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## THE BIOLOGICAL CONTROL OF CHEMICAL FACTORS IN THE ENVIRONMENT<sup>1</sup>

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IT IS a recognized principle of ecology that the interactions of organisms and environment are reciprocal. The environment not only determines the conditions under which life exists, but the organisms influence the conditions prevailing in their environment. The examples on which this principle rests are usually difficult to describe in quantitative terms and are frequently local in their application. In the ocean the principal interactions between organisms and environment are chemical. Because of its unity, its fluid nature, and the intensity of the mixing to which the water is subject their relations can be examined statistically and expressed in quantitative terms.

The purpose of this essay is to discuss the relations between the statistical proportions in which certain elements enter into the biochemical cycle in the sea, and their relative availability in the water. These relations suggest not only that the nitrate present in sea water and the oxygen of the atmosphere have been produced in large part by organic activity, but also that their quantities are determined by the requirements of the biochemical cycle. The argument is not simple and in order that it may be understood the nature of the biochemical cycle and the circulation of the elements involved are reviewed.

### *The Biochemical Cycle*

The production of organic matter in the sea is due to the photosynthetic activity of microscopic floating plants, the phytoplankton, and is limited to the surface layers where sufficient light is available. The formation of organic matter in the autotrophic zone requires all the elements in protoplasm, of which carbon, nitrogen, and phosphorus are

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of particular concern. These are drawn from the carbonate, nitrate, and phosphate of the water. Following the death of the plants the organic matter is destroyed, either by the metabolism of animals or the action of microorganisms. Normally, decomposition is completed by oxidation so that carbon, nitrogen, and phosphorus are returned to the sea water as carbonate, nitrate, and phosphate, while requisite quantities of free oxygen are withdrawn from the water.

The autotrophic zone has a depth of 200 meters at most and includes less than five per cent of the volume of the ocean. Below this zone, life depends on organic matter carried down by organisms sinking from above or by the vertical migrations of animals back and forth between the depths. Although the greater part of the nutrient chemicals absorbed in the autotrophic zone complete the cycle in this layer, the portion which sinks as organic matter tends to deplete the surface layers of these chemicals and, with the decomposition of the organic matter in the depths, to enrich this heterotrophic zone with the products of decomposition.

The existence of the vast reservoir of deep water in which organic matter may accumulate and decay out of reach of autotrophic resynthesis is a distinctive feature of the oceanic environment which enables one to separate, in observation and thinking, the constructive and destructive phases of the biochemical cycle.

The synthesis of organic matter is a highly selective process which results in products having specific composition. Differences in the composition of various species or individuals exist, of course, but the similarities on the whole are greater than the differences. When the population of a large region of the sea is considered it seems reasonable that its composition will be uniform in a statistical sense, and will be reflected in the changes in the chemistry of the water from which its materials are drawn or to which they are returned. In the decomposition of a given amount of organic matter the quantity of oxygen consumed must be determined exactly by the quantities of carbon, nitrogen, etc., to be oxidized, and the relative changes in the quantity of oxygen, phosphate, nitrate, and carbonate in the water must depend exactly on the elementary composition of the plankton [1].

The validity of this concept is shown by a comparison of the proportions in which the elements exist in the plankton and the proportions in which they vary in samples of water from the open sea. The analysis of many samples of plankton, taken in a variety of places with nets designed to take organisms of different size indicates that atoms of phosphorus, nitrogen, and carbon are present on the average in the ratios: 1:16:106 [2]. The oxidation of this material is estimated to require 276 atoms of oxygen. In comparison, data on the phosphate, nitrate, and carbonate content of sea water collected from various

depths in the several oceans show that the available phosphorus, nitrogen, and carbon vary from sample to sample in the atomic ratios: 1:15:105 and that about 235 atoms of oxygen disappear for each addition of one phosphorus atom, assuming the water to have been in equilibrium with the oxygen of the atmosphere when it was last at the sea surface [3-5]. It is as though various quantities of material containing phosphorus, nitrogen, and carbon in these ratios had decomposed in the water samples. The correspondence of these ratios with those obtained from the analysis of plankton, as shown in Table 1, leaves little doubt that these elements vary in sea water almost entirely as the result of the synthesis or decomposition of organic matter [1].

This conclusion permits one to approach the biochemical cycle in the sea in much the same way as the physiologist examines the general metabolism of an individual organism. It defines the quantitative relations of the cycles of the separate elements which are involved in the biochemical cycle as a whole. It provides a quantitative criterion, similar to the principle of combining proportions in chemistry, for examining many problems in marine ecology. Consider, for example, the question of the relative availability in the sea of the various substances required for the growth of organisms. In accordance with Liebig's law of the minimum, that constituent of the sea water present in smallest quantity relative to the requirement for growth of organisms will become the limiting factor. The ratios shown in Table 1 define precisely what these relative requirements are. When the composition of sea water is examined it is found that phosphorus and nitrogen are usually available in about the proportions, 1:15, required for the formation of the plankton. Carbon, as carbonate, in contrast, is present in great excess, the phosphorus-carbon ratio being about 1:1000 whereas the required ratio is 1:105. Consequently, carbonate never becomes a limiting factor. In a similar way sulfur, an important plant nutrient, is available in great quantities relative to phosphorus and nitrogen, and the same is true of calcium, magnesium, and potassium.

TABLE 1

## ATOMIC RATIOS OF ELEMENTS IN THE BIOCHEMICAL CYCLE

	P	N	C	O
Analyses of plankton	1	16	106	-276
Changes in sea water	1	15	105	-235
Available in sea water	1	15	1000	200-300

Phosphorus and nitrogen thus appear to be the constituents of sea water present in limiting quantities. It was pointed out by Harvey in 1926 that it is a remarkable fact that in the English Channel plant growth should strip sea water of both nitrates and phosphates at about

the same time [6]. To this coincidence I will return. Data for the oceans indicate that this is a world-wide occurrence in the surface waters of tropical and temperate seas. This would not be the case were other substances, such as the various trace elements, generally limiting factors for growth in the sea.

It should be recognized that in coastal waters and in the surface of the open ocean the ratios of the elements under discussion frequently depart widely from those which are here attributed to the oceans as a whole. This is due, in part at least, to the fact that where the elements are substantially depleted by the growth of plants, small unused residues of one or another element may greatly alter the ratios, and also because in the process of decomposition phosphorus tends to be regenerated more rapidly than nitrogen. It is believed, however, that in the great bulk of the open sea the ratios presented represent the statistical composition of the water and of the organisms living in it sufficiently well to serve for the argument to be developed. This argument depends upon the consideration that the physiology of marine plants places definite restrictions on the proportions in which certain elements participate in the biochemical cycle, rather than on the exactness with which these proportions can be stated at present.

#### *The Biochemical Circulation*

The withdrawal of nutrients from the autotrophic zone would soon exhaust its fertility and bring the cycle to a close if means did not exist to restore them to the surface. This is done by purely physical processes, the vertical mixing of water by turbulence and by direct upwelling of deeper water to the surface—frequently after transport for great distances by currents in the depths of the sea [7].

The production of organic matter in the autotrophic zone at the surface of the sea depends upon how fast the biochemical cycle runs its course. Many factors, such as the temperature and light intensity, may intervene, but it is clear that the cycle is limited by the return of nutrient materials to the surface by the motion of the water. This, in turn, depends in part upon the quantities of nutrients available in the subsurface waters. We may consequently inquire with interest into the concentrations of nutrients in the deeper layers of the sea as they are distributed throughout the world.

The sea water of the oceans may be considered to be thoroughly mixed. The major ions of sea water occur so nearly in the same proportions that by this criterion one cannot distinguish water from one part of the ocean from another. The principal variables used by oceanographers to distinguish different waters are the temperature and salinity. Changes in these properties are produced at the sea surface, and while the effects may be relatively large they influence only a

small part of the total mass of water. Ninety per cent of the water in the oceans differs by less than 3 per cent from the average in its salinity or its heat content.

In contrast, the principal elements involved in the biochemical cycle differ greatly in their abundance in different parts of the sea. It was first shown by the cruises of the Danish research vessel "Dana" and the "Carnegie" that phosphate and nitrate were much more abundant in the Pacific and Indian Oceans than in the Atlantic [8, 9]. A chart showing the quantities of phosphorus present in the world oceans at a depth of



Fig. 1. Distribution of phosphorus at depth of 2000 meters in Oceans of World. Contour interval 0.25 mg atoms/m<sup>3</sup>. This diagram is based on some 1600 measurements between depths of 1900 and 2100 meters. Data are available from about 75 per cent of the 10° squares. About half the observations fall within the designated contour interval, the remainder within the adjacent intervals.

2000 meters, which represents adequately the concentrations present in the great reservoir of deep water, is shown in Figure 1. The variation in phosphorus content is widespread and systematic, the values increasing from less than 1.25 mg atoms per cubic meter in the North Atlantic to more than 3.0 of these units in the North Pacific and Indian Oceans. In the Mediterranean Sea comparable values are less than 0.5 unit, so that there is a variation of more than sixfold in the potential fertility of the deep reservoirs of the major seas.

It is evident that there is some world-wide mechanism at work producing this distribution. Since the elements involved are those which enter the biochemical cycle this mechanism must be biological.

Since the distribution differs from that of the biologically inactive components of the water there must be a biochemical circulation which is different from, though dependent upon, the physical circulation of the water [10]. How can this difference in behavior be explained?

The presumptive agency of fractionation which separates the biochemical from the inactive elements in sea water is the selective absorption of the former in the synthesis of protoplasm near the surface, followed by the sinking of the organized matter to greater depths prior to its decomposition. In addition the differential motions of the water at different depths must be taken into account if substantial differences in concentration and their redistribution are to be explained.

The foregoing discussion is intended to bring out two points of importance, namely, that the principal elementary constituents of protoplasm enter the biochemical cycle statistically in definite proportions, and that the cycle of movement of these elements between the surface layers and the deep waters runs with sufficient intensity to influence markedly their distribution on an ocean-wide scale. We may now turn to two remarkable coincidences which have led to the inquiry which is our major concern.

#### *Correspondence Between Requirement and Availability of Phosphorus, Nitrogen, and Oxygen*

The stoichiometric relations summarized in Table 1 indicate that phosphorus, nitrogen, and oxygen are available in ocean water in very nearly the same proportions as those in which they enter the biochemical cycle. In discussing the remarkable coincidence in the supply and demand for nitrogen and phosphorus it has been pointed out that it might arise from: (1) a coincidence dependent on the accidents of geochemical history; (2) adaptation on the part of the organisms; or (3) organic processes which tend in some way to control the proportions of these elements in the water [1].

Of the first alternative not much can be said except that the probability that the ratio in the sea be what it is rather than any other is obviously small. That the coincidence applies to the oxygen as well as to the nutrient elements compounds the improbability.

For the second alternative, it may be said that the phytoplankton do have some ability to vary their elementary composition when one element or another is deficient in the medium in which they grow. Such physiology might account for the coincidence in the nitrogen-phosphorus ratios. However, it is not evident how adaptation could determine the oxygen relation since this depends more on the quantity than the quality of the organic matter formed, and the oxygen requirement is felt only after the death of the living plant.

For these reasons the third alternative deserves serious consideration. Mechanisms should be examined by which organic processes may have tended to control the proportions of phosphorus, nitrogen, and oxygen available for life in the sea.

#### *The Phosphorus-Nitrogen Ratio*

When the coincidence between the elementary composition of marine plankton and the proportions of available nitrogen and phosphorus in sea water was first noted, it was suggested that it might have been brought about by the activity of those microorganisms which form nitrogenous compounds from atmospheric nitrogen, or liberate nitrogen gas in the course of their metabolism. The composition of such organisms must be more or less fixed in regard to their relative phosphorus and nitrogen content. When living in an environment containing a deficiency of nitrate relative to phosphate, the growth and assimilation of the nitrogen-fixing organisms might tend continually to bring the proportions of nitrogen and phosphorus nearer to that characteristic of their own substance. Thus, in the case of *Azotobacter*, it has been found that for every atom of phosphorus available in the medium about 10 atoms of nitrogen are fixed or assimilated into microbial protein [11]. In an environment populated by organisms of this type, the relative proportion of phosphate and nitrate must tend to approach that characteristic of their protoplasm. Given time enough, and the absence of other disturbances, a relation between phosphate and nitrate such as observed in the sea may well have arisen through the action of such organisms.

Nitrogen fixation is employed practically in agriculture whenever leguminous plants are used to enrich the soil. It is not unreasonable to assume that the same process has been effective on a larger scale in nature. Hutchinson has estimated that nitrogen is being fixed on the earth's surface at the annual rate of 0.0034 to 0.017 mg/cm<sup>2</sup> [12]. At the lesser value it would require only 40,000 years to fix the  $7 \times 10^{14}$  kilograms of nitrogen estimated to be available as nitrate in the ocean.

Nitrogen fixation is so active that there is no difficulty in assuming that it might serve in adjusting the phosphorus nitrogen ratio in the sea. The difficulty is rather in explaining why there is not a great excess of nitrate nitrogen in the water. The ratio of nitrogen to phosphorus in fresh waters is higher than that in ocean water, while the ratio in sedimentary rocks is very much lower. Consequently the ratio in the sea must tend to increase, unless some process is returning nitrogen to the atmosphere. Denitrifying bacteria might operate in this sense, in which case the phosphorus-nitrogen ratio is fixed by a complex balance.

Biological mechanisms adequate to influence the phosphorus-nitrogen ratio in sea water are known. Whether they do in fact operate in a regulatory sense is a subject for future investigation.

### The Phosphorus-Oxygen Ratio

The relation between the quantity of phosphorus present in sea water and the amount of oxygen available for the decomposition of organic matter is less obvious than the relation of phosphorus and nitrogen. The quantity of oxygen dissolved in sea water when it is at the sea surface appears to be fixed by equilibrium with the atmosphere, which contains about 21 per cent oxygen. Consider what would happen if a unit volume of water, containing its characteristic quantities of plant nutrients, was brought from the depths of the ocean to the surface. There, under the influence of light, photosynthesis would convert the available nutrients to organic matter until all the phosphate is exhausted. At the same time the water is saturated with oxygen by equilibration with the atmosphere. If the unit volume of water is now returned to the depths where the organic matter is decomposed and oxidized, will the

TABLE 2

#### UTILIZATION OF OXYGEN IN OCEAN WATER

	Average S. W.	North Atlantic	North Pacific
Phosphorus content mg atoms/m <sup>3</sup>	2.3	1.25	3.0
Equivalent oxygen	6.9	3.75	9.0
Utilization * ml/liter	7.1	6.7	7.5
Oxygen content of saturated S. W.	0.2	2.95	-1.5
Excess oxygen		3.0	0.01
Oxygen in "minimum oxygen layer"			

\* Calculated allowing 276 atoms of oxygen to be used in oxidizing a quantity of organic matter containing one atom of phosphorus in which case 1 mg atom P/m<sup>3</sup> is equivalent to 3 milliliters O<sub>2</sub>/liter.

dissolved oxygen present be sufficient for the purpose, will there be a large excess of oxygen, or will the oxygen be deficient?

The answer can be given only within approximate limits, for two reasons. First, the quantities of nutrients are different in the deep waters of the several oceans, as we have seen. We can consider the extreme cases of the North Atlantic containing phosphorus in the concentration of 1.25 mg atoms per m<sup>3</sup>, the North Pacific containing 3.0 mg atoms per m<sup>3</sup>, and an "average" sea water containing, say, 2.3 mg atoms per m<sup>3</sup>. Second, the quantity of oxygen dissolved in the water when it is at the surface will vary depending upon the temperature, and to a lesser degree upon the salinity.

The lowest oxygen concentrations are not found at the bottom of the oceans, but at some intermediate depth, where also maximum con-

centrations of phosphate and nitrate occur. The temperature at this depth in the North Atlantic is about 8°C. and when at the surface at this temperature the water would have taken up 6.7 milliliters of oxygen per liter. The corresponding temperature of the minimum oxygen layer in the North Pacific is about 3°C. and the oxygen solubility 7.5 milliliters per liter.

From these numbers Table 2 has been prepared to show the excess oxygen which might be expected to remain in the minimum oxygen layer if all the phosphorus present has been derived from the oxidation of organic matter. In the case of the "average" sea water it appears that the quantity of organic matter which can be formed from the nutrients in a unit of volume of "average" sea water is almost exactly that which can be completely oxidized by the oxygen dissolved at the surface. In the North Atlantic, where the phosphorus content is reduced, only about one half of the dissolved oxygen would be consumed and the excess oxygen corresponds well with the quantities observed to remain in the zone of minimum oxygen content. In the North Pacific, the phosphate content of the deep water is so great that the dissolved oxygen would be more than exhausted if the process went to completion as postulated.

Actually the Pacific Ocean does not appear to be anaerobic at any depth. However, large volumes of water at intermediate depths contain only small traces of oxygen [4]. In high latitudes where the deep water of the oceans originates the photosynthetic processes do not convert all of the available nutrients into organic matter before the water sinks. Consequently, the deep water contains phosphates which have not been liberated by oxidation during the preceding turn of the cycle. Presumably this effect accounts for traces of oxygen which remain in the minimum oxygen layer of the North Pacific.

Although the oxygenation of the oceans appears to be adequate to oxidize the products of the biochemical cycle at present the margin is not large. Actually anaerobic conditions exist in a number of isolated areas, such as the Black Sea and the Sea of Azov, Kaøe Bay in the East Indies, the Cariaco Trench, and numerous fjords in Norway and elsewhere [4]. A decrease in the oxygen content of the atmosphere, an increase in surface ocean temperatures or reduction in the vertical circulation of the water might lead to the extension of anaerobic conditions over much wider areas.

It is widely held among geochemists that the primitive atmosphere was devoid of oxygen, or at least contained very much less oxygen than at present. During the course of geological history atmospheric oxygen is thought to have been produced by the photochemical dissociation of water in the upper atmosphere and by the photosynthetic reduction of carbon dioxide, previously present in much greater quantities [13].

Estimates of the quantity of reduced carbon present in the earth's crust as coal and petroleum indicate that photosynthetic processes have been much more than adequate to produce the present oxygen content of the atmosphere. It has not been suggested, to my knowledge, why this process has proceeded just so far as it has; that is, why there is 21 per cent of oxygen in the atmosphere at present, no more or no less. It is, however, on this fact that the quantity of oxygen dissolved in the sea depends.

My supposition is that the actual quantities of oxygen present in the sea may have been regulated by the activities of sulfate-reducing bacteria. This group of bacteria are known to have the ability to use sulfates as a source of oxygen when free oxygen is absent and organic compounds are present to supply a source of energy [14]. The over-all reaction is



The process should be broken down into two steps, each of which takes place in the sea under different environmental conditions, (1) Sulfate Reduction,  $\text{SO}_4^{2-} + 2\text{C} \rightarrow 2\text{CO}_2 + \text{S}^-$  which occurs at depth under anaerobic conditions, and (2) Photosynthesis  $2\text{CO}_2 \rightarrow 2\text{C} + \text{O}_2$  which occurs near the surface in the presence of light.

In these equations C represents the reduced carbon present in organic matter. The decomposition of this material by sulfate-reducing bacteria according to the first step also liberates a corresponding quantity of nitrogen and phosphorus, which permit the  $\text{CO}_2$  formed to re-enter the biological cycle when the second step comes into play. The  $\text{CO}_2$  produced in this way can thus contribute to the production of oxygen in a way in which the excess carbonate normally present in sea water cannot.

The first step, which depends upon the presence of organic matter in excess of the free oxygen required to complete its decomposition, will initiate a mechanism which will tend to increase the oxygen when, and only when, the quantity of available free oxygen is deficient. If the total mechanism has operated on a large enough scale in the course of geochemical history, it may have kept the supply of oxygen available in the sea adjusted to the requirements of the biochemical cycle.

There is very good evidence that sulfate reduction does operate on a large scale in the sea wherever anaerobic conditions exist. Figure 2 shows the relations between the phosphorus content and the combined utilization of oxygen and sulfate in the waters of the Black Sea and Cariaco Trench, both anaerobic basins. The phosphorus content may be taken as an indication of the quantity of organic matter which has decomposed in the water. The combined utilization is the quantity of free oxygen which has disappeared from the water since it left the surface, plus *four times* the quantity of sulfide present. That is to say, it is

assumed that for each ion of sulfide liberated in the water four atoms of oxygen have been produced by sulfate reduction and utilized in oxidizing organic matter. The figure shows that as increasing quantities of organic matter decompose in the water the utilization of oxygen increases approximately in the ratio of 235 atoms for each atom of phosphorus set free [3]. After the phosphorus content reaches a little more than 2 mg atoms per  $\text{m}^3$  the free oxygen is exhausted and hydrogen sulfide appears

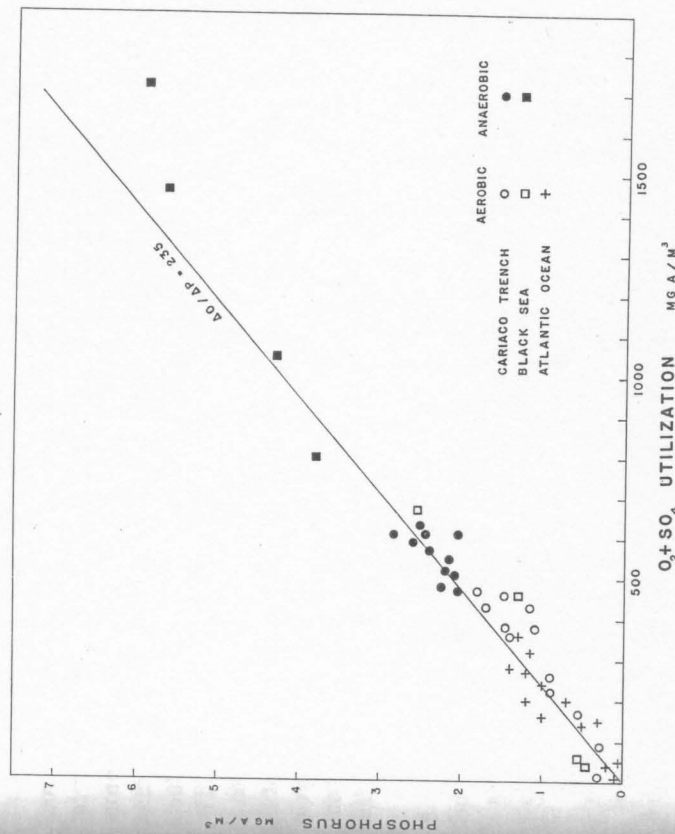


FIG. 2. Relation between the inorganic phosphorus and the combined utilization of oxygen and sulfate in waters of Cariaco Trench, Black Sea, and western Atlantic Ocean. After Richards and Vaccaro [3].

in the water. The increase in hydrogen sulfide continues as though it were produced by the reduction of the quantity of sulfate required to oxidize the accumulated organic matter. In the depths of the Black Sea more than two thirds of the phosphorus present may be attributed to the decomposition of organic matter through sulfate reduction. If the products of such decomposition find their way back to the surface, then the oxygen derived from sulfate will be liberated by the photosynthetic process and will be added to the supply of free oxygen in the environment.

At the present time, anaerobic basins such as the Black Sea and the Cariaco Trench are rarities and the greater part of the ocean is well

oxygenated. Extensive areas of marsh and estuary present anaerobic conditions, as do quite generally marine muds. At present the production of oxygen through sulfate reduction in such situations may not be more than sufficient to balance the losses due to the oxidation of eroding terrestrial surfaces. If, however, in the past the oxygen of the atmosphere were lower than at present, anaerobic conditions may have been much more prevalent. The reduction of sulfates may then have served to bring the oxygen content of the atmosphere and sea into correspondence with the requirements set by the quantities of phosphorus available.

In considering the influence of the biochemical cycle on the environment it should be remembered that the cycle can, and apparently for the most part does, run its course without adding more to the environment at one phase than it withdraws at another. Photosynthesis cannot increase the oxygen content of the environment unless the products of photosynthesis are in some way withdrawn from reoxidation. The reduction of sulfates will not make more oxygen available in the sea if the sulfides produced are reoxidized in the sea water. Fractionating mechanisms are required which separate the products of the cycle, so that they cannot re-enter it. Such mechanisms exist at the sea bottom, where materials may be buried in the sediments, and at the surface where volatiles may pass into the atmosphere.

Consider the fate of the sulfide and oxygen which are produced in anaerobic basins by the activity of sulfate-reducing organisms. When the water containing these products is brought to the surface layers of the sea by mixing processes the sulfide will be reoxidized to sulfate, consuming a quantity of free oxygen equivalent to that produced by the original reduction. No change in the total oxygen in the water column would result if this were the complete picture. However, if a portion of the sulfide forms insoluble compounds, such as iron sulfide, which settle into the bottom sediments, or if a portion of the oxygen liberated near the sea surface passes into the atmosphere, these portions cannot re-enter the cycle immediately and a net increase in the oxygen of the environment will be produced.

Conditions on the land, in contrast with the sea, appear to be much less favorable for producing changes in the free oxygen of the atmosphere, either by photosynthesis or in response to anaerobic conditions through sulfate reduction. The predominance of erosion does not permit the permanent entrapment of large quantities of organic matter on land. Soils are usually well aerated so that organic carbon does not remain long out of circulation. Anaerobic conditions do exist in swamps, and many coal deposits must represent reduced carbon formed in such places which have contributed oxygen to the atmosphere, but such withdrawals must be small compared to the quantities of organic matter accumulated in marine sediments.

The exchange of oxygen across the sea surface must be important in this connection. The solubility of oxygen in water is such that under equilibrium conditions more than twenty times as much oxygen occurs in a unit volume of air than in a comparable volume of water at the sea surface. Of any increase in the quantity of oxygen in the water, whether produced by the reduction of sulfates or the photosynthetic reduction of carbonates, only a small portion would remain in the water since a larger fraction would pass into the atmosphere.\* In this way the biochemical cycle of the sea can continue to add to the oxygen content of the environment until a new equilibrium is established between the atmosphere, the sea, and the available nutrient materials.

It appears, then, that the biochemical cycle in the sea may have produced the major amount of oxygen in the atmosphere and that conditions in the sea have adjusted its level to that which occurs at present. We think of the atmosphere as determining the oxygen content of the sea. This is because the atmosphere is the great reservoir of oxygen on the earth's surface and because the motion of the air gives it a conveniently constant composition. Perhaps it is more correct, however, to think of the sea, and particularly of its nutrient content, as determining the composition of the atmosphere.

### *Geochemical Considerations*

As a final check on these speculations, we can look at the relative availability of the principal materials of the biochemical cycle on the earth's surface, to see if they conform to the postulates. In Table 3 estimates are given of the total quantities of the pertinent elements in the atmosphere, the ocean, and the sedimentary rocks. The content of the atmosphere is quite accurately known; that of the ocean can be approximated since the greater part of its water is of relatively uniform composition. The values for the sedimentary rocks are quite uncertain, partly because of the variability in their composition and the incompleteness in sampling, and partly because the volumes in question are arbitrarily chosen. However, we are concerned with orders of magnitude so the numbers are useful.

The first column of numbers in Table 3 are the estimated weights of each element on the earth's surface. Divided by the phosphorus content of the ocean and adjusted for atomic weights, the second column gives the numbers of atoms relative to the atoms of phosphorus in the ocean.

\* The intensity of the exchange of oxygen across the sea surface is indicated by the observations that in the Gulf of Maine a quantity of oxygen sufficient to form a layer 0.9 meters in depth enters the atmosphere each spring as the result of photosynthetic activity by phytoplankton. This is about 15 per cent of the oxygen locally present to a depth of 200 m. This quantity of oxygen returns to the water during the following fall and winter to replace that used in the oxidation of the summer crop of organic matter [15].

So reduced, the relative quantities are indicated in Figure 3 which presents in diagrammatic form the biochemical cycle as described.

TABLE 3  
QUANTITIES AND PROPORTIONS OF ELEMENTS AT  
THE EARTH'S SURFACE\*

Ocean	P	$1 \times 10^{14}$	1
	N as $\text{NO}_3$	$7 \times 10^{14}$	15
	as $\text{N}_2$	$2.3 \times 10^{16}$	510
	C	$4 \times 10^{16}$	1,000
	S	$1 \times 10^{18}$	10,000
	O	$1.4 \times 10^{16}$	270
Atmosphere	N as $\text{N}_2$	$3.8 \times 10^{18}$	62,000
	C	$6.4 \times 10^{14}$	16
	O	$1.2 \times 10^{18}$	23,000
Earth's crust	P	$4 \times 10^{18}$	40,000
Sedimentary rocks	N	$4.4 \times 10^{17}$	10,000
	S	$1 \times 10^{18}$	10,000
	C	$1.5 \times 10^{19}$	400,000
	C	$6 \times 10^{18}$	160,000

\* Estimates are based on following sources: Atmosphere [19]; Ocean, volume  $1.37 \times 10^9 \text{ Km}^3$  [20], P  $71 \times 10^{-6} \text{ gr/Kg}$  (original), N as  $\text{NO}_3$   $15 \times \text{P}$ , N as  $\text{N}_2$   $17.3 \times 10^{-3} \text{ gr/Kg}$  assuming saturation at  $2^\circ\text{C}$ . and  $34.33 \%$  S [21], O as  $\text{O}_2$ , including consumption in biochemical cycle,  $10.7 \times 10^{-3} \text{ gr/Kg}$  assuming saturation at  $2^\circ\text{C}$ . and  $34.5 \%$  S [22], C as  $\text{HCO}_3$   $0.028 \text{ gr/Kg}$  [20] S as  $\text{SO}_4$   $0.884 \text{ gr/Kg}$  [20]; Earth's crust, area  $5.1 \times 10^{18} \text{ cm}^2$ , Sedimentary rocks  $170 \text{ Kg/cm}^2$ , P  $0.46$  per cent (arbitrary weighting of analyses by Stokes and Steiger) N  $0.051$  per cent, S =  $0.12$  per cent (arbitrary weighting of analyses by Stokes), C  $3 \text{ Kg/cm}^2$ , and coal and petroleum  $1.26 \text{ Kg/cm}^2$  after Kalle [19].

The diagram shows phosphate, nitrate, and carbonate entering the organic phase of the biochemical cycle near the sea surface, through the process of photosynthesis. Phosphorus, nitrogen, and carbon are selected by the synthetic process in the proportions of 1:15:105. This is the step which coordinates the cycles of the several elements in a unique way and gives meaning to the comparisons. The elements are carried in these proportions to the point of decomposition where they are oxidized to their original state as phosphate, nitrate, and carbonate. The oxygen required is just that set free by photosynthesis. Such a cycle could run indefinitely in an otherwise closed system so long as light is supplied.

To account for the correspondence in the ratios of phosphorus and nitrogen in the organic phase of the cycle and in the inorganic environment, bacterial processes of nitrogen fixation and denitrification are indicated at the upper right and, similarly, the sulfate reduction process is shown at the lower left. This latter is assumed to operate effectively

only when the environment becomes anaerobic. Finally, the exchanges with the atmosphere and the sediments of the sea bottom are shown. If these processes are operative it is necessary that supplies are adequate and that their products exist in suitable quantities.

Considering first nitrogen, there exist in sea water for each atom of phosphorus 15 atoms of nitrogen available as  $\text{NO}_3$  and a reserve of 510 atoms of nitrogen as dissolved  $\text{N}_2$  which may be drawn on by nitrogen-fixing bacteria. In addition, there is a reserve of nitrogen in the atmosphere equivalent to 86,000 atoms of phosphorus, which is available to replace that dissolved in the sea were it to be drawn on. The nitrogen of the sedimentary rocks is about one-sixth that in the atmosphere and twenty times that in the ocean. More than four-fifths of this is fossil nitrogen which may be assumed to be derived from organic matter [12]. Consequently, large quantities of nitrogen have passed through the biochemical cycle in its passage from the atmospheric reserves to be deposited in sediments at the sea bottom. The quantity withdrawn in this way is small, however, in comparison to the reserve in the atmosphere. Clearly, the nitrogen supply is adequate.

Sulfate is one of the most abundant ions in sea water. In this form there is present sulfur equivalent to 10,000 atoms of phosphorus. It would be capable of supplying oxygen equivalent to 40,000 atoms of phosphorus on reduction. Clearly, the sulfate reduction mechanism could continue to operate for a long time. If it has operated as postulated in the past much sulfide may have been removed from the sea. Sedimentary rocks are estimated to contain sulfur equivalent to 10,000 atoms of oceanic phosphorus. If this were all the product of sulfate reduction, this would have produced oxygen equivalent to 40,000 atoms of oceanic phosphorus, which is almost twice that present in the atmosphere. It is not clear how much of the sulfur in sedimentary rocks is present as sulfides, but much of it is. Clearly, much oxygen can have been produced in the past by sulfate reduction and possibly this process has contributed to an important degree in producing the oxygen of the atmosphere.

Carbon is present in the sea, chiefly as carbonate ions, in about ten times the quantity required for the biochemical cycle. Much of the large deposits of carbon in the sedimentary rocks is present as carbonates and cannot have contributed to the production of free oxygen. The estimated carbon present as coal and petroleum, equivalent to 160,000 atoms of oceanic phosphorus, is sufficient to yield oxygen on reduction equivalent to 320,000 atoms of oceanic phosphorus, which is more than ten times the present content of the atmosphere.

The known facts of geochemistry do not appear to contradict the suppositions presented on the mechanism which may have controlled the relative availability of phosphate, nitrate, and oxygen in the sea. Sources of nitrogen and sulfate are available in great excess and the by-



products of the reactions can be adequately accounted for. According to these suppositions, phosphorus is the master element which controls the availability of the others. How about phosphorus itself?

In the sedimentary rocks, formed for the most part by marine deposition, there are present some 40,000 atoms of phosphorus for every atom in the sea water. Evidently large quantities of phosphorus, carried into the sea from the rivers in past times, have passed through the sea to contribute to these deposits. The concentration of phosphorus in average sea water is very small, amounting to less than one part in 10 million. Probably this represents a condition determined by the low solubility of phosphates under the conditions existing in sea water at the sea bottom. Dietz, Emery, and Shepard [16] have suggested that sea water deeper than a few hundred meters is essentially saturated with  $\text{Ca}_3(\text{PO}_4)_2$ . It is not possible to be exact in this regard because the solubility will vary with the conditions, and the physical constants are not well known. However, they have described the presence of phosphate deposits on the floor of the North Pacific ocean which they explain in this way. The high ratio of phosphorus to nitrogen in sedimentary rocks, 4:1, when compared to the ratio characteristic of the plankton, 1:15, also suggests that phosphorus has been introduced into the sediments by some mechanism other than the entrapment of organic matter.

If the argument presented is sound it may be concluded that the quantity of nitrate in the sea, and the partial pressure of oxygen in the atmosphere are determined through the requirements of the biochemical cycle, by the solubility of phosphate in the ocean. This is a physical property of a unique chemical compound and as such is not subject to change except in so far as alterations in conditions may influence the activity coefficients of the ions involved. It follows then that the nutrient supplies in sea water, and the oxygen content of the atmosphere have been about as at present for a long time in the past and will remain at much the same level into the future. This argument may then be added to those reviewed by Rubey [17] that the composition of sea water and atmosphere has varied surprisingly little at least since early geologic time.

Speculations about geochemical history are obviously not subject to proof in the ordinary sense. The best one can do is to develop circumstantial evidence which shows that known processes occur which are adequate to produce the effects postulated, and to demonstrate that the quantities of matter and its distribution as presently observed are concordant with the hypotheses. The present hypothesis appears to be supported by evidence of this sort. What is lacking is direct evidence that the postulated processes do, in fact, act in a regulatory way so as to bring the atomic ratios of phosphate nitrate and oxygen in the

environment into conformity with the requirements of the biochemical cycle. It is desirable, and would seem quite possible, to set up controlled microcosms in the laboratory, such as von Brand, Rakestraw, and Renn [18] employed to demonstrate the steps in the nitrogen cycle, which would test whether the physiology of the nitrogen and sulfur manipulating bacteria is such as to provide the homeostatic regulation which has been assumed.

## REFERENCES

1. A. C. REDFIELD, "On the proportions of organic derivatives in sea water and their relation to the composition of plankton," James Johnstone Memorial Volume, pp. 176-192, Liverpool (1934).
2. R. H. FLEMING, "The composition of plankton and units for reporting populations and production," *Proc. Sixth Pacific Sci. Congress*, 2, pp. 535-540 (1940).
3. F. A. RICHARDS and R. F. VACCARO, "The Cariaco Trench, an anaerobic basin in the Caribbean Sea," *Deep-Sea Research*, 3, pp. 214-228 (1956).
4. F. A. RICHARDS, "Oxygen in the Ocean," Treatise on Marine Ecology and Paleocology, J. W. Hedgpeth, Ed., Vol. 1, Chapter 9, pp. 185-238 (1957).
5. L. H. N. COOPER, "On the ratio of nitrogen to phosphorus in the sea," *Jour. Marine Biol. Assn.*, 22, pp. 177-182 (1937).
6. H. W. HARVEY, "Nitrate in the Sea," *Jour. Marine Biol. Assn.*, n.s. 14, pp. 71-88 (1926).
7. A. C. REDFIELD, "The processes determining the concentration of oxygen, phosphate and other organic derivatives within the depths of the Atlantic Ocean," *Papers in Physical Oceanography and Meteorology*, 9(2) 22 pp. (1942).
8. H. THOMSEN, "Nitrate and phosphate contents of Mediterranean Water," Report on the Danish Oceanographical Expeditions 1908-1910 to the Mediterranean and Adjacent Seas. No. 10 (3) pp. 1-11 (1931).
9. H. W. GRAHAM and E. G. MOBERG, "Chemical results of the last cruise of the Carnegie," Sci. Results of Cruise VII of the Carnegie during 1928-29 under Command of Captain J. P. Ault, Chemistry I, v plus 58 pp., Washington (1944).
10. A. C. REDFIELD, "The hydrography of the Gulf of Venezuela," Papers in Marine Biology and Oceanography, Supplement to *Deep-Sea Research*, 3, pp. 115-133 (1955).
11. J. SNOBKLAŠA, "Biochemischer Kreislauf des Phosphat-Ions im Boden," *Zentralbl. Bakt.*, II, 29, 385-419 (1911).
12. G. E. HUTCHINSON, "Nitrogen in the biogeochemistry of the atmosphere," *Am. Scientist*, 32, pp. 178-195 (1944).
13. J. H. J. POOLIE, "The evolution of the atmosphere," *Royal Dublin Soc., Sci. Proc.*, 22 (n.s.), pp. 345-365 (1941).
14. S. A. WAKSMAN, "Principles of soil microbiology," Ed. 2, 894 pp., Baltimore (1932).
15. A. C. REDFIELD, "The exchange of oxygen across the sea surface," *Jour. Marine Research*, 7, pp. 347-361 (1948).
16. R. S. DIETZ, K. O. EMERY, and F. P. SHEPARD, "Phosphorite deposits on the sea floor off southern California," *Bull. Geol. Soc. America*, 53, pp. 815-847 (1942).
17. W. W. RUBEY, "Geologic history of sea water," *Bull. Geol. Soc. America*, 62, pp. 1111-1147 (1951).
18. T. VON BRAND, N. W. RAKESTRAW, and C. E. RENN, "Further experiments on the decomposition and regeneration of nitrogenous organic matter in sea water," *Biol. Bull.*, 77, 285-296 (1939).
19. K. RANKAMA and T. G. SAHAMA, "Geochemistry," 912 pp., Chicago (1950).
20. H. U. STERDRUP, M. W. JOHNSON, and R. H. FLEMING, "The Oceans," 1087 pp., New York (1942).
21. N. W. RAKESTRAW and V. M. EMMEL, "The solubility of nitrogen and argon in sea water," *Jour. Phys. Chem.*, 42, pp. 1211-1215 (1938).
22. F. A. RICHARDS and N. CORWIN, "Some oceanographic applications of recent determinations of the solubility of oxygen in sea water," *Limnology and Oceanography*, 1, pp. 263-267 (1956).