THE OXYGEN CYCLE

The oxygen in the atmosphere was originally put there by plants. Hence the early plants made possible the evolution of the higher plants and animals that require free oxygen for their metabolism

by Preston Cloud and Aharon Gibor

The history of our planet, as recorded in its rocks and fossils, is reflected in the composition and the biochemical peculiarities of its present biosphere. With a little imagination one can reconstruct from that evidence the appearance and subsequent evolution of gaseous oxygen in the earth's air and water, and the changing pathways of oxygen in the metabolism of living things.

Differentiated multicellular life (consisting of tissues and organs) evolved only after free oxygen appeared in the atmosphere. The cells of animals that are truly multicellular in this sense, the Metazoa, obtain their energy by breaking down fuel (produced originally by photosynthesis) in the presence of oxygen in the process called respiration. The evolution of advanced forms of animal life would probably not have been possible without the high levels of energy release that are characteristic of oxidative metabolism. At the same time free oxygen is potentially destructive to all forms of carbon-based life (and we know no other kind of life). Most organisms have therefore had to "learn" to conduct their oxidations anaerobically, primarily by removing hydrogen from foodstuff rather than by adding oxygen. Indeed, the anaerobic process called fermentation is still the fundamental way of life, underlying other forms of metabolism.

Oxygen in the free state thus plays a role in the evolution and present functioning of the biosphere that is both pervasive and ambivalent. The origin of life

and its subsequent evolution was contingent on the development of systems that shielded it from, or provided chemical defenses against, ordinary molecular oxygen (O_2), ozone (O_3) and atomic oxygen (O). Yet the energy requirements of higher life forms can be met only by oxidative metabolism. The oxidation of the simple sugar glucose, for example, yields 686 kilocalories per mole; the fermentation of glucose yields only 50 kilocalories per mole.

Free oxygen not only supports life; it arises from life. The oxygen now in the atmosphere is probably mainly, if not wholly, of biological origin. Some of it is converted to ozone, causing certain high-energy wavelengths to be filtered out of the radiation that reaches the surface of the earth. Oxygen also combines with a wide range of other elements in the earth's crust. The result of these and other processes is an intimate evolutionary interaction among the biosphere, the atmosphere, the hydrosphere and the lithosphere.

Consider where the oxygen comes from to support the high rates of energy release observed in multicellular organisms and what happens to it and to the carbon dioxide that is respired [see illustration on page 114]. The oxygen, of course, comes from the air, of which it constitutes roughly 21 percent. Ultimately, however, it originates with the decomposition of water molecules by light energy in photosynthesis. The 1.5 billion cubic kilometers of water on the earth are split by photosynthesis and reconsti-

tuted by respiration once every two million years or so. Photosynthetically generated oxygen temporarily enters the atmospheric bank, whence it is itself recycled once every 2,000 years or so (at current rates). The carbon dioxide that is respired joins the small amount (.03 percent) already in the atmosphere, which is in balance with the carbon dioxide in the oceans and other parts of the hydrosphere. Through other interactions it may be removed from circulation as a part of the carbonate ion (CO_3^-) in calcium carbonate precipitated from solution. Carbon dioxide thus sequestered may eventually be returned to the atmosphere when limestone, formed by the consolidation of calcium carbonate sediments, emerges from under the sea and is dissolved by some future rainfall.

Thus do sea, air, rock and life interact and exchange components. Before taking up these interactions in somewhat greater detail let us examine the function oxygen serves within individual organisms.

Oxygen plays a fundamental role as a building block of practically all vital molecules, accounting for about a fourth of the atoms in living matter. Practically all organic matter in the present biosphere originates in the process of photosynthesis, whereby plants utilize light energy to react carbon dioxide with water and synthesize organic substances. Since carbohydrates (such as sugar), with the general formula $(CH_2O)_n$, are the common fuels that are stored by plants, the essential reaction of photosynthesis can be written as $CO_2 + H_2O +$ light energy $\rightarrow CH_2O + O_2$. It is not immediately obvious from this formulation which of the reactants serves as the source of oxygen atoms in the carbohydrates and which is the source of free molecular oxygen. In 1941 Samuel Ruben and Mar-
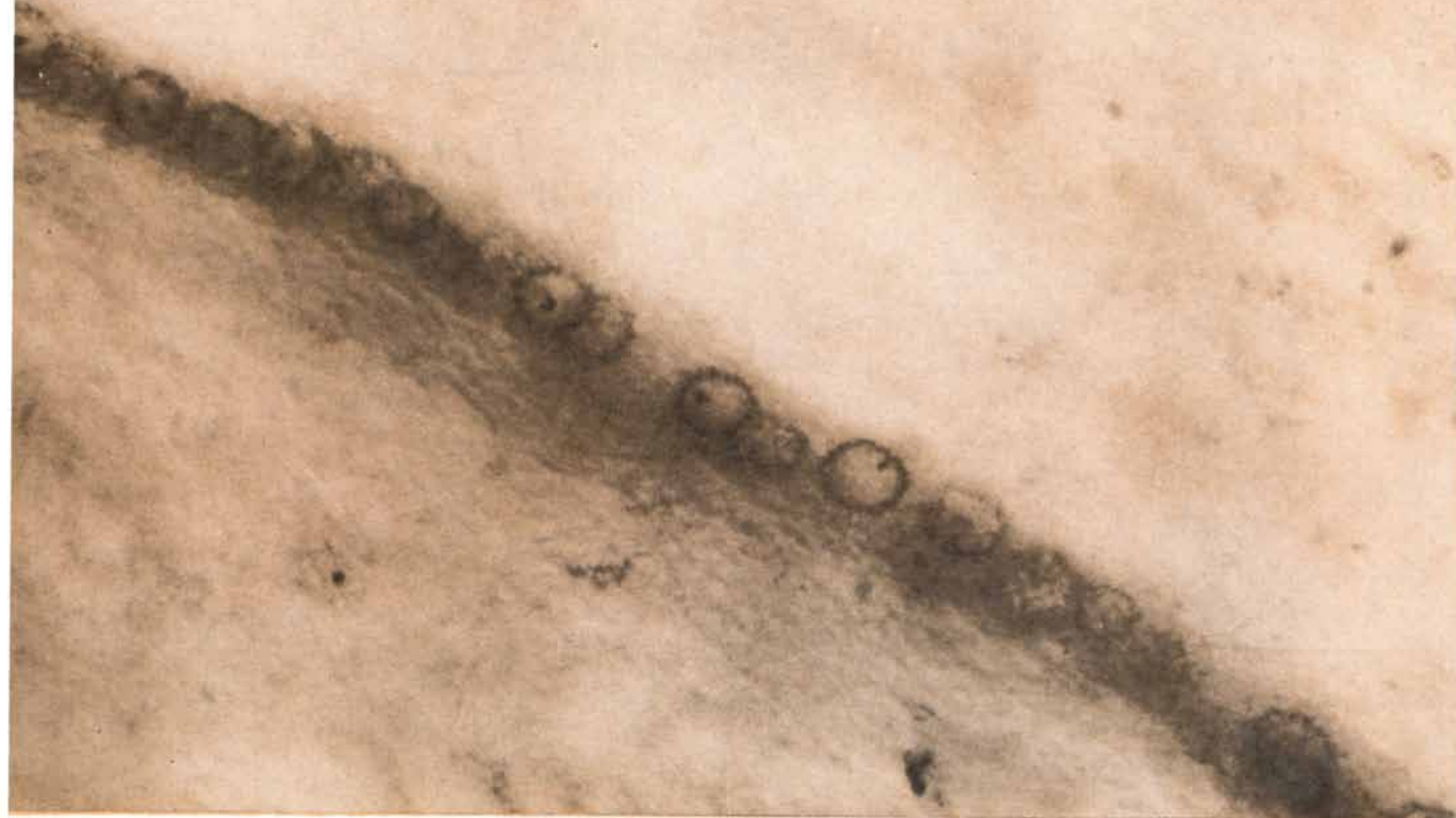
EUCARYOTIC CELLS, which contain a nucleus and divide by mitosis, were, like oxygen, a necessary precondition for the evolution of higher life forms. The oldest eucaryotes known were found in the Beck Spring Dolomite of eastern California by Cloud and his colleagues. The photomicrograph above shows eucaryotic cells with an average diameter of 14 microns, probably green algae. The regular occurrence and position of the dark spots suggest they may be remnants of nuclei or other organelles. Other cell forms, which do not appear in the picture, show branching and large filament diameters that also indicate the eucaryotic level of evolution.

PROCARYOTIC CELLS, which lack a nucleus and divide by simple fission, were a more primitive form of life than the eucaryotes and persist today in the bacteria and blue-green algae. Procaryotes were found in the Beck Spring Dolomite in association with the primitive eucaryotes such as those in the photograph at the top of the page. A mat of threadlike procaryotic blue-green algae, each thread of which is about 3.5 microns in diameter, is seen in the photomicrograph below. It was made, like the one at top of page, by Gerald R. Licari. Cells of this kind, among others, presumably produced photosynthetic oxygen before eucaryotes appeared.
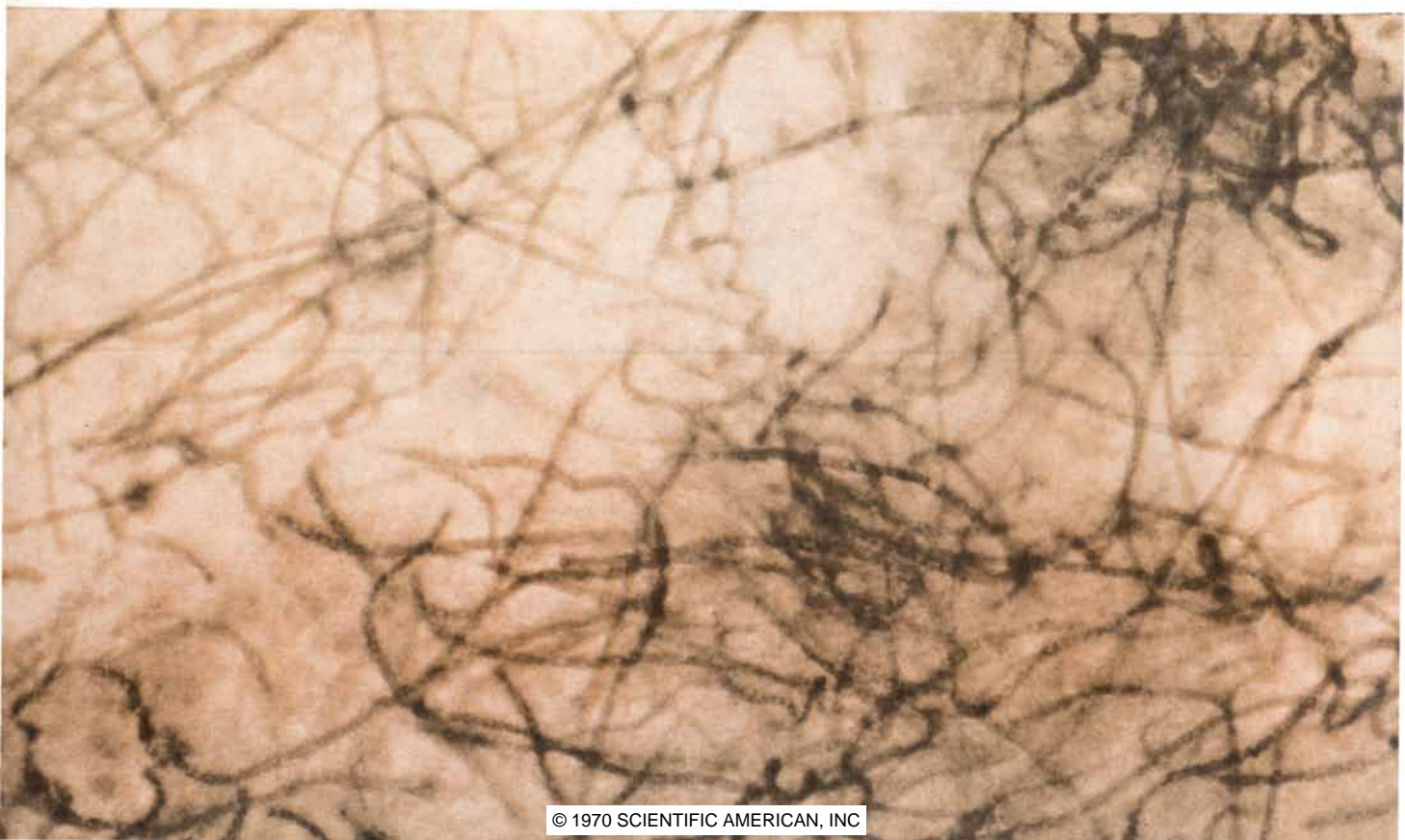
tin D. Kamen of the University of California at Berkeley used the heavy oxygen isotope oxygen 18 as a tracer to demonstrate that the molecular oxygen is derived from the splitting of the water molecule. This observation also suggested that carbon dioxide is the source of the oxygen atoms of the synthesized organic molecules.

The primary products of photosynthesis undergo a vast number of chemical transformations in plant cells and subsequently in the cells of the animals that feed on plants. During these processes changes of course take place in the atomic composition and energy content of the organic molecules. Such transformations can result in carbon compounds that are either more "reduced" or more "oxidized" than carbohydrates. The oxidation-reduction reactions between these compounds are the essence of biological energy supply and demand. A more reduced compound has more hydrogen atoms and fewer oxygen atoms per carbon atom; a more oxidized compound has fewer hydrogen atoms and more oxygen atoms per carbon atom. The combustion of a reduced compound liberates more energy than the combustion of a more oxidized one. An example of a molecule more reduced than a carbohydrate is the familiar alcohol ethanol (C_2H_6O); a more oxidized molecule is pyruvic acid ($C_3H_4O_3$).

Differences in the relative abundance of hydrogen and oxygen atoms in organic molecules result primarily from one of the following reactions: (1) the removal (dehydrogenation) or addition (hydrogenation) of hydrogen atoms, (2) the addition of water (hydration), followed by dehydrogenation; (3) the direct addition of oxygen (oxygenation). The second and third of these processes introduce into organic matter additional oxygen atoms either from water or from molecular oxygen. On decomposition the oxygen atoms of organic molecules are released as carbon dioxide and water. The biological oxidation of molecules such as carbohydrates can be written as the reverse of photosynthesis: $CH_2O + O_2 \rightarrow CO_2 + H_2O$ + energy. The oxygen atom of the organic molecule appears in the carbon dioxide and the molecular oxygen acts as the acceptor for the hydrogen atoms.

The three major nonliving sources of oxygen atoms are therefore carbon dioxide, water and molecular oxygen, and since these molecules exchange oxygen atoms, they can be considered as a common pool. Common mineral oxides such as nitrate ions and sulfate ions are also oxygen sources for living organisms,

which reduce them to ammonia (NH_3) and hydrogen sulfide (H_2S). They are subsequently reoxidized, and so as the oxides circulate through the biosphere their oxygen atoms are exchanged with water.

The dynamic role of molecular oxygen is as an electron sink, or hydrogen acceptor, in biological oxidations. The biological oxidation of organic molecules proceeds primarily by dehydrogenation: enzymes remove hydrogen atoms from the substrate molecule and transfer them to specialized molecules that function as hydrogen carriers [see top illustration on pages 116 and 117]. If these carriers become saturated with hydrogen, no further oxidation can take place until some other acceptor becomes available. In the anaerobic process of fermentation organic molecules serve as the hydrogen acceptor. Fermentation therefore results in the oxidation of some organic compounds and the simultaneous reduction of others, as in the fermentation of glucose by yeast: part of the sugar molecule is oxidized to carbon dioxide and other parts are reduced to ethanol.

In aerobic respiration oxygen serves as the hydrogen acceptor and water is produced. The transfer of hydrogen atoms (which is to say of electrons and protons) to oxygen is channeled through an array of catalysts and cofactors. Prominent among the cofactors are the iron-containing pigmented molecules called cytochromes, of which there are several kinds that differ in their affinity for electrons. This affinity is expressed as the oxidation-reduction, or "redox," potential of the molecule; the more positive the potential, the greater the affinity of the oxidized molecule for electrons. For example, the redox potential of cytochrome b is .12 volt, the potential of cytochrome c is .22 volt and the potential of cytochrome a is .29 volt. The redox potential for the reduction of oxygen to water is .8 volt. The passage of electrons from one cytochrome to another down a potential gradient, from cytochrome b to cytochrome c to the cytochrome a complex and on to oxygen, results in the alternate reduction and oxidation of these cofactors. Energy liberated in such oxidation-reduction reactions is coupled to the synthesis of high-energy phosphate compounds such as adenosine triphosphate (ATP). The special copper-containing enzyme cytochrome oxidase mediates the ultimate transfer of electrons from the cytochrome a complex to oxygen. This activation and binding of oxygen is seen as the fundamental step, and possibly

the original primitive step, in the evolution of oxidative metabolism.

In cells of higher organisms the oxidative system of enzymes and electron carriers is located in the special organelles called mitochondria. These organelles can be regarded as efficient low-temperature furnaces where organic molecules are burned with oxygen. Most of the released energy is converted into the high-energy bonds of ATP.

Molecular oxygen reacts spontaneously with organic compounds and other reduced substances. This reactivity explains the toxic effects of oxygen above tolerable concentrations. Louis Pasteur discovered that very sensitive organisms such as obligate anaerobes cannot tolerate oxygen concentrations above about 1 percent of the present atmospheric level. Recently the cells of higher organisms have been found to contain organelles called peroxisomes, whose major function is thought to be the protection of cells from oxygen. The peroxisomes contain enzymes that catalyze the direct reduction of oxygen molecules through the oxidation of metabolites such as amino acids and other organic acids. Hydrogen peroxide (H_2O_2) is one of the products of such oxidation. Another of the peroxisome enzymes, catalase, utilizes the hydrogen peroxide as a hydrogen acceptor in the oxidation of substrates such as ethanol or lactic acid. The rate of reduction of oxygen by the peroxisomes increases proportionately with an increase in oxygen concentration, so that an excessive amount of oxygen in the cell increases the rate of its reduction by peroxisomes.

Christian de Duve of Rockefeller University has suggested that the peroxisomes represent a primitive enzyme system that evolved to cope with oxygen when it first appeared in the atmosphere. The peroxisome enzymes enabled the first oxidatively metabolizing cells to use oxygen as a hydrogen acceptor and so reoxidize the reduced products of fermentation. In some respects this process is similar to the oxidative reactions of the mitochondria. Both make further dehydrogenation possible by liberating oxidized hydrogen carriers. The basic difference between the mitochondrial oxidation reactions and those of peroxisomes is that in peroxisomes the steps of oxidation are not coupled to the synthesis of ATP. The energy released in the peroxisomes is thus lost to the cell; the function of the organelle is primarily to protect against the destructive effects of free molecular oxygen.

Oxygen dissolved in water can diffuse
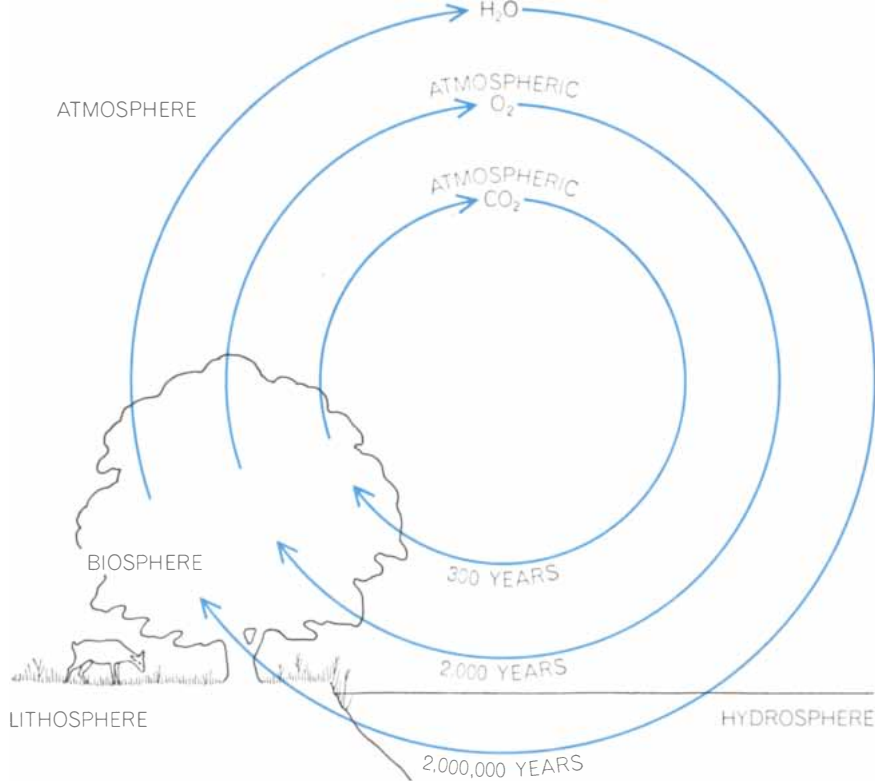
BIOSPHERE EXCHANGES water vapor, oxygen and carbon dioxide with the atmosphere and hydrosphere in a continuing cycle, shown here in simplified form. All the earth's water is split by plant cells and reconstituted by animal and plant cells about every two million years. Oxygen generated in the process enters the atmosphere and is recycled in about 2,000 years. Carbon dioxide respired by animal and plant cells enters the atmosphere and is fixed again by plant cells after an average atmospheric residence time of about 300 years.

across both the inner and the outer membranes of the cell, and the supply of oxygen by diffusion is adequate for single cells and for organisms consisting of small colonies of cells. Differentiated multicellular organisms, however, require more efficient modes of supplying oxygen to tissues and organs. Since all higher organisms depend primarily on mitochondrial aerobic oxidation to generate the energy that maintains their active mode of life, they have evolved elaborate systems to ensure their tissues an adequate supply of oxygen, the gas that once was lethal (and still is, in excess). Two basic devices serve this purpose: special chemical carriers that increase the oxygen capacity of body fluids, and anatomical structures that provide relatively large surfaces for the rapid exchange of gases. The typical properties of an oxygen carrier are exemplified by those of hemoglobin and of myoglobin, or muscle hemoglobin. Hemoglobin in blood readily absorbs oxygen to near-saturation at oxygen pressures such as those found in the lung. When the blood is exposed to lower oxygen pressures as it moves from the lungs to other tissues, the hemoglobin discharges most of its bound oxygen. Myoglobin, which acts as

a reservoir to meet the sharp demand for oxygen in muscle contraction, gives up its oxygen more rapidly. Such reversible bonding of oxygen in response to changes in oxygen pressure is an essential property of biochemical oxygen carriers.

Lungs and gills are examples of anatomical structures in which large wet areas of thin membranous tissue come in contact with oxygen. Body fluids are pumped over one side of these membranes and air, or water containing oxygen, over the other side. This ensures a rapid gas exchange between large volumes of body fluid and the environment.

How did the relations between organisms and gaseous oxygen happen to evolve in such a curiously complicated manner? The atmosphere under which life arose on the earth was almost certainly devoid of free oxygen. The low concentration of noble gases such as neon and krypton in the terrestrial atmosphere compared with their cosmic abundance, together with other geochemical evidence, indicates that the terrestrial atmosphere had a secondary origin in volcanic outgassing from the earth's interior. Oxygen is not known among the gases so released, nor is it
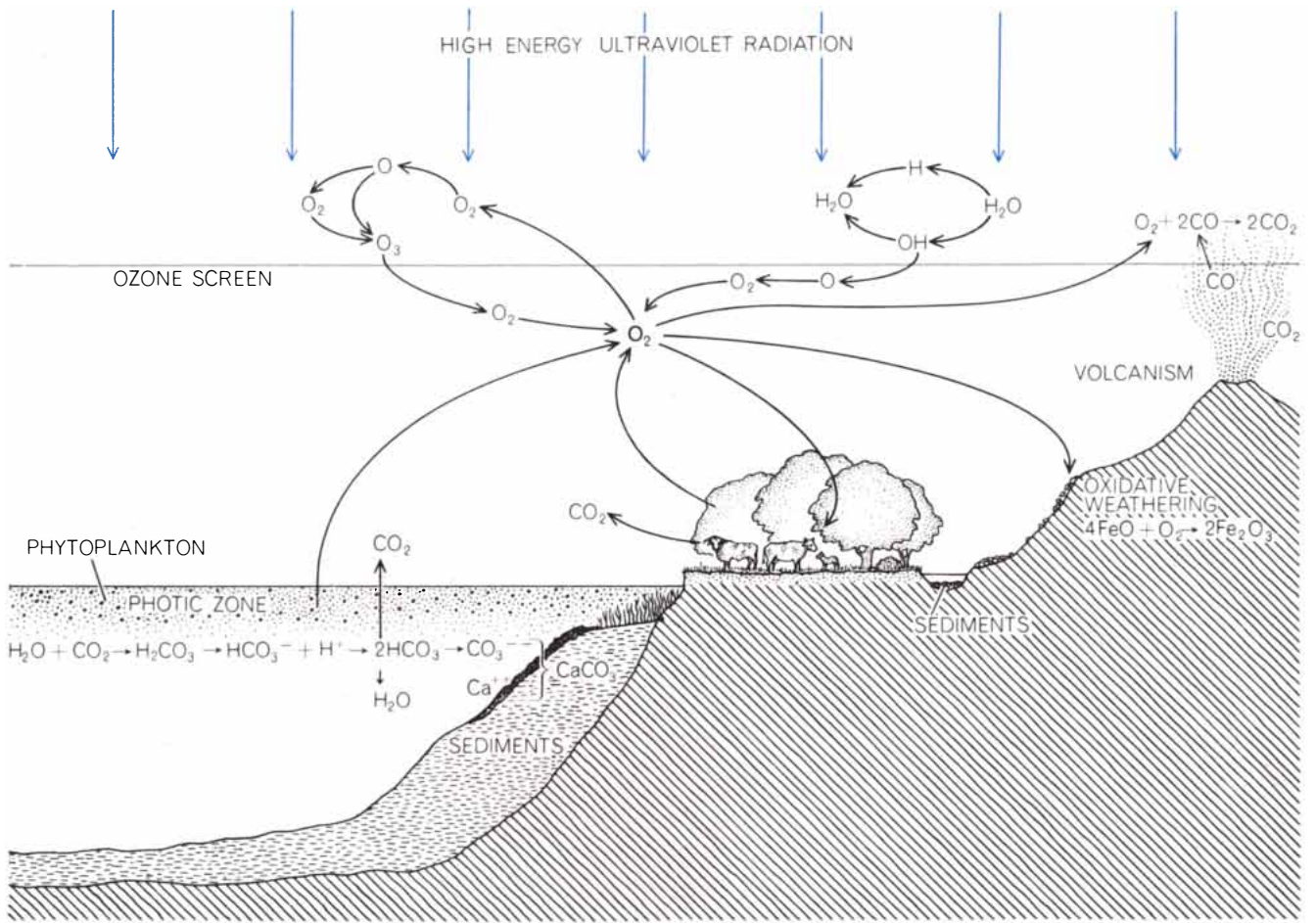
found as inclusions in igneous rocks. The chemistry of rocks older than about two billion years is also inconsistent with the presence of more than trivial quantities of free atmospheric oxygen before that time. Moreover, it would not have been possible for the essential chemical precursors of life—or life itself—to have originated and persisted in the presence of free oxygen before the evolution of suitable oxygen-mediating enzymes.

On such grounds we conclude that the first living organism must have depended on fermentation for its livelihood. Organic substances that originated in nonvital reactions served as substrates for these primordial fermentations. The first organism, therefore, was not only an anaerobe; it was also a heterotroph, dependent on a preexisting organic food supply and incapable of manufacturing its own food by photosynthesis or other autotrophic processes.

The emergence of an autotroph was an essential step in the onward march of biological evolution. This evolutionary step left its mark in the rocks as well as on all living forms. Some fated eobiont, as we may call these early life forms whose properties we can as yet only imagine, evolved and became an autotroph, an organism capable of manufacturing its own food. Biogeological evidence suggests that this critical event may have occurred more than three billion years ago.

If, as seems inescapable, the first autotrophic eobiont was also anaerobic, it would have encountered difficulty when it first learned to split water and release free oxygen. John M. Olson of the Brookhaven National Laboratory recently suggested biochemical arguments to support the idea that primitive photosynthesis may have obtained electrons from substances other than water. He argues that large-scale splitting of water and release of oxygen may have been delayed until the evolution of appropriate enzymes to detoxify this reactive substance.

We nevertheless find a long record of oxidized marine sediments of a peculiar type that precedes the first evidence of atmospheric oxygen in rocks about 1.8 billion years old; we do not find them in significant amounts in more recent strata. These oxidized marine sediments, known as banded iron formations, are alternately iron-rich and iron-poor chemical sediments that were laid down in open bodies of water. Much of the iron in them is ferric (the oxidized form, Fe^{+++}) rather than ferrous (the reduced form, Fe^{++}), implying that there was a source of oxygen in the column of water above them. Considering the

HIGH ENERGY ULTRAVIOLET RADIATION

OZONE SCREEN

O
O_2 O_2
O_3
O_2
O_2 ← O
O_2

H
H_2O H_2O
OH

$O_2 + 2CO \rightarrow 2CO_2$
CO
CO_2

VOLCANISM

PHYTOPLANKTON

CO_2

CO_2

PHOTIC ZONE

OXIDATIVE WEATHERING
$4FeO + O_2 \rightarrow 2Fe_2O_3$

$H_2O + CO_2 \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+ \rightarrow 2HCO_3 \rightarrow CO_3^-$

H_2O

Ca^+ $CaCO_3$

SEDIMENTS

SEDIMENTS

OXYGEN CYCLE is complicated because oxygen appears in so many chemical forms and combinations, primarily as molecular oxygen (O_2), in water and in organic and inorganic compounds. Some global pathways of oxygen are shown here in simplified form.

39×10^{20} GRAMS

551×10^{20} GRAMS

ATMOSPHERE

SULFATE IN SALT WATER

OTHER SOURCES

CARBONATE ROCKS

ORGANIC MATTER IN SEDIMENTARY ROCKS

SEDIMENTARY SULFATE

OXIDATION OF FeO to Fe_2O_3

TOTAL OXYGEN
590×10^{20} GRAMS

ATMOSPHERE, HYDROSPHERE AND BIOSPHERE

CARBONATE ROCKS AND AS CARBON IN SEDIMENTARY ROCKS

TOTAL CARBON
252×10^{20} GRAMS
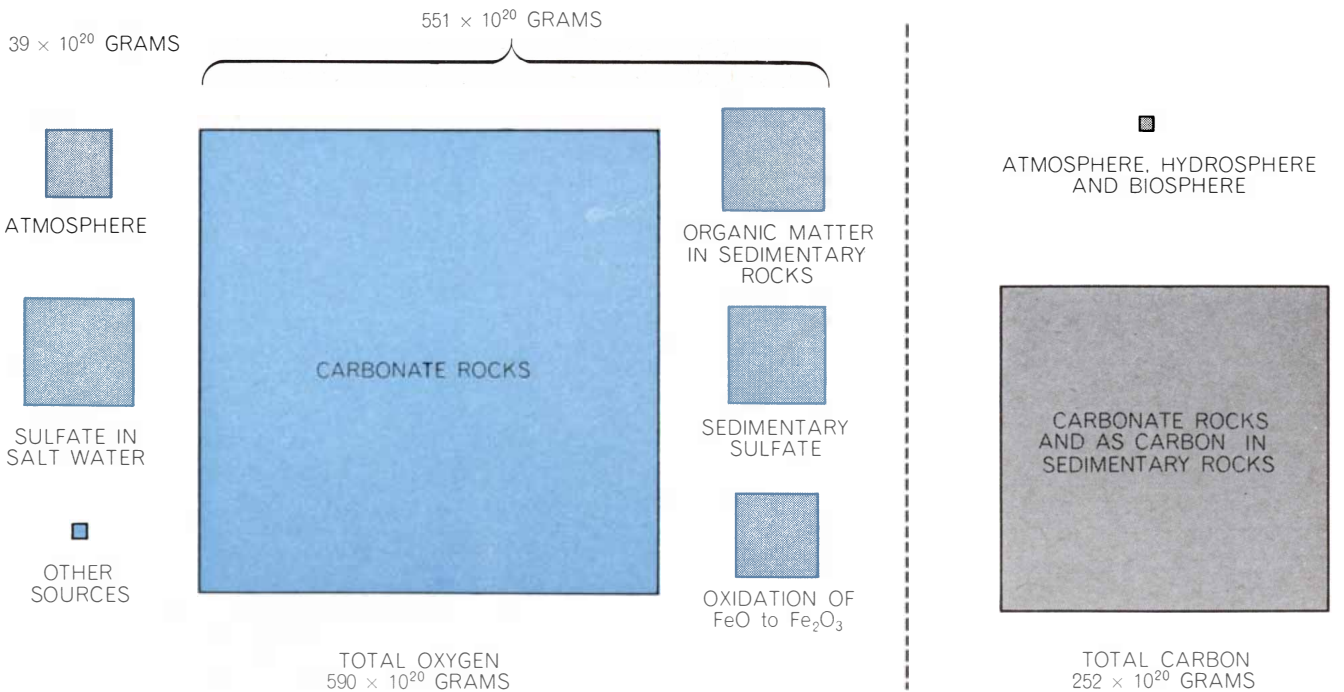
OXYGEN-CARBON BALANCE SHEET suggests that photosynthesis can account not only for all the oxygen in the atmosphere but also for the much larger amount of "fossil" oxygen, mostly in compounds in sediments. The diagram, based on estimates made by William W. Rubey, indicates that the elements are present in about the proportion, 12/32, that would account for their derivation through photosynthesis from carbon dioxide (one atom of carbon, molecular weight 12, to two of oxygen, molecular weight 16).

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a MYO-INOSITOL → (INOSITOL OXYGENASE, O_2, H_2O) → D-GLUCURONIC ACID

b SUCCINIC ACID → (SUCCINIC DEHYDROGENASE, FAD, $FADH_2$) → FUMARIC ACID
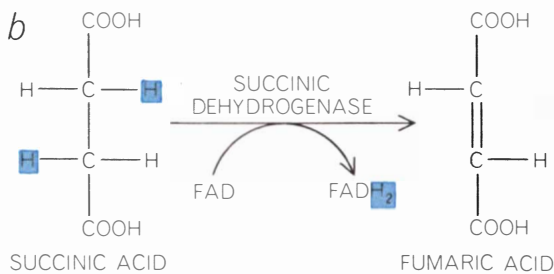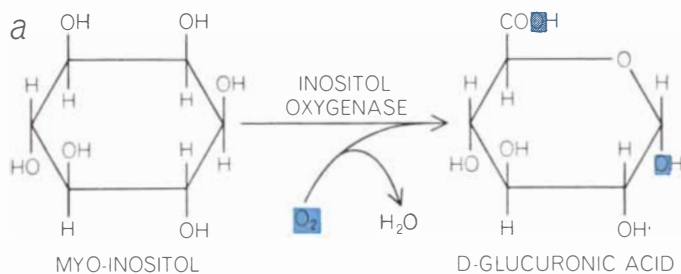
OXIDATION involves a decrease in the number of hydrogen atoms in a molecule or an increase in the number of oxygen atoms. It may be accomplished in several ways. In oxygenation (*a*) oxygen is added directly. In dehydrogenation (*b*) hydrogen is re-

problems that would face a water-splitting photosynthesizer before the evolution of advanced oxygen-mediating enzymes such as oxidases and catalases, one can visualize how the biological oxygen cycle may have interacted with ions in solution in bodies of water during that time. The first oxygen-releasing photoautotrophs may have used ferrous compounds in solution as oxygen acceptors—oxygen for them being merely a toxic waste product. This would have precipitated iron in the ferric form ($4FeO + O_2 \rightarrow 2Fe_2O_3$) or in the ferro-ferric form (Fe_3O_4). A recurrent imbalance of supply and demand might then account for the cyclic nature and differing types of the banded iron formations.
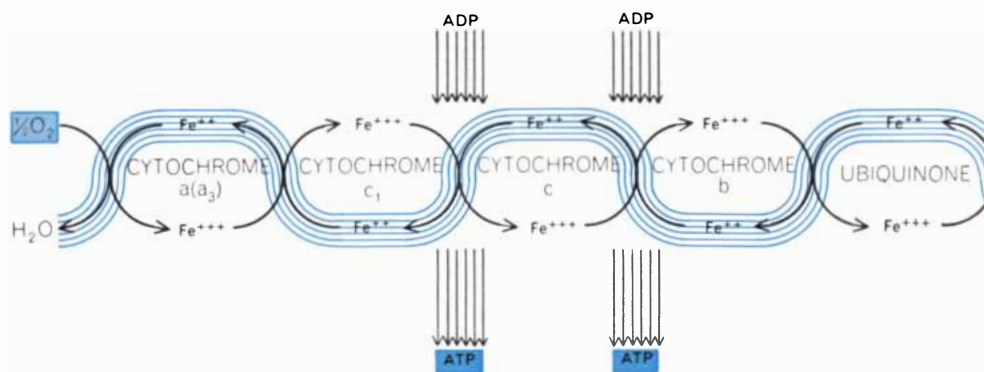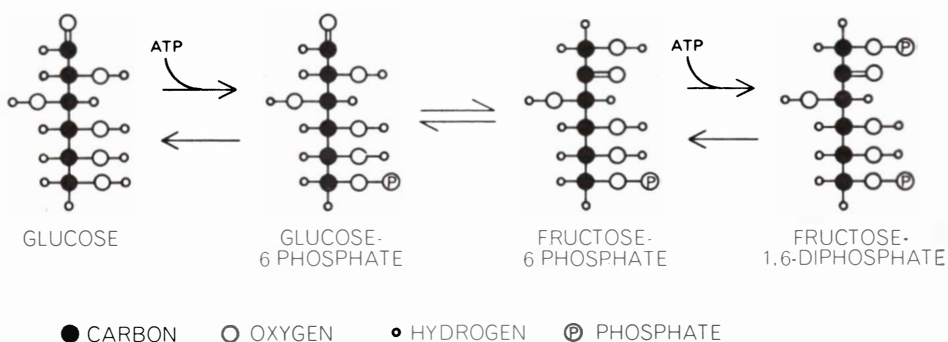
Once advanced oxygen-mediating enzymes arose, oxygen generated by increasing populations of photoautotrophs containing these enzymes would build up in the oceans and begin to escape into the atmosphere. There the ultraviolet component of the sun's radiation would dissociate some of the molecular oxygen into highly reactive atomic oxygen and also give rise to equally reactive ozone. Atmospheric oxygen and its reactive derivatives (even in small quantities) would lead to the oxidation of iron in sediments produced by the weathering of rocks, to the greatly reduced solubility of iron in surface waters (now oxygenated), to the termination of the banded iron formations as an important sedimentary type and to the extensive formation of continental red beds rich in ferric iron [*see illustration on page 110*]. The record of the rocks supports this succession of events: red beds are essentially restricted to rocks younger than about 1.8 billion years, whereas banded iron formation is found only in older rocks.

So far we have assumed that oxygen accumulated in the atmosphere as a consequence of photosynthesis by green plants. How could this happen if the entire process of photosynthesis and respiration is cyclic, representable by the reversible equation $CO_2 + H_2O + energy$ $\rightleftharpoons CH_2O + O_2$? Except to the extent that carbon or its compounds are somehow sequestered, carbohydrates produced by photosynthesis will be reoxidized back to carbon dioxide and water, and no significant quantity of free oxygen will accumulate. The carbon that is sequestered in the earth as graphite in the oldest rocks and as coal, oil, gas and other carbonaceous compounds in the younger ones, and in the living and dead bodies of plants and animals, is the equivalent of the oxygen in oxidized sediments and in the earth's atmosphere! In attempting to strike a carbon-oxygen balance we must find enough carbon to account not only for the oxygen in the present atmosphere but also for the "fossil" oxygen that went into the conversion of ferrous oxides to ferric oxides, sulfides to sulfates, carbon monoxide to carbon dioxide and so on.

Interestingly, rough estimates made some years ago by William W. Rubey,

GLUCOSE → (ATP) → GLUCOSE-6 PHOSPHATE ⇌ FRUCTOSE-6 PHOSPHATE → (ATP) → FRUCTOSE-1,6-DIPHOSPHATE

● CARBON   ○ OXYGEN   • HYDROGEN   Ⓟ PHOSPHATE

OXIDATIVE METABOLISM provides the energy that powers all higher forms of life. It proceeds in two phases: glycolysis (*top*), an anaerobic phase that does not require oxygen, and aerobic respiration (*bottom*), which requires oxygen. In glycolysis (or fermentation, the anaerobic process by which organisms such as yeast derive their energy) a molecule of the six-carbon sugar glucose is broken down into two molecules of the three-carbon compound pyruvic acid with a net gain of two molecules of adenosine triphosphate, the cellular

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C

FUMARATE HYDROTASE

MALIC ACID DEHYDROGENASE

FUMARIC ACID   L-MALIC ACID   OXALOACETIC ACID
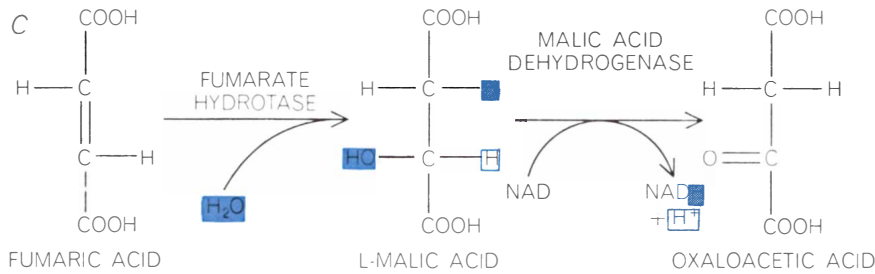
moved. In hydration-dehydrogenation (c) water is added and hydrogen is removed. Oxygenation does not occur in respiration, in which oxygen serves only as a hydrogen acceptor.

now of the University of California at Los Angeles, do imply an approximate balance between the chemical combining equivalents of carbon and oxygen in sediments, the atmosphere, the hydrosphere and the biosphere [see bottom illustration on page 115]. The relatively small excess of carbon in Rubey's estimates could be accounted for by the oxygen used in converting carbon monoxide to carbon dioxide. Or it might be due to an underestimate of the quantities of sulfate ion or ferric oxide in sediments. (Rubey's estimates could not include large iron formations recently discovered in western Australia and elsewhere.) The carbon dioxide in carbonate rocks does not need to be accounted for, but the oxygen involved in converting it to carbonate ion does. The recycling of sediments through metamorphism, mountain-building and the movement of ocean-floor plates under the continents is a variable of unknown dimensions, but

it probably does not affect the approximate balance observed in view of the fact that the overwhelmingly large pools to be balanced are all in the lithosphere and that carbon and oxygen losses would be roughly equivalent. The small amounts of oxygen dissolved in water are not included in this balance.

Nonetheless, water does enter the picture. Another possible source of oxygen in our atmosphere is photolysis, the ultraviolet dissociation of water vapor in the outer atmosphere followed by the escape of the hydrogen from the earth's gravitational field. This has usually been regarded as a trivial source, however. Although R. T. Brinkmann of the California Institute of Technology has recently argued that nonbiological photolysis may be a major source of atmospheric oxygen, the carbon-oxygen balance sheet does not support that belief, which also runs into other difficulties.

When free oxygen began to accumulate in the atmosphere some 1.8 billion years ago, life was still restricted to sites
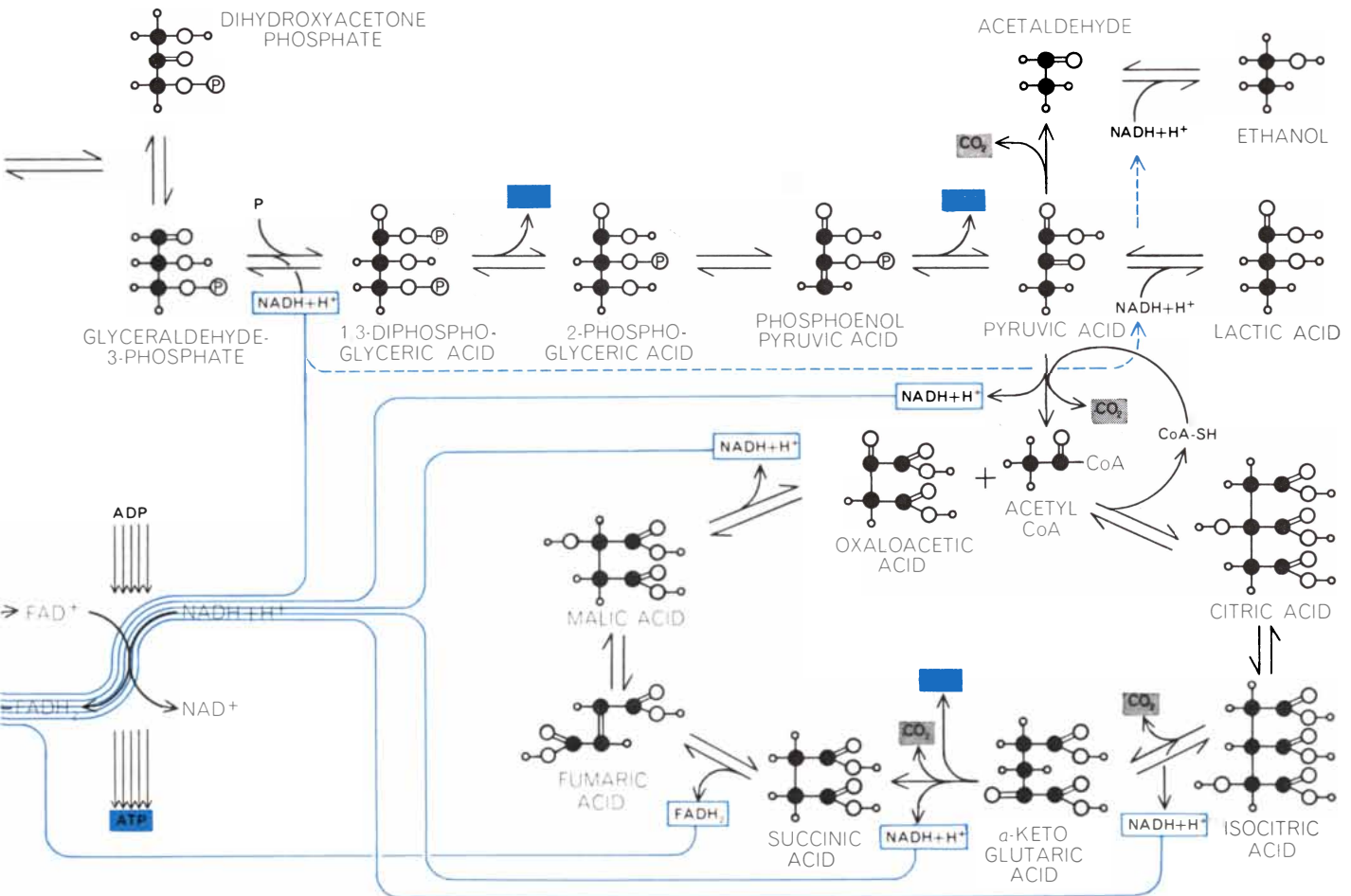
energy carrier. The pyruvic acid is converted into lactic acid in animal cells deprived of oxygen and into some other compound, such as ethanol, in fermentation. In aerobic cells in the presence of oxygen, however, pyruvic acid is completely oxidized to produce carbon dioxide and water. In the process hydrogen ions are removed. The electrons of these hydrogens (and of two removed in glycolysis) are passed along by two electron carriers, nicotinamide adenine dinucleotide (NAD) and flavin adenine dinucleotide (FAD), to a chain of respiratory enzymes, ubiquinone and the cytochromes, which are alternately reduced and oxidized. Energy released in the reactions is coupled to synthesis of ATP, 38 molecules of which are produced for every molecule of glucose consumed.

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shielded from destructive ultraviolet radiation by sufficient depths of water or by screens of sediment. In time enough oxygen built up in the atmosphere for ozone, a strong absorber in the ultraviolet, to form a shield against incoming ultraviolet radiation. The late Lloyd V. Berkner and Lauriston C. Marshall of the Graduate Research Center of the Southwest in Dallas calculated that only 1 percent of the present atmospheric level of oxygen would give rise to a sufficient level of ozone to screen out the most deleterious wavelengths of the ultraviolet radiation. This also happens to be the level of oxygen at which Pasteur found that certain microorganisms switch over from a fermentative type of metabolism to an oxidative one. Berkner and Marshall therefore jumped to the conclusion (reasonably enough on the evidence they considered) that this was the stage at which oxidative metabolism arose. They related this stage to the first appearance of metazoan life somewhat more than 600 million years ago.

The geological record has long made it plain, however, that free molecular oxygen existed in the atmosphere well before that relatively late date in geologic time. Moreover, recent evidence is consistent with the origin of oxidative metabolism at least twice as long ago. Eucaryotic cells—cells with organized nuclei and other organelles—have been identified in rocks in eastern California that are believed to be about 1.3 billion years old [*see top illustration on page 112*]. Since all living eucaryotes depend on oxidative metabolism, it seems likely that these ancestral forms did too. The oxygen level may nonetheless have still been quite low at this stage. Simple diffusion would suffice to move enough oxygen across cell boundaries and within the cell, even at very low concentrations, to supply the early oxidative metabolizers. A higher order of organization and of atmospheric oxygen was required, however, for advanced oxidative metabolism. Perhaps that is why, although the eucaryotic cell existed at least 1.2 billion years ago, we have no unequivocal fossils of metazoan organisms from rocks older than perhaps 640 million years.

In other words, perhaps Berkner and Marshall were mistaken only in trying to make the appearance of the Metazoa coincide with the onset of oxidative metabolism. Once the level of atmospheric oxygen was high enough to generate an effective ozone screen, photosynthetic organisms would have been able to spread throughout the surface waters of the sea, greatly accelerating the rate of oxygen production. The plausible episodes in geological history to correlate with this development are the secondary oxidation of the banded iron formations and the appearance of sedimentary calcium sulfate (gypsum and anhydrite) on a large scale. These events occurred just as or just before the Metazoa first appeared in early Paleozoic time. The attainment of a suitable level of atmospheric oxygen may thus be correlated with the emergence of metazoan root stocks from premetazoan ancestors beginning about 640 million years ago. The fact that oxygen could accumulate no faster than carbon (or hydrogen) was removed argues against the likelihood of a rapid early buildup of oxygen.

That subsequent biospheric and atmospheric evolution were closely interlinked can now be taken for granted. What is not known are the details. Did oxygen levels in the atmosphere increase steadily throughout geologic time, marking regular stages of biological evolution such as the emergence of land plants, of
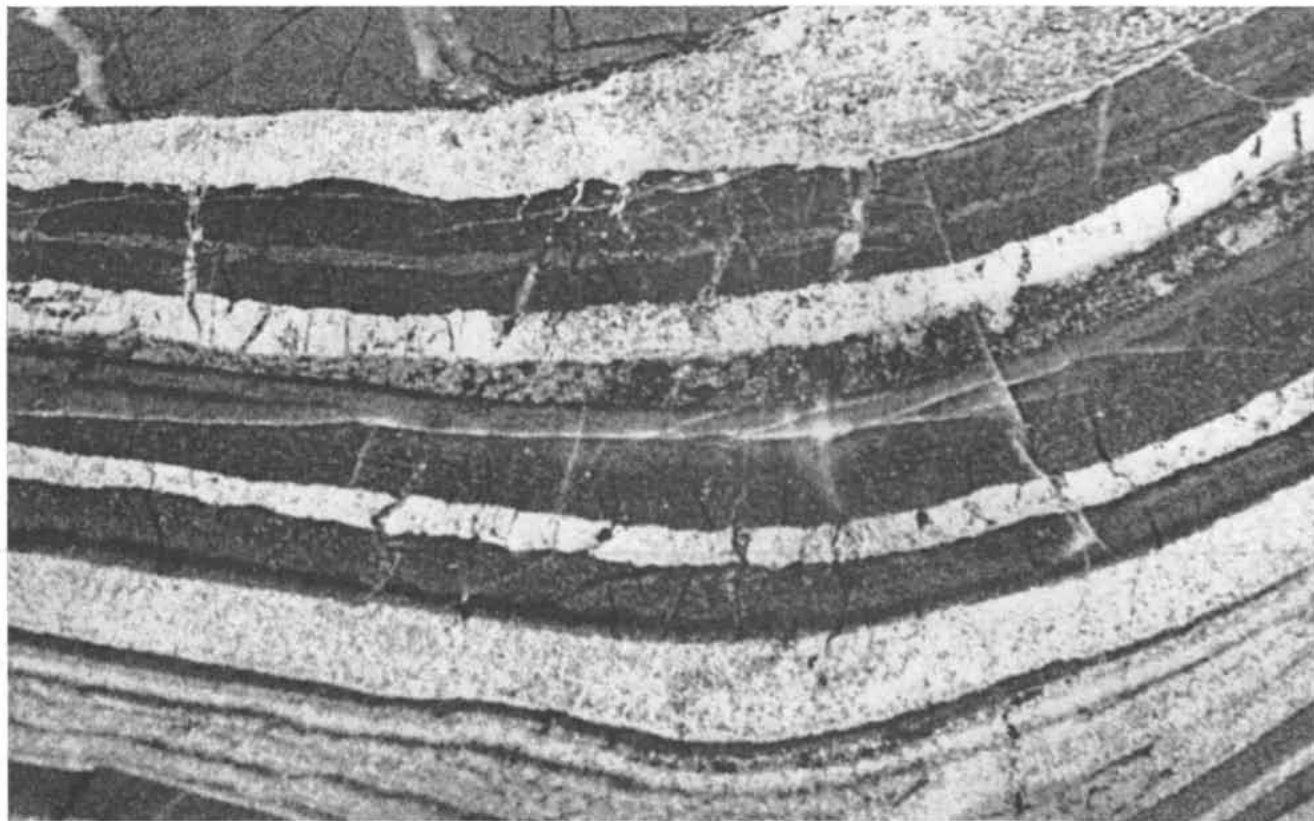
BANDED IRON FORMATION provides the first geological evidence of free oxygen in the hydrosphere. The layers in this polished cross section result from an alternation of iron-rich and iron-poor depositions. This sample from the Soudan Iron Formation in Minnesota is more than 2.7 billion years old. The layers, originally horizontal, were deformed while soft and later metamorphosed.
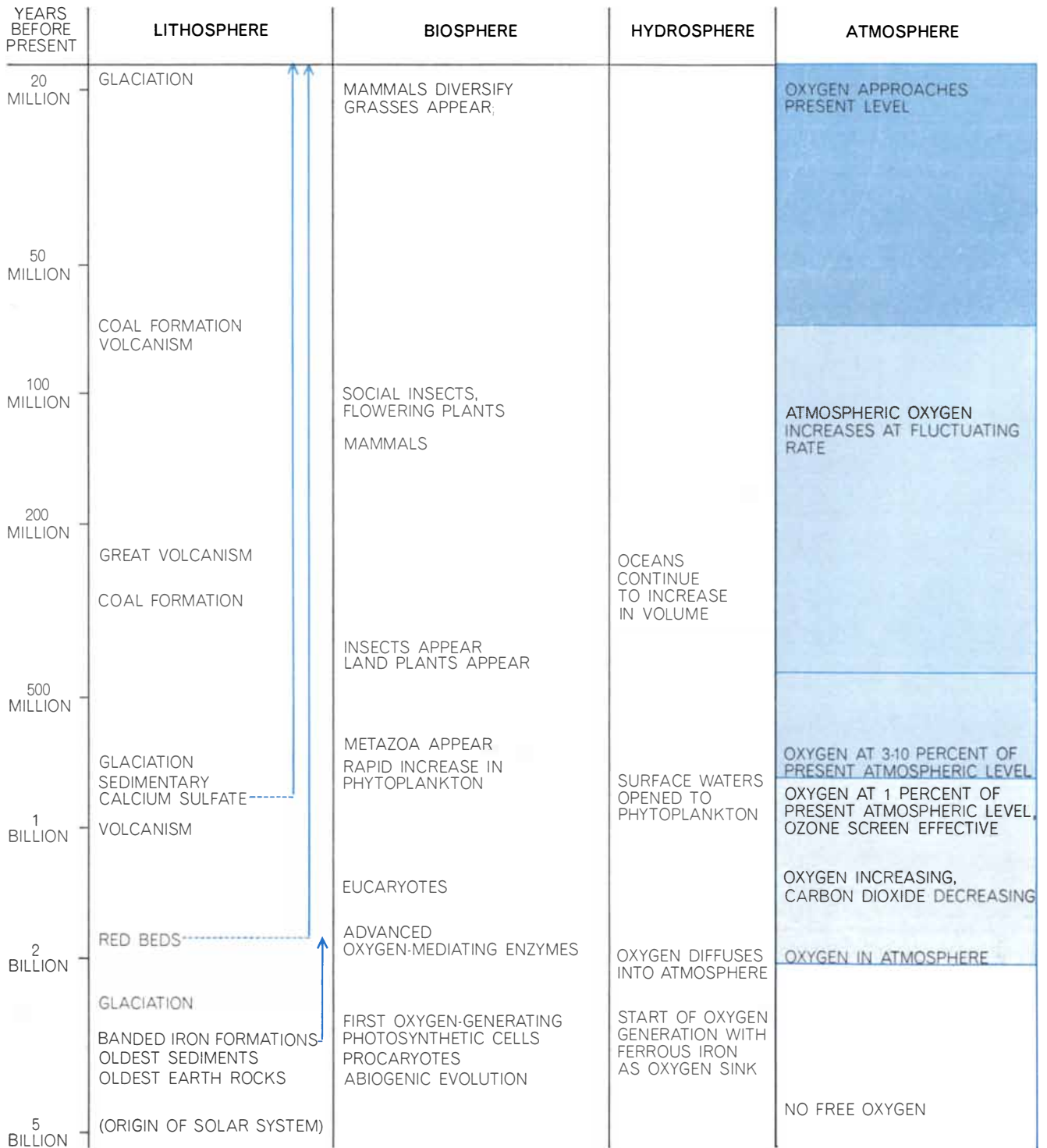
insets, of the various vertebrate groups and of flowering plants, as Berkner and Marshall suggested? Or were there wide swings in the oxygen level? Did oxygen decrease during great volcanic episodes, as a result of the oxidation of newly emitted carbon monoxide to carbon dioxide, or during times of sedimentary sulfate precipitation? Did oxygen increase when carbon was being sequestered during times of coal and petroleum formation? May there have been fluctuations in both directions as a result of plant and animal evolution, of phytoplankton eruptions and extinctions and of the extent and type of terrestrial plant cover? Such processes and events are now being seriously studied, but the answers are as yet far from clear.

What one can say with confidence is that success in understanding the oxy-

YEARS BEFORE PRESENT	LITHOSPHERE	BIOSPHERE	HYDROSPHERE	ATMOSPHERE
20 MILLION	GLACIATION	MAMMALS DIVERSIFY GRASSES APPEAR;		OXYGEN APPROACHES PRESENT LEVEL
50 MILLION				
	COAL FORMATION VOLCANISM			
100 MILLION		SOCIAL INSECTS, FLOWERING PLANTS MAMMALS		ATMOSPHERIC OXYGEN INCREASES AT FLUCTUATING RATE
200 MILLION	GREAT VOLCANISM COAL FORMATION		OCEANS CONTINUE TO INCREASE IN VOLUME	
		INSECTS APPEAR LAND PLANTS APPEAR		
500 MILLION	GLACIATION SEDIMENTARY CALCIUM SULFATE- - - - -	METAZOA APPEAR RAPID INCREASE IN PHYTOPLANKTON	SURFACE WATERS OPENED TO PHYTOPLANKTON	OXYGEN AT 3-10 PERCENT OF PRESENT ATMOSPHERIC LEVEL OXYGEN AT 1 PERCENT OF PRESENT ATMOSPHERIC LEVEL, OZONE SCREEN EFFECTIVE
1 BILLION	VOLCANISM			
		EUCARYOTES		OXYGEN INCREASING, CARBON DIOXIDE DECREASING
2 BILLION	RED BEDS - - - - - - - -	ADVANCED OXYGEN-MEDIATING ENZYMES	OXYGEN DIFFUSES INTO ATMOSPHERE	OXYGEN IN ATMOSPHERE
	GLACIATION BANDED IRON FORMATIONS OLDEST SEDIMENTS OLDEST EARTH ROCKS	FIRST OXYGEN-GENERATING PHOTOSYNTHETIC CELLS PROCARYOTES ABIOGENIC EVOLUTION	START OF OXYGEN GENERATION WITH FERROUS IRON AS OXYGEN SINK	
5 BILLION	(ORIGIN OF SOLAR SYSTEM)			NO FREE OXYGEN

CHRONOLOGY that interrelates the evolutions of atmosphere and biosphere is gradually being established from evidence in the geological record and in fossils. According to calculations by Lloyd V. Berkner and Lauriston C. Marshall, when oxygen in the atmosphere reached 1 percent of the present atmospheric level, it provided enough ozone to filter out the most damaging high-energy ultraviolet radiation so that phytoplankton could survive everywhere in the upper, sunlit layers of the seas. The result may have been a geometric increase in the amount of photosynthesis in the oceans that, if accompanied by equivalent sequestration of carbon, might have resulted in a rapid buildup of atmospheric oxygen, leading in time to the evolution of differentiated multicelled animals.

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gen cycle of the biosphere in truly broad terms will depend on how good we are at weaving together the related strands of biospheric, atmospheric, hydrospheric and lithospheric evolution throughout geologic time. Whatever we may conjecture about any one of these processes must be consistent with what is known about the others. Whereas any one line of evidence may be weak in itself, a number of lines of evidence, taken together and found to be consistent, reinforce one another exponentially. This synergistic effect enhances our confidence in the proposed time scale linking the evolution of oxygen in the atmosphere and the management of the gaseous oxygen budget within the biosphere [*see illustration on page 120*].

The most recent factor affecting the oxygen cycle of the biosphere and the oxygen budget of the earth is man himself. In addition to inhaling oxygen and exhaling carbon dioxide as a well-behaved animal does, man decreases the oxygen level and increases the carbon dioxide level by burning fossil fuels and paving formerly green land. He is also engaged in a vast but unplanned experiment to see what effects oil spills and an array of pesticides will have on the world's phytoplankton. The increase in the albedo, or reflectivity, of the earth as a result of covering its waters with a molecule-thick film of oil could also affect plant growth by lowering the temperature and in other unforeseen ways. Reductions in the length of growing seasons and in green areas would limit terrestrial plant growth in the middle latitudes. (This might normally be counterbalanced by increased rainfall in the lower latitudes, but a film of oil would also reduce evaporation and therefore rainfall.) Counteracting such effects, man moves the earth's fresh water around to increase plant growth and photosynthesis in arid and semiarid regions. Some of this activity, however, involves the mining of ground water, thereby favoring processes that cause water to be returned to the sea at a faster rate than evaporation brings it to the land.

He who is willing to say what the final effects of such processes will be is wiser or braver than we are. Perhaps the effects will be self-limiting and self-correcting, although experience should
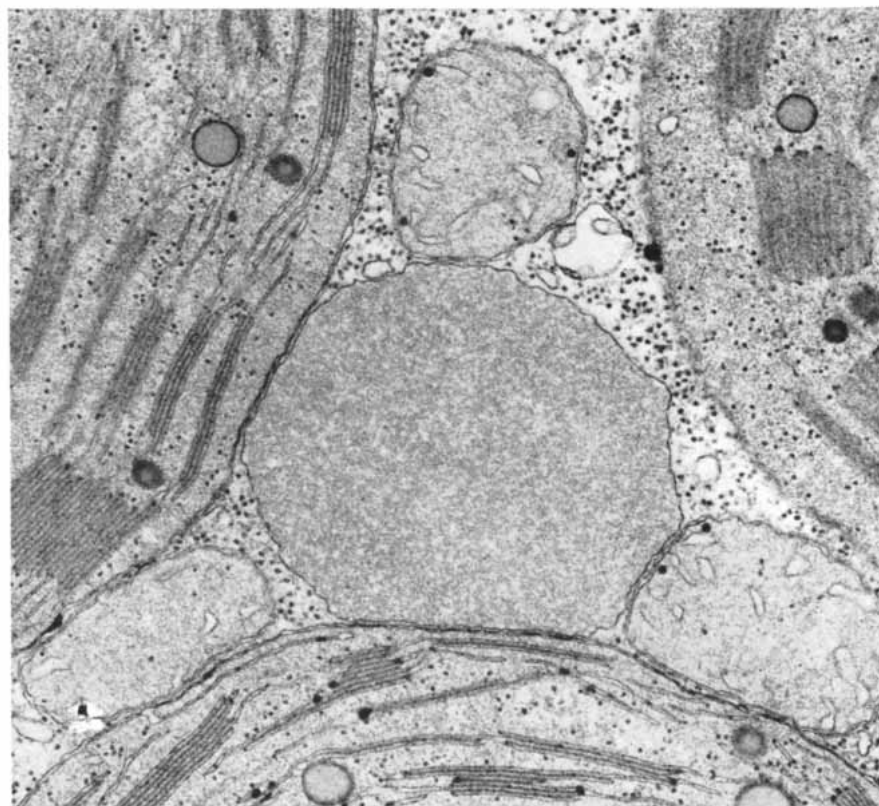
THREE ORGANELLES that are involved in oxygen metabolism in the living cell are enlarged 40,000 diameters in an electron micrograph of a tobacco leaf cell made by Sue Ellen Frederick in the laboratory of Eldon H. Newcomb at the University of Wisconsin. A peroxisome (*center*) is surrounded by three mitochondria and three chloroplasts. Oxygen is produced in the grana (*layered objects*) in the chloroplasts and is utilized in aerobic respiration in the mitochondria. Peroxisomes contain enzymes involved in oxygen metabolism.

warn us not to gamble on that. Oxygen in the atmosphere might be reduced several percent below the present level without adverse effects. A modest increase in the carbon dioxide level might enhance plant growth and lead to a corresponding increase in the amount of oxygen. Will a further increase in carbon dioxide also have (or renew) a "greenhouse effect," leading to an increase in temperature (and thus to a rising sea level)? Or will such effects be counterbalanced or swamped by the cooling effects of particulate matter in the air or by increased albedo due to oil films? It is anyone's guess. (Perhaps we should be more alarmed about a possible decrease of atmospheric carbon dioxide, on which all forms of life ultimately depend, but the sea contains such vast amounts that it can presumably keep carbon dioxide in the atmosphere balanced at about the present level for a long time to come.) The net effect of the burning of fossil fuels may in the long run be nothing more than a slight increase (or decrease?) in the amount of limestone deposited. In any event the recoverable fossil fuels whose combustion releases carbon dioxide are headed for depletion in a few more centuries, and then man will have other problems to contend with.

What we want to stress is the indivisibility and complexity of the environment. For example, the earth's atmosphere is so thoroughly mixed and so rapidly recycled through the biosphere that the next breath you inhale will contain atoms exhaled by Jesus at Gethsemane and by Adolf Hitler at Munich. It will also contain atoms of radioactive strontium 90 and iodine 131 from atomic explosions and gases from the chimneys and exhaust pipes of the world. Present environmental problems stand as a grim monument to the cumulatively adverse effects of actions that in themselves were reasonable enough but that were taken without sufficient thought to their consequences. If we want to ensure that the biosphere continues to exist over the long term and to have an oxygen cycle, each new action must be matched with an effort to foresee its consequences throughout the ecosystem and to determine how they can be managed favorably or avoided. Understanding also is needed, and we are woefully short on that commodity. This means that we must continue to probe all aspects of the indivisible global ecosystem and its past, present and potential interactions. That is called basic research, and basic research at this critical point in history is gravely endangered by new crosscurrents of anti-intellectualism.