

A possible sequence of events for the generalized glacial-interglacial cycle

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Received 4 January 2005; revised 8 November 2005; accepted 3 January 2006; published 25 May 2006.

[1] There is not yet widespread agreement as to the underlying cause of the 80–100 ppmv roughly 100-kyr-duration glacial-interglacial cycles in atmospheric pCO₂. Most of the mechanisms which have been proposed to account for the observed pCO₂ variations appear to in some way violate interpretations of paleo proxy data. The inability of a single mechanism to explain the observed cycles in atmospheric CO₂ (which show amazing similarity over the past 430,000 years) is perplexing, and leads us to consider whether a combination of mechanisms might be consistent with available evidence. Consistent with previous work, we find that physical changes (ocean circulation, temperature, mixing) can only explain part of the observed atmospheric pCO₂ variability; changes in ocean chemistry are invoked to explain the remainder. In order to account for the initial pCO₂ drawdown (from “interglacial” to “intermediate” levels), we invoke physical changes in the ocean (mixing, temperature). The transition from intermediate atmospheric pCO₂ levels to full glacial conditions involves a small increase in mean ocean nutrient levels and mean ocean alkalinity, accomplished by falling sea level and subsequent erosion of organic-rich shelf sediments. The first part of the transition out of full glacial conditions is achieved through increased temperature and increased mixing in the Southern Ocean. The final part of the atmospheric pCO₂ rise up to full interglacial conditions is accomplished through rising sea level and the subsequent change in mean ocean alkalinity and phosphate, and a rise in the Northern Hemisphere temperature and ocean mixing. The proposed sequence of events is consistent with most existing proxy evidence for paleo-nutrient levels and changes in export production over the last glacial-interglacial cycle. Furthermore, it is consistent with evidence for a whole-ocean shift in δ¹³C toward significantly more negative values in the late glacial. The proposed scenario is also consistent with ice core-based timing constraints, as summarized by Broecker and Henderson (1998). We show that we are able to explain the full magnitude of the glacial-interglacial cycle in atmospheric pCO₂ without the need to invoke iron-fertilization in the Southern Ocean.

Citation: Peacock, S., E. Lane, and J. M. Restrepo (2006), A possible sequence of events for the generalized glacial-interglacial cycle, *Global Biogeochem. Cycles*, 20, GB2010, doi:10.1029/2005GB002448.

1. Introduction

[2] Over the last half million years or so, Earth’s climate has cycled through a series of fairly regularly spaced glacial and interglacial eras. During this time, changes in atmospheric partial pressure of CO₂ (pCO₂) have been strongly correlated with fluctuations in global temperature and ice volume [Petit *et al.*, 1999]. During the Last Glacial Maximum (LGM), the pCO₂ of the atmosphere was around 200

ppmv, compared with 280 ppmv in the preindustrial era. In addition to this 80 ppmv drop, the terrestrial biosphere is thought to have added some 500 Pg of carbon to the atmosphere-ocean system during the last glacial, estimated to be equivalent to an effective 15 ppmv increase in atmospheric pCO₂ after CaCO₃ compensation [Sigman and Boyle, 2000]. While it is generally agreed that the ocean must somehow regulate glacial-interglacial changes in pCO₂ on timescales of tens of thousands of years [Broecker and Peng, 1982], the means by which such a coupling might be achieved is still under debate [Sigman and Boyle, 2000].

[3] The typical “glacial-interglacial” cycle over the past 430,000 years is characterized by a slow decline in temperature and CO₂ (lasting tens of thousands of years) under low background levels of dust deposition, followed by a period during which dust flux rises, while temperature and CO₂ fall

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still farther, culminating in maximum glacial conditions. The end of the LGM is marked by a rapid decline in dust levels and relatively rapid rise of temperature and CO₂ (taking place over <10,000 years) to full interglacial conditions. Interglacial periods are far shorter than the corresponding glacial; then the cycle repeats itself. Prior to 430,000 years ago this 100,000 year cyclicity between glacial and interglacial periods was somewhat more muted, but still clearly discernible back to about 740,000 years ago [Augustin *et al.*, 2004].

[4] Although a large number of mechanisms have been proposed to account for the glacial-interglacial pCO₂ variations, the combination of data-based constraints and timing constraints makes it highly unlikely that any single process can account for the entire change. We here use a box model to explore whether the observed pCO₂ cyclicity can be accounted for by a sequence of distinct processes, both physical and chemical. The proposed sequence of events is tested against both paleo-proxy data from deep-ocean sediment cores and timing constraints from ice cores. We demonstrate that relatively small physical changes (mixing, rate of circulation, temperature boundary conditions) which are consistent with proxy evidence, can only account for part (roughly 50 ppmv) of the observed glacial-interglacial pCO₂ shift. Examination of the relative timing of CO₂ rise and atmospheric δ¹⁸O suggests that in the transition from peak glacial to interglacial conditions, the last part of the pCO₂ rise is coincident with changing sea level. We therefore explore the possibility that changes in ocean chemistry triggered by sea level change could account for the remainder of the pCO₂ change. The proposed sequence of events is shown to be largely consistent with paleo-nutrient reconstructions, with recent estimates of export production, and with the timing constraints imposed by ice core records.

[5] In this study, we view the generalized glacial-interglacial cycle as consisting of three quite distinct periods. These we term “interglacial,” “intermediate,” and “glacial” (see Figure 1). The “intermediate” stage corresponds to Marine Isotope Stages 5a through 5d (roughly 110 kyr to 75 kyr B.P.; see Table 1), while “glacial” corresponds to the time from roughly 75 kyr through 10 kyr B.P. “interglacial” periods are those such as the Holocene, where atmospheric pCO₂ levels are close to 280 ppmv for a relatively short period of time. The intermediate stage is characterized by low background dust flux and relatively high (but decreasing) atmospheric pCO₂ (generally higher than 220 ppmv). The glacial period is characterized by high dust fluxes and low atmospheric pCO₂ (generally lower than 220 ppmv).

2. Constraints From Data

2.1. Proxy Data From the Glacial Ocean

[6] During the LGM, the sea surface temperature (SST) was lower than at the present day. Although the CLIMAP project (2001, <http://ingrid.ldeo.columbia.edu/sources/.climap/>) reported a minimal change in the low-latitude SST, more recent estimates [Beck *et al.*, 1992; Guilderson *et al.*, 1994] suggest the temperature dropped by between 4°C and 5°C. The evidence for change in the height of the snow

line near the equator also supports a sea surface temperature change of order 5°C [Broecker, 1995]. The drop in SST in high latitudes is limited by the freezing point of seawater. There is now substantial evidence indicating that the southern high latitude regions were around 1–2°C lower than at the present day, and the northern high latitudes around 3–4°C lower [Broecker, 1995] during the LGM. Martin *et al.* [2002] calculate that the temperature of the glacial bottom waters of the ocean were around 2–3°C cooler than the interglacial. The deep tropical glacial ocean may have been up to 4°C cooler than during the interglacial period.

[7] Eustatic sea level changes between the LGM and present day yield an estimate of mean ocean salinity of between 35.85‰ [Fairbanks, 1989] and 35.95‰ [Lambeck and Chappell, 2001; Rohling *et al.*, 1998; Yokoyama *et al.*, 2000]. Recent data from ocean-floor pore water profiles [Adkins *et al.*, 2002] imply that the LGM salinity was somewhat higher than this. It has been suggested that groundwater reserves or floating ice shelves may explain the discrepancy. On this basis we assume in this study that a mean ocean salinity of 36‰ is representative of the glacial ocean.

[8] There is evidence for increased sea-ice coverage in the Southern Ocean and a northward migration of the polar front in glacial times [e.g., Francois *et al.*, 1997]. These authors suggest that increased stratification in the Southern Ocean could be an important factor in lowering atmospheric pCO₂. In a similar vein, Toggweiler [1999] has also proposed increased stratification (reduced mixing) and reduced ventilation of deep water as a mechanism for lowering atmospheric pCO₂.

[9] There are various lines of evidence suggesting that the thermohaline flow in the North Atlantic was weaker during the last glacial. There is evidence from δ¹³C and Cd/Ca [Bacastow, 1987; Boyle and Keigwin, 1982; Boyle, 1992] that NADW was found at a considerably shallower depth during the last glacial than at the present day. Radiocarbon age differences between coexisting planktonic and benthic foraminifera suggest that deep water in the Southern Ocean and Pacific was considerably older during the LGM, perhaps implying a reduced rate of flow [Goldstein *et al.*, 2001; Shackleton *et al.*, 1988; Sikes *et al.*, 2000]. Measurements of the authigenic uranium in sediments have been used as a proxy for the amount of oxygen in deep water. This evidence implies that oxygen in the deep ocean was decreased during the glacial, but that the deep ocean was not anoxic [Francois *et al.*, 1997]. However, there is currently some debate as to the interpretation of paleo-circulation proxies. Wunsch [2003] argues that a reduced circulation is hard to reconcile with evidence for stronger winds in glacial times. There is also evidence from ²³¹Pa/²³⁰Th that contradicts the concept of reduced-flow during the glacial [e.g., Yu *et al.*, 1996]. More recently it has been shown that much of the observed variability in down-core δ¹³C records can be explained under a steady state circulation and changing boundary conditions [Rutberg and Peacock, 2006]. Until a consensus is reached on the interpretation of existing circulation proxy records, it is impossible to say definitively how much glacial large-scale ocean circulation differed from that of today.

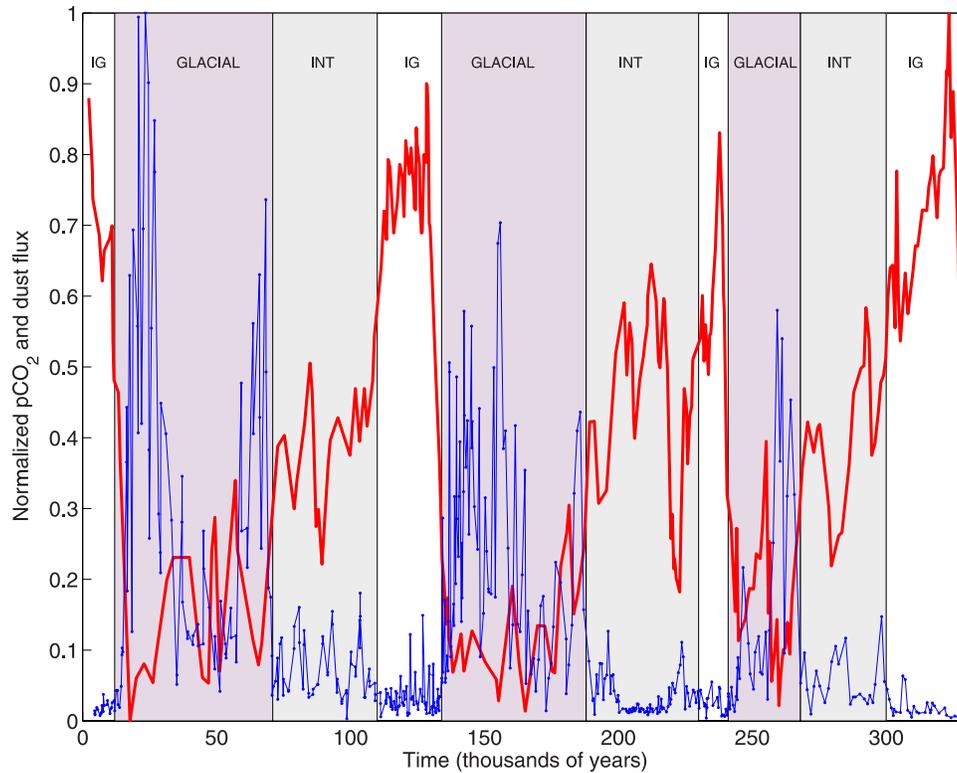


Figure 1. Atmospheric pCO₂ (red) and dust (blue) records from the Vostok ice core. Data are those reported by *Petit et al.* [1999]. Records have been normalized such that the maximum values over the time period 0–430,000 years scale to +1, and the minimum values to zero (in absolute terms, over the period shown in the figure, the minimum value of pCO₂ is 182 ppmv and the maximum is 298 ppmv). The shaded regions correspond to time periods discussed in the text, during which each model solution was obtained. The interglacial (IG) periods are those of high (roughly 278 ppmv) atmospheric pCO₂ and low background dust flux; “intermediate” (INT) periods occur between full interglacial and full glacial conditions (gray shading), and for the purposes of this study, “glacial” is used to refer to the period with coldest temperatures, lowest atmospheric pCO₂, and highest dust flux.

[10] Iron fertilization has been suggested as a mechanism by which to lower atmospheric CO₂ during glacial periods [*Martin, 1990*]. It has been shown that the addition of a limiting nutrient such as iron can have a very strong local effect on export production in high-nutrient, low-chlorophyll (HNLC) regions such as the Southern Ocean, which exhibit “underrealized utilization potential.” Even a small elevation in the input of iron (via dust) to the Southern Ocean might be expected to increase nutrient utilization, export production (and hence atmospheric pCO₂ drawdown).

[11] What about the evidence for past levels of export production? A recent compilation of various data from a large number of cores by *Kohfeld et al.* [2005] suggests that net export production was the same or lower than at the present day during much of the intermediate stage (Marine Isotope Stages (MIS) 5a through 5d). During the LGM, however, it appears from the *Kohfeld* compilation that outside of the Southern Ocean, export production may have been somewhat higher than today, whereas south of 50°S export production during the LGM appears somewhat lower than present-day levels. The small increase in dust flux

observed during the intermediate period (stages 5a–5d; Figure 1) appears not to have been associated with an increase in global export production [*Kohfeld et al., 2005*]. However, the much larger increase in dust flux during the glacial period (Figure 1) does correlate with generally higher global export production.

[12] There is an important distinction between net export production and nutrient utilization. If there is no change in circulation, an increase in nutrient utilization and an increase in export production will go hand in hand. However, if the supply of nutrients to the surface is decreased (for example through enhanced stratification, or reduced vertical mixing), the percentage of nutrients utilized could increase while export production remained constant. Evidence for the degree of nutrient utilization in the glacial Southern

Table 1. Definition of Time Periods Used in This Study

This Study	Age, years	Marine Isotope Stages
Interglacial	0–10	1
Glacial	10–75	2, 3, 4
Intermediate	75–110	5a–5d

Ocean is somewhat contradictory. There are a number of proxies which have been used in attempt to evaluate the degree of nutrient utilization in the glacial ocean. Nitrate uptake has been assessed from variations in ¹⁵N in organic matter through time (an increase in nitrate uptake would lead to an increase in the ¹⁵N of organic matter in the surface ocean). Past levels of phosphate in the glacial surface ocean have been estimated on the basis of Cd/Ca ratios in planktonic foraminifera. Uptake of silica in the surface ocean has been estimated on the basis of the ^δ³⁰Si concentration in diatoms (higher surface water silica uptake would lead to and increase in the ^δ³⁰Si of diatoms); and surface water CO₂ in the glacial ocean has been inferred on the basis of the ^δ¹³C of organic material (a decrease in surface water CO₂ would be reflected by a relative increase in the ^δ¹³C of organic material).

[13] Evidence from nitrogen-isotopes suggests that nutrient utilization in the Indian and Pacific sectors of the sub-Antarctic was somewhat greater during the glacial than in the modern (interglacial) ocean [Robinson *et al.*, 2005], whereas in the Atlantic sector, nutrient utilization was roughly the same as present-day levels [Robinson *et al.*, 2004]. Evidence from Cd/Ca ratios in planktonic foraminifera [Elderfield and Rickaby, 2000; Boyle, 1992] suggests little or no change in nutrient concentrations in the Antarctic surface ocean during the LGM. In fact, if anything, their evidence points to somewhat higher than present-day phosphate levels in the Antarctic, and roughly equivalent to present-day levels in the sub-Antarctic. It appears that the ^δ³⁰Si in diatoms was lower than at present in the glacial surface Southern Ocean [DeLaRocha *et al.*, 1998], and surface water CO₂ appears to have been higher than present-day levels [Rosenthal *et al.*, 2000]. Thus the majority of proxy data is consistent with both a decrease in nutrient utilization, and a decrease in export production. There are of course uncertainties associated with the Cd/Ca reconstruction; however, error bounds seem to constrain LGM Antarctic surface-ocean nutrient levels to within 30% of present-day levels. Nitrogen isotopes are the only proxy which suggest increased utilization, and this may be because controls over nitrogen isotope ratios are still not fully understood [Robinson *et al.*, 2005]. On the basis of the available evidence, we feel that increased nutrient draw-down via enhanced iron fertilization in the glacial ocean is somewhat at odds with the bulk of the evidence for past levels of nutrient utilization.

2.2. Evidence for Timing of CO₂ Change Versus Ice Sheet Melting

[14] Interesting observations were made by Broecker and Henderson [1998] pertaining to the relative timing of the rise in CO₂ and temperature versus atmospheric ^δ¹⁸O (a proxy for ice sheet melting) coming out of a glaciation. It was observed that in the transition from the penultimate glacial to interglacial, air temperature and atmospheric pCO₂ in the Southern Hemisphere rose together, some time after the high glacial dust flux had dropped to low interglacial levels; the decrease in ice volume and changes in the North Atlantic circulation (as recorded by ^δ¹³C in foraminifera) occurred later. The atmospheric CO₂ and tempera-

ture (inferred from deuterium) began to rise from low full glacial values a significant amount of time before the ^δ¹⁸O began to fall (indicating ice sheet melting and change in sea level). Dust had dropped to near-zero levels before the CO₂ rise began. Warming took about 8 thousand years (kyr). Changes in ^δ¹³C in the North Atlantic appear to occur synchronously with the change in ^δ¹⁸O (i.e., significantly after the start of the rise in Antarctic temperature and atmospheric pCO₂). The time gap for the last termination is order 2 kyr; for the penultimate termination it was order 4 kyr [Broecker and Henderson, 1998]. On the basis of the relative timing of events coming out of the penultimate glaciation, Broecker and Henderson [1998] suggest that the trigger for atmospheric pCO₂ change must lie in the tropics or Southern Ocean, not the North Atlantic.

2.3. Criteria Which Must Be Satisfied By Any Model of Glacial-Interglacial Atmospheric pCO₂ Variations

[15] Taking at face value the Kohfeld *et al.* [2005] and Elderfield and Rickaby [2000] results, and imposing the Broecker and Henderson [1998] timing constraints, there are certain criteria which should be satisfied by a model of glacial-interglacial atmospheric pCO₂ variations: (1) Glacial export production in the Southern Ocean should be the same as, or lower than, interglacial levels; (2) glacial export production in the nonpolar oceans should be the same as, or higher than, interglacial levels; (3) glacial surface-ocean phosphate concentrations in the Southern Ocean should be the same as, or higher than, interglacial levels; (4) glacial surface-ocean phosphate concentrations in the nonpolar oceans should be roughly the same as interglacial levels; (5) export production during the intermediate stage should be the same as, or lower than, interglacial levels almost everywhere in the ocean; (6) circulation changes in the North Atlantic and ice sheet melting (sea level rise) should occur after CO₂ and Antarctic temperatures have already started to rise; and (7) the compilation of global export production rates combined with the Vostok dust record suggests that if dust plays any role at all, it most likely does so in the glacial period.

3. Hypotheses for Glacial-Interglacial pCO₂ Variations

[16] The ultimate cause for the dramatic swings in atmospheric pCO₂ observed on glacial-interglacial timescales must lie in the ocean. How exactly such cycles are regulated, however, remains elusive. For an excellent review paper on the subject, the reader is referred to Sigman and Boyle [2000]. The main ocean-based mechanisms by which the atmosphere's pCO₂ can be altered on millennial timescales are the "solubility pump," the "soft-tissue pump" and the "carbonate pump." These refer to the oceans' ability to sequester excess CO₂ due to temperature-induced solubility; change in net amount or utilization of organic matter; and change in the CaCO₃/C_{org} rain ratio and/or dissolution rate of CaCO₃, respectively. Another possible way to regulate atmospheric pCO₂ is through changes in physical properties, such as sea-ice cover, mixing, or the ocean's velocity field [Bacastow, 1996; Heinze *et al.*, 1991]. While the

possible role of locally reduced air-sea gas exchange and/or increased sea-ice cover is still debated [Stephens and Keeling, 2000; Ridgwell, 2001; Archer et al., 2003], there appears to be general agreement that changes in circulation alone will have only a small effect on atmospheric pCO₂ change [Schultz and Paul, 2004; Winguth et al., 1999].

3.1. Temperature-Salinity Changes

[17] One parameter which is fairly well constrained is the change in mean temperature and salinity of the ocean. During glacial times, ocean temperatures were lower and mean salinity higher (owing to lower ocean volume). Decreasing temperature increases solubility, and hence increases the amount of dissolved CO₂ in the surface ocean; increasing salinity acts in the opposite direction. Results from many studies show that the combined temperature/salinity effect between peak glacial and interglacial times was order 20–30 ppmv [Sigman and Boyle, 2000], clearly not anywhere near large enough to explain the observed changes.

3.2. Shelf Hypothesis

[18] One of the earliest hypotheses put forward to try and account for the observed glacial-interglacial atmospheric pCO₂ changes was the so-called “shelf hypothesis” of Broecker [1982]. This involves a change in whole-ocean nutrient inventory through phosphorus deposition onto and erosion off shallow shelves which are alternately buried and exposed as sea level rises and falls. Sea level changes are the driving force behind this mechanism. Burial of phosphorus in interglacials would decrease mean phosphate; erosion in the low-sea level stand of the glacials would increase mean ocean phosphate. The impact on atmospheric pCO₂ is through changing the mean ocean ΣCO₂:PO₄ ratio, which would regulate the extent of pCO₂ drawdown by plants in the surface ocean. This hypothesis has been widely discredited for two reasons: First, it is closely tied to changing sea level, and second, because the amount of sediment required to be deposited and eroded on the glacial-interglacial timescale is in order for this mechanism to account for most of the atmospheric pCO₂ change appears to be far greater than observational evidence suggests.

3.3. Alkalinity-Change and Carbonate-Pump-Based Hypotheses

[19] Because the pCO₂ of surface water in the ocean is a function of both dissolved inorganic carbon (DIC, or ΣCO₂) and alkalinity, changes in the mean ocean inventory of either would have an impact on atmospheric pCO₂ levels. A number of the early hypotheses seeking to explain the glacial-interglacial atmospheric pCO₂ variations invoked a change in mean ocean alkalinity [Berger, 1982; Opdyke and Walker, 1992; Milliman, 1993], but again, these hypotheses have been widely discarded because they must be linked to changes in sea level, which occurred during the lattermost part of atmospheric pCO₂ rise.

[20] Hypotheses involving a change in the ocean’s carbonate pump seem unlikely because such a change would cause a significant shift in the depth of the lysocline (a transition zone which separates deep-sea sediments with no

preserved calcite from shallower sediments where calcite is preserved), which has not been observed. Archer and Maier-Reimer [1994] suggested a way around this problem with a hypothesis which invoked a higher rain rate of organic matter to the seafloor during glacial times. However, this idea calls for a separation between the saturation horizon and the lysocline, a scenario which Sigman et al. [1998] make a strong case against.

3.4. Changes in North Atlantic Circulation

[21] The jury is still out with regard to how to definitively interpret existing evidence for changes in North Atlantic circulation associated with the transition from glacial to interglacial periods. There clearly are changes in proxies such as δ¹³C, but whether such variability reflects changes in boundary properties or in the time-mean circulation remains open to debate [Rutberg and Peacock, 2006]. As we will discuss below, there is strong evidence that changes in the North Atlantic significantly lagged the onset of CO₂ and temperature rise as evident from the Vostok ice core record.

3.5. Polar Dominance (Increased Nutrient Utilization)

[22] Since the mid-1980s, the idea has reigned that polar regions of the ocean are more important in regulating atmospheric pCO₂ than are the low latitude regions. If correct, this would rule out many of the nonpolar-based mechanisms from having a significant impact on atmospheric pCO₂. Attempts have been made to quantify the “high latitude sensitivity” of a given model by metrics such as the “HBEI” (the “Harvardton Bear Equilibration index,” designed to estimate the relative importance of circulation and air-sea gas exchange [Broecker et al., 1999]) and “abiotic pCO₂” [Archer et al., 2000], but how the real ocean fits into all of this is still the subject of ongoing debate [Lane et al., 2006].

[23] Because nutrients are largely underutilized in the Southern Ocean today, it is possible that a significant increase in nutrient utilization in this region during glacial times could play an important role in the drawdown of atmospheric pCO₂. Many box model results [e.g., Siegenthaler and Wenk, 1984; Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984] suggest that increased utilization of the currently very underutilized Southern Ocean nutrients would account for most of the glacial-interglacial CO₂ drawdown; however, it seems unlikely that so dramatic a change in Southern Ocean nutrient concentrations occurred [Boyle, 1992; Elderfield and Rickaby, 2000]. Aside from the proxy evidence for small or no change in Southern Ocean nutrients is the likelihood that a large increase in high-latitude nutrient utilization would cause anoxia in the deep ocean, which also goes against observational evidence [Francois et al., 1997]. Furthermore, there is no clear mechanism for a sudden and large high-latitude nutrient drawdown. Iron fertilization is an obvious candidate [Martin, 1990]. However, there are problems with this idea. For example, very high dust fluxes are only observed in glacial times (as defined in Figure 1), and second, as Broecker and Henderson [1998] point out, the dust flux had fallen to almost zero before the temper-

ature and CO₂ began to rise in the Southern Hemisphere. As a way around this problem, Broecker and Henderson suggest an increase in the rate of nitrogen fixation in the ocean; the idea is that because of the long residence time of nitrate in the ocean, an iron-induced increase in fixed nitrate could take several thousand years to diminish to interglacial levels.

3.6. Increased Sea-Ice Coverage

[24] *Stephens and Keeling* [2000] recently proposed that covering most of the Southern Ocean with sea ice, and hence dramatically reducing air-sea gas exchange, could go a long way toward accounting for the glacial-interglacial atmospheric pCO₂ signal by isolating the deep ocean from the atmosphere, and hence increasing the deep ocean storage of ΣCO₂. However, a GCM-based study of the impact of increased sea ice on atmospheric pCO₂ levels [*Archer et al.*, 2003] suggests that the effect is minimal. There are also box-model-based results [*Ridgwell*, 2001; *Lane et al.*, 2006] which imply that the reduction in air-sea gas exchange that comes from increasing sea-ice cover only has a small net effect on atmospheric pCO₂. *Francois et al.* [1997] and *Toggweiler* [1999] suggest that it is more likely that reduced vertical mixing in the Southern Ocean in glacial times could be an important factor. *Gildor and Tziperman* [2001] propose a mechanism whereby changes in the North Atlantic are able to remotely trigger a change in extent of Antarctic sea ice (via deep-ocean circulation); however, their hypothesis relies upon the trigger lying in the North Atlantic, which contradicts timing constraints.

3.7. Silicate Leakage Hypothesis

[25] *Brzezinski et al.* [2002] suggested an alternative mechanism by which the export ratio of CaCO₃ to organic matter might be altered, involving the silicate cycle. Today there is a very strong gradient in silicate in the Antarctic, with high values to the south and low values to the north of the polar front. It is predominantly high-nitrate, low-silicate waters that are exported northward to lower latitudes as Subantarctic Mode Water. The possibility exists that an increase in dust deposition to the Southern Ocean might relieve diatoms from their iron stress, which would feed back to export significantly higher amounts of Si(OH)₄ to lower latitudes. This would enhance growth of diatoms over coccoliths, which would lead to a reduction in the export of CaCO₃ from the surface ocean, which could subsequently draw down atmospheric pCO₂. Support for this idea is given by the observation that there were higher opal accumulation rates south of the polar front during the LGM [*Kumar et al.*, 1995; *Francois et al.*, 1997], δ³⁰Si measurements indicating a depletion of surface silicic acid during the LGM [*DeLaRocha et al.*, 1998], and δ¹⁵N measurements which indicate higher nitrate utilization during the LGM [*Francois et al.*, 1997]. It was found in a box-model framework [*Matsumoto et al.*, 2002] that the net effect of such a process could be order 30–40 ppmv. However, it must be noted that all the sedimentary evidence, and the large increase in dust flux, occurs in the stage we denote as “glacial” [*Brzezinski et al.*, 2002, Figure 2]. By the start of the glacial (roughly 75,000 years ago for the last glacial-interglacial cycle), atmospheric pCO₂

had already dropped from the interglacial value of around 280 ppmv down to around 220 ppmv (see Figure 2). Therefore it seems that the silicate leakage hypothesis could only be invoked to explain the lattermost part of the glacial decline in atmospheric pCO₂, and not the bulk of the record.

4. Box Model

[26] In order to test our proposed sequence of events, we have constructed a dynamic-flow box model which incorporates a Michaelis-Menten-type feedback on nutrient levels. The model equations can be found in the auxiliary material¹. A depiction of the box model appears in Figure 3, and details of model construction and its sensitivity to parameters are given by *Lane et al.* [2006]. The parameters of the six box model were tuned to achieve the observed preindustrial pCO₂ of roughly 280 ppmv [*Barnola et al.*, 1992] while aiming to stay as close to observational constraints as possible. Initial conditions for each tracer were obtained from estimates of the ocean mean preindustrial tracer values.

[27] Mixing coefficients were estimated as follows: The eddy-mixing coefficient for vertical mixing in the interior nonpolar ocean was required to be between $1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ and $1 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, in line with observational evidence [*Polzin et al.*, 1997]. In the southern box, where intense mixing along steeply inclined isopycnals yields a very large effective vertical mixing coefficient in depth coordinates, and in the northern box, where deep convection also yields a high effective mixing, an effective vertical eddy-mixing coefficient of between $10^{-3} \text{ m}^2 \text{ s}^{-1}$ and $10^{-2} \text{ m}^2 \text{ s}^{-1}$ was required. The horizontal eddy-mixing coefficient was estimated to be between 2 and $3 \times 10^5 \text{ m}^2 \text{ s}^{-1}$, in line with values used in GCMs. The “best-guess” mixing coefficient was then multiplied by the area between adjacent boxes and divided by a mean length-scale in order to get an estimate of the volume flux of water exchanged by two boxes by mixing: $F_{Sv} \approx (K_v \times \text{Area})/\text{distance}$. The mixing coefficients are model parameters, and we therefore allowed them to be adjusted to within the ranges specified above. The mixing coefficients used, and the corresponding implied fluxes, are given in auxiliary material Table S1.

[28] Air-sea gas exchange velocities were set to match the mean air-sea gas exchange coefficient (piston velocity) estimated by *Broecker and Peng* [1982] of 3 m/day. The fraction of organic matter which dissolved in the deep (D) box, γ , was set at 80%, with the remainder dissolving in the bottom (B) box. There is no sedimentary reservoir included in our box model, so all particulate matter leaving the surface boxes is remineralized at depth. From (6) it can be seen that λ , which sets the absolute magnitude of the flows, is also a tunable parameter. This was adjusted to give the northern flow rate (Q_1) to be around 15 Sv in order to reflect the present magnitude of the NADW [*Schmitz*, 1995]. Table S3 in the auxiliary material gives the flow rates obtained on the basis of these requirements. The parameters used to obtain this solution are given in Table

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gb/2005gb002448>.

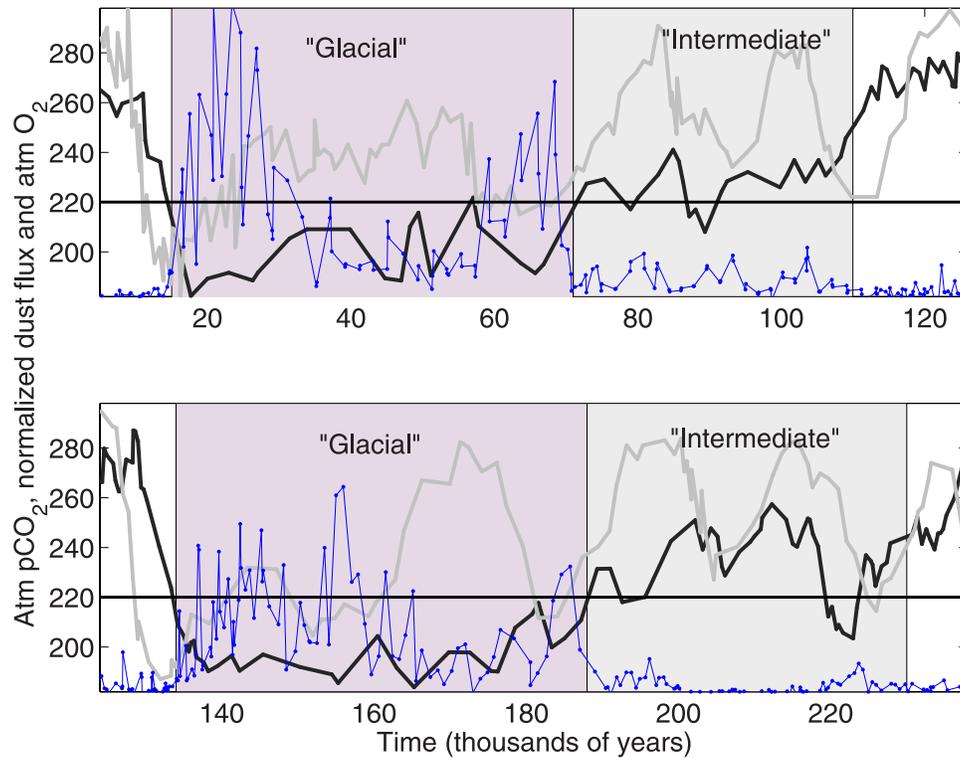


Figure 2. Records of normalized dust (blue), normalized, inverted atmospheric $\delta^{18}\text{O}$ (gray), and pCO_2 (black) from the Vostok ice core over the last two glacials. Dust and oxygen records were normalized such that the minimum and maximum values over the time period 0–430,000 years scale to the minima and maxima of atmospheric pCO_2 over the same time period. The shading shows the partitioning into “intermediate” and “glacial” periods, as defined in the text.

S2 in the auxiliary material and Table 2. The Redfield ratio $r_{C:P}$ was calculated assuming that 80% of the particulate flux was organic matter and the remainder CaCO_3 (see *Toggweiler* [1999] for details) and using the Redfield ratios of [*Anderson and Sarmiento, 1994*]. The Redfield ratio $r_{C:P} = 162.5$, is that of total carbon to phosphorus. This was obtained assuming an organic carbon to phosphorus ratio, $r_{\text{Corg:P}} = 130$, and that the sinking flux consists of 1 mole CaCO_3 for every 4 moles of organic carbon.

5. A Possible Sequence of Events for the Generalized Glacial-Interglacial Cycle

[29] We have used the box model described in section 4 to test the plausibility of various mechanisms in regulating atmospheric pCO_2 , keeping in mind the strong constraints from observational proxy evidence. The model we use improves on previous box models which have been applied to the glacial-interglacial pCO_2 problem in that it is not symmetrical (contains distinct high-latitude boxes); it includes a flow field which is dependent on the model’s density field; and includes a Michaelis-Menten type feedback on nutrient levels. Before using the model to test our proposed sequence of events, we present data from the modern (interglacial) ocean as a benchmark against which to test the model’s interglacial solution. We then present a

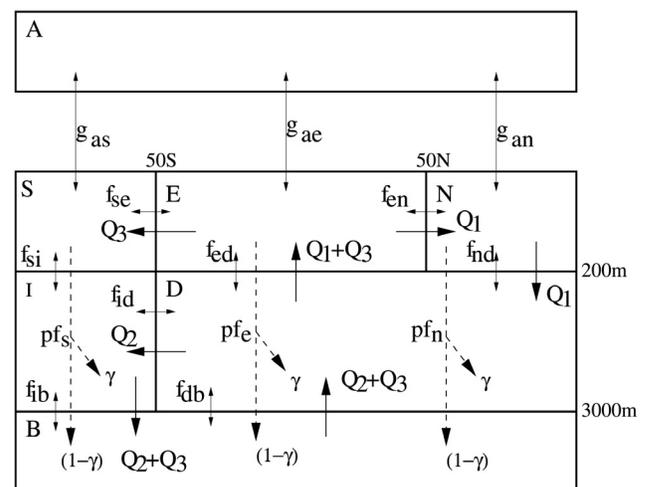


Figure 3. Diagram of the six-box model (not to scale). Shown are the atmosphere (A), the southern surface box (S), the nonpolar or equatorial surface box (E), the northern surface box (N), the deep southern or intermediate box (I), the deep box (D), and the bottom box (B). The density-driven thermohaline flow is shown as Q_1 , Q_2 , and Q_3 . Here f_{xy} denotes mixing between boxes x and y , and pf is the particulate flux.

Table 2. Parameter Values Used Which Differed for the Glacial, Intermediate, and Interglacial Solutions

Parameter	Interglacial	Intermediate	Glacial
Restoring temperature, °C			
Southern	0	-1.8	-1.8
Low latitude	20	16	16
Northern	5	1	1
Initial salinity, ‰	34.7	34.7	36.0

series of model solutions, each obtained by making sequential changes to the model which are consistent with existing data. The first step is to investigate the impact on atmospheric pCO₂ of changing only the external (T/S) boundary/initial conditions. We then explore whether the model can yield an “intermediate” solution (aiming for a pCO₂ of roughly 220 ppmv; see Figure 2) and consider whether, to achieve this, we are violating any of the glacial proxy data. We then investigate what changes must be made to the model in order to achieve the transition from intermediate pCO₂ (circa 223 ppmv) to the low pCO₂ (circa 204 ppmv) characteristic of full glacial conditions. Finally, we suggest how the transition from full glacial back to full interglacial conditions may have occurred.

5.1. Interglacial Data

[30] Using the Levitus ocean data [Conkright *et al.*, 1994], mean and standard deviations for the tracers temperature, salinity and oxygen were calculated for the different regions of our box model (Table 3). These values were used as a benchmark against which to compare the model’s interglacial solution (we are assuming that modern data is representative of the Holocene). Note that there are large standard deviations associated with all these numbers because boxes cover such a large volume of ocean. It is not to be expected that the model match the mean values reported in Table 3 exactly. Rather, the model values should ideally fall within the 1 standard deviation error bars on the data, and should also preserve the relative gradients observed in the tracer data.

[31] Data from Takahashi *et al.* [1999] was used to calculate the average difference in pCO₂ between each surface ocean box and the atmosphere. If the pCO₂ of the surface ocean is less than that of the atmosphere then the ocean will be a sink of pCO₂ and vice versa. In the present-day ocean, the northern high latitudes are by far the most important net sink of CO₂, with $\Delta pCO_{2n} = pCO_{2n} - pCO_{2a} \approx -26$ ppmv (see Figure 3 for boxes corresponding to subscripts). The mid- and low-latitude regions have a slight excess of pCO₂ with $\Delta pCO_{2e} \approx 3$ ppmv. The Southern Ocean is more-or-less neutral. Averaging the Takahashi data reveals that the ocean south of 50°S is only just a net sink of carbon dioxide with $\Delta pCO_{2s} \approx -1$ ppmv, but with large enough scatter in the data to make this small offset insignificant. There is also sensitivity to the boundaries selected to define high and low latitudes. For example, if the cutoff between high and low latitudes is taken to be 40°, rather than 50°, then ΔpCO_{2e} increases to 8 ppmv and ΔpCO_{2s} drops to -7 ppmv. Alkalinity in the deep ocean is around 2350 $\mu\text{-eq/kg}$; in the surface ocean it is around 2280 $\mu\text{-eq/kg}$; Total CO₂ in the deep

ocean averages around 2280 $\mu\text{moles/kg}$; in the low-latitude surface ocean it is roughly 1930 $\mu\text{moles/kg}$ [Toggweiler *et al.*, 2003]. The following mean ocean phosphate values were assumed: 1.5–1.6 $\mu\text{mol/kg}$ for the southern box; 0.7–0.8 $\mu\text{mol/kg}$ for northern box; 0.2 $\mu\text{mol/kg}$ for nonpolar box.

[32] To estimate global average rates of export production, we use estimates provided by Falkowski *et al.* [1998], who estimated a total net export production for the present day of order 16 Gt C/yr. The Falkowski study revealed the highest export production in the Northern Hemisphere; elevated levels in eastern mid- and low-latitude basins (upwelling related), with very high concentrations along western continental margins, and near-zero values in the subtropical gyres. The Southern Ocean is characterized by very sharp gradients in export production associated with the frontal systems.

5.2. Interglacial Model State

[33] The restoring ocean-surface temperature boundary condition used to obtain the interglacial (modern) solution was 0°C for the southern box, 20°C for the nonpolar box, and 5°C for the northern box. These values are not the exact average values computed from the Levitus data, but are well within the 1 standard deviation error bar. The reason for using values slightly lower than the averages in the high-latitude boxes is that this brings the deep-ocean temperature more into line with observations. In the real ocean, deep convection occurs on a very localized scale in cold high-latitude waters. The mean tracer values of the high-latitude boxes in the box model are somewhat different to the tracer properties which are communicated to the deep ocean via the process of deep convection. This is a fundamental shortcoming of box models in general, and one reason why it is quite difficult to match observed deep-ocean properties in such a framework.

[34] The parameters used in obtaining the interglacial solution are given in Tables S1–S4 in the auxiliary material and Table 2. Table 4 gives the model tracer concentrations for the interglacial solution. The salinity and oxygen concentrations predicted by the model are, for the most part, within the 1 standard deviation error bar computed from the data. However, in the bottom box, the model oxygen is slightly lower than 1 standard deviation from the Levitus average, and in the deep box, the oxygen concentration is

Table 3. Mean and Standard Deviations (s.d.) for Temperature, Salinity, and Oxygen in the Regions of the Ocean Corresponding to the Different Model Boxes^a

Tracer	Mean/s.d.	S	E	N	I	D	B
T, °C	mean	1.69	19.03	5.66	1.35	4.39	1.15
	s.d.	2.55	6.58	3.28	1.20	3.66	0.72
S, ‰	mean	34.13	35.17	33.95	34.64	34.70	34.73
	s.d.	0.23	0.98	1.16	0.14	0.46	0.08
O ₂ , $\mu\text{mol/kg}$	mean	304.02	202.24	275.24	203.97	145.44	184.66
	s.d.	33.76	53.81	47.98	12.89	71.75	36.79

^aValues were computed from the Levitus annual average data set, with the Arctic Ocean excluded from the averaging owing to spurious values in this region. Values are given for the southern surface box (S), the nonpolar or equatorial surface box (E), the northern surface box (N), the deep

Table 4. Solution for Interglacial Ocean^a

Tracer	A	S	E	N	I	D	B
T	...	0.1537	19.9543	5.2391	2.0076	4.7121	2.2567
S	...	34.5551	34.9824	34.7942	34.6229	34.7219	34.6320
PO ₄	...	1.5337	0.1589	0.7159	2.0294	2.2990	2.4052
ΣCO ₂	...	2136.07	1946.52	2053.82	2228.81	2290.39	2291.52
pCO ₂	278.20	287.62	280.18	243.97
ALK	...	2292.42	2266.43	2276.04	2315.43	2331.75	2330.27
O ₂	...	329.21	232.90	304.76	197.12	81.52	126.80

^aTemperature is given in °C, and salinity is given in ‰. The concentrations of PO₄, ΣCO₂, and O₂ are given in μmol/kg, pCO₂ is given in ppmv, and alkalinity is given in μeq/kg. A, S, E, N, I, D, and B correspond to the regions illustrated in Figure 1.

significantly lower than the mean (although within the 1 standard deviation error bar). This reveals a fundamental limitation of this model; in order to increase the deep and bottom oxygen, either the vertical mixing must be increased, or the high-latitude export production must be reduced. A significant decrease in export production is required to obtain a relatively modest increase in deep-ocean oxygen concentration, while increasing vertical mixing increases the high-latitude nutrient concentrations to values above those observed. Because the model includes a Michaelis-Menten type feedback on surface nutrient concentration (see Lane *et al.* [2006] for details), increasing the nutrient concentration also increases the particulate flux, which leads to higher oxygen consumption in the deep ocean. One possible resolution to this dilemma is to develop a model with higher vertical resolution. It does not seem possible with the current configuration of the model to have a significantly higher deep oxygen concentration and maintain a phosphate concentration in the northern box between 0.7 μmol/kg and 0.8 μmol/kg, which is in line with observational evidence. The approach taken with earlier box model studies [Sarmiento and Toggweiler, 1984; Knox and McElroy, 1984; Toggweiler, 1999] was to construct a model with just one high-latitude box, and to allow the mean phosphate concentration to be very high (much higher than Northern Hemisphere observations, closer to that in the Southern Hemisphere) in this box. This, combined with high vertical mixing, and a very low particulate flux (an order of magnitude lower than Falkowski *et al.* [1998] estimates) resulted in oxygen levels in the deep boxes somewhat higher than those reported here, but this is clearly at the expense of approximating reality in other areas.

[35] The phosphate concentrations in this solution are in good agreement with observational evidence. The southern box has a value of around 1.5 μmol/kg, the northern box of just over 0.7 μmol/kg, and the nonpolar box of 0.15 μmol/kg. It should be remembered that the nonpolar box extends to 50°N and 50°S. The surface pCO₂ is in fair agreement with the Takahashi *et al.* [1999] data. The model's northern high latitudes are a sink of CO₂, while the low latitudes and southern box are a source. Also in agreement with present-day observations, the northern ocean is much farther out of local equilibrium with the atmospheric pCO₂ than either the low latitude or southern box. The northern downwelling is just over 15 Sv. The southern downwelling is around 8 Sv giving a total surface downwelling of 23 Sv.

[36] The export production in the interglacial solution follows a similar spatial gradient to that of Falkowski *et al.* [1998], with a total global export production of 12.02 Gt C/yr. It should be noted that this number is significantly higher than the total export production in most carbon box models, which tend to be about an order of magnitude lower (see Archer *et al.* [2000] and Figure 7 therein for discussion).

5.3. “Interglacial” Through “Intermediate” Stages

[37] As can be seen from Figure 2, the “intermediate” stage is characterized for the most part by a low background dust flux, and pCO₂ levels intermediate between the interglacial and glacial stages. In order to explain the drop from interglacial atmospheric pCO₂ levels (278 ppmv) to roughly 220 ppmv during the intermediate stage, we wish to call upon mechanisms which are consistent with paleo proxy data. Dust levels are low throughout this period, and the results of the Kohfeld *et al.* [2005] study suggest export production was for the most part the same as, or lower than, at the present day. On the basis of these results, we seek a solution which does not invoke any increase in export production to draw down atmospheric pCO₂, nor do we want to invoke any hypotheses related to changing sea level at this stage. This is based on results from Lambeck and Chappell [2001] and Siddall *et al.* [2003], who show that most of the fall in sea level associated with the glacial-interglacial cycle occurred later in time. We are reluctant to change the CaCO₃/*C_{org}* rain ratio, as this presents difficulties with some of the paleo evidence (see Sigman and Boyle [2000] for discussion), and there seem to be persuasive arguments that the necessary decoupling of lysocline and calcite saturation depth is unlikely.

[38] So what options are left that do not fly in the face of proxy evidence? One obvious mechanism (which has been suggested before [e.g., see Toggweiler, 1999; Stephens and Keeling, 2000]) is a reduction in the amount of high-latitude mixing as sea ice begins to spread equatorward with declining temperatures. In the high latitudes there is evidence for advance of sea-ice with encroaching cold [Francois *et al.*, 1997]. One effect of increasing sea-ice coverage would be to increase ocean stratification beneath the sea ice (i.e., to reduce vertical mixing).

[39] The model described in section 4 (and in greater detail by Lane *et al.* [2006]) is used to explore whether or not the intermediate-stage CO₂ drawdown (278 ppmv to 223 ppmv) can be achieved by just changing the temperature restoring boundary condition, and allowing a modest reduction in high-latitude mixing in our model framework. Our imposed glacial change in restoring temperature represents northern and southern high-latitude cooling of 4°C and 1.8°C, respectively, and a cooling of the nonpolar box by 4°C (Table 2). If the only changes made in the model are to reduce the temperature restoring boundary conditions to glacial values, the atmospheric pCO₂ drops from 278 ppmv to 255 ppmv. Many previous studies have noted that the combined effect of a reduction in temperature boundary condition and an increase in mean salinity can only explain a small fraction of the observed glacial-interglacial pCO₂ difference [Sigman and Boyle, 2000]; the combined T-S

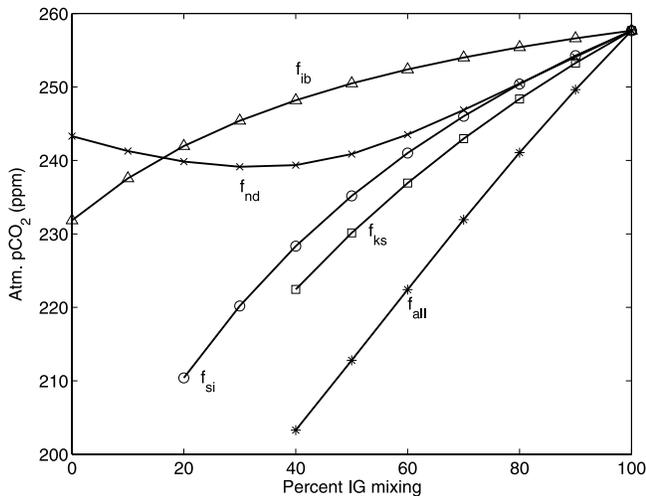


Figure 4. Dependence on atmospheric pCO₂ on various mixing terms in the box model. The starting point is 257 ppmv, achieved by imposing “glacial” temperature boundary conditions and salinity initial condition (Table 2) on the model. The triangles represent changes to only the term f_{ib} ; crosses represent changes to only the term f_{nd} ; open circles represent changes to only the term f_{si} (see Figure 3 for description of terms); squares represent changes to both the southern box mixing terms simultaneously; and stars represent changes to all three high-latitude mixing terms simultaneously.

effect has generally been found to be between 20 ppmv and 30 ppmv. Consistent with this, we find that the net effect of the glacial combined temperature/salinity boundary conditions would be a 21 ppmv reduction of atmospheric pCO₂ in our model. Because decreasing the mean salinity actually increases atmospheric pCO₂, the temperature effect alone is 23 ppmv. As discussed earlier, owing to the timing constraints on events, we require that the sea level change (and hence salinity change) occur after the temperature change.

[40] If the only change made to the interglacial model (after reducing the glacial temperature restoring boundary condition) is to lower the southern mixing term, f_{si} , by 50% (see Figure 3), the atmospheric pCO₂ drops to 232 ppmv. If both vertical mixing terms in the southern box (f_{si} and f_{ib}) are reduced by 50%, the resulting atmospheric pCO₂ is 227 ppmv. A 70% reduction in f_{si} from its interglacial value and no change in other mixing terms results in an atmospheric pCO₂ reduction to 217 ppmv; a reduction in both f_{si} and f_{ib} by 70% causes a drawdown to 210 ppmv. A measure of the sensitivity of atmospheric pCO₂ to various mixing terms is given in Figure 4, which shows how atmospheric pCO₂ responds when the high latitude mixing terms f_{si} , f_{ib} and f_{nd} are reduced either individually or in combination (the lines are terminated at a point at before which zero-oxygen concentrations are reached in the deep ocean.) Reducing the southern box mixing term f_{si} is slightly more effective at drawing down atmospheric pCO₂ than is reducing the f_{nd} term; this is also evident from the linearized sensitivity analysis discussed by Lane *et al.* [2006]. A

reduction of atmospheric pCO₂ to order 223 ppmv can be achieved either by reducing both the southern mixing terms to some 40% of their interglacial levels or by concurrently reducing all high-latitude mixing terms to around 60% of interglacial levels.

[41] The limitation one runs into when invoking reduced vertical mixing to achieve a drawdown of pCO₂ is that decreasing mixing causes a dramatic decrease in the amount of high-oxygen water supplied to the deep ocean. Approaching anoxic levels therefore becomes a problem. As discussed in section 5.2, this model has interglacial deep and bottom oxygen concentrations which are roughly 1 standard deviation below the mean. Because of this there is little room to maneuver as far as utilizing deep oxygen is concerned. If a solution can be found in which the deep ocean is still oxic, it is likely that the required level of oxygen consumption is entirely within reasonable bounds. In the reduced-mixing solutions mentioned above, the deep ocean oxygen levels are low, but nowhere is the ocean anoxic. Counteracting the decreased deep oxygen through vertical mixing is the particulate flux: lower mixing means less high-nutrient water is brought to the surface; this in turn leads to a reduction in the particulate flux, which will lead to less oxygen being consumed in the deep ocean. However, in the experiments mentioned above, this effect is small relative to the deep oxygen depletion by decreased mixing.

[42] To summarize, in going from the interglacial (278 ppmv) solution to the intermediate-stage (223 ppmv) solution, the following changes were made to the model. (1) The temperature boundary condition was reduced to glacial values (see Table 2). (2) The northern mixing term was reduced by 30% and the southern mixing terms by 40%.

[43] The results are shown in Table 5. In going from the interglacial solution (Table 4) to the intermediate-stage solution (Table 5), there was a global 20% reduction in net export production; nearly all of this reduction is in the nonpolar and northern surface boxes (there is very little change in export production in the southern box of the model). Lower net export production during the intermediate stage than at the present-day is consistent with the findings of Kohfeld *et al.* [2005]. The relatively high nutrients in our model solution in the polar oceans are consistent with the constraints from Cd/Ca and $\delta^{13}\text{C}$. The deep oxygen levels are reasonable (especially given the caveat of initially low deep oxygen discussed in section 5.2). The 223 ppmv intermediate-stage model therefore appears to be in fair agreement with much of the existing proxy data. The next step is to ask what parameter changes are necessary to achieve a transition from intermediate atmospheric pCO₂

Table 5. Solution for “Intermediate” Stage^a

Tracer	A	S	E	N	I	D	B
T	...	-1.72	15.97	1.21	0.21	2.15	0.51
S	...	34.44	35.07	34.83	34.58	34.73	34.61
PO ₄	...	1.52	0.06	0.39	2.10	2.22	2.60
ΣCO_2	...	2115.2	1939.5	2026.5	2239.1	2287.1	2324.4
pCO ₂	222.63	235.84	224.65	180.97
ALK	...	2284.70	2268.28	2266.13	2315.85	2329.29	2336.15
O ₂	...	341.00	253.41	327.94	165.61	69.16	69.18

^aSee footnote for Table 4.

levels of 223ppmv to the glacial values of circa 200 ppmv, and whether the changes required to achieve such a transition are consistent with proxy evidence and timing constraints.

5.4. “Intermediate” Through “Glacial” Stages

5.4.1. Meeting Proxy-Data and Timing Constraints

[44] During the “glacial stage” (marine isotope stages 2, 3, 4), temperatures continued to fall, ice volume continued to increase, and the dust flux spiked to values significantly above intermediate-stage and interglacial levels. As summarized in section 2.1, proxy evidence suggests that nutrient levels south of the polar front were if anything slightly higher than present-day levels [Elderfield and Rickaby, 2000], while export production in this region appears not to have been higher (possibly slightly lower) than today [Kohfeld *et al.*, 2005]. Interestingly, the Kohfeld *et al.* [2005] compilation suggests that export production in the nonpolar ocean during the glacial was actually higher than at the present day. The $\delta^{13}\text{C}$ records show significant trend toward strongly negative values in the glacial [Curry *et al.*, 1988; Duplessy *et al.*, 1988]. It is of interest to note that many cores exhibit a sharp drop in both benthic and planktonic $\delta^{13}\text{C}$ at around 65 kyr B.P. [e.g., Duplessy *et al.*, 1988, Figure 3]. This is roughly the time at which we defined the transition from intermediate stage to glacial. The very significant offset in whole-ocean $\delta^{13}\text{C}$ between these two time periods lends further support to the notion that there was a fundamental difference in mechanisms regulating the atmospheric pCO₂ content between the intermediate and glacial periods.

[45] It would be difficult to significantly increase the export production in the nonpolar ocean if nutrient levels were similar to present-day levels (phosphate is already close to zero in most of the nonpolar ocean) unless there was a corresponding increase in the supply of nutrients to the surface ocean. One way this could be accomplished is via increased upwelling. However, our model implies that if anything, the rate of upwelling was somewhat lower, owing to a slightly smaller lateral density gradient. Another way to increase nutrient levels would be to increase mean ocean nutrient inventory. This was one of the early ideas put forward to account for glacial-interglacial atmospheric pCO₂ drawdown, but has been widely discredited because the mechanism is crucially tied to sea level, and coming out of glaciations, much of the pCO₂ increase occurred before the change in sea level (ice sheet melting). Furthermore, it is unclear that there is sufficient organic-rich sediment deposited and eroded between glacial and interglacial periods to account for the full magnitude of the observed glacial-interglacial $\delta^{13}\text{C}$ change. Another possibility is that the mean ocean alkalinity increased during glacial periods.

[46] Both the whole-ocean nutrient (“shelf”) and alkalinity (“coral-reef”) hypotheses are intimately tied to changes in sea level. The shelf hypothesis relies on increased deposition of organic-rich material in shelf areas during interglacial (high sea level) periods and enhanced erosion of this material during glacial (low sea level) periods. Storage and release of phosphorus in marine shelf sediments on glacial-interglacial timescales would lead to changes in

whole-ocean phosphate inventory. By the beginning of full glacial conditions (circa 70 kyr for the most recent glacial-interglacial cycle), atmospheric $\delta^{18}\text{O}$ records suggest that ice sheets were significantly larger, and hence sea level was considerably lower than in interglacial times. This is supported by sea level reconstructions [Lambeck and Chappell, 2001; Siddall *et al.*, 2003]. A low-stand in sea level would expose phosphate-rich shelf sediments, the erosion of which could lead to an increase in mean ocean PO₄. Sea level changes are required to drive erosion from and deposition onto shallow shelves. If deposition of organic rich sediments occurs on shelves, it would happen during post-glacial sea level rise.

[47] The coral-reef hypothesis invokes an increase in the magnitude of and shift in the locus of carbonate deposition from the deep sea during glacials to shelves during interglacial periods. Existing evidence pertaining to the timing of sea level changes during the last glacial suggest that most of the sea level rise occurred in the latest stages of the glacial period, with a rise of 100–120 m occurring between 20 and 10 kyr B.P. [Lambeck and Chappell, 2001; Siddall *et al.*, 2003].

5.4.2. Changes in Whole-Ocean Nutrient Inventory

[48] In today’s ocean there exists a strong correlation between phosphate and $\delta^{13}\text{C}$. The reason for this is that variations in $\delta^{13}\text{C}$ are due mainly to photosynthesis and respiration; the distribution of phosphate is also mediated by biological activity. Because formation and destruction of temporary organic carbon reservoirs would be expected to leave a signature in the ¹²C/¹³C ratio of ocean ΣCO_2 , it might be expected that the glacial $\delta^{13}\text{C}$ distribution could yield information on phosphate levels in the glacial ocean.

[49] In general, glacial benthic foraminifera tend to have a lower ¹²C/¹³C than interglacial benthic forams. Broecker [1982] made an attempt to compile the deep-ocean $\delta^{13}\text{C}$ records existing at the time in order to estimate the mean ocean $\delta^{13}\text{C}$ shift between the LGM and the Holocene, and estimated a net shift of 0.7‰ toward lower mean ocean $\delta^{13}\text{C}$ in glacial times. More recently this estimate has been lowered to between 0.32‰ [Duplessy *et al.*, 1988] and 0.46‰ [Curry *et al.*, 1988]. An increase in mean ocean $\delta^{13}\text{C}$ from glacial to interglacial implies removal of carbon from the ocean at the end of the glacial period to form organic matter, which could be either shelf or terrestrial material. Because deposits of Holocene organic-rich shelf sediments sufficiently large to explain the observed $\delta^{13}\text{C}$ shift have not been found, there is general acceptance that most or all of this shift can be attributed to changes in the size of the terrestrial biosphere [Shackleton, 1977; Sigman and Boyle, 2000]. Deposition of organic-rich shelf sediments would cause a change in mean ocean phosphate and $\delta^{13}\text{C}$; storage of organic material in the terrestrial biosphere would change mean ocean $\delta^{13}\text{C}$ but would not have any impact on mean ocean phosphate.

[50] The shelf hypothesis requires that the loss of $\delta^{13}\text{C}$ to organic matter in the interglacial would be compensated by an equivalent loss of ΣCO_2 to CaCO₃, such that about a mole of carbon would be removed as CaCO₃ for each mole of carbon removed as organic material. In addition to this, roughly one unit of alkalinity would be lost for each unit of

ΣCO_2 . The deposition of organic material as shelf sediment would alter the $\text{PO}_4:\Sigma\text{CO}_2$ ratio in the deep ocean. This would lead directly to a larger reduction in pCO_2 due to plant growth in the surface ocean through an increase in export production.

[51] Assuming a mean ocean $\delta^{13}\text{C}$ change between peak glacial and interglacial times of 0.7‰, [Broecker, 1982] estimated that mean deep-ocean PO_4 rose from an interglacial value of around $2.25\ \mu\text{mol/kg}$ to a glacial value of about $3.2\ \mu\text{mol/kg}$. This estimate should be revised in light of more recent estimates of the whole-ocean change in $\delta^{13}\text{C}$ (current estimates range from 0.32–0.46‰; [Curry *et al.*, 1988; Duplessy *et al.*, 1988; Broecker and Henderson, 1998]). Following the methodology adopted by [Broecker, 1982], it is possible to put upper and lower bounds on the mean phosphate concentration in the glacial ocean (see auxiliary material for details). If we assume that the entire glacial-interglacial $\delta^{13}\text{C}$ shift can be attributed to the deposition of organic-rich sediments, the mean deep-ocean phosphate during glacial conditions must have been roughly $2.85\ \mu\text{mol/kg}$. If on the other hand it is assumed that the entire $\delta^{13}\text{C}$ shift in benthic forams between glacial and interglacial times can be attributed to a change in the size of the terrestrial biosphere, the mean deep-ocean phosphate during glacial times must have been roughly $2.3\ \mu\text{mol/kg}$. Assuming that a third of the observed $\delta^{13}\text{C}$ shift can be attributed to the storage and erosion of organic-rich sediments yields an estimate of $2.42\ \mu\text{mol/kg}$ for the mean ocean phosphate.

[52] Even if the observed benthic $\delta^{13}\text{C}$ change can be attributed wholly to changes in the terrestrial biosphere, the mean ocean phosphate concentration must have been slightly higher than today during the peak of the last glacial (the volumetric effect). It is to be expected that an increase in mean ocean phosphate will act to draw down atmospheric pCO_2 through increased nutrient utilization in the low-latitude ocean (where phosphate concentrations are currently close to zero). We have explored the effect of various assumptions about the degree to which glacial mean ocean phosphate was increased over present-day values in our model. If the mean phosphate concentration in the box model is increased so as to roughly achieve the mean deep-ocean phosphate value of $2.85\ \mu\text{mol/kg}$, atmospheric pCO_2 drops from 223 ppmv to 182 ppmv. In order to achieve a mean deep-ocean phosphate value of $2.42\ \mu\text{mol/kg}$, atmospheric pCO_2 drops from 223 ppmv to 209 ppmv. If only the volume-based phosphate change of $2.30\ \mu\text{mol/kg}$ is used, atmospheric pCO_2 drops from 223 ppmv to around 216 ppmv.

[53] It is important to note that the model we use does not allow for carbonate compensation, or any kind of feedback between CaCO_3 and atmospheric pCO_2 . Therefore, while recognizing that removal of carbon in the form of shelf and/or terrestrial organic matter in glacial periods would entail change in the average ΣCO_2 and alkalinity of the ocean, this is not a process we are able to accurately simulate in the current model. In exploring the effect of increased phosphate, we did not make corresponding increases in ΣCO_2 and alkalinity. Had we included these changes, the net effect would be to lower atmospheric pCO_2 still farther.

[54] The volume-based phosphate increase has only a very minor effect (order 6 ppmv) on atmospheric pCO_2 . If the entire benthic $\delta^{13}\text{C}$ change can be attributed to storage/erosion in organic-rich shelf sediments, the estimated change in mean ocean phosphate is large enough to account for a significant drawdown in atmospheric pCO_2 (order 40 ppmv). However, this appears to be at odds with the sedimentary record. (This magnitude of change would require the deposition of 1–2 m of sediment containing roughly 1% by weight carbon over the entire ocean shelf area [Broecker, 1982]). A shift in benthic $\delta^{13}\text{C}$ of -0.46‰ requires that roughly 6×10^{16} moles of carbon must have been converted to organic carbon at the end of the glacial. If only a third (i.e., 0.15‰) of the benthic $\delta^{13}\text{C}$ is attributed to storage in shelf sediments, this requires the burial of roughly 2×10^{16} moles carbon. Assuming organic-rich shelf sediment contains 1% wt carbon, this is equivalent to roughly a 1-m-thick layer of sediment spread over the entire ocean shelf area ($\approx 3 \times 10^{17}\ \text{cm}^2$), or equivalently, a 10-m-thick layer of sediment spread over a tenth the ocean shelf area ($\approx 3 \times 10^{16}\ \text{cm}^2$). On the largest of the world's shallow shelves, the Sunda Shelf, (area roughly $1.8 \times 10^{16}\ \text{cm}^2$ [Hanebuth *et al.*, 2000]), sediment cover is only a few centimeters, but Holocene sediments over 10 m thick have been observed, for example on the central Vietnamese Shelf [Schimanski and Stattegger, 2001]. Both the question of timescales of carbon removal/deposition, and the question of whether or not sufficient Holocene-age organic-rich sediment exists to account for burial and erosion of some 2×10^{16} moles carbon on a glacial-interglacial timescale, remain questions for future research.

5.4.3. Changes in Whole-Ocean Alkalinity

[55] Among the earliest explanations to be put forward to explain the glacial-interglacial variations in atmospheric pCO_2 involved an increase in the mean ocean alkalinity during glacial periods. Increasing alkalinity will cause a decrease in atmospheric pCO_2 . Addition to the ocean of alkalinity on glacial-interglacial timescales is primarily through continental weathering of carbonate rocks, and the dissolution of shallow and deep-ocean carbonates. Removal of alkalinity from the ocean on these timescales is achieved predominantly through the growth of coral reefs, and through burial of carbonate-shelled organisms in deep-sea sediments. (On glacial-interglacial timescales, it is possible that the calcium carbonate reservoir plays an important role in the input and removal of alkalinity.) Because the rate of growth and destruction of shallow coral reefs must vary as sea level changes between its interglacial highstand and the LGM lowstand (some 140 m lower), early hypotheses for glacial-interglacial variations in atmospheric pCO_2 looked to changes in mean ocean alkalinity through changes in coral-reef abundance [Berger, 1982; Opdyke and Walker, 1992; Milliman, 1993].

[56] Glacial periods might be expected to correlate with a decrease in coral-reef growth. This would increase mean ocean alkalinity and ΣCO_2 in the ratio 2:1, and would lead to a decrease in atmospheric pCO_2 . An increase in mean ocean alkalinity would cause an increase in deep ocean CO_3^{2-} which would cause deepening of the calcite lysocline (and hence higher CaCO_3 preservation in the deep ocean).

Table 6. Solution for “Glacial” Stage^a

Tracer	A	S	E	N	I	D	B
T	...	-1.72	15.97	1.22	0.20	2.14	0.50
S	...	35.73	36.38	36.14	35.88	36.03	35.91
PO ₄	...	1.60	0.08	0.45	2.21	2.34	2.73
ΣCO ₂	...	2132.83	1944.74	2036.06	2259.92	2309.29	2348.57
pCO ₂	203.81	216.74	205.63	164.13
ALK	...	2322.57	2302.91	2302.69	2354.59	2368.46	2375.68
O ₂	...	340.80	253.47	327.67	159.08	58.17	58.73

^aSee footnote for Table 4. In this “glacial” solution, the southern surface-ocean phosphate concentration is close to 1.6 μmol/kg, slightly higher than interglacial levels, which is in agreement with the Cd/Ca data [Elderfield and Rickaby, 2000]. Nutrient levels are relatively high in the northern box, and at near-zero levels in the nonpolar box. The deep oxygen concentration in this solution is around 60 μmol/kg, some 20 μmol/kg lower than in the interglacial solution.

Sigman and Boyle [2000] estimate that a 1-km-average deepening of the lysocline would account for roughly a 25 ppmv decrease in atmospheric pCO₂.

[57] There are two main reasons for the coral-reef hypothesis having been widely rejected. First, this mechanism must be closely correlated with changing sea level, and clearly much of the sea level change came after a significant portion of the atmospheric pCO₂ increase coming out of the last glaciation (see section 5.3 and Broecker and Henderson [1998]). Second, a change in mean ocean alkalinity would trigger a change in the depth of the calcite lysocline, and lysocline depth changes large enough to account for the glacial-interglacial atmospheric pCO₂ shift have not been observed. Although it is fairly difficult to assess glacial-interglacial changes in the mean calcite lysocline depth from the sedimentary record, in general, there appears to be a consensus that there was slightly higher CaCO₃ preservation during the glacial than at the present day in the Pacific and North Atlantic [Catubig et al., 1998; Farrell and Prell, 1989; Farrell, 1991], and that the calcite lysocline was probably only slightly (order 500 m) deeper than during interglacials [Farrell and Prell, 1989; Berger, 1982].

[58] With a closed-system model, we are not able to simulate how the lysocline will change in response to an alkalinity perturbation. However, we are able to explore how atmospheric pCO₂ in the model will respond to a change in mean ocean alkalinity. If, starting with the intermediate-stage (223 ppmv) solution, alkalinity is increased in the model by 40 μeq/kg, and ΣCO₂ by 20 μmol/kg, the response is a decrease in atmospheric pCO₂ from 223 ppmv to 210 ppmv. This magnitude of change would probably trigger a decrease of order 500 m in lysocline depth, which is within the error bars of observational estimates.

5.4.4. Combined Alkalinity and Nutrient Changes

[59] In order to reconcile our proposed mechanisms with existing observational evidence, it is necessary to invoke a combination of small increase in mean ocean alkalinity (sufficiently small that the average lysocline depth should be depressed only by a few hundred meters), and a small increase in mean ocean phosphate (sufficiently small that the thickness of carbonate-rich sediments recorded on existing shallow shelves can account for the change).

Starting with the intermediate-stage solution (see Table 5), the initial condition for alkalinity was increased by 40 μeq/kg and the initial condition for ΣCO₂ by 20 μmol/kg. In addition, the initial condition for PO₄ was modified such that there was an increase in mean ocean phosphate of 0.12 μmol/kg (this is the change expected by attributing roughly a third of the observed benthic δ¹³C shift to storage in shelf sediments). The solution obtained by making these changes is shown in Table 6. Together, the proposed alkalinity change and whole-ocean nutrient change can account for the remaining depletion of atmospheric pCO₂ from 223 ppmv down to LGM levels (204 ppmv).

[60] Benthic δ¹³C reached maximum negative values during the glacial [Duplessy et al., 1988; Curry et al., 1988]. By this stage, sea level had fallen sufficiently that large areas of shelf would have been exposed, and any organic material on them could slowly have been eroded into the sea. Our model results indicate that the hypothesized late glacial increase in mean ocean phosphate might account for between 6 ppmv (volumetric-based change) and 10 ppmv of the glacial atmospheric pCO₂ drawdown. For the remainder of the drawdown we invoke a small change in mean ocean alkalinity, a likely consequence of increased input of CaCO₃ to the ocean via erosion of carbonate-rich rocks on land and coral reefs.

[61] Without the combined action of increase mean ocean alkalinity and phosphate, it is difficult to explain the last part of the glacial atmospheric pCO₂ drawdown without violating proxy evidence. Increases in both alkalinity and nutrients are intimately tied to changing sea level. Because detailed sea level records exist coming out of the glacial into the Holocene, the feasibility of combined small changes in mean ocean alkalinity and nutrients can be tested with respect to timing constraints from ice core records in the transition out of the glacial.

5.5. Transitioning Out of the Glacial Period

[62] It has been observed on the basis of a comparison of the GISP II record of δ¹⁸O_{atm} and the Barbados sea level curve [Fairbanks, 1989] that δ¹⁸O_{atm} lags changes in sea level (ice volume) on roughly a 2-kyr timescale [Broecker and Henderson, 1998]. These authors make a strong case based on results of δ¹⁸O_{atm}, atmospheric pCO₂, and other proxies from the Vostok ice core, that the melting of the Northern Hemisphere ice sheets must have started only after the rise of CO₂ in the atmosphere was well underway. This can be seen from Figure 5, which shows the δ¹⁸O_{atm}, atmospheric pCO₂, and dust records from Vostok over the last two terminations.

[63] If the glacial solution of the model is modified as follows, (1) southern high latitude mixing is increased back to interglacial values and (2) the southern box restoring temperature boundary condition is increased from -1.8°C to 0°C (the interglacial value), and the nonpolar restoring temperature boundary condition is increased to 18°C (half-way between the glacial and interglacial values), the solution in Table 7 is obtained (237 ppmv). Note that there has, as yet, been no increase in the Northern Hemisphere restoring temperature boundary condition. Because this solution does not require any change in Northern

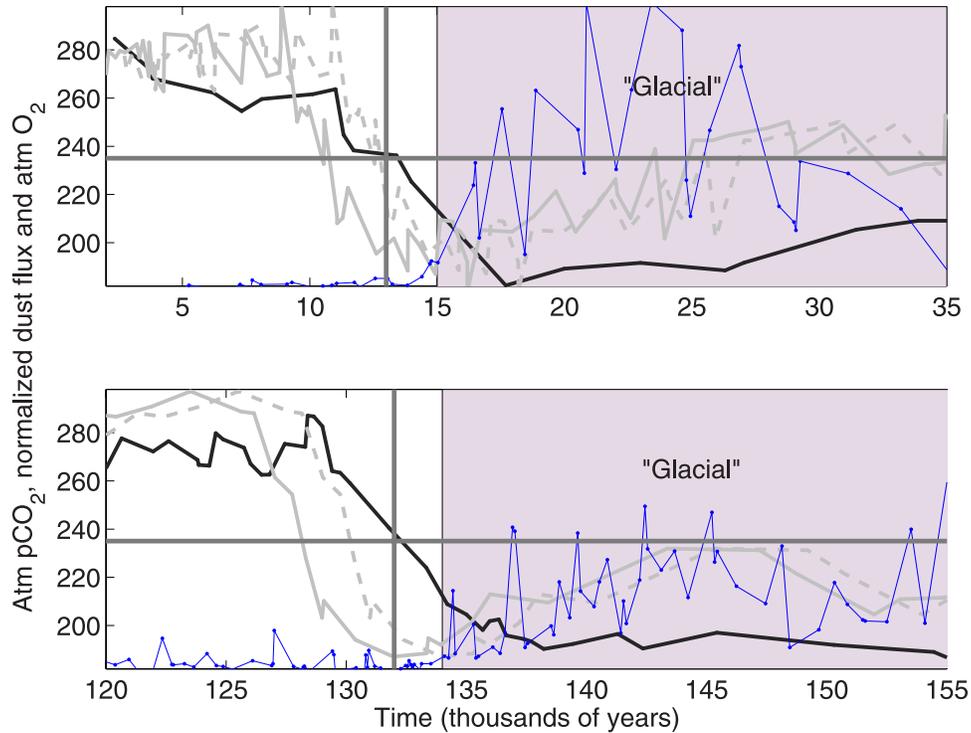


Figure 5. Records of normalized dust (blue), normalized inverted atmospheric $\delta^{18}\text{O}$ (gray), and pCO_2 (black) from the Vostok ice core over the last two terminations. The dashed line is the atmospheric $\delta^{18}\text{O}$ curve offset back in time by 2000 years (so it can be thought of as approximating sea level). The 237 ppmv (“transitional”) atmospheric pCO_2 solution is shown for reference. Dust and oxygen records were normalized such that the minimum and maximum values over the time period 0–430,000 years scale to the minima and maxima of atmospheric pCO_2 over the same time period.

Hemisphere temperature or circulation patterns, there are no timing constraints that have been violated.

5.6. Completing the Transition Into Full Interglacial Conditions

[64] What remains now is to explain the remainder of the transition back into full interglacial conditions; the 237–278 ppmv part of the record. Close inspection of the Vostok ice core record shows, during deglaciations, that the time at which atmospheric pCO_2 reached intermediate levels (237 ppmv) corresponds to the beginning of the steep rise in atmospheric $\delta^{18}\text{O}$ (measured in the air bubbles in ice; Figure 5). A decrease (increase on the scaled, inverted $\delta^{18}\text{O}$ shown in Figure 5) in $\delta^{18}\text{O}$ indicates a retreat of ice sheets over land, or an increase in sea level.

[65] Estimated sea level curves for the last deglaciation [Fairbanks, 1989; Hanebuth et al., 2000] suggest that the bulk of sea level rise occurred between 20 and 10 kyr B.P. This is consistent with the shifted $\delta^{18}\text{O}_{\text{atm}}$ record in the Vostok ice core (Figure 5). Let us therefore accept the Bender et al. [1994] estimate that sea level starts to rise about 2 kyr before atmospheric $\delta^{18}\text{O}$. The dashed gray line in Figure 5 shows $\delta^{18}\text{O}_{\text{atm}}$ offset by 2 kyr; the horizontal line shows the transitional 237 ppmv solution. It is clear that for both the last two terminations, the point at which atmospheric pCO_2 reached 237 ppmv during the deglaciation

corresponds fairly closely to the beginning of the steep rise in shifted $\delta^{18}\text{O}_{\text{atm}}$, which is here taken as a proxy for sea level (or Northern Hemisphere ice sheet melting). For Termination 1, sea level is about halfway to interglacial levels by the time atmospheric pCO_2 reaches 237 ppmv. For Termination 2, however, sea level is just starting to rise when atmospheric pCO_2 is at the 237 ppmv level. Because there will be some time lag between the time at which sea level starts to rise, and the flooding of the continental shelves, some fraction of total sea level rise must be accomplished before there is significant deposition of organic-rich shelf sediments.

[66] The entire atmospheric pCO_2 rise (from the glacial maximum to peak interglacial) takes order 8 kyr; the

Table 7. Solution for Partial Transition Out of Peak Glacial Conditions (235 ppmv)^a

Tracer	A	S	E	N	I	D	B
T	...	0.08	17.96	1.30	1.13	2.75	1.31
S	...	35.78	36.35	36.15	35.88	36.04	35.90
PO ₄	...	1.88	0.10	0.43	2.29	2.35	2.68
ΣCO_2	...	2160.29	1956.91	2051.33	2255.98	2311.59	2325.45
pCO_2	237.27	264.52	238.19	178.67
ALK	...	2336.03	2302.23	2302.62	2357.40	2368.85	2373.47
O ₂	...	329.91	243.22	327.02	192.53	76.70	113.41

^aSee footnote for Table 4.

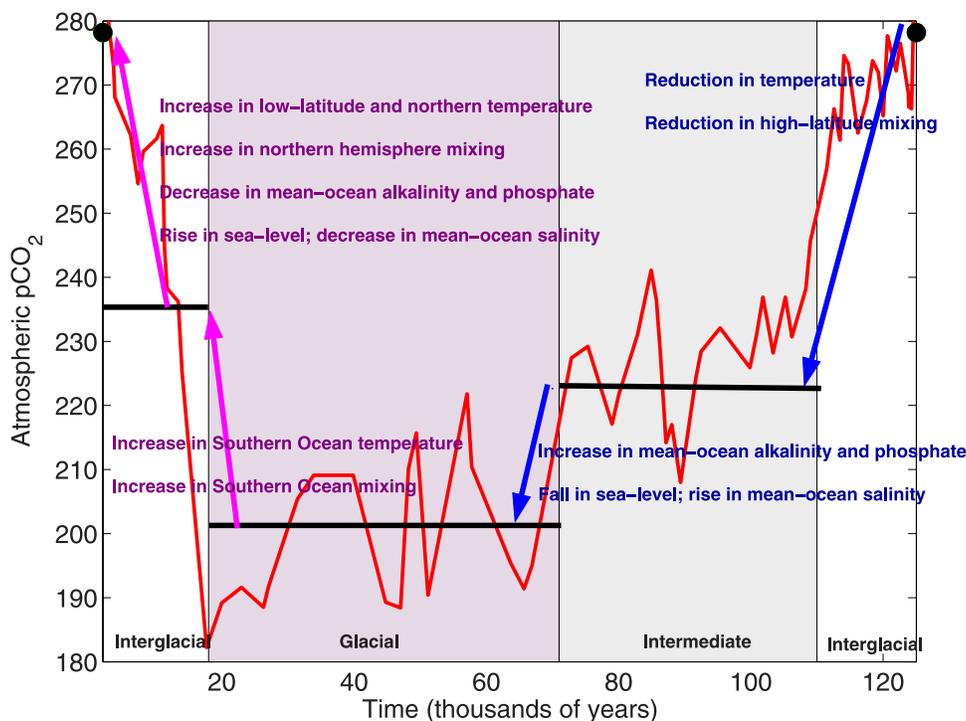


Figure 6. Summary figure showing atmospheric pCO₂ over last glacial-interglacial cycle (red), model solutions presented in this study (black horizontal lines), and mechanisms used to explain each part of the observed atmospheric pCO₂ variation (text).

mechanism put forth here requires that the first part of the rise (from 204 ppmv to 237 ppmv) was achieved through gradual Southern Hemisphere and low-latitude warming, melting of southern sea ice, and subsequent increase in mixing in the Southern Hemisphere. The latter part of the CO₂ rise requires a different explanation; in order to be consistent with our previous hypothesis, we require a sea level related mechanism. As sea level rose, it would become possible to bury phosphate in organic-rich sediment on the continental shelves, and hence lower the mean ocean phosphate value back to interglacial levels. Furthermore, growth of coral reefs in shallow seas would alter mean ocean CaCO₃, causing a slight lowering of both ΣCO₂ and alkalinity. It must be borne in mind that for the timing reasons outlined in the previous paragraph, this explanation works better for Termination 1 than for Termination 2.

[67] Changing the temperature restoring boundary condition alone (leaving the high glacial phosphate levels) back up to its interglacial values everywhere results in an increase in atmospheric pCO₂ up to 247 ppmv; restoring Northern Hemisphere high-latitude northern mixing back up to interglacial levels brings the solution to 253 ppmv; and finally, and decreasing mean ocean salinity, phosphate, alkalinity and ΣCO₂ back to those in the interglacial solution, brings us back to the interglacial solution presented in Table 4.

6. Discussion and Conclusions

[68] By considering a generalized glacial-interglacial cycle to consist of three distinct stages, an “interglacial,” “intermediate” and “glacial,” we have shown how a

distinct sequence of events might account for the observed change in atmospheric pCO₂ between interglacial and glacial periods. The initial pCO₂ drawdown, from interglacial to intermediate conditions, involves physical changes in the ocean (mixing, temperature/salinity). The transition from the intermediate to the glacial invokes a small increase in mean ocean nutrient levels and mean ocean alkalinity. Physical changes in the Southern Ocean (mixing, temperature) are invoked in order to explain the first part of the transition out of peak glacial conditions; the remaining increase in atmospheric pCO₂ (back up to interglacial levels) is accounted for through a combination of changing ocean chemistry, and changes in the salinity, temperature, and mixing in the Northern Hemisphere oceans. This sequence of events is summarized in Figure 6.

[69] The proposed scenario is consistent with most existing evidence on paleo-nutrient levels and changes in export production over a glacial-interglacial cycle. Furthermore, it is consistent with evidence for a whole-ocean shift in δ¹³C toward significantly more negative values in the late glacial. The proposed sequence of events is also consistent with ice core-based timing constraints, as summarized by *Broecker and Henderson* [1998]. A shortcoming of this study is that we have used a highly simplified “closed-system” model which does not include carbonate dynamics; future work should consider impact of the proposed changes on changes in lysocline depth, and timescales of adjustment, which could be tested in an “open system” model.

[70] The box model we have used here incorporates a dynamic flow field and a Michaelis-Menten type feedback on export production, and exhibits sensitivities which are

somewhat different to models which do not include these effects [Lane *et al.*, 2006]. Other distinguishing features of this model are a more realistic export flux than most box models, and parameter values in fair agreement with observations. The model is able to produce both glacial and interglacial pCO₂ levels. The model yields tracer distributions in good agreement with observational and proxy evidence. Moreover, as evidenced by the sensitivity analysis discussed by Lane *et al.* [2006], the model derivatives also appear to be reasonable.

[71] Although we utilized a time-dependent model, we have presented only the steady state solutions. In order to begin the gradual decline from peak interglacial to colder, intermediate-stage conditions, some manner of external forcing would be required. The question of what such a forcing may have been, and why it triggered a 100-kyr cycle (rather than, for example, a 23-kyr cycle, which would be in line with maxima in insolation change) lies beyond the scope of the present study.

[72] In previous studies it has been found that by invoking a single mechanism (e.g., changing mixing, sea-ice cover, or nutrient utilization), it is very difficult to account for the observed glacial-interglacial atmospheric pCO₂ variations. We are in accord with this view, and have therefore sought to explore whether a sequence of events can be found which does not violate the growing body of proxy evidence for variables such as nutrient levels, export production, etc. Modest changes in physical properties of the ocean (mixing, circulation, temperature) appear sufficient to account for about 55ppmv of the atmospheric pCO₂ drawdown. However, in order to account for the full atmospheric pCO₂ change, we are forced to invoke sea level related mechanisms. By allowing relatively small changes in mean ocean alkalinity, ΣCO₂ and phosphate, we show that the remaining 20 ppmv of the atmospheric pCO₂ drawdown can be accounted for, and further, that this mechanism does not violate the ice core-based timing constraints, nor evidence of mean ocean changes in lysocline depth. Without some storage of organic-rich material on shallow shelves we find are not able to account for the full atmospheric pCO₂ drawdown unless a larger alkalinity change is called upon, and this would require a change in lysocline depth greater than is observed.

[73] Support for the sequence of events proposed here would come from a robust record of the timing of changes in nutrient chemistry of the high-latitude oceans. With the existing database of proxy evidence for changes between the glacial and present-day ocean, the sequence of events we outline in this paper remains just one of many possible scenarios which may explain the observed changes in atmospheric pCO₂, albeit one that does not violate most existing paleoceanographic evidence. It should be noted that we do not require enhanced dust flux to the surface ocean to play a leading role in the proposed scenario. It appears that the role of the ocean in glacial-interglacial atmospheric pCO₂ variations is fairly complex, involving a number of tightly coupled changes. The remarkable similarity of the atmospheric pCO₂ record of each 100-kyr glacial-interglacial cycle over the past 430 kyr, as is evident from ice core records, indicates that whatever these changes in the ocean were, they must have been highly reproducible on time-

scales of hundreds of thousands of years. Better quantification of possible glacial-interglacial changes in ocean chemistry remains an important challenge for the future.

[74] **Acknowledgments.** Thanks are owed to Wally Broecker, who made useful comments on an early version of the manuscript. We are very appreciative of a very detailed and insightful review by Gideon Henderson, which served to greatly improve the manuscript. Thanks also are owed to an anonymous reviewer for valuable comments. J. M. R. was supported by NSF grant DMS0327642.

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