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## **COMMENTARY**

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This article is a commentary on Qin et al. (2022), https://doi.org/10.1029/2021GL097121.

#### **Key Points:**

 The deep Atlantic and Pacific Oceans accumulated carbon at different intervals during the mid-Pleistocene transition

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# **Deepening the Late Quaternary's Deep Ocean Carbon Mysteries**

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**Abstract** Changes to the carbon content of the deep ocean, the largest reservoir in the surficial carbon cycle, are capable of altering atmospheric carbon dioxide concentrations and thereby Earth's climate. While the role of the deep ocean's carbon inventory in the last ice age has been thoroughly investigated, comparatively little is known about whether the deep ocean contributed to the change in the pacing and intensity of ice ages around 1 million years ago during the Mid-Pleistocene Transition (MPT). Qin et al. (2022, https://doi. org/10.1029/2021GL097121) provide new reconstructions of deep ocean carbonate ion saturation, a proxy for carbon content, from the deep Pacific Ocean across the MPT. Intriguingly, their results show that a reduction in deep Pacific carbonate ion saturation across the MPT occurred at different intervals from carbonate ion saturation decline in the deep Atlantic Ocean. These results suggest a more nuanced contribution of whole-ocean carbon sequestration to the climate changes reconstructed across the MPT.

Plain Language Summary Earth's periodic ice ages became longer and more intense around 1 million years ago. While the underlying reasons for this climate change remain debated, it is widely understood that the deep ocean may have played an important role by storing the potent greenhouse gas carbon dioxide away from the atmosphere. New research by Qin et al. (2022, https://doi.org/10.1029/2021gl097121) shows that the deep Pacific Ocean did indeed accumulate additional carbon around the time of this million-year old climate transition. However, the new results also show that Pacific Ocean accumulated carbon over different intervals than the Atlantic Ocean, deepening the mystery around how and why this carbon uptake occurred.

# 1. Introduction

The deep ocean contains approximately 38,000 billion tons of dissolved inorganic carbon (DIC), a quantity  $\sim$ 50 times larger the carbon inventory of the preindustrial atmosphere (which is predominantly carbon dioxide  $[CO_2]$ ). The atmospheric and deep ocean carbon reservoirs are directly connected through the ocean's physical overturning circulation, by which deep ocean waters circulate through the high latitude surface oceans every  $\sim$ 1000 years. In addition, the deep ocean accumulates DIC from the atmosphere through the respiration of sinking organic material produced by photosynthesis in the surface ocean. Given the sheer magnitude of the deep ocean DIC inventory relative to atmospheric  $CO_2$ , processes leading to only small changes to deep ocean DIC could have manifest impacts on atmospheric  $CO_2$  concentrations and hence climate. For these reasons, understanding how and why the deep ocean DIC inventory has changed is of paramount importance in the search for the drivers of atmospheric  $CO_2$  and climate change during the Pleistocene ice age cycles (Broecker, 1982; Sigman et al., 2010), as well as the lengthening and amplification of these cycles during the mid-Pleistocene transition (MPT) (e.g., Farmer et al., 2019; Lear et al., 2016; Pena & Goldstein, 2014; Raymo et al., 1997).

Despite its importance, past deep ocean DIC is a challenging parameter to reconstruct. Recent progress in unraveling past DIC has been made with empirical proxies of deep ocean carbonate ion saturation state, defined as  $\Delta[{\rm CO_3}^{2-}]$ . Carbonate ion saturation state is largely driven by changes to deep sea carbonate ion concentration, which in turn responds to the balance of DIC and alkalinity in the deep ocean. (For a detailed background on ocean carbonate chemistry and definitions of these key parameters, please see Dickson et al. [2007] or Zeebe [2012]). Given this dependence, past deep ocean DIC change can be quantified from  $\Delta[{\rm CO_3}^{2-}]$  reconstructions given constraints on past changes in deep ocean alkalinity.

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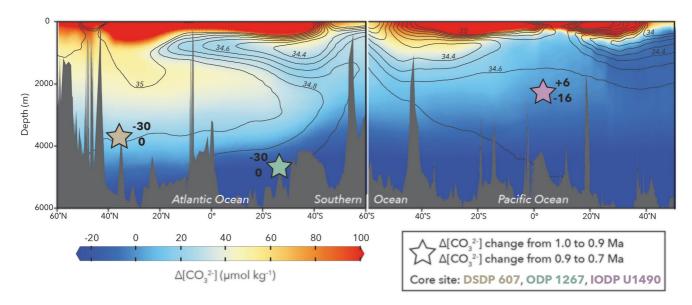


Figure 1. The modern distribution of salinity (contoured) and carbonate ion saturation state ( $\Delta[\text{CO}_3^{2-}]$  in  $\mu$ mol kg<sup>-1</sup>, colorbar) in the Atlantic and Pacific Oceans with sediment core reconstructions of  $\Delta[\text{CO}_3^{2-}]$  change during the mid-Pleistocene (stars). The superscript number next to each star indicates the reconstructed  $\Delta[\text{CO}_3^{2-}]$  change between 1.0 and 0.9 Ma, with the subscript number indicating the reconstructed  $\Delta[\text{CO}_3^{2-}]$  change between 0.9 and 0.7 Ma. Data sources: DSDP 607 B/Ca (Lear et al., 2016; Sosdian et al., 2018), ODP 1267 B/Ca (Farmer et al., 2019), and IODP U1490 *T. sacculifer* size-normalized weight (Qin et al., 2022). Plot created using Ocean Data View (Schlitzer, 2021) and hydrographic data from GLODAPv2.2021 (Lauvset et al., 2021).

# 2. Deep Ocean DIC Reconstructions Across the MPT

Ocean sediment measurements empirically related with deep ocean  $\Delta [CO_3^{2-}]$  include B/Ca ratios of benthic foraminifera (Yu & Elderfield, 2007) and planktonic foraminifer size-normalized shell weights (Broecker & Clark, 2001; Lohmann, 1995). For the MPT, previous benthic foraminifer B/Ca records from the deep Atlantic Ocean showed a ~30 µmol kg<sup>-1</sup>  $\Delta [CO_3^{2-}]$  decline between 1.0 and 0.9 million years ago (Ma) (Figure 1; Farmer et al., 2019; Lear et al., 2016; Sosdian et al., 2018). These results indicate pervasive DIC accumulation in the deep Atlantic linked to the reorganization of deep Atlantic overturning circulation at this time (Farmer et al., 2019; Pena & Goldstein, 2014; Raymo et al., 1997).

As the Atlantic Ocean represents less than one-third of the deep ocean's volume, a full accounting of surficial carbon cycle change across the MPT requires establishing whether DIC similarly accumulated in the deep Pacific, the most voluminous of the global oceans. Qin et al. (2022) address this with  $\Delta[{\rm CO_3}^2]$  reconstructions from IODP Site U1490 (Figure 1) using planktonic foraminifer shell-normalized weights. Intriguingly, their preferred reconstruction from weights of *Trilobatus sacculifer*, a surface-dwelling planktonic foraminifer (Schiebel & Hemblen, 2017) shows net DIC accumulation across the MPT that diverges from the deep Atlantic in its timing. In detail, Pacific  $\Delta[{\rm CO_3}^2]$  increased between 1.0 and 0.9 Ma when Atlantic  $\Delta[{\rm CO_3}^2]$  decreased, with a subsequent larger Pacific  $\Delta[{\rm CO_3}^2]$  decline from 0.9 to 0.7 Ma aligning with effectively no change in deep Atlantic  $\Delta[{\rm CO_3}^2]$  (Figure 1).

Qin et al. (2022) also reconstruct  $\Delta[\text{CO}_3^{2-}]$  based on the size-normalized weights of *Neogloboquadrina dutertrei*, a planktonic foramnifer that favors a deeper habitat near the deep chlorophyll maximum (Ravelo et al., 1990). The *N. dutertrei*-based  $\Delta[\text{CO}_3^{2-}]$  shows a pattern that differs from that of *T. sacculifer* in important aspects, with a continuous, albeit small,  $\Delta[\text{CO}_3^{2-}]$  decline from 1.0 to 0.7 Ma, and no evident  $\Delta[\text{CO}_3^{2-}]$  increase between 1.0 and 0.9 Ma as was observed in *T. sacculifer*. Qin et al. (2022) cite several reasons to discount the *N. dutertrei*-based  $\Delta[\text{CO}_3^{2-}]$  reconstruction, including its weaker core-top correlation to bottom water  $\Delta[\text{CO}_3^{2-}]$  than *T. sacculifer*. Additionally, *N. dutertrei* forms calcite crusts in the subsurface water column (Steinhardt et al., 2015), which could make its weight less sensitive to deep sea dissolution and thus a poor choice for deep ocean  $\Delta[\text{CO}_3^{2-}]$  reconstructions. While these arguments support using *T. sacculifer* size-normalized weights over those of *N. dutertrei*, as is done by Qin et al. (2022), more research is needed to assess the suitability of different planktonic foraminifer species for size-normalized weight  $\Delta[\text{CO}_3^{2-}]$  reconstructions.

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Assuming constant alkalinity, the increased deep Pacific  $\Delta[{\rm CO_3}^{2-}]$  implied by *T. sacculifer* weights between 1.0 and 0.9 Ma would imply a loss of ~60 Gt of DIC from the deep Pacific, which would fully counteract the reconstructed 30–50 Gt DIC increase in the deep Atlantic over this time (Farmer et al., 2019). Alternatively, the Pacific results could indicate a violation of the assumption of constant alkalinity. The  $\Delta[{\rm CO_3}^{2-}]$  increase could also result from the deep Pacific gaining alkalinity either in response to deep ocean DIC accumulation at this time (carbonate compensation), or as a consequence of sea-level lowering as ice sheets first expanded to their 100-kyr glacial configuration around 0.9 Ma (e.g., Kerr et al., 2017). In contrast, the subsequent deep Pacific  $\Delta[{\rm CO_3}^{2-}]$  decline between 0.9 and 0.7 Ma appears likely to represent a DIC increase, particularly as it parallels the development of enhanced stratification in the Southern Ocean (Hasenfratz et al., 2019) that would act to prevent carbon release from the deep Pacific (Qin et al., 2022).

# 3. Future Challenges

Qin et al. (2022)'s results raise fundamental questions about how changes to the deep ocean's carbon inventory contributed to the lengthening and amplification of glacial cycles at the MPT. Moving forward, addressing these questions would benefit from research on two fronts. The first is to expand the accuracy and spatial coverage of MPT-related deep ocean carbon changes using  $\Delta[{\rm CO_3}^{2-}]$  proxies. While benthic foraminifer B/Ca is well established for this purpose, planktic foraminifer size-normalized shell weights should benefit from further scrutiny, including in the choice of most sensitive planktonic foraminferal species to deep ocean dissolution, and in the isolation of dissolution driven by deep ocean  $\Delta[{\rm CO_3}^{2-}]$  from potential changes in size-normalized weights driven by surface ocean growth conditions (e.g., Bijma et al., 2002).

In spite of the uncertainities with the size-normalized weight proxy, this proxy clearly helps to address the issue of data limitation that currently limits our knowledge of deep ocean carbon change at the MPT (Figure 1). For example, Qin et al. (2022) effectively increased the number of high resolution MPT  $\Delta[\text{CO}_3^{2-}]$  records by 50%. Regarding this current data limitation, benthic foraminifer  $\delta^{13}\text{C}$  serves as an optimistic historical analogue: Starting from an underconstrained, ocean-wide perspective on deep ocean  $\delta^{13}\text{C}$  change (Shackleton et al., 1983), we now possess detailed depictions of deep ocean  $\delta^{13}\text{C}$  during past time intervals, including the MPT (e.g., Curry & Oppo, 2005; Poirier & Billups, 2014). We should aspire to generate similar synoptic maps of past deep ocean  $\Delta[\text{CO}_3^{2-}]$ , particularly given that this parameter may be translated to past DIC.

Second, following an increase in the density of  $\Delta[{\rm CO_3}^{2-}]$  reconstructions, we then need to refine our understanding of how these reconstructions quantitatively relate to deep ocean DIC and, in turn, atmospheric pCO<sub>2</sub>. Regarding the former, as  $\Delta[{\rm CO_3}^{2-}]$  is a function of both DIC and deep ocean alkalinity, converting  $\Delta[{\rm CO_3}^{2-}]$  to DIC requires an assumption about the local alkalinity history of a given core location (Farmer et al., 2019; Qin et al., 2022; Yu et al., 2016). The veracity of these assumptions is difficult to assess given the lack of established ocean alkalinity proxies, although alkalinity proxy development is ongoing. Regarding pCO<sub>2</sub>, more work is needed to understand how deep ocean DIC and atmospheric pCO<sub>2</sub> are related across different climate states. There have been several attempts to define the relationship between deep ocean DIC and pCO<sub>2</sub> from a carbon mass-balance approach (Skinner, 2009; Yu et al., 2016). Though elegant, unfortunately no simple mass-balance equivalence exists between deep ocean DIC and atmospheric pCO<sub>2</sub>, as their relationship highly sensitive to where, and by which pathways, CO<sub>2</sub> is sequestered into the ocean interior (e.g., Hain et al., 2010; Kwon et al., 2012). Thus, an expansion of  $\Delta[{\rm CO_3}^{2-}]$  reconstructions, to which size-normalized shell weights (Qin et al., 2022) can contribute, should be paralleled by a complimentary data/model effort to ascertain how and why the distribution of DIC and alkalinity changed in the ocean interior during the mid-Pleistocene.

# **Conflict of Interest**

The authors declare no conflicts of interest relevant to this study.

# **Data Availability Statement**

No new data was used in this paper.

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