Oxygen Production During the Evolution of the Earth's Atmosphere

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OXYGEN is the key element for the existence and development of life, based on carbon as the basic structural atom. This vital element, whose function was discovered by A. Lavoisier, 1774, has been appreciated even more since oxygen has come into use as an aid in high altitude flights and as a therapeutic means in certain diseases and emergency cases. Today, with the beginning of the Space Age, this bioelement attracts increased interest with regard to manned space operations to other celestial bodies. It may therefore be appropriate to discuss its origin and rate of production during the evolution of the earth's atmosphere and the processes by which oxygen was produced, with some side remarks about other planets. This should be of special interest to those who are professionally interested in aviation medicine, space medicine, astrobiology, paleobiology, and cosmology.

Two natural processes of oxygen production in the earth's primordial atmosphere must be considered—a physical and a biological one. The first has been discussed extensively in recent astrophysical and geochemical books by G. P. Kuiper,[5] K. Rankama, Th. G. Sahama[14] and H. Urey,[16] as well as in several textbooks and periodicals.[2,3,8,13,14] The intent of this paper is to concentrate on the biological aspects. However, in order to obtain a complete picture of the subject, the physical process must also be considered briefly.

During the early stages of the earth's formation, the protoatmosphere* contained no oxygen. The main constituents in the order of their abundance were hydrogen (H_2), helium (He), neon (Ne), water (H_2O), ammonia (NH_3), methane (CH_4), and argon (A). Because hydrogen and hydrogen compounds were the main components, this was a reduced and reducing atmosphere.

The question then arises: How, when, and in what amounts did oxygen (O_2) enter this oxygen-free protoatmosphere?

According to J. H. J. Poole,[8] and P. Harteck and H. G. D. Jensen,[4] the first oxygen was produced by photochemical dissociation of water at the outer border of the gaseous envelope of the earth. In this process, the water molecule was split by ultraviolet radiation into hydrogen and oxygen. The hydrogen escaped into space; the oxygen with its larger atomic weight remained in the atmosphere. This theory has now displaced an earlier one according to which the water molecules were decomposed by heat (thermodissociation) (G. Tamann,[14] L. Wild[17]). It has been calculated that the present amount of oxygen in the atmosphere could be produced by photodissociation within a period of 60 million years. But the merits of the two theories are still disputed by astrophysicists and geophysicists.

Be that as it may, an initial stock of oxygen appeared in the earth's protoatmosphere by a

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*The protoatmosphere of the earth was that gaseous envelope which surrounded our planet in its developmental stage as a protoplanet. This stage embraces the period of time during which the concentration of the dust cloud surrounding the sun into planetary bodies was completed or nearly completed, and the surface of the earth was a solid or semisolid crust. The time of this stage is estimated as 4 billion years in the past.

physical process. In this mode of oxygen production the parent molecule is water; the effective agent is solar ultraviolet radiation and the process is called *photolytic.*

Later on, a biological process became much more important. This process is *photosynthetic* in nature. It requires two kinds of parent molecules—water and carbon dioxide. Carbon dioxide originated in the proto-atmosphere through the oxidation of methane as soon as some photolytically produced oxygen was available. The photosynthetic process requires light-energy and the organic substance chlorophyll as an enzyme. In photosynthesis, organic compounds of the carbohydrate category are built up and at the same time oxygen is liberated, according to the overall formula:

$$6\ CO_2 + 6\ H_2O + \text{light energy} \rightarrow C_6\ H_{12}\ O_6 + 6\ O_2$$

In textbooks on botany, oxygen is usually considered a "by-product" of photosynthesis. This may be a proper appraisal for the present time where we enjoy an oxygen stock of more than one quadrillion tons in the atmosphere. From the standpoint of the evolution of the atmosphere, however, oxygen was just as much a main product of photosynthesis as the organic matter produced in this process.

The question now is: When did this process commence, and at what rate did oxygen accumulate during geological times?

Paleontology shows us that chlorophyll-bearing organisms such as green algae existed in the Precambrian age, more than 500 million years ago. From the Huronian era of the upper Precambrian or Proterozoic age, relics have been found that are properly identified as calcareous algae. They belong to the class of chlorophyceae, or green algae and it is evident that they must have reached a state of considerable evolution at that time. The Collenia bed in the Beltian series of the Glacier National Park in Montana, for instance, is formed by the alga collenia, which was a calcareous alga. These algae formed mold-like colonies, precipitating calcium carbonate in globular structures with fine concentric laminations. They are also found in this form in the upper Huronian layers on the Belcher Islands in Hudson Bay. This formation originated about one billion years ago. Similar structures have been found even in the upper part of the Keewatin system in Minnesota. The Keewatin period is the early phase of the Archaic era. It precedes the Laurentian orogeny, and may stem from a time more than 1.5 billion years ago (for more detail see C. O. Dunbar[3] and E. S. Borghoorn[1]). Very recently St. A. Tyler and E. S. Borghoorn[15] discovered blue-green algae in non ferrogenous cherts of the gunflint iron formation of southern Ontario. The age of this Precambrian formation may approach two billion years.

Thus, chlorophyll apparently existed 1.5 to 2 billion years in the past*—perhaps at first in other forms or as precursors of bacterial chlorophyll and protochlorophyll as we know them today. Protochlorophyll can be extracted from the inner coats of seeds of certain plants (pumpkin). It is of interest to note that in the absence of oxygen, etiolated seedlings (grown in the dark) do not produce chlorophyll even when properly illuminated.[6] This indicates that the formation of chlorophyll from its precursors involves the process of oxidation. If so, the development of chlorophyll requires a pre-existing store of oxygen. In the proto-atmosphere, oxygen would have been available from the stock produced by photochemical dissociation of water, as we have mentioned. New phylogenetic studies on chlorophyll may bring interesting results and shed new light on this problem.

It has been calculated that the present vegetation on all of the earth's continents could within 27,000 years replace the entire amount of oxygen in the atmosphere—about 1.2×10^{21}g. If we include the green vegetation in the oceans (plankton, etc.), the time decreases to as little as 3,000 years (see Rabinowitsch[9]). This estimate is of course based on present-day vegeta-

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*In contrast to chlorophyll, which is instrumental in producing oxygen, the blood pigments which serve as oxygen carriers like chlorocruerin, the precursor of hemoglobin, may not be much older than ½ billion years.

tion, not necessarily equal in amount to that found on earth in earlier times.

It may be of interest to speculate on the rate of oxygen production in the first phase after the appearance of chlorophyll. Let us assume that the earliest chlorophyll-bearing organisms were unicellular algae of the type of chlorella, belonging to the protococcacean group. Assuming that they multiplied from one parent cell at the rate of two per day, we would have one billion cells within thirty days. If the exponential growth could continue at this rate, we would get in six months as many cells as there are atoms on earth. This shows that once a single cell has evolved the process of filling all the earth's oceans to capacity is practically instantaneous as compared to the time scale of geological processes.

According to J. Meyers,[7] 2.3 kg of alga chlorella pyrenoidosa will under optimal conditions produce about 25 liters or 37 gm of oxygen per hour—the equivalent of one man's consumption. Hence, starting with 1 kg fresh weight of an alga of the protococcacean type with a multiplication factor of 2 per day and under undisturbed conditions, the present atmospheric amount of 1.2×10^{21} gm of oxygen could have been produced in just two months (sixty-one days).

All this is a purely mathematical speculation, assuming simplified conditions. Yet, it demonstrates the power of living matter in a most spectacular way. Actually, the growth of microorganisms follow the so-called logistic curve. Slow at the start, it rises exponentially until it finally finds environmental restrictions of a physical or biotic nature and levels off. This S-shaped curve is characteristic for the course of multiplication or growth of bacteria in a culture medium. There are no objections to the assumption that this growth function is applicable to the large scale rise and fall of many biological species in the vast culture medium of the oceans and on lands.

One important factor influencing the multiplication rate is temperature. If the temperature was higher than it is today, the multiplication rate might have been greater. We know that thermophilic bacteria are able to multiply every ten minutes. Similar observations have been made with algae. Assuming a higher temperature, it seems reasonable to suppose that the oxygen production in the photosynthetic stage of the protoatmosphere took even less time to change the environment into its present chemical composition than would be the case under present temperature conditions. Moreover, a higher carbon dioxide concentration may have been another factor favoring a rapid production of photosynthetic oxygen in the late phase of the protoatmosphere. And finally, there probably were fewer, if any, higher creatures to feed upon the algae than is the case today.

What, then, is the present turn-over rate of oxygen on the earth? Considering all types of land areas including forests, cultivated lands, underbrush or uncultivated land, and deserts and calculating their oxygen output based on the amount of carbon dioxide consumed (A. Schroeder[12])—we arrive at a total land oxygen production approaching fifty billion metric tons per year.

The oxygen production of green plankton and other ocean plants must also be taken into account. However, it is difficult to estimate (see Rabinowitsch[9] for more details). Furthermore, to appraise the actual oxygen level of the atmosphere and the sea, we have to allow for the consumption of oxygen by the living world, and for its absorption by the lithosphere. But this is beyond the scope of our discussion.

The appearance of oxygen has had a decisive influence on the composition of our atmosphere. Reduced compounds like ammonia and methane, found in the protoatmosphere, were oxidized to nitrogen and carbon dioxide. Thus the reduced and reducing conditions of the protoatmosphere have been transformed over a transitional period into the oxidized and oxidizing conditions of our present atmosphere.[5,16]

The initial stock of photolytically produced oxygen may have conditioned the environment for chlorophyll-bearing plants. They in turn set the stage, in a burst of photosynthetic activity, for the development of higher plants and animals.

Thus, oxygen is an essential element in the luxuriant development of life on our planet. Yet, due honor must be given to the parent chemicals which are water and carbon dioxide, and to solar radiation.

The consideration of the oxygen production during the evolution of the earth's atmosphere is of course of special interest with regard to the history of the atmospheres of other planets. The outer planets have still atmospheres of the primordial type. The atmospheres of the inner planets, Venus and Mars, went through the process of oxydation similarly to that of the earth; however, with different results due to different solar radiation intensities and different gravities. Whether or not biological processes have been involved in their atmospheric transformations remains to be explored on the spot by means of astronautical operations. Such a comparison would also lead to the problems of accidental contamination and intentional inoculation of other planets with terrestrial photosynthetically effective microorganisms, a subject matter which has recently become a frequent topic of scientific discussions.[11] This however goes beyond the frame of this paper and will be discussed elsewhere. But the history of the earth's atmosphere in its physical, chemical, and biological aspects will in this regard provide background information and serve as an astrobiological model.

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