Glacial/interglacial variations in atmospheric carbon dioxide

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Twenty years ago, measurements on ice cores showed that the concentration of carbon dioxide in the atmosphere was lower during ice ages than it is today. As yet, there is no broadly accepted explanation for this difference. Current investigations focus on the ocean's 'biological pump', the sequestration of carbon in the ocean interior by the rain of organic carbon out of the surface ocean, and its effect on the burial of calcium carbonate in marine sediments. Some researchers surmise that the whole-ocean reservoir of algal nutrients was larger during glacial times, strengthening the biological pump at low latitudes, where these nutrients are currently limiting. Others propose that the biological pump was more efficient during glacial times because of more complete utilization of nutrients at high latitudes, where much of the nutrient supply currently goes unused. We present a version of the latter hypothesis that focuses on the open ocean surrounding Antarctica, involving both the biology and physics of that region.

The past two million years have been characterized by large cyclic variations in climate and glaciation. During cold 'ice age' periods, large continental ice sheets cover much of the polar Northern Hemisphere. During intervening warm periods, or 'interglacials', Northern Hemisphere glaciation wanes drastically. The ultimate pacing of these glacial cycles is statistically linked to cyclic changes in the orbital parameters of the Earth, with characteristic frequencies of roughly 100, 41 and 23 kyr (refs 1, 2). These orbitally driven variations in the seasonal and spatial distribution of solar radiation incident on the Earth's surface, known as the 'Milankovitch cycles' after their discoverer, are thought to be the fundamental drivers of glacial/interglacial oscillations. However, the direct energy budget effects of the orbital variations are insufficient to drive the large amplitude of the glacial cycles that are observed, and orbital variations alone do not provide an obvious cause of the rapid climate transitions evident in palaeoclimatic and palaeoceanographic records. Positive feedbacks within the Earth's climate system must amplify orbital forcing to produce glacial cycles, but the operation of these internal feedbacks is poorly understood. One of the central goals of Earth science is to develop a mechanistic understanding of the Earth's climate feedbacks, the roles that they have played over glacial cycles, and the roles that we should expect them to play in the future.

The concentration of carbon dioxide (CO_2) in the atmosphere has varied in step with glacial/interglacial cycles[3,4] (Fig. 1). During interglacial times, such as the Holocene (roughly the past 10,000 years), the atmospheric partial pressure of CO_2 (p_{CO_2}) is typically near 280 parts per million by volume (p.p.m.v.). During peak glacial times, such as the Last Glacial Maximum about 18,000 years ago, atmospheric p_{CO_2} is 180–200 p.p.m.v., or roughly 80–100 p.p.m.v. lower. CO_2 is a greenhouse gas, and model calculations suggest that its changes play a significant role in the energetics of glacial/interglacial climate change[5]. However, we have not yet identified the cause of these variations in CO_2. How do the orbitally driven cycles in solar radiation set this particular positive feedback into motion?

This question has persisted for two decades, motivating intensive research by palaeoclimatologists and palaeoceanographers. From this research, we now recognize many processes that could regulate atmospheric CO_2 on the timescales of glacial/interglacial transitions, and it may well be that the actual cause of glacial/interglacial CO_2 change is among them. However, evaluating the importance of these mechanisms with data from the recent geological and glaciological record has been a challenging and controversial task, leading as yet to no consensus on a fundamental mechanism. It is possible that many factors contribute comparably to the observed changes. However, the regularity of the CO_2 variations and the consistency of the upper and lower limits of atmospheric CO_2 through multiple 100-kyr cycles (Fig. 1) are suggestive of a well-ordered set of dominant mechanisms, the 'holy grail' of glacial/interglacial CO_2 research.
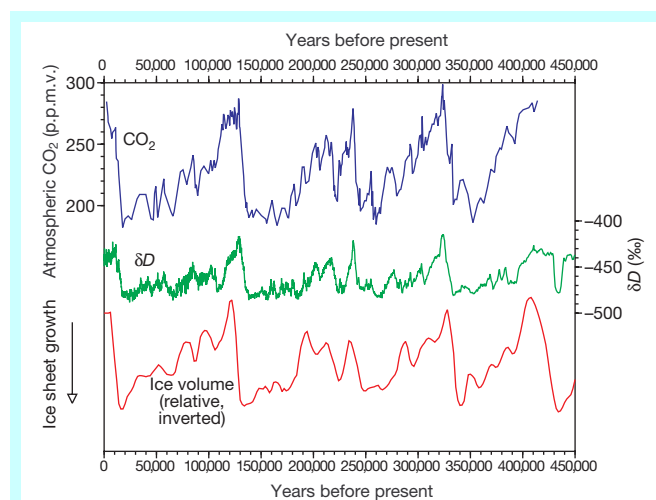

Figure 1 The history of atmospheric CO_2 back to 420 kyr ago as recorded by the gas content in the Vostok ice core from Antarctica[4]. The ratio of deuterium to hydrogen in ice (expressed as the term δD) provides a record of air temperature over Antarctica, with more negative δD values corresponding to colder conditions. The history of global ice volume based on benthic foraminiferal oxygen isotope data from deep-sea sediment cores[96] is plotted as relative sea level, so that ice ages (peaks in continental ice volume) appear as sea level minima, with a full glacial/interglacial amplitude for sea level change of about 120 m (ref. 18). During peak glacial periods, atmospheric CO_2 is 80–100 p.p.m.v. lower than during peak interglacial periods, with upper and lower limits that are reproduced in each of the 100-kyr cycles. Ice core records, including the Vostok record shown here, indicate that atmospheric CO_2 was among the early parameters to change at the termination of glacial maxima, roughly in step with Southern Hemisphere warming and preceding the decline in Northern Hemisphere ice volume.
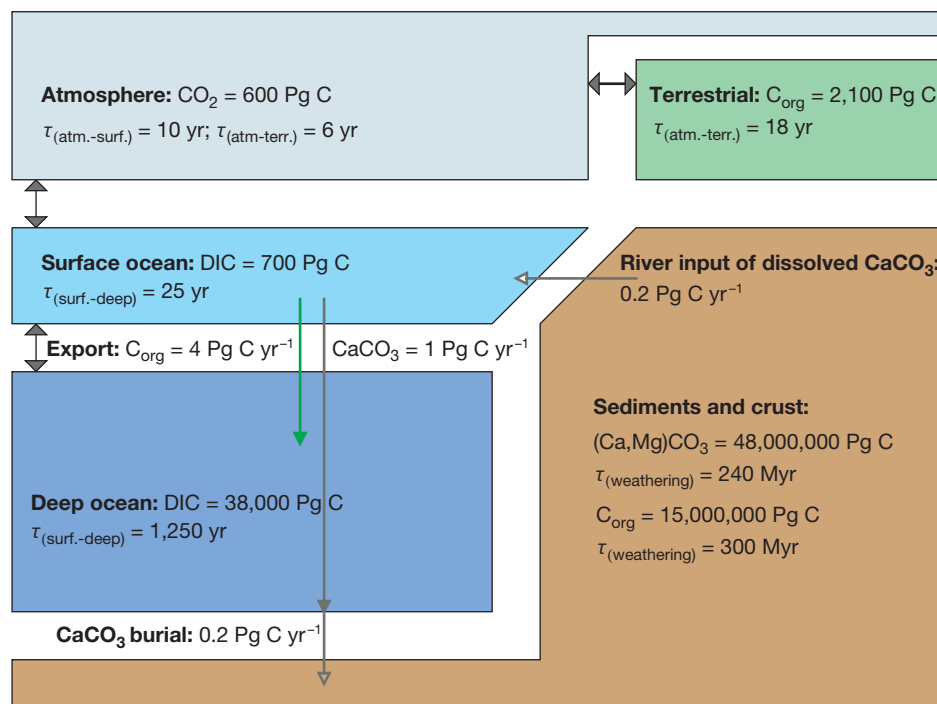
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Figure 2 A simplified view of the Holocene (pre-industrial) carbon cycle. Data is largely based on ref. 97 and includes only the reservoirs and fluxes thought to be most relevant for glacial/interglacial variations in atmospheric CO_2. Carbon that exchanges with atmospheric CO_2 on the timescale of glacial/interglacial transitions is stored in a number of reservoirs (given in units of Pg C, or 10^{15} g C), as dissolved inorganic carbon (DIC), calcium carbonate ($CaCO_3$), and organic carbon (C_{org}). For each of the carbon reservoirs, a residence time (τ, reservoir size divided by input or output) is given in relation to important exchange terms among reservoirs, which are indicated by double arrows. Relevant fluxes of C_{org} and $CaCO_3$ (including 'dissolved' $CaCO_3$) are indicated by single arrows. It is also informative to consider the fluxes that are excluded from this diagram. For instance, organic carbon burial (which occurs mostly along ocean margins), organic carbon weathering on land and volcanic/hydrothermal CO_2 release are generally thought to occur too slowly or to have the wrong sensitivities to play a major role in the consistent variation of atmospheric CO_2 over glacial/interglacial cycles.

The modern carbon cycle provides our first basis for discerning the processes that may have played an important role in glacial/interglacial CO_2 change (Fig. 2). Excluding recent anthropogenic changes, the atmospheric CO_2 reservoir is one-third to one-quarter of the size of the terrestrial biosphere and soil carbon reservoir, and is comparable to the amount of inorganic carbon stored in the warm upper ocean. However, all of these pools together are less than 10% of the inorganic carbon stored in the deep ocean. Deep water is exposed at the ocean surface roughly every 1,000 years, so that a change in atmospheric CO_2 driven by something other than oceanic processes would be diluted into the large reservoir of deep ocean inorganic carbon, greatly attenuating such CO_2 changes on the timescale of ice ages and interglacial periods. In addition, over thousands of years, the deep ocean regulates the exchange of inorganic carbon between the geosphere and the hydrosphere/atmosphere system through its control of the burial of calcium carbonate on the sea floor. From these facts, Broecker[6] concluded that oceanic changes must underlie the glacial/interglacial cycle in atmospheric CO_2.

Here, we review the potential causes of glacial/interglacial CO_2 change that have been recognized as well as the evidence for and against them. We will start with the relatively well-studied hypotheses and end with subjects of greater conjecture. Given that we still lack a proven mechanism for glacial/interglacial CO_2 changes, this approach is tantamount to first describing the processes that we believe cannot explain glacial/interglacial CO_2 changes (changes in terrestrial carbon storage and in ocean temperature, simple changes in the marine calcium carbonate budget) and then shifting to those processes that might (such as changes in the oceanic nutrient reservoir size) and finally to a hypothesis that is currently receiving special attention (changes in the completeness of nutrient consumption in high-latitude surface waters).

Carbon storage on land

With currently forested or vegetated regions covered under kilometres of ice, an increase in the extent of deserts, apparent conversion of tropical forest to grassland, and exposure of organic-rich sediments on continental shelves, it seems likely that the continental reservoir of organic carbon decreased during the last ice age, contributing CO_2 to the ocean/atmosphere system (ref. 7 and references therein). Based on reconstructions of biome distributions for the glacial world and information on carbon storage by different biomes, estimates[7,8] of the glacial/interglacial change in terrestrial carbon storage range between 700 and 1,350 Pg C (10^{15} g of carbon). An integrative indicator of the transfer of carbon from terrestrial sources during the last ice age is thought to be provided by the $^{13}C/^{12}C$ ratio of the calcitic shells of benthic foraminifera from deep sea sediments. The $^{13}C/^{12}C$ ratio of glacial-age shells is on average 0.3–0.4‰ lower than that of Holocene shells, a shift that has been interpreted as reflecting a transfer of continental organic carbon, which has a low $^{13}C/^{12}C$ ratio, to the ocean/atmosphere inorganic carbon reservoir during ice ages[9–11]. If this interpretation is correct, the $^{13}C/^{12}C$ change of 0.3–0.4‰ indicates that roughly 300–700 Pg of additional carbon were distributed throughout the ocean/atmosphere system during the last ice age[12]. While other possible explanations[13] have been raised for the observed decrease in foraminiferal $^{13}C/^{12}C$, the foraminiferal estimate of terrestrial carbon loss during the last ice age is already at the lower bound of values inferred from the terrestrial palaeoecological data, making it seem likely that changes in the terrestrial carbon pool dominated the benthic foraminiferal $^{13}C/^{12}C$ shift.

Given no other processes, a 500 Pg C addition, when distributed throughout the ocean/atmosphere system, would have raised atmospheric CO_2 by 45 p.p.m.v. However, this increase in inorganic

carbon would have driven a temporary increase in the dissolution of deep sea sedimentary calcite (see below), which would have reduced the effective CO_2 increase to 15 p.p.m.v. over about 5–10 kyr. Thus, while the terrestrial carbon reservoir was smaller during the last ice age, its effect on atmospheric CO_2 was probably modest because of buffering by the ocean carbon reservoir and the ocean $CaCO_3$ balance. Details aside, terrestrial carbon represents a source of CO_2 to the atmosphere, not a sink, during ice ages.

CO_2 storage in the ocean

The exchange of CO_2 between the atmosphere and the surface ocean would reach completion over the course of six to twelve months if there were no other processes redistributing inorganic carbon in the ocean. However, the p_{CO_2} of surface waters is continuously being reset by its interaction with the deep ocean reservoir of inorganic carbon, which is more than 25 times that of the atmosphere and surface ocean combined (Fig. 2).

Excluding the effect of anthropogenic additions of CO_2 to the atmosphere, we can consider the ocean and atmosphere to be in approximate steady state with respect to CO_2 exchange, with CO_2 uptake in some regions of the ocean balanced by CO_2 release in others. The air–sea exchange of CO_2 is determined largely by the p_{CO_2} of surface waters, with CO_2 transfer into the ocean occurring where the p_{CO_2} of surface waters is lower than that of the atmosphere, and transfer out of the ocean where it is higher. Surface water p_{CO_2}, in turn, is controlled by temperature and ocean chemical composition, which are separable in their responses to glacial/interglacial changes. CO_2 is more soluble in cold water, causing CO_2 invasion into cold surface waters and CO_2 evasion out of warm surface waters. The role of ocean chemical composition is more complicated, involving the dependence of surface water p_{CO_2} on its inorganic carbon content and acid/base chemistry, which are greatly affected by biological processes.

Ocean temperature

As ocean temperature was lower during ice ages, it is an obvious first step to consider its effect on atmospheric CO_2. The lower temperatures of the glacial ocean would have reduced the concentration of CO_2 in the atmosphere by drawing more of it into the ocean. The deep ocean, which is the dominant volume of ocean water, has a mean temperature of $2\,^\circ C$. Sea water begins to freeze at about $-2\,^\circ C$, producing buoyant ice. As a result, deep ocean water could not have been more than $4\,^\circ C$ colder during the last ice age, placing an upper bound on how much additional CO_2 this water could have sequestered simply by cooling. The potential cooling of surface waters in polar regions such as the Antarctic is also constrained by the freezing point of sea water. The temperature of the lower-latitude (equatorial, tropical and subtropical) surface ocean is far from the freezing point and thus lacks this constraint, and the pattern of low-latitude cooling is a subject of continuing research. The CLIMAP project[14] estimated that the tropical and subtropical sea surface was cooler by $3\,^\circ C$ or less during the last ice age. However, estimates from the continents and some of the more recent paleoceanographic work suggest greater cooling, for example, as much as $5\,^\circ C$ in the tropical Atlantic[15].

The cooling of different regions of the ocean surface affected ice age CO_2 levels to the degree that they altered the volume-averaged temperature of the ocean, the critical parameter for the mean solubility of CO_2 in the ocean. The similarity in temperature between the large volume of the deep ocean and polar surface waters implies that most of the ocean interior is ventilated in polar environments, so we expect a given temperature change in polar surface waters to have a greater influence on atmospheric CO_2 than would the same temperature change in the low-latitude surface. For instance, in the CYCLOPS ocean box model[16], a given cooling of the high-latitude surface causes roughly twice the CO_2 decrease that is
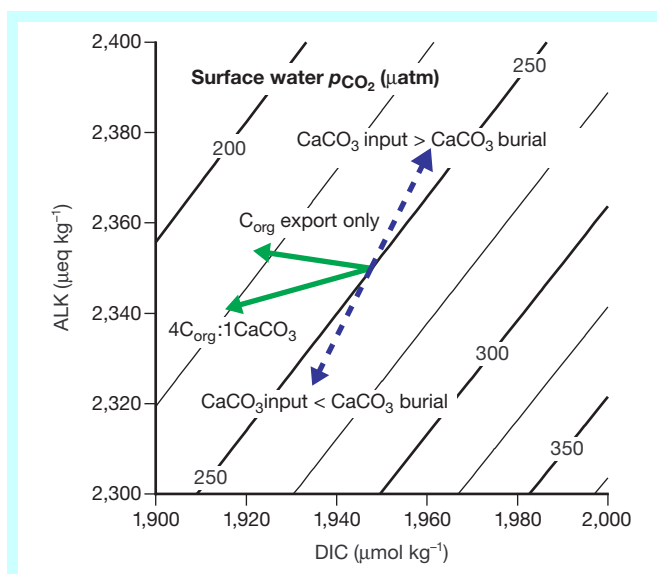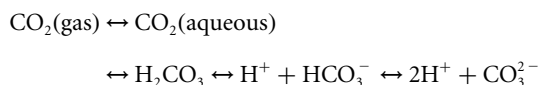

Figure 3 The p_{CO_2} of surface sea water at $20\,^\circ C$ and a salinity of 35 parts per thousand, as set by its dissolved inorganic carbon (DIC) content and alkalinity (ALK). The p_{CO_2} decreases as DIC decreases and/or ALK increases. The dashed arrows show the relative effects on ALK and DIC of imbalances in the $CaCO_3$ budget of the ocean. If $CaCO_3$ burial is less than the continental input of dissolved $CaCO_3$, then the ALK and DIC of the whole ocean increase in a 2:1 ratio. This lowers the p_{CO_2} of surface waters and transfers CO_2 from the atmosphere into the ocean. The solid arrows show the effect of the rain of biogenic materials out of the surface ocean ('export production'), for the cases that this rain is organic carbon (C_{org}) only and that it is a 4:1 molar ratio of C_{org} and $CaCO_3$. In general, the former composition applies to high nutrient polar surface ocean ecosystems, while the latter applies to the warm low-latitude ocean (references in ref. 98). Export production removes DIC from the surface ocean, sequestering it in the ocean interior. The modest ALK increase associated with C_{org} export only is due to the associated uptake of nitrate by phytoplankton. Export production also affects the DIC and ALK of the deep ocean, because C_{org} produced in the surface ocean and oxidized by bacteria in the ocean interior releases DIC and lowers the carbonate ion concentration of deep water. This affects the burial rate of $CaCO_3$ in the seafloor sediments, which further modifies the p_{CO_2} of surface waters through its effect on the whole-ocean $CaCO_3$ balance (dashed arrows).

caused by an identical cooling of the low-latitude surface. A reasonable estimate for ice age ocean cooling of $2.5\,^\circ C$ in the polar surface and $5\,^\circ C$ in the low-latitude surface leads to a CO_2 decrease of 30 p.p.m.v., with the low-latitude and polar temperature changes playing roughly equivalent roles in this decrease. It has recently been noted that ocean general circulation models predict a greater sensitivity of CO_2 to low-latitude surface conditions than do simple ocean box models like CYCLOPS[17]. However, the significance of this observation is a matter of intense debate.

An opposing effect on atmospheric CO_2 to that of glacial/interglacial temperature change is provided by the increased salinity of the glacial ocean, due to the storage of fresh water on land in extensive Northern Hemisphere ice sheets. Based on the approximately 120 m depression of sea level during the last ice age[18], the whole ocean was about 3% saltier than it is today. All else being constant, this increase would have reduced the solubility of CO_2 in sea water and raised atmospheric CO_2 by 6.5 p.p.m.v. Taking the estimated temperature and salinity effects together, we would expect the atmospheric CO_2 concentration of the ice age world to have been 23.5 p.p.m.v. lower. Folding in the effect of a 500 Pg C transfer from the continents to the ocean/atmosphere system, we are left with an 8.5 p.p.m.v. decrease in CO_2 (Table 1). There are uncertainties in each of these effects, but it seems that most of the 80–100 p.p.m.v. CO_2 change across the last glacial/interglacial transition must be explained by other processes. We must move on to the more complex aspects of the ocean carbon cycle.

Ocean carbon cycle

Upon dissolution in sea water, inorganic carbon maintains an acid/base equilibrium:

$$CO_2(gas) \leftrightarrow CO_2(aqueous)$$

$$\leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

Dissolved inorganic carbon (DIC) is defined as the sum of these different inorganic carbon species, excluding gas phase CO_2. The distribution of inorganic carbon among the above species depends on both the DIC concentration and the acid-titrating capacity of sea water, which we refer to as 'alkalinity' (ALK), the total equivalence of ions that must be protonated in order to lower the pH of sea water to the pK_a of carbonic acid (Fig. 3). If DIC increases while ALK remains constant, the proportion of the DIC pool present as carbonic acid and aqueous CO_2 increases. In addition, there is more inorganic carbon to partition among the different inorganic carbon species. Hence, p_{CO_2} increases as DIC increases. As ALK increases, the inorganic carbon reservoir is shifted away from aqueous CO_2, resulting in a lower p_{CO_2}.

The DIC and ALK of surface water are determined by two types of carbon cycle responses to oceanographic change, which can be referred to as 'closed-system' and 'open-system' responses. Closed-system responses redistribute DIC and ALK among the different volumes of the ocean. Open-system responses change the sizes of the whole-ocean reservoirs of DIC and ALK, through temporary imbalances between their input from weathering of calcium carbonate ($CaCO_3$) on the continents and their output by the burial of biogenic calcium carbonate in the ocean. The first geochemical hypotheses for the cause of glacial/interglacial CO_2 changes generally fell into two categories, based on whether they elicited a closed-system or open-system carbon-cycle response. Closed-system hypotheses focused on the 'biological pump', the sequestration of inorganic carbon in the deep ocean by photosynthesis in the sunlit surface and the subsequent rain of organic carbon out of the upper ocean[19]. Open-system hypotheses focussed on carbonate weathering and coral reef growth[20]. We have come to recognize that many geochemical changes, especially those involving the biological pump, would affect both the gradients and the reservoir sizes of ALK and DIC in the ocean, so that both closed- and open-system responses must be considered[21].

Ocean alkalinity

Alkalinity is added to the ocean largely by the weathering of emergent carbonates on land, and it is removed largely by the biogenic precipitation and burial of $CaCO_3$, in shallow coral reefs and carbonate banks, and in deep-sea sediments[22]. A complete treatment of ocean alkalinity would also include the input of alkalinity by the weathering of silicates on land and the consumption of alkalinity in the ocean by hydrothermal activity[23] and 'reverse weathering'[24]. However, on the timescales of glacial/interglacial transitions, it is believed that our view can be restricted to the input/output balance of $CaCO_3$. In reef environments, much of the buried $CaCO_3$ is precipitated in situ by corals and benthic algae as the mineral aragonite. In the open ocean, most $CaCO_3$ is precipitated as the mineral calcite in the microfossils of two groups of marine plankton, coccolithophorids and planktonic foraminifera. This $CaCO_3$ subsequently rains out of the surface ocean along with

sinking organic matter. Roughly 75% of the $CaCO_3$ rain dissolves in the deep sea, while the remaining 25% is buried in deep sea sediment and is thus removed from the ocean reservoir (Fig. 2). When weathered or buried, $CaCO_3$ adds or removes two equivalents of ALK per mole of DIC.

The balance between the input of alkalinity from the continents and the removal of alkalinity in sediments is maintained by the distribution of $CaCO_3$ burial in the deep sea, and this distribution also provides us with a powerful constraint on ocean alkalinity changes over glacial/interglacial cycles. Deep sea $CaCO_3$ burial is mediated by the depth of the 'calcite lysocline,' the transition separating shallower seafloor sediments where some calcite is preserved from deeper seafloor sediments where almost all of the calcite rain dissolves[25,26]. One of the primary controls on the depth of the lysocline is the calcite saturation depth, the depth at which the carbonate ion concentration of bottom water, $[CO_3^{2-}]_{bw}$, equals the carbonate ion concentration at calcite saturation, $[CO_3^{2-}]_{sat}$, occurring on average at 3.5 km depth[27]. Because calcite solubility increases with depth (a pressure effect), the water bathing the sea floor above the saturation depth is supersaturated, causing the preservation and eventual burial of $CaCO_3$ on the shallow sea floor, while water deeper than the saturation depth is undersaturated, dissolving the calcite rain and thus preventing $CaCO_3$ burial on the deeper sea floor.

Because of its effect on the calcite burial rate, the response of the lysocline to a change in $[CO_3^{2-}]_{bw}$ represents a negative feedback which drives deep-sea calcite burial towards a balance with the input of alkalinity from the continents[28]. For example, an increase in the weathering of limestone and other carbonate-bearing rocks on land (or similarly a decrease in coral reef growth in the shallow ocean) increases the whole ocean inventories of ALK and DIC in a 2:1 ratio. This inventory change causes a decrease in atmospheric CO_2 (Fig. 3). However, this increase in oceanic alkalinity also causes an increase in deep ocean $[CO_3^{2-}]$ (according to the relation $\Delta[CO_3^{2-}] \approx 0.6\Delta(ALK - DIC)$), which in turn deepens the calcite saturation horizon. This deepening of the saturation horizon deepens the lysocline, which increases the area of sea floor where $CaCO_3$ is buried, so that the $CaCO_3$ burial rate once again comes into balance with the rate of alkalinity input from rivers, and atmospheric p_{CO_2} stabilizes at a lower value.

Thus, the history of the mean lysocline depth provides a palaeoceanographic constraint on ocean alkalinity changes. An increase in carbonate weathering on land would deepen the lysocline by 1 km for every ~25 p.p.m. decrease in atmospheric p_{CO_2} that it would cause. This requires that the lysocline must have been deeper by more than 2 km during the last ice age for a change in the input of alkalinity to have played a dominant role in glacial/interglacial CO_2 changes. Data on seafloor $CaCO_3$ content suggest that the ocean-average lysocline of the last ice age was less than 1 km deeper than that of the Holocene[29]. This finding invalidates hypotheses that call upon increased weathering or decreased coral reef growth as the primary driver of lower ice age levels of atmospheric CO_2 (ref. 30).

An alternative mechanism for changes in ocean alkalinity involves the biological production of $CaCO_3$ microfossils. The low-latitude ocean (the combined equatorial, tropical, and subtropical regions), where the $CaCO_3/C_{org}$ ratio of the biogenic rain is roughly 1:4, is responsible for most deep-sea calcite burial[29]. We might expect the $CaCO_3/C_{org}$ rain ratio of the low-latitude ocean to have been lower during the last ice age if organic carbon export production rates were higher or more sporadic, amongst other possibilities[31]. Decreasing the $CaCO_3/C_{org}$ rain ratio of the low-latitude ocean drives a decrease in atmospheric CO_2, partly by leaving a larger fraction of the ocean's alkalinity reservoir in the surface ocean, where it enhances CO_2 solubility (a closed-system effect)[31], and partly by decreasing deep-sea $CaCO_3$ burial, which causes the whole ocean alkalinity reservoir to increase (an open-system effect)[32]. In the CYCLOPS ocean geochemistry model[16], assuming that only

Table 1 Atmospheric CO₂ effects of known changes	
Condition during the last ice age (as different from Holocene)	CO_2 change (p.p.m.v.)
Terrestrial carbon decrease (500 Pg C)	15
Ocean cooling (5° low latitude, 2.5° high latitude)	−30
Ocean salinity increase (3%)	6.5
Total CO_2 change	−8.5

bottom water undersaturation causes calcite dissolution on the sea floor[27], a halving of the $CaCO_3/C_{org}$ rain ratio causes atmospheric CO_2 to decrease by about 55 p.p.m.v., with 35 p.p.m. of this change arising from an increase in whole ocean alkalinity (Fig. 4)[33]. This whole ocean alkalinity change can be parsed into two separate effects. The first is 'CaCO_3 compensation'[21], in which the closed-system redistribution of ALK and DIC by the change in rain ratio causes a 'dissolution event' in the deep sea, reducing the depth of the lysocline (and thus the whole-ocean burial rate of $CaCO_3$) for a transient period (Fig. 4). The second open-system effect, which we call the 'steady-state lysocline shift'[33], is that the decrease in the rain rate of $CaCO_3$ to the sea floor in itself causes the burial rate of $CaCO_3$ to fall below the continental input rate of dissolved $CaCO_3$. This, in turn, causes ocean alkalinity to increase until the lysocline has deepened enough to allow for $CaCO_3$ burial to once again balance the continental input of alkalinity.

The 55 p.p.m.v. decrease in CO_2 due to this rain ratio change is significant relative to the observed glacial/interglacial variability of atmospheric CO_2. However, the record of deep sea calcite preservation provides a critical sticking point, just as it did with respect to an increase in the continental sources of alkalinity. The CO_2 decrease is associated with an ocean-average 1.1-km deepening of the calcite saturation horizon (Fig. 4) owing to the decrease in the

Figure 4 The time-dependent response of the CYCLOPS model to a sudden halving in the $CaCO_3/C_{org}$ ratio of the export flux out of the low-latitude surface ocean[33]. The low-latitude surface ocean comprises the equatorial, tropical and subtropical oceans. **a**, Atmospheric CO_2, for both 'closed' and 'open' system cases. **b**, Depth of calcite saturation (and the lysocline) in the open-system case. In the closed-system case, all of the $CaCO_3$ rain is dissolved in the ocean subsurface, with no burial, and there is no continental source of dissolved $CaCO_3$. In the open-system case, which is more realistic, $CaCO_3$ is buried on the deep sea floor, and there is a continental input of dissolved $CaCO_3$. The closed-system output has been offset to start at the same initial p_{CO_2} as the open-system case (280 p.p.m.v.). The closed-system effect of the $CaCO_3/C_{org}$ rain ratio decrease is to extract less alkalinity from the surface ocean, which causes a 20 p.p.m.v. decrease in atmospheric CO_2 within hundreds of years. In the open-system case, the $CaCO_3/C_{org}$ rain ratio decrease causes $CaCO_3$ burial to decrease below the input rate of alkalinity from the continents, both because of a transient dissolution event (evident as the early shoaling of the calcite saturation horizon, **b**) and because of a permanent decrease in the $CaCO_3$ rain rate onto the sea floor. Due to both of these effects, ocean alkalinity increases, which causes the p_{CO_2} of surface water to decrease, so that atmospheric CO_2 decreases more in the open-system case than in the closed-system case (**a**). The whole-ocean alkalinity increase associated with the permanent decrease in the $CaCO_3$ rain rate, while contributing to the decrease in atmospheric CO_2, also causes the deep-ocean carbonate ion concentration to increase through time, so that the calcite saturation horizon deepens. This deepening increases the area of sea floor on which $CaCO_3$ is preserved and buried so that global-ocean $CaCO_3$ burial increases back to equality with the river input of alkalinity, resulting in a new steady state with a deeper saturation horizon and lysocline. The model used here assumes that the carbonate ion concentration of deep water is the dominant control on the depth distribution of calcium carbonate burial in seafloor sediments (see text).

$CaCO_3$ rain rate to the sea floor. The compiled data indicating a smaller difference in the ocean-average lysocline depth between the modern and glacial oceans[29] argue against a glacial decrease in the $CaCO_3/C_{org}$ ratio as the sole driver of lower glacial CO_2 levels. What is needed to explain glacial/interglacial CO_2 variability is a mechanism to lower atmospheric CO_2 without causing a large deepening of the steady-state lysocline.

Early research demonstrated that the degree of seawater saturation with respect to calcite is a dominant control on seafloor $CaCO_3$ preservation. The observed correspondence of the lysocline depth with the depth of calcite saturation helped lead to this conclusion[27]. However, continued studies of seafloor dissolution have indicated that pore water undersaturation due to oxidation of organic matter within the sediments is also a significant driver of calcite dissolution (ref. 34 and references in ref. 35). The effect of sedimentary respiration on seafloor calcite dissolution amplifies the capacity of a decrease in the $CaCO_3/C_{org}$ ratio of low-latitude biological production to lower atmospheric CO_2 (ref. 30). When this 'respiratory dissolution' is included in an ocean geochemistry model, halving the $CaCO_3/C_{org}$ ratio causes an atmospheric CO_2 decrease comparable to the glacial/interglacial change. The greater CO_2 decrease is due to enhancement of the whole ocean alkalinity increase when respiratory dissolution is included in the seafloor dissolution model. One of the recognized requirements of this mechanism as a hypothesis for glacial/interglacial CO_2 changes is that the deepening of the calcite saturation horizon associated with this alkalinity increase would not be evident in the record of the glacial lysocline. In other words, it requires that the depth of lysocline did not correspond to the calcite saturation depth during glacial times. Instead, the lysocline must have occurred in supersaturated waters, representing the transition point at which bottom water supersaturation was low enough for respired CO_2 in sedimentary pore waters to drive almost complete dissolution of the calcite in the sediment.

When the $CaCO_3/C_{org}$ rain ratio is lowered in a range of models of seafloor calcite dissolution, however, respiratory dissolution does not effectively decouple the lysocline from the saturation depth until both are quite deep, so that a major deepening in the calcite saturation horizon would have been accompanied by a deepening of the lysocline[33]. The strong coupling between the lysocline and the saturation horizon results from the weak depth dependence of respiratory dissolution, relative to that of dissolution driven by bottom water undersaturation. With enhanced respiratory dissolution, calcite burial rates become less depth-dependent, with proportionally more dissolution occurring on the shallow sea floor. With less $CaCO_3$ burial on the sea floor of the shallow and mid-depth ocean, there must be an increase in $CaCO_3$ burial rates in the deeper ocean, and thus a deepening of the lysocline, to balance the river input of alkalinity. Thus, the relatively constant ocean-average lysocline depth remains as evidence against a glacial decrease in the $CaCO_3/C_{org}$ ratio as the sole driver of lower ice age CO_2 levels. Although seafloor $CaCO_3$ dynamics may have surprises in store for us, there are reasons to doubt the role of whole-ocean alkalinity changes as the sole driver of glacial/interglacial CO_2 change.

Nevertheless, most biological pump mechanisms for lowering atmospheric CO_2 also drive a change in whole-ocean alkalinity (see below), and in some cases, this contributes significantly to their capacity to lower atmospheric CO_2. The alkalinity changes which are most 'helpful' in this regard are due to $CaCO_3$ compensation[21], in which the oceanic redistribution of ALK and DIC causes a transient dissolution event, rather than a shift in the steady-state depth of the lysocline. This prevents violation of the palaeoceanographic constraint on the steady-state depth of the lysocline.

The ocean nutrient reservoir and low-latitude productivity

Broecker[19] first hypothesized a glacial increase in the strength of the biological pump as the driver of lower glacial CO_2 levels. This
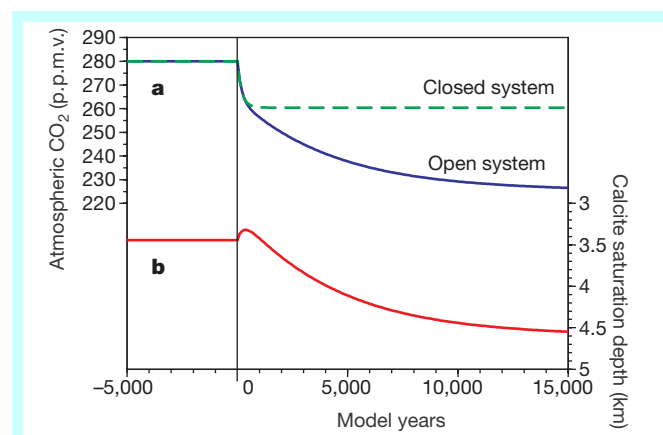
hypothesis has spawned many variants. These mechanisms can be separated into two groups: (1) those involving changes in the low- and mid-latitude surface ocean, where the major nutrients nitrate and phosphate ultimately limit the extraction of CO_2 by biological production; and (2) those involving changes in the polar and subpolar ocean regions, where the major nutrients are currently not completely consumed. In either case, the relevant quantity is 'export production', the organic matter produced by phytoplankton that is exported from the surface ocean, resulting in the sequestration of its degradation products (inorganic carbon and nutrients) in the ocean interior.

Biological production in the ocean tends to incorporate phosphate, nitrate, and inorganic carbon into biomass in the ratios of 1:16:106 (the 'Redfield ratios'[36]). These ratios determine the amount of inorganic carbon sequestered in the deep sea when the supply of nutrients to the surface is completely converted to export production, as is the case in the low- and mid-latitude ocean. For low-latitude carbon export to extract more CO_2 from the surface ocean and atmosphere, it must be driven by an increase in the deep-ocean nutrient reservoir and/or a change in the composition of the export production.

Broecker[19] and McElroy[37] described possible mechanisms by which the reservoirs of phosphate and nitrate might increase during glacial times, which would allow enhanced low-latitude biological production to lower atmospheric CO_2. However, it was recognized that large changes in nutrient reservoirs would be required to produce the entire observed amplitude of CO_2 change. In the modern polar oceans, biological production is limited by parameters other than the supply of phosphate or nitrate[38]. Therefore, it seems most reasonable to assume that high-latitude production would not respond to an increase in these nutrients. Making this assumption, box model calculations[33] indicate that the immediate effect of 30% increase in the oceanic nutrient reservoir, enhanced extraction of CO_2 from the surface ocean and its sequestration in the deep sea, lowers atmospheric CO_2 by 30–45 p.p.m.v. (Table 2).

The longer-term effect on CO_2 from the ocean alkalinity balance depends greatly on whether $CaCO_3$ export increases in step with C_{org} export[33]. If $CaCO_3$ export increases proportionately with C_{org} export, the increase in the $CaCO_3$ flux to the sea floor causes a loss of alkalinity from the ocean over 5–10 kyr, which works to raise atmospheric CO_2. As a result, the net drop in CO_2 from a 30% increase in the oceanic major nutrient reservoir would be only 15–25 p.p.m.v. (Table 2)[33]. However, if $CaCO_3$ production remains constant as C_{org} production increases, an increase in the oceanic nutrient reservoir is much more effective at lowering atmospheric CO_2. In this case, a 30% increase in the oceanic nutrient reservoir lowers atmospheric CO_2 by approximately 50 p.p.m.v. (Table 2), and an increase of more than 50% could lower atmospheric CO_2 by 80 p.p.m.v.[33]. The increase in the ocean nutrient reservoir required for an 80 p.p.m.v. decrease in CO_2 could be lowered from 50% to perhaps 30–40% by a coincident decrease in $CaCO_3$ export that was modest enough not to violate observations of the glacial-age lysocline depth[33]. Nevertheless, even a 30% increase in oceanic nutrients and in low- and mid-latitude export production would be a dramatic change.

Given a residence time of 16 kyr or more for oceanic phosphate and few appropriate mechanisms for phosphate addition and removal[39], it is difficult to imagine how oceanic phosphate could vary so as to cause the observed amplitude, rate and phasing of atmospheric CO_2 change[40]. On the other hand, there is growing evidence that the nitrogen cycle is adequately dynamic to allow for a large change in the oceanic nitrate reservoir on glacial/interglacial timescales[41]. Nitrogen isotope studies in currently active regions of denitrification[42–44] indicate that water column denitrification was reduced in these regions during glacial periods. In addition, Falkowski[45] has suggested that N_2 fixation rates were greater during glacial periods because of increased airborne supply of iron-bearing dust to the open ocean (iron being an important requirement for N_2 fixation). Both of these hypothesized changes, a decrease in water column denitrification and an increase in N_2 fixation, would have increased the oceanic nitrate reservoir. It has been suggested that such a nitrate reservoir increase would lead to significantly higher export production in the open ocean during glacial periods, potentially explaining glacial/interglacial atmospheric CO_2 changes[37,40,42,45].

The major questions associated with this hypothesis involve the oceanic reservoir of phosphate, the feedbacks of the nitrogen cycle, and the strictness with which marine organisms must adhere to the Redfield ratios, both N/P and C/N. Oceanic N_2 fixation provides a mechanism to add fixed nitrogen to the ocean when the other nutrients are present in adequate supply. By contrast, riverine input of phosphorus, the major source of phosphate to the ocean, is not directly controlled by marine phytoplankton. As a result, geochemists have traditionally considered phosphate to be the fundamentally limiting major nutrient on glacial/interglacial timescales[46]. For a nitrate reservoir increase to be the sole driver of an increase in low-latitude biological production, the nutrient requirements of the upper-ocean biota must be able to deviate from Redfield stoichiometry to adjust to changes in the N/P ratio of nutrient supply, so as to use the added nitrate fully in the absence of added phosphate. On the other hand, if this compensatory shift in biomass composition is incomplete, the surface ocean will tend to shift toward phosphate limitation.

It was originally suggested by Redfield[36], based on analogy with freshwater systems, that N_2 fixers in the open ocean will enjoy greater competitive success under conditions of nitrate limitation but will be discouraged in the case of phosphate limitation. If this sensitivity exists, then one would expect N_2 fixation to act as a negative feedback on the nitrate reservoir, varying so as to prevent large changes in the nitrate reservoir that are not associated with a coincident change in the phosphate reservoir[47]. On the grand scale, this feedback must occur to prevent drastic swings in the oceanic nitrate reservoir. However, the quantitative constraint that this negative feedback places on the global nitrate reservoir is not yet known, with one suggested possibility being that iron is so important to N_2 fixers that changes in its supply can, within some limits, overpower the nitrate/phosphate sensitivity described by Redfield, leading to significant variations in the nitrate reservoir over time[45]. Biogeochemical studies of the modern ocean[48] and the palaeoceanographic record[49] are both likely to play a role in the evaluation of these questions regarding Redfield stoichiometry and N_2 fixation, which are, in turn, critical for the hypothesis of the low-latitude biological pump as the driver of glacial/interglacial CO_2 change.

A number of palaeoceanographic studies suggest that export production was greater in low-latitude regions during ice ages[50,51]. However, proxy data for nutrient utilization[52] and pH[53] suggest that these changes were driven at least partially by enhanced upwelling, masking any potential sign of a change in the oceanic nutrient reservoir. Nutrient consumption is eventually complete in the modern low-latitude surface ocean, so that inorganic carbon is already stripped to the greatest possible degree, given the oceanic nutrient reservoir and the Redfield ratios. Vertical mixing and

Table 2 Atmospheric CO_2 effects of a 30% increase in the ocean nutrient inventory

Carbon cycle effect	CaCO_3 production	
	Proportional	Constant
Closed system effects	−34	−43
Open system effects		
CaCO_3 compensation	6	−3
Steady state lysocline shift	11	0
Total CO_2 change (p.p.m.v.)	−17	−46

upwelling supply excess inorganic carbon to the surface ocean in approximately Redfield proportions with the major nutrients, so that an increase in upwelling would increase the rate of export production from the surface ocean but would not enhance the extraction of DIC from the surface ocean. Increased export production driven by higher rates of vertical mixing or upwelling would only play a role in lowering atmospheric CO_2 if it caused a change in the chemical composition of the exported organic material (such as a decrease in its $CaCO_3/C_{org}$ ratio, as described above).

Nutrient utilization and high latitudes

Soon after Broecker's[19] low-latitude-based hypothesis, several groups[54–56] recognized the potential importance of the high-latitude surface ocean for glacial/interglacial CO_2 change, through its effect on the global efficiency of the biological pump. The thermocline of the world ocean outcrops at subpolar latitudes, allowing deep waters more ready access to the surface in the polar regions. In these regions, the nutrient-rich and CO_2-charged waters of the deep ocean are exposed to the atmosphere and returned to the subsurface before the available nutrients are fully utilized by phytoplankton for carbon fixation. This incomplete use of upwelled nutrients allows for the leakage of deeply sequestered CO_2 back into the atmosphere, raising the atmospheric p_{CO_2} (Fig. 5). On this basis, increased nutrient utilization in the high-latitude surface ocean has been invoked as the cause of the lower atmospheric p_{CO_2} of glacial times[16,54–58].

With regard to their nutrient status, it can be shown that surface ocean regions that ventilate the ocean subsurface have particular importance for atmospheric CO_2 (Fig. 5). Briefly, this involves the integrated potential of global ocean nutrient stocks to drive carbon sequestration as the water holding these nutrients cycles through the surface ocean and drives biological export production. The 'Southern Ocean' (the high-latitude ocean of the Southern Hemisphere) ventilates large volumes of the ocean interior, making its variations in nutrient utilization a potentially important driver of glacial/interglacial CO_2 change (Fig. 6a). The Antarctic zone, the most polar region in the Southern Ocean, is central in the formation of deep and intermediate-depth waters (Fig. 6b), making this region important to the atmosphere/ocean CO_2 balance. The subantarctic zone (to the north of the Antarctic) has a less clear effect on atmospheric CO_2, depending on the degree to which the nutrient status of the subantarctic surface influences the preformed nutrient concentration of newly formed subsurface water (Antarctic intermediate water and subantarctic mode water, Fig. 6b). In contrast to polar surface waters, the importance of the nutrient status of the low-latitude upwelling systems to atmospheric CO_2 does not extend to glacial/interglacial timescales because these regions do not ventilate the ocean interior. Put another way, nutrients upwelled in these environments are eventually consumed before the water holding them is folded back into the ocean interior, so nutrient utilization is complete today and would have been so during the last ice age as well.

In hypotheses of a change in Southern Ocean nutrient utilization, two causes have been considered: an increase in biological export production and a decrease in the exposure rate of deep waters at the polar surface. We might consider the first mechanism 'biological' and the second 'physical'. However, an increase in nutrient utilization by either mechanism requires certain sensitivities of the biological productivity in Southern Ocean surface waters. Specifically, both mechanisms would require that export production in the modern Southern Ocean is limited by something other than the major nutrients nitrate and phosphate that are supplied by the upwelling of deep water. Indeed, both light and trace metals such as iron are scarce commodities in the Southern Ocean[38]. We can easily imagine processes that would have increased Southern Ocean nutrient utilization by either of the two mechanisms mentioned above. For instance, an increase in the input of dust and its

associated trace metals to the Southern Ocean might have driven an increase in the rate of nutrient and carbon uptake by phytoplankton[58]. Alternatively, a strengthening of salinity-driven stratification in the Antarctic or a decrease in wind-driven upwelling in this region could have lowered the rate of nutrient and CO_2 transport to the surface[59].

With respect to rates of biological export production, palaeoceanographic work in the Southern Ocean indicates that the Antarctic and subantarctic have responded very differently to glacial/interglacial cycles. In the modern Antarctic, export production is dominated by diatoms, a group of phytoplankton that precipitate tests of hydrated silica, and these microfossils are frequently the dominant component of the underlying sediments. The accumulation of diatomaceous
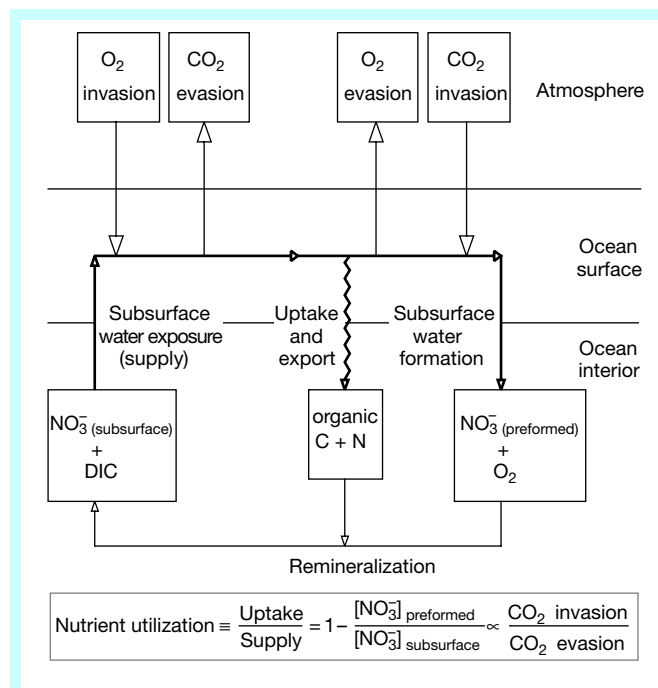

$$\text{Nutrient utilization} \equiv \frac{\text{Uptake}}{\text{Supply}} = 1 - \frac{[NO_3^-]_{preformed}}{[NO_3^-]_{subsurface}} \propto \frac{CO_2 \text{ invasion}}{CO_2 \text{ evasion}}$$

Figure 5 The effect on atmospheric CO_2 of the biological pump in a region of deep-ocean ventilation. Deep water is nutrient- and CO_2-rich because of the lower-latitude biological pump, which sequesters both nutrients and inorganic carbon in the ocean interior; the major nutrients nitrate and phosphate are represented here as nitrate (NO_3^-) only. In high-latitude regions such as the Antarctic, the exposure of deep water at the surface releases this sequestered CO_2 to the atmosphere. However, the uptake of nutrients and CO_2 in the formation of phytoplankton biomass and the eventual export of organic matter subsequently lowers the p_{CO_2} of surface waters, causing the surface layer to reabsorb a portion of the CO_2 that was originally lost from the upwelled water. Thus, the ratio between export production and the ventilation of CO_2-rich subsurface water, not the absolute rate of either process alone, controls the exchange of CO_2 between the atmosphere and high-latitude surface ocean. The nutrient concentration of water at the time that it enters the subsurface is referred to as its 'preformed' nutrient concentration. The preformed nutrient concentration of subsurface water provides an indicator of the cumulative nutrient utilization that this water underwent while at the surface, with a higher preformed nutrient concentration indicating lower cumulative nutrient utilization at the surface and thus a greater 'leak' in the biological carbon pump. The global efficiency of the biological pump can be evaluated in terms of the global mean preformed nutrient concentration of the ocean interior. In the calculation of this mean preformed nutrient concentration, each subsurface water formation term is weighted according to the volume of the ocean that it ventilates, because this corresponds to the amount of CO_2 that could be sequestered in a given portion of the ocean interior. As a result, surface ocean regions that are important in the ventilation of the ocean interior, such as the Antarctic, have particular importance for atmospheric CO_2. This simple view overlooks some important facts. For instance, ocean/atmosphere CO_2 exchange is not instantaneous[68], and variations in the chemical composition of export production also affects the p_{CO_2} of surface waters, as does sea surface temperature.

sediments in the Antarctic was clearly lower during the last ice age[60], and palaeoceanographic indicators also suggest that the biological export of carbon was lower in general[59,61,62]. However, given a possible bias in the proxies to record preferentially the carbon export associated with diatoms, it remains possible that the biological export of carbon from the glacial Antarctic surface was as high as or higher than export during interglacial times but that it occurred in a form that was poorly preserved in the sediment record[64,65]. In the subantarctic, there is very strong evidence for higher export production during glacial times and an associated increase in the relative importance of diatom production[59–61]. While these changes in export production are critical to the workings of the ice age Southern Ocean, they do not directly address the effect on atmospheric CO_2, which is largely determined by the history of nutrient utilization (Fig. 5).

In the Antarctic, nitrogen isotope data suggest that nitrate utilization during the last ice age was twice or more its current value[59,66]. These results seem to support the longstanding hypothesis that nutrient utilization changes in Antarctic waters are a fundamental driver of glacial/interglacial changes in atmospheric p_{CO_2}. A box model calculation predicts that 25–40% higher nitrate utilization (that is, 50–65% during the last ice age compared to 25% during the present interglacial) could lower atmospheric CO_2 by the full glacial/interglacial amplitude[66]. According to the model calculation, a significant part of this CO_2 change is due to an increase in ocean alkalinity, and this model calculation may underestimate its importance[67]. In addition, a glacial increase in wintertime sea ice coverage may have worked to lower atmospheric CO_2 by preventing gas exchange during this season[68], when Antarctic surface water is more likely to be supersaturated with CO_2. Because palaeoceanographic proxy data suggest that Antarctic export production was lower during the last ice age, we infer that more complete nitrate utilization in the Antarctic was due to a lower rate of nitrate supply from the subsurface, implying that the fundamental driver of the CO_2 change was an ice age decrease in the ventilation of deep waters at the surface of the Antarctic[59].

The interpretation from nitrogen isotopes of higher nitrate utilization in the Antarctic faces a number of apparent disagreements with other proxies of nutrient status, in particular, the Cd/Ca (refs 69, 70) and $^{13}C/^{12}C$ (ref. 71) of planktonic foraminiferal calcite. The Cd/Ca of surface water varies predictably with its nutrient content[69,72]. The same is roughly true of the $^{13}C/^{12}C$ of surface DIC, although with the additional influence of gas exchange[73]. Measurements of these ratios in planktonic foraminifera indicate no clear decrease in the nutrient concentration of Antarctic surface water during the last ice age, while such a decrease would have been expected on the basis of the nitrogen isotope data, assuming no major changes in the nutrient concentration of the Antarctic subsurface (Fig. 5). Unfortunately, each of the palaeochemical proxies has significant uncertainties. In the case of nitrogen isotopes, concerns currently revolve around the controls on the isotope fractionation of nitrate uptake by phytoplankton[74,75]. Foraminiferal proxies for surface conditions also have potential complications[13,72,76], with the water depth of shell growth[77] being one of the greatest concerns for the Antarctic, a region with the potential for very sharp vertical gradients within the upper water column.

Dissolved silicate is a major nutrient for diatom growth because of the silica tests that these phytoplankton precipitate. Much like nitrate and phosphate, silicate is nearly completely depleted in the low-latitude surface ocean but is found at higher concentrations in the Antarctic. The silicon isotopic composition of diatom microfossils implies that there was a reduction in Antarctic silicate utilization during the last ice age[78], in contrast to the evidence for enhanced nitrate utilization. While this may indicate a disagreement among proxies, the alternative is that the difference signals a real oceanographic change. Field observations, incubations and culture studies[79,80] indicate that iron-replete conditions (such as may have

resulted from the dustiness of the ice age atmosphere[81]) favour a higher nitrate/silicate uptake ratio in diatoms. Taking both the nitrogen and silicon isotope data at face value implies that the nitrate/silicate uptake ratio of phytoplankton was higher during the last ice age, leading to lower nitrate but higher silicate concentrations in the glacial Antarctic surface relative to modern times[78]. If the change in uptake ratio was great enough, it may actually have removed the tendency for preferential depletion of silicate relative to nitrate that is observed in the modern Southern Ocean surface.

In the subantarctic, planktonic foraminiferal Cd/Ca and the $^{13}C/^{12}C$ of diatom-bound organic matter both show changes that are consistent with an ice age state of higher nutrient utilization[62,82]. However, the consideration of proxy complications may argue against such a change[72]. The significance of the nitrogen isotope data for the glacial subantarctic is uncertain. On the one hand, bulk sediment nitrogen isotope records from the subantarctic can be interpreted as suggesting lower utilization during the last ice age, perhaps due to an increase in the supply of nutrients from below[59]. On the other hand, isotopic measurements of nitrate in the modern Southern Ocean indicate that downcore nitrogen isotope changes in the subantarctic may instead represent a shift in the nitrate source to the subantarctic surface, with the Antarctic surface providing most of this nitrate during interglacial times, but the subantarctic thermocline becoming the dominant nitrate source during glacial periods[75]. This latter interpretation has some merit in its consistency with the Antarctic nitrogen isotope data. If Antarctic nitrate utilization was higher during glacial times as suggested above, then the Antarctic surface would have had less nitrate to transport into the subantarctic surface, making other sources of nitrate proportionally more important.

In spite of the many uncertainties and conflicts, we propose a hypothesis for the Southern Ocean during the last ice age which would explain lower glacial atmospheric CO_2 concentrations through reduced deep-water ventilation and enhanced nutrient utilization (Fig. 6c and d). In this hypothesis, a cooler climate caused a northward shift in the belt of eastward winds that drives upwelling and northward surface flow in the modern Antarctic. This shift caused a decrease in the upwelling of deep water into the Antarctic surface[83], replacing it with upwelling of intermediate-depth water into the subantarctic surface. The hypothetical glacial Antarctic, because of reduced wind-driven upwelling, was able to develop a stable, fresh, frequently ice-covered surface layer[84], further reducing deep-ocean ventilation in the open Antarctic. These changes in circulation resulted in a lower rate of nutrient supply to the Antarctic surface[59] and reduced CO_2 outgassing[67,68].

From interglacial to glacial times, export production in the Antarctic decreased less than did the supply of nitrate and phosphate from below, that is, nutrient utilization increased during glacial times[66]. This response may indicate that the iron limitation of modern Antarctic phytoplankton was alleviated during glacial times by the increase in dust deposition from the continents[58,81]. Dissolved silicate may have been decoupled from nitrate and phosphate changes[78], owing to more frugal use of silicate by diatoms[79,80] and the possible importance of non-diatom phytoplankton in the glacial Antarctic[64].

The hypothetical glacial subantarctic was more productive, perhaps also because of an increased supply of iron from dust[61]. Subantarctic utilization of nitrate and phosphate may have increased[62,82] due to a combination of higher export production and a reduction in the supply of these nutrients from the Antarctic surface. However, increased nutrient supply from the thermocline below the subantarctic surface may have worked against such a change[59].

Higher utilization of nitrate and phosphate across the Antarctic and perhaps also the subantarctic lowered atmospheric p_{CO_2}, with the Antarctic dominating this effect because of the large volume of the ocean that it currently ventilates[67]. The reduced supply of nitrate

and phosphate from the Antarctic to the subantarctic represented a decrease in one of the most important routes by which these nutrients are fed from the cold, deep ocean into the mid-depth and upper ocean. In addition, the high export production of the glacial subantarctic may have worked to pump nutrients and DIC out of upper and mid-depth ocean by producing rapidly sinking particles that persist into the deep ocean (Fig. 6d). As a result, the nutrient content of the mid-depth ocean decreased while its oxygen content increased[16,42–44,85–87]. This change was balanced by an increase in nutrient content and a decrease in oxygen content in the abyssal ocean[59,85], as well as a calcite dissolution event in the abyssal ocean at the onset of ice ages, which further reduced the

atmospheric p_{CO_2} (refs 66, 67, 88). Since North Atlantic Deep Water formation and Antarctic upwelling are coupled in the modern ocean[89,90], a glacial reduction in Antarctic upwelling is consistent with the evidence for less North Atlantic Deep Water formation during the last ice age[91]. The proposed upwelling of intermediate-depth waters into the glacial subantarctic surface is akin to a shoaling of modern Southern Ocean overturning, with new inter-mediate-depth waters being supplied from the North Atlantic[99] and/ or North Pacific[100] (Fig. 6c).

This Southern Ocean hypothesis is controversial (for example, see ref. 72). Clearly, one of the major obstacles in the evaluation of this and other hypotheses is the uncertainty in our proxies for surface-
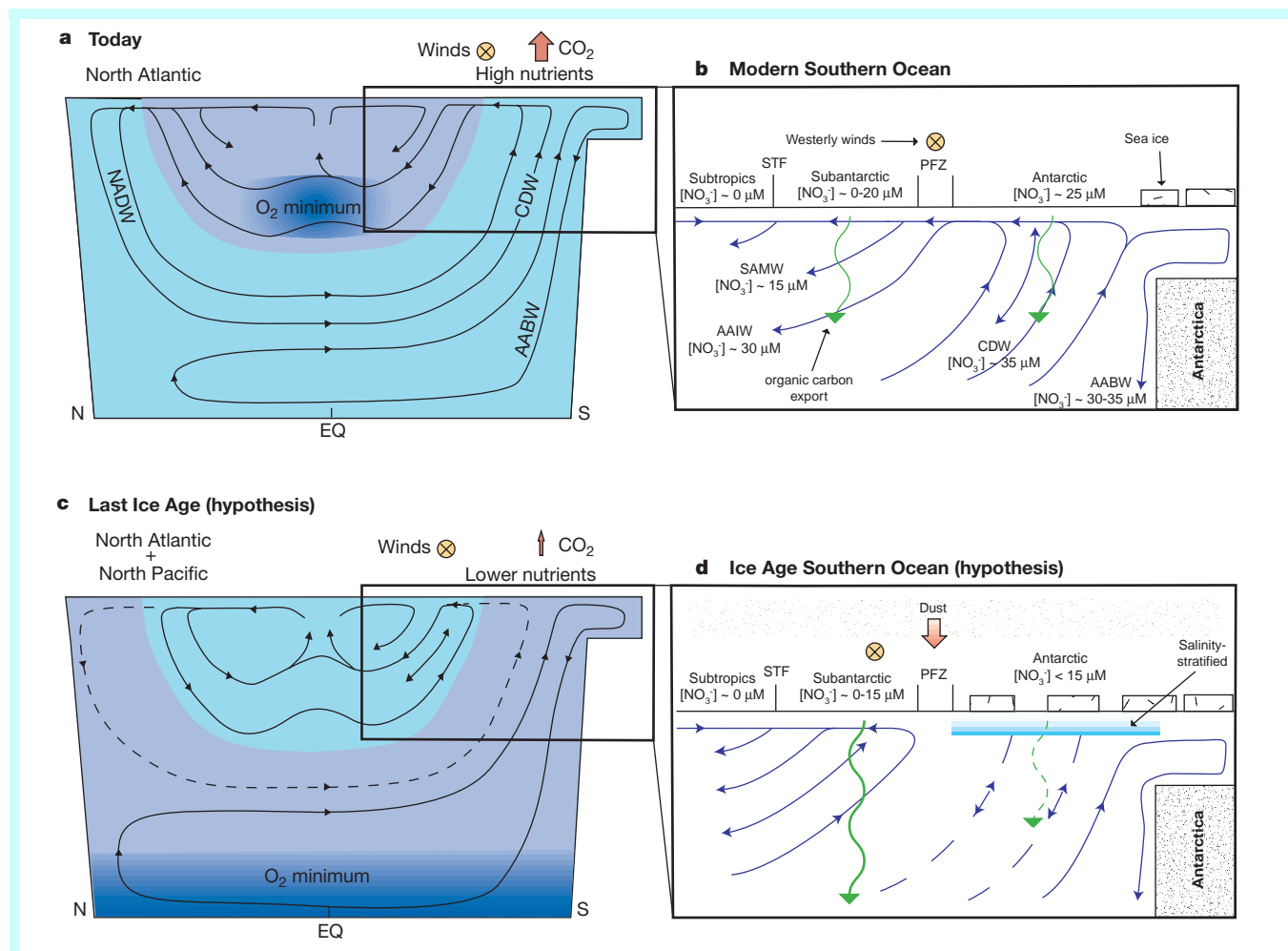

Figure 6 The modern ocean (**a**, **b**) and a Southern Ocean-based hypothesis for reduced levels of atmospheric CO_2 during glacial times (**c**, **d**). The figure shows a generalized depth section running from north to south (**a**, **c**) with an expanded view of the Southern Ocean (**b**, **d**). The north–south and vertical components of ocean circulation are shown (black flow lines in **a** and **c**, blue in **b** and **d**). The blue shading in **a** and **c** indicates changes in the intensity of circulation between modern and ice-age times, with the lighter shade representing more vigorous circulation, illustrating the hypothesis that ice-age circulation was less vigorous in the cold, dense, deep ocean but more vigorous in the warmer, less dense, upper ocean. In the modern ocean (**a**, **b**), circulation of the interior can be characterized as follows. New deep water forms in the high-latitude North Atlantic (North Atlantic Deep Water, NADW). NADW flows south and mixes with other deep waters (including Antarctic Bottom Water, AABW) to generate Circumpolar Deep Water (CDW). Eastward winds (orange circled cross) over the Polar Frontal Zone (PFZ) drive upwelling of CDW into the Antarctic surface, releasing deep-sequestered CO_2 to the atmosphere (upward red arrow in **a**). Antarctic surface water flows northward to the PFZ, where it sinks into the subsurface as Antarctic Intermediate Water (AAIW) or mixes with subantarctic surface water, some of which forms Subantarctic Mode Water (SAMW). The biological production and export of organic matter (green arrows) extracts nutrients and inorganic carbon from surface waters, causing the nitrate concentration ([NO_3^-]) of the Antarctic surface ($\sim 25\,\mu M$), the subantarctic surface (0–20 μM), and newly formed AAIW and SAMW (~ 30 and $\sim 15\,\mu M$, respectively) to be lower than that of the CDW that was originally upwelled ($\sim 35\,\mu M$). AAIW and SAMW ventilate the mid-depth ocean and supply nutrients to the lower-latitude surface. This nutrient supply fuels biological export production, the degradation of which causes a subsurface deficit in dissolved oxygen which is most intense at intermediate depths (the O_2 minimum in **a**). The hypothetical ice-age Southern Ocean described in the text includes the following changes (**c**, **d**). Upwelling into the Antarctic surface decreased, possibly due to an equatorward shift in the belt of eastward winds, and/or a freshening of the surface ('salinity-stratification') related to an increase in sea ice. In the subantarctic, the winds may have driven the upwelling of intermediate-depth waters, which formed in the North Atlantic and/or North Pacific. The supply of iron from dust was high (broad downward arrows and red stippling). Organic carbon export was higher in the subantarctic but lower in the Antarctic (green arrows). Possibly due to the greater supply of dust-borne iron, the degree of nitrate utilization was higher in both regions, leading to lower surface [NO_3^-] and less nutrient transport to the lower latitudes. This pattern of nutrient supply and export production caused the O_2 minimum to migrate into the abyssal ocean and reduced the release of CO_2 from the Southern Ocean.

ocean nutrient status and export production. However, more global properties such as the $^{13}C/^{12}C$ ratio of atmospheric CO_2 (refs 92, 93), the O_2 content of the ocean subsurface, and the relative timing of geochemical and climatic changes[40] are also important constraints on this and other hypotheses for glacial/interglacial CO_2 change. For instance, atmospheric CO_2 is among the early parameters to change going into an interglacial period, nearly coincident with the warming of high southern latitudes[94], which supports a Southern Hemisphere origin for glacial/interglacial CO_2 change.

Conclusion

The most viable hypotheses for the cause of glacial/interglacial CO_2 change involve the extraction of carbon from the surface ocean by biological production, either at low or high latitudes, necessarily allied with changes in the marine calcium carbonate budget. Much work remains to be done before a consensus can emerge on the specific driver of glacial/interglacial CO_2 changes. While our ability to reconstruct past environmental conditions requires continued effort, there also remain fundamental uncertainties about the sensitivity of atmospheric CO_2 to the oceanic changes discussed above[17]. Nevertheless, our understanding of the potential causes is much greater than when the CO_2 changes were first discovered.

Lessons learned from the investigation of glacial/interglacial CO_2 change inform our thinking on the critical issues of the modern carbon cycle. Several of the hypotheses for glacial/interglacial CO_2 change relate directly to considerations for purposeful mitigation of the anthropogenic CO_2 increase[45,58]. Other hypothetical causes for glacial/interglacial CO_2 change have been recognized as potentially important factors in possible situations of anthropogenic CO_2 increase and global warming[95]. More generally, the mystery of glacial/interglacial CO_2 change has provided a focus for study of the interaction among the diverse processes operating in the natural environment, resulting in real progress toward a science of the Earth system. □

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