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Critical review on the origin of atmospheric oxygen: Where is organic matter?



Vadim A. Davankov

Institute of Organo-Element Compounds, Russian Academy of Sciences, Moscow, 119991, Russia

A R T I C L E I N F O Keywords: Photosynthesis reaction Origin of oxygen Organic matter Oxygen/organics balance Photolysis of water Escape of hydrogen	A B S T R A C T In a short note of 1998 Davankov questioned the generally accepted notion that the unique features of the planet Earth, namely, the presence of life and atmospheric oxygen are inseparably bonded as a case and effect. Indeed, photosynthesis in terrestrial and aquatic phototrophs simultaneously produces oxygen and carbohydrates in almost equal amounts. Since the degradation of organic matter through burning or rotting also consumes an equivalent amount of oxygen, the total masses of oxygen and organic material must always remain comparable. This correlation for Earth appears to be drastically distorted in favor of oxygen, thus disproving the still wide- spread delusion of biogenic origin of atmospheric oxygen. Instead, by analyzing more recent data on the balance
	spread delusion of biogenic origin of atmospheric oxygen. Instead, by analyzing more recent data on the balance between oxygen and organics we arrive at the conclusion that radiolysis of water vapors with the preferential dissipation of hydrogen to space, most probably, was the major source of the free and oxidation-spent oxygen. The present review tries to illuminate the most important uncertainties that still remain to be clarified before an interdisciplinary and scientifically-balanced picture on the evolution of Earth gets settled.

1. Evolution of the early Earth's atmosphere

The matter that erupted from an infinitely small space as the Big Bang about 13.8 billion years (Gyrs) ago had a long history of evolution before Solar system started to form at a corner of the Milky Way galaxy. By that time, some 4.6 billion years ago, the matter in the universe was mainly presented by hydrogen and helium which, even nowadays, are more abundant by about 10,000–1,000,000 times than any of the other elements (Boyce et al., 1933). In fact, majority of elements heavier than helium had to have been produced later, in the long period of Universe evolution, in fission reactors of star cores and exploding supernova. At present, total amounts of each element in the universe rapidly decrease with their atomic numbers rising.

It is believed that our young proto-solar system presented a hot central part with a disc, or nebula, rotating around it. Besides gaseous elements, mainly hydrogen, helium, nitrogen, oxygen, neon and argon, the disc contained a lot of vapors and a mess of dust and rocky solid material. Due to the contraction of the core of the nebula its temperature rose and the Sun was born. At that point the very strong solar wind swept out most of light gases from the inner part of solar nebula. The remaining heavier components finally merged and grew into the rocky planets Mercury, Venus, Earth and Mars and, probably, concentrated in the cores of gas giants as Jupiter, Saturn, Uranus, and Neptune. The latter giant planets were able to capture more local gases so that their total composition can be expected to roughly represent that of the nebula at corresponding distances from the Sun while their atmospheres logically contain over 90% hydrogen, as on Jupiter and Saturn. The rocky planets were heavy enough to capture and retain only a portion of the initial gaseous matter in the form of their primordial atmospheres, (with the exception of the small Mercury that is practically deprived of any atmosphere).

Ruther early, Aston (1924a,b) noticed that concentration of neon in the Earth's atmosphere is particularly low, far below than that expected from its abundance in the universe. Neon is a noble gas, not prone to form compounds with other elements, so it must have concentrate in the atmosphere of the planet. Instead, Earth's atmosphere contains only 20 parts per million of neon, which is billion times less than in the atmosphere of Jupiter (Brown, 1949). The only rational explanation of this fact is that strong solar wind removed major part of light gaseous matter from the Sun' neighborhood and that modern secondary atmospheres of rocky planets have little to do with primordial ones, but largely resulted from their specific evolution processes.

Nevertheless, with hydrogen dominating among the interstellar gases and the initial nebula that gave birth to the solar system, we must accept that both solid matter and the primordial Earth's atmosphere were reductive.

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E-mail address: davank@ineos.ac.ru.

Strong additional arguments in favor of the reductive nature of the atmospheres of Earth and even Venus are presented in the extensive review by Zahnle, Schaefer and Fegley (Zahnle et al., 2010). They analyzed the degassing processes during the planet accretion from the initial planetesimals and planetary embryos, as well as the material delivered by numerous incoming meteorites, including various types of chondrites. On heating, they predominantly emit water, hydrogen and methane. It is also stressed in (Elkins-Tanton and Seager, 2008) that interaction of water with metallic iron that was present in large quantities in the above solid building blocks of planets would also deliver a lot of hydrogen to the evolving gases. Authors mention the fact that a radical change may have occurred some 30-100 million years (Myrs) after the formation of planets in the Solar system when Earth experienced the Moon-forming impact by another planet of the size of Mars. The collision energy may have caused melting and degassing of the mantle. This event could deliver large amounts of CO2 which is known to be one of major components of modern volcanic gases. (Typical gases collected during several eruptions of Kluchevskaya Sopka on Kamchatka peninsula in Russia contain some hydrogen-based compounds as H2, CH4, NH3, H2S, HCl, HF, but mainly oxygen-containing CO, CO₂, SO₂, as well as N₂, few noble gases and a lot of ash particles preferentially formed by compounds of Si, Fe and many other metals). Volcanoes emissions are important contributors to the atmosphere, though they do not contain free oxygen. Of volcanic emissions, only nitrogen will remain in the atmosphere while all other basic and acidic volatile molecules will be soon eliminated by water rains or slowly oxidized by free atmospheric O₂.

Still, all current hypothesis thus predict (Zahnle et al., 2010) "that an atmosphere generated by impact degassing would tend to have a composition reflective of the impacting bodies (rather than the mantle), and these are almost without exception strongly reducing".

It is only natural that within the nebula and early planet atmospheres, the abundant and active elements progressively formed most stable molecules, H_2 , H_2O , CH_4 , NH_3 , N_2 , CO, HCN, H_2S , CO_2 , etc. Compounds with high melting points as SiO₂, FeO and those incorporating all heavier elements finally formed solid bodies of the rocky planets. Oxygen, the third-most abundant in the universe element, exhibits very high affinity to other "light" elements as H, C, Si, Al, Fe and, therefore, could not emerge in the atmospheres in its atomic or molecular O_2 forms. Indeed, there is no free oxygen in the atmosphere of any other known planet.

Modern atmosphere of our Earth, a 100 km-thick layer of gas es, is composed of 78% nitrogen, 21vol-% (23.15 weight-%) oxygen and a few Ar, it has little in common with the initially reductive atmosphere and must have resulted from very complex evolution history of more than 4 Gyes. Oxygen was certainly formed and accumulated around Earth to its present proportion due to the slow and very specific type of the planet evolution. Generally, evolution of the young terrestrial planets was determined by a set of important parameters, such as the strength of gravitation, distance from the Sun, rates of rotation around their own axis and around the Sun, inclination of the rotation axis to the orbit, presence of a magnetic field, chemical processes within the body of the planet, volcanic activity, and many others, though less important. Due to the difference in some of these parameters, the present situation on the surface of all terrestrial planets that we know today looks so different. Atmospheres of Venus and Mars mainly consist of carbon dioxide, about 95-96%, and nitrogen, ~3%. At that, carbon dioxide on Venus actually exists in the form of a supercritical fluid (pressure 92 atm and temperature 475 °C, which is far beyond critical conditions), while Mars is about one order of magnitude lighter than Earth and its atmosphere is extremely thin (0.006 atm, -55 °C).

Nitrogen gas, being rather inert and water-insoluble, slowly accumulated in the atmosphere, while large amounts of water and methane dominated in the Earth's atmosphere for the first billion years. While being one of the major forms of existence of carbon in the gases of the nebula, methane was definitely largely entrapped by the matter that condensed to Earth. As mentioned above, along with water and hydrogen, methane comprised major product of degassing of impacting meteorites. We may assume the presence of methane in olivine inclusions to be an additional argument in favor of its presence in the initial nebula and accreting Earth matter in substantial quantities. There are evidences that it still may be present as methane-rich fluids in upper mantle masses (Matjuschkin et al., 2019). Methane can not co-exist with oxygen, so that it was gradually converted to carbon dioxide and largely disappeared from the atmosphere in the times when oxygen has been delivered there by one chemical process or another.

A peculiar and very lucky feature of Earth is that there is a lot of water on its surface. Most probably, water was one of significant components of the collapsing nebula matter. Indeed, water is one of the most abandoned molecules in the interstellar space and can also be observed as massive solid bodies in the cold parts of solar system. A part of water could be contributed later, in the times of intensive meteoritic rains. Another reliable source of water is volcanic gases which contain up to 90% water vapors.

In the times when Earth was hot, its atmosphere must have incorporated the whole water with a corresponding rise in the atmospheric pressure by several orders of magnitude. Thus, Earth's early atmosphere probably consisted of water vapor, methane, hydrogen, and smaller amounts of nitrogen, carbon mono- and dioxides. As the planet cooled down and liquid water began to form oceans, the initial and mainly additionally formed carbon dioxide was gradually eliminated from the atmosphere by rain waters. Simultaneously, running liquid waters brought to aqueous basins large amounts of calcium, magnesium and iron(II) salts. Over millions of years, enormous masses of calcium carbonate rocks were deposited from the oceans, so that the concentration of carbon dioxide in the atmosphere dropped to very low values. On planets without oceans, like Venus and Mars, carbon dioxide is still the main component of the atmosphere (Rosen et al., 2014a).

2. First emergence of oxygen in the Earth's atmosphere

In fact, Earth is the only known planet in the whole universe which atmosphere contains significant amounts of free oxygen. Extensive studies of mineralogy and geology specialists presented convincing evidences that free oxygen appeared in our atmosphere about 2.3 billion years ago (Chu, 2016), more accurately, between 2.4 and 1.8 Gyrs ago. So, during the first half of Earth's history its atmosphere remained reductive and rich in methane. Arguments of specialists in favor of this statement are well presented in the recent review by Rosen and Egger (2014b). They are based on considering the fate of water-soluble iron(II) salts that were washed by rivers into oceans from weathering and erosion of continental rocks. Note that iron is a light element rather abandoned in the universe and on Earth and in the initially reductive environment it existed both in the metallic form and oxidation II state. Important fact is that geologists report intensive Banded Iron Formation (or BIF) all over the world's oceans until about two billion years ago, and not later. These minerals are layered clay sediments rich in water-insoluble iron(III) oxides, magnetite (Fe₃O₄) and hematite (Fe₂O₃), which are dark brown colored, they alternate with bright silica-rich bands. Obviously, BIFs were formed by oxidation of large amounts of iron(II) accumulated in the oceans with oxygen that gradually emerged in ocean's waters by somewhat more than 3 Gyrs ago (Cloud, 1968).

Deposition of BIFs in the oceans suddenly stopped about 1.8 Gyrs ago. Instead, about this time, bright red-colored sediments start to appear around the world, commonly known as Redbeds (Rosen et al., 2014b). These are sediments which owe their red-brown color to iron(III) oxides, they could form near the weathering spots of iron(II)-incorporating rocks only under condition that certain amount of free oxygen appeared in the atmosphere. Thus, the current notion is that the Great Oxidation Event on Earth occurred between 2.4 and 1.8 Gyrs ago. By that time, iron(II) reserves in the ocean's waters as well as methane in the atmosphere-exposed parts of land started.

The same dating of the revolutionary conversion of the reductive state

of the atmosphere into oxidative one follows from the detailed study of isotopic composition of sulfur participating in the Earth's earliest sulfur cycle (Farquhar et al., 2000; Thiemens, 2012). It could be appropriate to mention here that the initial atmosphere as well as volcanic gases contained measurable amounts of H_2S .

3. Photosynthesis as a source of oxygen

It is a generally accepted belief that in the universe there exist only one significant source of free oxygen which is photosynthesizing living organisms. Though the origin of life still remains a subject of scientific debates, speculations, and fantasy, to the best of our knowledge, the biogenic origin of oxygen in Earth's atmosphere has not been seriously questioned, with the exception of the early publication by Davankov (1998).

At the first sight, the current notions are sufficiently logical. Indeed, in one way or another, first signs of life emerged on Earth rather early – already in Archean by the end of the bombardment with "meteoritic rains" - approximately 3.8–4.0 Gyrs ago (Schidlowski, 1988). Such a surprisingly quick evolution from the mineral to living matter was facilitated by the fact that hypervelocity collisions of cosmic bodies generate a whole pallet of organic molecules, including amino acids and carbohydrates with the predomination of molecular configurations that correspond to the required biological homochirality on Earth (Davankov, 2016, 2018; Managadze et al., 2016).

Schopf and co-workers eventually found mineralized structures in 3.5 Gyrs-old rocks from Western Australia that resemble phytoplankton (Schopf, 1993). This implies that the evolution of life in the oceans was already able to support there the existence and proliferation of one-cell photosynthesizing organisms. It was uncritically assumed that the latter managed to convert water and carbon dioxide molecules into oxygen and carbohydrate units by utilizing energy of light photons. Oxygen did not escape to the atmosphere prior to the times where most of iron(II) was oxidized to insoluble BIF matter. Certainly, oxygen was also consumed for the oxidation of other species as, for instance, dissolved H_2S .

The above assumption does not seem to be fully correct. First, the identification of the microfossils, which is based mainly on morphological resemblance to current microorganisms, is not convincing. Identical morphological characteristics can be easily attributed to other filamentous nonoxygen-evolving phototrophs such as green nonsulfur bacteria, including *Chloroflexus*, that are microscopically indistinguishable from many cyanobacteria. (Pierson, 1994).

Second, the overall consensus nowadays appears to be that primitive photosynthetic pigments first emerged in purple bacteria living near oceanic hydrothermal vents. The photosynthesis mechanism of these cells is anoxygenic and exploits infrared light as an additional source of energy (Nisbet et al., 1995, 2001).

Third, it has been shown that purple nonsulfur bacteria can oxidize soluble Fe(II) salts to brown precipitates of Fe(III) oxides and reduce CO_2 to cell material, implying that the Precambrian BIF may be of an alternative (or additional), anoxygenic origin (Widdel et al., 1993).

Most important are results of fundamental studies of Jin Xiong et al. The authors examined photosynthesis instruments of diverse photosynthetic bacteria and, using the rooted phylogenetic approach (Xiong et al., 1998, 2000), analyzed many pigment biosynthesis genes and enzymes. It was convincingly proven that the most of initial bacteriochlorophyll-synthesizing anoxygenic photosynthetic bacterial groups, through adaptation and extremely complicated and long pathways, finally evolved to chlorophyll-synthesizing oxygenic photosynthetic groups. Thus, an overwhelming support was presented to the fact that the oxygen-generating photosynthesis systems emerged much later than numerous anoxygenic systems. (Xiong and Bauer, 2002).

In any case, Earth's oceans were beginning to be dominated by cyanobacteria starting 2.7 Gyrs ago, almost one billion ears later than the supposed date of life emergence (Des Marais, 2000). Interestingly, the success of cyanobacteria was suggested to be due to not only the energetic advantage of photosynthesis, but also the inhibition of competitors through the creation of the potentially toxic agent O_2 (Nitschke et al., 1998).

Nevertheless, in hypersaline (salinity, $95\frac{1}{2}$) shallow waters of a lake in Mexico coexisting chemotrophic and heterotrophic cyanobacteriadominated mats have been found. Their photosynthetic bacteria actively produce H₂ and CH₄ in the dark and CO during daylight hours. Assuming that such kind of bacterial mats could have existed in the past, authors suggest that "H₂ escape might have contributed substantially to the oxidation of Earth's large reservoirs of reduced iron and sulfur, which must have preceded actual atmospheric oxygenation" (Hoehler et al., 2001). Still, both oceanic hydrothermal vents and shallow hypersaline waters are rather rare sites and could not be responsible for the formation of the whole mass of BIFs. Moreover, massive deposition of BIFs must have been accompanied by a comparable accumulation of organic matter, chemotropic bacterial residues, which however could not be found in corresponding amounts.

The evolution of cyanobacteria and advent of oxygenic photosynthesis in the oceans may have increased global oxygen production and biosphere productivity by a factor of 100 to 1000 (Hoehler et al., 2001). Especially efficient was the incorporation of photosynthetic cyanobacteria into eukaryotes as chloroplasts. Due to the proliferation of the newly emerging algae, some oxygen eventually appeared in the atmosphere. It is then, about 2 billion years ago, that the Great Oxidation Event took place and it changed the situation on Earth's surface in the most radical way. Nevertheless, for more than another billion years concentration of free oxygen remained rather low. Possibly, it was consumed for the oxidation of freshly appearing iron(II)- and sulfur(II)-salts on cites of intensive rock weathering and for the elimination of remaining amounts of methane in the atmosphere.

An enhanced concentration of oxygen was also required to build up an ozone layer in the stratosphere that started efficiently protecting the land from the deadly dangerous high-energy cosmic irradiation. (It could be mentioned here that equally dangerous charged particles of the solar wind are deflected from Earth's surface by the magnetic field. Venus and Mars do not have such kind of magnetic protection: Venus spins much too slowly - one turn takes 243 days, while Mars is small and, therefore, cooled down and became entirely solid). Magnetic field in cooperation with the emerging ozone layer finally created on Earth conditions for life organisms to move from the oceans to land. The descendants of algae, land plants, appeared on Earth not earlier than 0.5–0.6 Gyrs ago. Since that moment, green plants rapidly occupied most of land territories and the biogenic production of oxygen substantially accelerated. Finally, concentration of the latter rose to the level of over 21% in the present atmosphere.

Current oxygen concentration pO_2 in the atmosphere depends on a large number of factors. Most important appear to be the following: ocean nutrients content and productivity of biosynthesis in the ocean and on land, oxidative weathering intensity of available ablifted sedimentary organic carbon and sedimentary minerals as pyrite, rate of delivery of thermogenic methane and volcanic gases prone to oxidation, carbon burial rate, etc. Daines et al. pay special attention to the last factor and believe "that increased biological productivity and resultant organic carbon burial drove the Great Oxidation Event" (Daines et al., 2017). Still, even now we don't understand the modern oxygen control system that keeps pO_2 on a rather constant level since those times.

Thus, numerous generations of green plants and phytoplankton are credited to be the major, if not the only, producers of oxygen which presence makes Earth that unique in the solar system and known parts of the universe. As mentioned above, oxygen is generally considered as a byproduct of the photosynthesis reaction which converts carbon dioxide into organic matter of green plants (Paassivirta, 1991; Hutzinger, 1980; Post et al., 1990) by using energy of solar light. The annual production of oxygen in nature was estimated (Hutzinger, 1980; Schidlowsky, 1981) to be as follows:

x 10 ¹² mol	x 10 ⁶ t
4600	150,000
3790	120,000
0.007	0.224
	x 10 ¹² mol 4600 3790 0.007

Atmospheric oxygen	$>\!\!1\times10^{15}t$
Fossil fuels	$\overline{<}1\times10^{13}t$
Living matter	${<}3\times10^{12}t$
Humus in the soil and in sediments	$2\times 10^{12}t$

Green plants on land produce 150 billion tons of oxygen per year. Though the total biomass in the Ocean yields to that on land by a factor of about 10,000, phytoplankton is more efficient and consumes solar energy on a larger surface area, so that the annual oxygen output in the Ocean is almost as large as it is on land - 120 billion tons. Compared to these two oxygen sources, other natural processes that release oxygen are thought not to be worth mentioning. It is not without reason that we call forests lungs of our planet and express our concern by such facts as Brasilia loosing half a billion trees in the year 2018 alone, or several million hectares of coniferous and mixed forests burning down in Australia, Russian Siberia and Brazil.

Still, the above values of oxygen production have to be considered more critically. Green plants produce oxygen (and cellulose) *on the day time*, only, but up to half of that amount is consumed in the night for oxidation processes called plant respiration. Even worse, decomposition of fallen trees by fungi and bacteria eliminates both the biomass and oxygen. The fact that *only young and growing forests accumulate oxygen in the atmosphere and biomass in the form of wood* is often overseen. The truth is that an old mature forest actually does not contribute noticeable amounts of the above two photosynthesis products to the already existing inventory for the reason that bacterial decay and further oxidation of cellulose reverses the photosynthesis process and consumes atmospheric oxygen.

Still, for decades the total balance in the carbon and oxygen cycles was believed to be positive, implying that oxygen in the atmosphere and organic matter on land and in sediments are steadily accumulating. There have been rather early attempts and calls (Davankov, 1998; Vernadskyi, 1954; Ronov, 1976) for a more critical quantitative correlation between the total amounts of oxygen and organic carbon on Earth. Such correlations are essential for the verification or disproval of the still popular theory of the biogenic origin of oxygen.

Let us consider mass balance of the photosynthesis process presented as a normal chemical reaction in its most general form, as follows:

Photosynthesis

44 18 Degradation 30 32 (g/mole)

We notice that one molecule of carbon dioxide and one molecule of water produce, at the expense of solar energy, one oxygen molecule and one basic unit of carbohydrates. The latter mainly polymerize to cellulose. The reaction products are rich in energy and release the accumulated solar energy in the form of heat on reversing the synthesis process, i.e. on consuming oxygen through burning or rotting of the cellulose. Most important for the following consideration is that green plants cannot generate oxygen without increasing simultaneously their own biomass and that *the weight-amounts of oxygen and carbohydrates produced by the photosynthesis cycle are almost equal* (molecular weights 32 and 30, respectively). Total amounts of oxygen and organic matter that are present in the whole system at any moment must be comparable, (provided that no other mechanisms operate which produce or consume the same products – these aspects will be elaborated somewhat later).

The estimated amounts of oxygen and organic matter on Earth are presented below:

Fossil fuels, i.e. coal, oil, earth gas, brown coal and all other types of fuels, are the most important deposits of organic matter (Post et al., 1990). They exceed the amount of living matter by a factor of 3 or more.

In the above values, there is considerable uncertainty about how much dispersed organic carbon is stored in soils and sediments. In his classical paper, by analyzing the ratio between two stable carbon isotopes, ¹²C and ¹³C, in organic matter and mineral carbonates as well as in CO₂-emissions from the Earth's volcanoes (primordial carbon), Schidlowsky (1981) arrived at the conclusion that about 20% of carbonaceous sediments were formed with the participation of living matter. This amount would correspond to 1.4×10^{16} t carbon. However, though corrals and mollusks may well facilitate the process of formation of carbonate sediments, thus influencing the ratio between carbon isotopes, it must be emphasized that these marine organisms deposit carbon in its oxidized CaCO₃ form. The only exception represent proteins and carbohydrates which happened to survive consumption by other living organisms, slow oxidation or anaerobic degradation and can still be found as trace impurities in mineralized sediments. Thus, contrary to Schidlowsky, we do not refer the 20% of carbonaceous sediments as "organic carbon", since what matters for our considerations is the present oxidation state of carbon rather than its history. We assume that real organic matter survived in mineralized calcium carbonates in much smaller proportions, only.

Still, Ronov (1976) estimates the total mass of "organic carbon" buried in the continental and oceanic sediments during the post-Cambrian period (around 500 million years ago, as various multi-cellular organisms emerged and life started to occupy continents) as high as 9.1×10^{15} t, which would correspond to 24.3×10^{15} t oxygen. He adds later that during the same period of time, 94% of that oxygen amount (missing 22.8 \times 10¹⁵ t oxygen) were spent for the "oxidation processes of biosphere matter (living and dead) as well as for the oxidation of iron, manganese, sulfur and other polyvalent elements in mountain rocks, sediments and waters". This is an obscure statement, as the origin, nature and amounts of the "oxidized dead biosphere matter" (methane ?) are not specified and oxidation of the living biosphere matter would simultaneously eliminate both this organic carbon and the corresponding amount of oxygen. Important in Ronov's estimations is his statement that the major part of oxygen generated by living organisms has been spent for numerous oxidation processes.

Long-term carbon sink and recycling into the mantle has been treated in details by Hilton et al. (2002) and Barry et al. (2019). Still, organic matter in all kinds of sediments remains badly defined and its amounts remain poorly estimated.

As to the estimated reserves of earth gas and earth oil, there is another uncertainty about the origin of these hydrocarbons. Initially it was generally assumed that they present products of thermal degradation of the above residual organic matter transported with sediments into 2-4 km-deep layers and in exceptional cases - on the depth down to maximum 8 km. Besides the heat and high pressure, the degradation reactions of organics with the formation of oil and gas hydrocarbons could be well catalyzed there by certain minerals. At the same time more than 1000 commercial petroleum fields are known producing oil and/or natural gas from rocks at the depths of 4500-10,685 m (Sugisaki and Mimura, 1994), where the biogenic organics could hardly be delivered. Therefore, hypotheses on abiogenic origin of deep petroleum and natural gas deposits saying that they were mostly formed by inorganic means, rather than by the decomposition of organisms, steadily find many additional scientific arguments (Sugisaki and Mimura, 1994; Kutcherov, 2013). Indeed, conditions in the asthenosphere, the layer of the Earth between 80 and 200 km below the surface, are considered to enable reduction of carbonates and water by iron oxide to methane, according to the formal thermodynamically favorable reaction

 $CaCO_3 + 12FeO + H_2O = CaO + 4Fe_3O_4 + CH_4$

In the first reliable and reproducible laboratory experiments, in the temperature interval 900–1500 K at 2–5 GPa pressure which correspond to the upper mantle conditions, formation of heavier alkanes (ethane, propane, and butane) from methane was observed (Kutcherov et al., 2002; Kolesnikov et al., 2009). Besides, primordial hydrocarbons could also form from hydrolysis of metal carbides, since deep interior may contain more than 90% of total Earth's carbon in its various forms and compounds (Hazen et al., 2012). The occurrence of diamonds in kimberlite natural rocks is further evidence of the presence of reduced carbon in the Earth's interior. Interestingly, some diamonds were found to include hydrocarbon fluids and gases. Thus, "Presence of abiotic hydrocarbon fluids in the Mantle of the Earth is scientifically proved evidence" (Sugisaki and Mimura, 1994).

Some additional arguments and factors also speak in favor of very feasible abyssal abiogenic origin or formation of large amounts of earth oil and gas, such as.

- Methane is a highly abandoned form of existence of carbon in the Universe.
- Giant gas fields have been discovered to occur in very deep synclines where gas must be generated, rather than accumulated from decomposition of buried organic residues (Masters, 1979).
- The presence of methane and other hydrocarbons on Saturn's moon Titan and in the atmospheres and on the surface of Jupiter, Saturn, Uranus and Neptune testify for the presence of hydrocarbons in the initial nebula that gave birth to planets; these hydrocarbons were formed without any biogenic assistance.
- Extremely large deposits of methane hydrates in see-bottom sediments and permafrost areas (Makogon et al., 2007) are difficult to combine with the idea of biogenic origin of the gas.
- There is a lot of organic matter in carbonaceous meteorites, or chondrites, comets, asteroids.

Though of many estimations of all kinds of biogenic fossil fuel reserves and living and dead organic matter which could be found in the literature, we have deliberately selected the above presented most optimistic figures, the total sum of organic material that can be expected to exist on Earth at present times still yields to the amount of free oxygen in the atmosphere by at least two orders of magnitude.

Coming back to the estimation of amounts of oxygen hypothetically

generated by photosynthesis we can mention that, in addition to the free atmospheric oxygen, one should also add some less known quantities of oxygen that are dissolved in waters of rivers, lakes and oceans. However, incomparably greater amounts of oxygen have been used up for oxidizing methane, hydrogen, ammonia, etc. of the initial atmosphere, as well as oxidizing many iron(II) and sulfur(II)-containing salts and minerals to higher oxidation states. Thus, Schidlowsky (1981) estimates 57% of total oxygen being consumed by formation of Fe₂O₃ from salts of Fe(II) in the ocean and on land, and 38% of oxygen being used up for oxidation of sulfides to sulfates, with only 4% of "biologically produced" oxygen representing the free oxygen in the modern atmosphere and oceans. Anyway, the actual amount of oxygen that should be involved into our balance consideration is probably by two orders of magnitude larger than the existing in the atmosphere 10^{15} t O₂. Accordingly, if all oxygen present in the atmosphere and spent for manifold oxidation processes were generated by photosynthesis reactions, the amounts of simultaneously produced organic matter would exceed by nearly four orders of magnitude (!) the organic masses which we can find as living and estimated as hidden from our sight under Earth's surface. The above mentioned supposition that DIFs were formed by chemotropic bacteria without consumption of oxygen do not affect our arguments, since oxygen had to be consumed anyway by subsequent elimination of equivalent amounts of the "dead biosphere matter".

On the other hand, transformation of cellulose to pure carbon or coal with emission of water from carbohydrates reduces the weight of organic matter by a factor of 2.5, only, which does not solve the above dramatic contradiction between the amounts of oxygen and organic matter, at all.

4. Another look at the carbon/oxygen balance

Certainly, manipulating large figures does not sound very convincing. Let us try therefore to approach the same problem at a smaller scale. Air pressure at the Sea level amounts to 1 atm or 1 kg air per 1 cm². Each square meter of the surface carries 10 t air or 2.315 t oxygen. Simultaneously, over two tons of organic matter should have resulted from the photosynthesis of the above air oxygen. This would correspond to the weight of an old oak tree or a dozen elephants residing on each square meter of Earth's surface (living organisms mainly consist of water, but it is dry weight of organic carbon, only, that matters). That high concentration of organic matter should be characteristic of every spot on our Earth, including oceans, deserts and Polar Regions, in order to justify the now existing free oxygen, alone! Remembering that about 95% of total "biosphere-produced" oxygen has been spent for oxidation of minerals and methane, the amount of buried organic mater should be another hundred times greater (!). Meanwhile, estimates of the organic carbon held in tropical forest vary by region and forest type from 150 to 250 tones per hectare, with an additional 100 tones per hectare in the forest soils. This means that there is less than 50 kg carbon per m^2 or less than 200 kg cellulose per m^2 of tropical regions. There is nowhere sufficient organic matter in the rainforests that could balance the 2 tones of atmospheric oxygen still existing above each square meter of Earth's surface (!), not to mention the 100 times larger O2 masses spent for oxidation (!).

It is much easier to imagine several tons of coal or oil hidden under each square meter of the surface. But specialists find it absolutely impossible to be wrong by several orders of magnitude in their estimations of total amounts of biogenic fossil fuels and buried organic matter.

Several important conclusions should be made from the above severe contradiction between the known amounts of free oxygen and organic matter. First, an exhaustive global fire, when burning down everything on and under the Earth's surface, would not consume more than 1% of atmospheric oxygen. Maybe, just by intuition, when burning coal, earth oil and gas we are more concerned about the overproduction of carbon dioxide than about excessive consumption of oxygen. Second important conclusion is that oxygen in the atmosphere of our Earth was not produced by photosynthesis in green plants alone.

5. Water as a source of free and oxidation-spent oxygen

To find an additional, if not major, source of oxygen on Earth, we must pay more attention to the only one *steady* and *non-cyclic* natural process that generates oxygen. Water molecules, when irradiated in the outer layers of the atmosphere, are easily split into oxygen and hydrogen atoms. The latter, being extremely light, gradually escape to space, thus leaving heavy oxygen atoms in the gravitation field of the planet. Indeed, by multiplying the very early rough estimations of Earth's annual oxygen production through this process, a quarter million of tons (Hutzinger, 1980) to nearly two million tons (Brinkman, 1969), with the Earth's age of circa 4 billion years, we obtain figures of the same order of magnitude as is the current amount of free oxygen on Earth. Our idea thus is to examine intently the role of water as a possible source of free oxygen.

Water is the most abandoned three-atomic molecule in the Universe and, definitely, it was presented in sufficient amounts in the initial nebula around the young Sun. We do not know for certain how much water are hidden in the bodies of giant gas planets. But we can suggest that Earth-like planets Venus and Mars have received comparable to our Earth portions of water. Where is their water now?

Information gathered by the Curiosity rover, in particular studying the abundance and isotopes of argon in the Martian atmosphere, suggests that Mars once had a much thicker water reach atmosphere (Mahaffy et al., 2013) as well as a lot of liquid water. Estimated amounts of liquid waters vary between a few tens of meters global coverage (Plaut et al., 2007) and ~70% of the Earth's ocean (Erkaev et al., 2014). Mars still has preserved some frozen water in the coldest polar area. More recently a lake of liquid water was discovered at a depth of 1.5 km under the north pole of Mars. The most important distinguishing features of Mars are that it is about 10 times lighter than Earth and is not protected from the solar wind by a measurable magnetic field. Because of the low gravitation force, Mars lost almost all gaseous and volatile components of its initial atmosphere already three to four billion years ago. The thin remaining modern Mars' atmosphere mainly consists of heavier carbon dioxide and small admixtures of nitrogen and argon. Importantly, traces of hydrogen in the Martian atmosphere are highly enriched in deuterium. The latter fact implies that its water vapors experienced radiolysis and partial D/H discrimination when hydrogen dissipated to space (Erkaev et al., 2014; Greenwood et al., 2008). We can also speculate that at a certain point in time Mars' atmosphere above its oceans contained some oxygen due to the delay in its dissipation, compared to the escape of hydrogen atoms.

The mass of Venus is similar to that of Earth but it receives almost doubled irradiation because its distance from Sun is only 0.72 au and it has as little as no magnetic field. For the same reasons as well as because of the high content of carbon dioxide (96.5%) in its dense atmosphere (92 atm), the planet exerts strong greenhouse effect and its surface is very hot (~475 °C). Therefore, no liquid water could concentrate above the solid crust. Instead, being nearly tree times less heavy than carbon dioxide, water molecules must have occupied the outer layers of the atmosphere and were lost from there preferentially, regardless as such or after splitting into hydrogen and oxygen atoms. Therefore, current Venus is an arid planet (Dolezol, 1989). The large D/H ratio on Venus of about $1.6-2.2 \times 10^{-2}$ (Gillmann et al., 2009), which is two orders of magnitude higher than that on Earth, also implies that very large amounts of water have been split and lost in the early history of Venus. It is only logical to imagine that the initial atmosphere of the planet was mainly composed of water vapor and methane. Because of high temperature, water had no chance to condense to liquid state and was subjected to permanent irradiation. Oxygen converted all methane to the presently dominating carbon dioxide. Contrary to the situation on our Earth, the latter could not be dissolved in liquid water and subsequently precipitated from oceans in the form of carbonates. At a certain stage of evolution, Venus' atmosphere must have contained measurable concentration of oxygen, in addition to carbon dioxide. However, within the first 100 million years oxygen that was left behind the escaping hydrogen has been dissolved and used up for oxidation in the Venus magma ocean (Gillmann et al.,

2009; Lammer et al., 2008; Lichtenegger et al., 2016). Only stable carbon dioxide and some nitrogen compose current atmosphere of our neighbor planet.

When looking at the problem of photolysis of most important gas molecules in any planet's atmosphere, we have to take into account that water and methane molecules are light (molecular weights of water, methane, oxygen and carbon dioxide are 18, 16, 32 and 44 g/mol, respectively) and least stable from thermodynamic point of view (negative standard Gibb's energy of formation of methane, water and carbon dioxide, $G_{298,15}$, 50,8, 228.6 and 394,4 kJ/mol, respectively). These data imply that water and methane are preferably exposed to irradiation in the upper layers of atmosphere and readily convert on photolysis into heavier and more stable carbon dioxide. The latter could be washed out from the atmospheres of Earth and Mars (but not Venus) and converted in oceans into solid carbonates. (Traces of oxygen still detectable on Mars and Venus could descend from both H₂O and CO₂ molecules).

The intensity of water photolysis gradually decreased with the changing activity of Sun. It should be taken in consideration that the X-ray and ultraviolet radiation activity of the young Sun was, probably 10 to 100 times that of the present value (Ribas et al., 2005). It is only natural that the oxygen production by photolysis also depends on the current composition of the atmosphere. Oxygen flux was maximal when Earth was hot and its atmosphere mainly consisted of water vapors, methane and newly formed carbon mono- and dioxides. When water condensed to oceans, the content of water and carbon dioxide dropped dramatically while proportion of nitrogen gradually rose to the modern level. The intensity of water photolysis also varied with water partial pressure symbatic with the changing averaged temperature of Earth surface. Importantly, oxygen production by water photolysis is permanent and will never stop during the whole period of existence of wet atmospheres around Earth and other planets.

In a recent thorough theoretical study, Guo (2019) considers in detail the influence of irradiation on Earth's atmosphere. He discusses several photochemistry reactions of H₂O and the effect of photoionization on the differential dissipation of oxygen and hydrogen atoms as well as their ions under conditions of Earth's magnetic field. His model under consideration is the ion-atom mixed atmosphere that mostly includes four species: H, H⁺, O, and O⁺. In fact, with the increase of altitude the ions of H and O become more abundant because of the photoionization. According to the ion-atom model by Guo, enormous amounts of water could have escaped from the atmosphere of Earth-like planets: equivalent to 9.1 and 0.6 to-days Earth's oceans calculated for hydrogen and oxygen dissipation respectively. The enormous difference, 8.5 Earth's oceans, obviously, would correspond to the oxygen that stayed with the planet and was used to oxidize most of initially available oxidation-prone matter as well as for building up free oxygen content of modern Earth's atmosphere. The same model predicts possible loss of hydrogen content of 21.5 Earth's oceans and the loss of oxygen content of 2.6 Earth's oceans for early Venus-like planets.

An earlier model by Hunten et al. (1987) predicted smaller loss of water, namely, 2.8 Earth's oceans for hydrogen and 1.4 Earth's oceans for oxygen with about 1.4 Earth's oceans of oxygen remaining with the planet. Though 6 times less than the above estimations of Guo, the partially lost 1.4 Earth's oceans would contribute 1.6×10^{18} t oxygen to Earth's inventory, which overshoots the current atmospheric content by more than three orders of magnitude! These estimated enormous oxygen masses left with the planet at the expense of lost water could easily convert all primordial methane to carbonates as well as oxidize polyvalent metal ions of Earth' upper crust layers to higher oxidation states. Similarly to the case of Earth, on many exoplanets water photolysis could also result in possible formation of abiotic oxygen-containing atmospheres and partial oxidation of the initially reductive planet-forming matter (Lichtenegger et al., 2016; Wordsworth and Pierrehumbert, 2014).

We may also note here that planet Earth has already irretrievably lost major part of its initial water inventory. Among other, this fact implies that in the former times oceans covered almost the whole of Earth's surface and explains the remarkably large masses of sediments almost everywhere on to-days continents.

6. Conclusion

It has been repeatedly noted that photosynthesis must be considered as a chemical reaction that produces from carbon dioxide and water almost equal weight-amounts of oxygen and organic matter. As early as 1998 Davankov emphasized the drastic discrepancy between the free oxygen in the Earth's atmosphere and the at least 100 times smaller estimated amounts of all living and fossil organic matter. By questioning the notion on biogenic origin of oxygen, he pointed out another permanent but underestimated source of oxygen which is the photolysis of water into hydrogen and oxygen with the preferential escape of hydrogen to open space. Indeed, data generated in the last two decades strongly corroborate the above suggestions and bring to light the urgent necessity in the interdisciplinary reconsideration of the mass balance between available Earth's resources in oxygen and organic matter, on the one hand, and geochemical and geophysical processes involving water, carbon dioxide and oxygen, on the other hand. In view of recent data generated in various brunches of geophysics and life sciences it has become evident that oxygen of the Earth's atmosphere is not the unique specialty of our life-enriched planet, but a rather common evolution step of water-containing matter that was entrapped or acquired by any planet. Critical revision of common notions of the origins of Earth's oxygen will insistently require reconsideration of our views on such fundamental topics of Earth's evolution as the oceans-continents relations, erosion and formation of sediments and minerals, origin and reserves of fissile fuels and earth gas and oil, evolution of the atmosphere and biosphere as a whole, history of other planets, etc. It must be admitted that our knowledge in all these area is really insufficient, thus leaving room to entirely irrational idea like the hypotheses that water on Earth was formed through splitting of carbon dioxide into carbon and oxygen followed by recombination of the latter with protons of solar wind (Merkl, 2015).

Declaration of competing interest

This manuscript is my own scientific work. It has not been published earlier and is not submitted to other publisher.

References

- Aston, F.W., 1924a. Atomic species and their abundance on the earth. Nature 113, 393–395. https://doi.org/10.1038/113393a0.
- Aston, F.W., 1924b. The rarity of the inert gases on the Earth. Nature 114, 786. https:// doi.org/10.1038/114786a0.
- Barry, P.H., de Moor, J.M., Giovannelli, D., Schrenk, M., Hummer, D.R., Lopez, T., Pratt, C.A., Segura, Y.A., Battaglia, A., Beaudry, P., Bini, G., Cascante, M., d'Errico, G., di Carlo, M., Fattorini, D., Fullerton, K., Gazel, E., Gonzalez, G., Halldórsson, S.A., Iacovino, K., Kulongoski, J.T., Manini, E., Martinez, M., Miller, H., Nakagawa, M., Ono, S., Patwardhan, S., Ramirez, C.J., Regoli, F., Smedile, F., Turner, S., Vetriani, C., Yucel, M., Ballentine, C.J., Fischer, T.P., Hilton, D.R., Lloyd, K.G., 2019. Forearc carbon sink reduces long-term volatile recycling into the mantle. Nature 568, 487–492. https://doi.org/10.1038/s41586-019-1131-5.
- Boyce, J.C., Menzel, D.H., Payne, C.H., 1933. Forbidden lines in astrophysical sources. Proc. Natl. Acad. Sci. Unit. States Am. 19 (6), 581–591. https://doi.org/10.1073/ pnas.19.6.581.
- Brinkman, R.A., 1969. Dissociation of water vapor and evolution of oxygen in the terrestrial atmosphere. J. Geophys. Res. 74 (23), 5355–5368. https://doi.org/ 10.1029/JC074i023p05355.
- Brown, H., 1949. Rare gases and the formation of the Earth's atmosphere. In: Kuiper, G. (Ed.), The Atmospheres of the Earth and Planets. Chicago Press, Chicago, p. 258.
- Chu, J., 2016. Study Pinpoints Timing of Oxygen's First Appearance in Earth's Atmosphere. MIT News. http://news.mit.edu/2016/oxygen-first-appearance-earth -atmosphere-0513.
- Cloud, P.E., 1968. Atmospheric and hydrospheric evolution on the primitive Earth. Both secular accretion and biological and geochemical processes have affected Earth's volatile envelope. Science 160 (3829), 729–736. https://doi.org/10.1126/ science.160.3829.729.
- Daines, S.J., Mills, B.J.W., Lenton, T.M., 2017. Atmospheric oxygen regulation at low Proterozoic levels by incomplete oxidative weathering of sedimentary organic carbon. Nat. Commun. 8, 14379. https://doi.org/10.1038/ncomms14379.

Davankov, V.A., 1998. Mystery of earth atmosphere. Chem. Life X Century 6, 76.

- Davankov, V.A., 2016. Homochirality of organic matter objective law or curious incident? Isr. J. Chem. 56, 1036–1041. https://doi.org/10.1002/ijch.201600042, 2016.
- Davankov, V.A., 2018. Biological homochirality on the Earth, or in the Universe? A selective review. Symmetry 10, 749. https://doi.org/10.3390/sym10120749.
- Des Marais, D.J., 2000. When did photosynthesis emerge on Earth? Science 289, 1703–1705.
- Dolezol, T., 1989. Klima-Katastrophe ja oder nein? Teil II: erde und Venus. Droht uns das Schicksal des "hollischen" Planeten? P & M (Philos. Med.) N°11, 82–90.
- Elkins-Tanton, L.T., Seager, S., 2008. Ranges of atmospheric mass and composition of super-earth exoplanets. Astrophys. J. 1237–1246. https://doi.org/10.1086/591433, 685:1237Y1246, 2008 10.
- Erkaev, N.V., Lammer, H., Elkins-Tanton, L.T., Stökl, A., Odert, P., Marcq, E., Dorfi, E.A., Kislyakova, K.G., Kulikov, YuN., Leitzinger, M., Güdel, M., 2014. Escape of the martian protoatmosphere and initial water inventory. Planet. Space Sci. 98, 106–120. https://doi.org/10.1016/j.pss.2013.09.008.
- Farquhar, J., Bao, H., Thiemens, M., 2000. Atmospheric influence of Earth's earliest sulfur cycle. Science 289 (5480), 756–758. https://doi.org/10.1126/science.289.5480.756.
- Gillmann, C., Chassefière, E., Lognonné, Ph, 2009. A consistent picture of early hydrodynamic escape of Venus atmosphere explaining present Ne and Ar isotopic ratios and low oxygen atmospheric content. Earth Planet Sci. Lett. 286, 503–513. https://doi.org/10.1016/j.epsl.2009.07.016.
- Greenwood, J.P., Shouchi, I., Naoya, S., Edward, P.V., Hisayoshi, Y., 2008. Hydrogen isotope evidence for loss of water from Mars through time. Geophys. Res. Lett. 35, L05203. https://doi.org/10.1029/2007GL032721.
- Guo, J.H., 2019. The effect of photoionization on the loss of water of the planet. Astrophys. J. 872 https://doi.org/10.3847/1538-4357/aaffd4, 99 (21pp).
- Hazen, R.M., Hemley, R.J., Mangum, A.J., 2012. Carbon in Earth's interior: storage, cycling, and life. EOS. Trans. Am. Geophys. Union 93 (2), 17–18. https://doi.org/ 10.1029/2012EO020001.
- Hilton, D.R., Fischer, T.P., Marty, B., 2002. Noble gases in subduction zones and volatile recycling. Rev. Mineral. Geochem. 47 (1), 319–370. https://doi.org/10.2138/ rmg.2002.47.9.
- Hoehler, T.M., Bebout, B.M., Des Marais, D.J., 2001. The role of microbial mats in the production of reduced gases on the early Earth. Nature 412 (19), 324–327. https:// doi.org/10.1038/35085554.
- Hunten, D.M., Pepin, R.O., Walker, J.G.G., 1987. Mass fractionation in hydrodynamic escape. Icarus 69 (3), 532–549. https://doi.org/10.1016/0019-1035(87)90022-4.
- Hutzinger, O. (Ed.), 1980. The Handbook of Environmental Chemistry, vol. 1. Springer, Berlin. https://doi.org/10.1002/iroh.19880730514. Part A.
- Kolesnikov, A., Kutcherov, V.G., Goncharov, A.F., 2009. Methane-derived hydrocarbons produced under upper-mantle conditions. Nat. Geosci. 2 (8), 566–570. https:// doi.org/10.1038/ngeo591.

Kutcherov, V.G., 2013. Abiogenic deep origin of hydrocarbons and oil and gas deposits formation. In: Hydrocarbon, pp. 1–28. https://doi.org/10.5772/51549 (Chapter 1).

- Kutcherov, V.G., Bendiliani, N.A., Alekseev, V.A., Kenney, J.F., 2002. Synthesis of hydrocarbons from minerals at pressure up to 5 Gpa. Proc. Rus. Acad. Sci. 387 (6), 789–792. https://doi.org/10.1023/A:1021758915693.
- Lammer, H., Kasting, J.F., Chassefiere, E., Johnson, R.E., Kulikov, Y.N., Tian, F., 2008. Atmospheric escape and evolution of terrestrial planets and satellites. Space Sci. Rev. 139, 399–436. https://doi.org/10.1007/s11214-008-9413-5.
- Lichtenegger, H.I.M., Kislyakova, K.G., Odert, P., Erkaev, N.V., Lammer, H., Groeler, H., Johnstone, C.P., Elkins-Tanton, L., Tu, L., Guedel, M., Holmstroem, M., 2016. Solar XUV and ENA-driven water loss from early Venus' steam atmosphere. J. Geophys. Res.: Space Phys. 121, 4718–4732. https://doi.org/10.1002/2015JA022226.
- Mahaffy, P.R., Webster, C.R., Atreya, S.K., Franz, H., Wong, M., Conrad, P.G., Harpold, D., MSL Science Team, 2013. Abundance and isotopic composition of gases in the martian atmosphere from the Curiosity Rover. Science 341 (6143), 263–266. https:// doi.org/10.1126/science.1237966.
- Makogon, Y.F., Holdich, S.A., Makogon, T.Y., 2007. Natural gas-hydrates a potential energy source for the 21st Century. J. Petrol. Sci. Eng. 56, 14–31. https://doi.org/ 10.1016/j.petrol.2005.10.009.
- Managadze, G.G., Engel, M.H., Getty, S., Wurz, P., Brinckerhoff, W.B., Shokolov, A.G., Sholin, G.V., Terent'ev, S.A., Chumikov, A.E., Skalkin, A.S., Blank, V.D., Prokhorov, V.M., Managadze, N.G., Luchnikov, K.,A., 2016. Excess of L-alanine in amino acids synthesized in a plasma torch generated by a hypervelocity meteorite impact reproduced in the laboratory. Planet. Space Sci. 131, 70–78. https://doi.org/ 10.1016/j.pss.2016.07.005.
- Masters, J., 1979. Deep Basin gas trap. West Canada. Am. Assoc. Petrol. Geol. Bull. 63 (2), 152–181. https://doi.org/10.1306/C1EA55CB-16C9-11D7-8645000102C1865D.
- Matjuschkin, V., Woodland, A.B., Yaxley, G.M., January, 2019. Methane-bearing fluids in the upper mantle: an experimental approach. Contrib. Mineral. Petrol. 174, 1–14. https://doi.org/10.1007/s00410-018-1536-4.
- Merkl, H., 2015. On the origin of water on earth and Mars a new hypothesis. J. Geogr. Geol. 7 (2), 1–5. https://doi.org/10.5539/jgg.v7n2p1.
- Nisbet, E.G., Cann, J.R., van Dover, C.L., 1995. Origins of photosynthesis. Nature 373, 479–480. https://doi.org/10.1038/376026a0.
- Nisbet, E.G., Sleep, N.H., 2001. The habitat and nature of early life. Nature 409, 1083–1891. https://doi.org/10.1038/35059210.
- Nitschke, W., Muhlenhoff, U., Liebl, U., 1998. Evolution. In: Raghavendra, A. (Ed.), Photosynthesis: A Comprehensive Treatise. Cambridge Univ. Press, Cambridge, UK, pp. 286–304.

Paassivirta, J., 1991. Chemical Ecotoxicology. CRC Press. ISBN 0873713664.

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- Pierson, B.K., 1994. The emergence, diversification, and role of photosynthetic eubacteria. In: Bengston, S. (Ed.), *Early Life on Earth*, Nobel Symp. Columbia Univ. Press, New York, pp. 161–180. No. 84.
- Plaut, J.J., Picardi, G., Safaeinili, A., Ivanov, A.B., Milkovich, S.M., Cicchetti, A., Kofman, W., Mouginot, J., Farrell, W.M., Phillips, R.J., Clifford, S.M., Frigeri, A., Orosei, R., Federico, C., Williams, I.P., Gurnett, D.A., Nielsen, E., Hagfors, T., Heggy, E., Stofan, E.R., Plettemeier, D., Watters, T.R., Leuschen, C.J., Edenhofer, P., 2007. Subsurface radar sounding of the south polar layered deposits of Mars. Science 316 (5821), 92–95. https://doi.org/10.1126/science.1139672.
- Post, W.M., Peng, T.-H., Emanuel, W.R., King, A.W., Dale, V.H., DeAngelis, D.L., 1990. The global carbon cycle. Am. Sci. 78, 310–326. https://www.jstor.org/stable/ 29774118.
- Ribas, I., Guinan, E.F., Güdel, M., Audard, M., 2005. Evolution of the solar activity over time and effects on planetary atmospheres. I, High-energy irradiances (1-1700 A°). Astrophys. J. 622, 680–694. https://doi.org/10.1086/427977.
- Ronov, A.B., 1976. Volcanism, carbon sink, life. Regularities of global geochemistry of carbon. Geochemistry 8, 1252–1277.
- Rosen, J., Egger, A.E., 2014a. *History of Earth's atmosphere I*. The origin of the modern atmosphere. Visionlearning EAS-3 (2).
- Rosen, J., Egger, A.E., 2014b. *History of Earth's atmosphere II*. The rise of atmospheric oxygen. Visionlearning EAS-3 (3).
- Schidlowsky, M., 1981. Die Geschichte der Erdatmosphaere. Spectr. Wiss. Hefte 4, 17–27. Schidlowski, M., 1988. A 3800-million-year isotopic record of life from carbon in
- sedimentary rocks. Nature 333, 313–318. https://doi.org/10.1038/333313a0.
 Schopf, J.W., 1993. Microfossils of the early archean apex chert: new evidence of the antiquity of life. Science 260 (5108), 640–646. https://doi.org/10.1126/science.260.5108.640.

- Sugisaki, R., Mimura, K., 1994. Mantle hydrocarbons: abiotic or biotic? Geochem. Cosmochim. Acta 58 (11), 2527–2542. https://doi.org/10.1016/0016-7037(94) 90029-9.
- Thiemens, M.H., 2012. Oxygen origins. Nat. Chem. 4, 66. https://www.nature.com/art icles/nchem.1226.
- Vernadskyi, V.I., 1954. Ocherki Geochimii, Selected Vorks, vol. 1. Acad. of Sci. of USSR, Moscow (Rus).
- Widdel, F., Schnell, S., Heising, S., Ehrenreich, A., Assmus, B., Schink, B., 1993. Ferrous iron oxidation by anoxygenic photosynthetic bacteria. Nature 362, 834–836. https:// doi.org/10.1038/362834a0.
- Wordsworth, R., Pierrehumbert, R., 2014. Abiotic oxygen-dominated atmospheres on terrestrial habitable zone planets. Astrophys. J. Lett. 785 (2), 1–4. https://doi.org/ 10.1088/2041-8205/785/2/L20. L20 (4pp).
- Xiong, J., Inoue, K., Bauer, C.E., 1998. Tracking molecular evolution of photosynthesis by characterization of a major photosynthesis gene cluster from *Heliobacillus mobilis*. Proc. Natl. Acad. Sci. U.S.A. 95, 14851–14856. https://doi.org/10.1073/ pnas.95.25.14851.
- Xiong, J., Fischer, W.,M., Inoue, K., Nakahara, M., Bauer, C.E., 2000. Molecular evidence for the early evolution of photosynthesis. Science 289, 1724–1730. https://doi.org/ 10.1126/science.289.5485.1724.
- Xiong, J., Bauer, C.E., 2002. Complex evolution of photosynthesis. Annu. Rev. Plant Biol. 53, 503–521. https://doi.org/10.1146/annurev.arplant.53.100301.135212.
- Zahnle, K., Schaefer, L., Fegley, B., 2010. Earth's earliest atmospheres. Cold Spring Harb. Perspect. Biol. 1–17. https://doi.org/10.1101/cshperspect.a004895, 2010.