nature portfolio

Peer Review File

Contributions of biological and physical dynamics to deglacial CO2 release from the polar Southern Ocean

Corresponding Author: Dr Yuhao Dai

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Review of Dai and Yu, “Deglacial polar Southern Ocean carbon release driven by physical and biological dynamics,” submitted to Nature Communications, by Jesse Farmer

Dai and Yu present new deep ocean B/Ca-derived carbonate ion, Cd/Ca-derived phosphate concentration, and d13C gradient-derived oxygen reconstructions from a sediment core in the Southwest Pacific Ocean tracking (largely) the properties of Southern Sourced deep waters over the last deglaciation. The authors translate this proxy data into information on changes to preformed phosphate and air-sea carbonate ion change to track the influences of Southern Ocean biology and gas exchange on carbon dioxide partitioning between the ocean and atmosphere over the last deglaciation.

There is a lot to like in this manuscript. It is overall well written, the figures are excellent, and the combination of proxies applied is novel and potentially quite transformative. At the same time, I feel that the authors are trying to reach a conclusion on the role of sea ice cover in deglacial ocean-atmosphere CO2 exchange before they have fully “paved the road” of proxy understanding that would allow the reader to get on board with this interpretation and exclude other alternatives. For this reason, I think the results would actually be more influential as a longer contribution to a field-specific journal where the proxy interpretations, and, most crucially, the covariance between these new proxies (see below) can be more fully explored. It may even be beneficial to split this into two manuscripts, one longer-form outlining the combined proxy approach and its uncertainties, and the second a shorter-form application to the deglaciation with its climate system implications.

Major comments (not in order of importance):

1. Age model development. The C. wuellerstorfi d18O (ED Fig. 1) does not lend confidence in the age model construction that is based on G. bulloides Mg/Ca correlation to EDC dD (Dai et al., 2020). This is of crucial importance for the sea ice interpretation of outgassing in early HS1 – if the timing of HS1 is not correctly assigned in this sediment core, then the relationship of PO4* to sea ice (ice core ss Na) is uncertain. Unfortunately, I don’t find the chronological establishment here sufficiently compelling/precise as to allow for the discussion on L166 and onward, which is the crux of the current paper. Perhaps the published radiocarbon evidence can be brought in here, or other SST proxies can be measured to refine this alignment?

2. Sea ice, or not? The authors take a strong position on the role of sea ice in the abstract “…physical dynamics involving sea ice retreats (sic) dominated CO2 outgassing…” (L22) but are rightly more circumspect about this in the main text “However, relative roles of biological and physical processes to the PAZ outgassing remain ambiguous on both millennial and glacial-interglacial timescales…” (L157-158). More clarity on the relative contributions of sea ice and their timing would be beneficial.

3. Tracer interdependence. PO4* and [CO32-]as are not independent tracers, as both depend on Cd/Ca-derived [PO43-] (L48-49, 66-69). That suggests the difference between the two is largely driven by carbonate ion and oxygen… but it is not at all clear what to make of the distinctions between the two tracers. On the one hand, it’s interesting that the two show slightly offset patterns in time… but on the other, it’s not surprising that the two look similar (Fig. 2f, g). I would appreciate more guidance from the authors on what to make of this interdependence.

4. NSW and SSW endmembers + contributions over time. The authors note that the advantage of PO4* and [CO32-]as is that both tracers are quasi-conservative in the ocean interior (e.g., L50-60). However, the downside of this is that these proxies are set by the endmember values of NSW and SSW and their relative contributions to the core site. It is known from the authors' previous work that these endmember values are not stable over time (e.g., Yu et al., 2019 for [CO32-]as in the N. Atlantic); indeed, the goal of this study is essentially to reconstruct the SSW endmember PO4* and [CO32-]as over the last deglaciation (e.g., L63-65). To this end, it is critical that the authors know the contributions of the relative endmembers. In my mind, their approach of assuming a percentage contribution of SSW and allowing it to vary (e.g., L290) leaves much to be desired, especially as proxy data (Nd isotopes) may help address this question for them.

5. Presentation of results. The authors do not discuss their underlying proxy reconstructions, instead they move directly to the derived tracer products (PO4* and [CO32-]as). This is unfortunate – the most directly calculated results should be presented first, and only after that a discussion of the interpreted derived products. Such additional length would allow for further investigation of intriguing features in the proxy data – for instance the offsetting (in both depth + age space) of carbonate ion, oxygen, and phosphate concentration deglacial maxima/minima (Fig. 2c-e). Might this relate to the relative depth habitat of the foraminifer used? (C. wuellerstorfi being ~sediment/water interface, H. elegans perhaps being infaunal, G. affinis being deep infaunal)?

6. Uncertainty on PO4* and [CO32-]as. There does not appear to be an effort to estimate errors on PO4* and [CO32-]as aside from those relating to the individual proxy reconstruction of carbonate ion, oxygen concentration, and phosphate concentration. At the very least, the errors of each required measurement will add in quadrature; in addition, further error will result from assumption of Redfield stoichiometry (see modern ocean uncertainties in these ratios from Anderson & Sarmiento, 1994). A more comprehensive handling of uncertainty in these new tracers will be needed than is presented in the main text, figures and methods.

Minor methods comments.

L236. How was anthropogenic carbon calculated and deducted? I would not expect much detectible DICant at this water depth…
L262. Given all those contributions, the estimated uncertainty on phosphate concentration is only ±0.05 µmol/kg? Come on now, that is not realistic. For one point of comparison, the Cd/Ca measurement precision alone in Farmer et al. (2019) corresponded to a similar or larger phosphate concentration uncertainty. I have no doubt the authors are better analysts than myself, but the propagation of error should be handled appropriately.
L273-275. The effect of global alkalinity change on the reconstructed [CO32-]as is quite significant (ED Fig. 1i), and also there is no reason to expect that a single core site would experience the global ocean alkalinity change (see, e.g., regional deviations in benthic d18O for whole-ocean d18O change, Lisiecki & Stern, 2016 and references therein). Can the authors please further elaborate on/justify this correction and illustrate its uncertainty?

Reviewer #2

(Remarks to the Author)
Key Results:
It is difficult to parse apart the drivers of air-sea CO2 exchange (and by extension atmospheric CO2 variability), particularly in the Polar Antarctic Zone where carbonate archives are generally not present. The authors of this paper attempt to circumvent this challenge by inferring changes in quasi-conservative properties of deep ocean waters that are sourced from the PAZ; these properties are set by a combination of endmember values and water-mass mixing and should be recorded by benthic foraminifera at the study site. By the authors' logic, changes in these properties should reflect a combination of changes in circulation and changes in endmember composition (in this case largely set in the PAZ and delivered to the study site).
The authors have divided the discussion of their results by timescale. On glacial/interglacial timescales, they find that the deep pacific ocean was a net source of CO2 to the atmosphere, given the increase in [CO32-]as at the site. The concurrent increase in PO4* suggests that there was a combination of more preformed PO43- (and thus lower nutrient efficiency) and/or more preformed O2 as a result of a combination of biology and the removal of sea ice. The latter is corroborated by the decrease in ventilation age documented at the site in a previous publication by these authors.
On millennial timescales, the authors suggest that the deep South Pacific was a source of CO2 outgassing across HS1, and that this was matched by changes in preformed nutrients (and by extension nutrient utilization efficiency) and/or preformed O2 inferred from PO4*. Radiocarbon ventilation ages suggest that this was a period of better ventilation, perhaps as a result of sea-ice retreat and/or a shift southwards of the southern hemisphere westerlies during this period. The Antarctic Cold Reversal shows a decline in [CO32-]as and PO4 from the end of HS1, consistent with poorer ventilation of the waters reaching this region. Lastly, the Younger Dryas measurements of [CO32-]as and PO4* suggest that this region was again a source of CO2 outgassing as a result of biological and physical changes in the PAZ. These mechanisms are consistent with to those provided for the full glacial/interglacial change in these parameters.
On sub-millennial scales, the authors examine and attempt to delineate the timing of changes in [CO32-]as and PO4* at this site across HS1 using ~12 data points (the sedimentation rate of this core is 10-20 cm/kyr depending on chosen tie points from Dai, Yu and Rafter 2021). The authors suggest that the asynchrony between [CO32-]as and PO4* in early HS1 allows for the discrimination between the various influences on these parameters. They suggest that the lack of change in PO4* is consistent with an increased role for physical drivers (retreating sea ice and altered southern hemisphere westerlies) in early

HS1. In contrast, according to the authors interpretation, the change in PO4* across late HS1 is indicative that biological changes likely spurred mid-late HS1 outgassing.

Validity:

The authors make use of two quasi-conservative (and related) tracers: PO4* and [CO32-]as. PO4* is derived using inferred concentrations of PO43- and O2. The former is derived from the measured Cd/Ca ratio of the benthic foraminfera H. elegans using a local calibration for Cd/Ca to PO43-. The latter is derived from the gradient in carbon isotopes of co-occurring infaunal (G. affinis) and epifaunal (C. wuellerstorfi) species. Changes in PO4* thus reflect some combination of changes in nutrient utilization (via changes in preformed PO43-) and changes in oxygen related to either biology and/or physics.

The PO43- measurements are also used to calculate [CO32-]as, a parameter which reflects changes in CO32- (and by extension DIC and atmospheric CO2) with biological influences removed. When this parameter changes, it reflects changes in carbonate ion as a result of CO2 sequestration or outgassing as a result of air-sea gas exchange; increases in [CO32-]as reflect lower DICas and outgassing of atmospheric CO2. Because increased exchange of CO2 should also alter PO4*, differences in the behavior of [CO32-]as and PO4* downcore should provide constraints on the role of physical processes (relative to biological processes) in governing CO2 release to the atmosphere across the deglaciation.

In general the data appear to be of high-quality and their interpretation appears robust. However, there are some major flaws that I think need to be fixed if the paper is accepted for publication. In particular, the discussion of sub-millennial drivers of CO2 variability in HS1 relies on the statement that [CO32-]as increased throughout early HS1, in contrast to PO4* (line 166-167). It would be extremely helpful to the reader to delineate the exact magnitude of the change in these variables over the early HS1 time period. The change in [CO32-]as between 18- 16.3 ka appears to be on the order of 5 µmol/kg at most, and perhaps less than that if the lowest data point on the edge of HS1 is excluded. The data for PO4* looks as though it is also slightly increasing over the same time period, with the exception of a slight decrease right at 16.3 kyr (Figures 2 and 3). To make things more confusing, the onset of HS1 on Extended Data Figure 1 appears at a different place in the [CO32-]as and PO4* curves than in Figures 2 and 3. Because the figure is plotted against depth it makes interpretation and comparison difficult, but if Extended Data Figure 1 is used in interpretation it appears that [CO32-]as actually decreased between 18-16.3 kyr.

In other places in the text the authors refer to the change in N. Atlantic [CO32-]as as small across all of HS1 (lines 117-118), but the change in early HS1 in the NEAP-4K record is almost double that of the MD97-2106 core. How much of the small change in [CO32-]as in early HS1 could be from a change in NSW/SSW proportion and/or end member composition? Again this is unclear, but if the change in [CO32-]as is on the order of 5 µmol/kg, even a small change induced by circulation/water column structure change may represent a significant proportion of this inferred increase.

It is not convincing to me from Figures 2/3 or from Extended Figure 1 that the change in [CO32-]as is significant either relative to the lack of change in PO4* or its starting value at the beginning of HS1. Given that this is one of the 3 major findings of the paper and is used evidence for physical changes initiating CO2 outgassing, this needs to be addressed prior to publication. The other evidence cited (radiocarbon ventilation, sea ice extent, and δ15N) are convincing in this respect, but have all been published elsewhere.

Significance:

The authors' text is well-cited with regard to deglacial CO2 release from the deep Southern Ocean, including mechanisms and modelling. The literature they cite shows that, over the last 5-10 years, there have been numerous results connecting the deep Southern Ocean to the release of carbon from the deep across the deglaciation. There is, to my knowledge, already a consensus that the Pacific would have been a major player in this process both on glacial/interglacial and millennial timescales. Where this article therefore would be adding to the literature, then, would be if it could distinguish the role of physical and biological changes in driving this release for the PAZ. However, for the glacial/interglacial and millennial timescales of this article, the authors acknowledge that the co-variance of their tracers does not allow them to fully delineate between the dual roles of physics and biology. They do attempt to constrain the amount of carbon release implied by their data for glacial/interglacial transition, but this extrapolation is not fully explained nor is the role of the deep South Pacific (relative to, for example, the Atlantic) constrained by this extrapolation.

The authors suggest that the behavior of the two conservative tracers over HS1 allows them to discriminate between influence of physical and biological tracers at its onset. To me this would be a significant advance in understanding provided by this paper, as it would serve to confirm evidence from radiocarbon and sea-ice proxies. However, the authors must provide more information regarding the changes in these two tracers across this time period to better demonstrate their conclusions (regarding whether the change in [CO32-]as is significant relative to the lack of change in PO4*).

The significance of this paper would clearer with discussion in more detail of how the results can or cannot discern between mechanisms or how they could build upon the various modelling results that they cite. Khatiwala et al. (2019), for example, find that sea ice extent and ocean circulation are minor contributors to changes in carbon storage relative to the role of air-sea equilibrium in amplifying changes in ocean temperature and iron fertilization. Cliff et al. (2021) also suggests a minor role for circulation and the biological pump in driving deep ocean deoxygenation (and thus PO4*), but a large role for sea ice extent and iron fertilization. Such contradictions might be cleared up from paleoclimate-based inferences, but is largely not discussed here.

One major thing that is unclear to me is why the authors do not discuss existing PAZ δ15N data. The authors suggest that the lack of carbonate archives from the PAZ preclude analysis of nutrient utilization in the region, but diatom archives (plotted in Extended Figure 5) provide such a record. Likewise, deep sea corals provide a coherent and chronologically well-constrained record of δ15N. There is no discussion of these diatom records throughout the text, and only a single mention of deep sea coral-bound δ15N. Recent important work (Ai et al., 2020) provides important constraints on the role of Southern Hemisphere westerly winds and upwelling on nutrient conditions in the PAZ and should be discussed here in reference to the conclusions being drawn, especially with regard to the interpretation of δ15N records from the PAZ.

Another discussion point that should be addressed are the 'Late Holocene' values marked in Figure 2. It is not entirely clear from the methods section what age the "Late Holocene values reflect (Lines 214-215), but from inference (the disappearance of G. affinis until 0-17cm in the core) it seems likely these reflect values core top values. The values of [CO32-]as and PO4* are both equal to their value at 8-10 kyr. However, we know from Studer et al. (2018) that there was a substantial (20 ppm) rise in CO2 across the late Holocene (between 10 kyr and 2 kyr) that was accompanied by a large change in nitrate supply, reflected in the δ15N of Southern Ocean PAZ and Polar Frontal Zone diatom-bound N records, as well as in Coral-bound δ15N records from the PAZ. Presumably this change in δ15N should also be reflected in the authors' records of PO4*. The changes in overturning driven by migration of Southern

Hemisphere Westerly Winds (hypothesized by Studer et. al 2018) should also perhaps be reflected as changes in [CO32-]as. Please discuss why your core top values relative to 10 kyr do or do not contradict existing data regarding this period. Previous records from this same core (from the same authors in 2022) show a strong role for altered efficiency of the solubility pump over the same time period (inferred from data presented in Fig. 2A). No discussion of this in relation to the findings of this paper are made, yet the inference from the 2022 paper is that Southern Ocean outgassing as a result of an altered solubility pump makes up a significant proportion of the observed change between 19-15 kyr – but the current paper would suggest much of the action is taking place in the PAZ instead of the subantarctic.

Data and methodology:
The data appeared to be of high quality, and technically sound. I have minor comments that can be addressed line by line in the text. The main major comment I have is for readability: the authors here assume the reader has a detailed understanding regarding the calculation and interpretation of [CO32-]as, and rely on the reader to have a fairly detailed prior understanding of how this is calculated in order to follow the discussion. A short discussion of the tracer and its relationship to atmospheric CO2 and DIC would be helpful.

Methods:
There is evidence that morphotypes of C. wuellerstorfi (e.g. sensu lato vs. sensu stricto after Gottschalk et al. 2016 and references therein) can alter the values of δ13C and trace element ratios. Given their expertise in the field, the authors are likely aware of this – were selections made by morphotype within C. wuellerstorfi that are not mentioned in the text? If not, could this account for some of the variability in, for example, B/Ca and δ13C that would give rise to artificial changes in reconstructed [CO32-]as and PO4* values? δ13C in particular can vary by between 0.2-0.7‰, which would be significant for reconstructions of bottom water oxygen concentrations.
In lines 222-223, there is mention of splits of large samples into subsamples, which were presumably run in different batches and/or treated as independent samples. What is the standard deviation of these "true" replicates? Are they averaged and included in the figures (e.g. Extended Figure 1) or plotted independently? The 5th oldest point in Extended Figure 1g, for example, looks as if it may be 2 replicate samples, but one is significantly different than the other – but it is hard to tell.
Were the benthic foraminiferal tests for stable isotope analysis (lines 230-233) treated in any way (e.g. crushed and sonicated)? Why not use splits of C. wuellerstorfi from the trace element measurements?
δ18O is plotted in Extended Figure 1E but there is no reference to it in the text, and no discussion of the methodology (species?) for the δ18O measurements (line 233 is the only mention). It appears δ18O largely agree, but there are places with offsets of up to ~0.25‰ in co- occurring benthics. This difference is disguised by the scale of glacial/interglacial change in δ18O – is this a normal difference in δ18O between these two species? If so, perhaps this should be discussed, and if not, there should be a rationalization for how these particular points can be used for co-occurring measurements of δ13C gradients.
A table or a more organized discussion of the results of sensitivity tests would also be helpful for the reader – at the moment the discussion feels haphazard. The results of the sensitivity tests are presented parenthetically (Lines 91-93 for example), which makes it hard to follow. The methodology behind the sensitivity tests is straightforward and described in the text (lines 290 onwards) but the results of these tests as they are discussed in the text are not as clear.

Analytical approach:
There are places where the analytical approach is not always clear, though largely the authors have done a good job here. Several of the figures contain data that is not explained and/or referenced in the main text or supplement for the purpose of discussion. This includes Fig. 2A and 2B, Extended Data Fig 1B and 1E, Extended Data Fig. 3, Extended Data Fig. 4b, and most notably Extended Data Fig. 5C.
More and/or clearer discussion of the results of the sensitivity tests would also benefit the manuscript. It is not always clear what the tests and results of the test are (Lines 89-93 are a good example of this). More discussion of the sensitivity tests relative to the findings is necessary - for example, in lines 89-93 the authors discuss the range of sensitivities in SSW PO4* implied by potential changes in NSW PO4* - but neglect to then relate this finding back to their results (potentially because the order of magnitude of the sensitivity test is on par with the entire change in PO4* in SSW). If the sensitivity tests are included in discussion of the results (which they correctly are), they should also be discussed in greater detail. It is also unclear why the authors do not conduct sensitivity tests for other transitions (e.g. YD) where they are suggesting there must have necessarily been changes in the balance of NSW/SSW at the site.
A specific point that I found confusing in the sensitivity tests is that, with their help, the authors define the increased change at the site from the change in NSW endmember to be 7 μmol/kg and the SSW endmember contribution to be 30 μmol/kg. However, adding these up gives a change larger than the glacial interglacial change suggested in lines 73-74 (32 μmol/kg +/- 4). Apologies if I have misunderstood, but these numbers do not seem to add up correctly, even accounting for the sensitivity test results.
There is no discussion of whether the core used here is of high enough sedimentation rate to analyze the sub-millennial scale variability that makes up the latter part of the paper, with the exception of lines 163-165 which references chronological uncertainties in Extended Data Figure 1 that are not evident in the figure or discussed in detail anywhere I can find. If there are significant uncertainties then they need to be described. Regardless, Extended Data Figure 1 does not match Figure 2 or figure 3 with regard to the onset of HS1 in PO4* or [CO32-]as - as an example, there are 4 data points prior to the gray bar in

Extended Data Fig. 1i, and only 2 or 3 in Fig. 2g. Likewise, the upward trend in the oldest part of the PO4* record in Fig. 2F contradicts the data points in Extended Fig. 1h. Further confusing the analysis of this record, Extended Fig. 1 lacks the 16.3 kyr dashed line, making it difficult to analyze how many points constitute the trend the authors are inferring exists for [CO32-]as and not for PO4* between 18- 16.3 kyr.
The extrapolation of carbon release from the glacial-interglacial transition needs to be made clearer and discussed further, or removed. What is this amount relative, to say, the Atlantic or Indian – and if the amount released is comparable in size to the atmosphere then does this imply that the majority of the C release was accomplished through a reorganization of the deep Pacific alone? What was the role of the intermediate waters in this reorganization? Lines 110-113 are not clear to me and need further clarification.

Clarity and context:
There are several places where the writing is unclear and obscures the logic or
argument. The authors' use of the phrase "direct evidence" (lines 83-85) needs to be substantiated or made more clear - why is this "direct evidence" compared to the numerous other records of Southern Ocean deglacial carbon loss? These records also represent inferences, given that they are not from the PAZ and rely on inferred relationships between trace metal/calcium ratios, bottom water chemistry, pore water chemistry, etc, as well as sensitivity tests and assumptions regarding the characteristics of NSW, SSW, and their proportions. While the authors of existing δ15N records would not necessarily say their records record "direct" CO2 outgassing from the AZ, they might be inclined to argue that diatom records from the PAZ are a much more direct record of nutrient utilization efficiency than PO4* inferred here. Why is B-P radiocarbon from the site is not "direct" evidence (lines 103-106, for example)?
Text, minor comments:
Line 37: Key to this paper is the idea that these properties are conserved, adding "along flow paths moving away from the PAZ" might be clearer.
Lines 46-48 are confusing: PO4* is noted to be largely governed by surface nutrient conditions here, but in the methods explanation has a solubility/physical component (lines 276-289). The statement in lines 48-49 about deconvolving these tracers makes it sound much more straightforward than the methods imply, which is shown by the fact that their deconvolution can not be achieved for glacial-interglacial or millennial timescales.
Line 71: There are no calculation details for [CO32-]as.
Lines 75-76: Changes in SSW/NSW is vague wording: do you mean changes in the proportion of these or in the endmember composition?
Lines 76-79: This is confusing – if the proportion of NSW is increasing across the deglaciation, changes in NSW characteristics would have a larger impact as the proportion increased.
Lines 87: "Changes" could refer to proportion or endmember again.

Lines 107-110: "Data-based evidence" is a strong way to phrase this, given that most of the other studies cited (including those from this site) are also Data-based.
Line 118: This refers to extended data fig. 4, I believe, not certainly not 5. Line 119: decreased fraction of NWS during HS1 needs a citation.
Line 121-122: citation needed for this
Line 136-138: Are your results adding to these conclusions listed? A reader might have arrived at the same conclusions (Driven by biological and physical changes) from the δ15N, radiocarbon, and sea salt records alone. The paper needs to be more specific about the constraints that this data is providing.
Lines 156-159: Again, as noted immediately above, it remains unclear what additional constraints are provided given the ambiguous conclusion. The authors would be well-served to make their specific conclusions stronger and/or clearer, with regard to how these add to the existing literature.
Lines 166-167: This does not appear to be true, at least not significantly. This needs to be addressed with the actual data, and concentrations/values need to be given.
Lines 169-170: 0.1 represents 1/3 of the Glacial-Interglacial transition, so it is not as small as the authors imply here.
Lines 186-187: Callout to figure 3 would be helpful here.
Lines 210-212: The finding that the biological pump plays a large role is not surprising, but could be discussed further relative to recent papers finding a large role for the solubility pump and other physical mechanisms, particularly for intermediate Southern Ocean waters.
Figures, minor comments:
Caption Fig. 1 has the words "Lower Circumpolar Deep Water" but no explanation of what this is in reference to with regard to the rest of the sentence (Lines 323-324).
Fig. 2: The late Holocene values for Figure 2 [CO32-]as are not at all close to the values in Figure 1D. While some of the absolute value change is due to calibration, the values are significantly higher than those given for the modern ocean. Why is this the case, if the PO4values are accurately reflected in the core tops? Why does Fig. 2F increase at the oldest point in the record without a data point on the plot that is older than ~18 kyr?
Fig. 3: It is not clear what the gradient in the color bars on the triangles in b,c,e, f and h are reflecting given the depiction of timeseries. Also, should Fig. 3D say B-P and not B-A age?

Extended Fig. 1: This needs substantial improvements as it does not align with Figure 2 or 3, and does not have a marker for 16.3 kyr.
Extended Fig. 2: Typo for a instead of (a) in line 567.
Extended Fig. 3: Needs a better legend, given that there are actually 3 sets of data on the plot and not 2. This figure is not discussed in the main text. For example, hat does the substantial gradient (20 μmol/kg) between MD97-2106 and the S. Indian Core in reconstructed O2 imply for the deep South Pacific vs Indian Ocean during early HS1?
Extended Fig. 4: Is there a reason that the Yu 2022 data for the South Atlantic is not also included here? I assume the

reasoning is to show the endmembers for NSW and SSW, but the GGC90 record was used by Yu et al to infer significant release of carbon from the Atlantic sector of the Southern Ocean as well.
Extended Fig. 5: It would be helpful to discuss Fig. 5C in the text. Also, putting the late Holocene values for the δ15N records and for PO4* would be helpful for any discussion of the late Holocene evolution of these tracers.

References:
The paper is well-cited, though not many of the citations are used to further the discussion of the text (for example, δ15N references) despite being in the text. These citations may also be of interest for the discussion:
Ronge, Thomas A., et al. "Southern Ocean contribution to both steps in deglacial atmospheric CO2 rise." Scientific reports 11.1 (2021): 22117.
Moy, Andrew D., et al. "Varied contribution of the Southern Ocean to deglacial atmospheric CO2 rise." Nature Geoscience 12.12 (2019): 1006-1011.
Fogwill, C. J., et al. "Southern Ocean carbon sink enhanced by sea-ice feedbacks at the Antarctic Cold Reversal." Nature Geoscience 13.7 (2020): 489-497.

Reviewer #3

(Remarks to the Author)
Dai and Yu present a valuable dataset, interpreted in a cutting edge quantitative framework, to investigate glacial carbon storage and release. This is a really interesting contribution and following revisions would, I think, make a very suitable Nature Communications paper.
I have provided detailed line by line comments, which include key conceptual questions as well as more minor points and typos. Note there are other typos and sections lacking clarity too - the paper would benefit from further proof reading and an attempt to more clearly describe processes to the reader alongside their quantification in different tracer signals. I also pick out some of the most critical issues below.

[CO32-]as - better describe what it can and can't tell us
The [CO32-]as tracer has been introduced and used in a series of recent papers from Yu's group, yet is still relatively new and (as detailed below) needs further description to help the reader.
More critically, the interpretation I felt leaps in to this relatively derived quantity quite quickly, and would benefit from spelling out some of the signals in the raw data, and how these are brought together into [CO32-]as and other related properties. In particular, I was left wondering about the other components of ocean carbon storage (e.g. remineralised carbon) and their fingerprints on the carbonate chemistry and other reconstructions here. Can we learn something about remineralised carbon storage from these data or not? This is particularly important as the topic is currently in vogue (see e.g. the Volmer et al., 2023 paper in Paleo) and as this question naturally arises from several points in the text. For instance right from the abstract, line 19 highlights "carbon losses from the Deep South Pacific to the atmosphere"; this to many readers will I think give an image of release of a deep carbon reservoir which others have suggested has a large remineralised carbon component. But the main text description and discussion of the signals is very much focussed on preformed signals in the Southern Ocean surface. I can see ways to bring these different ends of the glacial carbon storage system together, but it would I think be very helpful for the authors to spell this out more explicitly, both by describing the tracer in more detail and its relationship with other ways of thinking about deep carbon storage and release (e.g. remineralised vs preformed carbon) in the introduction and the initial sections describing deglacial carbon loss from the deep ocean.

Which water are we really feeling?
The authors claim that their record is indicative of processes in the PAZ. However this needs to be better substantiated for a couple of reasons. While I agree with the authors that the core will be dominantly influenced by SSW, not all SSW is necessarily sourced from the PAZ. For instance in the Gebbie and Huybers (2010) deconvolution of deep water sources, this core site would have about 50% water from the PAZ, with additional, subequal contributions from the PFZ/SAZ and NSW (the NSW component is indeed nicely picked up in the low PO4* blob in the section figure).
[The proportion of SSW at this site and how this is tracked by PO4* is, in addition, strongly influenced by the role of entrainment in the SSW PO4* end member signature, discussed further below.] Related to the major comment above about preformed vs remineralised signatures, I'm also left wondering how I should think about timescales of change at this site compared to the atmosphere, given that it will have influences both from relatively recently ventilated water from the south alongside return flow from the Pacific. Should I think of this as being in water that has recently left the PAZ so quickly picks up changes sourced from PAZ-atmosphere interactions? Or does it also have a component of return flow from the Pacific, rich in remineralised carbon, having left its surface source regions perhaps several thousand years earlier? A mixture of these to me seems likely and I think some discussion of this, alongside the different carbon signatures being felt here as discussed above, would benefit the paper.

Structure of paper / structure of millennial vs HS1 changes
I read through the section on millennial changes wondering why the earlier and later parts of HS1, which clearly have very different signatures, were being lumped together. I then realised that they are discussed in more detail in the next section on Bio vs Physical carbon loss in HS1. However I think this current structure risks confusing readers. I'd suggest at least flagging in the millennial section that there are two distinct parts of HS1 that will be discussed further below.
I also suggest using the general/orbital section to better discuss the tracers and the nature of carbon loss, addressing the major comments above.

Early HS1 [CO32-]as change?

The text discusses there being a [CO32-]as change in both the early and late part of HS1, and from reading the text alone without looking at the figures one might assume these [CO32-]as changes are similar in size. However from looking at the figure, it's unclear whether there really is a significant [CO32-]as change in early HS1, whereas the late HS1 change is substantial. Modify the text to address this directly - is there perhaps even something interesting one can say about the different sizes of these changes are their relationship/slope compared to other tracers that may further point to mechanisms?

Plotting error - is there an interesting centennial signal?
The relative phasing of the data in Figure 2 and ED Figure 1 is not the same (and I realise that one is in age space, the other in depth - the issue lies in the phasing of proxy signals within the same core). In ED Figure 1 the notable spike to low [PO4] at 150 cm is simultaneous with a sharp jump up in [CO32-]as. Taken together these signatures are really interesting in terms of mechanism - and are also particularly interesting given some of the very rapid changes in deep sea coral data around this time (e.g. Li et al., 2020). However in Figure 2, the sharp drop in [PO4] at 16.3 ka has no accompanying feature in [CO32-]as - the jump up comes 500 years or so later.
If the jump up in [CO32-]as is associated with a drop in [PO4], then this does have implications for mechanisms and should be addressed. Specifically, at present the late HS1 rise in [CO32-]as is discussed as being associated with rising PO4, leading to the implication that this outgassing change comes about through reduced biological pump efficiency. However if this major jump up in [CO32-]as (which is about half the overall late HS1 change) is in detail associated with a drop in [PO4], then this surely challenges that interpretation, at least within this interval? Rather, it might fit better with the coral 14C younging that happen at this time, indicating a pulse of pronounced ventilation that outgasses CO2 and flushes well-ventilated, low nutrient waters through the water column.

Line by line comments

43-46 - [CO32-]as is the main focus of this paper and is still a relatively new tracer. I think the paper (and certainly its readers!) would benefit from some more description of this tracer here and also in the methods. This doesn't need to be exhaustive (you can reference the previous work for more details), but it should be enough for the reader to get a feeling how this is calculated and what it indicates in more detail than currently provided. It should also discuss how DIC is calculated from this tracer, which appears out of the blue later in the paper, and would similarly benefit from introduction.

73 - jumps straight in to very derived property/concept. My preference would be to step through the glacial state you have first and the different components to the carbon storage (e.g. both preformed and remineralised), then how they evolve over deglaciation.

78 - unclear as written - an increase in Northern water, which is increasing its [CO32]as, sounds like it could contribute to the signal of increasing [CO32]as. Key missing logical step is I think the different [CO32]as signatures of NSW vs SSW: as NSW has lower absolute [CO32]as, this may be expected to dominate. I realise this is what the mass balance calculation in the sentence that follows is meant to spell out, but it's not very clear for a non-expert. Add a short clause of descriptive explanation here and a fuller explanation to Figure ED4 caption, which is referenced here, but doesn't have this level of explanation in the caption.

81 - the NSW contribute to - unclear writing.

82/83 - this seems like it would also benefit from being shown in a figure - perhaps an additional panel to Figure ED4.
Also what does the PO4* suggest about water masses?

85 - a key point (also mentioned above) that is not discussed in enough detail is whether we can explicitly link changes at this site to the PAZ, vs other regions of the Southern Ocean. The core is not in a region of pure PAZ-sourced AABW and likely also has a component of water ventilated along sloping isopycnals in the PFZ/SAZ (as well as the NSW which is discussed).

86 - raised —> rose

90 - being —> is

92 - if of varying

91-93 - again I don't find this list of numbers particularly helpful in getting a sense for how big a deal this is - would much rather see in a figure or a table.

94 - "the latter of which" is odd here - would seem like it would only be referring to O2, but think you mean PO4 and O2?

110-111 - where do these numbers come from?! I understand how you calculate [CO32-]as, but not how you then go to (presumably) DIC to get total Pg carbon.
Also, critically, if you are going to extend the calculation to the whole deep Pacific, you really need to say something about the other proxy records in this basin (especially DCO32-, PO4, O2) - are they consistent with the signals here allowing you to extrapolate to the Pacific below 1500m?

112 - is this really sizeable? Pacific below 1500 m is likely main deep ocean carbon store. If need to account for at least another 400 PG and maybe as much as 800 or 1200, then where does the rest of the carbon come from?

115-129 - “throughout HS1” - actually the big change in [CO32-]as and PO4* is late HS1.
130-139 - linked but conversely to the point above, the 14C change happens entirely during early HS1, and is associated with no change in [CO32-]as! Seems like this is trying to tell us something. Alternatively, if the authors don’t think the age model is robust to this, need to be up front about it. What do the benthic-planktic data look like?

143 - Stewart et al. (2021) paper also nicely shows this and reaches similar conclusions.

166 - only significant change seems late HS1. Certainly a very different magnitude / slope of change if there is any change at all, and can’t just brush over this.

168-169 - this sentence is very hard to follow

171 - given what you say about sea ice I think best to omit “likely stay unchanged” - if your sea ice and 14C interpretation is correct, then it likely increases.

174 - if you are really in PAZ waters, then how influential is any likely change in temperature? Probably stays pretty cold!

176-177 - this is really not clear to me and I think will be completely opaque to majority of readers. Rephrase to make more clear what you mean. I’m left unsure whether these are expected to drive a change in PO4* or not.

180 - very unlikely that no change in physical O2 recharge if there is a change in 14C, as 14C takes much longer to equilibrate than O2.

186 - this younging in 14C occurs notably earlier than coral 14C data: with the exception of the transient younging pulse at 16.1 ka, the main younging is all in late HS1. This is also true of most of the younging in the Skinner record. Why the discrepancy?

191 - This is nicely supported by Gray et al. 2023 reconstruction.

195 - “14C further declined” - this makes it sound like it’s comparable to the much larger earlier change. As with the points made above on the magnitude of [CO32-]as change in the different parts of HS1, you need to be up front about the different magnitudes of these signals.

198-199 - hard to follow what is meant here. Even if more details are provided in the Yu et al. 2019 paper, the reader shouldn’t have to go to this to get a general sense for how this calculation works.
Also if this calculation is done for DIC in late HS1, what is the equivalent calculation for DIC in early HS1? I would think minimal as there’s to my eye very little [CO32-]as change, but the text discusses [CO32-]as change in early HS1, so maybe there’s something I’m missing? Having the equivalent calculation for both may be helpful.

200-201 - this might not be minor if there was a major change in sea ice

208-210 - interesting and important point but unclear as written

229 - 1 sigma or 2 sigma?

261-262 - rephrase - this isn’t considering *all* the uncertainties as it doesn’t take in the calibration uncertainty, which is more like ±0.2 umol/kg.

268 - need to at least give a brief description
269 - similar to point above, but even more importantly, you really need to give more information here (and ideally also in the main text). [CO32-]as is totally central to this paper and is still a relatively new tracer, being only previously used in a couple of other papers from this group. While I realise that thinking about [CO32-]as probably now seems very natural to Yu and co-workers, it is still new enough that the rest of the community will continue to need some explanation - especially when it’s as key to a paper as it is here. Indeed I think the paper would benefit from additional description in the main text too to help build intuition.

271-275 - I agree in principle with the correction for global alkalinity change and it’s very helpful to see figure ED1 that shows the [CO32-]as signatures both with and without this correction. However this figure (ED1i) also makes it apparent that the vast majority of the glacial-interglacial change in [CO32-]as from the oldest to the youngest samples comes about from this correction. This really needs to be discussed explicitly in the main text section on orbital scale changes.

286-287 - why does air sea gas exchange cause reduced nutrient utilisation?

303 - this is highly dependent on what end member is used for the SSW - the AABW signature in the source region vs the signature that incorporates entrained CDW. Rae and Broecker (2018) show this changes the SSW:NSW fraction in the deep Indo-Pacific between 50:50 and 75:25 respectively. Some discussion of this is needed, as it also has implications for what you are reconstructing in terms of SSW end member. Similarly, the influence of entrainment on the PO4* signature of the Southern end member should also be mentioned - this has an important influence today, is notably different in different

regions of the Southern Ocean, and may have also changed in the past. These are, I realise, not easy things to constrain, but it needs at least some discussion.

323-324 - LCDW - not really a sentence.

Figure 2
328—329 - if crosses really indicate age ties then these look unconvincing. Are the crosses 14C control points and the triangles the ties?

331 - is the PO4 data also really including calibration error? Based on the different choices possible in Figure ED2, I would expect calibration error to be larger?

Figure ED1
- Please show benthic-planktic 14C data here too

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
R1 review of Dai and Yu, "Deglacial polar Southern Ocean carbon release driven by biological and physical dynamics," submitted to Nature Communications, by Jesse Farmer

The authors have taken significant steps to revise their manuscript following detailed reviewer comments. I appreciated the time and care they put in the responses to reviewers and the clarifications added to the manuscript. There are still some outstanding issues that need addressing related to the clarity of the presentation; I've highlighted these as major comments. Ultimately, although I may not fully agree with the presented interpretations, I think the authors provide valuable additions to the discussion of the ocean's mechanistic role in deglacial atmospheric CO2 increases that should be open to broader discussion. Thus, I support publication once the below comments are addressed.

Major comment 1. L198-203. I'm not following how it is plausible for sea-ice to be sufficiently reduced to allow for CO2 isotopic equilibrium (and hence 14C equilibrium), but not CO2 concentration equilibrium (which is ~an order of magnitude faster). This is all the more confusing because the authors later call on a concurrence of CO2 isotopic and concentration equilibrium during the Younger Dryas (L257-261). The authors should revisit the explanation; they can also allow that their interpretation is not consistent with other paleodata and worth further investigation.

Major comment 2. L162-170. This paragraph needs some work. There should be a more clear comparison between the [CO32-]_as-derived DIC sequestration estimate and the [PO4*]-derived DIC sequestration estimate. For instance, you could add in on L166, "This DIC sequestration is larger than that estimated from [PO4*] of +58±18 µmol/kg". Then the sentence on L167-170 should be clarified: It appears you are ascribing the DIC sequestration from [PO4*] directly to biological processes, whereas the additional DIC sequestration from the [CO32-]_as indicates a further contribution from physical processes, such as a sea ice barrier (and add references for this mechanism).

Ultimately, the I found that the paragraph on L204-218 did the best job of outlining the various quantitative datasets, comparing them, and reaching conclusions on relevant mechanisms. This should be adopted to the other paragraphs.

Major comment 3. L116-136. As someone who loves thinking about endmember compositions, even my head is spinning from all the values presented here. I'd strongly recommend adding a table of modern NSW, modern SSW, LGM NSW and SSW endmember values, percentages estimated for the core site, and derived values for the core site to aid the reader through this text.

Minor comments.

Title: "driven by biological and physical dynamics" is rather vague. Perhaps "Biological and physical contributions to deglacial polar Southern Ocean carbon release" or similar?

L26-27. Suggest adding "during the Late Pleistocene glacial-interglacial transitions"

L39-40. Suggest specifying "…quasi-conservative properties of deep waters set by the PAZ surface".

L55. Remove unnecessary comma after "(3)"

L58. Cite refs. 19 and 20 at the end of this sentence.

L70-74 and Fig 1. This discussion has been greatly streamlined. One note, I'd highly recommend making the color step the same unit in panels a, d (5 or 10 µmol/kg) and b, e (0.1 µmol/kg). This allows the reader to simply visualize how much PO4 changes relative to PO4*.

L80. Change to “may allow for distinguishing the…”

L88-89. Strongly recommend briefly stating those proxies here in 1-2 sentences. There is space in the main text and it prevents the reader from having to flip to the methods three times.

L101 and throughout. Note that the new supplementary figures appear out of order with their presentation in the text; these will need to be reordered. For instance, Fig S5 should become Fig S2.

L105. Add space between [CO32-] and "at"

L108, L114 and elsewhere. Recommend changing to “organic matter” as "matter" is typically indicative of a plural quantity.

L111. Remove comma or swap “that” with “which”. The options are either “…change, which is” or “…change that is”

L142. Suggest adding hyphen: “physically-driven”

L144-145. The authors should cautiously note here that the atmosphere-ocean exchange times for O2 and CO2 are not equivalent (e.g., Broecker and Peng, 1974), but that difference may be expected to be mediated by the millennial-scale integration of their sediment records.

Reference: Broecker, W., and T. Peng (1974), Gas exchange rates between air and sea, Tellus, 26(1–2), 21–35.

L156. Suggest changing to “which are presumably biased toward the spring-summer seasonality of phytoplankton blooms that are offset from wintertime deep water formation”. Although the OAZ-PAZ difference might also be important, it would take more detail to explain why than is provided here, and so I think it best to not dwell on this difference. (Alternatively, the authors could devote several sentences to explaining why the OAZ would be expected to be distinct from the PAZ).

L167. Change to “combines”

L190. Change “using” to “in”

L200. Change to “enhanced”

L204-218. As noted above, nice paragraph here – I find this argument convincing.

L227. Delete the repetition of “at our site”

L230-239. See Major Comment 2. As you did in L204-218, you should include the magnitudes of DIC change inferred from both PO4* and CO32-_as to support the statement of physical changes being necessary (L238-239).

L257-261. See Major Comment 1. I find it really challenging to have radiocarbon ventilation work with CO2 outgassing at one point, but without it at a previous point.

L262. Suggest changing to “Conclusions”

L265. Change to “partitioning”

L267-268. Recommend changing to the following: “…were mediated by biological and physical processes both between the LGM and the Holocene interglacial, and on millennial timescales during the deglaciation”

L270. References should be added here.

L274-275. Specifically, PAZ CO2 outgassing as diagnosed in this study

L275. “was reduced”

L278. Change to variability (it is also plural)

L279-280. Specify your approach – namely, reconstructing CO2 exchange through PO4* and CO32-_as

L281 (Methods throughout). The equations should all be set on separate lines, and not in-text (see L312, 317, 336-337, 349, 355, 356, 358, vs. L415, 416, 419, 420...)

L301-304. How was d18O and d13C precision quantified? What standards were used for normalization?

L310-346. It appears the [CO32-] reconstruction paragraph should be presented first, as the Monte Carlo approach is referenced in the [PO4] reconstruction paragraph. However, as the [PO4] paragraph currently comes first, this Monte Carlo approach has not yet been introduced.

L313-314. Add comma before “which”

L351. Missing reference.

L383-385. I believe these should be combined into one sentence.

L506. Caption panel f. Specify “Deep-sea coral-bound”

Reviewer #2

(Remarks to the Author)
General remarks:

The authors have substantially reorganized the manuscript since the first submission, and the submission is much improved. The authors have clarified the conclusions of the paper in such a way as to make the significance clear, and there is considerably more discussion of the background necessary for the interpretation of the PO4* and [CO32-]as data. For example, the utility of the tracer pair is made clear, particularly by Fig. S1. They have removed discussion of the sub millennial scale variability in early HS1 (18-16.3 kyr) from the text, which I think was not justified in the previous draft given the lack of statistical significance in the measurement, and instead discuss on the lack of change during this time.

More detail has been added clarifying the significance of their reconstructions in the context of existing records of nutrient utilization efficiency (e.g. δ15N records), which I felt was unclear or not present before. The authors results serve to confirm the conclusions of existing δ15N records from the OAZ and provide a complementary constraint to existing records that may have been governed by different processes (although it appears that they are in fact consistent).

The discussion of the sensitivity tests was confusing before in the previous draft, and I think the text benefits from the authors' decision to summarize these in the supporting material. I think that the added sensitivity tests details in Fig. S6 and S7 also substantially improve the paper.

All in all the authors should be congratulated on an improved manuscript that reads logically and mostly clearly.

Specific Comments:

I was perhaps unclear with regard to the core top values of PO4* and [CO32-]as in the previous draft. My point was that, given the placement of the core top values in Fig. 2F and Fig. 2G, it would seem that the values you are calling Late Holocene (4.2-0 kyr) identify no change between 8 kyr to Late Holocene in PO4* and CO32-as , which I found surprising. I take your general point in your response that this study may not be suitable to examine these features between 8kyr and Late Holocene. However, upon looking at the latest version of the data (I believe Fig. 3F is comparable in the new paper to Fig. 2G in the first submission), it appears that there is now a substantial difference (~15 µmol/kg) between the Late Holocene and 8 kyr values in CO32-as. This wasn’t present in the previous version of the paper. What is changing between the two versions of the paper that is driving this large change? The change in the LH value is on the order of that observed across the YD or ACR in your data, so is a substantial change to be seeing between two separate submissions.

Line 101-102 is a bit misleading. You are discussing the increase in bottom water O2 from the LGM to the LH, which is ~75 µmol/kg – but then you say that that change is similar to previous records. The record you show in Fig. S5 has no Late Holocene data whatsoever. The two records are impressively close in behavior and magnitude, but Fig. S5 does not back up any statement about LGM to LH change being similar to previous records.

Forgive my confusion, but I thought you might clarify lines 110-112 a bit further. It feels like you are building towards an obvious conclusion for the reader about the sums of these multiple factors, but as I understand it, the measured increase in [CO32-] is 13 µmol/kg and the expected changes you list are an increase of 5 µmol/kg (PO4 decrease), a decrease of 26 µmol/kg (global alkalinity and DIC decline), and a decrease of 2 µmol/kg from T/S/Depth changes. I could easily be reading it wrong, but it feels like lines 110-112 imply that the numbers you give in the preceding lines should in some way sum or difference to 39 µmol/kg – but looking at the difference between reconstructed [CO32-] and the three factors listed above doesn’t give 39 µmol/kg (difference between an increase of 13 and a decrease of 23). I say this because the way you listed the factors driving your calculation of CO32-as in lines 52-57 make it feel like these factors should give you the number back for your LGM to LH change that you give in the paragraph.

Line 227 is also a bit confusing. It looks to me like the changes in of PO4* and [CO32-]as during the ACR are ~0.25 and ~10 µmol/kg, respectively (Fig. 3C and 3F). It seems like a 30% decline in SSW% (going from 100% to 70%) could then, in fact, account for the reconstructed magnitudes almost entirely. Unless I am missing something with the calculation, I feel that this statement is not supported.

Line 246: Why assuming little change in NSW%, if you mention that SSW% declined? I think I know what you mean but this could be clearer, as it seems like from line 242 you would assume some change in NSW%.

Line 251-252 is not clearly written. Should this be "driven by changes in SSW endmembers"?

There are small typos and grammatical errors throughout the text that I encourage the authors to correct prior to another resubmission. For example, the first line of the abstract is, to my understanding, not grammatically correct – I think you cannot be "deemed as a region regulating…", and I think "important implications" would be referring to changes in the polar Southern Ocean. I also was curious what the other part of "in part" is (line 13) – this seems like the main challenge for this region.

Another easy but obvious small error is that the references are not carefully formatted throughout -Line 35 for example. Also, they appear to have forgotten a reference listed in line 351 (ref. XX).

This is a personal preference, but the use of δ in the figure labels for Fig. 3 is not intuitive to me, given its common usage as other notation for isotopes. I would prefer personally if they were replaced with Δ if you are seeking to indicate change relative to some average (in this case LGM values). This would make it consistent with you calculations lines in the Methods section (Lines 354-360, for example).

Reviewer #3

(Remarks to the Author)

The authors have done a good job addressing my concerns and I found the paper significantly strengthened. I found the addition of the sensitivity tests in Figure 3 particularly helpful, along with the improved description of the [CO32-]as tracer and the restructuring. It is worth noting though that despite the improved description (and having thought about this quite a bit), it took me some time to get my head back into [CO32-]as space, and this will likely be true of your readers. I suggest taking on a description similar to that in Gruber et al., 2009, as per the comment on line 53.

I have a series of comments below that I think should be addressed prior to publication. These include minor typos and ways to improve the clarity and robustness of the argument, but also a couple of more major comments, including an important point on the sensitivity of the [CO32-] DIC calculation under altered whole ocean alkalinity.

12 – “is sparse” would be much better after “evidence”

14 – “challenges in obtaining”

21-22 – “biologically unutilized carbon as a key source for deglacial CO2 outgassing in the polar Southern Ocean” – not super clear. Suggesting leading this sentence with what you actually see in the signals in HS1 (e.g. rising PO4* and [CO32-]as) and how this allows you to infer a shift from lower preformed nutrients and high carbon uptake to higher preformed nutrients and lower carbon uptake.

22-23 – “relieved gas exchange disequilibrium” is confusing as written. This sentence and the abstract in general would also benefit from more explicitly discussing the HS1 and ACR as well as the YD change.
Also note that, as discussed in more detail in comments on lines 164-170 below, the whole ocean change in ALK and DIC is I think a significant contributor to the glacial-interglacial change in carbon uptake calculated from [CO32-]as.

30 – I think some more nuance is required here, as in general biological processes are not thought to have much influence in the PAZ. While biology is always somewhat tied in to carbon and nutrient balance, and may play a role indirectly too via global increase in respired carbon storage at the LGM, the observation that export is lower in PAZ at LGM and increases over deglacial goes in the wrong way, in isolation, for biology to be key in enhancing deglacial outgassing in the PAZ.

45 – “in deep-water formation regions”

49 – “Recently, a tracer of the air-sea exchange”

53 – both here and in figure 1 caption I think it would be very helpful to reference the Gruber et al. (2009; GBC) DC_gas-exch property. This is conceptually equivalent to [CO32-]as and that paper explains it very clearly.
More generally, while I found the revised manuscript easier to follow, I would still encourage the authors to expand their introductory description of this tracer at some point here or in the sections below, with a few lines on how it is set in the North Atlantic (which is a nice easy case) vs AAIW (another useful end member) vs SSW from the PAZ (which is less clear than NADW or AAIW yet is central to this paper).

64 – delete “on the other hand” as this sentence isn’t really in tension with the previous one – they both have the same general sense.

78 – not strictly quite true – you discuss below quite extensively that both biological and physical processes might influence PO4* via gas exchange influence on O2. I agree this may not be a super sensitive effect, but it’s not nothing.

93 – add “and uncertainties on derived properties are given at 1 sigma throughout”.

99 – 102 – briefly mention here or in text immediately prior to this results section above that only perform the derived tracer

calculations where you have paired data from the same sediment depth. This is important given the different temporal extents of the different datasets.

100 – unclear whether Late Holocene data is from forams or water column (line 483 says "late Holocene data" which seems like forams, but I can't find these data anywhere – they could for instance easily go into the supplemental figure on core depth). Forams would of course be preferable but I understand that this might be limited by abundances. Water column is ok especially as the youngest data in the core seem to align well with these values, however would still benefit from brief justification e.g. Have the youngest data (which from the figures appear to be ~8-10 ka) been aligned to water column values, such that the B/Ca data down core is anomaly from modern values (i.e. taking account of any calibration offset)? If so, there needs to be justification about why it's ok to do this with Early Holocene data and that we don't need to worry about an EH peak in e.g. B/Ca.

107 – add reference to figure 3 after "compared to the LGM"

110-111 – note here that this model dependent – stating just that it influences by 26 umol/kg makes it sound as if we know this precisely. It might be 26 umol/kg, but it could alternatively be 15 or 40, we really don't know. Should also note that while this is a big influence on the size of the glacial-interglacial change, it shouldn't substantially influence the structure or timing of the deglacial changes – can also reference S7.

116 – Fig S8   S6

138-139 – might it be possible to give some feel for how much is physical vs biological based on the O2 and PO4 signals themselves? i.e. O2 has a more striking change than PO4 – might this point to an important role for physical processes?

140 – I think jumping straight to DIC is a bit unclear. More straightforward would be clearer to say biologically unutilized phosphate and associated DIC.

148 – "declined … ratios" – unclear, rephrase

150-153 – there's some important nuance that I think should be added here (and below), in that biological export production in the PAZ is lower at the LGM compared to the late Holocene, so increased biological usage would need to be relative to supply. Many readers not super familiar with the field would read this sentence as indicating greater biological productivity, rather than utilisation relative to supply.

154-155 – I don't think "storage" is quite the right word here. Storage suggests carbon at depth, whereas these preformed signals are I think better linked to "uptake" or "reduced outgassing" or "improved nutrient and carbon usage efficiency". This could then lead to net improvement in deep storage; I think this nuance should be mentioned. This is particularly the case given the comparison to nitrogen isotopes that follows – these explicitly track surface utilisation efficiency, rather than deep storage.

162 – again slightly confusing sentence; at least needs an "improved" in front of efficiency

163 – maybe add "more directly" between "also" and "demonstrates"

164-167 – one key concern here is on the sensitivity of [CO32-]as to DIC change (which I think is assessed based on modern ocean data) and how this would change under overall higher ocean ALK and DIC at the LGM?
There are two related issues:
The first is that authors are using higher ALK and DIC based on model results and while this will not alter the structure of the deglacial change (as discussed above and in Figure S7), it will impact the value calculated here, and I think this should be acknowledged.
The second is that if the ocean has higher overall ALK and DIC, it seems the relationship between [CO32-]as will likely be different. I have tried looking in to the references given here about how this sensitivity was established but couldn't find an easy answer to this and I think it should be as least briefly discussed.

167 – "Different from PO4*" – there's the need for a bit more nuance here, as you've discussed above how physical processes can also influence PO4* via O2 disequilibrium, so this sentence jars a bit compared to the text above. I think the resolution to this point is your argument that at least some of that O2 disequilibrium may ultimately be derived from biological utilisation, and it would be helpful to reference this briefly again here.
The other important point here relates to the comment above, which is that a substantial portion of the [CO32-]as comes not from within ocean biological or physical processes, but from whole ocean carbon cycle change, so doesn't fit neatly within this biological vs physical partition. This should be explicitly discussed.

168 – "combines"

170 – again as above, a chunk of this is from whole ocean change and this should be specified.

182 – "contribution"

194 – "changes in"

202 – “only enhance CO_2 outgassing in the PAZ negligibly” “but had minimal impact on CO_2 outgassing”

203-205 – confusing as written – seems to imply that warming, which lowers solubility, limits outgassing! I think you are trying to say that it stays fairly cold, which means that there’s not much solubility-driven change

206 – here and elsewhere “late HS1” is I think neater than “the late HS1” – but feel free to ignore

209 – as above, is this really minor if O_2 change is much bigger than PO_4 change?

213 – again, I worry about sensitivity of this DIC value to higher ALK and DIC, as mentioned above

217 – the timing of this change in $[CO_3^{2-}]$ also fits carbon release during the deep convection pulse suggested by Li et al. (2020, Science Advances)

223-224 – again, thinking about O_2 in isolation likely useful here – high NSW input would be unlikely to drive low O_2. The low O_2 also nicely explains the gap in deep sea corals at this time (see Stewart et al., 2021, Paleo)

230 – why “possibly” given argument above – “likely” seems more likely!

241 – remove “in the both”

258 – 8 out of 40 would be better described as “minor” than “negligible”

353 – ref xx!

375 – unclear as written

380 – give the rationale for this (I went digging through the previous papers and found it but would be handy to mention briefly here)

484 – foram data or water?

Fig S2 – would be helpful to also see the Mg data

We thank all three reviewers for their very detailed and constructive comments. Below, we provide our point-to-point responses to the *reviewers' comments*.

Reviewer #1 (Remarks to the Author):

Review of Dai and Yu, "Deglacial polar Southern Ocean carbon release driven by physical and biological dynamics," submitted to Nature Communications, by Jesse Farmer

Dai and Yu present new deep ocean B/Ca-derived carbonate ion, Cd/Ca-derived phosphate concentration, and d13C gradient-derived oxygen reconstructions from a sediment core in the Southwest Pacific Ocean tracking (largely) the properties of Southern Sourced deep waters over the last deglaciation. The authors translate this proxy data into information on changes to preformed phosphate and air-sea carbonate ion change to track the influences of Southern Ocean biology and gas exchange on carbon dioxide partitioning between the ocean and atmosphere over the last deglaciation.

There is a lot to like in this manuscript. It is overall well written, the figures are excellent, and the combination of proxies applied is novel and potentially quite transformative. At the same time, I feel that the authors are trying to reach a conclusion on the role of sea ice cover in deglacial ocean-atmosphere CO2 exchange before they have fully "paved the road" of proxy understanding that would allow the reader to get on board with this interpretation and exclude other alternatives. For this reason, I think the results would actually be more influential as a longer contribution to a field-specific journal where the proxy interpretations, and, most crucially, the covariance between these new proxies (see below) can be more fully explored. It may even be beneficial to split this into two manuscripts, one longer-form outlining the combined proxy approach and its uncertainties, and the second a shorter-form application to the deglaciation with its climate system implications.

We thank the reviewer for the positive comments, and appreciation of the amount of work put into this study. Following the reviewer's comments, we have expanded discussions on original proxy records, contributions of original proxies to the derived tracers, and some alternative explanations for our data that we dismissed. These will follow the reviewer's comments.

Major comments (not in order of importance):

1. Age model development.

The C. wuellerstorfi d18O (ED Fig. 1) does not lend confidence in the age model construction that is based on G. bulloides Mg/Ca correlation to EDC dD (Dai et al., 2020). This is of crucial *importance for the sea ice interpretation of outgassing in early HS1 – if the timing of HS1 is not correctly assigned in this sediment core, then the relationship of PO4* to sea ice (ice core ss Na) is uncertain. Unfortunately, I don't find the chronological establishment here sufficiently compelling/precise as to allow for the discussion on L166 and onward, which is the crux of the current paper. Perhaps the published radiocarbon evidence can be brought in here, or other SST proxies can be measured to refine this alignment?*

We agree with the reviewer that a robust age model is the foundation to discuss changes during HS1. Our age model enables us to discuss these changes within our records from the same sediment core and between our records and other records. This point, which was not properly emphasized in the previous version, is now made clear in the main text (Line 92). Our age model during HS1 is based on planktic Mg/Ca-EDC δD correlation in (Dai et al., 2021), as well as 4 radiocarbon dates during HS1 reported in (Dai et al., 2022)(2 in the early HS1 and 2 in the late HS1). These age constraints allow us to resolve millennial timescale changes, including distinguishing the early and late HS1, despite uncertainties in absolute ages.

To demonstrate the robustness of our age model, we have plotted our data based on an alternative age model discarding the planktic Mg/Ca-based tie point. Similar patterns of the records to that shown in the main text, especially within HS1, prove that our age model is robust in discussing these features. (Fig. S3).

The second point raised by the reviewer is the slightly delayed benthic δ^{18}O decline during HS1. This appears to be a common pattern that has been observed in the region previously. In Fig. X1, it is shown that our data is consistent with another well-dated site nearby, which further lends support to our age model.

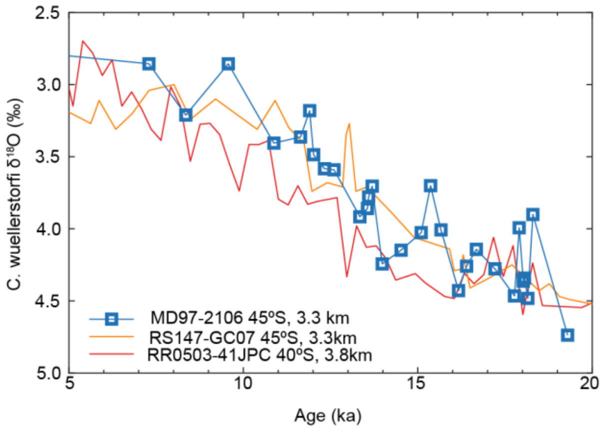

Fig X1. benthic δ^{18}O at site MD97-2106 compared to two other SW Pacific sites in (Sikes et al., 2016).

2. Sea ice, or not? The authors take a strong position on the role of sea ice in the abstract "…physical dynamics involving sea ice retreats (sic) dominated CO2 outgassing…" (L22) but are rightly more circumspect about this in the main text "However, relative roles of biological and physical processes to the PAZ outgassing remain ambiguous on both millennial and glacial-interglacial timescales…" (L157-158). More clarity on the relative contributions of sea ice and their timing would be beneficial.

We clarify the contribution of the gas exchange disequilibrium imposed by sea ice in the abstract (Line 22) and the main text (e.g., Line 255). In short, our PO_4* and $[CO_3^{2-}]_{as}$ changes show that sea-ice related gas exchange disequilibrium contributed to deglacial CO_2 outgassing during the YD and minimally contributed to HS1 CO_2 outgassing.

3. Tracer interdependence. PO4 and [CO32-]as are not independent tracers, as both depend on Cd/Ca-derived [PO43-] (L48-49, 66-69). That suggests the difference between the two is largely driven by carbonate ion and oxygen… but it is not at all clear what to make of the distinctions between the two tracers. On the one hand, it's interesting that the two show slightly offset patterns in time… but on the other, it's not surprising that the two look similar (Fig. 2f, g). I would appreciate more guidance from the authors on what to make of this interdependence.*

The reviewer's concern is valid in that Cd/Ca-derived $[PO_4^{3-}]$ contributed to both PO_4* and $[CO_3^{2-}]_{as}$. In the revised version, we add a new figure (Fig. 3) to show contributions of underlying proxies to PO_4* and $[CO_3^{2-}]_{as}$. As shown in this figure, $[PO_4^{3-}]$ is a minor contributor to millennial-timescale variabilities in PO_4* and $[CO_3^{2-}]_{as}$.

4. NSW and SSW endmembers + contributions over time. The authors note that the advantage of PO4 and [CO32-]as is that both tracers are quasi-conservative in the ocean interior (e.g., L50-60). However, the downside of this is that these proxies are set by the endmember values of NSW and SSW and their relative contributions to the core site. It is known from the authors' previous work that these endmember values are not stable over time (e.g., Yu et al., 2019 for [CO32-]as in the N. Atlantic); indeed, the goal of this study is essentially to reconstruct the SSW endmember PO4* and [CO32-]as over the last deglaciation (e.g., L63-65). To this end, it is critical that the authors know the contributions of the relative endmembers. In my mind, their approach of assuming a percentage contribution of SSW and allowing it to vary (e.g., L290) leaves much to be desired, especially as proxy data (Nd isotopes) may help address this question for them.*

In the new version, we focus on discussing SSW endmember changes based on our best estimation of SSW% and NSW endmembers determined from literature data (including Nd isotope (εNd) data for SSW%, previous North Atlantic records for NSW endmembers). Sensitivity tests (now moved to the supplementary materials, Fig. S8) support estimations based on our assumptions. This is because our site was dominantly affected by SSWs over the last deglaciation (with SSW% over 70%), any variability of the SSW% at our site during the last deglaciation would be expected to be small.

Our assumptions about SSW% at our site are based on εNd data in the region. However, we do not directly use εNd data to infer SSW% changes in the SW Pacific. This is because εNd has different endmembers (the North Atlantic and the North Pacific) from PO_4* and $[CO_3^{2-}]_{as}$ (the North Atlantic and the Southern Ocean).

5. Presentation of results. The authors do not discuss their underlying proxy reconstructions, instead they move directly to the derived tracer products (PO4 and [CO32-]as). This is unfortunate – the most directly calculated results should be presented first, and only after that a discussion of the interpreted derived products. Such additional length would allow for further investigation of intriguing features in the proxy data – for instance the offsetting (in both depth + age space) of carbonate ion, oxygen, and phosphate concentration deglacial maxima/minima (Fig. 2c-e). Might this relate to the relative depth habitat of the foraminifer used? (C. wuellerstorfi being ~sediment/water interface, H. elegans perhaps being infaunal, G. affinis being deep infaunal)?*

In this work, we aim to focusing on interpreting derived tracers, which have the advantage of avoiding some alternative explanations related to local processes for the most directly calculated proxies. However, the reviewer's point that in the previous version we moved on to discussing PO_4* and $[CO_3^{2-}]_{as}$ too quickly is valid.

To address the reviewer's concern, we now expand background of PO_4* and $[CO_3^{2-}]_{as}$ in the introduction, and use distribution of deep-water $[CO_3^{2-}]$, $[PO_4^{3-}]$, $[O_2]$, PO_4* and $[CO_3^{2-}]_{as}$ in the preindustrial ocean to better illustrate the strength of PO_4* and $[CO_3^{2-}]_{as}$ (Fig. 1, S1, Line 69). In this version, we also started our discussion from directly reconstructions (Line 98). We avoid directly interpreting their implications for carbon cycle changes but explain the contribution of their variabilities to the derived tracers aided by Fig. 3.

We discount the varying depth habitats of employed benthic foraminifera as the driver of the observed changes in the supplementary material (Line 385). The possibility that some of the subtle offsets between the proxies are caused by varying habitats of benthic foraminifera employed for proxy reconstructions cannot be fully ruled out. These features are however not the focus of our interpretation. We focus on millennial-timescale changes in our core (including the different changes during the early and late HS1), which are not affected by this effect, due to bioturbation and relative high sedimentation rate. This is can be supported by similar $\delta^{18}O$ patterns of the epifaunal species *C. wuellerstorfi* and the deep infaunal species *G. affinis* (Fig. S2e) (*H. elegans* being epifaunal to shallow-infaunal (within top 0.5 cm), thus between these two species in the habitat depth profile*)*.

6. Uncertainty on PO4 and [CO32-]as. There does not appear to be an effort to estimate errors on PO4* and [CO32-]as aside from those relating to the individual proxy reconstruction of carbonate ion, oxygen concentration, and phosphate concentration. At the very least, the errors of each required measurement will add in quadrature; in addition, further error will result from assumption of Redfield stoichiometry (see modern ocean uncertainties in these ratios from Anderson & Sarmiento, 1994). A more comprehensive handling of uncertainty in these new tracers will be needed than is presented in the main text, figures and methods.*

The method for propagating errors using an iterated LOESS smoothing method for individual proxies and the derived tracers are expanded (Lines 320, 339, 377). We also fixed the mistake associated with the $[PO_4^{3-}]$ estimation spotted by the reviewer (see reply to minor method comments) and updated related error envelopes in figures.

Consistent with previous works on proxies (e.g., (Lynch-Stieglitz et al., 2024)) and modelling (e.g., (Khatiwala et al., 2019)), we adopt a constant set of Redfield ratios to derive tracers and infer DIC changes. However, our conclusions are minorly influenced by variable Redfield ratios in the ocean, as shown by additional sensitivity tests in Figs. S6, S7. In these tests, we calculated PO_4^* using varying $R_{-O2:P}$ (160, 175, 180), and calculated $[CO_3^{2-}]_{as}$ using varying sensitivities of $[CO_3^{2-}]_{as}$ to $[PO_4^{3-}]$ changes with varying $R_{C:P}$ (127 or 140) and $R_{Corg:Ccarb}$ (4 or 8) defined in Yu et al. 2019. It is noted that, as shown in Yu et al 2019 (Shown here as Fig X2), the sensitivity of $[CO_3^{2-}]_{as}$ to $[PO_4^{3-}]$ is relatively insensitive to changes in $R_{C:P}$ and $R_{Corg:Ccarb}$ at the low $[CO_3^{2-}]_{norm}$ end ($[CO_3^{2-}]_{norm}$ is similar to $[CO_3^{2-}]_{as}$ without correcting for the constant offset of -78), where our data points are.

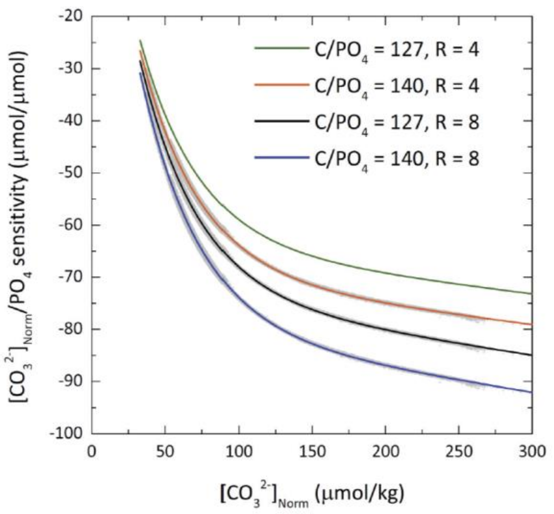

Fig. X2. Sensitivities of $[CO_3^{2-}]_{norm}$ changes to $[PO_4^{3-}]$ with varying $R_{C:P}$ and $R_{Corg:Ccarb}$.

Minor methods comments.

L236. How was anthropogenic carbon calculated and deducted? I would not expect much detectible DICant at this water depth…

Anthropogenic DIC is estimated from (Lauvset et al., 2016). It contributes negligibly to DIC in the deep SW Pacific indeed, but it does substantially contribute to the DIC in the N Atlantic. Correcting anthropogenic DIC is critical to reveal linear SSW-NSW mixing trend of $[CO_3^{2-}]_{as}$ in the ocean before the industrial era.

L262. Given all those contributions, the estimated uncertainty on phosphate concentration is only ±0.05 µmol/kg? Come on now, that is not realistic. For one point of comparison, the Cd/Ca measurement precision alone in Farmer et al. (2019) corresponded to a similar or larger phosphate concentration uncertainty. I have no doubt the authors are better analysts than myself, but the propagation of error should be handled appropriately.

This was a mistake, which is now corrected (~0.11 µmol/kg, ~0.05 of the estimated $[PO_4^{3-}]$, Line 323). The uncertainties of derived tracers are updated accordingly. We also provide more details about how the error of $[PO_4^{3-}]$ is derived (Line 320).

L273-275. The effect of global alkalinity change on the reconstructed [CO32-]as is quite significant (ED Fig. 1i), and also there is no reason to expect that a single core site would experience the global ocean alkalinity change (see, e.g., regional deviations in benthic d18O *for whole-ocean d18O change, Lisiecki & Stern, 2016 and references therein). Can the authors please further elaborate on/justify this correction and illustrate its uncertainty?*

Both data and models suggest that the average ocean alkalinity was substantially higher during the LGM than the Holocene. The effect of global alkalinity change on $[CO_3^{2-}]_{as}$ is significant, and correcting for it helps to better quantify $[CO_3^{2-}]_{as}$ in the past. Although regional alkalinity changes would deviate from the global trend to certain degree, the magnitude of change would be similar on the orbital timescale (also the case for $\delta^{18}O$).

The reviewer's concern about the uncertainty of the global alkalinity change is valid, as it could be the driving factor for some subtle feature in our record. For this reason, we no longer argue for an early-HS1 $[CO_3^{2-}]_{as}$ increase, which is dependent on the alkalinity correction and is not statistically significant compared to the updated $[CO_3^{2-}]_{as}$ reconstruction uncertainty. In comparison, the discussed changes from the late HS1 onwards are independent of the alkalinity correction (Fig. 3). We also use three different model outputs to calculate $[CO_3^{2-}]_{as}$ (Fig. S7). Although the magnitudes of $[CO_3^{2-}]_{as}$ changes vary, the millennial-timescale $[CO_3^{2-}]_{as}$ features are consistent (Fig. S7).

Reviewer #2 (Remarks to the Author):

Key Results:

It is difficult to parse apart the drivers of air-sea CO2 exchange (and by extension atmospheric CO2 variability), particularly in the Polar Antarctic Zone where carbonate archives are generally not present. The authors of this paper attempt to circumvent this challenge by inferring changes in quasi-conservative properties of deep ocean waters that are sourced from the PAZ; these properties are set by a combination of endmember values and water-mass mixing and should be recorded by benthic foraminifera at the study site. By the authors' logic, changes in these properties should reflect a combination of changes in circulation and changes in endmember composition (in this case largely set in the PAZ and delivered to the study site).

The authors have divided the discussion of their results by timescale. On glacial/interglacial timescales, they find that the deep pacific ocean was a net source of CO2 to the atmosphere, given the increase in [CO32-]as at the site. The concurrent increase in PO4 suggests that there was a combination of more preformed PO43- (and thus lower nutrient efficiency) and/or more preformed O2 as a result of a combination of biology and the removal of sea ice. The latter is corroborated by the decrease in ventilation age documented at the site in a previous publication by these authors.*

On millennial timescales, the authors suggest that the deep South Pacific was a source of CO2 outgassing across HS1, and that this was matched by changes in preformed nutrients (and by extension nutrient utilization efficiency) and/or preformed O2 inferred from PO4. Radiocarbon ventilation ages suggest that this was a period of better ventilation, perhaps as a result of sea-ice retreat and/or a shift southwards of the southern hemisphere westerlies during this period. The Antarctic Cold Reversal shows a decline in [CO32-]as and PO4 from the end of HS1, consistent with poorer ventilation of the waters reaching this region. Lastly, the Younger Dryas measurements of [CO32-]as and PO4* suggest that this region was again a source of CO2 outgassing as a result of biological and physical changes in the PAZ. These mechanisms are consistent with to those provided for the full glacial/interglacial change in these parameters.*

On sub-millennial scales, the authors examine and attempt to delineate the timing of changes in [CO32-]as and PO4 at this site across HS1 using ~12 data points (the sedimentation rate of this core is 10-20 cm/kyr depending on chosen tie points from Dai, Yu and Rafter 2021). The authors suggest that the asynchrony between [CO32-]as and PO4* in early HS1 allows for the discrimination between the various influences on these parameters. They suggest that the lack of change in PO4* is consistent with an increased role for physical drivers (retreating* *sea ice and altered southern hemisphere westerlies) in early HS1. In contrast, according to the authors interpretation, the change in PO4* across late HS1 is indicative that biological changes likely spurred mid-late HS1 outgassing.*

We thank the reviewer for the very comprehensive summary. We altered the interpretation of our data during HS1 based on the reviewers' comments, which will be detailed following the related comments.

Validity:

The authors make use of two quasi-conservative (and related) tracers: PO4 and [CO32-]as. PO4* is derived using inferred concentrations of PO43- and O2. The former is derived from the measured Cd/Ca ratio of the benthic foraminfera H. elegans using a local calibration for Cd/Ca to PO43-. The latter is derived from the gradient in carbon isotopes of co-occurring infaunal (G. affinis) and epifaunal (C. wuellerstorfi) species. Changes in PO4* thus reflect some combination of changes in nutrient utilization (via changes in preformed PO43-) and changes in oxygen related to either biology and/or physics.*

The PO43- measurements are also used to calculate [CO32-]as, a parameter which reflects changes in CO32- (and by extension DIC and atmospheric CO2) with biological influences removed. When this parameter changes, it reflects changes in carbonate ion as a result of CO2 sequestration or outgassing as a result of air-sea gas exchange; increases in [CO32-]as reflect lower DICas and outgassing of atmospheric CO2. Because increased exchange of CO2 should also alter PO4, differences in the behavior of [CO32-]as and PO4* downcore should provide constraints on the role of physical processes (relative to biological processes) in governing CO2 release to the atmosphere across the deglaciation.*

In general the data appear to be of high-quality and their interpretation appears robust. However, there are some major flaws that I think need to be fixed if the paper is accepted for publication. In particular, the discussion of sub-millennial drivers of CO2 variability in HS1 relies on the statement that [CO32-]as increased throughout early HS1, in contrast to PO4 (line 166- 167). It would be extremely helpful to the reader to delineate the exact magnitude of the change in these variables over the early HS1 time period. The change in [CO32-]as between 18- 16.3 ka appears to be on the order of 5 µmol/kg at most, and perhaps less than that if the lowest data point on the edge of HS1 is excluded. The data for PO4* looks as though it is also slightly increasing over the same time period, with the exception of a slight decrease right at 16.3 kyr (Figures 2 and 3).*

We recognized that the early-HS1 $[CO_3^{2-}]_{as}$ increase presented in the last version was not statistically significant compared to the updated reconstruction uncertainty (due to an error with the uncertainty associated with $[PO_4^{3-}]$, see responses to Reviewer 1's comments for details). We revised our discussion on HS1 changes focusing on the minimal changes in PO_4* and $[CO_3^{2-}]_{as}$ during the early HS1 and increases in these tracers during the late HS1.

To make things more confusing, the onset of HS1 on Extended Data Figure 1 appears at a different place in the [CO32-]as and PO4 curves than in Figures 2 and 3. Because the figure is plotted against depth it makes interpretation and comparison difficult, but if Extended Data Figure 1 is used in interpretation it appears that [CO32-]as actually decreased between 18-16.3 kyr.*

There was a mistake in depth of $[CO_3^{2-}]_{as}$ when plotting Figure ED1, which is corrected in Fig. S2 of this revision.

In other places in the text the authors refer to the change in N. Atlantic [CO32-]as as small across all of HS1 (lines 117-118), but the change in early HS1 in the NEAP-4K record is almost double that of the MD97-2106 core. How much of the small change in [CO32-]as in early HS1 could be from a change in NSW/SSW proportion and/or end member composition? Again this is unclear, but if the change in [CO32-]as is on the order of 5 μmol/kg, even a small change induced by circulation/water column structure change may represent a significant proportion of this inferred increase.

We reorganized the discussion on the minor contribution of NSWs to $[CO_3^{2-}]_{as}$ changes at our site during HS1. In short, even when overestimating the NSW% at our site during HS1 (20%) the NSW $[CO_3^{2-}]_{as}$ increase of ~7 μmol/kg can only make a small contribution to our site (~2 μmol/kg, Line 179).

It is not convincing to me from Figures 2/3 or from Extended Figure 1 that the change in [CO32-]as is significant either relative to the lack of change in PO4 or its starting value at the beginning of HS1. Given that this is one of the 3 major findings of the paper and is used evidence for physical changes initiating CO2 outgassing, this needs to be addressed prior to publication. The other evidence cited (radiocarbon ventilation, sea ice extent, and δ15N) are convincing in this respect, but have all been published elsewhere.*

We agree with the reviewer that this $[CO_3^{2-}]_{as}$ change during the early HS1 is not statistically significant compared to the updated reconstruction uncertainty as mentioned above.

Significance:

The authors' text is well-cited with regard to deglacial CO2 release from the deep Southern Ocean, including mechanisms and modelling. The literature they cite shows that, over the last 5-10 years, there have been numerous results connecting the deep Southern Ocean to the release of carbon from the deep across the deglaciation. There is, to my knowledge, already a consensus that the Pacific would have been a major player in this process both on glacial/interglacial and millennial timescales. Where this article therefore would be adding to the literature, then, would be if it could distinguish the role of physical and biological changes in driving this release for the PAZ. However, for the glacial/interglacial and millennial timescales of this article, the authors acknowledge that the co-variance of their tracers does not allow them to fully delineate between the dual roles of physics and biology. They do attempt to constrain the amount of carbon release implied by their data for glacial/interglacial transition, but this extrapolation is not fully explained nor is the role of the deep South Pacific (relative to, for example, the Atlantic) constrained by this extrapolation.

The authors suggest that the behavior of the two conservative tracers over HS1 allows them to discriminate between influence of physical and biological tracers at its onset. To me this would be a significant advance in understanding provided by this paper, as it would serve to confirm evidence from radiocarbon and sea-ice proxies. However, the authors must provide more information regarding the changes in these two tracers across this time period to better demonstrate their conclusions (regarding whether the change in [CO32-]as is significant relative to the lack of change in PO4).*

We made substantial changes to our manuscript to clarify that our conclusions on both orbital and millennial timescales are significant.

- Paired carbonate ion-phosphate-oxygenation reconstructions for deep-water preformed conditions

Our work is a first attempt to use these proxies to quantify two different deep-water preformed properties tracing different biogeochemical processes during the last deglaciation. Firstly, our reconstructions from the <u>deep ocean</u> are important in the context of the published surface records suggesting the influence of the nutrient utilization efficiency on PAZ CO_2 outgassing. As we explained in detail in the main text (Line 154), the deep-water reconstructions demonstrated that the surface nutrient utilization changes previously reconstructed, which are outside main deep-water forming region and offset from the deep water forming season, indeed were associated with deep-ocean biogeochemistry changes. Secondly, our approach focusing on reconstructing <u>preformed</u> properties can avoid some uncertainties associated with extrapolating local in-situ deep-water biogeochemistry changes to the global scale. (e.g., Line 70).

- Contributions of biological and physical processes to deglacial CO_2 outgassing

Our approach combines PO_4* (mostly linked to biology-related DIC change) and $[CO_3^{2-}]_{as}$ (including both biology- and physics- related DIC changes). On glacial-interglacial timescales, we provide strong evidence that both biological and physical processes are contributors of deglacial CO_2 outgassing. More importantly, by quantifying the DIC changes associated with other tracers, we reveal that the biological processes are a more dominant contributor during the early deglaciation, but the physical processes are more important during the late deglaciation.

Our work is the first attempt to distinguish mechanisms of the deep Southern Ocean CO_2 outgassing using proxy data. it is difficult to use single proxy for in-situ properties (such as $[O_2]$, radiocarbon, and $[CO_3^{2-}]$) to discern contributions of biological and physical processes as did in previous works on deep Southern Ocean carbon cycle changes.

The significance of this paper would clearer with discussion in more detail of how the results can or cannot discern between mechanisms or how they could build upon the various modelling results that they cite. Khatiwala et al. (2019), for example, find that sea ice extent and ocean circulation are minor contributors to changes in carbon storage relative to the role of air-sea equilibrium in amplifying changes in ocean temperature and iron fertilization. Cliff et al. (2021) also suggests a minor role for circulation and the biological pump in driving deep ocean deoxygenation (and thus PO4), but a large role for sea ice extent and iron fertilization. Such contradictions might be cleared up from paleoclimate-based inferences, but is largely not discussed here.*

Some of the modelling results mentioned by the reviewer is added to our introduction (Line 29). Our deep-water reconstructions can quantify CO_2 outgassing from the PAZ and distinguish contributions from biological and physical processes. For biological processes, our estimation is consistent with PAZ nutrient utilization efficiency changes inferred from previous $\delta^{15}N$ records. The key role of the PAZ as the key region modulating deep-ocean regenerated DIC changes can also be supported by moderate deglacial CO_2 outgassing from the SAZ attributable to iron fertilization (Dai et al., 2022). For the contribution of physical processes, we cannot distinguish contributions of sea ice extent, position and strength of westerlies, and ocean circulation, as these processes are not directly linked to the proxies we reconstructed.

One major thing that is unclear to me is why the authors do not discuss existing PAZ δ15N data. The authors suggest that the lack of carbonate archives from the PAZ preclude analysis of nutrient utilization in the region, but diatom archives (plotted in Extended Figure 5) provide such a record. Likewise, deep sea corals provide a coherent and chronologically well-constrained record of δ15N. There is no discussion of these diatom records throughout the text, and only a single mention of deep sea coral-bound δ15N. Recent important work (Ai et al., 2020) provides important constraints on the role of Southern Hemisphere westerly winds and upwelling on nutrient conditions in the PAZ and should be discussed here in reference to the conclusions being drawn, especially with regard to the interpretation of δ15N records from the PAZ.

In this revision, $\delta^{15}N$ data are discussed in more detail. We acknowledge that the idea of the PAZ control on air-sea CO_2 partition through nutrient utilization efficiency is from the $\delta^{15}N$ records (Line 152). However, we also explain why our deep-water records, showing the deep-water preformed changes is also significant. It is not yet known if the nutrient utilization changes inferred from $\delta^{15}N$ records led to changes in deep-water preformed properties and thus deep-water carbon storage. The reasons for this are that 1) the published $\delta^{15}N$ records are in the Open Antarctic Zone, not in the main region forming deep waters (although part of surface water in the OAZ contributes to the process), and 2) that the $\delta^{15}N$ records changes in seasons offset from deep-water forming season (Line 155). Our deep-water PO_4^* reconstruction provides strong evidence from the deep ocean to complement the surface $\delta^{15}N$ records for the PAZ nutrient utilization efficiency to affect deep-water chemistry.

We compare our reconstructions to records with comparable or better age models when discussing millennial-timescale changes. For this reason, we choose to discuss the coral-bound $\delta^{15}N$ records in the main text to support our observations during HS1. The $\delta^{15}N$ record at site MD12-3394 (Ai et al., 2020) indeed show a pattern nicely consistent with our PO_4^* record (Fig. S10). The reason that we did not discuss this record in detail is that its age model during the last deglaciation, which was determined by two tie-points at 11.7 and 18.2 ka (Table S2 in Ai et al., 2020), does not permit discussing millennial-timescale changes, despite the high sediment rate at this site. Lack of carbonates for ^{14}C dating during deglaciation and the LGM is common in high-latitude Southern Ocean sediment cores (e.g., at site MD12-3394), and it is one aspect of the challenge associated with PAZ reconstructions. We do now, however, refer to Ai et al (2020) when discussing westerlies' influence on deglacial CO_2 outgassing (Line 235) following the Reviewer's advice.

Another discussion point that should be addressed are the ‘Late Holocene’ values marked in Figure 2. It is not entirely clear from the methods section what age the “Late Holocene values reflect (Lines 214-215), but from inference (the disappearance of G. affinis until 0-17cm in the core) it seems likely these reflect values core top values. The values of [CO32-]as and PO4 are both equal to their value at 8-10 kyr. However, we know from Studer et al. (2018) that there was a substantial (20 ppm) rise in CO2 across the late Holocene (between 10 kyr and 2 kyr) that was accompanied by a large change in nitrate supply, reflected in the δ15N of Southern Ocean PAZ and Polar Frontal Zone diatom-bound N records, as well as in Coral-bound δ15N records from the PAZ. Presumably this change in δ15N should also be reflected in the authors’ records of PO4*. The changes in overturning driven by migration of Southern Hemisphere Westerly Winds (hypothesized by Studer et. al 2018) should also perhaps be reflected as changes in [CO32-]as. Please discuss why your core top values relative to 10 kyr do or do not contradict existing data regarding this period.*

The Late Holocene data are shown in the supplementary data table. The Late Holocene age of these samples is also mentioned in the supplementary material (Line 405).

The current study focuses on changes during the last deglaciation. The reviewer provides an interesting hypothesis for the partitioning between the Southern Ocean and the atmosphere, which our methodology can be employed to test. However, to test this hypothesis, more proxy data and age constraints during the Holocene are needed, which warrant a future study.

Previous records from this same core (from the same authors in 2022) show a strong role for altered efficiency of the solubility pump over the same time period (inferred from data presented in Fig. 2A). No discussion of this in relation to the findings of this paper are made, yet the inference from the 2022 paper is that Southern Ocean outgassing as a result of an altered solubility pump makes up a significant proportion of the observed change between 19-15 kyr – but the current paper would suggest much of the action is taking place in the PAZ instead of the subantarctic.

Changes in both PAZ and SAZ are both thought to be important to the air-sea CO_2 exchange in the Southern Ocean (e.g., (Jaccard et al., 2013)). The current study used materials from the same sediment core as our work in 2022. The current study mainly uses deep-water reconstructions at site MD97-2016 to infer changes in the PAZ and show that the air-sea CO_2 exchange in the PAZ are important during HS1. Dai et al. (2022) by contrast used surface-water reconstructions from the same site to track SAZ changes and suggested that solubility pump is important for SAZ surface carbon cycle changes. Taken together these studies provide insight about how different parts of the Southern Ocean contributed to changes in the air-sea CO_2 exchange during the last deglaciation.

We follow the reviewer's suggestion to better engage with our work in 2022. For example, the delayed carbon release from deep waters at our site during HS1 compared to the atmospheric CO_2 rise implies important contribution of the SAZ to the early-HS1 atmospheric CO_2 rise (Line 273).

Data and methodology:

The data appeared to be of high quality, and technically sound. I have minor comments that can be addressed line by line in the text. The main major comment I have is for readability: the authors here assume the reader has a detailed understanding regarding the calculation and interpretation of [CO32-]as, and rely on the reader to have a fairly detailed prior understanding of how this is calculated in order to follow the discussion. A short discussion of the tracer and its relationship to atmospheric CO2 and DIC would be helpful.

We expand description of the two tracers in the introduction, especially the main components of these tracers, and what they are related to (Lines 42-58). We also describe how $[CO_3^{2-}]_{as}$ is related to DIC changes, in the context of its distribution in the modern ocean (Line 63).

To more clearly explain downcore PO_4* and $[CO_3^{2-}]_{as}$ changes, we discuss in details distribution of these two tracers in the modern ocean, in comparison to their underlying components (Line 70). We also describe how variabilities in deep-water $[CO_3^{2-}]$, $[PO_4^{3-}]$, and $[O_2]$ contributed to downcore PO_4* and $[CO_3^{2-}]_{as}$ changes (Line 90) before moving on to discuss carbon cycle implications of the derived tracers.

More details about $[CO_3^{2-}]_{as}$ calculation are also given in the methods (Line 358).

Methods:

There is evidence that morphotypes of C. wuellerstorfi (e.g. sensu lato vs. sensu stricto after Gottschalk et al. 2016 and references therein) can alter the values of δ13C and trace element ratios. Given their expertise in the field, the authors are likely aware of this – were selections made by morphotype within C. wuellerstorfi that are not mentioned in the text? If not, could this account for some of the variability in, for example, B/Ca and δ13C that would give rise to artificial changes in reconstructed [CO32-]as and PO4 values? δ13C in particular can vary by between 0.2-0.7‰, which would be significant for reconstructions of bottom water oxygen concentrations.*

Both of our B/Ca and δ^{13}C data are minimally affected by potential differences related to *C. wuellerstorfi* morphotypes. We identified *C. wuellerstorfi* specimen following description in Holbourn et al (2013), which is largely in line with *C. wuellerstorfi* (sensu stricto) described by Gottschalk et al. (2016). The morphology of picked *C. wuellerstorfi* is consistent within the core, ruling out any possibility for systematic offset in B/Ca and δ^{13}C related to morphotype within the record between different periods. Any abrupt changes in morphotype of picked samples within the records would also likely lead to outliers in the B/Ca and δ^{13}C records, which is not seen in our relatively smooth records.

In lines 222-223, there is mention of splits of large samples into subsamples, which were presumably run in different batches and/or treated as independent samples. What is the standard deviation of these "true" replicates? Are they averaged and included in the figures (e.g. Extended Figure 1) or plotted independently? The 5th oldest point in Extended Figure 1g, for example, looks as if it may be 2 replicate samples, but one is significantly different than the other – but it is hard to tell.

The standard deviations of the replicated samples are added in the methods (Line 294), Replicated samples are plotted independently in Fig S2, but the averages of the subsamples are shown in Figs.2, 3, which are used to derive smoothed records. All data are shown in the supplementary data tables.

Were the benthic foraminiferal tests for stable isotope analysis (lines 230-233) treated in any way (e.g. crushed and sonicated)? Why not use splits of C. wuellerstorfi from the trace element measurements?

These samples are untreated, which is commonly done for benthic foraminifera (e.g., sample submission guidelines at MARUM, https://www.marum.de/en/Infrastructure/Guidelines-and-Terms-of-Use-Carbonates.html).

Although using splits of the *C. wuellerstorfi* shells for both trace element and stable isotopes may yield better records, using different *C. wuellerstorfi* shells for stable isotopes and trace elements is also common practice (e.g., (Allen et al., 2020)).

δ18O is plotted in Extended Figure 1E but there is no reference to it in the text, and no discussion of the methodology (species?) for the δ18O measurements (line 233 is the only mention). It appears δ18O largely agree, but there are places with offsets of up to ~0.25‰ in co- occurring benthics. This difference is disguised by the scale of glacial/interglacial change *in δ18O – is this a normal difference in δ18O between these two species? If so, perhaps this should be discussed, and if not, there should be a rationalization for how these particular points can be used for co-occurring measurements of δ13C gradients.*

The methodology is updated in the Methods (Line 298). The oxygen isotope data are used to shown synchroneity of varying proxy records downcore which is now specified in the supplementary materials (Line 389).

The deglacial trends of oxygen isotopes in *C. wuellerstorfi* and *G. affnis* are overall in good agreement as the reviewer mentioned. The $\delta^{18}O$ offset between *G. affnis (*corrected by the species offset of 0.94‰*)* and *C. wuellerstorfi* is 0.00±0.21‰ (1 standard deviation). Considering the deviation within the data set, it is not well-grounded to reject data with larger oxygen isotope offsets, although the reviewer's concern over these points is valid. Here, we show an alternative [O_2] record rejecting these few points in comparison with the one presented in the main text. The general trends of the two [O_2] records are the same.

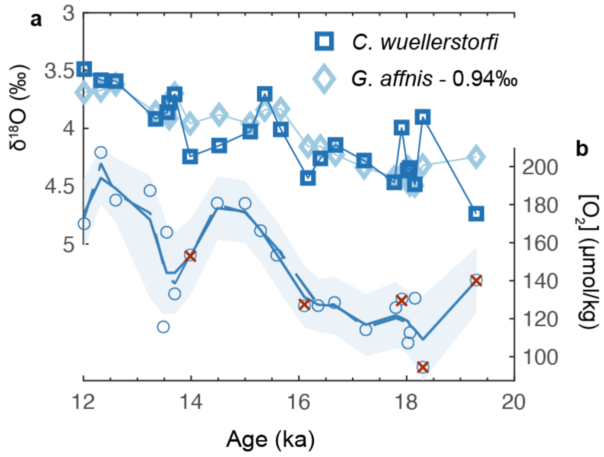

Fig X3. Upper panel: oxygen isotopes of C. wuellerstorfi and G. affinis. Lower panel: oxygen concentration estimated from carbon isotope gradients between C. wuellerstorfi and G. affinis. The dashed line is the smoothed curve without data points with large oxygen isotope offsets between C. wuellerstorfi and G. affinis (shown by crosses).

A table or a more organized discussion of the results of sensitivity tests would also be helpful for the reader – at the moment the discussion feels haphazard. The results of the sensitivity tests are presented parenthetically (Lines 91-93 for example), which makes it hard to follow. The methodology behind the sensitivity tests is straightforward and described in the text (lines 290 onwards) but the results of these tests as they are discussed in the text are not as clear.

We reorganized the way we present sensitivity tests. To be concise in the main text, we focus on interpreting SSW changes calculated from preferred SSW% at our site and NSW endmembers. Sensitivity tests are used to show that SSW changes we calculated are insensitive to uncertainties in SSW% at our site and NSW endmembers. Sensitivity tests are summarized in the supplementary material and the results are shown in Fig. S8.

Analytical approach:

There are places where the analytical approach is not always clear, though largely the authors have done a good job here. Several of the figures contain data that is not explained and/or referenced in the main text or supplement for the purpose of discussion. This includes Fig. 2A and 2B, Extended Data Fig 1B and 1E, Extended Data Fig. 3, Extended Data Fig. 4b, and most notably Extended Data Fig. 5C.

We now refer to the figures where appropriate, all supplementary figures are cited in main text and Methods.

More and/or clearer discussion of the results of the sensitivity tests would also benefit the manuscript. It is not always clear what the tests and results of the test are (Lines 89-93 are a good example of this). More discussion of the sensitivity tests relative to the findings is necessary - for example, in lines 89-93 the authors discuss the range of sensitivities in SSW PO4 implied by potential changes in NSW PO4* - but neglect to then relate this finding back to their results (potentially because the order of magnitude of the sensitivity test is on par with the entire change in PO4* in SSW). If the sensitivity tests are included in discussion of the results (which they correctly are), they should also be discussed in greater detail. It is also unclear why the authors do not conduct sensitivity tests for other transitions (e.g. YD) where they are suggesting there must have necessarily been changes in the balance of NSW/SSW at the site.*

We simplified discussion of the sensitivity tests in the main text (see responses to the previous comments). The purpose of our sensitivity test is to show that our estimated SSW changes are robust.

Sensitivity tests are employed for LGM-Late Holocene changes, as the Late Holocene levels of PO_4^* and $[CO_3^{2-}]_{as}$ of SSWs and NSWs along with SSW% at our site are constrained by preindustrial hydrographic data. For millennial-timescale changes, in most cases, NSW endmember values and SSW% at our site during neither of the two compared time periods is constrained. For simplicity, we maximized contributions from NSW endmembers to PO_4^* and $[CO_3^{2-}]_{as}$, and show that changes in NSW endmember values and SSW% cannot fully account for the observed changes in PO_4^* and $[CO_3^{2-}]_{as}$ at our site. The fraction of PO_4^* and $[CO_3^{2-}]_{as}$

changes at our site unexplained by NSW endmembers and SSW% are attributed to SSW changes (e.g., Line 247).

A specific point that I found confusing in the sensitivity tests is that, with their help, the authors define the increased change at the site from the change in NSW endmember to be 7 μmol/kg and the SSW endmember contribution to be 30 μmol/kg. However, adding these up gives a change larger than the glacial interglacial change suggested in lines 73-74 (32 μmol/kg +/- 4). Apologies if I have misunderstood, but these numbers do not seem to add up correctly, even accounting for the sensitivity test results.

We removed this part from our discussion.

There is no discussion of whether the core used here is of high enough sedimentation rate to analyze the sub-millennial scale variability that makes up the latter part of the paper, with the exception of lines 163-165 which references chronological uncertainties in Extended Data Figure 1 that are not evident in the figure or discussed in detail anywhere I can find. If there are significant uncertainties then they need to be described. Regardless, Extended Data Figure 1 does not match Figure 2 or figure 3 with regard to the onset of HS1 in PO4* or [CO32-]as - as an example, there are 4 data points prior to the gray bar in Extended Data Fig. 1i, and only 2 or 3 in Fig. 2g. Likewise, the upward trend in the oldest part of the PO4* record in Fig. 2F contradicts the data points in Extended Fig. 1h. Further confusing the analysis of this record, Extended Fig. 1 lacks the 16.3 kyr dashed line, making it difficult to analyze how many points constitute the trend the authors are inferring exists for [CO32-]as and not for PO4* between 18- 16.3 kyr.

We provide more information about the sediment core, including sediment rates and age model (Lines 92, 392). All the raw data are also provided in supplementary data table.

Fig. S2 (old ED Fig. 1) is improved, correcting for a few errors in depths, also adding a dashed line inicating 16.3 ka.

The extrapolation of carbon release from the glacial-interglacial transition needs to be made clearer and discussed further, or removed. What is this amount relative, to say, the Atlantic or Indian – and if the amount released is comparable in size to the atmosphere then does this imply that the majority of the C release was accomplished through a reorganization of the deep Pacific alone? What was the role of the intermediate waters in this reorganization? Lines 110-113 are not clear to me and need further clarification.

This part is removed.

Clarity and context:

There are several places where the writing is unclear and obscures the logic or argument. The authors' use of the phrase "direct evidence" (lines 83-85) needs to be substantiated or made more clear - why is this "direct evidence" compared to the numerous other records of Southern Ocean deglacial carbon loss? These records also represent inferences, given that they are not from the PAZ and rely on inferred relationships between trace metal/calcium ratios, bottom water chemistry, pore water chemistry, etc, as well as sensitivity tests and assumptions regarding the characteristics of NSW, SSW, and their proportions. While the authors of existing δ15N records would not necessarily say their records record "direct" CO2 outgassing from the AZ, they might be inclined to argue that diatom records from the PAZ are a much more direct record of nutrient utilization efficiency than PO4 inferred here. Why is B-P radiocarbon from the site is not "direct" evidence (lines 103-106, for example)?*

We no longer use the phrase "direct evidence", as we agree that it could be too strong as we used deep-water records to infer PAZ changes. Nevertheless, our approach to constrain changes in deep-water preformed values do have its unique advantages to infer PAZ change. All proxies, including δ^{15}N, radiocarbon, deep-water in-situ properties we reconstructed ($[CO_3^{2-}]$, $[PO_4^{3-}]$, and $[O_2]$), as well as deep-water preformed tracers we derived (PO_4^* and $[CO_3^{2-}]_{as}$), have to be interpreted with some assumptions. The strength of our approach is partly that we use our new proxy data and published data based on other proxies to show a comprehensive view of the PAZ's role in contributing to the release of carbon from the deep ocean to the atmosphere via the surface Southern Ocean. We test the robustness of our conclusion rigorously.

1. We reconstruct deep-water biogeochemistry using established proxies ($[CO_3^{2-}]$, $[PO_4^{3-}]$, and $[O_2]$) that have successfully been implemented in different regions and during various time periods.
2. The quasi-conservative nature of our derived preformed tracers is based on observations in preindustrial ocean (Figs. 1, S1), and tested against variabilities in assumptions made on Redfield ratios and rain ratios (Figs S6, S7).
3. Our site is predominantly affected by SSWs, and sensitivity tests show that despite uncertainties in SSW% and NSW endmember values, our conclusions on SSW endmember changes are robust (Fig. S8).

Text, minor comments:

Line 37: Key to this paper is the idea that these properties are conserved, adding "along flow paths moving away from the PAZ" might be clearer.

We revise the following sentence to stress that these properties are conservative: *Following deep water formation, signatures of surface source waters can be preserved as "preformed" properties that are quasi-conservative in the ocean interior* (Line 40)

Lines 46-48 are confusing: PO4 is noted to be largely governed by surface nutrient conditions here, but in the methods explanation has a solubility/physical component (lines 276-289). The statement in lines 48-49 about deconvolving these tracers makes it sound much more straightforward than the methods imply, which is shown by the fact that their deconvolution can not be achieved for glacial-interglacial or millennial timescales*.

We now mention that the LGM-Holocene change in physical component in PO_4* is small based on modelling study (Cliff et al., 2021) (Line 142). This component is often ignored in paleo reconstruction (e.g., deriving preformed [PO_4^{3-}] from AOU as in (Lynch-Stieglitz et al., 2024)).

Line 71: There are no calculation details for [CO32-]as.

This sentence is removed.

Lines 75-76: Changes in SSW/NSW is vague wording: do you mean changes in the proportion of these or in the endmember composition?

We added SSW% to make the sentence clear (Line 116).

Lines 76-79: This is confusing – if the proportion of NSW is increasing across the deglaciation, changes in NSW characteristics would have a larger impact as the proportion increased.

This sentence is not correct and removed. We reorganized the argument about limited influences of NSWs to [CO_3^{2-}]$_{as}$ changes observed at our site (Line 131).

Lines 87: "Changes" could refer to proportion or endmember again.

Lines 107-110: "Data-based evidence" is a strong way to phrase this, given that most of the other studies cited (including those from this site) are also Data-based.

These sentences are removed. (Line).

Line 118: This refers to extended data fig. 4, I believe, not certainly not 5.

Corrected.

Line 119: decreased fraction of NWS during HS1 needs a citation.

Reference added (Line 177).

Line 121-122: citation needed for this

Why PO_4* at our site can be used reflect that of SSW is expanded with references in the discussion (Line 179).

Line 136-138: Are your results adding to these conclusions listed? A reader might have arrived at the same conclusions (Driven by biological and physical changes) from the δ15N, radiocarbon, and sea salt records alone. The paper needs to be more specific about the constraints that this data is providing.

Lines 156-159: Again, as noted immediately above, it remains unclear what additional constraints are provided given the ambiguous conclusion. The authors would be well-served to make their specific conclusions stronger and/or clearer, with regard to how these add to the existing literature.

We now explain why our perspective from the deep-water preform properties is important for similar conclusions both on glacial-interglacial and millennial timescales (Lines). We focus on providing evidence of relative importance of the biological and physical processes during varying deglaciation stages (Line 22).

Lines 166-167: This does not appear to be true, at least not significantly. This needs to be addressed with the actual data, and concentrations/values need to be given.

As explained in responses to main points, we no longer discuss these features.

Lines 169-170: 0.1 represents 1/3 of the Glacial-Interglacial transition, so it is not as small as the authors imply here.

We agree 0.1µmol/kg change of PO_4* is not small. This however cannot be discussed with confidence due to the reconstruction uncertainty of PO_4*.

Lines 186-187: Callout to figure 3 would be helpful here.

Added.

Lines 210-212: The finding that the biological pump plays a large role is not surprising, but could be discussed further relative to recent papers finding a large role for the solubility pump and other physical mechanisms, particularly for intermediate Southern Ocean waters.

We agree with the potential importance of physical mechanism of other water masses, which is briefly discussed later (Line 276). Here, we choose to focus on the PAZ ventilated deep waters.

Figures, minor comments:

Caption Fig. 1 has the words "Lower Circumpolar Deep Water" but no explanation of what this is in reference to with regard to the rest of the sentence (Lines 323-324).

This is removed from the figure and caption as LCDW is not used in our discussion.

Fig. 2: The late Holocene values for Figure 2 [CO32-]as are not at all close to the values in Figure 1D. While some of the absolute value change is due to calibration, the values are significantly higher than those given for the modern ocean. Why is this the case, if the PO4values are accurately reflected in the core tops?

$[CO_3^{2-}]_{as}$ in Fig 2 of the last did not correct for the constant of -78 µmol/kg. Both late-Holocene PO_4* and $[CO_3^{2-}]_{as}$ are close to the pre-industrial levels (Figs. 1, 2).

Why does Fig. 2F increase at the oldest point in the record without a data point on the plot that is older than ~18 kyr?

This was generated by smoothed curves of $[PO_4^{3-}]$ and $[O_2]$, but was not explained. It is removed.

Fig. 3: It is not clear what the gradient in the color bars on the triangles in b,c,e, f and h are reflecting given the depiction of timeseries. Also, should Fig. 3D say B-P and not B-A age?

Colour bars with colour gradients are removed. The radiocarbon data shown is B-A age. A stands for atmosphere, and we change to Atm for clarity.

Extended Fig. 1: This needs substantial improvements as it does not align with Figure 2 or 3, and does not have a marker for 16.3 kyr.

This figure (now Fig. S2) is improved. Error in depth is corrected, and a line indicating depth corresponding to 16.3 ka is added.

Extended Fig. 2: Typo for a instead of (a) in line 567.

Corrected.

Extended Fig. 3: Needs a better legend, given that there are actually 3 sets of data on the plot and not 2. This figure is not discussed in the main text. For example, hat does the substantial gradient (20 μmol/kg) between MD97-2106 and the S. Indian Core in reconstructed O2 imply for the deep South Pacific vs Indian Ocean during early HS1?

This figure generally show that these deglacial deep Southern Ocean [O_2] records are similar, and is now discussed (Fig. S5, Line 101).

The difference in [O_2] between our site and the Indian Ocean site is close to the reconstruction uncertainty preventing detailed interpretation.

Extended Fig. 4: Is there a reason that the Yu 2022 data for the South Atlantic is not also included here? I assume the reasoning is to show the endmembers for NSW and SSW, but the GGC90 record was used by Yu et al to infer significant release of carbon from the Atlantic sector of the Southern Ocean as well.

GGC90 record is added (Fig. S8). GGC90 record mainly reflects intermediate depth carbon release, which complement with deep-water carbon release.

Extended Fig. 5: It would be helpful to discuss Fig. 5C in the text. Also, putting the late Holocene values for the δ15N records and for PO4 would be helpful for any discussion of the late Holocene evolution of these tracers.*

Not discussing $\delta^{15}N$ records other than the coral bound record is because these records lack well-defined age models allowing for discussing millennial scale changes, as well explained above.

Late Holocene $\delta^{15}N$ changes are omitted in this figure as this work focus on deglacial changes.

References:
The paper is well-cited, though not many of the citations are used to further the discussion of the text (for example, δ15N references) despite being in the text. These citations may also be of interest for the discussion:

Ronge, Thomas A., et al. "Southern Ocean contribution to both steps in deglacial atmospheric CO2 rise." Scientific reports 11.1 (2021): 22117.

Moy, Andrew D., et al. "Varied contribution of the Southern Ocean to deglacial atmospheric CO2 rise." Nature Geoscience 12.12 (2019): 1006-1011.

Fogwill, C. J., et al. "Southern Ocean carbon sink enhanced by sea-ice feedbacks at the Antarctic Cold Reversal." Nature Geoscience 13.7 (2020): 489-497.

In this revision, we pay attention to specifying the types of cited proxies and referring to references where appropriate in the discussion. We also refer to some of the recommended citations for discussion about changes during the Antarctic Cold Reversal (Line 235) and the Younger Dryas (Line 261).

Reviewer #3 (Remarks to the Author):

Dai and Yu present a valuable dataset, interpreted in a cutting edge quantitative framework, to investigate glacial carbon storage and release. This is a really interesting contribution and following revisions would, I think, make a very suitable Nature Communications paper.

I have provided detailed line by line comments, which include key conceptual questions as well as more minor points and typos. Note there are other typos and sections lacking clarity too - the paper would benefit from further proof reading and an attempt to more clearly describe processes to the reader alongside their quantification in different tracer signals. I also pick out some of the most critical issues below.

We thank the reviewer for the positive comments and apologize for typos in the last version.

[CO32-]as - better describe what it can and can't tell us

The [CO32-]as tracer has been introduced and used in a series of recent papers from Yu's group, yet is still relatively new and (as detailed below) needs further description to help the reader.

$[CO_3^{2-}]_{as}$ is now better described in the introduction. We explain the underlying component of $[CO_3^{2-}]_{as}$ when the tracer is introduced, the quasi-conservative property it quantifies, its relation to CO_2 air-sea exchange, and its limitation in understanding mechanisms for carbon cycle changes (Line 77). A new figure (Fig. 3) is introduced to help readers understand how $[CO_3^{2-}]_{as}$ is calculated.

More critically, the interpretation I felt leaps in to this relatively derived quantity quite quickly, and would benefit from spelling out some of the signals in the raw data, and how these are brought together into [CO32-]as and other related properties. In particular, I was left wondering about the other components of ocean carbon storage (e.g. remineralised carbon) and their fingerprints on the carbonate chemistry and other reconstructions here. Can we learn something about remineralised carbon storage from these data or not? This is particularly important as the topic is currently in vogue (see e.g. the Volmer et al., 2023 paper in Paleo) and as this question naturally arises from several points in the text. For instance right from the abstract, line 19 highlights "carbon losses from the Deep South Pacific to the atmosphere"; this to many readers will I think give an image of release of a deep carbon reservoir which others have suggested has a large remineralised carbon component. But the main text description and discussion of the signals is very much focussed on preformed signals in the Southern Ocean surface. I can see ways to bring these different ends of the glacial carbon *storage system together, but it would I think be very helpful for the authors to spell this out more explicitly, both by describing the tracer in more detail and its relationship with other ways of thinking about deep carbon storage and release (e.g. remineralised vs preformed carbon) in the introduction and the initial sections describing deglacial carbon loss from the deep ocean.*

- Discussing directly reconstructed proxies first then derived tracers

Similar points were raised by Reviewer 1. To address this point in this revision, provide more information about $[CO_3^{2-}]_{as}$ and PO_4^* in the introduction (Line 45), and discuss the derived tracers and their underline components in the modern ocean to help readers understand downcore $[CO_3^{2-}]_{as}$ and PO_4^* records. We also begin our discussion by describing how changes in deep-water $[CO_3^{2-}]$, $[PO_4^{3-}]$, and $[O_2]$ contributed to $[CO_3^{2-}]_{as}$ and PO_4^* changes from the LGM to the late Holocene (Line 98).

- Remineralized (regenerated) carbon storage change

We aim to constrain the deep-water preformed changes, which are more homogenous for the deep Indo-Pacific and deep Southern Ocean and can be tied the deep ocean changes to the PAZ processes.

The change in regenerated carbon/nutrient storage is the other side of the same token of the preformed changes. For example, deglacial increases in SSW PO_4^* (largely preformed $[PO_4^{3-}]$), when considering the minor changes in oceanic $[PO_4^{3-}]$ inventory during the last deglaciation, suggests declined concentrations of regenerated nutrient and thus regenerated carbon. Our deep-water reconstructions of $[CO_3^{2-}]$, $[PO_4^{3-}]$, and $[O_2]$ generally show deglacial loss of regenerated carbon <u>from this site</u>. This is consistent with previous deep-water records. However, these observed changes related to deep-water regenerated carbon storage, at anywhere in the deep ocean can be alternatively accounted by other processes (e.g., Line 71). Therefore, observed loss in deep-water regenerated carbon (as at our site) does not mean the lost carbon is necessarily ended up in the atmosphere. Moreover, in contrast to the preformed properties, regenerated carbon storage of deep waters is heterogenous in the deep ocean depending on where they are on the route of deep-water circulation (shown by the O_2 transect in Fig.1). These characters of regenerated carbon/nutrient, when compared with the preformed properties, show the advantage of preformed properties in inferring large scale ocean carbon cycle changes.

Which water are we really feeling?

The authors claim that their record is indicative of processes in the PAZ. However this needs to be better substantiated for a couple of reasons. While I agree with the authors that the core *will be dominantly influenced by SSW, not all SSW is necessarily sourced from the PAZ. For instance in the Gebbie and Huybers (2010) deconvolution of deep water sources, this core site would have about 50% water from the PAZ, with additional, subequal contributions from the PFZ/SAZ and NSW (the NSW component is indeed nicely picked up in the low PO4* blob in the section figure).*

[The proportion of SSW at this site and how this is tracked by PO4 is, in addition, strongly influenced by the role of entrainment in the SSW PO4* end member signature, discussed further below.] Related to the major comment above about preformed vs remineralised signatures, I'm also left wondering how I should think about timescales of change at this site compared to the atmosphere, given that it will have influences both from relatively recently ventilated water from the south alongside return flow from the Pacific. Should I think of this as being in water that has recently left the PAZ so quickly picks up changes sourced from PAZ-atmosphere interactions? Or does it also have a component of return flow from the Pacific, rich in remineralised carbon, having left its surface source regions perhaps several thousand years earlier? A mixture of these to me seems likely and I think some discussion of this, alongside the different carbon signatures being felt here as discussed above, would benefit the paper.*

- Contribution of the SAZ-ventilated SSWs to our site

SSWs are indeed ventilated in both the PAZ and SAZ. The SAZ-ventilated SSWs are however mainly at intermediate depths and a relatively minor contribution to the deep Indo-Pacific Ocean in the modern ocean. The minor impact is due to the even smaller influence of SAZ-ventilated SSWs at deep depths during the LGM owing to the shallower upper cell circulation, which is explained in the supplementary material (Line 407). We do not discuss contribution of SAZ-ventilated SSWs to our reconstructions in the main text for clarity, and attribute inferred changes in SSW $[CO_3^{2-}]_{as}$ and PO_4^* largely to PAZ processes.

- SSW at our site

Newly ventilated SSWs and recirculated SSWs from the North Pacific (PDW) have distinctive geochemical signatures ($[CO_3^{2-}]$, $[O_2]$, $[PO_4^{3-}]$, and radiocarbon). As can be shown by relatively high deep-water $[O_2]$ and well-ventilated radiocarbon, the returning PDWs are a minor contributor in the modern ocean. Due to the shoaled upper-cell overturning circulation, our site was more strongly affected by the newly ventilated SSWs during the LGM, and likely also the last deglaciation, as shown by εNd records.

By contrast, $[CO_3^{2-}]_{as}$ and PO_4^* of newly ventilated SSWs and PDW are similar in the preindustrial ocean (as shown in Fig. 1, S1), which is an advantage of using the quasi-conservative tracers, when considering past changes in water mass mixing. For this reason, contributions of PDWs to our site during the LGM, if different from Holocene, minimally affect $[CO_3^{2-}]_{as}$ and PO_4^* of deep waters, with the assumption that the LGM was close to a steady state similar to the Holocene.

During the last deglaciation, $[CO_3^{2-}]_{as}$ and PO_4^* of recently ventilated SSWs and PDW could differ due to changing preformed conditions in the Southern Ocean. Changes in $[CO_3^{2-}]_{as}$ and PO_4^* of PDWs theoretically lag recently ventilated SSWs by the time taken for deep waters to transit from the Southern Ocean to the North Pacific. However, such a difference does not significantly affect millennial-timescale $[CO_3^{2-}]_{as}$ and PO_4^* changes at our site for two reasons.

Firstly, the deep-water transit time from the Southern Ocean to the North Pacific is relatively short during the last deglaciation. It is estimated to be 550-850 years during the LGM, the longest since the LGM (Rafter et al., 2022). This suggests that $[CO_3^{2-}]_{as}$ and PO_4^* of the PDW would be similar to the recently ventilated SSWs on millennial timescale, and the difference of $[CO_3^{2-}]_{as}$ and PO_4^* between the PDW and recently ventilated SSWs driven by millennial-timescale changes are small. Secondly, our site was more dominantly affected by recently ventilated SSWs during the last deglaciation, as we explained above. Consequently, we do not discuss the potential influence of changing PDW to our site.

Structure of paper / structure of millennial vs HS1 changes

I read through the section on millennial changes wondering why the earlier and later parts of HS1, which clearly have very different signatures, were being lumped together. I then realised that they are discussed in more detail in the next section on Bio vs Physical carbon loss in HS1. However I think this current structure risks confusing readers. I'd suggest at least flagging in the millennial section that there are two distinct parts of HS1 that will be discussed further below.

I also suggest using the general/orbital section to better discuss the tracers and the nature of carbon loss, addressing the major comments above.

We have restructured the manuscript. After comparing LGM results with the Late Holocene, millennial timescales changes are presented in chronological order.

We also expanded discussion on the changes on LGM-Holocene changes. Specifically, we

- describe how deep-water $[CO_3^{2-}]$, $[PO_4^{3-}]$, and $[O_2]$ changes contribute to $[CO_3^{2-}]_{as}$ and PO_4^* changes (Line 102);
- use DIC changes related to $[CO_3^{2-}]_{as}$ and PO_4^* to show the carbon loss was driven by both biological and physical processes (e.g., Lines 149, 161).

Early HS1 [CO32-]as change?

The text discusses there being a [CO32-]as change in both the early and late part of HS1, and from reading the text alone without looking at the figures one might assume these [CO32-]as changes are similar in size. However from looking at the figure, it's unclear whether there really is a significant [CO32-]as change in early HS1, whereas the late HS1 change is substantial. Modify the text to address this directly - is there perhaps even something interesting one can say about the different sizes of these changes are their relationship/slope compared to other tracers that may further point to mechanisms?

As mentioned in responses to comments of Reviewers 1 and 2, the early HS1 $[CO_3^{2-}]_{as}$ change is not statistically significant and not discussed any more.

Plotting error - is there an interesting centennial signal?

The relative phasing of the data in Figure 2 and ED Figure 1 is not the same (and I realise that one is in age space, the other in depth - the issue lies in the phasing of proxy signals within the same core). In ED Figure 1 the notable spike to low [PO4] at 150 cm is simultaneous with a sharp jump up in [CO32-]as. Taken together these signatures are really interesting in terms of mechanism - and are also particularly interesting given some of the very rapid changes in deep sea coral data around this time (e.g. Li et al., 2020). However in Figure 2, the sharp drop in [PO4] at 16.3 ka has no accompanying feature in [CO32-]as - the jump up comes 500 years or so later.

If the jump up in [CO32-]as is associated with a drop in [PO4], then this does have implications for mechanisms and should be addressed. Specifically, at present the late HS1 rise in [CO32-]as is discussed as being associated with rising PO4, leading to the implication that this outgassing change comes about through reduced biological pump efficiency. However if this major jump up in [CO32-]as (which is about half the overall late HS1 change) is in detail associated with a drop in [PO4], then this surely challenges that interpretation, at least within this interval? Rather, it might fit better with the coral 14C younging that happen at this time, indicating a pulse of pronounced ventilation that outgasses CO2 and flushes well-ventilated, low nutrient waters through the water column.

We improved the discussed figure. The relation in Fig. ED1 in the previous version mentioned here is indeed due to a plotting error with the depth of $[CO_3^{2-}]_{as}$. The $[PO_4^{3-}]$ trough corresponds to the relative low part of the $[CO_3^{2-}]_{as}$ record at ~150 cm.

It is also worth mentioning that we tend not to compare $[CO_3^{2-}]_{as}$ or PO_4^* with the underlying proxies to avoid circular arguments.

Line by line comments

43-46 - [CO32-]as is the main focus of this paper and is still a relatively new tracer. I think the paper (and certainly its readers!) would benefit from some more description of this tracer here and also in the methods. This doesn't need to be exhaustive (you can reference the previous work for more details), but it should be enough for the reader to get a feeling how this is calculated and what it indicates in more detail than currently provided. It should also discuss how DIC is calculated from this tracer, which appears out of the blue later in the paper, and would similarly benefit from introduction.

We agree with the reviewer on this point. As mentioned above, we substantially increase background of the $[CO_3^{2-}]_{as}$ tracer in the introduction (Line 52) and details about its calculation in the methods (Line 362).

73 - jumps straight in to very derived property/concept. My preference would be to step through the glacial state you have first and the different components to the carbon storage (e.g. both preformed and remineralised), then how they evolve over deglaciation.

we now start our discussion from describing how directly reconstructed tracers contributed to the derived tracers. We tend not to interpret directly reconstructed tracers as they all contain both preformed and remineralized component that are hard to tease out. We would like to focus on the preformed properties derived from our derived tracers.

78 - unclear as written - an increase in Northern water, which is increasing its [CO32]as, sounds like it could contribute to the signal of increasing [CO32]as. Key missing logical step is I think the different [CO32]as signatures of NSW vs SSW: as NSW has lower absolute [CO32]as, this may be expected to dominate. I realise this is what the mass balance calculation in the sentence that follows is meant to spell out, but it's not very clear for a non-expert. Add a short clause of descriptive explanation here and a fuller explanation to Figure ED4 caption, which is referenced here, but doesn't have this level of explanation in the caption.

This sentence is removed. We simplify the discussion about the NSW endmember's contribution to $[CO_3^{2-}]_{as}$ at our site (Line 128). We use Fig 4 to demonstrate the $[CO_3^{2-}]_{as}$ difference between SSW and NSW.

81 - the NSW contribute to - unclear writing.

This sentence is removed.

82/83 - this seems like it would also benefit from being shown in a figure - perhaps an additional panel to Figure ED4.

The glacial NSW and SSW endmembers are shown in the new Fig. 4.

Also what does the PO4 suggest about water masses?*

PO_4* at our site is also driven by SSW PO_4* change (Line 128).

85 - a key point (also mentioned above) that is not discussed in enough detail is whether we can explicitly link changes at this site to the PAZ, vs other regions of the Southern Ocean. The core is not in a region of pure PAZ-sourced AABW and likely also has a component of water ventilated along sloping isopycnals in the PFZ/SAZ (as well as the NSW which is discussed).

This point is now mentioned in supplementary materials (Line 409) as mentioned in the response to a main point.

86 - raised —> rose

Corrected (Line 102).

90 - being —> is

92 - if of varying

Removed.

91-93 - again I don't find this list of numbers particularly helpful in getting a sense for how big a deal this is - would much rather see in a figure or a table.

Agreed. Sensitivity tests are now summarized in Fig S8.

94 - “the latter of which” is odd here - would seem like it would only be referring to O2, but think you mean PO4 and O2?

Removed.

110-111 - where do these numbers come from?! I understand how you calculate [CO32-]as, but not how you then go to (presumably) DIC to get total Pg carbon.

More details are provided how to use SSW $[CO_3^{2-}]_{as}$ change to derive DIC changes (Line 163).

Also, critically, if you are going to extend the calculation to the whole deep Pacific, you really need to say something about the other proxy records in this basin (especially DCO32-, PO4, O2) - are they consistent with the signals here allowing you to extrapolate to the Pacific below 1500m?

112 - is this really sizeable? Pacific below 1500 m is likely main deep ocean carbon store. If need to account for at least another 400 PG and maybe as much as 800 or 1200, then where does the rest of the carbon come from?

We discard the estimation of the ocean carbon inventory change. The reason is that we used modelled global alkalinity changes to derive $[CO_3^{2-}]_{as}$, and the argument would be slightly circular if we use the derived $[CO_3^{2-}]_{as}$ changes to infer global DIC change, which would be partly dependent on the modelled global alkalinity change we employ.

115-129 - “throughout HS1” - actually the big change in [CO32-]as and PO4 is late HS1.*

Agreed. We altered the way we describe the HS1 $[CO_3^{2-}]_{as}$ changes, and discuss early- and late- HS1 changes separately (Line 186).

130-139 - linked but conversely to the point above, the 14C change happens entirely during early HS1, and is associated with no change in [CO32-]as! Seems like this is trying to tell us something. Alternatively, if the authors don’t think the age model is robust to this, need to be up front about it. What do the benthic-planktic data look like?

Our age model resolves the early and late HS1 based on radiocarbon dates. We do not have enough planktic radiocarbon data to generate B-P age.

Due to the large reconstruction uncertainty associated with $[CO_3^{2-}]_{as}$, there could be a small physically driven outgassing during this period, consistent with radiocarbon data. It is notable that radiocarbon is always in disequilibrium with the atmosphere and can be more sensitive to improved air-sea exchange than CO_2.

143 - Stewart et al. (2021) paper also nicely shows this and reaches similar conclusions.

Cited (Line 237).

166 - only significant change seems late HS1. Certainly a very different magnitude / slope of change if there is any change at all, and can't just brush over this.

As explained above, we no longer argue for an early-HS1 $[CO_3^{2-}]_{as}$ increase.

168-169 - this sentence is very hard to follow

171 - given what you say about sea ice I think best to omit "likely stay unchanged" - if your sea ice and 14C interpretation is correct, then it likely increases.

174 - if you are really in PAZ waters, then how influential is any likely change in temperature? Probably stays pretty cold!

176-177 - this is really not clear to me and I think will be completely opaque to majority of readers. Rephrase to make more clear what you mean. I'm left unsure whether these are expected to drive a change in PO4 or not.*

180 - very unlikely that no change in physical O2 recharge if there is a change in 14C, as 14C takes much longer to equilibrate than O2.

Discussion related to above comments is removed.

186 - this younging in 14C occurs notably earlier than coral 14C data: with the exception of the transient younging pulse at 16.1 ka, the main younging is all in late HS1. This is also true of most of the younging in the Skinner record. Why the discrepancy?

The reviewer's observation is valid. However, this study does not focus on radiocarbon data, and thus we do not discuss this point in the main text, which could be related to the relative low resolution of LCDW-level coral based radiocarbon during the period between 18 and 16.3 ka (Li et al., 2020).

191 - This is nicely supported by Gray et al. 2023 reconstruction.

Cited (Line 261).

195 - “14C further declined” - this makes it sound like it’s comparable to the much larger earlier change. As with the points made above on the magnitude of [CO32-]as change in the different parts of HS1, you need to be up front about the different magnitudes of these signals.

This is removed.

198-199 - hard to follow what is meant here. Even if more details are provided in the Yu et al. 2019 paper, the reader shouldn’t have to go to this to get a general sense for how this calculation works.

Description of this calculation is expanded (Line 361).

Also if this calculation is done for DIC in late HS1, what is the equivalent calculation for DIC in early HS1? I would think minimal as there’s to my eye very little [CO32-]as change, but the text discusses [CO32-]as change in early HS1, so maybe there’s something I’m missing? Having the equivalent calculation for both may be helpful.

The discussion on the early-HS1 $[CO_3^{2-}]_{as}$ is removed.

200-201 - this might not be minor if there was a major change in sea ice

We specify that it is the purely physically driven preformed $[O_2]$ change is minor, as shown by (Cliff et al., 2021) (Line 142).

208-210 - interesting and important point but unclear as written

This point on relative contribution of biological and physical processes on millennial timescales is expanded when discussing changes during both HS1 and YD (Lines 211, 255).

229 - 1 sigma or 2 sigma?

Specified (1 sigma, Line 297).

*261-262 - rephrase - this isn’t considering *all* the uncertainties as it doesn’t take in the calibration uncertainty, which is more like ±0.2 umol/kg.*

We specified all the source of the uncertainty (Line 323).

268 - need to at least give a brief description

Calculation of $[CO_3^{2-}]_{as}$ is described in detail (Line 361).

269 - similar to point above, but even more importantly, you really need to give more information here (and ideally also in the main text). [CO32-]as is totally central to this paper and is still a relatively new tracer, being only previously used in a couple of other papers from this group. While I realise that thinking about [CO32-]as probably now seems very natural to Yu and co-workers, it is still new enough that the rest of the community will continue to need some explanation - especially when it's as key to a paper as it is here. Indeed I think the paper would benefit from additional description in the main text too to help build intuition.

Following the reviewer's comments, we expanded description of the tracer both in the main text (Line 52) and methods (Line 361).

271-275 - I agree in principle with the correction for global alkalinity change and it's very helpful to see figure ED1 that shows the [CO32-]as signatures both with and without this correction. However this figure (ED1i) also makes it apparent that the vast majority of the glacial-interglacial change in [CO32-]as from the oldest to the youngest samples comes about from this correction. This really needs to be discussed explicitly in the main text section on orbital scale changes.

Because of this concern, we discard discussion on the early HS1 $[CO_3^{2-}]_{as}$ change. However, the global alkalinity correction is necessary to reveal the deglacial $[CO_3^{2-}]_{as}$ change (although admittedly introducing uncertainty in our reconstruction).

The global alkalinity change is on the orbital timescale. We now show its contributions during the last deglaciation in Fig. 3. Sensitivity tests show that the millennial timescale changes are independent of the alkalinity correction (Fig. S7).

286-287 - why does air sea gas exchange cause reduced nutrient utilisation?

This sentence is removed from the methods. However, we expand the description of the relation between air-sea exchange and PO_4* in the main text (Line 75).

303 - this is highly dependent on what end member is used for the SSW - the AABW signature in the source region vs the signature that incorporates entrained CDW. Rae and Broecker (2018) show this changes the SSW:NSW fraction in the deep Indo-Pacific between 50:50 and 75:25 respectively. Some discussion of this is needed, as it also has implications for what you are reconstructing in terms of SSW end member. Similarly, the influence of entrainment on the PO4 signature of the Southern end member should also be mentioned - this has an important influence today, is notably different in different regions of the Southern Ocean, and may have also changed in the past. These are, I realise, not easy things to constrain, but it needs at least some discussion.*

As mentioned in responses to the reviewer's main comments, we now discuss entrained CDW with a substantial contribution from the deep North Pacific,

We agree that absolute values of estimated SSW changes indeed depend on how the SSW is defined, the influence of the SSW changes on the global carbon cycle changes is the same (a point made in Line). This is because regardless of the definition of SSWs, the SSW% at our site is comparable to the deep Indo-Pacific. We defined SSW and NSW endmembers following Rae and Broecker (2018) that gives the SSW:NSW of 75:25, which "best characterize(s) the ratio of deep Southern Ocean to North Atlantic water volume". If we adopt the Antarctic shelf-water definition of SSWs (also in (Rae & Broecker, 2018)), the SSW% at our site would be lower (~47% rather ~70%). Based on the LGM-Holocene changes at our site, projected changes in SSW $[CO_3^{2-}]_{as}$ and $[PO_4^{3-}]$ would be higher. However, due to the lower SSW% in the deep Indo-Pacific Ocean based on this definition (~50% rather than 75%), the carbon cycle changes attributable to SSWs would be the same.

323-324 - LCDW - not really a sentence.

Removed.

Figure 2

328—329 - if crosses really indicate age ties then these look unconvincing. Are the crosses 14C control points and the triangles the ties?

Yes, this is clarified in the caption.

331 - is the PO4 data also really including calibration error? Based on the different choices possible in Figure ED2, I would expect calibration error to be larger?

As in responses to reviewer 1, errors with [PO_4^{3-}] was not correct in the last version and corrected now. How [PO_4^{3-}] errors are calculated is also better explained.

Figure ED1

- Please show benthic-planktic 14C data here too

Benthic radiocarbon data at this site is compared to the atmospheric value not the planktic radiocarbon at this site. For this reason, benthic radiocarbon data have to be shown in the age scale, thus it is not included in this figure.

References

Allen, K. A., Sikes, E. L., Anderson, R. F., & Rosenthal, Y. (2020). Rapid Loss of CO2 From the South Pacific Ocean During the Last Glacial Termination. *Paleoceanography and Paleoclimatology, 35*(2). Unsp 2019pa003766

10.1029/2019pa003766

Anderson, R. F., Sachs, J. P., Fleisher, M. Q., Allen, K. A., Yu, J., Koutavas, A., & Jaccard, S. L. (2019). Deep-Sea Oxygen Depletion and Ocean Carbon Sequestration During the Last Ice Age. *Global Biogeochemical Cycles*. 10.1029/2018gb006049

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

Dai, Y., Yu, J., & Rafter, P. (2021). Deglacial Ventilation Changes in the Deep Southwest Pacific. *Paleoceanography and Paleoclimatology, 36*(2). 10.1029/2020pa004172

Dai, Y., Yu, J., Ren, H., & Ji, X. (2022). Deglacial Subantarctic CO2 outgassing driven by a weakened solubility pump. *Nature Communications, 13*(1). 10.1038/s41467-022-32895-9

Jaccard, S. L., C. T. Hayes, A. Martínez-García, Hodell, D. A., Anderson, R. F., D. M. Sigman, & Haug, G. H. (2013). Two Modes of Change in Southern Ocean Productivity Over the Past Million Years. *Science, 339*(1419-1423).

Khatiwala, S., Schmittner, A., & Muglia, J. (2019). Air-sea disequilibrium enhances ocean carbon storage during glacial periods. *Sci Adv, 5*(6), eaaw4981. 10.1126/sciadv.aaw4981

Lauvset, S. K., Key, R. M., Olsen, A., van Heuven, S., Velo, A., Lin, X., et al. (2016). A new global interior ocean mapped climatology: the 1° × 1° GLODAP version 2. *Earth System Science Data, 8*(2), 325-340. 10.5194/essd-8-325-2016

Li, T., Robinson, L. F., Chen, T., Wang, X. T., Burke, A., Rae, J. W. B., et al. (2020). Rapid shifts in circulation and biogeochemistry of the Southern Ocean during deglacial carbon cycle events. *Sci Adv, 6*(42). 10.1126/sciadv.abb3807

Lynch-Stieglitz, J., Vollmer, T. D., Valley, S. G., Blackmon, E., Gu, S., & Marchitto, T. M. (2024). A diminished North Atlantic nutrient stream during Younger Dryas climate reversal. *Science, 384*(6696), 693-696. 10.1126/science.adi5543

Rae, J. W. B., & Broecker, W. (2018). What fraction of the Pacific and Indian oceans' deep water is formed in the Southern Ocean? *Biogeosciences, 15*(12), 3779-3794. 10.5194/bg-15-3779-2018

Rafter, P. A., Gray, W. R., Hines, S. K. V., Burke, A., Costa, K. M., Gottschalk, J., et al. (2022). Global reorganization of deep-sea circulation and carbon storage after the last ice age. *Sci Adv, 8*(46), eabq5434. 10.1126/sciadv.abq5434

Sikes, E. L., Elmore, A. C., Allen, K. A., Cook, M. S., & Guilderson, T. P. (2016). Glacial water mass structure and rapid δ18O and δ13C changes during the last glacial termination in the Southwest Pacific. *Earth and Planetary Science Letters, 456*, 87-97. 10.1016/j.epsl.2016.09.043

Reviewer #1 (Remarks to the Author):

R1 review of Dai and Yu, "Deglacial polar Southern Ocean carbon release driven by biological and physical dynamics," submitted to Nature Communications, by Jesse Farmer
The authors have taken significant steps to revise their manuscript following detailed reviewer comments. I appreciated the time and care they put in the responses to reviewers and the clarifications added to the manuscript. There are still some outstanding issues that need addressing related to the clarity of the presentation; I've highlighted these as major comments. Ultimately, although I may not fully agree with the presented interpretations, I think the authors provide valuable additions to the discussion of the ocean's mechanistic role in deglacial atmospheric CO2 increases that should be open to broader discussion. Thus, I support publication once the below comments are addressed.

We thank the reviewer for the positive comments. We've revised our interpretation for the early HS1 data (Major comment 1). We've also improved writing for clarity, based on the detailed and constructive comments.

Major comment 1. L198-203. I'm not following how it is plausible for sea-ice to be sufficiently reduced to allow for CO2 isotopic equilibrium (and hence 14C equilibrium), but not CO2 concentration equilibrium (which is ~an order of magnitude faster). This is all the more confusing because the authors later call on a concurrence of CO2 isotopic and concentration equilibrium during the Younger Dryas (L257-261). The authors should revisit the explanation; they can also allow that their interpretation is not consistent with other paleodata and worth further investigation.

We've revised our interpretation of our $[CO_3^{2-}]_{as}$ reconstruction and literature radiocarbon records during early HS1. We now suggest that the large changes seen in radiocarbon records may be related to changes in the geometry of global overturning circulation, while the roughly stable $[CO_3^{2-}]_{as}$ at our site might be related to the lack of warming in the PAZ. Model simulations show that warming is important to promote CO_2 outgassing (Khatiwala et al., 2019). Thus, little warming would result in negligible outgassing with limited change in $[CO_3^{2-}]_{as}$ during early HS1. We fully appreciate that multiple processes can control air-sea CO_2 exchange and encourage further investigations to explain the contrasting changes in geochemical tracers during early HS1 (Lines 231-239).

Major comment 2. L162-170. This paragraph needs some work. There should be a more clear comparison between the [CO32-]_as-derived DIC sequestration estimate and the [PO4]-derived DIC sequestration estimate. For instance, you could add in on L166, "This DIC sequestration is larger than that estimated from [PO4*] of +58±18 µmol/kg". Then the sentence on L167-170 should be clarified: It appears you are ascribing the DIC sequestration from [PO4*] directly to biological processes,* *whereas the additional DIC sequestration from the [CO32-]_as indicates a further contribution from physical processes, such as a sea ice barrier (and add references for this mechanism).*

Ultimately, the I found that the paragraph on L204-218 did the best job of outlining the various quantitative datasets, comparing them, and reaching conclusions on relevant mechanisms. This should be adopted to the other paragraphs.

We've improved writing for all related paragraphs following your useful advice. We clarify that DIC changes derived from PO_4* is ascribed to biological processes, and the additional DIC changes derived from $[CO_3^{2-}]_{as}$ is ascribed to physical processes (Line 192). When DIC changes are inferred, $[CO_3^{2-}]_{as}$ and PO_4* changes that are used to make these inferences are mentioned alongside (e.g., Lines 161,191).

Major comment 3. L116-136. As someone who loves thinking about endmember compositions, even my head is spinning from all the values presented here. I'd strongly recommend adding a table of modern NSW, modern SSW, LGM NSW and SSW endmember values, percentages estimated for the core site, and derived values for the core site to aid the reader through this text.

We've added Table 1 to show various values used for calculations and discussions following the reviewer's suggestion.

Minor comments.

Title: "driven by biological and physical dynamics" is rather vague. Perhaps "Biological and physical contributions to deglacial polar Southern Ocean carbon release" or similar?

We changed the title to "Contributions of biological and physical dynamics to deglacial CO2 release from the polar Southern Ocean".

L26-27. Suggest adding "during the Late Pleistocene glacial-interglacial transitions"

L39-40. Suggest specifying "…quasi-conservative properties of deep waters set by the PAZ surface".

L55. Remove unnecessary comma after "(3)"

L58. Cite refs. 19 and 20 at the end of this sentence.

Changes were made following these comments.

L70-74 and Fig 1. This discussion has been greatly streamlined. One note, I'd highly recommend making the color step the same unit in panels a, d (5 or 10 μmol/kg) and b, e (0.1 μmol/kg). This allows the reader to simply visualize how much PO4 changes relative to PO4.*

We appreciate the reviewer's thought. After some trying, we found it is difficult to use the same color steps for Fig. 1a and d, due to the smaller variability of deep ocean $[CO_3^{2-}]_{as}$

(PO_4*) than [CO_3^{2-}] ([PO_4^{3-}]). We thus have decided to use the full color map to illustrate the differences between SSW and NSW [CO_3^{2-}]$_{as}$ and PO_4*. Given the reviewer's suggestion, we've added a short sentence in Fig. 1 caption to remind readers regarding different steps for various panels. (Line 534)

L80. Change to "may allow for distinguishing the…"

Changed.

L88-89. Strongly recommend briefly stating those proxies here in 1-2 sentences. There is space in the main text and it prevents the reader from having to flip to the methods three times.

Information added (Line 95).

L101 and throughout. Note that the new supplementary figures appear out of order with their presentation in the text; these will need to be reordered. For instance, Fig S5 should become Fig S2.

All supplementary figures are rearranged according to the cited order.

L105. Add space between [CO32-] and "at"
L108, L114 and elsewhere. Recommend changing to "organic matter" as "matter" is typically indicative of a plural quantity.
L111. Remove comma or swap "that" with "which". The options are either "…change, which is" or "…change that is"
L142. Suggest adding hyphen: "physically-driven"

Changes were made following these comments.

L144-145. The authors should cautiously note here that the atmosphere-ocean exchange times for O2 and CO2 are not equivalent (e.g., Broecker and Peng, 1974), but that difference may be expected to be mediated by the millennial-scale integration of their sediment records.
Reference: Broecker, W., and T. Peng (1974), Gas exchange rates between air and sea, Tellus, 26(1–2), 21–35.

We've clarified that the disequilibrium in O_2 must be accompanied by CO_2 disequilibrium due to the longer equilibration time of CO_2 (Line 162).

We've also added the reference (Line 163).

L156. Suggest changing to "which are presumably biased toward the spring-summer seasonality of phytoplankton blooms that are offset from wintertime deep water formation". Although the OAZ-PAZ difference might also be important, it would take more detail to explain why than is provided here, and so I think it best to not dwell on

this difference. (Alternatively, the authors could devote several sentences to explaining why the OAZ would be expected to be distinct from the PAZ).
L167. Change to “combines”
L190. Change “using” to “in”
L200. Change to “enhanced”
Changes were made following the above comments.

L204-218. As noted above, nice paragraph here – I find this argument convincing.
Thanks!

L227. Delete the repetition of “at our site”
Changed.

L230-239. See Major Comment 2. As you did in L204-218, you should include the magnitudes of DIC change inferred from both PO4 and CO32-_as to support the statement of physical changes being necessary (L238-239).*

L257-261. See Major Comment 1. I find it really challenging to have radiocarbon ventilation work with CO2 outgassing at one point, but without it at a previous point.
Please refer to our responses above (Major comment 1).

L262. Suggest changing to “Conclusions”
L265. Change to “partitioning”
L267-268. Recommend changing to the following: “…were mediated by biological and physical processes both between the LGM and the Holocene interglacial, and on millennial timescales during the deglaciation”
L270. References should be added here.
L274-275. Specifically, PAZ CO2 outgassing as diagnosed in this study
L275. “was reduced”
L278. Change to variability (it is also plural)
L279-280. Specify your approach – namely, reconstructing CO2 exchange through PO4 and CO32-_as*
L281 (Methods throughout). The equations should all be set on separate lines, and not in-text (see L312, 317, 336-337, 349, 355, 356, 358, vs. L415, 416, 419, 420...)

Changes were made following these comments.

L301-304. How was d18O and d13C precision quantified? What standards were used for normalization?

We added details for determining stable isotope precision in the Methods (Line 348). Normalization standards are commonly not reported.

L310-346. It appears the [CO32-] reconstruction paragraph should be presented first, as the Monte Carlo approach is referenced in the [PO4] reconstruction paragraph. However, as the [PO4] paragraph currently comes first, this Monte Carlo approach has not yet been introduced.
L313-314. Add comma before "which"
L351. Missing reference.
L383-385. I believe these should be combined into one sentence.
L506. Caption panel f. Specify "Deep-sea coral-bound"
Changes were made following these comments.

Reviewer #2 (Remarks to the Author):

General remarks:
The authors have substantially reorganized the manuscript since the first submission, and the submission is much improved. The authors have clarified the conclusions of the paper in such a way as to make the significance clear, and there is considerably more discussion of the background necessary for the interpretation of the PO4 and [CO32-]as data. For example, the utility of the tracer pair is made clear, particularly by Fig. S1. They have removed discussion of the sub millennial scale variability in early HS1 (18-16.3 kyr) from the text, which I think was not justified in the previous draft given the lack of statistical significance in the measurement, and instead discuss on the lack of change during this time.*
More detail has been added clarifying the significance of their reconstructions in the context of existing records of nutrient utilization efficiency (e.g. δ15N records), which I felt was unclear or not present before. The authors results serve to confirm the conclusions of existing δ15N records from the OAZ and provide a complementary constraint to existing records that may have been governed by different processes (although it appears that they are in fact consistent).
The discussion of the sensitivity tests was confusing before in the previous draft, and I think the text benefits from the authors' decision to summarize these in the supporting material. I think that the added sensitivity tests details in Fig. S6 and S7 also substantially improve the paper.
All in all the authors should be congratulated on an improved manuscript that reads logically and mostly clearly.
We thank the reviewer for the positive comments.

Specific Comments:

I was perhaps unclear with regard to the core top values of PO4 and [CO32-]as in the previous draft. My point was that, given the placement of the core top values in Fig. 2F and Fig. 2G, it would seem that the values you are calling Late Holocene (4.2-0 kyr) identify no change between 8 kyr to Late Holocene in PO4* and CO32-*

as , which I found surprising. I take your general point in your response that this study may not be suitable to examine these features between 8kyr and Late Holocene. However, upon looking at the latest version of the data (I believe Fig. 3F is comparable in the new paper to Fig. 2G in the first submission), it appears that there is now a substantial difference (~15 µmol/kg) between the Late Holocene and 8 kyr values in CO32-as. This wasn't present in the previous version of the paper. What is changing between the two versions of the paper that is driving this large change? The change in the LH value is on the order of that observed across the YD or ACR in your data, so is a substantial change to be seeing between two separate submissions.

We've updated the Late Holocene $[CO_3^{2-}]_{as}$ in the 2nd version which is ~10 µmol/kg higher than that in the 1st version. The ~10 umol/kg difference is caused by two factors below.

(1) A ~7 µmol/kg difference is due to the global alkalinity effects during the Holocene (Fig. X1), which was not considered in the 1st version (see Fig. X1); and

(2) A ~3 µmol/kg difference comes from different calculation method for the Late Holocene $[CO_3^{2-}]$ averages: one includes all $[CO_3^{2-}]$ reconstructions (n = 4) while the other only includes $[CO_3^{2-}]$ reconstructions (n = 2) with paired $[PO_4^{3-}]$ reconstructions (Supplement Data).

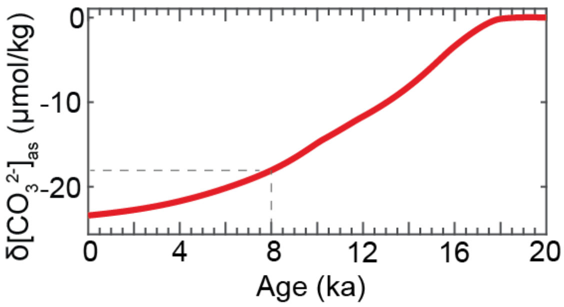

Fig. X1. Effects of the global alkalinity change on deep Southern Ocean $[CO_3^{2-}]$ assuming no air-sea CO_2 exchange.

Line 101-102 is a bit misleading. You are discussing the increase in bottom water O2 from the LGM to the LH, which is ~75 µmol/kg – but then you say that that change is similar to previous records. The record you show in Fig. S5 has no Late Holocene data whatsoever. The two records are impressively close in behavior and magnitude, but Fig. S5 does not back up any statement about LGM to LH change being similar to previous records.

Indeed, it would be ideal to have the LH $[O_2]$ reconstructions at site MD12-3396CQ, but such records do not yet exist. So, we now show the modern ocean $[O_2]$ to indicate the LH $[O_2]$ levels at sites MD12-3396CQ in Fig. S4. As can be seen

Supplementary Fig. 4, data from the two cores show similar changes between the LGM and the LH.

Forgive my confusion, but I thought you might clarify lines 110-112 a bit further. It feels like you are building towards an obvious conclusion for the reader about the sums of these multiple factors, but as I understand it, the measured increase in [CO32-] is 13 µmol/kg and the expected changes you list are an increase of 5 µmol/kg (PO4 decrease), a decrease of 26 µmol/kg (global alkalinity and DIC decline), and a decrease of 2 µmol/kg from T/S/Depth changes. I could easily be reading it wrong, but it feels like lines 110-112 imply that the numbers you give in the preceding lines should in some way sum or difference to 39 µmol/kg – but looking at the difference between reconstructed [CO32-] and the three factors listed above doesn't give 39 µmol/kg (difference between an increase of 13 and a decrease of 23). I say this because the way you listed the factors driving your calculation of CO32-as in lines 52-57 make it feel like these factors should give you the number back for your LGM to LH change that you give in the paragraph.

The confusion is largely due to different LH [CO_3^{2-}] averages as explained in the response to your first specific comment. To make numbers consistent, we've revised the amount of [CO_3^{2-}] change to 16 µmol/kg that is based on 2 data points with paired [PO_4^{3-}] reconstructions.

Line 227 is also a bit confusing. It looks to me like the changes in of PO4 and [CO32-]as during the ACR are ~0.25 and ~10 µmol/kg, respectively (Fig. 3C and 3F). It seems like a 30% decline in SSW% (going from 100% to 70%) could then, in fact, account for the reconstructed magnitudes almost entirely. Unless I am missing something with the calculation, I feel that this statement is not supported.*

We've improved our argument here. It is theoretically possible to explain the observed changes in PO_4^* and [CO_3^{2-}]$_{as}$ using SSW% changes as acknowledged in Lines 261-264. However, this was hardly the case, because SSW% was unlikely to 100% during HS1 and a large SSW% decrease would contradict with deep-water [O_2] changes during the ACR (Line 265).

Line 246: Why assuming little change in NSW%, if you mention that SSW% declined? I think I know what you mean but this could be clearer, as it seems like from line 242 you would assume some change in NSW%.

We've now clarified that we estimate the maximum influence on PO4* at MD97-2106 from changes in NSW endmember values by using 70% for SSW% at our site (Line 285). In other words, the influence from NSW endmember variations would be decreased if using higher SSW%.

Line 251-252 is not clearly written. Should this be "driven by changes in SSW endmembers"?

Revised following your suggestion (Line 292).

There are small typos and grammatical errors throughout the text that I encourage the authors to correct prior to another resubmission. For example, the first line of the abstract is, to my understanding, not grammatically correct – I think you cannot be "deemed as a region regulating…", and I think "important implications" would be referring to changes in the polar Southern Ocean. I also was curious what the other part of "in part" is (line 13) – this seems like the main challenge for this region. Another easy but obvious small error is that the references are not carefully formatted throughout -Line 35 for example. Also, they appear to have forgotten a reference listed in line 351 (ref. XX).

We have corrected typos and errors throughout the manuscript including those specifically pointed out here.

This is a personal preference, but the use of δ in the figure labels for Fig. 3 is not intuitive to me, given its common usage as other notation for isotopes. I would prefer personally if they were replaced with Δ if you are seeking to indicate change relative to some average (in this case LGM values). This would make it consistent with you calculations lines in the Methods section (Lines 354-360, for example).

We chose to use δ rather than Δ to denote changes to avoid potential confusions. Specifically, $\Delta[CO_3^{2-}]$ is often used to present calcite saturation state, not temporal changes/anomalies.

Reviewer #3 (Remarks to the Author):

The authors have done a good job addressing my concerns and I found the paper significantly strengthened. I found the addition of the sensitivity tests in Figure 3 particularly helpful, along with the improved description of the [CO32-]as tracer and the restructuring. It is worth noting though that despite the improved description (and having thought about this quite a bit), it took me some time to get my head back into [CO32-]as space, and this will likely be true of your readers. I suggest taking on a description similar to that in Gruber et al., 2009, as per the comment on line 53.

I have a series of comments below that I think should be addressed prior to publication. These include minor typos and ways to improve the clarity and robustness of the argument, but also a couple of more major comments, including an important point on the sensitivity of the [CO32-]◊DIC calculation under altered whole ocean alkalinity.

We thank the reviewer for positive reviews. In the revision, we've provided more information about $[CO_3^{2-}]_{as}$ and strengthened our arguments based on your comments.

12 – "is sparse" would be much better after "evidence"
14 – "challenges in obtaining"

Changes were made following these comments.

21-22 – "biologically unutilized carbon as a key source for deglacial CO2 outgassing in the polar Southern Ocean" – not super clear. Suggesting leading this sentence with what you actually see in the signals in HS1 (e.g. rising PO4 and [CO32-]as) and how this allows you to infer a shift from lower preformed nutrients and high carbon uptake to higher preformed nutrients and lower carbon uptake.*

22-23 – "relieved gas exchange disequilibrium" is confusing as written. This sentence and the abstract in general would also benefit from more explicitly discussing the HS1 and ACR as well as the YD change.
Also note that, as discussed in more detail in comments on lines 164-170 below, the whole ocean change in ALK and DIC is I think a significant contributor to the glacial-interglacial change in carbon uptake calculated from [CO32-]as.

We've revised the latter part of Abstract following these comments. We've specified that reduced biological nutrient utilization was a key process controlling the deglacial CO_2 outgassing.

In addition, we've clarified that contributions of physical processes to CO_2 outgassing is deduced from comparing carbon changes estimated using PO_4^* (reflecting biological impacts) and $[CO_3^{2-}]_{as}$ (reflecting impacts from all processes) as described in Lines 18-24.

30 – I think some more nuance is required here, as in general biological processes are not thought to have much influence in the PAZ. While biology is always somewhat tied in to carbon and nutrient balance, and may play a role indirectly too via global increase in respired carbon storage at the LGM, the observation that export is lower in PAZ at LGM and increases over deglacial goes in the wrong way, in isolation, for biology to be key in enhancing deglacial outgassing in the PAZ.

This sentence is rewritten to clarify that released carbon were previously sequestered via both biological and physical processes (Line 30).

45 – "in deep-water formation regions"
49 – "Recently, a tracer of the air-sea exchange"
Changes were made following these comments.

53 – both here and in figure 1 caption I think it would be very helpful to reference the Gruber et al. (2009; GBC) DC_gas-exch property. This is conceptually equivalent to [CO32-]as and that paper explains it very clearly.

More generally, while I found the revised manuscript easier to follow, I would still encourage the authors to expand their introductory description of this tracer at some point here or in the sections below, with a few lines on how it is set in the North Atlantic (which is a nice easy case) vs AAIW (another useful end member) vs SSW from the PAZ (which is less clear than NADW or AAIW yet is central to this paper).
We now refer to Gruber 2009 and 1996 when introducing $[CO_3^{2-}]_{as}$. (e.g., Line 51)

Following the reviewer's suggestion, we explain driving factors for deep ocean $[CO_3^{2-}]$ variation before describing how the air-sea exchange signature of $[CO_3^{2-}]$ can be calculated (Line 54). The reason why SSW $[CO_3^{2-}]_{as}$ is high is also explained (Line 69).

64 – delete "on the other hand" as this sentence isn't really in tension with the previous one – they both have the same general sense.
Removed.

78 – not strictly quite true – you discuss below quite extensively that both biological and physical processes might influence PO4 via gas exchange influence on O2. I agree this may not be a super sensitive effect, but it's not nothing.*
Added "largely" to be accurate (Line 84).

93 – add "and uncertainties on derived properties are given at 1 sigma throughout".
Added (Line 102).

99 – 102 – briefly mention here or in text immediately prior to this results section above that only perform the derived tracer calculations where you have paired data from the same sediment depth. This is important given the different temporal extents of the different datasets.
Added (Line 100).

100 – unclear whether Late Holocene data is from forams or water column (line 483 says "late Holocene data" which seems like forams, but I can't find these data anywhere – they could for instance easily go into the supplemental figure on core depth). Forams would of course be preferable but I understand that this might be limited by abundances. Water column is ok especially as the youngest data in the core seem to align well with these values, however would still benefit from brief justification e.g. Have the youngest data (which from the figures appear to be ~8-10 ka) been aligned to water column values, such that the B/Ca data down core is anomaly from modern values (i.e. taking account of any calibration offset)? If so, there needs to be justification about why it's ok to do this with Early Holocene data and that we don't need to worry about an EH peak in e.g. B/Ca.

We specify that these are core-top sediment samples in the caption of Fig. 2 (Line 553).

107 – add reference to figure 3 after "compared to the LGM"

Added.

110-111 – note here that this model dependent – stating just that it influences by 26 umol/kg makes it sound as if we know this precisely. It might be 26 umol/kg, but it could alternatively be 15 or 40, we really don't know. Should also note that while this is a big influence on the size of the glacial-interglacial change, it shouldn't substantially influence the structure or timing of the deglacial changes – can also reference S7.
We've added a sentence citing the sensitivity test to show that our conclusion (both biological and physical processes contributed to more carbon sequestration during the LGM) is independent of the choices of model simulation results (Line 124).

116 – Fig S8 ◊ S6
Supplementary figures were reordered and references to them were checked.

138-139 – might it be possible to give some feel for how much is physical vs biological based on the O2 and PO4 signals themselves? i.e. O2 has a more striking change than PO4 – might this point to an important role for physical processes?

We think in general it is difficult to tease out contributions of biological and physical processes by looking at in-situ properties, because of the large influence of organic matter respiration on them.

140 – I think jumping straight to DIC is a bit unclear. More straightforward would be clearer to say biologically unutilized phosphate and associated DIC.
We now adopt this suggestion throughout the manuscript.

148 – "declined … ratios" – unclear, rephrase

Rephrased.

150-153 – there's some important nuance that I think should be added here (and below), in that biological export production in the PAZ is lower at the LGM compared to the late Holocene, so increased biological usage would need to be relative to supply. Many readers not super familiar with the field would read this sentence as indicating greater biological productivity, rather than utilisation relative to supply.

Discussion here was reorganized to emphasize that it is the nutrient utilization that drove changes in carbon sequestration, and the lowered PAZ export productivity is also mentioned as a caveat (Line 182).

154-155 – I don't think "storage" is quite the right word here. Storage suggests carbon at depth, whereas these preformed signals are I think better linked to "uptake" or "reduced outgassing" or "improved nutrient and carbon usage efficiency". This could then lead to net improvement in deep storage; I think this nuance should be mentioned. This is particularly the case given the comparison to nitrogen isotopes that follows – these explicitly track surface utilisation efficiency, rather than deep storage.

Changed to "uptake" (Line 175).

We also expand the discussion about how our PO_4* reconstruction supports more deep-water carbon storage by surface Southern Ocean carbon uptake (Line 181).

162 – again slightly confusing sentence; at least needs an "improved" in front of efficiency
163 – maybe add "more directly" between "also" and "demonstrates"
Revised.

164-167 – one key concern here is on the sensitivity of [CO32-]as to DIC change (which I think is assessed based on modern ocean data) and how this would change under overall higher ocean ALK and DIC at the LGM?
There are two related issues:
The first is that authors are using higher ALK and DIC based on model results and while this will not alter the structure of the deglacial change (as discussed above and in Figure S7), it will impact the value calculated here, and I think this should be acknowledged.

We acknowledged that the estimated DIC change is partially dependent on the global alkalinity derived from model simulations, which has little effect on our conclusion (line 193).

The second is that if the ocean has higher overall ALK and DIC, it seems the relationship between [CO32-]as will likely be different. I have tried looking in to the references given here about how this sensitivity was established but couldn't find an easy answer to this and I think it should be as least briefly discussed.

Sensitivities of carbonate system to physical conditions, phosphate, and DIC are similar as shown by comparing results using preindustrial and LGM data sets (Yu et al., 2019). That is, global ALK changes have negligible impacts on the $[CO_3^{2-}]_{as}$ vs DIC sensitivities. We've clarified this point in the supplementary material (Line 415).

167 – "Different from PO4" – there's the need for a bit more nuance here, as you've discussed above how physical processes can also influence PO4* via O2* *disequilibrium, so this sentence jars a bit compared to the text above. I think the resolution to this point is your argument that at least some of that O2 disequilibrium may ultimately be derived from biological utilisation, and it would be helpful to reference this briefly again here.*

The commented discussion was reorganized. We now say that PO_4* is <u>dominantly/largely</u> driven by biological processes (Line 84). We've also clarified that DIC changes stoichiometrically associated with PO_4* are the upper limited of biologically-driven DIC uptake, should there be any effect of physical processes on PO_4* via changing the preformed $[O_2]$. Therefore, the larger DIC change associated with $[CO_3^{2-}]_{as}$ than PO_4*supports a physically-driven component in air-sea CO_2 changes (Line 195).

The other important point here relates to the comment above, which is that a substantial portion of the [CO32-]as comes not from within ocean biological or physical processes, but from whole ocean carbon cycle change, so doesn't fit neatly within this biological vs physical partition. This should be explicitly discussed.

In terms of the procedures to calculate $[CO_3^{2-}]_{as}$, we must use $[CO_3^{2-}]$, $[PO_4^{3-}]$, TSP, and global alkalinity changes. After the calculation, $[CO_3^{2-}]_{as}$ reflects air-sea exchange component CO_2 changes, attributions of which can be partitioned into influences from biological and physical processes.

Here we use the LH-LGM deep-water $[CO_3^{2-}]$ change (Fig. X2) to illustrate the relation between carbonate system changes caused by the whole ocean alkalinity-DIC changes related to $CaCO_3$ input/output imbalance and by air-sea exchange effects. If we consider the LH-to-LGM transition (that is backwards in time), reduced $CaCO_3$ burial during the transition would raise alkalinity and DIC at 2:1 along the trend defined by LH-LGM' (Fig. X2). [Note that from the LGM to the LH, increased deep-sea $CaCO_3$ preservation is observed (Cartapanis et al., 2018). Thus, $CaCO_3$ burial would be reduced from the LH to the LGM].

Without air-sea CO_2 exchange, in-situ $[CO_3^{2-}]$ would have been raised (LGM'). In contrast, the LGM $[CO_3^{2-}]$ is observed to be lower than the LH level (LGM). Therefore, during the LH-to-LGM transition, DIC must be raised by more CO_2 sequestration (LGM'-LGM). When calculating the magnitude of the DIC change (LGM'→LGM), the global alkalinity change is required; in other words, the global ALK change affect the length of the "LGM'→LGM" vector. However, the DIC change (LGM'→LGM) must be caused by air-sea exchange which can be classified into changed due to physical and biological processes.

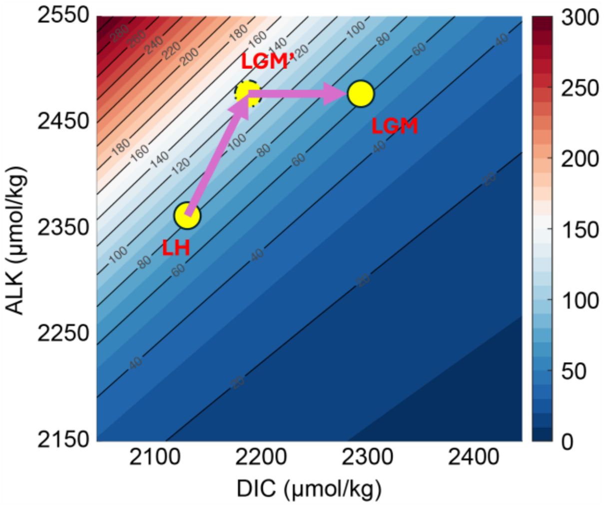

Fig. X2. Deep-water $[CO_3^{2-}]$ changes in the ALK- DIC space.

168 – "combines"

Fixed.

170 – again as above, a chunk of this is from whole ocean change and this should be specified.

See our response above and Fig X2.

182 – "contribution"
194 – "changes in"
202 – "only enhance CO2 outgassing in the PAZ negligibly" ◊ "but had minimal impact on CO2 outgassing"

Fixed.

203-205 – confusing as written – seems to imply that warming, which lowers solubility, limits outgassing! I think you are trying to say that it stays fairly cold, which means that there's not much solubility-driven change

This sentence has been revised to "the lack of strong CO_2 outgassing resolvable by our $[CO_3^{2-}]_{as}$ reconstruction might be related to minor surface warming in the PAZ and deep Southern Ocean during early HS1(Stewart et al., 2023), which has been shown by model simulations to be crucial to modulate physically-driven CO_2 outgassing(Khatiwala et al., 2019; Menviel et al., 2018)" Line (234).

206 – here and elsewhere "late HS1" is I think neater than "the late HS1" – but feel free to ignore

Changed throughout the manuscript following the advice.

209 – as above, is this really minor if O2 change is much bigger than PO4 change?
213 – again, I worry about sensitivity of this DIC value to higher ALK and DIC, as mentioned above
These were addressed in responses to previous comments.

217 – the timing of this change in [CO32-] also fits carbon release during the deep convection pulse suggested by Li et al. (2020, Science Advances)

We've cited Li et al. (2020) to suggest enhanced Southern Ocean convection as a potential physical process leading to CO_2 outgassing (Line 300).

223-224 – again, thinking about O2 in isolation likely useful here – high NSW input would be unlikely to drive low O2. The low O2 also nicely explains the gap in deep sea corals at this time (see Stewart et al., 2021, Paleo)
We've used the observation from Stewart et al. (2021) to support minimal increase in the NSW contribution to the deep Southern Ocean during the ACR (Line 266).

230 – why "possibly" given argument above – "likely" seems more likely!
241 – remove "in the both"
258 – 8 out of 40 would be better described as "minor" than "negligible"
353 – ref xx!
375 – unclear as written
Fixed.

380 – give the rationale for this (I went digging through the previous papers and found it but would be handy to mention briefly here)
The rationale has now been added (Line 448).

484 – foram data or water?
This is now specified that the data are based on core-top reconstructions (Line 552)

Fig S2 – would be helpful to also see the Mg data
Mg/Ca-based SST was added to this figure.

References

Cartapanis, O., Galbraith, E. D., Bianchi, D., & Jaccard, S. L. (2018). Carbon burial in deep-sea sediment and implications for oceanic inventories of carbon and alkalinity over the last glacial cycle. *Climate of the Past, 14*(11), 1819-1850. 10.5194/cp-14-1819-2018

Khatiwala, S., Schmittner, A., & Muglia, J. (2019). Air-sea disequilibrium enhances ocean carbon storage during glacial periods. *Sci Adv, 5*(6), eaaw4981. 10.1126/sciadv.aaw4981

Li, T., Robinson, L. F., Chen, T., Wang, X. T., Burke, A., Rae, J. W. B., et al. (2020). Rapid shifts in circulation and biogeochemistry of the Southern Ocean during deglacial carbon cycle events. *Sci Adv, 6*(42). 10.1126/sciadv.abb3807

Menviel, L., Spence, P., Yu, J., Chamberlain, M. A., Matear, R. J., Meissner, K. J., & England, M. H. (2018). Southern Hemisphere westerlies as a driver of the early deglacial atmospheric CO2 rise. *Nature Communications, 9*(1). 10.1038/s41467-018-04876-4

Stewart, J. A., Li, T., Spooner, P. T., Burke, A., Chen, T., Roberts, J., et al. (2021). Productivity and Dissolved Oxygen Controls on the Southern Ocean Deep‐Sea Benthos During the Antarctic Cold Reversal. *Paleoceanography and Paleoclimatology, 36*(10). 10.1029/2021pa004288

Stewart, J. A., Robinson, L. F., Rae, J. W. B., Burke, A., Chen, T., Li, T., et al. (2023). Arctic and Antarctic forcing of ocean interior warming during the last deglaciation. *Sci Rep, 13*(1), 22410. 10.1038/s41598-023-49435-0

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. *Nat Commun, 10*(1), 2170. 10.1038/s41467-019-10028-z