8.11
The Global Oxygen Cycle

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8.11.1 INTRODUCTION

One of the key defining features of Earth as a planet that houses an active and diverse biology is the presence of free molecular oxygen (O₂) in the atmosphere. Biological, chemical, and physical processes interacting on and beneath the Earth’s surface determine the concentration of O₂ and variations in O₂ distribution, both temporal and spatial. In the present-day Earth system, the process that releases O₂ to the atmosphere (photosynthesis) and the processes that consume...
8.11.2.1 The Atmosphere

Understanding of exactly why \( O_2 \) concentrations vary across the atmosphere, sea, and other natural waters is therefore important because, while an equable distribution of \( O_2 \) is central to life as we know it, our understanding of exactly why \( O_2 \) concentrations remain nearly constant over large spans of geologic time is very limited.

This chapter begins with a review of distribution of \( O_2 \) among various reservoirs on Earth’s surface: air, sea, and other natural waters. The key factors that affect the concentration of \( O_2 \) in the atmosphere and surface waters are next considered, focusing on photosynthesis as the major process generating free \( O_2 \), followed by various biological and abiotic processes that consume \( O_2 \). The chapter ends with a synopsis of current models on the evolution of an oxygenated atmosphere through 4.5 billion years of Earth’s history, including geochemical evidence constraining ancient \( O_2 \) concentrations and numerical models of atmospheric evolution.

### 8.11.2 DISTRIBUTION OF \( O_2 \) AMONG EARTH SURFACE RESERVOIRS

#### 8.11.2.1 The Atmosphere

The partial pressure of oxygen in the present-day Earth’s atmosphere is \( \sim 0.21 \) bar, corresponding to a total mass of \( \sim 34 \times 10^{18} \) mol \( O_2 \) (0.20946 bar (force/area) multiplied by the surface area of the Earth (\( 5.1 \times 10^{18} \) m\(^2\)), divided by average gravitational acceleration \( g \) (9.8 m s\(^{-2}\)) and the formula weight for \( O_2 \) (32 g mol\(^{-1}\)) yields \( \sim 34 \times 10^{18} \) mol \( O_2 \). There is a nearly uniform mixture of the main atmospheric gases (\( N_2 \), \( O_2 \), \( Ar \)) from the Earth’s surface up to \( \sim 80 \) km altitude (including the troposphere, stratosphere, and mesosphere), because turbulent mixing dominates over molecular diffusion at these altitudes. Because atmospheric pressure (and thus gas molecule density) decreases exponentially with altitude, the bulk of molecular oxygen in the atmosphere is concentrated within several kilometers of Earth’s surface. Above this, in the thermosphere, gases become separated based on their densities. Molecular oxygen is photodissociated by UV radiation to form atomic oxygen (O), which is the major form of oxygen above \( \sim 120 \) km altitude.

Approximately \( 21\% \) \( O_2 \) in the atmosphere represents an average composition. In spite of well-developed turbulent mixing in the lower atmosphere, seasonal latitudinal variations in \( O_2 \) concentration of \( \pm 15 \) ppm have been recorded. These seasonal variations are most pronounced at high latitudes, where seasonal cycles of primary production and respiration are strongest (Keeling and Shertz, 1992). In the northern hemisphere, the seasonal variations are anticorrelated with atmospheric \( p_{CO_2} \); summers are dominated by high \( O_2 \) (and high inferred net photosynthesis), while winters are dominated by lower \( O_2 \). In addition, there has been a measurable long-term decline in atmospheric \( O_2 \) concentration of \( \sim 10^{14} \) mol yr\(^{-1}\), attributed to oxidation of fossil fuels. This decrease has been detected in both long-term atmospheric monitoring stations (Keeling and Shertz, 1992, Figure 1(a)) and in atmospheric gases trapped in Antarctic firn ice bubbles (Figure 1(b)). The polar ice core records extend the range of direct monitoring of atmospheric composition to show that a decline in atmospheric \( O_2 \) linked to oxidation of fossil fuels has been occurring since the Industrial Revolution (Bender et al., 1994b; Battle et al., 1996).

#### 8.11.2.2 The Oceans

Air-saturated water has a dissolved \( O_2 \) concentration dependent on temperature, the Henry’s law constant \( k_H \), and ionic strength. In pure water at \( 0^\circ C \), \( O_2 \) saturation is \( 450 \) \( \mu \)M; at \( 25^\circ C \), saturation falls to \( 270 \) \( \mu \)M. Other solutes reduce \( O_2 \) solubility, such that at normal seawater salinities, \( O_2 \) saturation is reduced by \( \sim 25\% \). Seawater is, of course, rarely at perfect \( O_2 \) saturation. Active photosynthesis may locally increase \( O_2 \) production rates, resulting in supersaturation of \( O_2 \) and degassing to the atmosphere. Alternately, aerobic respiration below the sea surface can consume dissolved \( O_2 \) and lead to severe \( O_2 \)-depletion or even anoxia.

Lateral and vertical gradients in dissolved \( O_2 \) concentration in seawater reflect balances between \( O_2 \) inputs from air–sea gas exchange, biological processes of \( O_2 \) production and consumption, and advection of water masses. In general terms, the concentration of \( O_2 \) with depth in the open ocean follows the general structures described in Figure 2. Seawater is saturated to supersaturated with \( O_2 \) in the surface mixed layer (\( \sim 0–60 \) m water depth). Air–sea gas exchange and trapping of bubbles ensures constant dissolution of atmospheric \( O_2 \). Because gas solubility is temperature dependent, \( O_2 \) concentrations are greater in colder high-latitude surface waters than in waters near the equator. Oxygen concentrations in surface waters also vary strongly with...
season, especially in high productivity waters. Supersaturation is strongest in spring and summer (time of greatest productivity and strongest water column stratification) when warming of surface layers creates a shallow density gradient that inhibits vertical mixing. Photosynthetic O₂ production exceeds consumption and exchange, and supersaturation can develop. O₂ concentrations drop below the surface mixed layer to form O₂ minimum zones (OMZs) in many ocean basins. O₂ minima form where biological consumption of O₂ exceeds resupply through advection and diffusion. The depth and thickness of O₂ minima vary among ocean basins. In the North Atlantic, the OMZ extends several hundred meters. O₂ concentrations fall from an average of ~300 μM in the surface mixed layer to ~160 μM at 800 m depth. In the North Pacific, however, the O₂ minimum extends deeper, and O₂ concentrations fall to <100 μM. Along the edges of ocean basins, where OMZs impinge on the seafloor, aerobic respiration is restricted, sediments are anoxic at or near the sediment–water interface, and burial of organic matter in sediments may be enhanced. Below the oxygen minima zones in the open ocean, O₂ concentrations gradually increase again from 2000 m to the seafloor. This increase in O₂ results from the slow progress of global thermohaline circulation. Cold, air-saturated seawater sinks to the ocean depths at high-latitudes in the Atlantic, advecting in O₂-rich waters below the O₂ minimum there. Advection of O₂-rich deep water from the Atlantic through the Indian Ocean into the Pacific is the source of O₂ in deep Pacific waters. However, biological utilization of this deep-water O₂ occurs along the entire path from the North Atlantic to the Pacific. For this reason, O₂ concentrations in deep Atlantic water are slightly greater (~200 μM) than in the deep Pacific (~150 μM).

In some regions, dissolved O₂ concentration falls to zero. In these regions, restricted water circulation and ample organic matter supply result in biological utilization of oxygen at a rate that exceeds O₂ resupply through advection and diffusion. Many of these are temporary zones of
anoxia that form in coastal regions during summer, when warming facilitates greatest water column stratification, and primary production and organic matter supply are high. Such O₂-depletion is now common in the Chesapeake Bay and Schelde estuaries, off the mouth of the Mississippi River and other coastal settings. However, there are several regions of the world oceans where stratification and anoxia are more permanent features (Figure 3). These include narrow, deep, and silled coastal fjords, larger restricted basins (e.g., the Black Sea, Cariaco Basin, and the chain of basins along the southern California Borderlands). Lastly, several regions of the open ocean are also associated with strong O₂-depletion. These regions (the equatorial Pacific along Central and South America and the Arabian Sea) are associated with deep-water upwelling, high rates of surface water primary productivity, and high dissolved oxygen demand in intermediate waters.

Figure 2 Depth profiles of oxygen concentration dissolved in seawater for several latitudes in the Pacific (a) and Atlantic (b). Broad trends of saturation or supersaturation at the surface, high dissolved oxygen demand at mid-depths, and replenishment of O₂ through lateral advection of recharged deep water are revealed, although regional influences of productivity and intermediate and deep-water heterotropy are also seen (source Ingmanson and Wallace, 1989).

Figure 3 Map detailing locations of extensive and permanent oxygen-deficient intermediate and deep waters (Deuser, 1975) (reproduced by permission of Elsevier from Chemical Oceanography 1975, p.3).
Oxygen concentrations in the pore fluids of sediments are controlled by a balance of entrainment of overlying fluids during sediment deposition, diffusive exchange between the sediment and the water column, and biological utilization. In marine sediments, there is a good correlation between the rate of organic matter supply and the depth of O₂ penetration in the sediment (Hartnett et al., 1998). In coastal sediments and on the continental shelf, burial of organic matter is sufficiently rapid to deplete the sediment of oxygen within millimeters to centimeters of the sediment–water interface. In deeper abyssal sediments, where organic matter delivery is greatly reduced, O₂ may penetrate several meters into the sediment before being entirely consumed by respiration.

There is close coupling between surface water and atmospheric O₂ concentrations and air–sea gas exchange fluxes (Figure 4). High rates of marine primary productivity result in net outgassing of O₂ from the oceans to the atmosphere in spring and summer, and net ingassing of O₂ during fall and winter. These patterns of air–sea O₂ transfer relate to latitude and season: outgassing of O₂ during northern hemisphere high productivity months (April through August) are accompanied by simultaneous ingassing in southern latitudes when and where the productivity is lowest (Najjar and Keeling, 2000). Low-latitude ocean surface waters show very little net air–sea O₂ exchange and minimal change in outgassing or ingassing over an annual cycle.

8.11.2.3 Freshwater Environments

Oxygen concentrations in flowing freshwater environments closely match air-saturated values, due to turbulent mixing and entrainment of air bubbles. In static water bodies, however, O₂-depletion can develop much like in the oceans. This is particularly apparent in some ice-covered lakes, where inhibited gas exchange and wintertime respiration can result in O₂-depletion and fish kills. High productivity during spring and summer in shallow turbid aquatic environments can result in extremely sharp gradients from strong O₂ supersaturation at the surface to near O₂-depletion within a few meters of the surface. The high concentration of labile dissolved and particulate organic matter in many freshwater environments leads to rapid O₂-depletion where advective resupply is limited. High rates of O₂ consumption have been measured in many temperature and tropical rivers.

Figure 4 Zonal average monthly sea-to-air oxygen flux for world oceans. Outgassing and ingassing are concentrated at mid- to high latitudes. Outgassing of oxygen is strongest when primary production rates are greatest; ingassing is at a maximum during net respiration. These patterns oscillate during an annual cycle from northern to southern hemisphere (source Najjar and Keeling, 2000).
8.11.2.4 Soils and Groundwaters

In soil waters, oxygen concentrations depend on gas diffusion through soil pore spaces, infiltration and advection of rainwater and groundwater, air–gas exchange, and respiration of soil organic matter (see review by Hinkle, 1994). In organic-matter-rich temperate soils, dissolved O2 concentrations are reduced, but not entirely depleted. Thus, many temperate shallow groundwaters contain some dissolved oxygen. Deeper groundwaters, and water-saturated soils and wetlands, generally contain little dissolved O2. High-latitude mineral soils and groundwaters contain more dissolved O2 (due to lower temperature and lesser amounts of soil organic matter and biological O2 demand). Dry tropical soils are oxidized to great depths, with dissolved O2 concentration less than air saturated, but not anoxic. Wet tropical forests, however, may experience significant O2-depletion as rapid oxidation of leaf litter and humus occurs near the soil surface. Soil permeability also influences O2 content, with more clay-rich soils exhibiting lower O2 concentrations.

In certain environments, localized anomalously low concentrations of soil O2 have been used by exploration geologists to indicate the presence of a large body of chemically reduced metal sulfides in the subsurface. Oxidation of sulfide minerals during weathering and soil formation draws down soil gas \( p_{O_2} \) below regional average. Oxidation of sulfide minerals generates solid and aqueous-phase oxidation products (i.e., sulfate anion and ferric oxyhydroxides in the case of pyrite oxidation). In some instances, the volume of gaseous O2 consumed during mineral oxidation generates a mild negative pressure gradient, drawing air into soils above sites of sulfide mineral oxidation (Lovell, 2000).

8.11.3 MECHANISMS OF O2 PRODUCTION

8.11.3.1 Photosynthesis

The major mechanism by which molecular oxygen is produced on Earth is through the biological process of photosynthesis. Photosynthesis occurs in higher plants, the eukaryotic protists collectively called algae, and in two groups of prokaryotes: the cyanobacteria and the prochlorophytes. In simplest terms, photosynthesis is the harnessing of light energy to chemically reduce carbon dioxide to simple organic compounds (e.g., glucose). The overall reaction (Equation (1)) for photosynthesis shows carbon dioxide and water reacting to produce oxygen and carbohydrate:

\[
6CO_2 + 6H_2O \rightarrow 6O_2 + C_6H_{12}O_6 \quad (1)
\]

Photosynthesis is actually a two-stage process, with each stage broken into a cascade of chemical reactions (Figure 5). In the light reactions of photosynthesis, light energy is converted to chemical energy that is used to dissociate water to yield oxygen and hydrogen and to form the reductant NADPH from NADP⁺.

![Figure 5](image_url) The two stages of photosynthesis: light reaction and the Calvin cycle. During oxygenic photosynthesis, \( H_2O \) is used as an electron source. Organisms capable of anoxygenic photosynthesis can use a variety of other electron sources (\( H_2S, H_2, S^0, S_2O_3^{2-} \)) during the light reactions, and do not liberate free O2. Energy in the form of ATP and reducing power in the form of NADPH are produced by the light reactions, and subsequently used in the Calvin cycle to deliver electrons to \( CO_2 \) to produce sugars.
The next stage of photosynthesis, the Calvin cycle, uses NADPH to reduce CO₂ to phosphoglycerate, the precursor for a variety of metabolic pathways, including glucose synthesis. In higher plants and algae, the Calvin cycle operates in special organelles called chloroplasts. However, in bacteria the Calvin cycle occurs throughout the cytosol. The enzyme ribulose-1,5-biphosphate carboxylase (rubisco) catalyzes reduction of CO₂ to phosphoglycerate, which is carried through a chain of reactions that consume ATP and NADPH and eventually yield phosphoglycerate. Most higher plants are termed C₃ plants, because the first stable intermediate formed during the carbon cycle is a three-carbon compound. Several thousand species of plant, spread among at least 17 families including the grasses, precede the carbon cycle with a CO₂-concentrating mechanism which delivers a four-carbon compound to the site of the Calvin cycle and rubisco. These are the C₄ plants. This four-carbon compound breaks down inside the chloroplasts, supplying CO₂ for rubisco and the Calvin cycle. The C₄-concentrating mechanisms is an advantage in hot and dry environments where leaf stomata are partially closed, and internal leaf CO₂ concentrations are too low for rubisco to efficiently capture CO₂. Other plants, called CAM plants, which have adapted to dry climates utilize another CO₂-concentrating mechanisms by closing stomata during the day and concentrating CO₂ at night. All higher plants, however, produce O₂ and NADPH from splitting water, and use the Calvin cycle to produce carbohydrates. Some prokaryotes use mechanisms other than the Calvin cycle to fix CO₂ (i.e., the acetyl-CoA pathway or the reductive tricarboxylic acid pathway), but none of these organisms is involved in oxygenic photosynthesis.

Global net primary production estimates have been derived from variations in the abundance and isotopic composition of atmospheric O₂. These estimates range from $23 \times 10^{15}$ mol yr⁻¹ (Keeling and Shertz, 1992) to $26 \times 10^{15}$ mol yr⁻¹, distributed between $14 \times 10^{15}$ mol yr⁻¹ O₂ production from terrestrial primary production and $12 \times 10^{15}$ mol yr⁻¹ from marine primary production (Bender et al., 1994a). It is estimated that ~50% of all photosynthetic fixation of CO₂ occurs in marine surface waters. Collectively, free-floating photosynthetic microorganisms are called phytoplankton. These include the algal eukaryotes (dinoflagellates, diatoms, and the red, green, brown, and golden algae), various species of cyanobacteria (Synechococcus and Trichodesmium), and the common prochlororophytes Prochlorococcus. Using the stoichiometry of the photosynthesis reaction, this equates to half of all global photosynthetic oxygen production resulting from marine primary production. Satellite-based measurements of seasonal and yearly average chlorophyll abundance (for marine systems) and vegetation greenness (for terrestrial ecosystems) can be applied to models that estimate net primary productivity, CO₂ fixation, and O₂ production. In the oceans, there are significant regional and seasonal variations in photosynthesis that result from limitations by light, nutrients, and temperature. Yearly averages of marine chlorophyll abundance show concentrated primary production at high-latitudes in the North Atlantic, North Pacific, and coastal Antarctica, in regions of seawater upwelling off of the west coasts of Africa, South America, and the Arabian Sea, and along the Southern Sub-tropical Convergence. At mid- and high latitudes, marine productivity is strongly seasonal, with primary production concentrated in spring and summer. At low latitudes, marine primary production is lower and varies little with season or region. On land, primary production also exhibits strong regional and seasonal patterns. Primary production rates (in g C m⁻² yr⁻¹) are greatest year-round in the tropics. Tropical forests in South America, Africa, and Southeast Asia are the most productive ecosystems on Earth. Mid-latitude temperate forests and high-latitude boreal forests are also highly productive, with a strong seasonal cycle of greatest production in spring and summer. Deserts (concentrated at ~30° N and S) and polar regions are less productive. These features of seasonal variability in primary production on land and in the oceans are clearly seen in the seasonal variations in atmospheric O₂ (Figure 4).

Transfer of O₂ between the atmosphere and surface seawater is controlled by air–sea gas exchange. Dissolved gas concentrations trend towards thermodynamic equilibrium, but other factors may complicate dissolved O₂ concentrations. Degassing of supersaturated waters can only occur at the very surface of the water. Thus, in regions of high primary production, concentrations of O₂ can accumulate in excess of the rate of O₂ degassing. In calm seas, where the air–sea interface is a smooth surface, gas exchange is very limited. As seas become more rough, and especially during storms, gas exchange is greatly enhanced. This is in part because of entrainment of bubbles dispersed in seawater and water droplets entrained in air, which provide much more surface for dissolution or degassing. Also, gas exchange depends on diffusion across a boundary layer. According to Fick’s law, the diffusive flux depends on both the concentration gradient (degree of super- or undersaturation) and the thickness of the boundary layer. Empirically it is observed that the boundary layer thickness decreases with increasing wind speed, thus enhancing diffusion and gas exchange during high winds.
8.11.3.2 Photolysis of Water

In the upper atmosphere today, a small amount of O2 is produced through photolysis of water vapor. This process is the sole source of O2 to the atmospheres on the icy moons of Jupiter (Ganymede and Europa), where trace concentrations of O2 have been detected (Vidal et al., 1997). Water vapor photolysis may also have been the source of O2 to the early Earth before the evolution of oxygenic photosynthesis. However, the oxygen formed by photolysis would have been through reactions with methane and carbon monoxide, preventing any accumulation in the atmosphere (Kasting et al., 2001).

8.11.4 MECHANISMS OF O2 CONSUMPTION

8.11.4.1 Aerobic Cellular Respiration

In simple terms, aerobic respiration is the oxidation of organic substrates with oxygen to yield chemical energy in the form of ATP and NADH. In eukaryotic cells, the respiration pathway follows three steps (Figure 6). Glycolysis occurs throughout the cytosol, splitting glucose into pyruvic acid and yielding some ATP. Glycolysis does not directly require free O2, and thus occurs among aerobic and anaerobic organisms. The Krebs citric acid (tricarboxylic acid) cycle and oxidative phosphorylation are localized within the mitochondria of eukaryotes, and along the cell membranes of prokaryotes. The Krebs cycle completes the oxidation of pyruvate to CO2 from glycolysis, and together glycolysis and the Krebs cycle provide chemical energy and reductants (in the form of ATP, NADH, and FADH2) for the third step—oxidative phosphorylation. Oxidative phosphorylation involves the transfer of electrons from NADH and FADH2 through a cascade of electron carrying compounds to molecular oxygen. Compounds used in the electron transport chain of oxidative phosphorylation include a variety of flavoproteins, quinones, Fe–S proteins, and cytochromes. Transfer of electrons from NADH to O2 releases considerable energy, which is used to generate a proton gradient across the mitochondrial membrane and fuel significant ATP synthesis. In part, this gradient is created by reduction of O2 to H2O as the last step of oxidative phosphorylation. While eukaryotes and many prokaryotes use the Krebs cycle to oxidize pyruvate to CO2, there are other pathways as well. For example, prokaryotes use the glyoxalate cycle to metabolize fatty acids. Several aerobic prokaryotes also can use the Entner–Doudoroff pathway in place of normal glycolysis. This reaction still produces pyruvate, but yields less energy in the form of ATP and NADH.

Glycolysis, the Krebs cycle, and oxidative phosphorylation are found in all eukaryotes (animals, plants, and fungi) and many of the aerobic prokaryotes. The purpose of these reaction pathways is to oxidize carbohydrates with O2, yielding CO2, H2O, and chemical energy in the form of ATP. While macrofauna generally require a minimum of ~0.05–0.1 bar (~10 μM) O2 to survive, many prokaryotic microaerophilic organisms can survive and thrive at much lower O2 concentrations. Because most biologically mediated oxidation processes occur through the activity of aerotolerant microorganisms, it is unlikely that a strict coupling between limited atmospheric O2 concentration and limited global respiration rates could exist.

![Figure 6](image-url) The three components of aerobic respiration: glycolysis, the Krebs cycle, and oxidative phosphorylation. Sugars are used to generate energy in the form of ATP during glycolysis. The product of glycolysis, pyruvate, is converted to acetyl-CoA, and enters the Krebs cycle. CO2, stored energy as ATP, and stored reducing power as NADH and FADH2 are generated in the Krebs cycle. O2 is only directly consumed during oxidative phosphorylation to generate ATP as the final component of aerobic respiration.
8.11.4.2 **Photorespiration**

The active site of rubisco, the key enzyme involved in photosynthesis, can accept either CO\textsubscript{2} or O\textsubscript{2}. Thus, O\textsubscript{2} is a competitive inhibitor of photosynthesis. This process is known as photorespiration, and involves addition of O\textsubscript{2} to ribulose-biphosphate. Products of this reaction enter a metabolic pathway that eventually produces CO\textsubscript{2}. Unlike cellular respiration, photorespiration generates no ATP, but it does consume O\textsubscript{2}. In some plants, as much as 50% of the carbon fixed by the Calvin cycle is respired through photorespiration. Photorespiration is enhanced in hot, dry environments when plant cells close stomata to slow water loss, CO\textsubscript{2} is depleted and O\textsubscript{2} accumulates. Photorespiration does not occur in prokaryotes, because of the much lower relative concentration of O\textsubscript{2} versus CO\textsubscript{2} in water compared with air.

8.11.4.3 **C\textsubscript{1} Metabolism**

Beyond metabolism of carbohydrates, there are several other metabolic processes common in prokaryotes that consume oxygen. For example, methylotrophic organisms can metabolize C\textsubscript{1} compounds such as methane, methanol, formaldehyde, and formate, as in

\[
\begin{align*}
\text{CH}_4 + \text{NADH} + \text{H}^+ + \text{O}_2 & \rightarrow \text{CH}_3\text{OH} + \text{NAD}^+ + \text{H}_2\text{O} \\
\text{CH}_3\text{OH} + \text{PQQ} & \rightarrow \text{CH}_2\text{O} + \text{PQQH}_2 \\
\text{CH}_2\text{O} + \text{NAD}^+ + \text{H}_2\text{O} & \rightarrow \text{HCOOH} + \text{NADH} + \text{H}^+ \\
\text{HCOOH} + \text{NAD}^+ & \rightarrow \text{CO}_2 + \text{NADH} + \text{H}^+
\end{align*}
\]

These compounds are common in soils and sediments as the products of anaerobic fermentation reactions. Metabolism of these compounds can directly consume O\textsubscript{2} (through monooxygenase enzymes) or indirectly, through formation of NADH which is shuttled into oxidative phosphorylation and the electron transport chain. Oxidative metabolism of C\textsubscript{1} compounds is an important microbial process in soils and sediments, consuming the methane produced by methanogenesis.

8.11.4.4 **Inorganic Metabolism**

Chemolithothrophic microorganisms are those that oxidize inorganic compounds rather than organic substrates as a source of energy and electrons. Many of the chemolithotrophs are also autotrophs, meaning they reduce CO\textsubscript{2} to generate cellular carbon in addition to oxidizing inorganic compounds. In these organisms, CO\textsubscript{2} fixation is not tied to O\textsubscript{2} production by the stoichiometry of photosynthesis. Hydrogen-oxidizing bacteria derive most H\textsubscript{2} utilized by hydrogen-oxidizing bacteria from nitrogen fixation associated with nitrogen-fixing plants and cyanobacteria. Nitrifying bacteria are obligate autotrophs that oxidize ammonia. Ammonia is produced in many environments during fermentation of nitrogen compounds and by dissimilatory nitrate reduction. Nitrifying bacteria are common at oxic–anoxic interfaces in soils, sediments, and the water column. Other chemolithoautotrophic bacteria can oxidize nitrate to nitrite. Non-photosynthetic bacteria that can oxidize reduced sulfur compounds form a diverse group. Some are acidophiles, associated with sulfide mineral oxidation and tolerant of extremely low pH. Others are neutrophilic and occur in many marine sediments. These organisms can utilize a wide range of sulfur compounds produced in anaerobic environments, including H\textsubscript{2}S, thiosulfate, polythionates, polysulfide, elemental sulfur, and sulfite. Many of the sulfur-oxidizing bacteria are also autotrophs. Some bacteria can live as chemoaotrophs through the oxidation of ferrous-iron. Some of these are acidophiles growing during mining and weathering of sulfide minerals. However, neutrophilic iron-oxidizing bacteria have also been detected associated with the metal sulfide plumes and precipitates at mid-ocean ridges. Other redox-sensitive metals that can provide a substrate for oxidation include manganese, copper, uranium, arsenic, and chromium. As a group, chemolithoautotrophic microorganisms represent a substantial flux of O\textsubscript{2} consumption and CO\textsubscript{2} fixation in many common marine and terrestrial environments. Because the net reaction of chemolithoautotrophy involves both O\textsubscript{2} and CO\textsubscript{2} reduction, primary production resulting from chemoaotrophs has a very different O\textsubscript{2}/CO\textsubscript{2} stoichiometry than does photosynthesis. Chemolithoautotrophs use the electron flow from reduced substrates (metals, H\textsubscript{2}, and reduced sulfur) to O\textsubscript{2} to generate ATP and NAD(P)H, which in turn are used for CO\textsubscript{2}-fixation. It is believed that most aerobic chemoaotrophs utilize the Calvin cycle for CO\textsubscript{2}-fixation.

8.11.4.5 **Macroscale Patterns of Aerobic Respiration**

On a global scale, much biological O\textsubscript{2} consumption is concentrated where O\textsubscript{2} is abundant.
This includes surficial terrestrial ecosystems and marine surface waters. A large fraction of terrestrial primary production is consumed by aerobic degradation mechanisms. Although most of this is through aerobic respiration, some fraction of aerobic degradation of organic matter depends on anaerobic breakdown of larger biomolecules into smaller C1 compounds, which, if transported into aerobic zones of soil or sediment, can be degraded by aerobic C1 metabolizing microorganisms. Partially degraded terrestrial primary production can be incorporated into soils, which slowly are degraded and eroded. Research has shown that soil organic matter (OM) can be preserved for up to several millennia, and riverine export of aged terrestrial OM may be a significant source of dissolved and particulate organic carbon to the oceans.

Aside from select restricted basins and specialized environments, most of the marine water column is oxygenated. Thus, aerobic respiration dominates in open water settings. Sediment trap and particle flux studies have shown that substantial fractions of marine primary production are completely degraded (remineralized) prior to sediment infilling through time. Conversely, in deep-sea sediments, where organic matter delivery is minor and waters are cold and charged with O2 from sites of deep-water formation, O2 may penetrate uniformly 1 m or more into the sediment.

8.11.4.6 Volcanic Gases

Gases emitted from active volcanoes and fumaroles are charged with reduced gases, including CO, H2, SO2, H2S, and CH4. During explosive volcanic eruptions, these gases are ejected high into the atmosphere along with H2O, CO2, and volcanic ash. Even the relatively gentle eruption of low-silicon, low-viscosity-shield volcanoes is associated with the release of reduced volcanic gases. Similarly, reduced gases are released dissolved in waters associated with hot springs and fumaroles. Oxidation of reduced volcanic gases occurs in the atmosphere, in natural waters, and on the surfaces of minerals. This is predominantly an abiotic process, although many chemolithoautotrophs have colonized the walls and channels of hot springs and fumaroles, catalyzing the oxidation of reduced gases with O2. Much of biological diversity in hyperthermophilic environments consists of prokaryotes employing these unusual metabolic types.

Recent estimates of global average volcanic gas emissions suggest that volcanic sulfur emissions range, 0.1–1 × 1012 mol S yr−1, is nearly equally distributed between SO2 and H2S (Halmer et al., 2002; Arthur, 2000). This range agrees well with the estimates used by both Holland (2002) and Lasaga and Ohmoto (2002) for average volcanic S emissions through geologic time. Other reduced gas emissions (CO, CH4, and H2) are estimated to be similar in magnitude (Mörner and Etiope, 2002; Arthur, 2000; Delmelle and Stix, 2000). All of these gases have very short residence times in the atmosphere, revealing that emission and oxidative consumption of these gases are closely coupled, and that O2 consumption through volcanic gas oxidation is very efficient.

8.11.4.7 Mineral Oxidation

During uplift and erosion of the Earth’s continents, rocks containing chemically reduced minerals become exposed to the oxidizing conditions of the atmosphere. Common rock-forming minerals susceptible to oxidation include olivine, Fe2+ bearing pyroxenes and amphiboles, metal sulfides, and graphite. Ferrous-iron oxidation is a common feature of soil formation. Iron oxides derived from oxidation of Fe2+ in the parent rock accumulate in the B horizon of temperate soils, and extensive laterites consisting of iron and aluminum oxides develop in tropical soils to many meters of depth. Where erosion
rates are high, iron-bearing silicate minerals may be transported short distances in rivers; however, iron oxidation is so efficient that very few sediments show deposition of clastic ferrous-iron minerals. Sulfide minerals are extremely susceptible to oxidation, often being completely weathered from near-surface rocks. Oxidation of sulfide minerals generates appreciable acidity, and in areas where mining has brought sulfide minerals in contact with the atmosphere or O2-charged rainwater, low-pH discharge has become a serious environmental problem. Although ferrous silicates and sulfide minerals such as pyrite will oxidize under sterile conditions, a growing body of evidence suggests that in many natural environments, iron and sulfur oxidation is mediated by chemolithoautotrophic microorganisms. Prokaryotes with chemolithoautotrophic metabolic pathways have been isolated from many environments where iron and sulfur oxidation occurs. The amount of O2 consumed annually through oxidation of Fe2+ and sulfur-bearing minerals is not known, but based on sulfur isotope mass balance constraints is on the order of \((0.1–1) \times 10^{12} \text{mol yr}^{-1}\) each for iron and sulfur, similar in magnitude to the flux of reduced gases from volcanism.

### 8.11.4.8 Hydrothermal Vents

The spreading of lithospheric plates along mid-ocean ridges is associated with much undersea volcanic eruptions and release of chemically reduced metal sulfides. Volcanic gases released by subaerial volcanoes are also generated by submarine eruptions, contributing dissolved reduced gases to seawater. Extrusive lava flows generate pillow basalts, which are composed in part of ferrous-iron silicates. Within concentrated zones of hydrothermal fluid flow, fracture-filling and massive sulfide minerals precipitate within the pillow lavas, large chimneys grow from the seafloor by rapid precipitation of Fe–Cu–Zn sulfides, and metal sulfide-rich plumes of high-temperature “black smoke” are released into seawater. In cooler zones, more gradual emanations of metal and sulfide rich fluid diffuse upward through the pillow basalts and slowly mix with seawater. Convective cells develop, in which cold seawater is drawn down into pillow lavas off the ridge axis to replace the water released at the hydrothermal vents. Reaction of seawater with basalt serves to alter the basalt. Some sulfide is liberated from the basalt, entrained seawater sulfate precipitates as anhydrite or is reduced to sulfide, and Fe2+ and other metals in basalts are replaced with seawater-derived magnesium. Oxygen dissolved in seawater is consumed during alteration of seafloor basalts. Altered basalts containing oxidized iron-mineral can extend as much as 500 m below the seafloor. Much more O2 is consumed during oxidation of black smoker and chimney sulfides. Chimney sulfide may be only partially oxidized prior to transport off-axis through spreading and burial by sediments. However, black smoker metal-rich fluids are fairly rapidly oxidized in seawater, forming insoluble iron and manganese oxides, which slowly settle out on the seafloor, generating metalliferous sediments.

Because of the diffuse nature of reduced species in hydrothermal fluids, it is not known what role marine chemolithoautotrophic microorganisms may play in O2 consumption associated with fluid plumes. Certainly such organisms live within the walls and rubble of cooler chimneys and basalts undergoing seafloor weathering. Because of the great length of mid-ocean ridges throughout the oceans, and the abundance of pyrite and other metal sulfides associated with these ridges, colonization and oxidation of metal sulfides by chemolithoautotrophic organisms may form an unrecognized source of primary production associated with consumption, not net release, of O2.

### 8.11.4.9 Iron and Sulfur Oxidation at the Oxic–Anoxic Transition

In restricted marine basins underlying highly productive surface waters, where consumption of O2 through aerobic respiration near the surface allows anoxia to at least episodically extend beyond the sediment into the water column, oxidation of reduced sulfur and iron may occur when O2 is present. Within the Black Sea and many anoxic coastal fjords, the transition from oxic to anoxic environments occurs within the water column. At other locations, such as the modern Peru Shelf and coastal California basins, the transition occurs right at the sediment–water interface. In these environments, small concentrations of sulfide and O2 may coexist within a very narrow band where sulfide oxidation occurs. In such environments, appreciable sulfur recycling may occur, with processes of sulfate reduction, sulfide oxidation, and sulfur disproportionation acting within millimeters of each other. These reactions are highly mediated by microorganisms, as evidenced by extensive mats of chemolithoautotrophic sulfur-oxidizing Beggiatoa and Thioploca found where the oxic–anoxic interface and seafloor coincide.

Similary, in freshwater and non-sulfidic brackish environments with strong O2 demand, dissolved ferrous-iron may accumulate in groundwaters and anoxic bottom waters. Significant iron oxidation will occur where the water
table outcrops with the land surface (i.e., groundwater outflow into a stream), or in lakes and estuaries, at the oxic–anoxic transition within the water column. Insoluble iron oxides precipitate and settle down to the sediment. Recycling of iron may occur if sufficient organic matter exists for ferric-iron reduction to ferrous-iron.

The net effect of iron and sulfur recycling on atmospheric O$_2$ is difficult to constrain. In most cases, oxidation of sulfur or iron consumes O$_2$ (there are some anaerobic chemolithoautotrophic microorganisms that can oxidize reduced substrates using nitrate or sulfate as the electron acceptor). Reduction of sulfate or ferric-iron are almost entirely biological processes, coupled with the oxidation of organic matter; sulfate and ferric-iron reduction individually have no effect on O$_2$. However, the major source of organic substrates for sulfate and ferric-iron reduction is ultimately biomass derived from photosynthetic organisms, which is associated with O$_2$ generation. The net change derived from summing the three processes ($\text{S}^{2-}$- or Fe$^{3+}$-oxidation, SO$_4^{2-}$ or Fe$^{3+}$- reduction, and photosynthesis), is net gain of organic matter with no net production or consumption of O$_2$.

### 8.11.4.10 Abiotic Organic Matter Oxidation

Aerobic respiration is the main means by which O$_2$ is consumed on the Earth. This pathway occurs throughout most Earth-surface environments: soils and aquatic systems, marine surface waters supersaturated with O$_2$, within the water column and the upper zones of sediments. However, reduced carbon materials are also reacted with O$_2$ in a variety of environments where biological activity has not been demonstrated. Among these are photo-oxidation of dissolved and particulate organic matter and fossil fuels, fires from burning vegetation and fossil fuels, and atmospheric methane oxidation. Olefins (organic compounds containing double bonds) are susceptible to oxidation in the presence of transition metals, ozone, UV light, or gamma radiation. Low-molecular-weight oxidized organic degradation products form from oxidation reactions, which in turn may provide organic substrates for aerobic respiration or C$_1$ metabolism. Fires are of course high-temperature combustion of organic materials with O$_2$. Research on fires has shown that O$_2$ concentration has a strong influence on initiation and maintenance of fires (Watson, 1978; Lenton and Watson, 2000). Although the exact relationship between $p_{O_2}$ and initiation of fire in real terrestrial forest communities is debated (see Robinson, 1989, 1991), it is generally agreed that, at low $p_{O_2}$, fires cannot be started even on dry wood, although smoldering fires with inefficient oxidation can be maintained. At high $p_{O_2}$, even wet wood can support flame, and fires are easily initiated with a spark discharge such as lightning.

Although most methane on Earth is oxidized during slow gradual transport upwards through soils and sediments, at select environments there is direct injection of methane into the atmosphere. Methane reacts with O$_2$ in the presence of light or metal surface catalysts. This reaction is fast enough, and the amount of atmospheric O$_2$ large enough, that significant concentrations of atmospheric CH$_4$ are unlikely to accumulate. Catastrophic calving of submarine, CH$_4$-rich hydrates during the geologic past may have liberated large quantities of methane to the atmosphere. However, isotopic evidence suggests that this methane was oxidized and consumed in a geologically short span of time.

### 8.11.5 Global Oxygen Budgets and the Global Oxygen Cycle

One window into the global budget of oxygen is the variation in O$_2$ concentration normalized to N$_2$. O$_2$/N$_2$ ratios reflect changes in atmospheric O$_2$ abundance, because N$_2$ concentration is assumed to be invariant through time. Over an annual cycle, $\delta$(O$_2$/N$_2$) can vary by 100 per meg or more, especially at high-latitude sites (Keeling and Shertz, 1992). These variations reflect latitudinal variations in net O$_2$ production and consumption related to seasonal high productivity during summer. Observations of O$_2$/N$_2$ variation have been expanded beyond direct observation (limited to the past several decades) to records of atmospheric composition as trapped in Antarctic firn ice and recent ice cores (Battle et al., 1996; Sowers et al., 1989; Bender et al., 1985, 1994b). These records reflect a slow gradual decrease in atmospheric O$_2$ abundance over historical times, attributed to the release and oxidation of fossil fuels.

As yet, details of the fluxes involved in the processes that generate and consume molecular oxygen are too poorly constrained to establish a balanced O$_2$ budget. A summary of the processes believed to dominate controls on atmospheric O$_2$, and reasonable best guesses for the magnitude of these fluxes, if available, are shown in Figure 7 (from Keeling et al., 1993).

### 8.11.6 Atmospheric O$_2$ Throughout Earth’s History

#### 8.11.6.1 Early Models

Starting with Cloud (1976), two key geologic formations have been invoked to constrain the
The history of oxygenation of the atmosphere: banded iron formations (BIFs) and red beds (Figure 8). BIFs are chemical sediments containing very little detritus, and consist of silica laminae interbedded with layers of alternately high and low ratios of ferric- to ferrous-iron. As chemical sediments, BIFs imply the direct precipitation of ferrous-iron from the water column. A ferrous-iron-rich ocean requires anoxia, which by implication requires an O$_2$-free atmosphere and an anaerobic world. However, the ferric-iron layers in BIFs do reflect consumption of molecular O$_2$ (oxidation of ferrous-iron) at a rate much greater than supply of O$_2$ through prebiotic H$_2$O photolysis. Thus, BIFs may also record the evolution of oxygenic photosynthesis and at least localized elevated dissolved O$_2$ concentrations (Walker, 1979). Red beds are sandy sedimentary rocks rich in coatings, cements, and particles of ferric-iron. Red beds form during and after sediment deposition, and thus require that both the atmosphere and groundwater are oxidizing. The occurrence of the oldest red beds (~2.0 Ga) coincides nearly with the disappearance of BIFs (Walker, 1979), suggesting that some threshold of atmospheric O$_2$ concentration was reached at this time. Although the general concept of a low-O$_2$ atmosphere before ~2.0 Ga and accumulated O$_2$ since that time has been agreed on for several decades, the details and texture of oxygenation of the Earth’s atmosphere are still being debated.

Geochemists and cosmochemists initially looked to models of planetary formation and comparison with other terrestrial planets to understand the earliest composition of Earth’s atmosphere. During planetary accretion and core formation, volatile components were liberated...
from a molten and slowly convecting mixture of silicates, metals, and trapped gases. The gravitational field of Earth was sufficient to retain most of the gases released from the interior. These include CH₄, H₂O, N₂, NH₃, and H₂S. Much H₂ and He released from the interior escaped Earth’s gravitational field into space; only massive planets such as Jupiter, Saturn, Neptune, and Uranus have retained an H₂–He rich atmosphere. Photolysis of H₂O, NH₃, and H₂S produced free O₂, N₂, and S, respectively. O₂ was rapidly consumed by oxidation of CH₄ and H₂S to form CO₂, CO, and SO₂. High partial pressures of CO₂ and CH₄ maintained a strong greenhouse effect and warm average Earth surface temperature (~90 °C), in spite of much lower solar luminosity. Recognizing that the early Earth contained an atmospheric substantially richer in strong greenhouse gases compared with the modern world provided a resolution to subfreezing average Earth surface temperatures predicted for the early Earth due to reduced solar luminosity (Kasting et al., 2001, 1983; Kiehl and Dickinson, 1987).

Liquid water on the early planet Earth allowed a hydrologic cycle and silicate mineral weathering to develop. Fairly quickly, much of the atmosphere’s CO₂ was reacted with silicates to produce a bicarbonate-buffer ocean, while CH₄ was rapidly consumed by oxygen produced through photolysis of H₂O. Early microorganisms (and many of the most primitive organisms in existence today) used inorganic substrates to derive energy, and thrive at the high temperatures expected to be widespread during Earth’s early history. These organisms include Archea that oxidize H₂ using elemental sulfur. Once photolysis and CH₄ oxidation generated sufficient pCO₂, methanogenic Archea may have evolved. These organisms reduce CO₂ to CH₄ using H₂. However, sustainable life on the planet is unlikely to have developed during the first several hundred million years of Earth’s history, due to large and frequent bolide impacts that would have sterilized the entire Earth’s surface prior to ~3.8 Ga (Sleep et al., 1989; Sleep and Zahne, 1998; Sleep et al., 2001; Wilde et al., 2001), although recent work by Valley et al. (2002) suggests a cool early Earth that continually supported liquid water as early as 4.4 Ga.

Much of present understanding of the earliest evolution of Earth’s atmosphere can trace descent from Walker (1979) and references therein. The prebiological atmosphere (before the origin of life) was controlled principally by the composition of gases emitted from volcanoes. Emission of H₂ in volcanic gases has contributed to net oxidation of the planet through time. This is achieved through several mechanisms. Simplest is hydrodynamic escape of H₂ from Earth’s gravity. Because H₂ is a strongly reducing gas, loss of H₂ from the Earth equates to loss of reducing power or net increase in whole Earth oxidation state (Walker, 1979).

Today, gravitational escape of H₂ and thus increase in oxidation state is minor, because little if any H₂ manages to reach the upper levels of the atmosphere without oxidizing. Early in Earth’s history, sources of H₂ included volcanic gases and water vapor photolysis. The small flux of O₂ produced by photolysis was rapidly consumed by reaction with ferrous-iron and sulfaide, contributing to oxidation of the crust.

Today, volcanic gases are fairly oxidized, consisting mainly of H₂O and CO₂, with smaller amounts of H₂, CO, and CH₄. The oxidation state of volcanic gases derives in part from the oxidation state of the Earth’s mantle. Mantle oxygen fugacity today is at or near the quartz-fayalite-magnesite buffer (QFM), as is the fO₂ of eruptive volcanic gases. Using whole-rock and spinel chromium abundance from volcanogenic rocks through time, Delano (2001) has argued that the average oxidation state of the Earth’s mantle was set very early in Earth’s history (~3.6–3.9 Ga) to fO₂ at or near the QFM buffer. Magmas with this oxidation state release volcanic gases rich in H₂O, CO₂, and SO₂, rather than more reducing gases. Thus, throughout much of Earth’s history, volcanic gases contributing to the atmosphere have been fairly oxidized. More reduced magma compositions have been detected in diamond-bearing assemblages likely Hadean in age (>4.0 Ga) (Haggerty and Toft, 1985). The increase in mantle oxidation within several hundred million years of early Earth’s history reveals very rapid “mantle + crust” overturn and mixing at this time, coupled with subduction and reaction of the mantle with hydrated and oxidized crustal minerals (generated from reaction with O₂ produced through H₂O photolysis).

8.11.6.2 The Archean

8.11.6.2.1 Constraints on the O₂ content of the Archean atmosphere

Several lines of geochemical evidence support low to negligible concentrations of atmospheric O₂ during the Archean and earliest Proterozoic, when oxygenic photosynthesis may have evolved. The presence of pyrite and uraninite in detrital Archean sediments reveals that the atmosphere in the earliest Archean contained no free O₂ (Cloud, 1972). Although Archean-age detrital pyrites from South Africa may be hydrothermal in origin, Australian sediments of the Pilbara craton (3.25–2.75 Ga) contain rounded grains of
pyrite, uraninite, and siderite (Rasmussen and Buick, 1999), cited as evidence for an anoxic atmosphere at this time. Although disputed (Ohmoto, 1999), it is difficult to explain detrital minerals that are extremely susceptible to dissolution and oxidation under oxidizing conditions unless the atmospheric oxygen of the Archean was essentially devoid of O2.

Archean paleosols provide other geochemical evidence suggesting formation under reducing conditions. For example, the 2.75 Ga Mount Roe #2 paleosol of Western Australia contains up to 0.10% organic carbon with isotope ratios between −33‰ and −55‰ (Rye and Holland, 2000). These isotope ratios suggest that methanogenesis and methanotrophy were important pathways of carbon cycling in these soils. For modern soils in which the bulk organic matter is strongly 13C-depleted (−40‰), the methane fueling methanotrophy must be derived from somewhere outside the soil, because reasonable rates of fermentation and methanogenesis cannot supply enough CH4. By extension, Rye and Holland (2000) argue that these soils formed under an atmosphere rich in CH4, with any O2 consumed during aerobic methanotrophy having been supplied by localized limited populations of oxygenic photoautotrophs. Other paleosol studies have used lack of cerium oxidation during soil formation as an indicator of atmospheric anoxia in the Archean (Murakami et al., 2001). In a broader survey of Archean and Proterozoic paleosols, Rye and Holland (1998) observe that all examined paleosols older than 2.4 Ga indicate loss of iron during weathering and soil formation. This chemical feature is consistent with soil development under an atmosphere containing <10−5 atm O2 (1 atm = 1.01325 × 105 Pa), although some research has suggested that anoxic soil development in the Archean does not necessarily require an anoxic atmosphere (Ohmoto, 1996).

Other evidence for low Archean atmospheric oxygen concentrations come from studies of mass-independent sulfur isotope fractionation. Photochemical oxidation of volcanic sulfur species, in contrast with aqueous-phase oxidation and dissolution that characterizes the modern sulfur cycle, may have been the major source of sulfate to seawater in the Archean (Farquhar et al., 2002; Farquhar et al., 2000). Distinct shifts in δ33S and δ34S in sulfide and sulfate from Archean rocks occurred between 2.4–2.0 Ga, consistent with a shift from an O2-free early atmosphere in which SO2 photochemistry could dominate over sulfate sources to an O2-rich later atmosphere in which oxidative weathering of sulfide minerals predominated over photochemistry as the major source of seawater sulfate. Sulfur isotope heterogeneities detected in sulfide inclusions in diamonds also are believed to derive from photochemical SO2 oxidation in an O2-free atmosphere at 2.9 Ga (Farquhar et al., 2002). Not only do these isotope ratios require an O2-free atmosphere, but they also imply significant contact between the mantle, crust, and atmosphere as recently as 2.9 Ga.

Nitrogen and sulfur isotope ratios in Archean sedimentary rocks also indicate limited or negligible atmospheric O2 concentrations (Figure 9). Under an O2-free environment, nitrogen could only exist as N2 and reduced forms (NH3, etc.). Any nitrate or nitrite produced by photolysis would be quickly reduced, likely with Fe2+. If nitrate is not available, then denitrification (reduction of nitrate to free N2) cannot occur. Denitrification is associated with a substantial nitrogen-isotope discrimination, generating N2 that is substantially depleted in 15N relative to the NO3 source. In the modern system, this results in seawater nitrate (and organic matter) that is 15N-enriched relative to air. Nitrogen in kerogen from Archean sedimentary rocks is not enriched in 15N (as is found in all kerogen nitrogen from Proterozoic age to the present), but instead is depleted relative to modern atmospheric N2 by several ‰ (Beaumont and Robert, 1999). This is consistent with an Archean nitrogen cycle in which no nitrate and no free O2 was available, and nitrogen cycling was limited to N2-fixation, mineralization and ammonia volatilization. Bacterial sulfate reduction is associated with a significant isotope discrimination, producing sulfide that is depleted in 34S relative to substrate sulfate. The magnitude of sulfur isotope fractionation during sulfate reduction depends in part on available sulfate concentrations. Very limited differences in sulfur isotopic ratios among Archean sedimentary sulfide and sulfate minerals (≤2‰) indicate only minor isotope fractionation during sulfate reduction in the Archean oceans (Canfield et al., 2000; Habicht et al., 2002), best explained by extremely low SO42− concentrations (<200 µM) in contrast with modern concentrations of ∼28 mM) (Habicht et al., 2002). The limited supply of sulfate in the Archean ocean suggests that the major source of sulfate to Archean seawater was volcanic gas, because oxidative weathering of sulfide minerals could not occur under an O2-free atmosphere. The limited sulfate concentration would have suppressed the activity of sulfate-reducing bacteria and facilitated methanogenesis. However, by ∼2.7 Ga, sedimentary sulfides that are 34S-depleted relative to sulfate are detected, suggesting at least sulfate reduction, and by implication sources of sulfate to seawater through sulfate oxidation, may have developed (Canfield et al., 2000).
8.11.6.2.2 The evolution of oxygenic photosynthesis

In the early Archean, methanogenesis (reaction of H₂ + CO₂ to yield CH₄) was likely a significant component of total primary production. O₂ concentrations in the atmosphere were suppressed due to limited O₂ production and rapid consumption with iron, sulfur, and reduced gases, while CH₄ concentrations were likely very high (Kasting et al., 2001). The high methane abundance is calculated to have generated a hydrocarbon-rich smog that could screen UV light and protect early life in the absence of O₂ and ozone (Kasting et al., 2001). Other means of protection from UV damage in the O₂-free Archean include biomineralization of cyanobacteria within UV-shielded iron–silica sinters (Phoenix et al., 2001).

Biological evolution may have contributed to early Archean oxidation of the Earth. Catling et al., (2001) have recognized that CO₂ fixation associated with early photosynthesis may have been coupled with active fermentation and
methanogenesis. Prior to any accumulation of atmospheric $O_2$, $CH_4$ may have been a large component of Earth’s atmosphere. A high flux of biogenic methane is supported by coupled ecosystem–climate models of the early Earth (Pavlov et al., 2000; Kasting et al., 2001) as a supplement to Earth’s greenhouse warming under reduced solar luminosity in the Archean. $CH_4$ in the upper atmosphere is consumed by UV light to yield hydrogen (favored form of hydrogen in the upper atmosphere), which escapes to space. Because $H_2$ escape leads to net oxidation, biological productivity and methanogenesis result in slow oxidation of the planet. Net oxidation may be in the form of direct $O_2$ accumulation (if $CO_2$ fixation is associated with oxygenic photosynthesis) or indirectly (if $CO_2$ fixation occurs via anoxygenic photosynthesis or anaerobic chemotrophy) through production of oxidized iron or sulfur minerals in the crust, which upon subduction are mixed with other crustal rocks and increase the crustal oxidation state. One system that may represent a model of early Archean biological productivity consists of microbial mats found in hypersaline coastal ponds. In these mats, cyanobacteria produce $H_2$ and $CO$ that can be used as substrates by associated chemooautotrophs, and significant $CH_4$ fluxes out of the mats have been measured (Hoehler et al., 2001). Thus, mats may represent communities of oxygenic photosynthesis, chemooautotrophy, and methanogenesis occurring in close physical proximity. Such communities would have contributed to elevated atmospheric $CH_4$ and the irreversible escape of hydrogen from the Archean atmosphere, contributing to oxidation of the early Earth.

The earliest photosynthetic communities may have contributed to oxidation of the early Earth through production of oxidized crustal minerals without requiring production of $O_2$. Crustal rocks today are more oxidized than the mantle, with compositions ranging between the QFM and hematite-magnesite $f_o_2$ buffers. This is best explained as an irreversible oxidation of the crust associated with methanogenesis and hydrogen escape (Catling et al., 2001). It is unlikely that $O_2$ produced by early photosynthesis ever directly entered the atmosphere.

Maintaining low $O_2$ concentrations in the atmosphere while generating oxidized crustal rocks requires oxidation mechanisms that do not involve $O_2$. Among these may be serpentinization of seafloor basalts (Kasting and Siefer, 2002). During seafloor weathering, ferrous-iron is released to form ferric oxyhydroxides. Using $H_2O$ or $CO_2$ as the ferrous-iron oxidant, $H_2$ and $CH_4$ are generated. This $H_2$ gas (either produced directly, or indirectly through UV decomposition of $CH_4$) can escape the atmosphere, resulting in net oxidation of the crust and accumulation of oxidized crustal rocks. BIF formation in the Archean may be related to dissolved $Fe^{2+}$ that was oxidized in shallow-water settings associated with local oxygenic photosynthesis or chemooautotrophy (Kasting and Siefer, 2002). After the biological innovation of oxygenic photosynthesis evolved, there was still a several hundred million year gap until $O_2$ began to accumulate in the atmosphere, because $O_2$ could only accumulate once the supply of reduced gases ($CO$ and $CH_4$) and ferrous-iron fell below rates of photosynthetic $O_2$ supply.

### 8.11.6.2.3 Carbon isotope effects associated with photosynthesis

The main compound responsible for harvesting light energy to produce NADPH and splitting water to form $O_2$ is chlorophyll. There are several different structural variants of chlorophyll, including chlorophyll $a$, chlorophyll $b$, and bacteriochlorophylls $a$–$e$ and $g$. Each of these shows optimum excitation at a different wavelength of light. All oxygenic photosynthetic organisms utilize chlorophyll $a$ and/or chlorophyll $b$. Other non-oxygenic photautotrophic microorganisms employ a diverse range of chlorophylls.

The earliest evidence for evolution of oxygenic photosynthesis comes from carbon isotopic signatures preserved in Archean rocks (Figure 10). $CO_2$ fixation through the Calvin cycle is associated with a significant carbon isotope discrimination, such that organic matter produced through $CO_2$ fixation is depleted in $^{13}C$ relative to $^{12}C$ by several per mil. In a closed or semi-closed system (up to and including the whole ocean–atmosphere system), isotope discrimination during fixation of $CO_2$ then results in a slight enrichment in the $^{13}C/^{12}C$ ratio of $CO_2$ not taken up during photosynthesis. Thus, a biosignature of $CO_2$ fixation is an enrichment in $^{13}C/^{12}C$ ratio in atmospheric $CO_2$ and seawater bicarbonate over a whole-Earth averaged isotope ratio. When carbonate minerals precipitate from seawater, they record the seawater isotope value. Enrichment of the $^{13}C/^{12}C$ ratio in early Archean carbonate minerals, and by extension seawater bicarbonate, is taken as early evidence for $CO_2$ fixation. Although anoxygenic photautotrophs and chemooautotrophs fix $CO_2$ without generating $O_2$, these groups either do not employ the Calvin cycle (many anoxygenic photautotrophs use the acetyl-CoA or reverse tricarboxylic acid pathways) or require $O_2$ (most chemolithooautotrophs). Thus, the most likely group of organisms responsible for this isotope effect are oxygenic photautotrophs such as cyanobacteria. Kerogen and graphite that is isotopically depleted in $^{13}C$ is a common and continuous feature of the sedimentary record, extending as far back as $\sim 3.8 \text{ Ga}$ to the Isua.
Supracrustal Suite of Greenland (Schidlowski, 1988, 2001; Nutman et al., 1997). Although some isotopically depleted graphite in the metasediments from the Isua Suite may derive from abiotic hydrothermal processes (van Zuilen et al., 2002), rocks interpreted as metamorphosed turbidite deposits retain 13C-depleted graphite believed to be biological in origin. Moreover, the isotopic distance between coeval carbonate and organic matter (in the form of kerogen) can be used to estimate biological productivity through time. With a few exceptions, these isotope mass balance estimates reveal that, since Archean times, global scale partitioning between inorganic and organic carbon, and thus global productivity and carbon burial, have not varied greatly over nearly 4 Gyr of Earth’s history (Schidlowski, 1988, 2001).

Approximately 25% of crustal carbon burial is in the form of organic carbon, and the remainder is inorganic carbonate minerals. This estimate derives from the mass- and isotope-balance equation:

$$\delta^{13}C_{\text{avg}} = f \delta^{13}C_{\text{organic matter}} + (1 - f) \times \delta^{13}C_{\text{carbonate}}$$  (2)

where $\delta^{13}C_{\text{avg}}$ is the average isotopic composition of crustal carbon entering the oceans from continental weathering and primordial carbon emitted from volcanoes, $\delta^{13}C_{\text{organic matter}}$ is the average isotopic composition of sedimentary organic matter, $\delta^{13}C_{\text{carbonate}}$ is the average isotopic composition of carbonate sediments, and $f$ is the fraction of carbon buried as organic matter in sediments.

The observation that the proportion of carbon buried in sediments as organic matter versus carbonate has not varied throughout geologic time raises several intriguing issues. First, biogeochemical cycling of carbon exhibits remarkable constancy across 4 Gyrs of biological evolution, in spite of large-scale innovations in primary production and respiration (including anoxygenic and oxygenic photosynthesis, chemosynthesis, sulfate reduction, methanotrophy, and aerobic respiration). Thus, with a few notable exceptions expressed in the carbonate isotope record, burial flux ratios between organic matter and carbonate have remained constant, in spite of varying dominance of different modes of carbon fixation and respiration through time, not to mention other possible controls on organic matter burial and preservation commonly invoked for Phanerozoic systems (anoxia of bottom waters, sedimentation rate, selective preservation, or cumulative oxygen exposure time). Second, the constancy of organic matter versus carbonate burial through time reveals that throughout geologic time, the relative contributions of various sources and sinks of carbon to the “ocean + atmosphere” system have remained constant. In other words, to maintain a constant carbonate isotopic composition through time, not only must the relative proportion of organic matter versus carbonate burial have remained nearly constant, but the relative intensity of organic matter versus carbonate weathering also must have remained nearly constant. In the earliest stages of Earth’s history, when continents were small and sedimentary rocks were sparse, inputs of carbon from continental weathering may have been small relative to volcanic inputs. However, the several billion year sedimentary record of rocks rich in carbonate minerals and organic matter suggests that continental
8.11.6.2.4 Evidence for oxygenic consumption prior to accumulation of O$_2$ in the atmosphere. Rocks may have been active even in the Archean, that oxidative weathering of ancient sedimentary early in the Archean. Intriguingly, this indicates contribution to total oceanic carbon inputs fairly weathering must have formed a significant production of O$_2$ and organic matter weathering is equated to O$_2$ consumption.

### 8.11.6.3 The Proterozoic Atmosphere

#### 8.11.6.3.1 Oxygenation of the Proterozoic atmosphere

Although there is evidence for the evolution of oxygenic photosynthesis several hundred million years before the Huronian glaciation (e.g., Brocks et al., 1999) or earlier (Schidlowski, 1988, 2001), high fluxes of UV light reacting with O$_2$ derived from the earliest photosynthetic organisms would have created dangerous reactive oxygen species that severely suppressed widespread development of large populations of these oxygenic photoautotrophs. Cyanobacteria, as photoautotrophs, need to be exposed to visible light and have evolved several defense mechanisms to protect cell contents and repair damage. However, two key metabolic pathways (oxygenic photosynthesis and nitrogen fixation) are very sensitive to UV damage. Indisputably cyanobacterial fossil occur in 1,000 Ma rocks, with putative fossils occurring 2,500 Ma and possibly older (Schopf, 1992). Sediment mat-forming cyanobacteria and stromatolites are least ambiguous and oldest. Terrestrial encrusting cyanobacteria are only known in the Phanerozoic. Planktonic forms are not known for the Archean and early Proterozoic. They may not have existed, or they may not be preserved. Molecular evolution, specifically coding for proteins that build gas vesicles necessary for planktonic life, are homologous and conserved in all cyanobacteria. Thus, perhaps planktonic cyanobacteria existed throughout Earth’s history since the late Archean.

Today, ozone forms in the stratosphere by reaction of O$_2$ with UV light. This effectively screens much incoming UV radiation. Prior to the accumulation of atmospheric O$_2$, no ozone could form, and thus the UV flux to the Earth’s surface would be much greater (with harmful effects on DNA and proteins, which adsorb and are altered into protein form, and thus the UV flux to the Earth’s surface would be much greater (with harmful effects on DNA and proteins, which adsorb and are altered by UV). A significant ozone shield could develop at $10^{-2}$ PAL O$_2$ (Kasting, 1987). However, a fainter young Sun would have emitted somewhat lower UV, mediating the lack of ozone. Although seawater today adsorbs most UV light by 6–25 m (1% transmittance cutoff), seawater with abundant dissolved Fe$^{2+}$ may have provided an effective UV screen in the Archean (Olson and Pierson, 1986). Also, waters rich in humic materials, such as modern coastal oceans, are nearly UV opaque. If Archean seawater contained DOM, this could adsorb some UV. Iron oxidation and BIF at $2.5–1.9$ Ga would have removed the UV screen in seawater. Thus, a significant UV stress may have developed at this time. This would be mediated coincidentally by accumulation of atmospheric O$_2$.

In the early Archean before oxygenic photosynthesis evolved, cyanobacteria were limited.
Planktonic forms were inhibited, and limited by dissolved iron content of water, and existence of stratified, UV-screen refuges. Sedimentary mat-forming and stromatolite-forming communities were much more abundant. Iron-oxide precipitation and deposition of screen enzymes may have created UV-free colonies under a shield even in shallow waters.

Advent of oxygenic photosynthesis in the Archean generated small oxygen oases (where dissolved O₂ could accumulate in the water) within an overall O₂-free atmosphere waters containing oxygenic photautotrophs might have reached 10% air saturation (Kasting, 1992). At this time, both unscreened UV radiation and O₂ may have coincided within the water column and sediments. This would lead to increased UV stress for cyanobacteria. At the same time, precipitation of iron from the water would make the environment even more UV-transparent. To survive, cyanobacteria would need to evolve and optimize defense and repair mechanisms for UV damage (Garcia-Pichel, 1998).

Perhaps this explains the ∼500 Myr gap between origin of cyanobacteria and accumulation of O₂ in the atmosphere. For example, the synthesis of scytonemin (a compound found exclusively in cyanobacteria) requires molecular oxygen (implying evolution in anoxic environment); it optimally screens UV-a, the form of UV radiation only abundant in an oxygenated atmosphere.

Oxygenation of the atmosphere at ∼2.3–2.0 Ga may derive from at least three separate causes. First, discussed earlier, is the titration of O₂ with iron, sulfur, and reduced gases. The other is global rates of photosynthesis and organic carbon burial in sediments. If the rate of atmospheric O₂ supply (oxygenic photosynthesis) exceeds all mechanisms of O₂ consumption (respiration, chemosynthesis, reduced mineral oxidation, etc.), then O₂ can accumulate in the atmosphere. One means by which this can be evaluated is through seawater carbonate δ¹³C. Because biological CO₂ fixation is associated with significant carbon isotope discrimination, the magnitude of carbon fixation is indicated by the isotopic composition of seawater carbonate. At times of more carbon fixation and burial in sediments, relatively more ¹²C is removed from the atmosphere + ocean inorganic carbon pool than is supplied through respiration, organic matter oxidation, and carbonate mineral dissolution. Because carbon fixation is dominated by oxygenic photosynthesis (at least since the late Archean), periods of greater carbon fixation and burial of organic matter in sediments (observed as elevated seawater carbonate δ¹³C) are equated to periods of elevated O₂ production through oxygenic photosynthesis. The early Proterozoic Lomagundi event (∼2.3–2.0 Ga) is recorded in the sediment record as a prolonged period of elevated seawater carbonate δ¹³C, with carbonate δ¹³C values reaching nearly 10‰ in several sections around the world (Schidlowski, 2001). This represents an extended period of time (perhaps several hundred million years) during which removal of carbon from the “ocean + atmosphere” system as organic matter greatly exceeded supply. By implication, release of O₂ through photosynthesis was greatly accelerated during this time.

A third mechanism for oxygenation of the atmosphere at ∼2.3 Ga relies on the slow, gradual oxidation of the Earth’s crust. Irreversible H₂ escape and basalt-seawater reactions led to a gradual increase in the amount of oxidized and hydrated minerals contained in the Earth’s crust and subducted in subduction zones throughout the Archean. Gradually this influenced the oxidation state of volcanic gases derived in part from subducted crustal rocks. Thus, although mantle oxygen fugacity may not have changed since the early Archean, crustal and volcanic gas oxygen fugacity slowly increased as the abundance of oxidized and hydrated crust increased (Holland, 2002; Kasting et al., 1993; Kump et al., 2001). Although slow to develop, Holland (2002) estimates that an increase in fO₂ of less than 1 log unit is all that would have been required for transition from an anoxic to an oxic atmosphere, assuming rates of oxygenic photosynthesis consistent with modern systems and the sediment isotope record. Once a threshold volcanic gas fO₂ had been reached, O₂ began to accumulate. Oxidative weathering of sulfides released large amounts of sulfate into seawater, facilitating bacterial sulfate reduction.

There are several lines of geochemical evidence that suggest a rise in oxygenation of the atmosphere ∼2.3–2.0 Ga, beyond the coincident last occurrence of BIFs (with one late Proterozoic exception) and first occurrence of red beds recognized decades ago, and carbon isotopic evidence suggesting ample burial of sedimentary organic matter (Karhu and Holland, 1996; Bekker et al., 2001; Buick et al., 1998). The Huronian glaciation (∼2.3 Ga) is the oldest known glacial episode recorded in the sedimentary record. One interpretation of this glaciation is that the cooler climate was a direct result of the rise of photosynthetically derived O₂. The rise of O₂ scavenged and reacted with the previously high atmospheric concentration of CH₄. Methane concentrations dropped, and the less-effective greenhouse gas product CO₂ could not maintain equable surface temperatures. Kasting et al. (1983) estimate that a rise in pO₂ above ∼10⁻⁴ atm resulted in loss of atmospheric CH₄ and onset of glaciation.
Paleosols have also provided evidence for a change in atmosphere oxygenation at some time between 2.3–2.0 Ga. Evidence from rare earth element enrichment patterns and U/Th fractionation suggests a rise in \( O_2 \) to \( \sim 0.005 \) bar by the time of formation of the Flin Flon paleosol of Manitoba, Canada, 1.85 Ga (Pan and Stauffer, 2000; Holland et al., 1989; Rye and Holland, 1998). Rye and Holland (1998) examined several early Proterozoic paleosols and observed that negligible iron loss is a consistent feature from soils of Proterozoic age through the present. These authors estimate that a minimum \( p_{O_2} \) of \( >0.03 \) atm is required to retain iron during soil formation, and thus atmospheric \( O_2 \) concentration has been 0.03 or greater since the early Paleozoic. However, re-evaluation of a paleosol crucial to the argument of iron depletion during soil formation under anoxia, the Hekpoort paleosol dated at 2.2 Ga, has revealed that the iron depletion detected by previous researchers may in fact be the lower zone of a normal oxidized lateritic soil. Upper sections of the paleosol that are not depleted in iron have been eroded away in the exposure examined by Rye and Holland (1998), but have been found in drill core sections. The depletion of iron and occurrence of ferrous-iron minerals in the lower sections of this paleosol have been reinterpreted by Beukes et al., (2002) to indicate an abundant soil surface biomass at the time of deposition that decomposed to generate reducing conditions and iron mobilization during the wet season, and precipitation of iron oxides during the dry season.

Sulfur isotope studies have also provided insights into the transition from Archean low \( p_{O_2} \) to higher values in the Proterozoic. In the same studies that revealed extremely low Archean ocean sulfate concentrations, it was found that by \( \sim 2.2 \) Ga, isotopic compositions of sedimentary sulfates and sulfides indicate bacterial sulfate reduction under more elevated seawater sulfate concentrations compared with the sulfate-poor Archean (Habicht et al., 2002; Canfield et al., 2000). As described above, nitrogen isotope ratios in sedimentary kerogens show a large and permanent shift at \( \sim 2.0 \) Ga, consistent with denitrification, significant seawater nitrate concentrations, and thus available atmospheric \( O_2 \).

Prior to \( \sim 2.2 \) Ga, low seawater sulfate concentrations would have limited precipitation and subduction of sulfate-bearing minerals. This would maintain a lower oxidation state in volcanic gases derived in part from recycled crust (Holland, 2002). Thus, even while the oxidation state of the mantle has remained constant since \( \sim 4.0 \) Ga (Delano, 2001), the crust and volcanic gases derived from subduction of the crust could only achieve an increase in oxidation state once seawater sulfate concentrations increased.

A strong model for oxygenation of the atmosphere has developed based largely on the sulfur isotope record and innovations in microbial metabolism. The classical interpretation of the disappearance of BIFs relates to the rise of atmospheric \( O_2 \), oxygenation of the oceans, and removal of dissolved ferrous-iron by oxidation. However, another interpretation has developed, based largely on the evolving Proterozoic sulfur isotope record. During the oxygenation of the atmosphere at \( \sim 2.3–2.0 \) Ga, the oceans may not have become oxidized, but instead remained anoxic and became strongly sulfidic as well (Anbar and Knoll, 2002; Canfield, 1998 and references therein). Prior to \( \sim 2.3 \) Ga, the oceans were anoxic but not sulfidic. Ferrous-iron was abundant, as was manganese, because both are very soluble in anoxic, sulfide-free waters. The high concentration of dissolved iron and manganese facilitated nitrogen fixation by early cyanobacteria, such that available nitrogen was abundant, and phosphorus became the nutrient limiting biological productivity (Anbar and Knoll, 2002). Oxygenation of the atmosphere at \( \sim 2.3 \) Ga led to increased oxidative weathering of sulfide minerals on the continents and increased sulfate concentration in seawater. Bacterial sulfate reduction generated ample sulfide, and in spite of limited mixing, the deep oceans would have remained anoxic and now also sulfidic as long as \( p_{O_2} \) remained below \( \sim 0.07 \) atm (Canfield, 1998), assuming reasonable rates of primary production. Both iron and manganese form insoluble sulfides, and thus were effectively scavenged from seawater once the oceans became sulfidic. Thus, the Proterozoic oxygenation led to significant changes in global oxygen balances, with the atmosphere and ocean mixed layer becoming mildly oxygenated (probably \(<0.01 \) atm \( O_2 \)), and the deep oceans becoming strongly sulfidic in direct response to the rise of atmospheric \( O_2 \).

In addition to increased oxygen fugacity of volcanic gases, and innovations in biological productivity to include oxygenic photosynthesis, the oxygenation of the Proterozoic atmosphere may be related to large-scale tectonic cycles. There are several periods of maximum deposition of sedimentary rocks rich in organic matter through geologic time. These are \( \sim 2.7 \) Ga, \( 2.2 \) Ga, 1.9 Ga, and 0.6 Ga (Condie et al., 2001). The increased deposition of black shales at 2.7 Ga and 1.9 Ga are associated with superplume events: highly elevated rates of seafloor volcanism, oceanic crust formation. Superplumes lead to increased burial of both organic matter and carbonates (through transgression, increased atmospheric \( CO_2 \), accelerated weathering, and
nutrient fluxes to the oceans), with no net effect on carbonate isotopic composition. Thus, periods of increased absolute rates of organic matter burial and O$_2$ production may be masked by a lack of carbon isotopic signature. Breakup of supercontinents may be related to the black shale depositional events at 2.2 Ga and 0.6 Ga. Breakup of supercontinents may lead to more sediment accommodation space on continental shelves, as well as accelerated continental weathering and delivery of nutrients to seawater, fertilizing primary production and increasing organic matter burial. These supercontinent breakup events at 2.2 Ga and 0.6 Ga are clearly observed on the carbonate isotopic record as increases in relative burial of organic matter versus carbonate. Modeling efforts examining the evolution of the carbon, sulfur, and strontium isotope records have shown that gradual growth of the continents during the Archean and early Proterozoic may in fact play a very large role in controlling the onset of oxygenation of the atmosphere, and that biological innovation may not be directly coupled to atmospheric evolution (Goddéris and Veizer, 2000).

8.11.6.3.2 Atmospheric O$_2$ during the Mesoproterozoic

The sulfur-isotope-based model of Canfield and colleagues and the implications for limiting nutrient distribution proposed by Anbar and Knoll (2002) suggest that for nearly thousand million years (~2.2–1.2 Ga), oxygenation of the atmosphere above $p_{O_2} \sim 0.01$ atm was held in stasis. Although oxygenic photosynthesis was active, and an atmospheric ozone shield had developed to protect surface-dwelling organisms from UV radiation, much of the deep ocean was still anoxic and sulfidic. Removal of iron and manganese from seawater as sulfides generated severe nitrogen stress for marine communities, suggesting that productivity may have been limited throughout the entire Mesoproterozoic. The sluggish but consistent primary productivity and organic carbon burial through this time is seen in the carbonate isotope record. For several hundred million years, carbonate isotopic composition varied by no more than $\pm 2\%_e$, revealing very little change in the relative carbonate/organic matter burial in marine sediments. Anbar and Knoll (2002) suggest that this indicates a decoupling of the link between tectonic events and primary production, because although variations in tectonic activity (and associated changes in sedimentation, generation of restricted basins, and continental weathering) occurred during the Mesoproterozoic, these are not observed in the carbonate isotope record. This decoupling is a natural result of a shift in the source of the biological limiting nutrient from phosphorus (derived from continental weathering) to nitrogen (limited by N$_2$ fixation). Furthermore, the isotopic composition of carbonates throughout the Mesoproterozoic is 1–2‰ depleted relative to average carbonates from the early and late Proterozoic and Phanerozoic. This is consistent with a decrease in the relative proportion of carbon buried as organic matter versus carbonate during this time. It appears that after initial oxygenation of the atmosphere from completely anoxic to low $p_{O_2}$ in the early Proterozoic, further oxygenation was halted for several hundred million years.

Global-scale reinvigoration of primary production, organic matter burial and oxygenation of the atmosphere may be observed in the latest Mesoproterozoic. Shifts in carbonate $\delta^{13}$C of up to 4‰ are observed in sections around the globe at ~1.3 Ga (Bartley et al., 2001; Kah et al., 2001). These positive carbon isotope excursions are associated with the formation of the Rodinian supercontinent, which led to increased continental margin length, orogenesis, and greater sedimentation (Bartley et al., 2001). The increased organic matter burial and atmospheric oxygenation associated with this isotope excursion may be related to the first occurrence of laterally extensive CaSO$_4$ evaporites (Kah et al., 2001). Although the rapid 10‰ increase in evaporite $\delta^{34}$S across these sections is taken to indicate a much reduced seawater sulfate reservoir with much more rapid turnover times than found in the modern ocean, the isotope fractionation between evaporate sulfates and sedimentary sulfides indicates that the oceans were not sulfate-limiting. Atmospheric O$_2$ was of sufficient concentration to supply ample sulfate for bacterial sulfate reduction throughout the Mesoproterozoic.

8.11.6.3.3 Neoproterozoic atmospheric O$_2$

Elevated carbonate isotopic compositions (~4‰) and strong isotope fractionation between sulfate and biogenic sulfide minerals through the early Neoproterozoic indicates a period of several hundred million years of elevated biological productivity and organic matter burial. This may relate in part to the oxygenation of the atmosphere, ammonia oxidation, and increased seawater nitrate availability. Furthermore, oxidative weathering of molybdenum-bearing sulfide minerals, and greater oxygenation of the oceans increased availability of molybdenum necessary for cyanobacterial pathways of N$_2$-fixation (Anbar and Knoll, 2002). Much of the beginning of the Neoproterozoic, like the late Mesoproterozoic, saw gradual increases in
oxygenation of the atmosphere, and possibly of the surface oceans. Limits on the oxygenation of the atmosphere are provided by sulfur isotopic and molecular evidence for the evolution of sulfide oxidation and sulfur disproportionation. The increase in sulfate–sulfide isotope fractionation in the Neoproterozoic (~1.0–0.6 Ga) reflects a shift in sulfur cycling from simple one-step reduction of sulfate to sulfide, to a system in which sulfide was oxidized to sulfur intermediates such as thiosulfate or elemental sulfur, which in turn were disproportionated into sulfate and sulfide (Canfield and Teske, 1996). Sulfur disproportionation is associated with significant isotope effects, generating sulfide that is substantially more 34S-depleted than can be achieved through one-step sulfate reduction. The sulfur isotope record reveals that an increase in sulfate–sulfide isotope fractionation occurred between 1.0 Ga and 0.6 Ga, consistent with evolution of sulfide-oxidation at this time as derived from molecular clock based divergence of non-photosynthetic sulfide-oxidizing bacteria (Canfield and Teske, 1996). These authors estimated that innovation of bacterial sulfide oxidation occurred when much of the coastal shelf sediment (<200 m water depth) was exposed to water with 13–46 μM O2, which corresponds to 0.01–0.03 atm pO2. Thus, after the initial oxygenation of the atmosphere in the early Proterozoic (~2.3–2.0 Ga) to ~0.01 atm, pO2 was constrained to this level until a second oxygenation in the late Proterozoic (~1.0–0.6 Ga) to 0.03 atm or greater.

During the last few hundred million years of the Proterozoic (~0.7–0.5 Ga), fragmentation of the Rodinian supercontinent was associated with at least two widespread glacial episodes (Hoffman et al., 1998; Hoffman and Schrag, 2002). Neoproterozoic glacial deposits are found in Canada, Namibia, Australia, and other locations worldwide (Evans, 2000). In some of these, paleomagnetic evidence suggests that glaciation extended completely from pole to equator (Sumner, 1997; see also Evans (2000) and references therein). The “Snowball Earth”, as these events have come to be known, is associated with extreme fluctuations in carbonate stratigraphy strati, reoccurrence of BIFs after an ~1.0 Ga hiatus, and precipitation of enigmatic, massive cap carbonate sediments immediately overlying the glacial deposits (Figure 11). It has been proposed that the particular configuration of continents in the latest Neoproterozoic, with land masses localized within the middle–low latitudes, lead to cooling of climate through several mechanisms. These include higher albedo in the subtropics (Kirschvink, 1992), increased silicate weathering as the bulk of continents were located in the warm tropics, resulting in a drawdown of atmospheric CO2 (Hoffman and Schrag, 2002), possibly accelerated through high rates of OM burial, and reduced meridional Hadley cell heat transport, because tropical air masses were drier due to increased continentality (Hoffman and Schrag, 2002). Growth of initially polar ice caps would have created a positive ice–albedo feedback such that greater than half of Earth’s surface became ice covered, global-scale growth of sea ice became inevitable (Pollard and Kasting, 2001; Baum and Crowley, 2001). Kirschvink (1992) recognized that escape from the Snowball Earth becomes possible because during extreme glaciation, the continental hydrologic cycle would be shut down. He proposed that sinks for atmospheric CO2, namely, photosynthesis and silicated weathering, would have been eliminated during the glaciation. Because volcanic degassing continued during the glaciation, CO2 in the atmosphere could rise to very high concentrations. It was estimated that an increase in pCO2 to 0.12 bar would be sufficient to induce a strong enough greenhouse effect to begin warming the planet and melting the ice (Caldeira and Kasting, 1992). Once meltback began, it

Figure 11 Composite section of carbonate isotope stratigraphy before and after the Ghaub glaciation from Namibia. Enriched carbonates prior to glaciation indicate active primary production and organic matter burial. Successive isotopic depletion indicates a shut down in primary production as the world became covered in ice (source Hoffman et al., 1998).
would subsequently accelerate through the positive ice–albedo feedback. Intensely warm temperatures would follow quickly after the glaciation, until accelerated silicate weathering under a reinvigorated hydrologic cycle could consume excess $\text{CO}_2$ and restore $p_{\text{CO}_2}$ to more equable values. Carbonate mineral precipitation was inhibited during the global glaciation, so seawater became enriched in hydrothermally derived cations. At the end of glaciation, mixing of cation-rich seawater with high alkalinity surface runoff under warming climates led to the precipitation of massive cap carbonates.

Geochemical signatures before and after the Snowball episodes reveal rapid and short-lived changes in global biogeochemical cycles that impacted $\text{O}_2$ concentrations in the atmosphere and oceans. Prior to the Snowball events, the Neoproterozoic ocean experienced strong primary production and organic matter burial, as seen in the carbon isotopic composition of Neoproterozoic seawater in which positive isotope excursions reached 10‰ in some sections (Kaufman and Knoll, 1995). These excursions are roughly coincident with increased oxygenation of the atmosphere in the Neoproterozoic (Canfield and Teske, 1996; Des Marais et al., 1992). Although sulfur isotopic evidence suggests that much of the ocean may have become oxygenated during the Neoproterozoic, it is very likely that this was a temporary phenomenon. The global-scale glaciations of the late Neoproterozoic would have driven the oceans to complete anoxia through several mechanisms (Kirschvink, 1992). Ice cover inhibited air–sea gas exchange, and thus surface waters and sites of deep-water formation were cut off from atmospheric $\text{O}_2$ supplies. Intense oxidation of organic matter in the water column and sediment would have quickly consumed any available dissolved $\text{O}_2$. Extreme positive sulfur-isotope excursions associated with snowball–succession deposits reflect nearly quantitative, closed-system sulfate reduction in the oceans during glaciation (Hurtgen et al., 2002). As seawater sulfate concentrations were reduced, hydrothermal inputs of ferrous-iron exceeded sulfide supply, allowing BIFs to form (Hoffman and Schrag, 2002). Closed-system sulfate reduction and iron formations require ocean anoxia throughout the water column, although restricted oxygenic photosynthesis beneath thin tropical sea ice may be responsible for ferrous-iron oxidation and precipitation (Hoffman and Schrag, 2002).

Once global ice cover was achieved, it is estimated to have lasted several million years, based on the amount of time required to accumulate 0.12 bar $\text{CO}_2$ at modern rates of volcanic $\text{CO}_2$ emission (Caldeira and Kasting, 1992). This must have placed extreme stress on eukaryotes and other organisms dependent on aerobic respiration. Obviously, oxygenated refuge must have existed, because the rise of many eukaryotes predates the Neoproterozoic Snowball events (Butterfield and Rainbird, 1998; Porter and Knoll, 2000). Nonetheless, carbon isotopic evidence leading up to and through the intense glacial intervals suggests that overall biological productivity was severely repressed during Snowball events. Carbonate isotope compositions fall from extremely enriched values to depletions of $\sim$(-6‰) at glacial climax (Hoffman et al., 1998; Kaufman et al., 1991; Kaufman and Knoll, 1995). These carbonate isotope values reflect primordial (volcanogenic) carbon inputs, and indicate that effectively zero organic matter was buried in sediments at this time. Sustained lack of organic matter burial and limited if any oxygenic photosynthesis under the glacial ice for several million years would have maintained an anoxic ocean, depleted in sulfate, with low sulfide concentrations due to iron scavenging, and extremely high alkalinity and hydrothermally-derived ion concentrations. Above the ice, the initially mildly oxygenated atmosphere would slowly lose its $\text{O}_2$. Although the hydrologic cycles were suppressed, and thus oxidative weathering of sulfide minerals and organic matter exposed on the continents was inhibited, the emission of reduced volcanic gases would have been enough to fully consume 0.01 bar $\text{O}_2$ within several hundred thousand years. Thus, it is hypothesized that during Snowball events, the Earth’s atmosphere returned to pre-Proterozoic anoxic conditions for at least several million years. Gradual increases in carbonate $\delta^{13}\text{C}$ after glaciation and deposition of cap carbonates suggests slow restored increases in primary productivity and organic carbon burial.

Carbon isotopic evidence suggests that reoxygenation, at least of seawater, was extremely gradual throughout the remainder of the Neoproterozoic. Organic matter through the terminal Proterozoic derives largely from bacterial heterotrophs, particularly sulfate reducing bacteria, as opposed to primary producers (Logan et al., 1995). These authors suggested that throughout the terminal Neoproterozoic, anaerobic heterotrophy dominated by sulfate reduction was active throughout the water column, and $\text{O}_2$ penetration from surface waters into the deep ocean was inhibited. Shallow-water oxygen-deficient environments became widespread at the Precambrian–Cambrian boundary (Kimura and Watanabe, 2001), corresponding to negative carbonate $\delta^{13}\text{C}$ excursions and significant biological evolution from Ediacaran-type metazoans to emergence of modern metazoan phyla in the Cambrian.
8.11.6.4 Phanerozoic Atmospheric $O_2$

8.11.6.4.1 Constraints on Phanerozoic $O_2$ variation

Oxygenation of the atmosphere during the latest Neoproterozoic led to a fairly stable and well-oxygenated atmosphere that has persisted through the present day. Although direct measurement or a quantifiable proxy for Phanerozoic paleo-$pO_2$ concentrations have not been reported, multiple lines of evidence point to upper and lower limits on the concentration of $O_2$ in the atmosphere during the past several hundred million years. Often cited is the nearly continuous record of charcoal in sedimentary rocks since the evolution of terrestrial plants some 350 Ma. The presence of charcoal indicates forest fires throughout much of the Phanerozoic, which are unlikely to have occurred below $pO_2 = 0.17$ atm (Cope and Chaloner, 1985). Combustion and sustained fire are difficult to achieve at lower $pO_2$. The existence of terrestrial plants themselves also provides a crude upper bound on $pO_2$ for two reasons. Above the compensation point of $pO_2$/$pCO_2$ ratios, photorespiration outcompetes photosynthesis, and plants experience zero or negative net growth (Tolbert et al., 1995). Although plants have developed various adaptive strategies to accommodate low atmospheric $pCO_2$, or aridity (i.e., C$_4$ and CAM plants), net terrestrial photosynthesis and growth of terrestrial ecosystems are effectively inhibited if $pO_2$ rises too high. This upper bound is difficult to exactly constrain, but is likely to be $\sim$0.3–0.35 atm. Woody tissue is also extremely susceptible to combustion at high $pO_2$, even if the tissue is wet. Thus, terrestrial ecosystems would be unlikely above some upper limit of $pO_2$ because very frequent reoccurrence of wildfires would effectively wipe out terrestrial plant communities, and there is no evidence of this occurring during the Phanerozoic on a global scale. What this upper $pO_2$ limit is, however, remains disputed. Early experiments used combustion of paper under varying humidity and $pO_2$ (Watson, 1978) but paper may not be the most appropriate analog for inception of fires in woody tissue with greater moisture content and thermal thickness (Robinson, 1989; Berner et al., 2002). Nonetheless, the persistence of terrestrial plant communities from the middle Paleozoic through the present does imply that $pO_2$ concentrations have not risen too high during the past 350 Myr.

Prior to evolution of land plants, even circumstantial constraints on early Paleozoic $pO_2$ are difficult to obtain. Invertebrate metazoans, which have a continuous fossil record from the Cambrian on, require some minimum amount of dissolved oxygen to support their aerobic metabolism. The absolute minimum dissolved $O_2$ concentration able to support aerobic metazoans varies from species to species, and is probably impossible to reconstruct for extinct lineages, but modern infaunal and epifaunal metazoans can accommodate dissolved $O_2$ dropping to the tens of micromolar in concentration. If these concentrations are extrapolated to equilibrium of the atmosphere with well-mixed cold surface waters, they correspond to $\sim$0.05 atm $pO_2$. Although local and regional anoxia occurred in the oceans at particular episodes through Phanerozoic time, the continued presence of aerobic metazoans suggests that widespread or total ocean anoxia did not occur during the past $\sim$600 Myr, and that $pO_2$ has been maintained at or above $\sim$5% $O_2$ since the early Paleozoic.

8.11.6.4.2 Evidence for variations in Phanerozoic $O_2$

Several researchers have explored possible links between the final oxygenation of the atmosphere and explosion of metazoan diversity at the Precambrian–Cambrian boundary (McMenamin and McMenamin, 1990; Gilbert, 1996). While the Cambrian explosion may not record the origin of these phyla in time, this boundary does record the development of large size and hard skeletons required for fossilization (Thomas, 1997). Indeed, molecular clocks for diverse metazoan lineages trace the origin of these phyla to $\sim$400 Myr before the Cambrian explosion (Doolittle et al., 1996; Wray et al., 1996). The ability of lineages to develop fossilizable hardparts may be linked with increasing oxygenation during the latest Precambrian. Large body size requires elevated $pO_2$ and dissolved $O_2$ concentrations, so the diffusion can supply $O_2$ to internal tissues. Large body size provides several advantages, and may have evolved rather quickly during the earliest Cambrian (Gould, 1995), but large size also requires greater structural support. The synthesis of collagen (a ubiquitous structural protein among all metazoans and possible precursor to inorganic structural components such as carbonate or phosphate biominerals) requires elevated $O_2$. The threshold for collagen biosynthesis, and associated skeletonization and development of large body size, could not occur until $pO_2$ reached some critical threshold some time in the latest Precambrian (Thomas, 1997).

There is evidence to suggest that the late Paleozoic was a time of very elevated $pO_2$, to concentrations substantially greater than observed in the modern atmosphere. Coals from the Carboniferous and Permian contain a greater abundance of fusain, a product of woody tissue combustion and charring, than observed for any period of the subsequent geologic past (Robinson, 1989, 1991; Glasspool, 2000), suggesting more abundant forest fires and by implication possibly
higher $p_{O_2}$ at this time. Less ambiguous is the biological innovation of gigantism at this time among diverse arthropod lineages (Graham et al., 1995). All arthropods rely on tracheal networks for diffusion of $O_2$ to support their metabolism; active pumping of $O_2$ through a vascular system as found in vertebrates does not occur. This sets upper limits on body size for a given $p_{O_2}$ concentration. In comparison with arthropod communities of the Carboniferous and Permian, modern terrestrial arthropods are rather small. Dragonflies at the time reached 70 cm wingspan, mayflies reached 45 cm wingpans, millipedes reached 1 m in length. Even amphibians, which depend in part on diffusion of $O_2$ through their skin for aerobic respiration, reached gigantic size at this time. These large body sizes could not be supported by today’s 21% $O_2$ atmosphere, and instead require elevated $p_{O_2}$ between 350 Ma and 250 Ma. Insect taxa that were giants in the Carboniferous do not survive past the Permian, suggesting that declining $p_{O_2}$ concentrations in the Permian and Mesozoic led to extinction (Graham et al., 1995; Dudley, 1998).

Increases in atmospheric $O_2$ affect organisms in several ways. Increased $O_2$ concentration facilitates aerobic respiration, while elevated $p_{O_2}$ against a constant $p_{N_2}$ increases total atmospheric pressure, with associated changes in atmospheric gas density and viscosity (Dudley, 1998, 2000). In tandem these effects may have played a strong role in the innovation of insect flight in the Carboniferous (Dudley, 1998, 2000), with secondary peaks in the evolution of flight among birds, bats and other insect lineages corresponding to times of high $O_2$ in the late Mesozoic (Dudley, 1998).

In spite of elevated $p_{O_2}$ in the late Paleozoic, leading up to this time was an extended period of water column anoxia and enhanced burial of organic matter in the Devonian. Widespread deposition of black shales, fine-grained laminated sedimentary rocks rich in organic matter, during the Devonian indicate at least partial stratification of several ocean basins around the globe, with oxygen deficiency throughout the water column. One example of this is from the Holy Cross Mountains of Poland, from which particular molecular markers for green sulfur bacteria have been isolated (Joachimski et al., 2001). These organisms are obligately anaerobic chemophotoautotrophs, and indicate that in the Devonian basin of central Europe, anoxia extended upwards through the water column well into the photic zone. Other black shales that indicate at least episodic anoxia and enhanced organic matter burial during the Devonian are found at several sites around the world, including the Exshaw Shale of Alberta (Canada), the Bakken Shale of the Williston Basin (Canada/USA), the Woodford Shale in Oklahoma (USA), and the many Devonian black shales of the Illinois, Michigan, and Appalachian Basins (USA). Widespread burial of organic matter in the late Devonian has been linked to increased fertilization of the surface waters through accelerated continental weathering due to the rise of terrestrial plant communities (Algeo and Scheckler, 1998). High rates of photosynthesis with relatively small rates of global respiration led to accumulation of organic matter in marine sediments, and the beginnings of a pulse of atmospheric hyperoxia that extended through the Carboniferous into the Permian. Coalescence of continental fragments to form the Pangean supercontinent at this time led to widespread circulation-restricted basins that facilitated organic matter burial and net oxygen release, and later, to extensive infilling to generate near-shore swamps containing terrestrial vegetation which was often buried to form coal deposits during the rapidly fluctuating sea levels of the Carboniferous and Permian.

The largest Phanerozoic extinction occurred at the end of the Permian (~250 Ma). A noticeable decrease in the burial of organic matter in marine sediments across the Permian–Triassic boundary may be associated with a global decline in primary productivity, and thus, with atmospheric $p_{O_2}$. The gigantic terrestrial insect lineages, thought to require elevated $p_{O_2}$, do not survive across this boundary, further suggesting a global drop in $p_{O_2}$, and the sedimentary and sulfur isotope records indicate an overall increase in sulfate reduction and burial of pyritic shales (Berner, 2002; Beerling and Berner, 2000). Although a long-duration deep-sea anoxic event has been proposed as a cause for the Permian mass extinction, there are competing models to explain exactly how this might have occurred. Hotinski et al., (2001) has shown that while stagnation of the water column to generate deep-water anoxia might at first seem attractive, global thermohaline stagnation would starve the oceans of nutrients, extremely limiting primary productivity, and thus shutting down dissolved $O_2$ demand in the deep oceans. Large negative excursions in carbon, sulfur, and strontium isotopes during the late Permian may indicate stagnation and reduced ventilation of seawater for extended periods, coupled with large-scale overturn of anoxic waters. Furthermore, sluggish thermohaline circulation at this time could derive from a warmer global climate and warmer water at the sites of high-latitude deep-water formation (Hotinski et al., 2001). The late Permian paleogeography of one supercontinent (Pangea) and one superocean (Panthalassa) was very different from the arrangement of continents and oceans on the modern Earth. Coupled with elevated $p_{CO_2}$ at the time (Berner, 1994; Berner and Kothavala, 2001), GCM models predict warmer climate, weaker wind stress, and low equator to pole temperature
gradients. Although polar deep-water formation still occurred, bringing O\textsubscript{2} from the atmosphere to the deep oceans, anoxia was likely to develop at mid-ocean depths (Zhang et al., 2001), and thermohaline circulation oscillations between thermally versus salinity driven modes of circulation were likely to develop. During salinity driven modes, enhanced bottom-water formation in warm, salty low-latitude regions would limit oxygenation of the deep ocean. Thus, although sustained periods of anoxia are unlikely to have developed during the late Permian, reduced oxygenation of deep water through sluggish thermohaline circulation, coupled with episodic anoxia driven by low-latitude warm salty bottom-water formation, may have led to reoccurring episodes of extensive ocean anoxia over period of several million years.

Other researchers have invoked extraterrestrial causes for the End-Permian extinction and anoxia. Fullerenes (cage-like hydrocarbons that effectively trap gases during formation and heating) have been detected in late Permian sediments from southern China. The noble gas complement in these fullerenes indicates an extraterrestrial origin, which has been interpreted by Kaito et al., (2001) to indicate an unrecognized bolide impact at the Permian–Triassic boundary. The abrupt decrease in $\delta^{34}$S across this boundary (from 20‰ to 5‰) implies an enormous and rapid release of $^{34}$S-depleted sulfur into the ocean–atmosphere system. These authors propose that volatilized bolide- and mantle-derived sulfur (~0‰) oxidized in air, consumed atmospheric and dissolved O\textsubscript{2}, and generated severe oxygen and acid stress in the oceans. Isotope mass balance estimates require $\sim 10^{19}$ mol sulfur to be released, consuming a similar mass of oxygen. $10^{19}$ mol O\textsubscript{2} represents some 10–40% of the total available inventory of atmospheric and dissolved O\textsubscript{2} at this time, removal of which led to immediate anoxia, as these authors propose.

Other episodes of deep ocean anoxia and extensive burial of organic matter are known from the Jurassic, Cretaceous, Miocene, and Pleistocene, although these have not been linked to changes in atmospheric O\textsubscript{2} and instead serve as examples of the decoupling between atmospheric and deep-ocean O\textsubscript{2} concentrations through much of the geologic past. Widespread Jurassic black shale facies in northern Europe (Posidondien Schiefer, Jet Rock, and Kimmeridge Clay) were deposited in a restricted basin on a shallow continental margin. Strong monsoonal circulation led to extensive freshwater discharge and a low-salinity cap on basin waters during summer, and intense evaporation and antestuarine circulation during winter (Röhl et al., 2001), both of which contributed to water column anoxia and black shale deposition. Several oceanic anoxic events (OAEs) are recognized from the Cretaceous in all major ocean basins, suggesting possible global deep-ocean anoxia. Molecular markers of green sulfur bacteria, indicating photic zone anoxia, have been detected from Cenomanian–Turonian boundary section OAE sediments from the North Atlantic (Sinninghe Damsté and Köster, 1998). The presence of these markers (namely, isorenieratene, a diaromatic carotenoid accessory pigment used during anoxygenic photosynthesis) indicates that the North Atlantic was anoxic and euxinic from the base of the photic zone (~50–150 m) down to the sediment. High concentrations of trace metals scavenged by sulfide and an absence of bioturbation further confirm anoxia throughout the water column. Because mid-Cretaceous oceans were not highly productive, accelerated dissolved O\textsubscript{2} demand from high rates of respiration and primary production cannot be the prime cause of these OAEs. Most likely, the warm climate of the Cretaceous led to low O\textsubscript{2} bottom waters generated at warm, high salinity regions of low-latitude oceans. External forcing, perhaps through Milankovic-related precession-driven changes in monsoon intensity and strength, influenced the rate of salinity-driven deep-water formation, ocean basin oxygenation, and OAE formation (Wortmann et al., 1999). Sapropels are organic matter-rich layers common to late Cenozoic sediments of the eastern Mediterranean. They are formed through a combination of increased primary production in surface waters, and increased organic matter preservation in the sediment likely to be associated with changes in ventilation and oxygenation of the deep eastern Mediterranean basins (Stratford et al., 2000). The well-developed OMZ located off the coast of Southern California today may have been more extensive in the past. Variations in climate affecting intensity of upwelling and primary production, coupled with tectonic activity altering the depth of basins and height of sills along the California coast, have generated a series of anoxia-facies organic-matter-rich sediments along the west coast of North America, beginning with the Monterey Shale and continuing through to the modern sediments deposited in the Santa Barbara and Santa Monica basins.

As shown by the modeling efforts of Hotinski et al., (2001) and Zhang et al., (2001), extensive deep ocean anoxia is difficult to achieve for extended periods of geologic time during the Phanerozoic when $p_{o_2}$ were at or near modern levels. Thus, while localized anoxic basins are common, special conditions are required to generate widespread, whole ocean anoxia such as observed in the Cretaceous. Deep-water formation in highly saline low-latitude waters was likely in the geologic past when climates were warmer and equator to pole heat gradients were
reduced. Low-latitude deep-water formation has a significant effect on deep-water oxygenation, not entirely due to the lower O₂ solubility in warmer waters, but also the increased efficiency of nutrient use and recycling in low-latitude surface waters (Herbert and Sarmiento, 1991). If phytoplankton were 100% efficient at using and recycling nutrients, even with modern high-latitude modes of cold deep-water formation, the deep oceans would likely become anoxic.

8.11.6.4.3 Numerical models of Phanerozoic oxygen concentration

Although photosynthesis is the ultimate source of O₂ to the atmosphere, in reality photosynthesis and aerobic respiration rates are very closely coupled. If they were not, major imbalances in atmospheric CO₂, O₂, and carbon isotopes would result. Only a small fraction of primary production (from photosynthesis) escapes respiration in the water column or sediment to become buried in deep sediments and ultimately sedimentary rocks. This flux of buried organic matter is in effect “net photosynthesis”, or total photosynthesis minus respiration. Thus, while over timescales of days to months, dissolved and atmospheric O₂ may respond to relative rates of photosynthesis or respiration, on longer timescales it is burial of organic matter in sediments and ultimately sedimentary rocks. This process has been called “georespiration” by some authors (Keller and Bacon, 1998). It can be represented by Equation (6), the reverse of (5):

\[
\text{Weathering of organic matter from rocks:} \\
\text{O}_2 + \text{“CH}_2\text{O”} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (6)
\]

Both Equations (3) and (4) contain terms for addition and removal of O₂ from the atmosphere. Thus, if we can reconstruct the rates of burial and weathering of OM into/out of sedimentary rocks through time, we can begin to quantify sources and sinks for atmospheric O₂. The physical manifestation of this equation is the reaction of organic matter with O₂ during the weathering and erosion of sedimentary rocks. This is most clearly seen in the investigation of the changes in OM abundance and composition in weathering profiles developed on black shales (Petsch et al., 2000, 2001).

In addition to the C–O system, the coupled C–S–O system has a strong impact on atmospheric oxygen (Garrels and Lerman, 1984; Kump and Garrels, 1986; Holland, 1978, 1984). This is through the bacterial reduction of sulfate to sulfide using organic carbon substrates as electron donors. During bacterial sulfate reduction (BSR), OM is oxidized and sulfide is produced from sulfate. Thus, BSR provides a means of resupplying oxidized carbon to the “ocean + atmosphere” system without consuming O₂. The net reaction for BSR shows that for every 15 mol of OM consumed, 8 mol sulfate and 4 mol ferric-iron are also reduced to form 4 mol of pyrite (FeS₂):

\[
4 \text{Fe(OH)}_3 + 8 \text{SO}_4^{2-} + 15 \text{CH}_2\text{O} \rightarrow 4 \text{FeS}_2 + 15 \text{HCO}_3^- + 13 \text{H}_2\text{O} + (\text{OH})^- 
\]

Oxidation of sulfate using organic substrates as electron donors provides a means of restoring inorganic carbon to the ocean + atmosphere system without consuming free O₂. Every 4 mol of pyrite derived from BSR buried in sediments represents 15 mol of O₂ produced by photosynthesis to generate organic matter that will not be consumed through aerobic respiration. In effect, pyrite burial equates to net release of O₂ to the atmosphere, as shown by (8), obtained by the addition of Equation (7) to (5):

\[
4\text{Fe(OH)}_3 + 8\text{SO}_4^{2-} + 15\text{CH}_2\text{O} \\
\rightarrow 4\text{FeS}_2 + 15\text{HCO}_3^- + 13\text{H}_2\text{O} + (\text{OH})^- \\
+15\text{CO}_2 + 15\text{H}_2\text{O} \rightarrow 15\text{O}_2 + 15\text{“CH}_2\text{O”}
\]
Oxidative weathering of sedimentary sulfide minerals during exposure and erosion on the continents results in consumption of $O_2$ (Equation (8)):

$$4\text{Fe(OH)}_3 + 8\text{SO}_4^{2-} + 15\text{CO}_2 + 2\text{H}_2\text{O}$$
$$\rightarrow 4\text{FeS}_2 + 15\text{HCO}_3^- + (\text{OH})^- + 15\text{O}_2$$

Just as for the C–O geochemical system, if we can reconstruct the rates of burial and oxidative weathering of sedimentary sulfide minerals through geologic time, we can use these to estimate additional sources and sinks for atmospheric $O_2$ beyond organic matter burial and weathering.

In total, then, the general approach taken in modeling efforts of understanding Phanerozoic $O_2$ variability is to catalog the total sources and sinks for atmospheric $O_2$, render these in the form of a rate of change equation in a box model, and integrate the changing $O_2$ mass through time implied by changes in sources and sinks:

$$\frac{dM_{O_2}}{dt} = \sum F_{O_2} \text{ into the atmosphere}$$
$$- \sum F_{O_2} \text{ out of the atmosphere}$$
$$= F_{\text{burial of organic matter}}$$
$$+ (15/8) F_{\text{burial of pyrite}}$$
$$- F_{\text{weathering of organic matter}}$$
$$- (15/8) F_{\text{weathering of pyrite}}$$

One approach to estimate burial and weathering fluxes of organic matter and sedimentary sulfides through time uses changes in the relative abundance of various sedimentary rock types estimated over Phanerozoic time. Some sedimentary rocks are typically rich in both organic matter and pyrite. These are typically marine shales. In contrast, coal basin sediments contain much organic carbon, but very low amounts of sedimentary sulfides. Non-marine coarse-grained clastic sediments contain very little of either organic matter or sedimentary sulfides. Berner and Canfield (1989) simplified global sedimentation through time into one of three categories: marine shales + sandstone, coal basin sediments, and non-marine clastic sediments. Using rock abundance estimates derived from the data of Ronov and others (Budyko et al., 1987; Ronov, 1976), these authors estimated burial rates for organic matter and pyrite as a function of time for the past ~600 Myr (Figure 12). Weathering rates for sedimentary organic matter and pyrite were calculated as first order dependent on the total mass of sedimentary organic matter or pyrite, respectively. Although highly simplified, this model provided several new insights into global-scale coupling C–S–O geochemistry. First, the broad-scale features of Phanerozoic $O_2$ evolution were established. $O_2$ concentrations in the atmosphere were low in the early Paleozoic, rising to some elevated $p_{O_2}$ levels during the Carboniferous and Permian (probably to a concentration substantially greater than today’s 0.21 bar), and then falling through the Mesozoic and Cenozoic to more modern values. This model confirmed the suspicion that in contrast with the Precambrian, Phanerozoic $O_2$ evolution was a story of relative stability through time, with no great excursions in $p_{O_2}$. Second, by linking C–S–O cycles with sediments and specifically sedimentation rates, this model helped fortify the idea that a strong control on organic matter burial rates globally, and thus ultimately on release of $O_2$ to the atmosphere, may be rates of sedimentation in near-shore environments. These authors extended this idea to propose that the close linkage between sedimentation and erosion (i.e., the fact that global rates of sedimentation are matched nearly exactly to global rates of sediment production—in other words, erosion) may in fact be a stabilizing influence on atmospheric $O_2$ fluctuations. If higher sedimentation rates result in greater burial of organic matter and pyrite, and greater release of $O_2$ to the atmosphere, at the same time there will be greater rates of erosion on the continents, some of which will involve oxidative weathering of ancient organic matter and/or pyrite.

The other principal approach towards modeling the Phanerozoic evolution of atmospheric $O_2$ rests on the isotope systematics of the carbon and sulfur geochemical cycles. The significant isotope discriminations associated with biological fixation of CO$_2$ to generate biomass and with bacterial reduction of sulfate to sulfide have been mentioned several times previously in this chapter. Given a set of simplifications of the exogenic cycles of carbon, sulfur and oxygen, these isotopic discriminations and the isotopic composition of seawater through time ($\delta^{13}C$, $\delta^{34}S$) can be used to estimate global rates of burial and weathering of organic matter, sedimentary carbonates, pyrite, and evaporative sulfates (Figure 13).

(i) The first required simplification is that the total mass of exogenic carbon is constant through time (carbon in the oceans, atmosphere, and sedimentary rocks). This of course neglects inputs of carbon and sulfur from volcanic activity and metamorphic degassing, and outputs into the mantle at subduction zones. However, if these fluxes into and out of the exogenic cycle are small enough (or have no effect on bulk crustal carbon or sulfur isotopic composition), then this simplification may be acceptable.
Figure 12  Estimated organic carbon burial (a), pyrite sulfur burial (b), and atmospheric oxygen concentrations (c) through Phanerozoic time, derived from estimates of rock abundance and their relative organic carbon and sulfide content (source Berner and Canfield, 1989).
(ii) The second simplification is that the total mass of carbon and sulfur dissolved in seawater plus the small reservoir of atmospheric carbon and sulfur gases remains constant through time. For carbon, this may be a realistic simplification. Dissolved inorganic carbon in seawater is strongly buffered by carbonate mineral precipitation and dissolution, and thus it is unlikely that extensive regions of the world ocean could have become significantly enriched or depleted in inorganic carbon during the geologic past. For sulfur, this assumption may not be completely accurate. Much of the interpretation of sulfur isotope records (with implications for atmospheric O$_2$ evolution) in the Precambrian depend on varying, but generally low dissolved sulfate concentrations. Unlike carbonate, there is no great buffering reaction maintaining stable sulfate concentrations in seawater. And while the sources of sulfate to seawater have likely varied only minimally, with changes in the sulfate flux to seawater increasing or decreasing smoothly through time as the result of broad-scale tectonic activity and changes in bulk continental weathering rates, removal of sulfate through excessive BSR or rapid evaporate formation may be much more episodic through time, possibly resulting in fairly extensive shifts in seawater sulfate concentration, even during the Phanerozoic. Nonetheless, using this simplification allows us to establish that for C–S–O geochemical models, total weathering fluxes for carbon and sulfur must equal total burial fluxes for carbon and sulfur, respectively.

Referring to Figure 14, we can see that these simplifications allow us to say that

$$\frac{dM_{oc}}{dt} = F_{wg} + F_{wc} - F_{bg} - F_{bc} = 0 \tag{11}$$

$$\frac{dM_{os}}{dt} = F_{ws} + F_{wp} - F_{bs} - F_{bp} = 0 \tag{12}$$

Figure 13  Globally averaged isotopic composition of carbonates ($\delta^{13}C$) and sulfates ($\delta^{34}S$) through Phanerozoic time (source Lindh, 1983).

Figure 14  The simplified geochemical cycles of carbon and sulfur, including burial and weathering of sedimentary carbonates, organic matter, evaporites, and sulfides. The relative fluxes of burial and weathering of organic matter and sulfide minerals plays a strong role in controlling the concentration of atmospheric O$_2$. 
The full rate equations for each reservoir mass in Figure 14 are as follows:

\[ \frac{dM_c}{dt} = F_{bc} - F_{wc} \]  
(13)

\[ \frac{dM_g}{dt} = F_{bg} - F_{wg} \]  
(14)

\[ \frac{dM_s}{dt} = F_{bs} - F_{ws} \]  
(15)

\[ \frac{dM_p}{dt} = F_{bp} - F_{wp} \]  
(16)

\[ \frac{dM_{O_2}}{dt} = F_{bg} - F_{wg} + 15/8(F_{bp} - F_{wp}) \]  
(17)

This system of equations has four unknowns: two burial fluxes and two weathering fluxes.

(iii) At this point, a third simplification of the carbon and sulfur systems is often applied to the weathering fluxes of sedimentary rocks. As a first approach, it is not unreasonable to guess that the rate of weathering of a given type of rock relates in some sense to the total mass of that rock type available on Earth’s surface. If that relation is assumed to be first order with respect to rock mass, an artificial weathering rate constant for each rock reservoir can be derived. Such constants have been derived by assuming that the weathering rate equation has the form \( F_i = k_i M_i \). If we can establish the mass of a sedimentary rock reservoir \( i \), and also the average global river flux to the oceans due to weathering of reservoir \( i \), then \( k_i \) can easily be calculated. For example, if the total global mass of carbonate in sedimentary rock is \( 5000 \times 10^{18} \) mol C, and annually there are \( 20 \times 10^{12} \) mol C discharged from rivers to the oceans from carbonate rock weathering, then \( k_{\text{carbonate}} \) becomes \( (20 \times 10^{12} \text{ mol C yr}^{-1}) / (5,000 \times 10^{18} \text{ mol C}) \), i.e., \( 4 \times 10^{-3} \text{ Myr}^{-1} \). These simple first-order weathering rate constants have been calculated for each sedimentary rock reservoir in the C−S−O cycle, derived entirely from estimated preanthropogenic carbon and sulfur fluxes from continental weathering. Lack of a true phenomenological relationship relating micromass-scale and outcrop-scale rock weathering reactions to regional- and global-scale carbon and sulfur fluxes remains one of the primary weaknesses limiting the accuracy of numerical models of the coupled C−S−O geochronal cycles.

If weathering fluxes from eroding sedimentary rocks are independently established, such as through use of mass-dependent weathering fluxes, then all of the weathering fluxes in our system of equations above become effectively known. This leaves only the burial fluxes as unknowns in solving the evolution of the C−S−O system.

The exact isotope discrimination that occurs during photosynthesis and during BSR is dependent on many factors. For carbon, these include cell growth rate, geometry and nutrient availability (Rau et al., 1989, 1992), CO2 availability species-specific effects, modes of CO2 sequestration (i.e., C3, C4, and CAM plants). For sulfur, these can include species-specific effects, the degree of closed-system behavior and sulfate concentration, sulfur oxidation and disproportionation. However, as a simplification in geological modeling of the C−S−O cycles, variability in carbon and sulfur isotopic fractionation is limited. In the simplest case, fractionations are constant through all time for all environments. As a result, for example, the isotopic composition of organic matter buried at a given time is set at a constant 25‰ depletion relative to seawater dissolved carbonate at that time, and pyrite isotopic composition is set at a constant 35‰ depletion relative to seawater sulfate. Of course, in reality, \( \alpha_c \) and \( \alpha_s \) (the isotopic discriminations assigned between inorganic–organic carbon and sulfate–sulfide, respectively) vary greatly in both time and space. Regardless of how \( \alpha_c \) and \( \alpha_s \) are set, however, once fractionations have been defined, the mass balance equations given in (13)−(17) above can be supplemented with isotope mass balances as well.

Based on the first simplification listed above, the exogenic cycles of carbon and sulfur are regarded as closed systems. As such, the bulk isotopic composition of average exogenic carbon and sulfur do not vary through time. We can write a rate equation for the rate of change in (mass × isotopic composition) of each reservoir in Figure 14 to reflect this isotope mass balance. For example:

\[ \frac{d(\delta_{oc}M_{oc})}{dr} = \frac{\delta_{oc}dM_{oc}}{dr} + M_{oc}d\delta_{oc} \]

\[ = \delta_{oc}F_{wc} + \delta_{oc}F_{wg} - \delta_{oc}F_{bg} - (\delta_{oc} - \alpha_c)F_{bg} \]

(18)

Using the simplification that \( dM_{oc}/dr = 0 \), Equation (18) reduces to an equation relating the organic matter burial flux \( F_{bg} \) in terms of other known entities:

\[ F_{bg} = \left( \frac{1}{\alpha_c} \right) \left[ M_{oc} \left( \frac{d\delta_{oc}}{dr} \right) + F_{wc}(\delta_{oc} - \delta_c) \right. \]

\[ + F_{wg}(\delta_{oc} - \delta_g) \right] \]

(19)

Using (11) above,

\[ F_{bc} = F_{wg} + F_{wc} - F_{bg} \]

(20)

A similar pair of equations can be written for the sulfur system:
as well as the rate of change in the mass of O₂. The relationships provide a useful guide for evaluating changes in organic matter and pyrite burial fluxes and the impact these have on atmospheric O₂, simply by examining the isotopic records of marine carbonate and sulfate. Early efforts to model the coupled C–S–O cycles yielded important information. The work of Garrels and Lerman (1984) showed that the exogenic C and S cycles can be treated as closed systems over at least Phanerozoic time, without exchange between sedimentary rocks and the deep “crust + mantle.” Furthermore, over timescales of millions of years, the carbon and sulfur cycles were seen to be closely coupled, with increase in sedimentary organic carbon mass matched by loss of sedimentary pyrite (and vice versa). Other models explored the dynamics of the C–S–O system. One important advance was promoted by Kump and Garrels (1986). In these authors’ model, a steady-state C–S–O system was generated and perturbed by artificially increasing rates of organic matter burial. These authors tracked the shifts in seawater carbon and sulfur isotopic composition that resulted, and compared these results with the true sedimentary record. Importantly, these authors recognized that although there is a general inverse relationship between seawater δ¹³C and δ³⁴S, the exact path along an isotope–isotope plot through time is not a straight line. Instead, because of the vastly different residence times of sulfate versus carbonate in seawater, any changes in the C–S–O system are first expressed through shifts in carbon isotopes, then sulfur isotopes (Figure 15). The authors also pointed out large-scale divisions in C–S iso¬te coupling through Phanerozoic time. In the Paleozoic, organic matter and pyrite burial were closely coupled (largely because the same types of depositional environment favor burial of marine organic matter and pyrite). During this time, seawater carbonate and sulfur isotopes co-varied positively, indicating concomitant increases (or decreases) in burial of organic matter and pyrite. During the late Paleozoic, Mesozoic, and Cenozoic, terrestrial depositional environments became important settings for burial of organic matter. Because pyrite formation and burial in terrestrial environments is extremely limited, organic matter and pyrite burial became decoupled at this time, and seawater carbonate and sulfur isotopes co-varied negatively, indicating close matching of increased sedimentary organic matter with decreased sedimentary pyrite (and vice versa), perhaps suggesting a net balance in O₂ production and consumption, and maintenance of nearly constant, equable pO₂ throughout much of the latter half of the Phanerozoic. The model of Berner (1987) introduced the concept of rapid recycling: the effort to numerically represent the observation that younger sedimentary rocks are more likely to be eroded and weathered than are...
older sedimentary rocks. Because young sedimentary rocks are likely to be isotopically distinct from older rocks (because they are recording any recent shifts in seawater carbon or sulfur isotopic composition), restoring that isotopically distinct carbon or sulfur more quickly back into seawater provides a type of negative feedback, dampening excessively large or small burial fluxes required for isotope mass balance. This negative feedback serves to reduce calculated fluctuations in organic matter and pyrite burial rates, which in turn reduce fluctuations in release of O$_2$ to the atmosphere. Results from this study also predict large increases in OM burial fluxes during the Permocarboniferous (300 Ma) above values present earlier in the Paleozoic. This increase, likely associated with production and burial of refractory terrigenous organic matter (less easily degraded than OM produced by marine organisms), led to elevated concentrations of O$_2$ ~ 300 Ma.

One flaw with efforts to model the evolution of Phanerozoic O$_2$ using the carbon and sulfur isotope records is that unreasonably large fluctuations in organic matter and pyrite burial fluxes (with coincident fluctuations in O$_2$ production rates) would result. Attempts to model the whole Phanerozoic generated unreasonably low and high O$_2$ concentrations for several times in the Phanerozoic (Lasaga, 1989), and applications of what seemed to be a realistic feedback based on reality (weathering rates of sedimentary organic matter and pyrite dependent on the concentration of O$_2$) were shown to actually become positive feedbacks in the isotope-driven C–S–O models (Berner, 1987; Lasaga, 1989).

Phosphorus is a key nutrient limiting primary productivity in many marine environments. If phosphorus supply is increased, primary production and perhaps organic matter burial will also increase. Degradation and remineralization of OM during transit from surface waters into sediments liberates phosphorus, but most of this is quickly scavenged by adsorption onto the surfaces of iron oxyhydroxides. However, work by Ingall and Jahnke (1994) and Van Cappellen and Ingall (1996) has shown that phosphorus recycling and release into seawater is enhanced under low O$_2$ or anoxic conditions. This relationship provides a strong negative feedback between primary production, bottom water anoxia, and atmospheric O$_2$. As atmospheric O$_2$ rises, phosphorus scavenging on ferric-iron is enhanced, phosphorus recycling back into surface waters is reduced, primary production rates are reduced, and O$_2$ declines. If O$_2$ concentrations were to fall, phosphorus scavenging onto ferric-iron would be inhibited, phosphorus recycling back into surface waters would be accelerated, fueling increased primary production and O$_2$ release to the atmosphere. Van Cappellen and Ingall (1996) applied these ideas to a mathematical model of the C–P–Fe–O cycle to show how O$_2$ concentrations could be stabilized by phosphorus recycling rates. Petsch and Berner (1998) expanded the model of Van Cappellen and Ingall (1996) to include the sulfur system, as well as carbon and sulfur isotope effects. This study examined the response of the C–S–O–Fe–P system, and in particular carbon and sulfur isotope ratios, to perturbation in global ocean overturn rates, changes in continental

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**Figure 15** Twenty-million-year average values of seawater $\delta^{34}$S plotted against concomitant carbonate $\delta^{13}$C for the last 700 Myr (source Kump and Garrels, 1986).
weathering, and shifts in the locus of organic matter burial from marine to terrestrial depocenters. Confirming the idea promoted by Kump and Garrels (1986), these authors showed that perturbations of the exogenic C–S–O cycle result in shifts in seawater carbon and sulfur isotopic composition similar in amplitude and duration to observed isotope excursions in the sedimentary record.

Other proposed feedbacks stabilizing the concentration of atmospheric O2 over Phanerzoic time include a fire-regulated PO4 feedback (Kump, 1988, 1989). Terrestrial primary production requires much less phosphate per mole CO2 fixed during photosynthesis than marine primary production. Thus, for a given supply of PO4, much more CO2 can be fixed as biomass and O2 released from photosynthesis on land versus in the oceans. If terrestrial production proceeds too rapidly, however, pO2 levels may rise slightly and lead to increased forest fires. Highly weatherable, PO4-rich ash would then be delivered through weathering and erosion to the oceans. Primary production in the oceans would lead to less CO2 fixed and O2 released per mole of PO4.

Hydrothermal reactions between seawater and young oceanic crust have been proposed as an influence on atmospheric O2 (Walker, 1986; Carpenter and Lohmann, 1999; Hansen and Wallmann, 2002). While specific periods of oceanic anoxia may be associated with accelerated hydrothermal release of mantle sulfide (i.e., the Mid-Cretaceous, see Sinninghe-Damsté and Köster, 1998), long-term sulfur and carbon isotope mass balance precludes substantial inputs of mantle sulfur to the Earth’s surface of a different net oxidation state and mass flux than what is subducted at convergent margins (Petsch, 1999; Holland, 2002).

One recent advance in the study of isotope-driven models of the coupled C–S–O cycles is re-evaluation of isotope fractionations. Hayes et al., (1999) published a compilation of the isotopic composition of inorganic and organic carbon for the past 800 Myr. One feature of this dual record is that because each round of photosynthesis results in 13C-depletion in cellular carbon relative to CO2, cells with high rates of photorespiration will contain more 13C-depleted CO2 and thus will produce more 13C-depleted organic matter.

In controlled-growth experiments using both higher plants and single-celled marine photosynthetic algae, a relationship between ambient O2 concentration and net isotope discrimination has been observed (Figure 16) (Berner et al., 2000; Beerling et al., 2002). The functional form of this relationship has been expressed in several ways. The simplest is to allow isotope discrimination to vary linearly with changing atmospheric O2 mass:

$$\Delta C = 25 \times (M_{O2}/38)$$

More complicated relationships have also been derived, based on curve-fitting the available experimental data on isotopic fractionation as a function of [O2]. O2-dependent isotopic fractionation during photosynthesis has provided the first mathematically robust isotope-driven model of the C–S–O cycle consistent with geologic observations (Beerling et al., 2000). Results of this model show that allowing isotope fractionation to respond to changes in ambient O2...
provides a strong negative feedback dampening excessive increases or decreases in organic matter burial rates. Rates of organic matter burial in this model are no longer simply dependent on seawater carbonate δ¹³C, but now also vary with 1/αc. As fractionation becomes greater (through elevated O₂), less of an increase in organic matter burial rates is required to achieve the observed increase in seawater δ¹³C than if αc were constant.

The same mathematical argument can be applied to sulfate–sulfide isotope fractionation during BSR. As O₂ concentrations increase, so does sulfur isotope fractionation, resulting in a strong negative feedback on pyrite burial rates. This is consistent with the broad-scale changes in sulfur isotope dynamics across the Proterozoic, reflecting a large increase in Δ³⁴S (between sulfate and sulfide) when atmospheric O₂ concentrations were great enough to facilitate bacterial sulfide oxidation and sulfur disproportionation. Perhaps during the Phanerozoic, when O₂ concentrations were greater, sulfur recycling (sulfate to sulfide through BSR, sulfur oxidation, and sulfur disproportionation) was increased, resulting in greater net isotopic distance between sulfate and sulfide. Another means of changing net sulfur isotope discrimination in response to O₂ may be the distribution of reduced sulfur between sulfide minerals and organic matter-associated sulfides. Work by Werne et al., 2000, 2003) has shown that organic sulfur is consistently ~10 % enriched in ³⁴S relative to associated pyrite. This is believed to result from different times and locations of organic sulfur versus pyrite formation. While pyrite may form in shallow sediments or even anoxic portions of the water column, reflecting extreme sulfur isotope depletion due to several cycles of BSR, sulfide oxidation and sulfur disproportionation, organic matter is sulfurized within the sediments. Closed, or nearly closed, system behavior of BSR in the sediments results in late-stage sulfide (the source of sulfur in sedimentary organic matter) to be more enriched compared with pyrite in the same sediments. It is known that burial of sulfide as organic sulfur is facilitated in low O₂ or anoxic waters. If lower atmospheric O₂ in the past encouraged development of more extensive anoxic basins and increased burial of sulfide as organic sulfur instead of pyrite, the 10‰ offset between pyrite and organic sulfur would become effectively a change in net sulfur fractionation in response to O₂.

Applying these newly recognized modifications of carbon and sulfur isotope discrimination in response to changing O₂ availability has allowed development of new numerical models of the evolution of the coupled C–S–O systems and variability of Phanerozoic atmospheric O₂ concentration (Figure 17).

8.11.7 CONCLUSIONS

Molecular oxygen is generated and consumed by a wide range of processes. The net cycling of O₂ is influenced by physical, chemical, and most importantly, biological processes acting on and beneath the Earth’s surface. The exact distribution of O₂ concentrations depends on the specific interplay of these processes in time and space. Large inroads have been made towards
understanding the processes that control the concentration of atmospheric O2, especially regarding O2 as a component of coupled biogeochemical cycles of many elements, including carbon, sulfur, nitrogen, phosphorus, iron, and others.

Earth’s modern oxygenated atmosphere is the product of over four billion years of its history (Figure 18). The early anoxic atmosphere was slowly oxidized (although not oxygenated) as the result of slow H2 escape. Evolution of oxygenic photosynthesis accelerated the oxidation of Earth’s crust and atmosphere, such that by ~2.2 Ga a small but significant concentration of O2 was likely present in Earth’s atmosphere. Limited primary production and oxygen production compared with the flux of reduced volcanic gases maintained this low pO2 atmosphere for over one billion years until the Neoproterozoic. Rapid oscillations in Earth’s carbon and sulfur cycles associated with global Snowball glaciation may also have expression in a return to atmospheric anoxia at this time, but subsequent to the late Proterozoic isotope excursions, oxygenation of the atmosphere to near-modern concentrations developed such that by the Precambrian–Cambrian boundary, O2 concentrations were high enough to support widespread skeletonized metazoans. Phanerozoic seawater and atmospheric O2 concentrations have fluctuated in response to tectonic forcings, generating regional-scale anoxia in ocean basins at certain times when biological productivity and ocean circulation facilitate anoxic conditions, but in the atmosphere, O2 concentrations have remained within ~0.05–0.35 bar pO2 for the past ~600 Myr.

Several outstanding unresolved gaps in our understanding remain, in spite of a well-developed understanding of the general features of the evolution of atmospheric O2 through time. These gaps represent potentially meaningful directions for future research, including:

(i) assessing the global importance of mineral oxidation as a mechanism of O2 consumption;
(ii) the flux of reduced gases from volcanoes, metamorphism, and diffuse mantle/lithosphere degassing;
(iii) the true dependence of organic matter oxidation on availability of O2, in light of the great abundance of microaerophilic and anaerobic microorganisms utilizing carbon respiration as a metabolic pathway, carbon isotopic evidence suggesting continual and essentially constant organic matter oxidation as part of the sedimentary rock cycle during the entire past four billion years, and the inefficiency of organic matter oxidation during continental weathering;
(iv) stasis in the oxygenation of the atmosphere during the Proterozoic;
(v) contrasting biochemical, fossil, and molecular evidence for the antiquity of the innovation of oxygenic photosynthesis; and

\[ \text{Conclusions} \]

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**Figure 18** Composite estimate of the evolution of atmospheric oxygen through 4.5 Gyr of Earth’s history. Irreversible oxidation of the Earth resulted from CH4 photolysis and hydrogen escape during early Earth’s history. Evolution of oxygenic photosynthesis preceded substantial oxygenation of the atmosphere by several hundred million years. Relative stasis in atmospheric pO2 typified much of the Proterozoic, with a possible pulse of oxygenation associated with formation of the Rodinian supercontinent in the Late Mesoproterozoic, and possible return to anoxia associated with snowball glaciation in the Neoproterozoic (sources Catling et al., 2001; Kasting, 1992; Rye and Holland, 1998; Petsch, 2000; Berner et al., 2000).
(vi) evaluating the relative strength of biological productivity versus chemical evolution of the Earth’s crust and mantle in controlling the early stages of oxygenation of the atmosphere.

Thus, study of the global biogeochemical cycle of oxygen, the component of our atmosphere integral and crucial for life as we know it, remains a fruitful direction for Earth science research.

REFERENCES


