

# 6.18

## The Biological Pump in the Past

D. M. Sigman

*Princeton University, NJ, USA*

and

G. H. Haug

*Geoforschungszentrum Potsdam, Germany*

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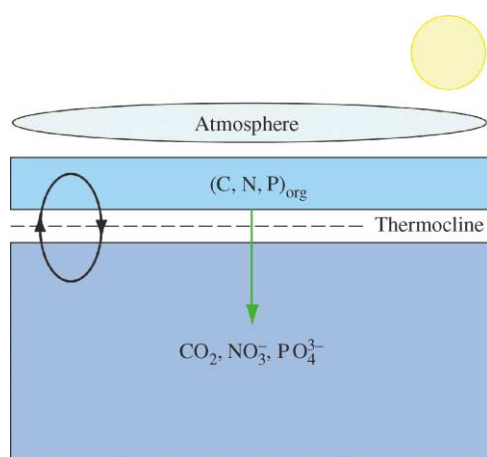
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### 6.18.1 INTRODUCTION

It is easy to imagine that the terrestrial biosphere sequesters atmospheric carbon dioxide; the form and quantity of the sequestered carbon, living or dead organic matter, are striking. In the ocean, there are no aggregations of biomass comparable to the forests on land. Yet biological productivity in the ocean plays a central role in the sequestration of atmospheric carbon dioxide, typically overshadowing the effects of terrestrial biospheric carbon storage on timescales longer than a few centuries. In an effort to communicate the ocean's role in the regulation of atmospheric carbon dioxide, marine scientists frequently refer to the ocean's biologically driven sequestration of carbon as the "biological pump." The original and strict definition of the biological (or "soft-tissue")

pump is actually more specific: the sequestration of carbon dioxide in the ocean interior by the biogenic flux of organic matter out of surface waters and into the deep sea prior to decomposition of that organic matter back to carbon dioxide (Volk and Hoffert, 1985) (Figure 1). The biological pump extracts carbon from the "surface skin" of the ocean that interacts with the atmosphere, presenting a lower partial pressure of carbon dioxide (CO<sub>2</sub>) to the atmosphere and thus lowering its CO<sub>2</sub> content.

The place of the biological pump in the global carbon cycle is illustrated in Figure 2. The atmosphere exchanges carbon with essentially three reservoirs: the ocean, the terrestrial biosphere, and the geosphere. The ocean holds ~50 times as much carbon as does the atmosphere, and



**Figure 1** A schematic of the ocean's "biological pump," the sequestration of carbon and nutrients (nitrogen and phosphorus) in the ocean interior (lower dark blue box) by the growth of phytoplankton (floating unicellular algae) in the sunlit surface ocean (upper light blue box), the downward rain of organic matter out of the surface ocean and into the deep ocean (green downward arrow), and the subsequent breakdown of this organic matter back to carbon dioxide ( $\text{CO}_2$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ). The nutrients and  $\text{CO}_2$  are reintroduced to the surface ocean by mixing and upwelling (the circling arrows at left). The biological pump lowers the  $\text{CO}_2$  content of the atmosphere by extracting it from the surface ocean (which exchanges  $\text{CO}_2$  with the atmosphere) and sequestering it in the isolated waters of the ocean interior. In most of the low- and mid-latitude ocean, the surface is isolated from the deep sea by a temperature-driven density gradient, or "thermocline," keeping nutrient supply low and leading to essentially complete consumption of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  by phytoplankton at the surface. At the higher latitudes, where there is no permanent thermocline, more rapid communication with the deep sea leads to incomplete consumption of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ .

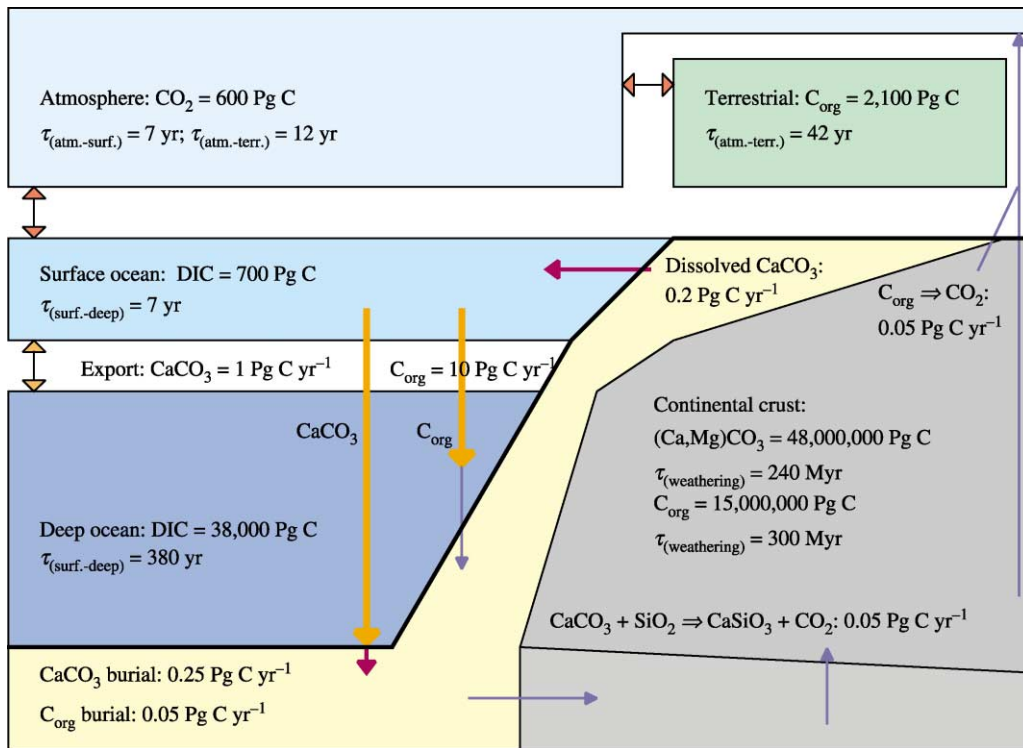
~20 times as much as the terrestrial biosphere. Thus, on timescales that are adequately long to allow the deep sea to communicate with the surface ocean and atmosphere ( $\geq 500$  yr), carbon storage in the ocean all but sets the concentration of  $\text{CO}_2$  in the atmosphere. The effect of the biological pump is not permanent on this timescale of ocean circulation; the downward transport of carbon is balanced by the net upward flux from the  $\text{CO}_2$ -rich waters of the deep sea, which, in the absence of the biological pump, would work to homogenize the carbon chemistry of the ocean, raising atmospheric  $\text{CO}_2$  in the process.

The dynamics of marine organic carbon can be described as a set of three nested cycles in which the biological pump is the cycle with flux and reservoir of intermediate magnitude (Figure 3). The cycle with the shortest timescale, which operates within the surface ocean, is composed of net primary production by phytoplankton

(their photosynthesis less their respiration) and heterotrophic respiration by zooplankton and bacteria that oxidize most of the net primary production back to  $\text{CO}_2$ . This cycle is by far the greatest in terms of the flux of carbon, but the reservoir of sequestered carbon that accumulates in surface waters (phytoplankton biomass, dead organic particles, and dissolved organic carbon) is small relative to the atmospheric reservoir of  $\text{CO}_2$ , and it has a short residence time (less than a year). A small imbalance in this cycle, between net primary production and heterotrophic respiration, feeds the next cycle in the form of organic carbon that sinks (or is mixed) into the deep sea. This "export production" drives the biological pump (Figure 3).

At the other extreme, a small fraction of the organic matter exported from the surface ocean escapes remineralization in the water column and sediments and is thus buried in the sediments, removing carbon from the ocean/atmosphere system (Figure 3). On the timescale of geologic processes, this carbon removal is balanced by the oxidation of the organic matter when it is exposed at the earth surface by uplift and weathering, or when it is released by metamorphism and volcanism. While the fluxes involved in this cycle are small, the reservoir is large, so that its importance increases with timescale, becoming clearly relevant on the timescale of millions of years.

The biological pump, in the strict sense, does not include the burial of organic matter in marine sediments. There are several related reasons for this exclusion. First, as described below, the variations in atmospheric carbon dioxide that are correlated with the waxing and waning of ice ages have driven much of the thinking about the role of organic carbon production on atmospheric composition. Only a very small fraction of the organic matter exported out of surface waters is preserved and buried in the underlying sediment, so that this process cannot sequester a significant amount of carbon on the timescale of millennia and thus is not a candidate process for the major carbon dioxide variations over glacial cycles. Second, on the timescale for which organic matter burial is relevant, i.e., over millions of years, it is thought to be only one of several mechanisms by which atmospheric  $\text{CO}_2$  is regulated. Most hypotheses regarding the history of  $\text{CO}_2$  over geological time involve weathering of rocks on land and the precipitation of carbonates in the ocean, due to both the larger fluxes and larger reservoirs involved in the geological trapping of  $\text{CO}_2$  as carbonate as opposed to organic carbon (Figure 2). Finally, the importance of biological productivity in determining the burial rate of organic carbon is not at all clear. While some examples of high organic carbon burial appear to be due to high

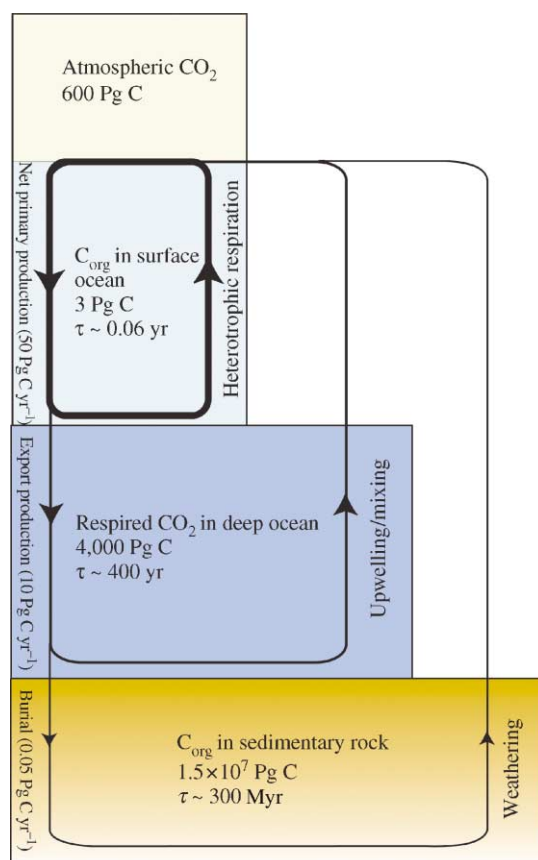


**Figure 2** A simplified view of the Holocene (pre-industrial) carbon cycle (largely based on Holmen (1992)). Units of carbon are petagrams (Pg,  $10^{15}$  g). The fluxes are colored according to the residence time of carbon in the reservoirs they involve, from shortest to longest, as follows: red, orange, purple, blue. Exchanges of the atmosphere with the surface ocean and terrestrial biosphere are relatively rapid, such that changes in the fluxes alter atmospheric  $\text{CO}_2$  on the timescale of years and decades. Exchange between the surface ocean and the deep ocean is such that centuries to millennia are required for a change to yield a new steady state. Because the deep-ocean carbon reservoir is large relative to the surface ocean, terrestrial biosphere, and atmosphere, its interactions with the surface ocean, given thousands of years, determine the total amount of carbon to be partitioned among those three reservoirs. In a lifeless ocean, the only cause for gradients in  $\text{CO}_2$  between the deep ocean and the surface ocean would be temperature (i.e., the “solubility pump” (Volk and Hoffert, 1985))—deep waters are formed from especially cold surface waters, and  $\text{CO}_2$  is more soluble in cold water. The biological pump, represented by the right downward arrow, greatly enhances the surface–deep  $\text{CO}_2$  gradient, through the rain of organic matter (“ $\text{C}_{\text{org}}$ ”) out of the surface ocean. The “carbonate pump,” represented by the left downward arrow, is the downward rain of calcium carbonate microfossils out of the surface ocean. Its effect is to actually raise the  $p_{\text{CO}_2}$  of the surface ocean; this involves the alkalinity of seawater and is discussed in Chapters 6.04, 6.10, 6.19, and 6.20. Almost all of the organic matter raining out of the surface ocean is degraded back to  $\text{CO}_2$  and inorganic nutrients as it rains to the seafloor or once it is incorporated into the shallow sediments; only less than 1% ( $\sim 0.05 \text{ Pg}$  out of  $\sim 10 \text{ Pg}$ ) is removed from the ocean/atmosphere system by burial (the downward blue arrow). This is in contrast to the calcium carbonate rain out of the surface (the downward purple arrow),  $\sim 25\%$  of which is buried. In parallel, the weathering rate of calcium carbonate on land is significant on millennial timescales (the left-pointing purple arrow), while the release of geologically sequestered  $\text{C}_{\text{org}}$  occurs more slowly, on a similar timescale as the release of  $\text{CO}_2$  from the metamorphism of calcium carbonate to silicate minerals.

oceanic productivity (Vincent and Berger, 1985), others involve diverse additional processes, such as the delivery of sediments to the ocean (France-Lanord and Derry, 1997), which influences the ease with which the organic matter rain enters the sedimentary record (Canfield, 1994). In the latter case, the distribution of oceanic productivity is of secondary importance to the effect of organic carbon burial on atmospheric  $\text{CO}_2$ .

The most direct evidence for natural variations in atmospheric  $\text{CO}_2$  comes from the air that is

trapped in Antarctic glacial ice. Records from Antarctic ice cores indicate that the concentration of  $\text{CO}_2$  in the atmosphere has varied in step with the waxing and waning of ice ages (Barnola *et al.*, 1987; Petit *et al.*, 1999) (Figure 4). During interglacial times, such as the Holocene (roughly the past  $10^4$  years), the atmospheric partial pressure of  $\text{CO}_2$  ( $p_{\text{CO}_2}$ ) is typically near 280 ppm by volume (ppmv). During peak glacial times, such as the last glacial maximum  $\sim 1.8 \times 10^4$  yr ago, atmospheric  $p_{\text{CO}_2}$



**Figure 3** The nested cycles of marine organic carbon, including (i) net primary production and heterotrophic respiration in the surface ocean, (ii) export production from the surface ocean and respiration in the deep sea followed by upwelling or mixing of the respired  $\text{CO}_2$  back to the surface ocean (the biological pump, the subject of this chapter), and (iii) burial of sedimentary organic carbon and its release to the atmosphere by weathering. The slight imbalance of each cycle fuels the longer-timescale cycles. The carbon reservoirs shown refer solely to the fraction affected by organic carbon cycling; for instance, the deep-ocean value shown is of  $\text{CO}_2$  produced by respiration, not the total dissolved inorganic carbon reservoir.

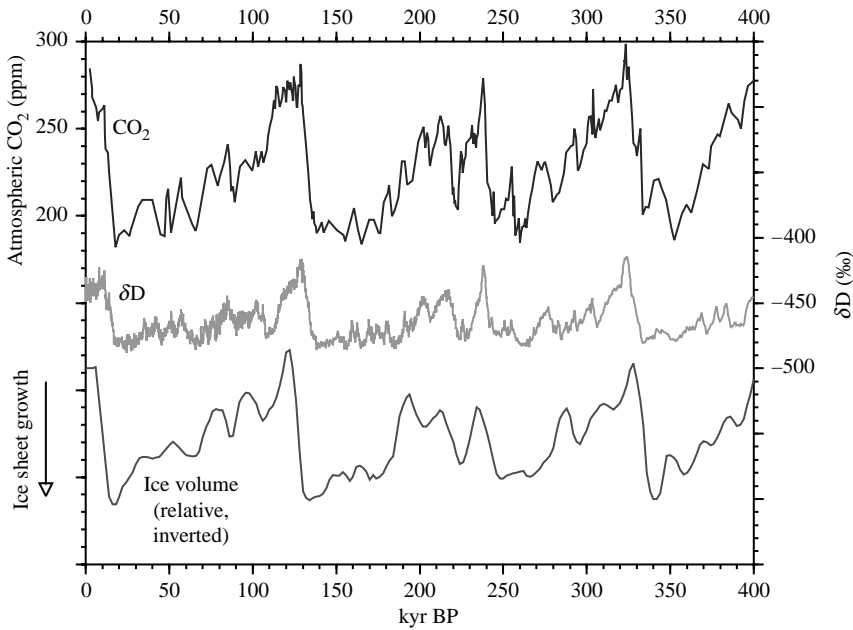
is 180–200 ppmv, or  $\sim 80$ –100 ppmv lower.  $\text{CO}_2$  is a greenhouse gas, and model calculations suggest that its changes play a significant role in the energetics of glacial/interglacial climate change (Weaver *et al.*, 1998; Webb *et al.*, 1997). However, we have not yet identified the cause of these variations in  $\text{CO}_2$ . The explanation of glacial/interglacial cycles in  $\text{CO}_2$  is a major motivation in the paleoceanographic and paleoclimatological communities, for three reasons: first, these  $\text{CO}_2$  changes are the most certain of any in our record of the past (excluding the anthropogenic rise in  $\text{CO}_2$ ); second, they show a remarkably strong connection to climate, inspiring considerations of both cause and effect; and third,

they are of a timescale that is relevant to the history and future of humanity.

The ultimate pacing of glacial cycles is statistically linked to cyclic changes in the orbital parameters of the Earth, with characteristic frequencies of approximately 100 kyr, 41 kyr, and 23 kyr (Berger *et al.*, 1984; Hays *et al.*, 1976). These orbitally driven variations in the seasonal and spatial distribution of solar radiation incident on the Earth surface, known as the “Milankovitch cycles”, are thought by many to be the fundamental driver of glacial/interglacial oscillations in climate. However, positive feedbacks within the Earth’s climate system must amplify orbital forcing to produce the amplitude and temporal structure of glacial/interglacial climate variations. Carbon dioxide represents one such feedback. The point of greatest uncertainty in this feedback is the mechanism by which atmospheric  $\text{CO}_2$  is driven to change.

Broecker (1982a,b) first hypothesized a glacial increase in the strength of the biological pump as the driver of lower glacial  $\text{CO}_2$  levels. This suggestion has spawned many variants, which we will tend to phrase in terms of the “major” nutrients, nitrogen and phosphorus. These nutrients are relatively scarce in surface ocean waters but are required in large quantities to build all algal biomass. In terms of the major nutrients, the biological pump hypotheses fall into two groups: (i) changes in the low and mid-latitude surface ocean, where the major nutrients appear to limit the extraction of  $\text{CO}_2$  by biological production, and (ii) changes in the polar and subpolar ocean regions, where the major nutrients are currently not completely consumed and not limiting. In both cases, the central biological process is “export production,” the organic matter produced by phytoplankton that is exported from the surface ocean, resulting in the sequestration of its degradation products (inorganic carbon and nutrients) in the ocean interior. Here, we review the concepts, tools, and observations relevant to variability in the biological pump on the millennial timescale, with a strong focus on its potential to explain glacial/interglacial  $\text{CO}_2$  change.

The biogenic rain to the deep sea has important mineral components: calcium carbonate, mostly from coccolithophorids (phytoplankton) and foraminifera (zooplankton), and opal, mostly from diatoms (phytoplankton) and radiolaria (zooplankton). The calcium carbonate ( $\text{CaCO}_3$ ) component is important for atmospheric carbon dioxide in its own right (Figure 2). In contrast to organic carbon, the production, sinking, and burial of  $\text{CaCO}_3$  acts to raise atmospheric carbon dioxide concentrations. This is unintuitive, in that  $\text{CaCO}_3$ , like organic carbon, represents a repository for inorganic carbon and a vector for the removal of



**Figure 4** The history of atmospheric  $\text{CO}_2$  back to 400 kyr as recorded by the gas content in the Vostok ice core from Antarctica (Petit *et al.*, 1999). The ratio of deuterium to hydrogen in ice (expressed as the term  $\delta\text{D}$ ) provides a record of air temperature over Antarctica, with more negative  $\delta\text{D}$  values corresponding to colder conditions. The history of global ice volume based on benthic foraminiferal oxygen isotope data from deep-sea sediment cores (Bassinot *et al.*, 1994) is plotted as relative sea level, so that ice ages (peaks in continental ice volume) appear as sea-level minima, with a full glacial/interglacial amplitude for sea level change of  $\sim 130$  m (Fairbanks, 1989). During peak glacial periods, atmospheric  $\text{CO}_2$  is 80–100 ppmv lower than during peak interglacial periods, with upper and lower limits that are reproduced in each of the 100 kyr cycles. Ice cores records, including the Vostok record shown here, indicate that atmospheric  $\text{CO}_2$  was among the first parameters to change at the termination of glacial maxima, roughly in step with southern hemisphere warming and preceding the decline in northern hemisphere ice volume.

this carbon from the surface ocean and atmosphere. The difference involves ocean “alkalinity.” Alkalinity is the acid-titrating capacity of the ocean. As it increases, the pH of seawater rises (i.e., the concentration of  $\text{H}^+$ , or protons, decreases), and an increasing amount of  $\text{CO}_2$  is stored in the ionic forms bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ( $\text{CO}_3^{2-}$ ). This “storage” is achieved by the loss of  $\text{H}^+$  from carbonic acid ( $\text{H}_2\text{CO}_3$ ), which is itself formed by the combination of dissolved  $\text{CO}_2$  with its host  $\text{H}_2\text{O}$ . Thus, an increase in ocean alkalinity lowers the  $p_{\text{CO}_2}$  of surface waters and thus the  $\text{CO}_2$  concentration of the overlying atmosphere. The carbonate ion holds two equivalents of alkalinity for every mole of carbon:  $\text{CO}_3^{2-}$  must absorb two protons before it can leave the ocean as  $\text{CO}_2$  gas. In the precipitation of  $\text{CaCO}_3$ ,  $\text{CO}_3^{2-}$  is removed from the ocean, lowering the alkalinity of the ocean water and thus raising its  $p_{\text{CO}_2}$ . We can describe this in terms of a chain of reactions: the  $\text{CO}_3^{2-}$  that was lost to precipitation is replaced by the deprotonation of a  $\text{HCO}_3^-$ , generating a proton. This proton then combines with another  $\text{HCO}_3^-$  to produce  $\text{H}_2\text{CO}_3$ , which dissociates to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , yielding the

summary reaction:  $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ . Thus, the biological precipitation of  $\text{CaCO}_3$  raises the  $p_{\text{CO}_2}$  of the water in which it occurs.

The biological formation of  $\text{CaCO}_3$  affects atmospheric  $\text{CO}_2$  from two perspectives. First, the precipitation of  $\text{CaCO}_3$  in surface waters and its sinking to the seafloor drives a surface-to-deep alkalinity gradient, which raises the  $p_{\text{CO}_2}$  of surface waters in a way that is analogous to the  $p_{\text{CO}_2}$  decrease due to the biological pump; this might be referred to as the “carbonate pump.” Just as with the  $\text{CO}_2$  produced in deep water by organic matter degradation, the chemical products of the deep redissolution of the  $\text{CaCO}_3$  rain are eventually mixed up to the surface again, undoing the effect of their temporary ( $\sim 1,000$  yr) sequestration in the abyss. Second,  $\sim 25\%$  of the  $\text{CaCO}_3$  escapes dissolution and is buried, thus sequestering carbon and alkalinity in the geosphere, on a timescale of thousands to millions of years (Figure 2). An excess in the loss of alkalinity by calcium carbonate burial rate relative to the input of alkalinity by continental weathering will drive an increase in the  $p_{\text{CO}_2}$  of the whole ocean on the



timescale of thousands of years. In summary,  $\text{CaCO}_3$  precipitation can alter atmospheric  $p_{\text{CO}_2}$  by generating a surface-to-deep gradient in seawater alkalinity (the carbonate pump) and by changing the total amount of alkalinity in the ocean.

The  $\text{CaCO}_3$  cycle is a central part of the effect of biological productivity on atmospheric  $\text{CO}_2$ . However, it is not within the strict definition of the biological pump, which deals specifically with organic carbon. Moreover, the effect of the  $\text{CaCO}_3$  rain is determined not only by the actual magnitude of the rain to the seafloor but also by its degree of preservation and burial at the seafloor, a relatively involved subject that is treated elsewhere in this volume. Thus, in our discussions below, we try as much as possible to limit ourselves to the geochemical effects of the biogenic rain of organic matter, bringing  $\text{CaCO}_3$  into the discussion only when absolutely necessary and then trying to focus on its biological production and not its seafloor preservation.

### 6.18.2 CONCEPTS

At the coarsest scale, phytoplankton abundance (Figure 5(a)) and nutrient availability (Figures 5(b)–(d)) are correlated across the global surface ocean, indicating that the supply of major nutrients is a dominant control on productivity. In this context, two types of environments emerge from the global ocean distributions (Figure 5): (i) the tropical and subtropical ocean, where productivity is low and limited by the supply of nitrate and phosphate, and (ii) the subpolar and polar regions, where the supply of nitrate and phosphate is high enough so as not to limit phytoplankton growth. This distinction frames much of the conceptual discussion that follows. One important result will at this point seem counterintuitive: the global biological pump is driven from the low-latitude regions, where the biological pump is working at maximal efficiency with respect to the major nutrient supply, and weakened by the high-latitude regions, which are not maximally efficient with respect to the major nutrients and which are thus allowing deeply sequestered  $\text{CO}_2$  to escape back to the atmosphere.

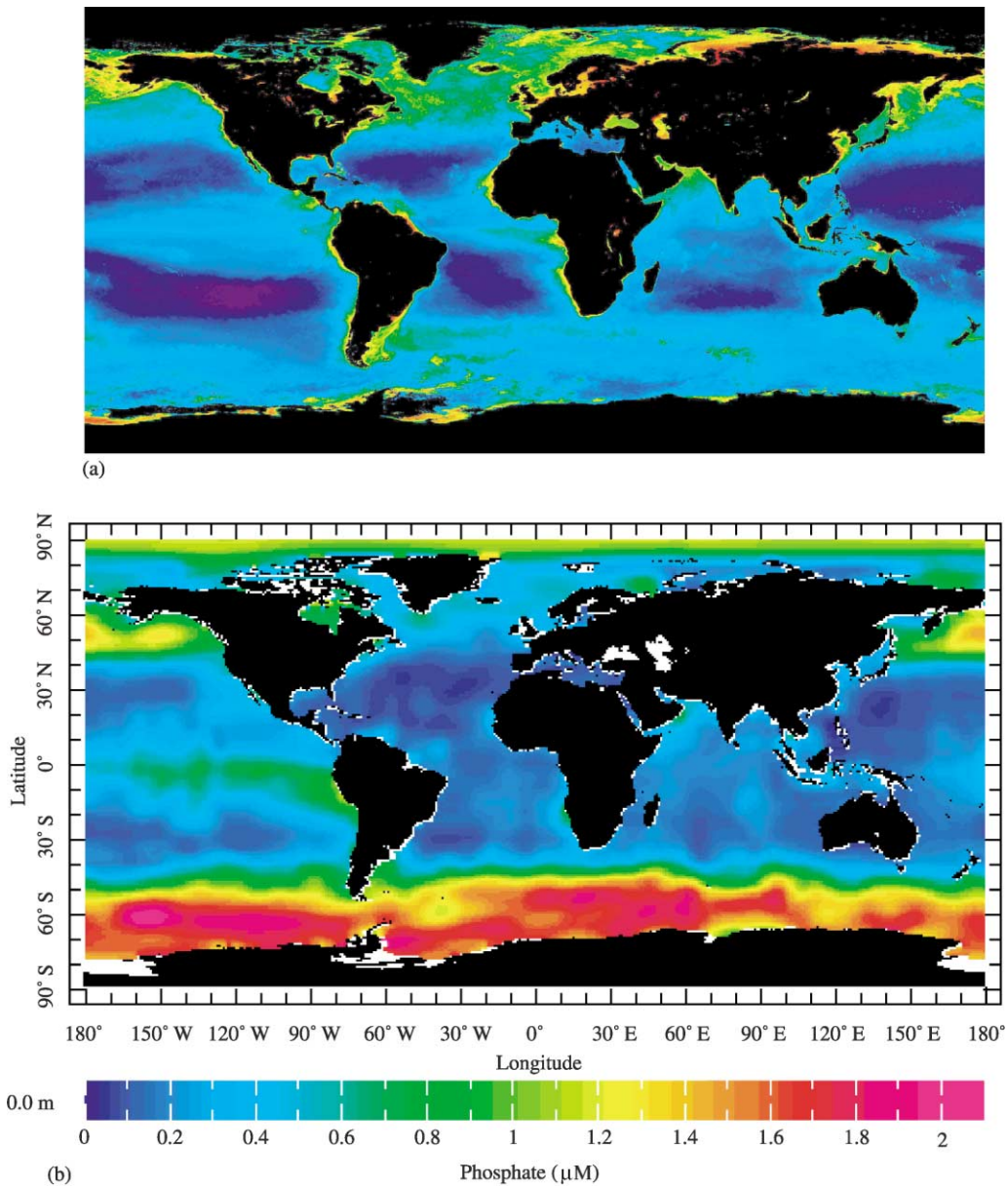
The relative importance of the low versus high latitudes in controlling atmospheric  $\text{CO}_2$  is currently a matter of debate, with the lines drawn between the two types of models that are used to study the biological pump: geochemical box models of the ocean, the first tools available for quantifying the role of the biological pump, and the newer ocean general circulation models. Relative to box models, at least some general

circulation models express a greater sensitivity of atmospheric  $\text{CO}_2$  to the low-latitude ocean and a lesser sensitivity to the high-latitude ocean (Archer *et al.*, 2000b). This difference in sensitivity has major implications for the feasibility of different oceanic changes to explain glacial/interglacial  $\text{CO}_2$  change. While some authors have argued that the discrepancy can be framed in terms of the amount of vertical mixing in the low versus high-latitude ocean (Broecker *et al.*, 1999), we are not convinced by this argument, as such differences should be captured by the deep-ocean temperatures in the two types of models. Rather, we favor the arguments of Toggweiler *et al.* (2003a) that the difference is mostly in the degree of air/sea equilibration of  $\text{CO}_2$  that is allowed in the high-latitude regions of the models. If this is so, there is good reason to believe that the high latitudes are as important in the biological pump as the box models suggest (Toggweiler *et al.*, 2003a). Regardless of our view, it must be recognized that the quantitative arguments made below are based largely on our experience with box models (Hughen *et al.*, 1997; Sigman *et al.*, 1998, 1999b, 2003), and that some workers would find different areas of emphasis, although the same basic processes would probably be described (e.g., see Archer *et al.*, 2000a).

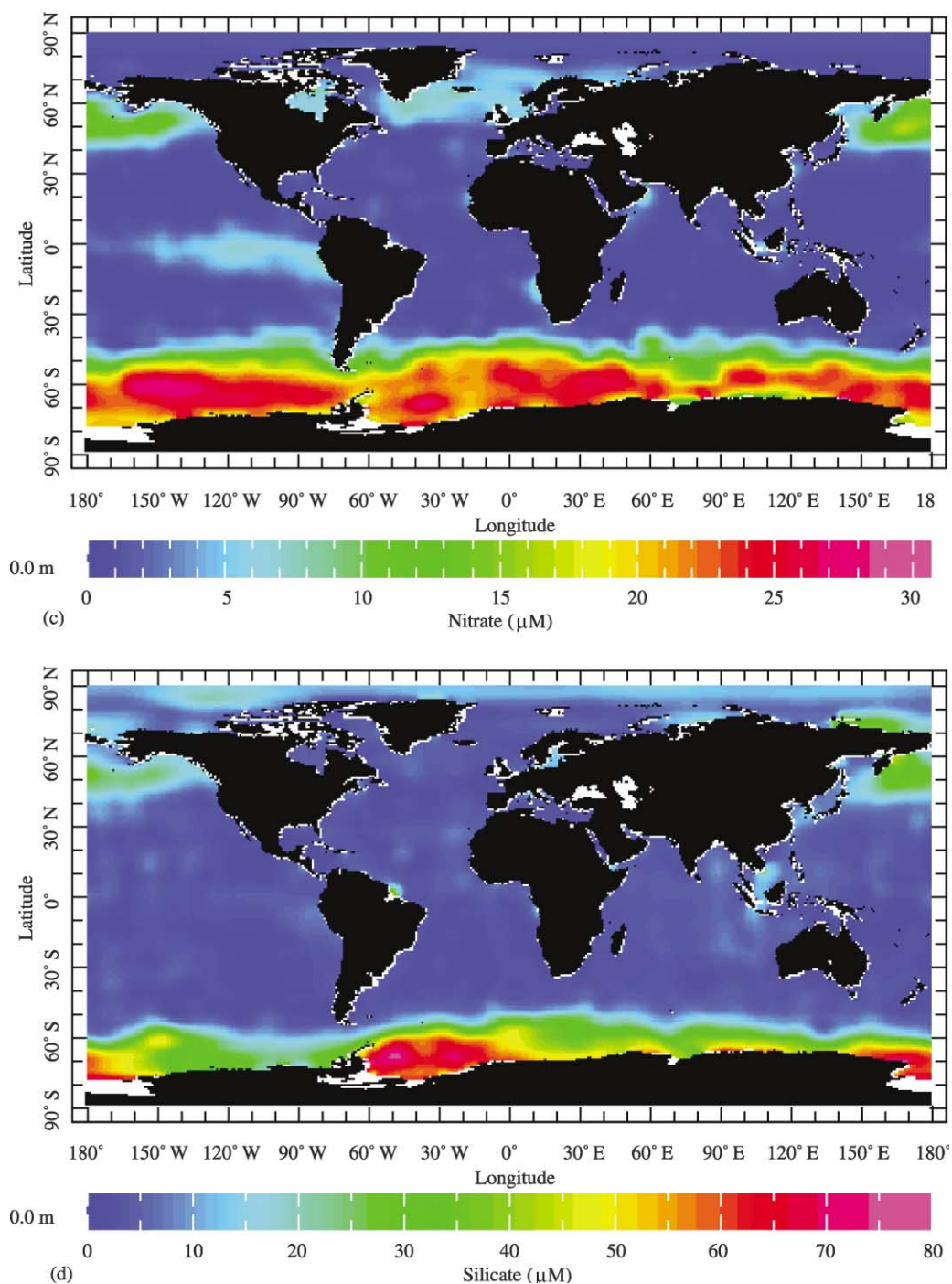
While the global correlation between nutrients and productivity is strong, it is far from perfect. For instance, the chlorophyll levels among the high-latitude regions do not correlate with their surface nutrient concentration, nor does such a correlation hold particularly well within a single high-latitude region (Figure 5). These discrepancies provide a starting point for addressing what controls polar productivity and how the different polar regions impact the biological pump. We also look to the current differences among the polar regions to understand how the high-latitude leaks in the biological pump might have changed in the past.

The general link between nutrient concentration and productivity is also broken in some low-latitude regions. For instance, coastal productivity is high even where there is no apparent elevation in major nutrients. While part of this discrepancy is probably due to nutrient inputs from the continents that are not captured in Figure 5 because they are sporadic and/or compositionally complex, the discrepancy also reflects the very rapid cycling of organic matter in the shallow ocean. We will see that the coastal regions, despite their extremely high productivity, are not central to the biological pump, illustrating the distinction between productivity and the biological pump.

While this comparison between “nutrients” and productivity is useful, the surface distributions of the nutrients are themselves not all identical.



**Figure 5** The concentrations in the surface ocean of chlorophyll (a qualitative index of phytoplankton abundance and thus net primary productivity, (a)), the “major nutrients” phosphate ( $\text{PO}_4^{3-}$ , (b)) and nitrate ( $\text{NO}_3^-$ , (c)), and the nutrient silicate ( $\text{SiO}_4^{4-}$ , (d)), which is required mostly by diatoms, a group of phytoplankton that builds opal tests. The chlorophyll map in (a) is from composite data from the NASA SeaWiFS satellite project collected during 2001 (<http://seawifs.gsfc.nasa.gov/SEAWIFS.html>). The nutrient data in (b), (c), and (d) are from 1994 World Ocean Atlas (Conkright *et al.*, 1994), and the maps are generated from the International Research Institute for Climate Prediction Data Library (<http://ingrid.ldeo.columbia.edu>). Comparison of (a) with (b), (c), and (d) demonstrates that phytoplankton abundance, at the coarsest scale, is driven by the availability of these nutrients, and these nutrients are generally most available in the polar ocean and along the equatorial upwellings where nutrient-rich deep water mixes more easily to the surface. However, among the nutrient-bearing high-latitude regions, there is not a good correlation between nutrient concentration and chlorophyll, indicating that other parameters come to limit productivity in these regions. The high-latitude ocean of the southern hemisphere, which has the highest nutrient concentrations, is known as the Southern Ocean. It is composed of the more polar Antarctic zone, where the silicate concentration is high and diatom productivity is extensive, and the more equatorward Subantarctic zone, where nitrate and phosphate remain high but silicate is scarce. The strong global correlation between phosphate and nitrate, originally recognized by Redfield (Redfield, 1942, 1958; Redfield *et al.*, 1963), allows us to group the two nutrients together when considering their internal cycling within the ocean, as they are exhausted in more or less the same regions. However, their input/output budgets may change over hundreds and thousands of years, and the relationship between these two nutrients may have been different in the past.



**Figure 5** (continued).

For instance, nitrate and phosphate penetrate much further north than does silicate in the Southern Ocean, the polar ocean surrounding Antarctica (Figures 5(b)–(d)). As silicate is needed by diatoms but not other types of phytoplankton, this difference has major implications for the ecology of the Southern Ocean, present and past. Moreover, since surface water from 40–50°S is fed into the thermocline that

supplies the low-latitude surface ocean with nutrients, the nutrient conditions of the Southern Ocean affect the nutrient supply and ecology of lower latitudes (Brzezinski *et al.*, 2002; Matsumoto *et al.*, 2002b). With regard to nitrate and phosphate (Figures 5(b) and (c)), a more careful comparison of their concentration variations would show lower nitrate-to-phosphate ratios in the Pacific than elsewhere, indicative of



the nitrate loss that is occurring in that basin (Deutsch *et al.*, 2001; Gruber and Sarmiento, 1997). The input/output budget of the marine nitrogen cycle and its affect on the ocean nitrate reservoir arises as a matter of great importance in the section that follows.

### 6.18.2.1 Low- and Mid-latitude Ocean

We can describe the global biological pump in terms of a balance of fluxes between the sunlit surface ocean and the cold, dark, voluminous deep ocean (Figure 1). Phytoplankton consume  $\text{CO}_2$  and nutrients (in particular, the major nutrients nitrogen and phosphorus) in the surface, and subsequent processing drives a downward rain of this organic matter that is degraded after it has sunk into the ocean interior, effectively extracting the  $\text{CO}_2$  and nutrients from the surface ocean and lowering atmospheric  $\text{CO}_2$ . Balancing this downward flux of particles is the net upward flux of dissolved inorganic carbon and nutrients into the surface, due to a combination of diffuse vertical mixing over the entire ocean and focused vertical motion (upwelling and downwelling) in specific regions.

This steady state can be described by the following expressions (Broecker and Peng, 1982), which indicate a balance between the gross upward (left-hand side) and gross downward (right-hand side) transport of phosphorus (Equation (1)) and carbon (Equation (2)):

$$[\text{PO}_4^{3-}]_{\text{deep}} \times Q = [\text{PO}_4^{3-}]_{\text{surface}} \times Q + \text{EP}_P \quad (1)$$

$$[\text{DIC}]_{\text{deep}} \times Q = [\text{DIC}]_{\text{surface}} \times Q + (\text{EP}_P \times \text{C/P}_{\text{EP}}) \quad (2)$$

where  $[\text{PO}_4^{3-}]$  is the phosphate concentration and  $[\text{DIC}]$  is the dissolved inorganic carbon concentration (the sum of dissolved  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) in the deep and surface layers,  $Q$  is the exchange rate of water between the deep and surface,  $\text{EP}_P$  is the export production in terms of phosphorus, and  $\text{C/P}_{\text{EP}}$  is the carbon to phosphorus ratio of the export production. In these expressions, phosphorus is intended to represent the major nutrients in general; the distinctions between phosphorus and nitrogen will be considered later.

The biological pump is the biologically driven gradient in  $[\text{DIC}]$  between the surface and the deep sea ( $[\text{DIC}]_{\text{deep}} - [\text{DIC}]_{\text{surface}}$ ). Because the deep ocean is a very large reservoir, increasing this gradient essentially means decreasing  $[\text{DIC}]_{\text{surface}}$ . Because the surface ocean equilibrates with the gases of the atmosphere, an increase in the gradient lowers atmospheric  $\text{CO}_2$  as well. Solving

Equation (2) for  $[\text{DIC}]_{\text{deep}} - [\text{DIC}]_{\text{surface}}$  gives

$$[\text{DIC}]_{\text{deep}} - [\text{DIC}]_{\text{surface}} = (\text{EP}_P \times \text{C/P}_{\text{EP}})/Q \quad (3)$$

Solving Equation (1) for  $\text{EP}_P$  gives:

$$\text{EP}_P = ([\text{PO}_4^{3-}]_{\text{deep}} - [\text{PO}_4^{3-}]_{\text{surface}}) \times Q \quad (4)$$

Substitution of Equation (4) into Equation (3) for  $\text{EP}_P$  gives the following expression for  $[\text{DIC}]_{\text{deep}} - [\text{DIC}]_{\text{surface}}$ :

$$[\text{DIC}]_{\text{deep}} - [\text{DIC}]_{\text{surface}} = ([\text{PO}_4^{3-}]_{\text{deep}} - [\text{PO}_4^{3-}]_{\text{surface}}) \times \text{C/P}_{\text{EP}} \quad (5)$$

Thus, given the assumptions above, the surface–deep gradient in inorganic carbon concentration (the “strength” of the biological pump) is determined by (i) the  $\text{C/P}$  of the organic matter that is exported from the surface ocean, and (ii) the nutrient concentration ( $[\text{PO}_4^{3-}]$ ) gradient between the surface and deep ocean.

In the low- and mid-latitude ocean, this balance is simplified by the nearly complete extraction of  $[\text{PO}_4^{3-}]$  and  $[\text{NO}_3^-]$  from the surface ocean (Figures 5(b) and (c)). The warm sunlit surface layer is separated by a strong temperature-driven density gradient (“thermocline”) from the cold deep ocean, preventing rapid communication between the low-latitude ocean surface and the ocean interior. As a result, nutrient supply from below occurs slowly, and phytoplankton completely strip surface waters of available nitrogen and phosphorus; i.e., low- and mid-latitude phytoplankton growth is limited by the major nutrients nitrogen and phosphorus. If the low-latitude surface ocean is so strongly limited by the major nutrients that  $[\text{PO}_4^{3-}]_{\text{surface}}$  would not be raised above zero for any imaginable increase in  $Q$  (i.e., if surface ocean plant productivity remains major-nutrient limited over a broad range of surface–deep mixing rates), then changes in upwelling and vertical mixing are balanced by equivalent changes in biological export production. In this case, changes in  $Q$  could cause changes in productivity over time, but these would not change the surface–deep gradient in  $[\text{DIC}]$  maintained by the biological pump.

If this is an adequate description of the real low-latitude ocean, then the strength of its biological pump (the amplitude of the surface–deep gradient in inorganic carbon concentration) is controlled solely by: (i) the carbon/nutrient ratio of the organic matter, and (ii) the nutrient content of the deep ocean (see Equation (5)). If the  $\text{C/P}$  ratio of export production increased or the  $[\text{PO}_4^{3-}]$  of the deep ocean increased, then biological production at the surface would drive an increase in the downward flux of carbon that is not at first matched by any change in the upward flux of carbon dioxide associated with surface–deep

mixing. A new balance between the downward and upward fluxes of carbon would eventually be reached as the [DIC] gradient between the surface and the deep increases, so that a given amount of mixing transports more  $\text{CO}_2$  back into the surface ocean. This increase in surface–deep [DIC] gradient would be mostly due to a drop in dissolved inorganic carbon concentration of the surface ocean, which would lower the  $p_{\text{CO}_2}$  of the surface ocean and drive an associated decrease in atmospheric  $\text{CO}_2$ .

Biological production in the ocean tends to incorporate carbon, nitrogen, and phosphorus into biomass in the ratios of 106/16/1 (Redfield, 1942, 1958; Redfield *et al.*, 1963). These ratios determine the amount of inorganic carbon that is sequestered in the deep sea when the supply of nutrients to the surface is completely converted to export production, as is the case in the modern low- and mid-latitude ocean. It is unclear at this point how variable the C/N/P ratios of export production might be through time. When Broecker (1982a) first hypothesized a glacial increase in the strength of the biological pump as the driver of lower glacial  $\text{CO}_2$  levels, he considered the possibility (suggested to him by Peter Weyl) that the C/P export production changes between ice ages and interglacials, with a higher C/P ratio during the last ice age, but he could find neither a mechanism nor direct paleoceanographic evidence for such a change.

Roughly the same situation persists today. We remain exceedingly uncertain about the robustness of the “Redfield ratios” through time and space. However, we do not yet have any mechanistic understanding of their variability (Falkowski, 2000), neither have we recognized a paleoceanographic archive that would help us to assess this variability. The organic matter preserved in the sediment record represents a minute and compositionally distinct fraction of the organic matter exported from the surface ocean. We have no reason to believe that variations in the elemental ratios of this residual sedimentary organic matter will reflect that of export production, especially in the face of changing seafloor conditions.

One of the persistent views of geochemists, to the frustration of their more biologically oriented colleagues, is that the complex recycling of elements in the low-latitude surface ocean has no major significance for the low-latitude biological pump. The argument is that, given the nutrient limitation that predominates in the low-latitude surface, the amount of carbon to be exported is determined by the supply of the major nutrients from the subsurface and the C/N/P uptake ratios of phytoplankton, regardless of the upper ocean recycling of a given nutrient element before export. However, the C/N/P ratios of export production may be altered by ecological effects

on the relationship between phytoplankton biomass and the organic matter actually exported from the surface ocean, even without changes in the elemental requirements of the phytoplankton themselves. As a result, the ecology of the surface ocean could drive variations in the strength of the biological pump, for instance, by changing the C/P ratio of export production independent of the C/P ratio of phytoplankton, so as to change the amount of carbon exported for a given phosphorus supply. It was with this reasoning that Weyl originally justified the idea of glacial/interglacial changes in the C/P ratio of export production (Broecker, 1982a). Terrestrial biogeochemists and limnologists are actively seeking a quantitative theory for the ecological constraints imposed by elemental cycling (Elser *et al.*, 2000); oceanographers may benefit from a similar focus on the controls on elemental ratios, in particular, in export production. In any case, while changes in the chemical composition of export production may play a role in the variability of the ocean’s biological pump, we are not yet in a position to posit specific hypotheses about such changes or to recognize them in the sedimentary record.

Broecker (1982b) and McElroy (1983) initially hypothesized that the oceanic reservoirs of phosphate and nitrate, respectively, might increase during glacial times, which would allow enhanced low-latitude biological production to lower atmospheric  $\text{CO}_2$ . However, it was recognized that this basic mechanism would require large changes in nutrient reservoirs to produce the entire observed amplitude of  $\text{CO}_2$  change. According to a box-model calculation, the immediate effect of an increase in the nutrient reservoir is to extract  $\text{CO}_2$  from the surface ocean and atmosphere, sequestering it in the deep sea, with a 30% increase in the oceanic nutrient reservoir driving a 30–40 ppmv  $\text{CO}_2$  decrease (Table 1, see “closed system effects”) (Sigman *et al.*, 1998). The longer-term effect on  $\text{CO}_2$  from the ocean alkalinity balance depends greatly on whether  $\text{CaCO}_3$  export increases in step with  $C_{\text{org}}$  export. It is not known whether a global increase in low-latitude production would increase the  $\text{CaCO}_3$  rain in step with the  $C_{\text{org}}$  rain—this would probably depend on the circumstances of

**Table 1** Atmospheric  $\text{CO}_2$  effects of a 30% increase in the ocean nutrient inventory.

$\text{CO}_2$ changes (ppm)	$\text{CaCO}_3$ production	
	Proportional to $C_{\text{org}}$	Constant
Closed system effects	– 34	– 43
Open system effects	+ 17	– 3
Total $\text{CO}_2$ change	– 17	– 46

the increase—so we should consider both possibilities.

If  $\text{CaCO}_3$  export increases proportionately with  $C_{\text{org}}$  export (see “ $\text{CaCO}_3$  production proportional to  $C_{\text{org}}$ ” in Table 1), the increase in the  $\text{CaCO}_3$  flux to the seafloor causes a gradual loss of alkalinity from the ocean, which works to raise atmospheric  $\text{CO}_2$  (see “open system effects” in Table 1). As a result, only a 15–25 ppmv drop in  $\text{CO}_2$  results from a 30% increase in the oceanic major nutrient reservoir (Table 1). However, if  $\text{CaCO}_3$  production remains constant as  $C_{\text{org}}$  production increases (see “ $\text{CaCO}_3$  production constant” in Table 1), the effects on the whole ocean reservoir of alkalinity are minimal (see “open system effects” in Table 1), and the increase in the oceanic nutrient reservoir is much more effective at lowering atmospheric  $\text{CO}_2$ . In this case, the box model calculation suggests that a 30% increase in the oceanic nutrient reservoir lowers atmospheric  $\text{CO}_2$  by ~50 ppmv (Table 1), while some general circulation models would suggest declines in  $\text{CO}_2$  of as much as 80 ppm (Archer *et al.*, 2000a). The required increase in the ocean nutrient reservoir could perhaps be lowered by a coincident decrease in  $\text{CaCO}_3$  export that was modest enough not to violate observations of the glacial-age sedimentary  $\text{CaCO}_3$  distribution (Archer and Maier-Reimer, 1994; Brzezinski *et al.*, 2002; Matsumoto *et al.*, 2002b; Sigman *et al.*, 1998). Nevertheless, a 30% increase in oceanic nutrients would require a dramatic change in ocean biogeochemistry.

Given a residence time of >6 thousand years for oceanic phosphate and the nature of the input/output terms in the oceanic phosphorus budget (Froelich *et al.*, 1982; Ruttenberg, 1993), it is difficult to imagine how oceanic phosphate could vary so as to cause the observed amplitude, rate, and phasing of atmospheric  $\text{CO}_2$  change (Ganeshram *et al.*, 2002). Entering an ice age, Broecker (1982a) considered the possibility of a large phosphorus input from the weathering of shelf sediments, as ocean water is captured in ice sheets and sea level drops. Ice-core studies dispatched with this admittedly unlikely scenario by demonstrating that, going into an interglacial period,  $\text{CO}_2$  begins to rise before sea level rises (Sowers and Bender, 1995), so that the phosphorus inventory decrease would occur too late to explain the rise of  $\text{CO}_2$  into interglacials.

There is growing evidence that the nitrogen cycle is adequately dynamic to allow for a large change in the oceanic nitrate reservoir on glacial/interglacial timescales (Codispoti, 1995; Gruber and Sarmiento, 1997). Denitrification, the heterotrophic reduction of nitrate to  $\text{N}_2$  gas, is the dominant loss term in the oceanic budget of “fixed” (or bioavailable) nitrogen. Nitrogen isotope studies in currently active regions of

denitrification provide compelling evidence that water column denitrification was reduced in these regions during glacial periods (Altabet *et al.*, 1995; Ganeshram *et al.*, 1995, 2002; Pride *et al.*, 1999). In addition, it has been suggested that  $\text{N}_2$  fixation, the synthesis of new fixed nitrogen from  $\text{N}_2$  by cyanobacterial phytoplankton, was greater during glacial periods because of increased atmospheric supply of iron to the open ocean (iron being a central requirement of the enzymes for  $\text{N}_2$  fixation) (Falkowski, 1997). Both of these changes, a decrease in water column denitrification and an increase in  $\text{N}_2$  fixation, would have increased the oceanic nitrate reservoir. It has been suggested that such a nitrate reservoir increase would lead to significantly higher export production in the open ocean during glacial periods, potentially explaining glacial/interglacial atmospheric  $\text{CO}_2$  changes (Broecker and Henderson, 1998; Falkowski, 1997; McElroy, 1983).

The major conceptual questions associated with this hypothesis involve the feedback of the nitrogen cycle and the strictness with which marine organisms must adhere to the Redfield ratios, both N/P and C/N. Oceanic  $\text{N}_2$  fixation provides a mechanism by which the phytoplankton community can add fixed nitrogen to the ocean when conditions favor it. By contrast, riverine input of phosphorus, the major source of phosphate to the ocean, is not directly controlled by marine phytoplankton. Because phytoplankton have no way to produce biologically available phosphorus when there is none available, geochemists have traditionally considered phosphorus to be the fundamentally limiting major nutrient on glacial/interglacial timescales (Broecker and Peng, 1982). For a nitrate reservoir increase alone to drive an increase in low-latitude biological production, the nutrient requirements of the upper-ocean biota must be able to deviate from Redfield stoichiometry to adjust to changes in the N/P ratio of nutrient supply, so as to fully utilize the added nitrate in the absence of added phosphate. Alternatively, if this compensatory shift in biomass composition is incomplete, the surface ocean will tend to shift toward phosphate limitation, and an increase in export production will be prevented.

It was originally suggested by Redfield (Redfield *et al.*, 1963), based on analogy with freshwater systems, that  $\text{N}_2$  fixers in the open ocean will enjoy greater competitive success under conditions of nitrate limitation but will be discouraged in the case of phosphate limitation. Having posited this sensitivity, Redfield hypothesized that  $\text{N}_2$  fixation acts as a negative feedback on the nitrate reservoir, varying so as to prevent large changes in the nitrate reservoir that are not associated with a coincident change in the phosphate reservoir (Redfield *et al.*, 1963).

On the grand scale, this feedback must exist and must put some bounds on the degree to which the oceanic nitrate reservoir can vary independently from phosphorus. However, the quantitative constraint that this negative feedback places on the global nitrate reservoir is not yet known, with one suggested possibility being that iron is so important to  $N_2$  fixers that changes in its supply can overpower the nitrate/phosphate sensitivity described by Redfield, leading to significant variations in the nitrate reservoir over time (Broecker and Henderson, 1998; Falkowski, 1997).

In summary, there are two components of the paradigm of phosphorus's control on the nitrate reservoir and the low-latitude biological pump, both stemming from Redfield's work: (i) oceanic  $N_2$  fixation proceeds in phosphorus-bearing, nitrogen-poor environments, but not otherwise, and (ii) export production has a consistent C/N/P stoichiometry. The first statement would have to be inaccurate for the nitrate reservoir to vary independently of the phosphate reservoir, and the second statement would have to be inaccurate for such an independent change in the nitrate reservoir to actually cause a change in the biological pump. Partly as a reaction to studies that have considered the influence of other parameters, in particular, the supply of iron to open ocean  $N_2$  fixation (Falkowski, 1997), some papers have restated the traditional Redfield-based paradigm (Ganeshram *et al.*, 2002; Tyrrell, 1999). However, the real challenge before us is to test and quantify the rigidity of the Redfield constraints relative to the influence of other environmental parameters. Biogeochemical studies of the modern ocean (Karl *et al.*, 1997; Sanudo-Wilhelmy *et al.*, 2001) and the paleoceanographic record (Haug *et al.*, 1998) are both likely to play a role in the evaluation of these questions regarding Redfield stoichiometry and  $N_2$  fixation, which are, in turn, critical for the hypothesis of the low latitude biological pump as the driver of glacial/interglacial  $CO_2$  change.

The mean concentration of  $O_2$  in the ocean interior would be lowered in the glacial ocean by an increase in low-latitude carbon export, regardless of whether it is driven by an increase in the ocean phosphorus reservoir, the ocean nitrogen reservoir, or a change in the carbon/nutrient ratio of sinking organic matter. As described below, this makes deep-ocean  $[O_2]$  a possible constraint on the strength and efficiency of the biological pump in the past. Here, however, we focus on this sensitivity of deep-ocean  $[O_2]$  as part of an additional negative feedback in the ocean nitrogen cycle. This feedback may restrict the variability of the oceanic nitrate reservoir, even in the case that Redfield's  $N_2$  fixation-based

feedback on the ocean nitrogen cycle is weak and ineffective.

Denitrification occurs in environments that are deficient in  $O_2$ . An increase in the ocean's nitrate content will drive higher export production (neglecting, for the moment, the possibility of phosphate limitation). When this increased export production is oxidized in the ocean interior, it will drive more extensive  $O_2$  deficiency. This will lead to a higher global rate of denitrification, which, in turn, will lower the ocean's nitrate content. Thus, the sensitivity of denitrification to the  $O_2$  content of the ocean interior generates a hypothetical negative feedback that may, like the  $N_2$  fixation-based feedback, work to stabilize the nitrate content of the ocean (Toggweiler and Carson, 1995).

While it is generally true that the major nutrients nitrate and phosphate are absent in low- and mid-latitude surface ocean, there are important exceptions (Figures 5(b) and (c)). Wind-driven upwelling leads to nonzero nutrient concentrations and high biological productivity at the surface along the equator and the eastern margins of the ocean basins (e.g., off of Peru, California, and western Africa). Why have we given such short shrift to these biologically dynamic areas in our discussion of the low- and mid-latitude biological pump?

While critically important for ocean ecosystems and potentially important for interannual variations in atmospheric  $CO_2$ , the nutrient status in equatorial and coastal upwelling systems does not greatly affect atmospheric  $CO_2$  on centennial or millennial timescales. Above, we demonstrated that greater vertical exchange between the nutrient-poor surface ocean and the deep sea causes higher export production but does not affect the [DIC] gradient between the surface and the deep sea, so that it would not drive a change in atmospheric  $CO_2$ . Following this same reasoning, low-latitude upwellings may generate much export production, but they are not millennial-scale sinks for atmospheric  $CO_2$  because the upwelling brings up both nutrients and respiratory  $CO_2$  from the ocean interior. Neither do the upwellings drive a net loss of  $CO_2$  from the ocean, because the high-nutrient surface waters of the low-latitude upwellings do not contribute appreciably to the ventilation of the ocean subsurface. Put another way, the nutrients supplied to the surface are eventually consumed as the nutrient-bearing surface water flows away from the site of upwelling, before the water has an opportunity to descend back into the ocean interior. This pattern is evident in surface ocean  $pCO_2$  data (Takahashi *et al.*, 1997). For instance, in the core of equatorial Pacific upwelling,  $pCO_2$  is high both because the water is warming and because deeply sequestered metabolic  $CO_2$  is brought to



the surface and evades back to the atmosphere. Adjacent to the equatorial upwelling, the tropical and subtropical Pacific is a region of low  $p_{\text{CO}_2}$  which is associated with the consumption of the excess surface nutrients that have escaped consumption at the site of upwelling. It does not matter for atmospheric  $\text{CO}_2$  whether the upwelled nutrients are converted to export production on-axis of the upwelling system or further off-axis. Thus, while changes in upwelling, biological production, and nutrient status are central to the history of the low-latitude ocean, they have limited importance for atmospheric  $\text{CO}_2$  changes on glacial/interglacial timescales. Increased export production driven by higher rates of vertical mixing or upwelling would only play a role in lowering atmospheric  $\text{CO}_2$  if it caused a change in the chemical composition of the exported organic material, such as a decrease in its  $\text{CaCO}_3/\text{C}_{\text{org}}$  ratio or an increase in the mean depth at which the organic rain is metabolized in the ocean interior (e.g., Boyle, 1988b; Dymond and Lyle, 1985).

The surface chlorophyll distribution shows that coastal environments, even in regions without upwelling, are among the most highly productive in the ocean (Figure 5(a)). However, it is believed that coastal ocean productivity does not have a dominant effect on atmospheric  $\text{CO}_2$  over centuries and millennia. As biomass does not accumulate significantly in the ocean, any long-term excess in net primary production relative to heterotrophy must lead to export of organic matter out of the surface layer, in particular, as a downward rain of biogenic particles. In the case of the coastal ocean, this export is stopped by the shallow seafloor, frequently within the depth range that mixes actively with the surface ocean. The high net primary productivity of the coastal ocean owes much to the presence of the shallow seafloor, as the nutrients released from the degradation of settled organic matter are available to the phytoplankton in the sunlit surface. Yet, just as the seafloor prevents the loss of nutrients from the coastal surface ocean, so too does it prevent the export of carbon. Almost as soon as the settled organic carbon is respired, the  $\text{CO}_2$  product is free to diffuse back into the atmosphere. Were the same export to have occurred over the open ocean, it would have effectively sequestered the carbon in that biogenic rain within the ocean interior for roughly a thousand years. Thus, the shallow seafloor of the ocean margin leads to high primary productivity while at the same time limiting its effect on the carbon cycle over the timescale of centuries and millennia. It should be noted, however, that the ocean margins are critically important in the global carbon cycle on the timescale of millions of years, due to their role in organic carbon burial.

It has been hypothesized that a significant fraction of the organic matter raining onto the shallow margin is swept over the shelf/slope break, thus transporting organic matter into the ocean interior (Walsh *et al.*, 1981). This has been interpreted as rendering ocean margin productivity important to atmospheric  $\text{CO}_2$  on millennial timescales, in that the organic matter being swept off the shelf would be an important route by which  $\text{CO}_2$  is shuttled into the deep sea. However, this view should be considered carefully. The ocean margins have high net primary production because of nutrient recycling, but the recycled nutrients were produced by the decomposition of organic matter that would have otherwise been exported out of the system. Mass balance dictates that export of organic carbon from the coastal surface ocean, like export production in the open ocean surface, is set by the net supply of nutrients to the system. If a low-latitude ocean margin receives most of its net nutrient supply from the deep sea, then it is no different than the neighboring open ocean in the quantity of carbon that it can export. There is one caveat to this argument: if organic matter deposited on the shelf can have its nutrients stripped out without oxidizing the carbon back to  $\text{CO}_2$  and this “depleted” organic carbon is then transported off the shelf and into the ocean interior, then ocean margin productivity, having been freed from the Redfield constraint on the elemental composition of its export production, could drive a greater amount of organic carbon export for a given amount of nutrient supply.

#### 6.18.2.2 High-latitude Ocean

Broecker’s (Broecker, 1981, 1982a,b; Broecker and Peng, 1982) initial ideas about the biological pump revolutionized the field of chemical oceanography. However, soon after their description, several groups demonstrated that his focus on the low-latitude ocean missed important aspects of the ocean carbon cycle. The thermocline outcrops at subpolar latitudes, allowing deep waters more ready access to the surface in the polar regions. In these regions, the nutrient-rich and  $\text{CO}_2$ -charged waters of the deep ocean are exposed to the atmosphere and returned to the subsurface before the available nutrients are fully utilized by phytoplankton for carbon fixation. This incomplete utilization of the major nutrients allows for the leakage of deeply sequestered  $\text{CO}_2$  back into the atmosphere, raising the atmospheric  $p_{\text{CO}_2}$ . Work is ongoing to understand what limits phytoplankton growth in these high-latitude regions. Both light and trace metals such as iron are scarce commodities in these regions and together probably represent the dominant controls

on polar productivity, with light increasing in importance toward the poles due to the combined effects of low irradiance, sea ice coverage, and deep vertical mixing (see [Chapters 6.02, 6.04, and 6.10](#)). The Southern Ocean, which surrounds Antarctica, holds the largest amount of unused surface nutrients ([Figures 5\(b\)–\(d\)](#)), yet the surface chlorophyll suggests that it is perhaps the least productive of the polar oceans; iron and light probably both play a role in explaining this pattern ([Martin \*et al.\*, 1990](#); [Mitchell \*et al.\*, 1991](#)).

The efficiency of the global biological pump with respect to the ocean's major nutrient content is determined by the nutrient status of the polar regions that ventilate the deep sea, or more specifically, the nutrient concentration of the new water that enters the deep sea from polar regions ([Figure 6](#)). Deep water is enriched in nutrients and  $\text{CO}_2$  because of the low- and mid-latitude biological pump, which sequesters both nutrients and inorganic carbon in subsurface. In high-latitude regions such as the Antarctic, the exposure of this  $\text{CO}_2$ -rich deep water at the surface releases this sequestered  $\text{CO}_2$  to the atmosphere. However, the net uptake of nutrients and  $\text{CO}_2$  in the formation of phytoplankton biomass and the eventual export of organic matter subsequently lowers the  $p_{\text{CO}_2}$  of surface waters, causing the surface layer to reabsorb a portion of the  $\text{CO}_2$  that was originally lost from the upwelled water. Thus, the ratio between export production and the ventilation of  $\text{CO}_2$ -rich subsurface water, not the absolute rate of either process alone, controls the exchange of  $\text{CO}_2$  between the atmosphere and high-latitude surface ocean. The nutrient concentration of water at the time that it enters the subsurface is referred to as its "preformed" nutrient concentration. The preformed nutrient concentration of subsurface water provides an indicator of the cumulative nutrient utilization that it underwent while at the surface, with a higher preformed nutrient concentration indicating lower cumulative nutrient utilization at the surface and thus a greater leak in the biological carbon pump. This picture overlooks a number of important facts. For instance, ocean/atmosphere  $\text{CO}_2$  exchange is not instantaneous, so water can sink before it has reached  $\text{CO}_2$  saturation with respect to the atmosphere. In polar regions, this typically means that deep water may leave the surface before it has lost as much  $\text{CO}_2$  to the atmosphere as it might have ([Stephens and Keeling, 2000](#)).

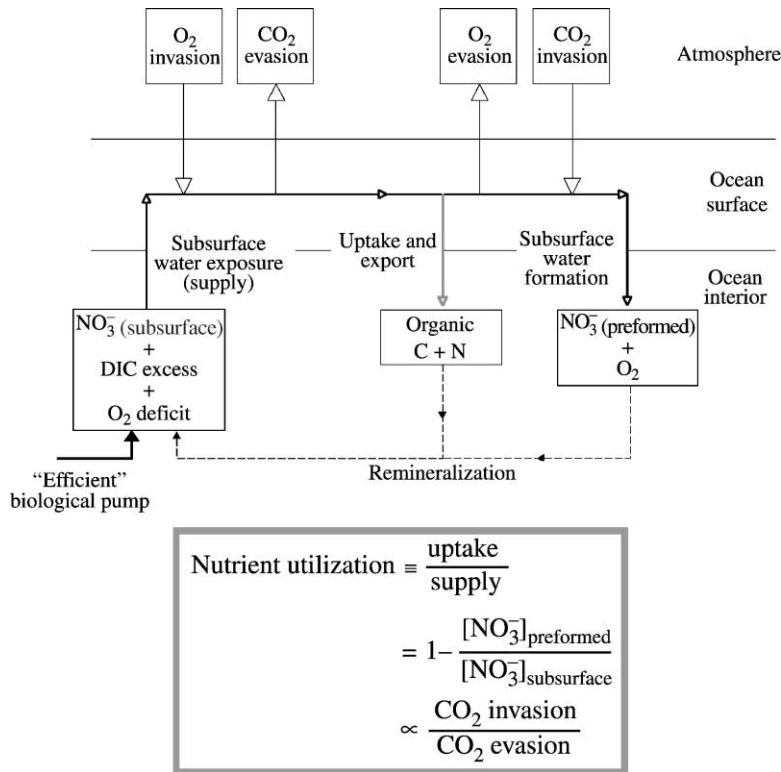
The global efficiency of the biological pump can be evaluated in terms of a global mean preformed nutrient concentration for surface water that is folded into the ocean interior. In the calculation of this mean preformed nutrient concentration, each subsurface water formation

term is weighted according to the volume of the ocean that it ventilates because this corresponds to the amount of  $\text{CO}_2$  that could be sequestered in a given portion of the ocean interior. As a result, the nutrient status of surface ocean regions that directly ventilate the ocean subsurface (deep, intermediate, or thermocline waters) have special importance for atmospheric  $\text{CO}_2$ .

The high-latitude North Atlantic and the Southern Ocean are the two regions that appear to dominate the ventilation of the modern deep ocean. Through the preformed nutrient concentrations of the newly formed deep waters, their competition to fill the deep ocean largely determines the net efficiency of the global biological pump ([Toggweiler \*et al.\*, 2003b](#)). Of these two regions, the North Atlantic has a low preformed nutrient concentration and thus drives the ocean toward a high efficiency for the biological pump. In contrast, the preformed nutrient concentration of Southern Ocean-sourced deep water is high and thus drives the global biological pump toward a low efficiency.

Within the polar oceans involved in deep water formation, certain regions are more important than others. The Antarctic Zone, the most polar region in the Southern Ocean, is involved in the formation of both deep and intermediate-depth waters, making this region important to the atmosphere/ocean  $\text{CO}_2$  balance. The quantitative effect of the Subantarctic Zone on atmospheric  $\text{CO}_2$  is less certain, depending on the degree to which the nutrient status of the Subantarctic surface influences the preformed nutrient concentration of newly formed subsurface water (Antarctic Intermediate Water and Subantarctic mode water), but its significance is probably much less than that of the Antarctic.

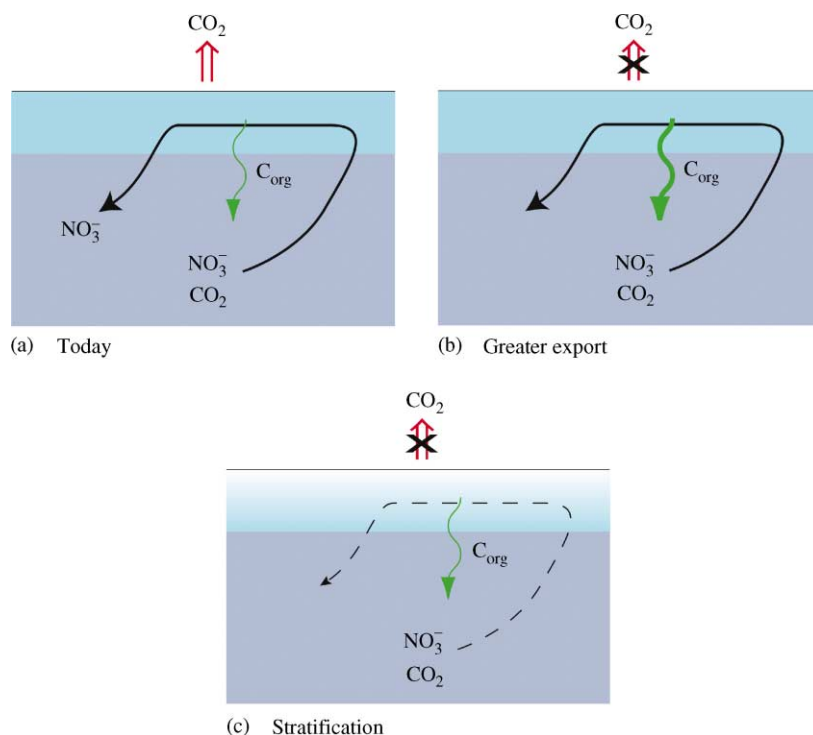
Questions regarding the most critical regions extend to even smaller spatial scales. For instance, with regard to deep-ocean ventilation in the Antarctic, it is uncertain as to whether the entire Antarctic surface plays an important role in the  $\text{CO}_2$  balance, or whether instead only the specific locations of active deep water formation (e.g., the Weddell Sea shelf) are relevant. This question hinges largely on whether the surface water in the region of deep water formation exchanges with the open Antarctic surface, or whether it instead comes directly from the shallow subsurface and remains isolated until sinking. If the latter is true, then the open Antarctic may be irrelevant to the chemistry of the newly formed deep water. This would be problematic for paleoceanographers, since essentially all of the reliable paleoceanographic records come from outside these rather special environments. There is, however, a new twist to this question. While deep water formation in the modern Antarctic has long been thought of as restricted to the shelves, efforts to reproduce



**Figure 6** The effect on atmospheric  $\text{CO}_2$  of the biological pump in a region of deep-ocean ventilation where the major nutrients are not completely consumed, such as the Antarctic zone of the Southern Ocean. In this figure,  $\text{NO}_3^-$  is intended to represent the major nutrients and thus should not be distinguished conceptually from  $\text{PO}_4^{3-}$ . The biological pump causes deep water to have dissolved inorganic carbon (DIC) in excess of its “preformed” [DIC] (the concentration of DIC in the water when it left the surface; see lower left box, which represents water in the ocean interior). The low- and mid-latitudes (and a few polar regions, such as the North Atlantic) house a biological pump that is “efficient” in that it consumes all or most of the major nutrient supply. As a result, it drives the DIC excess toward a concentration equivalent to the deep  $[\text{NO}_3^-]$  multiplied by the C/N ratio of exported organic matter (left lower arrow represents this influence on deep-water chemistry). The respiration of organic matter in the ocean interior also leads deep water to have an  $\text{O}_2$  deficit relative to saturation. In high-latitude regions such as the Antarctic, the exposure of this deep water at the surface releases this sequestered  $\text{CO}_2$  to the atmosphere and leads to the uptake of  $\text{O}_2$  from the atmosphere (upper left). However, the net uptake of nutrients and  $\text{CO}_2$  in the formation of phytoplankton biomass and the eventual export of organic matter (“uptake and export”) subsequently lowers the  $p_{\text{CO}_2}$  of surface waters, causing the surface layer to reabsorb a portion of the  $\text{CO}_2$  that was originally lost from the upwelled water (upper right). The net excess in photosynthesis to respiration that drives this export out of the surface also produces  $\text{O}_2$ , some of which evades to the atmosphere, partially offsetting the initial  $\text{O}_2$  uptake by the surface ocean. While the down-going water has lost its DIC excess by exchange with the atmosphere, a portion of the original DIC excess will be reintroduced in the subsurface when the exported organic matter is remineralized (the more complete the nutrient consumption in the surface, the greater the DIC excess that is reintroduced in the subsurface). The ratio between export and the ventilation of  $\text{CO}_2$ -rich subsurface water, which controls the net flux of  $\text{CO}_2$  between the atmosphere and surface ocean in this region, can be related to the nutrients. Nutrient utilization, defined as the ratio of the rate of nutrient uptake (and export) to the rate of nutrient supply, expresses the difference between nutrient concentration of rising and sinking water. Nutrient utilization relates directly (through the Redfield ratios) to the ratio of  $\text{CO}_2$  invasion (driven by organic matter export) relative to evasion (driven by deep-water exposure at the surface). The lower the nutrient utilization, the lower the ratio of invasion to evasion and thus the more this region represents a leak in the biological pump. This diagram overlooks a number of important facts. For instance, ocean/atmosphere  $\text{CO}_2$  exchange is not instantaneous, so water can sink before it has reached  $\text{CO}_2$  saturation with respect to the atmosphere.

deep-sea nutrient chemistry and radiochemistry raise the possibility that the deep ocean may also be ventilating in a more diffuse mode throughout the open Antarctic (Broecker *et al.*, 1998; Peacock, 2001). If this is the case, the significance of the open Antarctic in the  $\text{CO}_2$  balance is less

susceptible to uncertainties about lateral exchange with the shelf sites of deep water formation. In the discussion that follows, we assume that the open Antarctic does affect the  $\text{CO}_2$  exchanges associated with deep water formation, either by active exchange of surface water with the specific sites of



**Figure 7** Schematic illustrations of the  $\text{CO}_2$  leak from the Southern Ocean to the atmosphere that exists today and of two alternative scenarios by which this leak might have been stopped during ice ages. The incomplete consumption of nutrients in the modern Southern Ocean causes waters that come to the surface in the Southern Ocean to release  $\text{CO}_2$  to the atmosphere because not all of the nutrient supply to the surface drives a downward rain of organic material, allowing  $\text{CO}_2$  sequestered by the lower latitude biological pump to escape (a). During ice ages, atmospheric  $\text{CO}_2$  could have been reduced by increasing the nutrient efficiency of the biological pump in the Southern Ocean (b and c). This could have been driven by an increase in biological productivity (b), which would have actively increased the downward flux of carbon, or by density “stratification” of the upper ocean, allowing less nutrient- and  $\text{CO}_2$ -rich water to the Southern Ocean surface (c). As described in Figure 8, because of the existence of other regions of deep water formation, the evasion of  $\text{CO}_2$  is reduced upon stratification (c) even if the degree of nutrient consumption in the surface does not change.

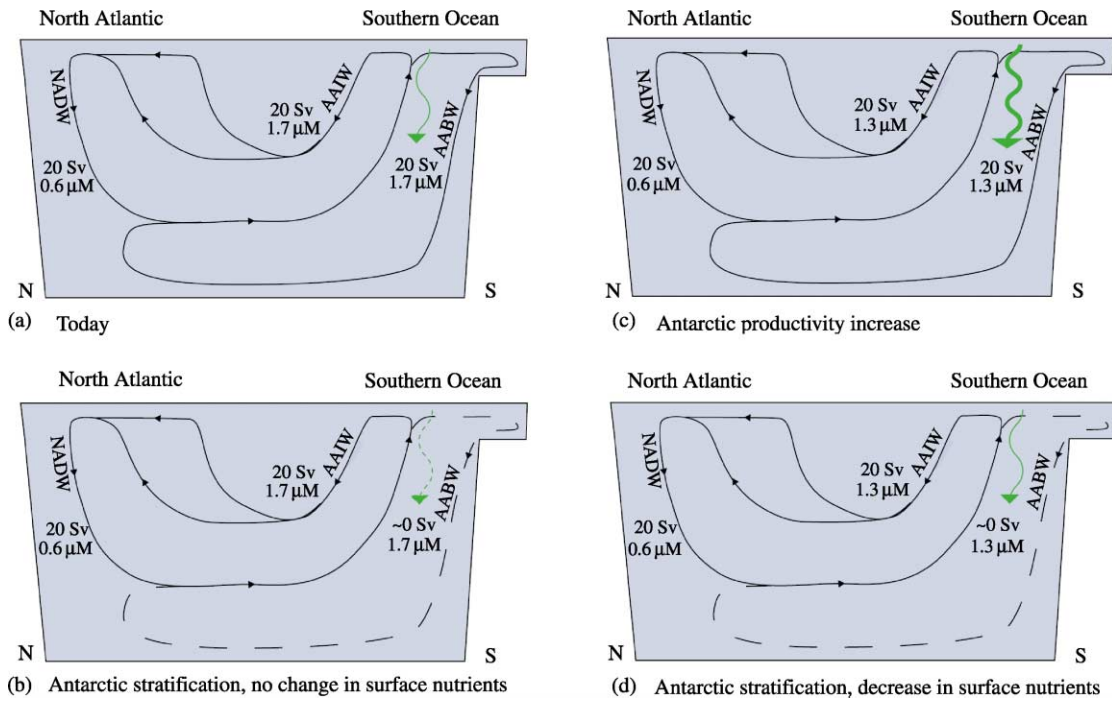
deep water formation or by its actual participation in the ventilation process. In any case, we must improve our understanding of the modern physical and chemical oceanography of the polar regions if we are to determine their roles in atmospheric  $\text{CO}_2$  change.

In their hypothesis of a glacial decrease in Southern Ocean  $\text{CO}_2$  leak, early workers considered two causes: (i) an increase in biological export production and (ii) a decrease in the exposure rate of deep waters at the polar surface (Figure 7). One can imagine processes that would have reduced the evasion of  $\text{CO}_2$  from the Southern Ocean by either of the two mechanisms mentioned above. For instance, an increase in the input of dust and its associated trace metals to the Southern Ocean might have driven an increase in the rate of nutrient and carbon uptake by phytoplankton (Martin, 1990). Alternatively, an increase in the salinity-driven stratification of the Antarctic and/or a decrease in wind-driven upwelling could have lowered the rate of nutrient and carbon dioxide supply to the surface

(discussed further in Section 6.18.3) (Francois *et al.*, 1997; Keeling and Visbeck, 2001; Sigman and Boyle, 2000, 2001; Toggweiler and Samuels, 1995). Under most conditions, these two hypothesized changes do not have the same quantitative effect on atmospheric  $\text{CO}_2$ . For instance, stratification can cause a significantly larger amount of  $\text{CO}_2$  decrease than does increased export production for a given amount of nutrient drawdown in Southern Ocean surface waters (Sigman *et al.*, 1999b).

These differences can be understood in the context of the mean preformed nutrient concentration of the ocean interior (Figure 8). There are two Southern Ocean mechanisms by which the global efficiency of the biological pump may be increased during glacial times: (i) decreasing the preformed nutrient concentration of Southern-Ocean-sourced deep water (Figures 8(c) and (d)), and (ii) decreasing the importance of Southern-Ocean-sourced deep waters in the ventilation of the deep ocean, relative to the North Atlantic or some other source of deep water with low





**Figure 8** Cartoons depicting the ventilation of the ocean interior by the North Atlantic and Southern Ocean and the preformed  $[\text{PO}_4^{3-}]$  of the different ventilation terms, for today (a) and three hypothesized ice-age conditions (b), (c), and (d)); calculation of the mean preformed  $[\text{PO}_4^{3-}]$  of the ocean interior for each of these cases (e); and the effects of the hypothesized glacial changes (b), (c), and (d) on atmospheric  $\text{CO}_2$  compared with the change in mean preformed  $[\text{PO}_4^{3-}]$ , as calculated by the CYCLOPS ocean geochemistry box model (f) (Keir, 1988; Sigman *et al.*, 1998). In the interglacial case (a), there are three sources of subsurface water shown: North Atlantic Deep Water (NADW), Antarctic Intermediate Water (AAIW), and Antarctic Bottom Water (AABW). In this simple picture, NADW and AAIW formation are related; NADW is drawn into the Antarctic surface by the wind-driven (“Ekman”) divergence of surface waters and then forms AAIW because of surface-water convergence further north (Gordon *et al.*, 1977; Toggweiler and Samuels, 1995). The rates of formation (in Sverdrups,  $10^6 \text{ m}^3 \text{ s}^{-1}$ ) and preformed  $[\text{PO}_4^{3-}]$  (in  $\mu\text{M}$ ) are from the CYCLOPS model. In (b), stratification is assumed to shut off AABW formation. Because we do not change NADW, we are forced to leave AAIW unchanged as well. In (b), export production in the Antarctic decreases proportionally with the decrease in upwelling to the surface, such that surface  $[\text{PO}_4^{3-}]$  remains at  $1.7 \mu\text{M}$ . This would be the expected outcome if, for instance, the Antarctic is iron limited and most of the iron comes from upwelling, during both interglacials and ice ages. In (d), the same circulation change occurs as in (b), but in this case export production does not decrease as upwelling decreases, so that surface  $[\text{PO}_4^{3-}]$  drops to  $\sim 1.3 \mu\text{M}$ . This would be the expected outcome if, for instance, the Antarctic iron is supplemented by a high dust input during ice ages. In (c), circulation remains constant but Antarctic export production increases (as indicated by the increase in the downward green arrow). This would be the expected outcome if, for instance, the combined input of iron from dust supply and deep water is greater during ice ages (Martin, 1990; Watson *et al.*, 2000). In (e), the mean preformed  $[\text{PO}_4^{3-}]$  of the ocean interior is calculated as the total phosphate input to the ocean interior divided by the ventilation rate (North Atlantic terms on the left, Antarctic terms on the right). In (f), the calculated change in atmospheric  $p_{\text{CO}_2}$  (relative to the interglacial case (a)) is plotted against the mean preformed  $[\text{PO}_4^{3-}]$  of each case, as calculated in (e). The strong correlation between these two parameters (a 170 ppm decrease in  $\text{CO}_2$  for a  $1 \mu\text{M}$  decrease in  $[\text{PO}_4^{3-}]$ ) indicates that the mean preformed  $[\text{PO}_4^{3-}]$  is an excellent predictor for the effect of a given change on the strength of the biological pump. In these experiments, the mean gas exchange temperature for the ocean interior was held constant, so that no change in the “solubility pump” was allowed (see text). In addition, calcium carbonate dynamics are included in these model experiments, so that a fraction of the  $\text{CO}_2$  response ( $\sim 25\%$ ) is not the result of the biological pump, in the most strict sense. Finally, none of these experiments address the evidence that NADW formation was reduced during glacial times (Boyle and Keigwin, 1982).

preformed nutrients (Figures 8(b) and (d)). Increasing surface productivity would lower the preformed nutrient concentration of the deep sea solely by reducing the preformed nutrient concentration of the Southern Ocean contribution

to deep water (Figure 8(c)). Stratification of the Southern Ocean surface would reduce the fraction of the deep ocean ventilated by the Southern Ocean, allowing the ocean interior to migrate toward the lower preformed nutrient concentration

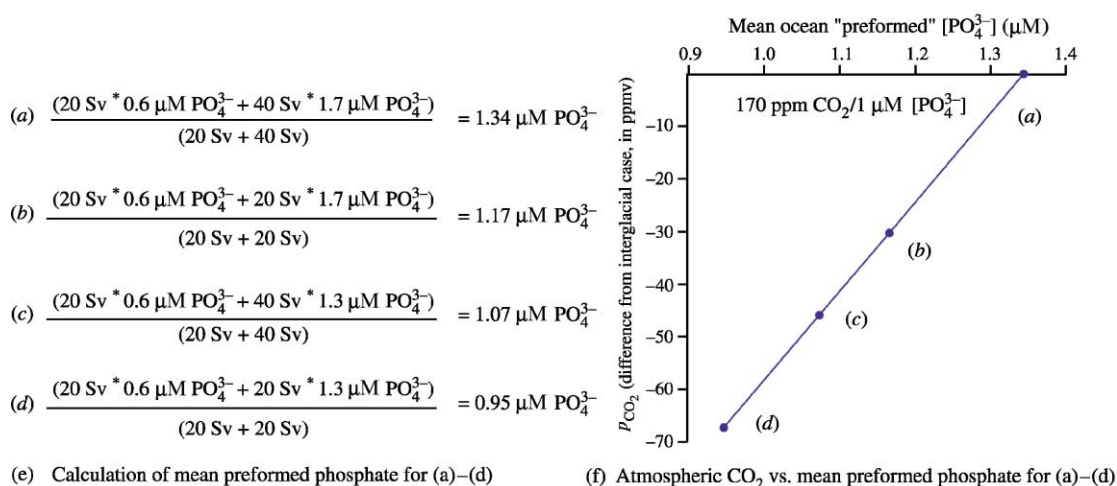
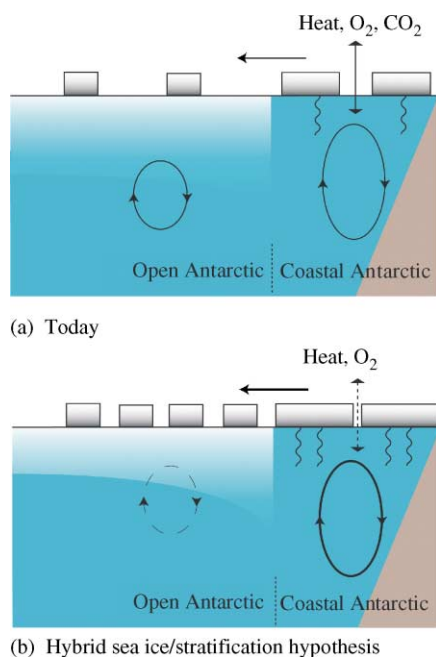


Figure 8 (continued).

of northern-sourced deep water (Figure 8(b)). In addition, if upon stratification phytoplankton growth rate does not decrease as much as does the supply of nutrients to the surface, then stratification would also lower the preformed nutrient concentration of southern-sourced deep waters (Figure 8(d)). In this case, stratification lowers the preformed nutrient concentration by both (i) and (ii) above, leading to a lower net preformed nutrient concentration for the ocean interior and thus making it a more potent mechanism for lowering atmospheric CO<sub>2</sub>. Of course, there are important additional considerations. First, a decrease in Southern Ocean deep water might allow the deep-sea temperature to rise, which would push CO<sub>2</sub> back into the atmosphere. This apparently did not occur during glacial times (Schrage *et al.*, 1996), suggesting that all glacial-age deep-water sources were very cold. Second, and more importantly, North Atlantic deep water formation may have been weaker during the last ice age (Boyle and Keigwin, 1982) (see Chapter 6.16). As this deep-water source is the low preformed nutrient end-member today, its reduction would have worked to increase the preformed nutrient concentration of the deep ocean during the last ice age, potentially offsetting the effects of a decrease in Southern-sourced deep water. These questions about actual events aside, the mean preformed nutrient concentration of the deep ocean provides an important predictive index for the effect of changes in the polar ocean on atmospheric CO<sub>2</sub>.

Some attention has focused on the prevention of CO<sub>2</sub> release from the Antarctic surface by sea ice cover as a potential driver of glacial/interglacial CO<sub>2</sub> change (Stephens and Keeling, 2000). Though the mechanism is essentially physical, it nevertheless would cause an increase in the global

efficiency of the biological pump by removing its polar leak. This is an important reminder that the biological pump is not solely a biological process, but rather arises from the interaction between the biology and physics of the ocean. For prevention of CO<sub>2</sub> release by sea ice cover to be the sole mechanism for glacial/interglacial CO<sub>2</sub> change, nearly complete year-round ice coverage of the Antarctic would be required. This seems unlikely to most investigators (Crosta *et al.*, 1998). As a result, a hybrid hypothesis has been proposed for the glacial Antarctic, in which intense surface stratification and nutrient consumption during the summer was followed by wintertime prevention of gas exchange due to ice cover (Moore *et al.*, 2000). While promising, this mechanism faces a discrepancy with the evidence for lower export production in the glacial Antarctic (see below). In the modern Antarctic, nutrients are supplied to the surface largely by wintertime vertical mixing. Thus, without year-round stratification, higher annual export production would have been required to lower the surface nutrient concentration below current summertime levels, even for a brief summer period. An alternative combined gas exchange limitation/stratification mechanism that does not violate the productivity constraint is that of spatial segregation of the two mechanisms within the Antarctic (Figure 9). Near the Antarctic continental margin, the formation of thick ice cover and its associated salt rejection could drive overturning, but the near-complete ice cover in that region could prevent CO<sub>2</sub> release. The ice formed along the coast would eventually drift into the open Antarctic, where it would melt, thus stratifying the water column and preventing the release of CO<sub>2</sub> from open Antarctic as well. In any case, ice cover provides an alternative or



**Figure 9** North-South (left-to-right) depth section of the shallow Antarctic, (a) under modern conditions, and (b) under glacial conditions as posited by a hybrid hypothesis involving both limitation of gas exchange by sea ice near the Antarctic continent and sea ice melt-driven stratification of the open Antarctic. During glacial times, sea ice formation was likely vigorous in the Antarctic, and the salt rejection during freezing would have worked to increase the density of the surface, perhaps driving vigorous overturning (bold loop close to the Antarctic continent) (Keeling and Stephens, 2001). While this alone would act to ventilate the deep sea and release CO<sub>2</sub> to the atmosphere, the ice coverage may have been adequately dense to prevent CO<sub>2</sub> outgassing, which occurs more slowly than the exchange of heat and O<sub>2</sub> (Stephens and Keeling, 2000). Here, we posit that this region of ice formation and ventilation was limited to the waters close to the Antarctic continent. The winds in the Antarctic would have drawn the ice northward, and some of it would have melted in the open Antarctic. This would have worked to strengthen the vertical stratification in the open Antarctic, which may have reduced CO<sub>2</sub> loss from the ocean in this region (Francois *et al.*, 1997). Depending on the predominant route of deep-ocean ventilation in the modern Antarctic (coastal or open ocean, see text), either the coastal sea ice coverage or the open Antarctic stratification may be taken as the most important limitation on CO<sub>2</sub> release. This hybrid hypothesis has a significant list of requirements in order to be feasible. For instance, the surface waters in the hypothesized region of convection must not mix laterally with the surface waters of the open Antarctic.

additional potential mechanism for preventing the release of biologically sequestered CO<sub>2</sub> from the Antarctic, and future paleoceanographic work must try to provide constraints on its actual importance.

### 6.18.3 TOOLS

While there are many aspects of biological productivity that one might hope to reconstruct through time, there are two parameters that are most fundamental to the biological pump: (i) export production and (ii) nutrient status. In regions where a deviation from major-nutrient limitation is highly unlikely, in particular, the tropical and subtropical ocean, export production is the major regional constraint that local paleoceanographic data can provide. For instance, if export production in the tropics was higher some time in the past, then there are at least two plausible explanations: (i) there was more rapid water exchange between the surface and the nutrient-bearing subsurface water, or (ii) there was an increase in the nutrient content of the subsurface water (and/or in N<sub>2</sub> fixation in the surface; see discussion above). While physically driven changes in nutrient supply (e.g., changes in upwelling intensity) have limited significance for the biological pump, changes in deep-ocean nutrient content could drive a strengthening of the pump and thus an associated decline in atmospheric CO<sub>2</sub> (see discussion above). Thus, it is critical for studies of the biological pump not only to reconstruct changes in low-latitude export production but also to determine what caused the changes.

In the polar ocean, both export production and nutrient status must be known to determine the impact on atmospheric CO<sub>2</sub>, because both of these terms are needed to determine the ratio of CO<sub>2</sub> supply from deep water to CO<sub>2</sub> sequestration by export production (Figure 7). For instance, a decrease in export production associated with an increase in surface nutrients would imply an increased leak in the biological pump, whereas a decrease in export production associated with reduced nutrient availability would imply a smaller leak in the pump. In low-latitude regions of upwelling, nutrient status is less important from the perspective of the global biological pump. Nevertheless, since nutrient status is potentially variable in these environments, it must be constrained to develop a tractable list of explanations for an observed change in productivity.

A great many approaches have been taken to study the biological pump in the past. While there are approaches that take advantage of virtually every aspect of the available geologic archives, we focus here on tools to reconstruct export production and nutrient status and limit ourselves to those that are largely based on geochemical measurement. We refer the interested reader to Fischer and Wefer (1999) for additional information and references.

#### 6.18.3.1 Export Production

Export production, as defined above, is the flux of organic carbon that sinks (or is mixed) out of

the surface ocean and into the deep sea. While it is extremely difficult to imagine how paleoceanographic measurements can provide direct constraints on this highly specific parameter, approaches exist for the reconstruction of the flux of biogenic debris to the seafloor. To the degree that sinking biogenic debris has a predictable chemical composition and that its export out of the surface ocean is correlated with its rain rate to the seafloor, these approaches can provide insight into export production variations (Muller and Suess, 1979; Ruhlemann *et al.*, 1999; Sarthain *et al.*, 1988) (see Chapter 6.04).

Only a very small fraction of the organic carbon exported out of the surface ocean accumulates in deep-sea sediments, with loss occurring both in the water column and at the seafloor. Moreover, various environmental conditions may influence the fraction of export production preserved in the sedimentary record (see Chapter 6.11). The mineral components of the biogenic rain (calcium carbonate, opal) do not represent a source of chemical energy to the benthos and thus may be preserved in a more predictable fashion in deep-sea sediments. Thus, paleoceanographers sometimes hope to reconstruct export production (the flux of organic carbon out of the surface ocean) from the biogenic rain of opal or carbonate to the seafloor (Ruhlemann *et al.*, 1999). We know that systematic variations in the ratio of opal or calcium carbonate to organic carbon in export production do occur, so there are many cases where changes in the mineral flux can be interpreted either as a change in the rate of export production or in its composition. Despite these limitations, we are better off with this information than without it.

The most basic strategy to reconstruct the biogenic rain to the seafloor is to measure accumulation rate in the sediments. This approach is appropriate for materials that accumulate without loss in the sediments or that are preserved to a constant or predictable degree. For the biogenic components of interest, organic carbon, opal, and calcium carbonate, the degree of preservation varies with diverse environmental variables, detracting from the usefulness of accumulation rate for the reconstruction of their rain to the seafloor. Nevertheless, because the environmental variables controlling preservation in the sediments are often linked to rain rate to the seafloor, accumulation rate can sometimes be a sound basis for at least the qualitative reconstruction of changes in some components of the biogenic rain. For instance, the fraction of the opal rain that is preserved in the sediment appears to be higher in opal-rich environments (Broecker and Peng, 1982). As a result, an observed increase in sedimentary opal accumulation rate may have been partially due to an increase in preservation. However, an increase in opal rain (and thus

diatom-driven export) would have been needed to increase the sedimentary opal content in the first place.

If an age model can be developed for a deep-sea sediment core, then the accumulation histories of the various sediment components can be reconstructed. Assuming that the age model is correct, the main uncertainty in the environmental significance of the reconstruction is then the potential for lateral sediment transport. Sediments can be winnowed from or focused to a given site on the seafloor.

The geochemistry of radiogenic thorium provides a way to evaluate the effect of lateral sediment transport and related processes (Bacon, 1984; Suman and Bacon, 1989) (see Chapter 6.09). Thorium-230 ( $^{230}\text{Th}$ ) is produced at a constant rate throughout the oceanic water column by the decay of dissolved  $^{234}\text{U}$ . As  $^{230}\text{Th}$  is produced, it is almost completely scavenged onto particles at the site of its production. As a result, the accumulation rate of  $^{230}\text{Th}$  in deep-sea sediments should match its integrated production in the overlying water column. If the accumulation of  $^{230}\text{Th}$  over a time period, as defined by a sediment age model, is more or less than should have been produced in the overlying water column during that period, then sediment is being focused or winnowed, respectively.

Thorium-230 is also of great use as an independent constraint on the flux of biogenic material to the seafloor (Bacon, 1984; Suman and Bacon, 1989). Because the production rate of  $^{230}\text{Th}$  in the water column is essentially constant over space and time, its concentration in sinking particles is diluted in high-flux environments with a large biogenic flux to the seafloor, yielding lower sedimentary concentrations of  $^{230}\text{Th}$  in these environments. One limitation on the use of  $^{230}\text{Th}$  is the radioactive decay of this isotope, which has a half-life of  $7.5 \times 10^4$  yr. Helium-3 can apparently be used in similar ways to  $^{230}\text{Th}$  and has the advantage that it is a stable isotope (Marcantonio *et al.*, 1996); however, it has been studied less than  $^{230}\text{Th}$ .

The addition of other scavenged elements further enhances the utility of  $^{230}\text{Th}$ .  $^{231}\text{Pa}$ , like  $^{230}\text{Th}$ , is produced throughout the ocean water column by radioactive decay of a uranium isotope ( $^{235}\text{U}$  in the case of  $^{231}\text{Pa}$ ). However, protactinium is somewhat less particle-reactive than thorium. As a result, the downward flux of  $^{231}\text{Pa}$  to the seafloor varies across the ocean. Protactinium from low-flux regions mixes into high-flux regions to be scavenged, resulting in higher  $^{231}\text{Pa}$  fluxes in environments with high biogenic rain rates. Thus, the  $^{231}\text{Pa}/^{230}\text{Th}$  ratio of sediments has been studied as an index of the particle flux through the water column. This index is potentially complementary to thorium-normalized accumulation rates in that the  $^{231}\text{Pa}/^{230}\text{Th}$  ratio



should not be affected by losses during sedimentary diagenesis. Limitations of this approach include (i) the tendency for the less easily scavenged isotope ( $^{231}\text{Pa}$ ) to adsorb preferentially to certain types of particles (e.g., diatom opal), which can make it difficult to distinguish a change in the flux of particles from a compositional change, and (ii) the scavenging of protactinium on basin margins, which can vary in importance as ocean circulation changes (Chase *et al.*, 2003b; Walter *et al.*, 1999; Yu *et al.*, 2001). Beryllium-10 may be used in similar ways to  $^{231}\text{Pa}$  but has been studied less (Anderson *et al.*, 1990).

The flux of barium to the seafloor appears to be strongly related to the rain of organic matter out of the surface ocean (Dehairs *et al.*, 1991). Apparently, the oxidation of organic sulfur produces microsites within sinking particles that become supersaturated with respect to the mineral barite ( $\text{BaSO}_4$ ). On this basis, barium accumulation has been investigated and applied as a measure of export production in the past, representing a more durable sedimentary signal of the organic carbon sinking flux than sedimentary organic carbon itself (Dymond *et al.*, 1992; Gingele *et al.*, 1999; Paytan *et al.*, 1996). While debates continue on aspects of the biogenic barium flux, some problems with preservation are broadly recognized. In sedimentary environments with low bottom water  $\text{O}_2$  and/or high organic carbon rain rates, active sulfate reduction in the shallow sediments can cause the barite flux to dissolve. In addition, there is some low level of barite dissolution under all conditions; if the biogenic barium flux is low, a large fraction of the barite can dissolve at the seafloor. Thus, barium accumulation studies appear to be most applicable to environments of intermediate productivity.

The rapidly growing field of organic geochemistry promises new approaches for the study of biological productivity in the past. By studying specific chemical components of the organic matter found in marine sediments, uncertainties associated with carbon source can be removed, and a richer understanding of past surface conditions can be developed (e.g., Hinrichs *et al.*, 1999; Martinez *et al.*, 1996). To some degree, organic geochemical approaches may allow us to circumvent the thorny problem of breakdown and alteration at the seafloor (Sachs and Repeta, 1999).

### 6.18.3.2 Nutrient Status

The measurable geochemical parameters currently available for addressing the nutrient status of the surface ocean include (i) the Cd/Ca ratio (Boyle, 1988a) and  $^{13}\text{C}/^{12}\text{C}$  of planktonic (surface-dwelling) foraminiferal carbonate (Shackleton *et al.*, 1983), which are intended to record the concentration of cadmium and the

$^{13}\text{C}/^{12}\text{C}$  of DIC in surface water, (ii) the nitrogen isotopic composition of bulk sedimentary organic matter (Altabet and Francois, 1994a) and microfossil-bound organic matter (Shemesh *et al.*, 1993; Sigman *et al.*, 1999b), which may record the degree of nitrate utilization by phytoplankton in surface water, (iii) the silicon isotopic composition (De La Rocha *et al.*, 1998) and Ge/Si ratio (Froelich and Andreae, 1981) of diatom microfossils, which may record the degree of silicate utilization in surface water (but see Bareille *et al.* (1998)), and (iv) the carbon isotopic composition of organic matter in sediments (Rau *et al.*, 1989) and diatom microfossils (Rosenthal *et al.*, 2000; Shemesh *et al.*, 1993), which may record the dissolved  $\text{CO}_2$  concentration of surface water and/or the carbon uptake rate by phytoplankton.

The concentration of dissolved cadmium is strongly correlated with the major nutrients throughout the global deep ocean, and the Cd/Ca ratio of benthic (seafloor-swelling) foraminifera shells records the cadmium concentration of seawater (Boyle, 1988a). As a result, benthic foraminiferal Cd/Ca measurements allow for the reconstruction of deep-ocean nutrient concentration gradients over glacial/interglacial cycles. Planktonic foraminiferal Cd/Ca measurements in surface water provide an analogous approach to reconstruct surface ocean nutrient concentration, although this application has been less intensively used and studied.

A number of factors appear to complicate the link between planktonic foraminiferal Cd/Ca and surface nutrient concentrations in specific regions. First, temperature may have a major effect on the Cd/Ca ratio of planktonic foraminifera (Elderfield and Rickaby, 2000; Rickaby and Elderfield, 1999). Second, planktonic foraminiferal shell growth continues below the surface layer (Bauch *et al.*, 1997; Kohfeld *et al.*, 1996) and probably integrates the Cd/Ca ratio of surface and shallow subsurface waters. This is of greatest concern in polar regions such as the Antarctic, where there are very sharp vertical gradients within the depth zone in which planktonic foraminiferal calcification occurs. Third, carbonate geochemistry on the deep seafloor may affect the Cd/Ca ratio of foraminifera preserved in deep-sea sediments (McCorkle *et al.*, 1995). Finally, the link between cadmium and phosphate concentration in surface waters is not as tight as it is in deeper waters (Frew and Hunter, 1992).

Because of isotopic fractionation during carbon uptake by phytoplankton, there is a strong correlation between the  $^{13}\text{C}/^{12}\text{C}$  of DIC and nutrient concentration in deep waters; as a result, the  $^{13}\text{C}/^{12}\text{C}$  of benthic foraminiferal fossils is a central tool in paleoceanography. The  $^{13}\text{C}/^{12}\text{C}$  of planktonic foraminiferal calcite has been used as a tool to study the strength of the biological

pump (Shackleton *et al.*, 1983). However, the exchange of CO<sub>2</sub> with the atmosphere leads to a complicated relationship between the <sup>13</sup>C/<sup>12</sup>C of DIC and the nutrient concentration in surface waters (Broecker and Maier-Reimer, 1992), such that even a perfect reconstruction of surface water <sup>13</sup>C/<sup>12</sup>C would not provide direct information of surface-ocean nutrient status. In addition, the <sup>13</sup>C/<sup>12</sup>C of planktonic foraminiferal fossils found in surface sediments appears to be an imperfect recorder of the <sup>13</sup>C/<sup>12</sup>C of DIC in modern surface waters, for a variety of reasons (Spero *et al.*, 1997; Spero and Lea, 1993; Spero and Williams, 1988). Finally, the same concerns about the calcification depth noted for Cd/Ca also apply to carbon isotopes or, for that matter, any geochemical signal in planktonic foraminiferal calcite.

During nitrate assimilation, phytoplankton preferentially consume <sup>14</sup>N-nitrate relative to <sup>15</sup>N-nitrate (Montoya and McCarthy, 1995; Waser *et al.*, 1998), leaving the surface nitrate pool enriched in <sup>15</sup>N (Sigman *et al.*, 1999a). This results in a correlation between the <sup>15</sup>N/<sup>14</sup>N ratio of organic nitrogen and the degree of nitrate utilization by phytoplankton in surface waters (Altabet and Francois, 1994a,b). There are major uncertainties in the use of this correlation as the basis for paleoceanographic reconstruction of nutrient status, which include (i) the isotopic composition of deep-ocean nitrate through time, (ii) temporal variations in the relationship between nitrate utilization and the nitrogen isotopes in the surface ocean (i.e., the “isotope effect” of nitrate assimilation), and (iii) the survival of the isotope signal of sinking organic matter into the sedimentary record (e.g., Lourey *et al.*, in press). The nitrogen isotope analysis of microfossil-bound organic matter (Sigman *et al.*, 1999b) and of specific compound classes such as chlorophyll-degradation products (Sachs and Repeta, 1999) promises to provide tools to evaluate and circumvent the effect of diagenesis. However, it remains to be seen whether selective nitrogen pools such as microfossil-bound nitrogen are tightly linked to the nitrogen isotope ratio of the integrated sinking flux, the parameter that theoretically relates most directly to the degree of nitrate utilization in surface waters (Altabet and Francois, 1994a).

The isotopic composition of silicon in diatom opal has been investigated as a proxy for the degree of silicate utilization by diatoms, based on the fact that diatoms fractionate the silicon isotopes (<sup>30</sup>Si and <sup>28</sup>Si) during uptake (De La Rocha *et al.*, 1997, 1998). This application is analogous to the use of nitrogen isotopes to study nitrate utilization, but with important differences. On the one hand, the upper ocean cycle is arguably simpler for silica than bio-available nitrogen, which bodes well for the silicon isotope system.

On the other hand, there are very few regions of the surface ocean that maintain high dissolved silicate concentrations (Figure 4(d)). As a result, in regions of strong silicate gradients, the link between silicate utilization and silicon isotopic composition may be compromised by mixing processes in surface waters.

The carbon isotopic composition of sedimentary organic matter was originally developed as a paleoceanographic proxy for the aqueous CO<sub>2</sub> concentration of Southern Ocean surface waters (Rau *et al.*, 1989). The aqueous CO<sub>2</sub> concentration is a nearly ideal constraint for understanding a region’s effect on the biological pump, as it would provide an indication of its tendency to release or absorb carbon dioxide. However, it has become clear that growth rate and related parameters are as important as the concentration of aqueous CO<sub>2</sub> for setting the <sup>13</sup>C/<sup>12</sup>C of phytoplankton biomass and the sinking organic matter that it yields (Popp *et al.*, 1998). In addition, active carbon acquisition by phytoplankton is also probably important for phytoplankton <sup>13</sup>C/<sup>12</sup>C in at least some environments (Keller and Morel, 1999). Thus, the <sup>13</sup>C/<sup>12</sup>C of organic carbon is a useful paleoceanographic constraint (Rosenthal *et al.*, 2000), but one that is currently difficult to interpret in isolation.

### 6.18.3.3 Integrative Constraints on the Biological Pump

Above, we have focused on approaches to reconstruct the role of a specific region of the surface ocean on the global biological pump. However, if our goal is to explain the global net effect of ocean biology on the carbon cycle, we must also search for less local, more integrative constraints on the biological pump. This is possible because the atmosphere, surface ocean and deep sea are each relatively homogeneous geochemical reservoirs, while being distinct from one another. There are a number of global scale geochemical parameters that may provide important constraints on the biological pump; we describe several of these below.

#### 6.18.3.3.1 Carbon isotope distribution of the ocean and atmosphere

As described above, the biological pump tends to sequester <sup>12</sup>C-rich carbon in the ocean interior. All else being equal, the stronger the global biological pump, the higher will be the <sup>13</sup>C/<sup>12</sup>C of dissolved inorganic carbon in the surface ocean and of carbon dioxide in the atmosphere. Broecker (1982a,b) and Shackleton (see Shackleton *et al.*, 1983) compared sediment core records of

the  $^{13}\text{C}/^{12}\text{C}$  of calcite precipitated by planktonic and benthic foraminifera, the goal being to reconstruct the  $^{13}\text{C}/^{12}\text{C}$  difference in DIC between the surface ocean and the deep sea, a measure of the strength of the global ocean's biological pump. Indeed, this work was the first suggestion that the biological pump was stronger during ice ages, thus potentially explaining the lower  $\text{CO}_2$  levels of glacial times. Our view of these results is now more complicated (e.g., [Spero et al., 1997](#)); however, the basic conclusion remains defensible ([Hofmann et al., 1999](#)). Reliable measurement of the  $^{13}\text{C}/^{12}\text{C}$  of atmospheric  $\text{CO}_2$  has proven challenging ([Leuenberger et al., 1992](#); [Marino and McElroy, 1991](#); [Smith et al., 1999](#)). Moreover, there are additional modifiers of the  $^{13}\text{C}/^{12}\text{C}$  of atmospheric  $\text{CO}_2$ , such as the temperature of gas exchange. Nevertheless, these data also seem consistent with the biological pump hypothesis for glacial/interglacial  $\text{CO}_2$  change ([Smith et al., 1999](#)).

#### 6.18.3.3.2 Deep-ocean oxygen content

The atmosphere/ocean partitioning of diatomic oxygen ( $\text{O}_2$ ) is a potentially important constraint on the strength of the biological pump; the stronger the pump, the more  $\text{O}_2$  will be shuttled from the deep ocean to the surface ocean and atmosphere. The rain of organic detritus into the deep ocean drives an  $\text{O}_2$  demand by the deep-ocean benthos as it sequesters carbon dioxide in the deep sea, while exposure of deep waters at the surface recharges them with  $\text{O}_2$  as it allows deep waters to degas excess  $\text{CO}_2$  to the atmosphere ([Figure 6](#)). A decrease in atmospheric  $\text{CO}_2$  due to the biological pump should, therefore, be accompanied by a decrease in the  $\text{O}_2$  content of the ocean subsurface.

The concentration of dissolved  $\text{O}_2$  in the ocean interior has long been a target for paleoceanographic reconstruction (the atmospheric change in  $\text{O}_2$  content would be minute). Sediments underlying waters with nearly no  $\text{O}_2$  tend to lack burrowing organisms, so that sediments in these regions are undisturbed by "bioturbation" and can be laminated; this is perhaps our most reliable paleoceanographic indicator of deep-water  $\text{O}_2$  content. Arguments have been made for surface area-normalized sedimentary organic carbon content as an index of  $\text{O}_2$  content in some settings ([Keil and Cowie, 1999](#)). It remains to be seen whether this is complicated by the potential for changes in the rain rate of organic matter to the sediments. There are a number of redox-sensitive metals, the accumulation of which gives information on the  $\text{O}_2$  content of the pore water in shallow sediments ([Anderson et al., 1989](#); [Crusius et al., 1996](#); [Crusius and Thomson, 2000](#)). Unfortunately, the  $\text{O}_2$  content of the sediment

pore waters can vary due to organic matter supply to the sediments as well as the  $\text{O}_2$  content of the bottom water bathing the seafloor, so that these two parameters can be difficult to separate (a situation that is analogous to that for sedimentary organic carbon content). While interesting data and arguments have been put forward in support of various approaches ([Hastings et al., 1996](#); [Russell et al., 1996](#)), it seems fair to argue that the paleoceanographic community still lacks a reliable set of methods for the global reconstruction of deep ocean dissolved  $\text{O}_2$  content, especially in environments far from complete  $\text{O}_2$  consumption.

Initial model results suggested that a biological pump mechanism for the glacial/interglacial  $\text{CO}_2$  change would have rendered the ocean subsurface so  $\text{O}_2$  deficient as to prevent the presence of burrowing organisms and oxic respiration over large expanses of the seafloor, which should leave some tell-tale signs in the sediment record. However, observations have changed this story significantly. For instance, the  $\text{O}_2$  minimum, which is at intermediate depths in the modern ocean, may have migrated downward into the abyssal ocean during the last ice age ([Berger and Lange, 1998](#); [Boyle, 1988c](#); [Herguera et al., 1992](#); [Marchitto et al., 1998](#)), so that the  $\text{O}_2$  decrease was apparently focused in waters which are currently relatively rich in  $\text{O}_2$ , perhaps avoiding widespread anoxia at any given depth ([Boyle, 1988c](#)). For this reason, testing the biological pump hypothesis by reconstructing deep ocean  $\text{O}_2$  will require that we do more than simply search for extensive deep-sea anoxia; rather, it will probably require a somewhat quantitative indicator of dissolved  $\text{O}_2$  that works at intermediate  $\text{O}_2$  concentrations.

#### 6.18.3.3.3 Phasing

With adequate dating and temporal resolution in paleoceanographic and paleoclimatic records, the sequence of past events and changes can be reconstructed, providing among the most direct evidence for cause and effect. There is much information on phasing that is relevant to the biological pump and its role in glacial/interglacial  $\text{CO}_2$  change. We limit ourselves here to one example that arises largely from ice core records: the timing of  $\text{CO}_2$  change relative to temperature and glaciation ([Broecker and Henderson, 1998](#) and references therein). Near the end of ice ages, atmospheric  $\text{CO}_2$  rises well before most of the deglaciation ([Monnin et al., 2001](#); [Sowers and Bender, 1995](#)); this was referred to above as strong evidence against Broecker's shelf phosphorus hypothesis for  $\text{CO}_2$  change (see [Section 6.18.2.1](#)). While the phasing of temperature is

still debated, it appears that most of the warming in the high-latitude southern hemisphere preceded most of the warming in the high-latitude northern hemisphere, and that the atmospheric CO<sub>2</sub> rise lagged only slightly behind the southern hemisphere warming. This latter observation is roughly consistent with a variety of hypotheses for changes in the biological pump, but appears inconsistent with alternative hypotheses that rely solely on changes in the oceanic calcium carbonate budget, which operates on a longer timescale than the biological pump (Archer and Maier-Reimer, 1994; Opdyke and Walker, 1992). With continued work, the detailed timing of CO<sub>2</sub> change may provide quantitative constraints on changes in the oceanic calcium carbonate budget as a partial contributor to CO<sub>2</sub> change; calcium carbonate plays a role in many of the biological pump hypotheses (Archer *et al.*, 2000a; Sigman *et al.*, 1998; Toggweiler, 1999).

#### 6.18.4 OBSERVATIONS

To this point, a number of central observations and concepts have already been described to motivate a search for changes in the biological pump over glacial/interglacial cycles. First, there are carbon dioxide variations over glacial/interglacial cycles that are of the right magnitude and temporal structure to be caused by changes in the biological pump. Second, carbon isotope data for carbon dioxide and foraminiferal carbonate appear consistent with a biological-pump mechanism. Third, changes in the nitrogen cycle have been recognized that would tend to increase the oceanic nitrate reservoir during glacial times, although an actual increase in this reservoir has not been demonstrated; such a reservoir change might be expected to strengthen the low-latitude pump during glacial times. Finally, observations about phytoplankton in polar regions, in particular, their incomplete consumption of the major nutrients and their tendency toward iron limitation, suggest that simple changes in either the iron supply to the Antarctic surface ocean or in polar ocean circulation could lead to an increase in the efficiency of the high-latitude biological pump during glacial times. These observations, together with other ideas about the operation of the ocean carbon cycle, warrant that we consider the basic regional observations on biological productivity and nutrient status over glacial/interglacial cycles.

##### 6.18.4.1 Low- and Mid-latitude Ocean

There have been many studies of the response of coastal and equatorial upwelling systems to glacial/interglacial climate change, and this

overview cannot do justice to the entire body of work. The coastal upwelling regions along the western continental margins show an Atlantic/Pacific difference in their response to glacial/interglacial climate change. Studies along the western coast of Africa suggest an increase in productivity during glacial times (Summerhayes *et al.*, 1995; Wefer *et al.*, 1996). However, in the eastern Pacific, the coastal upwelling zones off of California and Mexico in the north and off of Peru in the south were less productive during the last glacial period (Dean *et al.*, 1997; Ganeshram and Pedersen, 1998; Ganeshram *et al.*, 2000; Heinze and Wefer, 1992). This response has generally been explained as the effect of continental cooling (and a large North American ice sheet in the case of the California Current) on the winds that currently drive coastal upwelling in the eastern tropical Pacific (Ganeshram and Pedersen, 1998; Herbert *et al.*, 2001).

Early paleoceanographic studies in the equatorial Pacific found that export production was greater in the equatorial Pacific during ice ages (Lyle, 1988; Pedersen, 1983; Pedersen *et al.*, 1991; Rea *et al.*, 1991), and some subsequent studies have supported this conclusion (Herguera and Berger, 1991; Murray *et al.*, 1993; Paytan *et al.*, 1996; Perks *et al.*, 2000). However, this interpretation has been put in question by reconstructions using <sup>230</sup>Th- and <sup>3</sup>He-normalized accumulation rates, <sup>231</sup>Pa/<sup>230</sup>Th ratios (Marcantonio *et al.*, 2001b; Schwarz *et al.*, 1996; Stephens and Kadko *et al.*, 1997) and other evidence (Loubere, 1999). From studies along the eastern equatorial Atlantic, the consensus is for higher productivity during the last ice age than the Holocene; because of the limited extent of the Atlantic basin, it is difficult to differentiate this change from the glacial-age increase in productivity in African coastal upwelling (Lyle *et al.*, 1988; Martinez *et al.*, 1996; Moreno *et al.*, 2002; Rutsch *et al.*, 1995; Schneider *et al.*, 1996). Proxies for nutrient utilization (Altabet, 2001; Farrell *et al.*, 1995; Holmes *et al.*, 1997), pH (Sanyal *et al.*, 1997), and wind strength (Stutt *et al.*, 2002) would suggest that any export production increases that did occur in the low-latitude upwelling systems of the Pacific and Atlantic during the last glacial maximum were due to higher wind-driven upwelling, which increased the nutrient supply to the surface.

Upwelling associated with monsoonal circulation has apparently behaved predictably since the last ice age (Duplessy, 1982; Prell *et al.*, 1980). With less summertime warming of the air over Asia during the last glacial maximum, there was a weakening of the southwesterly winds of the summertime monsoon that drive coastal upwelling off the horn of Africa and Saudi Arabia, leading to a glacial decrease in export production in that



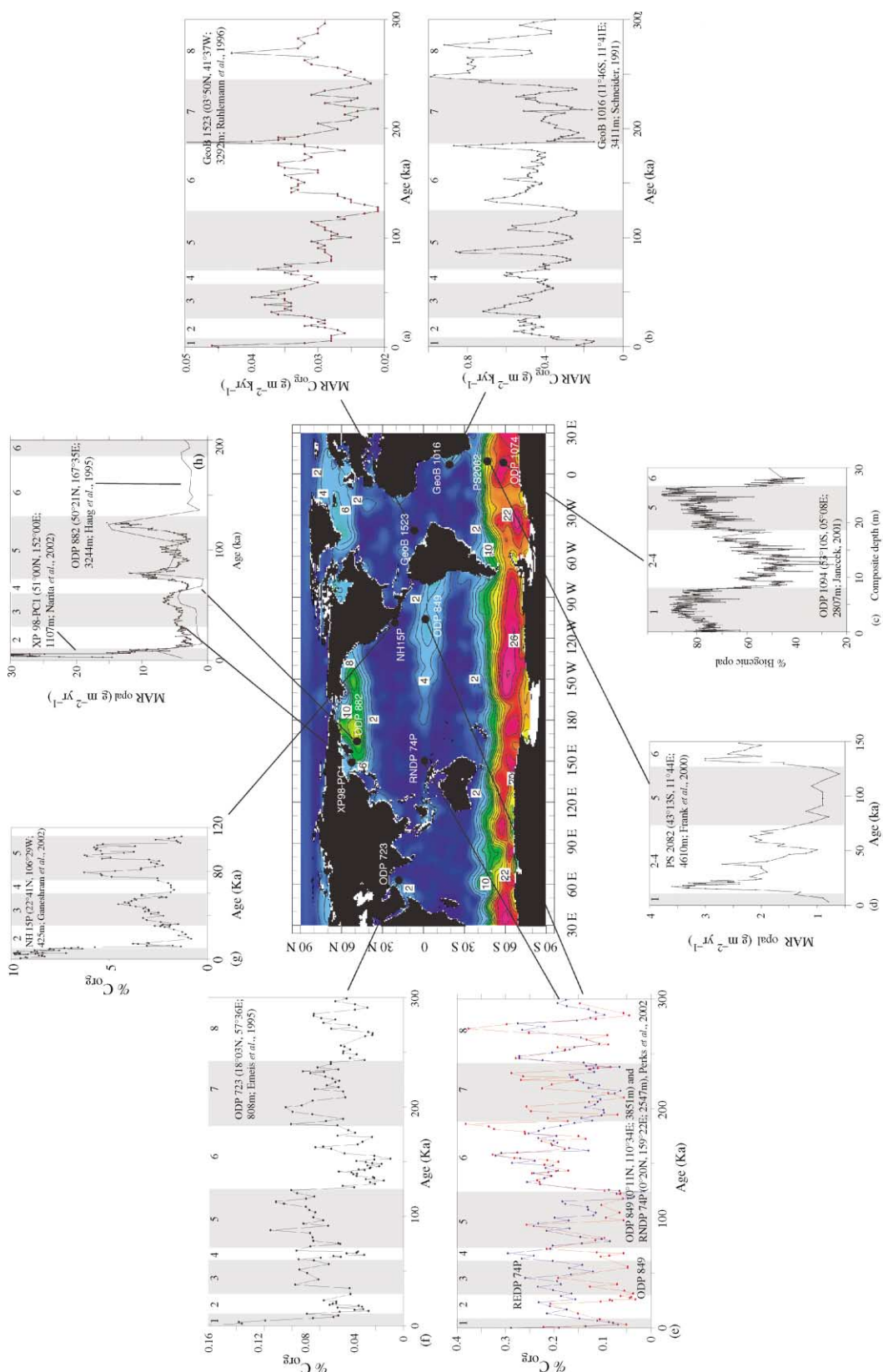
region (Altabet *et al.*, 1995; Anderson and Prell, 1993; Marcantonio *et al.*, 2001a; Prell *et al.*, 1980). To the east and in the more open Indian Ocean, where the (southward) wintertime monsoonal winds drive upwelling or vertical mixing, productivity was apparently higher during the last glacial maximum, again consistent with the expected effect of a cooler Eurasian climate on the monsoon cycle (Beaufort, 2000; Duplessy, 1982; Fontugne and Duplessy, 1986). In the South China Sea, where the winter monsoon (seaward flow) is responsible for the exposure of nutrient-rich deep waters, export production was apparently higher during the last glacial maximum, again suggesting a stronger winter monsoon associated with colder winter conditions over Eurasia (Huang *et al.*, 1997; Thunell *et al.*, 1992). The effect of the wintertime monsoon winds may also have impacted the western equatorial Pacific (Herguera, 1992; Kawahata *et al.*, 1998).

The low-productivity regions of the low- and mid-latitude ocean are an important source of information on the strength of the low-latitude biological pump, as they may be less susceptible to wind-driven changes in nutrient supply than are the upwelling regions discussed above, so that changes in productivity would be more closely tied to changes in the oceanic nutrient reservoir (and/or in  $N_2$  fixation). As mentioned above, studies in the western equatorial Pacific indicate that the sedimentary  $C_{org}$  was higher in these regions during glacial times (Figure 10; Perks *et al.* (2000)); however, studies from the more southern western Pacific appear to suggest lower productivity (Kawahata *et al.*, 1999). Studies in the western equatorial and tropical Atlantic indicate lower  $CaCO_3$  and  $C_{org}$  burial rates during glacial times (François *et al.*, 1990; Ruhlemann *et al.*, 1996). In the tropical Indian Ocean, away from the Arabian Sea, productivity was apparently higher during glacial times, but this has again been explained as the result stronger wind-driven mixing during the wintertime monsoon (Beaufort, 2000; Fontugne and Duplessy, 1986). Discrete sedimentation events of massive mat-forming diatoms are found in glacial-age sediments from the equatorial Indian; their significance is unclear (Broecker *et al.*, 2000).

As described in Section 6.18.2, there is substantial evidence for a change in the spatial pattern of denitrification across glacial/interglacial transitions (Altabet *et al.*, 1995, 2002; Emmer and Thunell, 2000; Ganeshram *et al.*, 1995; Pride *et al.*, 1999), and it seems likely that this led to a net global decrease in the loss rate of nitrate from the ocean during the last glacial maximum. Depending on the changes in  $N_2$  fixation over glacial/interglacial cycles and the role of phosphorus in these changes (see Section 6.18.2), low-latitude productivity may or may not have responded so as

to strengthen the biological pump. As discussed above, increased low-latitude productivity due to increased upwelling or vertical mixing has limited significance for the strength of the biological pump. It is a challenge to develop an approach to study past productivity changes that can distinguish between a change in the physical rate of vertical exchange and a change in the nutrient content of the subsurface. Thus, it is difficult to test the hypothesis that the ocean nutrient reservoir drove a significant glacial increase in the low- and mid-latitude biological pump, so as to explain glacial/interglacial  $CO_2$  changes. Nevertheless, it is notable that no direct support for the hypothesis has arisen without a focused search. Based on the overview above, the evidence for a net global increase in low-latitude productivity during the last ice age is not compelling. Moreover, the evidence that does exist for regional increases in low-latitude productivity seems easily explained in terms of changes in the wind-driven upwelling. Comparison of accumulation records for organic carbon and opal (Herguera and Berger, 1994) and of records from opposite sides of the South Atlantic basin (Ruhlemann *et al.*, 1999) has led to the suggestion that the nutrient content of the thermocline was lower during ice ages. If such was indeed the case, it could be associated with a tendency for nutrients to shift into the deeper ocean during ice ages (Boyle, 1988b,c); nevertheless, it provides little encouragement for hypotheses of a larger oceanic nutrient reservoir during glacial times.

While it is tempting to phrase orbitally driven climate variability in terms of “ice ages” and “interglacials,” this simplification breaks down frequently in the lower-latitude ocean (Clemens *et al.*, 1991; McIntyre and Molino, 1996; Sachs *et al.*, 2001). The precession component of the Earth’s orbital variations is by far the most directly important for the energy budget of the tropics. The Pleistocene variability of productivity in some tropical regions (Pailler *et al.*, 2002) and coastal and equatorial upwellings (Moreno *et al.*, 2002; Rutsch *et al.*, 1995; Summerhayes *et al.*, 1995) is dominated by the precession ( $\sim 23$  kyr) cycle, with the result that our focus on the Last Glacial Maximum/Holocene comparison can be misleading about the real timing of change. New data make this case very strongly for equatorial Pacific productivity (Perks *et al.*, 2000). As the variations in atmospheric  $CO_2$ , glacial ice volume, and polar temperature all have less variability at the precession frequency, one would surmise that the low-latitude productivity changes dominated by precession are not major drivers of variability in the biological pump or in atmospheric  $CO_2$ . This is consistent with the conceptual point that wind-driven changes in low-latitude productivity



are of limited importance to CO<sub>2</sub> transfer between the atmosphere and ocean.

#### 6.18.4.2 High-latitude Ocean

The global high-latitude open ocean includes the Arctic, the North Atlantic, the Southern Ocean, and the Subarctic North Pacific (Figure 5). We address each of these in turn.

The modern open Arctic appears to be relatively unproductive. Annually averaged solar insolation is low and sea ice cover is extensive, so that light limitation of phytoplankton growth is likely. Surface nitrate is also quite low in the Arctic surface (Figure 5(c)), at least partially due to a strong permanent “halocline,” or vertical salinity gradient, that drives a strong vertical density gradient in the upper Arctic ocean, isolating fresh surface waters from saltier and thus denser nutrient-rich deep water. However, as the major nutrients are not completely absent in the surface, the major nutrients are probably not the dominant limitation for phytoplankton in the open

Arctic. The few paleoproductivity studies of the open Arctic suggest that it was less productive during the last ice age (Schubert and Stein, 1996; Wollenburg *et al.*, 2001). A range of ice age conditions may have contributed to this decrease, including greater ice cover and thus more extreme light limitation as well as sea-level-driven loss of the nutrient supply from the Pacific that currently enters from the Bering Strait. Our current understanding of the Arctic would suggest that it is not in itself a central part of ocean/atmosphere CO<sub>2</sub> partitioning, so little energy has been expended to understand its glacial/interglacial cycle.

The high-latitude North Atlantic has a productive spring bloom but tends towards major-nutrient limitation in the summer. This tendency toward nutrient limitation is due at least partially to the formation of deep water in the high-latitude North Atlantic. The Gulf Stream extension provides salty, warm, low-nutrient water to the high-latitude surface, and the cooling of this water eventually leads to the formation of deep waters (see Chapter 6.16). As a result of this steady state, neither surface waters nor underlying deep waters

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**Figure 10** Paleooceanographic records relevant to the history of export production from various regions of the global ocean, overlain on a map of surface nitrate concentration (in  $\mu\text{M}$ ; Conkright *et al.*, 1994). The records are chosen to be somewhat representative as a crude first-order paleoproductivity record for their oceanic regime; the extreme uncertainty associated with some of these reconstructions is discussed at length in Section 6.18.2. The records are of the sedimentary concentration or accumulation of organic carbon or biogenic opal. While the concentration records are complicated by potential changes in dilution by other sediment components, there are some circumstances where accumulation rate estimates are also problematic. The referenced sources should be consulted for information on these concerns. The biogeochemical regime of the surface ocean is roughly indicated by surface nitrate concentration (see Figure 5), which indicates whether a record is from a nutrient-poor, low-latitude region, a nutrient-bearing low-latitude upwelling region, or a nutrient-bearing polar region. Records are plotted versus time (except core ODP 1094 in the Southern Ocean) and glacial–interglacial stages are numbered, with a gray shading during interglacials. (a) The  $C_{\text{org}}$  accumulation record from core GeoB 1523 for the last 300 ka (Ruhlemann *et al.*, 1996) conforms with the general finding that productivity was lower in the oligotrophic tropical Atlantic during the last ice age. (b) The  $C_{\text{org}}$  accumulation record from core GeoB 1016 for the last 300 ka (Schneider, 1991) is among the large body of evidence indicating that the Benguela upwelling system and the eastern equatorial Atlantic were more productive during the last ice age. However, all of the Atlantic records show a strong precessional response, indicating only a loose connection with ice volume. Ruhlemann *et al.* (1999) have noted an anti-correlation between eastern and western tropical Atlantic records. (c) Biogenic opal concentrations of ODP Site 1094 in the Antarctic zone of Southern Ocean (Janecek, 2001) conform with the large body of data indicating lower opal accumulation rates during ice ages. The upper 30 m of the composite sediment sequence represent approximately the last 135 ka. (d) Biogenic opal accumulation rate in core PS2062 (Frank *et al.*, 2000) over the last 150 ka conforms with a large body of data indicating higher opal and organic carbon accumulation in the Subantarctic zone of the Southern Ocean during ice ages, opposite to the temporal pattern observed in the Antarctic. (e) The  $C_{\text{org}}$  concentration in RNDP 74P from the western equatorial Pacific and in ODP Site 849 from the eastern equatorial Pacific over the last 300 ka (Perks *et al.*, 2000) suggests higher productivity across the entire equatorial upwelling during the last ice age but shows its dominant response to precession, not polar ice volume. (f) The  $C_{\text{org}}$  concentration in ODP Site 723 over the last 300 ka (Emeis *et al.*, 1995) conforms with the large body of data suggesting lower productivity in the Oman upwelling system during ice ages because of a weaker summer monsoon (and thus weaker upwelling) when Eurasia is cold. (g) The  $C_{\text{org}}$  concentration in core NH15P during the last 120 ka in the coastal upwelling zone off northwestern Mexico (Ganeshram and Pedersen, 1998) conforms with a large body of data indicating lower productivity during the last ice age because the North American ice sheet caused a reduction in wind-driven coastal upwelling. (h) Biogenic opal accumulation rates in the Subarctic North Pacific (ODP Site 882; Haug *et al.* (1995)) and the Okhotsk Sea (Core XP98-PC1 Narita *et al.* (2002)) suggest lower diatom export during glacials, perhaps because of stronger salinity stratification of the upper water column and thus reduced nutrient supply. See text for more references.

can supply large amounts of nutrients to the surface, with the largest nutrient source being the Antarctic Intermediate Water that penetrates from the south. The equivocal evidence for changes in North Atlantic productivity over glacial/interglacial cycles appears to suggest lower export production during the last ice age (Manighetti and McCave, 1995; Thomas *et al.*, 1995). This is consistent with the persistent formation of a low-nutrient subsurface water in the glacial North Atlantic (Oppo and Lehman, 1993), even though this water mass was distinct from modern North Atlantic Deep Water (again, see Chapter 6.16). If, during ice ages, the North Atlantic continued to import lower-latitude surface waters and produce a subsurface water mass with low preformed nutrients, then it would have played roughly the same role in the biological pump as it does today. However, a glacial weakening of the North Atlantic source would have had implications for the global mean preformed nutrient concentration of the deep ocean (Section 6.18.2.2 and Figure 8).

Paleoceanographic work in the Southern Ocean indicates a strong glacial/interglacial oscillation, but with very different responses in the (poleward) Antarctic than in the (equatorward) Subantarctic. In the modern Antarctic, biological export production is dominated by diatoms, the group of phytoplankton that precipitate tests of hydrated silica (“opal”), and these microfossils are frequently the dominant component of the underlying sediments. The accumulation of diatomaceous sediments in the Antarctic was clearly lower during the last ice age (Mortlock *et al.*, 1991), and other paleoceanographic indicators suggest that the biological export of carbon was also lower (Francois *et al.*, 1997; Kumar *et al.*, 1995; Rosenthal *et al.*, 2000). However, given an apparent bias of at least some of these proxies to preferentially record the carbon export closely associated with diatom microfossils (Chase *et al.*, 2003b; Yu *et al.*, 2001), it remains possible that the biological export of carbon from the glacial Antarctic surface was as high or higher than during interglacial times but that it occurred in a form that was poorly preserved in the sediment record (Arrigo *et al.*, 1999; Boyle, 1998; Brzezinski *et al.*, 2002; DiTullio *et al.*, 2000; Moore *et al.*, 2000; Tortell *et al.*, 2002).

In the Atlantic and Indian sectors of the Subantarctic, there is very strong evidence for higher export production during glacial times and an associated increase in the relative importance of diatom production (Chase *et al.*, 2001; Francois *et al.*, 1997; Kumar *et al.*, 1995; Mortlock *et al.*, 1991; Rosenthal *et al.*, 1995). This high glacial productivity has not yet been recognized in the Pacific sector (Chase *et al.*, 2003a). If this productivity increase was indeed absent in the Pacific sector of the Subantarctic, it provides

an important constraint on its cause. For instance, this finding may be consistent with iron fertilization as the dominant driver of the glacial increase in Subantarctic productivity, as the increase in iron input may have been extremely limited in parts of the Pacific sector (Chase *et al.*, 2003a).

While these changes in export production are critical to the workings of the ice age Southern Ocean, they do not address directly the effect of the Southern Ocean on atmospheric CO<sub>2</sub>, which is largely determined by the competition between the upwelling of respiratory CO<sub>2</sub> and nutrients to the surface and export of organic matter out of the surface (Section 6.18.2). In the Antarctic, nitrogen isotope data suggest that the fraction of the nitrate consumed during the last ice age was higher than its current value (Francois *et al.*, 1997; Sigman *et al.*, 1999b). These results seem to support the long-standing hypothesis that nutrient utilization changes in Antarctic waters are a fundamental driver of glacial/interglacial changes in the atmospheric concentration of CO<sub>2</sub>; box model calculations predict the 25–40% higher nitrate utilization (i.e., 50–65% in the glacial ocean compared to 25% during the present interglacial) could lower atmospheric CO<sub>2</sub> by the full glacial/interglacial amplitude under the relevant conditions (Sigman *et al.*, 1999b). Since paleoceanographic proxy data suggest that Antarctic export production was lower during the last ice age, one would infer that more complete nitrate utilization in the Antarctic was due to a lower rate of nitrate supply from the subsurface, implying that the fundamental driver of the CO<sub>2</sub> change was an ice age decrease in the ventilation of deep waters at the surface of the Antarctic (Francois *et al.*, 1997). Such a change in the Antarctic would also help to explain observations in the low-latitude ocean. For instance, the extraction of nutrients in the Antarctic should lower the nutrient content of the waters that subducted into the intermediate-depth ocean and thermocline at the equatorward margin of the Antarctic. This would work to prevent the transfer of nutrients from cold, deep ocean into the warmer, upper ocean, potentially explaining an apparent transfer of nutrients from the mid-depths to the deep ocean during glacial times (Boyle, 1988b; Herguera *et al.*, 1992; Keir, 1988; Matsumoto *et al.*, 2002a; Sigman and Boyle, 2000).

Two possible causes for Antarctic stratification have been discussed. First, the southern hemisphere westerlies winds apparently shifted northward during glacial times (Hebbeln *et al.*, 2002; McCulloch *et al.*, 2000), which should have reduced Ekman-driven upwelling in the Antarctic (Toggweiler *et al.*, 1999) (“wind-shift” mechanism). Second, the vertical gradient in density, as determined jointly by the vertical gradients in temperature and salinity, may have been stronger in the glacial Antarctic (“density” mechanism).



However, both of these mechanisms are currently incomplete as explanations for the glacial reduction in atmospheric CO<sub>2</sub> (Keeling and Visbeck, 2001; Sigman and Boyle, 2001). As an example, we consider the “density” mechanism in more detail. In the modern Antarctic, as in most polar regions, the vertical salinity gradient tends to stratify the upper ocean, while temperature tends to destabilize it. Thus, either an increase in the relative importance of salinity or a decrease in the importance of temperature could be the fundamental trigger for the development of strong stratification in the glacial Antarctic; once stratification begins, it will be reinforced by the accumulation of freshwater in the upper layer. Given the abundance of sea ice in the glacial Antarctic (Crosta *et al.*, 1998) and the typical association of sea ice with freshwater release, it is tempting to call upon sea ice as the initial driver of stratification. However, sea ice does not represent a source of freshwater *per se*, but rather a mechanism for transporting freshwater from one region of the Antarctic to another, with net ice formation in the coastal Antarctic and net melting in the open Antarctic. As a result, stratification of the open Antarctic by the melting of sea ice might occur at the expense of the coastal Antarctic, where sea ice formation would make surface waters more saline and thus more dense, leading to overturning and the accompanying release of CO<sub>2</sub> to the atmosphere. Thus, we are more encouraged by hypotheses that involve changes in temperature (i.e., cooling of the deep ocean) as the trigger for stratification (Gildor and Tziperman, 2001; Gildor *et al.*, 2002), although these have been tested only in simple physical models. In any case, if the evidence for stratification could be taken as overwhelming, we would still need to determine what caused it and how much it lowered atmospheric CO<sub>2</sub> during glacial times.

However, the evidence for Antarctic stratification is not overwhelming; indeed, many investigators are not convinced (e.g., Anderson *et al.*, 1998; Elderfield and Rickaby, 2000). The interpretation from nitrogen isotopes of higher nitrate utilization in the Antarctic faces a number of apparent disagreements with other proxies of nutrient status, in particular, the Cd/Ca (Boyle, 1988a; Keigwin and Boyle, 1989) and <sup>13</sup>C/<sup>12</sup>C (Charles and Fairbanks, 1988) of planktonic foraminiferal calcite. Measurements of these ratios in planktonic foraminifera indicate no clear decrease in the nutrient concentration of Antarctic surface water, while such a decrease would have been expected on the basis of the nitrogen isotope data. Each of the paleochemical proxies has significant uncertainties (see Section 6.18.3.2). Nevertheless, the need to define new interpretations of a variety of measurements to fit

the stratification hypothesis does not inspire confidence.

Dissolved silicate is a major nutrient for diatom growth because of the silica tests that these phytoplankton precipitate. Much like nitrate and phosphate, silicate is nearly completely depleted in the low-latitude surface ocean but is found at relatively high concentrations in the modern Antarctic (Figure 5(d)). The silicon isotopic composition of diatom microfossils implies that there was a reduction in Antarctic silicate utilization during the last ice age (De La Rocha *et al.*, 1998), in contrast to the evidence for enhanced nitrate utilization. While this may indicate a disagreement among proxies, the alternative is that the difference signals a real oceanographic change. Field observations, incubations and culture studies (Franck *et al.*, 2000; Hutchins and Bruland, 1998; Takeda, 1998) indicate that iron-replete conditions (such as may result from the dustiness of the ice age atmosphere (Mahowald *et al.*, 1999)) favor a higher nitrate/silicate ratio in diatoms, and phytoplankton species composition changes may have reinforced this shift (Tortell *et al.*, 2002). Indeed, taking both the nitrogen and silicon isotope data at face value implies that the nitrate/silicate uptake ratio of Antarctic phytoplankton was higher during the last ice age, leading to lower nitrate but higher silicate concentrations in the glacial Antarctic relative to modern times (Brzezinski *et al.*, 2002). From the perspective of our efforts to reconstruct the history of export production, this possibility is problematic in that the rain of biogenic silica out of the surface ocean would have decreased independently from the rain of organic carbon.

If the change in nitrate/silicate uptake ratio was adequately great, it may have actually removed the tendency for preferential depletion of silicate relative to nitrate that is observed in the modern Antarctic, possibly increasing the silicate/nitrate ratio of Southern-source water that supplies nutrients to the low-latitude surface (Brzezinski *et al.*, 2002). A greater supply of silicate to the low-latitude ocean could have driven an increase in the importance of silica-secreting phytoplankton (diatoms) relative to CaCO<sub>3</sub>-precipitating phytoplankton (coccolithophorids) (Matsumoto *et al.*, 2002b); this may explain a shift toward higher opal accumulation rates in some equatorial regions (Broecker *et al.*, 2000). If increased diatom productivity at low latitudes in the southern hemisphere occurred at the expense of coccolithophores, the high sinking rates of diatom-derived particulate matter may have facilitated the transport of organic matter through intermediate waters to the deep ocean (Boyle, 1988b), again consistent with evidence for the “nutrient deepening” during glacial times (Boyle, 1988c, 1992; Boyle *et al.*, 1995; Herguera *et al.*, 1992). In addition, a floral

shift away from coccolithophores to diatoms would have also lowered the  $\text{CaCO}_3$ /organic carbon rain ratio, weakening the ocean carbonate pump. Both the increase in the remineralization depth of organic carbon and a decrease in the rain ratio would have worked to lower-atmospheric  $\text{CO}_2$  (Archer and Maier-Reimer, 1994; Berger and Keir, 1984; Boyle, 1988b; Broecker and Peng, 1987; Brzezinski *et al.*, 2002; Dymond and Lyle, 1985; Keir and Berger, 1983; Matsumoto *et al.*, 2002b; Sigman *et al.*, 1998).

In the Subantarctic, planktonic foraminiferal Cd/Ca and the  $^{13}\text{C}/^{12}\text{C}$  of diatom-bound organic matter are consistent with an ice age state of higher nutrient utilization (Rosenthal *et al.*, 1997, 2000). However, the consideration of proxy complications argue against such a change (Elderfield and Rickaby, 2000). The significance of the nitrogen isotope data for the glacial Subantarctic is uncertain (François *et al.*, 1997; Sigman *et al.*, 1999a). Thus, while the Subantarctic was certainly more productive during glacial times, the history of its nutrient status is unclear and deserves further investigation. Given our current understanding of the role that the Subantarctic plays in the carbon cycle, the Subantarctic is less important in itself than in what it indicates about the nutrient status of the Antarctic zone at its (up-stream) southern end. The Subantarctic also represents the gateway by which the Antarctic affects the low-latitude ocean and is thus central in questions regarding the impact of Antarctic nutrient changes on low-latitude productivity (Brzezinski *et al.*, 2002; Matsumoto *et al.*, 2002b).

The Subarctic Pacific, like the Antarctic, is characterized by year-round nonzero concentrations of the major nutrients, nitrate and phosphate. However, the Subarctic Pacific maintains a higher degree of nutrient utilization (lower surface nutrient concentrations) than the Antarctic. In the open Subarctic Pacific, summer nitrate concentration frequently falls below  $8\ \mu\text{M}$  in surface water, despite nitrate concentrations of greater than  $35\ \mu\text{M}$  in the upwelling deep water below the permanent halocline. One important difference between the Subarctic Pacific and the Antarctic is the much stronger halocline in the former (Reid, 1969; Talley, 1993; Warren, 1983), where the extremely low salinity of the upper 400 m limits the exposure of nutrient- and  $\text{CO}_2$ -charged subsurface waters at the surface. It is roughly this salinity-driven stratification that has been proposed for the glacial Antarctic. Thus, the modern Subarctic Pacific provides something of a modern analogue for the glacial Antarctic stratification hypothesis (Haug *et al.*, 1999; Morley and Hays, 1983).

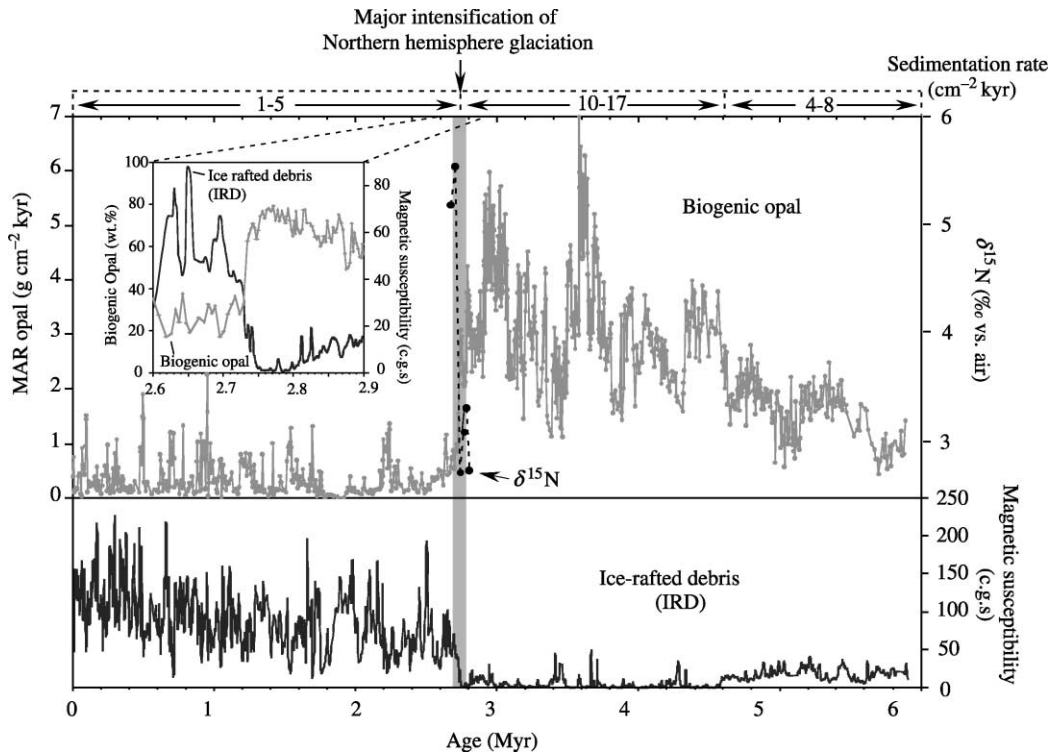
The Subarctic Pacific undergoes changes in productivity and nutrient regime over glacial/interglacial cycles, although these changes are of

smaller amplitude than is observed for the Southern Ocean. Opal accumulation was apparently lower during the last glacial maximum in the western Subarctic Pacific and its marginal seas (Gorbarenko, 1996; Haug *et al.*, 1995; Narita *et al.*, 2002). This has been interpreted, in much the same way as the Antarctic changes, as indicating intensified stratification during glacial times (Narita *et al.*, 2002). In this light, the smaller glacial/interglacial signal of this region relative to the Antarctic is explained by the fact the modern Subarctic Pacific is already strongly stratified. However, the dominant feature in most sediment records from western Subarctic Pacific and Bering Sea is of a high-productivity event upon the transition from the last ice age to the Holocene (Keigwin *et al.*, 1992; Nakatsuka *et al.*, 1995), for which there is as yet no well-supported explanation. Moreover, the eastern Subarctic Pacific seems to lack a glacial/interglacial signal, instead being characterized by abrupt events of opal deposition that are not clearly linked to global climate change (McDonald *et al.*, 1999).

## 6.18.5 SUMMARY AND CURRENT OPINION

While the early focus of hypotheses for glacial/interglacial  $\text{CO}_2$  change was on the biological pump (Broecker, 1982a,b), a number of alternative mechanisms, mostly involving the calcium carbonate budget, attracted increasing attention during the late 1980s and the 1990s (Archer and Maier-Reimer, 1994; Boyle, 1988b; Broecker and Peng, 1987; Opdyke and Walker, 1992). As problems have been recognized with these mechanisms as the sole driver of glacial/interglacial  $\text{CO}_2$  change (Archer and Maier-Reimer, 1994; Sigman *et al.*, 1998), the biological pump is receiving attention once again. Hypotheses exist for both low- and high-latitude changes in the biological pump. Their strengths, weaknesses, and central questions are now fairly clear.

Currently, the most popular low-latitude hypotheses depend largely on whether the nitrogen cycle alone can drive a large-scale change in low-latitude export production. As of the early 2000s, while this question has not yet been directly addressed, no new observations have arisen that would overturn the traditional view that the nitrogen cycle could have had only a limited effect without cooperation from the phosphorus cycle and that the phosphorus cycle could not have been adequately dynamic over glacial/interglacial cycles (e.g., Froelich *et al.*, 1982; Haug *et al.*, 1998; Redfield, 1942, 1958; Redfield *et al.*, 1963; Ruttenberg, 1993; Sanudo-Wilhelmy *et al.*, 2001). Thus, while the low-latitude biological pump has by no means been eliminated as the driver of glacial/interglacial cycles, our attention is focused on the polar ocean, the Antarctic in particular.



**Figure 11** A 6 Myr biogenic opal record from Ocean Drilling Program Site 882 in the western Subarctic Pacific (50°21' N, 167°35' E; water depth 3,244 m; figure from Haug *et al.* (1999)), showing an approximately fourfold decrease in opal accumulation rate at 2.73 Myr ago (top panel). This abrupt drop in opal occurred at isotope stage G6 (the former isotope stage 110) synchronously with the massive onset of ice rafted debris, as indicated by the increase in magnetic susceptibility (bottom panel). Maxima in opal accumulation during the last 2.73 Myr are generally linked to interglacial times or deglaciations, as reported by Keigwin *et al.* (1992) for the last deglaciation. Since silicate is supplied by the exposure of nutrient-rich deep water, the high opal flux rates of the mid-Pliocene Subarctic Pacific require a rate of deep-water exposure of a magnitude similar to that observed in the modern Antarctic. Because silicate consumption is nearly complete in the modern Subarctic Pacific (Figure 5(d)), the sharp drop in opal flux at 2.73 Myr ago cannot be attributed simply to a decrease in the completeness of silicate consumption. Rather, it must record a decrease in the rate of exposure of silicate-rich deep water at the Subarctic Pacific surface. Sediment  $\delta^{15}\text{N}$  ( $(^{15}\text{N}/^{14}\text{N}_{\text{sample}}/^{15}\text{N}/^{14}\text{N}_{\text{air}} - 1) \times 1,000$ ) increases concurrently with the sharp drop in opal accumulation at the event 2.73 Myr ago (from ~3‰ to 5‰, upper panel). This shift toward higher  $\delta^{15}\text{N}$  suggests an increase in nitrate utilization (Altabet and Francois, 1994a), providing additional evidence that the decrease in opal flux resulted from a decrease in the exposure of nutrient-rich deep water, which lowered the nitrate supply and thus forced more complete nitrate consumption while decreasing the silicate available for opal production (reproduced by permission of Nature Publishing Group from *Nature* 401, 779–782).

We have discussed three rough categories of Antarctic change that might drive a decline in  $\text{CO}_2$  during ice ages: (i) increased biological productivity, as in response to increased iron supply, (ii) vertical stratification of the upper ocean, and (iii) gas exchange limitation by ice cover. The productivity hypothesis is not supported by data, which suggest a smaller biogenic rain in the glacial Antarctic, although it remains possible that our proxies are telling us only about a reduction in the rain of bulk biogenic material (i.e., diatom-derived opal) and are leading us to overlook an increase in “export production,” the rain of organic carbon out of the surface ocean. The gas exchange hypothesis remains possible but is difficult to test and would seem to require extreme

conditions to be the sole cause for the observed amplitude of  $\text{CO}_2$  change. The stratification hypothesis is supported by some data but conflicts with other data, or at least with the traditional interpretations of those data. While there are major concerns about each of the polar hypotheses, these hypotheses have recently been strengthened by the realization that they would have impacted the lower-latitude ocean and the  $\text{CaCO}_3$  budget in ways that should have strengthened their overall effect on atmospheric  $\text{CO}_2$  (e.g., Brzezinski *et al.*, 2002; Matsumoto *et al.*, 2002b; Toggweiler, 1999).

As is clear from the treatment above, the stratification hypothesis has particular resonance with the authors of this chapter. This is driven

largely by the conceptual and observational links we observe between two nutrient-bearing polar ocean regions, the Antarctic and the Subarctic Pacific. As described above, there is a strong analogy between the Subarctic Pacific that we observe today and the glacial-age Antarctic that is posed by the stratification hypothesis. Moreover, at a major cooling event 2.7 Myr ago, it appears that the Subarctic Pacific underwent the transition to its current salinity-stratified condition (Figure 11) (Haug *et al.*, 1999), just as stratification has been hypothesized for the Antarctic on the transitions to ice age conditions. Ongoing work on other intervals of the climate record seems to support the existence of a strong generalized link between climate cooling and polar ocean stratification. The physical mechanism for this link, however, is still unresolved.

To these authors, there is no infallible recipe for the investigation of the biological pump in the past. Nevertheless, there are glaring uncertainties that require our attention, both in our concepts and our tools. The quantitative effects of the low latitude and polar ocean on atmospheric CO<sub>2</sub> are still a matter of debate (Broecker *et al.*, 1999; Toggweiler *et al.*, 2003a,b). Until our understanding of the modern ocean and carbon cycle has progressed to the degree that such major conceptual questions can be resolved, it will be extremely difficult to generate any consensus on the role of the biological pump in driving carbon dioxide change. After optimistic discussion of “proxy calibration” in the 1990s, we now recognize that the sedimentary and geochemical parameters we use to study the history of the biological pump are the product of multiple environmental variables, requiring that we think deeply about their significance in each case that they are applied. The quantity of work on the history of the biological pump has increased markedly over the last decade; a concerted effort to review, evaluate, and synthesize this information would greatly improve its usefulness. At the same time, we must continue to support a vanguard in search of untapped constraints. We have emphasized above that the biological pump is not strictly a biological phenomenon but rather results from the interaction of ocean biology, chemistry, and physics; as such, progress in its study is tied to our understanding of the history of the ocean in general, including its physical circulation and fundamental conditions (Adkins *et al.*, 2002).

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