

The Oceans

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INTRODUCTION

The Earth's waters constitute its hydrosphere. Only small quantities of freshwater contribute to the total; most water resides in the sea. In this chapter we examine the biogeochemistry of seawater and the contributions that oceans make to global biogeochemical cycles. We begin

with a brief overview of the circulation of the oceans and the mass balance of the major elements that contribute to the salinity of seawater. Then we examine net primary productivity (NPP) in the surface waters and the fate of organic carbon in the sea. Net primary productivity in the oceans is related to the availability of essential nutrient elements, particularly nitrogen and phosphorus. Conversely, biotic processes strongly affect the chemistry of many elements in seawater, including N, P, Si, and a variety of trace metals. We examine the biogeochemical cycles of essential elements in the sea and the processes that lead to the exchange of gaseous components between the oceans and the atmosphere.

OCEAN CIRCULATION

In [Chapter 3](#) we saw that the circulation of the atmosphere is driven by the receipt of solar energy which heats the atmosphere from the bottom, creating instability in the air column. Unlike the atmosphere, the oceans are heated from the top. Because warm water is less dense than cooler water, the receipt of solar energy conveys stability to the water column, preventing exchange between warm surface waters and cold deep waters over much of the ocean (Ledwell et al. 1993).

Global Patterns

At the surface, seawater is relatively well mixed by the wind (Thorpe 1985, Archer 1995) and by local changes in density that arise when the surface waters cool or increase in salinity. The mixed layers of the surface ocean range from 75 to 200 m in depth with a mean temperature of about 18°C. The surface temperature in some tropical seas may reach 30°C. The zone of rapid increase in density between the warm surface waters and the cold deep waters is known as the *pycnocline*. It roughly parallels the gradient in temperature, which is known as the thermocline ([Chapter 8](#)). The oceans' deep waters contain about 95% of the total volume with a mean temperature of 3°C.

Prevailing winds ([Chapter 3](#)) lead to the formation of surface currents in the oceans ([Figure 9.1](#)). These surface currents are now mapped at high resolution using the TOPEX/Poseidon satellite, which monitors small changes in the relative height of sea level (Ducet et al. 2000). Global wind patterns drive large gyres, circular rotating currents, that are observed at the surface of all ocean basins. These winds cause surface waters to converge in some areas and diverge in others. The horizontal pressure gradients that result from these areas of convergence and divergence drive motions in the ocean beneath the wind-driven flow at the surface.

These ocean currents are impacted by the Earth's rotation such that they circulate anticyclonically (clockwise in the Northern Hemisphere) around low-pressure centers (where surface waters have diverged). In the Northern Hemisphere, the currents are deflected to the right by the Coriolis force, which is observed when fluid motions occur in a rotating frame (see [Figure 3.3](#)). Thus, the Gulf Stream crosses the North Atlantic and delivers warm waters to northern Europe. In the Southern Hemisphere, the gyres move in a counter-clockwise direction and are deflected to the left.

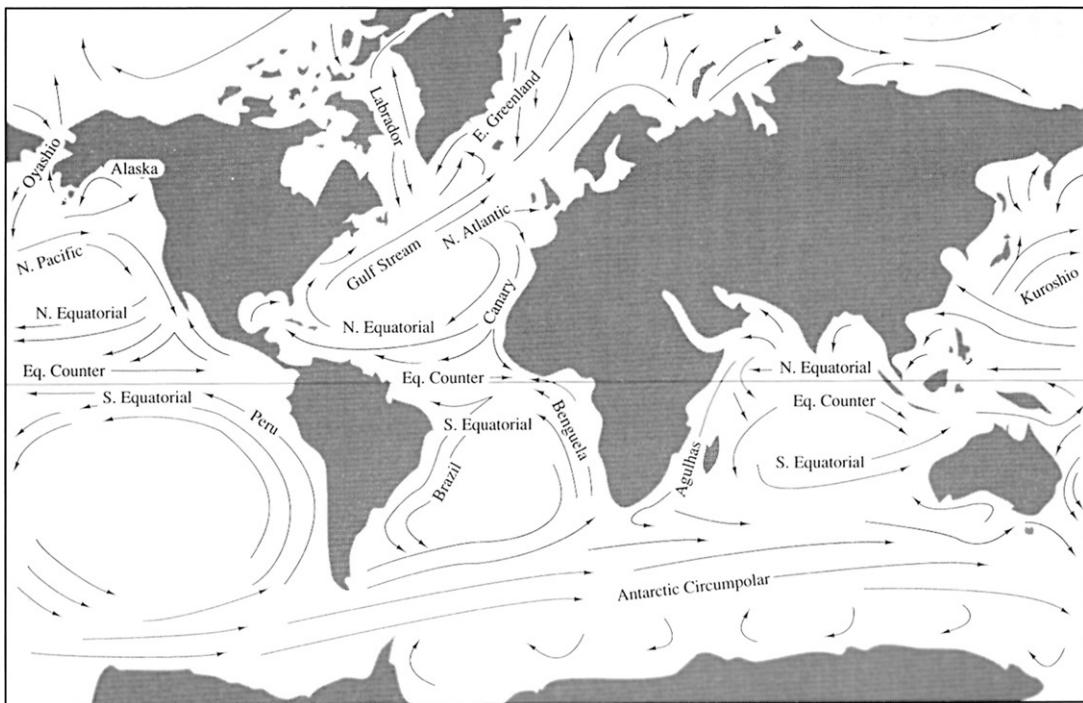


FIGURE 9.1 Major currents in the surface waters of the world's oceans. Source: From Knauss (1978). Used with permission of Dr. John Knauss.

The global circulation of the oceans transfers heat from the tropics to the polar regions of the Earth (Oort et al. 1994). About 10 to 20% of the net excess of solar energy received in the tropics is transferred to the poles by ocean circulation; the remainder is transferred through the atmosphere (Trenberth and Caron 2001). With the loss of heat at polar latitudes, the surface waters cool so that their density exceeds that of the underlying water. The resulting convective mixing permits exchange between the surface ocean and the deep waters. In contrast, deep convective mixing driven by winds is rarely observed (Wadhams et al. 2002, Gascard et al. 2002). During the winter in the Arctic and Antarctic oceans, the density of some polar waters also increases when freshwater is “frozen out” of seawater and added to the floating sea ice, leaving behind waters of greater salinity that sink to the deep ocean.

In contrast, during the summer, the polar oceans have lower surface salinity due to melting from the ice caps (Peterson et al. 2006). Because the seasonal downwelling of cold polar waters is driven by both temperature and salinity, it is known as *thermohaline circulation*. Global warming is anticipated to reduce the thermohaline circulation by increasing the density differences between surface and subsurface waters.

Our understanding of the circulation of the oceans has advanced with the deployment of sensors that are designed to follow currents at particular depths. Several thousand profiling floats compose the ARGO network, which transmits data to a satellite for subsequent relay to



FIGURE 9.2 Deployment of a RAFOS float in the North Atlantic Ocean. *Photograph courtesy of Susan Lozier, Duke University.*

ground stations. Among these, RAFOS floats¹ are subsurface floats that remain at depth, recording data for location, temperature, and pressure that are transmitted to a satellite when the floats rise to the sea surface after their mission is complete, typically after 2 years of deployment (Figure 9.2). These floats have documented an interior (mid-depth) circulation in the Atlantic, which returns polar waters to lower latitudes (Bower et al. 2009, Lozier 2010).

¹ ARGO derives from an ocean explorer in Greek mythology. RAFOS is SOFAR spelled backwards, reflecting that these floats receive signals from devices moored on the seafloor to record their position, whereas SOFAR (Sound Fixing and Ranging) devices emit signals that are received by moored devices.

Penetration of cold waters to the deep ocean at the poles, due to convective mixing, provides water for complete ocean mixing, or overturn. For example, North Atlantic deep water (NADW), which forms near Greenland, moves southward through the deep Atlantic, mixes with Antarctic water in the Southern Ocean, and eventually rounds the tip of Africa and enters the Indian and Pacific oceans (Lozier 2012; [Figure 9.3](#)). Major zones of upwelling are found in the Pacific Ocean and in the circumpolar Southern Ocean around 65°S latitude (Toggweiler and Samuels 1993). Deep waters are nutrient rich, so high levels of oceanic productivity are found in zones of upwelling. Upwelling along the western coast of South America yields high levels of net primary production that support the anchovy fishery of Peru. This global overturning circulation has traditionally been called the “conveyor belt” (Broecker 1991).

These patterns of ocean circulation have important implications for biogeochemistry. The overall mean residence time for seawater is 34,000 years with respect to river flow (i.e., total ocean volume/total annual river flow). In fact, most rivers mix only with the smaller volume of the surface ocean, which thus has a mean residence time of about 1700 years with respect to river water. If we account for the addition of rainwaters and upwelling waters to the surface ocean, the actual turnover time of the surface waters is even faster. For example, the mean residence time of surface waters in the North Pacific Ocean is about 9 to 15 years (Michel and Suess 1975). The surface water is also in rapid gaseous equilibrium with the atmosphere.

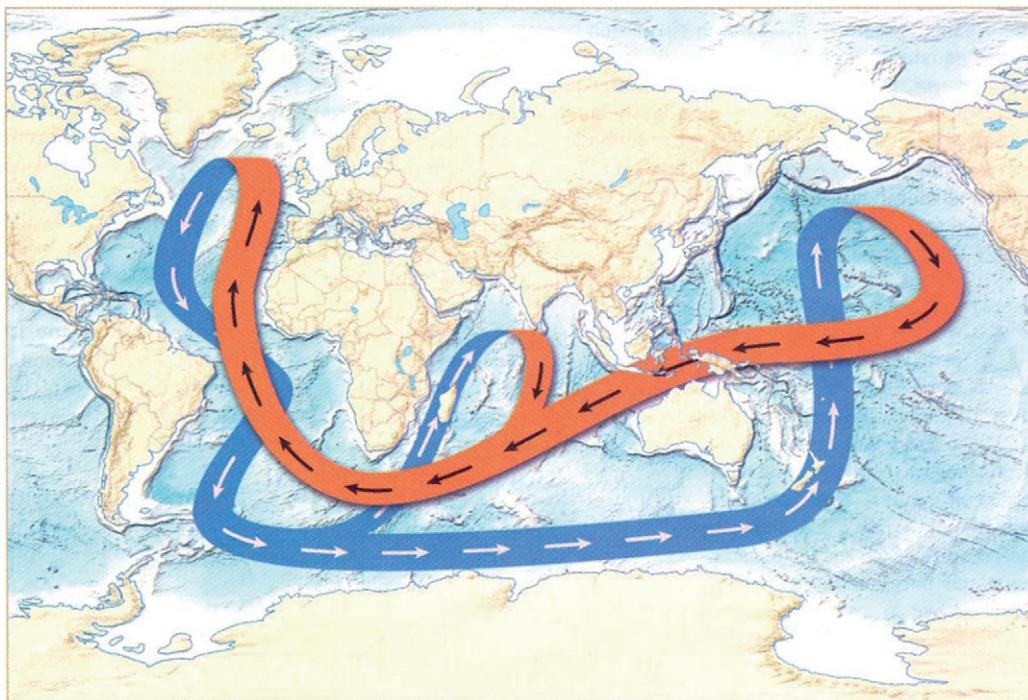


FIGURE 9.3 The global ocean thermohaline circulation forms a conveyor that moves water among the various ocean basins in surface (red) and deep-water (blue) currents. Source: From Lozier (2010). Used with permission of the American Association for the Advancement of Science.

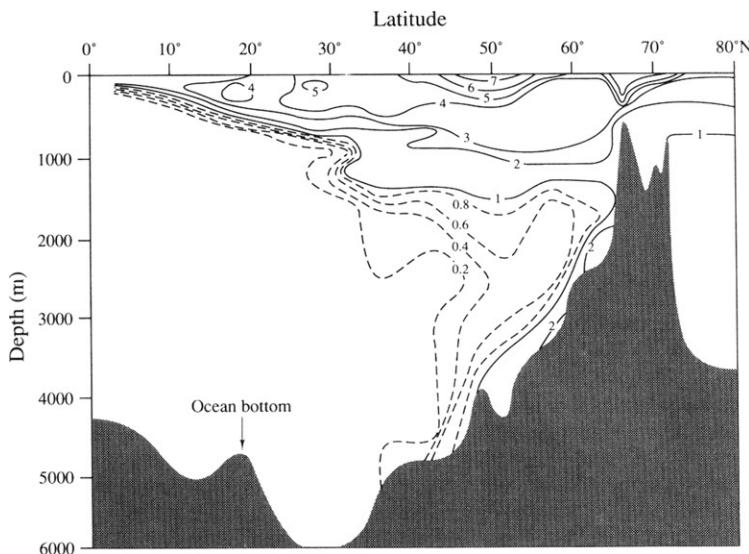


FIGURE 9.4 Penetration of bomb-derived tritium (${}^3\text{H}_2\text{O}$) into the North Atlantic Ocean. Data are expressed as the ratio of ${}^3\text{H}/\text{H} \times 10^{-18}$ for samples collected in 1972. Source: From Ostlund (1983).

Mean residence time for CO_2 dissolved in the surface waters of the Atlantic Ocean is about 6 years (Stuiver 1980).

Renewal or “ventilation” of the bottom waters is confined to the polar regions. Downward mixing of ${}^3\text{H}_2\text{O}$ and ${}^{14}\text{CO}_2$ produced from the testing of atomic bombs (Figure 9.4) and downward mixing of anthropogenic chemicals of recent origin (e.g., see Krysell and Wallace 1988) show the rate of entry of surface waters to the deep sea and the movement of deep water toward the equator. The downward transport in the North Atlantic is 15 Sv,² roughly 10 times greater than the total annual river flow to the oceans (Dickson and Brown 1994, Ganachaud 2003, Luo and Ku 2003). About 21 Sv sink in the Southern Ocean, including 4 to 5 Sv in the Weddell Sea, which is the origin of northward-flowing Antarctic bottom water (Hogg et al. 1982, Schmitz 1995). Because the volume of water entering the deep ocean is much greater than the total annual river flow to the sea, the mean residence time of the deep ocean is much less than 34,000 years. Estimates of the mean age of bottom waters using ${}^{14}\text{C}$ dating of total dissolved CO_2 range from 275 years for the Atlantic Ocean to 510 years for the Pacific (Stuiver et al. 1983), and the overall renewal of the oceans’ bottom waters is normally assumed to occur in 500 to 1000 years. Thus, the deep waters maintain a historical record of the conditions of the surface ocean several centuries ago.

Deep water currents also transfer seawater between the major ocean basins as a result of the Antarctic circumpolar current, which carries >130 Sv (Cunningham et al. 2003, Firing et al. 2011). In the Atlantic Ocean, evaporation exceeds the sum of river flow and precipitation, yielding higher seawater salinity than in the Pacific (Figure 9.5). The Atlantic receives a net

² As a unit to express the movement of large bodies of seawater, 1 Svedrup (Sv) = $10^6 \text{ m}^3/\text{sec} = 3.2 \times 10^{13} \text{ m}^3/\text{yr}$.

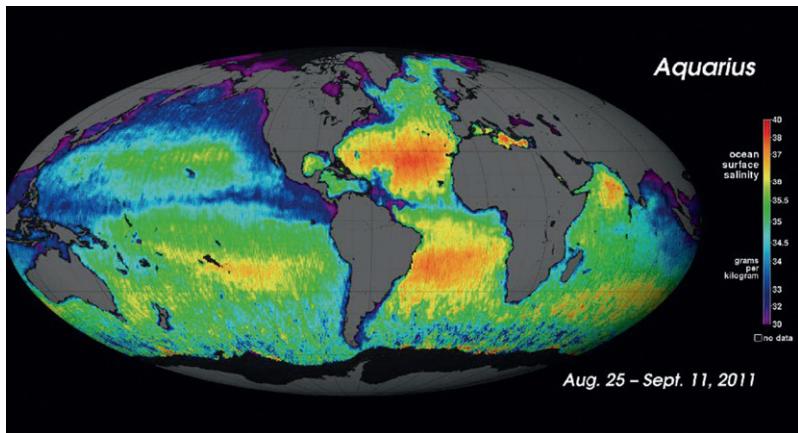


FIGURE 9.5 Salinity of the surface waters of the world's oceans. Source: From NASA Aquarius (http://www.nasa.gov/mission_pages/aquarius/multimedia/gallery/pia14786.html).

inflow of less saline waters from the Pacific, via the Antarctic circumpolar current, to restore the water balance (Figure 9.3). To maintain a mass balance in the overall volume of the deep sea, any increase in the formation of deep waters in polar regions must be associated with an increase in upwelling in other regions (Marshall and Speer 2012).

Changes in ocean currents, particularly the formation of deep waters, may be associated with changes in global climate. At the end of the last glacial epoch, the concentration of atmospheric CO₂ rose from 200 ppm to about 280 ppm in the atmosphere (Figure 1.2). An increase in the rate of upwelling of deep waters in the Southern Ocean may have been associated with the release of CO₂ to the atmosphere (Burke and Robinson 2012). There is some indication that the formation of polar deep waters has slowed in recent years, perhaps indicative of global warming and a greater density stratification of the surface waters in the North Atlantic (Cunningham and Marsh 2010). Climate change is also likely to affect the pattern of surface currents. During the last glacial epoch, the Gulf Stream, which carries about 30 Sv, appears to have shifted southward, producing a humid climate in southern Europe (Keffer et al. 1988). During the Little Ice Age, 200 to 600 years ago, a weakened flow of the Gulf Stream appears to have been related to cold conditions in Europe (Lund et al. 2006).

El Niño

Ocean currents also show year-to-year variations that affect biogeochemistry and global climate. One of the best known variations in current occurs in the central Pacific Ocean. Under normal conditions, the trade winds drive warm surface waters to the western Pacific, allowing cold subsurface waters to upwell along the coast of Peru. Periodically, the surface transport breaks down in an event known as the El Niño–Southern Oscillation (ENSO). During El Niño years, the warm surface waters remain along the coast of Peru, reducing the upwelling

of nutrient-rich water. Phytoplankton growth is limited and the normally productive anchovy fishery collapses (Glynn 1988).

Associated with these occasional warm surface waters in the eastern Pacific are changes in regional climate, for example, exceptionally warm winters and greater rainfall in western North America (Molles and Dahm 1990, Swetnam and Betancourt 1990, Redmond and Koch 1991). At the same time the absence of warm surface waters in the western Pacific reduces the intensity of the monsoon rainfalls in Southeast Asia and India. Working with atmospheric scientists, oceanographers now recognize that El Niño events are part of a cycle that yields opposite but equally extreme conditions during non-El Niño years, which are known as La Niña (Philander 1989). Although the switch from El Niño to La Niña is poorly understood, it is likely that the conditions at the beginning of each phase reinforce its development, with the cycle averaging between 3 and 5 years between El Niño events, which are recognized in sedimentary records extending to 5000 years ago (Rodbell et al. 1999). A similar but less powerful cyclic pattern of ocean circulation is seen in the Atlantic Ocean (Philander 1989).

The upwelling of cold, deep ocean waters during the La Niña years leads to lower atmospheric temperatures over much of the Northern Hemisphere. Thus, El Niño–La Niña cycles add variation to the global temperature record, complicating efforts to perceive atmospheric warming that may be due to the greenhouse effect. Moreover, the El Niño–La Niña cycle affects the concentrations of atmospheric CO₂, since the release of CO₂ from cold, upwelling waters is lower during years of El Niño (Bacastow 1976, Inoue and Sugimura 1992, Wong et al. 1993). During the 1991–1992 El Niño, the ocean released 0.3×10^{15} g C as CO₂ to the atmosphere, compared to its normal efflux of 1.0×10^{15} g C (Murray et al. 1994, 1995; Feely et al. 1999; compare Chavez et al. 1999 for the 1997–1998 El Niño), and the rate of CO₂ increase in the atmosphere slowed for several years (Keeling et al. 1995).

In addition to reducing marine net primary productivity in the eastern Pacific (Chavez et al. 1999, Behrenfeld et al. 2001, Turk et al. 2001), El Niño conditions can affect other aspects of biogeochemistry in the sea. Lower rates of denitrification in warm El Niño waters may decrease the total marine denitrification rate by as much as 25% over La Niña conditions (Codispoti et al. 1986, Cline et al. 1987).

THE COMPOSITION OF SEAWATER

Major Ions

Table 9.1 shows the concentration of major ions in seawater of average salinity, 35‰ (i.e., 35 g of salts per kilogram of seawater; Millero et al. 2008). Sodium and chloride dominate the mix, and in the surface waters the pH of seawater is close to 8.1. The mean residence time for each of these ions is much longer than the mean residence time for water in the oceans, allowing plenty of time for mixing. Although seawater varies slightly in salinity throughout the world (Figure 9.5), these ions are conservative in the sense that they maintain the same concentrations relative to one another in most ocean waters. For example, recent changes in the salinity of seawater, due to freshening of the North Atlantic by Greenland ice melt (Boyer et al. 2005, Curry and Mauritzen 2005), do not change the relationship between the concentration of

TABLE 9.1 Major Ion Composition of Seawater, Showing Relationships to Total Chloride and Mean Residence Times for the Elements with Respect to Riverwater Inputs

Constituent	Concentration in seawater ^a (g kg ⁻¹)	Chlorinity ratio ^a (g kg ⁻¹)	Concentration in river water ^b (mg/kg)	Mean residence time ^b (10 ⁶ yr)
Sodium	10.78145	0.556492	5.15	75
Magnesium	1.28372	0.066260	3.35	14
Calcium	0.41208	0.021270	13.4	1.1
Potassium	0.39910	0.020600	1.3	11
Strontium	0.00795	0.000410	0.03	12
Chloride	19.35271	0.998904	5.75	120
Sulfate	2.71235	0.140000	8.25	12
Bicarbonate	0.10481	0.005410	52	0.10
Bromide	0.06728	0.003473	0.02	100
Boron	0.02739	0.001413	0.01	10
Fluoride	0.00130	0.000067	0.10	0.05
Water	964.83496	49.800646		0.034

^a Source: Millero *et al.* (2008).

^b Source: Meybeck (1979) and Holland (1978).

various ions and Cl. Thus, a good estimate of total salinity can be calculated from the concentration of a single ion. Often chloride is used, and the relationship is

$$\text{Salinity} = (1.81) \times \text{Cl}^-, \quad (9.1)$$

with both values in g kg⁻¹. Table 9.1 shows the mean ratio between chloride and other major ions in standard seawater (Millero *et al.* 2008).

According to Table 9.1, the time for rivers to supply the elemental mass in the ocean, the mean residence time, varies from 120 million years for Cl to 1.1 million years for Ca. Biological processes, such as the deposition of calcium carbonate in the shells of animals, are responsible for the relatively rapid cycling of Ca. But even for Cl the mean residence time is much shorter than the age of the oceans; Cl has not simply accumulated in seawater through Earth's history.

Through geologic time, changes in the composition of seawater occurred when inputs and outputs of individual constituents were not in balance. In the face of continual inputs of ions in riverwater, the composition of seawater is maintained by processes that remove ions from the oceans. Processes controlling the composition of seawater must act differentially on the major ions, because their concentrations in seawater are much different from the concentrations in rivers. For example, whatever process removes Na from seawater must not be effective until the concentration of Na has built up to high levels (Drever 1988). On the other hand, Ca is the dominant cation in river water (Table 9.1), but the Ca concentration in seawater is relatively low. The Ca content of seawater has declined during the past 28 million years, as a

result of changes in the relative importance of inputs from rock weathering and sedimentary losses to carbonate sediments (De La Rocha and DePaolo 2000, Griffith et al. 2008).

A number of processes act to remove the major elements from seawater. Earlier, we saw that wind blowing across the ocean surface produces sea spray and marine aerosols that contain the elements of seawater ([Chapter 3](#)). A significant portion of the river transport of Cl from land is derived directly from the sea ([Figure 3.16](#)). The atmospheric transport of these “cyclic salts” removes ions from the sea roughly in proportion to their concentration in seawater ([Table 4.9](#)).

During some periods of the Earth’s history, vast deposits of minerals have formed when seawater evaporated from shallow, closed basins. Today, the extensive salt flats, or *sabkhas*, in the Persian Gulf region are the best examples. Although the area of such seas is limited, the formation of evaporite minerals has been an important mechanism for the removal of Na, Cl, and SO₄ from the oceans in the geologic past (Holland 1978). Huge deposits of salt laid down 400,000,000 years ago are now mined beneath Lake Erie, near Cleveland, Ohio.

Other mechanisms of loss occur in ocean sediments. Sediments are porous and the pores contain seawater. Burial of ocean sediments and their pore waters is significant in the removal of Na and Cl, which are the most concentrated ions in seawater. Biological processes are also involved in the burial of elements in sediments. As we will discuss in more detail in a later section Biogenic Carbonates (p. 363), the deposition of CaCO₃ by organisms is the major process removing Ca from seawater. Biological processes also cause the removal of SO₄, which is consumed in sulfate reduction and deposited as pyrite in ocean sediments (see [Chapters 7 and 8](#)).

Ions are removed from the oceans when the clays in the suspended sediments of rivers undergo ion exchange with seawater. In rivers, most of the cation exchange sites ([Chapter 4](#)) are occupied by Ca. When these clays are delivered to the sea, Ca is released and replaced by other cations, especially Na (Sayles and Mangelsdorf 1977, James and Palmer 2000). Most deep sea clays show higher concentrations of Na, K, and Mg than are found in the suspended matter of river water (Martin and Meybeck 1979). The clays eventually settle to the ocean floor, causing a net loss of these ions from ocean waters.

So far, the processes we have discussed for the removal of elements from seawater cannot explain the removal of much of the annual river flow of Mg and K to the sea. Marine geochemists have postulated several reactions of “reverse weathering,” whereby silicate minerals were reconstituted (authigenic) in ocean sediments, removing Mg and other cations from the ocean (MacKenzie and Garrels 1966). Reverse weathering is a major sink for Li from seawater (Misra and Froelich 2012), and the formation of authigenic clay minerals is apparently a small sink for Mg and K (Kastner 1974, Sayles 1981). Michalopoulos and Aller (1995) found that aluminosilicate minerals were reconstituted in laboratory incubations of marine sediments from the Amazon River, suggesting that this mechanism sequesters as much as 10% of the annual flux of K to the sea (compare Hover et al. 2002).

In the late 1970s, Corliss et al. (1979) examined the emissions from hydrothermal (volcanic) vents in the sea. One of the best-known hydrothermal systems is found at a depth of 2500 m near the Galapagos Islands in the eastern Pacific Ocean. Hot fluids emanating from these vents are substantially depleted in Mg and SO₄ and enriched in Ca, Li, Rb, Si, and other elements compared to seawater (Elderfield and Schultz 1996, de Villiers and Nelson 1999). Globally the annual sink of Mg in hydrothermal vents, where it leads to the formation of Mg-rich silicate rocks, exceeds the delivery of Mg to the oceans in river water. The flux of

Ca to the oceans in rivers, 480×10^{12} g/yr, is incremented by an additional flux of up to 170×10^{12} g/yr from hydrothermal vents (Edmond et al. 1979). Changes in the Mg/Ca ratio in seawater through geologic time are a good index of the relative importance of hydrothermal activities (Horita et al. 2002, Coggon et al. 2010).

In sum, it appears that most Na and Cl are removed from the sea in pore water burial, sea spray, and evaporites. Magnesium is largely removed in hydrothermal exchange, and calcium and sulfate by the deposition of biogenic sediments. The mass balance of potassium is not well understood, but K appears to be removed by exchange with clay minerals, leading to the formation of illite, and by some reactions with basaltic sediments (Gieskes and Lawrence 1981). Whitfield and Turner (1979) show an indirect correlation between the mean residence time of elements in seawater and their tendency to incorporate into one or more sedimentary forms (Figure 9.6). Over long periods of time, ocean sediments are subducted to the Earth's mantle, where they are converted into primary silicate minerals, with a portion of the volatile components being released in volcanic gases (H_2O , CO_2 , Cl_2 , SO_2 , etc.; Figure 1.3). The entire oceanic crust appears to circulate through this pathway in less than 300 million years (Muller et al. 2008), transferring sedimentary deposits to the mantle (Plank and Langmuir 1998).

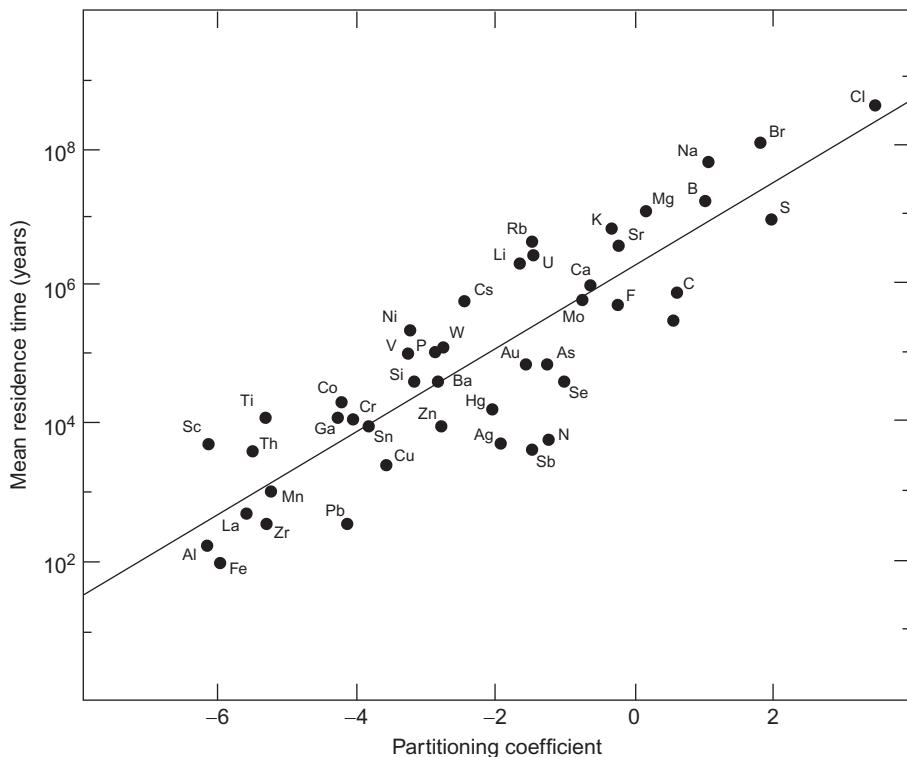


FIGURE 9.6 Mean residence time of elements in seawater as a function of their concentration in seawater divided by their mean concentration in the Earth's crust—with high values of the index indicating elements that are very soluble. Source: From Whitfield and Turner (1979). Reprinted with permission from Nature, copyright 1979 Macmillan Magazines Limited.

NET PRIMARY PRODUCTION

Measurement

Compared to massive forests, marine phytoplankton are easy to overlook, and much of their production of organic matter is rapidly decomposed in the surface waters. Thus, net primary production in the sea is often measured using modifications of the oxygen-bottle and ^{14}C techniques, as outlined for lake waters in [Chapter 8](#). Controversy surrounding the exact magnitude of marine production derives from the tendency for O_2 -bottle measurements of NPP to exceed those made using ^{14}C in the same waters (Peterson 1980). Part of the problem can be explained by the presence of a large biomass of picoplankton—small phytoplankton that pass through the filtration steps of the ^{14}C procedure. In the waters of the eastern tropical Pacific Ocean, Li et al. (1983) found that 25 to 90% of the photosynthetic biomass passes a 1- μm filter. Picoplankton are more important in warm, nutrient-poor waters than in the subpolar oceans (Agawin et al. 2000), and Stockner and Antia (1986) suggest that picoplankton may regularly account for up to 50% of ocean production. Marine phytoplankton also release large amounts of dissolved organic carbon to seawater (Baines and Pace 1991), and these compounds—technically a component of NPP—also pass through the filtration procedures of the ^{14}C method.

Acting to enhance estimates of marine NPP from ^{14}C methods, some ocean waters harbor anoxygenic photo-heterotrophic bacteria, which metabolize organic carbon when it is available and produce it by anoxygenic photosynthesis when it is not (Kolber et al. 2001). Photosynthesis by these bacteria constitutes 2 to 5% of total production in some waters, which would be overlooked by the O_2 -bottle method (Kolber et al. 2000).

With either method, water samples isolated in bottles contain a mix of photosynthetic and heterotrophic organisms, and the net change in O_2 is often said to indicate *net community production* (NCP) during the incubation period. Some workers have tried to avoid the problems associated with bottles by measuring net increases in O_2 (Craig and Hayward 1987, Najjar and Keeling 1997, Emerson and Stump 2010) or decreases in HCO_3^- (Lee 2001) in the upper water column when photosynthesis is occurring. The concentration of O_2 or HCO_3^- is compared to the concentration expected as a result of the equilibrium dissolution of gases in seawater from the atmosphere. As with bottle methods, a supersaturation of O_2 or depletion of HCO_3^- is best taken as an index of NCP in the water column.³

Yet another, new technique involves the measurement of dissolved O_2 and $\delta^{17}\text{O}$ in waters (Luz and Barkan 2009). Oxygen is affected by the rate of photosynthesis and respiration, whereas $\delta^{17}\text{O}$ is solely affected by photosynthesis. Differential changes in these parameters can be used to estimate NCP in ocean waters (Juranek and Quay 2010). In side-by-side comparisons, this $\delta^{17}\text{O}$ method gave values more than twice as high as the ^{14}C method for measuring marine production (Quay et al. 2010).

Remote sensing offers significant potential for improved regional and global estimates of marine NPP without complications associated with community respiration. Where ocean waters contain little phytoplankton, there is limited absorption of incident radiation by

³ Note that NCP is analogous to net ecosystem production (NEP) on land (Chapter 5), but NCP does not include deep-water and sediment respiration, which are supported by surface photosynthesis in the oceans.

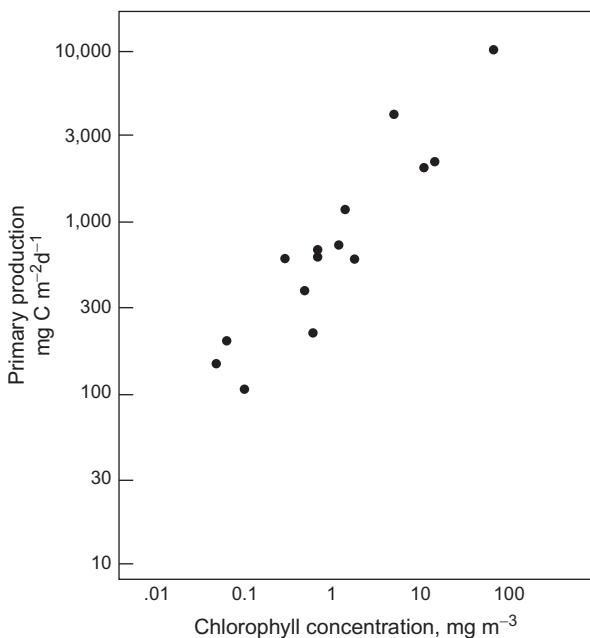


FIGURE 9.7 Net primary productivity as a function of surface chlorophyll in waters of coastal California. Source: From Eppley et al. (1985), Journal of Plankton Research. Reprinted by permission of Oxford University Press.

chlorophyll, and the reflected radiation is blue. Where chlorophyll and other pigments are abundant, the reflectance contains a greater proportion of green wavelengths (Prézelin and Boczar 1986). The reflected light is indicative of algal biomass in the upper 20 to 30% of the euphotic zone, where most NPP occurs (Balch et al. 1992). The reflectance data can be used to calculate the concentration of chlorophyll or organic carbon in the water column and hence production (Figure 9.7; Platt and Sathyendranath 1988; Najjar and Keeling 1997). With the deployment of the MODIS satellite (Chapter 5), multispectral images of the ocean are now available for worldwide estimates of marine NPP.

Global Patterns and Estimates

Differences in methodology account for much of the variation among published estimates of global marine production. Early estimates suggested that marine NPP was 23 to 27×10^{15} g C/yr (Berger 1989), but most workers now suggest that marine NPP may be $2\times$ larger and roughly equivalent to NPP on land (Table 9.2). Behrenfeld and Falkowski (1997) used satellite measurements of pigment concentration in surface waters to estimate marine NPP at 43.5×10^{15} g C/yr. More recently, Friend et al. (2009) estimated marine NPP at 52.5×10^{15} g C/yr (Figure 9.8), with a spatial pattern similar to that for dissolved O₂ in seawater (Najjar and Keeling 1997). Net community production, yielding organic matter that can sink into the deep ocean, is about 15 to 20% of total NPP (Lee 2001, Laws et al. 2000, Falkowski 2005, Quay et al. 2010), with higher values in cold polar waters where bacterial respiration is lower.

TABLE 9.2 Estimates of Total Marine Primary Productivity and the Proportion That Is New Production

Province	% of ocean	Area (10^{12} m^2)	Mean production ($\text{g C m}^{-2} \text{ yr}^{-1}$)	Total global production ($10^{15} \text{ g C yr}^{-1}$)	New production ^a ($\text{g C m}^{-2} \text{ yr}^{-1}$)	Global new production ($10^{15} \text{ g C yr}^{-1}$)
Open ocean	90	326	130	42	18	5.9
Coastal zone	9.9	36	250	9.0	42	1.5
Upwelling area	0.1	0.36	420	0.15	85	0.03
Total		362		51		7.4

^a New productivity defined as C flux at 100 m.

Source: From Knauer (1993). Used with permission of Springer-Verlag.

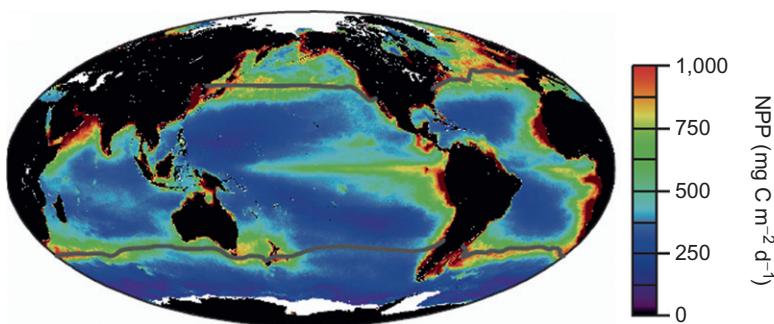


FIGURE 9.8 Global map of marine NPP. Source: From Behrenfeld et al. (2006).

The highest rates of NPP are measured in coastal regions, where nutrient-rich estuarine waters mix with seawater, and in regions of upwelling, where nutrient-rich deep water reaches the surface. NPP in beds of intertidal rockweed, *Ascophyllum nodosum*, in Cobscook Bay of eastern Maine is nearly $900 \text{ g C m}^{-2} \text{ yr}^{-1}$, similar to that of a temperate forest (Table 5.2; Vadas et al. 2004). In contrast, among open-water environments, even the most productive areas show NPP of $< 300 \text{ g C m}^{-2} \text{ yr}^{-1}$, roughly similar to the NPP of an arid woodland. As a result of their large area, the open oceans account for about 80% of the total marine NPP, with continental shelf areas accounting for the remainder (Table 9.2). Although massive beds of kelp are found along some coasts, such as the *Macrocystis* kelps of southern California, seaweed accounts for only about 0.1% of marine production globally (Smith 1981, Walsh 1984).

Dissolved Organic Matter

A large amount of dissolved organic matter is found in seawater (Martin and Fitzwater 1992). Based on its ^{14}C age and molecular properties, only a small fraction appears to derive from humic substances that have been delivered to the oceans by rivers (Opsahl and Benner

1997, Raymond and Bauer 2001, Hansell et al. 2004). Most marine DOC is derived from marine photosynthesis. It is well known that phytoplankton and bacteria leak dissolved organic compounds, and globally about 17% of net community production may leak from phytoplankton cells as dissolved organic carbon (DOC; Hansell and Carlson 1998b). DOC is also released following the death and lysis of phytoplankton cells (Agusti et al. 1998).

Most of this DOC is labile and rapidly decomposed in the surface ocean, where it supports bacterioplankton—free-floating bacteria (Kirchman et al. 1991, Druffel et al. 1992). However, a fraction of the DOC is relatively refractory, apparently composed of nitrogen compounds resynthesized by bacteria (Barber 1968, Ogawa et al. 2001, McCarthy et al. 1998, Jiao et al. 2010, Aluwihare et al. 2005). This DOC is entrained in downwelling waters and delivered to the deep sea (Aluwihare et al. 1997, Loh et al. 2004, Carlson et al. 1994). The mean residence time for DOC in the oceans, up to 6000 years, is longer than the time for deep-water renewal, implying that some DOC has made more than one cycle through the deep sea (Williams and Druffel 1987, Bauer et al. 1992).

Fate of Marine Net Primary Production

Most marine NPP is consumed by zooplankton and bacterioplankton in the surface waters. Bacterioplankton respire dissolved organic carbon and use extracellular enzymes to break down particulate organic carbon (POC) and colloids produced by phytoplankton (Druffel et al. 1992). Cho and Azam (1988) concluded that bacteria were more important than zooplankton in the consumption of POC in the North Pacific Ocean. Reviewing a large number of studies from marine and freshwater systems, Cole et al. (1988) found that net bacterial growth (production) is about twice that of zooplankton and accounted for the disappearance of 30% of NPP from the water column (compare del Giorgio and Cole 1998, Ducklow and Carlson 1992). In some areas, gross consumption by bacteria may reach 70% of NPP, especially when NPP is low (Biddanda et al. 1994).

Whereas zooplankton represent the first step in a trophic chain that eventually leads to large animals such as fish, bacteria are consumed by a large population of bacterivores that mineralize nutrients and release CO₂ to the surface waters (Fuhrman and McManus 1984). Thus, when bacteria are abundant, a large fraction of the carbon fixed by NPP in the sea is not passed to higher trophic levels (Ducklow et al. 1986). In areas where bacterial growth is inhibited, such as in cold waters, more NPP is available to pass to higher trophic levels, including commercial fisheries (Pomeroy and Deibel 1986, Rivkin and Legendre 2001, Laws et al. 2000). Many of the world's most productive fisheries are found in cold, polar waters.

Fisheries' production is directly linked to the primary production in the sea (Iverson 1990, Ware and Thomson 2005). Already humans extract a large harvest of fish and shellfish from the oceans, which can be traced to the consumption of 8% of marine net primary productivity at the base of the food web (Pauly and Christensen 1995). Recent declines in the populations of important commercial fishes—up to 90% for some preferred species—suggest that it is unlikely that the current harvest is sustainable for future generations (Myers and Worm 2003). If warmer surface waters accompany climate change, we can also expect reductions in zooplankton and ultimately in the commercial harvest of fish (Vazquez-Dominquez et al. 2007).

There is general agreement among oceanographers that about 80 to 90% of the NPP is degraded to inorganic compounds (CO_2 , NO_3 , PO_4 , etc.) in the surface waters, and the remainder sinks to the deep ocean. The sinking materials consist of particulate organic carbon (POC), including dead phytoplankton, fecal pellets, and organic aggregates, known as marine snow (Alldredge and Gotschalk 1990). The fraction (f_e) of net primary production that sinks out of the surface waters is known as *export production*—often called the *f-ratio*. Estimates of f_e are constrained, since high rates of sinking would remove unreasonably large quantities of nutrients from the surface ocean (Broecker 1974, Eppley and Peterson 1979).

The downward flux of organic matter varies seasonally depending on productivity in the surface water (Deuser et al. 1981, Asper et al. 1992, Sayles et al. 1994, Legendre 1998). Degradation continues as POC sinks through the water column of the deep ocean. With a mean sinking rate of about 350 m/day, the average particle spends about 10 days in transit to the bottom (Honjo et al. 1982). Bacterial respiration accounts for the consumption of O_2 and the production of CO_2 in the deep water.

As a result of progressive mineralization of the sinking debris, rates of oxygen consumption and bacterial activity show an exponential decline with depth below 200 m (Nagata et al. 2000, Andersson et al. 2004a). Honjo et al. (1982) found that respiration rates averaged $2.2 \text{ mg C m}^{-2} \text{ day}^{-1}$ in the deep ocean, where the rate of bacterial respiration is probably limited by cold temperatures. About 95% of the particulate carbon is degraded within a depth of 3000 m and only small quantities reach the sediments of the deep ocean (Suess 1980, Martin et al. 1987, Jahnke 1996, Hedges et al. 2001, Buesseler et al. 2007). Still, metabolically active bacteria are found at $\sim 11,000$ m depth in the bottom waters of the Mariana Trench (Kato et al. 1998).

Significant rates of decomposition also continue at the surface of the sediments (Emerson et al. 1985, Cole et al. 1987, Bender et al. 1989, Smith 1992a), where the rate of decay is determined by the length of exposure of the organic matter to oxygen (Figure 9.9; Gelinas et al. 2001, Arnarson and Keil 2007). Where burrowing organisms stir or *bioturbate* the sediments, O_2 may penetrate to considerable depth (e.g., Ziebis et al. 1996, Lohrer et al. 2004), stimulating degradation of buried organic matter (Hulthe et al. 1998).

If the current, higher estimates of marine NPP are correct, then at least $7.4 \times 10^{15} \text{ g C/yr}$ (i.e., global $f_e = 0.15$) sinks to the deep waters of the ocean (Knauer 1993, Falkowski 2005). The export production includes both particulate organic carbon ($5 \times 10^{15} \text{ g C/yr}$; Henson et al. 2011) and dissolved organic carbon (Hopkinson and Vallino 2005). Seiter et al. (2005) suggest that $0.5 \times 10^{15} \text{ g C}$ pass 1000-m depth. From a compilation of data from sediment cores taken throughout the oceans, Berner (1982) estimated that the rate of incorporation of organic carbon in sediments is $0.157 \times 10^{15} \text{ g C/yr}$. These values suggest that about 98% of the sinking organic materials are degraded in the deep sea (compare Martin et al. 1991). Degradation of organic carbon continues in marine sediments, and the ultimate rate of burial of organic carbon in the ocean is about $0.12 \times 10^{15} \text{ g C/yr}$ (Berner 1982, Seiter et al. 2005)—less than 1% of marine NPP.

Maps of the distribution of organic carbon in ocean sediments are similar to maps of the distribution of net primary production in the surface waters, except that a greater fraction of the total burial (83%) occurs on the continental shelf (Premuzic et al. 1982, Berner 1982). In most cases the delivery of materials to sediment ($\text{g C m}^{-2} \text{ yr}^{-1}$) is correlated to measured rates of respiration in the sediment, linking accumulations of sedimentary carbon to surface productivity (Bertrand and Lailler-Verges 1993, Legendre 1998). Where this is not the case,

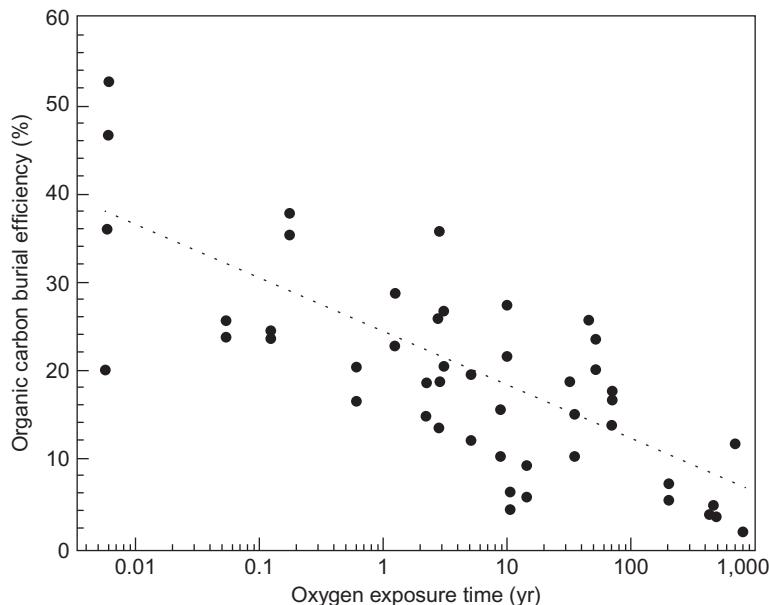


FIGURE 9.9 Organic carbon burial efficiency versus the time of its exposure to O₂ in sediments of the eastern North Pacific Ocean. Source: From Hartnett *et al.* (1998).

deposition from the episodic surface production or ancillary terrestrial sources is indicated (Smith *et al.* 1992a, 2001a). While near-shore sediments contain a large fraction of terrestrial material (Burdige 2005), isotopic analyses show that nearly all the sedimentary organic matter in the deep sea is derived from marine production and not from land (Hedges and Parker 1976, Prahl *et al.* 1994).

Indeed, most river-borne organic materials, both DOC and POC, must decompose in the ocean because the total burial of organic carbon in the ocean is less than the global delivery of organic matter in rivers, 0.4×10^{15} g C/yr (Schlesinger and Melack 1981). This has led to the curious suggestion that the ocean is a net heterotrophic system, because the ratio of total respiration to autochthonous production appears >1.0 (Smith and MacKenzie 1987, Serret *et al.* 2001, del Giorgio and Duarte 2002). However, net respiration is likely confined to near-shore regions and warm tropical waters, whereas photosynthesis and respiration are usually more closely balanced in the central ocean gyres (Williams 1998, Hoppe *et al.* 2002, Riser and Johnson 2008).

SEDIMENT DIAGENESIS

Organic Diagenesis

Slow metabolic rates characterize the inhabitants of sedimentary environments (D'Hondt *et al.* 2002, Røy *et al.* 2012), and archaea may be dominant in many of them (Lipp *et al.* 2008). Bacteria are found at 500-m depth in pelagic sediments (Parkes *et al.* 1994, Schippers *et al.*

2005, D'Hondt et al. 2004), and viable bacteria reported 1626 m below the seafloor near Newfoundland, Canada, where ambient temperatures range from 60 to 100°C, currently represent the maximum known extent of the biosphere into the Earth's crust (Roussel et al. 2008). Given the age of some deep sediments (e.g., 111,000,000 years; Roussel et al. 2008), it is not surprising that all but the most refractory organic compounds have disappeared. Nevertheless, the live biosphere in sediments may contain as much as 100×10^{15} g C (Parkes et al. 1994, Lipp et al. 2008), equivalent to about 15% of the biomass on land ([Chapter 5](#)). Note that this living biomass represents only a small fraction of the total organic carbon contained in sedimentary environments (Hartgers et al. 1994; [Table 2.3](#)).

Change in the chemical composition of sediments after deposition is known as *diagenesis*. Many forms of diagenesis are the result of microbial activities that proceed following the order of redox reactions outlined in [Chapter 7](#) (Thomson et al. 1993, D'Hondt et al. 2004). Within a few centimeters of the surface of sediments, NO_3^- and Mn^{4+} are exhausted by the anaerobic oxidation of organic matter. Supplementing the supply of NO_3^- that diffuses into the sediment from the overlying waters, some motile microbes appear to transport NO_3^- into the sediment, where it can be denitrified (Prokopenko et al. 2011). Sedimentary nitrogen can be oxidized anaerobically to NO_3^- (i.e., heterotrophic nitrification) in a coupling with the reduction of Mn^{4+} to Mn^{2+} (Hulth et al. 1999). In some cases, Mn^{3+} accumulates in Mn oxides in the suboxic zone, where it can act as an electron donor or an electron acceptor, depending on upward or downward shifts in redox potential (Anschtz et al. 2005, Trouwborst et al. 2006).

As in the case of freshwater sediments, the zone of Mn-reduction is underlain by zones of Fe-reduction and SO_4^{2-} -reduction ([Figure 9.10](#)). Organic marine sediments undergo substantial diagenesis as a result of sulfate reduction (Froelich et al. 1979, Berner 1984). In marine

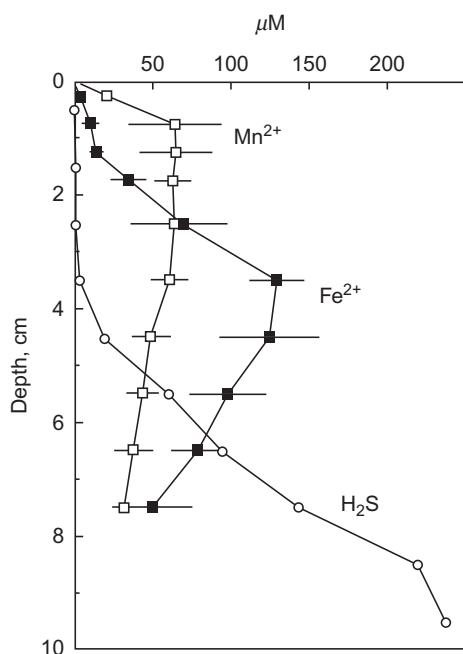


FIGURE 9.10 Pore water distribution of Mn^{2+} , Fe^{2+} , and H_2S in coastal sediments of Denmark, showing the approximate depth of Mn-reduction, Fe-reduction, and SO_4^{2-} -reduction, respectively. Source: From Thamdrup et al. (1994).

environments, sulfate reduction leads to the release of reduced sulfur compounds (e.g., H₂S) and to the deposition of pyrite in sediments (Eqs. 7.19 and 7.20). The rate of pyrite formation is often limited by the amount of available iron (Boudreau and Westrich 1984, Morse et al. 1992), so only a small fraction of the sulfide is retained as pyrite and the remainder escapes to the upper layers of sediment where it is reoxidized (Jorgensen 1977, Thamdrup et al. 1994). When the rate of sulfate reduction is especially high, reduced gases may also escape to the water column. Other metabolic couplings, including anaerobic oxidation of pyrite by NO₃⁻, Fe³⁺, and Mn⁴⁺, are seen when there is mixing of the sediment layers containing these substrates (Schippers and Jorgensen 2002).

Recently, oxidation/reduction reactions have been reported with electric currents transferring the electrons across local redox gradients in marine sediments (Nielsen et al. 2010). Mat-forming bacteria in the genus *Thiopioeca* provide the spatial connection within their own cells, by capturing NO₃⁻ from the overlying water column and transferring it intracellularly to the sediments, where they oxidize sulfides produced by sulfate reduction at depth (Fossing et al. 1995). *Thiopioeca* are related to the bacteria *Beggiatoa*, which oxidize upward diffusing hydrogen sulfide at the sediment surface.

In organic-rich sediments, sulfate reduction may begin within a few centimeters of the sediment surface where O₂ is depleted by aerobic respiration (e.g., Thamdrup et al. 1994). The various pathways of anaerobic metabolism are stimulated by increasing temperature with depth, which mobilizes acetate from buried organic matter (Wellsbury et al. 1997, Weston and Joye 2005). Simultaneously, adsorption of organic matter to clays and iron minerals tends to retard its degradation and lead to preservation (Keil et al. 1994, Kennedy et al. 2002a, Lalonde et al. 2012).

Globally, 9 to 14% of sedimentary organic carbon may be oxidized through anaerobic respiration, especially sulfate reduction (Lein 1984, Henrichs and Reeburgh 1987). The importance of sulfate reduction is much greater in organic-rich, near-shore sediments than in sediments of the open ocean (Skyring 1987, Canfield 1989b, 1991). Near-shore environments are characterized by high rates of NPP and a large delivery of organic particles to the sediment surface. Sulfate reduction generally increases with the overall rate of sedimentation, which is also greatest near the continents (Canfield 1989a, 1993).

Anoxic conditions develop rapidly as organic matter is buried in near-shore sediments. In a marine basin off the coast of North Carolina, Martens and Val Klump (1984) found that 149 moles C m⁻² yr⁻¹ were deposited, of which 35.6 moles were respired annually. The respiratory pathways included 27% in aerobic respiration, 57% in sulfate reduction leading to CO₂, and 16% in methanogenesis. In contrast, in pelagic sediments of the Pacific Ocean, net carbon burial was only 0.005 moles C m⁻² yr⁻¹ (D'Hondt et al. 2004). Near-shore environments promote the hydrogenation of sedimentary organic carbon, often by H₂S from sulfate-reducing bacteria (Hebing et al. 2006). These reduced organic residues are more resistant to decay and likely precursors to the formation of fossil petroleum (Gelinas et al. 2001).

The rate of burial of organic carbon depends strongly on the sedimentation rate (Figure 9.11; Muller and Suess 1979, Betts and Holland 1991). Greater preservation of organic matter in near-shore environments is likely to be due to the greater NPP in these regions (Bertrand and Lallier-Vergès 1993), rapid burial (Henrichs and Reeburgh 1987, Canfield 1991), and somewhat less efficient decomposition under anoxic conditions (Canfield

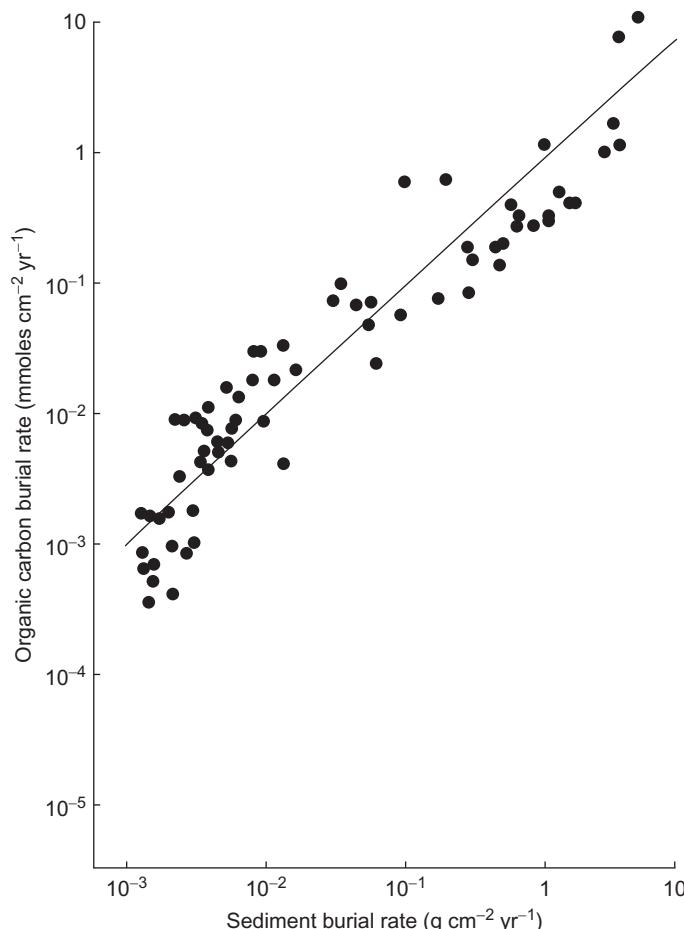


FIGURE 9.11 Burial of organic carbon in marine sediments as a function of the overall rate of sedimentation.
Source: From Berner and Canfield (1989). Reprinted by permission of American Journal of Science.

1994, Kristensen et al. 1995). As seen in soils (Chapter 5), the long-term persistence of organic matter in marine sediments is also enhanced by association with mineral surfaces (Keil et al. 1994, Mayer 1994).

In contrast, pelagic areas have lower NPP, lower downward flux of organic particles, and lower overall rates of sedimentation. The sediments in these areas are generally oxic (Murray and Grundmanis 1980, Murray and Kuivila 1990), so aerobic respiration exceeds sulfate reduction by a large factor (Canfield 1989b, Hartnett and Devol 2003). Little organic matter remains to support sulfate reduction at depth (Berner 1984). Among near-shore and pelagic habitats, there is a strong positive correlation between the content of organic carbon and pyrite sulfur in sediments (Figure 9.12), but it is important to remember that the deposition of pyrite occurs at the expense of organic carbon, namely,



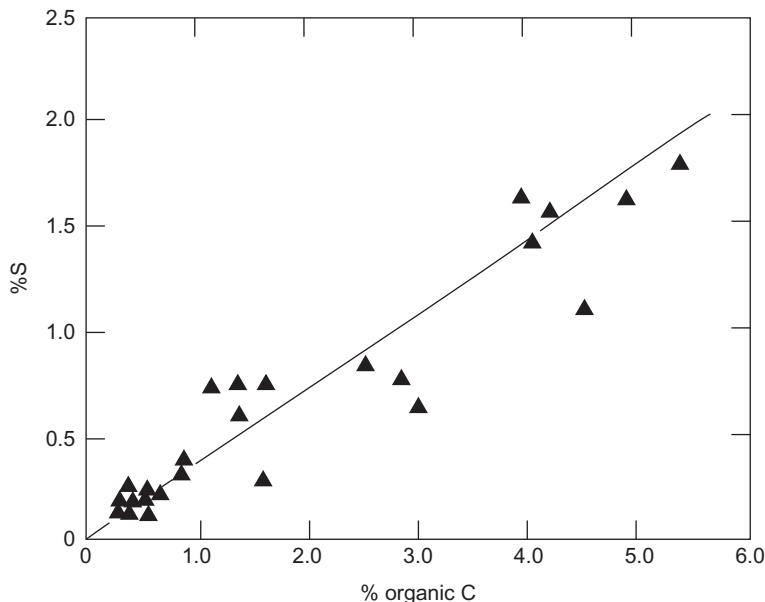


FIGURE 9.12 Pyrite sulfur content in marine sediments as a function of their organic carbon content. Source: From Berner (1984).

Thus, the net ecosystem production of marine environments is represented by the *total* of sedimentary organic carbon + sedimentary pyrite—with the latter resulting from the transformation of organic carbon to reduced sulfur (Eq. 9.2).

Permanent burial of reduced compounds (organic carbon and pyrite) accounts for the accumulation of O₂ in Earth's atmosphere (Chapter 3). The molar ratio is 1.0 for organic carbon, but the burial of 1 mole of reduced sulfur accounts for nearly 2.0 moles of O₂ (Raiswell and Berner 1986, Berner and Canfield 1989). The weight ratio of C/S in most marine shales is about 2.8—equivalent to a molar ratio of 7.5 (Raiswell and Berner 1986). Thus, through geologic time the deposition of reduced sulfur in pyrite may account for about 20% of the O₂ in the atmosphere. During periods of rapid continental uplift, erosion, and sedimentation, large amounts of organic substances and pyrite were buried and the oxygen content of the atmosphere increased (Des Marais et al. 1992). Rising atmospheric O₂ increases aerobic decomposition in marine sediments, consuming O₂ and limiting the further growth of O₂ in the atmosphere (Walker 1980).

In Chapter 7 we saw that redox potential controls the order of anaerobic metabolism by microbes in sediments. The zone of methanogenesis underlies the zone of sulfate reduction, because the sulfate-reducing bacteria are more effective competitors for reduced substrates. As a result of high concentrations of SO₄ in seawater, methanogenesis in ocean sediments is limited (Orem and Taylor 1978, Lovley and Klug 1986, D'Hondt et al. 2002). Nearly all methanogenesis is the result of CO₂ reduction, because normally acetate is depleted before SO₄ is fully removed from the sediment (Sansone and Martens 1981, Crill and Martens



FIGURE 9.13 Methane volatilized from a frozen clathrate can be burned at the Earth's surface. Source: Photo by Gary Klinkhammer, courtesy of NASA.

1986, Whiticar et al. 1986). There is, however, some seasonal variation in the use of CO₂ and acetate that appears to be due to microbial response to temperature (Martens et al. 1986).

In some sediments, methane produced in cold, high-pressure conditions crystallizes with water to form methane hydrates or *clathrates*, which are unstable and volatilize CH₄ when brought to the surface of the Earth (Zhang et al. 2011b; Figure 9.13). There is great interest in clathrates as a commercial source of natural gas as well as great concern that a catastrophic degassing of clathrates in response to global warming might release vast quantities of methane to the atmosphere, exacerbating further warming (Archer et al. 2009). Evidence for large releases of methane from clathrates during climate warming at the end of the last glacial epoch is controversial (Kennett et al. 2000; compare Petrenko et al. 2009, Sowers 2006).

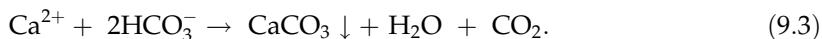
When methane produced at depth diffuses upward through the sediment, it is subject to anaerobic oxidation by methanotrophs (AOM) that use SO₄⁻², Mn⁴⁺, and Fe³⁺ as alternative electron acceptors in the absence of O₂ (Reeburgh 2007, Beal et al. 2009). Some anaerobic methanotrophs are archaea that appear to coexist in consortia with sulfate-reducing bacteria (Hinrichs et al. 1999, Boetius et al. 2000, Michaelis et al. 2002). When sediments are low in organic matter, the rate of sulfate reduction may be determined solely by the upward flux of methane that provides an organic substrate for metabolism (Hensen et al. 2003, Sivan et al. 2007). Methane-consuming archaea are known to fix nitrogen to support their growth in deep sediments, where nitrate has been depleted by denitrification (Dekas et al. 2009).

Methane released from ocean sediments, natural seeps, and hydrothermal vents is easily oxidized by microbes before it reaches the surface (Iversen 1996). For example, a large amount of natural gas associated with the blow out of the Deep-Water Horizon oil well in the Gulf of Mexico was apparently oxidized before it reached the surface (Kessler et al. 2011).

Nevertheless, many areas of the surface ocean are supersaturated in CH₄ with respect to the atmosphere (Ward et al. 1987, Kelley and Jeffrey 2002). This methane appears to result from methanogenesis in decomposing, sinking particles (Scranton and Brewer 1977, Burke et al. 1983, Karl and Tilbrook 1994, Holmes et al. 2000). Methane is not highly soluble in seawater, but the global flux of CH₄ from the oceans to the atmosphere, $\sim 10 \times 10^{12}$ g/yr, is small compared to that from other sources (Liss and Slater 1974, Conrad and Seiler 1988, Reeburgh 2007; Table 11.2).

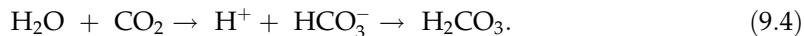
Biogenic Carbonates

A large number of marine organisms precipitate carbonate in their skeletal and protective tissues by the reaction:



Clams, oysters, and other commercial shellfish are the obvious examples, but a much larger quantity of CaCO₃ is produced by foraminifera, pteropods, and other small zooplankton that are found in the open ocean (Krumbein 1979, Simkiss and Wilbur 1989). Some carbonate formed in the guts of fish is carried to the deep sea in their fecal pellets (Wilson et al. 2009). Coccolithophores, a group of marine algae, are responsible for a large amount of CaCO₃ deposited on the seafloor of the open ocean.⁴ The annual production of CaCO₃ by these organisms is much larger than what could be sustained by the supply of Ca to the oceans in river flow (Broecker 1974, Feely et al. 2004). However, not all of the CaCO₃ produced is stored permanently in the sediment.

Recall that CO₂ is produced in the deep ocean by the degradation of organic materials that sink from the surface waters. Deep ocean waters are supersaturated with CO₂ with respect to the atmosphere as a result of their long isolation from the surface and the progressive accumulation of respiratory CO₂. Carbon dioxide is also more soluble at the low temperatures and high pressures that are found in deep ocean water. (Note that CO₂ effervesces when the pressure of a warm soda bottle is released on opening). The accumulation of CO₂ makes the deep waters undersaturated with respect to CaCO₃, as a result of the formation of carbonic acid:



When the skeletal remains of carbonate-producing organisms sink to the deep ocean, they dissolve:



Their dissolution increases the alkalinity, roughly equivalent to the concentration of HCO₃⁻, in the deep ocean. Small particles may dissolve totally during transit to the bottom, while large particles may survive the journey, and their dissolution occurs as part of sediment diagenesis (Honjo et al. 1982, Berelson et al. 1990). Degradation of organic matter in marine sediments, by aerobic or anaerobic processes, generates acidity, furthering the rate of dissolution of biogenic

⁴ Note that the precipitation of carbonate by phytoplankton supplies some of the CO₂ needed for photosynthesis, reducing the net uptake of CO₂ from seawater (Robertson et al. 1994).

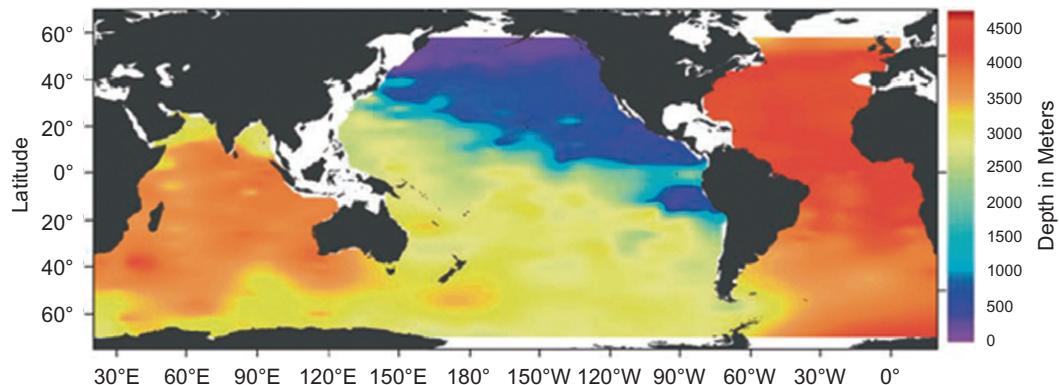


FIGURE 9.14 Calcite saturation depth in the world's oceans. Source: Feely et al. (2004). Used with permission of the American Association for the Advancement of Science.

carbonates that are coprecipitated (Jahnke et al. 1997, Ku et al. 1999, Berelson et al. 1990, Wenzhofer et al. 2001).

The depth at which the dissolution of CaCO_3 begins in the water column is called the carbonate lysocline and is an index of the *carbonate saturation depth* (CSD), the depth at which seawater is undersaturated with respect to CaCO_3 . This depth is roughly 3000 m in the southern Pacific and 4000 to 4500 m in the Atlantic Ocean (Biscayne et al. 1976, Berger et al. 1976; Figure 9.14). Slightly deeper, the *carbonate compensation depth* (CCD) is the depth where the downward flux of carbonate balances the rate of dissolution, so there are no carbonate sediments (Kennett 1982). The tendency for a shallower saturation depth and CCD in the Pacific is the result of the older age of Pacific deep water, which allows a greater accumulation of respiratory CO_2 (Li et al. 1969). Dissolution of sinking CaCO_3 means that calcareous sediments are found only in shallow ocean basins, and no carbonate sediments are found over much of the pelagic area where the ocean is greater than 4500 m deep. About 10×10^{15} g/yr of CaCO_3 are produced in the surface water, and about 0.8×10^{15} g are preserved in deep-ocean sediments (Berelson et al. 2007, Feely et al. 2004).

Added to the estimated carbonate preservation in shallow-water sediments (2.2×10^{15} g; Milliman 1993), this estimate of total carbonate deposition consumes more than the estimated flux of Ca to the oceans, suggesting that the Ca budget of the oceans is not currently in steady state. Today, the preservation ratio of organic carbon to carbonate carbon in ocean sediments is about 0.20 by weight, close to the ratio in the Earth's sedimentary inventory (0.26 in Table 2.3).

Many studies of carbonate dissolution have employed sediment traps that are anchored at varying depths to capture sinking particles. In most areas, biogenic particles constitute most of the material caught in sediment traps, and most of the CaCO_3 is found in the form of calcite. Pteropods, however, deposit an alternative form of CaCO_3 , known as aragonite, in their skeletal tissues. As much as 12% of the movement of biogenic carbonate to the deep ocean may occur as aragonite (Berner and Honjo 1981, Betzer et al. 1984). The downward movement of aragonite has been long overlooked because it is more easily dissolved than calcite and often

disappears from sediment traps that are deployed for long periods. The carbonate lysocline for aragonite is found at 500- to 1000-m depth (Milliman et al. 1999, Feely et al. 2004).

Geochemists have long puzzled that dolomite— $(\text{Ca}, \text{Mg})\text{CO}_3$ —does not appear to be deposited abundantly in the modern oceans, despite the large concentration of Mg in seawater and the occurrence of massive dolomites in the geologic record. There are few organisms that precipitate Mg calcites in their skeletal carbonates, but thermodynamic considerations would predict that calcite should be converted to dolomite in marine sediments (e.g., Malone et al. 1994). Baker and Kastner (1981) show that the formation of dolomite is inhibited by SO_4^{2-} , but dolomite can form in organic-rich marine sediments in which HCO_3^- is enriched and SO_4^{2-} is depleted by sulfate reduction (Eq. 9.2; Baker and Burns 1985). Dolomite is precipitated in laboratory cultures of the sulfate-reducing bacterium *Desulfovibrio* (Vasconcelos et al. 1995). Thus, the precipitation of dolomite is directly linked to biogeochemical processes in marine sediments. Although dolomite has been a significant sink for marine Mg in the geologic past, its contribution to the removal of Mg from modern seawater is likely to be minor.

Rising CO_2 in Earth's atmosphere, as it dissolves in seawater, will raise the acidity of seawater (Eq. 9.4), potentially increasing the dissolution of biogenic carbonates (Eq. 9.5; Hoffman and Schellnhuber 2010). Already, large-scale observations suggest rising dissolved CO_2 and lower pH in the surface of the Pacific Ocean, amounting to a drop of 0.06 in pH during the past 15 years (Takahashi et al. 2006, Byrne et al. 2010; compare Dore et al. 2009). Losses of corals, which are largely built from aragonite, are likely to be the most immediate consequence (Kleypas et al. 1999, Hoegh-Guldberg et al. 2007, Feely et al. 2012), but higher seawater acidity could affect the ability of a wide variety of plankton to build carbonate skeletons (Riebesell et al. 2000, Orr et al. 2005). Aragonite-depositing species are likely to be the most severely affected (Gruber et al. 2012). Differential responses among species can be expected (Iglesias-Rodriguez et al. 2008), disrupting the current food web of marine ecosystems. Of course, the drop in seawater pH is buffered by the dissolution of carbonates (Eq. 9.5), but unregulated CO_2 emissions could lead to a decline of seawater pH of 0.7 units in the next several centuries—a greater change than any observed during the past 300,000,000 years (Zeebe et al. 2008, Hönnisch et al. 2012).

THE BIOLOGICAL PUMP: A MODEL OF CARBON CYCLING IN THE OCEAN

CO_2 dissolves in seawater as a function of the concentration of CO_2 in the atmosphere. (Recall Henry's Law, Eq. 2.7.) The rate of dissolution increases with wind speed, which increases the turbulence of the surface waters⁵ and the downward transport of bubbles (Watson et al. 1991, Wanninkhof 1992, Farmer et al. 1993). As it dissolves in water, CO_2 disassociates to form bicarbonate, following Eqs. 2.4 and 9.3 (Archer 1995). The solubility of CO_2 in seawater depends on temperature; CO_2 is about twice as soluble at 0°C as it is at 20°C (Broecker 1974).

The temperature of the upper 1 mm of the ocean's surface, the "skin" temperature, is critical to determining the atmosphere-to-ocean flux. Over much of the oceans' surface, the skin

⁵ The term "piston velocity" is often used to describe the mixing of gases with seawater. A piston velocity of 5 m/day for CO_2 implies that atmosphere equilibrates with the amount of gas in the upper 5 m of seawater—as if pushed in by a piston—each day.

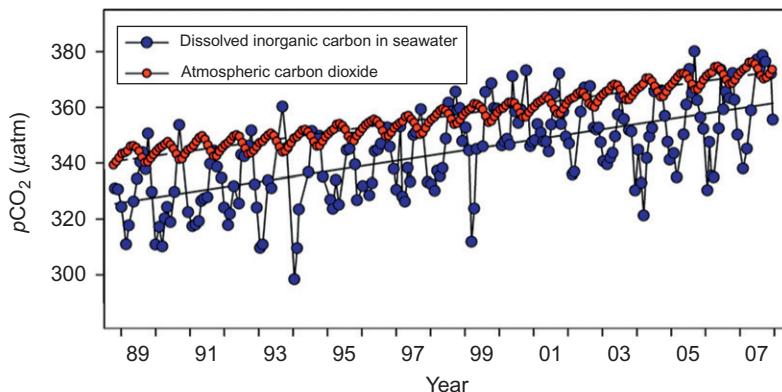


FIGURE 9.15 Dissolved carbon dioxide in seawater (dissolved inorganic carbon + total alkalinity) and $p\text{CO}_2$ in Earth's atmosphere at Mauna Loa, Hawaii, since 1989. Source: From Dore et al. (2009). Used with permission of the National Academy of Sciences.

temperature is about 0.3°C cooler than the underlying waters as a result of evaporation of water from the oceans' surface (Robertson and Watson 1992). Except in areas of upwelling, the surface waters of the oceans are undersaturated with respect to CO_2 in the atmosphere (Takahashi et al. 1997), allowing a net flux of CO_2 into the ocean. Indeed, surface waters show increasing concentrations of dissolved inorganic carbon during the past few decades presumably due to rising CO_2 in Earth's atmosphere (Figure 9.15; Takahashi et al. 2006, Inoue et al. 1995, Peng et al. 1998, Sabine et al. 2004, Dore et al. 2009).

Most CO_2 enters the deep oceans with the downward flux of cold water at polar latitudes. When cold waters form in equilibrium with an atmosphere of 400 ppm CO_2 (i.e., today), they carry more CO_2 than when they formed in equilibrium with an atmosphere of 280 ppm CO_2 —the historical origin of most of today's deep waters that are 300 to 500 years old. Brewer et al. (1989) report that North Atlantic deep water now carries a *net* flux of $0.26 \times 10^{15} \text{ g C/yr}$ southward because of the global rise in atmospheric CO_2 during this century.

In addition, the surface waters in many areas of the oceans are variably undersaturated in CO_2 as a result of photosynthesis. Sinking organic materials remove carbon from the surface ocean, and it is replaced by the dissolution of new CO_2 from the atmosphere. Taylor et al. (1992) found that during a 46-day period there was a net downward transport of carbon in the northeast Atlantic Ocean due to the sinking of live (2 g C/m^2) and dead (17 g C/m^2) cells and the downward mixing of living cells by turbulence (3 g C/m^2). Thus, biotic processes act to convert inorganic carbon (CO_2) in the surface waters to organic carbon that is delivered to the deep waters of the ocean.

As we have seen, the storage of organic carbon in sediments accounts for $<1\%$ of marine NPP, so most of the organic carbon that sinks is liberated by bacterial respiration in the deep ocean and released back to the atmosphere centuries later as CO_2 in zones of upwelling. Nevertheless, in the absence of a marine biosphere, the atmospheric CO_2 concentration would be much higher than today—perhaps as high as 470 ppm (Broecker and Peng 1993). More marine NPP and a more active “biotic pump” are postulated explanations for the lower concentrations of atmospheric CO_2 during the last glacial epoch (Broecker 1982, Paytan et al. 1996, Kumar et al. 1995a).

The biotic pump delivers other forms of carbon to the deep sea. Recall the production and leakage of DOC from phytoplankton in the surface waters. When DOC is entrained in downwelling water, it is delivered to the deep sea, where some of it is respired. As a result of deep-water circulation, concentrations of DOC are greatest in the Atlantic Ocean and lower in the Indian and Pacific Oceans, in which the deep waters are older (Hansell and Carlson 1998a).

Finally, the production and sinking of CaCO_3 also delivers carbon to the deep ocean. Most of the Ca^{2+} is derived from weathering on land and is balanced in riverwater by 2HCO_3^- (Figure 1.3). Whether it is preserved in shallow-water calcareous sediments or sinks to the deep ocean, each molecule of CaCO_3 carries the equivalent of one CO_2 and leaves behind the equivalent of one CO_2 in the surface ocean (Eq. 9.3). Globally, the carbon sink in sedimentary CaCO_3 is about four times larger than the sink in organic sediments (Li 1972). Near-shore environments contain most of the sedimentary storage of CaCO_3 and organic carbon; CaCO_3 delivered to the deep sea dissolves by reaction with H^+ , producing calcium and bicarbonate that return to the surface waters in zones of upwelling (Eq. 9.5; Berelson et al. 2007).

Thus, the biotic pump consists of three processes that remove carbon dioxide from the atmosphere—the fraction of NPP that sinks, downwelling of DOC, and sinking of carbonate skeletal debris (Figure 9.16). These biogeochemical processes are superimposed on a much larger, background flux of CO_2 that enters the oceans by dissolution of CO_2 in cold downwelling waters.⁶ The biotic pump responds to changes in the activity of the biosphere, whereas net downwelling of dissolved CO_2 responds only to changes in the concentration of CO_2 in the atmosphere and the circulation of deep ocean waters.

Equilibrium with ocean waters controls the concentration of CO_2 in the atmosphere, but the equilibrium can be upset when changes in CO_2 in the atmosphere exceed the rate at which the ocean system can buffer the concentration. The seasonal cycle of terrestrial photosynthesis and the burning of fossil fuels are two processes that affect the concentration of atmospheric CO_2 more rapidly than the ocean can react. As a result we observe a seasonal oscillation of atmospheric CO_2 and an exponential increase in its concentration in the atmosphere (Figure 1.1). Given enough time, the oceans could take up nearly all of the CO_2 released from fossil fuels, and the atmosphere would once again show stable concentrations at only slightly higher levels than today (Laurmann 1979, Archer et al. 1998). As the oceans take up CO_2 , they become more acid, with the acidity neutralized by the dissolution of marine carbonates.

A large number of models have been developed to explain the response of the ocean to higher concentrations of atmospheric CO_2 (Bacastow and Björkström 1981, Emanuel et al. 1985b). Most of these models are constructed to follow parcels of water as they circulate in a simplified ocean basin and to calculate the diffusion of CO_2 between layers that do not mix directly. Figure 9.17 on page 369 shows a multibox model in which the surface ocean is divided into cold polar waters and warmer waters. In this model, cold waters mix downward to eight layers of the deep ocean, while upwelling returns deep water to the surface, where it releases CO_2 to the atmosphere. The rate of mixing is calculated using oceanographic data for the rate at which ^{14}C and $^{3}\text{H}_2\text{O}$ from atomic bombs have entered the oceans (Killough and Emanuel 1981) and known constants for the dissolution of CO_2 in water as a function of

⁶ In discussions of the biotic pump, some workers refer to the sinking of NPP as the “soft tissue pump” and the sinking of carbonates as the “hard tissue pump,” both distinguished from the solubility pump, derived from the dissolution of CO_2 in downwelling waters.

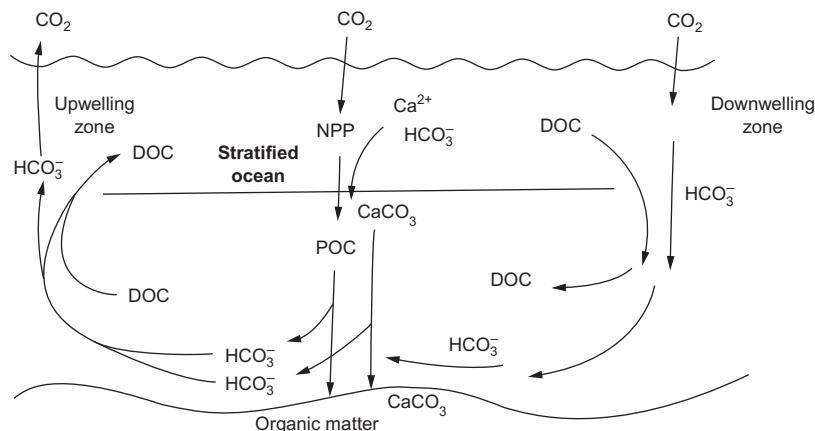


FIGURE 9.16 The marine biotic pump, showing the formation of organic matter (POC) and carbonate skeletons in the surface ocean and their downward transport and the downwelling of DOC and bicarbonate to the deep ocean.

temperature and pressure (Sundquist et al. 1979, Archer 1995). The models then adjust the chemistry of the water in each layer according to the carbonate equilibrium reactions given above.

As atmospheric carbon dioxide increases, we would expect an increased dissolution of CO_2 in the oceans, following Henry's Law. However, the surface ocean provides only a limited volume for CO_2 uptake, and the atmosphere is not in immediate contact with the much larger volume of the deep ocean. In the absence of large changes in NPP, it is the rate of formation of bottom waters in polar regions that limits the rate at which the oceans can take up CO_2 . Reductions in the upwelling and CO_2 degassing of deep waters in the Southern Ocean may have had a large impact on the low concentrations of atmospheric CO_2 during the last glacial epoch (Francois et al. 1997, Kohfeld et al. 2005, Sigman et al. 2010; compare Kumar et al. 1995a). Conversely, greater upwelling may have led to rising CO_2 and warmer temperatures at the end of the last glacial period (Burke and Robinson 2012).

NUTRIENT CYCLING IN THE OCEAN

Net primary productivity in the sea is limited by a scarcity of nutrients. Production is highest in regions of high nutrient availability—the continental shelf and regions of upwelling (Figure 9.8)—and lower in the open ocean, where the concentrations of available N, P, Fe, and Si are normally very low. In most areas of the ocean, nitrate is not measurable in surface waters, and phytoplankton respond to nanomolar additions of nitrogen to seawater (Glover et al. 1988). Nutrients are continuously removed from the surface water by the downward sinking of dead organisms and fecal pellets. Working off the California coast, Shanks and Trent (1979) found that 4 to 22% of the nitrogen contained in particles (PON) was removed from the surface waters each day. The mean residence time of N, P, and Si in the surface ocean is much less than the mean residence time of the surface waters, and there are wide differences in the concentration of these elements between the surface and the deep ocean

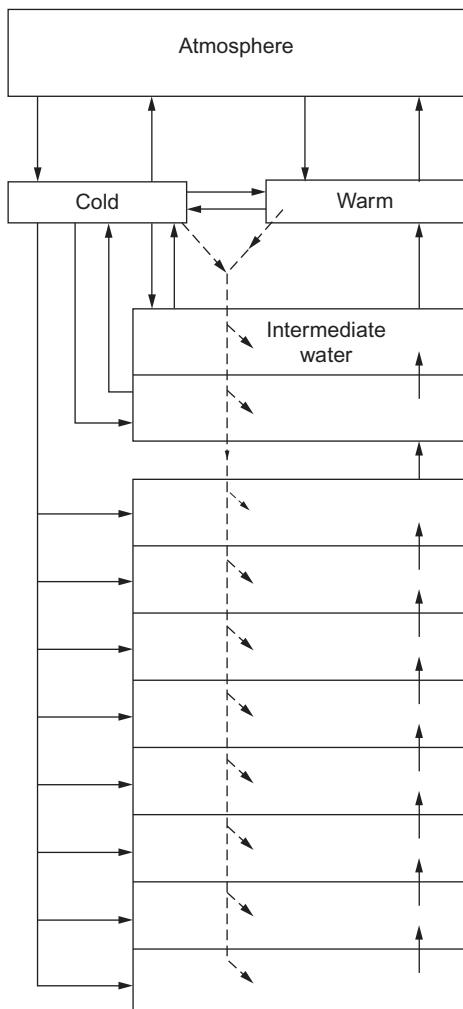


FIGURE 9.17 A box-diffusion model for the oceans, separating the surface oceans into cold polar waters and warmer waters at other latitudes. Cold polar waters mix with deeper waters as a result of downwelling. Other exchanges are by diffusion. *Source: From Emanuel et al. (1985a).*

(Figure 9.18). N, P, and Si are nonconservative elements in seawater; their behavior is strongly controlled by the presence of life.

Nutrients are regenerated in the deep ocean, where the concentrations are much higher than in surface waters. Recalling that the age of deep water in the Pacific Ocean is older than that in the Atlantic, we note that nutrient concentrations are higher in the deep Pacific Ocean (Figure 9.18), because its waters have had a longer time to receive sinking debris that are remineralized at depth. Similarly, in the Atlantic Ocean, nutrient concentrations increase progressively as North Atlantic deep water “ages” during its journey southward (Figure 9.19). Nutrients are also remineralized from DOC that mixes into the deep sea (Hopkinson and Vallino 2005). Nutrients are returned to the surface waters in the upwelling zones of the global thermohaline circulation (Figure 9.3; Sarmiento et al. 2004).

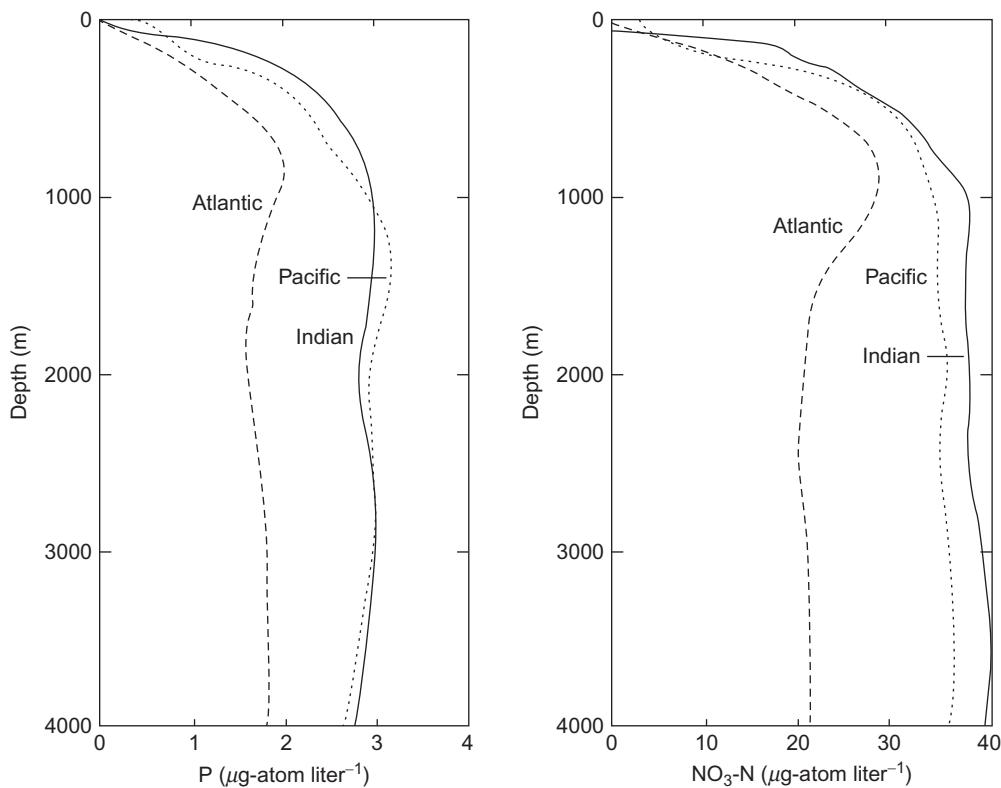
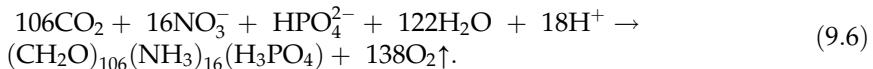


FIGURE 9.18 Vertical distribution of phosphate and nitrate in the world's oceans. Source: From Sverdrup *et al.* (1942).

Internal Cycles

In 1958, Albert Redfield published a paper that has served as a focal point in marine biogeochemistry for the past 50+ years. Redfield noted that marine phytoplankton contain N and P in a fairly constant molar ratio to the content of carbon, 106 C : 16 N : 1P (Redfield *et al.* 1963),⁷ as a result of the incorporation of these elements in photosynthesis and growth:



The molar N/P ratio of 16 may reflect fundamental relationships between the requirements for protein and RNA synthesis common to all plants (Loladze and Elser 2011). Despite differences in nutrient concentration among the major oceans (Figure 9.18), upwelling waters contain available C, N, and P (i.e., HCO_3^- , NO_3^- , and HPO_4^{2-}) in the approximate ratio of

⁷ Equivalent to a mass ratio of 40 C : 7 N : 1P. Thus, the N/P mass ratio in marine phytoplankton is lower than that in terrestrial plants (~15; Chapter 6).

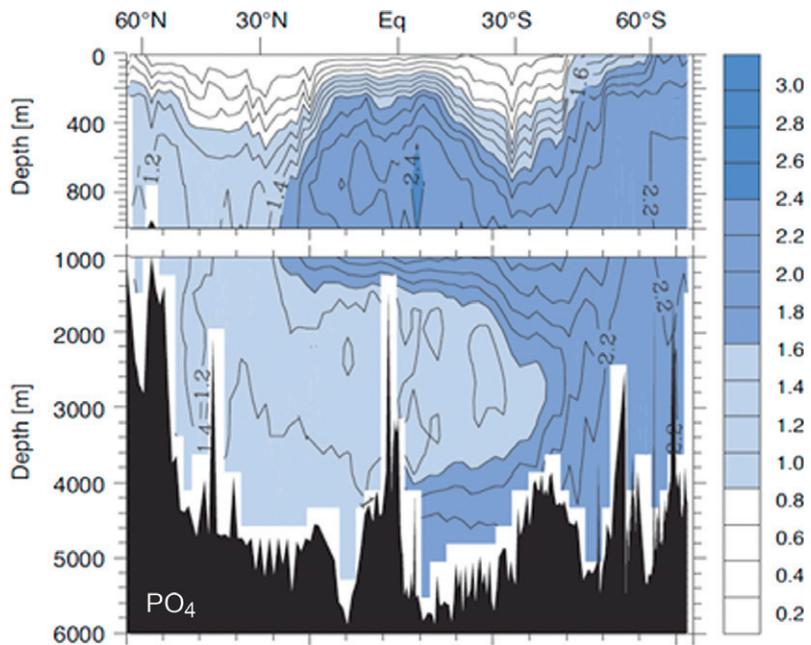


FIGURE 9.19 Phosphorus in the Atlantic Ocean, showing the increase in its concentration in deep waters as they travel from north to south. *Source: From Sarmiento and Gruber (2006). Used with permission of Princeton University Press.*

800 C : 16 N : 1P. Thus, even in the face of the high productivity found in upwelling waters, only about 10% of the HCO_3^- can be consumed by photosynthesis before the N and P are exhausted. Significantly, Redfield (1958) noted that the biota determined the relative concentrations of N and P in the deep sea, and that the biotic demand for N and P was closely matched to the availability of these elements in upwelling waters (Holland 1978).

Recognizing that the downward flux of biogenic particles carries CaCO_3 as well as organic carbon, Broecker (1974) recalculated Redfield's ratios to include CaCO_3 . His modified Redfield ratio in sinking particles is 120 C : 15 N : 1P : 40Ca. The ratio in upwelling waters is 800 C : 15 N : 1P : 3200Ca. Based on these quantities, net production in the surface water could remove all the N and P but only 1.25% of the Ca in upwelling waters. Although biogenic CaCO_3 is the main sink for Ca in the ocean, the biota exerts only a tiny control on the availability of Ca in surface waters. Thus, calcium is a well-mixed and conservative element in seawater (Table 9.1).

It is important to remember that the Redfield ratio is an average value. The nutrient concentrations in individual plankton species may differ from the Redfield ratio depending on season and environmental conditions (Klausmeier et al. 2004, Weber and Deutsch 2010). Nevertheless, as an average value, the Redfield ratio allows us to compare the importance of riverflow, upward transport, and internal recycling for their contributions to the annual net primary production of the surface ocean. To sustain a global marine NPP of $50 \times 10^{15} \text{ g C/yr}$ (Table 9.2), phytoplankton must take up about $8.8 \times 10^{15} \text{ g N}$ and $1.2 \times 10^{15} \text{ g P}$ each year (Table 9.3). Rivers supply about $0.050 \times 10^{15} \text{ g N/yr}$ and $0.002 \times 10^{15} \text{ g/yr}$ of

TABLE 9.3 Calculation of the Sources of Nutrients That Would Sustain a Global Net Primary Productivity of 50×10^{15} g C/yr in the Surface Waters of the Oceans

Flux	Carbon (10^{12} g)	Nitrogen (10^{12} g)	Phosphorus (10^{12} g)
New primary production ^a	50,000	8800	1200
Amounts supplied			
By rivers ^b	50		2
By atmospheric deposition ^c	67		1
By N fixation ^d	150		—
By upwelling	700		100
Recycling (by difference)	7800		1100

Note: Values taken from Figures 9.21 and 9.22, with rounding. Based on an approach developed by Peterson (1981).

^a Assuming a Redfield atom ratio of 106:16:1.

^b N from Galloway et al. (2004); P from Meybeck (1982).

^c Duce et al. (2008).

^d Deutsch et al. (2007).

reactive P to the oceans (Chapters 8 and 12). However, the total nutrient supply from rivers, atmospheric inputs, and vertical movements (upwelling + diffusion + eddy convection) provides only a small fraction (11% for N and 9% for P) of the total nutrient requirement in the surface ocean, so nutrient recycling in the surface waters must supply the rest. Rapid turnover of nutrients is consistent with the rapid turnover of 80 to 90% of the organic carbon in the surface ocean.

In the face of nutrient-limited growth and efficient nutrient uptake, phytoplankton maintain very low concentrations of N and P in surface waters (Figure 9.18). McCarthy and Goldman (1979) showed that much of the nutrient cycling in the surface waters may occur in a small zone, perhaps in a nanoliter (10^{-9} liter) of seawater, which surrounds a dying phytoplankton cell. Growing phytoplankton in the immediate vicinity are able to assimilate the nitrogen as soon as it is released. Often it is difficult to study nutrient cycling on such a small scale, but various workers have applied isotopic tracers (e.g., $^{15}\text{NH}_4$ and $^{15}\text{NO}_3$) to measure nutrient uptake by phytoplankton and bacteria (Glibert et al. 1982, Goldman and Glibert 1982, Dickson and Wheeler 1995). Leakage of dissolved organic nitrogen compounds (DON) from phytoplankton may also account for a significant amount of the bacterial uptake and turnover of nitrogen in the surface waters (Kirchman et al. 1994, Bronk et al. 1994, Kroer et al. 1994). During decomposition of organic particles in the surface ocean, nitrogen is mineralized more rapidly than carbon, so that surviving particles carry C/N ratios that are somewhat greater than the Redfield ratio (Sambrotto et al. 1993) and that increase with depth (Honjo et al. 1982, Takahashi et al. 1985, Anderson and Sarmiento 1994, Alldredge 1998, Schneider et al. 2003).

Nutrient demand by phytoplankton is so great that it has been traditional to assume that little of the NH_4 released by mineralization remains for nitrification in the surface waters, and NH_4 dominates phytoplankton uptake of recycled N (Dugdale and Goering 1967; Harrison et al. 1992, 1996; but see Yool et al. 2007). In contrast, most of the nitrogen mineralized in

the deep ocean is converted to NO_3^- —some by nitrifiers recently recognized as archaea (Konneke et al. 2005, Francis et al. 2005).⁸ Nitrate also dominates the nitrogen supply in rivers, so oceanographers can use the fraction of NPP that derives from the uptake of NH_4^+ versus that derived from NO_3^- to estimate the sources of nutrients that sustain NPP in the surface waters (Figure 9.20).

For example, Jenkins (1988) estimated that the upward flux of NO_3^- from the deep ocean near Bermuda would support an NPP of about $36 \text{ g C m}^{-2} \text{ yr}^{-1}$ —about 38% of observed NPP (Michaels et al. 1994). The remaining production must depend on NH_4^+ supplied by recycling in the surface waters. The fraction of NPP that is sustained by nutrients delivered from atmospheric inputs (including N fixation), rivers, and upwelling is known as *new production*. Globally, new production is about 10 to 20% of total NPP, but the fraction, f_n , is greatest in areas of cold, upwelling waters (Sathyendranath et al. 1991).

Rivers dominate the sources of N in many coastal waters, but in the pelagic oceans, the relative role of nutrient recycling in the surface waters and nutrient delivery by upwelling depends strongly on location. Outside of the major areas of thermohaline upwelling (Figure 9.3), nutrients are delivered to the surface waters by convection in eddies (McGillicuddy et al. 1998, Oschlies and Garçon 1998, Siegel et al. 1999, Johnson et al. 2010) and other processes of large-scale mixing (Uz et al. 2001) and advection (Palter et al. 2005). The vertical migration of diatoms is also known to transport nitrate to the surface (Villareal et al. 1999), and the vertical movements of whales transport nutrients from great depths, where whales feed, to the surface waters, where they defecate (Roman and McCarthy 2010).

Low, steady-state nutrient concentrations in the surface waters of the oceans—near the Redfield N/P ratio of 16—indicate that the sources of nutrients that sustain new production globally are about equal to the annual losses of nutrients in organic debris that sink through the thermocline to the deep ocean—that is, export production (f_e) (Eppley and Peterson 1979). However, it is now recognized that the traditional separation of new and recycled production based solely on the form of nitrogen taken up (NO_3^- vs. NH_4^+ , respectively) is complicated by significant nitrogen fixation in the marine environment, atmospheric deposition of NH_4^+ , and the presence of nitrifying bacteria and archaea that produce NO_3^- in the surface waters (Yool et al. 2007, Martens-Habbena et al. 2009).

Air–Sea Exchange of Nitrogen

In many pelagic waters, nitrogen fixation provides inputs of nitrogen for new production. Observations of significant nitrogen fixation in the pelagic oceans are relatively new, stemming from the widespread occurrence of filamentous cyanobacteria, *Trixochodesmium*, in warm, tropical waters (Carpenter and Romans 1991; Capone et al. 1997, 2005; Davis and McGillicuddy 2006) and unicellular cyanobacteria in other areas (Zehr et al. 2001, Montoya et al. 2004; Moisander et al. 2010).

⁸ Nitrification in the deep sea is a form of chemoautotrophy (Eqs. 2.17 and 2.18) in which carbon is fixed in the dark. Chemoautotrophic nitrification and sulfide oxidation in the oceans is estimated to account for the addition of 0.77 Pg C/yr or 1.5% to NPP (Middelburg 2011).

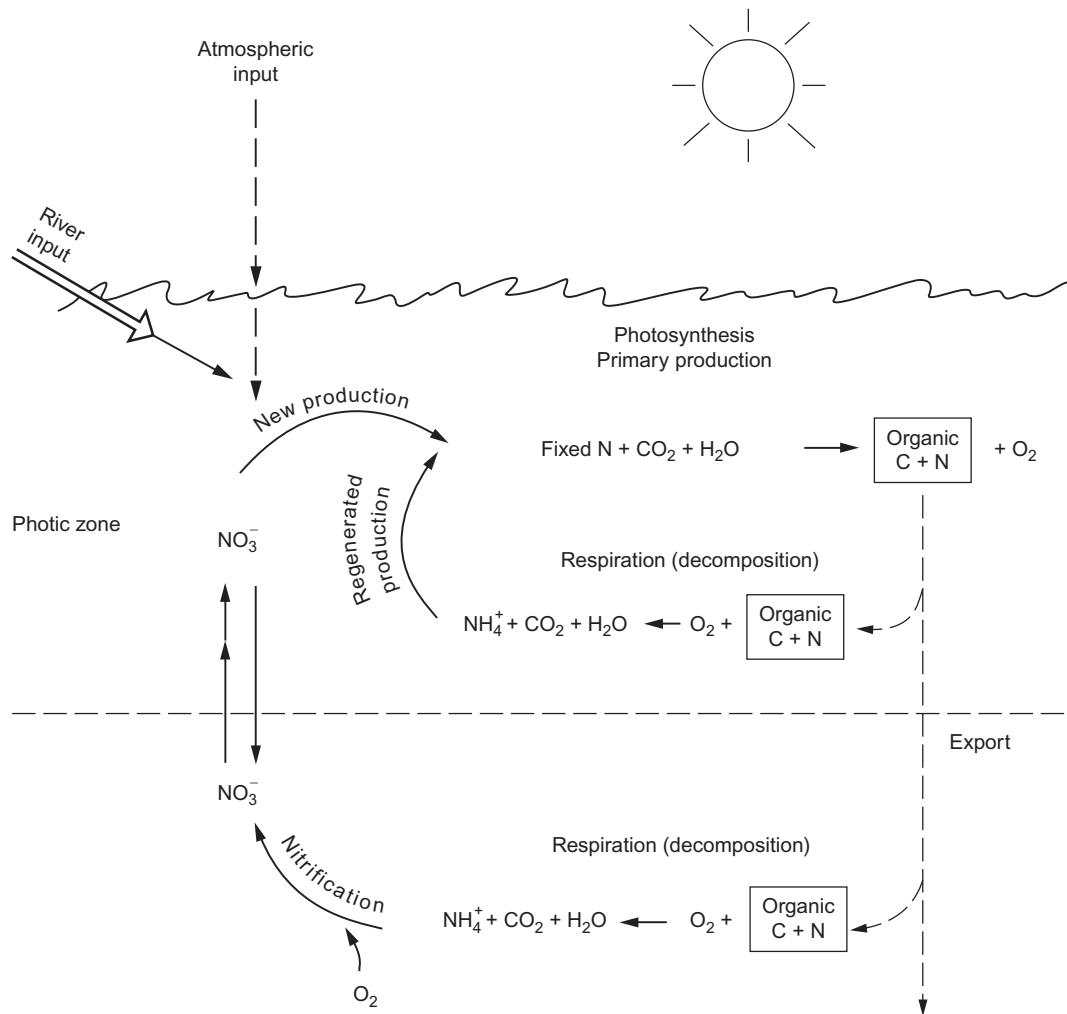


FIGURE 9.20 Links between the nitrogen and the carbon cycles in the surface ocean. Nitrogen regenerated in the surface waters is largely assimilated by phytoplankton as NH₄, while that diffusing and mixing up from the deep ocean is NO₃. When organic matter sinking to the deep ocean is mineralized, its nitrogen content is initially released as NH₄ and converted to nitrate by nitrifying bacteria. “New production” can be estimated as the fraction of net primary production that is derived from nitrate from rivers, atmospheric deposition, nitrogen fixation, and upwelling from the deep sea. *Source: From Jähnke (1990).*

External Inputs

Recalling that the nitrogen-fixing enzyme, nitrogenase, contains iron (Fe) and molybdenum (Mo) in its molecular structure (Chapter 2), the rate of nitrogen fixation in the oceans may be limited by the availability of these elements (Karl et al. 2002). Mo is a well-mixed and conservative element in seawater, but its uptake by phytoplankton appears inhibited by high concentrations of SO₄²⁻ (Howarth and Cole 1985). Fe is largely delivered to the pelagic

oceans by the deposition of desert dusts, which also provide P and Si to surface waters (Jickells et al. 2005). Iron appears to limit nitrogen fixation over much of the pelagic oceans, where Fe inputs are low (Falkowski 1997, Berman-Frank et al. 2001a, Mills et al. 2004; compare Moore et al. 2009, Okin et al. 2011).

Paulsen et al. (1991) found that additions of carbohydrates to seawater stimulated N fixation and postulated that these compounds created local zones of active decomposition, where oxygen is depleted, so nitrogenase activity is possible. Natural aggregations of organic matter, forming “marine snow,” create small microzones of anoxic conditions in seawater, in which a greater availability of trace micronutrients and low redox potentials can stimulate N fixation (Alldredge and Cohen 1987, Paerl and Carlton 1988). Anoxic microzones also develop in bundles of blue-green algae (Paerl and Bebout 1988) and in the endosymbiotic bacteria in diatoms (Martínez et al. 1983), both of which show significant N fixation in the sea. *Trichodesmium* shows spatial and temporal segregation of nitrogen fixation and photosynthesis within the cell to provide anoxic conditions for nitrogenase (Berman-Frank et al. 2001b).

Current estimates suggest global N fixation may account for about 150×10^{12} g N/yr added to the sea—roughly 10× higher than estimates only a couple of decades ago (Mahaffey et al. 2005, Deutsch et al. 2007). As in terrestrial plants, nitrogen fixation in the phytoplankton is associated with $\delta^{15}\text{N}$ of $\sim 0\text{\textperthousand}$ in plankton biomass and in organic debris in sediments (Karl et al. 2002). This isotopic signature can be used to estimate nitrogen fixation in the water column (Mahaffey et al. 2003). Through glacial-interglacial cycles, the rate of nitrogen fixation in the oceans appears to relate to the distribution of desert dust in the atmosphere; high marine NPP during the last glacial may have derived from a greater deposition of Fe in the oceans from desert dust (Falkowski et al. 1998). The deposition of desert dust in the oceans links marine NPP to soil biogeochemistry of distant terrestrial ecosystems. Thus, in many areas primary productivity in the sea appears limited by available N, but the amount of N is largely determined by the deposition of Fe for the synthesis and activity of nitrogenase (Falkowski 1997, Wu et al. 2000, Moore and Doney 2007).

In the open ocean, direct atmospheric deposition of nitrogen in rainfall and dryfall is a small additional source of nutrients for new production, since these areas are distant from rivers and upwelling. Prospero and Savoie (1989) found that 40 to 70% of the nitrate in the atmosphere over the North Pacific Ocean was derived from soil dusts, presumably from the desert regions of China. Humans have increased the transport of reactive nitrogen from land to sea, largely as air pollutants (Duce et al. 2008). In some coastal regions downwind of pollution sources, an increased deposition of reactive nitrogen compounds from air pollution may cause higher marine NPP (Paerl 1995, Fanning 1989, Kim et al. 2011). Since reactive nitrogen is quickly removed from the atmosphere, its transport and deposition are more important in coastal areas than in the pelagic oceans.

Gaseous Losses of Nitrogen from the Sea

NPP in many ocean waters shows a tendency for limitation by available N (Howarth 1988, Falkowski 1997). What processes lead to N limitation in the sea? Denitrification in a zone of low O₂ concentration in the eastern Pacific Ocean may result in the loss of $50 \text{ to } 60 \times 10^{12}$ g N from the oceans each year (Codispoti and Christensen 1985, Deutsch et al. 2001). Other regions with suboxic conditions in the water column also provide local areas for marine denitrification. Often these are regions of high NPP, with oxygen depletion in the mid-water

column due to the decomposition of sinking organic debris. The anoxic microzones created by flocculations of organic matter allow significant rates of denitrification in the oceans, despite the high redox potential of seawater (Allredge and Cohen 1987).

As we saw in terrestrial ecosystems (Chapter 6), $^{14}\text{NO}_3^-$ is used preferentially as a substrate in the production of N_2 during denitrification. Denitrification results in a high content of ^{15}N in the residual nitrate in seawater (Liu and Kaplan 1989, Sigman et al. 2000, Voss et al. 2001). Denitrification is estimated from measures of $\delta^{15}\text{N}$ in the residual nitrate pool, as well as excess concentrations of dissolved N_2 gas in seawater (Chang et al. 2010). The pool of nitrate left in the ocean, which is taken up by phytoplankton, leaves an enriched ^{15}N signature in organic sediments. Recall we used this signature to ascertain the origin of denitrification in the geologic history of the Earth (Chapter 2).

Denitrification is also observed in ocean sediments, where it is performed by bacteria and a few specialized benthic eukaryotes (Piña-Ochoa et al. 2010). Christensen et al. (1987) estimate that over 50×10^{12} g N/yr may be lost from the sea by sedimentary denitrification in coastal regions. Devol (1991) found that nitrification occurring within the sediments supplied most of the nitrate for denitrification on the continental shelf of the western United States. Denitrification in sediments leaves the NO_3^- pool in the pore space enriched in ^{15}N (Lehmann et al. 2007). Including sediments, the overall rate of denitrification in the oceans is estimated between 270 and 482×10^{12} g N/yr (Brandes and Devol 2002, Codispoti et al. 2001, Galloway et al. 2004, Bianchi et al. 2012), which is slightly in excess of the current estimate of N inputs to the oceans. Changes in the balance of nitrogen fixation and denitrification have controlled the nitrogen content of the oceans through geologic time (Ganeshram et al. 1995, Ren et al. 2009).

Most of the gaseous nitrogen lost from marine environments by denitrification is N_2 ; however, seawater is supersaturated with N_2O in many regions (e.g., Walter et al. 2004b), and the oceans supply about 25% of the annual source of N_2O to the atmosphere (Table 12.4). Much of this N_2O may be derived from the oxidation of ammonia by archaea and other nitrifying species in the water column (Santoro et al. 2011).

Just a few years ago, several investigators reported an unusual microbial metabolism: the anaerobic oxidation of ammonium, using nitrite as an alternative electron acceptor in place of oxygen (Mulder et al. 1995, Strous et al. 1999, Kuypers et al. 2003, Schmidt et al. 2002). The reaction is performed by *Planctomyces* and a few other bacteria:



and the mechanism of the reaction has recently been elucidated at the molecular level (Kartal et al. 2011). Known as *anammox*, the reaction produces N_2 gas, so it is difficult to separate anammox from denitrification. Both occur only in portions of the water column that are highly depleted in O_2 . While significant in some high-productivity waters (Dalsgaard et al. 2003, Kuypers et al. 2005), the flux of N_2 from anammox is lower than that from denitrification in the suboxic waters of the Arabian Sea where both have been measured together (Ward et al. 2009, Bulow et al. 2010). In coastal sediments of the eastern United States and Sweden, Engstrom et al. (2005) found that 7 to 79% of the N_2 flux from sediments was due to anammox.

Finally, a small amount of ammonia is lost from the surface of the sea, where NH_4^+ is deprotonated to form gaseous NH_3 in the slightly alkaline conditions of seawater

(Eq. 6.4; Quinn et al. 1988, Jickells et al. 2003). This source of ammonia contributes about 15% to the annual global flux of NH_3 to the atmosphere (Chapter 12).

A Global Budget for Nitrogen in the Oceans

A global model for the N cycle of the oceans (Figure 9.21) offers a deceptive level of tidiness to our understanding of marine biogeochemistry, and the reader should realize that many fluxes, for example, nitrogen fixation, denitrification, and sedimentary preservation, are not known to better than a factor of two. Nevertheless, the model shows that most NPP is supported by nutrient recycling in the surface waters, and only small quantities of nutrients

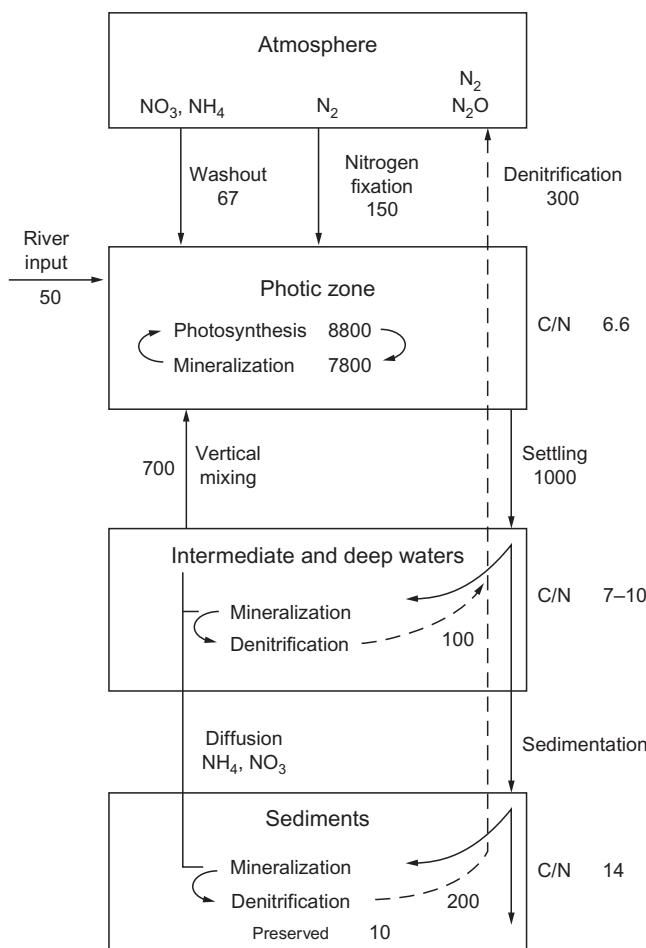


FIGURE 9.21 Nitrogen budget for the world's oceans, showing major fluxes in units of 10^{12} gN/yr . From an original conception by Wollast (1981), but with newer data added for atmospheric deposition (Duce et al. 2008), nitrogen fixation (Deutsch et al. 2007), riverflow (Galloway et al. 2004), denitrification (Brandes and Devol 2002), and nutrient regeneration in surface waters (compare Table 9.3). The global values have been rounded.

are lost to the deep ocean. Assuming that the total N pool in marine biota is $\sim 500 \times 10^{12}$ gN (Galloway et al. 2004), the mean residence time of the available nitrogen (inorganic and organic) in the surface ocean is about 125 days, whereas the mean residence time of organic N is about 20 days. Thus, each atom of N cycles through the biota many times.

In the absence of upwelling, the biotic pump would remove the pool of nutrients in the surface water in less than a year. After sinking and mineralization in the deep ocean, N enters pools with a mean residence time of about 500 years—largely controlled by the circulation of water through the deep ocean. The nitrogen cycle is dynamic; the overall mean residence time for N in the oceans is estimated to be ~ 2000 years, so the nitrogen cycle is responsive to global changes over relatively short periods (Brandes and Devol 2002).

Vertical mixing includes upwelling, upward convection, and diffusion from the deep ocean. Upwelling accounts for about half of the global upward flux, and it is centered in coastal areas where the resulting nutrient-rich waters yield high productivity. Away from areas of upwelling, diffusion and convection dominate the upward flux (Table 9.4), but diffusion rates are low (Ledwell et al. 1993), so the total supply of nutrients is limited in most of the open ocean (Lewis et al. 1986, Martin and Gordon 1988). Diffusion appears globally significant only as a result of the large area of pelagic ocean compared to the small area of upwellings.

Phosphorus

Phosphorus is nearly undetectable in most surface seawaters. Upwelling waters deliver N and P in amounts close to the Redfield ratio of 16, so it is reasonable to surmise that N and P would be depleted in tandem by the growth of phytoplankton. The long-standing debate over N versus P limitations to ocean NPP now appears settled in favor of N, as a result of the substantial rates of denitrification recently reported in marine environments. Nevertheless, phosphorus appears to limit phytoplankton activity in some regions (Wu et al. 2000), and

TABLE 9.4 Sources of Fe, PO₄, and NO₃ in Surface Waters of the North Pacific Ocean

Source	Fe	PO ₄	NO ₃
Concentration at 150 m ($\mu\text{mol m}^{-3}$)	0.075	330	4300
Upwelling ($\mu\text{mol m}^{-2} \text{ day}^{-1}$)	0.00090	4.0	52
Net upward diffusion ($\mu\text{mol m}^{-2} \text{ day}^{-1}$)	0.0034	30	400
Atmospheric flux ($\mu\text{mol m}^{-2} \text{ day}^{-1}$)	0.16	0.102	26
Total fluxes ($\mu\text{mol m}^{-2} \text{ day}^{-1}$)	0.164	34	480
Percent from advective input	0.5	12	11
Percent from diffusive input	2	88	83
Percent from atmospheric input	98	0	5

Source: From Martin and Gordon (1988).

Fe and P appear to colimit the growth of nitrogen-fixing *Trichodesmium* in the Atlantic Ocean (Mills et al. 2004). *Trichodesmium* appears to have evolved specialized mechanisms to assimilate dissolved organic P compounds, known as phosphonates, from seawater (Dyhrman et al. 2006), and various phytoplankton appear to reduce the phospholipid content of cellular membranes when P is in particularly short supply (van Mooy et al. 2009).

As seen in Chapter 8, only a small portion of the total phosphorus transport in rivers (21×10^{12} g P/yr) is carried in dissolved forms; the remainder is adsorbed to Fe and Al oxide minerals that are carried as suspended particles. Some of the adsorbed P is released following the mixing of freshwater and seawater (Chase and Sayles 1980, Caraco et al. 1990), but most is probably buried with the deposition of terrigenous sediments on the continental shelf (Filippelli 1997). The total flux of “bioreactive” P to the oceans is about 2.0×10^{12} g/yr (Ramirez and Rose 1992, Delaney 1998), giving an atom ratio of ~ 55 for N/P(reactive) in global riverflow.

Deposition of P on the ocean surface from the dust of deserts may play a special role in stimulating new production in areas of the open ocean that are distant from rivers and zones of upwelling (Wu et al. 2000; Mills et al. 2004). However, as seen for N, recycling of P in the surface waters accounts for the vast majority of the P uptake by phytoplankton (Figure 9.22). Most of the phosphorus pool in plankton is remineralized within a few days (Benitez-Nelson and Buesseler 1999). Phosphorus appears to be mineralized selectively from the phosphonate

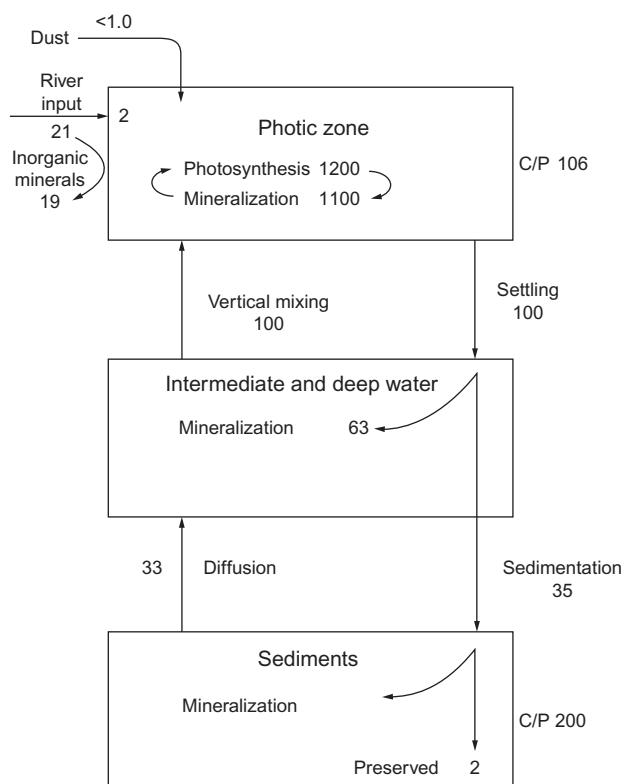


FIGURE 9.22 A phosphorus budget for the world’s oceans, with important fluxes shown in units of 10^{12} g P/yr. From an original conception by Wollast (1981), but with newer data added for dust inputs (Graham and Duce 1979), riverflow (Meybeck 1982), sedimentary preservation (Wallman 2010), and nutrient regeneration in surface waters (compare Table 9.3). The global values have been rounded.

component of DOC (Clark et al. 1999). Each year a small amount of organic debris, with C/P ratios somewhat greater than the Redfield ratio, sinks through the thermocline to the deep ocean (Honjo et al. 1982). An average of 500 years later, mineralized P (i.e., HPO_4^{2-}) returns to the surface waters in upwelling.

The C/P ratio in organic matter that is buried in marine sediments is about 200 (Mach et al. 1987, Ingall and Van Cappellen 1990, Ramirez and Rose 1992), suggesting that P is mineralized more rapidly than C during the downward transport and sedimentary diagenesis of organic matter in the sea (Honjo et al. 1982, Froelich et al. 1979, Loh and Bauer 2000). Phosphorus release and C/P ratios are greatest in anoxic sediments (Ingall et al. 1993, Ingall and Jahnke 1997; [Figure 9.23](#)). Anoxic environments have lower concentrations of oxidized Fe minerals that can adsorb P as it is mineralized from organic matter (Krom and Berner 1981, Sundby et al. 1992, Berner and Rao 1994, Blomqvist et al. 2004). Both dissolved and inorganic P are adsorbed to iron oxide minerals, especially less crystalline forms (Ruttenberg and Sulak 2011; compare [Chapter 4](#)).

In contrast to N, there are no significant gaseous losses of P from the sea. At steady state, the inputs to the sea in river water must be balanced by the burial of phosphorus in ocean sediments. Most of the P carried in suspended sediments is probably deposited near the coast of continents, where P burial parallels overall rates of sedimentation (Filippelli 1997). Burial of biogenic P compounds in sediments of the open ocean is estimated between about 2.0×10^{12} g P/yr—similar to the delivery of bioreactive P in rivers (Howarth et al. 1995a, Delaney 1998, Wallman 2010). Burial occurs with the deposition of organic matter or CaCO_3 (Froelich et al. 1982), with at least a portion of the burial being in biogenic polyphosphates (Diaz et al. 2008). During sediment diagenesis, organic- and Fe-bound P are converted to phosphorites (authigenic apatite), which ultimately dominate the P storage in sediments (Ruttenberg 1993, Filippelli and Delaney 1996, Rasmussen 1996).

Phosphorite is formed when the PO_4^{3-} produced from the mineralization of organic P combines with Ca and F to form fluorapatite, in a mineral known as francolite (Ruttenberg and Berner 1993, Krajewski et al. 1994, Anderson et al. 2001). Organic P disappears from sediments in parallel with an increase in francolite formed within them (Filippelli and Delaney

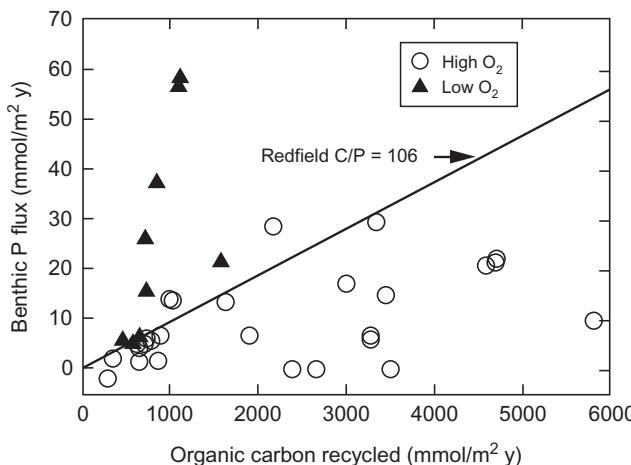


FIGURE 9.23 Flux of phosphorus from sediments to the water column as a function of the decomposition of organic carbon in areas of high and low O_2 in the overlying waters. Source: From Ingall and Jahnke (1997).

1996, Delaney 1998). In coastal California sediments, Kim et al. (1999) found that francolite sequestered about 30% of the P mineralized from organic compounds or adsorbed to Fe-oxides. The F is supplied by inward diffusion from seawater (Froelich et al. 1983, Schuffert et al. 1994). In some areas of the ocean, phosphorite nodules up to several centimeters in diameter accumulate on the seafloor. These nodules are an enigma; they remain on the surface of the sediment despite growing at rates slower than the rate of sediment accumulation (Burnett et al. 1982).

The mean residence time for reactive P in the oceans, relative to the input in rivers or the loss to sediments, is >25,000 years (Ruttenberg 1993, Filippelli and Delaney 1996, Delaney 1998). Thus, each atom of P that enters the sea may complete 50 cycles between the surface and the deep ocean before it is lost to sediments. The major sinks include the formation of authigenic phosphorites (francolite) and uptake at hydrothermal vents (Elderfield and Schultz 1996, Wheat et al. 2003). All forms of buried phosphorus complete a global biogeochemical cycle when geologic processes lift sedimentary rocks above sea level and weathering begins again. Thus, relative to N, the global cycle of P in the oceans turns very slowly ([Chapter 12](#)).

Human Perturbations of Marine Nutrient Cycling

The riverine input of N and P to the coastal oceans has increased in recent years, the result of direct human effluents and an increasing global use of nitrogen fertilizers (Howarth 1998, Boyer et al. 2006; [Chapter 8](#)). Fossil fuel pollutants and emissions of NH₃ from agricultural soils and livestock have also increased the atmospheric deposition of N on the ocean surface (Duce et al. 2008). These inputs have probably enhanced the productivity of coastal and estuarine ecosystems ([Chapter 8](#)) and perhaps the productivity of the entire ocean (Paerl 1995). Pahlow and Riebesell (2000) report a rising N/P ratio in export production from pelagic oceans in the Northern Hemisphere during the past 50 years, perhaps reflecting the widespread impacts of nitrogen deposition in the sea. Greater net primary production in the surface ocean should result in a greater transport of particulate carbon to the deep sea, potentially serving as a sink for increasing atmospheric CO₂.

Net primary production of $\sim 50 \times 10^{15}$ g C/yr is supported by nitrogen derived from a variety of sources ([Table 9.3](#)). If an additional 54×10^{12} g N/yr is deposited in the surface waters from atmospheric pollution (Duce et al. 2008), this “excess” nitrogen could result in an increase in the downward flux of organic carbon of about 0.30×10^{15} g/yr, assuming a Redfield atom ratio of 106 C/16 N in new production ([Figure 9.24](#)). Paerl et al. (1999) noted a significant stimulation of NPP in coastal and pelagic waters of the western Atlantic with the addition of synthetic rainfall containing small amounts of N.

Similar calculations using the “excess” flux of N in rivers (Schlesinger 2009) suggest an increased new production of $< 0.20 \times 10^{15}$ g C/yr in coastal zones (Wollast 1991), although many studies indicate that much of the river flux of N is largely denitrified in coastal sediments (Seitzinger et al. 2006). For comparison, the current release of carbon dioxide to the atmosphere from fossil fuel combustion is about 9×10^{15} g C/yr ([Chapter 11](#)). This increased NPP in the oceans offers an additional sink for atmospheric CO₂ (Rabouille et al. 2001, Krishnamurthy et al. (2007), but it is associated with significant problems of coastal eutrophication (Diaz and Rosenberg 2008, Doney 2010; [Chapter 8](#)). Globally marine NPP has probably

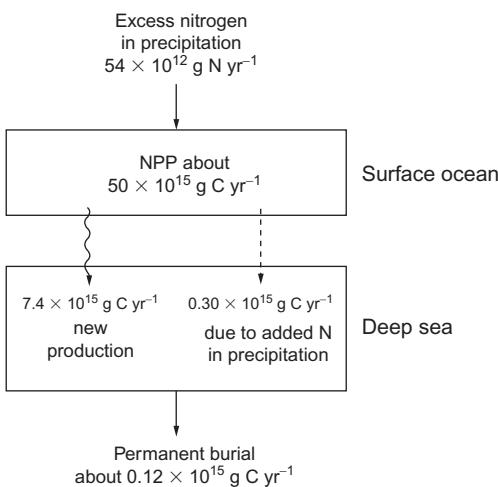


FIGURE 9.24 Estimated increase in the sedimentation of organic carbon that might be caused by human additions of nitrogen to the world's oceans by precipitation. Updated from an original conception by Peterson and Melillo (1985), based on current anthropogenic atmospheric inputs of Duce et al. (2008).

increased ~3% from anthropogenic nitrogen deposition from the atmosphere (Duce et al. 2008). The major ocean sink for anthropogenic CO₂, about 2.3×10^{15} g C/yr (Table 11.1), is found as a result of an increased dissolution of CO₂ in cold waters of the polar oceans (Shaffer 1993). As we discussed earlier, this inorganic sink for CO₂ is limited by the area of polar oceans and the amount of downwelling water.

Human perturbations of marine ecosystems are greatest in estuarine, coastal, and continental shelf waters (Chapter 8). These areas occupy only about 8% of the ocean's surface, but they account for about 18% of ocean productivity (refer to Table 9.2), and 83% of the carbon that is buried in sediments. Globally averaged models (e.g., Figures 9.21 and 9.22) mask the comparative importance of these regions to the overall biogeochemical cycles of the sea. For example, a significant amount of organic carbon may be transported from the continental shelf to the deep sea (Walsh 1991, Wollast 1993). If global climate change alters the rate of coastal upwelling (Bakun 1990), significant changes in the ocean's overall biogeochemistry can be expected (Walsh 1984).

Silicon, Iron, and Trace Metals

Phytoplankton acquire micronutrients from seawater, leaving an imprint on the distribution of trace elements in the sea. The concentrations of many essential elements, such as Si, Fe, Zn, Cu, Co, and Ni, are depleted in the surface waters and increase with depth (Bruland et al. 1991, Donat and Bruland 1995, Shelley et al. 2012). A few nonessential elements, such as Ti and Ba, which adsorb to sinking particles, also show this nonconservative behavior in seawater. Meanwhile, essential elements that are abundant in seawater (e.g., K, Mg, B, Sr, Mo, and SO₄) show conservative behavior, with long mean residence times and similar concentrations at all depths.

These patterns suggest that the geochemistry of many trace elements in seawater is controlled directly and indirectly by biota. Cherry et al. (1978) show that the mean residence time for 14 trace elements in seawater is inversely related to their concentration in sinking fecal

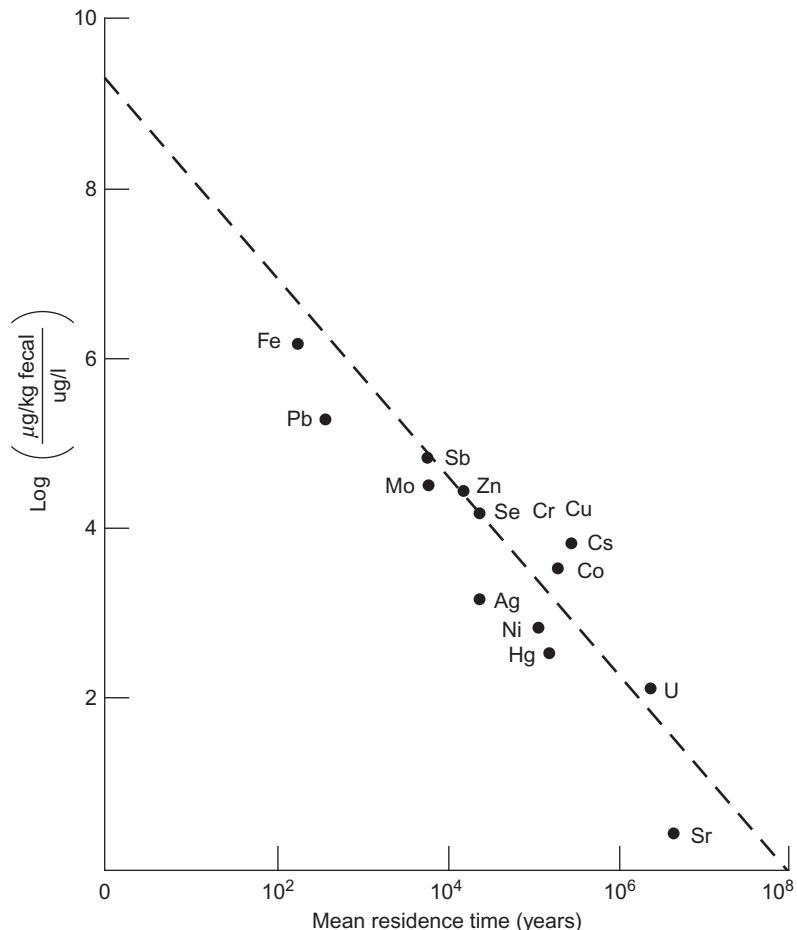


FIGURE 9.25 The ratio between the concentration of an element in sinking fecal pellets ($\mu\text{g}/\text{kg}$) and its concentration in seawater ($\mu\text{g}/\text{l}$), plotted as a function of its mean residence time in the ocean. Source: From Cherry *et al.* (1978). Reprinted with permission from Nature, copyright 1978 Macmillan Magazines Limited.

pellets (Figure 9.25). Some of these elements are remineralized by grazing zooplankton (Reinfelder and Fisher 1991) or by the degradation of POC by bacteria in the deep ocean. But the fate for many trace constituents is downward transport in organic particles and burial in the sediments of the deep sea (Turekian 1977, Lal 1977, Li 1981). Elements with less interaction with biota remain as the major constituents of seawater (refer to Table 9.1).

Diatoms compose a large proportion of the marine phytoplankton, and they require silicon (Si) as a constituent of their cell walls, where it is deposited as opal. As a result of biotic uptake, the concentration of dissolved Si in the surface waters is very low, usually $< 2 \mu\text{M}$, with the highest concentrations in the Southern and the North Pacific Oceans (Ragueneau *et al.* 2000). Globally, the annual uptake of Si by diatoms is about $6000 \times 10^{12} \text{ g}$ (Nelson *et al.*

1995). After the death of diatoms, a large fraction of the opal dissolves, and the Si is recycled in the surface waters, where bacterioplankton mediate the dissolution process (Bidle and Azam 1999).

Silicate concentrations generally increase with depth, but the dissolution of opal is dependent on temperature, so the rate of dissolution in the deep ocean is relatively slow (Honjo et al. 1982, Bidle et al. 2002, Van Cappellen et al. 2002). The average Si concentration in deep waters is about $70 \mu\text{M}$. In sinking particles and in ocean sediments, Si/C ratios increase with depth, suggesting that C is mineralized more readily than Si (Nelson et al. 2002). Globally, the burial efficiency for opaline Si is about 3% of production—significantly greater than for organic carbon (<1%) (DeMaster 2002). Silicon loss is retarded when dissolved silicon complexes with Al in the sediments (Dixit et al. 2001).

A mass-balance model for Si in the oceans shows that rivers ($156 \times 10^{12} \text{ g/yr}$), dust ($14 \times 10^{12} \text{ g/yr}$), and hydrothermal vents ($17 \times 10^{12} \text{ g/yr}$) are the main sources, and sedimentation of biogenic opal is the only significant sink (DeMaster 2002). The mean residence time for Si in the oceans is about 15,000 years, which is consistent with its nonconservative behavior in seawater. Most of the Si input is delivered by tropical rivers, as a result of high rates of rock weathering in tropical climates (Chapter 4). Sedimentation in the cold waters of the Antarctic Ocean accounts for 70% of the global sink (Ragueneau et al. 2000, DeMaster 2002), largely as a result of massive seasonal diatom blooms in the Southern Ocean near Antarctica (Nelson et al. 2002). About 10% of the sink is found in coastal regions, where the growth of diatoms in nutrient-enriched waters may be limited by silicon (Justic et al. 1995). Increasing deposition of desert dusts to the ocean surface, potentially stimulating diatom productivity and export production with a higher organic carbon content relative to CaCO_3 , may explain periods with lower CO_2 in Earth's atmosphere (Harrison 2000).

Similar to the use of Si by diatoms, marine protists known as acantharians require strontium (Sr). These organisms precipitate celestite (SrSO_4) as a skeletal component. As a result of the uptake of Sr in surface waters and the sinking of acantharians to the deep sea, the Sr/Cl ratio in seawater varies from about $392 \mu\text{g/g}$ in surface waters to $>405 \mu\text{g/g}$ with depth—relatively conservative behavior (Bernstein et al. 1987). The biotic demand for Sr leaves only a slight imprint on the large pool of Sr in the oceans; its overall mean residence time is about 12,000,000 years (Table 9.1).

All phytoplankton require a suite of micronutrients, for example, iron (Fe), copper (Cu), and zinc (Zn), in their biochemistry, where they are cofactors in metabolic enzymes (Morel and Price 2003). These elements are taken up in surface waters and mineralized when dead organisms sink to the deep ocean. Many of these elements are relatively insoluble in seawater, which typically has high redox potential (Chapter 7). Most metals are found at low concentrations in the surface waters, and concentrations increase with depth in the deep sea (e.g., Figure 9.26). In response to low concentrations of Fe, some bacterioplankton release organic compounds, known as siderophores, that chelate dissolved Fe and enhance its assimilation from seawater (Wilhelm et al. 1996, Butler 1998, Mendez et al. 2010). Organic complexes dominate the total concentrations of Fe, Zn, and Cu in surface waters (Bruland et al. 1991, Morel and Price 2003).

Near continents, the concentration of Fe in seawater is normally adequate to support phytoplankton growth, as a result of the inputs from rivers and local upwelling of waters (Hutchins et al. 1998, Firme et al. 2003, Elrod et al. 2004). In the central Pacific Ocean, however, Martin and Gordon (1988) found that internal sources of Fe could sustain only a small

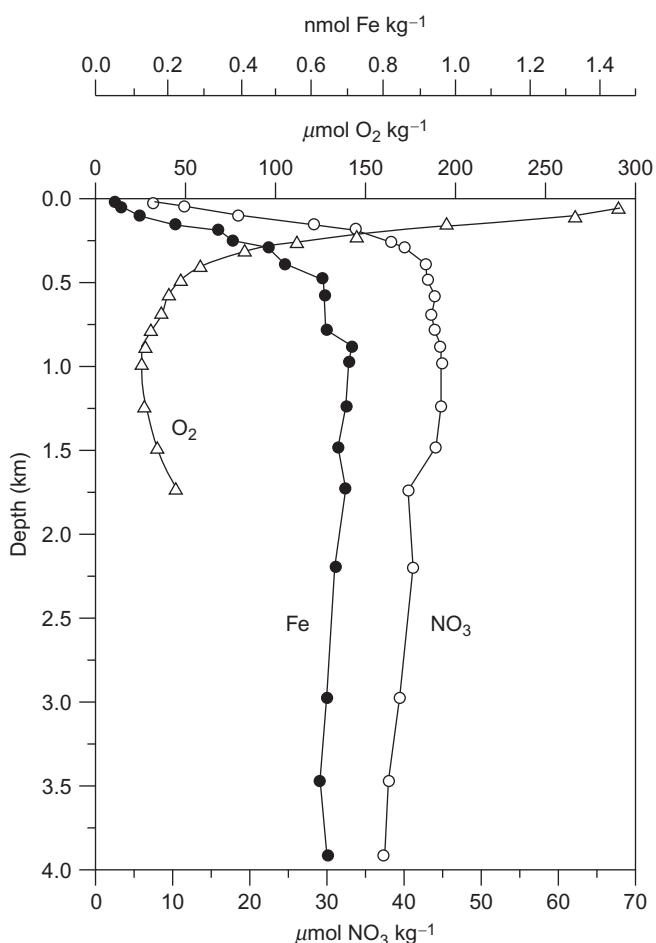


FIGURE 9.26 Vertical distribution of Fe, NO_3 , and O_2 in the central North Pacific Ocean. Source: From Martin et al. (1989).

percentage of the observed NPP. They suggested that as much as 98% of the new production in this area is supported by Fe derived from dust deposited from the atmosphere (Table 9.4). Most of the dust deposited in this region is probably transported from the deserts of central China (Duce and Tindale 1991, Uematsu et al. 2003). Growth of phytoplankton appears to be limited by iron, so small quantities of NO_3 and PO_4 remain in surface seawaters even during periods of peak production (Figure 9.26). These waters are known as the HNLC—high nutrient, low chlorophyll—zones of the ocean.

During the last glacial epoch, arid environments were more widespread and more continental shelf area was exposed because of lower sea level. It is likely that there was greater wind erosion and atmospheric transport of Fe (Lambert et al. 2008). This added Fe deposition may have enhanced marine NPP (Kumar et al. 1995a, Martinez-Garcia et al. 2011). Simultaneously, bubbles of gas trapped in Antarctic ice 18,000 years ago show lower levels of atmospheric CO_2 (Figure 1.2). Several workers have suggested that fertilizing the oceans with Fe might be an

effective way to stimulate marine NPP and export production, which would lower future levels of atmospheric CO₂. Export production is correlated to natural variations in dust deposition in the North Pacific (Bishop et al. 2002) and Southern oceans (Cessar et al. 2007), whereas the upwelling of Fe-rich waters controls NPP in other areas (Coale et al. 1996a, Blain et al. 2007).

Over a period of 10 years, a number of iron fertilization experiments were conducted in the Pacific (e.g., the IronEX experiment) and the Southern Ocean (SOFeX) to test the “iron hypothesis” (Boyd et al. 2007). In every case, the rate of net primary production by phytoplankton increased significantly—sometimes by a factor of 10—when Fe was added to the ocean surface (Martin et al. 1994; Coale et al. 1996b, 2004; Boyd et al. 2000), which lowered the concentration of CO₂ dissolved in the surface waters (Watson et al. 2000, Cooper et al. 1996). Iron increased the photosynthetic capacity of phytoplankton, in which it serves as an essential cofactor in several enzymes (Behrenfeld et al. 1996). Export production was calculated from the C/Fe ratio in POC, an extension of the Redfield ratio. For Fe-enrichment experiments in the Southern Ocean, this ratio was 3000, but increases in the export of POC to the deep ocean were modest (Buesseler et al. 2004). Smetacek et al. (2012) report increases in POC sinking below 1000-m depth during an Fe-enrichment experiment in the Antarctic ocean.

Fe in desert dust is normally found as Fe³⁺, which is much less soluble than the organic complexes that normally dominate the pool of available Fe in seawater (Rue and Bruland 1997). Most Fe in the oceans is found in particulate matter (Johnson et al. 1997), which sinks quickly (Croot et al. 2004). The Fe added experimentally to the ocean surface rapidly disappeared from the upper water column, so the bloom of phytoplankton was short-lived (Boyd et al. 2007). In experiments of longer duration, the development of an active community of zooplankton might have regenerated Fe in surface waters through their grazing activities (Reinfelder and Fisher 1991, Hutchins et al. 1993). Heterotrophic bacteria accumulate Fe (Tortell et al. 1996) and are sometimes fed on by phytoplankton (Maranger et al. 1998).

Iron fertilization is probably not a cure for rising anthropogenic atmospheric CO₂ in Earth’s atmosphere (Aumont and Bopp 2006, Zeebe and Archer 2005). In some iron-fertilization experiments, the flux of N₂O, another greenhouse gas, from the ocean surface increased significantly, potentially negating the uptake of CO₂ (Law and Ling 2001). Marine biologists warn of the disruptive effects of iron fertilization on the marine biosphere (Chisholm et al. 2001); by leading to other nutrient deficiencies, iron fertilization effects are likely to be short-lived, and the use of fossil fuels to mine, refine, and distribute Fe to the oceans may release more CO₂ than balanced by enhanced uptake in seawater.

Zinc (Zn) is an essential component of carbonic anhydrase—the enzyme that allows phytoplankton to convert HCO₃⁻ in seawater to CO₂ for photosynthesis (Morel et al. 1994). Low concentrations of Zn in surface waters can limit the growth of phytoplankton in marine environments (Brand et al. 1983, Sunda and Huntsman 1992). Zn is also an essential cofactor for alkaline phosphatase, which allows phytoplankton to extract P from dissolved organic forms (DOP) in low-phosphorus waters (Shaked et al. 2006). Like Fe, the concentrations of Zn increase with depth in the deep sea (Bruland 1989). Among samples of surface and deep waters, the concentrations of Fe and Zn are often well correlated to those of N, P, and Si, suggesting that biological processes control the distribution of all these elements in seawater. For example, Zn is correlated to Si in the northeast Pacific (Bruland et al. 1978a).

Uptake of trace metals also occurs for some nonessential, toxic metals, such as cadmium (Cd), which accumulates in phytoplankton. Cadmium appears to substitute for zinc in

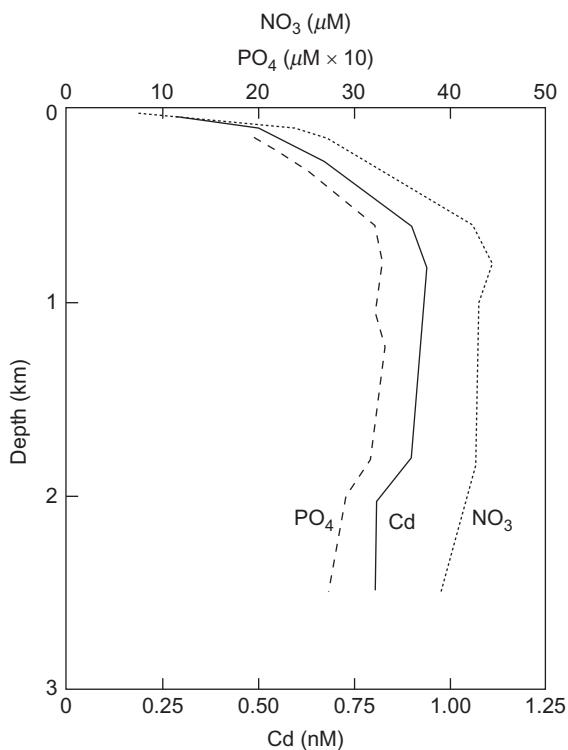


FIGURE 9.27 Depth distribution of nitrate, phosphate, and cadmium in the coastal waters of California. Source: From Bruland et al. (1978b).

biochemical molecules, allowing diatoms to maintain growth in zinc-deficient seawater (Price and Morel 1990, Lane et al. 2005, Park et al. 2008, Xu et al. 2008b). Cadmium is well correlated with available P in waters of the Pacific Ocean (Figure 9.27; Boyle et al. 1976, Abe 2002), and the concentration of Cd in marine sediments is sometimes used as an index of the availability of P in seawater in the geologic past (Hester and Boyle 1982, Elderfield and Rickaby 2000). When marine phosphate rock is used as a fertilizer, cadmium is often an undesirable trace contaminant (Smil 2000).

When nonessential elements (e.g., Al, Ti, Ba, and Cd) and essential elements (e.g., Si and P) show similar variations in concentration with depth, it is tempting to suggest that both are affected by biotic processes, but the correlation does not indicate whether the association is active or passive. Organisms actively accumulate essential micronutrients by enzymatic uptake, whereas other elements may show passive accumulations, as a result of coprecipitation or adsorption on dead, sinking particles. For instance, titanium (Ti), which is not essential for biochemistry, shows nonconservative behavior in seawater, with concentrations ranging from 10 μM at the surface to $> 200 \mu\text{M}$ at depth (Orians et al. 1990). The mean residence times for Ti, Ga (gallium), and Al (aluminum) in seawater range from 70 to 150 years (Orians et al. 1990).

Widespread observations of nonconservative behavior of barium (Ba) in seawater do not appear to result from direct biotic uptake (Sternberg et al. 2005). BaSO₄ precipitates on dead,

sinking phytoplankton, especially diatoms and acantharians, as a result of the high concentrations of SO_4^{2-} that surround these organisms during decomposition (Bishop 1988, Bernstein and Byrne 2004). The precipitation of barite (BaSO_4) is an indication of the productivity of oceans in the past (Paytan et al. 1996).

In the Mediterranean Sea, Al (aluminum) shows a concentration minimum at a depth of 60 m, where Si and NO_3^- are also depleted. MacKenzie et al. (1978) suggested that this distribution is the result of biotic activity, and active uptake has been confirmed in laboratory studies (Moran and Moore 1988). Other workers have found that organic particles carry Al to the deep ocean, but that the association is passive (Hydes 1979, Deuser et al. 1983). High Al in surface waters is due to atmospheric inputs of dust (Orians and Bruland 1986, Measures and Vink 2000, Kramer et al. 2004). Aluminum declines in concentration with depth as a result of scavenging by organic particles and sedimentation of mineral particles.

Manganese (Mn), an essential element for photosynthesis (Chapter 5), is found at higher concentrations in the surface waters ($0.1 \mu\text{g/liter}$) than in the deep waters ($0.02 \mu\text{g/liter}$) of the ocean. Calculating an Mn budget for the oceans, Bender et al. (1977) attribute the high surface concentrations to the input of dust to the ocean surface (Guieu et al. 1994, Shiller 1997, Mendez et al. 2010). Manganese appears less limiting than Fe and Zn for the growth of marine phytoplankton in surface waters (Brand et al. 1983). As in the case of Al, the deposition of Mn in dust in surface waters must exceed the rate of biotic uptake, downward transport, and re-mineralization of Mn in the deep sea.

The Mn budget of the ocean has long puzzled oceanographers, who recognized that the Mn concentration in ocean sediments greatly exceeds that found in the average continental rock (Broecker 1974, Martin and Meybeck 1979). Other sources of Mn are found in riverflow and in releases from hydrothermal vents (Edmond et al. 1979). Various deep-sea bacteria appear to concentrate Mn by oxidizing Mn^{2+} in seawater to Mn^{4+} that is deposited in sediment (Krumbein 1971; Ehrlich 1975, 1982). The most impressive sedimentary accumulations are seen in Mn nodules that range in diameter from 1 to 15 cm and cover large portions of the seafloor (Broecker 1974, McKelvey 1980). As we discussed for phosphorus nodules, the rate of growth of Mn nodules, about 1 to 300 mm per million years (Odada 1992), is slower than the mean rate of sediment accumulation (1000 mm per million years; Sadler 1981), yet they remain on the surface of the seafloor. Various hypotheses invoking sediment stirring by biota have been suggested to explain the enigma, but none is proven. In addition to a high concentration of Mn (15–25%), these nodules also contain high concentrations of Fe, Ni, Cu, and Co and are a potential economic mineral resource.

BIOGEOCHEMISTRY OF HYDROTHERMAL VENT COMMUNITIES

At a depth of 2500 m in the east Pacific Ocean, a remarkable community of organisms is found in association with hydrothermal vents. Discovered in 1977, this community consists of bacteria, tube worms, mollusks, and other organisms, many of which are recognized as new species (Corliss et al. 1979, Grassle 1985; Figure 9.28). Similar communities are found at hydrothermal vents in the Gulf of Mexico and other areas, including some located 15 km from mid-ocean rifts in the Atlantic Ocean (Kelley et al. 2005). In total darkness, these communities are supported by bacterial chemosynthesis, in which hydrogen sulfide (H_2S)



FIGURE 9.28 Medusa jellyfish at a hydrothermal vent at 2850-m depth on the East Pacific Rise, photographed from the ROV Jason II. Photo courtesy of Emily M. Klein, chief scientist, Duke University.

from the hydrothermal emissions is metabolized using O₂ and CO₂ from the deep sea waters to produce carbohydrates (Jannasch and Wirsen 1979, Jannasch and Mottl 1985):



Consumption of H₂S by chemosynthetic bacteria is correlated with declines in O₂ when seawater mixes with hydrothermal water (Johnson et al. 1986b). At first glance the reaction would appear to result in the production of organic matter without photosynthesis. We must remember, however, that the dependence of this reaction on O₂ links chemosynthesis in the deep sea to photosynthesis occurring in other locations on Earth. Other bacteria at hydrothermal vents employ chemosynthetic reactions based on methane, hydrogen, and reduced metals that are emitted in conjunction with H₂S (Jannasch and Mottl 1985, Petersen et al. 2011).

On the basis of the chemosynthetic reactions, bacterial growth feeds the higher organisms found in the hydrothermal communities (Grassle 1985, Levesque et al. 2005). Some of the bacteria are symbiotic in higher organisms. Symbiotic bacteria in the tube worm *Riftia* deposit elemental sulfur, leading to the rapid growth of tubular columns of sulfur up to 1.5 m long (Cavanaugh et al. 1981, Lutz et al. 1994). Filter-feeding clams up to 30 cm in diameter occur in dense mats near the vents. These communities are dynamic, and a particular vent may be active for only about 10 years. Because they are below the carbonate compensation depth, the clam shells slowly dissolve when the vent activity ceases (Grassle 1985). The offspring of these organisms must continually disperse to colonize new vent systems.

Various metallic elements and silicon are soluble in the hot, low-redox conditions of hydrothermal seawater. After mixing with seawater, the precipitation of metallic sulfides may remove as much as 100×10^{12} g S/yr from the ocean (Edmond et al. 1979, Jannasch 1989), although we have chosen a lower value (27×10^{12} g S/yr) in the sulfur cycle of Figure 9.29 (Elderfield and Schultz 1996). Mn and Fe are also deposited as insoluble oxides (MnO₂, FeO) and nodules on the seafloor. The iron oxides act to scavenge vanadium (V) and other elements from seawater and may remove 25% of the annual riverine input of V to the oceans each year (Trefry and Metz 1989).

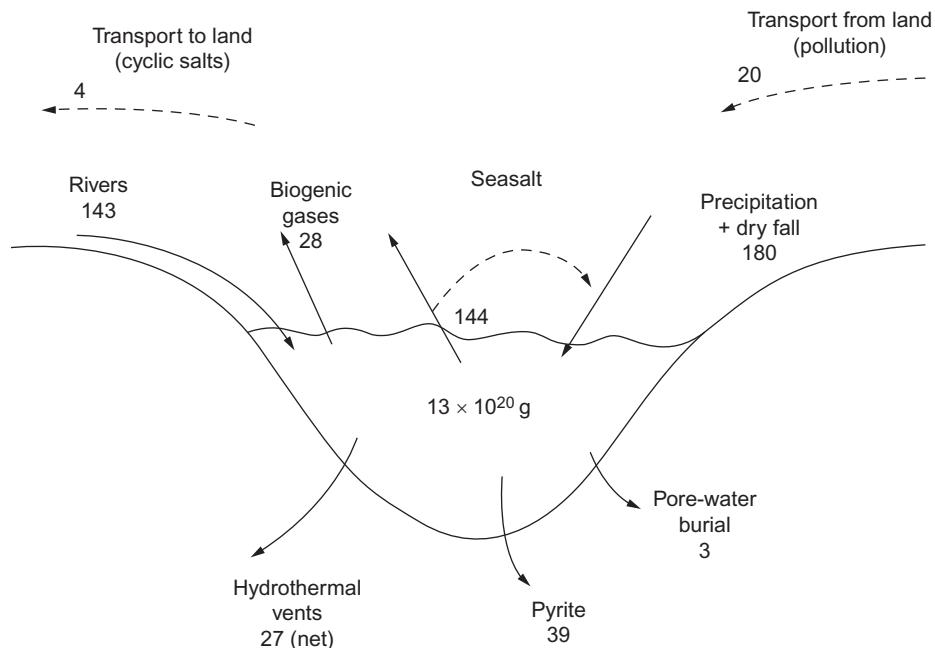


FIGURE 9.29 Sulfur budget for the world's oceans, showing important fluxes in units of 10^{12} g S/yr. (See also Figure 13.1.) Sources: Riverflux from Meybeck (1979), gaseous output from Lana et al. (2011), hydrothermal flux from Elderfield and Schultz (1996), and pyrite deposition from Berner (1982).

Hydrothermal vents attain global significance for their effect on the Ca, Mg, and SO₄ budgets of the oceans, and these bizarre chemosynthetic communities speak strongly for the potential for life to exist in unusual locations where oxidized and reduced substances are brought together by biogeochemical cycles. Persistent life in hydrothermal vent communities may be analogous to some of the earliest environments for the evolution of life on Earth and other planets (Chapter 2).

THE MARINE SULFUR CYCLE

Sulfur is the second most abundant anion in the oceans, where it is found overwhelmingly as SO₄²⁻ (refer to Table 9.1). Rivers and atmospheric deposition are the major sources of SO₄ in the sea (Figure 9.29), but most of the atmospheric deposition is derived from seasalt aerosols that are quickly redeposited on the ocean's surface (i.e., cyclic salt). Metallic sulfides precipitated at hydrothermal vents and biogenic pyrite forming in sediments are the major marine sinks. Sulfur is incorporated into protein by assimilatory reduction of SO₄ from seawater by marine phytoplankton and bacteria (Giordano et al. 2005). Sulfate shows a highly conservative behavior in seawater, with a mean residence time of about 10 million years relative to inputs from rivers.

Despite its high redox potential, seawater harbors various reduced sulfur compounds, presumably in anoxic microsites and suboxic waters. Rapid cycling of sulfur between reduced and oxidized forms is postulated, and gene sequences show the presence of chemoautotrophic sulfur-oxidizing pathways (Eq. 2.16; Canfield et al. 2010, Swan et al. 2011).

The oceans are recognized as a major source of dimethylsulfide— $(\text{CH}_3)_2 \text{S}$ —to the atmosphere. Trace quantities of this gas contribute to the “odor of the sea” in coastal regions (Ishida 1968). Dimethylsulfide (DMS) is produced during the decomposition of dimethylsulfoniopropionate (DMSP) from dying phytoplankton cells (Kiene 1990). The reaction is mediated by the enzyme DMSP-lyase. Grazing by zooplankton seems to be important to the release of DMS to seawater (Dacey and Wakeham 1986, Wolfe et al. 1997). As a form of organic S, DMSP can account for 10% of the carbon content in phytoplankton (Stefels et al. 2007) and up to 15% of the carbon that flows through the grazing food chain (Kiene et al. 2000, Simo et al. 2002). However, not all DMSP is converted to DMS following release from a phytoplankton cell (Kiene and Linn 2000). Certain bacterioplankton appear to convert a substantial fraction of DMSP to other sulfur compounds (Howard et al. 2006), and some bacteria and phytoplankton can assimilate DMSP as a sulfur source (Kiene et al. 2000, Tripp et al. 2008, Vila-Costa et al. 2006, Reisch et al. 2011). Finally, only a small portion of the total production of DMS is lost to the atmosphere; the rest is degraded by microbes in the surface waters (Kiene and Bates 1990, del Valle et al. 2009). The mean residence time of DMS in seawater is about 2 days.

In an effort to balance the global sulfur cycle, DMS was first proposed as a major gaseous output of the sea by Lovelock et al. (1972), but it wasn’t until 1977 that Maroulis and Bandy were able to measure DMS as an atmospheric constituent along the eastern coast of the United States. DMS is now widely recognized as a trace constituent in seawater and in the marine atmosphere, and the diffusion gradient of DMS across the sea-air interface indicates a global flux of 10 to 30×10^{12} g S/yr to the atmosphere (Lana et al. 2011; Figure 9.30). This is the largest natural emission of a sulfur gas to the atmosphere (Kjellstrom et al. 1999).

In contrast to terrestrial and freshwater wetland environments, where H_2S dominates the losses of gaseous sulfur, the oceans emit only small quantities of H_2S (Andreae et al. 1991, Shooter 1999). The oceans are also a source of carbonyl sulfide (COS) in the atmosphere, but the flux of COS is only a small component of the marine sulfur budget (about 0.04×10^{12} g S/yr; Chapter 13). Thus, dimethylsulfide is the major form of gaseous sulfur lost from the sea. Dimethylsulfide is also an important sulfur gas emitted from salt marshes (Steudler and Peterson 1985, Hines et al. 1993). Iverson et al. (1989) showed that the concentrations of DMS and its precursor DMSP increase as a function of increasing salinity in estuaries of the eastern United States.

In the atmosphere, DMS is rapidly oxidized by OH radicals, forming SO_2 and then sulfate aerosols that are deposited in precipitation (Shon et al. 2001, Falloona et al. 2009; Chapter 3). Nearly 80% of the nonseasalt sulfate (nss) in the atmosphere over the North Pacific Ocean appears to be derived from DMS, with the soil dust and pollution contributing the rest (Savoie and Prospero 1989). Marine DMS is estimated to contribute up to 10% of the atmospheric sulfur over industrial Europe (Tarrasón et al. 1995). The potential effects of DMS and SO_4^{2-} aerosols on climate are treated in detail in Chapter 13.

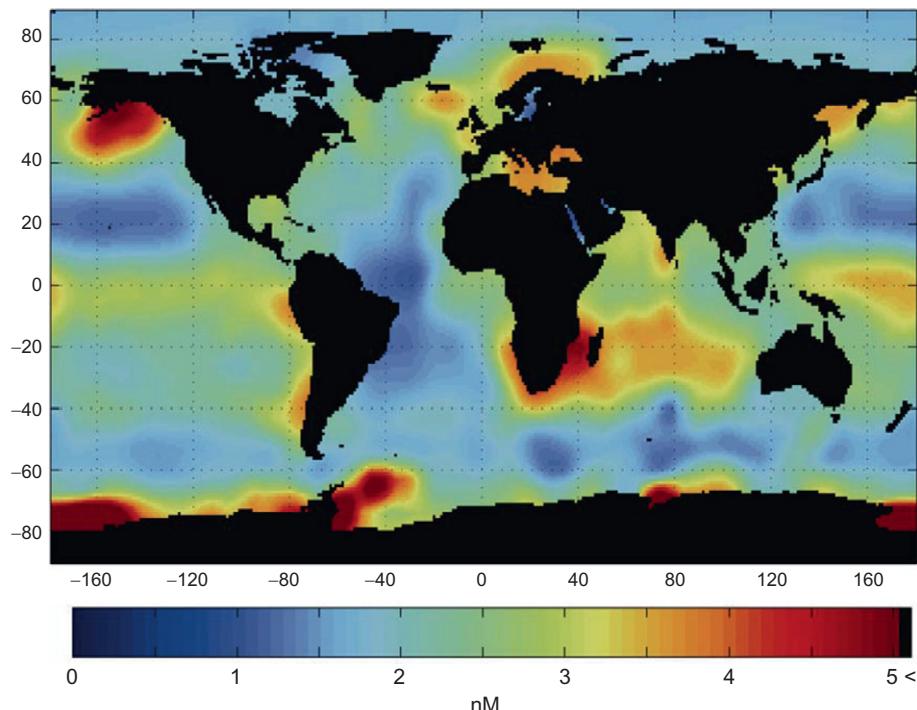


FIGURE 9.30 Mean annual dimethylsulfide concentration in the surface ocean (nM), showing zones of high concentrations in the high-latitude oceans. *Source: Redrawn from Lana et al. (2011). Used with permission of the American Geophysical Union. All rights reserved.*

THE SEDIMENTARY RECORD OF BIOGEOCHEMISTRY

Marine sediments contain a record of the conditions of the oceans through geologic time (Kastner 1999). Sediments and sedimentary rocks rich in CaCO_3 (calcareous ooze) show the past location of shallow, productive seas, where foraminifera and coccolithophores were abundant. Sediments deposited in the deep sea are dominated by silicate clay minerals, with high concentrations of Fe and Mn (red clays). Opal indicates the past environment of diatoms, whereas sediments with abundant organic carbon are associated with near-shore areas, where burial of organic materials is rapid (Figure 9.11). Changes in the species composition of preserved organisms have also been used to infer patterns of ocean climate, circulation, and productivity during the geologic past (Weyl 1978, Corliss et al. 1986). For instance, the ratio of germanium (Ge) to silicon (Si) in diatomaceous sediments has been used to infer variations in the past rates of continental weathering (Froelich et al. 1992).

Calcareous sediments contain a record of paleotemperature. When the continental ice caps grew during glacial periods, the water they contained was depleted in H_2^{18}O , relative to ocean water, because H_2^{16}O evaporates more readily from seawater and subsequently contributes more to continental rainfall and snowfall. When large quantities of water were lost from the ocean and stored in ice, the waters that remained in the ocean were enriched in

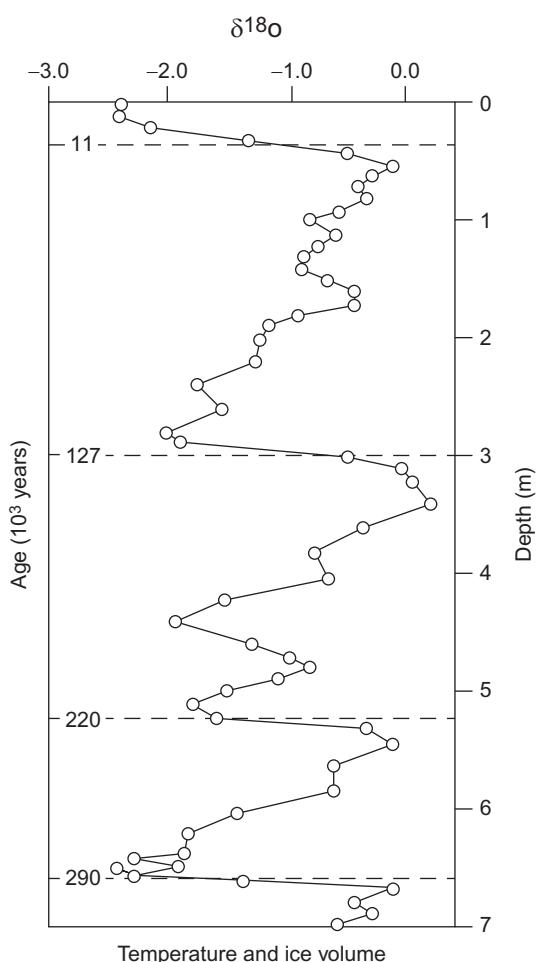


FIGURE 9.31 Changes in the $\delta^{18}\text{O}$ in sedimentary carbonates of the Caribbean Sea during 300,000 years. Enrichment of $\delta^{18}\text{O}$ during the last glacial epoch (20,000 years ago) is associated with lower sea levels and a greater proportion of H_2^{18}O in seawater. Source: From Broecker (1973).

H_2^{18}O compared to today. Carbonates precipitate in an equilibrium reaction with seawater (Eqs. 9.3–9.5), so an analysis of changes in the ^{18}O content of sedimentary carbonates is an indication of past changes in ocean volume and temperature (Figure 9.31).

The history of the Sr content of seawater is also of particular interest to geochemists because its isotopic ratio changes as a result of changes in the rate of rock weathering on land (Dia et al. 1992). Most strontium is ultimately removed from the oceans by coprecipitation with CaCO_3 (Kinsman 1969, Pingitore and Eastman 1986). During periods of extensive weathering, the ^{87}Sr content of seawater increases as a result of high content of that isotope in continental rocks. Thus, changes in the ^{87}Sr content of marine carbonate rocks offer an index of the relative rate of rock weathering over long periods (Richter et al. 1992). For calcium, changes in the rate of rock weathering versus the rate of carbonate sedimentation are reflected in the $\delta^{44}\text{Ca}$ ratio of calcium in carbonate sediments (De La Rocha and DePaolo 2000, Griffith et al. 2008). High rates of weathering are implicated for the Miocene, when atmospheric CO_2 levels were higher than today.

Carbonates are a small sink (20%) of boron in the oceans (Park and Schlesinger 2002), and the isotopic ratio of boron in carbonate varies as a function of seawater pH. The ratio measured in sedimentary foraminifera of the Miocene (21 mya) indicates that seawater pH was lower (7.4) than it is today (8.1), consistent with suggestions of higher atmospheric CO₂ during that period (Spivack et al. 1993, Pearson and Palmer 2000). Similarly, the boron isotope ratios of sedimentary carbonate indicate a higher seawater pH during the last glacial, when atmospheric CO₂ was low (Sanyal et al. 1995). As in all studies of sediments, the time resolution of the method is constrained by the mean residence time of the element in seawater, which for boron is >1,000,000 years (Park and Schlesinger 2002).

Sedimentary deposits of ¹³C in organic matter and in CaCO₃ contain a record of the biotic productivity of Earth. Recall that photosynthesis discriminates against ¹³CO₂ relative to ¹²CO₂, slightly enriching plant materials in ¹²C compared to the atmosphere (Chapter 5). When large amounts of organic matter are stored on land and in ocean sediments, ¹³CO₂ accumulates in the atmosphere and the ocean (i.e., ¹³HCO₃). Arthur et al. (1988) suggest that the relatively high ¹³C content of marine carbonates during the late Cretaceous reflects a greater storage of organic carbon from photosynthesis. Similar changes are seen in the ¹³C of coal age (Permian) brachiopods (Brand 1989). When the storage of organic carbon is greater, there is the potential for an increase in atmospheric O₂, as postulated for the Permian (Berner and Canfield 1989).

SUMMARY

Biogeochemistry in the oceans offers striking contrasts to that on land. The environment on land is spatially heterogeneous; within short distances there are great variations in soil characteristics, including redox potential and nutrient turnover. In contrast, the sea is relatively well mixed. Large, long-lived plants dominate the primary production on land, versus small, ephemeral phytoplankton in the sea. A fraction of the organic matter in the sea escapes decomposition and accumulates in sediments, whereas soils contain little permanent storage of organic matter. Terrestrial plants are rooted in the soil, which harbors most of the nutrient recycling by bacteria and fungi. The soil is sometimes dry, which limits NPP in many areas. In contrast, marine phytoplankton are bathed in the medium of nutrient cycling and never limited by water.

Through their buffering of atmospheric composition and temperature, the oceans exert enormous control over the climate of Earth. At a pH of 8.1 and a redox potential of +200 mV, seawater sets the conditions for biogeochemistry on the 71% of the Earth's surface that is covered by seawater. Most of the major ions in the oceans have long mean residence times and their concentration in seawater has been relatively constant for at least the past 1 million years or more. All of this reinforces the traditional, and unfortunate, view that the ocean is a body that offers nearly infinite dilution potential for the effluents of modern society. As we find high concentrations of mercury and other toxins in pelagic fish and birds, we realize that this is no longer true (Monteiro and Furness 1997, Vo et al. 2011).

Looking at the sedimentary record, we see that the ocean has been subject to large changes in volume, nutrients, and productivity, due to changes in global climate. Already, we have strong reason to suspect that the productivity of coastal waters is affected by human inputs

of N and P (e.g., Beman et al. 2005). Changes in the temperature and productivity of the central ocean basins may well indicate that global changes are affecting the oceans as a whole (Behrenfeld et al. 2006, Polovina et al. 2008). Several studies report a decline in the oxygen content of the global ocean waters (Whitney et al. 2007, Helm et al. 2011). With warming climate, the overturning circulation of the oceans will decline, leading to lower NPP in the surface waters (Schmittner 2005, but see Lozier et al. 2011). The oceans of the future are likely to be warmer, more acidic, and less productive than those of today—just at a time when the growing human population will expect greater productivity from them.

Recommended Readings

- Berner, E.K., and R.A. Berner. 2011. *Global Environment* (third ed.). Princeton University Press.
- Broecker, W.S. 1974. *Chemical Oceanography*. Harcourt Brace Jovanovich.
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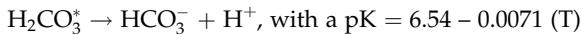
PROBLEMS

- What is the maximum concentration of dissolved inorganic phosphate that might be expected in seawater?
- What is the recycling efficiency in the deep ocean for C, N, and P? Of the total annual inputs of each element to the ocean from the land and atmosphere, what fraction is deposited in the sediments?
- For the major constituents in seawater (Table 9.1), plot the mean residence time in years versus the ratio of the concentration in seawater divided by the mean concentration in the Earth's crust (Table 4.1). How do you interpret your results?
- Using Equation 8.2, estimate the alkalinity (meq/l) of seawater (Table 9.1). Then, referring to Equation 8.1, and remembering that the pH of seawater is about 8.1, what is the contribution of CO_3^{2-} to the total alkalinity?
- The equilibrium between the concentration of CO_2 in the atmosphere and that dissolved in seawater $[\text{H}_2\text{CO}_3^*]$ is determined by Henry's Law, where

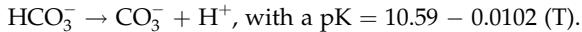
$$[\text{H}_2\text{CO}_3^*]/\text{pCO}_2 = 0.0347 \text{ mol liter}^{-1} \text{ atm}^{-1} \text{ at } 25^\circ\text{C} \text{ and 1 atmosphere pressure.}$$

(H_2CO_3^* refers to the sum of dissolved CO_2 plus carbonic acid, H_2CO_3 .)

Carbonic acid disassociates in seawater to form HCO_3^- . Following:



and HCO_3^- dissociates to form CO_3^{2-} , following:



If the atmospheric concentration of CO_2 increases from 400 $\mu\text{l/l}$ to 560 $\mu\text{l/l}$ during the next 50 years, how much CO_2 will enter the surface ocean (1–100 m)?