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STABILITY OF ATMOSPHERIC OXYGEN

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ABSTRACT. Estimation of the sources and sinks of atmospheric oxygen yields rates that are large enough, compared to the atmospheric reservoir, to cause substantial changes in 4 m.y. The fossil record indicates that atmospheric oxygen has been relatively constant in amount during a period of time larger by two orders of magnitude. Some negative feedback mechanism must, therefore, control the amount of oxygen in the atmosphere. The important sink is the weathering of reduced material, principally organic carbon, in sedimentary rocks. It is argued that this sink is independent of the oxygen content of the atmosphere under present conditions. The feedback mechanism must therefore be sought in the source, which is stoichiometrically equal to the rate of burial of organic carbon in new sediments. Control appears to be exercised by the relative rates of supply of dissolved oxygen and reduced organic matter to the deeper levels of the ocean. Since the solubility of oxygen decreases with increasing temperature, the warmer global climate that prevailed during much of the Phanerozoic may have produced oxygen partial pressures about 25 percent larger than at present.

INTRODUCTION

In terms of composition, the feature of the atmosphere that most distinguishes Earth from the other planets is the presence of abundant oxygen. The evolution of our oxygen-rich atmosphere and its relationship to the evolution of terrestrial life are subjects that have attracted considerable interest and will continue to do so. We will be most likely to unravel the history of the abundance of atmospheric oxygen if we understand what determines the oxygen content of the atmosphere today. Accordingly, this paper discusses the processes that produce or consume atmospheric oxygen and presents estimates of the rates at which these processes operate. With these processes evaluated, it is possible to examine the factors that control their rates and to arrive at a tentative model for the abundance of atmospheric oxygen. The model may not be correct in every respect, but it is sufficiently quantitative to allow predictions to be made. Thus it may be possible to test and refine the model by reference to the geological record.

GEOCHEMICAL BUDGET

Since the Earth is reducing in overall composition, the presence of free oxygen in the atmosphere must be considered in terms of processes that separate oxygen from its compounds and sequester the reducing material produced (Redfield, 1958; Sillén, 1966). Thus, figure 1 includes not only processes that directly affect the atmospheric reservoir of oxygen but also processes that affect the reservoirs of reduced matter

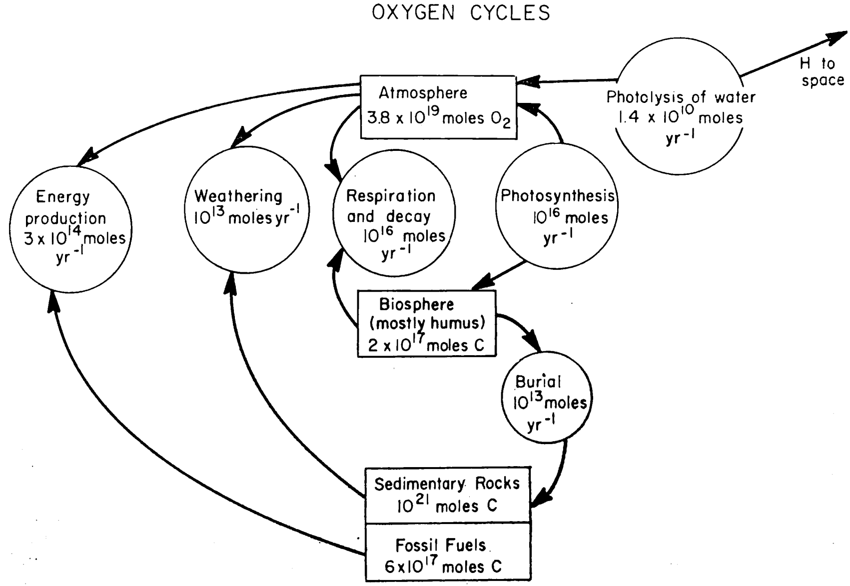

Fig. 1. The geochemical budget of atmospheric oxygen. Sources are cited in the text. In the lower portion of the figure, C denotes reduced carbon, sulfur, and iron; carbonate minerals are not included.

with which oxygen might combine. Since the arguments that follow are stoichiometric in nature, it is convenient to express both reservoirs and rates in terms of moles of oxygen and moles of reduced material. Many of the values presented in figure 1 are subject to large uncertainty, as the discussion will show.

In an effort to keep the model as simple and therefore as comprehensible as possible, I have ignored in figure 1 and in the discussion that follows many processes that affect atmospheric oxygen but that do not appear to me to play a dominant role in determining the oxygen abundance. Thus, for example, I have lumped all the reduced species in sedimentary rocks together and called them organic carbon, rather than treating explicity the oxidation of sulfide and ferrous iron and the reduction of sulfate and ferric iron. These processes are important but not essential.

Escape of hydrogen to space.—The dissociation of atmospheric water vapor by solar ultraviolet radiation initiates a chain of photochemical reactions leading either to the reformation of the water vapor or to the escape of hydrogen from the upper atmosphere to space. Escaping hydrogen atoms leave behind the oxygen with which they were at one time associated, constituting a net source of atmospheric oxygen (compare Kuiper, 1949).

The magnitude of this source may be estimated from data on the density of atomic hydrogen in the exosphere and theoretical values of the rate of escape as a function of density and temperature. Using ion composition data, Joseph (1967) has estimated an escape flux of hydrogen atoms equal to 2×10^8 cm^{-2} sec^{-1}, independent of solar activity. More recent data on ion composition (Brinton and Mayr, 1971) and on ultraviolet airglow (Meier and Mange, 1970; Tinsley and Meier, 1971) yield essentially the same value. The rate at which water vapor suffers photodissociation in the present day atmosphere has been calculated by Brinkmann (1969), who obtains a value of 2×10^9 cm^{-2} sec^{-1}. Evidently most photodissociations are followed by reformation of water and not by escape of hydrogen. Estimates of the oxygen source based on the assumption that every photodissociation is followed by escape are therefore incorrect, at least for the atmosphere as it is today.

Adopting Joseph's value for the escape flux of hydrogen, we calculate an atmospheric oxygen source of 1.4×10^{10} moles yr^{-1}. This is several orders of magnitude smaller than the other sources we shall consider.

Since photodissociation followed by escape is the only oxygen source we know of that does not involve biological activity, it is possible that this source was important in the era before life developed, even though it is negligible today. The rate of photodissociation of water vapor would have been very much larger ($\sim 2 \times 10^{11}$ cm^{-2} sec^{-1} [Brinkmann, 1969]) in the prebiological atmosphere if this atmosphere resembled the present atmosphere in most respects but contained little or no oxygen (Berkner and Marshall, 1965; Brinkmann, 1969). It is not at all clear, however, that the rate of escape of hydrogen would also have been larger (Van Valen, 1971).

In the absence of a theoretical treatment of the relevant photochemical problem, we may consider the evidence from Venus as an example of what can happen in an atmosphere containing very little oxygen. On Venus the rate of photodissociation of water vapor is in the range 2.5×10^9 to 2.5×10^{11} cm^{-2} sec^{-1} (McElroy and Hunten, 1969; Fink and others, 1972), which is larger than the rate of photodissociation of water vapor in the terrestrial atmosphere. The rate of escape of hydrogen from the atmosphere of Venus is very much smaller, however. The estimate of Walker, Turekian, and Hunten (1970), based on the measurements of Barth, Wallace, and Pearce (1968), is 2×10^5 cm^{-2} sec^{-1}. Thus, in the oxygen-poor atmosphere of Venus, only 10^{-4} to 10^{-6} of the photodissociations are followed by escape whereas in the oxygen-rich terrestrial atmosphere the fraction is about 10^{-1}. This argument is far from conclusive, but it suggests the need for caution concerning any assertion that the net source of atmospheric oxygen provided by photodissociation and escape would have been larger in the prebiological atmosphere than it is today.

Most of the processes we shall discuss in this paper are cyclic, with oxygen being released to the atmosphere at one point of the cycle and consumed at another. Photolysis of water vapor followed by escape of hydrogen to space is non-cyclic, however, causing a net gain in the level of oxidation of the atmosphere and crust. There are several non-cyclic sinks of oxygen also, among them the oxidation of primitive igneous rocks and volcanic gases and the accretion of hydrogen from space (Van Valen, 1971). We do not know enough about these sinks to judge whether they are larger or smaller than the non-cyclic source. If they are smaller, then the atmosphere and crust are becoming more highly oxidized; if they are larger, the level of oxidation is decreasing. There is no conclusive evidence as to which of these alternatives is correct.

The non-cyclic sources and sinks of oxygen are important for the long-term evolution of the atmosphere but not for the stability of atmospheric oxygen over time scales of a few hundred million years or less. We shall therefore follow Holland (1973) in concentrating on the more rapid cyclic processes.

Photosynthesis.—For present purposes we may think of photosynthesis as a process in which green plants add reduced organic material and oxygen at equal rates to the biospheric reservoir and the atmospheric reservoir (compare Hutchinson, 1954). We may keep track of the organic material with adequate accuracy by referring simply to the reduced organic carbon. Approximately one mole of organic carbon is produced for each mole of oxygen added to the atmosphere (compare Riley and Chester, 1971, p. 230).

Because of substantial differences in the productivities of different plant communities, it is difficult to estimate with precision the total rate at which photosynthesis produces organic carbon. The value we use in figure 1 is that of Bowen (1966; compare Gilbert, 1972). Bowen's estimate of production by oceanic plants differs little from previous values and agrees with a more recent result, based on a large body of radiocarbon data, of Koblentz-Mishke, Volkovinsky, and Kabanova (1970; compare Ryther, 1969). Bowen, basing his estimate on a review by Westlake (1963), concludes that land plants contribute approximately four times as much to total production as do oceanic plants, a value that is higher than previous estimates for reasons that Bowen describes. We shall argue below that production by land plants has little effect on the oxygen balance of the atmosphere, so the uncertainty in this figure is of little concern.

Respiration and decay.—We may think of respiration and decay as the reverse of photosynthesis, consuming biospheric carbon and atmospheric oxygen at equal rates. From the values presented in figure 1 we can calculate that the average time spent by organic carbon in what we have called the biospheric reservoir is only 20 years. Our value for the size of this reservoir is taken from Bowen (1966, p. 52). The reservoir includes living and dead organic matter on the land, in the soil, and in the ocean. About one quarter of the biosphere reservoir consists of living organisms, mostly plants. About 80 percent of the remainder is in solution in sea water. Some portion of the organic carbon contained in the surface layers of ocean sediments should probably be included in the biospheric reservoir since this carbon is subject to oxidation on a relatively short time scale. The inclusion of this component would increase the size of the biospheric reservoir by approximately a factor of 2.

The arguments that follow, however, depend only on the fact that the biospheric reservoir of carbon is very much smaller than the atmospheric reservoir of oxygen, so we will ignore this correction.

From the short residence time of organic carbon in the biospheric reservoir and the rapid rate of photosynthesis compared with all of the other processes in figure 1, we may conclude that respiration and decay must almost exactly balance photosynthesis (Van Valen, 1971; Holland, 1973) over times longer than about a hundred years (burial of organic carbon is a much slower process, which we shall consider below). Thus we arrive at the rate of respiration and decay shown in figure 1.

From the relatively small size of the biospheric reservoir some useful conclusions can be drawn. Suppose, for example, that the rate of photosynthesis were to be increased slightly by some change in world climate or by efficient agricultural techniques. The biospheric reservoir would increase at a rate proportionately very much greater than the rate of increase of atmospheric oxygen. We may assume that the rate of respiration and decay would increase as the biospheric mass increased, so we may predict that a new equilibrium would be achieved, in due course, with an increase in the amount of organic carbon in the biospheric reservoir but with no significant change in atmospheric oxygen (Van Valen, 1971).

We can see, therefore, that the cycle of photosynthesis followed by respiration and decay, which links a large reservoir of atmospheric oxygen to a small reservoir of biospheric carbon, serves to control not the size of the oxygen reservoir but the size of the biospheric reservoir. This conclusion indicates that the oxygen content of the atmosphere is not directly affected by changes in the rate of photosynthesis such as might be caused, for example, by changes in the partial pressure of carbon dioxide or, through the Warburg effect (compare Turner and Brittain, 1962; Gibbs, 1970), in the partial pressure of oxygen (Broecker, 1970b; Holland, 1973).

The relatively small size of the biospheric reservoir implies, also, that changes in the rate of photosynthesis and thus in the amount of carbon in the biosphere are possible, if they occur slowly, without causing any significant depletion in the supply of the raw materials of photosynthesis, carbon dioxide (3×10^{18} moles in the oceans), and water (10^{23} moles).

The time scale of these hypothetical changes is important as far as the supply of carbon dioxide is concerned. Photosynthesis removes carbon dioxide from the atmosphere and the surface layer of the ocean. The atmosphere contains 5.7×10^{16} moles of carbon dioxide, and the surface ocean contains about 5×10^{16} moles, mostly in the form of bicarbonate ions (Broecker, Li, and Peng, 1971); together they could be exhausted in 10 years if photosynthesis were not balanced by respiration and decay. A much larger amount of carbon dioxide, 3.2×10^{18} moles, resides in the deep ocean, and the rate of transfer of carbon from the deep ocean to the surface is sufficiently rapid to replenish the surface-atmosphere reservoir in about 50 years (Broecker, Li, and Peng, 1971). Thus, substantial growth in the size of the biospheric reservoir over times of a few decades or less will be limited by the supply of carbon dioxide. Changes over times longer than a few centuries can draw on the relatively large deep sea reservoir.

Under what circumstances could a sufficiently large excess of the rate of photosynthesis over the rate of respiration and decay deplete the deep sea reservoir of carbon (Garrels and Perry, 1973)? In terms of Broecker's (1971) model of kinetic controls on the composition of sea water, it appears that changes sufficiently large to affect the rate of photosynthesis would not occur unless the rate of extraction of carbon were to exceed the rate of supply of new carbon resulting from weathering, principally of carbonate rocks. This rate is about 2×10^{13} moles yr^{-1} (Garrels and Perry, 1973). The residence time of carbon in the deep sea is about 10^5 yr (Broecker, 1971), so we can probably neglect possible fluctuations in the abundance of carbon dioxide if we limit our considerations to changes occurring over times longer than 10^6 yr.

Burial of organic carbon.—Even at equilibrium there is a small imbalance between the rates of photosynthesis and of respiration and decay which arises because some of the organic carbon is preserved by burial in sediments. Corresponding to this "fossilization" of organic carbon is a small net source of atmospheric oxygen (Van Valen, 1971; Holland, 1973).

The rate of fossilization of organic carbon can, in principle, be estimated from data on the carbon content and the rate of accumulation of recent sediments. Since both these quantities exhibit substantial variation with position, a reliable estimate is not possible without a very much larger compilation of data than is presently available. We shall assume, rather arbitrarily, that the net source of oxygen due to burial of organic carbon is equal to the rate of consumption of oxygen by weathering, to be discussed below. The following very rough estimates of the rate of burial of carbon show that this assumption is at least reasonable.

According to the values presented in figure 1, we are looking for a rate of burial of organic carbon of about 10^{13} moles yr^{-1}. Consider first the deep sea non-hemipelagic sediments. According to Broecker (1970b) we may take the average carbon content of deep sea sediments as 0.5 percent[1] and the average accumulation rate as 10^{-3} cm yr^{-1} (Ku, Broecker, and Opdyke, 1968). Corrections for the water content of the sediment and its dry density cancel out at this level of approximation, so with an area of 3.6×10^{18} cm^2 (Sverdrup, Johnson, and Fleming, 1942, p. 15) we find a burial rate of 1.5×10^{12} moles C yr^{-1}. Deep sea sediments evidently make a small contribution to the burial of organic carbon.

Consider next some anaerobic basins. For the Black Sea, Deuser (1971) deduces an average burial rate of 4×10^{-4} g C cm^{-2} yr^{-1}. The

[1] This value is probably too high (Romankevich, 1968; R. A. Berner, personal commun.).

area of the Black Sea is 4.1 x 10^{15} cm^2 (Richards, 1965a), so the total burial rate is 1.3 x 10^{11} moles C yr^{-1}. For the basins off Southern California we derive a value of 1.2 x 10^{10} moles C yr^{-1} using data presented by Emery (1960, p. 257). It appears that the role of anaerobic basins is negligible at the present time.

The possibility that burial is occurring mainly in fresh water lakes needs to be examined. Deevey and Stuiver (1964) have derived a rate of burial of organic carbon in Linsley Pond, Conn., of 3 x 10^{-3} g cm^{-2} yr^{-1}. If we assume that Linsley Pond is representative of all the lakes in the world and use an area of 2.4 x 10^{15} cm^2 (Bowen, 1966, p. 44), we obtain a total burial rate of 6 x 10^{11} moles C yr^{-1}. This estimate, which may be too large (R. A. Berner, personal commun.), is negligibly small compared with the 10^{13} moles C yr^{-1} that we are trying to account for.

Consider now the terrigenous oceanic sediments known as hemipelagic "blue mud". They have an average carbon content of 1.7 percent (Clarke, 1924), an accumulation rate of 10^{-2} cm yr^{-1} (Kuenen, 1950, p. 384), and an area of 5.6 x 10^{17} cm^2 (Kuenen, 1950, p. 346). The total burial rate is 8 x 10^{12} moles C yr^{-1}. An alternative estimate of the same burial rate may be made using data presented by Emery (1960, p. 254) for a core on the continental slope off Southern California. In this core the rate of burial of organic material was 8 x 10^{-4} g cm^{-2} yr^{-1}, equivalent to 5 x 10^{-4} g C cm^{-2} yr^{-1}. If we assume that this burial rate is characteristic of all of the sea floor at depths between 200 and 3000 m and use an area of 5.4 x 10^{17} cm^2 (Sverdrup, Johnson, and Fleming, 1942, p. 21; Menard and Smith, 1966), we obtain a total burial rate of 2.2 x 10^{13} moles C yr^{-1}.

We conclude that a rate of burial of organic carbon of 10^{13} moles yr^{-1} is consistent with the limited data available and that almost all the burial occurs as hemipelagic "blue mud" on the continental slopes (Garrels and Mackenzie, 1971, p. 219), where carbon contents and sediment accumulation rates are both high.

Although the rate of burial of organic carbon in lake sediments is negligibly small compared with oceanic sediments and the rate of burial in sub-aerial sediments is probably also negligible (Redfield, 1958), we may not conclude without further examination that land plants do not contribute to the net source of atmospheric oxygen that corresponds to the carbon buried. It is possible that organic material particularly resistant to decay is synthesized on land and washed into the sea, making a significant contribution to the carbon in terrigenous sediments. There is a difference between the isotopic compositions ($^{13}C/^{12}C$) of organic carbon produced by land plants and by phytoplankton that makes it possible to evaluate this hypothesis. The evidence has been reviewed by Degens (1969) and by Williams (1971). While the presence of land-derived organic detritus is clearly discernible in river estuaries, it becomes undetectable in carbon isotope data outside the immediate environs of the river mouth. This evidence is not universally accepted; nevertheless, we shall assume that the net source of atmospheric oxygen corresponding to burial of organic carbon is almost entirely derived from photosynthesis by phytoplankton rather than by land plants.

From this it follows that the cycle of photosynthesis followed by respiration and decay on land is to all intents and purposes closed. Although the total rate of photosynthesis on land exceeds that in the ocean, photosynthesis on land makes no significant contribution to the oxygen budget of the atmosphere. Oxygen is released to the atmosphere at a rate corresponding to the rate of burial of organic carbon in marine sediments, and most of the organic material that is buried is produced by oceanic plants, not by land plants. If this was true also in the past, then the evolution of land plants in the late Silurian was not a significant stage in the evolution of atmospheric oxygen.

Fossilized organic carbon.—A substantial amount of reduced organic carbon has accumulated in sedimentary rocks as a result of burial over the ages. Estimation of the total amount is subject to considerable uncertainty in the volumes of various types of rocks. The value shown in figure 1 for the size of the sedimentary carbon reservoir is that of Ronov and Yaroshevskiy (1967; compare Garrels and Perry, 1973). A smaller estimate was given by Rubey (1951), but the arguments that follow depend only on the fact that the amount of fossilized carbon is considerably larger than the amount of atmospheric oxygen, and this is true of Rubey's estimate as well as of the one we use. In any event, these estimates refer only to material in the crust of the Earth; it is, however, possible that the crust is not isolated from the mantle and that significant quantities of material have been exchanged between the two throughout geological history (Armstrong, 1968, 1971; Armstrong and Hein, 1973). The true size of the fossil carbon reservoir may therefore be much larger than the value given here, and our estimate of the residence time of material in this reservoir may be too small.

Most of the fossil carbon occurs in highly dispersed form, with an average concentration in sedimentary rocks of only 0.5 percent (Ronov and Yarashevskiy, 1967, 1969). The proportion of the total that occurs in sufficient concentrations to be considered a recoverable fossil fuel is very small indeed (Hubbert, 1969).

By dividing the rate of burial of organic carbon into the fossil carbon reservoir, we may calculate that carbon spends 10^8 years in sedimentary rocks, on the average. Sediments do not accumulate indefinitely on the floor of the ocean. In due course processes of sea floor spreading and tectonism recycle the sediments, either by way of volcanism or by raising them above the surface of the sea where they are subject to erosion and weathering. When this happens, the reduced material that the sediments contain is subject to oxidation, constituting a sink for atmospheric oxygen.

Consumption of oxygen in weathering.—We follow Holland (1973) in estimating this quantity by calculating the total rate at which rivers are carrying material from the continents into the sea today and the average composition of the eroded material.

Turekian (1971) has discussed the amount of material carried into the sea by rivers. With an average suspended load of 330 mg l^{-1}, an average bed load approximately 10 percent as large, and dissolved solids[2] contributing 100 mg l^{-1}, he concludes that 500 mg l^{-1} is the average amount of terrigenous material in river water. With an average runoff of 3.6×10^{16} l yr^{-1}, the total flux into the sea is 1.8×10^{16} g yr^{-1} (compare Holeman, 1968; Gregor, 1970). Man's influence on this quantity is probably no larger than a factor of 2 or 3 (Judson, 1968), and it may be much smaller. If windblown material is neglected (Garrels and Mackenzie, 1971, p. 112) the riverborne flux must, in the long run, be equal to the rate of erosion, so we adopt this figure for the erosion rate.

As the principal reducing species in the eroded rocks we consider organic carbon, sulfide, and ferrous iron, assuming that the carbon is oxidized, upon erosion, to carbon dioxide, the sulfide to sulfate, and the ferrous iron to ferric (Holland, 1973). We shall examine below the possibility that not all the reduced material is oxidized during its exposure to the air before it is once again buried in sediments at the bottom of the sea. For the average compositions of continental rocks we use the compilation of Ronov and Yaroshevskiy (1967, 1969).

The average sediment on the continents contains 0.47 percent reduced carbon, 0.15 percent sulfide, and 2.82 percent ferrous iron, computed as FeO. When 100 g of this sediment are completely oxidized the carbon consumes 1.25 g of oxygen, the sulfide consumes 0.30 g, and the iron consumes 0.31 g, for a total of 1.86 g of oxygen per 100 g of sediment. For granitic rocks, 0.17 percent carbon consumes 0.45 g of oxygen, 0.04 percent sulfide consumes 0.08 g of oxygen, and 2.86 percent ferrous iron consumes 0.32 g of oxygen, for a total of 0.85 g of oxygen consumed per 100 g of granitic crust weathered. For basaltic rocks, 0.11 percent carbon consumes 0.29 g of oxygen, 0.03 percent sulfide consumes 0.06 g of oxygen, and 4.78 percent FeO consumes 0.53 g of oxygen, for a total of 0.89 g of oxygen consumed per 100 g of basaltic crust weathered. As far as oxygen consumption is concerned, we may consider granitic and basaltic rocks together, consuming 0.87 g of oxygen per 100 g of igneous rock weathered.

From considerations of the areas of igneous and sedimentary rocks exposed at the surface, Gilluly, Reed, and Cady (1970) conclude that sedimentary rocks contribute 85 percent of eroded material in the United States, whereas igneous rocks contribute 15 percent. We shall assume that these proportions hold throughout the world. Then, for 100 g of rock weathered, sedimentary rocks consume 1.52 g of oxygen and igneous rocks consume 0.13 g of oxygen, for a total of 1.65 g of oxygen per 100 g of eroded material. With the figure already presented for the total rate of erosion we calculate that weathering consumes atmospheric oxygen at a rate of 3×10^{14} g yr^{-1} or 10^{13} moles yr^{-1}, as shown in figure 1. There is disagreement over some of the numbers that have been used in

[2] Correction for bicarbonate ion contributed by atmospheric carbon dioxide is not necessary at this level of approximation.

this calculation, but the result is close to similar estimates by Holland (1973) and Garrels and Perry (1973).

The weathering of igneous rocks plays a very minor role, so we may think of weathering as the process that closes a cycle that commenced with the burial of reduced organic material produced by photosynthesis. Carbon is the most important reducing constituent of the sediments, and it is on carbon that we focus our attention. The other reducing constituents are largely produced by the oxidation of buried organic carbon during diagenesis (compare Berner, 1971), so most of the reduced sulfur and iron in sediments has taken the place of a stoichiometrically equal amount of reduced carbon that was in the sediments when they were first deposited. It is for this reason that it is not necessary to consider the oxidation and reduction of sulfur explicitly in a simple model of the oxygen budget. Although there is isotopic evidence of substantial changes in the relative sizes of the reduced and oxidized sulfur reservoirs over geological time (Holser and Kaplan, 1966), these changes have probably been accompanied by equivalent changes in the reduced carbon reservoir, not in the abundance of atmospheric oxygen (compare Garrels and Perry, 1973).

Photosynthesis followed by burial of organic carbon adds oxygen to the atmosphere and carbon to the sedimentary reservoir whereas weathering closes the cycle by consuming atmospheric oxygen and sedimentary carbon. In figure 1 we have shown this cycle in balance, but the data are by no means good enough to determine whether this is true at the present time.

Volcanism.—A rough estimate of the rate of consumption of oxygen in the oxidation of volcanic gases has been made by Holland (1973) using sea floor spreading rates. His value is 7×10^{10} moles yr^{-1}. Although the uncertainties are large, it is not likely that volcanism is comparable to weathering as a sink for atmospheric oxygen.

Energy production by combustion of fossil fuels.—In terms of the cyclical processes we have been discussing, we may think of the combustion of fossil fuels as an accelerated form of weathering. The rate at which man is currently using up atmospheric oxygen in this process (Hubbert, 1969) is substantially larger than the rate of oxygen consumption by natural weathering, as figure 1 shows. The fossil fuel reservoir, however, is small. From the values in figure 1 we can see that the present rate of fossil fuel consumption can be maintained for only 2000 years. Combustion of all of the fossil fuel reserves would reduce the oxygen content of the atmosphere by less than 2 percent. While energy production by combustion of fossil fuels may cause many environmental problems, the disappearance of atmospheric oxygen is not one of them (Machta and Hughes, 1970; Broecker, 1970b).

The role of photosynthesis in maintaining the oxygen content of the atmosphere.—Some insights into the workings of the oxygen cycles shown in figure 1 are obtained by imagining what would happen if photosynthesis were to cease altogether, possibly as a result of man's activities. If we were to kill all the green plants, photosynthesis would no longer add oxygen to the atmosphere and carbon to the biosphere. Respiration and decay would continue to consume oxygen and carbon, however, so the atmospheric oxygen content and the biospheric carbon content would decline. The decline would continue until the biospheric carbon reservoir was completely exhausted, after a time of order 20 years. At this time, the amount of oxygen in the atmosphere would have decreased by less than 1 percent (Broecker, 1970b; Van Valen, 1971). Atmospheric carbon dioxide would increase initially, but most of the excess would be taken up by the deep sea in 100 years or so.

With no carbon left in the biospheric reservoir, the burial of organic carbon in sediments would now cease, but weathering would continue. The oxygen content of the atmosphere would therefore continue to decline, but much more slowly than before. It would take approximately 4 m.y. for weathering to consume all the oxygen in the atmosphere. Consumption of all the atmospheric oxygen would reduce the reservoir of sedimentary organic carbon by only 4 percent.

We may conclude that the oxygen crisis that would result from the cessation of photosynthesis would, from man's point of view, occur in the very remote future.

CONTROL OF THE OXYGEN CONTENT OF THE ATMOSPHERE

With the sources and sinks of atmospheric oxygen enumerated and evaluated we are now in a position to consider what processes determine the amount of oxygen there is. It is clear, from the thought experiments discussed above, that control is not exercised directly by the rapid cycle of photosynthesis followed by respiration and decay, which links the atmospheric oxygen reservoir to the biospheric carbon reservoir. Because the biospheric reservoir is so much smaller than the atmospheric reservoir, this cycle controls the mass of biospheric carbon not the mass of atmospheric oxygen. Although the atmospheric reservoir of carbon dioxide is smaller than the biosphere reservoir, it is probable that the abundance of carbon dioxide averaged over times of order 10^6 years is controlled by processes of weathering and precipitation of carbonate minerals (Broecker, 1971) and not by the cycle of photosynthesis followed by respiration and decay.

Therefore, since other processes we have examined are quantitatively insignificant, control of atmospheric oxygen must be exercised by the cycle of burial of organic carbon followed by weathering, which links the reservoir of atmospheric oxygen to a much larger reservoir of sedimentary organic carbon (Holland, 1973). The rates are such that imbalances in this cycle, if they were to occur, could cause substantial fluctuations in the oxygen content of the atmosphere in times of the order of 4 m.y.

As Van Valen (1971) and Holland (1973) have pointed out, 4 m.y. is a short time compared with the history of terrestrial life. Mammals have been sucessful inhabitants of the Earth for approximately 65 m.y., since the beginning of the Cenozoic, and mammals are sensitive to the oxygen content of the atmosphere. Multicelled animals with oxidative metabolisms have been abundant for a period ten times as long, since before the beginning of the Paleozoic. It is hard to draw quantitative conclusions from these observations, but we can probably say quite definitely that oxygen has not been completely absent from the atmosphere in the last 600 m.y. at least, and it is possible that we could argue further that atmospheric oxygen hasn't fluctuated by factors larger than 2 or 3 since the advent of the mammals.

For oxygen to have survived in the atmosphere for so long a period in the presence of processes that replace it every 4 m.y., there must be a negative feedback mechanism that provides a measure of stability (Holland, 1973). Where, in the geochemical cycle we have described, does this feedback mechanism operate?

Variation of the weathering sink with oxygen partial pressure.—An obvious possibility is that the rate at which atmospheric oxygen is consumed by weathering increases as the oxygen content of the atmosphere increases (Holland, 1973). We shall show in this section that this does not appear to be the case under present conditions.

We note, first, that there is an upper limit to the rate at which oxygen can be consumed by weathering, which is governed by the rate at which reduced material is exposed to the atmosphere by erosion. Sedimentary organic carbon can not be oxidized faster than it is uncovered. With this in mind, let us think of the weathering sink as the product of three factors. The first factor is the erosion rate, which is the rate at which material is carried from the continents into the sea. Among the circumstances that might influence the erosion rate are topography, climate, and biological activity, but over a long period of time the erosion rate must be equal to the rate at which tectonic activity raises up new material to replace that which has worn away. The erosion rate, therefore, does not depend directly on the oxygen content of the atmosphere.

The second factor entering into the expression for the weathering sink is the content of reducing material in the eroded rocks. As shown above, this is principally sedimentary organic carbon. For present purposes, we need simply note that this factor does not depend on the oxygen content of the atmosphere.

The third factor is the fraction of the organic carbon (and iron and sulfur) that suffers oxidation during the period between erosion and reburial when the reducing material is exposed to the atmosphere. This factor does depend on the oxygen content of the atmosphere, at least at low oxygen levels (Holland, 1973). If there were no oxygen in the atmosphere, essentially all the organic carbon would survive its journey from the mountains to the sea, to be incorporated, once again, in new sediments. The fraction oxidized and the weathering sink would both be close to zero.

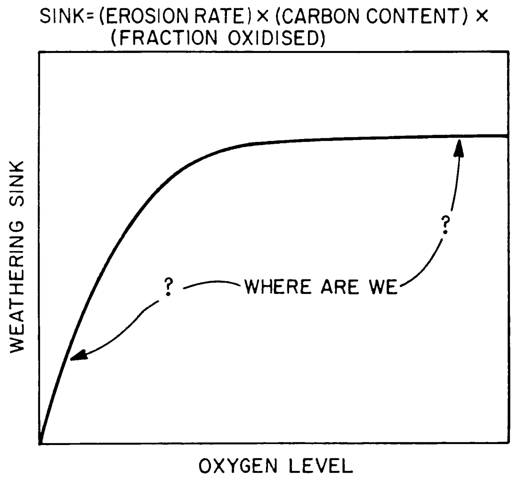

Fig. 2. Schematic representation of the rate of consumption of oxygen in weathering as a function of the amount of oxygen in the atmosphere.

Increasing atmospheric oxygen would lead to the oxidation of an increasingly large fraction of the exposed material until, at sufficiently high oxygen levels, oxygen would cease to be limiting, essentially all of the exposed carbon would be oxidized before new sediments were laid down, and the weathering sink would become independent of the oxygen content of the atmosphere (Van Valen, 1971), while remaining dependent on the erosion rate. This behavior is sketched in figure 2 (compare Holland, 1973). The question we must now consider is whether we are at the low oxygen end of this figure, where the oxygen sink depends on the oxygen partial pressure, as Holland (1973) has suggested, or at the high oxygen end where the sink is constant.

The isotopic composition of organic carbon in sediments on the sea floor differs significantly from that in ancient sedimentary rocks (Degens, 1969). The implication is that these sediments do not contain a large proportion of fossilized carbon that has been recycled. Indeed, as we have already noted, the isotopic composition suggests that most of the organic matter has been freshly synthesized by phytoplankton. Since the average carbon content of new sediments is approximately equal to the average carbon content of the ancient sediments undergoing erosion (Holland, 1973) this observation suggests, in turn, that most of the fossilized carbon is oxidized upon erosion.

We can argue, moreover, that each time a given volume of sediment passes through the cycle of erosion and deposition, it receives a new charge of freshly synthesized organic matter. If this new material is not all oxidized during the subsequent cycle of erosion and deposition, the carbon content of the sediment will increase with the passage of time. Broecker (1970a), however, has presented an argument based on the invariance with time of the isotopic composition of carbonate carbon, which shows that the sedimentary reduced carbon reservoir accumulated before the opening of the Paleozoic and has not been increasing at a significant rate since then. The isotopic composition of the organic carbon in Phanerozoic sediments (Degens, 1969) supports Broecker's deduction, and scattered data from the Precambrian (Keith and Weber, 1964; Schopf and others, 1971; Oehler, Schopf, and Kvenvolden, 1972) suggest that the accumulation of the sedimentary organic carbon reservoir may have occurred as much as 3 b.y. ago.

Some additional support for the conclusion that the sedimentary carbon reservoir is not now growing is provided by data on the average carbon content of sediments of different ages (Ronov, 1958), which show no clear evidence of a secular increase (Gregor, 1971).

If the sedimentary carbon reservoir is not now growing we may conclude that any sedimentary carbon that is recycled is very old (Precambrian) and inert; it has survived many cycles of erosion and deposition without suffering oxidation. All the reduced matter that is susceptible to oxidation is, in fact, oxidized upon erosion. Therefore, we are on the flat portion of the curve in figure 2, and the weathering sink for present day oxygen is independent of the oxygen content of the atmosphere (compare Van Valen, 1971).

This being the case, we must look elsewhere for the feedback mechanism that stabilizes the oxygen content of the atmosphere. Since it is not associated with the sink of oxygen, it must be associated with the source.

Burial of organic carbon as a source of atmospheric oxygen.—We now wish to examine more closely the processes that lead to burial of organic carbon in sediments, thereby providing the net oxygen source that, in the long run, balances the oxygen sink caused by weathering.

Since the sedimentary rocks that consume most of the oxygen upon weathering contain, on the average, about 0.5 percent carbon, and since the mass of the sediments is largely conserved during erosion, weathering, and transport to the sea (Garrels and Mackenzie, 1971), it is evident that the deposition of new sediments containing less than 0.5 percent carbon results, overall, in a net loss of atmospheric oxygen. The important oxygen source regions are therefore those where the new sediments contain more than 0.5 percent carbon. Figure 3 shows for the Pacific that these regions are very restricted indeed (Romankevich, 1968), occurring only in narrow belts along the ocean margins. Ancient sediments also show a concentration of carbon in marine near-shore deposits (Ronov, 1958). In spite of the great disparity in the areas of the carbon-rich and carbon-poor sediments, it is possible for balance to be maintained in the oxygen and carbon budgets, as we have already shown, because the sediment accumulation rate is approximately 10 times as large in the near-shore areas as in the deep sea.

There are two factors that appear to contribute to the relatively high carbon content of the near-shore sediments (Romankevich, 1968). The first of these is the rapid accumulation of sediments. Organic detritus lies on the sea floor or in the surface layers of the sediments for a time that is inversely proportional to the sediment accumulation rate. During this time it is exposed to oxygenated water and is subject to attack by benthic organisms and aerobic microorganisms. The more rapidly the detritus is buried, the more likely it is to escape oxidation.

The second factor is the supply of organic matter to the sediments, which is much greater along the coasts than in the open ocean because the primary organic productivity is higher (Koblentz-Mishke, Volkovinsky, and Kabanova, 1970; Riley and Chester, 1971). A large supply of carbon to the sediments can obviously lead directly to a high carbon content of the sediments, but there is an indirect effect of large carbon supply that is probably more important. A large supply of organic carbon promotes the establishment of anaerobic conditions.

As a simple model of what happens to the carbon in newly-deposited sediments, consider a sample of material that has been completely

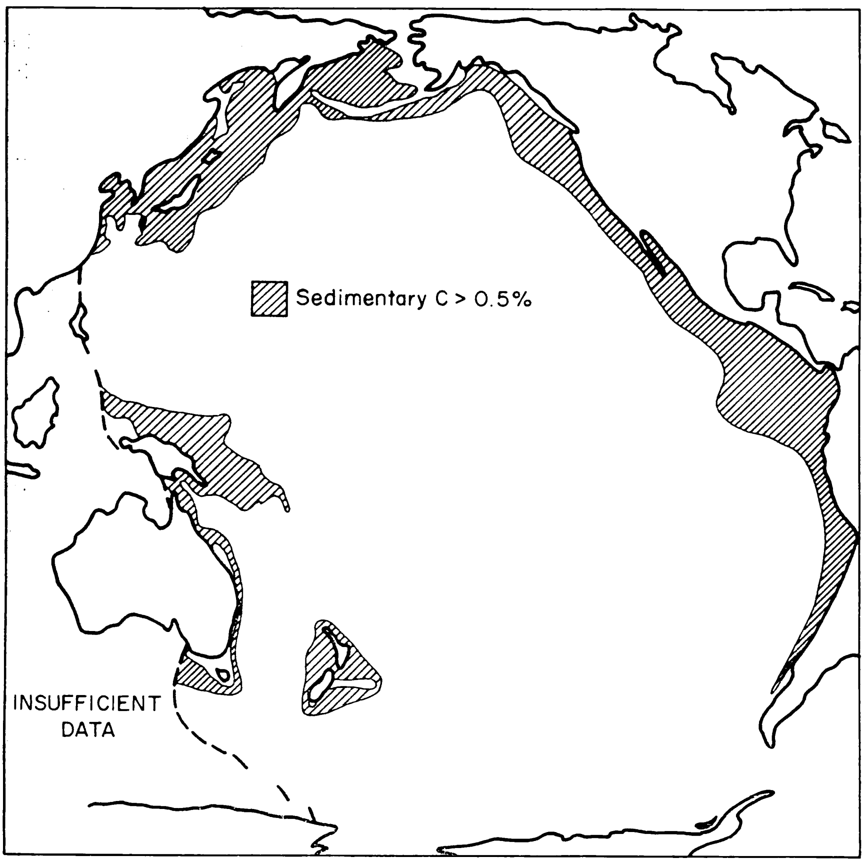

Fig. 3. Areas in the Pacific Ocean where recent sediments contain more than 0.5 percent organic carbon (after Romankevich, 1968).

isolated by subsequent deposition. If this sample contains more moles of oxygen dissolved in pore waters than of organic carbon, most of the carbon will in due course be oxidized, the sediment will remain aerobic, and little or no carbon will be fossilized. If, on the other hand, because of a greater initial supply of carbon, the sample contains more carbon than oxygen, the oxygen will be depleted in due course, and the sediment will become anaerobic. The remaining organic material will still be subject to oxidation by microorganisms utilizing dissolved nitrate or sulfate ions as their sources of oxygen (fermentation does not change the amount of reduced material unless methane escapes from the sediment), but these organisms work much more slowly than aerobic organisms (Thimann, 1963) and are less able to attack resistant organic substrates (Postgate, 1968). Sulfate reduction, moreover, does not as a rule lead to a decrease in the total content of reduced material in the sediments. Carbon is oxidized, but the sulfate is reduced to hydrogen sulfide, which reacts with iron (Berner, 1970, 1972). Burial of sedimentary iron sulfide is equivalent to burial of organic carbon as far as the net production of atmospheric oxygen is concerned (Redfield, 1958). Only if the sediments are deficient in reactive iron and the hydrogen sulfide escapes into the sea will oxidation of organic carbon by sulfate reduction lead to a decrease in the oxygen source.

Our description of the processes affecting the decay of organic carbon in isolated sediment samples is, of course, greatly simplified. A more realistic model would allow for diffusion of dissolved constituents and for the activities of burrowing organisms (Berner, 1971; Rhoads, 1973). Our conclusion, nevertheless, is valid. A large supply of organic carbon to the sediments promotes the establishment of anaerobic conditions, and these, in turn, enhance the preservation of the carbon. In the world ocean today, it is in the near-shore sediments that anaerobic conditions are found.

Given the highly restricted areas in which significant carbon burial occurs and the complex and non-linear interactions which determine the carbon content of sediments, it would appear that the total rate of carbon burial and thus the net source of atmospheric oxygen would vary quite markedly with time. Changes in the distribution of the continents, in world climate, and in the circulation of the oceans will lead to new areas of high primary productivity, high sediment accumulation rate, and high rate of burial of organic carbon; alternatively, areas of significant carbon burial may disappear. Thus it seems most probable that the oxygen content of the atmosphere can vary (Holland, 1973), possibly by a substantial amount. Nevertheless, as we have already argued, there must be a feedback mechanism that prevents oxygen from disappearing altogether.

Stabilization of the oxygen content of the atmosphere.—Control appears to be exercised by the relative rates of supply of organic matter and of oxygen to the deeper levels of the ocean (Redfield, 1958; Broecker, 1971; Holland, 1973). If the oxygen content of the atmosphere were to decrease, there would be larger areas of the ocean in which the supply of organic material would exceed the supply of oxygen. Anaerobic conditions would become more widespread, increasing the rate of burial of organic carbon and thus the net production of atmospheric oxygen; this mechanism would counteract the initial decrease.

The plausibility of this suggestion can be examined with the help of a very simple model of the chemical circulation of the ocean. Imagine bringing an isolated sample of water from the deep sea to the surface. At the surface allow photosynthesis to proceed until the limiting nutrients in the water are exhausted and allow the oxygen content of the water to equilibrate with the atmosphere. Now take the sample with its burden of organic material and oxygen back down to the depths and allow decay to proceed to completion. Redfield (1958) has worked out the stoichiometry of this thought experiment, using the average nutrient content of sea water, the solubility of oxygen, and the average chemical composition of plankton. He finds that the dissolved oxygen and the organic material would be exhausted simultaneously at the present level of atmospheric oxygen. If there were less oxygen, however, the water would become anaerobic, and organic carbon would survive to be buried.

This is a greatly oversimplified description of a complex set of interactions. For one thing, most sea water, when it leaves the surface, does not have all of its limiting nutrients incorporated in organic material. Deep water is produced at high latitudes where primary productivity may be limited by illumination rather than by nutrient supply. Thus, water descending to the deeps may have its full load of oxygen but may not carry as much organic material as it would have if photosynthesis had proceeded to completion. For this reason, the deep waters of the world ocean are not entirely depleted in oxygen, although the depletion is very substantial for a large volume of the Pacific (Duedall and Coote, 1972). The model we have described also neglects the transport of nutrients and oxygen by eddy diffusion and the transport of organic matter in particulate form by settling.

In addition, there are very marked variations in the nutrient content of deep water in different parts of the ocean as a result of the interaction of biological processes and ocean circulation (Redfield, Ketchum, and Richards, 1963), which means that the coincidence we have described between the nutrient content of sea water and the oxygen content of the atmosphere exists only in the sense of an ill-defined average.

The average is nonetheless significant. As Redfield (1958) has shown, there is a suggestive coincidence between the oxygen content of the atmosphere, which governs the oxygen content of saturated sea water, and the amount of oxygen that is released when photosynthesis exhausts the nutrients in sea water (equal to the amount consumed when decay restores these nutrients to inorganic form). Consequently, if the oxygen content of the atmosphere were decreased or the nutrient content of sea water increased, anaerobic conditions would be created at depth, not everywhere, but in situations where circulation and productivity were favorable. The formation of these anaerobic areas would cause an increase in the rate of burial of organic carbon and thus in the net source of oxygen. Since the rate of consumption of oxygen in weathering would not be changed by small perturbations of the kind we are considering, the abundance of atmospheric oxygen would increase. Similarly, if the atmosphere contained too much oxygen relative to the nutrient content of average sea water, anaerobic environments would be rare; there would be little burial of organic carbon, and so little net production of oxygen. Oxygen consumption, however, would not be changed, so the level of atmospheric oxygen would decline.

This general mechanism for stabilizing the oxygen content of the atmosphere by means of a net oxygen source that varies inversely with oxygen partial pressure has been described by Broecker (1971) and Holland (1973). The present model draws on the work of Redfield (1958) to make this general idea more quantitative. According to the model, the equilibrium level of oxygen depends in a calculable way on the nutrient content of sea water, the composition of plankton, and the solubility of oxygen.

Palaeoclimate and atmospheric oxygen.—As an example of how the model can be used, consider the effect on oxygen partial pressure of changes in the average temperature of surface sea water. According to Brooks (1951), climate during much of the Phanerozoic was warmer than the present by about 10°C. These higher temperatures would have reduced the solubility of oxygen in sea water by 20 percent (Richards, 1965b), thereby increasing the partial pressure of oxygen required for equilibrium between production and consumption. Assuming no other changes in the system, the oxygen content of the atmosphere would have increased by 25 percent during the warm periods in order to sustain the supply of oxygen to the bottom of the sea.

CONCLUSION

As Holland (1973) has pointed out, the existence of a negative feedback mechanism does not imply that the oxygen content of the atmosphere has not varied with time. The equilibrium level can be expected to have varied as a result of the temperature effect just described, or to cite a few other possibilities, as a result of tectonic activity, changes in the configuration of the ocean basins, and changes in ocean circulation. Moreover, it takes the atmosphere a few million years to adjust to any shift in the equilibrium abundance of oxygen, so departures from the equilibrium value are to be expected.

Subject to these fluctuations, atmospheric oxygen is stabilized, over the long term, by the requirement that the average rate of supply of oxygen to the deeper levels of the ocean be equal to the average rate of supply of organic material. As explained above, this means that the equilibrium oxygen content of the atmosphere is related to the average nutrient content of sea water, by way of the carbon to nutrient ratio in plankton and the solubility of oxygen. The limiting nutrients are phosphate and nitrate, which are frequently exhausted simultaneously in surface waters (Harvey, 1926; Redfield, 1958; Broecker, 1971; Riley and Chester, 1971). There is little evidence for Holland's (1973) suggestion that a significant proportion of the nitrate is provided by inorganic processes acting at a rate that increases with oxygen partial pressure (Hutchinson, 1944, 1954; Commoner, 1970). It is more probable that the nitrate content of sea water is related to the phosphate content by the activities of organisms that fix nitrogen when they encounter water deficient in nitrogen relative to phosphorus (Strickland, 1965, p. 544; Ryther and Dunstan, 1971; Hutchinson, 1973). If this is true, we conclude that phosphate is the important nutrient and that the equilibrium oxygen content of the atmosphere depends on the average phosphate content of sea water. The extent to which oceanic phosphate may have varied over geological history is not clear (Holland, 1973).

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