Chapter 9

Carbon in the Oceanic Coastal Margin

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In this chapter we address the behavior of inorganic and organic carbon in the shallow coastal ocean where a large part of the biological production and sediment accumulation occur. At present, the coastal zone is more or less synonymous with the continental shelf that is covered by ocean water as a result of ice melting and sea level rise of 120 meters since the end of the Last Glacial Maximum about 18,000 years ago. In some intervals of the geologic past, shallow epicontinental seas were much more widespread during the periods of marine transgressions when the land was covered by seawater due to a rising sea level, caused by such factors as change in the relative elevation of land and(or) displacement of the ocean-water volume by the growth of spreading ridges on the ocean floor. In fact, a large part of marine sediments preserved on the continents was formed in shallow seas of the past that covered parts of the cratons of what are now different continents. The importance of the coastal ocean in the regulation of the global carbon cycle is primarily related to its position at the junction of the land, atmosphere, and open ocean, with all of which it interacts differently and modifies the transport fluxes of carbon. We emphasize in this chapter the inorganic and organic carbon cycles in the coastal ocean at the time scale of the Industrial Era, the last approximately 300 years, and up to three centuries into the future that are the time of increasing perturbations of the global carbon cycle by human activities.
1 The Global Coastal Zone

The coastal zone is the environment of continental and insular shelves to 180 to 200 m depth, including bays, lagoons, estuaries, and near-shore banks that occupy, in various estimates, 7 to 8% of the surface area of the ocean (24 × 10^6 to 29 × 10^6 km^2; Table 9.1). The mean depth of coastal zone water is approximately 130 m. The occurrence and extent of continental shelves are shown on the world map in Fig. 9.1 and on the hypsometric curve in Fig. 9.2. Estuaries are the main points of input from land to the coastal zone and their total area was estimated as about 1 × 10^6 km^2 (Borges, 2005) or less than 5% of the shelf area. The zone of 0 to −200 m accounts for about 5% of the global surface area. The continental shelves average 75 km in width, with a bottom slope of 1.7 m/km, and they are generally viewed as divisible into the interior or proximal shelf, and the exterior or distal shelf (Drake and Burk, 1974). The depth of the outer edge of the global continental shelf is usually taken as the depth of the break between the continental shelf and slope at approximately 200 m, although this depth varies throughout the world oceans. In the Atlantic, Emery and Uchupi (1984) gave the median depth of the shelf-slope break at 120 m, with the range from 80 to 180 m. The depths of the continental shelf are near 200 m in the European section of the Atlantic, but they are close to 100 m on the African and North American coasts.

The sea level stand at the Last Glacial Maximum 18 ka ago was about 120 m below the present level (Fig. 9.3), making the shelf ice-free area about 30% of the present area. Notice in Fig. 9.3 the relatively rapid rise in sea level of approximately 95 cm per century between 18,000 and 7000 years ago and the slowing down of sea level rise to 12 to 20 cm per century in younger time. The sea level curve of Fig. 9.3 from Barbados has been confirmed to a variable extent from other areas of the world, including other oceanic islands such as Bermuda. The flooding of continental shelves during the late Pleistocene and Holocene has been responsible for major changes in land-sea exchange of materials, including organic carbon and nutrients, and has modified the behavior of the global carbon cycle and increased the ocean area of air-sea exchange of atmospheric CO₂, as

<table>
<thead>
<tr>
<th>Area (10^6 km^2)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.8</td>
<td>Rabouille et al. (2001)</td>
</tr>
<tr>
<td>28.3</td>
<td>Milliman (1993)</td>
</tr>
<tr>
<td>28.1</td>
<td>Lagrula (1966)</td>
</tr>
<tr>
<td>28.0</td>
<td>From ETOPO5 (Fig. 9.5)</td>
</tr>
<tr>
<td>27.1</td>
<td>Drake and Burk (1974)</td>
</tr>
<tr>
<td>27.0</td>
<td>Tsunogai et al. (1999)</td>
</tr>
<tr>
<td>26.0</td>
<td>Borges (2005)</td>
</tr>
<tr>
<td>25.2</td>
<td>Gattuso et al. (1998)</td>
</tr>
<tr>
<td>24.6</td>
<td>From P. W. Sloss (Fig. 9.2)</td>
</tr>
<tr>
<td>24.3</td>
<td>World Resources Institute (2000)</td>
</tr>
</tbody>
</table>
Figure 9.1  Global coastal zone of 0 to −200 m depth. Lambert azimuthal projection, from ETOPO5 data. The parallels are 15° apart and the meridians 30° apart. Coastal zone is dark shaded area.
Figure 9.2 Global hypsometric curve showing the surface areas of the ocean floor and land surface in 100-meter intervals. Areas deeper than −7000 m and higher than 5500 m are too small to be seen in the graph. Total global surface area is $510 \times 10^6$ km$^2$. Coastal zone area between 0 and −200 m (darker shaded 2 bars) is $24.6 \times 10^6$ km$^2$. From P. W. Sloss (personal communication of unpublished data, 2003, based onETOPO2 Gridded Elevation Data, NOAA National Geophysical Data Center, Boulder, Colorado http://www.ngdc.noaa.gov/mgg/fliers/01mgg04.html).

discussed later in this chapter. This concept of the coastal zone includes essentially all of the continental shelves and the points of input from land, yet it differs from some other definitions of the coastal zone that extend from some elevation on land above mean sea level to some depth on the continental shelf; for example, the international program on Land-Ocean Interactions in the Coastal Zone (LOICZ) defines the coastal zone as extending from +200 m on land to −200 m on the continental shelves (Pernetta and Milliman, 1995). Global continental shelves have a very uneven distribution around the continents, as the maps in Figs. 8.3 and 9.1 show. Bearing in mind that the Mercator projection of the map in Fig. 8.3 exaggerates the extent of the continental shelves in the Arctic Ocean, the prominence of the continental shelves is readily apparent in Northern Europe, East Asia, Southeast Asia, North Australia, and the Eastern coasts of the Americas.

The main drainage basins of the rivers are major areas of input from the continents to the coastal zone (Fig. 9.4), where it can also be noted that some of the larger river outflows occur on relatively narrow or poorly developed continental shelves (Northeast coast of South America, East and West coasts of Africa). This physiographic feature shows that the bigger and wider continental shelves are not merely physical links on the path between river mouths or deltas and the open ocean, but they play a broader role in the global transport and transformation of materials in the land-atmosphere-ocean system.
Estimated amounts of particulate matter transported from land by rivers at present are 13 to $20 \times 10^9$ ton/yr (Chapter 8). Riverine input of particulate organic carbon to the oceans increased from about $0.19 \times 10^9$ ton C/yr in pre-industrial time to about $0.24 \times 10^9$ ton C/yr in the year 2000, and this carbon is likely to be derived from soil humus of an average C:N:P atomic ratio of 268:17:1 (Lerman et al., 2004; Mackenzie et al., 2002). Thus the particulate organic carbon flux accounts for a fraction of 1 to 2% of the total particulate matter input by rivers to the oceans. The particulate inorganic carbon (PIC) flux has been estimated as 0.18 Gt C/yr.

The water volume of the coastal zone to 100 m mean depth is 2.2 to 3.3% of the volume of the surface ocean layer (300 m deep, $108 \times 10^6$ km$^3$) and its surface area is approximately 8% of the ocean surface. The present-day coastal zone comprises important sites of deposition and regeneration of organic carbon and of calcium carbonate produced in situ: 45% of total carbonate and approximately 85% of total organic
carbon accumulation in the ocean occur in the coastal margin, and 10 to 30% of total oceanic biological production takes place in this region (Mackenzie et al., 2004; Milliman, 1993; Turner and Adger, 1996; Wollast, 1994, 1998). Eighty percent of the mass of riverine terrigenous materials reaching the ocean is deposited in the coastal zone (Milliman and Syvitski, 1994). Active depositional areas in the coastal ocean may have sedimentation rates as high as 30 to 60 cm/1000 yr, as compared to average rates for hemipelagic and pelagic sediments of 20 cm/1000 yr and 0.1 to 1 cm/1000 yr, respectively. It is thus understandable why the coastal zone is regarded as both a filter and a trap for natural as well as anthropogenic materials transported from the continents to the open ocean (Mantoura et al., 1991). Coastal environments are also regions of higher biological productivity relative to that of average oceanic surface waters, making them an important reservoir in the global carbon cycle. The higher primary productivity is variably attributable to the nutrient inflows from land, as well as most importantly from upwelling of deeper ocean waters along certain sections of the global coastal margin. The global role of the coastal zone as a whole must be viewed through the geographic distribution of its latitudinal sections that is shown in Fig. 9.5.

In the Northern Hemisphere, above the latitude N60°, the shelves make a relatively large fraction of the total surface area, about 20%. This is also a region of major inputs by some of the rivers in North America and Siberia (Fig. 9.4). The shelves in the Northern Hemisphere occupy a much larger area than in the Southern Hemisphere. The climatic differences between the latitudinal zones affect primary production and
biological calcification. Carbonate production on the shelves by corals, calcareous algae, and foraminifera is greater in the warmer latitudes, but it should be kept in mind that there are significant deposits of biogenic calcareous sediments at higher latitudes (cool-water carbonates). In addition, significant carbonate mineral production occurs in areas dominated by terrigenous inputs, such as in the river deltaic areas of the coastal ocean, but the carbonate accumulating there is diluted by the detrital input and difficult to quantify in terms of accumulation flux.

Despite its relatively small size, the coastal ocean is an important interface between the land and open ocean, and it is also in direct exchange with the atmosphere. Large river drainage basins connect the vast interiors of continents with the coastal zone through river and groundwater discharges. The ocean surface links the coastal ocean to the atmosphere via gas exchange at the air-sea interface, production of sea aerosols, and atmospheric deposition on the sea surface; substances released at the air-sea interface of the coastal zone may be subsequently transported through the atmosphere and deposited on land as wet and dry depositions; conversely, emissions from land to the atmosphere are in part deposited in the coastal zone. Additionally, physical exchange processes at coastal margins, involving for example coastal upwelling (water rising from the deeper ocean) and onwelling (water that moves on and across the shelf), and net advective transport of water, dissolved solids, and particles from the coastal zone offshore connect the coastal ocean with the surface and intermediate
depths of the open ocean. The processes of settling, deposition, resuspension, remineralization of organic matter, dissolution and precipitation of mineral phases, and accumulation of materials connect the water column and the sediments of the coastal zone.

In general, interfaces between the larger material reservoirs (that is, the land, atmosphere, and ocean) are important in the control of the biogeochemical cycling of three of the major bioessential elements found in organic matter: carbon (C), nitrogen (N), and phosphorus (P), because they act as relatively fast modifiers of transport and perturbation processes at geologically short time scales. Over the past several centuries, activities of humankind have significantly modified the exchange of materials between the land, atmosphere, and ocean on a global scale. Humans have become, along with natural processes, agents of environmental change. For example, rapid population growth, increasing population density in the areas of the major river drainage basins and close to oceanic coastlines (about 40% of the world population lives within 100 km of the shoreline; Cohen et al., 1997), and changes in land-use practices in past centuries have increased discharges of industrial, agricultural, and municipal wastes into oceanic coastal waters. Land-use activities include the conversion of land for food production (grazing land, agricultural land), for urbanization (building human settlements, roads, and other structures), for energy development and supply (building dams, hydroelectric plants, and mining of fossil fuels), and for resource exploitation (mining of metals, harvest of forest hardwood) (e.g., Mackenzie, 2003). These activities on land have contributed to increased soil degradation and erosion, eutrophication of river and coastal ocean waters through addition of chemical fertilizers to agricultural land and sewage discharge, degradation of water quality, and alteration of the coastal marine food web and community structure. It is estimated that only about 20% of the world’s drainage basins have pristine water quality at present (Meybeck and Ragu, 1995). Estuarine and coastal regions showing much human-induced change are located, for example, along the coasts of the North Sea, the Baltic Sea, the Adriatic Sea, the East China Sea, and the East and South coasts of North America (Fig. 9.4; De Jonge et al., 1994; Richardson and Heilmann, 1995).

2 Carbon Cycle in the Coastal Ocean

2.1 Cycle Structure and Main Processes

For the global coastal ocean as described in the preceding section, a conceptual model of the broad features of the carbon cycle is shown in Fig. 9.6. The inorganic carbon reservoir exchanges CO₂ with the atmosphere (±F_{CO₂}) and receives inputs of dissolved inorganic carbon from land via rivers, surface runoff and groundwater flow (F₁₁), from the CO₂ released by the precipitation of calcium carbonate (curved arrow 1), and by upwelling from the deeper ocean (F₁₅). Upwelling refers to the various processes responsible for the transport of water, dissolved inorganic and organic carbon and nutrients from mainly intermediate-depth waters of the ocean to the surface,
in this case to the coastal zone waters. Outflows of inorganic carbon are via net water
outflow from the coastal ocean (\(F_{i4}\)), accumulation of calcium carbonate formed in the
coastal zone, in coastal marine sediments (deposition less dissolution, \(F_{i3}\)), and used
as CO\(_2\) in photosynthesis (\(F_{i2}\)). The organic carbon cycle is linked to the inorganic
cycle through biologically driven reduction and oxidation processes, corresponding to
primary production (\(F_{o2}\)) utilizing CO\(_2\), and respiration and decay (\(F_{DIC}\), where DIC
stands for total dissolved inorganic carbon). Analogous to the inorganic carbon cycle,
there are inputs of organic carbon from land (dissolved and particulate, \(F_{o1}\)) and by
transport of dissolved organic carbon from the deeper ocean, referred to as coastal
upwelling (\(F_{o5}\)). Removal of organic carbon from the coastal zone is through net out-
flow to the open ocean (\(F_{o4}\)), accumulation in coastal sediments (in situ produced and
land-derived, \(F_{o3}\)), and respiration and decay or remineralization (\(F_{DIC}\)). Remineralized

Figure 9.6 Conceptual model of the inorganic and organic carbon cycles in the coastal ocean
and their interactions. \(F_i\) refer to the fluxes from reservoir i to j (after Mackenzie et al., 1998a).
See text for explanation.
organic carbon produced in situ (curved arrow 2) or imported from land (curved arrow 3) contributes to \( F_{\text{DIC}} \).

The material balance for the organic carbon reservoir in the coastal margin, using the flux notation in Fig. 9.6 for a period \( \Delta t = 1 \text{ yr} \), can be written as:

\[
\Delta C_{\text{org}} = (F_{o1} + F_{o2} + F_{o5}) - (F_{o4} + F_{o3} + F_{\text{DIC}}),
\]

(9.1)

where \( C_{\text{org}} \) is the mass of organic carbon in the reservoir, in mol C. Gross photosynthesis \((F_{o2})\) and respiration and decay \((F_{\text{DIC}})\) are the linkages between the organic and inorganic carbon cycles. The balance of inorganic carbon, \([\text{DIC}]\) in mol C, is:

\[
\Delta[\text{DIC}] = (F_{i1} + F_{i5} + F_{\text{DIC}}) - (F_{i3} + F_{i4} + F_{i2}) \pm F_{\text{CO}_2}
\]

(9.2)

Inputs and outputs of carbon produce changes in DIC that equilibrates with atmospheric CO\(_2\). A change in the DIC concentration from an initial value of \([\text{DIC}_0]\) to a new equilibrium value after all the input and output fluxes have been accounted for, \([\text{DIC}_{\text{eq}}]\), is the difference

\[
\Delta[\text{DIC}] = [\text{DIC}_{\text{eq}}] - [\text{DIC}_0]
\]

(9.3)

The mass of air-sea exchange of CO\(_2\), flux \( F_{\text{CO}_2} \times 1 \text{ yr} \), can be obtained by substitution of \( F_{\text{DIC}} \) from equation (9.1) for \( F_{\text{DIC}} \) in (9.2) and also writing the individual terms as fluxes that are shown in Fig. 9.6 as follows:

\[
F_{\text{CO}_2} = (F_{i4} - F_{i1} - F_{i5}) + F_{i3} + (F_{o4} + F_{o3}) - (F_{o1} + F_{o5}) + \Delta C_{\text{org}} + \Delta[\text{DIC}]
\]

\[
= (F_{\text{DIC}_{\text{outflow}}} - F_{\text{DIC}_{\text{inflow}}}) + (F_{\text{CaCO}_3, \text{ppt}} - F_{\text{CaCO}_3, \text{diss}})
\]

\[
+ (F_{\text{CaCO}_3, \text{outflow}} + F_{\text{CaCO}_3, \text{sed}} - F_{\text{CaCO}_3, \text{inflow}}) + \Delta C_{\text{org}} + \Delta[\text{DIC}]
\]

(9.4)

In the notation of Fig. 9.6 and equation (9.4), \( F_{\text{CO}_2} \) is negative when the net CO\(_2\) flow is from seawater to the atmosphere and the coastal ocean is a CO\(_2\) source; \( F_{\text{CO}_2} \) is positive when the CO\(_2\) flow is to seawater and the coastal ocean is a CO\(_2\) sink.

2.2 CO\(_2\) Air-Sea Exchange

The individual inorganic and organic carbon fluxes that determine the CO\(_2\) exchange between seawater and the atmosphere are discussed in this section.

The change in DIC and the equilibrium value \([\text{DIC}_{\text{eq}}]\) depend not only on the atmospheric CO\(_2\) concentration, but also on the shift in the carbonate equilibria because of the net removal of CaCO\(_3\) from seawater and a resultant increase in the dissolved CO\(_2\) as a fraction of DIC. A calculation of \([\text{DIC}_{\text{eq}}]\) that is needed for the CO\(_2\) air-sea flux is based on the changes in total alkalinity and DIC of seawater that are discussed in Chapter 5. A simplified calculation, presented below, is based on the parameter \( \theta \) that defines a relationship between the net removal of CaCO\(_3\) and change in DIC due to production of CO\(_2\) in seawater of normal salinity. The ratio of CO\(_2\) released from seawater of normal salinity to CaCO\(_3\) removed by precipitation, between 15\(^\circ\)C, and 25\(^\circ\)C, and the atmospheric CO\(_2\) concentration between the pre-industrial 280 ppmv and the
near-present 375 ppmv, is (Table 5.5):
\[
\theta = \frac{\Delta[DIC]}{F_{\text{CaCO}_3} \Delta t} = 0.51 \text{ to } 0.66 \tag{9.5}
\]

In the coastal zone, where most of the CaCO\textsubscript{3} is produced by biological processes, \((F_{\text{CaCO}_3} \text{ppt} - F_{\text{CaCO}_3} \text{diss})\) has been called net ecosystem calcification or NEC in the marine ecological literature.

The balance of the organic carbon inputs and outputs to the coastal ocean is called net ecosystem production (NEP) or net ecosystem metabolism (NEM):
\[
NEM = F_{\text{o4}} + F_{\text{o3}} - F_{\text{o1}} + \Delta C_{\text{org}} \approx F_{\text{o4}} + F_{\text{o3}} - F_{\text{o1}} \tag{9.6}
\]

Net ecosystem metabolism is essentially equivalent to the difference between gross primary production (GPP) and the production of CO\textsubscript{2} by autotrophic and heterotrophic respiration of organic carbon that includes organic carbon from external inputs and \textit{in situ} primary production. NEM is a negative quantity when the input of organic carbon to the coastal ocean \((F_{\text{o1}})\) is greater than its removal by outflow to the open ocean \((F_{\text{o4}})\) and net storage in sediments \((F_{\text{o3}})\). In this algebraic notation, the excess of organic carbon input over its removal is a contribution to the CO\textsubscript{2} flux out of the coastal zone.

A relationship between a change in DIC of seawater due to a change in atmospheric CO\textsubscript{2} concentration was developed by Bacastow and Keeling (1973) and approximated by Revelle and Munk (1977) in the form of:
\[
R = \frac{C_{\text{atm},t}/C_{\text{atm},0} - 1}{C_{\text{DIC},t}/C_{\text{DIC},0} - 1} \tag{9.7}
\]
\[
R \approx R_0 + D \times (C_{\text{atm},t}/C_{\text{atm},0} - 1) \tag{9.8}
\]

where \(C_{\text{atm}}\) is CO\textsubscript{2} concentration in the atmosphere and \(C_{\text{DIC}}\) is the dissolved inorganic carbon concentration [DIC] in surface ocean water, subscript 0 denotes the initial value and subscript \(t\) a value at a later time \(t\). Subsequently, \(R\) became known as the Revelle factor and its different forms have been discussed by Zeebe and Wolf-Gladrow (2001). Equation (9.8) with constants \(R_0 = 9\) and \(D = 4\) is Revelle and Munk's (1977) approximation to the curve of \(R\) calculated by Bacastow and Keeling (1973) for an average surface ocean water of total alkalinity \(2.435 \times 10^{-3}\) mol-equivalent/liter, temperature 19.59°C, chlorinity 19.24 per mil, and initial pH = 8.271. With \(R_0 = 9\), the buffer mechanism of seawater causes a fractional rise of DIC in coastal ocean surface seawater that is one-ninth of the increase of CO\textsubscript{2} in the atmosphere. The change in DIC, as written in equation (9.3), becomes:
\[
\Delta[DIC] = \frac{(C_{\text{atm},t} - C_{\text{atm},0})C_{\text{DIC},0}}{R_0 C_{\text{atm},0} + D \times (C_{\text{atm},t} - C_{\text{atm},0})}. \tag{9.9}
\]

A time-dependent change of [DIC], \(d[DIC]/dt\), is obtained by differentiation of equation (9.8) that gives a simpler approximate relationship in equation (9.10a) and a
more complete relationship (9.10b) with a second-order term:

\[
\frac{d[DIC]}{dt} = \frac{[DIC_0]}{R_0 C_{atm,0} + D \times (C_{atm,t} - C_{atm,0})} \times \frac{dC_{atm}}{dt}
\]  

(9.10a)

\[
\frac{d[DIC]}{dt} = \left\{ \frac{[DIC_0]}{R_0 C_{atm,0} + D \times (C_{atm,t} - C_{atm,0})} - \frac{D \times [DIC_0] \times (C_{atm,t} - C_{atm,0})}{[R_0 C_{atm,0} + D \times (C_{atm,t} - C_{atm,0})]^2} \right\} \times \frac{dC_{atm}}{dt}
\]  

(9.10b)

The CO₂ air-sea flux in equation (9.4), using the preceding definitions of the other flux terms, can now be written as:

\[
F_{CO_2} = (F_{t4} - F_{t1} - F_{t5}) + NEC + NEM + \frac{d[DIC]}{dt}
\]  

(9.11)

Table 9.2  Estimates of measured air-sea CO₂ exchange from worldwide shallow-water locations (estuaries, reefs, shelves)

<table>
<thead>
<tr>
<th>Location/Region</th>
<th>Net CO₂ flux (mol C m⁻² yr⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Global coastal zone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>without estuaries</td>
<td>+1.17</td>
<td>Borges (2005)</td>
</tr>
<tr>
<td>including estuaries</td>
<td>-0.38</td>
<td></td>
</tr>
<tr>
<td>Global estuaries</td>
<td>-41</td>
<td>Borges (2005)</td>
</tr>
<tr>
<td>European estuaries (Elbe, Ems, Rhine, Scheldt, Tamar, Thames, Gironde, Duoro, Sado)</td>
<td>-36.5 to -277</td>
<td>Frankignouille et al. (1998)</td>
</tr>
<tr>
<td>Oregon, Cape Perpetua</td>
<td>+7.29</td>
<td>Hales et al. (2003)</td>
</tr>
<tr>
<td>New Jersey</td>
<td>+0.43 to +0.84</td>
<td>Boehme et al. (1998)</td>
</tr>
<tr>
<td>Bermuda, Hog Reef flat</td>
<td>-1.20</td>
<td>Bates et al. (2001)</td>
</tr>
<tr>
<td>Mid Atlantic Bight (MAB)</td>
<td>+1.00</td>
<td>DeGrandpre et al. (2002)</td>
</tr>
<tr>
<td>South Atlantic Bight (SAB)</td>
<td>-2.50</td>
<td>Cai et al. (2003)</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>+0.90</td>
<td>Thomas and Schneider (1999)</td>
</tr>
<tr>
<td>North Sea</td>
<td>+1.35</td>
<td>Kempe and Pegler (1991)</td>
</tr>
<tr>
<td>North Sea average</td>
<td>+0.95 to +1.33</td>
<td>Thomas et al. (2004)</td>
</tr>
<tr>
<td>range from South to North</td>
<td>-0.5 to +2</td>
<td></td>
</tr>
<tr>
<td>Scheldt Estuarine plume</td>
<td>-1.10 to -1.90</td>
<td>Borges and Frankignouille (2002)</td>
</tr>
<tr>
<td>Gulf of Biscay</td>
<td>+1.75 to +2.88</td>
<td>Frankignouille and Borges (2001)</td>
</tr>
<tr>
<td>Galician Coast</td>
<td>+0.66 to +1.17</td>
<td>Borges and Frankignouille (2001)</td>
</tr>
<tr>
<td>Northern Arabian Sea</td>
<td>-0.46</td>
<td>Geyt et al. (1998)</td>
</tr>
<tr>
<td>East China Sea</td>
<td>+2.91</td>
<td>Tsunogai et al. (1999)</td>
</tr>
<tr>
<td>East China Sea</td>
<td>+1.20 to +2.80</td>
<td>Wang et al. (2000)</td>
</tr>
<tr>
<td>Moorea, French Polynesia</td>
<td>-0.55</td>
<td>Gattuso et al. (1993)</td>
</tr>
</tbody>
</table>

Note: Negative values denote CO₂ flux from ocean to the atmosphere; positive values denote flux from the atmosphere to ocean water. Some of the values are annual integrated flux measurements and others monthly or occasional measurements.
The preceding equation defines the CO$_2$ flux across the air-sea interface of the coastal ocean as an algebraic sum of four terms: the difference between the outflows and inflows of DIC (Fig. 9.6) into the coastal ocean, dissolved CO$_2$ produced by precipitation of calcium carbonate in net ecosystem production, net ecosystem metabolism that is the net difference of the inputs and outputs of organic carbon, and the change in the DIC concentration caused by a change in the atmospheric CO$_2$ concentration.

The relative importance of the individual processes that determine the CO$_2$ air-sea flux in equation (9.11) is discussed in the next section. Some of the measurements of the present-day CO$_2$ flux at different locations in coastal and open oceanic sections, and estuaries are summarized in Table 9.2, showing flux values that are highly variable both in their magnitude and direction.

An example of this variability is shown in Fig. 9.7 for the air-sea exchange of CO$_2$ in the major estuary of Kaneohe Bay, Oahu, Hawaii. Although the estuary, about 14 km
long and up to 5 km wide, on an annual basis is a source of CO$_2$ to the atmosphere from calcification processes involving major coral reef development in the bay, the direction, magnitude, and spatial distribution of the net CO$_2$ flux vary considerably during the year. The bay on an annual basis is net autotrophic and immediately following storms that deliver large subsidies of nutrients to the estuary from the land, via river and groundwater flows, the bay for some period of time, because of the enhanced organic productivity in phytoplankton blooms resulting from the storm-derived nutrient loading, becomes a sink of atmospheric CO$_2$. As the productivity declines, the bay returns to its more normal state of being a source of CO$_2$ to the atmosphere. These observations, particularly characteristic of many proximal coastal ocean ecosystems of the world, support two major conclusions: determining the air-sea exchange CO$_2$ flux for coastal environments and the integrated global coastal ocean is a difficult task because of the high variability of this flux and must involve time series carbon measurements of

![Diagram of the carbon cycle in the coastal ocean](image)

Figure 9.8 Inorganic (carbonate) part of the carbon cycle in the coastal ocean in pre-industrial time (from Andersson et al., 2005, and Ver et al., 1999a). Reservoir masses in italics are in units of $10^{12}$ mol C. Arrows denote carbon fluxes between reservoirs in units of $10^{12}$ mol C/yr (shown inside parentheses). Two major domains are the water column (surface water and dissolved inorganic carbon) and the pore water-sediment system (pore water, dissolved inorganic carbon, river-derived particulate inorganic carbon (PIC), calcite, aragonite, and 15 mol % magnesian calcite, a mean composition representing the range in composition of magnesian calcites). For two-way arrows the direction of the net flux is shown next to the flux estimate. The dashed lines indicate carbon flux owing to CaCO$_3$ production, equations (9.4), (9.5), and (9.12).
sufficient duration and spatial distribution to determine the flux quantitatively; and the net air-sea CO₂ flux is in part a reflection of both the net ecosystem metabolism (NEM) and net ecosystem calcification (NEC) rates.

3 Inorganic and Organic Carbon

3.1 A More Detailed Conceptual Model

It is clear from the preceding discussion that the inorganic or carbonate part of the carbon cycle is intimately linked to its organic part through the reduction of CO₂ in photosynthesis by primary producers, and oxidation of organic matter in autotrophic respiration and by microbial activity. Nevertheless, it is instructive to consider the inorganic and organic parts separately, as they are schematically shown in Figs. 9.8 and 9.9. The masses of carbonate and organic carbon in the different reservoirs of the

Figure 9.9 Organic (Cₐ₉) part of the carbon cycle in the coastal ocean in pre-industrial time (from Andersson et al., 2005, and Ver et al., 1999a). Reservoir masses in italics are in units of 10¹² mol C. Arrows denote carbon fluxes between reservoirs in units of 10¹² mol C/yr (shown inside parentheses). Two major domains are the water column (surface water, dissolved inorganic carbon, and organic matter) and the pore water—sediment system (pore water and organic matter in sediments). The dashed lines indicate carbon flux owing to the net imbalance between GPP and total remineralization of organic matter or net ecosystem metabolism, NEM, equations (9.6) and (9.11).
coastal ocean and the interreservoir fluxes have been used in the global carbon cycle models TOTEM (Terrestrial Ocean aTmosphere Ecosystem Model, Mackenzie et al., 2001; Ver et al., 1999) and SOCM (Shallow-water Ocean Carbonate Model, Andersson and Mackenzie, 2004; Andersson et al., 2003). One of the prominent features of the carbonate cycle is the dominant abundance of land-derived detrital calcite and biogenic aragonite in coastal sediments, followed by magnesian calcites and calcite. For the sediment layer 1 m in thickness (Fig. 9.8), total residence time of inorganic carbon calculated with respect to inputs is about 1850 years, with the main removal flux being the burial in sediments of the detrital calcite and in situ produced carbonates. Water residence time in the coastal water column is shown as about 4 years, although there are also shorter estimates of 2 to 3 years (Chavez and Toggweiler, 1995).

The organic carbon reservoir of the coastal water column includes dissolved organic carbon (DOC) and particulate organic carbon (POC), in part transported from land and in part formed in situ by primary production. Input from land consists of DOC and part of POC classified as a reactive particulate fraction and taken as 50% of total POC in rivers (Fig. 8.4; Smith and Hollibaugh, 1993). The remaining 50% of POC is considered a refractory fraction, at least on a short time scale. Organic carbon that is exported to the open ocean is eventually remineralized, in whole or in part. The uncertainties in the published estimates of the carbonate and organic carbon fluxes in the Holocene and earlier, during the Last Glacial period, are considerable, and a variation within a factor of two is to be expected in the storage rates. Since the end of pre-industrial time, the inputs of dissolved and particulate inorganic and organic carbon to the coastal zone have increased significantly and the projected trend is that of a continued increase on a centurial time scale (Lerman and Mackenzie, 2004; Mackenzie et al., 2004; Fig. 8.4).

3.2 Remineralization of Organic Matter

Degradation of organic matter in sediments by microbial processes generally produces aqueous CO$_2$ and bicarbonate ions. A number of such reactions involving the reduction of oxygen, nitrate, ferric iron, and sulfate are given in Table 9.3 and their energy yields are also shown in Fig. 9.10. The latter depend on the reaction stoichiometry and the reactants and products. Overall, the energy change decreases from remineralization of organic matter by oxygen through the reduction of nitrate, Fe$^{3+}$ iron, and sulfate to anaerobic decomposition of organic matter that produces methane, CO$_2$, and hydrogen.

A major benthic process involving the interaction between the inorganic and organic carbon cycles that was initially observed for shallow-water carbonate sediments and then extended to open ocean sediments was that involving the degradation of organic matter by a bacterially mediated oxygen reaction (Emerson and Bender, 1981; Table 9.3, reaction 1) and the consumption of the produced CO$_2$ in the process of dissolution of calcium carbonate. In an abbreviated and idealized form, comparable to reaction (5.23):

$$\text{CH}_2\text{O} + \text{O}_2 + \text{CaCO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (9.12)$$
Table 9.3  Organic matter oxidation (1), reduction by organic matter of nitrate, ferric iron, and sulfate (2-4), and anaerobic decomposition to methane and byproducts (5)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction(^{(2)})</th>
<th>(\Delta G_f^{\circ})(^{(1)}) (kJ/mol C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Remineralization</td>
<td>(\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O})</td>
<td>-478.4</td>
</tr>
<tr>
<td>2. a. Denitrification</td>
<td>5(\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ = 5\text{CO}_2 + 2\text{N}_2 + 7\text{H}_2\text{O})</td>
<td>-486.2</td>
</tr>
<tr>
<td>b.</td>
<td>2(\text{CH}_2\text{O} + 2\text{NO}_3^- + 2\text{H}^+ = 2\text{CO}_2 + \text{N}_2\text{O} + 3\text{H}_2\text{O})</td>
<td>-436.1</td>
</tr>
<tr>
<td>c.</td>
<td>2(\text{CH}_2\text{O} + 2\text{NO}_3^- = \text{N}_2\text{O} + 2\text{HCO}_3^- + \text{H}_2\text{O})</td>
<td>-391.4</td>
</tr>
<tr>
<td>3. a. Fe(^{3+}) iron reduction</td>
<td>(\text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 8\text{H}^+ = \text{CO}_2 + 4\text{Fe}^{2+} + 11\text{H}_2\text{O})</td>
<td>-412.6</td>
</tr>
<tr>
<td>b.</td>
<td>(\text{CH}_2\text{O} + 4\text{FeOOH} + 8\text{H}^+ = \text{CO}_2 + 4\text{Fe}^{2+} + 7\text{H}_2\text{O})</td>
<td>-278.3</td>
</tr>
<tr>
<td>c.</td>
<td>(\text{CH}_2\text{O} + 7\text{CO}_2 + 4\text{Fe(OH)}_3 = 4\text{Fe}^{2+} + 8\text{HCO}_3^- + 3\text{H}_2\text{O})(^{(3)})</td>
<td>-55.0</td>
</tr>
<tr>
<td>d.</td>
<td>2(\text{Fe(OH)}_3 + \text{H}_2 = 2\text{Fe(OH)}_2 + 2\text{H}_2\text{O}) (kJ/mol Fe)</td>
<td>-31.5</td>
</tr>
<tr>
<td>4. a. Sulfate reduction</td>
<td>3(\text{CH}_2\text{O} + 4\text{H}^+ + 2\text{SO}_4^{2-} = 3\text{CO}_2 + 5\text{H}_2\text{O} + 2\text{S})</td>
<td>-140.1</td>
</tr>
<tr>
<td>b.</td>
<td>2(\text{CH}_2\text{O} + 2\text{H}^+ + \text{SO}_4^{2-} = 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{H}_2\text{S})</td>
<td>-120.0</td>
</tr>
<tr>
<td>c.</td>
<td>2(\text{CH}_2\text{O} + \text{SO}_4^{2-} = 2\text{HCO}_3^- + \text{H}_2\text{S})</td>
<td>-75.3</td>
</tr>
<tr>
<td>5. a. Methanogenesis</td>
<td>2(\text{CH}_2\text{O} = \text{CO}_2 + \text{CH}_4)</td>
<td>-69.4</td>
</tr>
<tr>
<td>b.</td>
<td>3(\text{CH}_2\text{O} + \text{H}_2\text{O} = 2\text{CO}_2 + \text{CH}_4 + 2\text{H}_2)</td>
<td>-47.7</td>
</tr>
<tr>
<td>c.</td>
<td>(\text{CH}_3\text{COOH} = \text{CO}_2 + \text{CH}_4)</td>
<td>-27.6</td>
</tr>
</tbody>
</table>

Note: Standard Gibbs free energy of the reaction at 25°C in kJ per 1 mol carbon of organic matter, written in a shorthand notation \(\text{CH}_2\text{O}\) for glucose, \(\text{C}_6\text{H}_{12}\text{O}_6\)\(^{(3)}\).

\(^{(1)}\) Standard free energy of formation of glucose \((\text{C}_6\text{H}_{12}\text{O}_6)\) \(\Delta G_f^{\circ} = -918.78\) kcal/mol computed from the free energy change of the photosynthesis reaction, taken as \(\Delta G_f^{\circ} = 2870\) kJ/mol or 478.4 kJ/mol C (Chapter 2).

\(^{(2)}\) Standard Gibbs free energy of formation values from Lide (1994) and Drever (1997).

Gaseous species: \(\text{O}_2, \text{CO}_2, \text{N}_2, \text{N}_2\text{O}, \text{H}_2, \text{and CH}_4\). Liquid: \(\text{H}_2\text{O}\). Aqueous species: \(\text{H}^+, \text{H}_2\text{S, NO}_3^-, \text{Fe}^{3+}, \text{and SO}_4^{2-}\). Solids: ferrihydrite \(\text{Fe(OH)}_3\), goethite \(\text{FeOOH}\), ferrous hydroxide \(\text{Fe(OH)}_2\), and rhombic sulfur S.

\(^{(3)}\) This reaction is the sum of 3a and 8\(\text{CO}_2 + 8\text{H}_2\text{O} = 8\text{H}^+ + 8\text{HCO}_3^-\). Canfield (1993) gives for this reaction \(-114\) kJ/mol \(\text{CH}_2\text{O}\).

or with the organic matter based on the C:N:P Redfield ratio of marine phytoplankton:

\[
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 138 \text{O}_2 + 124 \text{CaCO}_3 = 16 \text{H}_2\text{O} + 16 \text{NO}_3^- + \text{HPO}_4^{2-} + 124 \text{Ca}^{2+} + 230 \text{HCO}_3^- \tag{9.13}
\]

This reaction is only possible if the pore waters are undersaturated with a carbonate phase and there are no competing reactions that increase pore water carbonate saturation state, such as ammonia release from the decaying organic matter that may increase the pore water pH. Figure 9.11 shows the increase in total alkalinity versus the increase in DIC for shallowly buried pore waters bathing sediments containing nearly pure calcite, aragonite, and magnesian calcites with up to 20 mol % MgCO₃ occurring in the Gulf of Calvi in Corsica. Notice that the slope of this relationship is 1.04, close to the slope predicted in equation (9.13), 2 \(\times\) 124/230 = 1.08 and not 2 as would
be expected if the dissolution were simply related to undersaturation with carbonate minerals: \( \text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-} \). The fact that the regression line does not pass through 0 in Fig. 9.11 reflects the fact that dissolved CO\(_2\) has been added to the pore waters from aerobic bacterial respiration of organic matter prior to carbonate dissolution thus lowering the carbonate saturation state of the pore water sufficiently for dissolution to occur. Moulin et al. (1985) showed that due to this very early diagenetic reaction in carbonate deposits, principally containing particles of the red alga \textit{Lithothamnium} sp. in Calvi Bay, nearly 75% of the carbonate sediment initially deposited is dissolved.

Another benthic process that can be important in the dissolution (and precipitation) of carbonate minerals in sediments is that of sulfate reduction (Table 9.3, reactions 4a-c). This is a complex process, but it can be described schematically by the following equation:

\[
\frac{1}{53}(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + \text{SO}_4^{2-} = 2\text{HCO}_3^- + \text{HS}^- + 16/53 \text{NH}_3 + 1/53 \text{H}_3\text{PO}_4 + \text{H}^+ \quad (9.14)
\]

This reaction results in the decrease in sulfate and pH and the concomitant increase in alkalinity, hydrogen sulfide, phosphate, ammonia, and DIC, commonly observed in anoxic sediment pore waters with increasing depth. During the early stages in sulfate reduction (range of approximately 2 to 35% decrease in sulfate concentration), the pore
water may become undersaturated with respect to carbonate minerals (Fig. 9.12), particularly the highly soluble magnesian calcites and aragonite, and carbonate phases may dissolve. As the extent of sulfate reduction increases further, the pore water becomes supersaturated with respect to carbonate minerals and a carbonate phase may precipitate. The extent of the reaction depends strongly on the organic carbon available and the C/N ratio of the labile carbon. This reaction pathway has been demonstrated both in model calculations and has been observed in pore waters (Mackenzie et al., 1995; Morse et al., 1985). The relative importance of carbonate dissolution in aerobic pore water environments and that of dissolution in anaerobic pore waters is not well known because of the lack of data on pore water composition accompanied by solid phase chemistry and mineralogy, particularly for shallow-water sediments. Suffice it to mention that both processes may occur during early diagenesis and are used in a model, discussed in the subsequent sections of this chapter, to assess changes in shallow-marine pore water chemistry and carbonate saturation state under rising atmospheric CO₂ concentrations and temperature and enhanced burial of organic carbon.

3.3 Carbon Fluxes

For the carbon cycle in the coastal zone near the end of pre-industrial time, taken as the year 1700, the direction and magnitude of the CO₂ exchange between coastal ocean waters and the atmosphere can be estimated from the fluxes shown in Figs. 9.8 and
Figure 9.12  A. Model calculation of the saturation state (\( \Omega \)) of marine pore waters of sediments with respect to aragonite as a function of the percentage of dissolved sulfate reduced in the pore waters starting with a pore water sulfate concentration of 0.028 mol/kg of seawater (Ben-Yaakov, 1973; recalculated by Morse and Mackenzie, 1990). B. The observed saturation state of Mangrove Lake, Bermuda marine pore waters with respect to calcite. Notice the undersaturation with respect to calcite at shallow depths and the supersaturation at deeper depths in the sediment. At the shallower depths in the sediment, calcite, aragonite and the highly soluble magnesian calcites could dissolve, and at deeper depths a carbonate phase(s) could precipitate (Mackenzie et al., 1995).

9.9 and equation (9.4). Below, three estimates of the exchange are given, based on somewhat different approaches.

For dissolved inorganic carbon (DIC), there are two main inputs, from land by rivers (\( 32 \times 10^{12} \) mol C/yr) and from intermediate ocean depths by coastal upwelling, and exchange with the open surface ocean. DIC is also removed as CO\(_2\) in primary production and calcium carbonate formation and storage in sediments. For organic carbon, there is the riverine input of reactive and particulate organic carbon (the latter considered as at least temporarily refractory) and its removal by export to the ocean and storage in sediments. Taking these fluxes with no change in the organic carbon concentration in the coastal ocean and no increase in the atmospheric CO\(_2\) concentration, the sea-air flux from equation (9.4) is:

\[
F_{CO_2} = (1503 - 32 - 1504.2) + (24.5 - 6) + (18 + 9 - 26 - 8) + 0 \\
= (-33.2 + 18.5 - 7) \times 10^{12} = -21.7 \times 10^{12} \text{ mol/yr}
\]  \( (9.15) \)

This value is shown as the sea-to-air flux in Figs. 9.8 and 9.9, which also show the individual contributions to the CO\(_2\) flux from DIC (in units of \( 10^{12} \) mol C/yr), \(-33.2 + 18.5 = -14.7\), and from the net imbalance between GPP and total remineralization of
organic matter. \(\dot{-}7.\) The increase in DIC due to an increase in atmospheric CO\(_2\) on a yearly basis that is given by the term \(d[\text{DIC}]/dt\) in equation (9.11) is relatively small in comparison to the other terms.

A more detailed solution, based on the preceding flux values and the CO\(_2\)-transfer computation that is described in Chapter 5, gives a slightly higher pre-industrial sea-to-air CO\(_2\) flux:

\[
F_{\text{CO}_2} = -24.7 \pm 0.1 \times 10^{12} \text{ mol/yr} \tag{9.16}
\]

An approximate value of the sea-air CO\(_2\) exchange can also be obtained from the balance of dissolved CO\(_2\) in the DIC inflow and outflow, CO\(_2\) production in CaCO\(_3\) net deposition, and remineralization of organic matter. Then, as explained in Section 2.2 and below, the CO\(_2\) flux at a steady state can be written from equation (9.11) as:

\[
F_{\text{CO}_2} \approx \alpha_{\text{sw}} \cdot (F_{\text{DIC out}} - F_{\text{DIC in}})_{\text{sw}} - \alpha_{\text{rw}} \cdot F_{\text{DIC in}, \text{rw}} - \theta \cdot NEC + NEM \tag{9.17}
\]

The DIC input to the coastal ocean, as shown in Fig. 9.8, consists of an upwelling flux of ocean water and riverine inflow, and the DIC outflow of seawater. Dissolved CO\(_2\) represents different fractions of DIC in fresh and ocean water: in river water, taken as pure water at a pH of 7.5, the CO\(_2\) fraction is \(\alpha_{\text{rw}} = 0.077\) at \(15^\circ\) and \(0.066\) to \(25^\circ\)C, but it is much smaller in seawater at the same temperatures because of its higher alkalinity, \(\alpha_{\text{sw}} = 0.0050\) to \(0.0038\), at a pH of 8.2. Using these values of the CO\(_2\) fractions \(\alpha_{\text{sw}}\) and \(\alpha_{\text{rw}}\) with the DIC outflow and inflow values, other fluxes as in equation (9.15), the sea-to-air flux is:

\[
F_{\text{CO}_2} \approx -20.4 \pm 0.2 \times 10^{12} \text{ mol/yr} \tag{9.18}
\]

The three estimates of the global sea-air CO\(_2\) exchange are comparable, although it should be borne in mind that they are all based on one set of inflow and outflow values in the model of the coastal ocean and sediments.

The calculated CO\(_2\) flux since the beginning of industrial time to the early years of the 21st century and beyond is shown in Fig. 9.13. This calculation, done using the model SOCM, takes into account increases in the inputs of carbon, nitrogen, and phosphorus from land to the coastal zone owing to human activities and the documented historical increase in atmospheric CO\(_2\) concentrations and their projection into the future. The greater delivery of nutrients to the coastal ocean, the rising atmospheric CO\(_2\), and a possibly increasing global temperature of the Earth's surface affect the main processes of the inorganic and organic carbon cycles in the coastal zone: primary production, storage of organic matter in sediments, seawater chemistry, and precipitation, dissolution, and storage of calcium carbonate minerals, all of which control the air-sea exchange of carbon dioxide.

Figure 9.13 also shows Borges's (2005) mean values of the coastal zone air-sea exchange of CO\(_2\) based on synthesis of most of the observational measurements available to date. It should be kept in mind that these data are of variable quality and still do not cover a major proportion of the global coastal zone area. In addition, few time-series data are available. The open circle in Fig. 9.13 is the mean air-sea CO\(_2\) exchange flux
Figure 9.13  Net air-sea CO$_2$ exchange ($10^{12}$ mol C yr$^{-1}$) between 1700 and 2100 calculated by SOCM adopting the coastal water residence time ($\tau$) of 4 and 12 years. The solid line indicates the average flux of the two scenarios. The data points (Borges, 2005) indicate that the coastal zone including estuaries (solid circle) is a net source of CO$_2$ to the atmosphere, and excluding estuaries (open circle) it is a net sink of CO$_2$. The small area of the estuaries ($\sim 1 \times 10^6$ km$^2$), less than 5% of the global continental shelf ($\sim 26 \times 10^6$ km$^2$), indicates that the strength of the estuarine source of CO$_2$ is unusually high; that is, its specific area CO$_2$ flux is significantly greater than the specific area CO$_2$ flux of the whole coastal zone that is dominantly shelf area (Andersson et al., 2005).

if one does not include estuaries in the estimate; the filled circle includes the data from estuaries. The area specific global coastal zone air-sea CO$_2$ flux without including the estuaries is $+1.17$ mol C m$^{-2}$ yr$^{-1}$ (a sink of atmospheric CO$_2$) and including estuaries is $-0.38$ mol C m$^{-2}$ yr$^{-1}$ (a source of atmospheric CO$_2$). The strong role of the estuaries in the global coastal zone air-sea CO$_2$ exchange balance is evidenced by their very significant area-specific mean air-sea CO$_2$ exchange flux of $-35.8$ mol C m$^{-2}$ yr$^{-1}$. Thus the model results in Fig. 9.13 agree very well with the observational data of Borges (2005) and show that in the future, the whole global coastal ocean will likely become a sink of atmospheric CO$_2$ owing to a combination of the rising atmospheric CO$_2$ with increased biological production that leads to a greater net storage of organic carbon in sediments. The global shelf area is already a sink of atmospheric CO$_2$. The magnitudes of the biogeochemical mechanisms that ultimately control the air-sea CO$_2$ exchange are shown in Fig. 9.14, calculated for the 300 years of the immediate past and projected for 300 years of the future Industrial Age.

A striking feature of the projected trends is the reversal of the coastal ocean's role from being a CO$_2$ source to a CO$_2$ sink owing to the change in the carbon cycle
dynamics. The contribution of the atmospheric CO$_2$ rise is small, as was mentioned earlier. Net ecosystem metabolism ($NEM$) changes from negative to positive, generating an excess of organic carbon in the coastal ocean that is in part stored in sediments and in part exported to the open ocean. Remineralization of organic matter also contributes to DIC in coastal water, increasing the DIC concentration in outflow. Even a more pronounced change takes place in the inorganic carbon cycle, as shown by the decrease in net ecosystem calcification, $NEC$. Excess of CaCO$_3$ mineral precipitation over dissolution declines until the magnitudes of the two processes are reversed and there is a net loss of CaCO$_3$ from sediment ($NEC < 0$) from approximately the middle of the 22nd century to the year 2300. The reason behind this carbonate loss is the dissolution of the relatively soluble Mg-calcites and aragonite, as discussed in the next section, that occurs because of a higher dissolved CO$_2$ concentration in coastal water due to the increase in atmospheric CO$_2$ and remineralization of organic carbon in carbonate sediments. Dissolved CO$_2$ lowers the degree of seawater saturation with respect to the carbonate minerals and promotes their dissolution. Remineralization or decay of organic matter in sediments (Figs. 9.9 and 9.12) generates at the beginning of the modeling period, year 1700, a flux of $31 \times 10^{12}$ mol C/yr that increases with time (Fig. 9.15), contributing to the carbonate mineral dissolution in sediments according to the reactions of equations (9.13) and (9.14).
Figure 9.15  Calculated rates of sedimentation and remineralization or decay of organic matter in the coastal ocean (Andersson et al., 2005).

4 Marine Calcifying Organisms and Ecosystems

4.1 Calcium Carbonate Saturation State and Calcification

Increasing atmospheric CO₂ and subsequently decreasing carbonate saturation state of surface ocean water (ocean acidification) may have a negative effect on marine calcifying organisms because their ability to calcify depends in part on the carbonate saturation state. The rate of calcification or the rate at which marine organisms make their CaCO₃ skeletons depends on the carbonate saturation state of seawater with respect to the mineral phase formed by the biomineralization processes. Greater supersaturation is usually accompanied by faster calcification rates. This relationship has been demonstrated for such different calcifying organisms as coccolithophorids (Riebesell et al., 2000; Sciandra et al., 2003; Zondervan et al., 2001), foraminifera (Bijma et al., 1999; Spero et al., 1997), coralline algae (Agegian, 1985; Borowitzka, 1981; Gao et al., 1993; Mackenzie and Agegian, 1989; Smith and Roth, 1979), and scleractinian corals (Gattuso et al., 1998; Marubini and Thake, 1999; Marubini et al., 2001, 2003; Reynaud et al., 2003). Similar results were obtained from experiments with typical calcareous communities in incubation chambers and mesocosms, and on the artificial reef of Biosphere 2 (Halley and Yates, 2000; Langdon et al., 2000, 2003; Leclercq et al., 2000, 2002). Although substantial variations have been observed between species and communities, the major results and conclusions of most studies have been similar: the rate of calcification has been observed to decrease as a function of decreasing carbonate saturation state, as shown in Fig. 9.16 for different communities of carbonate organisms. In addition, the saturation state and temperature of seawater also have an effect on the Mg-content of calcite in a species of a
coralline alga (Fig. 9.17). The degree of saturation of seawater with respect to carbonate minerals was discussed in Chapter 5 and it may be reiterated here that because the Ca$^{2+}$-ion concentration in seawater does not vary much, the saturation state depends on the CO$_3^{2-}$-ion, the concentration of which is a function of atmospheric CO$_2$. Dissolution of CO$_2$ in seawater decreases the carbonate-ion concentration, as shown in the reaction below, and it consequently decreases the saturation state with respect to the carbonate minerals:

$$\text{CO}_2 + \text{H}_2\text{O} + \text{CO}_3^{2-} = 2\text{HCO}_3^- \quad \text{(9.19)}$$

A reaction between dissolved CO$_2$ and carbonate minerals (Chapter 5) adds alkalinity to seawater, also buffering the change in the H$^+$-ion concentration that would be caused by adding CO$_2$ to pure water:

$$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} = \text{Ca}^{2+} + \text{HCO}_3^- \quad \text{(9.20)}$$
Empirical relationships for the increase of the calcification rates of corals and other calcifying organisms as a function of increasing degree of supersaturation of seawater have been proposed by a number of investigators (Gattuso et al., 1998, 1999; Leclercq et al., 2002; see also Chapter 4).

The degree of supersaturation of surface ocean water with respect to calcite has been decreasing due to the increase in atmospheric CO$_2$ (Fig. 9.18). In addition, recent observations from open ocean environments have shown a shoaling of the carbonate saturation horizon in several regions of all major ocean basins (Feely et al., 2004). Based on current experimental results and the observed increase in atmospheric CO$_2$ since the onset of the Industrial Age, one would expect the rate of calcification of marine calcifying organisms to have already declined by 6 to 14% and to decrease further by 11 to 44% owing to a doubling of the atmospheric CO$_2$ concentration relative to pre-industrial conditions (Buddemeier et al., 2004; Gattuso et al., 1999; Kleypas et al., 1999; Langdon, 2002).

However, no observations of such a decline exist at this time. On the contrary, analyses of drill cores taken from *Porites* colonies along the Great Barrier Reef suggest that the rate of calcification of these corals has increased rather than decreased between 1880 and the later part of the 20th century, a phenomenon attributed to an increase in...
the average annual sea surface temperature during the 20th century (Lough and Barnes, 2000). Similar results showing increased calcification rates toward the present have also been obtained from a coral core taken in French Polynesia (Bessat and Buiges, 2001). It is important to recognize that the rate of calcification is not controlled only by carbonate saturation state and temperature that is discussed in the next section, but also by light, as shown by the data in Fig. 9.16 and Marubini et al. (2001), nutrients, and metabolic and photosynthetic activity of the organism if the organism is autotrophic or dependent on autotrophic symbionts (Ferrier-Pages et al., 2000; Marubini and Atkinson, 1999; Paasche and Brubak, 1994; Sciandra et al., 2003).

The question that remains to be answered is whether lower carbonate saturation state and decreased rates of calcification will negatively affect corals and other calcifying organisms ecologically. Obvious adaptational advantages given to organisms that calcify include such functions as structural support and protection from predators and desiccation, whereas other hypotheses suggest that calcification may facilitate nutrient and/or bicarbonate uptake through an increase in surface area (Cohen and McConnaughey, 2003; McConnaughey and Whelan, 1997; McConnaughey et al., 2000).

As a result of the lower carbonate saturation state of surface water, the physical strength and structure of the skeletons and shells formed by marine calcifiers may become weaker and more susceptible to environmental stress in general, both natural
and anthropogenic. As a consequence, calcareous organisms may not thrive in a world characterized by high CO₂ and low carbonate saturation state and may be at an evolutionary disadvantage in their environment relative to other non-calcifying organisms that occupy the same habitats. For example, it would be anticipated that coral reef habitats might experience a successive transition from being dominated by corals and coralline algae to being dominated by seaweeds and fleshy macro algae. A recent report from the Caribbean goes so far as indicating that the average hard coral cover on reefs in this region has declined from 50% to 10% in the last three decades (Gardner et al., 2003). Although local factors, both natural and anthropogenic, such as disease, storms, temperature stress, predation, over-fishing, sedimentation, eutrophication, and habitat destruction were attributed to the reported decline, the effect of decreasing carbonate saturation state cannot be ruled out as a co-factor. Numerous worldwide observations report similar significant declines in coral reef health, which along with future climate projections has lead to the statement of a global “coral reef crisis” (Buddemeier et al., 2004).

4.2 Surface Water Temperature and Calcification

Different relationships have been reported between the rates of biological calcification and sea surface temperature. A positive linear relationship between the rate of calcification and sea surface temperature for the species of the coral genus Porites was postulated by Lough and Barnes (2000) from data from different geographical locations characterized by different annual average sea surface temperatures: the Hawaiian archipelago (Grigg, 1982, 1997), Phuket, Thailand (Scoffin et al., 1992), and the Great Barrier Reef (Lough and Barnes, 2000). In contrast to these conclusions, a negative parabolic relationship between the rate of calcification and temperature was reported for individual coral colonies and coralline algae (Andersson et al., 2005; Clausen and Roth, 1975; Mackenzie and Agegian, 1989; see Chapter 4). The projections on how calcification rates may be affected in the future by increasing temperature significantly depend on such relationships. The results of SOCM suggest that global shallow-water carbonate production could either increase by almost 70% or decrease by approximately 44% by the year 2100 depending on the temperature and saturation state relationships adopted in the model. Similar projections made by McNeil et al. (2004), adopting a positive linear temperature and a positive linear saturation-state dependence, suggest that net coral calcification significantly increases between the years 1900 and 2100 by approximately 40% as the positive effect of ocean warming outweighs the negative effect of decreasing carbonate saturation state.

The positive linear relationship observed between coral calcification and the average annual temperature in different geographic locations is most likely due to increased metabolism and/or increased photosynthetic activity by symbiotic zooxanthellae (Buddemeier et al., 2004). In calcifying organisms hosting symbiotic algae, photosynthesis and calcification are strongly coupled. Calcification rates are approximately three to five times higher in light conditions when photosynthesis is active than in the dark when this process is inactive (Fig. 9.16). It has been suggested that primary
production in some algae may be limited by CO₂ concentration (Raven, 1993, 1997; Riebesell, 1993). If carbon fixation by symbiotic algae is limited by the availability of CO₂, photosynthesis and consequently calcification may increase in the future owing to increasing concentrations of CO₂ that would then partly counteract the effects of a lower carbonate-mineral saturation state of surface water (Leclercq et al., 2002). However, there is currently no conclusive evidence confirming that the primary production of coral reef ecosystems is limited by the availability of CO₂ and its potential to compensate for a decrease in calcification rate.

Present-day corals and other calcifying organisms have evolved in their environment for thousands of years under relatively constant, but naturally changing, conditions of temperature and salinity, allowing them to adapt and acclimate to the prevailing regional climate conditions. We are now living in a world in which the rate of accumulation of CO₂ in the atmosphere from human activities and, possibly, the rate of temperature rise during the past 30 years are outside the conditions that characterized the Earth’s surface for most of the past 740,000 years of the data available for the period before the Industrial Age (Chapter 10, Section 4.1). Human activities have driven the Earth’s system away from the environmental conditions that bracket the interglacial-glacial dynamics (Chapter 10) and it is difficult to make projections for the future. However, the response of marine calcifying organisms to increasing sea surface temperature probably depends to some extent on the rate of temperature change. Certainly in a warmer world and one that is warming quickly, it is likely that there will be more bleaching events affecting corals. In addition, if the future temperature change in the tropics were smaller than the average as predicted (Houghton et al., 2001), the direct effect of temperature on the marine calcification rates of shallow, warm water benthic communities (Fig. 9.19)

![Figure 9.19 Distribution of warm- and cool-water shelf carbonates in the present (modified from Nelson, 1988; by permission of Elsevier, publishers of Sedimentary Geology).]
of hermatypic corals, green and red algae, benthic foraminifera, and bivalves might be relatively small. It might be the case that the cooler water benthic carbonate communities of bryozoans, mollusks, echinoderms, and coralline algae of predominantly the high and temperate latitudes might be more directly affected by temperature change than those in the tropics. In addition, as CO$_2$ continues to invade the ocean in the future, the carbonate saturation state of surface waters at high latitudes could drop below that of saturation with respect to aragonite and even calcite (Fig. 5.6). This along with rising sea surface temperatures could have a significant impact on the calcification rates of these cool-water carbonate communities and even their skeletal mineralogy and chemical composition.

5 Present and Future of the Coastal Ocean Carbon System

5.1 Carbonate Sediments and Pore Water

Carbonate sediments in the coastal ocean are mixtures of calcite, aragonite, and magnesian calcites of variable composition, ranging up to more than 20 mol % MgCO$_3$. The carbonate sediment composition shown in Fig. 9.8 consists of 48% calcite, of detrital origin and produced in situ, 38% aragonite, and 15% magnesian calcite (Ca$_{0.85}$Mg$_{0.15}$CO$_3$). However, among the minerals produced in the coastal zone, aragonite is the most abundant (63%), followed by magnesian calcite (24%) and calcite (13%). As discussed in Chapters 4 and 5, the mineral solubility increases from calcite to aragonite and Mg-calcite with 15 mol % and higher MgCO$_3$. In general, in undersaturated solutions, inorganic aragonite dissolves faster than calcite and the latter dissolves faster than 15 mol % Mg-calcite. However, the dissolution kinetics of biogenic materials depends on a variety of factors, such as skeletal microstructure and not simply mineralogy, and hence is quite complex (Chapter 4).

During early diagenetic reactions on the seafloor, dissolution of carbonate minerals generally follows a sequence based on mineral thermodynamic stability, progressively leading to removal of the more soluble phases until the most stable phases remain. Such selective dissolution of metastable carbonate minerals has been observed both in experimental and natural environments by many investigators (Balzer and Wefer, 1981; Chave, 1962; Halley and Yates, 2000; Leclercq et al., 2002; Morse and Mackenzie, 1990; Neumann, 1965; Schmalz and Chave, 1963; Wollast et al., 1980). According to SOCM calculations, global surface waters of the coastal ocean in the year 2300 would still be supersaturated with respect to calcite, aragonite and a 15 mol % Mg calcite, but undersaturated with respect to higher magnesian calcite compositions (Fig. 9.20A). Thus the calcites with a higher Mg-content could dissolve in contact with surface waters upon death of the organisms forming them. More significant perhaps is the forecast that because reactive organic matter loading of coastal sediments is anticipated to increase in the future, the enhanced decomposition of organic carbon in the pore waters of these sediments will result in a more substantial decrease in carbonate saturation state of the pore waters than overlying surface waters due to the
Figure 9.20 Saturation state of the coastal water column and pore water with respect to calcite, aragonite and 15 mol % magnesian calcite at 25°C and S = 35 psu. A. Surface water. B. Pore water and total carbonate dissolution between 1700 and 2300 (from Andersson et al., 2005).

reactions of equations (9.13) and (9.14). Consequently, magnesian calcite compositions that were once in metastable equilibrium with the pore water or with which the pore water was once supersaturated would have a greater tendency to dissolve. The global pore waters of coastal sediments may even become undersaturated with respect to a 15 mol % Mg calcite and nearly undersaturated with respect to aragonite by the year 2300 (Fig. 9.20B).

The dissolution curve in Fig. 9.20B represents model-calculated values for all the carbonate minerals, starting with the dissolution flux from sediments of $6 \times 10^{12}$ mol C yr$^{-1}$ at the beginning of industrial time that is about 25% of the total CaCO$_3$ precipitation rate (Fig. 9.8). In coastal ocean seawater that is supersaturated with respect to calcite, aragonite, and only some of the magnesian calcite compositions, dissolution may affect mainly the higher-Mg-calcite compositions, with about 20 mol % or higher
MgCO₃, and it may be taking place in microenvironments around the carbonate mineral particles that are close to the organic matter remineralized by bacterial reactions. In sediments, the continuous decomposition of organic matter by microbes, releasing CO₂ and maintaining a low carbonate saturation state within the sediment pore water, is the major factor controlling the extent of calcium carbonate dissolved (Fig. 9.20B), as discussed in Section 3.1.

5.2 Carbonate System Balance and Industrial CO₂

The partitioning of industrial CO₂ between the atmosphere and surface ocean water was discussed in Chapter 5. For the surface ocean water to be buffered against increasing acidity and a lower pH by the rising atmospheric CO₂, dissolution of CaCO₃ minerals in the global surface ocean essentially has to balance the net invasion of anthropogenic CO₂, about 160 × 10¹² mol C/yr or 2 Gt C/yr. Even if dissolution of CaCO₃ in the surface sediment layer were equal to the current rates of CaCO₃ production of about 95 × 10¹² mol C/yr (Milliman, 1993), the surface water would be still only partially buffered. However, dissolution rates of this magnitude are very unlikely since most of the CaCO₃ produced in pelagic environments, about 70 × 10¹² mol C/yr, sinks and dissolves at greater depths. Thus because the physical exchange of water between the shallow-water ocean environment and the open ocean is much faster than the turnover time of the ocean, substantial dissolution of metastable carbonate minerals in the shallow-ocean region is necessary to produce sufficient alkalinity to counteract any changes in the surface water chemistry owing to increasing atmospheric CO₂. Current estimates of CaCO₃ dissolution in the global coastal ocean range from 6.7 × 10¹² mol C/yr (Milliman, 1993) to 10 × 10¹² mol C/yr (Langdon, 2002), the higher estimate corresponding to about 7% of the average net anthropogenic invasion of CO₂ into the global ocean during the 1980s, at the rate of 160 × 10¹² mol C/yr (Sarmiento and Gruber, 2002). Direct measurements of carbonate dissolution range from 0 to 13.7 mmol CaCO₃ m⁻² day⁻¹, which corresponds to 0 to 140 × 10¹² mol C/yr, if extrapolated to the entire shallow-water ocean environment (Langdon, 2002). Dissolution of this magnitude is more than 5 times the amount of CaCO₃ produced annually within the global coastal region (24.5 × 10¹² mol C/yr, Fig. 9.8; Milliman, 1993) and it implies a substantial loss of calcium carbonate minerals from reef structures and sediments. Continued increase in atmospheric CO₂ and the lowering of the saturation state of surface water would result in a relatively faster dissolution of magnesian calcites with their higher Mg-content, thereby changing somewhat the mineral composition of the sediment toward a higher fraction of low-Mg calcites and pure calcite.

As can be surmised from the discussion above, the observed changes in the carbonate saturation state of the world’s oceans, including its surface coastal waters and the model predictions of saturation state for the future, do not bode well for reefs and other carbonate ecosystems. In addition, because the effects of temperature on individual calcifying organism and communities is still not well established, it is difficult to conclude that these organisms will acclimate rapidly enough, particularly if the future sea surface temperature changes are in the upper range of predictions for the future
(Chapter 11). Many corals and other marine calcifying organisms are currently living near the upper threshold of their temperature range. Thus the problem of changing carbonate saturation state of the world’s coastal and open ocean waters, ocean acidification, and the consequences of increasing temperature are of concern to the ecological well-being of the coastal ocean and its carbonate communities.

We are now in a position in this book to discuss in more detail the behavior and evolution of the natural carbon cycle through geologic time (Chapter 10). This in turn sets the stage for further discussion of the human influences on the carbon cycle during the past 200 to 300 years of the industrialized era known as the Anthropocene and on into the future (Chapter 11).