

DISCUSSION

WATER RADIOLYSIS, A POSSIBLE SOURCE OF ATMOSPHERIC OXYGEN

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The paper deals with the radiolysis of World-ocean water and underground water as a possible source of molecular oxygen emission into the Earth's atmosphere. Empirical facts proving this concept are reported. A suggestion is made that in the early stages of the Earth's development when its radioactivity was almost two orders of magnitude higher than at present, radiolysis could be the principal source of atmospheric oxygen, which ensured the conditions for the origin and development of life on our globe. The authors do not rule out the supposition that radiolytic oxygen may support primitive life forms on Jupiter's satellites: Europa, Io, and Ganymede. It was suggested that it is necessary to investigate water and ice radiolysis both under natural conditions and in a series of laboratory experiments, and to consider the expediency of choosing the deposits of radioactive Dictyonema shales and waters of Cambrian-Wendian water-bearing horizon in northern Estonia and in Leningrad District, as well as dumps of radioactive waste of "Silmet" metal works in Estonia as a ground for natural on-site observation.

At present the reduction of biological oxygen regeneration and a decrease (at a rate of 3.8 ppm annually) in the concentration of free oxygen in the atmosphere are observed [1, 2]. By the end of the 70ies the regeneration was $\sim 2 \cdot 10^{11}$ tons/year according to Budyko's data [3]. This reduction is caused by continuing intensive increase in industrial consumption of atmospheric oxygen, the destruction of forests, the advance of deserts, and World ocean and seas pollution by oil products, etc. [4]. This alarming situation draws our attention to non-biological natural processes, which can contribute to the reserve of free oxygen in the Earth's atmosphere. It is usually considered that this contribution is provided by nitrogen monoxide photolysis and hydrogen dissipation from the atmosphere into space. However, the overall power of these two sources is negligible: it is only 11.2 million tons/year according to Walker [3].

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In addition to the above factors, there is another natural process, which has not been studied in detail but can possibly compensate for oxygen depletion in the atmosphere caused by industrial oxygen consumption and large-scale felling of timber. This is water radiolysis due to natural radioactivity and producing oxygen and hydrogen. V. Vernadsky has paid attention to it long ago [6]. He wrote: "Free oxygen isolation without the influence of life has been proven or is extremely likely in connection with radioactive decay processes" and "can be evaluated: this is the decay of water molecules due to the effect of α - and partly β -radiations of radioactive element atoms which are found everywhere" [6].

It is not possible to determine a reliable balance of free oxygen in the Earth's atmosphere without taking into account the powers of all its emission sources and consumption items. Corresponding researches at the dumps of radioactive waste of the *Silmet* metallurgical enterprise (the town of Silamäe, Estonia) could be informative in this respect, for 5.7 million tonnes of water-saturated industrial wastes of processing of Dictyonema shales, uranium ores and loparite, containing ca. 1200 t uranium, 800 t thorium and 12 kg radium [46] are buried there creating favorable conditions for radiolytic oxygen developing process.

Why Oxygen Isolation during Natural Water Radiolysis Should Be Studied?

Radiolysis phenomenon has been known since the discovery of radioactivity. As early as in 1901 P. Curie et al. observed gas evolution from radium salts. In 1903, Ramsay and Soddy proved that the evolving gas is a mixture of oxygen and hydrogen ("fire-damp") [7]. During the following hundred years extensive literature was published on the problems of the radiolysis of water, chemical compounds, and minerals. Some examples of this literature published in the second half of the 20th century are given in references [7–39]. They deal mainly with analyses and description of observation of natural phenomena and oxygen evolution. In a fundamental book by Vovk [7], this problem is considered more globally. The author reports data on oxygen balance of the Earth's crust oxidation. They show that "the amount of radiolytic oxygen and oxidants formed during water radiolysis and equivalent in chemical effects could more than ensure the observed degree of the Earth's crust oxidation". The problem of increasing the amount of atmospheric oxygen by oxygen formed during water radiolysis was neglected by the author because it was assumed that radiolytic oxygen is completely consumed in processes of rock oxidation in the Earth's bowels.

The comparison of approximately calculated amounts of oxygen formed in Phanerozoic during the radiolysis of waters in the Earth's crust (up to $1.8 \cdot 10^{17}$ t) and ocean ($8.5 \cdot 10^{11}$ t) [8] and those emitted in the photosynthesis processes ($24.3 \cdot 10^{15}$ t) [9] shows that for the past 500 million years the

amount of radiolytic oxygen exceeds that of photosynthetic oxygen approximately seven times [8]. Assuming that the quantity of free oxygen in the contemporary atmosphere, $\sim 1.5 \cdot 10^{15}$ t, is the residue of oxidizing processes taking place for this period in the Earth's bowels and on its surface, it can be seen that this residue is only 0.7–1.8 % of all radiolytic and photosynthetic oxygen formed during this period. All the rest was consumed for oxidation of rocks, minerals and mineralization of organics. The uncompensated increase in industrial oxygen consumption which already in 1995 reached a level of $3.1 \cdot 10^{10}$ t/year was accompanied by a simultaneous decrease in O_2 total annual reproduction in photosynthetic processes to $\sim 1.9 \cdot 10^{11}$ t/year [11]. Taking this into consideration, it is urgent to answer the question whether radiolytic oxygen from the Earth's bowels is introduced into the atmosphere and if it does, what is its quantity.

It is traditionally assumed that oxygen in underground waters, spontaneous and other natural gases should not exist beyond the aeration zone which depending on local conditions is spread to a depth from several meters to half a kilometer. However, in samples of mineralized water collected in the Dnieper-Donets depression at depths from 1220 to 3335 m, oxygen content usually ranged from 10 to 20 % increasing in some bore-holes to 50 % [10]. In Yakutia in the waters of one tin-ore deposit, oxygen content reached 30 % [7]. Also in Yakutia, on a diamond deposit of the "Mir tube", samples of spontaneous gases in mineralized waters of Cambrian limestones and beds of rock-salt collected from water-level decreasing bore-holes 500–600-m deep in 61.5 % of cases contained more than 40 % oxygen. The age of this gas determined by the helium-argon method corresponded to that of rocks from which water saturated with gas originated [8].

In 1985 during the drilling of a water well at the Kopli promontory in Tallinn (Estonia), gas ejection from a depth of 100 m took place. The main rock at this depth is sandstone of the Voronkov and Gdov suites of the Wendian age. The gas contained 96 % N_2 , 4 % O_2 and He traces [12]. Coefficients of correlation between the contents of oxygen in spontaneous gases of the Cambrian-Wendian water-bearing complex (Gdov and Voronkov horizons) and concentrations of uranium-238, radium-226, and polonium-210 in the corresponding waters suggested radiolytic origin of oxygen in these natural waters [13]. These water-bearing horizons spread beyond Estonia to the Leningrad Region from Ivangorod to Ladoga and in many cases exhibit high radioactivity [14]. Therefore, it is desirable to take them into account as a possible testing ground for studying the water radiolysis effect under natural conditions.

While studying natural radiolysis of waters in northern Estonia and Leningrad Region, it is necessary to consider that in those regions, in Lower Ordovician rocks there occurs a layer (up to ~ 7 -m thick) of Dictyonema shales inclined to self-ignition. They are characterized by high uranium content [40, 41] reaching, in some places, industrial concentrations [42] that creates conditions for radiolysis of the impregnating water.

Dependence between γ -activity of shale and value of its kinetic constant of oxygen sorption velocity \bar{U}_s , $\text{ml}^{-2} \text{h}^{-1}$ (according to the technique of Prof. V. Veselovski [43; 44]) was established. At shale γ -activity $< 165 \mu\text{R h}^{-1}$ the dependence is direct, and at greater values it is inverse [45]. We assume that at low γ -activity of shale, ionizing radiations activate shale oxidizability. At higher γ -activity of U-rich Dictyonema shales, more radiolytic oxygen is formed. Relatively rapid and greater oxidizing passivation of uranium-rich shales by radiolytic oxygen reduces their kinetic constant of the oxygen sorption velocity [45]. Detailed research of relationship between the process of water radiolysis and those of oxidation of fossil fuels and industrial materials is interesting from the practical point of view: for preventing self-ignition of Dictyonema argillites and mine fires as well as for studying processes of chemical weathering of rocks.

If future studies will show that the amount of oxygen formed radiolytically from water is sufficient not only for oxidation of rocks in the Earth's bowels and on its surface but also even for partial compensation for industrially consumed atmospheric oxygen, the situation of humanity may be considered less catastrophic than it seems to us at present [4, 8, 11]. Hence, the study of oxygen formation during the radiolysis of water and aqueous solutions with different compositions induced by ionizing radiations of different types, energies, and intensities is not only a vitally important but also a very urgent task. If these processes are sufficiently effective, humanity could compensate for the deficiency of natural oxygen by the radiolysis of water media caused by powerful radiations of spent nuclear fuel and radioactive waste of atomic power plants.

Origin of the Earth's Oxygen Atmosphere

The appearance of the oxygen atmosphere is usually attributed to the beginning of photosynthesis of primitive green aquatic plants. Some researchers believe that this happened in some 2–2.5 billion years ago, and others think that it happened even earlier (more than three billion years ago [47, 48] and base this view on the existence of traces of oxygen-producing organisms in rocks of that age. The initial Earth's atmosphere is considered to be oxygenless. The activity of anaerobic bacteria formed in the primary ocean led to the formation of free oxygen in such an amount that it was sufficient for all natural oxidizing processes and for the formation of free oxygen resources in the atmosphere, which we are still using. These are the general features of the most wide-spread model for the formation of the atmosphere on our globe [48]. However, another model differing from the above view also has the right to exist.

Oxygen is one of the most wide-spread elements in our Solar system [49]. In the bound state in the form of various compounds, its content (wt%) is as follows:

- In the chemical composition of some planets:

Mercury	13.44 %
Venus	30.90 %
Earth	29.85 %
Mars	34.11 %
- In the Moon's rocks 37.5–43.4/40.0 %
- In meteorite substance 32.3 %
 - In stone chondrites 35.0 %
 - In carbon-bearing chondrites 45.3 %
- In the Earth's rocks:

Ultrabasic rocks (dunites, peridotites, pyroxenites, diallagites, kimberlites, etc.)	42.0 %
Basic rocks (basalts, gabbro, etc.)	43.0 %
Medium rocks (diorites, andesites, etc.)	46.0 %
Acid rocks (granites, granodiorites, etc.)	48.7 %
Sedimentary rocks	52.8 %
- Average O₂ content in the Earth's living substance according to A. Vinogradov [49] 70.0 %
- In the organic substance of organisms:

Wood (O + S)	43.7 %
Meadow and steppe grasses, peat-forming plants (O + S)	42.5 %
Aquatic flower plants and bottom algae (O + S)	43.8 %
Plankton algae (O + S)	36.9 %
Zoobenthos and land invertebrates (O + S)	29.9 %
Zooplankton, fish, and land vertebrates	28.0 %
- In the Earth's hydrosphere 85.7 %
- In the atmospheres of the Earth and some planets (the free form):
 In the Earth's atmosphere (vol.%) 20.95% (or 23.15 wt.%, which is equivalent to $1.184 \cdot 10^{15}$ t O₂) [47,48, 52]. According to some data, at present O₂ content of the atmosphere is 20.6–20.7 vol.% [3, 5, 6, 30].
 In the atmosphere of Mars [49–51] 0.1–0.15 %
 In the atmosphere of Venus [49, 50] $<10^{-3}$ %

There are no data about O₂ content of the atmosphere of other planets and other objects of the Solar system at the authors' disposal.

Consequently, the bound oxygen content in all objects of the Solar system ranging from planets and meteorites to minerals and living organisms of the Earth varies from 13.44 % (planet Mercury) to 85.7 % (the Earth's hydrosphere). In all other objects, O₂ content ranges from 28.0 % (zooplankton, fish, land vertebrates) to 52.8 % (sedimentary rocks) with a mean value of 39.5 ± 7.2 %. This relatively regular distribution and high concentrations of bound oxygen in our Solar system and in all objects in it naturally leads to the conclusion that oxygen and its compounds could actively participate from the very beginning in all processes and in all stages of the formation and development of objects in the Solar system. Therefore, it is possible that the Earth's primary atmosphere was already oxygenous, and only the radio-

lysis of ice, underground waters, and waters of the primary ocean of our globe could have been the oxygen source.

An additional argument for this hypothesis is provided in the initial stages of the Earth's development. The total energy release of still existing natural radionuclides (^{238}U , ^{235}U , ^{40}K , ^{85}Rb), and a whole series of radionuclides extinct at present owing to a relatively short half-life periods (^{107}Pd , ^{129}I , ^{146}Sm , ^{205}Pb , ^{236}U , ^{237}Np , ^{244}Pu , ^{247}Cm etc.) 4.5 billion years ago was almost hundred-fold higher than the contemporary release [49, 5 2, 53]. Radiolysis is continuing at present, probably emitting even now a considerable part of free oxygen. It is so far only a supposition and its justification requires serious theoretical development and laborious experimental testing.

Origin of the Life and Water Radiolysis

V. Vernadsky has already written: "Studying the history of the Earth's development we encounter a tremendously important fact the consequences of which are usually ignored: it is *constant chemical aspect* of the Earth's crust during the entire geological time. It is beyond doubt that minerals formed during this time are always identical. Everywhere and always, not only since the Cambrian era but also from the Archean eras the same minerals are formed. There is no change not only in minerals themselves, but their paragenesis also remains the same and their mutual ratios seem identical in all times.

Hence, it should be concluded that geochemical phenomena did not change noticeably from the Archean epoch. It also follows from this fact that the average quantities and the composition of the living substance remained approximately the same during all this tremendously long time. Otherwise, because of the significance of organisms in the geochemical history of all chemical elements, neither minerals nor their compounds could remain identical all the time. *Hence, the quantity of the living matter is probably a planetary constant from the Archean epoch, i.e., during all geological time*" [6].

This conclusion has been confirmed by subsequent investigations including data of super deep drilling. In 3.8 billion years of "the Earth's history known to us now ranging from the Precambrian to our days, the rate of biogenic carbon accumulation in sediments remained approximately the same and was about $3 \cdot 10^{13}$ t/million years" [54].

"Hence, we have not found empirically any indications of the time when the living matter on our globe did not exist. Life on it is geologically eternal" [55].

"Life creates free oxygen but the principal process is related to the creation of organic matter, i.e. of carbon, hydrogen, and oxygen compounds forming all organisms..." In the limits of geological time, "its concentration in the troposphere always remained very close to the contemporary concen-

tration because all land organisms were adapted to it." Consequently, Vernadsky logically concludes that "...free oxygen mass in the biosphere remains constant and geologically eternal..." [56].

It is possible to calculate the quantity of oxygen formed and entering the atmosphere from the content of carbon deposited in sedimentary rocks. One gram of carbon corresponds to 2.66 g of oxygen liberated a long time ago [57]. For example, at the formation of a kukersite oil shale layer (original resource ~9.84 billion t [58]) 2.3 billion t C was accumulated and 6.4 billion t O₂ liberated into the atmosphere, and at the formation of a Dictyonema shale layer (resource ~64 billion t) 6.7 billion t C was accumulated and 17.8 billion t O₂ liberated into the atmosphere.

Proceeding from these data [54] it is possible to evaluate the average annual increase in oxygen mass in the atmosphere during the entire geological history of the Earth known to us. It is $\sim 0.8 \cdot 10^8$ t/year and is only 0.035–0.04 % of the amount of oxygen annually produced by photosynthesis in geological epochs and equal to $(2-2.3) \cdot 10^{11}$ t/year, according to Bgatov's data [47]. These figures show how vulnerable is the equilibrium between biological reproduction and natural oxygen consumption if it is not supported by the flow of non-photosynthetic (radiolytic) oxygen from the Earth's bowels and oceans' waters.

On the Earth the age of which is about $(4.2-6.0) \cdot 10^9$ years (which differs only slightly from that of the Sun and the Universe) [59] a developed organic life existed already 3.8 billion years ago. It deposited the same average amount of carbon in sedimentary rock, and hence emitted the same amount of oxygen into the atmosphere as at present. The composition of ancient sedimentary and metamorphized rocks does not differ from their contemporary composition either. Comparing the Earth's age with data on the time of procaryotes existence in the geological manuscript, G. Zavarzin has drawn the conclusion that they "completely displace the origin of life from the Earth's limits into space" [57]. E. Lippmaa has reached the same conclusion. He wrote: "There is an impression that such a supercomplex structure as nucleohistones was being formed during a longer time period and, possibly, in a larger system than the Earth" [60].

Vernadsky also denies the possibility of abiogenesis. He writes: "Studying the geochemical history of carbon we did not see in it any traces of abiogenesis: organic compounds independent of the living matter, which would evidence the existence of this process during geological time, do not exist". Further, he remarks: "From geochemical and geological viewpoints the problem is not the synthesis of an individual organism but the origin of the biosphere" [6].

Consequently, it is reasonable to assume that the oxygen atmosphere with approximately the same composition as now should have existed on the Earth before bacteria arrived on it from the space. Finding here the conditions favorable for life and development (temperature, water, and oxygen) they multiplied rapidly and colonized the Earth. The only sufficiently power-

ful non-biological source of the formation of the primary oxygen atmosphere indispensable for development of life on the Earth before the appearance of green plants could probably be only water radiolysis.

Hence, the problem of water radiolysis is directly connected not only with those of compensating for the loss of atmospheric oxygen but also with the solution of such fundamental scientific problems as the formation of the oxygen atmosphere and the origin of life on the Earth as well as on other planets.

Water and Ice Radiolysis on Space Objects

Many useful and interesting facts for solving the problem of the origin of the oxygen atmosphere and life on our globe could be found in the information about space investigations already carried out and being carried out now. For this purpose it would be necessary to analyze them from the standpoint of the possibility of radiolysis of water (ice) present on space objects and the manifestations of free oxygen in their atmosphere or dissolved in the hydrosphere (in seas and in water of their bowels). Consequently, we deal with the problem of the existence of conditions sufficient to ensure the possibility of oxidation processes and development of organic or other forms of life on the Solar system's objects.

Mars is of greatest interest in this respect at present. On its surface traces of flowing waters (meandering river beds and ravines) have been detected as well as outcrops similar to those of a series of strata of sedimentary rocks which had been formed in water reservoirs [61,62]. The possible existence of water and free oxygen on Mars in the past is also proved by wide-spread iron oxides on its surface, which cause its red color. At present the following substances are detected in the Mars atmosphere: O_2 – 0.1–0.15 %, O_3 – 10^{-5} %, CO_2 – 95 % и CO – 0.08 % [49, 51]. Free oxygen concentration is low but there is another question: what is its origin? Furthermore, was its content formerly greater than at present and if so, what is the reason for its decrease? Whether it is a product of radiolysis of water residues, which takes place in its bowels or that of the organisms activity, is not known. Life on Mars has not yet been detected. Possibly, it existed in the past. It is supposed that some meteorites with traces of organic life are of Martian origin [63].

The presence of large ice and water masses and the manifestations of volcanism have been found by an American space probe "Galileo" on the satellites of Jupiter: Io, Ganymede, and Europa [64–66]. It is assumed that the heating of internal zones of these moons and volcanism are due to the radioactivity of their bowels. On Europa, the energy of radioactive decay maintains the water of its ocean in the liquid state. The depth of the ocean attains ~100 km (under a ~ 20 km ice layer) [64]. If so, the indications of radiolytic oxygen should probably be expected in the waters of this ocean on Europa as well as on Ganymede and Io because the conditions for its formation exist. It

is necessary to note, however, that NASA's Hubble space telescope has already found ozone's spectral "fingerprint" during observations of Jovian moon Ganymede and detected a thin oxygen atmosphere on Europa, the other moon [67]. Some scientists even hope to find primitive microbes in the ice and waters of these moons considering that the conditions in Europa's ocean are similar to those of the "Vostok" lake with a primitive ecosystem found in Antarctica under the 4 km ice layer [68]. In this respect the new geothermal theory of life origin on the Earth with the catalytic participation of Fe, Ni, and Co sulfides is of interest [69].

Conclusions

It follows that the problem of water radiolysis is directly related not only to the necessity of replacing atmospheric oxygen losses caused by its present intensive industrial consumption and insufficient photosynthetic reproduction. A number of other fundamental global problems not yet completely solved should be regarded from a new angle and require further study as well. They include the formation of the oxygen atmosphere on the Earth and other planets and objects of the Solar system, the appearance of life on the Earth, the share of non-biological sources in the debit item of the oxygen balance of the atmosphere, etc. The main task of primary importance is to elucidate the following problems:

- 1) Is the radiolysis of underground and sea waters under contemporary conditions a really significant source of increasing oxygen resources in the Earth's atmosphere?
- 2) Is it probable that radiolysis could have been this source in the early stages of the Earth's development as well as under the conditions of the planets Mars, Neptune, and Pluto, and of Jupiter's moons?

The solution of these problems will, first, make it possible to evaluate objectively the present situation of oxygen in the Earth's atmosphere and, second, to confirm or reject the hypothesis about the Earth's initial oxygen atmosphere. The Dictyonema shale layer and waters of Cambrian-Wendian water-bearing horizon containing radionuclids in northern Estonia and in Leningrad District, as well as dumps of radioactive waste of "Silmet" metal works in Estonia could be objects for natural on-site observation.

These investigations are in essence fundamental but at the same time they are of practical importance for humanity. They will permit to establish impartially and completely the role of water radiolysis as a tentatively most important non-biological source of molecular oxygen in the oxygen balance of the Earth's atmosphere. Researches on interrelation between radiolysis of water/moisture of combustible minerals, rocks and industrial materials, and processes of their oxidation/weathering are of practical interest from the point of view of struggle against deterioration of their quality and self-ignition.

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