CAPILLARY WAVES

See **SURFACE, GRAVITY AND CAPILLARY WAVES**

CARBON CYCLE

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Introduction

Why is carbon an important element? Carbon has several unique properties that make it an important component of life, energy flow, and climate regulation. It is present on the Earth in many different inorganic and organic forms. Importantly, it has the ability to form complex, stable carbon compounds, such as proteins and carbohydrates, which are the fundamental building blocks of life. Photosynthesis provides marine plants (phytoplankton) with an ability to transform energy from sunlight, and inorganic carbon and nutrients dissolved in sea water, into complex organic carbon materials. All organisms, including autotrophs and heterotrophs, then catabolize these organic compounds to their inorganic constituents via respiration, yielding energy for their metabolic requirements. Production, consumption, and transformation of these organic materials provide the energy to be transferred between all the trophic states of the ocean ecosystem.

In its inorganic gaseous phases (carbon dioxide, CO_2; methane, CH_4; carbon monoxide, CO), carbon has important greenhouse properties that can influence climate. Greenhouse gases in the atmosphere act to trap long-wave radiation escaping from Earth to space. As a result, the Earth's surface warms, an effect necessary to maintain liquid water and life on Earth. Human activities have led to a rapid increase in greenhouse gas concentrations, potentially impacting the world's climate through the effects of global warming. Because of the importance of carbon for life and climate, much research effort has been focused on understanding the global carbon cycle and, in particular, the functioning of the ocean carbon cycle. Biological and chemical processes in the marine environment respond to and influence climate by helping to regulate the concentration of CO_2 in the atmosphere. We will discuss (1) the importance of the ocean to the global carbon cycle; (2) the mechanisms of carbon exchange between the ocean and atmosphere; (3) how carbon is redistributed throughout the ocean by ocean circulation; and (4) the roles of the 'solubility', 'biological,' and 'carbonate' pumps in the ocean carbon cycle.

Global Carbon Cycle

The global carbon cycle describes the complex transformations and fluxes of carbon between the major components of the Earth system. Carbon is stored in four major Earth reservoirs, including the atmosphere, lithosphere, biosphere, and hydrosphere. Each reservoir contains a variety of organic and inorganic carbon compounds ranging in amounts. In addition, the exchange and storage times for each carbon reservoir can vary from a few years to millions of years. For example, the lithosphere contains the largest amount of carbon (10^{23} g C), buried in sedimentary rocks in the form of carbonate minerals ($CaCO_3$, $CaMgCO_3$, and $FeCO_3$) and organic compounds such as oil, natural gas, and coal (fossil fuels). Carbon in the lithosphere is redistributed to other carbon reservoirs on timescales of millions of years by slow geological processes such as chemical weathering and sedimentation. Thus, the lithosphere is considered to be a relatively inactive component of the global carbon cycle (though the fossil fuels are now being added to the biologically active reservoirs at unnaturally high rates). The Earth's active carbon reservoirs contain approximately 43×10^{18} g of carbon, which is partitioned between the atmosphere (750×10^{15} g C), the terrestrial biosphere (2190×10^{15} g C), and the ocean ($39\,973 \times 10^{15}$ g C; **Figure 1**). While the absolute sum of carbon found in the active reservoirs is maintained in near steady state by slow geological processes, more rapid biogeochemical processes drive the redistribution of carbon among the active reservoirs.

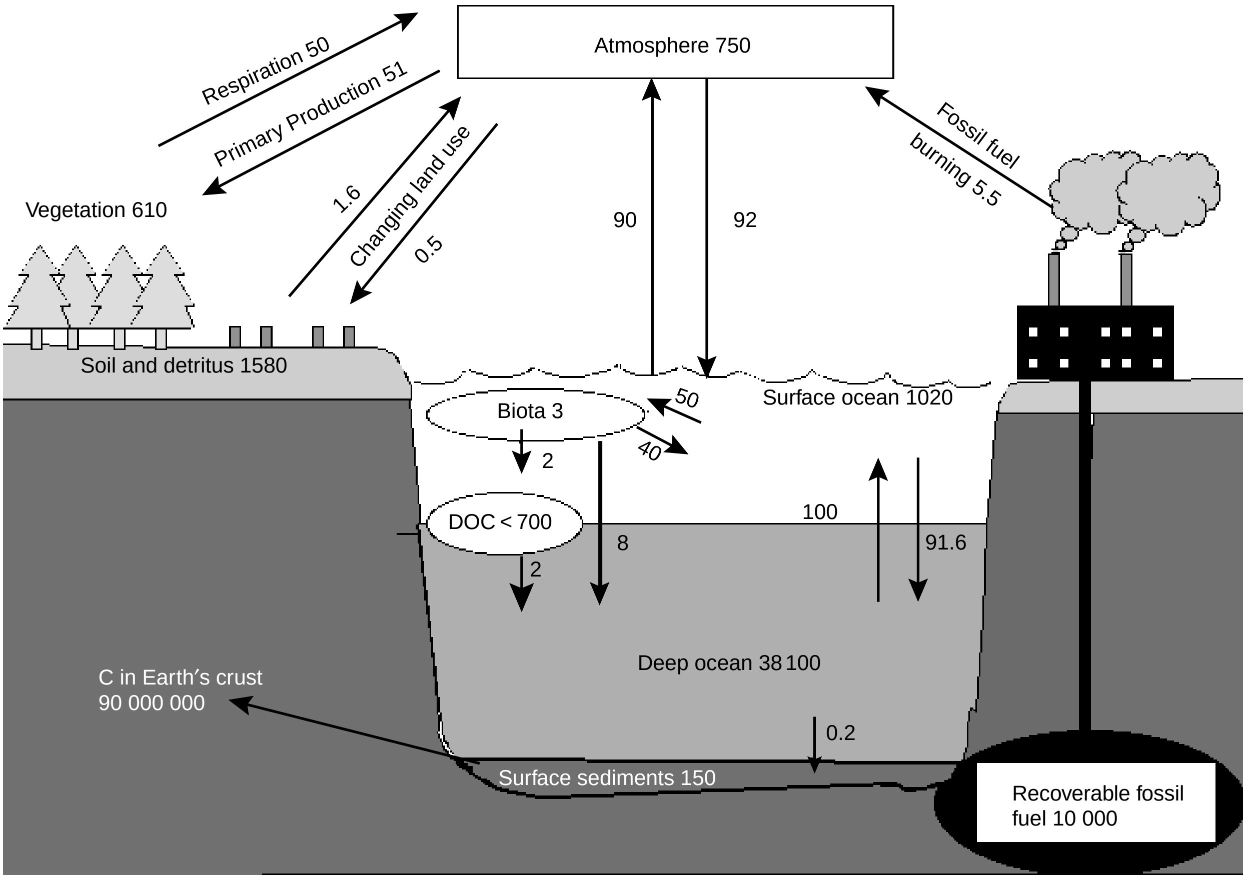

Figure 1 The global carbon cycle. Arrows indicate fluxes of carbon between the various reservoirs of the atmosphere, lithosphere, terrestrial biosphere, and the ocean. All stocks are expressed as 10^{15} g C. All fluxes are decadal means and expressed as 10^{15} g C y^{-1}. (Adapted with permission from Sigenthaler and Sarmiento 1993), copyright 1993, Macmillan Magazines Ltd.). Data used to construct this figure came from Sigenthaler and Sarmiento (1993), Hansell and Carlson (1998), and Sarmiento and Wofsy (1999).

Human activities, such as use of fossil fuels and deforestation, have significantly altered the amount of carbon stored in the atmosphere and perturbed the fluxes of carbon between the atmosphere, the terrestrial biosphere, and the ocean. Since the emergence of the industrial age 200 years ago, the release of CO_2 from fossil fuel use, cement manufacture, and deforestation has increased the partial pressure of atmospheric CO_2 from 280 ppm to present day values of 360 ppm; an increase of 25% in the last century (**Figure 2**). Currently, as a result of human activities, approximately 5.5×10^{15} g of 'anthropogenic' carbon is added to the atmosphere every year. About half of the anthropogenic CO_2 is retained in the atmosphere, while the remaining carbon is transferred to and stored in the ocean and the terrestrial biosphere. Carbon reservoirs that remove and sequester CO_2 from the atmosphere are referred to as carbon 'sinks'. The partitioning of anthropogenic carbon between oceanic and terrestrial sinks is not well known. Quantifying controls on the partitioning is necessary for understanding the dynamics of the global carbon cycle. The terrestrial biosphere may be a significant sink for anthropogenic carbon, but scientific understanding of the causative processes is hindered by the complexity of terrestrial ecosystems.

Global ocean research programs such as Geochemical Ocean Sections (GEOSEC), the Joint Global Ocean Flux Study (JGOFS), and the JGOFS/World Ocean Circulation Experiment (WOCE) Ocean CO_2 Survey have resulted in improvements in our understanding of physical circulation and biological processes of the ocean. These studies have also allowed oceanographers to better constrain the role of the ocean in CO_2 sequestration compared to terrestrial systems. Based on numerical models of ocean circulation and ecosystem

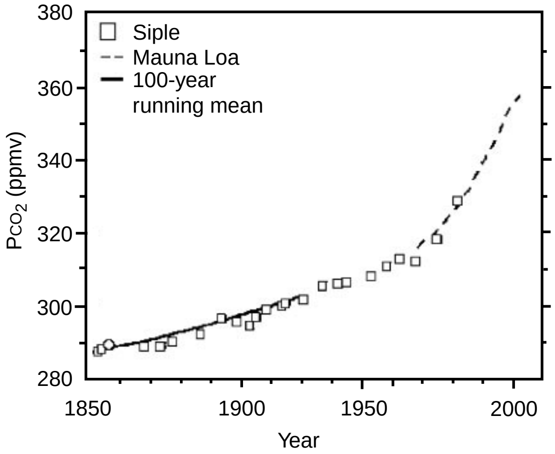

Figure 2 Atmospheric CO_2 concentrations from 1850 to 1996. These data illustrate an increase in atmospheric CO_2 concentration from pre-industrial concentration of 280 ppmv to present-day concentrations of 360 ppmv. Human activities of fossil fuel burning and deforestation have caused this observed increase in atmospheric CO_2. (Adapted from Houghton *et al.* (1996) with permission from Intergovernmental Panel on Climate Change (IPCC). The original figure was constructed from Siple ice core data and (from 1958) data collected at the Mauna Loa sampling site.)

processes, oceanographers estimate that 70% (2×10^{15} g C) of the anthropogenic CO_2 is absorbed by the ocean each year. The fate of the remaining 30% (0.75×10^{15} g) of anthropogenic CO_2 is unknown. Determining the magnitude of the oceanic sink of anthropogenic CO_2 is dependent on understanding the interplay of various chemical, physical, and biological factors.

Oceanic Carbon Cycle

The ocean is the largest reservoir of the Earth's active carbon, containing $39\,973 \times 10^{15}$ g C. Oceanic carbon occurs as a variety of inorganic and organic forms, including dissolved CO_2, bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and organic compounds. CO_2 is one of the most soluble of the major gases in sea water and the ocean has an enormous capacity to buffer changes in the atmospheric CO_2 content.

The concentration of dissolved CO_2 in sea water is relatively small because CO_2 reacts with water to form a weak acid, carbonic acid (H_2CO_3), which rapidly dissociates (within milliseconds) to form HCO_3^- and CO_3^{2-} (eqn [I]).

$$CO_2(\mathrm{gas}) + H_2O \rightleftharpoons H_2CO_3(\mathrm{aq}) \rightleftharpoons H^+(\mathrm{aq}) + HCO_3^-(\mathrm{aq}) \rightleftharpoons 2H^+(\mathrm{aq}) + CO_3^{2-}(\mathrm{aq}) \qquad [\mathrm{I}]$$

For every 20 molecules of CO_2 absorbed by the ocean, 19 molecules are rapidly converted to HCO_3^- and CO_3^{2-}; at the typical range of pH in sea water (7.8–8.2; see below), most inorganic carbon is found in the form of HCO_3^-. These reactions (eqn [I]) provide a chemical buffer, maintain the pH of the ocean within a small range, and constrain the amount of atmospheric CO_2 that can be taken up by the ocean.

The amount of dissolved CO_2 in sea water cannot be determined analytically but can be calculated after measuring other inorganic carbon species. Dissolved inorganic carbon (DIC) refers to the total amount of CO_2, HCO_3^- plus CO_3^{2-} in sea water, while the partial pressure of CO_2 (P_{CO_2}) measures the contribution of CO_2 to total gas pressure. The alkalinity of sea water (A) is a measure of the bases present in sea water, consisting mainly of HCO_3^- and CO_3^{2-} ($A = [HCO_3^-] + 2[CO_3^{2-}]$) and minor constituents such as borate (BO_4) and hydrogen ions (H^+). Changes in DIC concentration and alkalinity affect the solubility of CO_2 in sea water (i.e., the ability of sea water to absorb CO_2) (see below).

The concentrations of inorganic carbon species in sea water are controlled not only by the chemical reactions outlined above (i.e., eqn [I]) but also by various physical and biological processes, including the exchange of CO_2 between ocean and atmosphere; the solubility of CO_2; photosynthesis and respiration; and the formation and dissolution of calcium carbonate ($CaCO_3$).

Typical surface sea water ranges from pH of 7.8 to 8.2. On addition of acid (i.e., H^+), the chemical reactions shift toward a higher concentration of CO_2 in sea water (eqn [IIa]) and pH decreases from 8.0 to 7.8 and then pH will rise from 8.0 to 8.2.

$$H^+ + HCO_3^- \rightarrow H_2CO_3 \rightarrow CO_2(\mathrm{aq}) + H_2O \, [\mathrm{IIa}]$$

If base is added to sea water (eqn [IIb]), then pH will rise.

$$H_2CO_3 \rightarrow H^+ + HCO_3 \qquad [\mathrm{IIb}]$$

Solubility and Exchange of CO_2 between the Ocean and Atmosphere

The solubility of CO_2 in sea water is an important factor in controlling the exchange of carbon between the ocean and atmosphere. Henry's law (eqn [1]) describes the relationship between solubility and sea water properties, where S equals the solubility of gas in liquid, k is the solubility constant (k is a function mainly of temperature) and P is the overlying

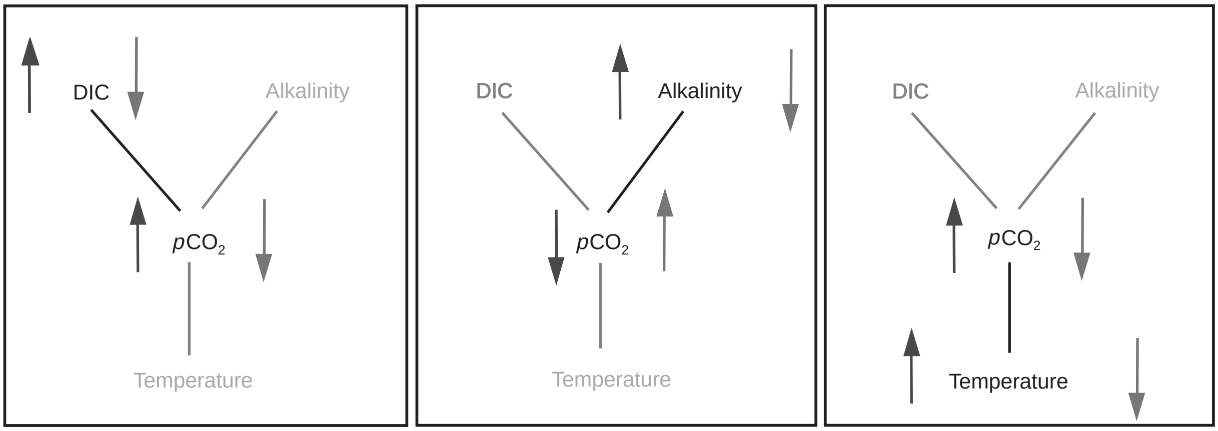

Figure 3 The response of $P\text{CO}_2$ to changes in the sea water properties of (A) DIC concentration, (B) alkalinity and (C) temperature. Each panel describes how $P\text{CO}_2$ will respond to the changes in the relevant sea water property. The blue arrows illustrate the response of $P\text{CO}_2$ to an increase in the sea water property and the red arrows illustrate the response to a decrease in the sea water property. For example, as DIC or temperature increases, $P\text{CO}_2$ increases; whereas an increase in alkalinity results in a decrease in $P\text{CO}_2$.

pressure of the gas in the atmosphere.

$$S = kP \qquad [1]$$

Sea water properties such as temperature, salinity, and partial pressure of CO_2 determine the solubility of CO_2. For example, at 0°C in sea water, the solubility of CO_2 is double that in sea water at 20°C; thus colder water will tend to absorb more CO_2 than warmer water.

Henry's law also describes the relationship between the partial pressure of CO_2 in solution ($P\text{CO}_2$) and its concentration (i.e., $[CO_2]$). Colder waters tend to have lower $P\text{CO}_2$ than warmer waters: for every 1°C temperature increase, sea water $P\text{CO}_2$ increases by $\sim 4\%$. Sea water $P\text{CO}_2$ is also influenced by complicated thermodynamic relationships between the different carbon species. For example, a decrease in sea water DIC or temperature acts to decrease $P\text{CO}_2$, while a decrease in alkalinity acts to increase $P\text{CO}_2$ (**Figure 3**).

Carbon dioxide is transferred across the air–sea interface by molecular diffusion and turbulence at the ocean surface. The flux (F) of CO_2 between the atmosphere and ocean is driven by the concentration difference between the reservoirs (eqn [2]).

$$F = \Delta P\text{CO}_2 K_\text{W} \qquad [2]$$

In eqn [2] $\Delta P\text{CO}_2$ is the difference in $P\text{CO}_2$ between the ocean and atmosphere and K_w is the transfer coefficient across the air–sea interface, termed the piston velocity. In cold waters, sea water $P\text{CO}_2$ tends to be lower than atmospheric $P\text{CO}_2$, thus driving the direction of CO_2 gas exchange from atmosphere to ocean (**Figure 3**). In warmer waters, sea water $P\text{CO}_2$ is greater than atmospheric $P\text{CO}_2$, and CO_2 gas exchange occurs in the opposite direction, from the ocean to the atmosphere. The rate at which CO_2 is transferred between the ocean and the atmosphere depends not only on the $P\text{CO}_2$ difference but on turbulence at the ocean surface. The piston velocity of CO_2 is related to solubility and the strength of the wind blowing on the sea surface. As wind speed increases, the rate of air–sea CO_2 exchange also increase. Turbulence caused by breaking waves also influences gas exchange because air bubbles may dissolve following entrainment into the ocean mixed layer.

Ocean Structure

Physically, the ocean can be thought of as two concentric spheres, the surface ocean and the deep ocean, separated by a density discontinuity called the pycnocline. The surface ocean occupies the upper few hundred meters of the water column and contains approximately 1020×10^{15} g C of DIC (**Figure 1**). The absorption of CO_2 by the ocean through gas exchange takes place in the mixed layer, the upper portion of the surface ocean that makes direct contact with the atmosphere. The surface ocean reaches equilibrium with the atmosphere within one year. The partial pressure of CO_2 in the surface ocean is slightly less than or greater than that of the atmosphere, depending on the controlling variables as described above, and varies temporally and spatially with changing environmental conditions. The deeper ocean represents the remainder of the ocean volume and is supersaturated with CO_2, with a DIC stock of 38 100 × 10^{15} g C (**Figure 1**), or 50 times the DIC contained in the atmosphere.

CO_2 absorbed by the ocean through gas exchange has a variety of fates. Physical and biological mechanisms can return the CO_2 back to the atmosphere or transfer carbon from the surface ocean to the deep ocean and ocean sediments through several transport processes termed the 'solubility', 'biological', and 'carbonate' pumps.

The Solubility Pump, Oceanic Circulation and Carbon Redistribution

The 'solubility pump' is defined as the exchange of carbon between the atmosphere and the ocean as mediated by physical processes such as heat flux, advection and diffusion, and ocean circulation. It assists in the transfer of atmospheric CO_2 to the deep ocean. This transfer is controlled by circulation patterns of the surface ocean (wind-driven circulation) and the deep ocean (thermohaline circulation). These circulation patterns assist in the transfer of atmospheric CO_2 to the deep ocean and help to maintain the vertical gradient of DIC found in the ocean (**Figure 4**). The ability of the ocean to take up anthropogenic CO_2 via the solubility pump is limited by the physical structure of the ocean, the distribution of oceanic DIC, ocean circulation patterns, and the exchange between the surface and deep ocean layers. To be an effective sink for anthropogenic carbon, CO_2 must be transferred to the deep ocean by mixing and biological processes (see below).

Wind-driven circulation occurs as a consequence of friction and turbulence imparted by wind blowing over the sea surface. This circulation pattern is primarily horizontal in movement and is responsible for transporting warm water from lower latitudes (warm) to higher latitudes (cold). Surface currents move water and carbon great distances within ocean basins on timescales of months to years. As surface sea water moves from low latitudes to high latitudes, the increasing solubility of CO_2 in the sea water (due to sea surface cooling) allows atmospheric CO_2 to invade the surface mixed layer (**Figures 5** and **6A**).

Exchange of surface waters with the deep ocean through wind-driven mixing is limited because of strong density stratification of the water column over the majority of the world's oceans. However, thermohaline (overturning) circulation at high latitudes provides a mechanism for surface waters to exchange with the deep ocean. Passage of cold and dry air masses over high-latitude regions, such as the Greenland and Labrador Seas in the North Atlantic or the Weddell Sea in the Southern Ocean, forms cold and very dense sea water ('deep water' formation). Once formed, these dense water masses sink vertically until they reach a depth at which water is of similar density (i.e., 2000–4000 m deep). Following sinking, the dense waters are transported slowly throughout all of the deep ocean basins by advection and diffusion, displacing other deep water that eventually is brought back to the surface by upwelling (**Figure 5**).

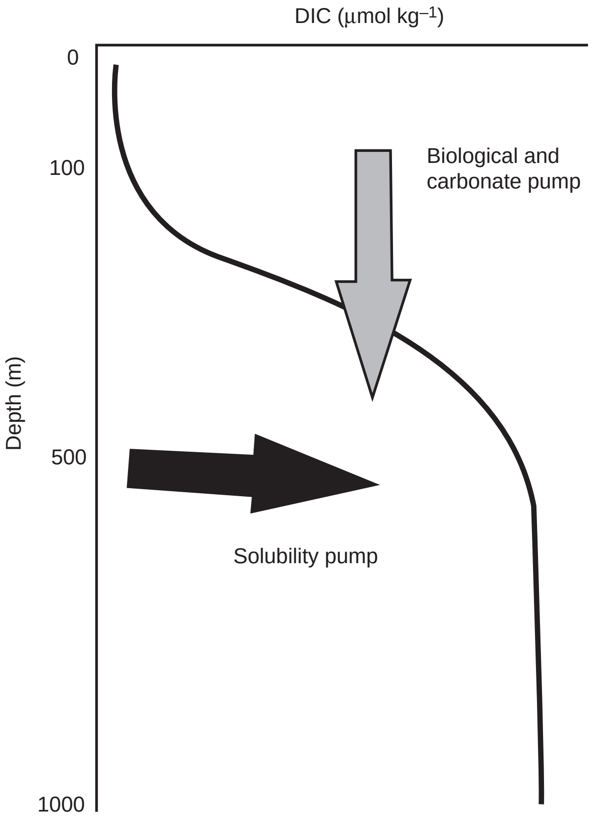

Figure 4 Illustration of the vertical gradient of DIC in the ocean. The uptake of DIC by phytoplankton and conversion into sinking organic matter ('biological pump'; gray arrow) and sinking calcium carbonate skeletal matter ('carbonate pump'; gray arrow) contributes to the maintenance of the vertical gradient. Introduction of DIC to the deep waters via the 'solubility pump' at high latitudes and subsequent deep water formation also helps maintain this vertical gradient (black arrow; see **Figure 5**).

Because of the smaller volume and faster circulation, the residence time of the surface ocean is only one decade compared to 600–1000 years for the deep ocean. The process of deep water formation transfers CO_2, absorbed from the atmosphere by the solubility pump, into the deep ocean. The effect is that DIC concentration increases with depth in all ocean basins (**Figures 4**, **5** and **6A**). As a result of the long residence time of the deep ocean, carbon, once removed from the surface ocean to the deep

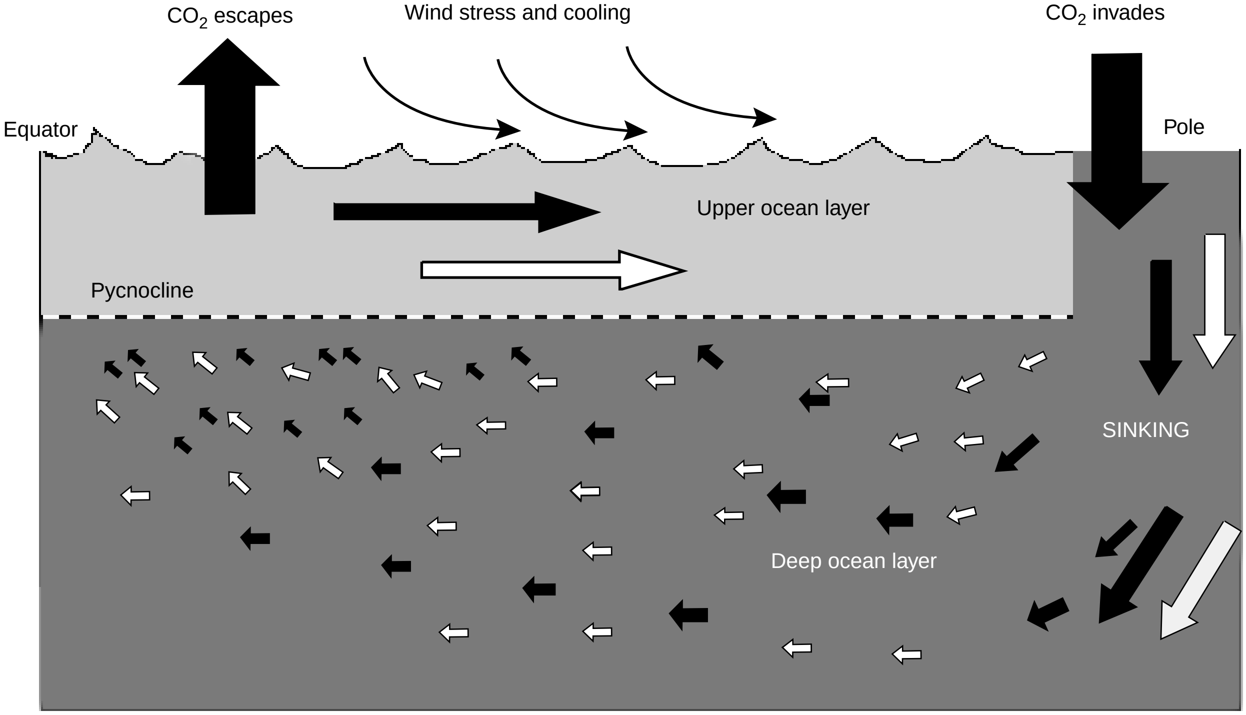

Figure 5 Conceptual model of the 'solubility pump'. White arrows represent movement of water; black arrows represent movement of CO_2 within, and into and out of, the ocean. Cooling increases the solubility of CO_2 and results in a flux of CO_2 from the atmosphere to the surface ocean. At subpolar latitudes the water density increases and the CO_2-enriched water sinks rapidly. At depth, the CO_2-enriched water moves slowly as is it is dispersed throughout the deep ocean. The sinking water displaces water that is returned to the surface ocean in upwelling regions. As the water warms, $P\text{CO}_2$ increases, resulting in escape of CO_2 from the surface water to the atmosphere.

ocean through the effects of solubility and deep water formation, is stored without contact with the atmosphere for hundreds to thousands of years. At present, deep water formed at the surface that is in equilibrium with the atmosphere (sea water $P\text{CO}_2$ of ~ 360 ppm), carries more CO_2 to depth than deep water formed prior to the industrial age (e.g., ~ 280 ppm). Furthermore, $P\text{CO}_2$ of upwelled deep water is less than that in the recently formed deep water, indicating that the deep water formation and the 'solubility pump' allow the ocean to be a net sink for anthropogenic CO_2. The vertical gradient in DIC (**Figure 4**) and the ability of the ocean to take up atmospheric CO_2 is augmented by biological processes known as the 'biological pump'.

The Biological Pump

Although the standing stock of marine biota in the ocean is relatively small (3×10^{15} g C), the activity associated with the biota is extremely important to the cycling of carbon between the atmosphere and the ocean. The largest and most rapid fluxes in the global carbon cycle are those that link atmospheric CO_2 to photosynthetic production (primary production) on the land and in the ocean. Globally, marine phytoplankton are responsible for more than one-third of the total gross photosynthetic production (50×10^{15} g C y^{-1}). In the sea, photosynthesis is limited to the euphotic zone, the upper 100–150 m of the water column where light can penetrate. Photosynthetic organisms use light energy to reduce CO_2 to high-energy organic compounds. In turn, a portion of these synthesized organic compounds are utilized by heterotrophic organisms as an energy source, being remineralized to CO_2 via respiration. Eqn [III] represents the overall reactions of photosynthesis and respiration.

$$CO_2(\text{gas}) + H_2O \underset{\text{Metabolic energy (respiration)}}{\overset{\text{Light energy (photosynthesis)}}{\rightleftarrows}} (CH_2O)_n + O_2(\text{gas}) \qquad \text{[III]}$$

In the sea, net primary production (primary production in excess of respiration) converts CO_2 to organic matter that is stored as particulate organic carbon (POC; in living and detrital particles) and as dissolved organic carbon (DOC). In stratified

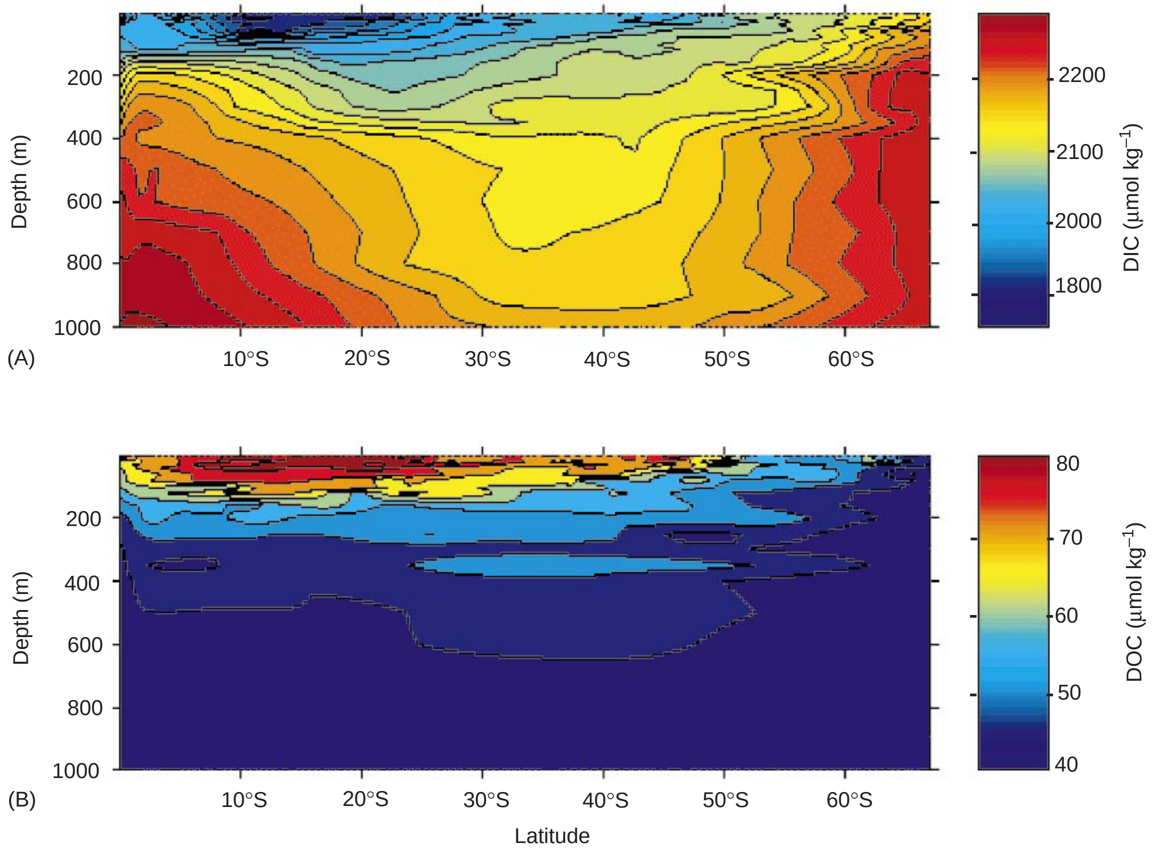

Figure 6 Contour plot of (A) DIC and (B) DOC along a transect line in the South Pacific between the equator (0°; 170° W) and the Antarctic Polar Front (66° S; 170° W). Note that in the low-latitude stratified waters DIC concentrations are depleted in surface water relative to deep water, as a result of net primary production and air–sea exchange. DOC concentrations are elevated relative to deep water. In high-latitude regions, DIC concentration are elevated in the surface water as a result of increased solubility of cooler surface waters.

regions of the ocean (lower latitudes), net primary production results in a drawdown of DIC and an accumulation of organic matter as POC and DOC (**Figure 6B**). However, it is the portion of organic carbon production that can be exported from the surface ocean and remineralized in the deep ocean that is important in the exchange of CO_2 between the atmosphere and the ocean. The biological pump refers to the processes that convert CO_2 (thereby drawing down DIC) to organic matter by photosynthesis, and remove the organic carbon to depth (where it is respired) via sinking, mixing, and active transport mechanisms (**Figure** 7). Once at great depth, it is effectively removed from exchange with the atmosphere. As living biomass is produced, some particles becomes senescent and form sinking aggregates, while other particles are consumed by herbivores and sinking fecal pellets (POC) are formed. These sinking aggregates and pellets remove carbon from the surface to be remineralized at depth via decomposition by bacteria or consumption by zooplankton and fish (**Figure** 7). In addition, DOC produced by phytoplankton or by animal excretion in surface waters can also be transported downward by subduction or convective mixing of surface waters (**Figure** 7). Finally, vertically migrating zooplankton that feed in the surface waters at night and return to deep waters during the day actively transport dissolved and particulate material to depth, where a portion is metabolized (**Figure** 7).

Production via photosynthesis can occur only in the surface ocean, whereas remineralization can occur throughout the water column. The biological pump serves to spatially separate the net photosynthetic from net respiratory processes. Thus, the conversion of DIC to exportable organic matter acts to reduce the DIC concentration in the surface water and its subsequent remineralization increases DIC concentration in the deep ocean (**Figure** 6). The biological pump is important to the maintenance of a vertical DIC profile of undersaturation in the surface and supersaturation at depth (**Figures** 4 and

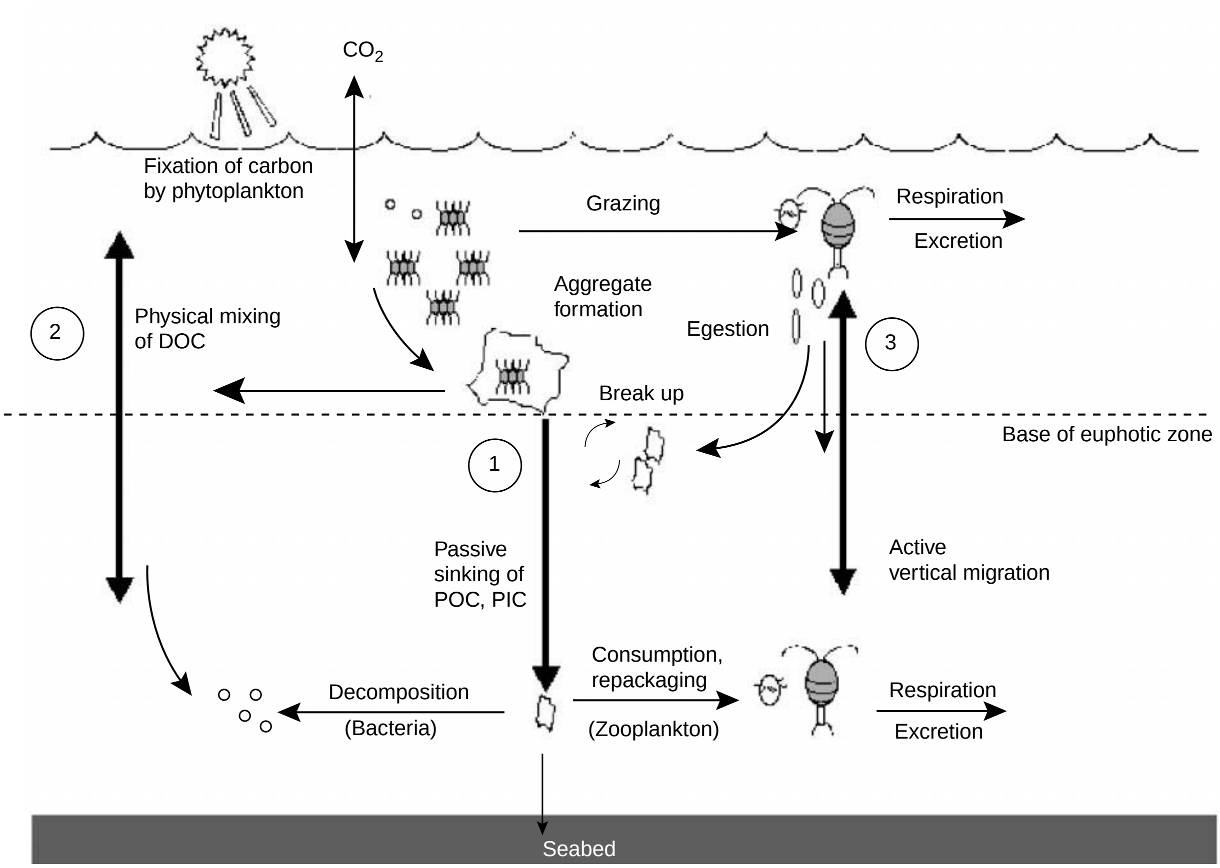

Figure 7 Conceptual diagram depicting components of the 'biological pump'. CO_2 is taken up by phytoplankton and organic matter is produced. As this organic matter is processed through the marine food web, fecal pellets or aggregates are produced, a portion of which sink from the surface waters to depth (1). As organic matter is processed through the food web, DOC is also produced. DOC is removed from the surface waters to depth via physical mixing of the water by convective overturn (2). DOC and DIC are also actively transported to depth by vertically migrating organisms such as copepods that feed in surface waters and excrete and respire the consumed organic carbon at depth (3).

5A). Undersaturation of DIC in the surface mixed layer, created by the biological pump, allows for the influx of CO_2 from the atmosphere (see Henry's law above; **Figure 7**).

Gross export of organic matter out of the surface waters is approximately $10 \times 10^{15}\,g\,C\,y^{-1}$ (**Figure 1**). Less than 1% of the organic matter exported from the surface waters is stored in the abyssal sediment. In fact, most of the exported organic matter is remineralized to DIC in the upper 500 m of the water column. It is released back to the atmosphere on timescales of months to years via upwelling, mixing, or ventilation of high-density water at high latitudes. It is that fraction of exported organic matter that actually reaches the deep ocean ($>1000\,m$) that is important for long-term atmospheric CO_2 regulation. Once in the deep ocean, the organic matter either remains as long-lived DOC or is remineralized to DIC and is removed from interaction with the atmosphere on timescales of centuries to millennia. Thus, even though less than 1% of the exported carbon is stored in marine sediments, the activities of the biological pump are very important in mediating the air–sea transfer of CO_2. Without this pump in action, atmospheric CO_2 concentration might be as high as 500 to 1000 ppm versus the 360 ppm observed today.

Contribution of POC Versus DOC in the Biological Pump

Historically, sinking particles were thought of as the dominant export mechanism of the biological pump and the primary driver of respiration in the ocean's interior. However, downward mixing of surface water can also transport large quantities of DOC trapped within the sinking water mass. In order for DOC to be an important contributor to the biological pump two sets of conditions must exist. First, the producer–consumer dynamics in the surface waters must yield DOC of a quality that is resistant to rapid remineralization by bacteria and lead to net DOC production. Second, the physical system must undergo periods of deep convective mixing or subduction in order to remove surface waters and DOC to depth. Although approximately 80% of the globally exported carbon is in the form of POC, DOC can represent 30–50% of carbon export in the upper 500 m of the water column at specific ocean sites. The biological/physical controls on DOC export are complex and are currently being assessed for various regions of the worlds' ocean.

Factors That Affect the Efficiency of the Biological Pump

An efficient biological pump means that a large fraction of the system's net production is removed from the surface waters via export mechanisms. Factors that affect the efficiency of the biological pump are numerous and include nutrient supply and plankton community structure.

Nutrient supply Does an increased partial pressure of atmospheric CO_2 lead to a more efficient biological pump? Not necessarily, since net primary production is limited by the availability of other inorganic nutrients such as nitrogen, phosphorus, silicon and iron. Because these inorganic nutrients are continuously being removed from the surface waters with vertical export of organic particles, their concentrations are often below detection limits in highly stratified water columns. As a result, primary production becomes limited by the rate at which these nutrients can be re-supplied to the surface ocean by mixing, by atmospheric deposition, or by heterotrophic recycling. Primary production supported by the recycling of nutrients in the surface ocean is referred to as 'regenerative' production and contributes little to the biological pump. Primary production supported by the introduction of new nutrients from outside the system, via mixing from below or by atmospheric deposition (e.g. dust), is referred to as 'new' production. New nutrients enhance the amount of net production that can be exported (new production). Because CO_2 is not considered to be a limiting nutrient in marine systems, the increase in atmospheric CO_2 is not likely to stimulate net production for most of the world's ocean unless it indirectly affects the introduction of new nutrients as well.

Community structure Food web structure also plays an important role in determining the size distribution of the organic particles produced and whether the organic carbon and associated nutrients are exported from or recycled within the surface waters. The production of large, rapidly settling cells will make a greater contribution to the biological pump than the production of small, suspended particles. Factors such as the number of trophic links and the size of the primary producers help determine the overall contribution of sinking particles. The number of trophic steps is inversely related to the magnitude of the export flux. For example, in systems where picoplankton are the dominant primary producers there may be 4–5 steps before reaching a trophic level capable of producing sinking particles. With each trophic transfer, a percentage (50–70%) of the organic carbon is respired, so only a small fraction of the original primary production forms sinking particles. Although picoplankton may dominate primary production in oceanic systems, their production is considered 'regenerative' and contributes little to the production of sinking material. Alternatively, production by larger phytoplankton such as diatoms ($>20\,\mu m$ in size) may represent a smaller fraction of primary production, but their contribution to the biological pump is larger because fewer trophic steps are taken to produce sinking particles.

The Carbonate Pump

A process considered part of the biological pump (depending how it is defined) is the formation and sinking of calcareous skeletal material by some marine phytoplankton (e.g., coccolithophores) and animals (e.g., pteropods and foraminifera). Calcification is the process by which marine organisms combine calcium with carbonate ions to form hard body parts. The resulting calcium carbonate ($CaCO_3$) is dense and sinks out of the surface water with export production (**Figure 8**). The global mean ratio for carbon sinking from the surface ocean as $CaCO_3$ or organic carbon is 1:4. However, unlike organic matter, $CaCO_3$ is not remineralized as it sinks; it only begins to dissolve in intermediate and deep waters, waters undersaturated with respect to $CaCO_3$. Complete dissolution of $CaCO_3$ skeletons typically occurs at depths of 1–4 km (in the north Pacific Ocean) to 5 km (in the North Atlantic). This depth zone is known as the carbonate compensation depth. $CaCO_3$ is only found in sediments shallower than the carbonate compensation depth. Globally, the CO_2 sink in sedimentary rock is four times greater than the sink in organic sediments.

Summary

In summary, the biological and physical processes of the oceanic carbon cycle play an important role in

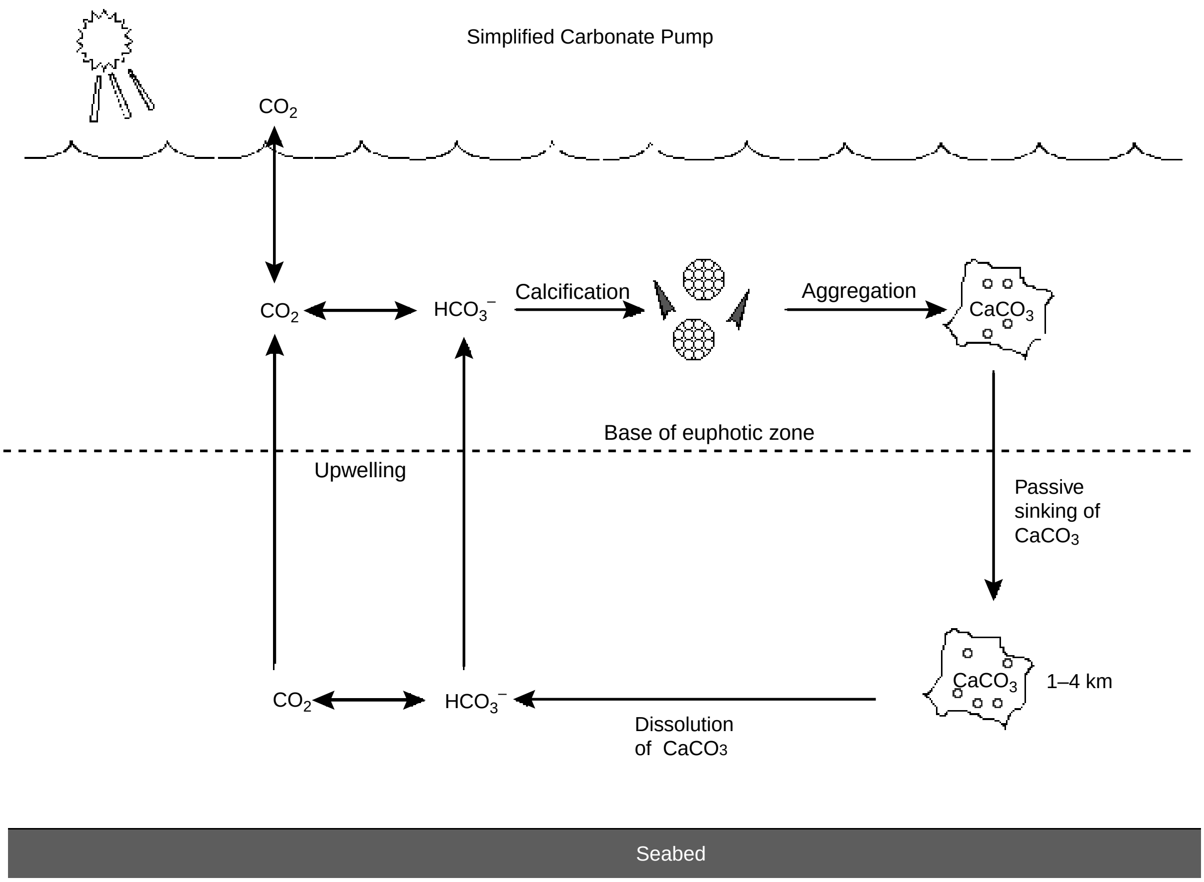

Figure 8 Conceptual diagram of a simplified 'carbonate pump'. Some marine organisms form calcareous skeletal material, a portion of which sinks as calcium carbonate aggregates. These aggregates are preserved in shallow ocean sediments or dissolve at greater depths (3000–5000 m), thus increasing DIC concentrations in the deep ocean. The calcium and bicarbonate are returned to the surface ocean through upwelling.

the regulation of atmospheric CO_2. However, the intricacies of the oceanic carbon cycle are vast and continued ocean research is essential to better understand the controls of the Earth's climate.

See also

Atmospheric Input of Pollutants. Carbon Dioxide (CO_2) Cycle. Network Analysis of Food Webs.

Glossary

Reservoir A reservoir is a region that is capable of holding a certain mass or volume of a substance of interest, i.e., carbon.

Flux A flux is the rate of transfer of material, i.e. carbon, into or out of a reservoir.

Lithosphere All the sediments, rocks, minerals, and soils of the Earth.

Biosphere All living (and dead) organisms of the Earth; organic matter.

Hydrosphere All water on Earth including the ocean, rivers, lakes, groundwater, sea ice, and glacial ice.

Further Reading

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CARBON DIOXIDE (CO_2) CYCLE

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Introduction

The oceans, the terrestrial biosphere, and the atmosphere are the three major dynamic reservoirs for carbon on the earth. Through the exchange of CO_2 between them, the atmospheric concentration of CO_2 that affects the heat balance of the earth, and hence the climate, is regulated. Since carbon is one of the fundamental constituents of living matter, how it cycles through these natural reservoirs has been one of the fundamental questions in environmental sciences. The oceans contain about 50 times as much carbon (about 40 000 Pg-C or 10^{15} g as carbon) as the atmosphere (about 750 Pg-C). The terrestrial biosphere contains about three times as much carbon (610 Pg-C in living vegetation and 1580 Pg-C in soil organic matter) as the atmosphere. The air–sea exchange of CO_2 occurs via gas exchange processes across the sea surface; the natural air-to-sea and sea-to-air fluxes have been estimated to be about 90 Pg-C y^{-1} each. The unperturbed uptake flux of CO_2 by global terrestrial photosynthesis is roughly balanced with the release flux by respiration, and both have been estimated to be about 60 Pg-C y^{-1}. Accordingly, atmospheric CO_2 is cycled through the ocean and terrestrial biosphere with a timescale of about 7 years.

The lithosphere contains a huge amount of carbon (about 100 000 000 Pg-C) in the form of limestones ((Ca, Mg) CO_3), coal, petroleum, and other forms of organic matter, and exchanges carbon slowly with the other carbon reservoirs via such natural processes as chemical weathering and burial of carbonate and organic carbon. The rate of removal of atmospheric CO_2 by chemical weathering has been estimated to be of the order of 1 Pg-C y^{-1}. Since the industrial revolution in the nineteenth century, the combustion of fossil fuels and the manufacturing of cement have transferred the lithospheric carbon into the atmosphere at rates comparable to the natural CO_2 exchange fluxes between the major carbon reservoirs, and thus have perturbed the natural balance significantly (6 Pg-C y^{-1} is about an order of magnitude less than the natural exchanges with the oceans (90 Pg-C y^{-1} and land (60 Pg-C y^{-1})). The industrial carbon emission rate has been about 6 Pg-C y^{-1} for the 1990s, and the cumulative industrial emissions since the nineteenth century to the end of the twentieth century have been estimated to be about 250 Pg-C. Presently, the atmospheric CO_2 content is increasing at a rate of about 3.5 Pg-C y^{-1} (equivalent to about 50% of the annual emission) and the remainder of the CO_2 emitted into the atmosphere is absorbed by the oceans and terrestrial biosphere in approximately equal proportions. These industrial