Drivers of atmospheric CO$_2$ concentrations over glacial to interglacial time scales

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Resum

Les concentracions de CO$_2$ han canviat de forma regular durant els darrers 650,000 anys, entre uns valors fixos màxims durant breus períodes interglacials, i mínims durant períodes glacials molt més prolongats. Aquesta variabilitat natural té lloc en paral·lel a canvis en diferents variables climàtiques durant el mateix interval la qual cosa suggereix una connexió causal entre el clima i el CO$_2$. No obstant això, trobar una explicació a les variacions de CO$_2$ entre períodes glacials i interglacials és un problema de difícil atribució. No hi ha un únic mecanisme que s'hagi identificat que expliqui tot sol les raons darrera les fluctuacions naturals totals del CO$_2$ atmosfèric. Sembla probable que un conjunt de mecanismes hagin actuat en concert, incloent processos físics, biològics i químics, i que és probable que l'oceà hi jugui un paper important donat que és un reservori molt gran de carboni i degut a les taxes de renovació del cicle marí de carboni. El repte no és tan sols explicar l'amplitud de les variacionals glacials-interglacials de CO$_2$, però també la complexa evolució del CO$_2$ atmosfèric i el clima de manera consistent.

Paraules claus: diòxid de carboni, cicles glacial-interglacial, cicle de carboni

Abstract

Atmospheric CO$_2$ concentrations have regularly alternated over the last 650,000 years, between fixed maxima during short interglacial periods and minima over prolonged glacial intervals. This natural variability has taken place alongside major and simultaneous changes in climatic variables, which suggests a strong causal link between climate and CO$_2$. However, the reason for these glacial-interglacial CO$_2$ variations remains difficult to explain. No single mechanism has been identified that accounts for the full range of natural fluctuations of atmospheric CO$_2$. It appears likely that numerous mechanisms have acted in concert. These are likely to encompass physical, biological, and chemical processes and to involve the ocean, given its large carbon reservoir and high turnover rates. Moreover, the challenge is not only to explain the amplitude of glacial-interglacial CO$_2$ variations, but also the complex temporal evolution of atmospheric CO$_2$ and climate.

Keywords: carbon dioxide, glacial-interglacial cycles, carbon cycle

The investigation of ice cores retrieved from the Antarctic ice cap has afforded several major breakthroughs in the investigation of the natural mechanisms of climate change. Analyses of the composition of air trapped in these cores revealed that the CO$_2$ concentration in the atmosphere has varied between 180 and 300 parts per million per volume (ppmv) over the glacial-interglacial (G-IG) cycles of the last 650 thousand years before the present (kyr BP) (Figure 1) [1,2]. During the last glacial maximum (LGM, ~21 kyrs BP; [3]), the atmospheric CO$_2$ concentration was ~190 ppmv, compared to ~280 ppmv in the pre-industrial atmosphere and 385 ppmv today.

The onset of a typical glacial cycle during the late Pleistocene was characterized by a slow decline in both temperature and CO$_2$ (lasting tens of thousands of years). In contrast, the end of the glacial maximum and onset of a glacial termination was marked by a rapid rise of temperature and CO$_2$ (taking place over <10 kyr) to full interglacial conditions. Interglacial periods were far shorter than the corresponding glacial stages. This sequence of events has repeated itself during the last 740 kyr, with a cycle of ca. 100 kyr, although prior to 430 kyr BP the frequency of G-IG periods was somewhat more muted, but still clearly discernible. In fact, the dominant periodicity of the G-IG cycles for most of the Pleistocene, prior to 900 kyr BP, was 41 kyr. The reason for the change in the frequency of the G-IG remains unclear.

The excellent temporal correlation between records of atmospheric CO$_2$, temperature, and continental ice volume (Figure 2) can be taken as evidence that atmospheric CO$_2$ has played a prominent role in past global climate changes [4]. The nature of the climate-CO$_2$ relationship, as depicted by these

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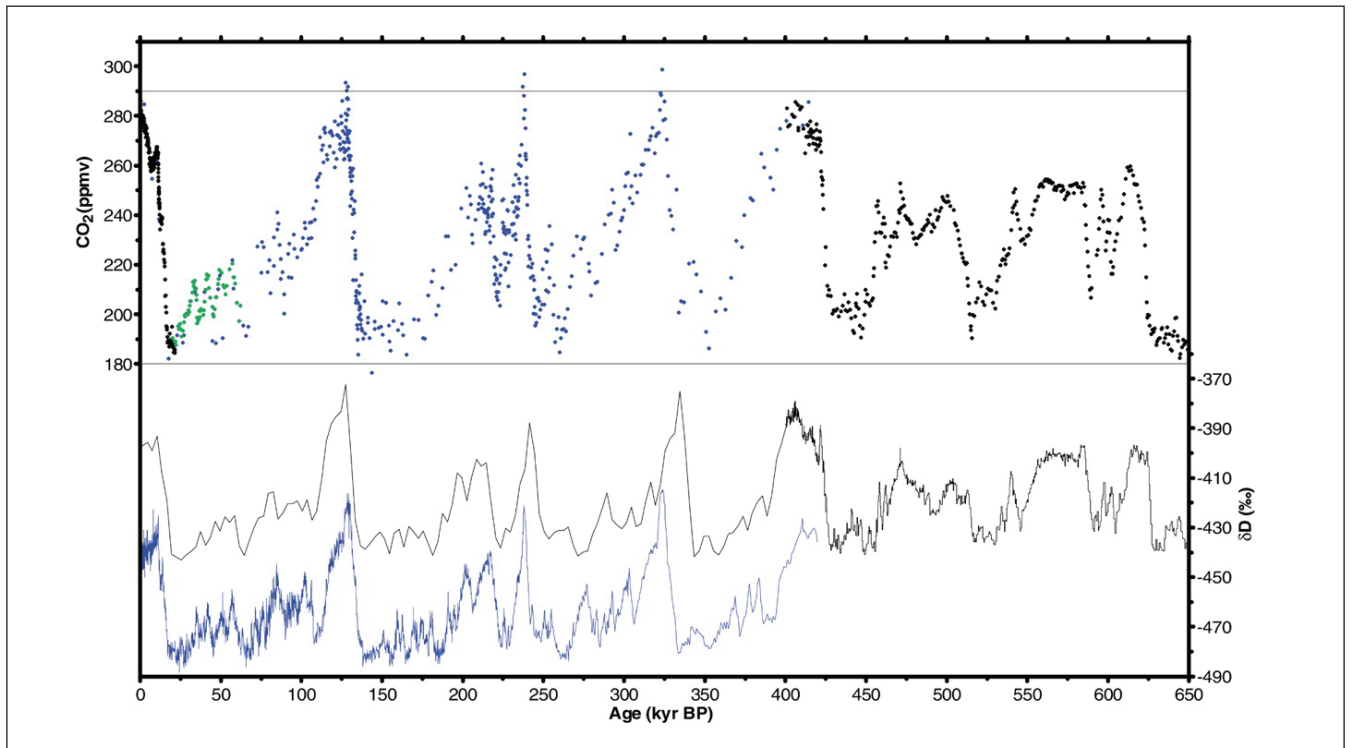
Figure 1. A composite record of atmospheric CO_2 over six and a half ice-age cycles, back to 650 thousand years before present (kyr BP). The record results from the combination of CO_2 data from three Antarctic ice cores: Dome C (black), 0–22 kyr BP and 390–650 kyr BP; Vostok (blue), 0–420 kyr BP; and Taylor Dome (light green), 20–62 kyr BP. The black line indicates δD (proxy for air temperature in Antarctica) from Dome C, 0–650 kyr BP. The blue line indicates δD from Vostok, 0–420 kyr BP. (Source and data references in [1]).
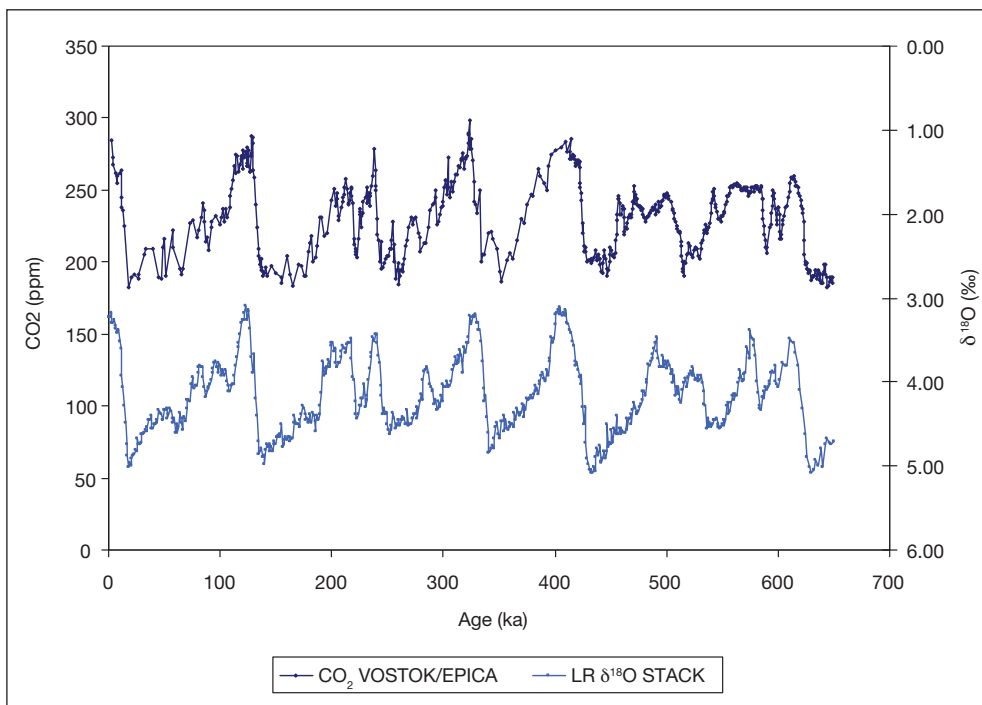

Figure 2. Record of atmospheric CO_2 [1] as shown in Fig. 1 (in dark blue) and record of global continental ice volume [46] (light blue) over the last 650,000 years.

data, offers insight into the future response of the Earth to anthropogenic forcing. However, the mechanisms responsible for G-IG CO_2 cycles have not been elucidated. For example, it is unclear whether CO_2 is a primary driver or a secondary amplifier of glacial cycles. The Milankovitch orbital theory for glacial cycles would seem to imply the latter, because there is a clear physical link between Northern Hemisphere summer heating and ice sheets [5]; however, there is no simple link between orbital variations and atmospheric CO_2. Furthermore, CO_2 variability clearly leads changes in continental ice volume over several thousand years, implying that CO_2 is driving this change [4]. Thus, elucidation of the mechanisms involved in G-IG CO_2 cycles is vital to our understanding of the key feedbacks operating in the present-day Earth system.

Role of the oceanic carbon reservoir

Over the last several decades, a range of processes that regulate atmospheric CO$_2$ have been proposed. These may operate in the atmosphere, oceans, marine sediments, and/or on land, and include the dynamics of sea ice and ice sheets. However, reconstructions from proxy data that could be used to test the various hypotheses are relatively scarce, uncertain, and their interpretation is controversial [6]. Nevertheless, of the planet's various carbon reservoirs or pools, that of the ocean is bound to play a major role.

Most of the carbon on Earth is incorporated into calcium carbonate (CaCO$_3$) rocks. This carbon pool, however, turns over too slowly to account for changes in CO$_2$ over the glacial cycles [7]. On a time scale of decades and even less, the terrestrial biosphere exerts significant control over atmospheric composition, with a pronounced seasonal signal [8]. However, the reservoir of carbon in the oceans is 14 times greater than that of the atmosphere and terrestrial biosphere combined [6]. Terrestrial changes cannot explain the low glacial values because terrestrial storage was lower during glacial periods than during interglacial periods (equivalent to a CO$_2$ concentration of 10–45 ppmv) and the terrestrial biosphere released carbon during the former, which is contradictory to an explanation of the lower glacial CO$_2$ values [9,10,11]. Thus, the mechanisms responsible for longer-term variability in the concentration of atmospheric CO$_2$ are more likely to involve the ocean [6,12].

The Southern Ocean has long been regarded as a pivotal region for G-IG change in the global carbon cycle. It has achieved its climatic status biochemically, as a result of the pool of excess nutrients found there, and through its physical oceanographic characteristics, as a pathway of relatively low resistance linking the carbon reservoirs of the atmosphere and deep ocean [13]. While the Southern Ocean represents less than 10% of the open ocean its waters account for more than 20% of the modern global ocean carbon sink [14,15].

Drivers

The existence of a single mechanism or process that would explain CO$_2$ G-IG cycles may seem desirable and conceptually attractive. Nonetheless, in recent years it has become increasingly apparent that, for the millennial time scales of the G-IG, atmospheric CO$_2$ is bound to be governed by a combination of processes. These encompass the interplay between ocean circulation, marine biological activity, ocean-sediment interactions, seawater carbonate chemistry, and air-sea exchange. They are often grouped under the terms "solubility pump", "soft-tissue or organic carbon pump," and "carbonate pump", which refer to the ocean's ability to sequester excess CO$_2$ due to temperature-induced solubility, change in net amount or utilization of organic matter, and change in the CaCO$_3$/Corg rain ratio and/or dissolution rate of CaCO$_3$, respectively. In addition, another possible way to regulate the partial pressure of atmospheric CO$_2$ (pCO$_2$) is through changes in physical properties,

such as sea-ice cover, mixing, or the ocean's velocity field. Since any of these mechanisms alone fall short of simultaneously meeting the constraints dictated by the various marine, terrestrial, and ice-core paleoclimatic records [11], the challenge lies in determining the important mechanisms involved and constraining their relative overall contribution to the dynamics of the system.

Physical processes

The transfer of CO$_2$ into the ocean occurs where the pCO$_2$ of surface waters is lower than that of the atmosphere, and transfer out of the ocean where it is higher. pCO$_2$, in turn, is controlled by the temperature and chemical composition of the ocean, including salinity. The latter are separable with respect to their responses to G-IG changes.

Changes in ocean temperature (and salinity)

As CO$_2$ is more soluble in cold than in warm water, the sequestration of atmospheric CO$_2$ in the ocean interior is mainly controlled by the formation of cold, dense water masses at high latitudes, especially in the North Atlantic and in the Southern Ocean confluence [6]. Accordingly, changes in surface and deep-ocean temperature have the potential to alter atmospheric CO$_2$. Ocean temperatures were lower during glacial times, which increased the solubility of CO$_2$ and the potential of the surface ocean to capture CO$_2$. However, the increased salinity of the glacial ocean (3% saltier) had an opposite effect to that of G-IG temperature change on atmospheric CO$_2$, due to the development of large ice sheets in the Northern Hemisphere that land-locked huge amounts of freshwater. Estimations of the net effect of G-IG temperature and salinity on reducing atmospheric CO$_2$ are around 23.5 ppmv [11], which is less than one-third of the observed G-IG change.

Deep-ocean ventilation

The concentration of total dissolved inorganic carbon in the ocean increases markedly below the upper 300 m, and it remains significantly above the surface ocean-atmosphere equilibrium value in all ocean basins. The higher concentration of inorganic carbon in the ocean interior results from the combination of two fundamental processes: the "solubility pump" and "biological pumps" (carbonate and organic carbon). The efficiency of the solubility pump depends on the thermohaline circulation as well as on latitudinal and seasonal changes in ocean ventilation. As these water masses sink into the ocean interior and are transported among the ocean basins, CO$_2$ is effectively prevented from re-equilibrating with the atmosphere by a cap of lighter overlying water. Re-equilibration occurs only when water from the ocean interior is brought back to the surface, decades to several hundreds of years later [6]. Most of this re-equilibration process occurs in the Antarctic region, where the deep ocean (below 2500 m) comes into contact with the atmosphere [16]. Recent estimations of the atmosphere-ocean CO$_2$ flux are in good agreement
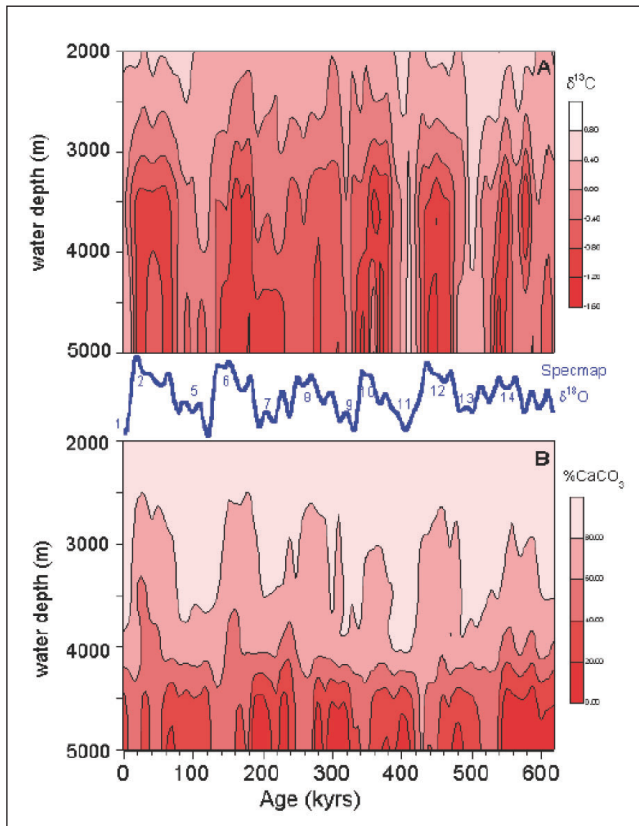
Figure 3A, B. Composite records of proxies that indicate changes in deep-water circulation of the North Atlantic over the last 600,000 years BP., as discussed in the text. (**A**) Contoured benthic $\delta^{13}C$ as a function of water depth and time in the South Atlantic. (**B**) Contoured weight-percent carbonate as a function of water depth and time in the South Atlantic. The reference curve for global continental ice volume, i.e., the Specmap $\delta^{18}O$ record [47] (blue line), is shown for reference. (Adapted from [17]).

with this suggestion, as they show that out-gassing of natural CO_2 from deep water takes place mainly in the Southern Ocean [14]. According to this view, processes that could interfere with ventilation of the deep ocean have the potential to affect atmospheric CO_2 concentrations.

The geologic record shows some evidences of changes in the ventilation of the deep ocean in G-IG timescales by means of the $\delta^{13}C$ distribution, which reflects the proportion of the isotopes $^{12}C/^{13}C$. This ratio is dependent on fractionation during organismal respiration; therefore, a depleted $\delta^{13}C$ signal in the record indicates that the ocean retains more respired CO_2. Reconstruction of the $\delta^{13}C$ distribution through time shows that, during glacial periods, the deep ocean (below 2500 m) was particularly depleted in $\delta^{13}C$, and hence enriched in respired CO_2 compared to interglacial periods (Figure 3) [17] The most likely explanation for this change involves a change in the ventilation that isolated the water below 2500 m and blocked the evasion of respired CO_2 back to the atmosphere [18].

The potential of this mechanism for causing the G-IG changes in atmospheric CO_2 concentrations recorded in the ice cores (Figure 1) has been confirmed by several models. However, these propose different processes capable of reducing deep-ocean ventilation during glacial times, including reduced Ekman-induced upwelling south of the polar front (PF)

[16,18], reduced deepwater mixing due to the reduced buoyancy flux [19], suppression of air-sea gas exchange by the increased sea-ice cover [20], and enhanced surface-water stratification [11,21,22]. The relative importance of these processes is still unclear and model-dependent; however, the fact that the different hypothesis are closely related and are not mutually exclusive suggests that a complete explanation probably involves a combination of them [19].

Reduced upwelling

According to this hypothesis, the process that exposes the deepwater to the atmosphere is the upwelling around Antarctica, which is driven mainly by the effect of the westerly winds over the Antarctic circumpolar current (ACC). In this view, the position of the westerlies with respect to the ACC is thought to be the critical factor that maintains upwelling [16,18]. If the westerlies are aligned with the ACC, as is the case today, upwelling of deepwater south of the PF and CO_2 out-gassing are maintained. However, during glacial periods, northward migration of the westerly winds results in a reduction in upwelling intensity and hence a decrease in deepwater ventilation that keeps the atmospheric CO_2 concentration low [18]. Although there is some proxy evidence of a shift of the westerly winds towards the equator, the data are limited and the issue is still a matter of debate in the paleoclimate community. An alternative version of this hypothesis that does not require a change in the westerlies considers that, during glacial times, upwelling is suppressed due to the reduced buoyancy flux as a consequence of the formation of denser deepwater in the Antarctic region [19].

Suppression of air-sea gas exchange by sea ice

Stephens and Keeling [20] proposed that the covering of most of the Southern Ocean with sea ice, which would dramatically reduce air-sea gas exchange, could go a long way towards accounting for the low glacial atmospheric pCO_2 signal by isolating the deep ocean from the atmosphere, hence increasing the deep-ocean storage of CO_2. This model reproduces the G-IG atmospheric CO_2 variations in the range of 67–82 ppmv. Furthermore, it explains the close relationship between atmospheric temperatures and CO_2 observed in the ice-core reconstructions (Fig. 1). In this view, colder temperatures favor Antarctic sea-ice expansion, reducing both ocean-atmosphere CO_2 out-gassing and atmospheric CO_2 concentrations. However, the fact that sea-ice was not extensive in summer, even in glacial times, could affect the validity of this model [19].

Increased stratification

Greater stratification of the surface waters around Antarctica has also been invoked to explain the reduced upwelling of carbon and nutrient-rich waters in the Southern Ocean during glacial times [21]. Stratification may have caused a depletion of nutrients and carbon at the surface, but proxy evidence for surface nutrient utilization is still controversial [11]. This mechanism has also been criticized recently, as observations of ocean dynamics show that diapycnal mixing rates near the surface are low in the modern Southern Ocean; hence, it is
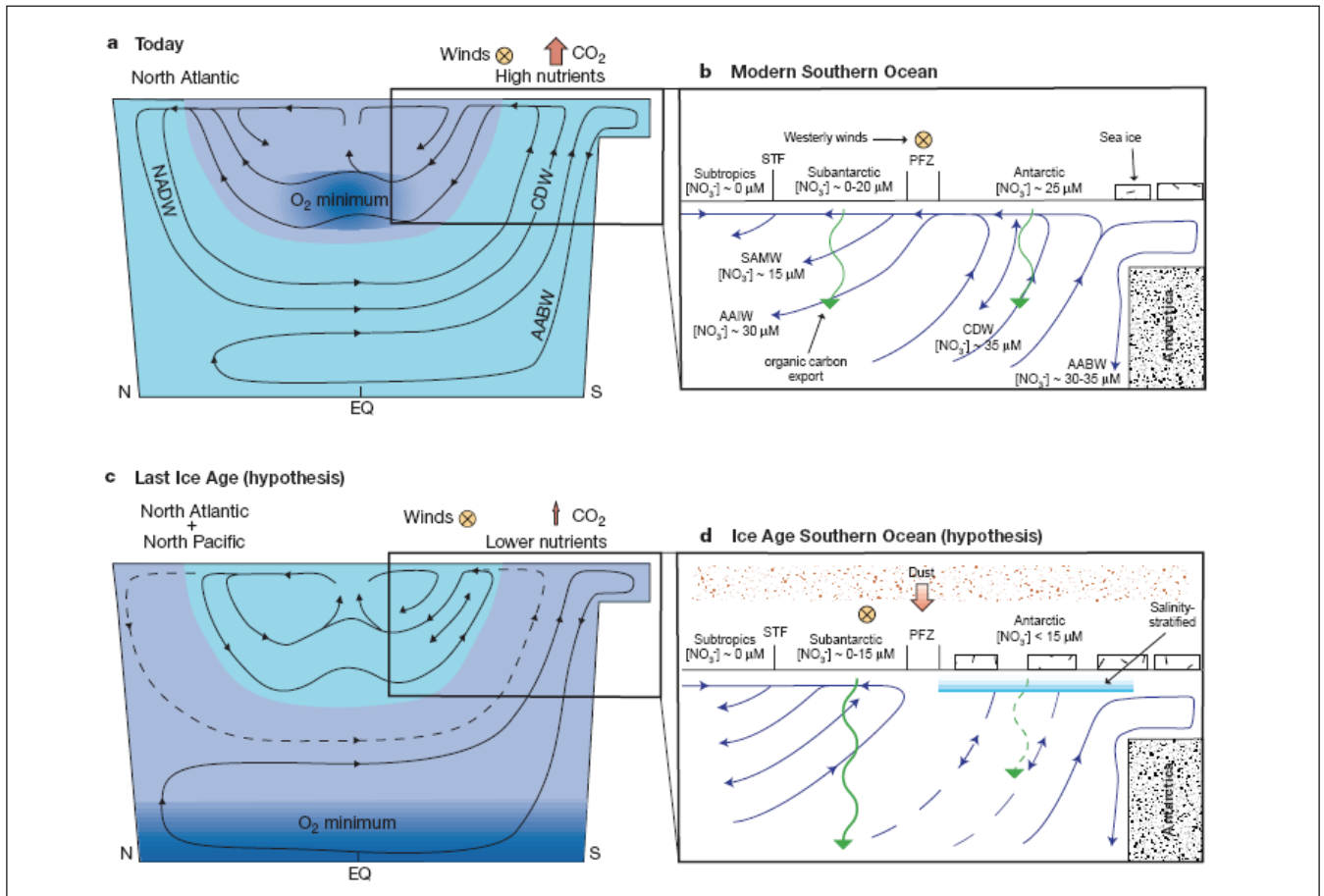
Figure 4. Graphical representation of the hypothesis for reduced levels of atmospheric CO$_2$ between the modern ocean (**a, b**) and a Southern Ocean during glacial times (**c, d**) as proposed by Sigman and Boyle [11]. The figure shows a generalized depth section running from north to south (**a, c**) 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. Acronyms: North Atlantic deep water, NADW; Antarctic bottom water, AABW; circumpolar deep water, CDW; polar frontal zone, PFZ; Antarctic intermediate water, AAIW; sub-Antarctic mode water, SAMW. (Adapted from [11]).

not clear how increased near-surface stratification could affect the transport between the surface and the underlying waters [19].

Sigman and Boyle [11] proposed a conceptual model to explain G-IG atmospheric CO$_2$ variations that considered the combined effect of some of the mechanisms described above (Figure 4). In their model, the configuration of the interglacial Southern Ocean was similar to that of the present-day. Upwelling of cold CO$_2$-rich deepwater driven by the eastward westerly winds occurred south of the PF. This well-ventilated ocean was characterized by the release of deeply sequestered CO$_2$ to the atmosphere in the Antarctic region, and by relatively low organic carbon export both in the Antarctic and sub-Antarctic regions. This scenario maintains the high atmospheric CO$_2$ levels characteristic of the interglacial periods. In contrast, during glacial periods the cooler climate promoted a northward shift of the eastward winds, causing a decrease in the upwelling of deepwater south of the Antarctic region. The reduced upwelling and the cooler climate at the same time favored stratification of the surface waters and the development of a stable ice cover, which in turn reduced further deep-ocean ventilation and CO$_2$ out-gassing [11,18]. In contrast, in the sub-Antarctic, these changes, together with the observed increase

in iron (Fe) supply, produced an increase in export productivity (discussed in the next section), which contributed further to the reduction of atmospheric CO$_2$ concentrations. Despite the positive results of this model and the relatively good agreement of the hypothesis with proxy data, a general-circulation model (GCM)-based study of the impact of increased sea ice and enhanced surface-water stratification on atmospheric pCO$_2$ levels suggested that the effects of sea-ice cover and surface-water stratification are minimal [23], challenging the results of the box model [11,16,20,21] Although the reason for the discrepancy between the models is far from clear, it may be related to the fact that the Southern Ocean is considered to be less important in the regulation of atmospheric CO$_2$ in the GCM than in the box model [23]. This issue should be revised considering recent estimates of atmospheric CO$_2$ sources and sinks in the modern ocean [14]..

Biological activity

Broecker [24,25] first proposed a glacial increase in biological activity as the mechanism lowering pCO$_2$ over millennial time scales. Phytoplankton photosynthesis incorporates inorganic

carbon into the synthesis of new organic matter in the photic zone, lowering the partial pressure of CO_2 in the upper ocean and thus promoting the absorption of CO_2 from the atmosphere. The sinking of marine plankton and its detritus represents an effective pathway of exporting carbon (i.e., export production) from the surface ocean to the deep sea, creating a net flux of carbon to the ocean interior ("biological pump"). An increment in the efficiency of the biological pump in the ocean contributes to a major sequestration of carbon from the atmosphere to the deep sea. Approximately 25% of the carbon fixed in the upper ocean sinks into the interior [26,27]. It is then oxidized through heterotrophic respiration such that just a small percentage is finally buried in the sediment. Since the turnover time of lithospheric carbon is too slow to account for changes in millennial time scales, organic-carbon transfer into the deep sea plays a key role in sequestering carbon within G-IG cycles [22].

Biological production requires optimal physical and chemical factors in the oceans that are not distributed homogenously in space and time. Phytoplankton creates new biomass by consuming CO_2, macronutrients (mainly nitrogen and phosphorous) and micronutrients (in the form of trace metals, such as Fe). When nutrients are not limited, the molar element ratio of the new organic matter created by phytoplankton tends to follow the Redfield ratio of 106C:16N:1P. The existence of a constant ratio restricts phytoplankton activity when there is a scarcity of one basic element. Thus, in most oceanic regions, the availability of major nutrients is the dominant controlling aspect of productivity.

The hypothesis arguing changes in the efficiency of the biological pump as a driver of the G-IG CO_2 cycles requires changing one or more of: (i) the availability of nutrients in surface waters, (ii) the consumption of unused nutrients in "high-nutrient, low-chlorophyll" (HNLC) regions, (iii) the Redfield ratio in the organic material exported, or (iv) the export ratio of $CaCO_3$ and organic material to the deep ocean (see "A change in the export ratio of $CaCO_3$ to organic matter to the deep ocean").

Fertilization of phytoplankton growth by increased deposition of iron-containing dust from the atmosphere

The ocean Fe cycle is replenished by atmospheric deposition of dust, at a rate that varies widely over the world's oceans. Mesoscale Fe-addition experiments have shown that the Fe supply limits production in one-third of the world's oceans [28]. It is known that the supply of Fe via the aeolian transport of Fe-rich dust from the continents to the oceans increased during glacial periods [29] and was at least an order of magnitude higher than during interglacial periods [30]. This Fe supply to the ocean has been suggested to play a key role in stimulating biological production during glacial periods, in particular in HNLC regions such as the North Pacific, equatorial Pacific, and Southern Ocean, where there is incomplete consumption of macronutrients by phytoplanktonic organisms due to a scarcity of Fe. The sub-Antarctic zone (SAZ) of the Southern Ocean is one of the best candidate regions for Fe fertilization because it

falls in the same latitude band as the major dust sources of the southern hemisphere. The higher productivity reported in at least some sectors of the SAZ and evidence from other studies that focused on the LGM [30,31,32] have been interpreted as supporting the glacial "Fe hypothesis"[33]. This hypothesis proposes that Fe fertilization in HNLC regions is the process regulating the strength of the biological pump via an increment in marine export production and the LGM reduction of pCO_2. The enhanced Fe supply to the oceans would not only have further stimulated biological production in the HNLC regions, but would also have stimulated the rate of nitrogen fixation [12,34], increasing the oceanic nitrate pool. Small variations in the ratio of nitrogen fixation to denitrification can significantly change the efficiency of the biological pump [27], especially in the most oligotrophic areas in the oceans, the "low-nutrient, low-chlorophyll" regions (i.e., the subtropical gyres). However, model simulations suggest a limited role for Fe in regulating past atmospheric CO_2 concentration because this family of mechanisms cannot account for the full amplitude of the reconstructed CO_2 variations when constrained by the available information [31]. The atmospheric pCO_2 had already dropped from the interglacial value of around 280 ppmv to around 220 ppmv by the start of the last glacial period (roughly 75,000 years ago), before the large increases in Fe-containing dust flux and nutrient uptake changes occurred. This argues against the Fe fertilization hypothesis as the trigger of reduced atmospheric pCO_2; therefore, this mechanism can only be invoked to explain the lattermost part of the glacial decline in atmospheric pCO_2.

Increase in the whole ocean nutrient content or the C/N/P ratio
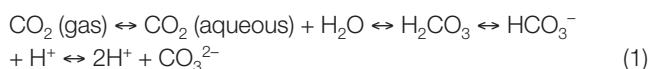
A postulated increased in ocean nutrient reservoirs alleviates nutrient limitation and allows a global increase in marine biomass and carbon export to the deep ocean. However, a distinction needs to be made between oceanic regions where productivity is limited by the supply of the major nutrients N and P, such as the tropical and subtropical oceans, and other regions, such as the polar and subpolar oceans, where the availability of nutrients is high enough so as not to limit phytoplankton growth. Whereas phytoplankton in polar regions cannot complete the consumption of major nutrients due to a scarcity of light and trace metals, in low-latitude oceans phytoplankton productivity depends mainly on the supply of the major nutrients from the subsurface and the C/N/P uptake ratios of phytoplankton. Broecker and McElroy [24,35] described possible mechanisms by which the reservoirs of phosphate and nitrate might increase during glacial times; however, to produce the observed entire drawdown of CO_2 in glacials would require a large increment in nutrient reservoirs.

Alternatively, if the Reldfield ratios of exported material to the ocean interiors differed in the past, the amount of inorganic carbon sequestered in the deep sea would have been greater during glacials with the same amount of available nutrients. This would mean more efficient utilization of major nutrients to capture inorganic carbon into the organic matter. Unfortunate-

ly, it is unknown how variable the Redfield ratios might have been through time; thus, although changes in the chemical composition of the material exported to the deep sea can alter the capacity of the biological pump and, in turn, pCO_2, we are not able yet to reconstruct glacial conditions.

Carbonate chemistry (acid/base equilibrium) and inorganic-ion redistribution

Inorganic carbon in the ocean exists as several species that maintain the equilibrium expressed in the following equation:

$$CO_2 \text{ (gas)} \leftrightarrow CO_2 \text{ (aqueous)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^-$$
$$+ H^+ \leftrightarrow 2H^+ + CO_3^{2-} \tag{1}$$

As CO_2 dissolves in seawater, it forms carbonic acid (H_2CO_3), which rapidly decomposes into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, lowering the pH of the ocean (production of H^+). Dissolved inorganic carbon (DIC) is defined as the sum of these different inorganic carbon species, excluding gas-phase CO_2 and considering the concentration of H_2CO_3 to be negligible. Another important concept is alkalinity (ALK), which refers to the total negative charges supplied by the species involved in an acid/base equilibrium. Alkalinity is defined as:

$$ALK = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \tag{2}$$

where the contribution of boron species to total alkalinity is usually negligible. The addition (or removal) of CO_2 to a solution does not change the alkalinity because the production of negatively charged species (HCO_3^- and/or CO_3^{2-}) is compensated by the production of positively contributing species (H^+), as expressed in Eq. (1).

Due to its acid/base equilibrium, the carbonate system has a buffering effect. Thus, if atmospheric CO_2 increases, more CO_2 dissolves in seawater and lowers the pH of the ocean until the buffering capacity restores the equilibrium by the dissolution of carbonates (which increases the concentration of negatively charged species and eventually leads to the consumption of H^+). The reactions involved in the carbonate buffer system maintain total inorganic carbon and alkalinity as conserved quantities [36]. However, not only chemistry determines the inorganic carbon composition of the ocean, as living organisms also play a role. In addition to the production of soft organic tissue, several phytoplankton and zooplankton species, such as coccolithophorids and foraminifers, form calcite ($CaCO_3$) shells. The process of calcification can be summarized as:

$$2HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + CO_2 + H_2O \tag{3}$$

The synthesized $CaCO_3$ shells eventually rain out of the surface ocean along with sinking organic matter. At depth, roughly 75% of the $CaCO_3$ rain dissolves and again becomes available for organisms, while the remaining 25% is buried in deep-sea sediment and is thus removed from the ocean reser-

voir [11]. This inorganic carbon cycle leads to a reduction in surface ocean DIC relative to the deep ocean and is therefore sometimes called the "carbonate pump." Another interesting outcome of this calcification and sinking process is the decrease of surface ocean alkalinity and an increase in pCO_2, as can be deduced from Eq. (3). The mean residence time of Ca^{2+} in the oceans is 8.5×10^5 years. Consequently, the rate of $CaCO_3$ production by marine organisms is not limited by the amount of available Ca^{2+}. In fact, over time scales of millions of years, as the Ca^{2+} supply from weathering keeps pace with the precipitation of carbonates, this 25% of carbonate burial becomes a significant sink for CO_2. Nevertheless, carbonates are the largest reservoir of carbon on Earth.

With this understanding of the carbonate system, we can examine several mechanisms that could account for the observed changes in atmospheric CO_2 at G-IG time scales. As we deduced from Eq. (3), ocean alkalinity and pCO_2 are closely related; thus, a mechanism to lower glacial atmospheric pCO_2 is to change the alkalinity of the entire ocean. In the following, mechanisms that could provide the ultimate reason for the glacial reduction of atmospheric CO_2 are explained.

An increase of CaCO₃ weathering on land and/or a decrease of coral-reef growth in the shallow ocean

Alkalinity is added to the ocean largely by the weathering of emergent carbonates on land and their subsequent transport into the interior of the ocean by runoff. By contrast, alkalinity is removed largely by the biogenic precipitation and burial of $CaCO_3$, not only in deep-sea sediments (i.e., sinking of calcareous shells) but also in shallow coral reefs and carbonate banks. The balance between the input of alkalinity from the continents and its removal in sediments is maintained by the distribution of $CaCO_3$ burial in the deep sea. $CaCO_3$ dissolution occurs when the actual $[CO_3^{2-}]$ of the water is lower than the $[CO_3^{2-}]$ at $CaCO_3$ saturation, as easily explained by the solubility equilibrium. As calcite solubility increases at depth (a pressure effect), the carbonate concentration at the saturation point also increases with depth, thus becoming higher than the carbonate concentration of the water at a certain level. This determines the "calcite lysocline" depth, the transition separating shallower sea-floor sediments where some calcite is preserved from deeper sea-floor sediments where almost all of the calcite rain dissolves. In the present ocean, the lysocline occurs at an average depth of 3.5 km [37] .

The hypothesis holds that 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) would increase the whole-ocean inventories of alkalinity and DIC in a 2:1 ratio, given that one mole of carbonate bears two equivalent moles of negative charges. This increase in oceanic alkalinity would cause a decrease in atmospheric CO_2 and an increase in deep-ocean $[CO_3^{2-}]$, as a result of the dissolution of carbonate rocks (see the reverse reaction of Eq. 3). The rise in water $[CO_3^{2-}]$, in turn, would deepen the lysocline because $[CO_3^{2-}]$ would become lower than calcite saturation $[CO_3^{2-}]$ at a greater depth. It is easy to imagine that lowering

of the lysocline would increase the area of sea floor where $CaCO_3$ is buried to compensate the extra input of alkalinity from land or the decreased coral-reef growth in shallow seas [11]. The lysocline would gradually return to its original depth once the alkalinity was restored to initial values, and the atmospheric CO_2 would stabilize at a lower value. The calculated time response of the lysocline is on the order of several thousands of years.

In a quantitative approach, an increase in carbonate weathering on land would deepen the lysocline by 1 km for every ~25 ppmv decrease in atmospheric pCO_2 that it would cause. If this mechanism was to explain the G-IG change in CO_2, the glacial lysocline must have been more than 2 km deeper. However, data on the evolution of buried $CaCO_3$ on the sea floor suggest that the average lysocline of the last ice age was less than 1 km deeper than that of the Holocene [38]. Thus, increased weathering or decreased coral-reef growth alone cannot explain the amplitude of the atmospheric CO_2 decrease during the ice ages.

A change in the export ratio of $CaCO_3$ to organic matter to the deep ocean

The rain ratio of calcite to organic matter ($CaCO_3/C_{org}$) connects the two main export processes of the biological pump. Changes in this ratio on G-IG time scales have been proposed to explain observed variations in atmospheric pCO_2 [39]. Most deep-sea calcite burial takes place in the low-latitude ocean (the combined equatorial, tropical, and subtropical regions), where the $CaCO_3/C_{org}$ ratio of biogenic rain is roughly 1:4 [11]. Thus, if there was a decrease in the $CaCO_3/C_{org}$ rain ratio of the glacial low-latitude ocean, this would have driven a decrease in atmospheric CO_2. The reason is twofold. First, reduced $CaCO_3$ export to the deep ocean leaves a larger fraction of the ocean's alkalinity reservoir in the surface ocean, where pCO_2 decreases (see Eq. 3), and thus atmospheric CO_2 solubility is enhanced. In other words, with higher amounts of carbonates in the surface ocean, the buffering effect will enhance the solubilization of CO_2 to produce the carbonic acid needed to restore the equilibrium. Second, the reduced $CaCO_3$ export also leads to decreasing deep-sea $CaCO_3$ burial, which causes the whole-ocean alkalinity reservoir to increase. As discussed in the previous section, this would cause the lysocline to shoal in order to increase calcite dissolution and restore the balance.

Some models predict that a halving of the $CaCO_3/C_{org}$ rain ratio will cause atmospheric CO_2 to decrease by about 55 ppmv, which is a significant quantity relative to the observed G-IG variability of atmospheric CO_2 [40]. Of this amount, 35 ppmv are due to the increase in whole-ocean alkalinity. However, this expected CO_2 decrease is associated with an ocean-average 1.1 km deepening of the lysocline, which is again larger than the record of deep-sea calcite preservation suggests [38]. Therefore, we should focus on a mechanism capable of explaining the lower glacial atmospheric CO_2 but one that does not imply a large deepening of the steady-state lysocline. The glacial decrease in the $CaCO_3/C_{org}$ ratio of the biogenic flux is hardly the only cause of this drop in glacial atmospheric CO_2.

Silica leakage hypothesis: redistribution of limiting nutrients

Brzezinski et al. [41] suggested an alternative mechanism, involving the silicate cycle, by which the export $CaCO_3/C_{org}$ ratio might be altered. In the present Southern Ocean, diatoms consume large amounts of silicic acid relative to nitrate. However, incubation experiments suggest that this preferential uptake is reversed if diatoms are released of their Fe stress [42]. In fact, dust records in the Antarctic ice cores indicate that aeolian Fe delivery in this region was higher during glacials [2]. If the glacial diatom population in the Southern Ocean consumed less silicic acid, the excess of this nutrient could have leaked to lower latitudes, transported by ocean currents. This convection of water from high to low latitudes is seen today as sub-Antarctic mode water. When the high-silicic-acid-containing waters reached silicon-limited regions at low latitudes, diatom production would be enhanced, probably at the expense of coccolithophorids (calcite-producing plankton). In that case, there might be a lowering of the $CaCO_3/C_{org}$, which could subsequently draw down atmospheric pCO_2, as described in the previous section.

Support for this hypothesis is given by the higher opal accumulation rates south of the PF during the LGM [21], δ^{30}Si measurements indicating a depletion of surface silicic acid during the LGM [43], and δ^{15}N measurements suggesting higher nitrate utilization during the LGM [21]. Models predicting that the net effect of this process would reduce atmospheric CO_2 by 30–40 ppmv have been described [44]. However, as in the case of the Fe fertilization hypothesis (see above), the fact that the decrease in atmospheric CO_2 concentration occurred before the large increase in the Fe flux observed in the ice cores [45] suggests that this mechanism can only account for the lattermost part of the glacial decline in atmospheric pCO_2.

Acknowledgements

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The Institute of Environmental Science and Technology (ICTA) was created in 2003 as a natural expansion of the previous Centre for Environmental Studies (1996-2002) at the Universitat Autònoma de Barcelona *(UAB). Its aims are to promote interdisciplinary research and training in the area of environmental sciences and technology. ICTA has established priority areas of research. These include: Climatic Change and Global Change, Water Management, Industrial Ecology, Environmental Risks, Sustainability, and Conservation Biology. The authors are members of the GEPOC group (Ocean and climate Processes Study group), one of the two research groups at ICTA formally recognized by the Catalan government and the UAB. A key focus of the research undertaken within GEPOC is to study the connections between ocean circulation, the marine carbon cycle and climate.*

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