

Review of Karancz et al., “Glacial-interglacial contrasts in the marine inorganic carbon chemistry of the Benguela Upwelling System,” submitted to *Climate of the Past*, by Jesse Farmer

Karancz and colleagues present a reconstruction of ocean carbonate chemistry and its proximal drivers in the Benguela Upwelling System (BUS) covering the last ~27 kyr based on a combination box-piston core from the Walvis Ridge. I commend the authors for applying a wide range of analytically challenging proxies in their attempt to understand past carbonate chemistry in the BUS. The manuscript is overall well written, especially the detailed and extensive methods, and the top-line interpretation/conclusion of increased intermediate ocean carbon storage based on the difference between alkenone ϵ_P and boron-based pCO_2 proxies is quite novel.

For the bad news: I found several deficiencies that temper my enthusiasm for publication. Given that I think some major rewrites (and possibly additional data) will be needed, I recommend major revisions that allow for sufficient time to address this. I want to emphasize that, given the quality and quantity of data here already, I fully expect a revised paper would be worthy of publication in *Climate of the Past*.

Response: Hereby we would like to thank you for the valuable comments which helped to clarify and improve the manuscript. Below we provide answers to all comments point by point and indicate how they will be implemented.

Major comments.

1. Core stratigraphy. I found the combined stratigraphy from BC6 and PC8 to be lacking. If I read this correctly, the authors took the length of BC6 (41.5 cm) and appended PC8 to the bottom to create a composite depth scale of 141.5 cm. While this is probably in the general ballpark given the radiocarbon dates, this approach is far too simplified. The authors would have to be incredibly lucky to have it such that the total recovery of the box core (41.5 cm) just happened to align with the total amount of lost material from the top of the piston core! (In my experience, this has never once happened).

To address this, the authors should use physical properties measurements on the two cores to align them in depth space and create a composite depth scale. This can be any measurable property – bulk density, reflectance/color, XRF, etc. Once they have this data, they can then align the two cores based on these properties and create a single depth-age model in rBacon using the ^{14}C dates vs. composite depth.

Response: Thank you for pointing this issue out and we agree that the creation of the composite record on a time scale requires stronger underpinning and rephrasing for clarity. In the adjusted manuscript we will refrain from using a composite depth scale and, instead, discuss the individual age models of the BC and PC records, and try to align those appropriately. The total dated length of BC6 needs to be corrected in the manuscript text to be 40.59 cm (figures and interpretations are not affected, as the age model is based on the 40.59 cm length), providing a continuous record of 4.863 to 9.636 ka BP. From sediment core PC8, only the top 65.5 cm was considered in this study based on the radiocarbon dates and the rBacon age-depth model, as there is potentially a hiatus below this depth (as illustrated in Figure 3). The top 4.24 cm of PC8 is disturbed likely due to the piston coring.

We used, as suggested by the reviewer, brightness (I*) from the core scanner to align the two cores. This way we show that there is some overlap between BC6 and PC8, based on detailed line-scan pictures of the two cores. As the reviewer already indicates, the cores do obviously not exactly follow, but have an overlap of 4.24 cm interval (~5.360 to 9.635 ka BP). This implies that, the top 4.24 cm of PC8, which is disturbed likely due to the coring technique, overlaps with 30.14 cm of BC6 (i.e., from 10.45 to 40.59 cm), suggesting severe compression of the top of PC8 (and absence of material above that). Deformation at the top of piston

cores is not unusual, and much more likely than the box core being disturbed. Hence, this overlap can be used to align and tie together the two age models of BC6 and PC8 to produce a near-continuous record of 27.75 ka BP. Although the records are clearly very well correlated, we decided to use the box core at the top section as the compressed section (even with the very high correlation observed) might be somewhat disturbed. The manuscript text will be modified accordingly, including this new information. The figure showing the alignment of the two cores based on reflectance data will be included as a Supplementary Figure:

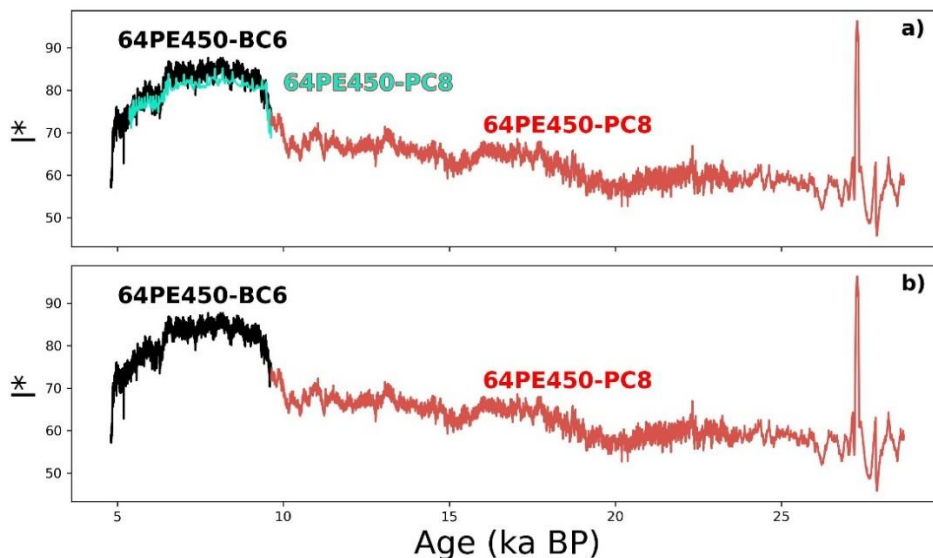
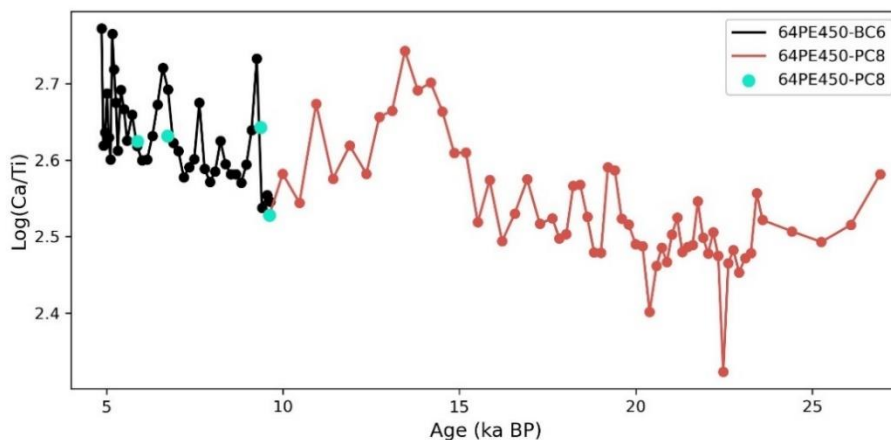


Figure S1. Light reflectance (I^*) measured in sediment cores 64PE450-BC6 (black line) and 64PE450-PC8 (red and green lines) plotted over the last 27 ka BP. Panel a) shows the record including the overlap of 64PE450-BC6 with the top 4.24 cm of 64PE450-PC8, which has been excluded from this study due to sediment disturbance likely caused by the coring technique used (green line). Panel b) shows the alignment of 64PE450-BC6 and 64PE450-PC8 that produces a near continuous record from 27 to 4.8 ka BP.

Moreover, for the reviewer, we here also present the alignment based on Ca/Ti ratio measured by XRF-scanning of both cores. Although the measured ratios of PC8 align well with those measured in BC6, the age model cannot be confirmed by this data alone due to the lower resolution of the XRF-scanning analysis (1-cm resolution) compared to the color line-scan data (63- μ m resolution). Hence, we will add only the line-scan data to the corrected manuscript.

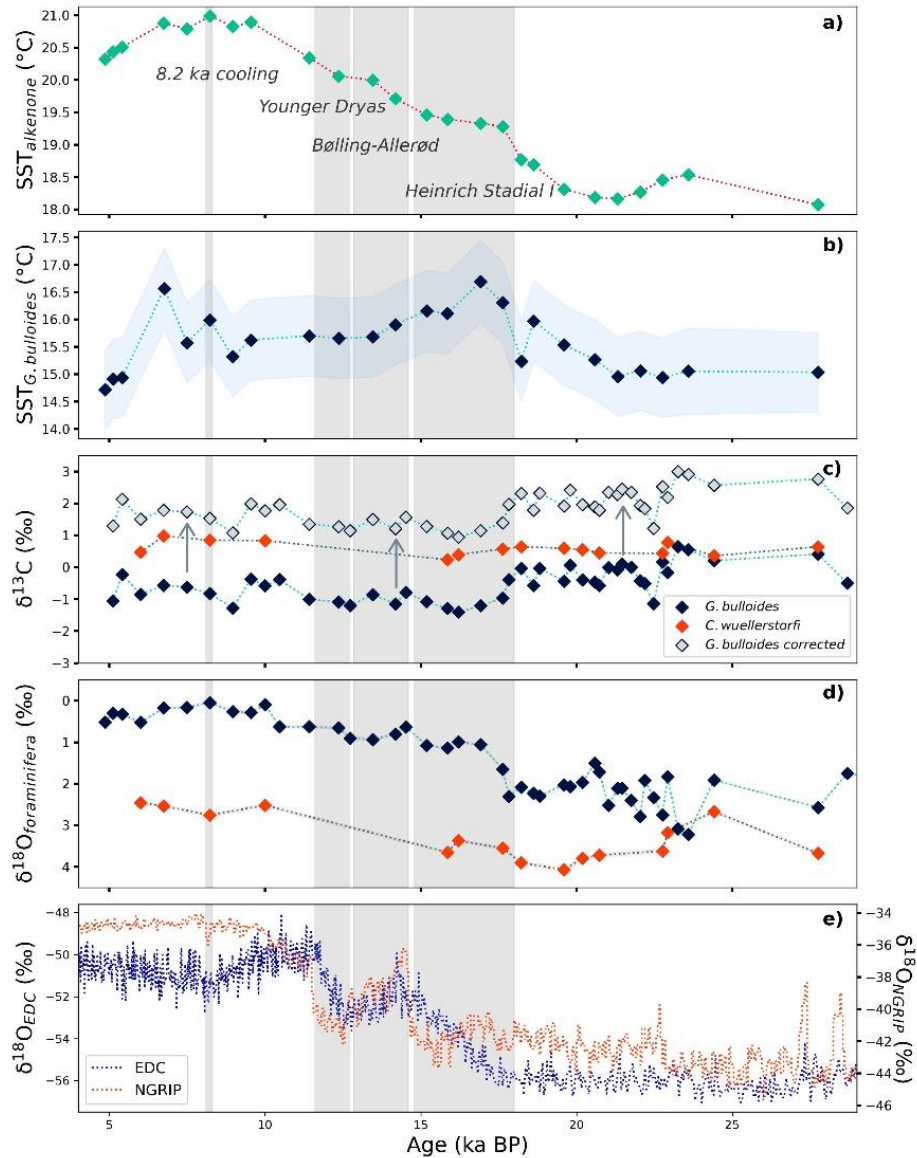


Additional Figure for the reviewer. Log(Ca/Ti) ratio (XRF-scanning element intensities) of 64PE450-BC6 (black line) and 64PE450-PC8 (red line and green circles) plotted over the last 27 ka BP. The top 4.24 cm of 64PE450-PC8 marked with green circles is not included in this study.

I don't ask for new data lightly in what is already an impressive multiproxy work. But there is very little other than ^{14}C (and then, only six of the eight shown dates) to benchmark this chronology. What else exists does not inspire much confidence – the benthic $\delta^{18}\text{O}$ record (Figure 4b) is effectively missing the entire deglacial section and so is of minimal utility. And I do not see at all the assignment of millennial-scale deglacial events in Figure 6 (it should be noted that *G. bulloides* $\delta^{18}\text{O}$ does not look like EDC). To this end, significant age model refinement will be needed if the authors wish to discuss millennial-scale features in their records during the deglaciation.

Response: We agree that correlations on a sub-Milankovitch time scale cannot be made with confidence here. For the overall aim of the paper, these detailed correlations are not needed as we mainly compare glacial to interglacial differences. Still, as we have the data at quite a high resolution, in the original manuscript we compared our data to existing records.

We noticed the resemblance of our records to the Southern Hemisphere climate responses based on the gradual increase of U_{37}^K temperatures from 23 ka BP onwards. This increase is also visible in a parallel decrease in $\delta^{18}\text{O}$ values for *G. bulloides*. The early deglaciation is to our opinion very much like that observed on the Southern Hemisphere. Comparing our record with both northern and southern hemisphere records, we also notice that individual climate events show similarities to the trends observed in Northern Hemisphere records, suggesting that the location of our sediment core was affected by both Northern and Southern Hemisphere processes. Acknowledging that our records miss the features necessary to make detailed correlations for individual events, we still would like to allow the readers to appreciate potential correlations for themselves. Hence in the revised manuscript, we will also add (to Figure 6) a key Northern Hemisphere record (NGRIP) and adjust the text accordingly within our discussion. We do believe that our independent age model acquired through ^{14}C -dating allows to at least compare large-scale deglacial trends and potentially multi-millennial changes within our record to key climate records from both hemispheres.



Adjusted Figure 6: Reconstructed sea surface temperatures (SST) based on a) the alkenone unsaturation index, U_{37}^K , and b) foraminiferal Mg/Ca, c) $\delta^{13}\text{C}$ analysed in benthic (*C. wuellerstorfi*) and planktonic (*G. bulloides*) foraminifera with corrected values, d) $\delta^{18}\text{O}$ of benthic (*C. wuellerstorfi*) and planktonic (*G. bulloides*) foraminifera, and e) $\delta^{18}\text{O}$ ice core record from EPICA-Dome C (EDC; Jouzel et al., 2007) and North Greenland Ice Core Project (NGRIP; North Greenland Ice Core Project members, 2004) shown for the past 27 ka BP. Modern day SST at core site 64PE450-BC6-PC8 is approximately 20.7 °C (GLODAPv2023; Lauvset et al., 2024; Santana-Casiano et al., 540 2009). Grey shaded areas mark climate events as labelled on the uppermost panel. Blue shaded area in panel b) indicates the error propagated from temperature calibration uncertainty and $\pm 1\sigma$ standard deviation of the duplicate measurement of the samples. Analysis of the stable isotopes (panel c and d) provided an error smaller than the symbols shown on the figure. Arrows in panel c) indicate the direction of the correction on the planktonic foraminiferal $\delta^{13}\text{C}$ values.

2. Presentation of alkenone ϵ_P -derived pCO_2 . Keeping in mind my affinity toward boron isotope approaches, the presentation of alkenone ϵ_P -derived pCO_2 stuck me as rather outdated. Namely, the approach outlined in the methods Section 3.8 does not acknowledge any of the vigorous discussion around the feasibility of this approach or its potential limitations. (Note that the authors do start to tackle this much further down on L651-678). I think the authors need to be more up front about what is known regarding the limitations of this proxy and how they sought to address these. Do haptophyte CCMs matter in an upwelling region? Is Ba/Ca actually a functional phosphate proxy in an upwelling region, where high OM remineralization rates can lead to $BaSO_4$ precipitation? Even if that problem is overcome, is Ba/Ca-derived PO_4 by itself enough of a constraint on the physiology of the alkenone producing community to address these issues?

Ultimately, it does matter that the authors' ϵ_P -derived pCO_2 is in reasonable agreement with ice core pCO_2 , and the authors could use this to argue that these recognized proxy complications may not be as significant in this particular setting. But the complications must be addressed head-on, and the reasoning for the authors' choices on calculation of pCO_2 should be made explicit to the reader.

Response: We acknowledge issues and uncertainties with using the $\delta^{13}C$ of alkenones in a low- $[CO_2]$ time interval, and apply this proxy here as an additional, independent method to reconstruct pCO_2 . Accordingly, we will add a section to introduce limitations of this approach within the Introduction section.

Sensitivity of the alkenone-based pCO_2 reconstructions to the 'b' factor (i.e., all physiological parameters affecting carbon isotope fractionation) has been tackled in various ways to improve the application of this proxy. While the approaches include compensation for e.g., nutrient levels, cell size and growth rate, these parameters do not necessarily correlate with each other (e.g., Riebesell et al., 1993), which makes it complicated to estimate carbon isotope fractionation during photosynthesis.

We agree with the reviewer that even though these uncertainties are known, they may not apply to this particular setting considering the good agreement between the alkenone-based pCO_2 and the ice core pCO_2 reconstructions. Results of this study using the Ba/Ca ratio as a nutrient proxy suggests, that the application potential of these various approaches may be regionally different, and the primary mechanisms controlling the 'b' factor need to be reevaluated for distinct environments, such as upwelling regions. Adaptation of active carbon uptake through CCM in haptophyte algae has been shown to potentially hamper the use of ϵ_P in pCO_2 reconstructions under low, for instance glacial, $[CO_2]$ conditions (Badger et al., 2021). However, the mechanisms and controls on how coccolithophores apply CCM is not fully constrained (e.g., Reinfelder, 2011) and CCM activity may also vary between species (e.g., Goulet et al., 2020).

The reviewer is referring to Ba remobilization as a complicating factor for using Ba. This applies to sedimentary Ba. Whereas here we use Ba measured on calcite shells. The correlation between seawater Ba and shell Ba has been published by e.g., Hönisch et al. (2011) and is not affected as long as the shells are adequately cleaned.

3. B isotope results, S/Mg and calculation of pCO_2 . There are a few issues here:

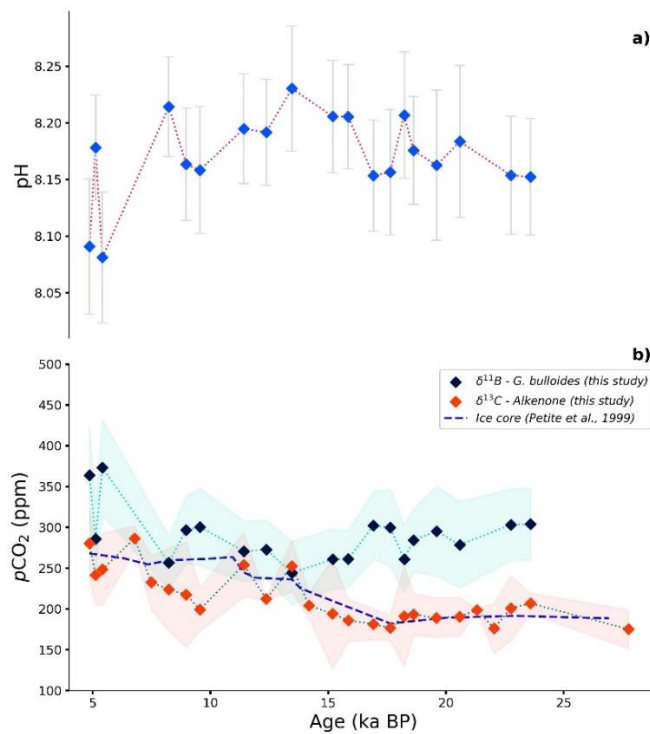
- *G. bulloides* size fractions and their $\delta^{11}B$. Numerous studies indicate that different size fractions of planktic foraminifera possess different B isotope ratios (Hönisch and Hemming, 2004; Henahan et al., 2013, 2016). Although I do not think this has been demonstrated explicitly in *G. bulloides*, the community tends to work in quite limited size fractions when measuring B isotopes in *G. bulloides*: 300-355 μm (Martinez-Boti et al., 2015) or 315-355 μm (Raitzsch et al., 2018, cited in the manuscript). In

this study, however, size fractions are not constrained; it appears the authors used specimens from 150 to 425 μm (Section 3.1). This adds an additional source of uncertainty that should be propagated into uncertainty on the reconstructed pH (L285), and it may be quite significant (in excess of 1‰, Hennehan et al. 2013 Figure 6).

Response: We are aware of potential impacts of ontogenetic variability on $\delta^{11}\text{B}$. Yet, unpublished data of Paulhac Buisson et al. (under review) suggest that $\delta^{11}\text{B}$ in *G. bulloides* is not affected by the foraminifer's size and confirms that the ontogenetic variability of $\delta^{11}\text{B}$, as presented from various species before, derives from the symbiont's activity. The impact of ontogenetic variability on foraminiferal $\delta^{11}\text{B}$ values has been shown for *T. sacculifer* (Hönisch and Hemming, 2004), *G. ruber* (Hennehan et al., 2013), and *O. universa* (Hennehan et al., 2016) which are all symbiont-bearing planktonic foraminifera. In their microenvironment, the pH is affected by the symbionts' physiological processes, such as respiration and photosynthesis, and the degree of pH alteration depends on symbiont abundance and density, and hence size of the foraminifera. We here used *G. bulloides*, which is a symbiont-barren species. We will add a statement about this to the Methods section.

- *Poor precision in some G. bulloides $\delta^{11}\text{B}$ replicates.* Looking at Figure 5a, there are a few datapoints where the replicate precision on the sample is $> \pm 0.5\%$. Boron is a tricky isotope system to measure, so I wonder if there was some plasma instability during these measurements. But regardless, the authors may wish to exclude these data as they don't appear sufficiently well-constrained to be useful for calculating pH or $p\text{CO}_2$.

Response: While seasonal differences of *G. bulloides* may contribute somewhat to a higher uncertainty in the pH reconstruction, we agree that datapoints with replicate precision as high as $\pm 0.5\%$ gives only an estimate and do not provide sufficient constraints on the $p\text{CO}_2$ reconstruction. These datapoints will be removed accordingly: this removal, however, does not affect the interpretation of the results.



*Adjusted Figure 7: Reconstruction of a) pH based on $\delta^{11}\text{B}$ of *G. bulloides* and b) $p\text{CO}_2$ based on $\delta^{11}\text{B}$ of *G. bulloides* combined with a constant total alkalinity of $2349 \pm 11.07 \mu\text{mol kg}^{-1}$ (dark blue diamonds) and $\delta^{13}\text{C}$ of alkenones (red diamonds). Modern day $p\text{CO}_2$ of the AAIW is approximately 326 ppm (Lauvset et al., 2024; Salt et al., 2015). Blue dashed line shows the Vostok ice core record of $p\text{CO}_2$ (Petit et al., 1999). Light green and red shaded area represent propagated error for the foraminifera and alkenone based reconstructions, respectively. See further details on uncertainty propagation in the text.*

- *Using carbonate ion alongside pH to constrain the carbonate system.* If I follow the authors' approach correctly, they seek to employ *G. bulloides* S/Mg or B/Ca as a separate constraint on the carbonate system to address uncertainty in paleoalkalinity (L680 and supplement). Unfortunately, this does not work well for a reason not included in the study: carbonate ion and pH strongly covary in the modern ocean ranges of alkalinity and DIC (see Figure 10 in Rae et al., 2011). For this reason, error propagation alone is not sufficient; the true uncertainty in the carbon system parameters derived using pH from B isotopes and carbonate ion from S/Mg, B/Ca would need to account for covariance of these parameters. Given this, I think it would be better just to remove this text/approach.

Response: Thank you for pointing this out. We agree and, therefore, the application of S/Mg and B/Ca for $p\text{CO}_2$ reconstruction will be removed from this study.

4. $\delta^{13}\text{C}$ gradients and estimation of BCP. In section 5.2, the authors do a pretty good job of laying out the complications to using $\delta^{13}\text{C}$ gradients as a proxy for the biological carbon pump (see also section 4.4 in Farmer et al., 2021). After laying out these significant complications, they state on L611-615 “a larger difference between planktonic and benthic foraminiferal $\delta^{13}\text{C}$ values during the LGM compared to the Holocene is evident (Fig. 6 c; and Supplementary Fig. S3), suggesting a more efficient BCP”. After re-reading this section, I do not agree with this conclusion. The data could more simply be explained as a change to lower $\delta^{13}\text{C}$ in AAIW source waters due to inefficient air-sea CO_2 exchange in a seasonally sea-ice covered Southern Ocean. To remove this influence, the authors could difference their benthic $\delta^{13}\text{C}$ record from one of similar depth in the South Atlantic not under the influence of Benguela Upwelling.

Response: We agree that variation in the water mass source present at the core location is an important aspect when foraminiferal $\delta^{13}\text{C}$ values are evaluated. Not only seasonal air-sea exchange but also organic matter decay and consequently lower pore water $\delta^{13}\text{C}$ may impact foraminiferal $\delta^{13}\text{C}$ values (Bickert and Wefer, 1999). Hence, we measured the carbon isotopes of the foraminifera in our record and compare our data to that of other sites in the South Atlantic, which suggests that the values measured here represent a stable South Atlantic water mass signal. We do acknowledge that this integrated signal actually may represent different processes, which is actually one of the main points of discussion.

In the manuscript, we suggested and applied a 2.4 ‰ offset assuming a continuous presence of AAIW at the site (at lines 610-611), which is based on observing similar benthic foraminiferal $\delta^{13}\text{C}$ values compared to those previously reported by Curry and Oppo (2005) from the western Atlantic. They measured $\delta^{13}\text{C}$ of *Cibicidoides* (various species) from the South Atlantic along the Brazil margin spanning a depth range of 400 to 3000 m, which is affected by the same water mass (AAIW) as our core site (1375 meter water depth). They present an average glacial $\delta^{13}\text{C}$ value of 0.5 ‰ at a depth of 1500 m, which agrees well with the values measured here. Their results suggest a glacial-interglacial $\delta^{13}\text{C}$ difference of -0.1 ‰ whereas we observe a difference of -0.2 ‰. Although a difference of 0.1 ‰ may still be the result of seasonal water mass

instability (or many other processes), it does not affect our final conclusions. We will rephrase and clarify this in Section 5.2.

5. Impact of Benguela Upwelling on atmospheric pCO₂. The manuscript sort of kicks around this idea that changes in upwelling intensity and/or its carbon content might have altered atmospheric pCO₂. In the biological carbon pump/preformed nutrient content view of ocean CO₂ uptake/release (e.g., Sigman et al. 2010), though, whether or not the BUS was a CO₂ source or sink would have minimal impact on global atmospheric CO₂. This is because any excess upwelled nutrients in the region would then be advected to regions where they would be consumed. That is, even a high rate of local CO₂ outgassing at the core site due to upwelling > productivity would be offset by adjacent regions, where productivity > upwelling and CO₂ uptake would occur. Put another way, the only places where upwelling has the capacity to alter atmospheric CO₂ is in regions where that upwelling adds nutrients to newly formed deep water, either around Antarctica or in the high latitude Northern Hemisphere. In all other regions, local imbalances are evened out spatially.

Response: We agree with this comment, which is very much in line with what we are trying to argue. As this was apparently not completely clear we will rephrase our text accordingly. Results of our study suggest that even though an enhanced amount of CO₂ was likely stored at intermediate depth, this was not outgassed during the glacial due to enhanced productivity.

Minor comment (just one for now). Suggest changing the title to “Contrasts in the marine inorganic carbon chemistry of the Benguela Upwelling System since the Last Glacial Maximum”. “Glacial-interglacial” implies that there are multiple data realizations of glacial intervals and interglacial intervals, so I found myself surprised when the data only went back to 27 ka.

Response: The title will be changed to “Contrasts in the marine inorganic carbon chemistry of the Benguela Upwelling System since the Last Glacial Maximum”.

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