The Late Quaternary History of Biogeochemical Cycling of Carbon

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4.1. Introduction

The cycling of carbon between the atmosphere, ocean and continents controls the concentration of atmospheric CO_2 (pCO_2), which in turn impacts the earth's radiation balance. Correlations between the concentration of atmospheric pCO_2 measured in air bubbles in ice cores with climatic indices such as inferred global temperature (Chapter 3, Figure 4.3) strongly suggest that some link exists between pCO_2, "greenhouse" warming and global climate (Shackleton 2000, and others). Late Quaternary climatic variability occurs predominantly at the 100 ky frequency associated with orbital eccentricity, ε. Since changes in ε result in relatively small changes in incoming solar radiation, non-linear internal feedback mechanisms must be invoked to explain climate variations at this frequency. In this context, the rapid collapse but slow growth of northern hemisphere continental ice sheets has often been suggested as an important influence (Imbrie and Imbrie 1980). The spectral analysis of Shackleton (2000) and the direct multiple-parameter comparisons of ice-core data recently published by Alley et al. (2002) reveal however that most indices of global climate changes (deep water temperature; inferred Vostok air temperature) precede ice volume by up to several thousand years. Although ice sheet dynamics are clearly an important component of the climate system on these timescales, such observations rule them out as the trigger of deglaciations.

On the other hand, CO_2 changes are in phase with orbital eccentricity, which reinforces the potential importance of CO_2 in influencing global climate changes, and highlights the importance of understanding the mechanisms that control the concentration of this gas in the atmosphere. Such mechanisms are the focus of this chapter.

The global carbon cycle can be viewed as a series of nested loops, all of which include atmospheric CO_2 (Figure 4.1). The amplitude of changes in pCO_2 is controlled by feedbacks that effect the magnitudes of fluxes between reservoirs. Paleodata, on the other hand, tend to constrain the size of carbon reservoirs rather than fluxes. This disparity between processes that are primarily distinguished by their influence on *fluxes* and data that primarily tell us about reservoirs is one of the fundamental reasons why developing an understanding of the long term operation of the carbon cycle remains a daunting task (LeGrand and Alverson 2001). The rapidity of the changes is dictated by the intrinsic response time of the processes involved and the rates of change of the external forcings that drive them (e.g. insolation intensity and distribution, or tectonics).

We can distinguish variability on five temporal scales, listed from short to long:

1) Changes on seasonal timescales, which mainly involve the insolation-driven cycle of respiration/photosynthesis of land biomass.
2) Changes on annual to decadal timescales, which involve climatically-driven exchanges between atmosphere, land biomass, litter, and the upper ocean.
3) Changes on decadal to centennial timescales. These involve transfers between the atmosphere, the upper and intermediate ocean, and

soil carbon, as well as climatically forced changes in land biomass.

4) Changes on millennial timescales. These comprise exchanges between the atmosphere, the entire ocean, the upper sediment layer, and the "reactive" crust, and include climatically-forced changes in land biomass and soil carbon.
5) Changes on million year timescales controlled by tectonically-driven (orogeny, volcanism, subduction) exchange of carbon with the lithosphere.

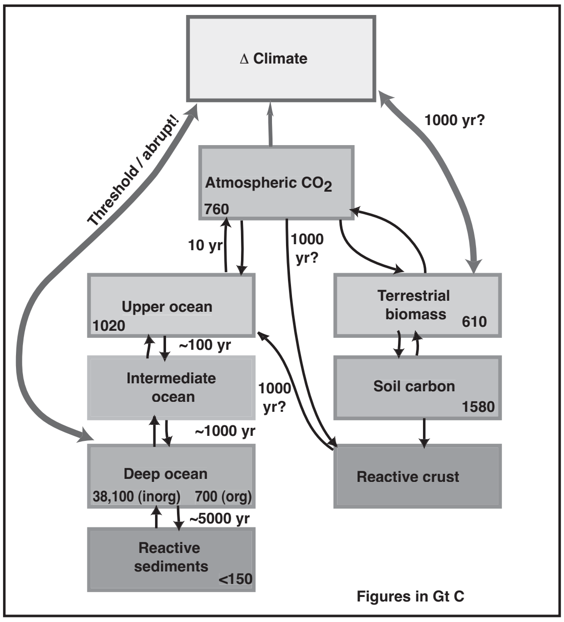

Fig. 4.1. Schematic showing the major reservoirs that exchange carbon on millenial and sub-millenial timescales, thereby participating in climate change (represented by the uppermost box). Black arrows indicate the directions of the exchanges with mean time constants. Thick double-headed arrows are meant to convey the potential for abrupt impacts on pCO_2 and thus climate from oceanic processes (left side) and more gradual impacts from continental processes. Numbers inside the boxes indicate estimated reservoir sizes in Gt C.

We discuss here only the terrestrial and marine reservoirs and processes that affect the cycling of carbon on century to multimillennial timescales. Within this temporal context, the steady-state level of atmospheric CO_2 is forced by exchanges between the atmosphere and the largest reservoirs (i.e. the deep ocean, reactive sediments and the reactive crust). In contrast, the smaller reservoirs (terrestrial biomass, soil carbon and the upper ocean) have only limited influence on the long-term steady-state level of atmospheric CO_2, but they can potentially respond much faster and produce transient excursions in atmospheric CO_2 levels on decadal to millennial timescales.

4.2. Continental processes and their impact on atmospheric CO_2

4.2.1. Biospheric carbon

During the LGM, the climate was colder and drier. These conditions induced a dramatic reorganisation of the vegetation at the Earth's surface (Chapter 5). Ice sheets prevented the growth of plants in the northern hemisphere at high latitudes. At lower latitudes, vegetation colonized the exposed shelf (following the ~125-129 m sea level drop; Peltier 2002; see also other papers in Mix and Clark 2002, and Chapter 3, Section 4, Figures 3.2 and 3.5) and deserts were much more widespread (eg. Sarnthein 1978; Petit-Maire 2000). Under the prevailing lower atmospheric CO_2 level, C4 plants were favoured. C3 plants did not thrive during times of low pCO_2 as they lacked the strong fertilization effect that CO_2 exerts on them, and they suffered from a decline in water use efficiency due to enhanced stomatal openings at low partial pressures of CO_2 (Polley et al. 1993). Grasslands, steppes and savannas expanded at the expense of forests (Adams et al. 1990). This is the general view of the LGM world that can be drawn from palynological and other continental data (Figure 4.2), although these are still too sparse to provide a precise picture.

Many attempts to reconstruct the carbon budget associated with the terrestrial biosphere at the LGM have been performed during the last decade. These studies agree that the land biosphere contained less carbon at the LGM than today, indicating that the terrestrial biospheric carbon reservoir must have been a source, rather than a sink for atmospheric CO_2. The magnitude of the deglacial increase is still intensively debated, however. Studies based on palynological and sedimentological data provide the highest estimates (740-1500 Gt C) of the increase in biospheric storage between the LGM and the present (Adams et al. 1990; Van Campo et al. 1993; Crowley 1995; Peng et al. 1995; Adams and Faure 1998). However, these estimates have been obtained by extrapolating a very limited set of data. Moreover, they usually rest on the assumption that the average carbon storage density (kg C m^{-2}) of a given biome was the same at the LGM as it is today. Most of these estimates include uptake of C by peatlands, which formed during the mid and late Holocene (Franzén 1994) and today cover roughly 2.3-5.0 x 10^6 km^2 of the Earth's surface. These deposits are estimated to store 110-455 Gt C (Botch et al. 1995), with a best guess of roughly 200 Gt C.

If the 0.3-0.4 ‰ rise in the global value of oceanic $\delta^{13}C$ recorded in foraminifera from the LGM to the present (Curry et al. 1988; Duplessy et al. 1988;

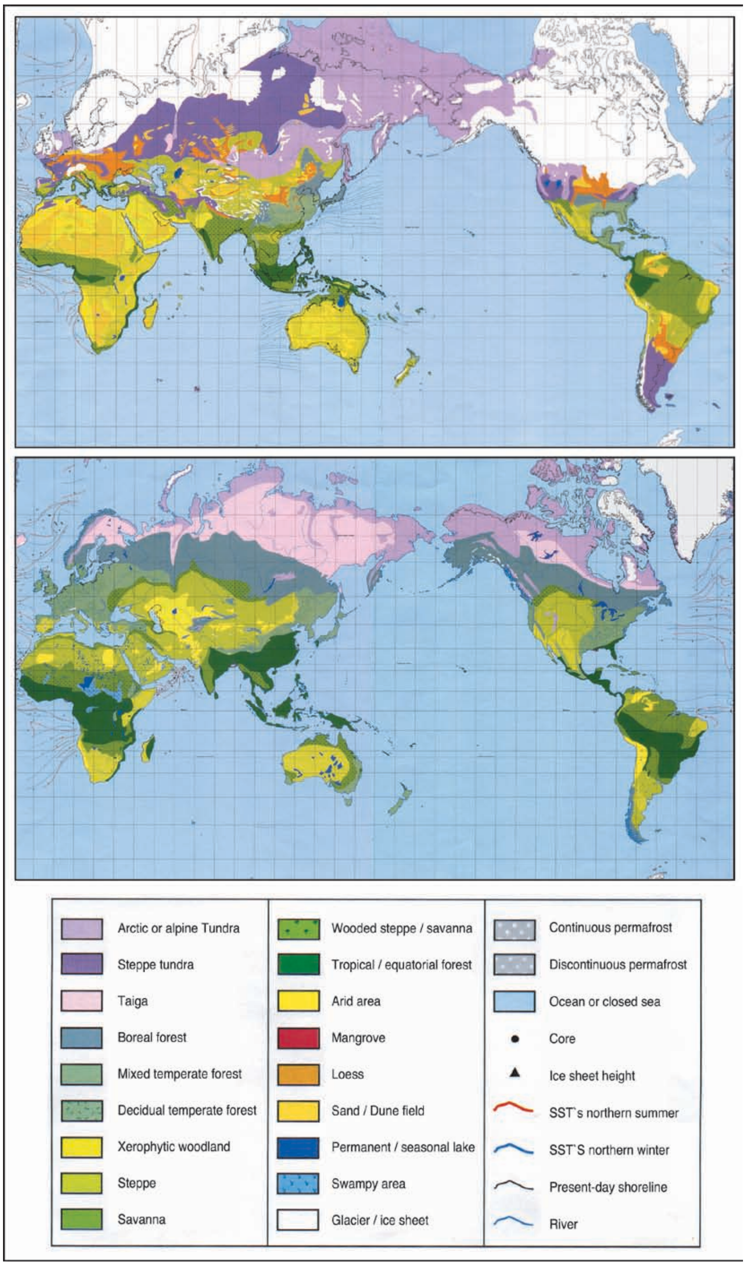

Fig. 4.2. A) Ice and biome distribution 6000 years BP. B) Ice and biome distribution at the Last Glacial Maximum (21,000 years ago). From Petit-Maire et al. (1999).

Crowley 1995) is fully attributed to carbon reservoir changes, it suggests a somewhat lower range for the increase in biospheric carbon stock of 270-720 Gt C (Bird et al. 1994). This range incorporates the possibility that isotope discrimination in C3 plants was reduced at the LGM (Van de Water et al. 1994). Bird et al. argue that the true change was probably at the lower end of this range, since C4 plants were more widespread during glacial times (Cole and Monger 1994). However, laboratory experiments on two species of foraminifera by Spero et al. (1997) showed that the $\delta^{13}C$ of carbonate shells decreases linearly with increasing concentration of carbonate ion in the water in which the organisms grow. This observation suggests that a significant portion of the observed 0.3-0.4 ‰ rise in the $\delta^{13}C$ of benthic foraminifera might reflect a decrease of seawater carbonate ion concentration ($[CO_3^{=}]_{sw}$) from the LGM to the present, rather than land-sea reservoir shifts. Using the estimate of Spero et al. of 40 μmol kg^{-1} for this drop in $[CO_3^{=}]_{sw}$, the "true" range of seawater $\delta^{13}C$ rise from the LGM to the present becomes 0.06-0.16 ‰. Based on the methodology of Bird et al. (1994), we estimate that the range of biospheric carbon change between the last glacial and the present would then span from –160 Gt C (i.e. lower carbon storage at the LGM) to +240 Gt C. The implications of the work by Spero et al. are thus that the biospheric carbon stock at LGM may have been quite close to, or even somewhat higher than, its present value. However, these isotope-based estimates rest on the hypothesis that the land biosphere was the only reservoir that exchanged significant amounts of isotopically-light carbon with the ocean-atmosphere system over the last deglaciation. Exchanges with isotopically light soil carbonate could also have played a role, as discussed below.

Other attempts to estimate the post-glacial uptake of carbon by the biosphere have used GCM climate reconstructions for the LGM as inputs to land biosphere models of varying complexity. The range of estimates yielded by these studies is 0-700 Gt C yr^{-1} (Prentice and Fung 1990, Friedlingstein et al. 1992, 1995, Prentice et al. 1993, Esser and Lautenschlager 1994, François et al. 1998, 1999). The uncertainties associated with this model-based methodology are well illustrated through the results of the recent PMIP intercomparison (*PMIP-Carbon*; François et al. 2000). In this work, three land biosphere models (ALBIOC, Roelandt 1998; BIOME4, Kaplan 2000; CARAIB, Warnant et al. 1994) were forced with a subset of the LGM climatic fields reconstructed within PMIP. The advantage of this intercomparison was that all participating biosphere models were forced with an identical set of climate reconstructions, so as to determine if discrepancies originated from differences in the adopted climate forcings or in the biosphere models themselves. The first experiment tested the model sensitivity to the atmospheric CO_2 increase that occurred between the LGM (200 ppmv) and the Pre-industrial (280 ppmv). CO_2 fertilization results in higher rates of photosynthesis, biomass growth and hence higher amounts of carbon in vegetation, litter and soil reservoirs during the Holocene. This trend was reproduced by all models (Figure 4.3), but the amplitude of the increase in biosphere carbon storage varied considerably among them (from 230 Gt C in ALBIOC to 890 Gt C in BIOME4). Such a wide range in sensitivities to CO_2 probably reflects our poor quantitative understanding of the mechanisms involved in CO_2 fertilization and the lack of observational data to constrain this process. This gap must be filled to produce reliable reconstructions of LGM carbon storage. This problem is not inherent only to model-based reconstructions, but also to those based on palynological and sedimentological data, since the biome carbon densities used to translate biome areas into carbon stocks are also dependent on CO_2 fertilisation.

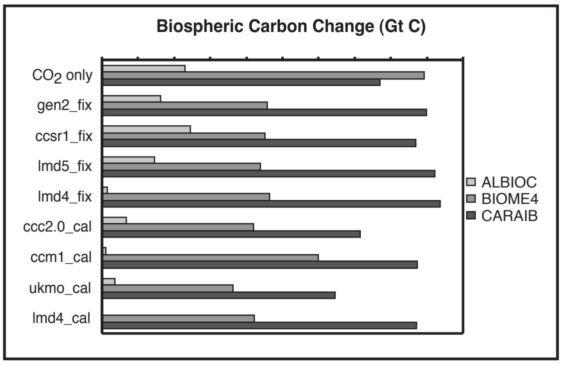

Fig. 4.3. Estimates of the increase in biosphere carbon storage since the Last Glacial Maximum for three land-biospheric models used in the Paleoclimate Model Intercomparison Project (PMIP). Boundary conditions in each case are described in the text. Data from François et al. (2000).

Other experiments tested the model response to the combined CO_2, land area (sea level) and climate changes that occurred from the LGM to the Pre-industrial. Again, the responses to these changes were strongly model-dependent. For example, land area and climate shifts strongly mitigate the effects of the CO_2 fertilisation in BIOME4, while an opposite but smaller trend is usually observed with CARAIB. Furthermore, the variability of carbon storage estimates associated with the use of different LGM climate reconstructions was much smaller than the intrinsic variability among the biosphere models. Indeed, the overall range of carbon storage changes predicted in the intercomparison (an increase of 9-935 Gt C from the LGM to pre-industrial times) was larger than the range exhibited by all previous model reconstructions. Presumably, one reason for such large contrasts among present models is that the calculated LGM biosphere carbon stock is the net result of several factors with opposite effects. For instance, the LGM cool climate results in an overall decrease of carbon storage in living vegetation, but the same cooling reduces organic matter decomposition rates by bacteria and, hence, tends to increase carbon storage in the soil.

In summary, Figure 4.4 shows a synthesis of all existing estimates of the increase in carbon storage by the biosphere between the LGM ~21,000 years ago and the present. These estimates range from –160 to 1900 Gt C. The lower end of this range corresponds to the isotopic estimate with inclusion of $[CO_3^{=}]_{sw}$ effects or to model-based estimates without CO_2 fertilization, while the upper end relates to the largest increase derived from continental data. Inclusion of $[CO_3^{=}]_{sw}$ effects on carbonate shell $\delta^{13}C$ reinforces the discrepancy between isotope-based and continental data-based estimates of the LGM-to-present shift in biospheric carbon storage. It is essential to find the reasons for this discrepancy in order to obtain more precise constraints on long term temporal variability in carbon cycling. A value of 600 Gt C represents the intersection of three different types of estimate (paleodata, models, and carbon isotopic budget excluding $[CO_3^{=}]_{sw}$ effects) and can be considered to be the 'best current guess'. The assimilation of this net amount of C by the terrestrial biosphere during the last deglaciation could have provided significant compensation for the CO_2 released during the deglacial reorganization of the ocean (Section 4 below).

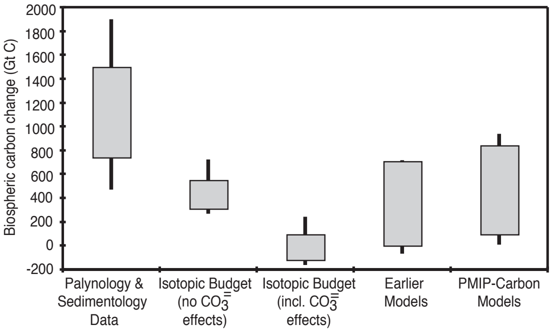

Fig. 4.4. Compilations of existing estimates of the increase in biospheric carbon storage between the Last Glacial Maximum and the present. Note that the range exceeds three orders of magnitude. Data sources are listed in François et al. (2000).

A few estimates of the change in biospheric carbon storage between the mid-Holocene (6000 yr B.P.) and the present have also been derived. The magnitude is much smaller than the shift that occurred between the LGM and the present. Using continental data, Adams and Faure (1998) estimated that biosphere carbon storage decreased by 27 Gt C from the mid-Holocene to the present. This is similar to the 36 Gt C decrease calculated by Foley (1994) from a biosphere model forced with GCM climatic fields. These estimates can be compared to the 195 Gt C decrease in biosphere carbon stock between 7000 and 1000 years BP obtained by Indermühle et al. (1999) by inversion of the pCO_2 and $\delta^{13}C_{air}$ signals archived by ice cores (see Chapter 2, Section 5). It must be noted, however, that the estimate by Indermühle et al. implicitly contains a contribution from the development of agriculture, while the present reference state in the other studies is defined by potential natural vegetation. Moreover, Adams and Faure (1998) and Foley (1994) both neglected CO_2 fertilisation in response to the 20 ppmv increase in pCO_2 from the mid-Holocene to the immediate pre-industrial period. This may have induced an increase in biospheric carbon storage of ~120 Gt C (François et al. 1999), which if added to these continental estimates would bring them up to the range suggested by Indermühle et al. (1999).

4.2.2 Soil carbonate

A major implication of the larger desert areas during the LGM is that the inventory of soil carbonate carbon (calcrete) in arid soils should have been higher at that time. Calcrete often occurs as layers and nodules, and represents an often-overlooked reservoir in the global budget. The current carbon content of calcrete and other soil carbonates is estimated to be some 700 Gt C (Batjes 1996). A first-order estimate of the change in magnitude of this reservoir since the LGM has been produced by Adams and Post (1999) using paleovegetation maps from the Quaternary Environment Network Atlas (QEN 1995; Adams and Faure 1997). They estimate that there was a decline in the storage of inorganic C in soils of ~500 Gt C from the LGM to the mid-Holocene, and an increase in storage of ~100 Gt C from the mid-Holocene to the present, yielding a net change of ~-400 Gt C in this reservoir over the last 21,000 years. This transfer of carbon to the ocean-atmosphere system over the last 21,000 years presumably had very limited impact on atmospheric CO_2 evolution, since carbon is transferred together with alkalinity. Moreover, a substantial fraction of the mobilized C probably re-precipitated as calcium carbonate on the ocean floor. However, calcrete and soil carbonates may have played a non negligible role on the isotopic budget of the ocean-atmosphere system. Precipitation of soil carbonates uses soil CO_2 with a negative carbon isotopic signature that is derived at least partly from vegetation. Indeed, the $\delta^{13}C$ of soil carbonates ranges from –2 to –10 ‰ (Cerling 1991). Dissolution of soil carbonates over the last deglaciation and their addition to the sea would then have lowered the $\delta^{13}C$ of the ocean, thus reducing the rise in oceanic $\delta^{13}C$ induced by the expansion of the biosphere by roughly 0.02 to 0.1 ‰. This effect is in the right direction to help reconcile continental data- and isotope-based estimates of the LGM biospheric carbon stock (Section 2.1), although it is far too small to explain the full difference between both estimates.

4.2.3. Weathering and river transport

Ludwig et al. (1999) have estimated using models that the delivery of riverine particulate and dissolved organic carbon to the ocean by rivers during the LGM was reduced by at least 10%. About two-thirds of the modern flux of riverine DOC and POC is respired to CO_2 in the coastal region and returned to the atmosphere (Smith and Hollibaugh 1993); thus, the lower riverine input of carbon during the LGM coupled with reduced glacial-age temperatures (and associated respiration rates) presumably represented a slight net decline in the CO_2 flux to the atmosphere from this source during glacial times. However, the smaller shelf area during the LGM limited the burial of particulate organic carbon in relatively rapidly accumulating nearshore or shelf deposits; this would have countered the reduced CO_2 flux. Ludwig and Probst estimate that the shelf-area effect would have dominated. Thus, reduced burial of the riverine terrestrial particulate C flux in marine sediments would have had a net effect of marginally increasing the CO_2 flux to the atmosphere.

The residence time of CO_2 in the atmosphere, if weathering were the only process operating to remove it, would be ~7000 to 8000 years (Kasting and Walker 1992). Thus, changes in continental weathering rates could have influenced glacial-interglacial pCO_2 directly, through either more or less consumption of carbon dioxide. An indirect effect would have been associated with any change in the alkalinity flux to the ocean (see Section 3.3). However isotopic tracers suggest that there was little change in weathering rates between the LGM and today. The high-precision $^{87}Sr/^{86}Sr$ measurements of Henderson et al. (1994) constrain glacial-interglacial changes in the riverine flux of Sr to $\leq$30%, while the $^{187}Os/^{186}Os$ data of Oxburgh (1998) show no evidence of enhanced chemical weathering during periods of intense continental glaciation. These results imply collectively that changes in chemical weathering intensity were unlikely to have exerted a significant impact on atmospheric pCO_2 on the timescales of interest here.

4.3 Marine processes that affect atmospheric CO_2

The ocean can be subdivided into four carbon reservoirs (Figure 4.1) each of which influences atmospheric CO_2 on a different timescale:

(1) *The upper ocean:* This is a comparatively small reservoir that exchanges CO_2 with the atmosphere on a subannual to decadal timescale. When integrated over space and time, localized areas of supersaturation, as in upwelling regions, are compensated by regions of undersaturation, often associated with regions of seasonally high productivity.

(2) *The intermediate ocean:* On longer timescales, the PCO_2 of surface water and the pCO_2 of the atmosphere are primarily controlled by the exchange of total dissolved inorganic carbon (ΣCO_2) and carbonate alkalinity (CA) between surface and deeper waters. We can define an “intermediate ocean” reservoir that supplies CO_2, CA and nutrients to the upper ocean. The rate of supply is controlled by vertical mixing and upwelling. Atmospheric CO_2 exchanges with this reservoir on century to millennial timescales.

(3) *The deep ocean:* The deep ocean is the largest reservoir of inorganic carbon relevant to the Quaternary (the much larger sedimentary carbon reservoirs exchange with atmospheric CO_2 on much longer timescales). It encompasses most of the ocean, and controls the steady-state level of atmospheric CO_2 on a timescale equivalent to the turnover period of the entire ocean (ca. 1000 y). The latter is a function of the rate of thermohaline circulation.

(4) *The reactive surficial carbonate sediment:* The balance between carbonate burial and dissolution in surface sediment also affects carbonate alkalinity and ΣCO_2 of deep water. Carbonate sediment in contact with bottom water is thus also a comparatively large reservoir of inorganic carbon that can affect atmospheric CO_2 with a multi-millenial response time (Catubig et al. 1998).

4.3.1 Air-sea flux

Transfer of carbon between the atmosphere and the ocean requires that there be a difference between the partial pressures of carbon dioxide in the lower troposphere (pCO_2) and the surface water of the ocean (PCO_2). The PCO_2 of seawater is determined primarily by its carbonate alkalinity (CA, = $[HCO_3]$ + $2[CO_3^{2-}]$) and total CO_2 (ΣCO_2) concentrations, via:

$$PCO_2 = \frac{(2\Sigma CO_2\text{-}CA)^2}{K'(CA - \Sigma CO_2)}$$

where K' is related to the first and second dissociation constants for carbonic acid, and can be summarized as $K' = ([HCO_3^-]^2)/(pCO_2[CO_3^{2-}])$. At $S = 35$ and 1 atm. pressure, K' decreases with increasing T, from ~11.3×10^4 mmol $L^{-1}atm^{-1}$ at 0° C to ~3×10^4 mmol $L^{-1}atm^{-1}$ at 30° C (Broecker and Peng 1982, Table 3-7); thus, atmospheric pCO_2 increases significantly as water temperature rises, by about 4 % per °C. Salinity has a more restricted effect on CO_2 solubility in the surface ocean – a 1 psu increase in S (from say 34 to 35) would decrease pCO_2 by only ~10 μatmospheres. Furthermore, pCO_2 is also influenced by the carbonate buffering system in surface seawater, via the summary reaction $CO_2 + H_2O + CO_3^{2-} = 2HCO_3^-$. Simply stated, for a given δCO_2, an increase in the carbonate ion content in surface water will decrease pCO_2.

In addition to depending on the difference (ΔpCO_2), the air-sea exchange of carbon has a strong, nonlinear and poorly understood dependence on wind speed. Calibrations in the modern context are summarized by Wanninkhof (1992), who suggests a quadratic wind speed dependence. The bulk formulae used in numerical models to parameterize the air-sea flux associated with a given ΔpCO_2 and wind speed are accurate to within about 25%. On a global scale, the generally accepted uncertainty in modern air-sea CO_2 flux climatologies, which includes uncertainties in both wind speed effects and the air-sea CO_2 partial pressure difference, is of order 100% (Doney et al. 2000). For the LGM, when wind speeds were likely to have been significantly higher, the situation is even worse. For example, if, over a given region, modern average wind speed is 5 m s^{-1}, and the LGM average was 7 m s^{-1}, the air-sea flux at LGM in this region, as a result of the necessity to square these values, would be approximately double its modern value, based on wind speed change alone. Of course regional wind speeds may have been less during the LGM, further complicating things. As a result, even if glacial ΔpCO_2 fields were perfectly known, the resulting pattern of air-sea carbon fluxes could not be estimated to within a factor of two, because of uncertainties in the wind fields. Sea ice can also influence the exchange of CO_2 between ocean and atmosphere by almost entirely blocking gas exchange across the interface, although greatly enhanced fluxes in leads (large gaps that open periodically in sea ice cover due to its dynamic nature) counter this effect somewhat. Although sea ice is restricted to high latitude areas it may nonetheless be important for the global carbon cycle. Stephens and Keeling (2000), for example, attribute the bulk of the increase in pCO_2 between glacial and preindustrial times to a decrease in the extent of sea ice in the Southern Ocean, thereby allowing more efficient outgassing of CO_2 from this high-latitude region.

In summary, the exchange of CO_2 between atmosphere and ocean can be driven by changes in sea surface temperature (SST) and salinity (SSS), changes in the supply and removal of total CO_2 and alkalinity to and from surface water, changes in the surface winds and variations in sea ice cover. These various influences and their operation on a spectrum of timescales will be assessed in the following sections.

4.3.2 SST and SSS control (the solubility pump)

The solubility pump is classically defined as the physical transfer of CO_2 into the deep ocean driven by solubility and meridional overturning. Because CO_2 solubility in seawater decreases with increasing temperature and salinity, as noted in the previous section, the effects on pCO_2 induced by an average decrease in sea-surface temperature and increase in sea-surface salinity, as would occur during a glacial period, would be opposite. The meridional overturning circulation also influences solubility-driven CO_2 drawdown. CO_2 fluxes into the ocean interior are enhanced when by warm low-latitude surface water advects poleward. As this water cools it absorbs CO_2 from the atmosphere and, as it sinks, this CO_2 is sequestered in the deep ocean. Variability in the deep and intermediate-water circulation through time could then have impacted pCO_2, as discussed in Section 4.3 below.

4.3.3 Removal of ΣCO_2 from surface waters by sinking C_{org} (the biological pump)

The biologically-mediated export of particulate organic matter from surface waters into the ocean interior promotes invasion of atmospheric CO_2 into the sea, while the resupply of regenerated CO_2 to the surface (and thus the atmosphere) by vertical mixing and upwelling counters this flux (e.g. Karl et al. 1997). The efficiency of the biological pump thus depends on the balance between the rate at which organic carbon is exported from surface waters and the rate at which regenerated CO_2 is resupplied from deep water. While the latter is controlled on a global scale by the rate of ventilation of the deep ocean, export production is controlled on regional scales and is often restricted by the rate of supply of a limiting nutrient to the euphotic zone.

Although light limitation and grazing pressure have also been invoked as alternative controls on primary production, only in restricted coastal upwelling regions such as along the Peru and Namibian margins are surface waters likely to be replete in all nutrients.

Four limiting nutrients, nitrate, phosphate, silicate and iron, have so far been clearly identified and their effect recognized in different areas of the ocean. They are all supplied to the ocean by river runoff, but iron and nitrate have important additional sources. Whereas Fe transported by rivers is readily removed in estuaries (Boyle et al. 1977), restricting its impact to coastal waters, eolian (dust) inputs add iron to the surface ocean, particularly in the open sea. Nitrate is added to seawater by nitrogen fixation, which predominantly occurs in the warm, stratified nutrient-poor (oligotrophic) regions of the ocean (Karl et al. 1997; Gruber and Sarmiento 1997). In these areas Cyanobacteria such as *Trichodesmium* spp. fix dissolved dinitrogen (N_2) into organic N, which is subsequently released to seawater as dissolved organic N species or ammonium and oxidized to NO_3^-.

The factors controlling the rates of supply of limiting nutrients to the euphotic zone depend on the limiting nutrient and vary from region to region. For nitrate, phosphate and silicate, rates of supply are mainly controlled by their concentration in intermediate waters and rates of vertical mixing or upwelling. In turn, their concentrations in subsurface waters are controlled by their inventories in the ocean, their regeneration rates, and deep water circulation. In contrast, while some Fe can also be supplied by vertical mixing (e.g. Watson et al. 2000), its main source in the open ocean is often dust deposition onto the surface. Likewise, in oligotrophic regions, nitrate supply from below is typically supplemented by direct fixation of N_2 (Karl et al. 1997; Gruber and Sarmiento 1997). These two modes of nutrient addition are distinguished by an important difference in their relative effectiveness in "pumping" CO_2 to the deep sea. Limiting nutrients supplied by vertical mixing are accompanied by stochiometrically equivalent amounts of ΣCO_2, so that increasing their supply rate simply by increasing vertical mixing or upwelling rates will not remove more CO_2 to the deep sea. Enhanced removal can only be achieved by increasing the oceanic inventory of these nutrients, thereby increasing the nutrient/ΣCO_2 ratio in deep and intermediate waters. On the other hand, aeolian iron supply and N_2 fixation occur independently of ΣCO_2 supply by vertical mixing and their utilization and subsequent removal from surface water with sinking organic matter amounts to a net export of ΣCO_2.

In the subtropical oligotrophic gyres, thermal stratification inhibits the upward diffusion of dissolved nutrients, thereby greatly constraining export production. Both nitrate and phosphate are added to surface waters by slow diffusion or intermittent vertical mixing associated with mesoscale eddies (McGillicuddy et al. 1998), but because phosphate is more efficiently recycled within the euphotic zone than fixed nitrogen (NH_4^+ and NO_3^-) there is often a slight excess of dissolved P in the upper water column (e.g. Gruber and Sarmiento 1997) relative to fixed nitrogen concentrations which often drop below detection limits. This makes fixed nitrogen the limiting nutrient, but only on short ("proximal": Tyrrell 1999) time scales. Over longer periods, the surface excess in phosphate sustains N fixation, so that phosphate is the ultimate limiting nutrient (Tyrrell 1999; Ganeshram et al. 2002) that dictates the export flux of organic matter supported by vertical supply of nitrate and N_2 fixation. This ecological feedback is thought to control the atomic ratio of these elements in average phytoplankton and seawater (the so-called Redfield ratio).

N_2 fixation also demands a large supply of iron, and it has been suggested that, instead of phosphate, Fe may limit N fixation and thus export production in oligotrophic regions (Falkowski 1997). While there is strong circumstantial evidence for Fe limitation of nitrogen fixation in areas of the Pacific Ocean (Wu et al. 2000; Deutsch et al. 2001), a recent study has shown that in the Atlantic, which receives a high iron input, N_2 fixers are in fact phosphate limited (Sanudo-Wilhelmy et al. 2001). By analogy to N vs P limitation (Tyrrell 1999), it could be argued that while iron may be the "proximal" limiting nutrient for N_2 fixers in oceanic regions with low iron input, P is their "ultimate" limiting nutrient, i.e. an abundant iron supply rapidly translates into P limitation.

Because of its longer regeneration scale length, the rate of supply of silicate to the surface waters of central oligotrophic gyres is even lower than those for N and P. This severely limits diatom production in such regions. Nonetheless, large diatoms can grow at the nutricline or after sporadic mixing events that supply nitrate and silicate into the euphotic zone (Siegel et al. 1999). Although these events can contribute a significant fraction of the organic material exported to the ocean interior, the mean annual rates of export in oligotrophic regions are still very low (Longhurst et al. 1995).

In stark contrast to the oligotrophic gyres, the surface waters of the equatorial and high latitude northern Pacific and the Southern Ocean are characterized by perennially large excesses of nitrate, phosphate and sometimes silicate. There is increasing evidence for Fe limitation in many of these regions (Martin et al. 1990; Kolber et al. 1994; Behrenfeld et al. 1996; Boyd et al. 1996; Coale et al. 1996; Van Leeuwe et al. 1997; Watson et al. 2000). In the subAntarctic and some areas of the equatorial Pacific, surface waters are also depleted in silicate raising the possibility that this is the limiting nutrient in these regions (Dudgale and Wilkerson 1998). The recent finding that Si/N uptake of diatoms increases with Fe limitation implies that silicate limitation could actually be induced by low Fe supply (Takeda 1998; Hutchins and Bruland 1998).

4.3.4 Supply of carbonate ions to surface waters (the alkalinity pump)

The CO_3^{2-} content of the sea is governed by the balance between the input of calcium and carbonate ions from the chemical weathering of rocks on land and the burial of $CaCO_3$ on the sea floor. The upper open ocean is everywhere supersaturated with $CaCO_3$ but because solubility increases with pressure and decreases with temperature, and because the weathering supply of calcium and carbonate ions is less than the demand from organisms that manufacture carbonate shells, the deep ocean is undersaturated deep waters compensate for the imbalance between continental supply and demand in shallow waters. The water depth of the saturation horizon is poised so that the rate of $CaCO_3$ burial on the seafloor balances the rate of addition from weathering, and any changes in the latter is opposed by an adjustment in the level of the saturation horizon and the net area of the sea floor hostile to carbonate-shell burial. Since the residence time of Ca in seawater is ~ 10^6 y, the dissolved Ca concentration can be considered constant on 10^3 to 10^4 year timescales, and the level of the saturation horizon must be controlled by carbonate ion concentration. Thus, deepening the saturation horizon to respond to higher weathering input requires a higher carbonate ion concentration in seawater, which engenders a lower pCO_2.

The alkalinity pump can also play an important role even in the absence of significant changes in continental weathering rates. For instance, the growth of carbonate formations in shallow waters, such as coral reefs, can be viewed as a means of preventing weathering products from reaching the deep sea and are thus equivalent to reducing weathering input, decreasing carbonate ion concentration and promoting higher pCO_2 (e.g. Opdyke and Walker 1992). Likewise, if the rate of carbonate production in surface waters of the open ocean increases, the resulting increase in carbonate burial rate will temporarily exceed weathering supply, prompting a gradual decrease in seawater carbonate ion concentration, a shoaling of the saturation horizon to a new level that will again compensate for weathering input, and a rise in pCO_2.

The alkalinity pump is also closely linked to the biological pump through the so-called "carbonate compensation" effect (Broecker and Peng 1987; Boyle 1988). Lower export of organic matter (or higher rates of deep water ventilation) for example, decreases CO_2 concentration in deep water, thereby increasing $[CO_3^{2-}]_{deep}$ without immediately changing the oceanic carbonate alkalinity inventory. This is because the increase in carbonate concentration is compensated by a decrease in bicarbonate concentration. The higher $[CO_3^{2-}]_{deep}$ deepens the carbonate saturation horizon, such that carbonate burial exceeds weathering input. This perturbation results in a gradual decrease in the oceanic inventory of carbonate alkalinity until the $[CO_3^{2-}]_{deep}$ and the level of the saturation horizon regain their initial values. The gradual lowering of seawater carbonate alkalinity required to regain this initial state thus augments any increase in pCO_2 initiated by decreasing the biological pump.

Another link between the biological and alkalinity pumps is provided by the generation of metabolic CO_2 from the decomposition of organic matter in sediments, which dissolves $CaCO_3$ and decreases the rate of $CaCO_3$ burial. From initial conditions at steady state, lowering C_{org} input into sediments increases carbonate burial in the deposits above that driven by weathering input, without initially changing the depth of the carbonate saturation horizon in the water column or the mean $[CO_3^{2-}]$ of seawater. In response, carbonate alkalinity gradually decreases, engendering higher pCO_2, lower $[CO_3^{2-}]$, and a shallower saturation horizon (Archer and Maier-Raimer 1994; Sigman et al. 1998). Thus, in contrast to the previous mechanism (accumulation of CO_2 in deep waters), which only produces a transient shoaling of the saturation horizon, lowering the rate of metabolically-driven dissolution of carbonate in sediment would result in a shallower steady-state saturation horizon. This result would be the same if carbonate production rates were increased or continental weathering rates were lowered.

Given known ocean mixing rates and considering how fast carbonate sediments on the sea floor can be chemically eroded, the temporal response for "carbonate compensation" has been estimated, using a coupled ocean/sediment carbon cycle model, at 5-10 ky (Catubig et al. 1998).

4.3.5 The export ratio (biological versus alkalinity pumps)

Oceanic productivity has opposing effects on the "biological" and "alkalinity" CO_2 pumps. While export of organic matter decreases pCO_2 and ΣCO_2 in surface water, the ensuing export of calcium carbonate from the surface ocean decreases carbonate alkalinity, thus increasing surface water and atmospheric pCO_2. Atmospheric CO_2 is thus also in part controlled by ecological factors that regulate the relative export of organic carbon and calcium carbonate, primarily through the relative contribution of carbonate producing (mainly coccolithophoridae) and non-carbonate producing (mainly diatoms) phytoplankton (e.g. Dymond and Lyle 1985).

4.4 Impact of marine processes on atmospheric CO_2

Based on the above discussion, it is apparent that a wide range of factors must have come into play to arrive at the net decrease in pCO_2 recorded in the glacial sections of Antarctic ice cores. Data from the Vostok ice core record indicate that increases in pCO_2 associated with the last several deglaciations occurred gradually over periods of 7 to 14 ka (Petit et al. 1999). Within such a time frame, mechanisms that contributed to the observed increases could include a wide combination of processes, some with rapid but relatively small impacts on CO_2 that could have occurred at any time during the transition, some with potentially rapid responses but forced externally at a slow rate, and some with intrinsically slow response times.

4.4.1 Contribution from the solubility pump

Cooler SST in areas of deep water formation during LGM (e.g. Shackleton 2000) would have enhanced the transfer of CO_2 to the deep sea. Using the CYCLOPS box model, Sigman and Boyle (2000) estimated that the competing effects of the global average glacial salinity increase of about 1 psu and a decrease in temperature of roughly 2.5 degrees in high-latitude surface waters and 5 degrees in the tropics would have lead to a net change in pCO_2 of about 20-25 μatm. This result is similar to previous estimates: Broecker and Peng (1998) for example, suggested that the combined effect of ΔS and ΔT between the LGM and today was some 10 μatmospheres, "small potatoes" in their terms. Legrand and Alverson (2001) note however that estimates of this type are heavily dependent on model assumptions and under-represent the range of possible effects of salinity and temperature variations on pCO_2. Their work suggests that the impact of S and T shifts between the LGM and the present cannot yet be prescribed with confidence.

4.4.2 Global export of ΣCO_2 from surface waters

It is now clear that over large areas of the world ocean biological productivity is limited by the supply of one or another limiting nutrient. Thus, the only way to enhance the efficiency of the biological pump in such regions to lower pCO_2 is to change the rate at which the limiting nutrient is supplied to the euphotic zone. On the other hand, in regions where all nutrients are available in surface waters, environmental changes that promote their utilization until one of the nutrients becomes limiting (e.g. water column stratification) would lower atmospheric CO_2. Both effects (i.e. increased supply of a limiting nutrient and environmental changes that promote its utilization) can also occur concurrently.

Changes in N and P supply in oligotrophic regions
Changes in the ocean N and P inventories may have occurred on glacial/interglacial timescales. The oceanic inventory of P is controlled by the balance between weathering input and sediment burial, but its response time is relatively long (e.g. 20 to 30 ka; Delaney, 1998). On the other hand, the inventory of fixed nitrogen (mainly nitrate) is controlled by the balance between N_2 fixation and denitrification, and its response time to perturbations is significantly shorter (~3 ka; Codispoti 1995).

Increasing evidence suggests that the extent of water column (Ganeshram et al. 1995; Altabet et al. 1995; Altabet et al. 2002) and sediment (Delaney 1998; Ganeshram et al. 2000) denitrification was lower during LGM, which would have resulted in a higher nitrate inventory in the glacial ocean. However, if the "Redfield ratios" C/N and C/P remain fixed, an increase in nitrate inventory alone, without an equivalent increase in phosphate inventory, could not have translated into higher export production in oligotrophic regions and a lowering in atmospheric CO_2. Excess nitrate would simply have remained unutilized in surface waters once phosphate was depleted, and the amount of surface-water ΣCO_2 removed to the deep sea would have remained equivalent to the unchanged supply of phosphate. On the other hand, if nitrogen fixers are ultimately limited by P supply (Sanudo-Wilhelmy et al. 2001), increasing P availability will promote N_2 fixation and the more dynamic ocean nitrate inventory will be anchored to the P inventory (Tyrrell 1999). Thus, in an ocean with fixed "Redfield" ratios, the key to lowering pCO_2 by increasing export of C_{org} in oligotrophic regions is to increase the phosphate inventory. The increase in the stock of both nutrients that would result would lead to a more extensive removal of ΣCO_2 from surface oligotrophic waters, contributing to the lowering of atmospheric CO_2. However, while the oceanic P inventory might have been somewhat higher during glacial times, as a result of reduced burial of authigenic carbonate fluorapatite in upwelling regions (Ganeshram et al. 2002), both the low amplitude of change and the slow response time of the P inventory should have contributed to minimizing its impact on glacial-interglacial changes in atmospheric CO_2.

It has also been proposed that if N_2 fixation in the modern ocean is limited by Fe instead of P, abundant dust supply during glacial periods could have enhanced export production, leading to reduced δCO_2 in surface oligotrophic waters and lower pCO_2 (Falkowski 1997; Broecker and Henderson 1998). But even if N_2 fixers in the modern ocean are Fe limited, relaxation of that limitation during glacial periods should have rapidly brought about P limitation (Sanudo-Wilhelmy et al. 2001); thus, significantly increased N_2-fixation during glacial periods seems unlikely (Ganeshram et al. 2002).

Changes in Fe supply in HNLC regions

Large excesses of nitrate and phosphate remain unutilized in the surface waters of large areas of the world ocean (the so-called High Nutrients Low Chlorophyll, or HNLC, regions). These regions are currently confined to areas where vertical mixing (North Pacific and Southern Ocean) or upwelling (Eastern Equatorial Pacific) supply abundant nitrate and phosphate to the euphotic zone. Evidence is mounting that many of these regions are Fe-limited (Martin et al. 1994; Coale et al. 1996; Boyd et al. 2000; Watson et al. 2000), which prevents the complete utilization of nitrate and phosphate and further lowering of surface ΣCO_2.

Of the three main HNLC regions, the Southern Ocean has elicited the most attention to explain the low glacial atmospheric CO_2, because that is the only area whose surface waters are directly connected to the large reservoir of ΣCO_2 stored in the deep sea. As such, the region can be viewed as a direct CO_2 "leak" from the deep sea to the atmosphere that can be variably "plugged" by a more or less efficient utilization of the upwelled macronutrients (and stochiometrically equivalent ΣCO_2) by phytoplankton (e.g. Sarmiento and Toggweiler 1984; Sigman and Boyle 2000; Watson et al. 2001; Legrand and Alverson 2001).

South of the modern position of the Polar Front, evidence based on the $\delta^{15}N$ of bulk sediment and diatom frustules supports higher surface nitrate utilization and a contribution from this region to lowering atmospheric CO_2 during LGM (François et al. 1997; Sigman et al. 2000; Figure 4.5). If the modern Southern Ocean is Fe-limited, higher utilization of surface nitrate and ΣCO_2 during the LGM could have been attained by increasing the supply of Fe relative to nitrate (and phosphate). This, in turn, could have been achieved by increasing the eolian input of Fe (Kumar et al. 1995), or by reducing the vertical supply rate of macronutrients by intensifying water column stratification (François et al. 1997; Stephens and Keeling 2000; Sigman and Boyle 2000). The dust record from Antarctic ice cores (Petit et al. 1999) indicates that the dust supply to the Southern Ocean was indeed higher during glacial periods. If the implied relaxation of Fe limitation occurred without a decrease in the rate of supply of macronutrients by vertical mixing, there should have been dramatically higher rates of export production in the region during the LGM. This is not unequivocally corroborated by the sedimentary record, primarily because of the difficulty in developing reliable proxies for paleoproductivity.

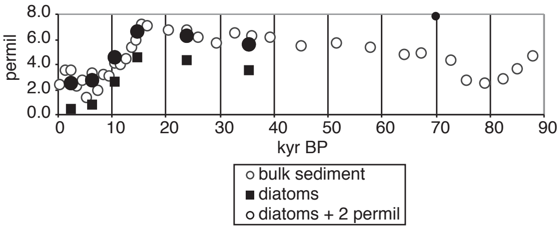

Fig. 4.5. $\delta^{15}N$ in bulk sediment and diatom frustules (Sigman et al., 1999) from core MD 84-552 taken south of the polar front in the Indian sector of the Southern Ocean (55°55'S; 73°50'E; 1780m)

Accumulation of sedimentary organic carbon, opal, biogenic Ba, and authigenic U, as well as $^{231}Pa/^{230}Th$ and $^{10}Be/^{230}Th$ ratio profiles have been used in attempts to define paleoproductivity history in the Southern Ocean (e.g. Kumar et al. 1995; François et al. 1997; Frank et al. 1999). However, the interpretation of each of these proxies is plagued by uncertainties that still need to be resolved. Productivity estimates from the accumulation of organic carbon in sediment are complicated by the extent of organic matter preservation in sediment and the factors that control it (e.g. Hedges and Keil 1995; Ganeshram et al. 2000). Likewise, opal preservation and changes in the C_{org}/opal rain rate from ecological changes (e.g. Phaeocystis vs diatoms) or Fe availability (Takeda 1998; Hutchins and Bruland 1998) obscure the interpretation of sedimentary opal flux (Anderson et al. 1998). Accumulation of biogenic Ba, which appears linked to export production (e.g. François et al. 1995), may also be affected by ecological factors (Dehairs et al. 2000) and its preservation in sediment is redox-sensitive and poorly constrained (McManus et al. 1999). Accumulation of authigenic U depends not only on the labile organic carbon flux reaching the seafloor, but also on bottom water oxygen concentration. $^{231}Pa/^{230}Th$ ratios of settling particles and sediments increase with particle flux over most of the ocean, as a result of differential scavenging between the two natural radionuclides (Bacon 1988; Chase et al. 2001; Yu et al. 2001). In regions dominated by opal, however, as in the Southern Ocean, differential scavenging is minimized and $^{231}Pa/^{230}Th$ is insensitive to changes in particle flux (Walter et al. 1997). Much remains to be done to refine our understanding of these proxies to obtain eventually reliable estimates of paleoproductivity in the Southern Ocean.

Notwithstanding the persisting uncertainty concerning the process involved (i.e. increased stratification vs increased export production), the $\delta^{15}N$ record indicates that the Southern Ocean CO_2 "leak" was partially "plugged" during the LGM south of the modern position of the Polar Front, and this contributed to lower pCO_2. Universal acceptance of this interpretation, however, still requires that it be reconciled with several seemingly divergent observations. Elderfield and Rickaby (2000) have interpreted changes in the Cd/Ca of planktonic foraminifera as an indication of higher surface phosphate concentration during glacial periods south of the modern Polar Front. This would be consistent with increased relative nitrate (and presumably phosphate) utilization only if the rate of vertical nutrient supply (and export production) were dramatically increased. The interpretation preferred by Elderfield and Rickaby is that the high glacial $\delta^{15}N$ signal is due to the predominance of ice algae, which have been shown to have high $\delta^{15}N$. This observation, however, is not consistent with recent analysis of sediment trap material collected in a region of the Southern Ocean affected by sea ice formation and melting (Altabet and François 2001). Alternatively, the planktonic Cd record could be reconciled with increased relative nutrient utilization and stratification in surface waters if the chemical composition of foraminifera shells were affected by secondary gametogenic calcification (Lohmann 1995; Kohfeld et al. 1996) within the nutrient-enriched pycnocline of the stratified glacial water column. In support of the work by Elderfield and Rickaby (2000), a preliminary Si isotope study suggests lower surface silicate utilization during the glacial periods (De la Rocha et al. 1998). But this approach too must be qualified in light of the recent finding that the Si/N uptake-rate ratio of diatoms decreases significantly when the cells grow in Fe-replete conditions. It is therefore conceivable that relaxation of Fe limitation in the glacial Southern Ocean could have produced an increase in relative nitrate utilization concurrent with a decrease in the proportion of silicate utilized. Alternatively, such dual but opposite impacts on relative nutrient inventories could have been caused by an ecological shift in which *Phaeocystis* sp. dominated diatoms, although the latter appear to be favored by highly stratified conditions (e.g. Arrigo et al. 1999).

In contrast, north of the Polar Front, opal accumulation rates increased during the LGM (Kumar et al. 1995) providing strong evidence for the increased export of C_{org}, possibly as a result of Fe fertilization. However, in this region the $\delta^{15}N$ of bulk sediment was actually somewhat lower than its Holocene value (François et al. 1997; Sigman and Boyle 2000), suggesting that increased Fe supply must have been matched by increased vertical supply of macronutrients and ΣCO_2. Notwithstanding higher export production, the $\delta^{15}N$ data suggest that this region should not have contributed to lower glacial pCO_2, although the interpretation of the $\delta^{15}N$ record in this region is more ambiguous (Sigman et al. 1999), and should still be considered tentative.

Increases in pCO_2 during deglaciations occur over time intervals longer than 5 ky (Petit et al. 1999), either because of the intrinsic response time of the mechanisms involved or that of their forcing. While changes in stratification or export production can have a very rapid effect on atmospheric CO_2, factors that force the changes (e.g. retreating sea-ice cover) can be geographically gradual. Change in Fe input also appears to have been gradual at high southern latitudes, but it may be dangerous to extrapolate the dust input function at Vostok to the entire Southern Ocean. An accurate evaluation of the impact and timing of Southern Ocean productivity, stratification and Fe fertilization on the deglacial increase in atmospheric CO_2 will require synoptic mapping of the timing of changes in $\delta^{15}N$, paleoproductivity and eolian dust over the entire region. Given the existing uncertainties in such proxies and what they mean, it remains a considerable challenge to estimate quantitatively the collective impact on pCO_2 of the processes that have been inferred to have operated in the glacial Southern Ocean. Model-based approaches face similar uncertainties. For example, while box model simulations suggest that surface nutrient depletion in high latitude oceans could produce a large drop in pCO_2 (Sarmiento and Toggweiler 1984; Sigman et al. 1999; Sigman and Boyle 2000; Watson et al. 2001; Legrand and Alverson 2001) simulations using ocean general circulation models are unable to replicate these results (Heinze and Maier-Reimer 1991; Archer et al. 2000). One reason for the lack of sensitivity of General Circulation Models is the relatively large and unrealistic diapycnal mixing often employed. Until this variable is better constrained in the modern and past ocean, and better controlled in the models that are used to estimate the response of pCO_2 to oceanic changes, quantification of the contribution of the biological pump in the Southern Ocean to the glacial lowering of atmospheric CO_2 will remain prone to large uncertainties.

Like the Southern Ocean, the perennial pool of "excess" nitrate, phosphate and silicic acid concentrations that characterizes the North Pacific represents a potential oceanic CO_2 sink. Although mean annual primary production in the region today is similar to that of equatorial Pacific waters (some 140 $gC \cdot m^{-2} \cdot yr^{-1}$, Wong et al. 1999), export production is lower that in the equatorial belt and comprises only 20 to 30 % of total production (Varela and Harrison 1999). Regenerated production dominates; excretion and remineralization are the prominent nitrogen sources for primary producers, rather than upwelling of "new" nitrate. The low new production can be fundamentally attributed to two factors: a) the permanent shallow halocline of the relatively fresh North Pacific, which inhibits physical mixing of the upper water column; and b) iron limitation, which favours the growth of small algal cells that have a characteristically low Fe requirement (Muggli and Harrison 1996; Sunda and Huntsman 1995). Microzooplankton apply essentially constant grazing pressure on the small phytoplankton, and it is this factor that prevents the occurrence in the Northeast Pacific of the spring blooms seen in most other high-latitude oceanic regions in both hemispheres. Large phytoplankton are present, but only as a small component of the total assemblage, and their growth is now known to be controlled by availability of Fe – recent grazer-replete iron-enrichment experiments conducted with Gulf of Alaska surface water in bottles at sea (Boyd et al. 1999) have shown that the addition of small amounts of iron stimulate rapid increases in diatom growth rate, particularly large-celled species (e.g. *Nitzchia*).

Could utilization of the presently unused pool of nutrients in the North Pacific have contributed to the pCO_2 drawdown of the LGM? The answer appears to be no, at least for the eastern sector of the region. The net annual CO_2 exchange across the air-sea interface in the Northeast Pacific today is slightly negative; that is, the region is a minor net sink for CO_2 (Wong and Chan 1991; Zeng et al. 2002). Based on data published by McDonald et al. (1999), the direction and magnitude of this exchange appears to have changed little over the last 30,000 years. McDonald et al. (1999) used the sedimentary record at ODP Site 887 under the HNLC waters of the Gulf of Alaska to show that there was no significant enhancement of carbon burial during the LGM in the area. This observation is supported by lack of biobarium enrichment and isotopically light (-24 to –23 ‰) $\delta^{13}C$ values in bulk organic matter, probably indicating little relative deficiency of CO_2 (aq) in euphotic zone waters (McDonald et al. 1999), similar to the case today. $\delta^{15}N$ measurements made on bulk sediments across the same time interval (Figure 5.6) show light values during the LGM, suggesting that relative nutrient utilization in the area was, if anything, reduced during that time. The available data collectively imply that there was no enhancement of export production during the LGM.; indeed, it may have been reduced. This inference would appear to rule out a strengthened biological pump in the Northeast Pacific as a contributor to the glacial drawdown in pCO_2.

Unlike the high northern latitudes of the Pacific, the Eastern Equatorial Pacific region has long been recognized as a principal source region for CO_2 to the atmosphere. Supersaturation and outgassing from the surface waters in the area results from warming of newly-upwelled CO_2- and nutrient-rich waters in the equatorial divergence (Chavez and Barber 1987; Feely et al. 1999). Although rates of primary production along the divergence are high, the influence of upwelling and warming dominates the impact of export production of C. The modern net air-sea exchange of CO_2 is therefore strongly positive (i.e. out of the ocean).

But did the sign of the flux change in the past? A number of studies have implied that export production was higher in the far eastern equatorial Pacific (EEP) during glacial periods (Pedersen and Bertrand 2000, and references therein). But very recent work suggests that this pattern may not be applicable to the entire equatorial belt east of about 150° W; Loubere (1999) for example used a novel benthic-foram transfer-function approach to suggest that export production in the LGM was not significantly higher than that today, at least along the equator west of the Galapagos Islands. The critical issue here, however, is not whether export production was or was not enhanced during the LGM, but whether or not the EEP ceased to be a source region for CO_2 during that time. All evidence currently available, which comprises a range of isotopic, faunal and sedimentary geochemical proxies, suggests that it did not (Pedersen and Bertrand 2000), although it remains possible that the magnitude of the efflux decreased. When coupled with the results from the Northeast Pacific, this conclusion reinforces the perception that the Southern Ocean was the critical oceanic sink for CO_2 during the LGM.

Changes in Si supply

Although characteristically replete in NO_3^- and HPO_4^{2-}, some HNLC regions are low in surface silicate concentration. This is the case for the subantarctic zone of the Southern Ocean and regions of the equatorial Pacific, both of which are areas that could be silicate-limited (Dugdale and Wilkerson 1998). In such regions, increasing the silicate inventory could potentially enhance transfer of atmospheric CO_2 to the deep sea. Glacial/interglacial changes in the supply rate of silicate to the ocean by weathering, riverine transport and aeolian dust input have not yet been adequately constrained in order to estimate the amplitude of this effect (Froelich et al. 1992; Archer et al. 2000) although the strontium and osmium isotopic evidence published to date suggests that an increased silicate flux to the LGM ocean via weathering at least was unlikely (Section 2.1.3). Alternatively, relieving Fe-limitation would decrease the Si/C_{org} export ratio, which would be equivalent to increasing the silicate supply to Si-limited regions. In addition, the thinner shells produced by Fe-replete diatoms would be more susceptible to dissolution, regenerating silicate at shallower depth and increasing the silicate/nitrate supply rate ratio by vertical mixing. These possibilities have not yet been systematically investigated and should be the subject of future studies.

4.4.3 Global rate of supply of ΣCO_2 to surface waters

The rate at which metabolic CO_2 regenerated in deep waters is brought back towards the surface depends on the strength of the meridional overturning and the rate of diapycnal mixing.

Comparing modeling results obtained with box models, z-coordinate and isopycnic general circulation models have highlighted the sensitivity of diapycnal mixing in establishing the response of atmospheric CO_2 to ocean perturbations (Archer et al. 2000). However, this mixing parameter is poorly constrained even in the modern ocean. Quantifying and understanding the mechanisms that control diapycnal mixing (e.g. Ledwell et al. 1993; Polzin 2000) are thus prerequisite to a quantitative evaluation of the impact of ocean processes on pCO_2.

The main contribution of thermohaline circulation to global climate is in transporting heat from low to high latitude as a result of North Atlantic Deep Water (NADW) formation (e.g. Stommel 1980; Gordon 1986). It may also have an indirect climatic role through the C cycle, however, as it partly controls the sequestration of CO_2 to the deep-sea. The global rate of thermohaline circulation in the modern ocean can be fairly well constrained from direct observations in which current meter measurements, tracer data and geostrophic flow calculations are combined (Ganachaud and Wunsch 2000). But its evolution in the past is more difficult to determine and must rely on reconstructions based on the distribution of chemical tracers that can be measured in sediments. Further, in order to establish the effect of deep circulation on the C cycle, we must reconstruct not only the rate of overturn of the global ocean but also water-mass geometry. The main tracers that have been used to estimate both rate and geometry of thermohaline circulation during the LGM are nutrient proxies, including $\delta^{13}C$, Cd/Ca and Ba/Ca in benthic foraminifera (e.g. Boyle 1992, Lea and Spero 1994; Duplessy et al. 1988). While these tracers disagree at some key locations, notably in the Southern Ocean, they clearly document an increase in nutrient concentration in the deep Atlantic during the LGM and a decrease in intermediate depths shallower than 2,000 m (Boyle 1992). This has been taken as evidence for a glacial shoaling of NADW, increased northward penetration of the Antarctic Bottom Water (AABW) and a general decrease in the rate of thermohaline circulation. Nutrient tracers, however, are not uniquely dependent on circulation, but also on biological uptake and remineralization. As a result, they are difficult to translate in terms of absolute rates of deep water formation (Legrand and Wunsch 1995). Evaluating the impact of possible change in the rate of thermohaline circulation thus still awaits the further developments of tracers that are more quantifiably linked to rates of ocean overturn, such as ^{14}C in foraminifera (Broecker et al. 1988; Hughen et al. 1997), $^{231}Pa/^{230}Th$ in sediments (Yu et al. 1996; Marchal et al. 2000) or “paleo” geostrophic calculations (Lynch-Stieglitz et al. 1999).

4.4.4 Contributions from the alkalinity pump

Changes in seawater alkalinity and attendant shifts in pCO_2 will ineluctably follow variations in continental weathering rate and oceanic production rates of organic carbon and carbonate. While the alkalinity of surface waters will respond rapidly to a changing rate of carbonate export, shifts in the actual rate are likely to be climatically controlled and gradual. Similarly, changes in whole-ocean alkalinity, resulting from variation in weathering rates or deep water acidity (or ΣCO_2 concentration) are inherently slow with a 5 to 10 ky response time (Boyle 1988; Catubig et al. 1998; Archer et al. 2000). Thus, changes in the operation of the oceanic alkalinity pump have the potential to drive multi-millennial variations in pCO_2, but not shifts on shorter time scales.

Temporal variations in sedimentary $CaCO_3$ concentration and burial rates can provide clues about past changes in the position of the carbonate saturation horizon (e.g. Catubig et al. 1998) and thereby shed light on the history of alkalinity distribution in the sea. However, there is not a unique relationship between changes in saturation depth and ocean alkalinity (Sigman et al. 1998; Sigman and Boyle 2000). Augmenting alkalinity by enhancing continental weathering rates or decreasing coral reef formation results in a gradual deepening of the saturation horizon and a concomitant drop in pCO_2 (by about 25 μatm for each km of deepening according to Sigman and Boyle 2000). Decreasing pelagic carbonate production relative to total primary production forces a change in the same direction, in part by extracting less alkalinity from the surface ocean (thereby increasing CO_2 solubility and drawing down atmospheric CO_2), and in part by promoting increased carbonate dissolution in the deep sea (thereby increasing the whole-ocean alkalinity inventory).

Did such changes occur? There is as yet no clear answer. Glacial/interglacial variations in the saturation depth are complex and remain poorly constrained by existing data. In very broad terms, the saturation horizon appears to have shoaled in the Atlantic and deepened in the Pacific during the LGM (e.g. Crowley 1985), while global carbonate accumulation appears to have been similar during the two periods, albeit with increases in carbonate production in the open equatorial and North Atlantic (Catubig et al. 1998). High-resolution reconstruction of carbonate burial rates in the equatorial Atlantic document a deglacial dissolution maximum, followed by a mid-Holocene preservation maximum (François et al. 1990). This progression is opposite to that observed in sediments of similar age elsewhere (e.g. the Indian Ocean: Peterson and Prell 1985). Such variations highlight the complexity associated with postulated changes in the strength of the alkalinity pump, for they could be the result of multiple influences which have variable geographic expression. The dissolution-preservation doublet in the Atlantic described by François et al. (1990) could have been caused for example by changes in the relative penetration of deep water from northern and southern sources. Such variations have not been predicted by any of the models or processes suggested in previous work. Alternatively, the doublet could reflect induction of lower alkalinity in deep waters by increasing ΣCO_2 through vertical transport of metabolizable carbon, followed by a relaxation to an initial position. A third hypothesis is that regional changes in the rain rate ratio of $CaCO_3/C_{org}$ could induce more or less dissolution of carbonate in the uppermost sediments. A lower ratio would cause increased dissolution as "excess" organic carbon was oxidized and lowered the carbonate ion concentration in shallow pore waters (Archer et al. 2000). In addition, there remain uncertainties in estimating continental weathering rates; these may have played a role in the alkalinity balance globally, although the limited evidence available suggests not (e.g. Henderson et al. 1994; Oxburgh 1998). Finally, deglacial and post-deglacial increases in coral reef and shallow carbonate accumulation did occur (Opdyke and Walker 1992), and these should have induced general shoaling of the saturation-horizon depth in the sea. Further progress in assigning weight to these various possible explanations and their geographic impact awaits detailed regional studies; it is only via this approach that the history and causation of relative movement of the saturation boundary will be defined.

4.4.5 Contributors to transient excursions in atmospheric CO_2

Significant changes in pCO_2 on the centennial-millennial time scale have been documented in ice cores (Chapter 2). Although much smaller in magnitude than the observed glacial-interglacial variability, such variations are nevertheless indicative of important global-scale processes. Progress in understanding controls on these higher-frequency changes has been slowed by the combination of a relatively small signal, complications arising from chronological uncertainties and the potential for naturally occurring artefacts within the glacial ice, particularly in Greenland ice cores. Nevertheless, recent studies of the less problematic Antarctic ice recovered from Byrd Station (Stauffer et al. 1998) and Taylor Dome (Indermühle et al. 2000) have confirmed that robust changes of 20±1 μatm tracked millennial-scale climate cycles during the last ice age, as noted in Chapter 2.

The relatively ephemeral persistence of these events rules out carbonate-compensation or alkalinity-pump explanations for their origin. Instead, the millennial-scale character coupled with their small magnitude points to changes in thermohaline circulation (THC) as the likely cause. Model studies indicate variability in THC can account for rapid changes in atmospheric composition, and that THC shutdowns could result in CO_2 increases of the observed magnitude (Marchal et al. 1998; Stocker and Marchal 2000). Modeled changes in pCO_2 result from Southern Ocean warming (Marchal et al. 1998) which occurs as part of the contrasting bipolar surface temperature response (Broecker 1998; Stocker 1998) when North Atlantic Deep Water production is curtailed. In addition, associated changes in alkalinity and dissolved inorganic carbon in Atlantic Ocean surface waters would amplify the CO_2 increase relatively rapidly (Indermühle et al. 2000).

Not all high-frequency climate changes are associated with pCO_2 variations, however. Some individual Dansgaard-Oeschger events (see Chapter 3) show no association with pCO_2 shifts (Chapter 2). This may reflect limited freshwater forcing due to smaller iceberg discharges (Indermühle et al. 2000) and lack of a thermohaline response sufficient to perturb pCO_2. Alternatively, the response time for pCO_2 to reach equilibrium with a new ocean circulation regime may be large relative to the quasi-1500 year duration of many D-O cycles (Stauffer et al. 1998), and this may have muted ΣpCO_2 shifts in the ice-core archives.

While these observations draw links between high-frequency, low-magnitude pCO_2 variability and physical oceanographic changes, it is also true that the warmest and longest interstadials of the D-O cycles occurred at the times of the highest concentrations of pCO_2 during the last ice age. This association implies a climatic response to the increased CO_2 and feedbacks potentially related to it, such as atmospheric water vapor content.

4.5 Summary and critical areas for future research

Atmospheric CO_2 changes on glacial/interglacial timescales are primarily controlled by oceanic processes. Although variations in continental carbon storage could have mitigated the amplitude of pCO_2 shifts during transition periods, such effects are likely to have been small. They are also very difficult to quantify. Estimates from isotopic mass balances, palynological data, and land biosphere models are widely divergent and need to be reconciled. Limited evidence suggests that there was little change in continental weathering rate variability on the global scale between glacial and interglacial times. If true, this rules out weathering-related effects as major controlling influences in the late Quaternary pCO_2 evolution.

While the importance of oceanic processes is well established, there is no consensus, as yet, on the precise mechanism or series of events responsible for the timing and amplitude of pCO_2 changes. The potential importance of high latitude oceans in regulating atmospheric pCO_2 has often been highlighted and has lead paleoceanographic carbon research to concentrate on the Southern Ocean. It is now apparent, however, that this perception is primarily model-driven (Broecker et al. 1999). The sensitivity of pCO_2 to high latitude surface oceanic processes, which is clearly recognized in box and zonally-averaged ocean circulation models, is not found in three-dimensional depth-coordinate ocean general circulation models, while isopycnic GCM's display an intermediate behavior (Archer in press). This discrepancy needs to be resolved and its consequences fully understood. If the 3-D models are shown to yield a closer representation of ocean circulation, a shift of focus toward lower latitude regions may be indicated.

Even though the Southern Ocean has been an area of focus, the paleoceanographic reconstruction of its carbon cycle remains uncertain. While a recent study of N isotopes in the modern Southern Ocean corroborates the interpretation of the $\delta^{15}N$ record in sediments as reflecting an increase in surface nitrate utilization during glacial periods (Altabet and François 2001), the mechanism whereby this higher depletion arises is still in doubt due to our inability to constrain properly past changes in export production. In addition, there remains a need to reconcile the sedimentary $\delta^{15}N$ record with those of the Cd/Ca ratio in planktonic foraminifera (Elderfield and Rickaby 2000) and silicon isotopes (De la Rocha et al. 1998). The history of vertical shifts in the depth of the lysocline and its relation to the thermodynamic saturation horizon in the water column and the compensation depth in sediments must also be better documented (e.g. Sigman et al. 1998; Catubig et al. 1998). Regional, high-resolution reconstruction of lysocline depth can be obtained by measuring ^{230}Th-normalized carbonate fluxes on the flanks of topographic features (e.g. François et al. 1990). This could help distinguish between the various factors that affect ocean alkalinity which include weathering rates, shallow carbonate accumulation, pelagic carbonate production, the length scale of organic matter remineralization, and deep water circulation.

Developing tools to estimate past changes in bottom water oxygen concentration would also bring important constraints to verify the validity of proposed circulation- and productivity-change scenarios. Such proxies do not exist in a well-verified sense, but the accumulation of redox sensitive metals with different redox potentials or geochemical behaviors holds promise (Crusius et al. 1996; Nameroff et al. 2002)

Accurately documenting eolian inputs to the deep-sea has now gained new urgency with the realization that many HNLC regions are Fe limited and might not have been so during glacial periods. Measurements of the terrigenous fraction of deep-sea sediments do not always provide an accurate reflection of eolian input, as nepheloid transport of resuspended shelf and slope sediments can also be significant, particularly during glacial periods (François and Bacon 1991). This is particularly well illustrated in the southern ocean, where ^{230}Th-normalized fluxes of terrigenous material in Holocene sediments far exceeds estimates of eolian input in this region (Kumar et al. 1995; François et al. 1997). Input of volcanic ash can also obscure the eolian fraction, or make difficult its measurement. Thus, developing a geochemical means of distinguishing eolian dust from other terrigenous sediment constituents would be very useful in reconstructing regional history of dust input and Fe fertilization.

A promising technique in this regard is the measurement of ^{4}He in the non-biogenic fraction of the bulk sediments, or in isolates of specific components. Geologically old rocks and soils such as those in the deserts of north-central Asia contain a relatively high ^{4}He content. The ^{4}He is derived from the decay of U and Th isotopes, and a U-rich mineral phase such as zircon is particularly enriched in ^{4}He because alpha particles cannot readily escape from the dense atomic structure of that mineral phase, at least when the zircon grain is larger than the typical recoil length of 10-30 μm (Farley et al. 1995). Analysis of the ^{4}He content of zircons extracted from a sediment core could potentially yield information on the provenance of the grains. In a region such as the northeast Pacific, where "old" ^{4}He-rich Asian dust is delivered to the sea surface (Boyd et al. 1998) along with "young" Alaskan dust, ^{4}He analyses could allow specific determination of the Asian dust input through time. Such an approach has been used successfully elsewhere. Patterson et al. (1999) used ^{4}He analyses to map Asian dust input through time to sediments on the Ontong-Java Plateau in the western equatorial Pacific (Patterson et al. 1999). Developing this fingerprinting technique further would be beneficial in mapping the time history of aeolian contributions to the open ocean. Having such information could prove very valuable in determining the influence of iron fertilization on the strength of the open-ocean biological pump during the Quaternary.

Finally, we suggest that the ca. 80 μatm difference in atmospheric CO_2 recorded in ice cores should not be used as a reference against which to appraise the significance of every proposed change in the C cycle. Many potential mechanisms may have acted in parallel or in sequence during the course of the late Quaternary glacial-interglacial seesaw, resulting in a vast reorganization of the earth's carbon cycle. Although we cannot rule out a simple one- or two-process control for the decline in pCO_2 seen in glacial maxima, such a spare explanation seems unlikely. The 80 μatm glacial decrease recorded in ice cores should therefore be viewed as a net effect and not a specific target that any one single process has to explain. Future progress will come from quantification of specific contributions from multiple sources and sinks, from reducing the uncertainties inherent in such estimates, and by working to gain an integrated understanding of the causalities and feedbacks among the processes involved.

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