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GEOPHYSICAL FACTORS OF ASYMMETRY ORIGINATION IN PRECURSORS OF BIOLOGICAL SYSTEMS

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A hypothesis is formulated which holds that breaking of symmetry in nature occurred in the prebiological evolution stage at the nonequilibrium ocean–atmosphere interface, and origination of aerosols from the ocean surface layer with inverted composition predetermined subsequent biological evolution.

INTRODUCTION

Numerous experiments carried out over the past decades have helped roughly clarify and model the mechanism of formation and accumulation of various organic compounds, including the basic components of biopolymers (such as amino acids, sugars, and nucleotides) on the surface of the primordial Earth [1]. Yet, it remains unclear what particular factors predetermined the possible origination of biologically advantageous nonequilibrium structures that are cell precursors.

Origination of a prebiological state represents a process of producing new information [2]. In this paper we made an effort to consider some aspects of the general problem of establishing a primary order.

1. A characteristic feature of the world around us is broken mirror symmetry: in contrast to the inanimate nature, the biosphere uses only levorotatory (L) molecules of amino acids and only dextrorotatory (D) molecules of sugars rather than their enantiomers. This asymmetry is one of the most important manifestations of the thermodynamic nonequilibrium of the biosphere.

In order to describe the state of the substance we have introduced the term "chiral polarization" $\eta = ([L] - [D])/([L] + [D])$ of a substance, where $[L]$ and $[D]$ are the concentrations of appropriate isomeric forms. A solution in which equal quantities of levo- and dextrorotatory molecules are randomly intermixed and which is characterized by $\eta = 0$ is referred to as racemate. If a solution contains molecules of one isomeric form, $\eta = \pm 1$ (chirally pure state). Transition $\eta = 0 \rightarrow \eta = \pm 1$ is a disorder-order transition with a marked disruption of chiral symmetry, which is well known in statistical physics [3].

At the stage of chemical evolution, as far as we know, only racemic mixtures of enantiomers could arise abiogenically [4]. Having analyzed the experimental data on biopolymer formation and replication processes, Gol'danskii and co-authors [5] suggested that breaking of chiral symmetry must have occurred at the stage of prebiological evolution as a prerequisite for subsequent biological evolution, while self-replication could arise and be sustained only in a chirally pure environment since polymers of chirally pure elements have crucial advantages over chirally impure elements: the former are faster polymerized, attain large sizes, and, what is particularly important, are capable of forming two-dimensional ordered helix structures. We believe that the stereospecific nature of the biosphere arose and stabilized in a dynamic cycle of the L amino acids (enzymes)/D sugars (nucleic acids) pair in the biosynthesis system.

2. Another important indication of symmetry breaking in nature is the nonequilibrium and asymmetric distribution of cations between cells and the environment.

The nonsymmetric ion distribution as information initially built into precell structures was essential for subsequent biological evolution. The nonequilibrium ion distribution facilitated the initiation and coordination of important metabolic and transport processes, as well as biosynthesis processes. Inorganic ions were used for sustaining integrity and individualization of primary cells. Rupture of the cell membrane or a change of conditions led to their redistribution [6].

We believe that a decisive role in the appearance of a primary order could be played by the nonequilibrium ocean–atmosphere interface.

It is well known that an open nonlinear thermodynamic system can form dissipative ordered structures if external conditions keep it in a state substantially removed from equilibrium. The ocean and the atmosphere

are a single thermodynamic system. The temperature of the ocean exceeds the atmospheric temperature by 0.1–0.4°C on the average due to high transparency of the atmosphere and the low albedo of the ocean. This leads to a spontaneous heat and mass exchange manifested in the evaporation, an effective IR radiation from the ocean surface and a contact heat exchange. These processes actually occur at the very surface of the ocean in a so called "radiating" layer 10 to 20 μm thick. Heat losses in the radiating layer are high and cannot be compensated for by the heat supplied by solar radiation absorption. Cooling of the radiating layer induces a compensation flow from underlying water layers, which gives rise to considerable temperature gradients in the ocean surface layer. The nonequilibrium state of the ocean–atmosphere system results in the appearance of a cold film—a phenomenon universally observed on the surface of the World Ocean [7].

Today the redistribution of ions in the thin surface layer of the ocean is a well-known fact. The surface film is more enriched with K^+ and Ca^{2+} ions than with Na^+ and Mg^{2+} ions compared to the subsurface sea water. The content of some microelements in the film is hundreds of times higher than in the sea water. The results of many years' full-scale investigations of the ionic composition of the ocean surface film revealed that ion redistribution in the sea surface layer depends on nonequilibrium processes at the ocean–atmosphere interface [8].

Thus, the radiant energy flux coming from the sun to the ocean surface gives rise to a dissipative structure with a nonequilibrium temperature distribution over depth and an asymmetric distribution of substances in the cold film.

Analysis of the ion distribution in the sea subsurface layer suggested a hypothesis that it is the salt composition of the sea water and of its surface film that predetermined the nature of ion asymmetry observed in biological systems [6].

This prompted us to investigate the possibilities of element stereoselection at the water–air interphase boundary and protobiont origination from the ocean surface microlayer.

EXPERIMENTAL RESULTS AND DISCUSSION

We set ourselves the task of elucidating whether a redistribution of L- and D-isomers of amino acids is possible in the surface layer. We used racemic solutions of amino acids in the experiments. We could observe a nonhomogeneous enrichment of the surface layer with various isomers from the optical rotation of a surface layer sample (the angle of rotation of the light polarization plane in the sample is proportional to the concentration difference $[L]-[D]$: $\alpha = [\alpha]^t_\lambda l([L]-[D])$, where $[\alpha]^t_\lambda$ is the specific rotation of the L amino acid at temperature t and wavelength λ and l is the cell length. The specific rotation of the initial solution did not exceed 0.02°).

The sampling technique of a thin (2–5 μm) surface layer of the solution is based on collecting small film droplets produced by artificial bubbling of the solution surface with large air bubbles (no less than 8 mm in diameter) [8]. The schematic diagram of the setup is presented in Fig. 1. An aqueous solution of the amino acid was poured into glass 5. The solution surface was bubbled with bubbles of air preliminarily humidified in vessel 2 by peristaltic pump 1 at a frequency from 2 to 4 s^{-1}. The aerosol was collected on nuclear lavsan filter 4 (the hole diameter 0.1 μm) by pump 3. The rate of sampling of the surface layer substance was $(2.5 \pm 0.5) \times 10^{-2}$ ml/h. The setup made it possible to control the intensity of evaporation from the solution surface by varying the solution temperature using thermostat 6 and blowing off the surface by pump 7. Prior to surface ventilation and bubbling the air was purified by Petryanov filters (PF) 8. In order to study the surface under equilibrium conditions (the evaporation heat flux is zero) the glass with the solution, the bubbler, and the sucking-in funnel were placed in an air-tight mist chamber 9 with water on its bottom. This greatly increased the surface area of the liquid, and manipulations in the chamber did not affect the equilibrium between liquid and vapor.

The sample was washed off the filter by distilled water (8 ml). The angle of polarization plane rotation for the solution obtained was measured by a Perkin–Elmer 241 MC polarimeter (λ = 360, 407, 436, and 579 μm).

The sampling technique introduces no error (outside the rotation angle measurement error) in the measurement results:

(1) The wash-off solution from the unused filter has no optical activity.

(2) The filter is L- and D-forms indiscriminant because the racemate (valine, 10^{-2} and 10^{-6} g ml^{-1}), in which the filter was held for 24 h, acquired no rotation; racemate droplets applied on the filter by a pipette and washed off after drying acquired no rotation either.

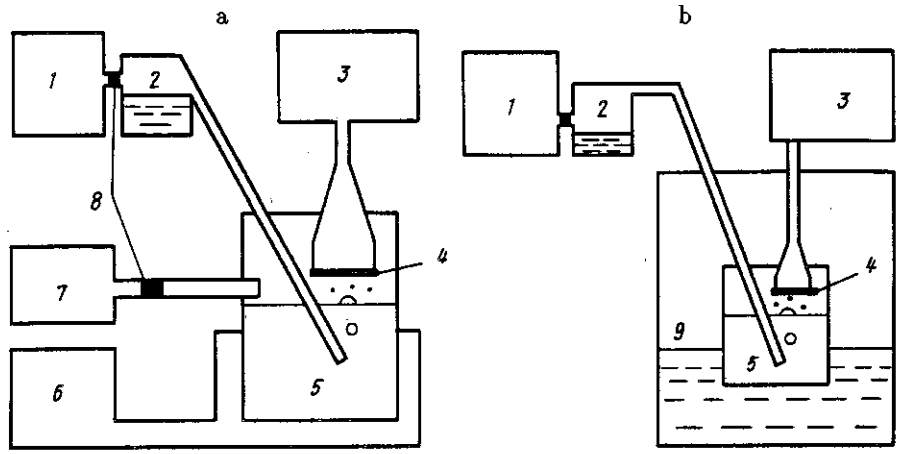

Fig. 1

Schematic representation of the device for sampling the surface layer (2 μm) in the conditions of evaporation from the surface (a) and a thermodynamic equilibrium (b).

(3) Samples collected in a bubbling-free system do not rotate the polarization plane.

Racemic solutions of alanine (10^{-2} g ml^{-1}), aspartic acid (0.5×10^{-2} g ml^{-1}), valine (10^{-2} g ml^{-1}), glutamine (10^{-2} g ml^{-1}), and leucine (0.99×10^{-2} g ml^{-1}) were used for the experiments. The samples were taken under different regimes of evaporation from the surface approaching the natural conditions (the heat fluxes from 0 to 1 kW m^{-2}).

The values of η in the surface layer samples of valine, glutamine, and leucine racemic solutions are given in Fig. 2. The error in determining η, including the measurement error for the angle of polarization plane rotation and the mean-root-square error of the $(L + D)$ determination in the sample, does not exceed 0.02. Note that the highest η values are observed under conditions of intensive evaporation from the surface, whereas in the surface layer under equilibrium η is within the error.

For a correct interpretation of the results obtained it was important to clarify whether the rotation of the plane-polarized light in the sample is related to a redistribution of the isomers or to the presence of an impurity chiral agent in the amino acid racemate that could be concentrated on the solution surface. NMR spectroscopic studies of amino acids (a VXR-300 Varian spectrometer, 300 MHz for ^{1}H nuclei) have shown that the racemates used are indeed contaminated (up to 5% impurities). Yet only the valine-contaminating impurity, the nonchiral molecule of sodium acetate, can be identified. Therefore, it is only for valine that one can assert with confidence that the racemate solution surface layer is enriched with molecules of an L isomer. Similar statements with respect to other amino acids can only be made by using the following indirect evidence. The specific rotation of amino acid solutions in H_2O and in HCl is different, and for leucine $[\alpha]_{H_2O}$ differs from $[\alpha]_{HCl}$ not only in absolute value but also in sign. We measured samples that had been washed off the filter with distilled water, acidified them to 1 N HCl, and measured them once more. We found a change of the angle of rotation proportional to $[\alpha]_{H_2O}/[\alpha]_{HCl}$.

The η values observed correspond to a decrease in entropy of a surface layer area of 1 m^2 by about 10^{-5} J K^{-1}. Such an ordering requires a supply of energy to the system not exceeding 10^{-2} W m^{-2}, because the characteristic times of microconvective motions in the water surface layer that can break the structure formed are no less than 1 s [9]. Note that the scale of the energy fluxes in the ocean–atmosphere system significantly exceeds this level (the mean total heat flux from the ocean to the atmosphere is 220 W m^{-2}).

In the most general case we can assume that in a situation when we have a magnetic field, a constant electric field at the interphase boundary (or a variable electric field in spray generation) and a local rotation of the medium (microconvection in the surface layer, including that in spray generation), a slight but locally regular fractionation of amphiphilic diamagnetic chiral molecules in the solution surface layer is possible.

Formation of isolated structures with an initially inverted composition with respect to the environment could become one of possible ways of origination of living forms at the initial stages of prebiological evolution. This process could occur as follows.

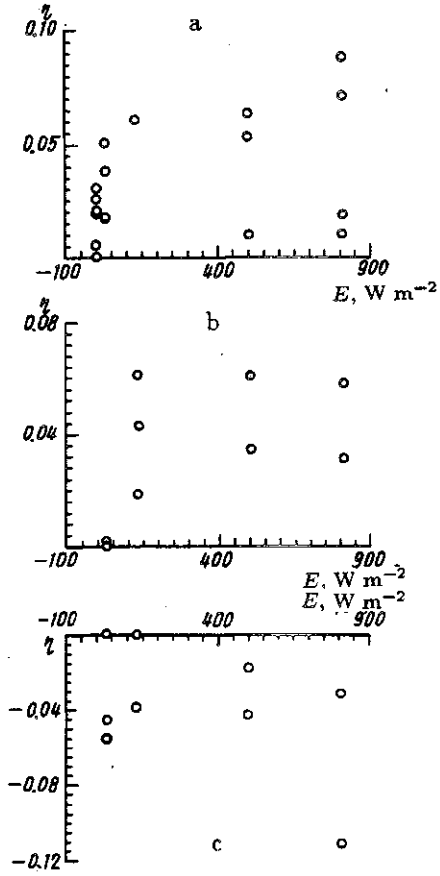

Fig. 2

Variation of η in the surface samples of racemic solutions of valine (a), glutamine (b), and leucine (c) at various values of heat flux expended in evaporation from the solution surface.

The surface of the ancient ocean could be covered by a thin monolayer of abiogenically produced lipids possessing the surface-active properties [10–12]. During aerosol formation particles of water whose composition conforms to that of the surface layer break loose from the water surface [13]. In the course of evaporation in air, the microdrops could diminish and be gradually coated by a lipid mono- and multilayer. When these vesicle-microdrops got into the sea water they could have already been coated with a lipid bilayer constituting a structural base for all kinds of membrane and could have a composition different from that of the environment (Fig. 3). Probably, these vesicles could exist for a long time in the sea water because liposomes are known to be capable of keeping a nonequilibrium concentrations of substances for at least a few hours and of existing for several days or even weeks [14]. This time could be quite sufficient for actuating some simplest life processes.

We modeled the process of formation of these vesicles under laboratory conditions. A thin lipid monolayer (standard lecithin) was applied to the surface of a NaCl aqueous solution (33‰). Figure 4 shows photographs of vesicles found in the solution after a prolonged treatment of its surface with air bubbles and taken using a JEM-MX electron microscope with a ×80 000 magnification by the method of negative contrast with a 2% solution of uranyl acetate.

Such cell-resembling structures can be produced in other experiments often reported in the literature [15]. The suggested process of protocell origination in the ocean surface layer under conditions of heat and mass exchange in the ocean–atmosphere system makes it possible to pass over from the morphological similarity of these structures with cells to the functional one.

It should be noted that asymmetry of the initial distribution of substance between a protocell and the

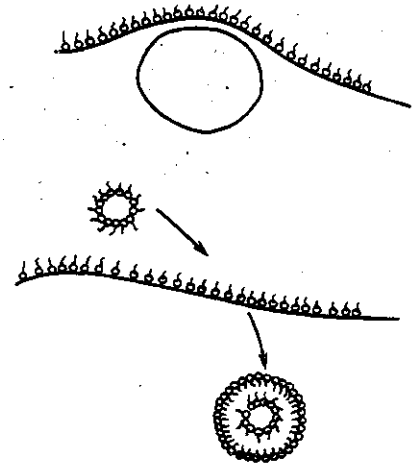

Fig. 3

Formation of vesicles from the monomolecular layer of polar lipid molecules during aerosol formation.

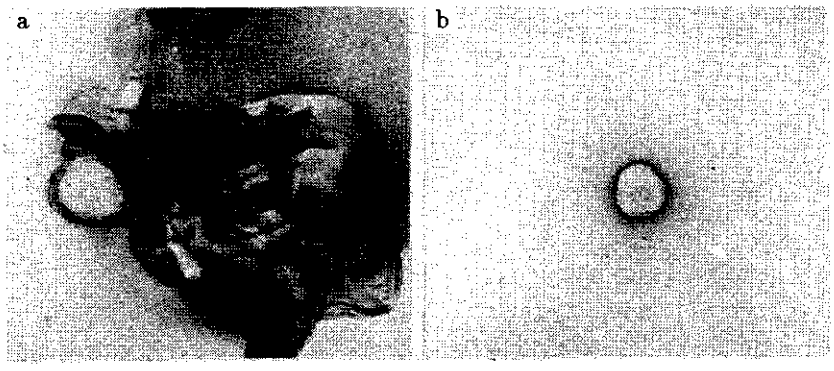

Fig. 4

A vesicle. ×80 000 magnification.

environment could grow substantially due to the following factors. The appearance of dissipative structures in the cold surface film can be facilitated by the presence of a surfactant layer of molecular thickness on the ocean surface. The phospholipid monolayers show a transition from one aggregate state to another of the phase transition type in the narrow temperature range from 15 to 25°C. The change in the phase state of the monolayer is accompanied by a change in the heat exchange conditions, and this causes a reverse transition. Similar systems are discussed in detail in [16, 17]. Additional feedback mechanisms in the system can result from changes of the monolayer sorption capacity with respect to inorganic ions during a phase transition.

At the ocean–atmosphere interface, reactions proceed under conditions when the reactants are separated in space. The primordial atmosphere had a fairly high H_2S concentration. In the conditions of surface sorption of bivalent cations, such as Cd^{2+}, Zn^{2+}, and Cu^{2+} on the surfactant monolayers, these cations could react with H_2S to form insoluble sulfides. Distribution of sulfides over the surface could be very nonuniform due both to the formation of dissipative structures and to differing sorption on monolayer regions at different phase state. The incorporation of these semiconducting microparticles into the membranes of primary cells could give rise to a photoinduced potential difference at the membrane and be the first step in the evolution of photosynthesis and electron transport systems.

Thus, we believe that breaking of symmetry in nature took place at the stage of prebiological evolution due to the initial asymmetry of processes at the ocean–atmosphere interface and the formation of aerosols from the ocean surface film with inverted composition created conditions for the subsequent biological evo-

lution.

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