

The Natural History of Oxygen

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ABSTRACT The nuclear reactions occurring in the cores of stars which are believed to produce the element oxygen are first described. Evidence for the absence of free oxygen in the early atmosphere of the earth is reviewed. Mechanisms of creation of atmospheric oxygen by photochemical processes are then discussed in detail. Uncertainty regarding the rate of diffusion of water vapor through the cold trap at 70 km altitude in calculating the rate of the photochemical production of oxygen is avoided by using data for the concentration of hydrogen atoms at 90 km obtained from the Meinel OH absorption bands. It is estimated that the present atmospheric oxygen content could have been produced five to ten times during the earth's history. It is shown that the isotopic composition of atmospheric oxygen is not that of photosynthetic oxygen. The fractionation of oxygen isotopes by organic respiration and oxidation occurs in a direction to enhance the O^{18} content of the atmosphere and compensates for the O^{18} dilution resulting from photosynthetic oxygen. Thus, an oxygen isotope cycle exists in nature.

I. INTRODUCTION

Although it is estimated that oxygen is only the third most abundant element cosmically (1) coming behind hydrogen and helium, in that order, it is the most abundant element on the earth's crust, which is important for the living race as oxygen is essential for life.

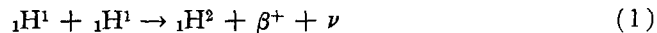
As we shall see later, oxygen was very probably not present in the early atmosphere of the earth, so it is interesting to consider how oxygen arose in the atmosphere, whether its abundance is now changing, what its isotopic composition is, and how the latter varies between samples of oxygen from different sources. Furthermore, there is probably a close connection between the origin of life on this planet and the growth in the abundance of atmospheric oxygen as recently emphasized by Berkner and Marshall (2). Before considering the interesting factors involved in the development of atmospheric oxygen, however, we shall take up first the history of the formation of the element oxygen in the cosmos. It should be emphasized that many of the conclusions described below must be considered not in the same light in which we view well grounded scientific laws and principles, but rather as the best

intelligent guesses and deductions that we can now make on the basis of presently available facts and theory.

II. COSMIC FORMATION OF OXYGEN

It is believed that the energy radiated by a star throughout most of its life comes from the so called hydrogen-burning nuclear reaction in which hydrogen is converted to helium (3). If this is true, then at zero time the universe must have consisted largely and probably solely of hydrogen, because there are few nuclear reactions which spontaneously produce hydrogen. In other words, hydrogen is continually being converted to helium and heavier elements and because it is the most abundant element in the universe today it must have been present in overwhelming amount and very possibly completely pure at zero time.

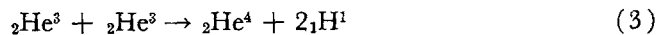
The hydrogen-burning reaction in which helium is produced is the most efficient energy producer, but the actual mechanism probably depends on the temperature of the star. At relatively low temperatures and in the early stages of a star's life before much He^4 has been produced, the hydrogen-burning chain reaction consists of the following steps:



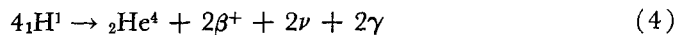
where β^+ represents the positron and ν the neutrino,



and

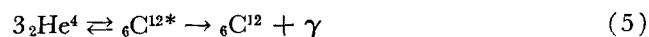


where γ represents a gamma ray photon. The total energy yield is 26.2 Mev (equivalent to 6×10^8 kcal per mole of ${}_2\text{He}^4$) for the net process which is



(There is a 2 per cent energy loss due to the production of the neutrino.) There are other mechanisms for He formation but the above is believed to be the most important.

As the hydrogen is consumed in the core of the star to form helium, no further nuclear transformations can take place until both the temperature and density have greatly increased. At temperatures of 10^8 °K and densities of 10^5 gm cm^{-3} ${}_6\text{C}^{12}$ can be produced by the nuclear reaction



with an energy release of 7.3 Mev per atom of ${}_6\text{C}^{12}$. This reaction probably

occurs during the red-giant phase of a star's evolution and this era of the star's life may last 10^7 to 10^8 years. The helium-burning phase is also responsible, it is believed, for oxygen formation inasmuch as when ${}_6\text{C}^{12}$ becomes sufficiently abundant the following exothermic reaction is possible

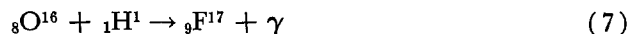


whose energy release is 7.2 Mev per atom of ${}_8\text{O}^{16}$.

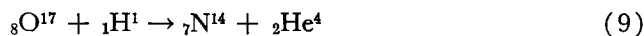
TABLE I
THE ISOTOPES OF OXYGEN (5, 6)

Isotope	Nuclide mass	Atom percentage in air	Nuclear reactions for their preparation	Half-life	Radiation emitted	Cost \$/gm as water (44)
				<i>sec.</i>		
O^{14}	14.0085	0	$\text{N}^{14}(p, n)\text{O}^{14}$	76.5	β^+, γ	
O^{15}	15.0030	0	$\text{N}^{14}(d, n)\text{O}^{15}$	118	β^+	
O^{16}	15.994915	99.7587				
O^{17}	16.999134	0.0374				1,000 (15 per cent)
O^{18}	17.999160	0.2039				400 (97 per cent)
O^{19}	19.0027	0	$\text{F}^{19}(n, p)\text{O}^{19}$	29.5	β^-, γ	
O^{20}	20.0040 (45)	0	$\text{O}^{18}(t, p)\text{O}^{20}$	13.6	β^-, γ	

Oxygen has two stable isotopes, masses 17 and 18, discovered by Giauque and Johnston (4) in 1929. O^{17} can be produced by the sequence of reactions



whose net energy release is slightly exothermic, but the O^{17} is mostly destroyed by the even less exothermic reaction



and by neutron capture to make the somewhat more abundant isotope of oxygen, ${}_8\text{O}^{18}$, viz.



with an energy release of 8.0 Mev.

All the other known isotopes of oxygen are radioactive with quite short half-lives (see Table I). These half-lives are so short that tracer studies using radioactive oxygen are not practical. Instead, the stable isotope O^{18} is used, or possibly the much more expensive O^{17} which has a nuclear spin of $\frac{5}{2}$ and

can be detected, therefore, through nuclear magnetic resonance measurements.

We now pass through the speculative phases (7) in the earth's history of its formation beginning with the breaking up of the solar nebula, continuing on to the condensation of some of its matter into protoplanets, the slow evaporation and escape of 99 per cent of the mass of the earth's protoplanet into interplanetary space lasting about 10^8 years until we come to the earth with its present mass and primitive atmosphere.

III. THE EARLY ATMOSPHERE OF THE EARTH

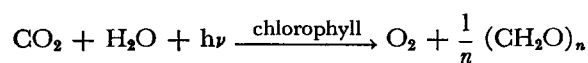
The earth now has an atmosphere completely different from that of any other celestial body in the universe whose atmosphere is known (see Table II), but

TABLE II
COMPOSITION OF PLANET ATMOSPHERES (8)
Units, centimeters of gas at standard temperature and pressure above the visible surface*

Planet	Mean distance from sun	H ₂	Ar	N ₂	O ₂	CO ₂	CH ₄	NH ₃	H ₂ O
	<i>miles</i> × 10 ⁻⁴								
Mercury	35.99								
Venus	67.24			?	<200	50,000	<20	~<4	<100
Earth	92.91	<1	7,400	625,000	168,000	200	2	0	2000
Mars	141.74		2,000	178,000	<200	420	<10	<2	10
Jupiter	483.90	D					15,000	<0	
Saturn	887.2	D					35,000	<250	
Uranus	1,785.0	2×10 ⁶					150,000		
Neptune	2,797.0	D					250,000		
Pluto	3,670.0								

* D signifies that the gas is undetectable but probably is a dominating component.

it was not always so unique. There is abundant evidence that oxygen was not present in the original earth's atmosphere. Chamberlin (9) has summarized the facts which briefly may be listed as follows: the earth's crust is still sub-oxidized, the rocks of which can and do take up oxygen primarily to oxidize ferrous iron to ferric and to a lesser extent to oxidize manganous and sulfur compounds. Ferrous iron in hot lava absorbs free oxygen and even extracts oxygen from water to form Fe₃O₄ and H₂. The reactions in a hot volcanic eruption are an important source of free hydrogen in the atmosphere. The oxygen that today is found in the atmosphere was produced by the photo-synthetic reaction



in which 1 mole of the product oxygen is chemically equivalent to 1 mole of the reactant carbon dioxide. If the carbohydrates formed in the reaction eventually are reduced to coal or fossil fuels, then the sum of the carbon in the latter should be chemically equivalent to the free oxygen of the atmosphere. Actually a considerable excess of carbon is now recognized, hence there is no necessity for assuming the presence of any free oxygen in the initial atmosphere of the earth. In fact, Rubey (10) has estimated that the entire carbon-oxygen ratio of the earth's crust, atmosphere, hydro-, and biospheres, can be accounted for by an approximately 3 to 2 ratio of CO_2 and CO "which is within the range of occluded CO_2 and CO proportions actually found in igneous rocks."

The reason that we made the statement above that all of the oxygen of the present atmosphere was produced by the photosynthetic reaction is that only approximately 2000 years are required to produce all of the atmospheric oxygen (2). This is a very short time on the geologic time scale.

Two other arguments against the existence of free atmospheric oxygen in the primeval atmosphere are the following: It is generally assumed that life on this planet could not have arisen in an oxidizing atmosphere. For example, Miller (11) was able to synthesize amino acids by passing an electric spark through a mixture of CH_4 , NH_3 , H_2 , and H_2O , but no organic compounds were formed when the gas mixture was only CO_2 and H_2O . Abelson (12) found that $\text{CH}_4 + \text{N}_2 + \text{H}_2\text{O}$ gave amino acids in an electric discharge, but not when $\text{CO}_2 + \text{N}_2 + \text{H}_2\text{O}$ was the gas mixture. In the presence of oxygen and light, especially ultraviolet light, the lifetime of amino acids would be very short. Thus, these authors believe that for life to have started, free oxygen must have been absent from the early atmosphere.

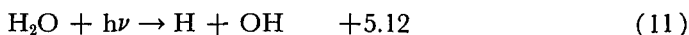
The second reason for the absence of oxygen in the early atmosphere stems from the deduction of Brown (13) that because most of the neon and a large fraction of the other inert gases escaped from the earth during its formation from its protoplanet, no free gas could have existed in the atmosphere. Only those gases were retained that could be retained chemically, H_2O , CO_2 , O_2 , and N_2 . For oxygen to exist as free gaseous oxygen it had to be liberated from chemical combination. Possible mechanisms for such liberation *via* photochemical means are discussed in the next section.

IV. THE PHOTOCHEMICAL THEORY OF THE FORMATION OF ATMOSPHERIC OXYGEN

A. Photochemical Reactions

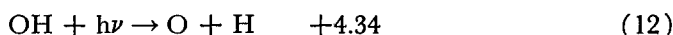
Although the greatest energy of the sunlight striking the earth per 50 Å range of wavelength is in the visible (2) at about 4500 Å wavelength, nevertheless, there is considerable energy in the ultraviolet region of the spectrum. As the wavelength is decreased to 2000 Å or lower, water and then carbon dioxide

begin to absorb the ultraviolet light. At 2000 Å the photons have enough energy on absorption to dissociate water vapor according to the reaction

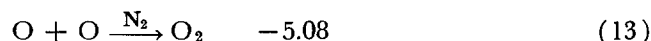


(The energies of reactions will be given in units of electron volts per event; a plus sign signifies energy absorbed. Energies of many reactions have been collected by the author (14). $h\nu$ represents the photon.)

The hydroxyl radical, OH, produced in reaction (11) can also absorb at even longer wavelengths than the water molecule itself and undergo further decomposition according to the reaction

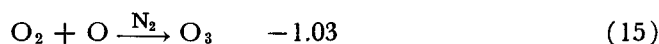
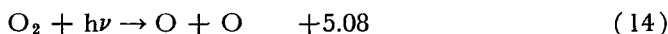


Atomic oxygen formed in this reaction can unite with another atom of oxygen in the presence of a third body such as a nitrogen molecule to form molecular oxygen

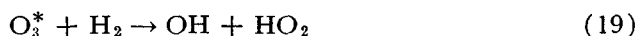
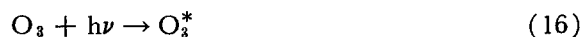


Thus, it is not difficult to understand how molecular oxygen could have arisen in the earliest times. There are serious problems, however.

In the presence of ultraviolet light, oxygen also absorbs (see Fig. 1) to form atomic oxygen which then reacts in the presence of a third body to produce ozone according to the reactions



The ozone absorbs ultraviolet light up to considerably higher wavelengths than does oxygen or water. This energy absorption produces electronically excited ozone molecules which can become deactivated by collisions, or which decompose to atomic and molecular oxygen, or which can react with H or H_2 , *viz.*



or



Further reaction of these radicals would lead to water formation. The yield of the reaction is one-half molecule of hydrogen reacted per quantum of light absorbed by the ozone (15). For each molecule of water formed one atom of free oxygen is lost and reactions (11) and (12) essentially reversed.

Obviously, for oxygen to build up in the atmosphere it is necessary for hydrogen to escape into outer space. The author some time ago (14) considered many possible reactions that might trap atomic hydrogen and pre-

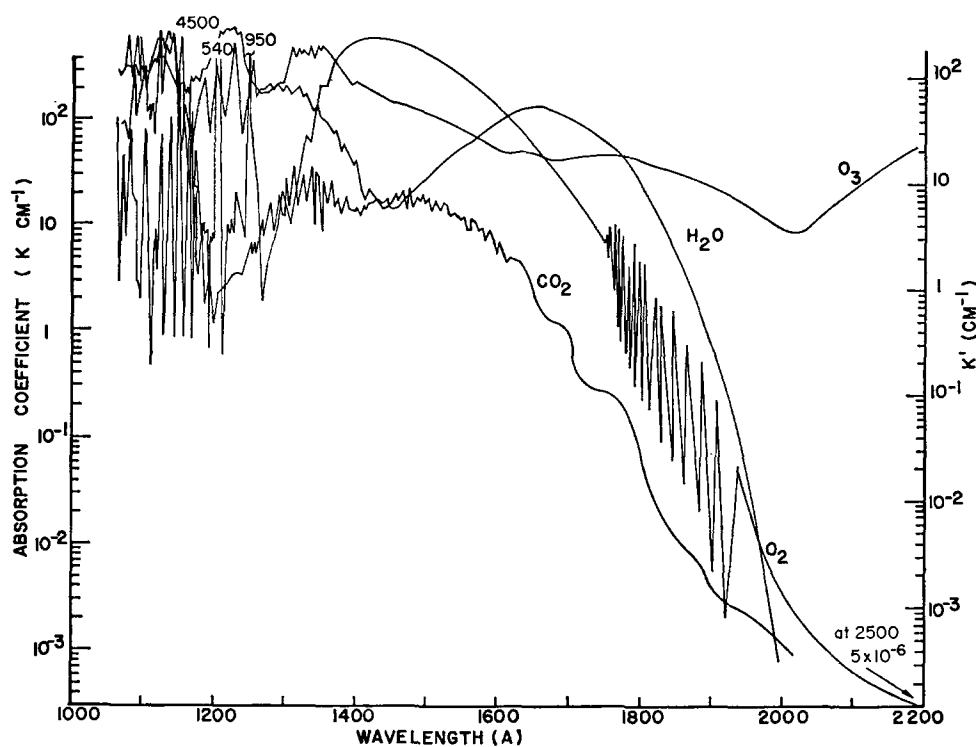
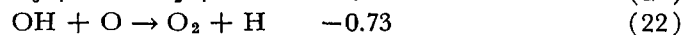
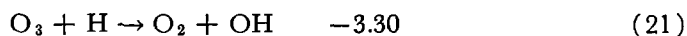


FIGURE 1. Ultraviolet absorption coefficients at different wavelengths for some atmospheric gases from Berkner and Marshall (2). *Figure reprinted by permission of the Faraday Society from Discussions of the Faraday Society, 1964, 37, 122.*

vent it from escaping, but he could find none that looked very plausible. Even at heights in the atmosphere where both ozone (16) and atomic hydrogen can be produced, about 90 km, the following reactions are believed to occur (17)



The net result is simply $\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2$ leaving the H atom concentration unchanged. Evidence for these reactions is found in the Meinel OH bands at

10,400 Å in the spectrum of the night sky (17). The energy, 3.30 eV of reaction (21), is just sufficient to excite OH to the 9th vibrational level and the transitions from this level are found to be the most intense.

B. Rate of Hydrogen Escape

The velocity that any body must have to escape from the earth, v_e , is given by the equation (18)

$$v_e = \sqrt{2gr_e} \quad (23)$$

where g is the acceleration due to gravity, 981 cm sec.⁻², and r_e is the mean radius of the earth, 6.38×10^8 cm. The escape velocity is calculated to be 11.2 km sec.⁻¹ or about 24,000 miles per hour. The temperature required so that the greatest number of hydrogen atoms would have this velocity is 7500°K, an enormously high temperature. But due to the Boltzmann distribution even at normal temperatures a certain fraction of molecules will have velocities equal to the escape velocity. The equation for the number of molecules leaving unit area per second with an upward component of velocity and speeds greater than v_e is (18)

$$\frac{n}{2\beta\sqrt{\pi}} (\beta^2 v_e^2 + 1) e^{-\beta^2 v_e^2} \quad (24)$$

where n is the number of atoms per cm³ at a height in the atmosphere where the temperature is equal to T°K and β is defined by the equation

$$\beta^2 = \frac{M}{2RT} \quad (25)$$

where M is the molecular weight of the gas and R is the gas constant.

At a height of 90 km in the atmosphere where the pressure is about 10^{-6} atm and the temperature about 200°K, Harteck and Reeves (19) have estimated that there are 1.5×10^9 H atoms cm⁻³. Under these conditions the number of H atoms escaping per cm² per second is 0.15. At this height a shell about the earth would have a surface area of 5.26×10^{18} cm² so that the total number of H atoms escaping per second would be 7.50×10^{17} or in terms of moles of H₂O, 0.62×10^{-6} . There are 3.15×10^7 seconds per year, so that 19.6 moles of water are lost per year. Inasmuch as there are 7.6×10^{19} gm atoms of oxygen in the present atmosphere, it would take $7.6 \times 10^{19}/19.6$ or about 4×10^{18} years to produce all of the oxygen of the atmosphere by this mechanism, a fantastically long time. However, if the hydrogen atoms are at a height of about 125 km where the temperature is 500°K (20), then the number escaping per cm² per second becomes 5.8×10^8 H atoms, or

1.62×10^{11} gm atoms of H per year from the earth. This is equivalent to 0.95×10^9 years to produce all of the atmospheric oxygen. Thus, during the earth's estimated age of 5×10^9 years, the entire amount of atmospheric oxygen could have been produced about 5 times if all the escaping H atoms came from the photochemical dissociation of water molecules.

The next problem concerns the rate at which H atoms can diffuse to the 125 km layer and the rate at which water molecules can migrate from the troposphere to high enough regions in the stratosphere to be dissociated by the ultraviolet light from the sun.

C. *Rate of Upward Diffusion of Water and Hydrogen*

Some years ago Harteck and Jensen (15) considered the rate at which water vapor could diffuse from the 12 to 20 km height where the temperature is -55 to -60°C to altitudes where photochemical dissociation could occur. They derived the following equation for the diffusional flux, J , in the vertical direction in units of moles cm^{-2} years $^{-1}$:

$$J = c_0 \frac{\rho D}{l} \cdot \frac{1}{1 - e^{-x_0/l}} \quad (26)$$

where c_0 is the mole fraction of the diffusing gas at the lower height, ρ is the density of the atmosphere, and D the gas diffusion coefficient (ρD is a constant at constant temperature and is assumed to be independent of pressure and height), x_0 is the height where the gas concentration is zero, and l is defined by

$$l = \frac{RT}{(M_{\text{air}} - M_{\text{H}_2\text{O}})g} \quad (27)$$

Under normal conditions, ρ is 4×10^{-5} mole/ cm^3 , D is 0.3 $\text{cm}^2/\text{sec.}$, and l , 2×10^6 cm. Estimating the water vapor pressure to be 0.045 mm Harteck and Jensen calculated that in 10^7 years 2 moles of water would diffuse upward per cm^2 of earth's surface. In 3×10^9 years, enough oxygen could be produced to generate the oxygen of the present atmosphere 50 times. Later Kuiper (7) repeated Harteck and Jensen's calculations using better values for the water vapor pressure and obtained a result one-tenth that of Harteck and Jensen, namely a fivefold rather than a 50-fold generation of the earth's oxygen in 3×10^9 years. Kuiper concluded that the "photochemical decomposition of water is an efficient mechanism of O_2 production, having the present rate of roughly twice the atmospheric content per 10^9 years."

Urey (21) also made a detailed calculation of the rate of oxygen production by stratospheric photochemical processes. Using more refined equations in which he assumed a linear increase of temperature with height, and an esti-

mate of the water vapor pressure considerably lower than that of Harteck or Kuiper, he deduced a rate of H atom escape about 500 times less than the rates given above. However, any turbulence or mixing in the stratosphere would raise Urey's estimate. But the whole problem of the partial pressure of water vapor can be avoided by considering only the rate of H atom escape as explained below. Although some of the H atoms of reaction (21) may have come from the photodissociation of CH_4 , the low abundance of the latter and the probability of its reaction with ozone or nitrogen oxides at lower levels indicate that this source of H atoms can be neglected.

But for the O_2 photochemical process to leave a residue of free atmospheric oxygen, the H atoms must diffuse from the lower cold levels to higher hot levels where their kinetic energy will be sufficient for escape. Using equation

TABLE III
RESULTS OF ESCAPE AND DIFFUSION CALCULATIONS
(Assuming H atom concentration at 90 km to be 1.5×10^9 atoms/cm³)
H atom escape

Conditions		No. of H atoms escaping/cm ² sec.	Yrs. to reproduce O ₂ in present atmosphere
Height	Temperature		
90 km	200°K	0.15	4×10^{18}
125	500	5.80×10^8	0.95×10^9
Water diffusion calculations			
20	260 (Harteck and Jensen, 1948)		0.83×10^8
40	270 (Kuiper, 1952)		0.62×10^9
H atom diffusion			
90	220 (average)	1.5×10^9	0.42×10^9
Estimated age of earth			5×10^9

(26) to make this calculation from the 90 km level assuming the H atom concentration to be 1.5×10^9 /cm³ as before, it turns out that 0.42×10^9 years would be required for enough H atoms to diffuse so that the present atmospheric O₂ content could be generated. The results of the diffusion and escape calculations are collected in Table III.

If the H atom concentration is 1.5×10^9 atoms/cm³ at 90 km, the concentration would probably be somewhat less than this at 125 km; therefore, the calculation of the rate of the H atom escape at 125 km may be too fast by the ratio of these concentrations. Nevertheless, it would appear that these new estimates based on recent determinations of the H atom abundance at 90 km confirm the earlier deductions of Harteck and Jensen and of Kuiper, that the photochemical dissociation of water vapor to oxygen and hydrogen during the lifetime of the earth has been of considerable geological significance.

V. OXYGEN AND THE ORIGIN OF LIFE

A. *Obstacles to Life in the Earliest Times*

Intelligent life as we know it requires an extremely specialized environment whose temperature and composition have to be carefully regulated within rather narrow limits for life to survive, as was pointed out in a masterly fashion many years ago by L. J. Henderson (22). In the earliest times because of less intense radiation from the sun, the earth may have been somewhat colder than it is today (23), in which case the oceans may have either not yet been formed or may have been too cold, *i.e.* frozen, so that photosynthesis could not have occurred. The initiation of life may have had to await, therefore, a certain warming up of the earth.

Another obstacle to the creation of life in the earliest times must have been the intense ultraviolet radiation striking the earth's surface. In Fig. 1 the absorption coefficients in the ultraviolet are plotted for a number of gases and it can be seen that only ozone has a significant absorption coefficient for wavelengths greater than about 2000 Å. In fact, the absorption coefficient of ozone goes through a maximum (24) at 2537 Å equal to about 135 cm^{-1} . This means that in the early atmosphere before the high altitude accumulation of ozone, the ultraviolet intensity at the earth's surface must have been great enough to be lethal to many organisms. Especially the combination of oxygen, even if the latter is present only at low concentrations, with ultraviolet light would be particularly deleterious (12). Berkner and Marshall (2) have recently reemphasized the need for a protective ozone layer to shield the earth from the lethal ultraviolet radiation. More importantly, they have shown a possible connection between the various stages in the evolution of life and the levels of oxygen concentration in the atmosphere. It should be noted, however, that Urey (21) has suggested that there may have been organic components in the early atmosphere of sufficient abundance to have provided a primeval ultraviolet screen.

B. *The Early Chemistry of Atmospheric Oxygen*

As soon as the water vapor content of the atmosphere rose to significant levels, *i.e.* as soon as the earth warmed up if it had been cold, the photochemical process for the production of oxygen must have started. At altitudes of 10 km and above the processes going on would be little affected if at all by the condition of the earth's surface. As soon as oxygen was produced it would begin diffusing downwards. As soon as it reached the top of the troposphere, about 10 km, it would rapidly mix with all the gases of the troposphere because of winds and turbulence in the latter.

Because the formation of free atmospheric oxygen depends on the escape of hydrogen from the earth and because the latter may have occurred slowly,

probably the oxygen that diffused to the earth in the earliest time was entirely consumed by oxidation of components of the earth's crust. However, oxygen would build up in the upper atmosphere until its rate of production equalled its rate of diffusion to the earth's surface. If we assume that the rate of production is correctly given by the value calculated from the H atom diffusion, namely 3.7×10^8 molecules of O_2 /sq. cm sec. (Table III), then by the use of equation (26) we can calculate the value of c_o necessary to make J equal to 3.7×10^8 . In this calculation we assumed that the diffusion occurred over the height from 40 to 10 km, that the average temperature was 270°K, and that ρD was equal to 7.5×10^{-6} moles/cm sec.; c_o is the ratio of molecules of oxygen to that of nitrogen. The calculation yielded about 3×10^{-4} for c_o or about 1.2×10^{-3} of the present ratio. This abundance of oxygen is very small, and not enough to screen effectively the earth from the ultraviolet rays of the sun.

We conclude that for many millions of years there was not enough oxygen in the earth's atmosphere to be of significance in protecting the earth from the lethal ultraviolet sunlight.

C. *Photosynthetic Production of Oxygen*

Following Berkner and Marshall (2) it seems evident that the simplest life forms must have arisen in the oceans, perhaps in relatively stagnant bays (example, Phosphorescence Bay off the coast of La Parguera, Puerto Rico), at depths great enough so that the water protected them from the lethal ultraviolet rays, up to 30 feet (2). As soon as algae developed, photosynthesis could begin, thereby greatly accelerating oxygen production. Berkner and Marshall (2) associate the rise of oxygen in the atmosphere to 1 per cent of its present level with the beginning of the Cambrian era, about 550,000,000 years ago, when there was an evolutionary explosion.

VI. THE ISOTOPIC COMPOSITION OF ATMOSPHERIC AND PHOTOSYNTHETIC OXYGEN

A. *The Isotopic Composition of Various Oxygen Sources Compared*

The present oxygen of the atmosphere must have been produced by the photosynthesis reaction, because it takes only about 2000 years to regenerate photosynthetically all of the free oxygen of the atmosphere. It would therefore be expected that its isotopic composition would be that of photosynthetic oxygen. Very surprisingly it is not.

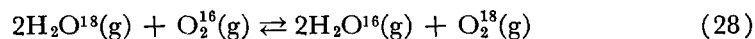
During the first third of this century, one would not have even thought to question oxygen's isotopic composition. In the first place the isotopes of oxygen were not discovered (4) until 1929, and in the second place it was one of the principles of chemistry that no isotope separation could occur in

any chemical reaction, that the element oxygen always had exactly the same ratio of isotopes irrespective of the substance in which the oxygen was combined. Even after the discovery of heavy hydrogen by Urey, Brickwedde, and Murphy (25) and of the rather rapid electrolysis separation method by Washburn and Urey (26) which was carried to an exciting completion by G. N. Lewis (27), there was still some question whether such separations would be possible with other elements. The author recalls talking with the late Professor R. H. Fowler of the University of Cambridge in the summer of 1933, just after Fowler had returned there from a visit to Lewis at Berkeley. Fowler suggested then that whereas light and heavy hydrogen could be separated because of the 100 per cent differences in their masses, this might not be possible with any other elements. In other words, the hydrogen isotopes might be unique.

TABLE IV
ISOTOPIC COMPOSITION OF OXYGEN
FROM VARIOUS SOURCES

Source	Atomic weights	Atom per cent O ¹⁸
Air	15.9993 ₈ (6)	0.2039
Photosynthesis (in Lake Michigan water)	15.9992 ₈	0.1990
Lake Michigan water	15.9992 ₆	0.1980
Atlantic Ocean water	15.9992 ₈	0.1990
Carbonate rocks	15.9994 ₉	0.2050
CO ₂ (at 0°C in the presence of fresh water)	15.9994 ₃	0.2067

However, Urey and Greiff (28) computed the partition function ratios of various isotope pairs such as [O¹⁸]/[O¹⁶] and [H₂O¹⁸]/[H₂O¹⁶] and concluded that in many isotopic exchange equilibrium reactions like the following



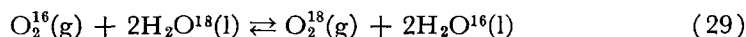
the equilibrium constant would be slightly greater than unity. Within a month or two after the publication of this paper the author (29, 30) discovered a significant difference in the atomic weight of oxygen in the air as compared to the oxygen in Lake Michigan water. A review contains more recent data (31). Other sources of oxygen such as the oxygen in carbonate rocks and iron oxide ores gave still different oxygen isotope ratios (32). Obviously, the element oxygen was not a good standard for the atomic weight scale so the International Committee on Atomic Weights in 1961 abandoned (6) oxygen and chose the carbon-12 isotope as the standard, giving to it an atomic weight of exactly 12.0000.

Table IV summarizes the atomic weights of oxygen from various sources.

The International Committee chose air as the source of oxygen for their table. Dole, Lane, Rudd, and Zaukelies (33) showed that oxygen in air samples taken from all over the world and up to altitudes of 87,000 feet had the atomic weight of oxygen in Evanston air within $\pm 0.000,002$ atomic weight units.

B. *Isotopic Composition of Photosynthetic Oxygen*

As mentioned above, when the relatively rapid turnover of atmospheric, water, and carbon dioxide oxygen is considered, one would have expected atmospheric oxygen to have the isotopic composition of oxygen from the photosynthesis process. A number of investigators (for a review see Kirshenbaum, 34), including the author, have demonstrated that the oxygen liberated in the photosynthesis reaction comes from the water rather than from the carbon dioxide. Dole and Jenks (35) concluded that the liberated oxygen had the isotopic composition to be expected if the following isotopic exchange equilibrium between oxygen and water were established at the temperature of and during the photosynthesis reaction:



The Soviet scientist, A. P. Vinogradov (36, 37), and his group of geochemists believe, on the other hand, that the isotopic composition of the oxygen liberated in the photosynthesis reaction has exactly the isotopic composition of water oxygen and that the very slightly enhanced O^{18} content of photosynthetic oxygen over that of the oxygen of water observed by Dole and Jenks was due to concentration of O^{18} in the gas phase due to plant respiration during the experiment. Fractionation of oxygen isotopes on respiration is discussed below. In Dole and Jenks's experiments the photosynthesizing algae were continuously illuminated while in the work of Vinogradov *et al.* the illumination was natural with a dark period at night. During the latter there would be relatively more respiration than in Dole and Jenks's experiments. Whether the isotopic exchange equilibrium of reaction (29) was established or not, the fact remains that the oxygen liberated in photosynthesis in ocean water has a smaller O^{18} content than atmospheric oxygen.

C. *Isotopic Composition of Oxygen in Air Dissolved in Ocean Water*

Rakestraw, Rudd, and Dole (38) made a careful study of the isotopic composition of the oxygen in air obtained by evacuation of ocean water taken at different depths in the ocean. Their data are illustrated in Fig. 2. A remarkable correlation is seen between the decrease in the percentage of oxygen in the air and the increase in the O^{18} percentage. To quote Rakestraw, Rudd, and Dole, "The conclusion is almost inescapable that marine vegetation,

plankton, bacteria and other sea life which consume oxygen must preferentially metabolize O^{16} at a higher rate than O^{18} to produce this marked isotope fractionation." Further work by Dole, Lane, Rudd, and Zaukelies

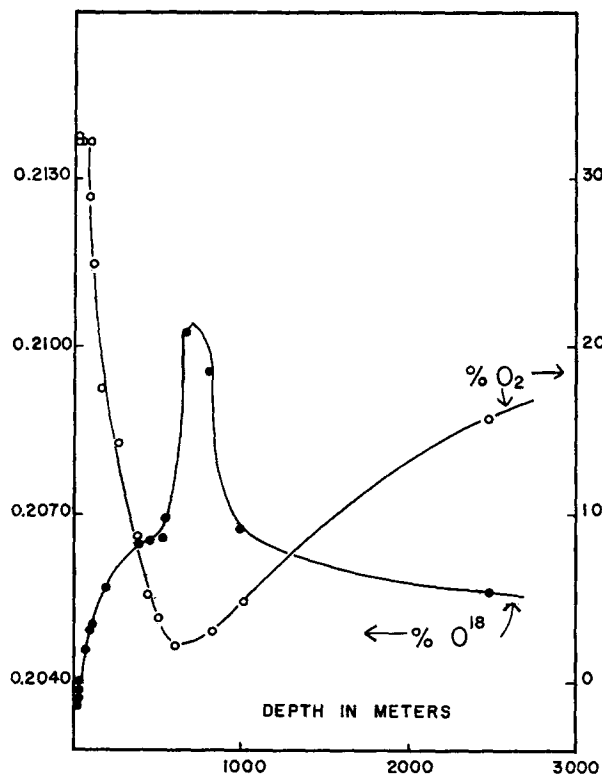


FIGURE 2. Atom per cent of O^{18} in dissolved ocean air at different depths in the Pacific Ocean at $32^{\circ} 10' N$ and $120^{\circ} 19' W$. Also plotted is the volume percentage of oxygen in the air.

(33) confirmed these results and led to a mathematical description of the data in terms of the following equation

$$\frac{1 - \alpha}{\alpha} \ln \frac{c_2}{c_1} = \ln \frac{y_{w,2}}{y_{w,1}} \quad (30)$$

where c_2 and c_1 are the concentrations of oxygen in the ocean water at two different depths, $y_{w,2}$ and $y_{w,1}$ are the O^{18} percentages in the dissolved oxygen at the two depths, and α is the isotope fractionation factor defined by the ratio y_w/y_B where y_B is the average O^{18} percentage in the oxygen consumed by all the living organisms or oxidation reactions going on in the ocean (assumed to be independent of depth and defined at the same depth as y_w). A plot of $\ln c$ versus $\ln y_w$ yielded roughly a straight line from whose slope α was

calculated to be 1.009. There was considerable scatter to the data at low oxygen percentages due in part to the difficulty of making accurate O^{18} percentage measurements in samples of air containing small concentrations of oxygen.

Vinogradov *et al.* (37) explain the above mentioned scatter in terms of variations in temperature of the water at the four different geographical stations at which the dissolved ocean air was collected. Isotope fractionation factors usually change with the temperature. However, the average value of α found by Vinogradov *et al.* (37) in their extensive work was 1.010 which is within the limits of error equal to that found by Dole and coworkers, namely 1.009.

D. Theories of the Enhanced O^{18} Content of Atmospheric Oxygen

We have seen above that the oxygen produced in the photosynthesis reaction does not have the same isotopic composition as the oxygen already in the air, hence there must be some mechanism which tends to enhance the O^{18} abundance in air. Calculations show that the atmospheric O^{18}/O^{16} ratio cannot be the result of the isotopic exchange equilibrium reaction because the equilibrium constant of the latter is much too close to unity. Inasmuch as the oxygen of the air and the waters of the oceans covering most of the earth's surface are in continual contact, there cannot be any isotope exchange going on between the molecular species H_2O and O_2 , otherwise the equilibrium would be established. In fact, there is no known mechanism by which H_2O and O_2 can undergo oxygen isotope exchange in aqueous systems at room temperature; high temperatures and catalysts like platinum are required.

Without taking space here to describe other possibilities which we have considered and rejected, let us turn at once to two reasonable possibilities. The fractionation of oxygen isotopes during the consumption of oxygen in the ocean suggested that this mechanism might explain the enhanced O^{18} content of the atmosphere. Accordingly, Lane and Dole (39) investigated fractionation during respiration of a number of organisms, including *Homo sapiens*. For the small organisms the apparatus used was that of Brown (40). For *Homo sapiens*, oxygen was breathed in through a tube from a reservoir of air whose oxygen supply was continually replenished, and breathed out through another tube. The exhaled breath passed through two large KOH bottles, then through a sampling flask before it was rebreathed. Two rubber balloons attached to the KOH reservoirs enabled the gas volume of the system to expand and contract with each breathing cycle and made it possible to make quick estimates of the amount of additional oxygen required. After a large fraction of the oxygen had been consumed, the isotopic composition of the unreacted oxygen was determined in a mass spectrometer. The fractionation factor α was then calculated from the equation

$$\alpha = \frac{y - y_0 e^{-m/\alpha}}{x_0 - x_0 e^{-m/\alpha}} \quad (31)$$

where y is the atom percentage of O^{18} in the sample at the end of the experiment, y_0 is the O^{18} percentage in the reservoir at the start of the experiment, x_0 is the O^{18} percentage in the oxygen added to the reservoir during the experiment, and m is equal to the ratio of oxygen consumed to the amount initially present. If much oxygen is respired so that m/α is equal to 3 or 4, the exponential terms can be neglected and α calculated directly from the ratio y/x_0 . The results of this work are illustrated in Fig. 3 where the dotted

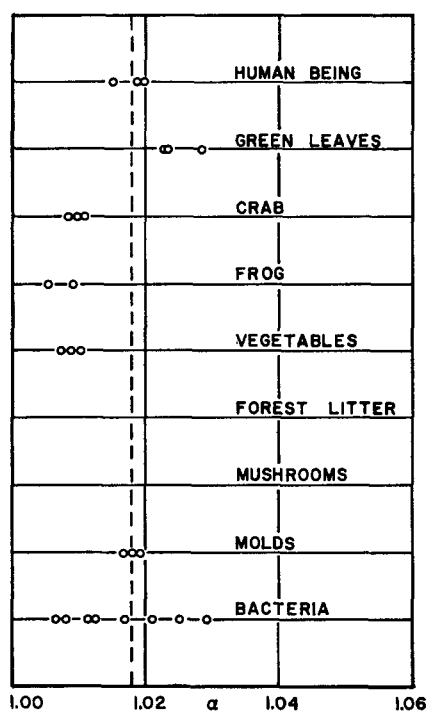


FIGURE 3. Oxygen isotope fractionation factors observed during respiration or organic oxidation.

vertical line represents the fractionation factor necessary to account for the enhanced O^{18} content of the atmosphere. As shown by Dole, Hawkings, and Barker (41) the equation describing the changes per year in the oxygen isotope ratio of atmospheric oxygen is

$$N_1 - N_0 = \frac{\Delta n}{n_{O,16}} [r_2 - r_1] [1 + N_1] \quad (32)$$

where

$N_1 = [O^{18}]/[O^{16}]$ in atmosphere at end of year.

$N_0 = [O^{18}]/[O^{16}]$ in atmosphere at start of year.

Δn = number of gram atoms of oxygen removed from atmosphere or returned to it per year.

$n_{o,16}$ = number of gram atoms of oxygen of mass 16 in atmosphere at beginning of year.

r_2 = $[O^{18}]/([O^{18}] + [O^{16}])$ in oxygen added to atmosphere *via* the photosynthesis reaction

r_1 = $[O^{18}]/([O^{18}] + [O^{16}])$ in oxygen removed from atmosphere *via* respiration or oxidation.

For a constant O^{18}/O^{16} atmospheric ratio it is necessary that r_2 and r_1 be equal. From the photosynthesis experiments r_2 was determined to be 0.2003 atom per cent; if r_1 is also 0.2003, then the fractionation factor on respiration should be 0.2039/0.2003 or 1.018. A value of this factor greater than unity means that O^{16} is consumed at a relatively greater rate than O^{18} .

It will be observed that the measured respiration fractionation factors cluster about the value 1.018. If we assume that the consumption of oxygen is entirely by respiration with allocation to various organisms according to the schedule bacteria, 75 per cent, leaves and roots, 15 per cent, molds and mushrooms, 5 per cent each, a composite α equal to 1.016 results in good agreement with the value required.

However, Vinogradov (37) and his Soviet school point out that respiration accounts for only 15 per cent of the yearly oxygen consumption, the remaining 85 per cent is by organic oxidation. Our forest litter experiments were thought to represent in part, at least, oxygen consumption in the oxidation of organic matter. Note that the two litter experiments yielded values quite close to 1.018, the value required to explain the enhanced O^{18} content of the atmosphere.

In all the studies of respiration and oxidation isotope fractionation, it should be realized that no fractionation will be observed if all the oxygen in any sample of air is consumed. For example, if a pocket of air is trapped in a capillary and all of its oxygen is consumed, there will be no oxygen isotope fractionation. Complete mixing of the gas phase should exist at all times.

Another possible explanation of the enhanced O^{18} content of the atmosphere should be mentioned as this is the theory which Vinogradov *et al.* support. When carbon dioxide is brought into isotopic exchange equilibrium with ocean water, which occurs rather readily, the O^{18} percentage in the carbon dioxide rises to about 0.2078 atom per cent (Vinogradov *et al.* (37) quote 0.2083 per cent) depending on the temperature. If this carbon dioxide is carried into the stratosphere where under the dissociative action of the ultraviolet light of the sun it can *irreversibly* and randomly exchange its oxygen atoms with those of molecular oxygen, then the O^{18} content of atmospheric oxygen will be enhanced. This idea was first investigated by Roake and Dole (42) who demonstrated that oxygen atoms would exchange between carbon

dioxide and molecular oxygen in an electric discharge, but that no exchange could occur between water vapor and oxygen. Vinogradov (37) has calculated that this mechanism could account for the enhanced O^{18} content of the atmosphere. The calculations given below, however, indicate that this process is too slow by about two orders of magnitude.

From radioactive fall-out measurements Vinogradov quotes 10 years as the time for the gases of the stratosphere to mix with those of the troposphere. Let us accept this estimate. The exchange between CO_2 and O_2 can only be assumed to occur above the ozone layer because of the screening effect of the latter on solar ultraviolet radiation. If we adopt the 25 km height and above as the locus of the exchange, we have to realize that the CO_2 - O_2 oxygen atom "scrambling" can occur in only about 2 per cent of the atmosphere. The percentage of O^{18} in the stratosphere above 25 km as the result of all the oxygen in the CO_2 becoming scrambled with the molecular oxygen of the atmosphere is readily calculated from the equation

$$\text{per cent } O^{18} \text{ in stratosphere} = (0.2039) (0.998427) + (0.2078) (0.001573) \quad (33)$$

where 0.998427 and 0.001573 are the total atom fractions in the mixture of oxygen in the O_2 and CO_2 , respectively. In calculating the latter we have used the volume percentages of O_2 and CO_2 in the atmosphere given by Glueckauf (43). The per cent O^{18} in the stratosphere after the exchange between all the CO_2 and O_2 is 0.203,906,134. In 1 year one-tenth of this oxygen will mix with all the oxygen below the 25 km level raising the per cent O^{18} in the troposphere as calculated by the equation

$$\begin{aligned} \text{per cent } O^{18} \text{ in troposphere after mixing with one-tenth of the} \\ \text{CO}_2\text{-exchanged } O_2 &= (0.2039) (0.998) + (0.203,906,134) (0.002) \\ &= 0.203,900,012. \quad (34) \end{aligned}$$

Thus, the CO_2 - O_2 scrambling process should increase the O^{18} percentage in the troposphere by 0.006 ppm.

In 1 year one-two thousandth or 0.0005 of the atmospheric O_2 will be produced by the photosynthesis reaction. This will decrease the O^{18} per cent as calculated according to the equation

$$\begin{aligned} \text{per cent } O^{18} \text{ in troposphere after 1 year's } O_2 \text{ production by} \\ \text{photosynthesis} &= (0.2039) (0.9995) + (0.2003) (0.0005) \\ &= 0.203,898,200 \quad (35) \end{aligned}$$

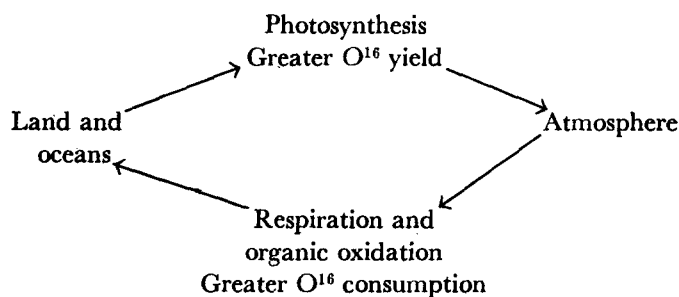
The difference between this number and 0.2039 is 1.8×10^{-6} or 0.9 ppm. Hence the photosynthesis process reduces the O^{18} percentage by 0.9 ppm per year, but the CO_2 - O_2 scrambling process raises it by only 0.006 ppm; hence

the latter is an inadequate explanation of the enhanced O^{18} content of the atmosphere.

The theory of Lane and Dole (39) that fractionation of the oxygen isotopes by respiration and organic oxidation causes the increase in the O^{18} content of the atmosphere seems to be the best from a quantitative standpoint.

E. *The Oxygen Isotope Cycle in Nature*

We can now set up the following steady state cycle of the oxygen isotopes in nature:



In summary, photosynthesis yields oxygen containing a higher O^{16}/O^{18} ratio than the oxygen of the atmosphere, while respiration consumes oxygen containing a higher O^{16}/O^{18} ratio than the oxygen of the atmosphere and the same ratio as that of photosynthetic oxygen, thus leading to the non-equilibrium steady state value of the O^{16}/O^{18} ratio in the atmosphere. In other words, the O^{16} ratio of the atmosphere has been automatically adjusted to just the right value so that the ratios for photosynthetic oxygen delivered to the atmosphere and the oxygen extracted from the atmosphere by respiration and organic oxidation are equal.

VII. THE FUTURE OF ATMOSPHERIC OXYGEN

Berkner and Marshall (2) suggest that during periods of high rates of photosynthesis without much organic matter to consume the oxygen produced, the oxygen may have "overswung" its present level of abundance to a somewhat higher value. During the ice ages of the Permian period, the earth cooled, photosynthesis was reduced "leading to a radical loss of atmospheric oxygen." Thus, it is highly likely that the oxygen content of the atmosphere has slowly fluctuated about a steady state concentration. Furthermore, inasmuch as the H atom escape must still be continuing, even if only at a very slow rate, the net oxygen content of the atmosphere may be slowly rising. Unfortunately, the problem of determining experimentally the atmospheric oxygen percentage over millions of years in the past seems to be insuperable.

The author acknowledges gratefully stimulating conversations with Professor Paul Harteck, Dr. Bertram Donn, and Dr. Walter Weller and the gift of pertinent reprints and manuscripts from these authors as well as from Dr. L. C. Marshall, Dr. D. L. Gilbert, Dr. B. J. Mair, Dr. F. O. Rice, and Dr. F. C. Schmehl.

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