

## CHAPTER 11

# Effect of Life on the Atmosphere

## The Rise of Oxygen and Ozone

### Key Questions

- What were the earliest forms of life, and how did they affect atmospheric composition?
- When and why did atmospheric  $O_2$  become abundant?
- When did the ozone layer form, and how did its formation affect Earth's surface environment and the evolution of the biota?
- By how much has atmospheric  $O_2$  varied over the last 540 million years?
- What controls the atmospheric  $O_2$  concentration today?

### Chapter Overview

Earth's present atmosphere is rich in molecular oxygen and has a well-developed ozone layer that shields the planet's surface from harmful solar ultraviolet radiation. This oxygen is produced by photosynthesis and, hence, would not have been present prior to the origin of photosynthetic life. The first organisms to evolve were probably not photosynthesizers. Rather, they lived in other ways, for example, by converting carbon dioxide and hydrogen into methane. Oxygenic photosynthesis originated at or before 2.4 b.y. ago, the time when atmospheric  $O_2$  levels first rose. Indeed, photosynthesis was probably occurring for several hundred million years prior to this time, but the initial rise of  $O_2$  was delayed for reasons that are not entirely understood. Atmospheric  $O_2$  has varied by modest amounts for the past few hundred million years because of changes in the rate of organic carbon burial. The fluctuations in  $O_2$  are small, however, because of a negative feedback mechanism that appears to involve the oxygenation of the deep oceans and the availability of dissolved phosphorus.

### INTRODUCTION

In the last chapter, we saw that the prebiotic Earth probably had an atmosphere dominated by carbon dioxide and molecular nitrogen ( $N_2$ ). But we also saw that life probably originated very early—within the first 700 m.y. of Earth's history—even though some of the evidence in favor of this idea has been questioned. As soon as life had evolved, it began to be a force that could change the composition of the atmosphere and eventually the surface as well. What was the nature of these earliest organisms, and how did they alter atmospheric composition? We can gain some insight into these questions by studying the structure of the ribosomal RNA tree and deducing which modern organisms look most “primitive.”

An even bigger change in atmospheric composition occurred when organisms evolved that were capable of oxygenic photosynthesis. The production of oxygen by such organisms eventually led to the establishment of our modern,  $O_2$ -rich atmosphere. But this change from reduced to oxidized atmospheric conditions appears to have occurred well after the invention

of photosynthesis, for reasons that are poorly understood. What other nonbiological changes in the planet were needed in order to allow atmospheric  $O_2$  to accumulate?

A related change in atmospheric composition that has affected both microbial and advanced life has been the development of a protective ozone layer. We have already seen that ozone is important because it blocks out harmful solar ultraviolet (UV) radiation. But, if the concentration of atmospheric  $O_2$  was initially very low, there must have been a time when the ozone layer did not exist. How did life cope with the solar UV flux at that time? When was an effective solar UV screen established? These are also questions that we address in this chapter.

### EFFECT OF LIFE ON THE EARLY ATMOSPHERE

As we saw in the previous chapter, we still do not know how life originated on Earth. We also do not know exactly when it originated because both the 3.5 b.y.-old Apex Chert microfossils and the 3.85 b.y.-old carbon isotopic evidence for life have been called into question. Starting



**FIGURE 11-1** Stromatolites from the 3.5 b.y.-old Warrawoona formation in Australia. (Source: Princeton University Press.)

at about 3.5 Ga, geologists have also found layered structures called **stromatolites** that are believed to be the fossilized remains of bacteria that form layered, sedimentary mats (Figure 11-1). The organisms that formed them are thought to have been similar to communities of photosynthetic bacteria that inhabit the shallow, salty waters of Shark Bay on the coast of western Australia (Figure 11-2).



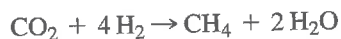
**FIGURE 11-2** [See color section] Shark Bay in western Australia. These "living stromatolites" are formed by communities of microbes and may be an analog to early microbial life. (Source: Fred Bavendam/Minden Pictures.)

How did the presence of life affect the composition of the atmosphere? The organisms that formed stromatolites were almost certainly photosynthetic—the fact that they lived in layers implies that they needed sunlight. However, this does not necessarily imply that they were producing oxygen. “Normal,” **oxygenic photosynthesis** is carried out by higher plants and algae today. But some bacteria make their living by a related process called anoxygenic photosynthesis. In **anoxygenic photosynthesis**,  $\text{H}_2\text{S}$  or  $\text{H}_2$  is used instead of  $\text{H}_2\text{O}$  to reduce  $\text{CO}_2$  to organic carbon; this process does not yield  $\text{O}_2$ . Finally, certain bacteria called **cyanobacteria**, formerly referred to as blue-green algae, can perform both oxygenic and anoxygenic photosyntheses. In practice, some cyanobacteria switch back and forth between these two metabolic processes in response to changes in their local environment. When hydrogen sulfide,  $\text{H}_2\text{S}$ , is present, these cyanobacteria photosynthesize anoxygenically; when  $\text{H}_2\text{S}$  is absent, they generate  $\text{O}_2$ .

Until just recently, it was widely believed—based on their relatively large sizes—that the Apex Chert microfossils (Figure 10-7) were the remains of cyanobacteria. The new evidence from Brasier’s group (see Chapter 10), however, indicates that the environment in which they were living was similar to the modern, hydrothermal vents in the deep ocean. No light penetrates to these depths, so if these fossilized structures were indeed organisms, they are unlikely to have been photosynthetic. Instead, they probably survived on the energy produced from chemical reactions. Such organisms are termed **chemosynthetic**. Today, many organisms that live near the hydrothermal vents derive energy from reacting  $\text{H}_2\text{S}$  from the vent fluids with  $\text{O}_2$  dissolved in the surrounding ocean water. On the early Earth, free  $\text{O}_2$  is unlikely to have been present, for reasons discussed in the previous chapter. How might these organisms have been making their living?

### Production of Methane

To get some idea of what types of organisms may have been living on the primitive Earth, we can turn once again to the “Universal” Tree of Life derived from sequencing of ribosomal RNA. In the last chapter, we saw that many of the organisms near the root of the tree appear to be *hyperthermophiles*—organisms that live at high temperatures. Only slightly further away from the root, along one branch of the Archaea, are the methanogenic bacteria (Figure 11-3). **Methanogenic bacteria**, or **methanogens** for short, produce energy from chemical reactions that generate methane. The simplest of these is



Both  $\text{CO}_2$  and  $\text{H}_2$  are abundant in modern vent fluids and in surface volcanic gases. On the early Earth, they would have been abundant in the atmosphere as well.  $\text{CO}_2$  may have built up to very high levels and probably played an important role in keeping Earth warm, despite reduced solar luminosity. (See Chapter 12.) The abundance of  $\text{H}_2$  can be

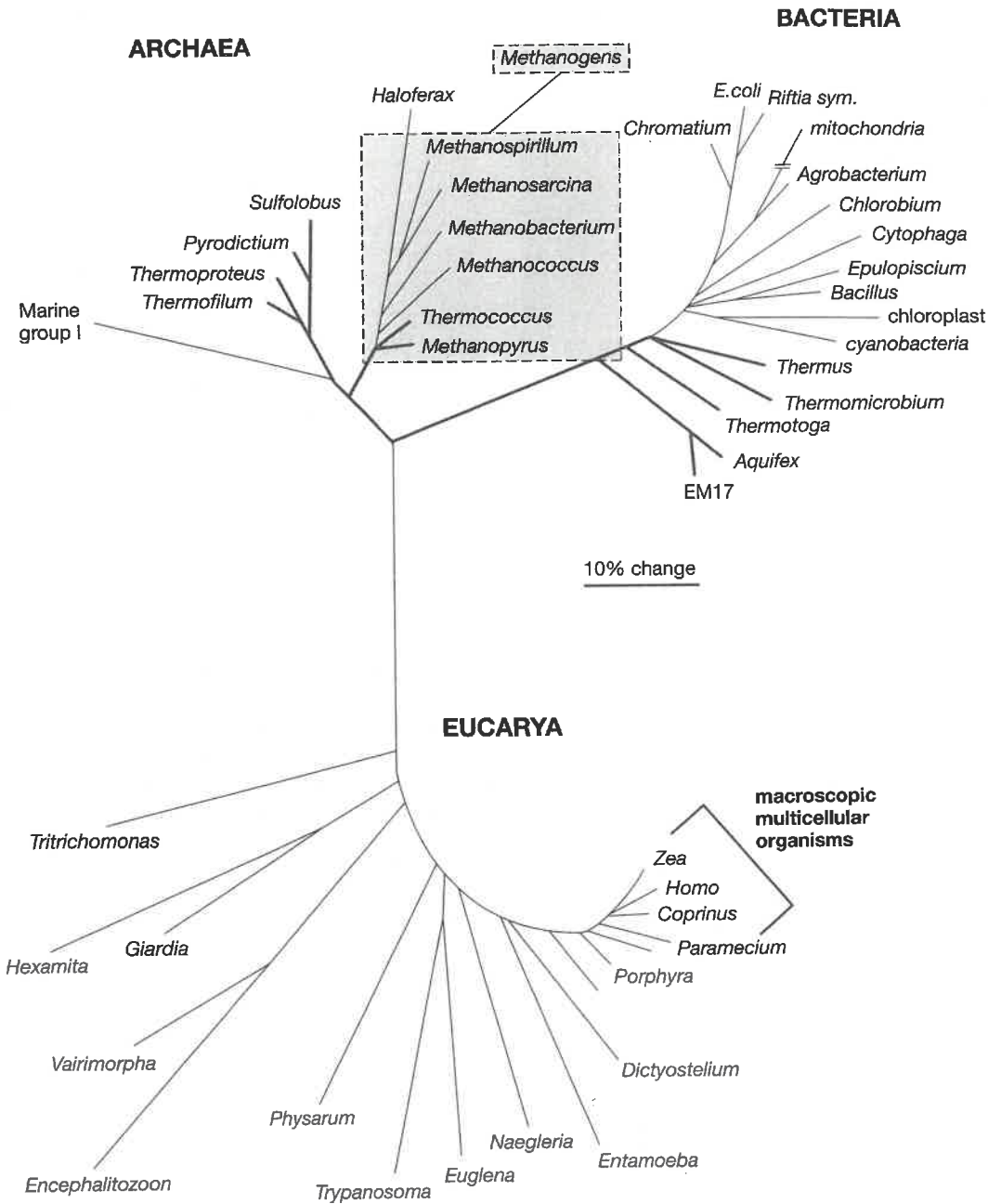
estimated by balancing the rate of escape of hydrogen to space with the rate at which hydrogen and other reduced gases were outgassed from volcanos. Such a calculation predicts that hundreds to thousands of ppm of  $\text{H}_2$  should have been present (possibly even more if hydrogen escape was slower than it is today because the upper atmosphere was colder). Many methanogens can survive at these  $\text{H}_2$  concentrations, although most require about 1%  $\text{H}_2$  (0.01 bar) to reproduce. Methanogens can also metabolize other reduced substances, such as formate ion ( $\text{HCOO}^-$ ), which is formed when carbon monoxide ( $\text{CO}$ ) dissolves in water.  $\text{CO}$ , like  $\text{H}_2$ , is thought to have been an important constituent of the early atmosphere. Thus, there is good reason to believe that methanogens were widespread on the early Earth. If primitive methanogens produced methane at the same rate that it is produced biologically today, the atmospheric methane concentration could have exceeded 1000 ppm, more than 600 times its present level (1.6 ppm). The higher abundance results from the fact that methane would have been destroyed less rapidly in a low- $\text{O}_2$  atmosphere.

The presence of high concentrations of methane may have caused the early atmosphere to look quite different from today’s atmosphere. We can get some idea of what it might have looked like by observing Saturn’s moon, Titan. Titan has a dense (1.5-bar) atmosphere that consists of about 98%  $\text{N}_2$  and 2%  $\text{CH}_4$ . But the most striking feature of Titan is that it is enveloped in an orangish haze layer that completely obscures the surface (Figure 11-4). This haze layer is thought to consist of hydrocarbon aerosols formed from photolysis and charged particle bombardment of atmospheric  $\text{CH}_4$ . Although Titan is not a perfect analog for early Earth—its surface temperature is only 94 K—computer models predict that the same type of haze could have formed in Earth’s early atmosphere if  $\text{CH}_4$  was more than about one-tenth the abundance of  $\text{CO}_2$ . In the next chapter, we will show that this condition may indeed have been satisfied.

Although this discussion is highly speculative, the geologic record provides indirect evidence that something like this actually happened. In particular, some of the sedimentary organic carbon from the Late Archean (around 2.7 b.y. ago) is highly depleted in  $^{13}\text{C}$  (Figure 11-5)—more so than can be explained by photosynthesis alone. This depletion is thought to be an indication of widespread methanogenic activity. The methane produced by methanogens is depleted in  $^{13}\text{C}$  relative to  $^{12}\text{C}$ . If this methane was taken up by other organisms, its low- $^{13}\text{C}$  carbon may have made its way into sediments and could account for the low- $^{13}\text{C}$  carbon preserved in the geologic record. Other indirect evidence from sulfur isotopes, discussed later in this chapter, also suggests that a methane-based organic haze could have been present at around this time.

### Cycling of Atmospheric Nitrogen

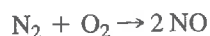
A second way in which organisms might have affected the atmosphere is by cycling nitrogen through the atmosphere–ocean system. Organisms need nitrogen for



**FIGURE 11-3** The ribosomal RNA tree, showing where methanogens and cyanobacteria fit into the picture. (Source: Courtesy Norman Pace, University of Colorado.)

making proteins and nucleic acids as well as for other biochemical functions. However, most of them cannot use nitrogen in its normal molecular form,  $N_2$ . Instead, they require **fixed nitrogen**, in which nitrogen atoms are bonded to other types of atoms. Ammonia ( $NH_3$ ) and nitrate ion ( $NO_3^-$ ) are two examples of fixed-nitrogen compounds.

Modern marine organisms acquire fixed nitrogen in two ways. One of these is from lightning. In the high-temperature region surrounding a lightning discharge, nitrogen and oxygen react to form nitric oxide, NO:

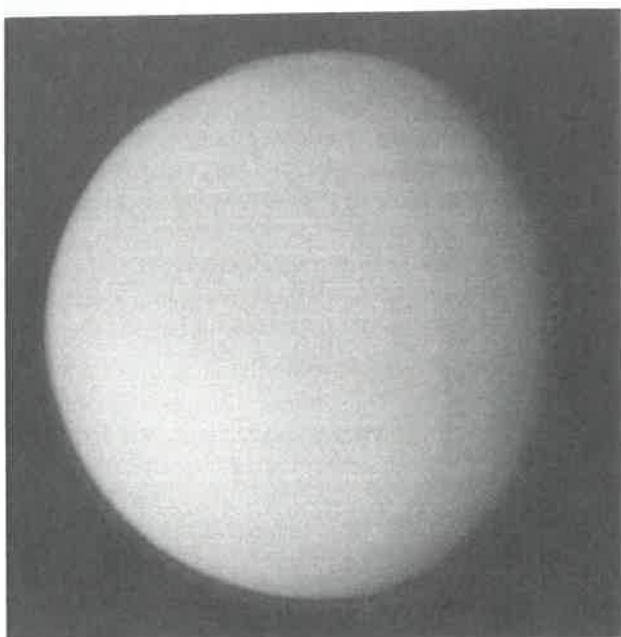


Nitric oxide is a radical that plays an important role in ozone photochemistry. In today's atmosphere it is eventually oxidized to nitric acid,  $HNO_3$ . Nitric acid is soluble in water and, thus, is quickly rained out of the troposphere. In solution, it **dissociates** (comes apart) to form hydrogen ions and nitrate ions:



The resulting nitrate ion can be directly used by organisms as a source of fixed nitrogen.

Some marine organisms can make their own fixed nitrogen by a process termed **nitrogen fixation**. Most of

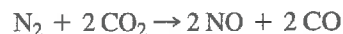


**FIGURE 11-4** [See color section] Saturn's moon, Titan, showing the orangish organic haze. (Source: Calvin Hamilton/NASA.)

the biologically available nitrogen in the oceans is fixed by cyanobacteria, the same type of organisms that we believe were responsible for the initial rise in  $O_2$ . However, the first nitrogen-fixers were probably not cyanobacteria. The ability to fix nitrogen is widespread among **prokaryotes**, which are single-celled organisms that lack *cell nuclei*—structures that house genetic material (Figure 11-6a). (In prokaryotes, the genetic material is not concentrated within a specific structure.) The prokaryotes include both the Bacteria and the Archaea. Methanogens are prokaryotes, and many of them can fix nitrogen. Most **eukaryotes** (organisms with cell nuclei) cannot fix nitrogen (Figure 11-6b). Prokaryotes are thought to be more primitive than eukaryotes because their cell structure is simpler. They are also more resistant to UV radiation, which is consistent with the idea that they evolved under a low- $O_2$  atmosphere that lacked a protective ozone layer.

How did the very earliest organisms acquire fixed nitrogen? Lightning is the most likely answer, although the reaction between  $N_2$  and  $O_2$  could not have been the source

because there would have been little  $O_2$  available. However, the analogous reaction

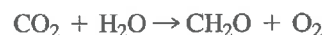


could have provided fixed nitrogen at a modest rate.

If nitrogen fixation were not balanced by some reverse process,  $N_2$  would be completely removed from the atmosphere in only about 20 million years. This does not happen, however, because atmospheric nitrogen is recycled by several different processes. Today, the dominant recycling mechanism is bacterial **denitrification**. Some organisms can derive energy by reacting nitrate with organic matter. In the process, nitrogen is released as either  $N_2$  or as nitrous oxide,  $N_2O$ . Most of the nitrous oxide is converted back into  $N_2$  by photolysis, although some of it reacts in the stratosphere to form  $NO$ . Denitrification is particularly rapid in **anoxic** (oxygen-free) regions of the ocean and in anoxic soils.

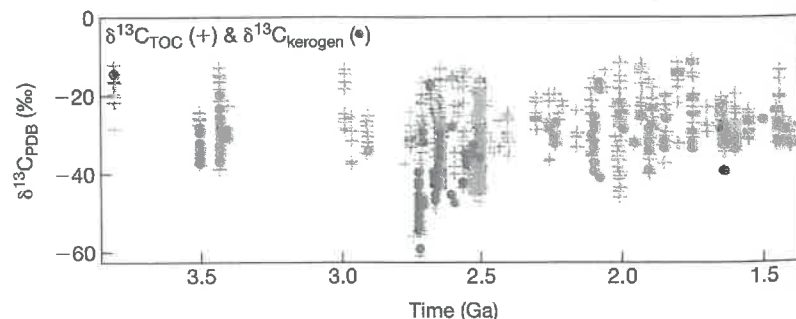
## THE RISE OF OXYGEN

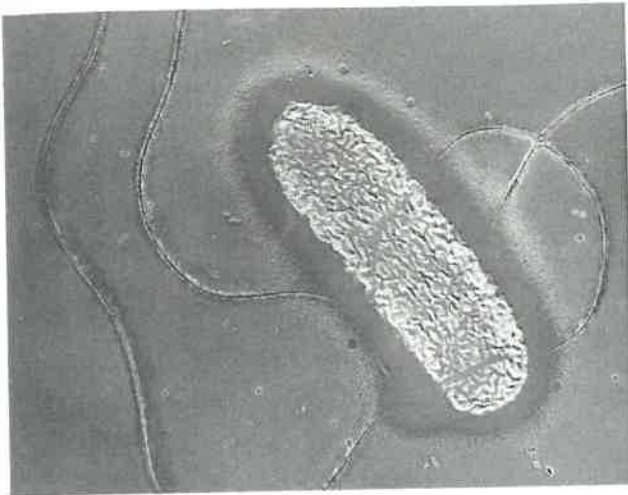
At some point in Earth's history, a historic biological event occurred. An organism evolved that was capable of producing  $O_2$  through oxygenic photosynthesis:



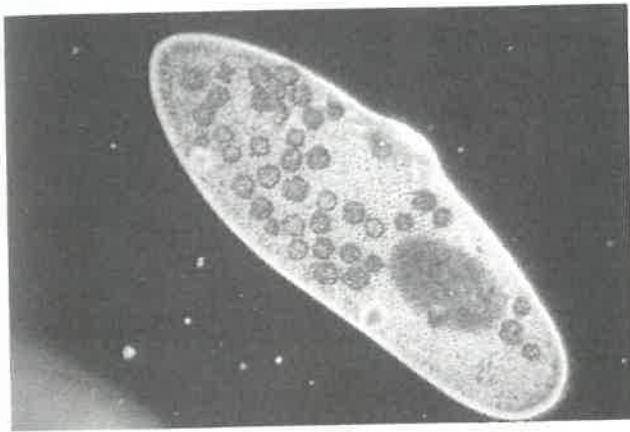
We have already seen that these first photosynthetic organisms were the *cyanobacteria*. These organisms are still important components of the ecosystems in modern oceans, lakes, and rivers. They have many different forms: some are round, or *coccolid*, and live as individual cells, while others grow in long, multicellular filaments (Figure 11-7). As mentioned earlier, many of them are able to fix nitrogen from the atmosphere. This is quite an extraordinary feat for cyanobacteria because the enzyme used to reduce  $N_2$ , *nitrogenase*, is poisoned by  $O_2$ . Thus, cyanobacteria have been forced to find ways to protect their nitrogenase from the  $O_2$  that they produce photosynthetically. Some types of filamentous cyanobacteria do this by developing special cells called **heterocysts** that are devoted to fixing  $N_2$  (see Figure 11-7c). No  $O_2$  is

**FIGURE 11-5** Carbon isotope values from organic carbon (kerogen) in ancient rocks. Organic carbon produced by oxygenic photosynthesis typically has  $\delta^{13}C$  values near  $-25\text{‰}$  to  $-30\text{‰}$ . The extremely "light" ( $-50\text{‰}$  to  $-60\text{‰}$ ) values around 2.7–2.8 b.y. ago probably require cycling of carbon through methane. (Source: A. A. Pavlov et al., *Geology* 29, 2001, pp. 1003–1006.)





(a)



(b)

**FIGURE 11-6** [See color section] (a) Prokaryotes have no nucleus, and the DNA is dispersed within the cell. (b) Eukaryotes have their DNA enclosed within a cell nucleus. (Sources: (a) A. B. Dowsett/SPL/Photo Researcher and (b) Eric V. Grave/Photo Researchers.)

produced within a heterocyst, so the inside of the cell can be kept virtually oxygen-free. Other types of cyanobacteria photosynthesize during the day and fix nitrogen at night, so they protect their nitrogenase in a different way. Still others, for example the abundant tropical marine species *Trichodesmium*, fix nitrogen in the morning and photosynthesize in the afternoon. Clearly, even though they are “simple” prokaryotes, cyanobacteria are very advanced organisms in a metabolic sense.

Cyanobacteria are important for yet another reason. Most photosynthesis today is carried out by eukaryotic algae or by higher plants. But we are virtually certain that these organisms did not reinvent photosynthesis on their own. A glance at the universal, ribosomal RNA tree (Figure 11-3) shows why. As the diagram shows, cyanobacteria are closely related to the chloroplasts in higher plants. **Chloroplasts** are the parts of plant cells in which oxygenic photosynthesis takes place. Chloroplasts

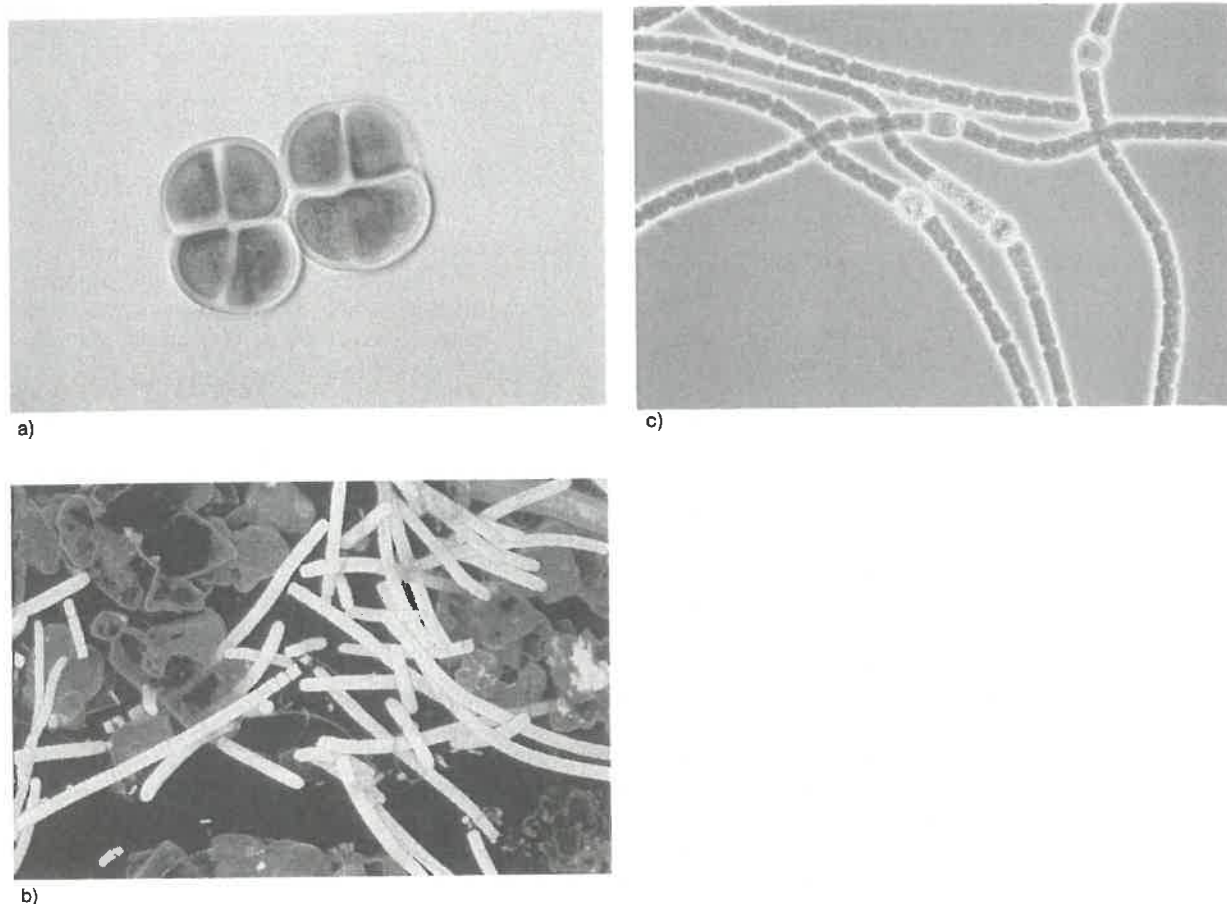
contain their own DNA, which is why they can be placed on the Tree of Life along with free-living organisms. As biologist Lynn Margulis of the University of Massachusetts pointed out more than 30 years ago, this shows conclusively that all higher plants (including algae) acquired their ability to produce oxygen by way of an **endosymbiotic** event: some eukaryotic organism ingested, or enveloped, a prokaryotic cyanobacterium without killing it. After that, the two organisms lived together in a mutually beneficial arrangement. The eukaryotic host cell provided nutrients to the cyanobacterium, and the cyanobacterium in turn provided  $O_2$  to the host. This  $O_2$  could then be used as an energy source (via respiration) by the host cell.

### When Did Cyanobacteria Evolve?

A critical question from the standpoint of understanding Earth history is: when did the cyanobacteria evolve? Or, to be more precise, the question could be phrased: When did cyanobacteria evolve the capability of producing  $O_2$ ? We have seen (Figure 10-7) that organisms, or at least structures, resembling modern cyanobacteria were already present by 3.5 b.y. ago. But, even if they were indeed alive, these organisms could not have been producing oxygen by photosynthesis because they lived in a deep-ocean, hydrothermal vent environment where light levels were extremely low.

Somewhat better evidence for the existence of cyanobacteria comes from organic chemicals in 2.7 b.y.-old sedimentary rocks from the Fortescue Group in western Australia. (Western Australia is a haven for Precambrian geologists because it contains very old rocks *and* it is extremely dry, so that these rocks are not covered up by vegetation.) These rocks contain organic carbon that has not been as highly degraded as most organic material of that age. In essence, they contain 2.7 b.y.-old oil. In this oil are compounds called *2 $\alpha$ -methylhopanes* (Figure 11-8). These compounds are thought to derive from the breakdown of *lipid* molecules that are present in the cell walls of modern cyanobacteria. If the oil in these rocks formed at the same time that the rocks were deposited, rather than migrating in at some later date, then cyanobacteria may have been around by this time. However, this argument has recently been shown to be inconclusive, because the precursors to *2 $\alpha$ -methylhopanes* have now been found in other organisms, specifically, two different strains of purple nonsulfur bacteria. These are phototrophic (“light-loving”) organisms that do not produce  $O_2$ . They live in lakes and streams today, rather than in the oceans, so they may not have been the source of the methylhopanes in ancient rocks. But this shows that our understanding of when cyanobacteria evolved is far from certain.

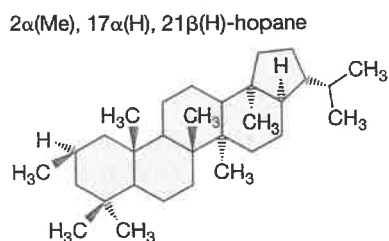
Even if the methylhopanes are indeed from ancient cyanobacteria, the geochemical evidence does not by itself prove that those cyanobacteria were producing oxygen.



**FIGURE 11-7** [See color section] Three different types of cyanobacteria: (a) *Chroococcus* (coccoid), (b) *Oscillatoria* (filamentous), (c) *Nostoc* (heterocystic). (Source: (a) Tom Adams/Visuals Unlimited, (b) Dr. Gernot Arp, and (c) Susan Barns and Norman R. Pace.)

Like the Apex Chert microfossils discussed earlier, these organisms may have resembled modern cyanobacteria—in this case by having a similar cell wall—but they did not necessarily have the same metabolism. We mention this because the first evidence for the presence of free  $O_2$  in the atmosphere does not come until almost 300 m.y. later. Thus, if  $O_2$  was being produced photosynthetically 2.7 b.y. ago, it must have been entirely consumed by reactions with reduced substances.

Additional evidence that  $O_2$  was being produced at this time comes from the presence of other organic com-



**FIGURE 11-8** A 2 $\alpha$ -methylhopane molecule, thought to be an indicator for cyanobacteria. (Source: Courtesy Jen Eigenbrode, Pennsylvania State University.)

pounds called **steranes** in these same 2.7-b.y.-old sediments. Steranes derive from the breakdown of organic compounds such as **cholesterol** that are thought to be produced exclusively by eukaryotes. (Cholesterol is familiar to us as the fatty substance that builds up in one's arteries as one gets older and that can lead to heart attacks.) Most eukaryotes use  $O_2$  for respiration and, hence, require at least 1 percent of present dissolved oxygen in the water in which they are living. And the biochemical synthesis of sterols requires free  $O_2$  during one key step of the process. So, the presence of steranes in ancient rocks implies that  $O_2$  was being produced within the water column, presumably by cyanobacteria. The presence of  $O_2$  in surface water does *not* necessarily imply the presence of  $O_2$  in the atmosphere because the rate at which oxygen (or any gas) can flow between the surface ocean and atmosphere is limited by diffusion through the gas-liquid interface, and so the atmosphere and surface ocean need not have been in chemical equilibrium.

To determine when  $O_2$  first rose to appreciable concentrations in the atmosphere, we must turn once again to the geologic record. Until a few years ago, the question of when  $O_2$  first rose was hotly debated. The reason is that most of the



**FIGURE 11-9** [See color section] A banded iron-formation, or BIF. (Source: J. William Schopf.)

geologic evidence bearing on the  $O_2$  rise is difficult to interpret. As we will see, new evidence from sulfur isotopes may have finally resolved this long-standing question. Let us begin, however, by discussing the various types of geologic evidence that have been used to try to track atmospheric  $O_2$ .

### Banded Iron-Formations

One type of geologic evidence that bears on the rise of oxygen is the occurrence of banded iron-formations. **Banded iron-formations (BIFs)** are laminated sedimentary rocks that consist of alternating, millimeter-thick layers of iron-rich minerals and chert (Figure 11-9). Such minerals include *magnetite* ( $Fe_3O_4$ ) or *hematite* ( $Fe_2O_3$ ), and *chert* ( $SiO_2$ ). They are of enormous economic importance today. Much of the iron that is used in making steel and automobiles come from BIFs in Canada and Australia. But these deposits do not form today; nor have they done so at any time in the recent past. Radiometric age dating shows that almost all BIFs formed prior to 1.9 b.y. ago. The only exceptions are a few BIFs that formed in the Late Proterozoic, about 0.6–0.8 b.y. ago. As we will discuss

further in the next chapter, the Late Proterozoic is unusual for several reasons, the most intriguing of which is the evidence of low-latitude glaciation. Some researchers have suggested that the two phenomena are linked: extensive ice cover inhibited oxygen transfer between the atmosphere and ocean, and this led to the reappearance of BIFs. This is one piece of evidence that the so-called Snowball Earth events actually occurred.

The reason that BIFs are useful as oxygen indicators is that iron can exist in more than one oxidation state. The **oxidation state** of an atom, molecule, or compound is its degree of oxidation. Substances with a low oxidation state have a large number of available electrons; substances with a high oxidation state do not (see the Box “Useful Concepts: Oxidation States of Iron”). We have already mentioned one oxidation state of iron, **ferrous iron** ( $Fe^{2+}$ ). A second, more oxidized state is termed **ferric iron** ( $Fe^{3+}$ ). Iron ions in these two oxidation states have very different chemical properties:  $Fe^{2+}$  is soluble in seawater, whereas  $Fe^{3+}$  is not. Because iron switches from  $Fe^{2+}$  to  $Fe^{3+}$  when oxygen is present, it can provide indirect information about past  $O_2$  levels.

To make use of this information, we need to understand the process by which BIFs formed. Although no consensus has been reached regarding the precise mechanism, there is general agreement on some parts of the story. To explain the voluminous quantities of iron deposited in BIFs, large portions of the deep oceans must have been anoxic. This condition would have allowed iron to be transported as dissolved  $Fe^{2+}$ . The iron was probably supplied originally from continental weathering and from mid-ocean ridge hydrothermal vent fluids. Trace element patterns in BIFs, especially those of the **rare earth elements** (atomic numbers 57–71 in the periodic table), show that at least some of the iron must have come from the vents. What happened next is not well understood. We know that BIFs did not form on the floor of the deep ocean. If they had, they would have been destroyed when the seafloor was subducted. Instead, the dissolved iron must have been transported to the margins

## USEFUL CONCEPTS

### Oxidation States of Iron

Iron occurs in three oxidation states in nature: elemental (or metallic), ferrous, and ferric. The elemental form is located mostly in Earth's core, which is composed largely of iron–nickel alloy. Ferrous and ferric iron occur in the mantle and crust. They exist in dissolved form as  $Fe^{2+}$  and  $Fe^{3+}$  ions, respectively. The positive charges arise because these ions are missing electrons:  $Fe^{2+}$  is missing two electrons, and  $Fe^{3+}$  is missing three. We say that these two ions are in the 2+ and 3+ oxidation states. Elemental iron, by comparison, has an oxidation state of zero.

When iron reacts with oxygen, the oxidation state of the iron atom determines the number of oxygen atoms

with which it combines. Oxygen, when it reacts, can be thought of as having a valence of  $-2$ . It has six electrons in its outer shell, and it wants two more in order to complete the shell. Thus, to produce a neutral molecule, one  $Fe^{2+}$  ion combines with one  $O_2^{-2}$  ion to form the mineral FeO (wüstite). Two  $Fe^{3+}$  ions combine with three oxygen ions to form  $Fe_2O_3$  (hematite).

Most of the iron in BIFs consists of magnetite,  $Fe_3O_4$ . This is equivalent to one molecule of FeO bonded to one molecule of  $Fe_2O_3$ . So, BIFs contain a 1:2 mixture of ferrous iron and ferric iron.



of the continents, where it was deposited on stable continental shelves. To be precipitated, the iron must first have been oxidized from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .

Exactly how this occurred is still a subject of debate. One suggestion is that the iron was brought to the surface by wind-induced upwelling of the type that occurs in some modern coastal settings. (Recall from Chapter 5 that this upwelling is produced by Ekman pumping.) The fine, millimeter-scale banding observed in the BIFs could have been caused by seasonal changes in winds that produced upwelling at certain times of the year but not at others. Iron-rich sediments would have formed when the upwelling was strong; silica-rich sediments would have formed when upwelling was weaker. Once the dissolved ferrous iron was brought to the surface, it could have been oxidized by dissolved  $\text{O}_2$  produced by photosynthetic cyanobacteria. Alternatively, the iron could have been oxidized abiotically. Laboratory experiments have shown that dissolved  $\text{Fe}^{2+}$  can be oxidized to  $\text{Fe}^{3+}$  by UV radiation. (In the process,  $\text{H}_2\text{O}$  is reduced to  $\text{H}_2$ .) A third possibility is that  $\text{Fe}^{2+}$  could have been oxidized by **phototrophic** bacteria (bacteria that use sunlight) that did not produce  $\text{O}_2$ . Whether the iron in BIFs was oxidized by UV radiation or by biologically generated  $\text{O}_2$  is still unresolved.

Because the oxygen in BIFs could have come from several sources, we cannot use them directly to infer the  $\text{O}_2$  content of the atmosphere. We can, however, safely conclude that the deep oceans must have been anoxic prior to 1.9 b.y. ago, during the time that BIFs formed. This in turn implies that the atmospheric  $\text{O}_2$  concentration was lower than it is today. So, BIFs are a strong indicator that the atmosphere has changed during recorded geologic history.

### Detrital Uraninite and Pyrite

More direct information on atmospheric  $\text{O}_2$  levels can be obtained from other types of geologic indicators. Elements other than iron are also capable of changing their oxidation state. Uranium, for example, has two common oxidation states:  $\text{U}^{4+}$  and  $\text{U}^{6+}$ . As with iron, these two ions differ in their solubilities. In this case, however, it is the oxidized (6+) form that is soluble and the more reduced (4+) form that is not.

The  $\text{U}^{4+}$  ion combines with oxygen to form **uraninite**,  $\text{UO}_2$ . This mineral occurs in rocks today, but it is normally oxidized to the soluble, 6+, state during weathering. (Notable exceptions to this rule occur in some of the rivers that drain the Himalayas, where the eroded sediments are redeposited very quickly, before the uranium can be oxidized.) Dissolved uranium is transported to the oceans, where it diffuses into anoxic sediments, is reduced, and precipitates as  $\text{UO}_2$ .

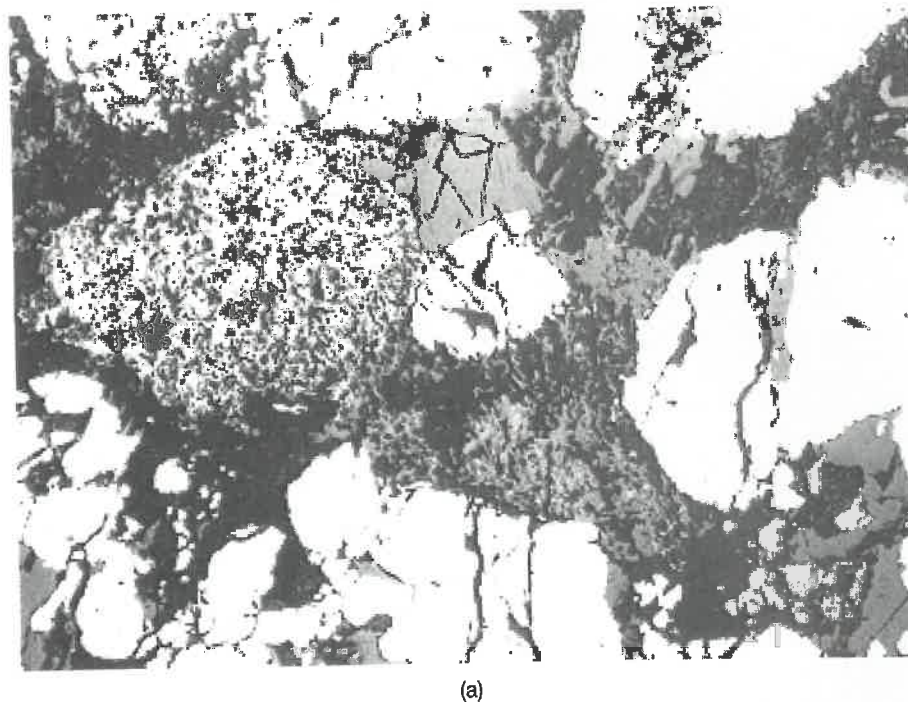
This modern cycle of uranium weathering and deposition does not seem to have operated early in Earth's history. Sedimentary rocks older than about 2.4 b.y. contain uraninite in *detrital* form (Figure 11-10a). A **detrital mineral** is a mineral that survived the weathering process and was transported to the site of deposition as a solid particle rather

than in solution. Such a mineral can often be identified by its appearance, which closely resembles the texture of the source rock. These minerals also have rounded edges, produced by grinding as they were transported down streams as pebbles. The presence of the detrital form implies that, at the time when the source rock was weathered, the atmospheric  $\text{O}_2$  content was too low to oxidize uraninite. Quantitative analysis suggests that the  $\text{O}_2$  concentration during this time was less than  $10^{-3}$  bars, or 0.005 PAL. (PAL means "times the present atmospheric level.") Unfortunately, this is only an upper bound. The actual  $\text{O}_2$  concentration prior to 2.4 b.y. ago could have been much lower than this. Indeed, in most places it might have been essentially the same as on the prebiotic Earth, where the surface  $\text{O}_2$  concentration is thought to have been on the order of  $10^{-13}$  PAL (see the Box "A Closer Look: Prebiotic  $\text{O}_2$  Concentrations" in the previous chapter). But during the Late Archean, this largely anoxic atmosphere may have been punctuated by plumes of free  $\text{O}_2$  rising from productive areas of the surface ocean.  $\text{O}_2$  was a pollutant in the anoxic Archean atmosphere, just as the reduced gas CO (carbon monoxide) is a pollutant in today's oxidized atmosphere.

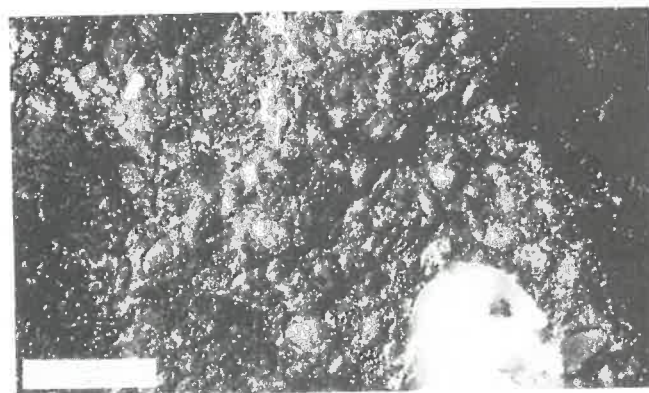
A second mineral that was deposited in detrital form prior to about 2.2 b.y. ago, but not since then, is **pyrite**,  $\text{FeS}_2$  (Figure 11-10b). It tells essentially the same story as uraninite. When pyrite is weathered under today's oxidizing atmospheric conditions, the sulfur is oxidized to sulfate,  $\text{SO}_4^{2-}$ , and the iron is oxidized to  $\text{Fe}^{3+}$ . But this oxidation apparently did not happen on the early Earth. Eroded grains of pyrite were transported long distances by streams and rivers, as evidenced by the rounded appearance of some samples, and were deposited in chemically unaltered form. This evidence is another indication that atmospheric  $\text{O}_2$  was low during the Archean eon.

### Paleosols and Redbeds

Other geologic indicators that have been used to study the rise of atmospheric  $\text{O}_2$  include **paleosols** (ancient soils) and **redbeds** (reddish-colored sandy and silty sediments). Heinrich Holland, now retired from Harvard University, has conducted chemical analyses of numerous Precambrian paleosols. He has found that most paleosols older than about 2.2 b.y. have lost significant amounts of iron, whereas paleosols younger than 1.9 b.y. have retained it. This finding is consistent with the story outlined previously, although the age dates in Holland's study (which are old ones) may need to be revised. Prior to 2.2 (or, more likely, 2.4) b.y. ago, atmospheric  $\text{O}_2$  was low, so the iron released during weathering remained as soluble  $\text{Fe}^{2+}$  and was carried away by groundwater. The resultant paleosols are iron-poor. After 1.9 b.y. ago, atmospheric  $\text{O}_2$  was relatively abundant, so the iron released by weathering was oxidized to insoluble  $\text{Fe}^{3+}$  and was retained in the soil. Holland's detailed calculations predict that atmospheric  $\text{O}_2$  was less than 0.01 PAL before 2.2 b.y. ago and greater than 0.15 PAL after 1.9 b.y. ago.



(a)



(b)

**FIGURE 11-10** [See color section] Samples of the detrital form of (a) uraninite and (b) pyrite. (Source: (a) and (b) J. William Schopf.)

Redbeds are sandy sediments that were deposited on land by rivers or as windblown dust (Figure 11-11). They form today in arid regions, such as the American Southwest. The reddish color of these deposits comes from a thin layer of **hematite**,  $\text{Fe}_2\text{O}_3$ , that coats the surfaces of the sediment grains. The iron in hematite is the oxidized,  $\text{Fe}^{3+}$ , variety, so redbeds indicate oxidizing atmospheric conditions at the time of their formation. The earliest confirmed redbeds are thought to have formed about 2.2 b.y. ago, which is consistent with the other evidence for a rise in atmospheric  $\text{O}_2$  at about this time.

Even better evidence for the rise of atmospheric  $\text{O}_2$  comes from sulfur isotopes. The arguments here are more complex, so the reader who doesn't care about the details may choose to bypass this discussion. For those who are interested, though, the data are described in the Box: "A Closer Look: Mass-Independent Sulfur Isotope Ratios and



**FIGURE 11-11** A sequence near Uranvan, Colorado, showing Triassic redbeds overlying Upper Jurassic sandstones. (Source: Estate of Preston Cloud.)

## A CLOSER LOOK

### Mass-Independent Sulfur Isotope Ratios and What They Tell Us about the Rise of Atmospheric O<sub>2</sub>

As mentioned earlier, new evidence from sulfur isotopes may have clinched the question of when atmospheric O<sub>2</sub> first rose. Sulfur is unusual in that it has four stable isotopes that occur naturally: <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S, and <sup>36</sup>S. These isotopes can be separated, or **fractionated**, by a variety of physical and chemical processes. In such processes, the lighter sulfur isotopes typically react faster than do the heavier isotopes. For example, **biological sulfate reduction**, in which certain bacteria use sulfate to oxidize organic matter, discriminates strongly against the heavier isotopes. Scientists usually measure just the two most abundant isotopes, <sup>32</sup>S and <sup>34</sup>S. The reduced sulfur that is formed from this reaction is preserved as pyrite (FeS<sub>2</sub>), which we have just discussed. The pyrite produced by bacterial sulfate reduction is strongly depleted in <sup>34</sup>S relative to <sup>32</sup>S. Indeed, such "isotopically light" pyrite is considered evidence for biological activity. (We say that the pyrite is "light" because it is enriched in the light isotope of sulfur compared to the heavier one.)

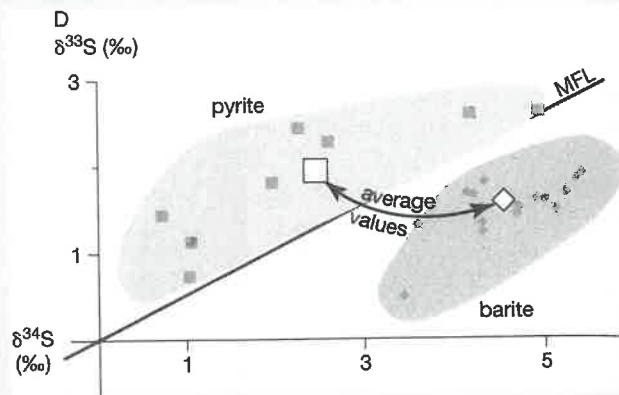
If one examines modern, sulfur-bearing rocks, one observes that the four sulfur isotopes are distributed in a highly predictable manner. <sup>33</sup>S is fractionated relative to <sup>32</sup>S by about half as much as is <sup>34</sup>S, and <sup>36</sup>S is fractionated by about twice as much. This is because the mass difference between <sup>33</sup>S and <sup>32</sup>S (1 atomic mass unit) is half that between <sup>34</sup>S and <sup>32</sup>S (2 atomic mass units), whereas the mass difference between <sup>36</sup>S and <sup>32</sup>S (4 atomic mass units) is twice as much. We say that all of the sulfur isotopes fall along the normal *mass fractionation line (MFL)*. But if one examines sulfur isotopes in Archean sediments, the results are quite different (Box Figure 11-1). In Box Figure 11-1, the pyrite sediments have more <sup>33</sup>S than would be expected and the barite (BaSO<sub>4</sub>) sediments have less.

The units used in Box Figure 11-1 deserve some explanation. Isotopic abundances are measured in parts per thousand (‰), also called "parts per mil." The standard way of expressing isotope abundances is to use *delta (δ) notation*. For <sup>34</sup>S, for example, we write

$$\delta^{34}\text{S}(\text{‰}) = \left[ \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}} - (^{34}\text{S}/^{32}\text{S})_{\text{standard}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} \right] \times 1000$$

Negative  $\delta^{34}\text{S}$  values mean that the sample is depleted in <sup>34</sup>S relative to the standard. The standard employed is FeS (the mineral *troilite*) from the Canyon Diablo meteorite. Hence, sulfur isotopes are said to be measured on the *CDT scale*.

Box Figure 11-1 by itself does not tell us when atmospheric O<sub>2</sub> first rose. However, if one replots these data in terms of the ages of the various samples, adding new datapoints that have been obtained during the past few years, a very clear result appears (Box Figure 11-2). In Box Figure 11-2,  $\Delta^{33}\text{S}$  represents the deviation of the measured  $\delta^{33}\text{S}$  values from the normal mass fractionation line. The solid bar through  $\Delta^{33}\text{S} = 0$  represents 73 samples of Phanerozoic age, that is, younger than 540 m.y. old. The data show that so-called mass-independent fractionation of sulfur isotopes is observed in sedimentary rocks older than about 2.4 b.y. of age but not in younger rocks. This marked change in the sulfur isotope distribution occurs



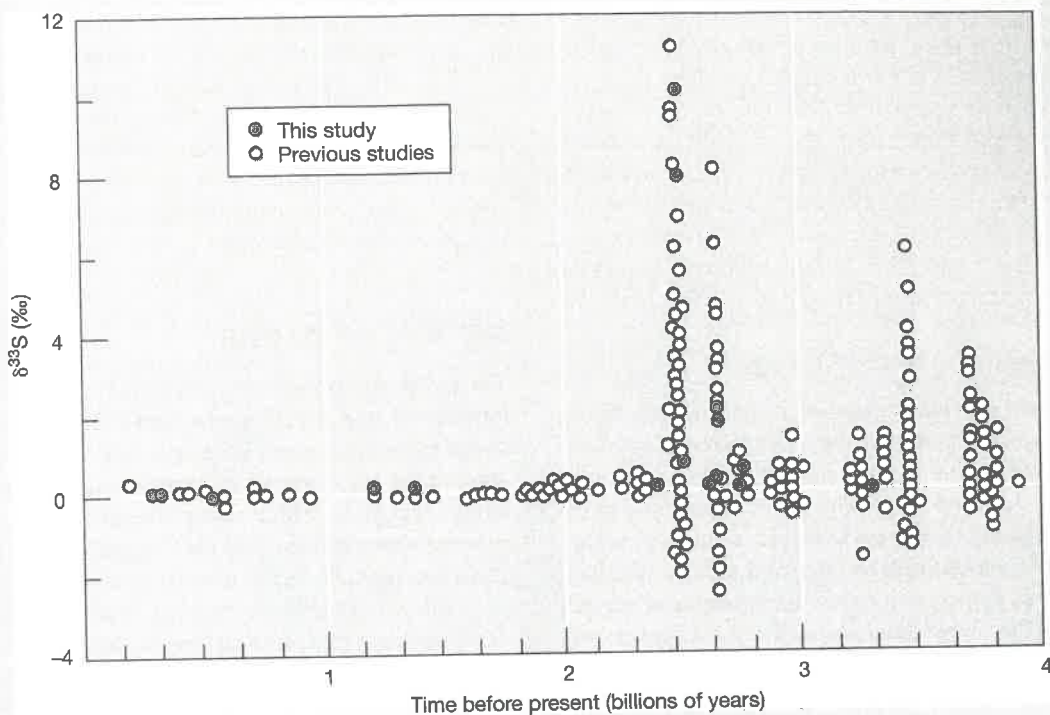
**BOX FIGURE 11-1** Diagram showing sulfur isotope concentrations measured in Archean rocks. Barite is BaSO<sub>4</sub>; pyrite is FeS<sub>2</sub>. (Source: J. Farquhar et al., *Journal of Geophysical Research* 106, 2001, pp. 1–11.)

at exactly the same time that other, conventional types of geologic evidence indicate that oxygen levels first rose.

The data in Box Figure 11-2 also show more complicated patterns that were not obvious until just a few years ago. Between about 2.8 and 3.2 b.y. ago, the  $\Delta^{33}\text{S}$  values are much smaller than before or after that time, but are still distinctly non-zero. Exactly what this means is a topic of current debate. Some researchers have suggested that atmospheric O<sub>2</sub> increased transiently during this time (see the following discussion), then went back down again, only to rise for good at 2.4 b.y. ago. Alternatively, this decrease in  $\Delta^{33}\text{S}$  may have been caused by the buildup of high-altitude organic haze, which prevented solar ultraviolet radiation from reaching the lower atmosphere.

How are sulfur isotopes in sediments affected by atmospheric O<sub>2</sub>? Laboratory experiments show that isotopes can be fractionated in a mass-independent manner by photochemical reactions occurring in the atmosphere. In particular, photolysis of sulfur dioxide (SO<sub>2</sub>) fractionates sulfur isotopes in this unusual way. The reason is probably related to slight shifts in the absorption lines of SO<sub>2</sub> molecules containing different isotopes of sulfur. This causes SO<sub>2</sub> molecules containing the most abundant isotope, <sup>32</sup>S, to be photolyzed at higher altitudes than those containing minor sulfur isotopes. Today, SO<sub>2</sub> is not photolyzed in the atmosphere because the ultraviolet radiation needed to cause this reaction is absorbed by O<sub>2</sub>. Much lower O<sub>2</sub> levels would be needed in order to allow this reaction to occur. Even more importantly, today all the sulfur that enters the atmosphere is eventually oxidized to sulfur dioxide or to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). These gases are soluble in water; hence, they are removed by rainout and end up in the ocean as dissolved sulfate (SO<sub>4</sub><sup>2-</sup>). Even if some photochemical reaction within the atmosphere did cause mass-independent fractionation of sulfur isotopes, the effects would disappear because all of the byproducts of the reactions would be recombined as oceanic sulfate before they entered into sediments.

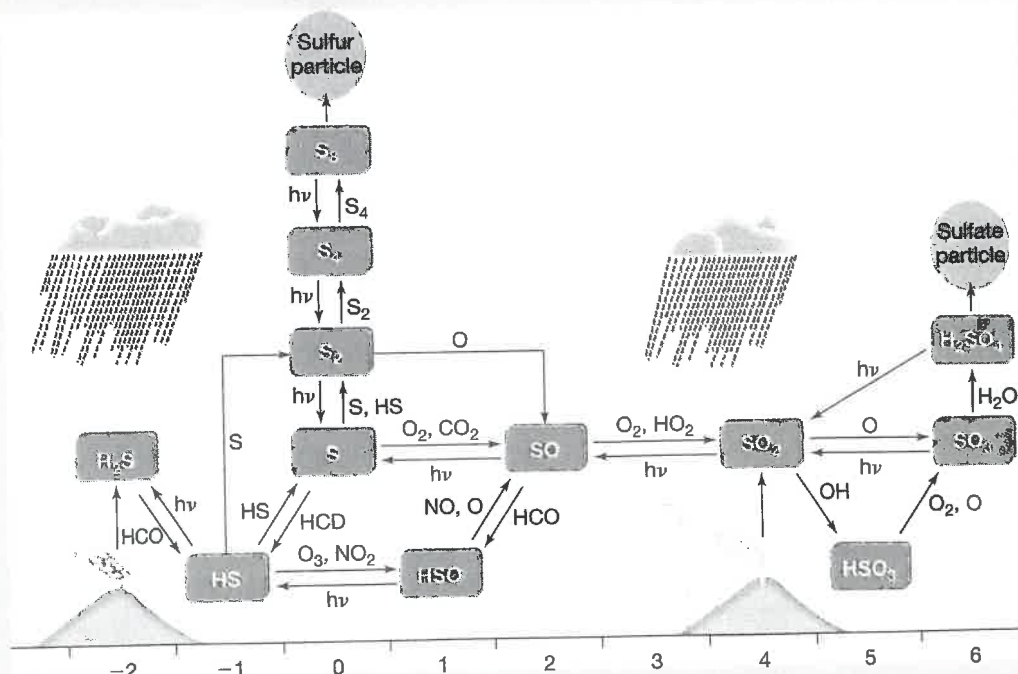
By contrast, in a low-O<sub>2</sub> atmosphere, sulfur photochemistry is much more complex (Box Figure 11-3). Here, the horizontal scale represents the oxidation state of sulfur,



**BOX FIGURE 11-2** Diagram illustrating the deviation of  $\delta^{33}\text{S}$  from the normal mass fractionation line. Phanerozoic samples fall close to zero on this scale. (Source: Domagal-Goldman et al., *Earth Planetary Science Letters* 269, 2008, pp. 29–40. Data courtesy J. Farquhar and D. T. Johnston.)

which ranges from  $-2$  for hydrogen sulfide ( $\text{H}_2\text{S}$ ) to  $+6$  for sulfuric acid. Because of the absence of  $\text{O}_2$ , sulfur photochemistry can proceed in both directions, left and right in the figure. Sulfur outgassed as  $\text{SO}_2$  can be reduced to elemental sulfur ( $\text{S}_8$ ) or to  $\text{H}_2\text{S}$ . Conversely, sulfur outgassed as  $\text{H}_2\text{S}$  can be oxidized all the way to  $\text{H}_2\text{SO}_4$ . The important point is that sulfur can leave the atmosphere in a variety of different oxidation states, and it does not all end up as

dissolved sulfate in the ocean. Hence, mass-independent fractionation patterns produced in the atmosphere can, in theory, be preserved in sediments. Detailed photochemical modeling shows that atmospheric  $\text{O}_2$  concentrations must have been at least  $10^5$  times lower than today in order for this type of chemistry to occur. Hence, the new data on sulfur isotopes provide strong evidence that the Archean atmosphere was essentially anoxic.



**BOX FIGURE 11-3** The atmospheric sulfur cycle in an anoxic, Archean atmosphere. The horizontal scale represents the oxidation state of sulfur. (Source: J. F. Kasting, *Science* 293, 2001, pp. 819–820.)

What They Tell Us about the Rise of Atmospheric O<sub>2</sub>.” To geochemists interested in Earth’s early evolution, these sulfur isotope data are fascinating. Not only do they confirm the basic story told earlier, they also provide indirect evidence of other changes in atmospheric composition prior to the rise of O<sub>2</sub>. In particular, they may show that an organic haze was indeed present during the Mid-Archean eon, around 2.8–3.2 b.y. ago. We’ll return to this question in the next chapter, as it may be related to Earth’s climate record.

### What Delayed the Rise of Oxygen?

When combined with the other geologic evidence bearing on the rise of atmospheric oxygen, the sulfur isotope data tell us fairly conclusively that O<sub>2</sub> first rose to appreciable levels some time close to 2.4 b.y. ago. This creates a puzzle, though, because the organic biomarker evidence mentioned earlier suggests that cyanobacteria had evolved at least 300 m.y. before this time. Hence, a question that researchers are still working on is this: What delayed the rise of atmospheric O<sub>2</sub> by almost half a billion years? One commonly held idea is that it simply took this long for photosynthetic O<sub>2</sub> to remove all the reduced ferrous iron that was initially present in the oceans. This idea is probably incorrect, however, because if oxygen was produced at today’s rate, it would have oxidized all the dissolved iron in the oceans in only a few thousand years. Something else must have been suppressing O<sub>2</sub>. Several possibilities have been suggested. Perhaps the organisms that generated the 2.7 b.y.-old 2 $\alpha$ -methylhopanes were merely the precursors to cyanobacteria, or entirely unrelated organisms like the purple nonsulfur bacteria, and were not generating oxygen. Or, perhaps cyanobacteria were indeed generating oxygen at this time, but they had not yet learned to fix nitrogen simultaneously, and so their production of O<sub>2</sub> was extremely limited. (We saw earlier that modern cyanobacteria have evolved complicated mechanisms for protecting their nitrogenase from the O<sub>2</sub> that they produce.) A third idea is that volcanic gases were more reduced prior to 2.4 b.y. ago, and that this additional sink for oxygen kept atmospheric O<sub>2</sub> levels suppressed. But there is no evidence

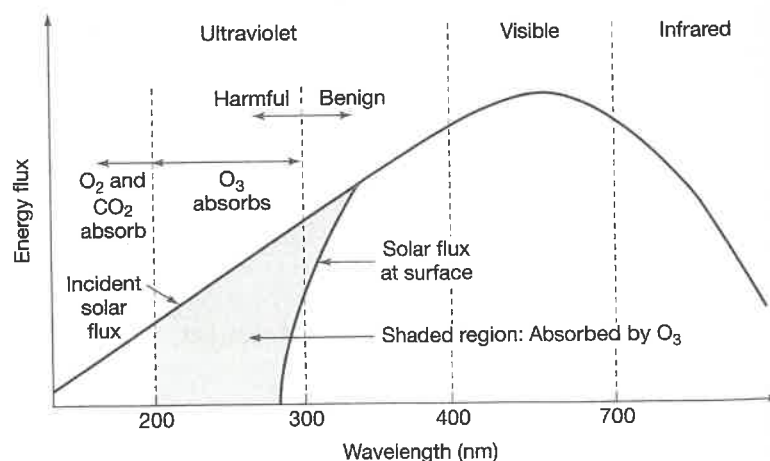
for a corresponding change in the oxidation state of Earth’s mantle, and so the mechanism for causing such a change in volcanic gas composition remains unresolved. We will not dwell on this problem any further, except to point out that many questions regarding the rise of atmospheric oxygen remain to be investigated. Scientists, as always, find new questions when old questions are answered.

### THE RISE OF OZONE

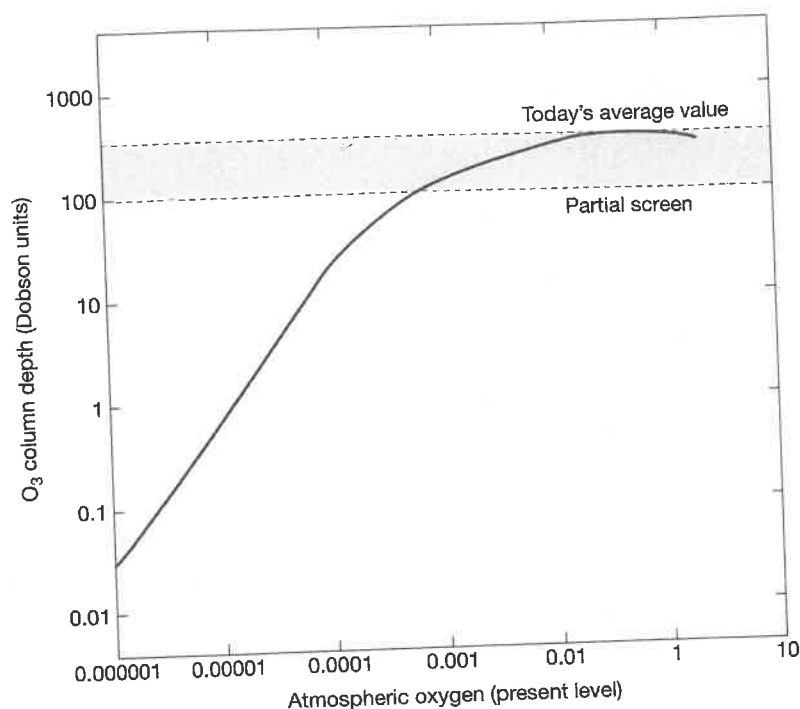
The rise of atmospheric oxygen would have been accompanied by an increase in stratospheric ozone. As we mentioned previously, ozone is critical for life because it shields out harmful solar ultraviolet radiation. The principal wavelength region in which ozone shielding is important is between about 200 and 300 nm (Figure 11-12). (Recall that 1 nm [nanometer] = 10<sup>-9</sup> m = 10<sup>-3</sup>  $\mu$ m.) Ultraviolet radiation with wavelengths shorter than 200 nm is also harmful to organisms, but it is effectively absorbed by both O<sub>2</sub> and CO<sub>2</sub>. Thus, it should not have been a problem even in an anoxic atmosphere. Ultraviolet radiation between 300 and 400 nm is much less harmful to organisms and is not considered to be a threat, even though a substantial flux of such radiation reaches Earth’s surface today.

As we mentioned in Chapter 1, the amount of UV radiation absorbed by ozone depends on the ozone *column depth*, that is, the total amount of ozone between the surface and the top of the atmosphere. The column depth is usually measured in *Dobson units*. One Dobson unit (DU) is equivalent to a layer of pure ozone 0.01 mm thick at the ground. The average ozone column depth today is about 320 DU, equivalent to a 0.32-cm-thick layer of pure ozone at 1 atm pressure.

How much ozone would have been present if the atmospheric O<sub>2</sub> concentration were lower than it is today? **Photochemical models** can be used to address this question: From a model calculation that is capable of reproducing today’s average ozone column depth, O<sub>2</sub> is gradually removed from the model atmosphere. The results of one such calculation are shown in Figure 11-13. The calculation



**FIGURE 11-12** The wavelength region where absorption by ozone is important.



**FIGURE 11-13** Ozone column depth at different atmospheric O<sub>2</sub> levels, as calculated by a photochemical model. "PAL" stands for "times the present atmospheric level."

shows that the ozone column depth increases nonlinearly with atmospheric O<sub>2</sub> level: Even a small amount of O<sub>2</sub> produces a substantial ozone column depth. The reasons have to do with the details of ozone photochemistry, which we will save for Chapter 17. Exactly when a biologically effective UV screen would have been established is not clear because organisms differ greatly in their tolerances for UV radiation. However, examination of the calculated UV fluxes shows that most of the harmful UV radiation would already have been absorbed once the ozone column depth exceeded about 100 DU, or roughly one-third of today's value. As Figure 11-13 demonstrates, this column depth would have been reached at an O<sub>2</sub> level of only 0.01 PAL. For comparison, the paleosol evidence discussed earlier indicates that atmospheric O<sub>2</sub> was greater than 0.15 PAL by 1.9 b.y. ago. So, we can infer that a reasonably effective UV screen was already established by this time.

### VARIATIONS IN ATMOSPHERIC O<sub>2</sub> OVER THE LAST 2 BILLION YEARS

The initial rise of atmospheric oxygen and ozone occurred over 2 b.y. ago. This does not necessarily imply, however, that O<sub>2</sub> concentrations immediately jumped up to the modern value of 21% by volume. Indeed, although the available evidence is far from conclusive, we have reason to believe that O<sub>2</sub> concentrations remained well below the present level until shortly before the dawn of the Cambrian period. One line of reasoning is the following. Recall that eukaryotes (organisms whose cells have nuclei) had already evolved by 2.7 b.y. ago, according to organic biomarker evidence. Recall also that the same Archean "oil" that

contained 2 $\alpha$ -methylhopanes from cyanobacteria contains steranes. These compounds are formed by the breakdown of cholesterol, which is thought to be manufactured only by eukaryotes. Most eukaryotes are aerobes, that is, they require oxygen, so their presence at 2.7 b.y. ago implies that free O<sub>2</sub> was present in their immediate environment, most likely the shallow surface ocean or lakes. Free O<sub>2</sub> was not present in the atmosphere, however, because this is conclusively ruled out by the geologic evidence just described.

### The Ediacaran Fauna

The curious thing is this: multicellular organisms did not appear in the fossil record until about 560 m.y. ago during a time period referred to as the Vendian. Until then, all eukaryotic organisms were single-celled. Why did the evolution of multicellular organisms take so long if eukaryotes were already present by 2.7 b.y. ago? One possible answer is that atmospheric O<sub>2</sub> levels were too low to support them. A study performed more than 30 years ago by Donald Rhoads and John Morse showed that animal life disappears below a few tens of meters depth in the anoxic Gulf of California. Their results indicate that modern multicellular organisms need at least 10–20% of present dissolved oxygen in order to survive. The evolution of multicelled animals could have been delayed because atmospheric O<sub>2</sub> concentrations and, hence, dissolved O<sub>2</sub> concentrations as well were below this level prior to the Vendian.

Another clue that atmospheric oxygen levels were still low in the Vendian period comes from the nature of the multicellular organisms that did evolve at that time. The animals of the Vendian period, termed the *Ediacaran fauna* because they were first discovered in the Ediacaran hills



**FIGURE 11-14** The Ediacaran organism, *Dickinsonia*. (Source: Simon Conway Morris.)

of Australia, have flattened bodies that may have been designed to maximize surface uptake of oxygen. For example, the Ediacaran fossil *Dickinsonia* (Figure 11-14) was about 30 cm in length but only 1 or 2 cm in thickness. Bruce Runnegar of the University of California, Los Angeles, has argued that *Dickinsonia* lacked a circulatory system, so that it had to acquire all of its oxygen through its skin. His analysis of this fossil organism indicates that  $O_2$  concentrations had to be above 0.1 times the present level in order for *Dickinsonia* to survive. However, oxygen levels were probably not much higher than this, if  $O_2$  limitation was the reason for this animal's flattened shape.

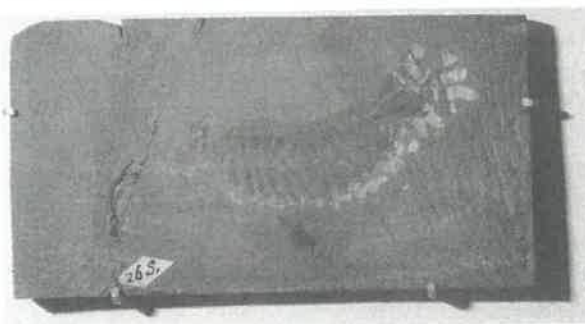
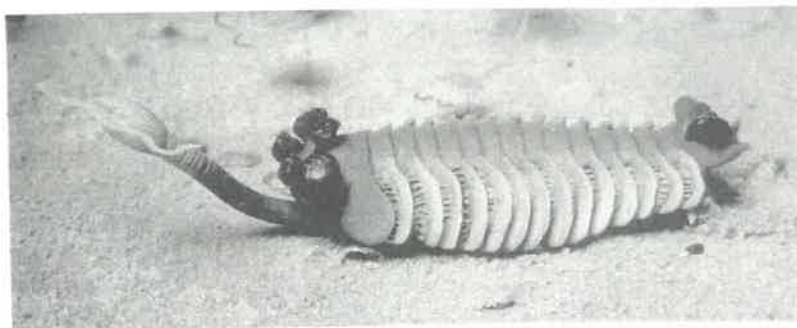
### Variations in Atmospheric $O_2$ during the Phanerozoic

The Phanerozoic eon—the time during which advanced, multicellular life has thrived—began 542 m.y. ago with what is often termed the *Cambrian explosion*. At about this time, organisms acquired the capability of making hard shells. As a result of this invention, the fossil record becomes much more detailed after this time. Figure 11-15 shows a sample of the early Cambrian fauna collected from the famous Burgess shale in western Canada. These organisms almost certainly required high levels of atmospheric oxygen, perhaps approaching those of the modern

Earth. Indeed, numerous researchers, beginning with Lloyd Berkner and William Marshall back in the 1960s, have suggested that the Cambrian explosion was triggered by an increase in atmospheric  $O_2$ . This speculation remains unproven, but it remains a leading hypothesis for why multicellular life diversified so rapidly beginning at that time.

The record of atmospheric  $O_2$  variations since that time is almost as poor as it is during the Proterozoic. However, we can make some estimates of how much  $O_2$  has varied by looking at carbon isotopes. Carbon, like sulfur, has more than one stable isotope, and these isotopes behave differently in chemical reactions. For carbon, the two isotopes of interest are  $^{12}C$  and  $^{13}C$ . During photosynthesis, plants consume  $CO_2$  that contains both of these carbon isotopes. The lighter isotope,  $^{12}C$ , reacts faster, however; thus, the organic matter that is formed is depleted in  $^{13}C$ . For typical rates of photosynthesis, the depletion in  $^{13}C$  is about 25 parts per mil. (Carbon isotope concentrations are expressed using “delta” notation as well. For carbon, the standard is carbonate from the Peedee belemnite, a fossil cuttlefish which is related to modern squid. Hence, the carbon isotope scale is referred to as the *PDB* scale.)

Carbon isotopes can be used to estimate the rates of  $O_2$  production in the following way. As we saw in Chapter 8, it is burial of photosynthetically produced organic carbon that results in net production of  $O_2$ . The organic carbon

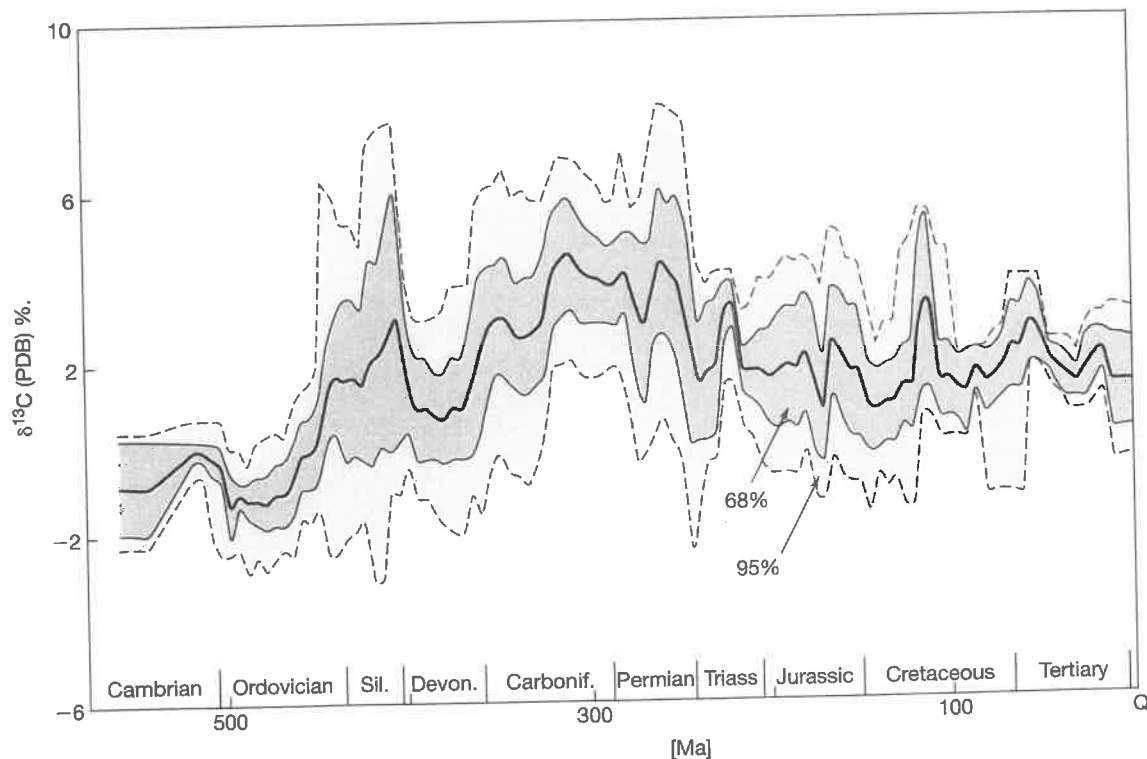


**FIGURE 11-15** Early Cambrian fauna from the Burgess shale. (Source: (a) Chip Clark and (b) A. J. Copley/Visuals Unlimited.)

that is buried is isotopically light, that is, it is depleted in <sup>13</sup>C. Hence, the carbon that remains in the atmosphere and in the ocean as dissolved bicarbonate and carbonate ion becomes isotopically heavy. The carbonate sediments that are formed are in equilibrium with dissolved carbonate and bicarbonate; thus, they are isotopically heavy as well compared to the buried organic carbon. And the faster

that organic carbon is buried, the heavier the carbonates become.

Figure 11-16 shows the carbon isotope composition of carbonate sediments during the last 540 m.y. Today, carbonate sediments are at about 0 per mil on the PDB scale. It can be shown from mass balance arguments (see the Box “Thinking Quantitatively: Carbon Isotopes and Organic



**FIGURE 11-16** The carbon isotope record from carbonate rocks deposited during the Phanerozoic. Solid curve is the running mean. Shaded areas include 68% and 95% of all the data. (Source: J. Veizer et al., *Chemical Geology* 161, 1999, pp. 59–88.)



## THINKING QUANTITATIVELY

## Carbon Isotopes and Organic Carbon Burial

Carbon isotopes provide a useful way of analyzing the behavior of the organic carbon cycle in the distant past. The reason is that organisms fractionate carbon isotopes when they convert  $\text{CO}_2$  into organic matter during photosynthesis. As described in the text,  $^{13}\text{C}$  is taken up faster during photosynthesis than is  $^{12}\text{C}$ . By measuring the  $^{13}\text{C}/^{12}\text{C}$  ratio in carbonate sediments, we can determine how fast organic carbon was being buried and, hence, how fast  $\text{O}_2$  was being produced.

We can analyze the carbon isotope record mathematically by keeping track of the total amount of  $^{12}\text{C}$  and  $^{13}\text{C}$  flowing through the system. For the purposes of this analysis we can treat the atmosphere and oceans as one combined reservoir. Carbon enters the atmosphere–ocean system in two different ways: (1) outgassing of  $\text{CO}_2$  from volcanoes, and (2) weathering of carbonate rocks and sedimentary organic carbon (**kerogen**) on land. Carbon leaves the system in the form of sedimentary organic carbon and carbonates. Let

$F_{\text{in}}$  = flux of carbon into the atmosphere–ocean system

$F_{\text{carb}}$  = burial rate of carbonates

$F_{\text{org}}$  = burial rate of organic carbon

$\delta_{\text{in}}$  = isotopic composition of carbon entering the system

$\delta_{\text{carb}}$  = isotopic composition of buried carbonate carbon

$\delta_{\text{org}}$  = isotopic composition of buried organic carbon

The total amount of carbon (including both  $^{12}\text{C}$  and  $^{13}\text{C}$ ) leaving the system must be equal to the amount of carbon entering it. Thus

$$(1) \quad F_{\text{in}} = F_{\text{carb}} + F_{\text{org}}$$

The amount of  $^{13}\text{C}$  leaving the system must also equal the amount that enters. Because the ratio of  $^{13}\text{C}$  to  $^{12}\text{C}$  is small, we can express this mathematically by the equation

$$(2) \quad F_{\text{in}}\delta_{\text{in}} = F_{\text{carb}}\delta_{\text{carb}} + F_{\text{org}}\delta_{\text{org}}$$

To make use of this system of two equations, we need one additional piece of information. During photosynthesis, most plants (and photosynthetic algae) fractionate carbon isotopes by about 25‰. Or, to say it another way, the organic matter that is formed from photosynthesis is depleted in  $^{13}\text{C}$  by this amount. Let

$$\Delta_{\text{B}} = \delta_{\text{carb}} - \delta_{\text{org}} \approx 25\text{‰}$$

Carbon Burial”) that this implies that about 20% of the  $\text{CO}_2$  entering the system from volcanic outgassing and weathering of carbonate and organic carbon-containing rocks on land is buried as organic carbon, while the other 80% is buried as carbonates. Figure 11-16 shows, however, that this has not always been the case. Carbonates were isotopically

To simplify things still further, let

$$f_{\text{carb}} = F_{\text{carb}}/F_{\text{in}} = \text{fraction of carbon entering the system that is buried as carbonate}$$

$$f_{\text{org}} = F_{\text{org}}/F_{\text{in}} = \text{fraction of carbon entering the system that is buried as organic carbon.}$$

Dividing equation (1) by  $F_{\text{in}}$  yields the relationship

$$(3) \quad 1 = f_{\text{carb}} + f_{\text{org}}$$

This just tells us an obvious result: all of the carbon entering the system must leave either as carbonate carbon or organic carbon. Meanwhile, dividing equation (2) by  $F_{\text{in}}$  yields

$$(4) \quad \delta_{\text{in}} = f_{\text{carb}}\delta_{\text{carb}} + f_{\text{org}}\delta_{\text{org}}$$

Now, we can make use of equation (3) to write:  $f_{\text{carb}} = 1 - f_{\text{org}}$ . Thus,

$$(5) \quad \delta_{\text{in}} = (1 - f_{\text{org}})\delta_{\text{carb}} + f_{\text{org}}\delta_{\text{org}} \\ = \delta_{\text{carb}} - f_{\text{org}}(\delta_{\text{carb}} - \delta_{\text{org}})$$

But the quantity  $(\delta_{\text{carb}} - \delta_{\text{org}})$  is just  $\Delta_{\text{B}}$ , the average fractionation produced during photosynthesis. Thus

$$(6) \quad \delta_{\text{in}} = \delta_{\text{carb}} - f_{\text{org}}\Delta_{\text{B}}$$

or, rearranging terms and solving for  $f_{\text{org}}$

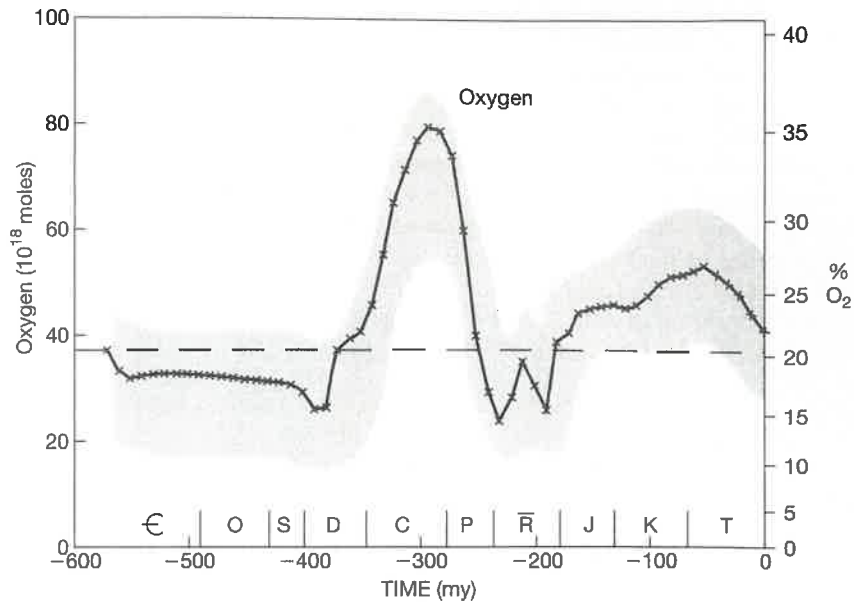
$$(7) \quad f_{\text{org}} = (\delta_{\text{carb}} - \delta_{\text{in}})/\Delta_{\text{B}}$$

Finally, we assume that the average isotopic composition of carbon entering the atmosphere–ocean system is the same as the carbon isotopic composition of the mantle, about –5‰. Using this value for  $\delta_{\text{in}}$  and setting  $\Delta_{\text{B}} = 25\text{‰}$  gives

$$(8) \quad f_{\text{org}} = (\delta_{\text{carb}} + 5)/25$$

When  $\delta_{\text{carb}} = 0\text{‰}$ , as it does today for marine carbonates, equation (8) predicts that  $f_{\text{org}} = 0.2$ . This is consistent with the value given in the text: about 20% of the  $\text{CO}_2$  entering the atmosphere–ocean system is reduced to organic carbon and leaves the system in that form. Figure 11-16 shows that  $\delta_{\text{carb}}$  was greater than +5‰ around 300 m.y. ago. According to equation (8), this implies that the fraction of carbon leaving the system as organic carbon was  $>0.4$ , or more than twice the modern value. If the carbon input rate from weathering and outgassing was the same as today, then the rate of  $\text{O}_2$  production was more than twice as much. So, it would not be at all surprising if the atmospheric  $\text{O}_2$  concentration was higher at that time as well.

heavy during the Carboniferous and early Permian periods, 360–250 m.y. ago, and again during the Cretaceous period, 144–65 m.y. ago. By the logic that we just went through, this implies lots of organic carbon burial, and hence lots of  $\text{O}_2$  production during both time periods. The biggest excursion in the carbon isotope record and, hence, the biggest increase



**FIGURE 11-17** Calculated variation in atmospheric O<sub>2</sub> during the Phanerozoic. (Source: R. A. Berner and D. Canfield, *American Journal of Science* 289, 1989, pp. 333–361.)

in organic carbon burial, was during the Mid-Carboniferous period. Carbonate sediments were about 5‰ heavier at that time, indicating that organic carbon was being buried about twice as fast as today. It is not hard to understand why if one considers what was happening at that time. The Carboniferous period gets its name from the extensive coal deposits that were formed during this time interval. The peak of this long-lived period of coal formation was during the Pennsylvanian epoch, 318–299 m.y. ago. The coal formed during that time has been the basis for the coal mining industry of western Pennsylvania and West Virginia.

Robert Berner and Donald Canfield of Yale University put these carbon isotope data into a model of the global carbon cycle and used them to estimate atmospheric O<sub>2</sub> levels. Their results are shown in Figure 11-17.

Atmospheric O<sub>2</sub> concentrations were probably higher than today during both the Carboniferous and the Cretaceous periods. The predicted variations in O<sub>2</sub> are not as large as one might anticipate from Figure 11-16 because the actual situation is more complicated than just described. Some of the excess oxygen that was produced was taken up by the sulfur cycle in oxidizing sulfide to sulfate. One can see evidence for this from sulfur isotopes, which covary with carbon isotopes in just the manner one would expect if oxygen was shuttling back and forth between the two reservoirs. However, Berner and Canfield's prediction is probably at least qualitatively correct. Other researchers have picked up on this idea and have suggested that the giant dragonflies of the Carboniferous (Figure 11-18) and the dinosaurs of the Mesozoic may both have been breathing an enriched blend



**FIGURE 11-18** [See color section] A Carboniferous dragonfly with a wingspan of 60 cm (2 ft.). (Source: John Weinstein/The Field Museum.)

of air. Like the Ediacaran organism *Dickinsonia* mentioned earlier, insects take in  $O_2$  through their “skin”; thus, some paleontologists have suggested that it was the higher  $O_2$  levels during the Carboniferous that allowed them to achieve their gigantic size. On the other hand, other researchers have pointed out that the level of biological competition was not as great then as it is today. One wonders how long 2-foot dragonflies would have survived in the presence of modern eagles or falcons. The gigantic pterosaurs of the Mesozoic would probably have made short work of them as well. So, the giant dragonflies of the Carboniferous could have existed simply because there was no one around to eat them. If this was true, they are not very reliable oxygen indicators.

### MODERN CONTROLS ON ATMOSPHERIC $O_2$

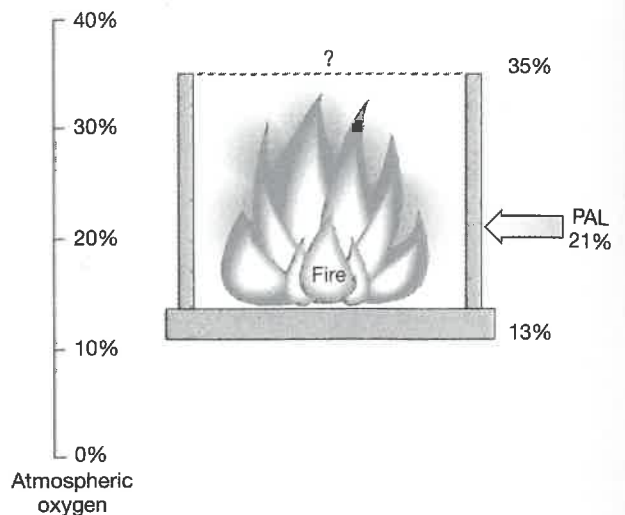
Let us now turn our attention to the modern system. We have offered some suggestions for why atmospheric  $O_2$  concentrations may have increased when they did. A related question, which we might hope would be somewhat easier, is this: What controls the atmospheric  $O_2$  concentration today?

The answer, surprisingly, is that we do not know for sure, although researchers do have a number of ideas. Whatever the oxygen control mechanism is, it appears to be very efficient. The modern atmospheric  $O_2$  level is 21% by volume, or 0.21 bar. It seems unlikely that the  $O_2$  concentration has strayed from this level by more than  $\pm 50\%$  since the late Devonian period, about 360 m.y. ago. The evidence is that forests have existed since that time and, while they have always been able to burn, they have never disappeared entirely.

### Forest Fires and Atmospheric Oxygen

Fires burn more intensely when the oxygen content of the air is increased. A graphic, and tragic, illustration of the phenomenon occurred in the mid-1960s, when an *Apollo* space capsule burned up on its test pad in Houston with three astronauts aboard. At that time, NASA was using pure  $O_2$  in its spacecraft to minimize launch weight. After the fire, the space agency returned to using normal air because they realized, belatedly, that pure  $O_2$  was too flammable.

A similar problem could occur globally if the atmospheric  $O_2$  content got too high. Forest fires, ignited by lightning or other mechanisms, might rage out of control and burn everything within reach. It is difficult to determine the exact  $O_2$  level at which this would occur, but laboratory experiments using wet matchsticks and shredded paper suggest that an  $O_2$  concentration of 35% by volume would be enough to destroy most of the global biota (Figure 11-19). A catastrophe of this magnitude may actually have taken place in the aftermath of the K-T impact event, 65 m.y. ago. But, as we will discuss in Chapter 13, this was a very special



**FIGURE 11-19** The oxygen “fire window,” showing proposed minimum and maximum atmospheric  $O_2$  levels consistent with the continuous record of charcoal deposition since the Devonian period. (Source: T. P. Jones and W. G. Chaloner, *Global and Planetary Change* 97, 1991, p. 39.)

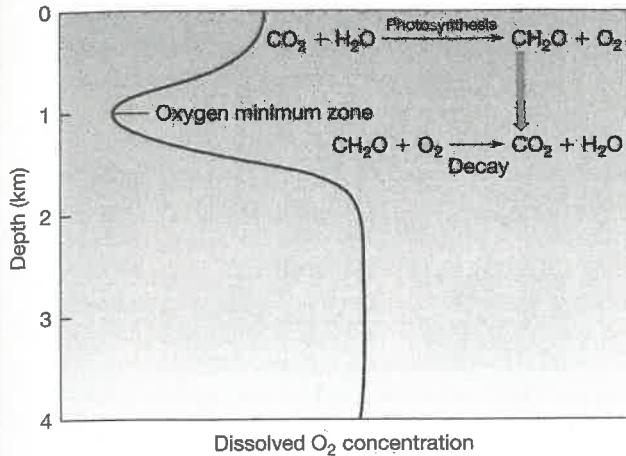
event in which fires may have been ignited all over the globe by finely dispersed ejecta reentering Earth’s atmosphere. Other than that scenario, there is no evidence that such widespread forest fires have occurred. We can infer that the atmospheric  $O_2$  concentration has probably remained below 35% by volume ever since forests first appeared.

Forest fires can also be used to place a lower bound on atmospheric  $O_2$  levels. Fires will not ignite when the  $O_2$  concentration falls below about 13% by volume. This limit is somewhat firmer than the upper bound on  $O_2$  because it depends on simple physics: At  $O_2$  concentrations below 13%, a flame loses heat by convection more rapidly than it gains heat by combustion. Sedimentary rocks preserve a more-or-less continuous record of charcoal since the late Devonian period. Charcoal is produced from the incomplete combustion of organic matter by fire, so forest fires must have burned on and off throughout this period. Hence, we conclude that the atmospheric  $O_2$  concentration has not fallen below 13% by volume during the last 360 m.y.

What mechanism could have stabilized atmospheric  $O_2$  within the “fire window” during the past few hundred million years? The main loss processes for  $O_2$ , surface weathering and the oxidation of reduced volcanic gases, are thought to be independent of  $O_2$  concentration within this range. The control mechanism must therefore act on the  $O_2$  source—namely, photosynthesis followed by burial of organic carbon. Let us consider the factors that affect the organic carbon burial rate.

### Oxygenation of the Deep Ocean

Most of the organic matter being buried today is deposited in marine sediments rather than on land. The same seems to have been true during most of the past few hundred



**FIGURE 11-20** The vertical profile of dissolved O<sub>2</sub> in the (low-latitude) ocean.

million years, except during the Carboniferous period, when the great coal beds were forming. Thus, the control of organic carbon burial appears to lie in the ocean.

For many years, researchers have believed that the feedback mechanism that stabilizes atmospheric O<sub>2</sub> involves the deep oceans. The deep oceans today contain relatively high concentrations of dissolved O<sub>2</sub>. Indeed, over much of the globe, the dissolved O<sub>2</sub> content of deep water is higher than that of surface water (Figure 11-20; see also the Box “A Closer Look: Oxygen Minimum Zone” on p. 156 in Chapter 8). The reason is that the water in the deep ocean originates at the surface at high latitudes, where temperatures are very cold. Like most other gases, O<sub>2</sub> increases in solubility as the temperature goes down. Thus, cold, high-latitude surface water contains more dissolved O<sub>2</sub> than does surface water at lower latitudes. This high O<sub>2</sub> content is passed on to the deep ocean when the cold surface water sinks as part of the global thermohaline circulation.

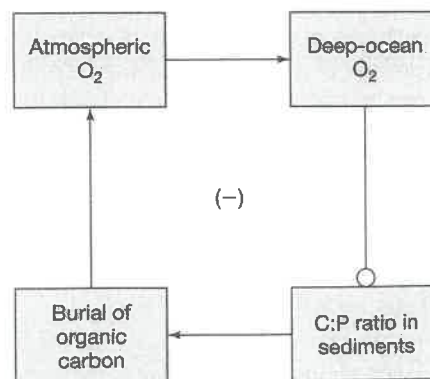
Oxygen concentrations in the deep ocean would drop dramatically, however, if the atmospheric O<sub>2</sub> concentration were lowered. Even today, over much of the ocean a pronounced **oxygen minimum zone** exists at a depth of about 1 km (see Figure 11-20). The low O<sub>2</sub> concentrations at this depth are caused by the decay of organic matter that falls from the surface ocean. In some regions—the Black Sea, for example—the rate of vertical mixing is slow enough to cause the deep ocean itself to become anoxic. If the atmospheric O<sub>2</sub> concentration were to decrease from its present level, the area covered by such **anoxic basins** would expand. The lower O<sub>2</sub> content of deep water could, in principle, allow more organic carbon to be buried on the ocean floor because the organic matter would decay less quickly. This, in turn, could provide a negative feedback that might stabilize atmospheric O<sub>2</sub>. Unfortunately, however, measurements do not support this idea. There is no direct correlation between the concentration of dissolved O<sub>2</sub>

and the organic carbon content of marine sediments. Evidently, organic carbon in sediments can be oxidized quite efficiently by bacteria that utilize either sulfate or nitrate rather than O<sub>2</sub>.

### Dissolved Oxygen and Sedimentary C:P Ratios

The actual O<sub>2</sub> control mechanism appears to be slightly more complicated than that outlined above. Recall from Chapter 8 that marine productivity is usually limited by the availability of key nutrients, especially nitrogen (N) and phosphorus (P). Of these, P is thought to be the most critical, because N can be fixed by organisms such as cyanobacteria. The concentration of P in seawater is controlled by the rate of supply of P from the weathering of rocks on the continents and by the loss of P due to incorporation in sediments. The C:P ratio in sediments is related to the dissolved oxygen concentration in seawater. Sediments overlain by well-oxygenated water have lower C:P ratios (i.e., they contain more phosphorus) than do sediments overlain by anoxic water. The reasons are complex: Apparently, bacteria in sediments store phosphorus when oxygen is available and use this stored material as an energy source when oxygen levels become too low. Phosphorus also tends to be bound up with iron compounds in sediments when oxygen is present. Both processes tend to create higher C:P ratios in sediments deposited under anoxic conditions.

The existence of such a relationship means that the dissolved O<sub>2</sub> content of deep water can affect the burial rate of organic carbon indirectly by altering the availability of phosphorus. This effect creates a negative feedback loop that may stabilize atmospheric oxygen (Figure 11-21). If atmospheric O<sub>2</sub> were to decrease for some reason, deep-ocean O<sub>2</sub> would decrease, and the C:P ratio in sediments would increase. This change would allow more organic carbon to be buried without removing any additional phosphorus. Increased burial of organic carbon would result in increased O<sub>2</sub> production, which would help restore atmospheric O<sub>2</sub> to its original level.



**FIGURE 11-21** A likely feedback loop for controlling atmospheric O<sub>2</sub>, involving dissolved O<sub>2</sub> concentrations and the C:P ratio in marine sediments.

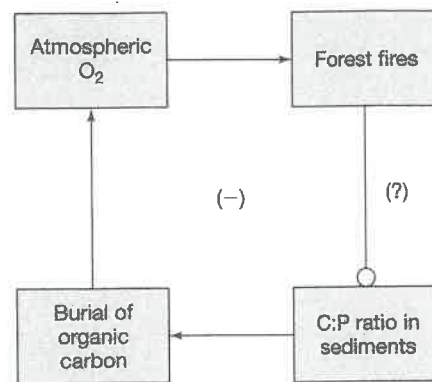
Although this mechanism may help stabilize atmospheric  $O_2$ , it does not imply that  $O_2$  levels have remained constant. Atmospheric  $O_2$  levels can be affected by changes in the rate of organic carbon burial on land, such as those that occurred during the Carboniferous period. Furthermore, the degree of deep-ocean oxygenation may depend on the details of ocean circulation. Periods such as the Mesozoic, when the poles were much warmer, are unlikely to have had the same type of thermohaline circulation that operates today. Data from oxygen isotopes indicate that during most of this time deep water was 10–15°C warmer than it is today. Warmer deep water would have contained less dissolved  $O_2$ . Thus, anoxia should have tended to be more prevalent if other factors had remained the same.

If the oxygen control mechanism suggested is correct, however, the atmospheric  $O_2$  concentration should have responded to this change. Larger areas of anoxia would have promoted the deposition of sediments with high C:P ratios. This deposition in turn should have led to increased oxygen production and higher atmospheric  $O_2$  levels. So, as suggested earlier, the dinosaurs may have breathed a somewhat enriched mixture of air. The possible connection between deep ocean circulation and atmospheric  $O_2$  concentration illustrates yet another interesting linkage in the highly intertwined Earth system.

### Forest Fires and C:P Ratios in Sedimentary Organic Matter

Although the control mechanism described previously is attractive, it leaves one important question unanswered: If the control of atmospheric  $O_2$  lies in the oceans, why have  $O_2$  levels always remained within the fire window for forests? Either this is just a coincidence, or forests themselves must have something to do with regulating  $O_2$ . But forests are not part of the control mechanism outlined earlier.

The answer to this question may also involve sedimentary C:P ratios. The C:P ratios of marine sediments and terrestrial sediments are very different. The C:P ratio of typical marine organisms is 105:1, whereas organic matter derived from trees has a characteristic C:P ratio of about 1,000:1. Thus, the burial of terrestrial organic carbon removes much less phosphorus than does the burial of an equivalent amount of marine organic matter. And, although the burial rate of organic matter on land is relatively low,



**FIGURE 11-22** A possible feedback loop by which forests might help control atmospheric  $O_2$ . The link between forest fires and the C:P ratios in near-shore marine sediments is not well established. Some such control mechanism may be required to keep atmospheric  $O_2$  levels within the “fire window.”

some of the organic matter produced there is carried away by rivers and buried in river deltas.

Could this mechanism create a feedback loop that keeps atmospheric  $O_2$  within the fire window? Suppose that atmospheric  $O_2$  levels were to become so high that the forests all burned down. The phosphorus that was being utilized by terrestrial vegetation would go directly into rivers and, thence, to the oceans, where it would be utilized to make low C:P marine organic matter. The burial of this marine organic matter would generate less oxygen than would the burial of the same amount of terrestrial organic matter. Oxygen production would go down, causing atmospheric  $O_2$  levels to decrease. The net result would be a negative feedback cycle, which could conceivably help to keep atmospheric  $O_2$  within the limits acceptable to terrestrial vegetation (Figure 11-22).

For reasons that are not entirely understood, however, the C:P ratio of river delta sediments collected to date does not appear to be much higher than that of normal marine sediments. Either other plants and algae with low C:P ratios provide most of the terrestrial organic material, or else sufficient reprocessing of material occurs during sediment deposition to smooth out the C:P differences between terrestrial and marine organic matter. Most of the work done so far has been on passive margins, though, where reprocessing times are long. Current work on active margins, where terrestrial organic matter is rapidly buried, may reveal the site of high C/P organic matter burial.

## Chapter Summary

1. Evidence from ribosomal RNA, combined with our knowledge of the early environment, suggests that methanogenic bacteria were among the earliest organisms. Once methanogens evolved, they changed the composition of the atmosphere by converting hydrogen into methane. The biota should also have increased the

rate at which nitrogen was cycled between the atmosphere and ocean.

2. The first  $O_2$ -producing organisms, the cyanobacteria, are thought to have originated at or prior to 2.7 b.y. ago, based on the presence of organic biomarkers (2-methylhopanes) in ancient rocks, along with the

- presence of steranes from eukaryotes. Nevertheless, the geologic record indicates that atmospheric  $O_2$  did not become abundant until sometime after 2.4 b.y. ago. Prior to that time,  $O_2$  levels were suppressed by reaction with reduced volcanic gases. A variety of different types of geologic evidence, including mass independently fractionated sulfur isotopes, show when the initial rise in  $O_2$  took place.
- Accompanying the rise in atmospheric  $O_2$  was a corresponding rise in the abundance of ozone. A reasonably efficient UV shield should have developed once the  $O_2$  concentration exceeded about 1% of its present level. Based on the geologic evidence, this threshold should have been passed by 1.9 b.y. ago, or perhaps a few hundred million years earlier.
  - Atmospheric  $O_2$  levels have probably fluctuated over the last 2 b.y. as a consequence of changes in the rate of organic carbon burial.  $O_2$  concentrations may have increased markedly just before the beginning of the Cambrian period, 542 m.y. ago, perhaps triggering the explosion of multicellular life at that time.  $O_2$  levels were probably also higher during the Carboniferous and Cretaceous periods, based on evidence from carbon isotopes. The formation of the Carboniferous coal beds created the largest positive excursion in atmospheric  $O_2$  during the Phanerozoic era.
  - Despite these changes in the rate of organic carbon burial, atmospheric  $O_2$  concentrations have probably not changed by more than  $\pm 50\%$  during the past 360 million years, as evidenced by the continuity of the fossil charcoal record. The most plausible control mechanism involves the degree of oxygenation of deep water and the C:P ratio of marine sediments. Less-oxygenated deep water promotes a higher sedimentary C:P ratio that, in turn, allows more organic carbon to be buried for a given burial rate of phosphorus. The burial of terrestrial organic matter in river deltas may also influence the C:P ratio of sediments, allowing forests to exert some control over ambient  $O_2$  levels.

## Key Terms

anoxic	eukaryotes	oxygenic photosynthesis
anoxic basin	ferric iron	paleosols
anoxygenic photosynthesis	ferrous iron	photochemical models
banded iron-formation (BIF)	fixed nitrogen	photochemical reactions
biological sulfate reduction	fractionated	phototrophic
chemosynthetic	hematite	prokaryotes
chloroplasts	heterocysts	pyrite
cholesterol	kerogen	rare earth elements
cyanobacteria	methanogenic bacteria	redbeds
denitrification	methanogens	steranes
detrital mineral	nitrogen fixation	stromatolites
dissociate	oxidation state	uraninite
endosymbiotic	oxygen minimum zone	

## Review Questions

- To which domain of life do methanogens belong? Why are they thought to be evolutionarily ancient?
- What is the difference between prokaryotes and eukaryotes? Which are seen first in the fossil record?
- What types of organisms have heterocysts and what are they used for?
- Which organisms were the first to produce  $O_2$ ?
- What types of geologic evidence are used to study the rise of atmospheric  $O_2$ ?
- How did plants and algae acquire their ability to photosynthesize?
- When did the ozone layer become thick enough to provide an effective UV screen?
- What do carbon isotopes tell us about the rise of atmospheric  $O_2$ ?
- What does the fossil charcoal record tell us about atmospheric  $O_2$  levels?
- How is the atmospheric  $O_2$  content maintained at its current level?

## Critical-Thinking Problems

1. a. The atmosphere consists of 78% N<sub>2</sub>, 21% O<sub>2</sub>, 1% <sup>40</sup>Ar, and about 350 ppm CO<sub>2</sub>. What is the mean molecular weight of air? Round your answer to three significant figures. (*Note:* The atomic weights of N and O are 14 and 16, respectively.)
  - b. The total mass of the atmosphere is about  $5 \times 10^{18}$  kg. How many moles of air does it contain? How many moles of O<sub>2</sub> and CO<sub>2</sub> are present? (*Note:* Calculate the latter two answers from the first one, not by computing the mass of O<sub>2</sub> and CO<sub>2</sub>. The concentrations listed for the various gases are percentages by volume, not by mass, so you need to work in moles.)
  - c. Forests and soils contain roughly 2160 Gton of carbon in the form of wood, leaves, and humus. (The actual value is not known this accurately, but this choice makes the numbers work out well.) Suppose that all of the world's forests were to burn down instantaneously and that all of the soil carbon was oxidized as well. By how much would atmospheric CO<sub>2</sub> increase? By how much would O<sub>2</sub> decrease? Express your answers in percentages. Assume that the burning equation is the same as that for respiration and decay:  $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ .
2. The combined burial rate of organic carbon in marine sediments and in coal is approximately 0.05 Gton(C) per year. This burial is the net source of atmospheric O<sub>2</sub>. In steady state, this source of oxygen is balanced by the weathering of reduced materials in rocks (kerogen, sulfides, and iron). If the weathering rate were to remain constant following the disaster in Problem 1c, and if all photosyntheses were shut off (in the oceans as well as on land), how long would it take for atmospheric O<sub>2</sub> to disappear?

## Further Reading

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