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The Oceans

Introduction

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

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 will 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 will 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

Global Patterns

In Chapter 3 we saw that the circulation of the atmosphere was driven by the receipt of solar energy which heated 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 deep, cold waters over much of the ocean (Ledwell et al. 1993).

Within the surface layers, seawater is relatively well mixed by the wind (Thorpe 1985, Archer 1995). Depending upon the incident radiation, the surface waters 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 7). The ocean's deep waters contain about 95% of the volume with a mean temperature of 3°C.

Atmospheric winds (Chapter 3) lead to the formation of currents in the oceans, such as the well-known Gulf Stream in the Atlantic Ocean (Fig. 9.1). In each ocean the trade winds (Fig 3.3a) drive surface currents from east to west along the equator. When these currents encounter land, the waters divide to form currents moving north and south along the eastern borders of the continents. As they move toward the poles, the currents are deflected to the right by the Coriolis Force (Fig. 3.3c), so the Gulf Stream crosses the North Atlantic and delivers warm waters to northern Europe. Water returns to the tropical latitudes in cold surface currents that flow along the west side of continents. The cyclic pattern of surface currents in each of the major oceans is called a *gyre*. The global circulation of surface currents transfers heat from the tropics to the polar regions of the Earth (Oort et al. 1994). More than half of the net excess of solar energy received
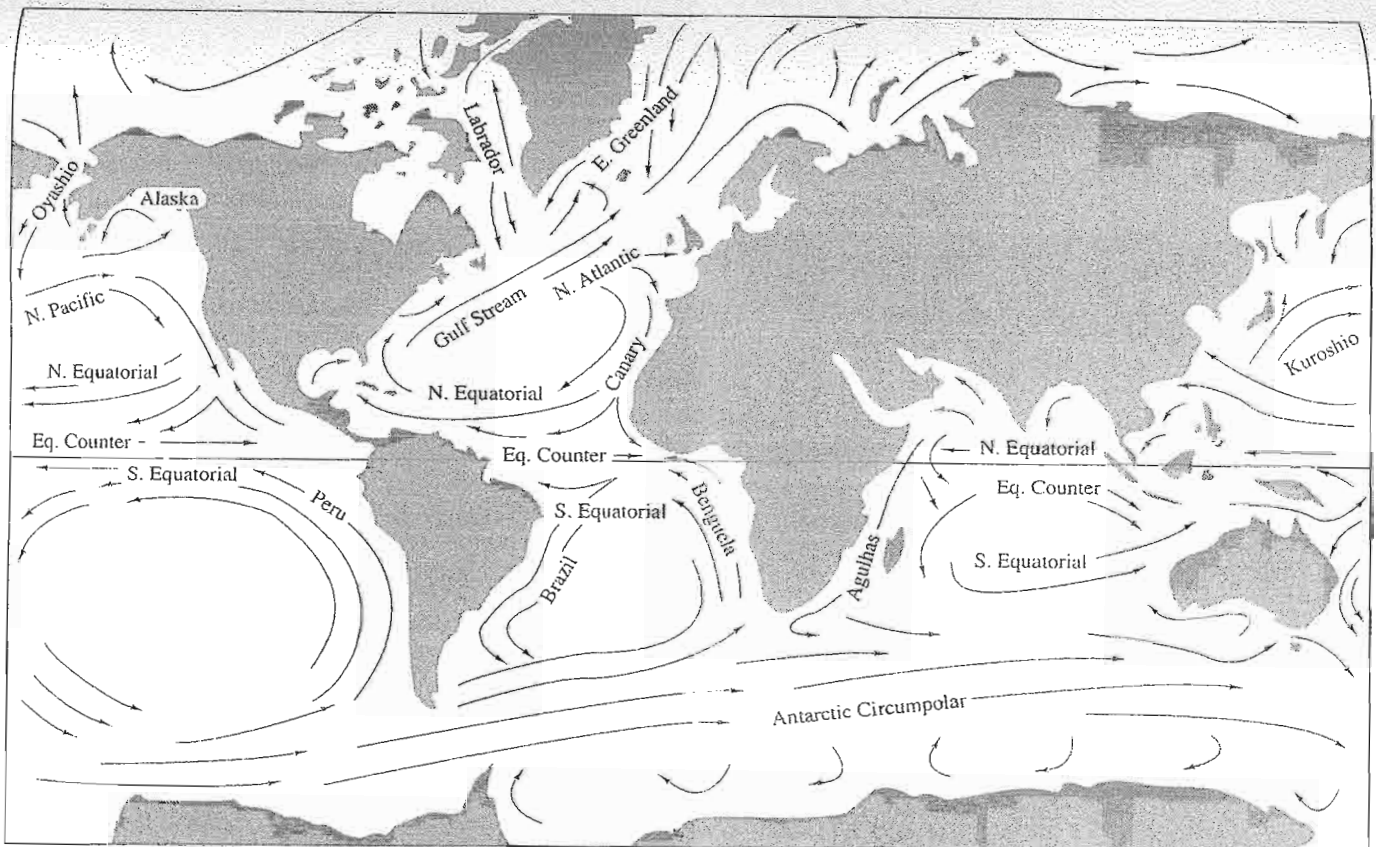

Figure 9.1 Major currents in the surface waters of the world's oceans. From Knauss (1978).

in the tropics is transferred to the poles by ocean circulation; the remainder is transferred through the atmosphere (Vonder Haar and Oort 1973).

With the loss of heat at polar latitudes, the density of seawater increases. Exchange between the surface ocean and the deep waters is possible when the surface waters cool and their density increases to that of the underlying water. Mixing of waters of equal density is known as *isopycnal mixing*. During the winter in the Arctic and Antarctic oceans, the density of some polar waters also increases when fresh water is "frozen out" of seawater and added to the polar ice caps, 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 icecaps. Because the seasonal downwelling of cold polar waters is driven by both temperature and salinity, it is known as *thermohaline circulation*.

Penetration of cold waters to the deep ocean at the poles, which is known as downwelling, creates deep sea currents. For example, North Atlantic deep water (NADW), which forms near Greenland, moves southward through the deep Atlantic, rounding the tip of Africa and entering the Indian and Pacific Oceans. 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.

These patterns of ocean circulation have important implications for biogeochemistry. One might calculate an overall mean residence time of 34,000 years for seawater with respect to river flow (i.e., total ocean volume/annual river flow). In fact, most rivers mix only with the volume of the surface ocean, which has a mean residence time of about 1700 years with respect to river water. If we account for the addition of rain waters and upwelling waters to the volume of 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 9–15 years (Michel and Suess 1975). The surface water is also in rapid gaseous equilibrium with the atmosphere. Mean residence time for CO_2 in the surface ocean is about 6 years (Stuiver 1980).

Renewal of the bottom waters is confined to the polar regions. Downward mixing of ^3H_2O produced from the testing of atomic bombs (Fig. 9.2) 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 13–17 Sv[1]—roughly 10× the annual rate of riverflow to the oceans (Dickson and Brown 1994, MacDonald and Wunsch 1996). Similarly, about 4–5 Sv sink in the Weddell Sea to form

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 oceans, 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}C dating of dissolved CO_2 range from 275 years for the Atlantic Ocean to 510 years for the Pacific (Stuiver et al. 1983). 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. In the Atlantic Ocean, evaporation exceeds the sum of riverflow and precipitation, yielding a higher seawater salinity than in the Pacific (Fig. 9.3). The Atlantic receives a net inflow of less saline waters from the Pacific to restore the water balance. At the same time, dense, saline water flows out of the deep Atlantic to enter the Indian and Pacific Oceans.

Changes in ocean currents, particularly the formation of deep waters, may be associated with changes in global climate. For example, an increase in the rate of downwelling of cold, saline water in the North Atlantic at the start of the last glacial epoch may have led to a decline in atmospheric
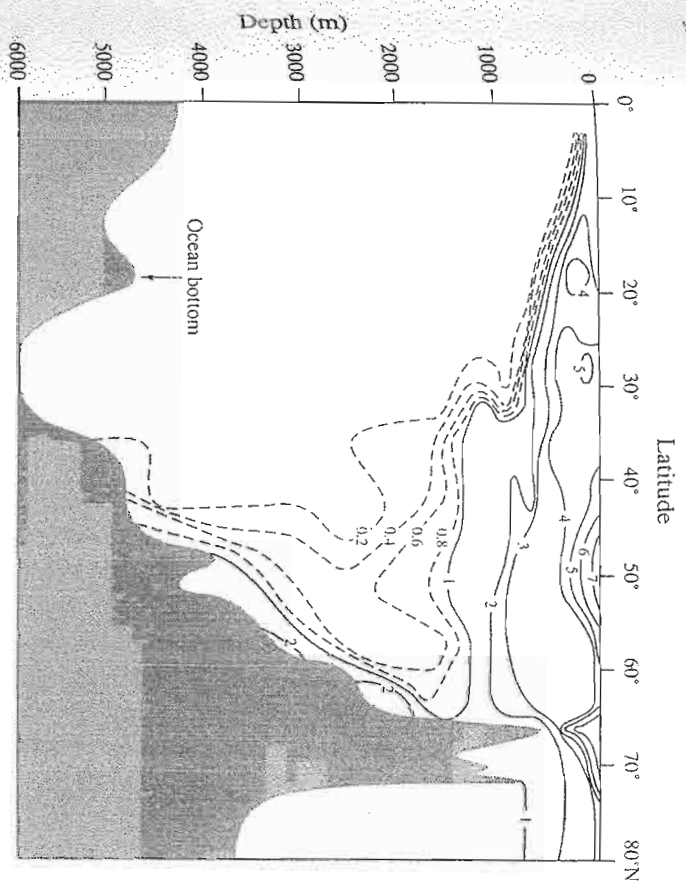

Figure 9.2 Penetration of bomb-derived tritium (^3H_2O) into the North Atlantic Ocean. Data are expressed as the ratio of $^3H/H \times 10^{-18}$ for samples collected in 1972. From Ostlund (1983).

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[1] 1 Sverdup (Sv) $= 10^6 \text{ m}^3/\text{sec} = 3.2 \times 10^{13} \text{ m}^3/\text{yr}.$

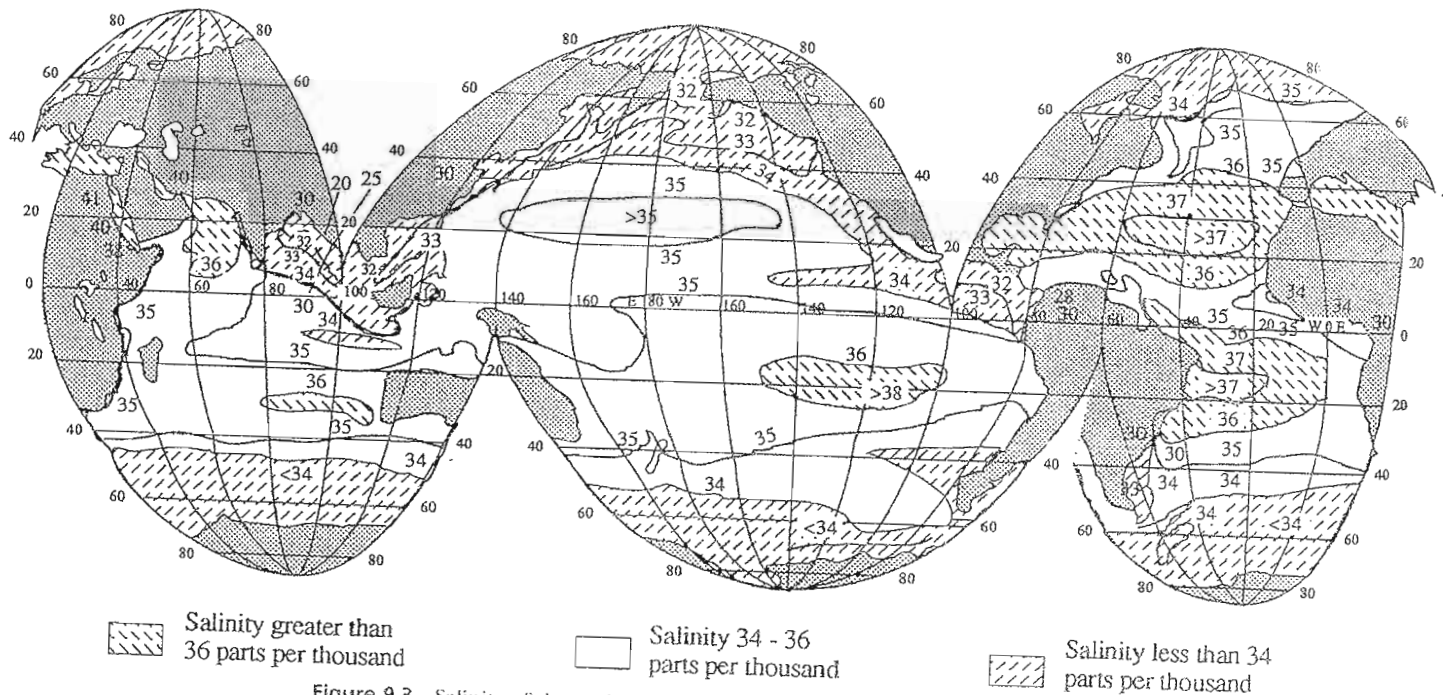| Salinity greater than 36 parts per thousand | Salinity 34 - 36 parts per thousand | Salinity less than 34 parts per thousand |

Figure 9.3 Salinity of the surface waters of the world's oceans. From Gross (1977).

CO_2, because CO_2 is more soluble in cold waters (Broecker and Peng 1987). During the last glacial epoch, the concentration of atmospheric CO_2 was about 200 ppm, compared to 280 ppm in the preindustrial atmosphere (Fig. 1.5). However, because the production of deep water is dependent upon the density difference between a warm surface layer and the cold waters that sink beneath it, once the glacial epoch was fully developed, the production of Atlantic deep water was likely to decline, reducing the transport of atmospheric CO_2 to the deep ocean and allowing warmer conditions to return. Climate changes are also likely to have affected the pattern of surface currents; the Gulf Stream appears to have shifted southward, producing a humid climate in southern Europe during the last glacial epoch (Keffer et al. 1988).

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 bottom 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, preventing the upwelling of nutrient-rich water. Phytoplankton growth is limited and the fisheries industry collapses (Glynn 1988).

Associated with the warm surface waters in the eastern Pacific are changes in global 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. These are known as La Niña conditions (Philander 1989). Although the switch from El Niño to La Niño 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. 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 CO_2, since the release of CO_2 from cold,

Table 9.1 Major Ion Composition of Seawater, Showing Relationships to Total Salinity and Mean Residence Times for the Elements with Respect to River Water Inputs

Constituent	Concentration in seawater[a] (mg/kg)	Chlorinity ratio[a]	Concentration in river water[b] (mg/kg)	Mean residence time (10^6 yr)
Sodium	10,760	0.5561	5.15	75
Magnesium	1,294	0.0668	3.35	14
Calcium	412	0.0213	13.4	1.1
Potassium	399	0.0206	1.3	11
Strontium	7.9	0.00041	0.03	12
Chloride	19,350	1.0000	5.75	120
Sulfate	2,712	0.1400	8.25	12
Bicarbonate	145	0.0075	52	0.10
Bromide	67	0.00035	.02	100
Boron	4.6	0.000921	.01	10.0
Fluoride	1.3	0.000067	0.10	0.5
Water				0.034

[a] Holland (1978).
[b] Meybeck (1979) and Holland (1978).

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 east Pacific ocean released 0.3×10^{15} g C as CO_2 to the atmosphere, compared to its normal efflux of 1.0×10^{15} g C (Murray et al. 1995), and the rate of CO_2 increase in the atmosphere slowed for several years (Keeling et al. 1995). In addition to its effects on ocean productivity, El Niño conditions 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). Efforts to understand and predict El Niño events are an important component of global change research.

The Composition of Seawater

Major Ions

Table 9.1 gives the concentration of the major ions in seawater of average salinity, 35‰ (i.e., 35 g of salts per kilogram of water). The mean residence times for these ions are much longer than the mean residence time for water in the oceans, so these elements are uniformly distributed. Although seawater varies slightly in salinity throughout the world (Fig. 9.3), these ions are conservative in the sense that they maintain the same concentrations relative to one another in most ocean waters. 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

$$\text{salinity} = 1.81(\text{Cl}). \qquad (9.1)$$

with both values in ‰. Table 9.1 shows the mean ratio between chloride and other major ions in seawater over a wide range of salinity.

Like the atmosphere, the composition of the major elements of seawater has been relatively constant for long periods of time. In the face of continual inputs of new ions in river water, the constant composition of seawater must be maintained by processes that remove ions from the oceans. Table 9.1 shows that 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.

A number of processes act to remove the major elements from seawater. Earlier, we saw that wind blowing on the ocean surface produces seaspray 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 (Table 8.6). The atmospheric transport of these "cyclic salts" removes ions from the sea roughly in proportion to their concentration in seawater. Other processes 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 it's concentration in seawater is relatively low.

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). Some K and Mg may also be taken up by illite and montmorillonite clays that are delivered to coastal oceans by rivers (Chapter 4). 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.

Other mechanisms of loss occur in ocean sediments. Sediments are porous and the pores contain seawater. Burial of ocean sediments and their porewaters 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, the deposition of $CaCO_3$ by organisms is the major process removing Ca from seawater. Biological processes also cause the removal of

SO_4, which is consumed in sulfate reduction and deposited as pyrite in ocean sediments (see Chapters 7 and 8).

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 SO_4 from the oceans in the geologic past (Holland 1978).

So far, the processes that we have discussed for the removal of elements from seawater cannot explain the removal of much of the annual riverflow of Mg and K to the sea. For a time, marine geochemists postulated several reactions of "reverse weathering," whereby silicate minerals were reconstituted in ocean sediments, removing Mg and other cations from the ocean (MacKenzie and Garrels 1966). Although some deep-sea sediments appear to be a small sink for Mg and K (Kastner 1974, Sayles 1981), direct evidence of reverse weathering has proven elusive (Drever 1988). Recently, however, Michalopoulos and Aller (1995) found that aluminosilicate minerals are reconstituted in laboratory cultures of marine sediments from the Amazon River, perhaps sequestering as much as 10% of the annual flux of K to the sea.

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 SO_4, and enriched in Ca, Li, Rb, Si, and other elements compared to the seawaters that feed the hydrothermal system. 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).

In sum, it appears that most Na and Cl are removed from the sea in porewater 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 (Fig. 9.4). Over long periods of time, ocean sediments are subducted to the Earth's mantle, where they are converted into primary silicate minerals, with volatile components being released in volcanic gases (H_2O, CO_2, Cl_2, SO_2, etc.; Fig. 1.4).

Mean Residence Time (years)
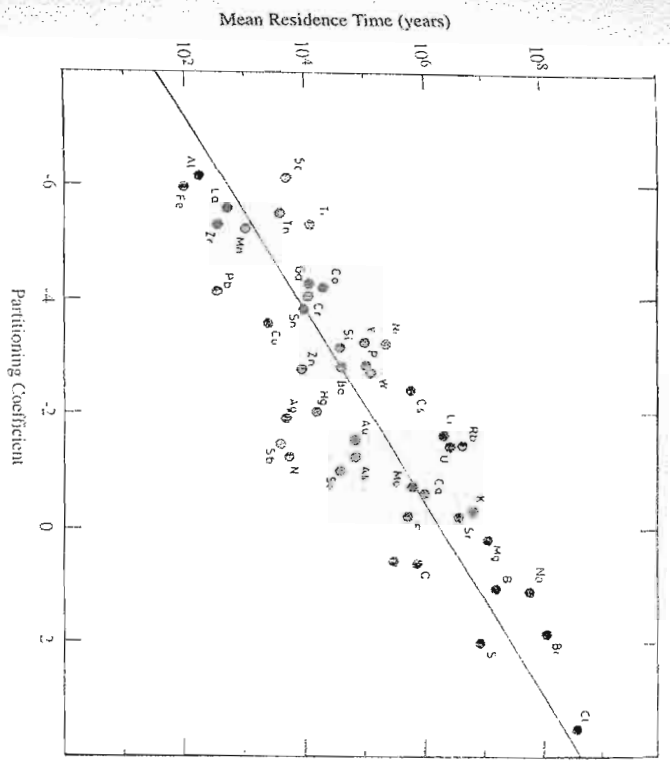
Partitioning Coefficient

Figure 9.4 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. From Whitfield and Turner (1979).

Net Primary Production

Global Patterns

As much as half of the Earth's photosynthesis may occur in the sea (cf. Tables 5.2 and 9.2). Compared to massive forests, the organic carbon produced in the ocean is easy to overlook, because it is largely the result of phytoplankton that are small and ephemeral. Phytoplankton production occurs in the surface mixed layer, in which the distribution of dissolved O_2 is an indirect measure of the rate of photosynthesis (Fig. 9.5). Net primary production in the sea is usually measured using the oxygen-bottle and ^{14}C techniques, as outlined for lake waters in Chapter 7. A new technique based on measurements of the O_2 supersaturation of seawater from photosynthesis has yet to be applied widely in marine environments (Craig and Hayward 1987).

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 recent observations of a large biomass of picoplankton, which passes through the filtration steps of the ^{14}C procedure.

Table 9.2 Estimates of Total Marine Primary Productivity and the Proportion That Is, New Productivity[a]

Province	% of ocean	Area (10^{12} m²)	Mean production (g C m⁻² yr⁻¹)	Total global production (10^{15} g C yr⁻¹)	New production[b] (g C m⁻² yr⁻¹)	Global new production (10^{15} 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] From Knauer (1993).
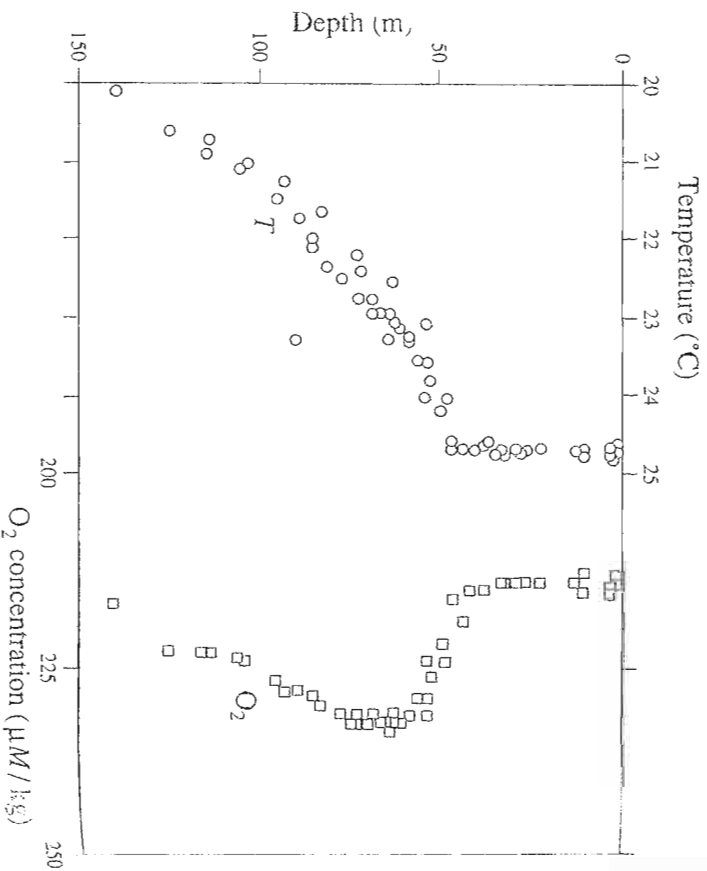[b] New productivity defined as C flux at 100 m.

Figure 9.5 Distribution of temperature and O_2 with depth in the North Pacific Ocean. The peak in O_2 at 50 m is not unusual: it reflects the frequent observation that maximum photosynthesis does not occur at the surface, but at a lower level of the euphotic zone where there is maximum nutrient remineralization. From Craig and Hayward (1987). See also Fig. 9.19 for the distribution of O_2 to 1700 m.

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-em filter, and Stockner and Antia (1986) suggest that such picoplankton may regularly account for up to 50% of ocean production. Marine phytoplankters also release large amounts of dissolved organic carbon to seawater (Baines and Pace 1991), and these compounds—technically a component of NPP—pass through the filtration procedures of the ^{14}C method. Another source of error stems from the possibility that many past studies of NPP have contaminated the seawater samples during application of the ^{14}C technique (Martin et al. 1987).

These methodological problems account for much of the variation among estimates of global marine production. Berger (1989) suggested that global marine NPP was 27×10^{15} g C/yr (Fig. 9.6), but some workers now suggest that marine NPP may be nearly twice that large (Table 9.2). Clearly, biogeochemists must work to improve their estimate of this critical component of the marine biosphere. Despite disagreement on the total value, all workers find that the highest individual values 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 (Fig. 9.6). However, 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).

Remote sensing offers significant potential for improving estimates of marine NPP. In 1978 the National Oceanic and Atmospheric Administration (NOAA) launched the Coastal Zone Color Scanner (CZCS) aboard the Nimbus-7 satellite (Hovis et al. 1980, Walsh and Dieterle 1988). The CZCS records the various wavelengths of radiation reflected from the ocean surface. Where ocean waters contain little phytoplankton, there is limited absorption of incident radiation by chlorophyll, and the reflected radiation is blue. Where chlorophyll is 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 20–30% of the euphotic zone, where most NPP occurs (Balch et al. 1992). CZCS images show dramatically the distribution of chlorophyll in the coastal ocean (Plate 2). The reflectance data can be used to calculate the concentration of chlorophyll and hence production (Fig. 9.7, Platt and Lewis 1987, Platt and Sathyendranath 1988). Recently, Antoine et al. (1996) used this approach to estimate that marine NPP lies between 36.5 to 45.6×10^{15} g C/yr globally.

A new spectral radiometer (MODIS) being developed by NASA for the Earth Observing System will allow greater satellite coverage of the world's oceans and the potential to monitor suspected long-term trends in oceanic
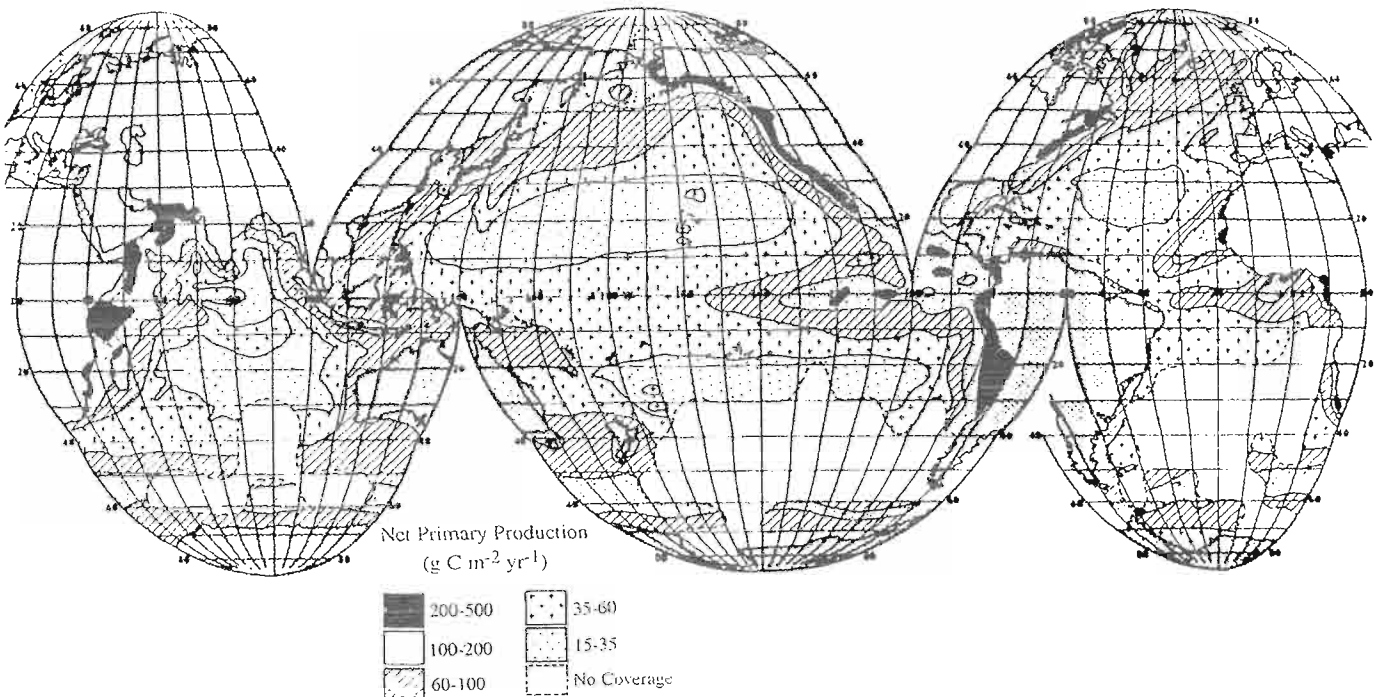
Figure 9.6 Net primary production in the world's oceans in units of g C m^{-2} yr^{-1}. From Berger (1989). Compare to Fig. 5.12, which shows the distribution of net primary production on land.
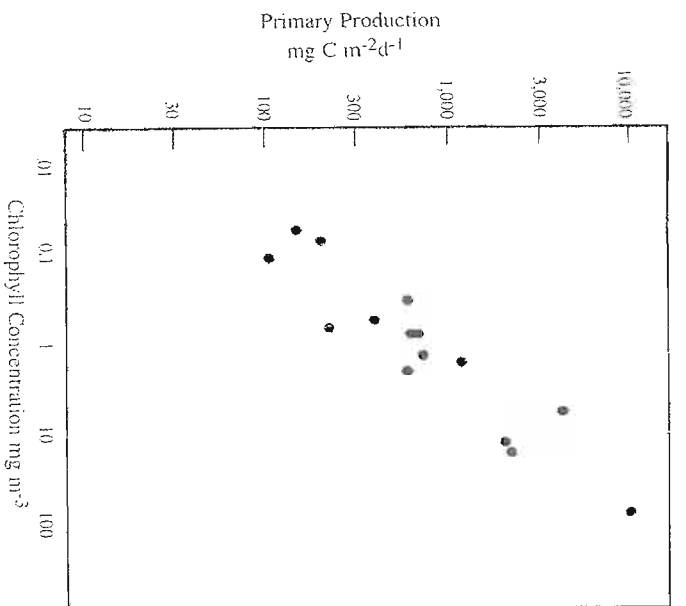
Figure 9.7 Net primary productivity as a function of surface chlorophyll in waters of coastal California. From Eppley et al. (1985).

NPP (e.g., Venrick et al. 1987, Falkowski and Wilson 1992). Future satellites can monitor trends in the marine phytoplankton of the Antarctic ocean (Sullivan et al. 1993), where the loss of stratospheric ozone allows an increasing flux of damaging ultraviolet radiation to the ocean's surface (R.C. Smith et al. 1992).

Fate of Marine Net Primary Production

Most marine NPP is consumed by zooplankton and free-floating bacteria, known as bacterioplankton, in the surface waters. The bacterioplankton also appear to decompose a large fraction of the dissolved organic carbon and organic colloids produced by phytoplankton (Kirchman et al. 1991, Druffel et al. 1992, Moran and Buesseler 1992, Huh and Prahl 1995). Cho and Azam (1988) concluded that bacteria were more important than zooplankton in the consumption of particulate organic carbon in the North Pacific Ocean. Reviewing a large number of studies from marine and freshwater systems, Cole et al. (1988) foun' that net bacterial growth (production) is about twice that of zooplankton and accounted for the disappearance of 30% of NPP from the photic zone (cf. 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 CO_2 to the surface waters. 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 by cold waters, more NPP is available to pass to higher trophic levels, including commercial fisheries (Pomeroy and Deibel 1986).

There is general agreement among oceanographers that about 80–90% of the NPP is degraded to inorganic compounds (CO_2, NO_3, PO_4, etc.) in the surface waters, and the remainder sinks below the euphotic zone to the deep ocean. The estimates of sinking are constrained, since greater 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 upon productivity in the surface water (Deuser et al. 1981, Asper et al. 1992, Sayles et al. 1994). Bacterial degradation continues as particulate organic material (POM) sinks through the water column of the deep ocean. The mean sinking rate is about 350 m/day, so 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. Honjo et al. (1982) found that respiration rates averaged 2.2 mg C m^{-2} 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). Significant rates of decomposition also continue in the sediments (Emerson et al. 1985, Cole et al. 1987, Bender et al. 1989, K.L. Smith 1992).

If the current, higher estimates of marine NPP are correct, then approximately 7.4×10^{15} g C/yr may sink to the deep waters of the ocean (Knauer 1993). From a compilation of data from sediment cores taken throughout the oceans, Berner (1982) estimates that the rate of incorporation of organic carbon in sediments is 0.157×10^{15} g C/yr. These values suggest that about 98% of the sinking organic debris is degraded in the deep sea (cf. Martin et al. 1991). Degradation of organic carbon continues in marine sediments, and the ultimate rate of burial of organic carbon in the ocean sediments is about 0.085 to 0.126×10^{15} g C/yr (Lein 1984, Berner 1982, Dobrovolsky 1994, p. 168). Even the larger value is much 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 (Fig. 9.6), except that a greater fraction of the total burial (83%) occurs on the continental shelf (Premuzic et al. 1982, Berner 1982). 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, degradation of river-borne organic materials must continue in the ocean, because the total burial of organic carbon in the ocean is less than the global delivery 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 is >1.0 (Smith and MacKenzie 1987).

Sediment Diagenesis

Organic Diagenesis

Changes in the chemical composition of sediments after deposition are 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). Organic marine sediments undergo substantial diagenesis after burial as a result of sulfate reduction (Froelich et al. 1979, Thamdrup et al. 1994). In organic-rich sediments, sulfate reduction may begin within a few centimeters of the sediment surface, where O_2 is depleted by aerobic respiration (e.g., Thamdrup et al. 1994). Viable anaerobic bacteria extend to depths of >500 m in Pacific Ocean sediments, adding a considerable dimension to the realm of the biosphere on Earth (Parkes et al. 1994).

Globally, Lein (1984) suggests that 14% of sedimentary organic carbon may be oxidized through anaerobic respiration, especially sulfate reduction. In marine environments, sulfate reduction leads to the release of reduced sulfur compounds (e.g., H_2S) and to the deposition of pyrite in sediments (Eqs. 7.17–7.19). The rate of pyrite formation is often limited by the amount of available iron (Boudreau and Westrich 1984), 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 (Jørgensen 1977, Thamdrup et al. 1994). When the rate of sulfate reduction is especially high, reduced gases may also escape to the water column.

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 flux of organic particles to the sediment surface. Sulfate-reduction generally increases with the overall rate of sedimentation, which is greatest near the continents and is buried in these sediments. In a marine basin off the coast of North Carolina (USA), Martens and 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 CO_2, and 16% in methanogenesis.

In contrast, pelagic (open-ocean) 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), and 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 (Fig. 9.8), but it is important to remember that the deposition of pyrite occurs at the expense of organic carbon (Fig. 1.1). Thus, the net ecosystem production of marine organic carbon 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. 7.17).

The rate of burial of organic carbon depends strongly on the sedimentation rate (Fig. 9.9). 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 1994, Kristensen et al. 1995). As seen in soils (Chapter 5), the long-term persistence of organic matter in marine sediments is also
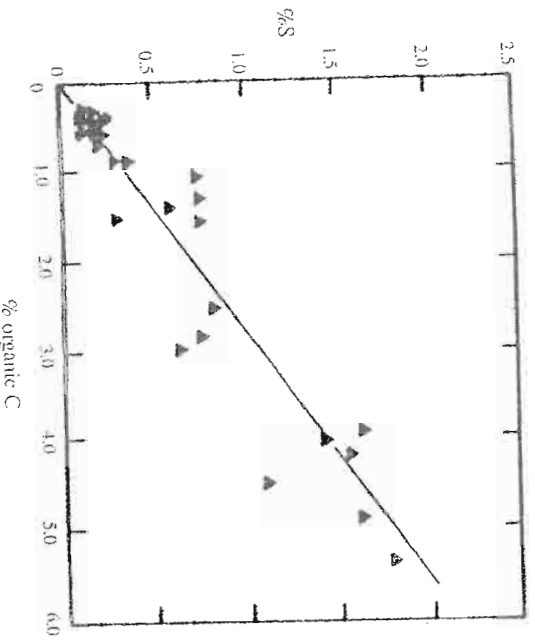

Figure 9.8 Pyrite sulfur content in marine sediments as a function of their organic carbon content. From Berner (1981).
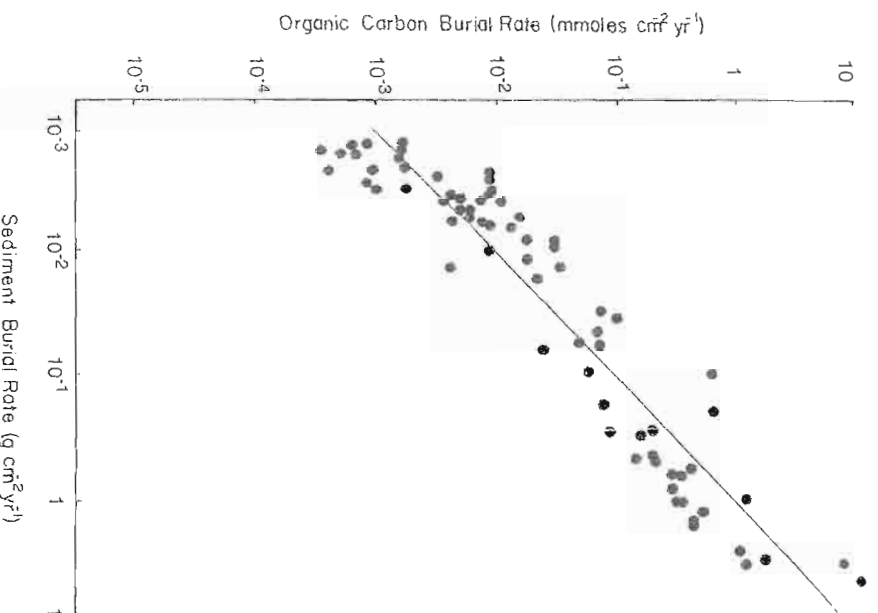
Figure 9.9 Burial of organic carbon in marine sediments as a function of the overall rate of sedimentation. From Berner and Canfield (1989).

enhanced by association with mineral surfaces (Keil et al. 1994, Mayer 1994).

Permanent burial of reduced compounds (organic carbon and pyrite) accounts for the release of O_2 to the atmosphere. 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 O_2 (Raiswell and Berner 1986, Berner and Canfield 1989; Fig. 1.1). 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 O_2 in the atmosphere. As discussed in Chapter 3, the burial of reduced substances through geologic time is thought to regulate the content of O_2 in the atmosphere. During periods of rapid continental uplift, erosion, and sedimentation, large amounts of organic

substances were buried and the oxygen content of the atmosphere increased (Des Marais et al. 1992). Rising atmospheric O_2 increases aerobic decomposition in marine sediments, consuming O_2 and limiting the further growth of O_2 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 SO_4 in seawater, methanogenesis in ocean sediments is limited (Oremland and Taylor 1978, Lovley and Klug 1986). Nearly all methanogenesis is the result of CO_2 reduction, because normally acetate is depleted before SO_4 is fully removed from the sediment (Crill and Martens 1986, Whiticar et al. 1986). There is, however, some seasonal variation in the use of CO_2, and acetate that appears to be due to microbial response to temperature (Martens et al. 1986).

Methane is not highly soluble in seawater, and in many areas the surface ocean is supersaturated in CH_4 with respect to the atmosphere (Ward et al. 1987). This methane appears to be due to methanogenesis in decomposing, sinking particles (Scranton and Brewer 1977, Burke et al. 1983, Karl and Tilbrook 1994). Methane released from ocean sediments and hydrothermal vents is easily oxidized by microbes before it reaches the surface (Iversen et al. 1990). The global flux of CH_4 from the oceans to the atmosphere, $<10 \times 10^{12}$ g/yr, is small compared to that from other sources (Liss and Slater 1974, Conrad and Seiler 1988; Table 11.2).

Biogenic Carbonates

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

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \downarrow + H_2O + CO_2. \qquad (9.2)$$

Clams, oysters, and other commercial shellfish are the obvious examples, but a vast quantity of $CaCO_3$ is produced by foraminifera, pteropods, and other small zooplankton that are found in the sea (Krumbein 1979, Simkiss and Wilbur 1989). Coccolithophores, a group of marine algae, are responsible for a large amount of $CaCO_3$, deposited on the seafloor of the open ocean.[2] The annual production of $CaCO_3$ by these organisms is much larger than what could be sustained by the supply of Ca to the oceans in river flow (Broecker 1974). However, not all of the $CaCO_3$ produced is stored permanently in the sediment.

[2] Note that the precipitation of carbonate by phytoplankton supplies some of the CO_2 needed for photosynthesis, reducing the net uptake of CO_2 from seawater (Robertson et al. 1994).

Recall that CO_2 is produced in the deep ocean by the degradation of organic materials that sink from the surface waters. Deep ocean waters are supersaturated with CO_2, with respect to the atmosphere as a result of their long isolation from the surface and the progressive accumulation of CO_2. Carbon dioxide is also more soluble at the low temperatures and high pressures that are found in deep ocean water. (Note that CO_2 effervesces when the pressure of a warm soda bottle is released upon opening). The accumulation of CO_2 makes the deep waters undersaturated with respect to $CaCO_3$, as a result of the formation of carbonic acid:

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons H_2CO_3. \qquad (9.3)$$
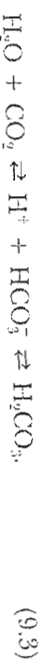
When the skeletal remains of $CaCO_3$-producing organisms sink to the deep ocean, they dissolve:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-. \qquad (9.4)$$
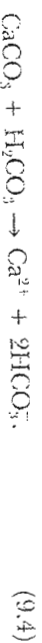
Their dissolution increases the alkalinity, roughly the concentration of HCO_3^-, in the deep ocean. Small particles may dissolve totally during transit to the bottom, while large particles may survive the journey, and their dissolution occurs as part of sediment diagenesis (Honjo et al. 1982, Berelson et al. 1990). The depth at which dissolution begins is called the carbonate lysocline; carbonate dissolution is complete below the *carbonate compensation depth* (CCD). The CCD occurs at roughly 4200–4500 m in the Pacific and 5000 m in the Atlantic Ocean (Kennett 1982). The tendency for a shallower CCD in the Pacific is the result of the longer mean residence time of Pacific deep water, which allows a greater accumulation of respiratory CO_2 (Li et al. 1969).

Dissolution of $CaCO_3$ 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 5.8×10^{15} g/yr of $CaCO_3$ are produced in the surface layer, and about 3.2×10^{15} g are preserved in shallow, calcareous sediments (Milliman 1993). This recent estimate of carbonate deposition consumes more than the known inputs of Ca to the oceans, suggesting that the Ca budget of the oceans is not now in steady state.

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. 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. 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).

Geochemists have long puzzled that dolomite [$(Ca,Mg)CO_3$] does not appear to be deposited abundantly in the modern ocean, 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. 7.17; 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.

Models of Carbon in the Ocean

CO_2 dissolves in seawater as a function of the concentration of CO_2 in the overlying atmosphere. (Recall Henry's Law, Eq. 2.7). The rate of dissolution increases with wind speed, which increases the turbulence of the surface waters² 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 Eq. 9.3 (Archer 1995). The solubility of CO_2 in seawater depends on temperature; CO_2 is about twice as soluble at 0°C than 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 ocean's surface the skin temperature is about 0.3°C cooler than the underlying waters as a result of evaporation of water from the ocean's surface (Robertson and Watson 1992).

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 360 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 upwelling waters that are 300 to 500 years old. Brewer et al. (1989) report that North Atlantic deep water now carries a net flux of 0.26×10^{15} g C/yr that is presumably due to the global rise in atmospheric CO_2 during this century.

Although the surface ocean is in theoretical equilibrium with atmospheric CO_2, the surface waters over large areas are often variably undersaturated in CO_2, as a result of photosynthesis (Tans et al. 1990, Watson et al. 1991). 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 living cells by turbulence (3 g C/m²). Thus, biotic processes act to convert inorganic carbon 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; most of the carbon is liberated by bacterial respiration in the deep ocean and released back to the atmosphere 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's—perhaps as high as 470 ppm (Broecker and Peng 1993). A more active "biotic pump" is one postulated explanation for the lower concentrations of atmospheric CO_2 during the last glacial epoch (Broecker 1982, Ganeshram et al. 1995, N. Kumar et al. 1995).

The biosphere also supplies a large quantity of dissolved organic carbon (DOC) to the surface waters of the ocean (Baines and Pace 1991). Most of this is labile and rapidly decomposed in the surface ocean (Kirchman et al. 1991, Druffel et al. 1992). Downwelling waters may carry some DOC to the deep sea, where it is decomposed, adding to the CO_2 content of the deep oceans (Carlson et al. 1994). In this regard, the labile carbohydrates in marine DOC (Benner et al. 1992, Pakulski and Benner 1994) must be distinguished from a large quantity of refractory DOC that is found well mixed throughout the oceans. Most marine DOC shows ^{14}C ages in excess of 6000 years (Williams and Druffel 1987), and some of it may derive from resistant humic substances supplied to seawater by rivers (Moran and Hodson 1994).

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 $2HCO_3^-$ (Fig. 1.4). Whether it is preserved in a shallow-water calcareous sediment 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. 9.2). Globally, the CO_2 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, producing calcium and bicarbonate that return to the surface waters in zones of upwelling (Eq. 9.4).

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

² 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 upper 5 m of seawater—as if pushed in by a piston—each day.

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 buffer the system. As a result we observe a seasonal oscillation of atmospheric CO_2, and an exponential increase in its concentration in the atmosphere (Fig. 1.3). 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). As the oceans take up additional CO_2, the pH of seawater will be buffered at about 8.0 by the dissolution of carbonates (Eqs. 9.3 and 9.4). Already, there is some indication that the concentration of CO_2 dissolved in the surface ocean has increased in response to increasing concentrations in the atmosphere (Fig. 9.10; Inoue et al. 1995), but there is little evidence for greater dissolution of marine carbonates (Broecker et al. 1979).

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, Holligan and Robertson 1996).
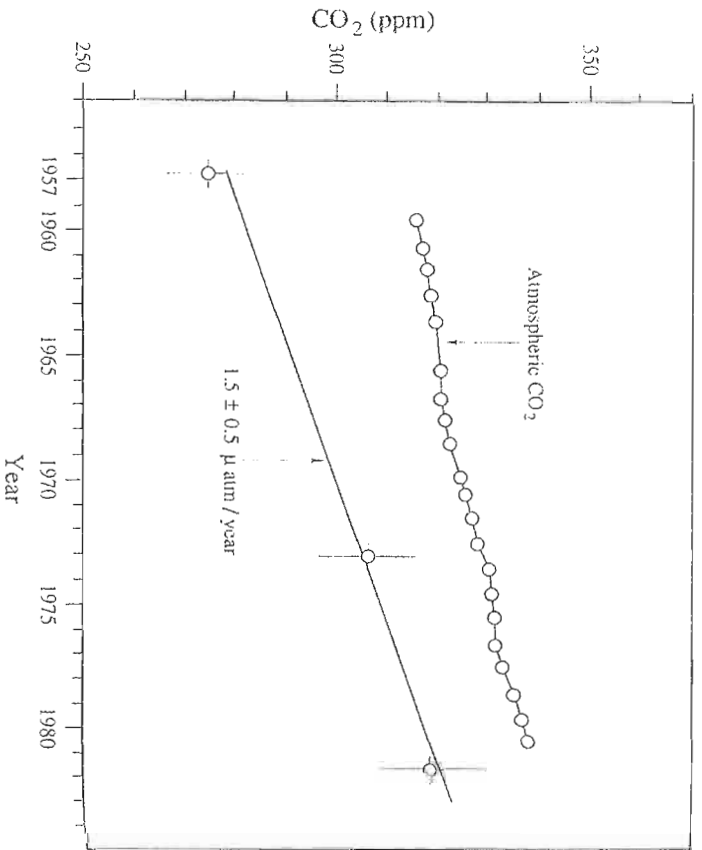
9. The Oceans

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 9.11 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 ^3H_2O 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 temperature and pressure for the dissolution of CO_2 in water as a function of temperature and pressure.

Figure 9.10 Measured changes in CO_2 dissolved in surface waters of the central Atlantic Ocean, showing an increase of 1.5 µatm/yr during recent decades. The trend in atmospheric CO_2 over the same period is shown for comparison. From Takahashi et al. (1983).
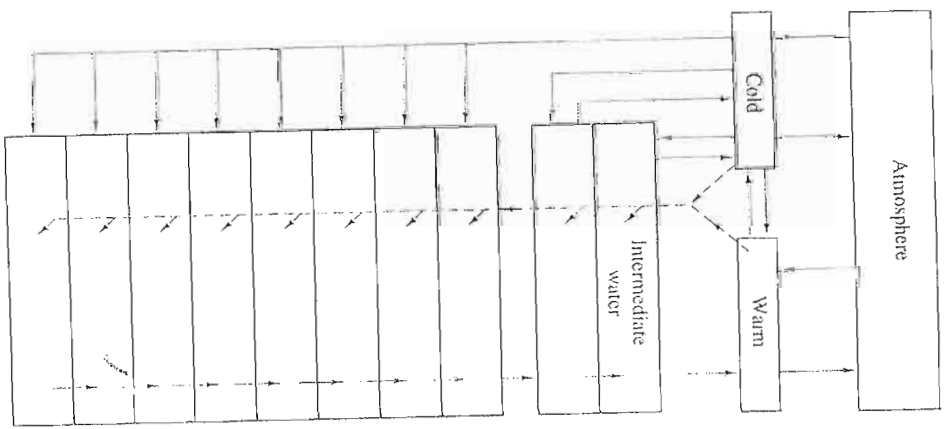

Figure 9.11 A box-diffusion model for the oceans, separating the surface oceans into cold polar waters and warmer waters at other latitudes. Cold polar waters mix with deeper waters as a result of downwelling. Other exchanges are by diffusion. From Emanuel et al. (1985b).

(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 (Tans et al. 1990). 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. Although most of the ocean models do not yet incorporate the effects of biotic productivity in the sea, nor do they incorporate the full three-dimensional complexity of ocean basins in both hemispheres of the globe, they do allow predictions about future global conditions and hypotheses for further testing (Shaffer 1993, Shaffer and Sarmiento 1995, Semtner 1995).

Nutrient Cycling in the Ocean

Net primary productivity in the sea is limited by nutrients. Production is highest in regions of high nutrient availability—the continental shelf and regions of upwelling (Fig. 9.6)—and in the open ocean the concentrations of available N, P, and Si are normally very low. Nutrients are continuously removed from the surface water by the downward sinking of dead organisms and fecal pellets. 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 water, and there are wide differences in the concentration of these elements between the surface and the deep ocean (Fig. 9.12). These are the nonconservative elements of seawater; their behavior is strongly controlled by biogeochemistry.

Nutrients are regenerated in the deep ocean, where the concentrations are much higher than those at the surface. 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 deep Pacific Ocean (Fig. 9.12), because its waters have had a longer time to receive sinking debris which is remineralized at depth. Similarly, in the Atlantic Ocean, nutrient concentrations increase progressively as North Atlantic deep water "ages" during its journey southward (Fig. 9.13).

Internal Cycles

In 1958, Albert Redfield published a paper that has served as a focal point in marine biogeochemistry for the last 40 years. Redfield noted that marine phytoplankters contained N and P in a fairly constant atom ratio to the
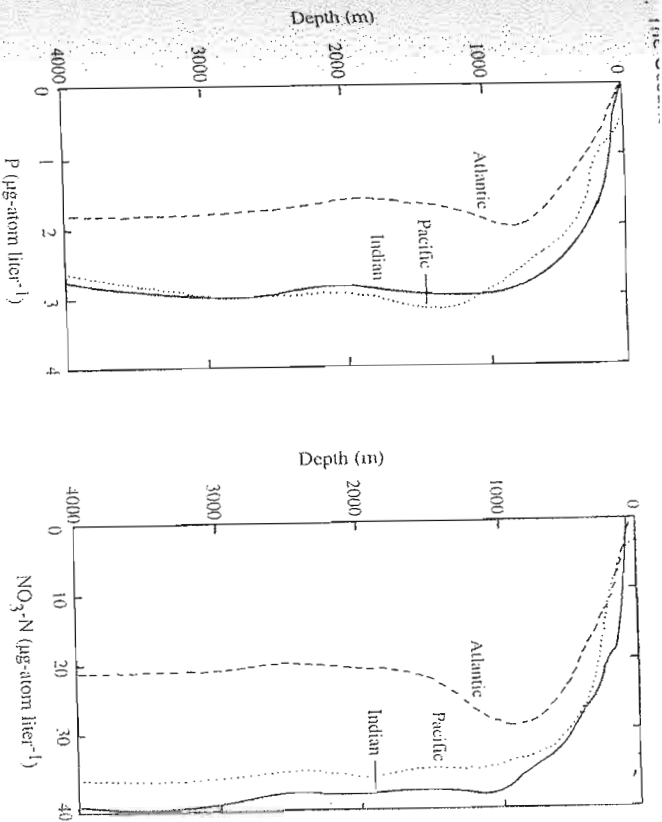
Figure 9.12   Vertical distribution of phosphate and nitrate in the world's oceans. From Svedrup et al. (1942).
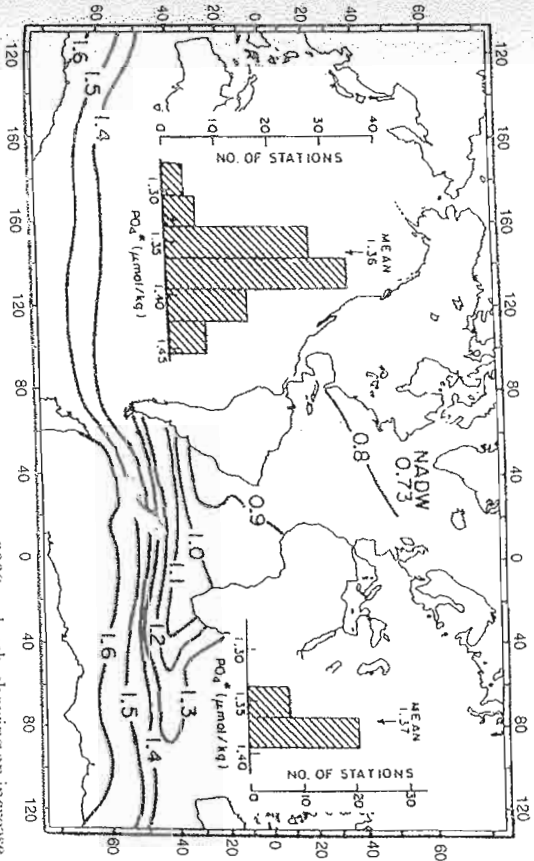
Figure 9.13   Phosphorus in North Atlantic deep waters at 3000-m depth, showing an increase from a mean of 0.73 $\mu M/kg$ near Greenland to 1.67 $\mu M/kg$ in the waters that upwell in the southern hemisphere. From Broecker (1991).

content of carbon, 106 C:16 N:1 P (Redfield et al. 1963), as a result of the incorporation of these elements in photosynthesis and growth:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+$$
$$\rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2. \qquad (9.5)$$
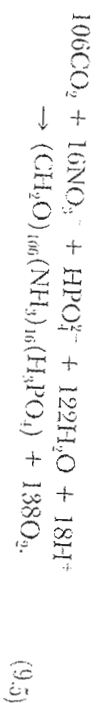
Despite differences in nutrient concentration among the major oceans (Fig. 9.12), upwelling waters contain available C, N, and P (i.e., HCO_3^-, NO_3^-, and HPO_4^{2-}) in the approximate ratio of 800 C:16 N:1 P. Thus, even in the face of the high productivity found in upwelling waters, only about 10% of the HCO_3^- can be consumed by photosynthesis before the N and P are exhausted. In areas of upwelling, the remaining HCO_3^- is lost to the atmosphere as CO_2 (e.g., Murray et al. 1994). 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.

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:1 P:40 Ca. The ratio in upwelling waters is 800 C:15 N:1 P:3200 Ca. 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, biota exert only a tiny control on the availability of Ca in surface waters. Thus, calcium is a constant, well-mixed, and conservative element in seawater (Table 9.1).

The Redfield ratio allows us to compare the importance of riverflow, upward transport, and internal recycling for their contributions to the net primary production of the surface ocean. To sustain a global marine NPP of 50 × 10^15 g C/yr (Table 9.2), phytoplankton must take up about 8.8 × 10^15 g N and 1.2 × 10^15 g P each year (Table 9.3). Rivers supply about 0.036 × 10^15 g N/yr and 0.002 × 10^15 g/yr of reactive P to the oceans (Chapter 8). Rivers and vertical movements (upwelling + diffusion) provide only a small fraction (15%) of the total nutrient requirement in the surface ocean (Table 9.3), and nutrient recycling in the surface waters must supply the rest. Rapid turnover of nutrients is consistent with the rapid turnover of 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 (Fig. 9.12). 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 phytoplankters 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

Table 9.3 Calculation of the Sources of Nutrients to Sustain a Global Net Primary Production of 50 × 10^15 g C/yr in the Surface Waters of the Oceans[a]

Flux	Carbon (10^12 g)	Nitrogen (10^12 g)	Phosphorus (10^12 g)
Net primary production[a]	50,000	8838	1219
Amounts supplied			
By rivers[b]		36	2
By atmosphere[c]		45	1
By upwelling		1189	106
Recycling (by difference)		7568	1110

[a] Based on an approach developed by Peterson (1981).
[b] Assuming a Redfield atom ratio of 106:16:1.
[c] Meybeck (1982).
[d] Figure 9.16.

isotopic tracers (e.g., $^{15}NH_4$ and $^{15}NO_3$) to measure nutrient uptake by phytoplankton and bacteria (Glibert et al. 1982, Goldman and Glibert 1982, Harrison et al. 1992, Dickson and Wheeler 1995). Leakage of dissolved organic nitrogen (DON) from phytoplankters may also account for a significant amount of the bacterial uptake and turnover in the surface waters (Kirchman et al. 1994, Bronk et al. 1994, Kroer et al. 1994). During decomposition of organic materials 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).

Nutrient demand by phytoplankters is so great that little of the NH_4 released by mineralization is nitrified in the surface waters, and NH_4 dominates phytoplankton uptake of recycled N (Dugdale and Goering 1967, Harrison et al. 1992, 1996). In contrast, most of the nitrogen mineralized in the deep ocean is converted to NO_3. 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 (Fig. 9.14). For example, Jenkins (1988) estimated that the upward flux of NO_3 from the deep ocean near Bermuda would support a NPP of about 36 g C m^-2 yr^-1—about 58% of total NPP (Michaels et al. 1994). The remaining production must depend on NH_4, supplied by recycling. The fraction of NPP that is sustained by nutrients delivered from rivers and upwelling is known as *new production*. Globally, new production is about 10–20% of total NPP, but the fraction, f_w, is greatest in areas of cold, upwelling waters (Sathyendra-nath et al. 1991). To maintain low, steady-state nutrient concentrations in

Figure 9.14 diagram labels: Atmospheric input · River input · Photic zone · New production (NP) · Regenerated production (RP) · Photosynthesis · Primary production (PP) · Fixed N + CO_2 + H_2O · Organic C + N + O_2 · NO_3^- · Nitrification · O_2 · Respiration (decomposition) · $NH_4^+ + CO_2 + H_2O \leftarrow O_2 +$ Organic C + N · Export
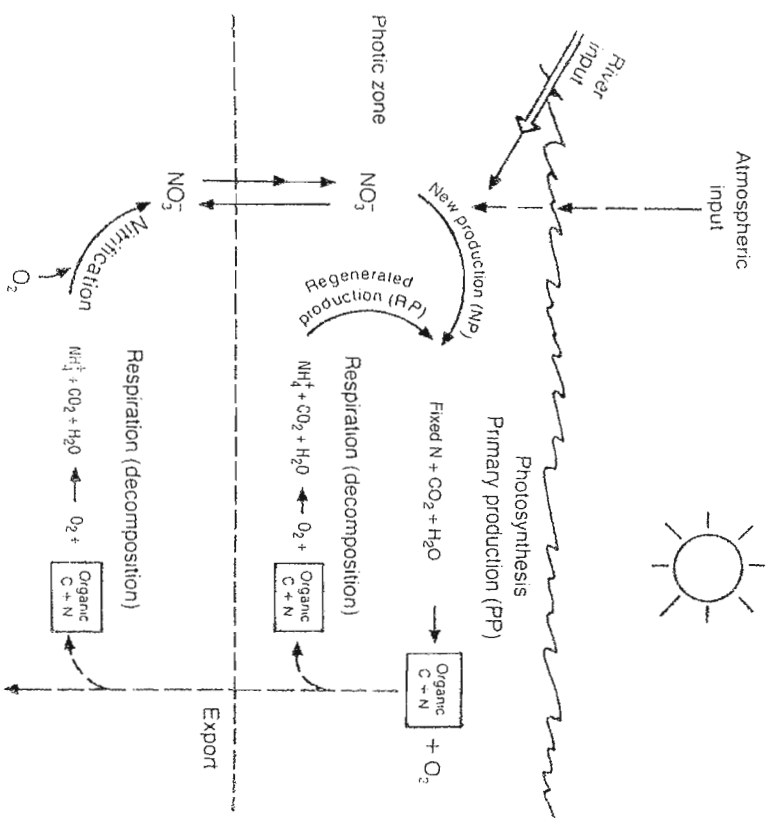
Figure 9.14 Links between the nitrogen and the carbon cycles in the surface ocean. Nitrogen regenerated in the surface waters is largely assimilated by phytoplankters as NH_4, while that diffusing and mixing up from the deep ocean is NO_3. When organic matter sinking to the deep ocean is mineralized, its nitrogen content is initially released as NH_4 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, and the deep sea. From Jahnke (1990).

the surface waters of the oceans, 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 sea (Eppley and Peterson 1979).

Nitrogen and Phosphorus Budgets for the Sea

Redfield ratios suggest that the demand for N and P by phytoplankton is closely matched to their concentrations in upwelling waters. Both elements show low concentrations in surface waters (Fig. 9.12), and the concentrations of N and P are correlated with a slope near the Redfield ratio (Holland 1978). These observations suggest that both N and P might simultaneously limit marine productivity, in contrast to the widespread limitation by P in

freshwaters (Chapter 7). In fact, NPP in many ocean waters shows a tendency for limitation by available N (Howarth 1988, Vitousek and Howarth 1991). What processes lead to a N limitation in the sea?

In contrast to the high rates of nitrogen fixation by blue-green algae in freshwater habitats, N-fixation in the sea is very limited (Capone and Carpenter 1982, Howarth et al. 1988a, Walsh and Dieterle 1988). Recall that the enzyme of nitrogen fixation, nitrogenase, requires molybdenum and iron in its molecular structure (Chapter 2). Howarth and Cole (1985) showed that the uptake of molybdenum is inhibited by the high concentrations of SO_4 in seawater, and they suggest that the assimilation of molybdenum generally limits N-fixation in the sea (Fig. 9.15). The lower concentration of SO_4 in most lake waters does not inhibit molybdenum uptake (Cole et al. 1993), so blue-green algae dominate lakes with low N/P ratios, adding nitrogen to these ecosystems by nitrogen fixation (Chapter 7).

Paerl et al. (1987) tested this hypothesis in coastal marine waters. They found that additions of Mo, Fe, and P did not affect N-fixation, but additions of organic materials increased the rate significantly. Paulsen et al. (1991) also found that additions of carbohydrates stimulated N-fixation and postulated that these compounds created local zones of active decomposition, where oxygen was depleted and nitrogenase activity is possible. Natural aggregations of organic matter, forming "marine snow," create small microzones of anaerobic conditions in seawater, in which a greater availability of trace micronutrients and low redox potentials could stimulate N-fixation (Alldredge and Cohen 1987, Paerl and Carlton 1988). Anaerobic microzones also develop in bundles of blue-green algae (Paerl and Bebout 1988)

Graph axes: MoO_4^{2-} uptake 4 pmol l^{-1} hr^{-1}; 0.0, 0.4, 0.8. X-axis: SO_4^{2-} or Cl^- added (µM); 0, 600, 1200. Curves labeled Chloride and Sulfate.
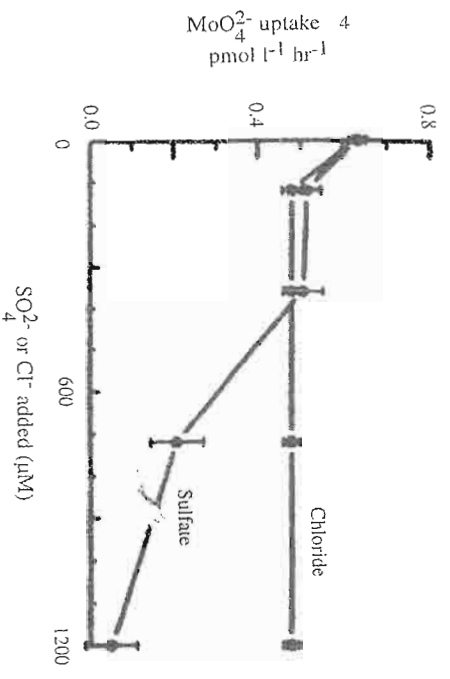
Figure 9.15 Effect of adding SO_4^{2-} and Cl^- on the molybdenum uptake of freshwater phytoplankton. High levels of Cl^- have no effect, while added SO_4 yields a precipitous decline in Mo uptake. From Howarth and Cole (1985).

and in the endosymbiotic bacteria in diatoms (Martínez et al. 1983), both of which show significant N-fixation. N-fixation in the oceans depends on anaerobic microzones in seawater, it may be limited by turbulent conditions that disrupt these microenvironments (Paerl 1985a, but see also Howarth et al. 1993).

Regardless of the mechanism (i.e., Mo deficiency or widespread turbulence) that limits N-fixation in seawater, this nitrogen input contributes significantly to new production only in the oligotrophic waters of the open ocean. For example, fixation by the blue-green algae, *Trichodesmium*, sustains an important component of new production in the tropical Atlantic Ocean, which is distant from sources of upwelling (Carpenter and Romans 1991). Global N-fixation may account for about $10–15 \times 10^{12}$ g N/yr added to the sea (Capone and Carpenter 1982, Walsh and Dieterle 1988, Carpenter and Romans 1991).

The anaerobic microzones created by flocculations of organic matter allow significant rates of denitrification in the oceans, despite the high redox potential of seawater (Alldredge and Cohen 1987). Denitrification in a zone of low O_2 concentration in the eastern Pacific Ocean may result in the loss of 50 to 60×10^{12} g N/yr from the sea (Liu and Kaplan 1989, Codispoti and Christensen 1985, Lipschultz et al. 1990). This denitrification explains the high content of ^{15}N in the residual nitrate in seawater (Liu and Kaplan 1989). As we saw in terrestrial ecosystems (Chapter 6), $^{14}NO_3$ is used preferentially as a substrate in the production of N_2 during denitrification.

Denitrification is also observed in ocean sediments. Christensen et al. (1987) estimate that over 50×10^{12} gN/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. Most of the gaseous nitrogen lost from marine environments is N_2—losses of N_2O are less important (Seitzinger et al. 1984, Jørgensen et al. 1984).

Limited inputs of nitrogen in river waters and by nitrogen fixation, and the potential for large losses by denitrification, all reinforce N limitation in the sea. 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). In the open ocean, direct atmospheric deposition of nitrogen in rainfall and dryfall may assume special significance, 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. The deposition of dust links the NPP of the ocean to the soil biogeochemistry of distant terrestrial ecosystems. An increased deposition of nitrate and organic nitrogen compounds from air pollution may now be responsible for higher marine NPP in areas that are

downwind of continental sources (Paerl 1985b, Fanning 1989, Owens et al. 1992, Cornell et al. 1995).

The global model for the N cycle of the oceans (Fig. 9.16) 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 mineralization in the surface waters, and only
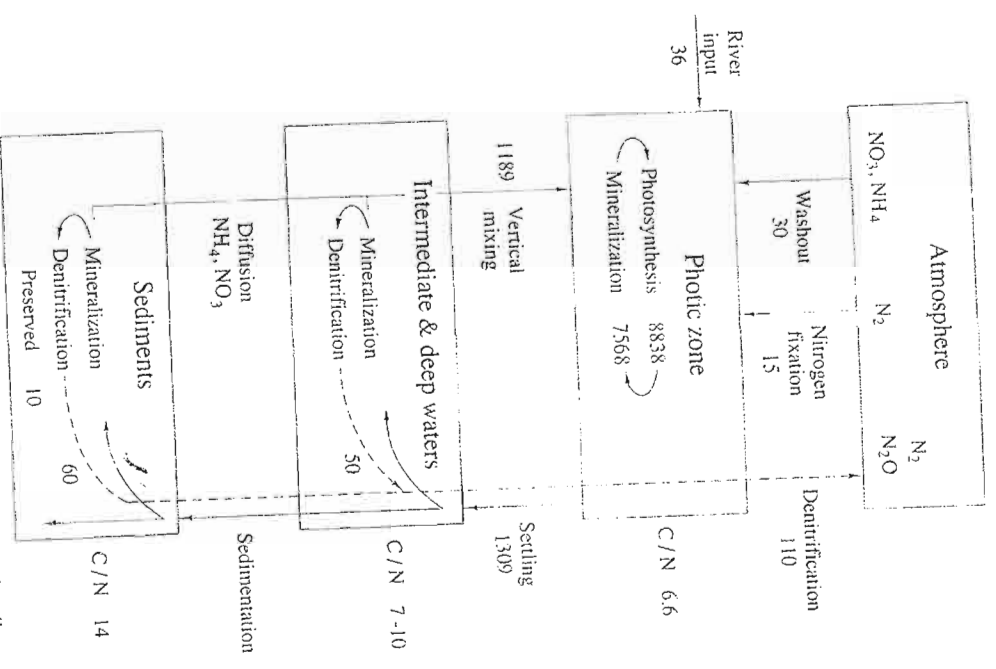
Figure 9.16 Nitrogen budget for the world's oceans, showing major fluxes in units of 10^{12} g N/yr. From an original conception by Wollast (1981), but with newer data added for atmospheric deposition (Duce et al. 1991), nitrogen fixation (Carpenter and Romans 1991), riverflow (Meybeck 1982), denitrification (Christensen et al. 1987), and nutrient regeneration in surface waters (cf. Table 9.3).

Figure labels:
Atmosphere — N_2, N_2O; NO_3, NH_4
River input 36
Washout 30 — Nitrogen fixation 15 — Denitrification 110
Photic zone — Photosynthesis 8838; Mineralization 7568; C/N 6.6
Vertical mixing 1189 — Settling 1309
Intermediate & deep waters — Mineralization; Denitrification 50; C/N 7-10
Diffusion NH_4, NO_3 — Sedimentation
Sediments — Mineralization; Denitrification 60; Preserved 10; C/N 14

small quantities of nutrients are lost to the deep ocean. The mean residence time of available nitrogen in the surface ocean is ≤1 year, while the mean residence time of the *total* pool in the surface ocean is about 10 years. Thus, each atom of N cycles through the biota many times. Upon 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.

Vertical mixing includes both upwelling and upward 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 dominates 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 open ocean compared to the small area of upwellings.

Although the estimates are subject to large uncertainty, the model of Fig. 9.16 indicates a net loss of nitrogen from the oceans. The overall gaseous losses of nitrogen from the ocean exceed the inputs from rivers and the atmosphere, so that the oceans may be declining in nitrogen content (McElroy 1983, Christensen et al., 1987, Smith and Hollibaugh 1989). Various workers have suggested that, in the absence of denitrification, higher concentrations of N_2 would be found in the ocean and lower concentrations of N_2 in the atmosphere (Chapters 2 and 12).

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 upon the mixing of freshwater and seawater (Chase and Sayles 1980, Caraco et al. 1989,

Table 9.4 Sources of Fe, PO_4 and NO_3 in Surface Waters of the North Pacific Ocean[a]

Source	Fe	PO_4	NO_3
Concentration at 150 m (μmol m^{-3})	0.075	330	4300
Upwelling (μmol m^{-2} day^{-1})	0.00090	4.0	52
Net upward diffusion (μmol m^{-2} day^{-1})	0.0034	30	400
Atmospheric flux (μmol m^{-2} day^{-1})	0.16	0.102	26
Total fluxes (μmol m^{-2} 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

[a] From Martin and Gordon (1988).

1990), but most is probably buried with the deposition of river sediments on the continental shelf. The total flux of "bioreactive" P to the oceans is about 2.0×10^{12} g/yr (Ramirez and Rose 1992, Howarth et al. 1995), giving an atom ratio of about 40 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 (Talbot et al. 1986). However, as seen for N, recycling in the surface waters accounts for the vast majority of the P uptake by phytoplankters (Fig. 9.17). 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.
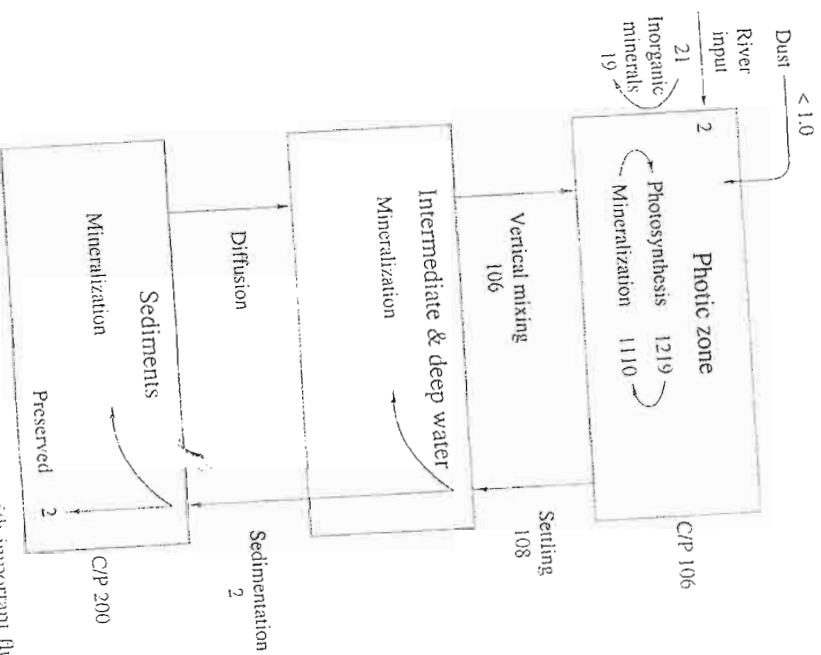

Figure 9.17 A phosphorus budget for the world's oceans, with important fluxes shown in units of 10^{12}g P/yr. From an original conception by Wollast (1981), but with newer data added for dust inputs (Graham and Duce 1979), riverflow (Meybeck 1982), sedimentary preservation (Howarth et al. 1995), and nutrient regeneration in surface waters (cf. Table 9.3).

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). Phosphorus release and C/P ratios are greatest in anoxic sediments (Ingall et al. 1993, Ingall and Jahnke 1994). 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). Indeed, Van Cappellen and Ingall (1996) suggest a negative-feedback mechanism by which changes in the concentration of O_2 in the deep ocean control the availability of P, which in turn stabilizes the level of O_2 in Earth's atmosphere through geologic time. For instance, if the concentration of O_2 in the atmosphere falls to low levels, available P becomes more plentiful in seawater, marine NPP increases, and O_2 is released to the atmosphere and oceans. This subsequently lowers the abundance of P due to its adsorption on Fe minerals in oxic sediments; marine NPP declines and less O_2 is produced.

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. Burial of biogenic P compounds in sediments of the open ocean is estimated between 1.0 and 2.0 × 10^{12} g P/yr—similar to the riverflux of bioreactive P (Howarth et al. 1995). Burial occurs with the deposition of organic matter or $CaCO_3$ (Froelich et al. 1982). During sediment diagenesis, organic- and Fe-bound P are converted to phosphorite (authigenic apatite) and other minerals, which may ultimately dominate the P storage in sediments (Ruttenberg 1993, Filippelli and Delaney 1996, Rasmussen 1996). Phosphorite is formed when PO_4^{3-} produced from the mineralization of organic P combines with Ca and F to form fluorapatite (Ruttenberg and Berner 1993). 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 accumulate on the sea floor. 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 about 25,000 years (Ruttenberg 1993, Filippelli and Delaney 1996; cf. Fig. 9.4). 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. 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 turns very slowly (Chapter 12).
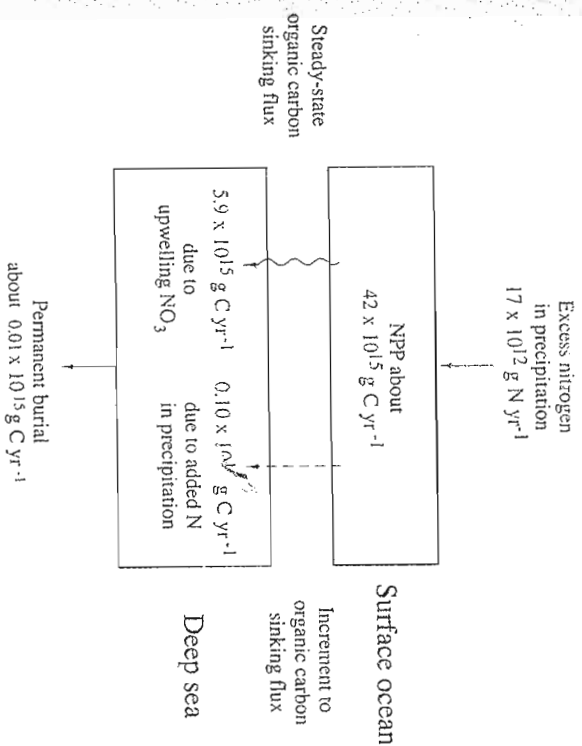
Human Perturbations of Marine Nutrient Cycling

Through the direct release of sewage and indirect losses of fertilizers, the river input of N and P to the oceans has increased in recent years (Meybeck 1982). Fossil fuel pollutants have also increased the atmospheric deposition of N and S on the ocean surface (Whelpdale and Galloway 1994, Cornell et al. 1995). These inputs have probably enhanced the productivity of coastal and estuarine ecosystems (Chapter 8) and perhaps the productivity of the entire ocean. 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 CO_2.

In the open ocean, the net primary production of 42 × 10^{15} g C/yr (Table 9.2) is supported by nitrogen derived from the atmosphere, from upward diffusion, and from internal recycling (Fig. 9.18). If an additional 17 × 10^{12} g N/yr is deposited in the surface waters from atmospheric pollution (Galloway et al. 1995), this "excess" nitrogen could result in an increase in the downward flux of organic carbon of about 0.10 × 10^{15} g/ yr, assuming a Redfield atom ratio of 106 C/16 N in new production. Similar calculations using the "excess" flux of N in rivers suggest an increased storage of <0.30 × 10^{15} g C/yr in coastal zones (Wollast 1991). In the face of a net release of carbon dioxide to the atmosphere of about

Figure 9.18 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).

6×10^{13} g C/yr, these ocean sinks are relatively small (MacKenzie et al. 1993). The major ocean sink for CO_2 is found as a result of an increased dissolution of CO_2 in cold waters of the polar oceans (Shaffer 1993). As we discussed earlier, this inorganic sink for CO_2 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 10% of the ocean's surface, but they account for about 18% of ocean productivity (Table 9.2), and 83% of the carbon that is buried in sediments. Globally averaged models (e.g., Figs. 9.16 and 9.17) 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 1991, 1993). If global climate change alters the rate of coastal upwelling (Bakun 1990), significant changes in the ocean's overall biogeochemistry should be expected (Walsh 1984).

Silicon, Iron, and Trace Metals

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 $<2 \mu M$. Globally, the annual uptake of Si by diatoms is about 6×10^{15} g (Nelson et al. 1995). Upon the death of diatoms, a large fraction of the opal dissolves, and the Si is recycled in the surface waters. Si 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). The average concentration in deep waters is about $70 \mu M$.

A mass-balance model for Si in the oceans shows that rivers (1.6×10^{14} g/yr), dust (0.14×10^{14} g/yr), and hydrothermal vents (0.06×10^{14} g/yr) are the main sources, and sedimentation of biogenic opal is the only significant sink (Tréguer et al. 1995). 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 (White and Blum 1995, Chapter 4). Sedimentation in the cold waters of the Antarctic Ocean accounts for 70% of the global sink (Tréguer et al. 1995). Other cold water areas provide most of the remaining sinks (DeMaster 1981), but about 10% of the sink is found in coastal regions, where the growth of diatoms in nutrient-enriched waters may now be limited by silicon (Justić et al. 1995).

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 their 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 $\mu g/g$ in surface waters to >405 $\mu g/g$ with depth (Bernstein et al. 1987). Thus, biotic processes maintain a slightly nonconservative behavior (i.e., $\pm 1.5\%$) for Sr in seawater, despite its overall mean residence time of 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. 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, due to its 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., Fig. 9.19). In response to low concentrations of Fe, some phytoplankton release organic compounds that chelate Fe, increasing its availability in seawater (Wilhelm et al. 1996). In contrast, cyanobacteria avoid toxic levels of Cu by releasing chelators that render Cu less available to biotic uptake (Moffett and Brand 1996).

Near the continents, the concentration of Fe in seawater is normally adequate to support phytoplankton growth, but in the central Pacific Ocean, Martin and Gordon (1988) found that internal sources of Fe could sustain only a small 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 is probably transported from the deserts of central China (Duce and Tindale 1991). 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 (Fig. 9.19). Some workers have even suggested that fertilizing the oceans with Fe might be an effective way to stimulate new production and lower atmospheric CO_2.

During 1993 and 1995, the "iron hypothesis" was tested by fertilizing patches of the Pacific Ocean with $FeSO_4$. During this experiment, the rate of photosynthesis by phytoplankton increased significantly in the surface waters (Martin et al. 1994, Kolber et al. 1994). When Fe was supplied continuously, the fertilization produced a massive bloom of phytoplankton, which removed a large portion of the dissolved CO_2 from the surface water (Coale et al. 1996). Iron fertilization is probably not a cure for rising atmospheric CO_2, but it is interesting to speculate that a greater global dispersal of iron-rich dust during the last glacial period may have stimulated marine production, drawing down atmospheric CO_2 (Martin 1990, N. Kumar et al. 1995).

Zinc (Zn) is an essential component of carbonic anhydrase—the enzyme that allows phytoplankton to covert HCO_3^- in seawater to CO_2 for photosynthesis (Morel et al. 1994). Low concentrations of Zn in surface waters can limit the growth of phytoplankton in different marine environments (Brand
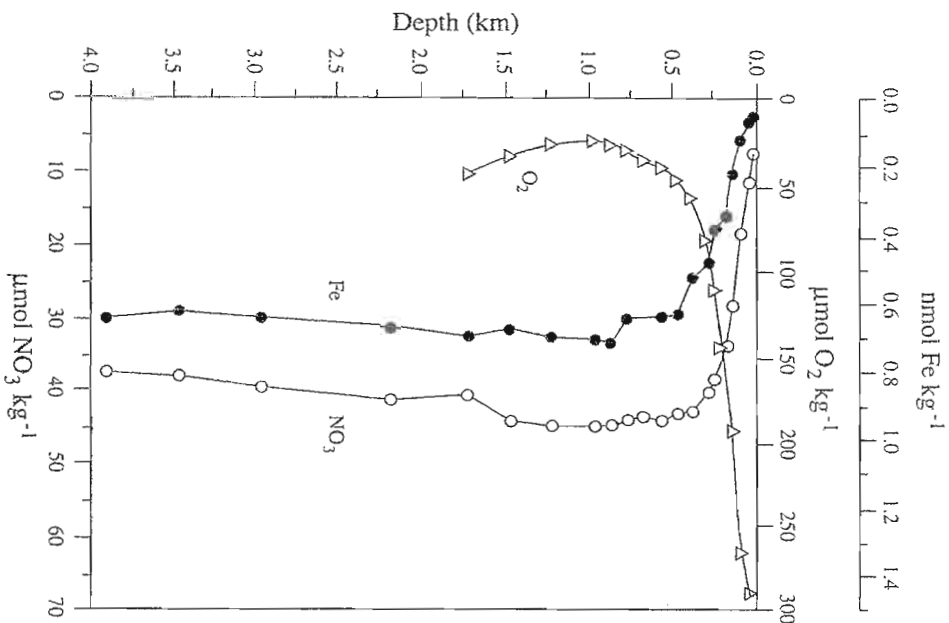
et al. 1983, Sunda and Huntsman 1992). Like Fe, the concentrations of Zn increase with depth in the deep sea (Bruland 1989). Among samples of surface and deep waters, the concentrations of Fe, Zn, and other metals are often well correlated to those of N, P, and Si, suggesting that biological processes control the distribution of these elements in seawater. For example, Zn is correlated to Si in the northeast Pacific (Bruland et al. 1978a); and Ni is correlated to P in most seawater (Sclater et al. 1976). Nickel appears to be an essential element for diatoms that use urea as a nitrogen source (Price and Morel 1991).

Uptake and accumulation of trace metals also extends to the tendency for some nonessential, toxic metals, such as cadmium (Cd) and mercury

Figure 9.19 Vertical distribution of Fe, NO_3, and O_2 in the central North Pacific Ocean. From Martin et al. (1989).

(Hg), to accumulate in phytoplankton (Table 9.5). Cadmium appears to substitute for zinc in biochemical molecules, allowing diatoms to maintain growth in zinc-deficient seawater (Price and Morel 1990, Lee et al. 1995). Cadmium (Cd) is well correlated with available P in waters of the Pacific ocean (Fig. 9.20; Boyle et al. 1976), and the concentration of Cd in marine sediments is often taken as an index of the availability of P in seawater of the geologic past (Hester and Boyle 1982). When marine phosphate rock is used as a fertilizer, cadmium is often an undesirable trace contaminant.

Mercury enters the ocean by deposition from the atmosphere, where the concentrations are increasing by >1%/yr (Slemr and Langer 1992). Most of the mercury entering the oceans is revolatilized, so the oceans do not constitute a large sink in the global cycle of mercury (Mason et al. 1994). However, in areas of seawater where oxygen is depleted, inorganic mercury is converted to methylmercury (Mason and Fitzgerald 1993) by processes similar to those in freshwater wetlands (Chapter 7). Methylmercury is the major form accumulating in fish (Cross et al. 1973), leading to concerns for human health.

When nonessential elements (e.g., Al, Ti, Ba, Hg, 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. Titanium (Ti) shows nonconservative behavior in seawater, with concentrations ranging from 10 μM at the surface to >200 μM at depth (Orians et al.

Table 9.5 Ratio of the Concentration of Elements in Phytoplankton to the Concentration of Elements in Seawater[a]

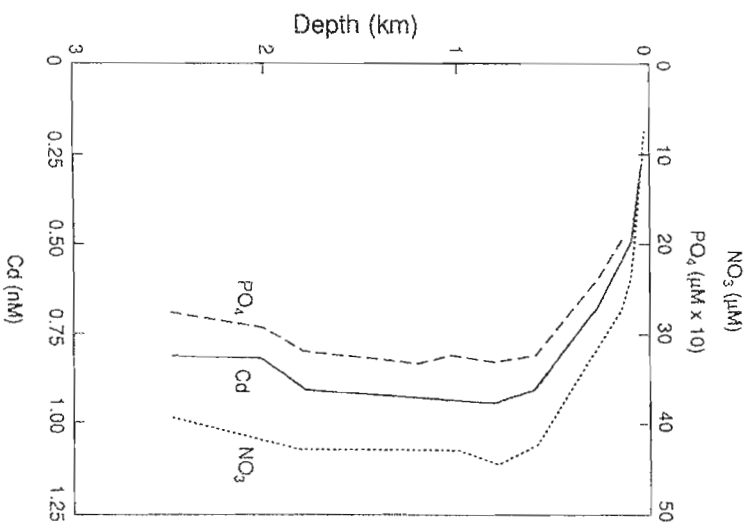| Element	Ratio
Al	25,000
Cd	910
Cu	17,000
Fe	87,000
Mg	0.59
Mn	9,400
Na	0.14
N	19,000
N:P	1700
P	15,000
Zn	65,000

[a] From Bowen (1966).

Figure 9.20 Depth distribution of nitrate, phosphate, and cadmium in the coastal waters of California. Bruland et al. (1978).

1990). Widespread observations of nonconservative behavior of barium (Ba) in seawater do not appear to result from direct biotic uptake. $BaSO_4$ precipitates on dead, sinking phytoplankton, especially diatoms, as a result of the high concentrations of SO_4 that surround these organisms during decomposition (Bishop 1988).

In the Mediterranean Sea, 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 1985, 1986). Aluminum declines in concentration with depth as a result of scavenging by organic particles and by sedimentation of mineral particles.

Manganese (Mn), an essential element for photosynthesis (Chapter 5), is found at higher concentrations in the surface waters (0.1 µg/liter) than

in the deep waters (0.02 µg/liter) of the ocean. Calculating a 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). 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 must exceed the rate of biotic uptake, downward transport, and remineralization 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/million years (Odada 1992), is slower than the mean rate of sediment accumulation, 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.

These diverse observations 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 ocean water is inversely related to their concentration in sinking fecal pellets (Fig. 9.21). Some of these elements are mineralized 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 (Table 9.1).

Biogeochemistry of Hydrothermal Vent Communities

At a depth of 2500 m a remarkable community of organisms is found in association with hydrothermal vents in the east Pacific Ocean. 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). Similar communities are found at hydrothermal vents in the Gulf of Mexico and other areas. In total darkness, these communities are supported by bacterial chemosynthesis, in which hydrogen sulfide (H_2S) from the hydrothermal emissions is metabolized using O_2 and CO_2
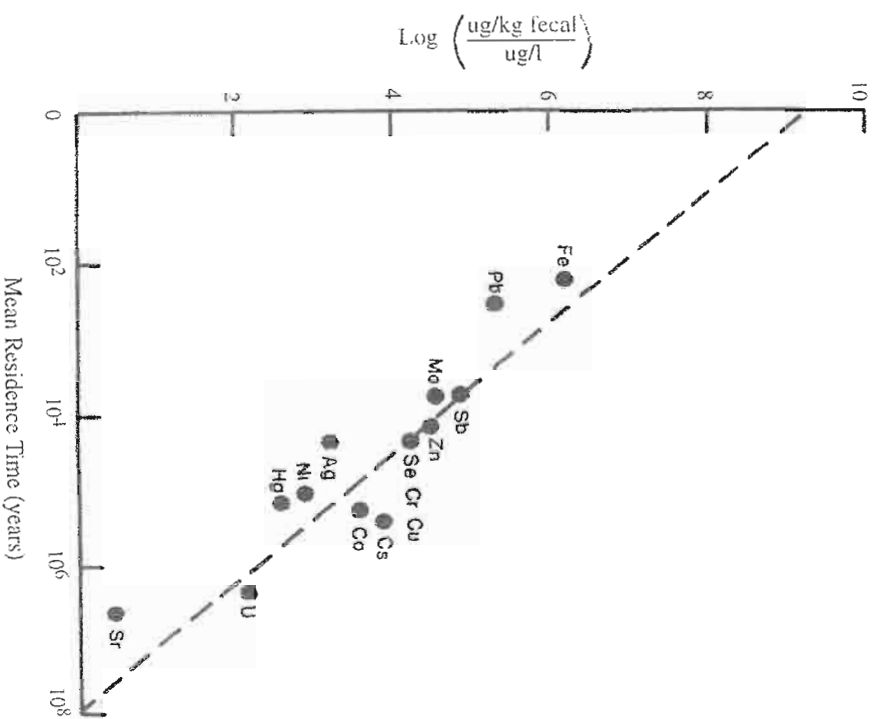
Figure 9.21 The ratio between the concentration of an element in sinking fecal pellets (µg/kg) and its concentration in seawater (µg/liter), plotted as a function of its mean residence time in the ocean. From Cherry et al. (1978).

from the deep sea waters to produce carbohydrate (Jannasch and Wirsen 1979, Jannasch and Mottl 1985):

$$O_2 + 4H_2S + CO_2 \rightarrow CH_2O + 4S\downarrow + 3H_2O. \quad (9.6)$$

Consumption of H₂S by chemosynthetic bacteria is correlated with declines in O₂ when seawater mixes with hydrothermal water (K.S. Johnson et al. 1986). 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).

On the basis of the chemosynthetic reactions, bacterial growth feeds the higher organisms found in the hydrothermal communities (Grassle 1985). 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; 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 vents. Upon mixing with seawater, the precipitation of metallic sulfides removes about 96×10^{12} g S/yr from the ocean (Edmond et al. 1979, Jannasch 1989). Mn and Fe are also deposited as insoluble oxides (MnO₂, FeO) and nodules on the sea floor. 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 ocean each year (Trefry and Metz 1989).

Hydrothermal vents attain global significance for their effect on the Ca, Mg, and SO₄ budgets of the oceans, but 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.

The Marine Sulfur Cycle and Global Climate

Sulfur is abundant in the oceans, where it is found as SO_4^{2-}. Rivers and atmospheric deposition are the major sources of SO_4 in the sea (Fig. 9.22), but most of the atmospheric deposition is derived from seasalt aerosols that are simply redeposited on the ocean's surface. Metallic sulfides precipitated at hydrothermal vents and biogenic pyrite in sediments are the major marine sinks. Sulfate shows a highly conservative behavior in seawater, with a mean residence time of about 10 to 12 million years relative to inputs from rivers (Table 9.1).

Our understanding of the marine sulfur cycle has developed rapidly within the last 20 years. Of greatest significance, the oceans are now recognized as a major source of dimethylsulfide [(CH₃)₂S] in the atmosphere. Trace quantities of this gas impart he "odor of the sea" to coastal regions (Andreae 1986). Dimethylsulfide (DMS) is produced during the decomposition of dimethylsulfoniopropionate (DMSP) from dying phytoplankton cells (Andreae and Barnard 1984, Andreae 1990,
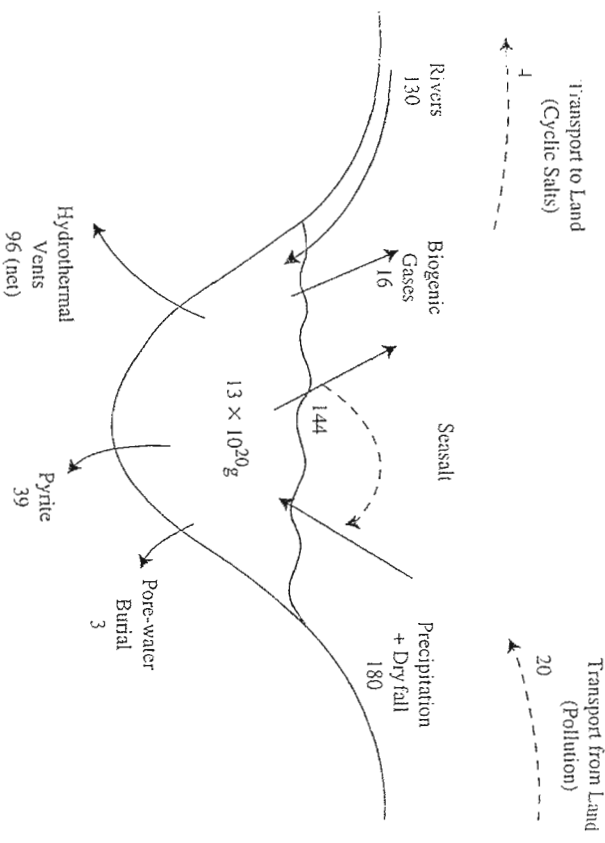
Processes and Reactions

Transport to Land (Cyclic Salts) 4

Rivers 130

Biogenic Gases 16

Transport from Land (Pollution) 20

Seasalt

Precipitation + Dryfall 180

13 × 10²⁰ g

144

Hydrothermal Vents 96 (net)

Pyrite 39

Pore-water Burial 3

Figure 9.22 Sulfur budget for the world's oceans, showing important fluxes in units of 10^{12} g S/yr. Riverflux from Husar and Husar (1985), gaseous outputs from Bates et al. (1992), hydrothermal flux from Jannasch (1989), and pyrite deposition from Berner (1982). See also Fig. 13.1.

Kiene 1990). The reaction is mediated by an enzyme, dimethyl sulfoxide (DMSO) reductase, which contains Mo (Stiefel 1996). Grazing by zooplankton seems to be important to the release of DMS to seawater (Dacey and Wakeham 1986). Only a small percent 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). 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). In 1977, Maroulis and Bandy were able to measure DMS as an atmospheric constituent along the eastern coast of the United States. It 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 at least 15×10^{12} g S/yr to the atmosphere (Erickson et al. 1990, Bates et al. 1992). This is the largest *natural* emission of a sulfur gas to the atmosphere globally (Möller 1984, Spiro et al. 1992).

In the atmosphere, DMS is rapidly oxidized by OH radicals, forming sulfate aerosols that are deposited in precipitation (Chapter 3). Nearly 80% of the non-seasalt sulfate in the atmosphere over the North Pacific Ocean appears to be derived from DMS, with the soil dust and pollution contribut-

ing 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).

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 (T.W. Andreae et al. 1991). 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 0.2×10^{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) show that the production of DMS increases as a function of increasing salinity, as river water mixes with seawater in estuaries of the eastern United States.

In addition to helping balance the marine sulfur budget, dimethylsulfide attains global significance for its potential effects on climate. Charlson et al. (1987) recognized that the oxidation of DMS to sulfate aerosols would increase the abundance of cloud condensation nuclei in the atmosphere, leading to greater cloudiness (Bates et al. 1987). Clouds over the sea reflect incoming sunlight, leading to global cooling (Chapter 3). The production of DMS is directly related to the growth of marine phytoplankton (Andreae and Barnard 1984, Turner et al. 1988, T.W. Andreae et al. 1994), so an increase in marine NPP increases the production of DMS. If higher NPP is associated with warmer sea surface temperatures, then the flux of DMS would have the potential to act as a negative feedback on global warming that might otherwise occur by the greenhouse effect.

This hypothesis for a biotic regulation on global temperature is intriguing, for it may be responsible for the moderation of global climate throughout geologic time. Given the strong arguments in favor of global warming by increased atmospheric CO_2, the potential negative feedbacks of DMS are the subject of intense scientific scrutiny and debate. The flux of DMS from the sea is greater in summer than winter, as a result of greater sea surface temperature (Prospero et al. 1991, Tarrasón et al. 1995). The concentration of DMS in seawater is well correlated to that in the air over the North Pacific Ocean (Watanabe et al. 1995). Cloud condensation nuclei also appear to be well correlated to the atmospheric burden of DMS in nonpolluted areas (Ayers and Gras 1991, Putaud et al. 1993, Andreae et al. 1995), and the ice-core record of methanesulphonate (MSA)—a DMS degradation product—suggests higher concentrations during the last glacial epoch than today (Legrand et al. 1991). Certainly the ocean's temperature was lower during the last glacial, but, for other reasons (e.g., a greater deposition of iron-rich dust), marine productivity was higher during the last glacial, an increased flux of DMS may have reinforced the global cooling of Earth's climate (Turner et al. 1996).

Schwartz (1988) argued that anthropogenic emissions of SO_2 should have the same effect as natural emissions of DMS, because SO_2 is also oxidized to produce condensation nuclei in the atmosphere. Using a general circulation model for global climate, Wigley (1989) suggested that climatic cooling by SO_2 may have offset some of the temperature change expected from the greenhouse effect. Because SO_2 has a short atmospheric lifetime (Chapter 3), its effect is regional and centered on areas of industry (Kiehl and Briegleb 1993, Falkowski et al. 1992, Langner et al. 1992). Nevertheless, it is possible that an increased flux of both SO_2 and DMS will act to dampen the greenhouse effect during the next century.

The Sedimentary Record of Biogeochemistry

Marine sediments contain a record of the conditions of the oceans through geologic time. Sediments and sedimentary rocks rich in $CaCO_3$ (calcareous ooze) show the past location of shallow, productive seas, where foraminifera and coccolithopores 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 (Fig. 9.9). Direct identification of preserved organisms and changes in their species composition have also been used to infer patterns of ocean climate, circulation, and productivity during the geologic past (Weyl 1978, Corliss et al. 1986).

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 $H_2^{18}O$ compared to today. Because carbonates precipitate in an equilibrium reaction with seawater (Eq. 9.2), an analysis of changes in the ^{18}O content of sedimentary carbonates is an indication of changes in the ocean volume and temperature (Fig. 9.23).

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 the 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).
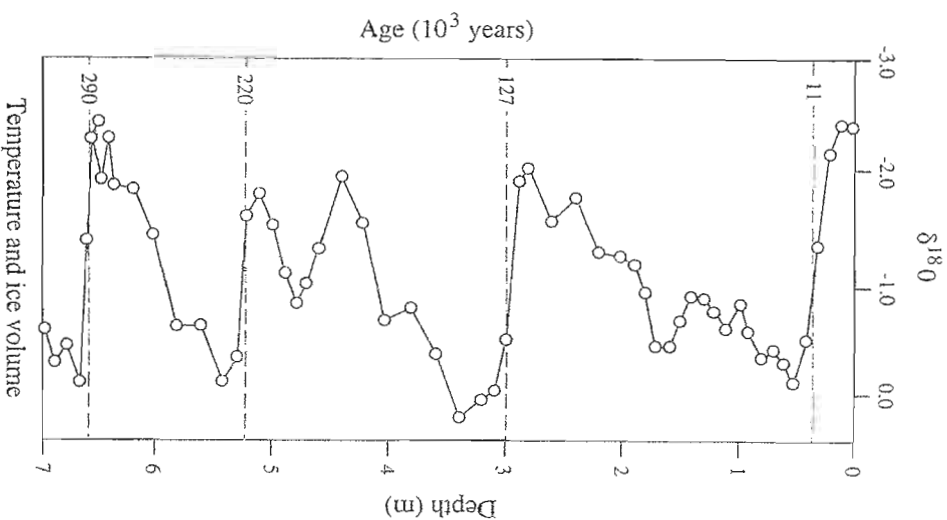
Figure 9.23 Changes in the $\delta^{18}O$ in sedimentary carbonates of the Caribbean Sea during the last 300,000 years. Enrichment of $\delta^{18}O$ during the last glacial epoch (20,000 ybp) is associated with lower sea levels and a greater proportion of $H_2^{18}O$ in seawater. From Broecker (1973).

Carbonates are also a major sink (20%) of boron in the oceans (Vengosh et al. 1991), and the isotopic ratio of boron in carbonates as a function of seawater pH. The isotopic ratio of boron in sedimentary foraminifera of the Miocene (21 million years ago) indicates that seawater pH was lower (7.4) than that of today (8.2), consistent with suggestions of higher atmospheric CO_2 during that period (Spivak et al. 1993). Similarly, the boron isotope ratios of sedimentary carbonate indicate a higher seawater pH during the last glacial, when atmospheric CO_2 was low (Sanyal et al. 1995).

The sedimentary record of ^{13}C in organic matter and in $CaCO_3$ contains a record of the biotic productivity of Earth. Recall that photosynthesis discriminates against $^{13}CO_2$ relative to $^{12}CO_2$ (Chapter 5), slightly enriching plant materials in ^{12}C compared to the atmosphere. When large amounts of organic matter are stored on land and in ocean sediments, $^{13}CO_2$ accumulates in the atmosphere and the ocean (i.e., $^{13}HCO_3$). Arthur et al. (1988) suggest that the relatively high ^{13}C content of marine carbonates during the late Cretaceous reflects a greater storage of organic carbon from photosynthesis. Similar changes are seen in the ^{13}C of coal age (Permian) brachiopods (Brand 1989). When the storage of organic carbon is greater, there is the potential for an increase in atmospheric O_2, as postulated for the Permian (Berner and Canfield 1989).

Summary

Biogeochemistry in the sea 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.

Through its buffering of atmospheric composition and temperature, the oceans exert enormous control over the climate of Earth. At a pH of 8.2 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 water. Most of the major ions in the oceans have long mean residence times and their concentration in seawater has been constant for nearly all of geologic time. All of this reinforces the traditional, and unfortunate, view that the ocean is a constant body that offers nearly infinite dilution potential for the effluents of modern society.

Looking at the sedimentary record, however, we see that the ocean is subject to large changes in volume and productivity, due to changes in global climate and nutrient flux. Already, we have strong reason to suspect that the productivity of coastal waters is affected by human inputs of N and P. Changes in the temperature and productivity of the central ocean basins may well indicate that global climate change is affecting the oceans as a whole (Venrick et al. 1987, Strong 1989, Polovina et al. 1995). Humans extract a large harvest of fish and shellfish from the oceans—amounting to 8% of marine net primary productivity (Pauly and Christensen 1995). Recent declines in the populations of important commercial fishes suggest that it is doubtful that this harvest is sustainable for future generations.

Recommended Readings

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