PROBLEMS, TRENDS IN DEVELOPMENT, AND IMPORTANT TASKS OF PHYSICAL CHEMISTRY

The Riddle of Atmospheric Oxygen: Photosynthesis or Photolysis?

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Abstract—The stoichiometry of the photosynthetic reaction requires that the quantities of the end products (organic biomaterial and free oxygen) be equal. However, the correct balance of the amounts of oxygen and organic matter that could have been produced by green plants on the land and in the ocean since the emergence of unique oxygenic photosynthetic systems (no more than 2.7 billion years ago) is virtually impossible, since the vast majority of oxygen was lost in oxidizing the initially reducing matter of the planet, and the bulk of organic carbon is scattered in sedimentary rocks. In recent decades, convincing information has been obtained in favor of the large-scale photolysis of water molecules in the upper atmosphere with the scattering of light hydrogen into space and the retention of heavier oxygen by gravity. This process has been operating continuously since the formation of the Earth. It is accompanied by huge losses of water and the oxidation of salts of ferrous iron and sulfide sulfur in the oceans and methane in the atmosphere. The main stages of the evolution of the atmosphere and surface layers of the Earth's crust are analyzed for the first time in this work by considering the parallel processes of photosynthesis and photolysis. Large-scale photolysis of water also provides consistent explanations for the main stages in the evolution of the nearest planets of our Solar System.

Keywords: evolution of the Earth's atmosphere, photosynthesis, photolysis of water, origin of oxygen, atmospheres of planets

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INTRODUCTION

In 1998, Davankov published the article "The Mystery of Atmospheric Oxygen" [1], which questioned for the first time the generally accepted theory that the emergence of life on Earth and the appearance of free oxygen in its atmosphere were related as cause and effect. This theory is based on our knowledge that cells of higher plants and algae, using sunlight as a source of energy, convert carbon dioxide and water molecules into molecules of organic matter with the simultaneous release of oxygen molecules. It is believed that this process of photosynthesis led both to the generation of all (free and consumed) oxygen, and to the accumulation of all organic matter and hydrocarbon reserves in the Earth's crust. However, Davankov considered the process of photosynthesis as an elementary chemical reaction in which oxygen and biomatter should form in equal amounts. Although the meeting of this requirement of stoichiometry is currently not subject to correct verification, the author of [1, 2] believed the amount of living and buried organic matter is less than that of free and consumed oxygen. We must therefore consider the photolysis of water molecules in the upper layers of the atmosphere as a constant and extremely important source of oxygen on Earth that proceeds independently of wildlife. Over the last two decades, a huge volume of new infor-

mation has been accumulated in different branches of the natural sciences that allows us to substantiate this new hypothesis with a high degree of reliability. This work, in addition to the recently published [2], compares photosynthesis and photolysis as parallel processes of oxygen generation and shows the highly important role of photolysis.

ORIGIN AND EVOLUTION OF THE EARTH'S PRIMARY ATMOSPHERE

The Big Bang, which is estimated to have occurred 13.8 billion years ago, should have produced identical numbers of high-energy photons, baryons, and antibaryons. According to the latest concepts, baryons and antibaryons are not only particles and antiparticles, but also pairs of steric enantiomers [3−5]. They quicky annihilated one another (i.e., turned into photons). For some reason, the number of baryons initially turned out to be slightly larger than that of antibaryons, so the latter did not survive at all. There are currently 10^6 times more photons than baryons, but it is the latter that make up all matter we can detect.

The primordial baryonic matter roughly 20 min after the Big Bang consisted almost exclusively of hydrogen, helium, and lithium. Some other elements formed later in the nuclear reactions of stars, convert-

ing hydrogen mainly into helium, and then into lithium and light elements up to iron with atomic number 26. The fusion of three helium nuclei thus produces a stable isotope of carbon ^{12}C; four, oxygen ^{16}O; five, neon ^{20}Ne; and so on. The heavier elements are believed to have originated in supernova explosions. The amount of each chemical element of observed matter falls rapidly as their atomic weight rises in the order hydrogen, helium, oxygen, carbon, nitrogen, neon, silicon, sulfur, iron, and so on. Even now, the number of hydrogen atoms in the Universe exceeds the number of any other element by tens of thousands (and even millions) of times [6]. This information about the elemental composition of matter in the Universe is extremely important for understanding that by the time the Solar System formed (around 4.6 billion years ago), the chemical composition of matter in the primary self-compacting nebula on the sidelines of our galaxy (the Milky Way) was mainly hydrogen, helium, and chemical compounds of light elements *with hydrogen*. The most common polyatomic chemical compounds in this primary nebula (and throughout the Universe) were thus H_2, H_2O, CH_4, NH_3, and (to a lesser extent) N_2, CO, HCN, H_2S, SiO_2, CO_2, FeO, and ionized fragments of these molecules. Heavier elements were naturally parts of solid and refractory compounds, silicates, oxides, sulfides, and so on. They made up the bulk of cosmic dust and small and large asteroids and protoplanets—the remnants of former worlds.

Oxygen, as the third element in the total amount of matter, is too active. It is completely bound in chemical compounds with other elements: H, C, Al, Si, Fe, Ni, and so on. It is clear that with the dominance of hydrogen in the primary nebula, which compacted into the forming star (the Sun) and its system of planets, the general state of matter was *reducing* [7]. Hydrogen still makes up the bulk of the Sun's mass. The atmosphere of giant gas planets like Jupiter and Saturn are also more than 90% hydrogen. It must be emphasized that there was no free oxygen in the primordial nebula.

The number of planets around the stars of the Milky Way is estimated at 40 billion, of which around 3500 have been discovered and documented. It is believed that 30 planets are in the habitable zones of their stars. However, free oxygen is not found either there or on any planet in our Solar System, except for Earth. The *only* exception is the modern atmosphere of our Earth. It is clear that it has little in common with the composition of the gases of the primary nebula; instead, it formed as a result of the long evolution of our planet.

The initial luminosity of the flaring Sun was tens or even hundreds of times greater than its modern activity. Photons and the solar wind therefore almost completely removed the lightest components (hydrogen, helium, and neon) from the inner part of the nebula and the primary atmospheres of the newly formed planets. The gravitational forces of the inner planets could retain only a small fraction of hydrogen, but more of the heavier molecules (H_2O, CH_4, NH_3, N_2, HCN, H_2S, CO, CO_2, and Ar).

The first three to four compounds and hydrogen probably formed the basis of the primary hot and massive reducing atmosphere of the Earth. Substantial amounts of additional gases were introduced into the atmosphere by meteorites, which actively bombarded the Earth in the first 500−700 million years of its formation, and the eruptions of numerous volcanoes. When falling to the ground at high speeds, the meteorites themselves heated up and resulted in strong heating of the surrounding rock. As was shown by detailed studies of the thermal degassing of meteorite material [8], the main products of chondrite degassing are water, hydrogen, and methane. It was also emphasized that interaction between equally widespread iron-nickel meteorites and water proceeds with the release of hydrogen. Only the atmospheric emissions of modern volcanoes include a number of oxygen-rich compounds (CO, CO_2, SO_2) in addition to water (more than 90%), a number of hydrogen-containing gases (H_2, CH_4, NH_3, H_2S, HCl, HF), nitrogen, and noble gases. There should nevertheless be no doubt as to the general *reducing* nature of both the bulk of the now solid matter and the primary atmosphere of the Earth, which must have consisted mainly of *water vapor and methane* (though smaller amounts of ammonia, carbon oxides, nitrogen, and traces of other gases were also present in the atmosphere) [7, 9].

As the planet cooled, the water condensed and formed huge oceans. Rains washed compounds readily soluble in water (NH_3, HCN, H_2S, and CO_2) out of the atmosphere. Atmospheric pressure dropped by several orders of magnitude. The greenhouse effect weakened somewhat, and was now determined not by water but by methane.

From a purely chemical and thermodynamic point of view, it follows from the above that of all the oxygen-containing compounds found on planet Earth in significant quantities (water, silica (SiO_2), silicates and some oxides) *the only potential source of free oxygen is water*.

The modern atmosphere of the Earth is about a hundred-kilometer layer of air that is 78% nitrogen, 21% (23.15 wt %) oxygen, and a small amount of argon. It is interesting that the proportions of the main gaseous components of the atmosphere have remained close to this for a very long period of time.

Such great scientists of the past as Scheele, Priestley, Lavoisier, and Lomonosov made significant contributions to our study of the composition of the atmosphere.

PHOTOSYNTHESIS AS A SOURCE
OF OXYGEN AND ORGANIC MATTER

Free oxygen did not appear in the Earth's atmosphere immediately. It did so somewhere between 2.4 and 1.8 billion years ago, though oxidative processes in the atmosphere (and especially ocean waters) were active long before that. In the oceans, oxidative processes clearly manifested in the formation and deposition of poorly soluble hydroxides and oxides of ferrous iron. (Large amounts of soluble salts of ferrous iron were carried into the ocean by streams of water from weathered continental rocks). The oxidation of Fe^{2+} ions led to the formation of layered red-brown sedimentary rocks—iron ores containing mainly magnetite (Fe_3O_4) and hematite (Fe_2O_3) [10, 11]. The formation of these rocks in the oceans ended suddenly around 1.8 billion years ago. More scattered masses of brown ferric oxides then began to form directly near areas of intense weathering of rocks that contained ferrous compounds. The most obvious example of such rocks is those of the Grand Canyon in Arizona (United States). The transfer of iron oxidation from the ocean to the continents is obviously difficult to explain other than by the depletion of the main reserves of ferrous iron in the ocean and the emergence of certain amounts of free oxygen in the atmosphere.

The change in the isotopic composition [12, 13] of sulfur-containing sedimentary rocks is also attributed to approximately the same time period—around 2 billion years ago. Let us recall that sulfur was initially present in a bivalent state in the form of H_2S and metal sulfides. After contact with oxygen in an aqueous medium, it transitions to the hexavalent state of sulfates, and it is in this oxidation that the isotopic kinetic effect becomes apparent.

The transition from an initially reductive atmosphere to an oxidative one (referred to as the Global Oxygen Catastrophe) occurred in the middle life of our planet. We emphasize that it could not have occurred before the completion of the main oxidative processes in the ocean, or the complete oxidation of the huge amount of gaseous methane in the primordial atmosphere. (It should be noted here that the final removal of methane from the atmosphere dramatically weakened the greenhouse effect and contributed to the start of a long period of global glaciation). The oxidation of one methane molecule consumes four oxygen atoms. The resulting carbon dioxide was quickly transported by rains to the oceans and reacted there with calcium and magnesium ions carried from the continents, forming massive sedimentary rocks of carbonates (limestones and dolomites). Limestone formations are 3−5 km thick; those of dolomites, 1 km thick. Carbonates account for 20−25% of all sedimentary rocks (stratispheres). They immobilize the bulk of carbon and a notable fraction of oxygen, which have been chemically transformed during the evolution of the Earth. It is clear that the oxidation of methane and the deposition of carbonates took more than one million years. The accumulation of free oxygen then started at a faster pace.

The biosphere is considered the only important engine of oxidative processes and a source of molecular oxygen. Life on Earth appeared strikingly early—shortly after the end of the meteorite bombardment period (i.e., between 4.0 and 3.8 billion years ago). This important event was facilitated by the accumulation of different organic compounds in the warm waters of small bodies of water [14] and the entire ocean [15]. They formed in large quantities from carbon-containing inorganic matter during the collision of different space objects with ultra-high speeds [16]. An important additional incentive for the origin of life must have been the recently hypothesized and experimentally confirmed direct synthesis from elements, which leads to the predominant formation of amino acids of precisely the L-configuration needed for life [4, 5, 17].

Fossil inclusions that resemble phytoplankton cells in morphology are in any case found in the rocks of eastern Australia [18]. Their age is at least 3.5 billion years. The emergence of photosynthetic biosystems is attributed to this period of time, or even 200−300 million years earlier (i.e., to the very beginning of the formation of the biosphere). However, most groups of the first archaea bacteria practiced *anoxygenic* photosynthesis [19, 20]. To reduce CO_2 molecules to fragments of biomatter, they used the energy of thermal infrared photons (about 1000 nm), emitted in areas of such hot hydrothermal springs as black smokers, and a number of easily oxidized substrates. These bacteria oxidized H_2S molecules, elemental sulfur, Fe^{2+} ions, methane, and hydrogen, transferring oxygen from water molecules to them. This proceeds *without the release of free oxygen*, but with the obligatory accumulation of biomass. If anaerobic bacteria really did make a significant contribution to the oxidative processes in the ocean waters, we would simultaneously detect buried organic matter near iron ore deposits. This assumption still requires careful attention and analysis on the part of geologists.

Although the estimated data in the literature can differ greatly, it is generally believed that the emergence of *oxygenic* photosynthesis and traces of oxygen on the planet Earth can be attributed to the period of 2.8−2.7 billion years ago [21]. In the subsequent period (2.45−1.85 billion years ago), O_2 was mainly spent on the oxidation of salts dissolved in water, along with rocks of the seabed. The Oxygen Catastrophe occurred with the emergence of oxygen in the atmosphere, which it rapidly penetrated starting 1.85−0.85 billion years ago, when it still had to eliminate methane and oxidize surface rocks.

The generation of oxygen in the sunlit surface layers of the ocean was clearly associated with the appear-

ance of cyanobacteria or blue-green algae. These one-celled photosynthetic organisms use two hydrogen atoms of a water molecule to reduce CO_2 molecules to an elementary carbohydrate (HCOH), especially starch or cellulose, with the release of an oxygen molecule:

$$CO_2 + H_2O = -(HCOH)- + O_2.$$
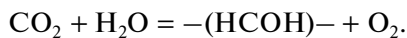
The energy for this endothermic reaction is supplied by photons absorbed by the pigment of the cell—quanta of the visible part (400−700 nm) of the sunlight spectrum.

Completion of oxidative processes in the atmosphere and on land and the accumulation of free oxygen in the air gradually led to the emergence of the ozone layer of the atmosphere. Despite the extremely small amount of ozone (at atmospheric pressure, the ozone layer would be no larger than 1 mm), it protected the Earth's surface from hard ultraviolet radiation. This allowed the higher green algae and plants to reach land and quickly populate all the continents. This happened only 500−600 million years ago! The rate of generation of oxygen and organic matter then grew dramatically. Land plants produce about 1.8×10^{11} tons of dry biomass annually, which is more than the amount produced in the World Ocean.

If we present in weight proportions the above formula of photosynthesis in its most general form (according to the molecular weights of all its participants), we find that by weight, 44 parts of carbon dioxide and 18 parts of water are converted into 30 parts of biomass and 32 parts of oxygen. It is important that the reaction products—biomass and oxygen—emerge in equal amounts. It is also important that photosynthesis is reversible, since the reverse process of combustion or decay of biomass destroys equal amounts of oxygen without disturbing the weight balance between these two products.

Let us see what resources of photosynthesis products the Earth now has. The atmospheric pressure at sea level is 1 kg/cm^2. This means that over each square meter of the Earth's surface there are 10 tons of air or 2.3 tons of free oxygen, so there must be at least 2 tons of biomass on each m^2 of the surface or under it. This should be true for any point on the surface, including those hidden by oceans and glaciers! With regard to *dry* biomass, this amount corresponds to a hundred-year-old oak tree, or several elephants, or two tons of coal, peat, or oil, if the latter are considered products of biomass transformation. Each square meter has 2 tons! And what are the estimates [22, 23] of the currently observed total reserves of biosynthesis products on our planet?

Oxygen	$>1 \times 10^{15}$ t,
Fossil fuels	$<1 \times 10^{13}$ t,
Living matter	$<3 \times 10^{12}$ t.

These estimated amounts seem to indicate a deficit of living and fossil organic matter of almost two orders of magnitude, relative to the amount of atmospheric oxygen! However, correct calculations of the balance should include the scattered organic carbon of sedimentary rocks as a product of the degradation of organic biomass on the one hand, and oxygen consumed for the oxidation of many of the original components of the atmosphere and the surface of continents on the other.

Unfortunately, there are no direct and accurate ways of selectively identifying of *organic* carbon against the background of a multiple excess of *inorganic* (carbonate) carbon for a variety of sedimentary rocks. The thickness of sedimentary rocks at different points on the Earth's surface also varies from 0 to 10 km, and the statistics of samples analyzed at different depths and in different areas of land and oceans is clearly insufficient for correct averaging. Indeed, "the figures given by different authors vary quite significantly. For example, according to the old calculations of Clark and Washington, the total carbon content in the earth's crust is 0.087%. G. Berg takes a value of 0.08%, while A.E. Fersman and V.I. Vernadsky believe that this value should be much higher 0.35−0.40%" [24].

Moreover, not all fossil fuels and even not all organic carbon of sedimentary rocks can be clearly attributed to the transformation products of buried biomass. The planet's original methane was not only in its atmosphere; it was also captured by the masses of compacted solid matter. Huge accumulations of methane are now found at depths of 10 km or more, where the surface biomass could not reach. It is also argued that at the great depths of the Earth's crust, there are entire layers of the Mantle that are saturated with hydrocarbons of *abiogenic* origin [24−26]. The category of scattered organic carbon thus includes both hydrocarbons embedded or adsorbed by sedimentary rocks that seep to the surface, and the carbon introduced into the Earth's crust by numerous carbonaceous meteorites (3.6% of all strikes, up to 7% carbon) and asteroids. (Hundreds of different organic compounds are found in meteorites, including ones that resemble proteins [27].)

On the other hand, atmospheric oxygen is only a small fraction of the amount consumed in the oxidation of metallic meteorites, salts of ferrous iron, sulfur and other elements of a low oxidation state in the earth's crust, along with primary hydrogen, methane, ammonia, hydrogen sulfide, and so on in the atmosphere. According to Schidlowski [23], at least 95% of the oxygen synthesized by plants has been irretrievably lost to different processes of the oxidation of the primary matter of the planet. It is clear that the estimate of the fraction of consumed oxygen is just as arbitrary as the fraction of organic carbon in the crust.

If we agree with the most optimistic estimate of the average organic carbon content of 0.5% and the average estimate of the thickness of sedimentary rocks at 2.2 km, we have 30 times more organic matter than would correspond to the free oxygen in the atmosphere, but it could be comparable to the amount of oxygen consumed.

It is surprising that after the discovery of photosynthesis at the turn of the 20th century, oxygen began to be considered a simple by-product of plant life [9]. The need to revise the accumulated amounts of oxygen and biomass was not raised in the literature, except for the two works by Davankov mentioned above [1, 2]. We believe that the chemical evolution of the Earth's surface matter cannot be studied properly if the role of other sources of natural oxygen is ignored.

PHOTOLYSIS OF WATER IS A POWERFUL SUPPLIER OF OXYGEN

As a primary and (after the emergence of photosynthesis) additional source of oxygen, the photolytic decomposition of water molecules into atoms or ions of hydrogen and oxygen is subject to analysis. It has always been under way in the upper layers of the atmosphere under the effects of solar radiation and the flow of corpuscular wind. Atoms or ions of hydrogen, being extremely light particles, meanwhile leave the stratosphere, while atoms or ions of oxygen that are 16 times heavier are to a greater extent held by the Earth's gravitational field [28]. As a result, the Earth continuously loses water, but has a constant source of oxygen in return. The intensity of this process varies depending on the Sun's activity, which was much higher at the beginning of the formation of the Solar System.

It should be remembered that molecules of water and methane (molecular weights 18 and 16, respectively) are much lighter than those of nitrogen and carbon dioxide (28 and 44 a.u.) and are therefore present in the upper layers of the stratosphere in increased proportions. N_2 and CO_2 are also thermodynamically more stable and less susceptible to photolysis. There is no doubt that from the beginning, active oxygen atoms and ions were partially spent on the oxidation of gases that predominated in the original reducing atmosphere (CH_4, NH_3, H_2S, H_2). In the recombination of O atoms into O_2 molecules, however, oxygen was quickly washed out by rains into the oceans and onto the surfaces of continents (at 10 g/m³ at 15°C, oxygen is not poorly soluble in water). It is important that molecular oxygen in the aquatic environment rapidly oxidizes Fe^{2+} ions, depositing insoluble Fe^{3+} hydroxides in the oceans and products of rock weathering. In contrast, oxygen does not interact with methane in the air under normal conditions. Even in today's oxygen-rich atmosphere, methane has a lifetime of 8−12 years. Oxidation is apparently promoted by the photolytic activation of methane and/or oxygen molecules.

This explains why oxygen participated mainly in oxidative processes in the ocean as it formed in the atmosphere. Only after the completion of the main redox processes in the ocean did oxygen begin to accumulate in the atmosphere, complete the removal of methane, and finally create the ozone layer, which ensured the emergence of green plants on land and the rise of forests—an additional powerful source of free oxygen.

The photolysis of water molecules as a constant source of oxygen was underestimated until very recently. However, the intense study of physical and chemical phenomena in outer space in recent decades has accumulated a great deal of experimental data that allows us to formulate and verify new concepts by computational means [28]. The photolysis of water in the stratosphere and the differentiated dissipation of hydrogen and oxygen into space thus unexpectedly turned out to be intense processes that play a crucial role in the evolution of the primary reductive matter of the planets.

As the most common chemical compound, water to one degree or another participated in the formation of all planets without exception. For planets close to the Sun, however, water remains in the vapor state and actively undergoes photolysis with partial loss of oxygen and almost complete dissipation of hydrogen. After a certain period of evolution, these processes can even form the oxidizing gas shell of a planet. By a happy coincidence, the Earth initially acquired a great deal of water and now has both oxygen and water (though there was no oxygen earlier, and there was much more water).

In 1987, Hunten et al. [29] calculated from possible losses of hydrogen that the Earth could have lost water in the amount of 2.8 modern volumes of the ocean as a result of photolysis. Calculations for oxygen yield a water loss of 1.4 ocean volumes. The 1.4 volume difference corresponds to the amount of oxygen stored on the planet. This amount (1.6×10^{18} tons) would be more than enough for the complete conversion of methane from the initial atmosphere into carbon dioxide (and then into carbonates), along with the oxidation of all other elements of the atmosphere and the upper layers of continents (N, S, Si, P, Fe, and other metals) to the currently observed higher states of. A very recent theoretical model by Guo [30] includes the radiation ionization of H and O atoms in its calculations and considers the dissipation of four components (H, H^+, O, and O^+). This model results in even greater possible losses of water by planet Earth: 9.1 and 0.6 ocean volumes in terms of hydrogen and oxygen, respectively.

Without attempting to discuss the adequacy of these computational models, we must still recognize the photolysis of water as a powerful and constant source of oxygen on the planets. From these positions, a number of facts could find a new, logical explanation. Thus, we therefore know that the outcroppings of

primary basaltic crustal rocks occupy only a small part of continental territory, while oceanic sedimentary rocks or products of their transformation are found over most of the surface. It could not be otherwise, if we accept there was much more water on the Earth before, and it could well have covered almost the entire surface.

Another thing that has yet to be satisfactorily explained, the stabilization of the concentration of oxygen in the atmosphere at a level of 20−30% over the past 500 million years, also does not agree with the idea that the green plants of continents and oceans continue to produce large amounts of oxygen (about 3.6×10^{11} tons per year). We must assume that at the beginning of this period, we were dealing not only with a sharp increase in the rate of biomass growth, but with intensification of the oxidation of the newly produced and previously buried biomass [31] as well, so the accumulation of free oxygen in the atmosphere was minimized. An alternative logical explanation can be proposed if we allow for the reversibility of the photolysis of water molecules. An increase in the total concentration of oxygen in the atmosphere to a noticeable level inevitably led to acceleration of the reverse process — the recombination of oxygen atoms or ions with fluxes of protons and hydrogen atoms in the solar wind. It is believed that the Sun loses up to one million tons of its mass every second, due to the streams of emitted particles, most of which are hydrogen. (At ground level, these are streams of protons, electrons, and alpha particles with speeds of 300−800 km/s.) Upon entering Earth's atmosphere, hydrogen cannot help but bind with oxygen atoms to form water molecules. As a result, this large-scale process should lead to the establishment of a stationary state whose position is mainly determined by the *quasi-equilibrium* oxygen concentration in the upper atmosphere and the intensity of the solar wind.

ATMOSPHERES OF THE SOLAR SYSTEM'S PLANETS

Unlike photosynthesis by green plants, the generation of oxygen by photolysis of water molecules should be a universal process characteristic not only of the planets of the Solar System, but for all other worlds as well. The evolution of the atmosphere and surface layers of the crust of any planet should be determined by a set of factors, the most important of which must be considered:

• the distance of the planet from its central star,

• the activity of the central star,

• the mass of the planet,

• the speed of the planet as it revolves around the star and rotates on its own axis,

• the presence of the planet's magnetic field.

Small differences in the values of one or several of these factors lead to fundamental differences in the results of a planet's evolution at each moment of their existence, even those that form in a more or less limited volume of a cosmic gas−dust cloud. The Earth and its closest neighboring planets therefore now differ radically.

Little Mercury (0.55 Earth masses) is located too close to the Sun (0.38 AUs) and has long lost both its initial atmosphere and all volatile components, so the side facing the Sun is heated to 430°C (while the shadowed side can cool to −180°C).

Venus is the closest in its parameters to our planet: its mass and distance from the Sun are 0.815 and 0.72 those of Earth, respectively. Its initial atmosphere contained both methane and water [32] in sufficient quantities (about 5 volumes of Earth's oceans). However, Venus receives a much higher load of radiation, so the powerful greenhouse effect created by these main gases did not allow its surface to cool to the point where water could condense and form oceans. Water vapor was constantly undergoing photolysis, decomposing into oxygen and hydrogen. The latter escaped into space, as shown by the high enrichment of its remnants with deuterium (150 times more than on Earth). Oxygen, the partial pressure of which could rise to 10 atm, was completely consumed for the conversion of methane into heavy and stable carbon dioxide, and possibly the partial oxidation of the surface layers of the hot land [33]. There is now a great deal of carbon dioxide surrounding the planet: its pressure reaches 90 atm at the surface, and the greenhouse effect does not allow it to cool below 460°C. These parameters correspond to the state of supercritical fluid $scCO_2$. The high mobility and heat capacity of the fluid equalize the high temperature of the illuminated and shadowed sides of Venus's surface. Our now very dry and hot neighbor Venus never had a chance to become a cradle of life.

Mars is much more interesting in searching for traces of living matter. However, it is too small: it is almost 10 times lighter than the Earth and could not retain an appreciable gas envelope. Residual amounts of CO_2 with admixtures of 3% nitrogen and inert gases create only 0.1 atm of pressure at its surface. Insufficient lighting and a very weak greenhouse effect allowed the surface to cool to −58 °C. During the first billion years of Mars's history, however, it was much warmer and richer in water [34, 35]. With an even distribution, the surface would be covered with at least 10 meters of water. Careful analysis of the topography of the planet's surface indicates the existence in the past of vast lakes, rivers, and even glaciers, up to a period of 500 million years ago, and perhaps much longer [36]. Powerful streams of water left indelible marks on the surface of the planet [37]. Some canyons were formed quite recently—only 200 million years ago [38]. Water has survived to this day in the form of snow caps in the circumpolar regions and probably in the form of a huge lake at a depth of 1.5 km under the

cold surface of the South Pole. The active processes of photolysis and dissipation of the split components of water are apparent from the great enrichment of its residues with deuterium [39]. It is assumed that the atmosphere was at one time oxidizing; otherwise, it is difficult to explain the detection of perchlorates in the salt deposits of dried seas. It can be argued that during this period, the conditions on the planet were quite suitable for supporting life, and traces of it could well remain under layers of surface dust. (Despite the low pressure of the atmosphere, dust storms are rampant on Mars, due to the weakness of the planet's gravitational field.) The most recent detailed review [40] of the latest results from studying of Mars confirms the presence of huge amounts of water in the past, and subsurface ice masses in the present period of the planet's evolution. There is a high probability of an oxidizing atmosphere existing on Mars, created either by primitive photosynthetic living organisms or by the photolysis of water ("abiogenic photosynthesis"). The photosynthesis/photolysis riddle we are considering has already been picked up and adopted by space researchers.

In analogy with the Earth, Mars and Venus, the initial presence of large amounts of water may well be assumed for the rest of the planets of the Solar System, and for exoplanets throughout the Universe [41]. Water exists on planets at great distances from their central stars, and is stored in the form of ice. For inner planets, intense photolysis and loss of water vapor are inevitable, along with the oxidation of atmospheric components and solid near-surface rocks [28]. Modern astrophysics predicts that in the next billion years, even before the Sun turns into a Red Giant and absorbs the inner planets of the system, the Earth, like Mars, will lose all available water and oxygen as a result of photolysis, but anaerobic bacteria will retain their viability for some time under a surface layer of dust and in ice deposits.

CONCLUSIONS

According to the stoichiometry of the process, photosynthesis produces equal amounts of biomaterial and free oxygen. The reverse processes of biodegradation or combustion destroy these products in equal proportions. However, a reliable assessment and comparison of the amounts of free oxygen and consumed for oxidation on the one hand, and living and reserves of transformed biomatter on the other, is hardly possible at present. We nevertheless believe that the amount of oxygen that participated in the evolution of the initially reductive matter of the Earth exceeded that of the oxygen and biomatter produced by photosynthesis in the cells of living organisms. Oxygenic synthesis in the surface layers of the oceans illuminated by the sun appeared only as a result of 1 billion years of the evolution of living cells [20, 21], while the generation of oxygen accelerated quite recently—only 500 million years ago, with the formation of the ozone layer and the emergence of plants on land.

On the other hand, the astrophysics of the 21st century has reliably proved the existence of another powerful and constant process of oxygen generation: the photolysis of vaporous water molecules with the dissipation of hydrogen and the retention of heavier oxygen molecules. The latter is generated constantly until the supply of water is exhausted. Our study of the chemical evolution of the living and inorganic matter of the Earth therefore can no longer ignore the role played by the photolysis of water, relative to the results obtained in studying other planets, especially Mars and Venus.

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