

Western Pacific physical and biological controls on atmospheric CO2 concentration over the last 700 kyr

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Article

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Abstract

We present new geochemical evidence of changes in the vertical dissolved inorganic carbon (DIC) distribution in the western tropical Pacific over the last 700 kyr, derived from stable carbon isotope (δ^{13} C) signals recorded in epifaunal benthic (*Cibicidoides wuellerstorfi*) and thermocline-dwelling planktonic (*Pulleniatina obliquiloculata*) for a minifera extracted from the Calypso Core MD06-3047. We further analyse the results of a transient numerical experiment of the Last Glacial Maximum (LGM) and the last deglaciation performed with the carbon isotope-enabled earth system model LOVECLIM, to understand the deglacial changes in DIC distribution and verify the proxy-based hypothesis. During glacial periods of the past 700 kyrs, the distinct negative deep water $\delta^{13}C_{DIC}$ values obtained from the benthic foraminifera suggest a carbon increase in the deep ocean, which could have been caused by weakening of deep Southern Ocean (SO) ventilation and enhanced marine biological productivity driven by dust-induced iron fertilization. During glacial terminations, a decrease of thermocline $\delta^{13}C_{DIC}$ associated with an increase in deep water $\delta^{13}C_{DIC}$ indicate a reduced vertical DIC gradient and the net transmission of ¹²C from the deep waters to the thermocline, caused mainly by the physical process (enhanced SO ventilation). On longer time scales, the largest increase in the Pacific deep carbon reservoir $\delta^{13}C_{DIC}$ during the marine isotope stage (MIS) 12/11 transition coincided with the mid-Brunhes climatic shift, which implies that the extent of oceanic carbon release during this interval was much larger than that during other deglaciations since 700 ka B.P. We infer that this could have been caused by reorganization of the oceanic carbon system. These findings provide new insights into the Pleistocene evolution of the carbon-cycle system in the Pacific Ocean.

Introduction

On glacial-interglacial (G-IG) timescales, gas exchange between the ocean and atmosphere regulates fluctuations in the partial pressure of atmospheric carbon dioxide $(pCO_2^{atm})^1$, which in turn may amplify the impacts of longer term external climate forcing on Earth's climate². Critically, this exchange involves the lower and upper cells of the global meridional overturning circulation (MOC), which are separated (approximately) by the 27.6 kg m⁻³ density surface^{3,4}. The MOC is thought to play a key role in the efficiency of the so-called biological soft-tissue pump (STP) in two ways: first, by facilitating the upward transport of nutrient- and CO₂-rich waters along the density surface, outcropping south of the polar front all the way around Antarctica; and second, by modulating the export of biologically fixed carbon into the ocean interior, where it is remineralized to dissolved inorganic carbon (DIC) and may effectively be isolated from the atmosphere^{3,5,6}. Either decreasing the rate of vertical exchange or enhancing export production would raise DIC concentrations in deep waters, thereby lowering pCO₂^{atm}. Increased DIC levels, in turn, enhance deep water corrosivity, possibly dissolving carbonate (CaCO₃) minerals and thereby increasing ocean alkalinity, which produces a further CO₂ drawdown⁷.

Although the STP efficiency in the Atlantic sector of the Southern Ocean (SO) has received much attention in recent years^{5,6,8}, the STP efficiency of the Pacific Ocean has received little attention and so remains poorly understood, despite the Pacific Basin dominating the world ocean volumetrically (3× larger than the Atlantic) and deriving its chemical characteristics from the SO. Furthermore, the Pacific Ocean has likely been the potential repository for a large portion of the carbon removed from the atmosphere during glacial periods^{9,10,11}. This raises questions concerning the impact of the significant Pacific "organic carbon pump" on pCO₂^{atm}, in particular the balance between biological and physical processes. The Antarctic Intermediate Water (AAIW) originates mainly from the upwelled carbon-rich Pacific Deep Water (PDW)¹². AAIW forms close to the Sub-Antarctic Front (SAF)¹³, with subsequent northward advection into the Pacific subtropical gyre through the low-latitude thermocline. On the other hand, the SO upwelling induced respired carbon outgassing from deep ocean to the atmosphere, may have left an isotopic footprint on the global upper ocean through air-sea exchange¹⁴. Hence, oceanic and atmospheric teleconnections may be able to propagate geochemical signals to low latitudes¹⁵. In this context, estimates of the vertical DIC distribution in the low-latitude Pacific obtained through paleoproxies could possibly provide information on past changes in SO ventilation.

Carbon isotopic gradients derived from benthic and planktonic foraminiferal calcite ($\delta^{13}C_b$ and $\delta^{13}C_p$) can be used to estimate the chemical differences between southern-sourced bottom and upper ocean thermocline waters^{16,17}. This approach exploits the recognition that the $\delta^{13}C$ of inorganic carbon dissolved in seawater ($\delta^{13}C_{DIC}$) can be used to trace the nutrient cycling associated with the biological pump in the ocean, because the photosynthetic carbon fixation preferentially removes ¹²C from the surface layer, leaving the surface ocean enriched in ¹³C. ¹²C-enriched carbon exported as organic material is later released to the deeper water column via remineralization, lowering deep ocean $\delta^{13}C_{DIC}$. The balance of biological versus physical (that is, transport and mixing of nutrient- and CO₂-rich water masses) processes therefore controls the magnitude of the vertical $\delta^{13}C_{DIC}$ gradient ($\Delta\delta^{13}C_{DIC}$) between bottom and upper ocean waters. As a result of these competitive processes, nutrients are, in general, negatively correlated with $\delta^{13}C_{DIC}$, and nutrient-rich waters such as the Antarctic Bottom Water (AABW) have relatively low $\delta^{13}C_{DIC}$ values¹⁸.

Here, we present new geochemical evidence of changes in the STP efficiency and vertical DIC distribution over the last 700 kyr, derived from co-registered δ^{13} C signals recorded in epifaunal benthic (*Cibicidoides wuellerstorfi*) and thermocline-dwelling planktonic (*Pulleniatina obliquiloculata*) foraminifera extracted from the Calypso Core MD06-3047. Altogether, the combination of our carbon isotope results with other proxy data and transient climate simulations performed with the carbon-isotopes enabled Earth system model LOVECLIM¹⁹, help understand G-IG marine carbon cycle changes.

Materials And Methods

Calypso Core MD06-3047 (890 cm long) was retrieved from the Benham Rise of the western Philippine Basin (17°00.44'N, 124°47.93'E; Fig. 1) during the joint Chinese and French cruise MARCO POLO 2/IMAGES XIV in 2006. The core was recovered from a water depth of 2510 m, within PDW. The chemical composition of this water mass is obtained in the Southern Ocean¹². The bottom water is located beneath the 27.6 kg m⁻³ isopycnal surface, which is the approximate boundary between the upper and lower cells of the global MOC⁴. Here, the subsurface thermocline waters are thought to be strongly influenced by the AAIW²⁰. Core MD06-3047 was composed mainly of yellow–brown silty clay and showed no evidence of turbidites or mass redeposition. A detailed description of the geological setting (e.g., topography, ocean current, and wind) in the Philippine Sea was provided by Xu et al^{21,22} and Wan et al²³. The Benham Rise is an oceanic plateau that formed along the Central Basin Ridge at 45–50 Ma²⁴. The core site was located about 240 km east of Luzon (Fig. 1). The continental shelves along eastern Luzon are very narrow (< 10 km on average), and the core site was located relatively far from the shelf (~ 230 km), so the effects of sea level variation on fluvial input from Luzon to this site are expected to be negligible. The region of Luzon is dominated by a subtropical East Asian monsoon climate²⁵.

The core was subsampled at 2-cm intervals and a total of 445 samples were obtained for analysis. The dry weight of these samples was determined and divided by the wet volume of the sample to obtain the dry bulk density. After being dried at 50°C, each sample (5 g dry weight) was treated with 5% H_2O_2 and washed through a 63 µm sieve to recover the foraminiferal tests. Analysis was carried out on planktonic foraminifera samples containing 10–15 specimens of *Pulleniatina obliquiloculata* from the 300–400 µm fraction, and also on the benthic foraminifera *Cibicidoides wuellerstorfi*, using 3–8 specimens picked from the 300–450 µm fraction. To minimize contamination, we were careful not to pick any broken, discoloured, or filled tests for isotopic measurement. The stable isotope ratios of the foraminiferal tests were measured on a GV IsoPrime mass spectrometer at the Key Laboratory of Marine Geology and Environment, Institute of Oceanography, Chinese Academy of Sciences. The analytical precision was better than ± 0.03‰ for δ^{13} C and ± 0.06‰ for δ^{18} O. Calibration against the Vienna Pee Dee Belemnite (VPDB) was performed using the standard NBS19.

Below, we will compare the signatures from Calypso cores ODP1090 and ANT30/P1-03 (Fig. 1), recovered from the sub-Antarctic zone (SAZ) and Antarctic zone (AZ), respectively, with our record from core MD06-3047, to trace the SO processes in the global carbon cycle.

Model setup and experimental design.

The LGM is a representative period of the glacial patterns in G-IG cycles. In addition, the subsequent Heinrich stadial 1 (HS1), at the beginning of the last deglaciation, is a crucial period to understand as it represents a major phase of atmospheric CO_2 rise and the transition out of the glacial period^{11,26}. To better understand the DIC distribution in G-IG cycles and verify the proxy-based hypothesis, we further analyse the results of a transient numerical experiment of the LGM and the last deglaciation performed with the carbon isotope-enabled Earth system model LOVECLIM²⁶. LOVECLIM includes an ocean general

circulation model (3° × 3°, 20 vertical levels), a dynamic–thermodynamic sea ice model, a quasigeostrophic atmospheric model (T21, three vertical levels), a land surface scheme, a dynamic global vegetation model and a marine carbon cycle model²⁷. The transient simulation starts from the Last Glacial Maximum (LGM) state with weak (11.2 Sv) and shallow NADW, and very weak AABW (5.1 Sv) obtained through 20% weaker SH westerlies and a 0.1 Sv meltwater input into the Southern Ocean¹¹. This LGM simulation featured the best model-data agreement in oceanic δ^{13} C and ventilation age distributions, and include a global mean 0.38 permil lower oceanic δ^{13} C at the LGM compared to Pre-industrial (PI) interval.

From this LGM state, the model is transiently integrated by varying the orbital parameters²⁸, and Northern Hemispheric ice-sheet extent, topography and albedo²⁹. To simulate a shutdown of NADW during Heinrich stadial 1, meltwater is added to the northern North Atlantic (0.04 Sv until 17.6 ka B.P., 0.07 Sv between 17.6 and 16.2 ka B.P.), while AABW is enhanced by decreasing the buoyancy forcing and strengthening the southern hemispheric westerly windstress.

Results And Discussion

Chronological framework

The chronological framework of core MD06-3047 was obtained by comparing the benthic foraminifera *C. wuellerstorfi* δ^{18} O curve from this core³⁰ with that of the LR04 δ^{18} O stack³¹, and also upon consideration of the last appearance datum (LAD) of *G. ruber* (pink). The LAD of *G. ruber* (pink) appeared at a depth of 160 cm, with a known age of 120 ka B.P³². Based on this chronology, the period of sediment accumulation spans marine isotope stages (MIS) 1–17, and thus potentially records the paleoceanographic history of the western Pacific (WP) over the last 700 kyr (Fig. 2).

Increased deep carbon storage and STP efficiency in the glacial tropical Pacific

Among genera of benthic foraminifera, the epibenthic dweller *C. wuellerstorfi* seems to record the $\delta^{13}C_{DIC}$ most reliably^{33,34}. During glacial intervals, we found distinct negative deep water $\delta^{13}C_{DIC}$ values in benthic foraminifera in our core (Fig. 3C), which is consistent with the benthic $\delta^{13}C$ records from the glacial Pacific deep water (below 2000–2500 m)³⁵⁻³⁷ and indicates the sequestration of more respired DIC and nutrients in the deep relative to the interglacials. The very negative glacial deep water $\delta^{13}C$ values are also present in benthic foraminifera from the Atlantic^{33,38}, Indian Ocean^{33,39}, and SO (Fig. 3I)^{40,41}, suggesting that the deep water reservoir stored more carbon in the glacial ocean. This large-scale phenomenon is consistent with the global stacked benthic foraminifera $\delta^{13}C$ record (Fig. 3D)⁴². Here we analyse a numerical experiment of the LGM¹¹, and hypothesise that it is representative of glacial periods. This LGM simulation displays higher oceanic DIC concentration in the deep ocean compared to PI (Fig. 5A).

Our reconstruction of the $\delta^{13}C_{DIC}$ gradient between the thermocline and deep waters ($\Delta\delta^{13}C_{DIC}$) shows that the largest difference coincides with full glacial conditions, indicating a more efficient STP in the western tropical Pacific, when pCO₂^{atm} was at its lowest (Fig. 3E, N), which is consistent with recent STP records from the SO reported in recent studies^{5,6,8}. Processes that impact the whole-ocean δ^{13} C, such as the transport of terrestrial organic material with relatively low levels of δ^{13} C to the oceans during glacial periods, are unlikely to result in $\delta^{13}C_{DIC}$ gradient variation as they impact the entire water column equally. During glacial intervals, relatively high Antarctic sea ice cover (Fig. 3L)⁴³ and the northward movement and/or weakening of the Southern Hemisphere (SH) westerlies (Fig. 3M)⁴⁴ are believed to have the potential to significantly attenuate the ventilation of the ocean's interior^{3,7,45}, which is in line with the isolated old glacial water masses identified in the North and South Pacific, as well as in the South Atlantic^{11,46-48}. The higher glacial export production in the WP, as recorded by variations in production of total organic carbon and mass accumulate rate (TOC*MAR; Fig. 3F)⁴⁹, could also reinforce the STP in the tropical Pacific. The observed close correlation between variations in dust supply and export production (Fig. 3F, G) indicates a dust-driven strengthening of the biological organic pump in the WP⁴⁹. The glacial enhanced iron-bearing dust inputs to the WP caused by the strengthened winter monsoon winds/westerlies and increased aridity in central Asia (Fig. 3G)^{22,23,49}, might stimulate nutrient utilization and phytoplankton growth, thus leading to high biological productivity (Fig. 3F)^{49,50}. Moreover, an increased WP nutrient drawdown and carbon transfer to the deep ocean stimulates an alkalinity feedback through the dissolution of carbonate in the abyss⁵¹. From the above, the weakening of the deep SO ventilation and the enhanced organic biological productivity by dust-induced iron fertilization via the synergy of both physical and biological processes led to a more efficient STP in the glacial tropical Pacific, hence contributing to the pCO_2^{atm} drawdown.

Role of SO ventilation in the vertical DIC distribution of the tropical Pacific

Pulleniatina obliquiloculata is the subsurface-dwelling planktonic foraminifera that is most abundant in middle to upper thermocline depths^{52,53}. The significant carbon isotope minimum events (CIMEs) that occurred during glacial terminations (Fig. 3B) resemble planktonic δ^{13} C profiles that are found in the equatorial Pacific⁵⁴⁻⁵⁶ as well as in the high- and mid-latitude SO^{8,41}. The CIMEs could reflect the collapse of deep ocean stratification, enhanced upwelling in the SO of low- δ^{13} C_{DIC} and CO₂-laden aged deep waters^{45,57}. The negative- δ^{13} C signal might be transmitted to thermocline of low-latitude ocean via ocean circulation (formation and advection of AAIW)⁵⁴, and the air-sea equilibration (strong outgassing in the SO and the ocean-atmosphere equilibrium thermodynamic exchange)^{14,57}.

The pronounced decreases in the ¹⁴C ventilation age in the South Pacific^{47,58} and in the δ^{13} C of atmospheric CO₂⁵⁹ during glacial terminations provide further evidence of enhanced ventilation of old and low- δ^{13} C_{DIC} deep Southern water mass to the surface and subsequent CO₂ outgassing. The

prominence of CIMEs in our record updates evidence that the δ^{13} C record of *P. obliquiloculata* reliably traces the enhanced SO ventilation.

During glacial terminations, the significant CIMEs reveal the migration of DIC and nutrients from the deep carbon pool to the low-latitude thermocline by intense SO ventilation and subsequently oceanic and atmospheric teleconnections^{14,45,54,57}. As a result of the ventilation-caused "DIC transmission", we hypothesize that not only the ocean upper layer and atmospheric CO_2 could receive the low- $\delta^{13}C_{DIC}$ signal during deglaciations (Fig. 4C)⁵⁹, but the southern-sourced deep carbon reservoir would receive the rising $\delta^{13}C_{DIC}$ signal. The most compelling support for our hypothesis comes from the antiphase variation of the thermocline and deep water $\delta^{13}C_{DIC}$ recorded in core MD06-3047 during each termination (Fig. 4C, D). If our hypothesis is correct, more widely distributed records of deep-ocean benthic δ^{13} C would capture the release of the deep low- $\delta^{13}C_{DIC}$ carbon reservoir. During Termination I–VII, the sub-Antarctic Zone (SAZ) deep water $\delta^{13}C_{DIC}$ from ODP 1090 (Fig. 4B)⁴⁰ and global stacked benthic foraminifera $\delta^{13}C$ increased as expected (Fig. 4E), possibly suggesting a transfer of a low- $\delta^{13}C_{DIC}$ signal from the depth to the surface. It is worth noting that the planktonic and benthic δ^{13} C did not always vary in antiphase in ODP 1090 (i.e., T-I and T-IV in Fig. 4A, B). In addition, their inverse trends began earlier and lasted longer (Fig. 3H, I). We suggest that the relatively reduced distance between ODP 1090 and the SO upwelling outcropping south of the Polar Front made the deep and upper layers of the core more sensitive and direct to the enhanced SO ventilation.

To further understand the ventilation-driven vertical DIC antiphase and verify our proxy-based hypothesis, we analyse the results of a transient numerical modelling experiment performed LOVECLIM²⁶. Because at the beginning of the last deglaciation, HS1 represents a major phase of atmospheric CO₂ rise and the transition out of the glacial periods, we chose HS1 in the last glacial-interglacial transition as a representative of the glacial terminations in G-IG cycles. Enhanced upwelling of DIC-rich CDW at the surface of the SO leads to a DIC increase in the upper 500m depth. The associated stronger AABW, and AAIW transport, lead to a DIC decrease in the SO and in the Pacific Ocean below ~1000m depth (Fig. 5B). Due to oceanic and atmospheric teleconnections, North Pacific Intermediate Waters (NPIW) also strengthen and ventilate during HS1⁶⁰. This leads to a DIC decrease at intermediate depth of the North Pacific, not far above our core-site depth (Fig. 5B), and thus might potentially contributes to the DIC decrease in our record (Fig. 4D). These changes in oceanic circulation leads to a δ^{13} C increase in the intermediate and deep Pacific, while δ^{13} C decreases at the surface of the ocean (Fig. 5C). This is consistent with our proxy record of $\delta^{13}C_{DIC}$ (Fig. 4C, D).

The SO ventilation has the potential to drive the antiphase variation of the vertical DIC distribution during glacial terminations. Meltwater input in the northern Atlantic/Arctic, due to Northern Hemisphere ice sheet retreat induced a cessation of the Atlantic MOC⁶¹⁻⁶³. This process, in conjunction with Antarctic local orbital forcing^{44,64}, might have triggered the decline in sea ice^{43,65}(Fig. 4G) and southward movement/enhancement of the SH westerlies^{45,66-68}(Fig. 4H). Stronger westerlies would have enhanced

the SO upwelling^{4,45}. This would have led to CO₂ outgassing and a decrease in δ^{13} C of atmospheric CO₂^{26,59}(Fig. 4J). This is also consistent with enhanced diatom productivity in the SO^{45,69,70} (Fig. 4I). In addition, through oceanic and atmospheric teleconnections, cessation of the Atlantic MOC enhances the formation of NPIW, thus ventilating the intermediate North Pacific^{26,60,71}. This might lead to a DIC decrease at intermediate and deep depth of the North Pacific, in agreement with the Ice-rafted debris (IRD) record in northern Atlantic⁷²(Fig. 4F) and our paleo and model results (Fig. 4D, Fig. 5B). So we suggest the NPIW enhancement might might potentially contributes to the DIC decrease at intermediate depth of the North Pacific.

The cause of STP efficiency collapse during glacial terminations

The graphical consistency of STP efficiency in the tropical Pacific and pCO₂^{atm} may point to the role of the low-latitude biological pump in changing the global climate (Fig. 3E, N), especially during glacial terminations. In glacial-interglacial transitions, the STP efficiency collapses corresponded to significant increases in pCO₂^{atm}. However, it remains to be determined whether the observed decrease in "organic carbon pump" efficiency resulted primarily from decreases in export productivity, or increases in ocean "ventilation". We address this question by reference to our export productivity and the $\delta^{13}C_{DIC}$ of the thermocline and deep waters. The export productivity, as recorded by the variation in TOC*MAR (Fig. 3F) reduced significantly during Termination I, III, IV, and V, but the changes during Termination II and VI were too small to have altered the STP. Increases in $\delta^{13}C_b$ and reductions in $\delta^{13}C_p$ during glacial terminations indicate ¹²C transmission through ventilation from the deep to the upper layer. However, photosynthetic carbon fixation preferentially removes ¹²C from the surface-layer DIC to the deeper water column. This process could explain the net transmission of ¹²C from deep to thermocline only be the enhanced ventilation, disagree with the proposition that a more poorly ventilated deep Pacific (relative to today) did not or could not exist^{73,74}. During glacial terminations, the physical process (enhanced SO ventilation) was far more effective than the biological process (export productivity) in driving the STP efficiency collapse (Fig. 3E).

Coordination of physical and biological controls on pCO2^{atm} changes

Our findings reveal insights into the coordination between physical and biological controls on pCO₂^{atm} changes over glacial cycles in the WP, and these are consistent with recently published sedimentary redox records from the AZ and SAZ^{5,6}. This suggests that the coordination is not only confined to the high- and mid-latitudes in the SO, but also occurs in the low latitudes in the WP, and is related to changes in the interhemispheric oceanic and atmospheric circulations⁸. During glacial periods, the intense stratification of the ocean interior induced by extensive Antarctic sea ice cover⁴³ (Fig. 3 and 7A) and northward movement and/or weakening of the SH westerlies⁴⁴(Figs 3 and 7A), combined with the high biological productivity caused by strengthened winter monsoon winds and increased aridity in central Asia, induced elevated iron-bearing dust inputs into the WP^{22,23,49}(Figs 3 and 7A), which led to the

continuous "recharge" of the abyssal carbon reservoir. In this light, it may seem remarkable that changes in dust fluxes and deep ventilation were coordinated, reinforcing their synergistic impacts on the STP.

We suggest that there was a mechanistic link between the coordinated physical and biological processes, which involved ventilation and Fe supply, in the high and low latitudes. Owing to this coupling of oceanic and atmospheric circulations, enhanced deglacial deep SO ventilation generally co-occurred with the southward migration of the SH westerlies. The subsequent warming of the atmosphere would have weakened the winter monsoon, which would have led to lower dust inputs to the WP^{23,49}, causing limited nutrient utilization and facilitating CO₂ outgassing (Fig. 7B). As such, the Fe fertilization processes may be viewed as a positive feedback process in response to initial forcing related to changes in the interhemispheric ocean–atmosphere system⁸. Thus, shifts in atmospheric circulation, coupled with changes in the MOC, would have caused the intensity of Fe limitation and deep convection to co-vary over glacial cycles. These large-scale coupled processes (i.e., coordinating the input flux of carbon to the deep sea and deep ventilation-caused carbon leakage in both high and low latitudes) could together modify the whole-ocean STP efficiency and atmospheric CO₂ levels. Further use of paleoclimate modelling to precisely quantity the contributions of biological/physical processes and high/low latitudes to STP efficiency will be required if we are to fully understand the natural variability of atmospheric CO₂.

Largest-amplitude DIC changes in deep waters at the MIS 12/11 transition

The most significant feature of the MD06-3047 deep-water $\delta^{13}C_{DIC}$ record may be the increase of ~0.97‰ (from -0.50‰ to 0.47‰) between late MIS 12 (ca. 438 ka B.P.) and mid-MIS 11 (ca. 405 ka B.P.), which represents the largest change of this type during the past 700 kyr (Fig. 3C). This peculiar interval also coincided with the largest change in the marine δ^{18} O record of the last 5 Myr³¹, and has been described as a major step change in global climate conditions⁷⁵.

This largest increase in the Pacific deep carbon reservoir $\delta^{13}C_{DIC}$ was generated by the most enhanced ventilation-caused "DIC" transmission", which led to a transfer of carbon from the deep ocean to the atmosphere^{45,76}. Meanwhile, the breakdown of oceanic stratification would raise the deep-water carbonate ion concentration ([CO₃^{2–}]) and CaCO₃ preservation^{51,77}. In a recent study, the reconstructed deep water [CO₃^{2–}] in this water column (from the same sediment core MD06-3047B) reached its maximum at the MIS12/11 termination⁷⁸(Fig. 6B). Furthermore, the "Pacific-style" CaCO₃ content records⁷⁹(Fig. 6C) also show their preservation maxima at the MIS 12/11 boundary. The extremely high values of these records during the MIS 12/11 transition imply that the extent of oceanic carbon release during this interval was much larger than during other deglaciations since 700 ka B.P.

Conclusions

Our reconstruction of vertical DIC distribution for the western tropical Pacific since 700 ka B.P. using a combination of carbon isotope results and climate simulations generated the following conclusions.

(1) The distinct negative deep water $\delta^{13}C_{DIC}$ values obtained from the benthic foraminifera suggest that the deep reservoir stored more carbon in the glacial ocean over the past 700 kyr. The more efficient STP in the glacial tropical Pacific and the drawdown of pCO₂^{atm}, possibly caused by the weakening of the deep SO ventilation and the enhanced organic biological productivity driven by dust-induced iron fertilization, via the coordination of physical and biological controls.

(2) The antiphase variation of the thermocline and deep water $\delta^{13}C_{DIC}$ in our record during each termination is consistent with the deglacial modelling result, suggesting that SO ventilation has the potential to drive the inverse variation of the vertical DIC distribution during glacial terminations.

(3) The increase in δ^{13} Cb and decrease in δ^{13} Cp during glacial terminations indicates the net transmission of ¹²C from the deep waters to the thermocline, and this suggests that the physical process (enhanced SO ventilation) was far more effective than the biological process (export productivity), thus driving the STP efficiency collapse and significant pCO₂^{atm} increase.

(4) This largest increase in the Pacific deep carbon reservoir $\delta^{13}C_{DIC}$ during the MIS 12/11 transition coincided with the mid-Brunhes climatic shift, which implies that the extent of oceanic carbon release during this interval was much larger than that during other deglaciations since 700 ka B.P. We infer that this could have been caused by reorganization of the oceanic carbon system.

Declarations

Acknowledgments

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Author contributions

Zheng Tang carried out the foraminifera picking and stable isotope measurements, and together with Zhifang Xiong and Tiegang Li analyzed the data. Zheng Tang contributed the combination of data and model. Tiegang Li helped shape the initial concept and contribute to data interpretation. Zheng Tang wrote the manuscript with contribution from Zhifang Xiong. All the co-authors contributed to the interpretation of the results and provided inputs to the final version.

Competing interests

The authors declare no competing interests.

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Figures



Figure 1

Map showing the locations of Calypso cores investigated in this study and modern ocean DIC concentration (shaded) in bottom waters80. Core MD06-3047 (white circle) is located in the West Philippine Sea, and Cores ODP 1090 and ANT30/P1-03 (blue circles) in the SO. The map was created using the Ocean Data View software81.



Figure 2

Chronological framework for core MD06-304730, obtained by graphical comparison between the δ 180 record of epibenthic foraminifera C. wuellerstorfi and the stacked global benthic LR04 δ 180 record31, with additional refinement based on the last appearance datum (LAD) of Globigerinoides ruber (pink). Blue crosses represent oxygen-isotope events, and the black arrow indicates the LAD of G. ruber (pink).



Figure 3

Records of (A) The stacked global benthic LR04 δ 18031, (B) MD06-3047 δ 13Cp extracted from thermocline-dwelling planktonic foraminifera (Pulleniatina obliquiloculata), and (C) MD06-3047 δ 13Cb extracted from epibenthic foraminifera (Cibicidoides wuellerstorfi). Horizontal red and blue lines in panels B and C represent the average δ 13Cp and δ 13Cb values of the respective Marine Isotope Stage. (D) Stacked δ 13Cb of the global ocean42. (E) MD06-3047 δ 13Cp-b; the green line is the five-point running average. (F) MD06-3047 TOC MAR49. (G) MD06-3047 dust MAR49. (H and I) ODP 1090 δ13Cp and δ13Cb40. (J) Accumulation rate of n-alkenone from ODP 109082. (K) Dust accumulation rate from ODP 109082. (L) Sea-salt sodium (ssNa) flux at EPICA Dome C43(EDC). (M) Accumulation Rate at EDC83. (N) pC02 record from EDC84. Grey shading indicates interglacial periods.



Figure 4

Records of (A and B) δ13Cp and δ13Cb, respectively, from core ODP-109040, as well as (C and D) δ13Cp and δ13Cb, respectively, from core MD06-3047 (this study). (E) Stacked δ13Cb time series for the global ocean42. (F) Ice-rafted debris (IRD) record from ODP 983 in the northeast Atlantic72. (G) ssNa flux at EPICA Dome C43 (EDC). (H) Accumulation Rate at EDC83. (I) Biogenic opal concentration from P1-0369. (J) pC02 record from EDC84. Green shading indicates glacial terminations.



Figure 5

Simulated ocean DIC and δ 13C anomalies in model LOVECLIM. Simulated (A) DIC concentration (µmol/L) anomalies at the LGM compared to pre-industrial (PI) at 2500 m depth near the study-core11 (left) and at the bottom (right). (B) DIC concentration (µmol/L) and (C) δ 13C (‰) anomalies at HS1 compared with LGM zonally averaged over the Indo-Pacific26. Circle B indicates the position of benthic foraminifera C. wuellerstorfi in core MD06-3047 (17°00.44'N, 124°47.93'E, 2,510 m water depth) and circle P indicates where the subsurface-dwelling planktonic foraminifera P. obliquiloculata records middle to upper thermocline properties.



Figure 6

Schematic representation of the South and tropical Pacific overturning circulation. (A) Glacial pattern with more dust input, efficient biological nutrient export, a northernmost extent of sea ice and SWW, a stratified Southern Ocean, DIC sequestration in deep, decreased atmospheric CO2, and a large $\Delta\delta$ 13CDIC. (B) Deglacial pattern with upwelling induced by southward shift of Antarctic sea ice and SWW, less dust input, inefficient biological nutrient export, outgassing of CO2, DIC transmission from deep to upper layer, and a consequently small $\Delta\delta$ 13CDIC. Grey arrows: overturning circuit; green arrows: biological nutrient export to the ocean interior; light-blue rectangles: sea ice; SWW: Southern Westerly Winds; major water masses (SAMW, AAIW, AABW, CDW, and PDW). Circle B: the position of benthic foraminifera C. wuellerstorfi in core MD06-3047 (17°00.44'N, 124°47.93'E, 2,510 m water depth); and circle P: where the subsurface-dwelling planktonic foraminifera P. obliquiloculata records middle to upper thermocline properties. The thickness of the arrow represents its strength. The color shading of the ocean section represents the DIC concentrations.



Figure 7

Records of (A) δ13Cb from MD06-3047 (this study) and (B) Deep-water [CO32-] from MD06-3047B78 (same location). (C) Pacific-pattern of deep-sea sedimentary calcium carbonate content change at site ODP 108979 (note that although ODP1089 is from a site in the South Atlantic, it is bathed in Indo-Pacific deep water, rather than North Atlantic Deep Water). (D) pC02 record from EDC84. Grey shading indicates interglacial periods, light blue shading indicates the MIS12/11 transition.