

Web Supplement 8.6

8.6 THE INFLUENCE OF ORGANIC MATTER ON THE GLOBAL BIOGEOCHEMICAL OXYGEN CYCLE

The marine cycle of organic matter has played an important role in the development and stabilization of atmospheric O_2 levels and, hence, seawater concentrations. Climate change has the potential to overwhelm these stabilizing loops. Evidence already supports a decline oxygen concentrations arising from warming of the oceans. This is likely to have profound consequences on fish distributions. Paleooceanographic records indicate that the global ocean has become anoxic for extended periods. These ocean anoxic events coincide with mass extinction events and periods of rapid climate change. Can we expect this to happen in the future? In this section, we consider how Earth's atmosphere became oxic and how marine plankton and the cycling of organic matter have contributed to setting and stabilizing atmospheric O_2 and seawater O_2 concentrations. In turn, the development of an oxic atmosphere has had a profound effect in directing evolutionary trajectories of marine microbes and animals (as well as those on land). A redox history of Earth is presented in Figure W8.1 and discussed in the following section.

8.6.1 Redox Conditions in the Precambrian Eon

The presence of free oxygen (O_2) in Earth's atmosphere is a unique feature among the planets of our solar system. Another of Earth's unique features, life, is largely responsible for accumulation of this O_2 . The planet's atmosphere was not always O_2 -rich. During the early stages of Earth's formation, all of its atmospheric gases were derived from volcanic emissions or the degassing of volcanic rocks. These atmospheric gases were mostly reduced species, e.g., N_2 , NH_3 , H_2 , and CH_4 . Halides were emitted as acidic species, including HCl and HF. As the early Earth cooled, its interior differentiated into layers with the densest materials, e.g., metallic iron, forming the core. Because this iron is strongly reducing, its concentration in the core led to a decline in the reducing nature of the mantle and, hence, in the volcanic gases released to the atmosphere. This

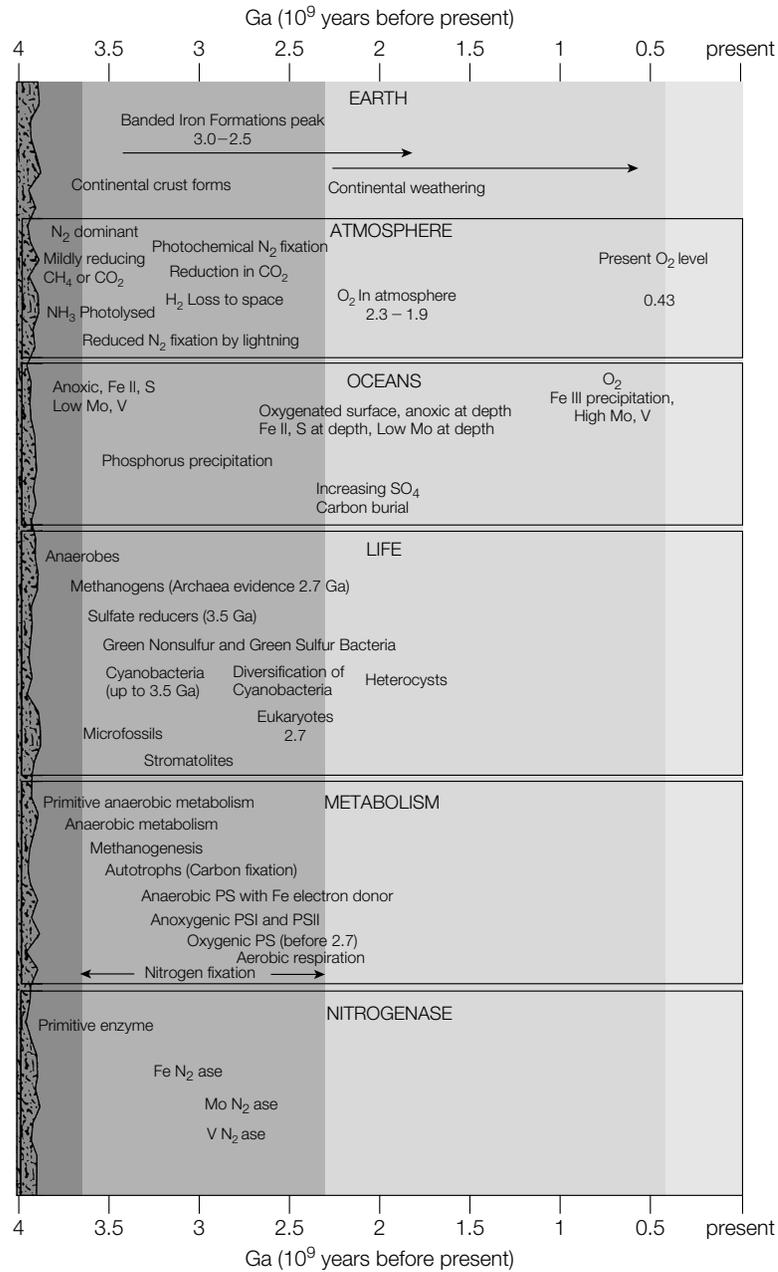


FIGURE W8.1

Major events in the evolution of the Earth, the atmosphere, oceans, and life. Meteor bombardments ended 3.8 bybp, allowing the planet to become habitable. *Source:* From Zehr, J. P., M. J. Church, and P. H. Moisaner (2006). Diversity, distribution and biogeochemical significance of nitrogen-fixing microorganisms in anoxic and suboxic ocean environments, pp. 337–369 in *Past and Present Water Column Anoxia*, L. N. Neretin, ed. Springer-Verlag.

process is thought to have occurred early in Earth's history, causing the volcanic gas composition to be dominated by H₂O, CO₂, N₂ with traces of H₂, H₂S, SO₂, and CO.

Before life evolved on the planet, O₂ was produced solely through the process of photodissociation,



This reaction occurs in the upper atmosphere when ultraviolet radiation from the sun strikes water molecules. The rate of this photodissociation has always been slow. The O₂ produced from photodissociation did not accumulate in the atmosphere as it was thermodynamically unstable, reacting either with H₂(g) or with the reduced chemicals that composed the fresh volcanic rocks and gases. One likely product of this crustal oxidation was CO₂.

Because of its low molecular weight, H₂(g) is continually escaping from the outer atmosphere into space. On the early Earth, the major sources of H₂ were volcanic emission, photolysis of water (Eq. W8.1), and the photolytic oxidation of methane to CO₂. Thus, the escape of H₂ to outer space caused the oxidation state of the crustal-ocean-atmosphere factory to increase over time. By 3.5 bypb, the mantle seems to have reached its current oxidation state such that volcanic gases now contain SO₂, CO₂, and CO. The ensuing buildup of atmospheric CO₂ and CH₄ from volcanic and biogenic sources acted to increase surface temperatures. Because CO₂ generates acid when it dissolves in water, natural waters became acidic, enhancing chemical weathering of the crust and, hence, the delivery of important solutes to the ocean.

The First Life Forms: Hydrogen and Iron Oxidizers

The isotopic composition of carbon in ancient rocks and fossilized remains indicated that life was present on Earth by 3.8 bypb. The early life forms were probably bacteria and/or archaea. The first metabolic strategies exploited free energy differences between reduced and oxidized species: for example, the reaction of H₂ with CO₂ to form methane. Modern-day methanogens exhibit characteristics that suggest they are descendants of these early life forms, because they are strict anaerobes and tend to be thermophilic. The early methanogens would have lowered the atmospheric levels of H₂ and CO₂ and increased CH₄ levels. These changes have potent consequences for weathering and climate control, because CH₄ is a more powerful greenhouse gas than CO₂ and CO₂ is a very effective weathering agent because it forms acid upon hydrolysis. Thus, bioengineering of the crustal-ocean-atmosphere factory probably commenced with the very first life forms. Other types of early chemolithotrophy were likely based on the oxidation of Fe(II), thereby reducing CO₂ to organic matter and converting the iron to an insoluble oxide. The remains of this process are seen in the ancient massive banded ironstone deposits found worldwide.

Anoxygenic and Oxygenic Photosynthesis

Anoxygenic photosynthesis was another likely early metabolic strategy due to the large energy benefit associated with using highly reduced species such as H_2 , H_2S , and elemental S as electron donors. If Fe(II) also served as an electron donor, anoxygenic photosynthesis could have played a role in creation of the banded ironstone formations. The eventual depletion of these reduced chemicals stimulated evolution of oxygenic photosynthesizers that use water as an electron donor. The first oxygenic photoautolithotrophs to evolve were the cyanobacteria. This seems to have occurred as early as 3.7 bybp. As the H_2 escaped to outer space and oxygenic photosynthesis came into being, the atmosphere partial pressure of O_2 began to rise. A partial pressure of 10^{-6} atm was attained by 3.6 bybp as illustrated in Figure W8.2. The pace of this rise was dictated by the relative rates of O_2 production and consumption. Production increased as oxygenic photosynthesizers increased in numbers and consumption declined as the primordial reduced rocks and gases became permanently oxidized. By 2.5 bybp, the P_{O_2} had reached 10^{-5} atm. This gradual buildup of atmospheric O_2 also enabled the photochemical production of O_3 . Ozone adsorbs UV radiation that would otherwise cause damage to DNA. Hence, the buildup of a stratospheric O_3 layer was critical to the continued development of life.

A rapid increase in atmospheric O_2 occurred around 2.3 bybp, bringing the partial pressure up to 10^{-2} atm. Three causes for this rapid rise have been proposed: (1) enough

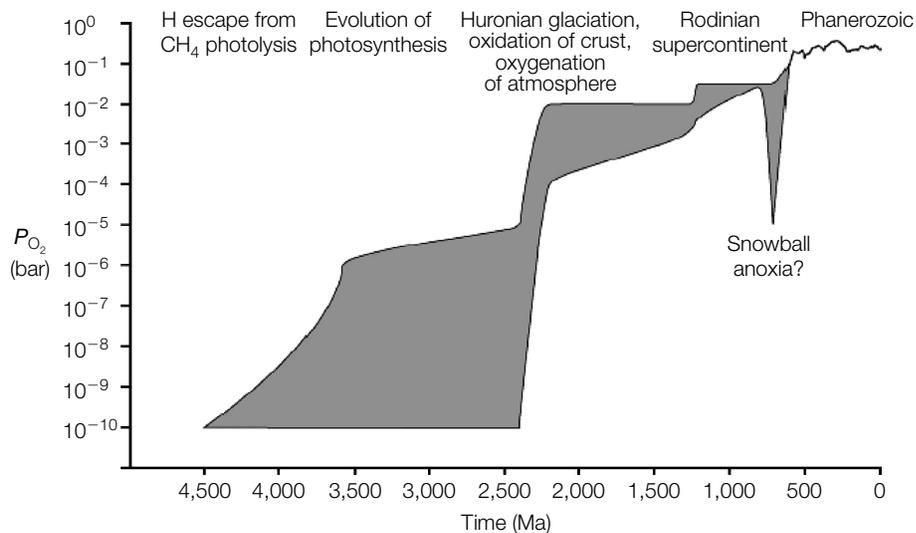


FIGURE W8.2

Composite estimate of the evolution of atmospheric oxygen through 4.5 billion years of Earth's history. *Source:* From Petsch, S. T. (2004). The global oxygen cycle. In *Treatise in Geochemistry*, H. Holland and K. Turekian, eds, pp. 515–555. Academic Press, Orlando, FL.

H₂ had escaped to outer space for the oxidation state of the crustal-ocean-atmosphere factory to favor the accumulation of atmospheric O₂, (2) the rate of photosynthetic O₂ production increased, and (3) a new O₂ source developed. The last is thought to be the burial of organic matter in marine sediments. If organic matter is preserved via burial in sediments, it cannot consume O₂. Thus, the products of photosynthesis, O₂ and organic matter, need to be physically separated to prevent their back reaction via aerobic respiration of organic matter. This separation is now being achieved by concurrent burial of organic matter on the seafloor with retention of O₂ in the atmosphere. A small fraction of the O₂ is dissolved in the ocean.

Increased rates of photosynthesis are attributed to an accelerated nutrient supply from continental weathering supported by an increasing area of continental land. The accompanying formation of continental shelves would also have favored organic matter burial by providing shallow water depths, making a shorter trip for sinking POM and, hence, a greater likelihood of sedimentation. An important weathering product, called clay minerals, also assists in enhancing POM burial rates by forming mineral aggregates that shield organic matter from microbial attack.

At some point, the production of O₂ would have been sufficient to have oxidized all the atmospheric CH₄ and other reduced chemicals in the crustal rocks. In the case of the latter, sulfide minerals were oxidized to sulfate, which was then transported to the ocean via river runoff. Since the oceans were still quite hypoxic, this infusion of sulfate supported evolution of sulfate-reducing organisms. These microbes returned the sulfur back to sulfide, which in seawater would have formed precipitates with iron and manganese. The removal of dissolved iron from seawater is thought to have slowed photosynthesis because it is a critical component of the enzymes used by the cyanobacterial N₂ fixers. This put a cap on any further increase in P_{O₂}. Nevertheless, continuing photosynthesis led to a substantial reduction in the two major greenhouse gases, CO₂ (from photosynthetic uptake) and CH₄ (from oxidation by O₂). This is thought to have played an important role in causing the Earth to enter a period of global glaciation called a Snowball Earth. Several such snowball events have taken place over Earth's history. Other factors thought to be important in triggering these massive glaciations include (1) an increased rate of CO₂ uptake via crustal weathering caused by increased production of igneous rock through volcanism and (2) the periodic passage of the solar system through dense clouds of interstellar dust that absorb and reflect insolation. The impact of Snowball Earths on the marine carbon cycle is discussed in Chapter 25.4.2.

Atmospheric O₂ concentrations remained at 0.01 atm until 1.3 bybp, when another period of continent building seems to have again enhanced the rate of nutrient supply via runoff of terrestrial weathering products, leading to an increased burial of POM. The ensuing rise in oxygen brought P_{O₂} up to 0.03 atm. Under these redox conditions, sulfide oxidation is favored. Toward the end of the Precambrian eon, around 0.7 bybp, plate tectonics had shifted most of the land masses to low latitudes. This is thought to have caused another series of massive glacial events in which more than half of the planet was covered by ice for the next 200 million years. During these snowball

glaciations, the ocean became anoxic, probably because the ice prevented both the air-sea exchange of O₂ and POM burial. Photosynthesis was also probably slowed such that the rate of O₂ uptake by various oxidations (crust and volcanic gases) exceeded the rate of supply. The net result was a significant decline of atmospheric O₂ levels. Recovery from this Snowball Earth is attributed to an eventual buildup of the greenhouse gas, CO₂, from continuing volcanic emissions.

8.6.2 Redox Conditions in the Phanerozoic Eon

The third and final jump in P_{O_2} occurred between 0.6 to 0.5 bybp, bringing atmospheric concentrations close to modern-day levels. As with the other sudden jumps, the influence of plate tectonics on arranging continental land masses is thought to have played a role. Other likely influences include the evolution of lichens that enhanced continental weathering and, hence, the rates of supply of nutrient and clay minerals to the ocean. The presence of a highly oxidic atmosphere is considered to be the key environmental change that stimulated evolutionary development of multicellular lifeforms (metazoans). The subsequent evolution of zooplankton is thought to have contributed enhanced POM burial rates because they produce organic-rich and dense fecal pellets that sink rapidly, effectively protecting them from microbial degradation.

An important consequence of this final O₂ rise was an explosion in biological diversity leading the rapid development of the major groups within the animal kingdom (aerobic heterotrophs). This is the point in the sedimentary record where the fossil record becomes dominated by metazoans. This period, 543 mybp, is defined as the end of the Precambrian and the beginning of the Phanerozoic eon. The role of O₂ in stimulating this diversification is attributed to an increase in biochemical options for genomic and metabolic complexity, which in turn enabled evolution of a great variety of strategies for improving survival. The latter include mechanisms for protection against predation, for winning in competitions for limited resources, and for reproductive success.

During the Phanerozoic, atmospheric oxygen levels have generally remained constant at around 0.21 atm. The present set point and its great stability are probably the result of negative feedback loops that operate over time scales on the order of millions of years. These loops are thought to involve the processes that constitute the biogeochemical cycle of O₂, namely biogenic POM production, remineralization and burial in marine sediments. The present-day O₂ cycle is shown in Figure W8.3.

Stabilizing Negative Feedbacks

For any set of processes to function as this feedback loop, they must be collectively dependent on atmospheric O₂ levels and vice versa. As shown in Figure W8.3, respiration of all the organic matter in the biosphere including the soils and detritus would lower the atmospheric O₂ level by only

$$\frac{191.4 \times 10^{15} \text{ mol}}{37,000 \times 10^{15} \text{ mol}} \times 100 = 0.5\%. \quad (\text{W8.2})$$

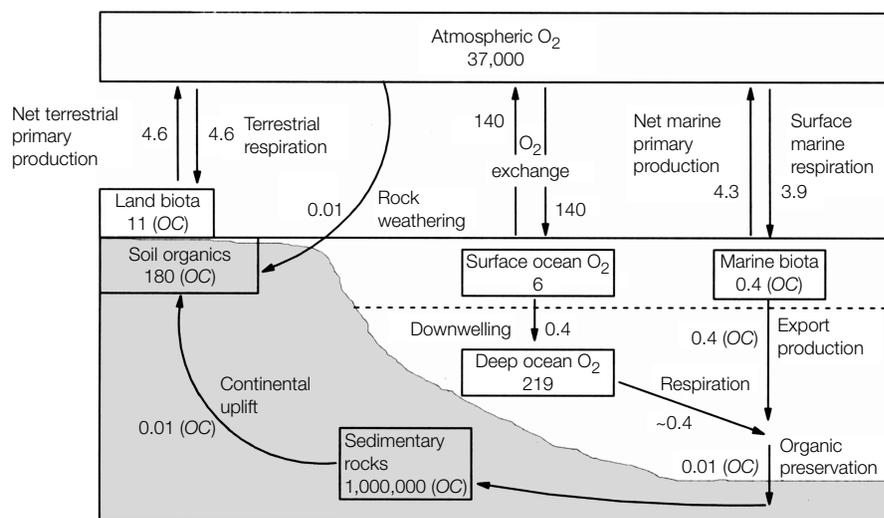


FIGURE W8.3

The global cycle of molecular oxygen. All reservoirs and fluxes (per year) are in units of 10¹⁵ mol O₂. (OC) indicates that the molar O₂ equivalent occurs in the form of organic carbon, whose flux directions are inverted from their O₂ counterpart. *Source:* From Hedges, J. I. (2002) Sedimentary organic matter preservation and atmospheric O₂ regulation, pp. 105–123 in *Chemistry of Marine Water and Sediments*, A. Gianguzza, E. Pelizzetti, and S. Sammartano, eds. Springer Verlag.

Thus, this reservoir is not a likely component of the O₂ feedback loop because it is too small to have a significant impact. The igneous rocks contain reduced chemicals, such as Fe(II). Uplift and exposure to atmospheric O₂ oxidizes these rocks, but is thought to be an unimportant O₂ sink because the production rate of new igneous rock is presently slow and the oxidation state of the mantle has remained relatively constant over the past 4 billion years. In contrast, oxidation of sedimentary rocks, such as shale and pyrite, have been the largest crustal weathering sink for atmospheric O₂ during the Phanerozoic. Shales contain reduced carbon, and pyrite contains reduced iron and sulfur. These rocks are rapidly oxidized upon uplift and exposure to atmospheric O₂. In other words, their oxidation rates are presently limited by the rate of uplift and erosion rather than atmospheric O₂ levels. Changes in the rates of various processes associated with plate tectonics, such as continent building and volcanism, have the potential to impact atmospheric O₂ levels by affecting crustal weathering rates, but do not serve as a stabilizing feedback mechanism. Furthermore, the relative stability of atmospheric O₂ levels over most of the Phanerozoic indicates that the stabilizing mechanism operates over fairly short time scales, e.g., millions of years.

The mechanism that stabilizes the atmospheric O₂ level is most likely one that regulates processes involved in net O₂ production, such as the burial of POM. As noted earlier, the greater the amount of POM buried, the higher the atmospheric O₂ levels and vice versa. This relationship suggests that the amount of POM buried should be

inversely related to the atmospheric O_2 level. This process has the potential to act as a stabilizing mechanism only if the amount of POM buried is large enough to have a significant impact on the amount of O_2 in the atmosphere.

The continental margins are the only locations where the amount of buried sedimentary organic carbon is large enough to account for a substantial amount of O_2 production. These sediments have relatively high carbon contents because they lie in areas where primary productivity is unusually high. This ensures a large flux of POM to the sediments. In addition, a greater percentage of POM is preserved in these sediments because (1) high sedimentation rates cause the POM to be rapidly buried and preserved from oxidation, (2) the POM takes less time to reach the seafloor due to the relatively shallow water depths reducing the time over which it can become oxidized, (3) the large POM flux creates oxygen-deficient conditions under which remineralization rates are relatively slow, and (4) the nearshore is close to the terrestrial source of clay minerals that form aggregates with organic matter, protecting it from oxidation.

The negative feedback thought to counter an atmospheric O_2 decline is illustrated by the following scenario. A decreased atmospheric partial pressure of O_2 eventually leads to lowered seawater concentrations of O_2 . This increases the rate of POM burial because remineralization is less efficient under suboxic conditions, leading to a larger rate of O_2 supply. A further indirect control is thought to be exerted through control of phosphorus burial in marine sediments by O_2 . This burial is most efficient under oxic conditions because it involves the sorption of phosphate onto particulate iron oxyhydroxides. Under suboxic condition this binding is less efficient, causing less phosphorus to be buried. The increased availability of phosphorus fertilizes the phytoplankton, thereby increasing photosynthetic production of O_2 ; enabling atmospheric levels to rise. This rise is kept in check by a negative feedback that involves increased oxidation rates of POM with increasing O_2 levels.

Another negative feedback is thought to involve an increased tendency toward forest fires at high O_2 . Fires consume O_2 and act to lower the partial pressure of O_2 . Another possible indirect mechanism invokes a fire-driven ecological shift to grasslands that are less efficient at weathering than forests. This should lead to a lower terrestrial input of phosphorus to the ocean and, hence, less photosynthesis and POM burial. Finally, photosynthesis is inhibited by high partial O_2 pressures due to the inactivation of an important enzyme via reaction with O_2 .

Some of the redox stabilization of the crustal-ocean-atmosphere factory is also provided by the global biogeochemical sulfur cycle. Sulfate reduction serves as a net source of O_2 through the burial of sulfide, primarily in the form of pyrite. Changes in the burial rate of pyrite thus serve the same function as changes in the burial rate of POM. As noted earlier, uplift and exposure of biogenic pyrite and shale to O_2 leads to oxidative weathering of sedimentary rocks, which has been the largest crustal O_2 sink in the Phanerozoic. (Shale is produced from the lithification of organic-rich marine sediments.)

If the burial of POM stabilizes the atmospheric O_2 level, the set point of P_{O_2} must be determined by factors that influence the production and destruction of POM. These include any processes that affect (1) the nutrient content of seawater, (2) the elemental composition of the plankton, (3) the solubility of O_2 , and (4) the exposure and

weathering of formerly buried POM. These processes are, in turn, at the mercy of plate tectonics and astronomical events, such as the Milankovitch cycles that affect insolation. It is certainly fortunate that several negative feedback loops seem to stabilize P_{O_2} .

The relative importance of the production of marine POM in determining the current set point is given by the following observation. The concentration of nutrients in a parcel of newly created deep water is currently such that if they were to be converted into POM by phytoplankton, the respiration of this amount of reduced carbon would consume all the dissolved O_2 in that water. This O_2 concentration is set by equilibration with the atmosphere. This suggests that the atmospheric O_2 content is a result of marine POM formation and burial, which are largely controlled by nutrient availability. The turnover time of O_2 with respect to burial of carbon in marine sediments is:

$$\frac{\text{Total amount of atmospheric } O_2}{\text{Burial rate of sedimentary organic matter in the crust}} = \frac{37,000 \times 10^{15} \text{ mol } O_2}{0.01 \times 10^{15} \text{ mol } O_2/\text{y}} \approx 3.7 \text{ million years} \quad (\text{W8.3})$$

Thus, any feedback that relies on this process operates on time scales of millions of years, making short-lived perturbations possible.

Oxygen Catastrophes in the Phanerozoic

An important exception to the overall stability of atmospheric P_{O_2} during the Phanerozoic occurred during the Carboniferous and Permian periods about 300 mybp. As shown in Figure W8.4, O_2 levels rose to nearly 0.3 atm. The reason for this is likely the

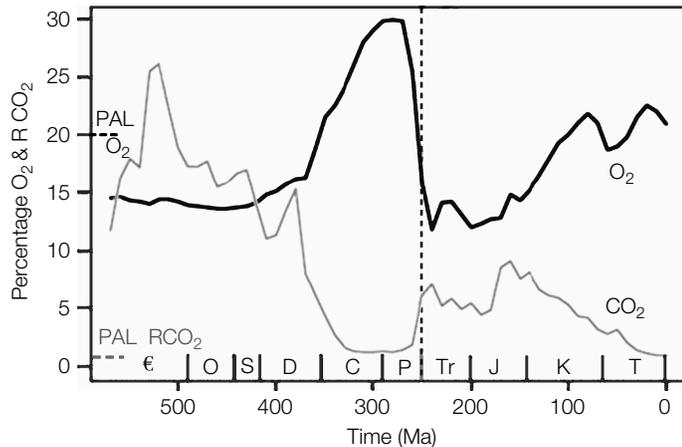


FIGURE W8.4

Percent atmospheric O_2 over time and the concentration of atmospheric CO_2 , relative to present day atmospheric level (PAL RCO_2). Dashed line marks mass extinction event at the Permian-Triassic Boundary. PAL O_2 = present-day atmospheric level (%) of O_2 . Source: From Huey, R. B., and P. D. Ward (2005). *Science* 308 (5720), 398–401.

burial of huge amounts of POM in freshwater swamps. In contrast, little terrestrial organic matter burial is occurring in the present day due to nearly complete oxidation of soils. The surge in POM deposition during the Permo-Carboniferous is thought to have been caused by an increase in the extent of freshwater swamps. This was a consequence of a favorable arrangement of land masses and rapid changes in sea level that acted to isolate sections of the ocean that eventually filled in and became shallow aquatic environments. During this time large woody plants colonized the land. These plants use cellulose for structural strength. Cellulose is highly resistant to microbial decomposition and, hence, lead to an enhanced burial efficiency of swamp POM (peat). These organic-rich deposits have since been transformed into black shales and coal.

The occurrence of high P_{O_2} during the Permo-Carboniferous period is thought to have resulted in an evolutionary increase in body size for many arthropods and some amphibians. The upper limit to atmospheric levels was probably provided by an increased tendency for forest fires and through the inactivation of a key photosynthetic enzyme. Nevertheless, the Permian period ended with the largest mass extinction event that has yet occurred on planet Earth. The paleoceanographic record also indicates that the oceans became anoxic, the P_{CO_2} was very high, and the climate was very warm. An increase in volcanism is thought to have lead to increased emissions of the greenhouse gases CO_2 and H_2O . The increased methane is attributed to the melting of methane ice in marine sediments. As the methane bubbled up through the ocean, most was oxidized by oxygen-utilizing methanotrophs, causing the entire ocean to become anoxic. The remainder escaped into the atmosphere where its oxidation is thought to have to caused a decline in P_{O_2} to 0.16atm. As shown in Figure W8.4, recovery from all these perturbations took close to 20 million years because of the severe degree of disruption to marine and terrestrial life and, hence, to the global biogeochemical cycles of carbon, oxygen, and nutrients.

Several other ocean anoxic events (OAEs) have occurred during the Phanerozoic, most recently in the Cretaceous (Figure W8.5). The causes of most of these OAEs are not known, but most are associated with perturbations in the global carbon cycle. These perturbations seem to have been caused by increased rates of CO_2 supply from tectonism and/or changes in nutrient and micronutrient supply to the oceans. Some OAEs appear to have been quite widespread, if not global in nature.

8.6.3 Can Humans Cause an Oxygen Catastrophe?

Some evidence exists for growing anthropogenic impacts on the global O_2 cycle. First, burning of fossil fuels seems to be leading to a decline in P_{O_2} (Figure W8.6). This is somewhat surprising given that fossil fuel carbon reservoir (in molar O_2 equivalents) represents only 2% of the atmospheric O_2 reservoir. A second line of evidence has established that the oceanic O_2 reservoir seems to be declining at a rate of $0.03 \pm 0.04 \times 10^{15}$ mol O_2 /y. This is thought to be caused by global warming, which lowers

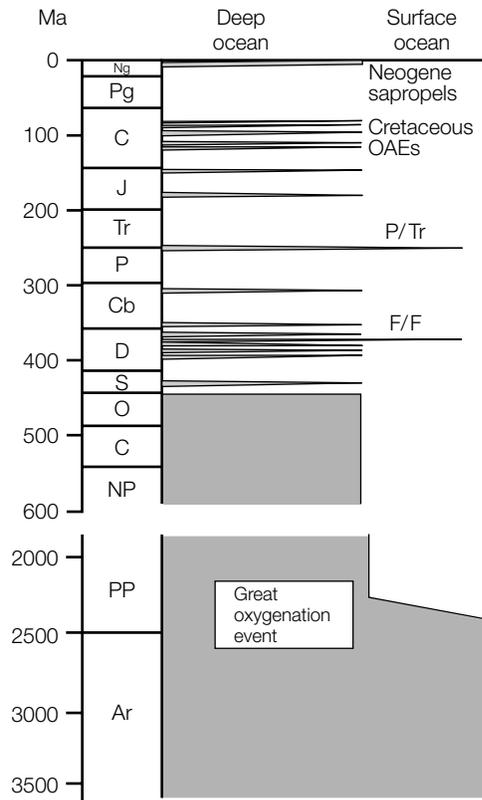


FIGURE W8.5

The temporal record of widespread anoxic conditions (gray shaded areas) in the shallow and deep ocean. P/Tr = Permian-Triassic and F/F = Famennian-Frasnian boundaries. *Source:* From Strauss, H. (2006). Anoxia through time, pp. 3–20 in *Past and Present Water Column Anoxia*, L. N. Neretin, ed. Springer Verlag.

gas solubility and increases the stratification of ocean. The latter slows the rate of return of deep water to the sea surface and, hence, the rate at which nutrients remineralized in these waters are returned to the euphotic zone, thereby reducing future rates of POM production and remineralization. We do not know enough about the feedbacks in the crustal-ocean-atmosphere factory to determine whether future climate change could lead to an OAE, but negative effects on oceanic fish populations are already being detected. As mentioned earlier, the extent and frequency of coastal hypoxia is increasing at low and mid-latitudes because of nutrient loading in terrestrial runoff. This is also putting stress on coastal fish populations.

