Paleoceanography and Paleoclimatology

COMMENTARY

10.1029/2023PA004775

Key Points:

- Proxies indicate less dissolved O_2 in the ocean interior during ice ages than during interglacials
- This suggests an increase in CO_2 storage by the ocean's biological pump adequate to explain the lower atmospheric CO_2 of the ice ages
- Reconstructed nutrient use implicates the Southern Ocean but does not yet resolve the roles of circulation, biology, and gas exchange

Correspondence to:

D. M. Sigman,
sigman@princeton.edu

Citation:

Sigman, D. M., & Hain, M. P. (2024). Ocean oxygen, preformed nutrients, and the cause of the lower carbon dioxide concentration in the atmosphere of the last glacial maximum. *Paleoceanography and Paleoclimatology*, *39*, e2023PA004775. https://doi.org/10.1029/2023PA004775

Received 2 OCT 2023
Accepted 9 JAN 2024

Author Contributions:

Conceptualization: Daniel M. Sigman
Writing – original draft: Daniel M. Sigman, Mathis P. Hain
Writing – review & editing: Daniel M. Sigman, Mathis P. Hain

Ocean Oxygen, Preformed Nutrients, and the Cause of the Lower Carbon Dioxide Concentration in the Atmosphere of the Last Glacial Maximum

Daniel M. Sigman[1] **and Mathis P. Hain**[2]

[1]Department of Geosciences, Princeton University, Princeton, NJ, USA, [2]Department of Earth and Planetary Sciences, University of California, Santa Cruz, CA, USA

Abstract All else equal, if the ocean's "biological [carbon] pump" strengthens, the dissolved oxygen (O_2) content of the ocean interior declines. Confidence is now high that the ocean interior as a whole contained less oxygen during the ice ages. This is strong evidence that the ocean's biological pump stored more carbon in the ocean interior during the ice ages, providing the core of an explanation for the lower atmospheric carbon dioxide (CO_2) concentrations of the ice ages. Vollmer et al. (2022, https://doi.org/10.1029/2021PA004339) combine proxies for the oxygen and nutrient content of bottom waters to show that the ocean nutrient reservoir was more completely harnessed by the biological pump during the Last Glacial Maximum, with an increase in the proportion of dissolved nutrients in the ocean interior that were "regenerated" (transported as sinking organic matter from the ocean surface to the interior) rather than "preformed" (transported to the interior as dissolved nutrients by ocean circulation). This points to changes in the Southern Ocean, the dominant source of preformed nutrients in the modern ocean, with an apparent additional contribution from a decline in the preformed nutrient content of North Atlantic-formed interior water. Vollmer et al. also find a lack of LGM-to-Holocene difference in the preformed $^{13}C/^{12}C$ ratio of dissolved inorganic carbon. This finding may allow future studies to resolve which of the proposed Southern Ocean mechanisms was most responsible for enhanced ocean CO_2 storage during the ice ages: (a) coupled changes in ocean circulation and biological productivity, or (b) physical limitations on air-sea gas exchange.

Plain Language Summary Recent studies have sealed the case that the concentration of oxygen was reduced in the deep ocean during the ice ages. Vollmer et al. (2022, https://doi.org/10.1029/2021PA004339) combine the oxygen results with data on deep ocean nutrient concentrations. They find that, relative to modern, more of the ice age deep ocean's nutrient reservoir arrived as sinking organic matter from surface waters, leading to more storage of carbon dioxide in the deep ocean. Moreover, they calculate that the entire observed drawdown in atmospheric carbon dioxide levels during ice ages can be explained by this strengthening of the ocean's "biological carbon pump." The findings bring the scientific community an important step closer to explaining why and how ice ages occur and end. The Southern Ocean, the ocean region around Antarctica, must have played a major role. However, it remains unclear whether the carbon dioxide was trapped in the Southern Ocean by changes in its circulation and biology or by limitations on air-sea gas exchange across the Southern Ocean surface, such as might have occurred due to sea ice cover. Vollmer et al.'s reconstruction of the carbon isotopes in Southern Ocean surface waters may help to answer this question.

Main Text

Photosynthesis by phytoplankton floating in the sunlit surface ocean converts CO_2 into the organic carbon of biomass. This reduces the concentration of dissolved inorganic carbon (DIC), which raises surface water *p*H and thereby lowers the CO_2 concentration of surface waters. Diatomic oxygen (O_2) is generated as a byproduct of photosynthesis. Respiration by the ecosystem as a whole, which includes such processes as microbial metabolism and the feeding and respiration by zooplankton and higher trophic levels, oxidizes the biomass organic carbon. These processes reverse the carbonate chemistry effects of biomass growth, also reconsuming the oxygen that had been produced. However, a portion of the photosynthetically produced organic matter is exported from the surface ocean before being respired. This exported organic matter (known as "export production") is only "regenerated" to DIC and nutrients once it reaches the ocean interior or the seabed. In net, these processes "pump" DIC from surface waters into the ocean interior, lowering the CO_2 concentrations of the surface ocean and the atmosphere with which it equilibrates—the ocean's "biological pump" (Sundquist & Broecker, 1985). While the biological pump drives a downward flux of DIC, we can think of it as an upward flux of oxygen: It consumes oxygen in the ocean interior, while producing it in surface waters. Because of air-sea exchange with the huge reservoir of oxygen gas in the atmosphere, the surface water elevation in oxygen due to the biological pump is barely measurable. In contrast, the oxygen depletion in the ocean interior is large in proportion to the reservoir size and thus both paleoceanographicly observable and biogeochemically important. Ocean circulation counters these net fluxes of carbon and oxygen, returning deeply stored carbon to the surface and delivering new oxygen to the ocean interior. However, the biological pump is maintained so long as subsequent upwelling of the respired nutrients and carbon back to the surface leads to another cycle of biological production and organic matter export from the surface.

The ocean's biological pump was recognized early in the search for the origin of glacial/interglacial CO_2 change (Broecker, 1982). Broecker (1982) identified oxygen depletion as a possible test of his hypothesis that the biological pump strengthened during ice ages. One cause of early skepticism regarding the biological pump hypothesis was that, for it to drive the observed decline in atmospheric CO_2, the required ocean interior oxygen concentration decline, when applied homogenously, should have caused oxygen to be completely depleted in some regions of the ocean. This conflicted with the consensus that laminated (unbioturbated) sediments, indicative of an absence of oxygen ("suboxia") in bottom waters, were not notably more common during the ice ages. However, Boyle (1988a, 1988b) found that, in the ice age ocean, the distribution of dissolved nutrients was altered, with less nutrients in the shallower subsurface (i.e., "intermediate depths") and more nutrients in the deep ocean. All else equal, this also would have shifted the burden of oxygen consumption out of the intermediate depths, where oxygen is currently lowest, and into the deep ocean, where oxygen is relatively abundant. Thus, widespread suboxia during the ice ages is not a necessary consequence of a strengthening in the biological pump adequate to explain the lower CO_2 of the ice age atmosphere. In this sense, Boyle's findings of "vertical ocean nutrient [and chemical] fractionation" rescued the biological pump hypothesis from an "oxygen crisis."

Biological pump hypotheses first revolved around the low- to mid-latitude open ocean. In these regions, the "major nutrients" (i.e., phosphate and nitrate) are, and probably have always been, completely consumed from surface waters. In Broecker's (1982) treatment of the biological pump, it was implicitly assumed that the North Atlantic was responsible for returning ocean surface waters to the interior, through the formation of North Atlantic Deep Water and its flow through the global deep ocean. Further, Broecker made the approximation that NADW is entirely composed of nutrient-poor surface waters of low latitude origin that had flowed into the high latitude North Atlantic. Under these assumptions, all of the nutrients dissolved in the ocean interior enter by the sinking of organic matter; that is, Broecker assumed that the nutrients of the ocean interior are entirely "regenerated." In this case, the strength of the biological pump can only be changed by increasing (a) the ocean's major nutrient reservoirs and/or (b) the carbon-to-nutrient ratios of organic matter exported from the surface ocean. In both of these cases, due to the average composition of sinking organic matter and thus the amount of oxygen required to regenerate it, oxygen in the ocean interior would decline by roughly 1.5 units for every unit of additional carbon storage by the biological pump (Anderson & Sarmiento, 1994).

The strong sensitivity of the global ocean's biological pump to conditions of the polar ocean surface then came into focus (Knox & McElroy, 1984; Sarmiento & Toggweiler, 1984; Siegenthaler & Wenk, 1984). The Southern Ocean in particular produces the coldest and densest deep water, filling much of the deep ocean interior with water rich in nutrients that were not consumed at the ocean surface surrounding Antarctica. This ventilation with water rich in unused (i.e., preformed) nutrients is a "missed opportunity" for biological storage of CO_2 in the ocean interior. Put another way, it is a "leak" in the ocean's biological pump, as CO_2 that was sequestered with regenerated nutrients by low latitude productivity is allowed to return to the atmosphere when interior water comes to the Southern Ocean surface and the CO_2 and its accompanying nutrients are not reassimilated (Figure 1a). The latter perspective explains why the coupling between deep ocean CO_2 sequestration and oxygen depletion in the ocean interior is maintained: The interior waters that emerge in the Southern Ocean take up oxygen from the atmosphere as they release the once-sequestered CO_2, returning to the interior with the newly absorbed oxygen but without their previous burden of excess CO_2.

Reconstruction of ocean oxygen concentrations has been a major goal of paleoceanography since the birth of the field. Perhaps the greatest challenge has been that most of the potential proxies are held in the sediments, and sedimentary porewater oxygen depends not only on the oxygen in the overlying bottom water but also on

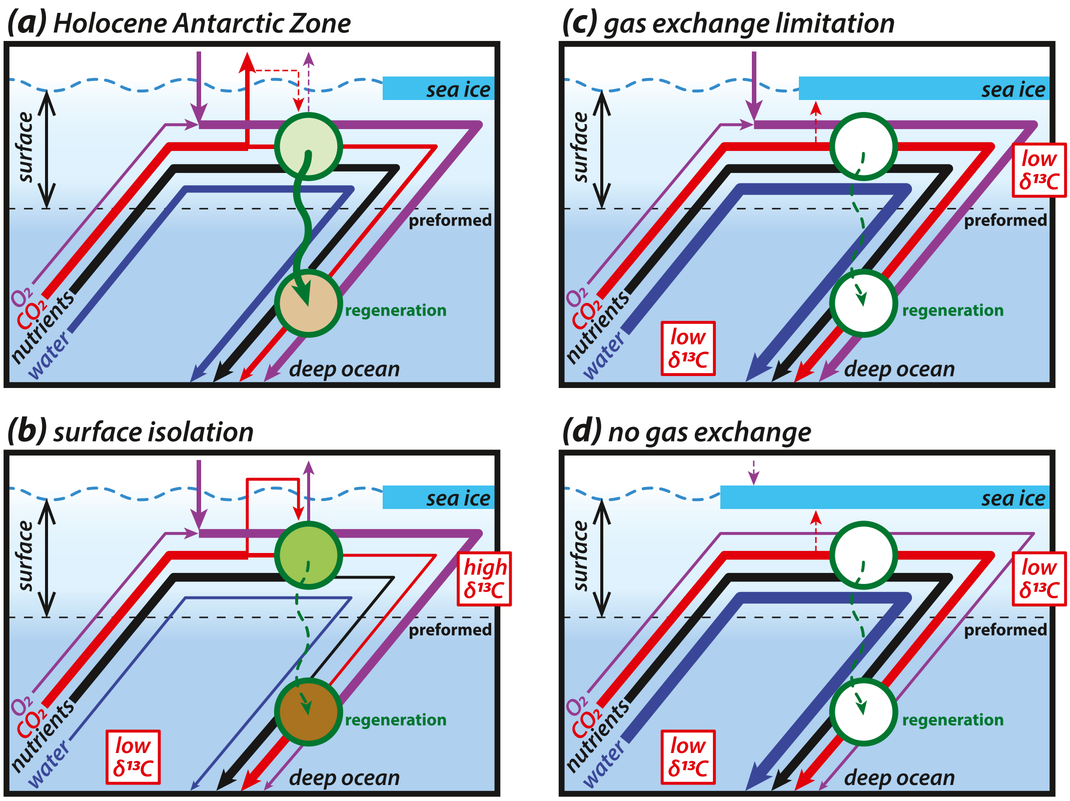

Figure 1. Changes in aspects of the biological pump and carbon cycle in response to hypothetical ice age conditions in the Antarctic Zone of the Southern Ocean. Each panel shows a single cycle of subsurface water from the low latitudes being imported into the Antarctic surface, undergoing air-sea gas exchange, biological production and sinking organic matter export, and return of the water to the deep ocean (with southward to the right). The blue arrow thickness indicates water circulation rate, and the green wavy arrow thickness indicates export production rate; dashing emphasizes low rates. The vertical red and purple arrows indicate air-sea CO_2 and oxygen transfer rates, as a rough proportion of the water circulation, not necessarily the absolute rate. The thicknesses of the arrows associated with dissolved nutrients (phosphate or nitrate; black), CO_2 (red), and oxygen (purple) indicate their concentrations in the water, not their transport rates. Panel (a) represents Holocene conditions in the Antarctic, with moderately fast overturning circulation and low surface nutrient consumption, providing the point of comparison for three LGM scenarios (b, c, d). For simplicity, the chemical parameters associated with the water upwelling to the Antarctic surface layer are shown as the same in all cases, with the pertinent point being the change in the arrows as they pass through the Antarctic. The green and brown shading of the circles indicates the degree to which productivity, export production, and regeneration affect preformed and regenerated concentrations, not the absolute rate of export production. The reconstructed decline in export production during the LGM (e.g., Kumar et al., 1993) is indicated as the thinner, dashed wavy arrows (b, c, d). However, in the case of reduced surface-subsurface water fluxes (b), the export production causes greater concentration changes than in the Holocene case (e.g., François et al., 1997). This case is titled "surface isolation," to encompass a range of physical changes that might have reduced water exchange between the ocean interior and the Antarctic surface. Panels (c) and (d) indicate LGM scenarios in which Antarctic air-sea gas exchange is limited or prevented by sea ice cover so as to prevent net CO_2 leakage, with (c) allowing oxygen exchange but (d) preventing it. Qualitative implications for the $\delta^{13}C$ of DIC in the Antarctic Zone surface and the global deep ocean, relative to the $\delta^{13}C$ of atmospheric CO_2, are indicated in red boxes.

the decomposition of sedimentary organic matter, which lowers the oxygen concentration of sediment porewater relative to bottom water. Early evidence for ice age reductions in oxygen, such as from benthic foraminifera species occurrence and redox-sensitive metals, were plagued by uncertainties related to sedimentary organic matter decomposition. As an example from the Southern Ocean, Kumar et al. (1995) measured elevation in the uranium content of Subantarctic Zone sediments during the Last Glacial Maximum (LGM), an observation explicable as either lower bottom water oxygen or higher biogenic fluxes (see also Rosenthal et al. (1997) for similar findings with cadmium). Kumar et al. (1995) found abundant evidence for an LGM increase in Subantarctic biogenic fluxes, which they attributed to dust-borne iron fertilization of the region, and they related the uranium increase to the resulting organic matter flux to the seabed. However, François et al. (1997) subsequently observed elevated authigenic uranium in LGM sediments from the Antarctic Zone of the Southern Ocean, in sediment cores that recorded the decline in biogenic fluxes that appears to have characterized the Antarctic during the LGM. It was argued that, in this case, the higher uranium must reflect a lower bottom water oxygen concentration during the LGM. This suggested an oxygen decline in most of the deep ocean during the last ice age, consistent with a biological pump explanation for lowering ice age atmospheric CO_2.

Since this early work, the data on ice age ocean interior oxygen has expanded and diversified, with a range of approaches for parsing the effects of bottom water and sedimentary porewater changes (e.g., Jacobel et al., 2020). The outcome has been confirmation of reduced oxygen concentrations in deep waters during the ice ages and an apparent rise in the oxygen concentrations of mid-depths ventilated by intermediate and mode waters (e.g., Jaccard & Galbraith, 2011). The overall picture is consistent with Boyle's (1988a, 1988b) finding of "vertical ocean nutrient fractionation" (also known as "nutrient deepening") but with even more deep ocean oxygen decline than nutrient deepening alone would have caused (Jaccard et al., 2009; Jacobel et al., 2017).

Among the approaches currently being applied to reconstruct bottom water oxygen is one proposed by McCorkle and Emerson (1988), which uses the stable carbon isotope ratio (i.e., $\delta^{13}C$) difference between two benthic foraminifera species living at distinct depths in the same sediment column, an "epifaunal" species that putatively captures bottom water DIC $\delta^{13}C$ and an "infaunal" species that captures porewater DIC $\delta^{13}C$ at the depth of complete oxygen consumption (see also Luz & Reiss, 1983; Schmiedl & Mackensen, 2006; Zahn et al., 1986). The concept is that when bottom water oxygen is higher, it can fuel more organic carbon decomposition in the sediments, leading to a larger inter-species $\delta^{13}C$ difference. More recently, the method was revisited, recalibrated, and applied by Hoogakker et al. (2015, 2016, 2019), with Hoogaker et al. (2019) reconstructing an ice age reduction in deep Pacific oxygen. Motivated by compelling results, the benthic foraminiferal "$\delta^{13}C$ difference method" for ocean interior oxygen reconstruction is now garnering intense interest.

There has been a need to merge the ocean interior oxygenation findings with other constraints on deep water chemistry to confirm and clarify the ice age connections of changes in oxygen, nutrients, and DIC. For the LGM, Vollmer et al. (2022) compiled data to undertake a core-by-core comparison of bottom water oxygen as reconstructed by the $\delta^{13}C$ difference method with reconstructions of bottom water DIC $\delta^{13}C$ and estimates of phosphate concentration based on the cadmium-to-calcium ratio (Cd/Ca) of benthic foraminifera. An outcome of this analysis is that, on average, the oxygen concentration of the deep ocean declined while its nutrient concentration changed much less. This indicates that a greater fraction of the ocean's nutrient reservoir was regenerated (rather than preformed) during the LGM, which corresponds to a more efficient biological pump that would have driven atmospheric CO_2 to a lower steady state concentration. Moreover, the greater storage of regenerated CO_2 in the deep ocean should have driven a transient dissolution of $CaCO_3$ in the deep ocean, further lowering atmospheric CO_2 (Boyle, 1988b; Broecker & Peng, 1987).

The results are not entirely surprising, given the data used for the compilation. On the one hand, benthic foraminiferal Cd/Ca data do not suggest an increase in the ocean phosphate reservoir during the LGM (Boyle, 1992), which was the mechanism for strengthening the biological pump that Broecker (1982) originally proposed. On the other hand, the evidence for lower ocean interior oxygen indicates that the concentration of regenerated phosphate was higher during the LGM (Jacobel et al., 2020). Given a constant total phosphate reservoir, a higher concentration of regenerated phosphate requires a lower concentration of preformed phosphate during the LGM. Importantly, the global ocean's input/output budgets for cadmium and phosphorus may not be tightly coupled (e.g., de Souza et al., 2022), so there is substantial uncertainty in the use of cadmium as a measure of changes in the ocean phosphorus reservoir over the ice age cycles. This concern aside, the calculation of preformed nutrients by Vollmer et al. links the data directly to theoretical insights that quantify the impact on atmospheric CO_2 concentration (Ito & Follows, 2005). This allows the authors to conclude that the oceanic decrease in preformed phosphate (and the complementary increase in regenerated carbon storage), when coupled with the response of seafloor calcium carbonate, can explain the entire reduction in atmospheric CO_2 during the LGM. Moreover, using an ocean model, Vollmer et al. (2022) show that the calculated distributions of preformed and regenerated nutrients are consistent with proposed mechanisms by which changes in the Southern Ocean (as well as the North Atlantic; Yu et al., 2019) may have strengthened the global ocean's biological pump (reviewed by Sigman et al., 2021). In net, the analysis by Vollmer et al. (2022) capstones a growing body of data pointing to Southern Ocean modulation of the biological pump as a key driver of glacial/interglacial CO_2 change.

In addition, Vollmer et al. (2022) preliminarily reconstruct the preformed $\delta^{13}C$ of DIC in the ocean interior, a constraint that may ultimately resolve a longstanding debate as to the specific ice age mechanism for preventing biologically stored CO_2 from venting from the Southern Ocean (Figure 1; Keeling & Visbeck, 2001; Sigman & Boyle, 2001). One category of possible mechanisms involves ice age strengthening of the DIC concentration gradient between the Southern Ocean surface layer and the underlying subsurface ocean. In this category are enhanced biological productivity in the surface layer (e.g., due to iron fertilization; Martin, 1990)) and reduction in the physical exchange between the surface layer and the underlying ocean interior ((Hain et al., 2010; Sigman & Boyle, 2000; Toggweiler et al., 2006) (The latter is shown as "surface isolation" in Figure 1b). An alternative category of Southern Ocean mechanisms for lowering atmospheric CO_2 involves strengthening the CO_2 concentration gradient between the Southern Ocean surface layer and the overlying atmosphere, through the restriction of air-sea gas exchange, especially in the Antarctic Zone. In this mechanism, following initial sequestration by the biological pump in another ocean region, regenerated CO_2 is returned to the Antarctic surface but fails to be released back to the atmosphere (Figures 1c and 1d). Increased coverage of the Southern Ocean by sea ice could drive such a change (Marzocchi & Jansen, 2019; Stephens & Keeling, 2000). In addition, if the biological pump were strengthened by processes such as iron fertilization in the Subantarctic Zone, models suggest that the additional regenerated CO_2 in the ocean interior would not have had adequate time to outgas when it reemerged in the Antarctic Zone surface, with or without an increase in sea ice cover (Ito & Follows, 2013; Khatiwala et al., 2019). It is a matter of definition as to whether these mechanisms involving limitations to air-sea gas exchange (Figures 1c and 1d) are categorized as strengthening of the biological pump (as unambiguously applies to Figure 1b) or as a separate CO_2 "disequilibrium" mechanism (Cliff et al., 2021). There are paleoproxy data in support of both iron fertilization in the Subantarctic Zone (Kumar et al., 1995; Martinez-Garcia et al., 2014) and "surface isolation" in the Antarctic Zone (Ai et al., 2020; Anderson et al., 2009; François et al., 1997; Studer et al., 2015; Wang et al., 2017). However, simulations with physical climate-and-ocean models do not support the surface isolation category of mechanisms (Jansen, 2017; Stouffer & Manabe, 2003), causing the modeling community to favor air-sea gas exchange restriction mechanisms for preventing CO_2 escape from the ice age Antarctic Zone (Galbraith & Skinner, 2020; Manabe & Broccoli, 2019). Given the findings of Vollmer et al. of an LGM decline in deep ocean oxygen adequate to explain roughly the entire atmospheric CO_2 decline, if air-sea gas exchange limitation was important during the LGM, it would have needed to limit the exchange of both CO_2 and oxygen (i.e., more akin to Figure 1d than to Figure 1c).

The carbon isotopes of DIC and atmospheric CO_2 take much longer to equilibrate across the sea surface than do oxygen or the partial pressure of CO_2 (Lynch-Stieglitz et al., 1995). If restrictions on gas exchange were responsible for keeping biological pump CO_2 in the ocean interior during the ice ages, then one would expect the preformed $\delta^{13}C$ of DIC to be far lower than expected from air-sea equilibrium expectations and thus lower than the Holocene value (Figures 1c and 1d). In contrast, if Subantarctic iron fertilization and/or a reduction in Antarctic surface/subsurface exchange were responsible for reduced Southern Ocean CO_2 leakage during the ice ages, then the preformed $\delta^{13}C$ of DIC sourced from the Southern Ocean surface should have more closely approached the air-sea equilibrium value or could have been higher than it, likely making it higher than the Holocene value (Figure 1b). Combining the findings of Vollmer et al. (2022) with atmospheric CO_2 $\delta^{13}C$ reconstructions (e.g., Eggleston et al., 2016) suggests that the Holocene and LGM had similar differences between the ocean's preformed $\delta^{13}C$ of DIC and atmospheric CO_2 $\delta^{13}C$. It is too early to say which set of the mechanisms is favored by this finding. In a scenario of air-sea exchange limitation for the concentration or $\delta^{13}C$ of CO_2 that still allowed for equilibration of oxygen (Figures 1c), Vollmer et al. (2022) should have reconstructed a low preformed DIC $\delta^{13}C$, in conflict with their actual calculations. However, if air-sea exchange of oxygen was also far from equilibrium during the LGM (Cliff et al., 2021), then the approach of Vollmer et al. (2022) would have overestimated the preformed DIC $\delta^{13}C$ (Figure 1d), complicating the interpretation. Moreover, the carbon isotope effects of air-sea CO_2 exchange depend on multiple factors, including temperature and the time scale of the opportunity for air-sea exchange, with kinetic and equilibrium isotopic fractionation potentially counteracting each other on short time scales (Lynch-Stieglitz et al., 1995). Numerical ocean models can include this broad range of dynamics. So they could be used to test whether the findings of Vollmer et al. (2022) are more consistent with ice age mechanisms for lowering atmospheric CO_2 that place the strongest CO_2 gradient between the surface ocean and the underlying ocean interior (Figure 1b) or between the surface ocean and the atmosphere (Figures 1c and 1d).

Vollmer et al. (2022) have brought paleoceanographic data on the concentrations of oxygen and nutrients in the ocean interior into a quantitative framework for estimating the role of the global ocean's biological pump in the decline of atmospheric CO_2 during the LGM, and they find that it can explain essentially all of it. Their findings should encourage researchers to continue with this approach, with carbon isotopes and other proxies, to determine the specific mechanisms that strengthened the ice age ocean's biological pump.

Data Availability Statement

Data were neither used nor generated for this research.

Acknowledgments
We thank editor Matthew Huber for soliciting this Commentary and a thoughtful anonymous reviewer for improving it at multiple levels. D.M.S. was supported by US NSF Grants 1401489, 2148921, and 2303548, and M.P.H. was supported by US NSF Grant 2032343.

References

Ai, X. E., Studer, A. S., Sigman, D. M., Martínez-García, A., Fripiat, F., Thöle, L. M., et al. (2020). Southern Ocean upwelling, Earth's obliquity, and glacial-interglacial atmospheric CO_2 change. *Science*, *370*(6522), 1348–1352. https://doi.org/10.1126/science.abd2115

Anderson, L. A., & Sarmiento, J. L. (1994). Redfield ratios of remineralization determined by nutrient data-analysis. *Global Biogeochemical Cycles*, *8*(1), 65–80. https://doi.org/10.1029/93gb03318

Anderson, R., Ali, S., Bradtmiller, L., Nielsen, S., Fleisher, M. Q., Anderson, B. E., & Burckle, L. H. (2009). Wind-driven upwelling in the Southern Ocean and the deglacial rise in atmospheric CO_2. *Science*, *323*(5920), 1443–1448. https://doi.org/10.1126/science.1167441

Boyle, E. A. (1988a). The role of vertical chemical fractionation in controlling late Quaternary atmospheric carbon dioxide. *Journal of Geophysical Research*, *93*(C12), 15701–15714. https://doi.org/10.1029/jc093ic12p15701

Boyle, E. A. (1988b). Vertical oceanic nutrient fractionation and glacial/interglacial CO_2 cycles. *Nature*, *331*(6151), 55–56. https://doi.org/10.1038/331055a0

Boyle, E. A. (1992). Cadmium and $\delta^{13}C$ paleochemical ocean distributions during the stage 2 glacial maximum. *Annual Review of Earth and Planetary Sciences*, *20*, 245–287.

Broecker, W. S. (1982). Ocean chemistry during glacial time. *Geochimica et Cosmochimica Acta*, *46*(10), 1689–1706. https://doi.org/10.1016/0016-7037(82)90110-7

Broecker, W. S., & Peng, T. (1987). The role of $CaCO_3$ compensation in the glacial to interglacial atmospheric CO_2 change. *Global Biogeochemical Cycles*, *1*, 15–29. https://doi.org/10.1029/gb001i001p00015

Cliff, E., Khatiwala, S., & Schmittner, A. (2021). Glacial deep ocean deoxygenation driven by biologically mediated air–sea disequilibrium. *Nature Geoscience*, *14*(1), 43–50. https://doi.org/10.1038/s41561-020-00667-z

Eggleston, S., Schmitt, J., Bereiter, B., Schneider, R., & Fischer, H. (2016). Evolution of the stable carbon isotope composition of atmospheric CO_2 over the last glacial cycle. *Paleoceanography*, *31*(3), 434–452. https://doi.org/10.1002/2015pa002874

François, R., Altabet, M. A., Yu, E., Sigman, D., Bacon, M., Frank, M., et al. (1997). Contribution of Southern Ocean surface-water stratification to low atmospheric CO_2 concentrations during the last glacial period. *Nature*, *389*(6654), 929–935. https://doi.org/10.1038/40073

Galbraith, E. D., & Skinner, L. C. (2020). The biological pump during the last glacial maximum. *Annual Review of Marine Science*, *12*(1), 559–586. https://doi.org/10.1146/annurev-marine-010419-010906

Hain, M. P., Sigman, D. M., & Haug, G. H. (2010). Carbon dioxide effects of Antarctic stratification, North Atlantic Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and synthesis in a geochemical box model. *Global Biogeochemical Cycles*, *24*(4), GB4023. https://doi.org/10.1029/2010gb003790

Hoogakker, B. A. A., Elderfield, H., Schmiedl, G., McCave, I. N., & Rickaby, R. E. M. (2015). Glacial-interglacial changes in bottom-water oxygen content on the Portuguese margin. *Nature Geoscience*, *8*(1), 40–43. https://doi.org/10.1038/ngeo2317

Hoogakker, B. A. A., Lu, Z., Umling, N., Jones, L., Zhou, X., Rickaby, R. E. M., et al. (2019). Glacial expansion of oxygen-depleted seawater in the eastern tropical Pacific. *Nature*, *562*(7727), 1–11. https://doi.org/10.1038/s41586-018-0589-x

Hoogakker, B. A. A., Thornalley, D. J. R., & Barker, S. (2016). Millennial changes in North Atlantic oxygen concentrations. *Biogeosciences*, *13*(1), 211–221. https://doi.org/10.5194/bg-13-211-2016

Ito, T., & Follows, M. J. (2005). Preformed phosphate, soft tissue pump and atmospheric CO_2. *Journal of Marine Research*, *63*(4), 813–839. https://doi.org/10.1357/0022240054663231

Ito, T., & Follows, M. J. (2013). Air-sea disequilibrium of carbon dioxide enhances the biological carbon sequestration in the Southern Ocean. *Global Biogeochemical Cycles*, *27*(4), 1129–1138. https://doi.org/10.1002/2013gb004682

Jaccard, S. L., & Galbraith, E. D. (2011). Large climate-driven changes of oceanic oxygen concentrations during the last deglaciation. *Nature Geoscience*, *5*(1), 1–6. https://doi.org/10.1038/ngeo1352

Jaccard, S. L., Galbraith, E. D., Sigman, D. M., Haug, G. H., Francois, R., Pedersen, T. F., et al. (2009). Subarctic Pacific evidence for a glacial deepening of the oceanic respired carbon pool. *Earth and Planetary Science Letters*, *277*(1–2), 156–165. https://doi.org/10.1016/j.epsl.2008.10.017

Jacobel, A. W., Anderson, R. F., Jaccard, S. L., McManus, J. F., Pavia, F. J., & Winckler, G. (2020). Deep Pacific storage of respired carbon during the last ice age: Perspectives from bottom water oxygen reconstructions. *Quaternary Science Reviews*, *230*, 106065. https://doi.org/10.1016/j.quascirev.2019.106065

Jacobel, A. W., McManus, J. F., Anderson, R. F., & Winckler, G. (2017). Repeated storage of respired carbon in the equatorial Pacific Ocean over the last three glacial cycles. *Nature Communications*, *8*(1), 1727. https://doi.org/10.1038/s41467-017-01938-x

Jansen, M. F. (2017). Glacial ocean circulation and stratification explained by reduced atmospheric temperature. *Proceedings of the National Academy of Sciences of the United States of America*, *114*(1), 45–50. https://doi.org/10.1073/pnas.1610438113

Keeling, R. F., & Visbeck, M. (2001). Palaeoceanography: Antarctic stratification and glacial CO_2. *Nature*, *412*(6847), 605–606. https://doi.org/10.1038/35088129

Khatiwala, S., Schmittner, A., & Muglia, J. (2019). Air-sea disequilibrium enhances ocean carbon storage during glacial periods. *Science Advances*, *5*(6), eaaw4981. https://doi.org/10.1126/sciadv.aaw4981

Knox, F., & McElroy, M. (1984). Changes in atmospheric CO_2 influence of the marine biota at high latitude. *Journal of Geophysical Research*, *89*(D3), 4629–4637. https://doi.org/10.1029/jd089id03p04629

Kumar, N., Anderson, R. F., Mortlock, R. A., Froelich, P. N., Kubik, P., Dittrich-Hannen, B., & Suter, M. (1995). Increased biological productivity and export production in the glacial Southern Ocean. *Nature*, *378*(6558), 675–680. https://doi.org/10.1038/378675a0

Kumar, N., Gwiazda, R., Anderson, R. F., & Froelich, P. N. (1993). $^{231}Pa/^{230}Th$ ratios in sediments as a proxy for past changes in Southern Ocean productivity. *Nature*, *362*(6415), 45–48. https://doi.org/10.1038/362045a0

Luz, B., & Reiss, Z. (1983). Stable carbon isotopes in quaternary foraminifera from the Gulf of Aquaba (Elat), Red Sea. *Utrecht Micropaleontological Bulletins*, *3*, 129–140.

Lynch-Stieglitz, J., Stocker, T. F., Broecker, W. S., & Fairbanks, R. G. (1995). The influence of air-sea exchange on the isotopic composition of oceanic carbon—Observations and modeling. *Global Biogeochemical Cycles*, *9*(4), 653–665. https://doi.org/10.1029/95gb02574

Manabe, S., & Broccoli, A. J. (2019). Beyond global warming, how numerical models revealed the secrets of climate change. https://doi.org/10.1515/9780691185163

Martin, J. H. (1990). Glacial-interglacial CO_2 change: The iron hypothesis. *Paleoceanography*, *5*, 1–13. https://doi.org/10.1029/pa005i001p00001

Martinez-Garcia, A., Sigman, D. M., Ren, H., Anderson, R. F., Straub, M., Hodell, D. A., et al. (2014). Iron fertilization of the subantarctic ocean during the last ice age. *Science*, *343*(6177), 1347–1350. https://doi.org/10.1126/science.1246848

Marzocchi, A., & Jansen, M. F. (2019). Global cooling linked to increased glacial carbon storage via changes in Antarctic sea ice. *Nature Geoscience*, *12*(12), 1001–1005. https://doi.org/10.1038/s41561-019-0466-8

McCorkle, D. C., & Emerson, S. R. (1988). The relationship between pore water carbon isotopic composition and bottom water oxygen concentration. *Geochimica et Cosmochimica Acta*, *52*(5), 1169–1178. https://doi.org/10.1016/0016-7037(88)90270-0

Rosenthal, Y., Boyle, E. A., & Labeyrie, L. (1997). Last glacial maximum paleochemistry and deepwater circulation in the Southern Ocean: Evidence from foraminiferal cadmium. *Paleoceanography*, *12*(6), 787–796. https://doi.org/10.1029/97pa02508

Sarmiento, J. L., & Toggweiler, J. R. (1984). A new model for the role of the oceans in determining atmospheric pCO_2. *Nature*, *308*(5960), 621–624. https://doi.org/10.1038/308621a0

Schmiedl, G., & Mackensen, A. (2006). Multispecies stable isotopes of benthic foraminifers reveal past changes of organic matter decomposition and deepwater oxygenation in the Arabian Sea. *Paleoceanography*, *21*(4). https://doi.org/10.1029/2006pa001284

Siegenthaler, U., & Wenk, T. (1984). Rapid atmospheric CO_2 variations and ocean circulation. *Nature*, *308*(5960), 624–626. https://doi.org/10.1038/308624a0

Sigman, D. M., & Boyle, E. A. (2000). Glacial/interglacial variations in atmospheric carbon dioxide. *Nature*, *407*(6806), 859–869. https://doi.org/10.1038/35038000

Sigman, D. M., & Boyle, E. A. (2001). Antarctic stratification and glacial CO_2. *Nature*, *412*, 606. https://doi.org/10.1038/35088132

Sigman, D. M., Fripiat, F., Studer, A. S., Kemeny, P. C., Martínez-García, A., Hain, M. P., et al. (2021). The Southern Ocean during the ice ages: A review of the Antarctic surface isolation hypothesis, with comparison to the North Pacific. *Quaternary Science Reviews*, *254*, 106732. https://doi.org/10.1016/j.quascirev.2020.106732

Sundquist, E. T., & Broecker, W. S. (Eds.). (1985). *The carbon cycle and atmospheric CO_2: Natural variations archean to present*. *Geophysical Monograph Series*. American Geophysical Union. ISBN: 9781118664322. https://doi.org/10.1029/gm032

de Souza, G. F., Vance, D., Sieber, M., Conway, T. M., & Little, S. H. (2022). Re-assessing the influence of particle-hosted sulphide precipitation on the marine cadmium cycle. *Geochimica et Cosmochimica Acta*, *322*, 274–296. https://doi.org/10.1016/j.gca.2022.02.009

Stephens, B. B., & Keeling, R. F. (2000). The influence of Antarctic sea ice on glacial-interglacial CO2 variations. *Nature*, *404*(6774), 171–174. https://doi.org/10.1038/35004556

Stouffer, R. J., & Manabe, S. (2003). Equilibrium response of thermohaline circulation to large changes in atmospheric CO_2 concentration. *Climate Dynamics*, *20*(7–8), 759–773. https://doi.org/10.1007/s00382-002-0302-4

Studer, A. S., Sigman, D. M., Martínez-García, A., Benz, V., Winckler, G., Kuhn, G., et al. (2015). Antarctic Zone nutrient conditions during the last two glacial cycles. *Paleoceanography*, *30*(7), 845–862. https://doi.org/10.1002/2014pa002745

Toggweiler, J. R., Russell, J. L., & Carson, S. R. (2006). Midlatitude westerlies, atmospheric CO_2, and climate change during the ice ages. *Paleoceanography*, *21*(2). https://doi.org/10.1029/2005pa001154

Vollmer, T. D., Ito, T., & Lynch-Stieglitz, J. (2022). Proxy-based preformed phosphate estimates point to increased biological pump efficiency as primary cause of last glacial maximum CO_2 drawdown. *Paleoceanography and Paleoclimatology*, *37*(11). https://doi.org/10.1029/2021pa004339

Wang, X. T., Sigman, D. M., Prokopenko, M. G., Adkins, J. F., Robinson, L. F., Hines, S. K., et al. (2017). Deep-sea coral evidence for lower Southern Ocean surface nitrate concentrations during the last ice age. *Proceedings of the National Academy of Sciences of the United States of America*, *114*(13), 3352–3357. https://doi.org/10.1073/pnas.1615718114

Yu, J., Menviel, L., Jin, Z. D., Thornalley, D. J. R., Foster, G. L., Rohling, E. J., et al. (2019). More efficient North Atlantic carbon pump during the last glacial maximum. *Nature Communications*, *10*(1), 2170. https://doi.org/10.1038/s41467-019-10028-z

Zahn, R., Winn, K., & Sarnthein, M. (1986). Benthic foraminiferal $\delta^{13}C$ and accumulation rates of organic carbon: Uvigerina Peregrina group and Cibicidoides Wuellerstorfi. *Paleoceanography*, *1*(1), 27–42. https://doi.org/10.1029/pa001i001p00027