



Glacial expansion of carbon-rich deep waters into the Southwestern Indian Ocean over the last 630 kyr

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ABSTRACT

Oceanic carbon storage is one of the main sinks for atmospheric CO₂, and thought to be the major contributing factor for CO₂ drawdown during past glacial periods. Both physical and biogeochemical processes control the capacity of carbon storage in the ocean. During glacial periods of the Pleistocene the larger volume of deep-water masses of Southern Hemisphere origin in the Atlantic has been shown to promote carbon storage in the Southern Ocean. However, the latitudinal extension of this water mass in the Indian Ocean has been scarcely studied. In this study, we combine foraminiferal ϵ_{Nd} and benthic $\delta^{13}C$ of two sediment cores in the southwest Indian Ocean (MD96–2077, 33°S, 3781 m water depth; MD96–2052, 19°S, 2627 m water depth), to reconstruct the spatial and temporal evolution of glacial carbon-rich deep waters in the SW Indian over the last 630 kyr. The combined use of foraminiferal ϵ_{Nd} and benthic $\delta^{13}C$ allows to distinguish $\delta^{13}C$ changes related to water mass mixing and from respired carbon accumulation within the water masses. Nutrient-rich deep waters, which cannot be explained by the enhanced proportion of southern-sourced waters, were present at core sites deeper than 2700 m during glacial periods and extended at least until 33°S into the SW Indian Ocean. From Marine Isotope Stage (MIS) 14 to MIS 10, glacial carbon storage increased gradually until reaching its highest capacity during the extreme glacial periods MIS 12 and 10. Orbital forcing (100-kyr eccentricity, 41-kyr obliquity), restricted air-sea exchange and enhanced ocean stratification, fostered higher carbon storage during periods of relatively lower eccentricity and obliquity. Furthermore, after MIS 10, a progressive transition was observed from 100-kyr eccentricity to 41-kyr obliquity cycles in benthic $\delta^{13}C$ and $\delta^{18}O$ records of core MD96–2077 and sea-ice cover changes derived from ice-rafted debris of the Agulhas Plateau composite core site.

1. Introduction

Ocean carbon cycle plays a fundamental role in sequestering CO₂ during glacial periods (Sarmiento and Toggweiler, 1984; Stephens and Keeling, 2000; Sigman et al., 2010). Glacial ice sheets on land, contributing to increased aridity and colder temperatures, reduced terrestrial carbon storage (Peterson et al., 2014). This resulted in most of the terrestrial carbon stored in the ocean, which is the largest carbon reservoir. The Last Glacial Maximum (LGM) to Holocene global ocean $\delta^{13}C$ ($^{13}C/^{12}C$ carbon isotopic composition) change was $0.34 \pm 0.19\%$,

implying an oceanic carbon variation of 330–694 Gt C (Peterson et al., 2014). One of the most important regions regarding the oceanic carbon cycle is the Southern Ocean, where under glacial conditions higher seawater CO₂ solubility, larger sea-ice, restricted air-sea exchange, stronger ocean stratification, sluggish deep-water circulation and enhanced nutrient utilization, reduced atmospheric CO₂ and favored ocean carbon storage (Sigman and Boyle, 2000; Stephens and Keeling, 2000; Sigman et al., 2010; Adkins, 2013; Lear et al., 2016; Lhardy et al., 2021). During glacial periods, larger ice sheets along with higher iron fertilization enhancing nutrient utilization and low air-sea exchange

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resulted in reduced $\delta^{13}\text{C}$ of dissolved inorganic carbon ($\delta^{13}\text{C}\text{-DIC}$) (Mix and Fairbanks, 1985; Gebbie, 2014). Indeed, in the Atlantic sector of the Southern Ocean, deep-water (> 3000 m) benthic foraminiferal $\delta^{13}\text{C}$ glacial values were lower than those of the deep equatorial Pacific (Mix et al., 1995; Hodell et al., 2003), suggesting an important role of the Southern Ocean to storage of respired carbon. More extensive sea ice cover combined with ocean stratification in the Southern Ocean may reduce the atmospheric CO_2 by 40 ppm (Stein et al., 2020). It has been proposed, based on benthic $\delta^{13}\text{C}$ records, that glacial carbon-rich Southern Ocean waters might have extended into the abyssal North Atlantic during the LGM in relation to weaker and shallower North Atlantic Deep Water (NADW) (Curry and Oppo, 2005; Gebbie, 2014). However, sustained production of NADW was suggested during the LGM from foraminiferal authigenic Nd isotopic composition ($^{143}\text{Nd}/^{144}\text{Nd}$ or ϵ_{Nd}) (Howe et al., 2016). Discrepancies of proxy reconstructions imply that reduced glacial NADW alone cannot fully explain the increased oceanic carbon storage. Different models reconstructing LGM circulation and related CO_2 drawdown also show discrepancies due to model resolution, simulation of ocean circulation and climate, representation of atmosphere and ocean physics and carbon cycle model completeness (Lhardy et al., 2021).

Glacial deep waters with a significant amount of respired carbon might have extended into other oceans in addition to the Atlantic Ocean, increasing their volume (Ferrari et al., 2014). Expanded southern-sourced nutrient-rich deep waters may enhance the total marine carbon inventory by trapping more CO_2 during glacial periods (Skinner, 2009). The Indian Ocean is one of the areas in which glacial carbon-rich waters could have arrived since southern-sourced waters, such as Circumpolar Deep Water (CDW), both the southwestern part of this ocean (Fig. 1). To test if glacial deep waters, enriched in respired carbon, extended to the SW Indian, one of the most insightful approaches is to combine authigenic ϵ_{Nd} and benthic foraminiferal $\delta^{13}\text{C}$ records from deep water sites from the SW Indian. The present-day seawater ϵ_{Nd} values at water depths >1500 m trace water-mass provenances and behave semi-conservatively when the influence of local inputs is small (e.g. Goldstein and Hemming, 2003; Tachikawa et al., 2017). Benthic $\delta^{13}\text{C}$ reflects different factors including organic carbon export and remineralization, respired carbon accumulation and air-sea exchange (Mix and Fairbanks, 1985; Howe et al., 2016). Therefore, combining benthic $\delta^{13}\text{C}$ with ϵ_{Nd} will allow distinguishing $\delta^{13}\text{C}\text{-DIC}$ changes related to water mass mixing from those produced by respired carbon accumulation.

In order to investigate the extension of carbon-rich deep waters under different mean climate states, it is necessary to obtain records covering several glacial-interglacial cycles. Climate states, with different average temperatures, may have modified differently ocean carbon storage, and, therefore, extension of carbon-rich deep waters. Previous studies of deep-water (>2500 m) benthic $\delta^{13}\text{C}$ records from the SW Indian are scarce (Pichon et al., 1992; Ziegler et al., 2013), and to date, the combination of $\delta^{13}\text{C}$ and ϵ_{Nd} covering several climate cycles has never been realized.

Here, we present new combined foraminiferal ϵ_{Nd} and epibenthic foraminiferal $\delta^{13}\text{C}$ records from two sites in the SW Indian Ocean over the past 630 kyr (Fig. 1): 1) core MD96–2077 (33°10.1'S, 31°14.8'E, 3781 m water depth), and 2) core MD96–2052 (19°52.7'S, 41°49.9'E, 2627 m water depth). This time interval covers different climate states, including extreme glacial conditions during MIS10 and 12 (Bard and Rickaby, 2009). The benthic $\delta^{13}\text{C}$ and foraminiferal authigenic ϵ_{Nd} relationship permitted distinguishing changes in water-mass contributions from ventilation and related accumulation of respired carbon. These new data, together with previously published benthic $\delta^{13}\text{C}$ records, allowed us to define the vertical and horizontal extension of glacial carbon-rich deep waters entering the SW Indian, which can contribute to the modification of marine carbon inventory and, consequently, oceanic CO_2 uptake.

2. Present-day deep-water circulation

In the study area, two main deep-water currents flow from the SE Atlantic to the SW Indian Ocean: the shallower North Atlantic Deep Water (NADW), and the deeper Circumpolar Deep Water (CDW) (Fig. 1). In the present SW Indian Ocean, the southern-sourced water at deep water depths of locations northern than 50°S is essentially lower circumpolar deep water (CDW) according to neutral density distribution (Orsi et al., 1999). Antarctic Bottom Water (AABW) flows in the deepest part of the Indian Ocean below 3800 m, entering the Mozambique basin (SW of Madagascar) (Tomczak and Godfrey, 1994) (Fig. 1a). This water mass formation results from brine rejection during sea ice formation or super-cooling of ice shelf water (Carmack and Foster, 1975).

The NADW, with higher salinity and potential temperature, occurs between 2000 and 3500 m (Figs. 1b and 2). This water mass is formed in the North Atlantic Ocean. It travels southward along the western Atlantic until it bifurcates around the equator into two branches, one flowing in the western Atlantic and the other flowing in the eastern Atlantic (Larqué et al., 1997). Around 40°S, the eastern branch deflects to the east, entering the SW Indian Ocean (Larqué et al., 1997). The NADW is part of the upper overturning cell of the Atlantic Meridional Overturning Circulation (AMOC) (Kuhlbrodt et al., 2007). In the SW Indian Ocean, the NADW flows northward, entering the Mozambique Channel (de Ruijter et al., 2002). It deflects and turns south at around 20°S (Charles et al., 2020) (Fig. 1a). The CDW is found deeper than 3500 m (Fig. 1b) and divided into Upper and Lower CDW (UCDW, LCDW), with LCDW being colder and saltier than UCDW (Fig. 2). The CDW is colder and fresher than NADW (Figs. 1a and 2). The origin of CDW is the mixing of NADW, Indian and Pacific deep waters, along with the local Antarctic dense waters (Talley, 2013). The CDW enters the Indian Ocean from the SE Atlantic, flowing along the SW coast of S Africa (Fig. 1a). It also flows northward from the Southern Ocean to the Indian Ocean along the eastern side of Madagascar (Fig. 1a). At the present day, the potential temperature-salinity diagram and water-mass properties (Amakawa et al., 2019) reveal that core MD96–2077 location is affected by LCDW, while the core MD96–2052 location is bathed by the NADW (Fig. 2).

3. Material and methods

3.1. Studied cores

3.1.1. Core MD96–2077

Sediment core MD96–2077 was collected off East London in the Natal Valley (SW Indian Ocean, 33°10.1'S, 31°14.8'E, 3781 m water depth) (Fig. 1). The core is 3554 cm long and mainly composed of biogenic carbonates (coccoliths and foraminifera) (Bertrand and Shipboard Scientific Party, 1997; Chen et al., 1998). The chronology of this core was initially constrained by *Globoconella inflata* $\delta^{18}\text{O}$ record (Bard and Rickaby, 2009). We refined the age model by a new benthic foraminiferal *Cibicides wuellerstorfi* $\delta^{18}\text{O}$ record and a new ^{14}C date on *G. inflata* from the uppermost part of the core (Fig. A.1 and Table B.1). The benthic foraminiferal $\delta^{18}\text{O}$ record was tuned to the LR04 global stack (Lisiecki and Raymo, 2005) (Fig. A.1). The age model is based on linear interpolation using 25 tie points, one based on radiocarbon dating and 24 based on benthic $\delta^{18}\text{O}$ stratigraphy (Table B.1). The radiocarbon age was calibrated using the Marine20 calibration curve (Heaton et al., 2020), with a ΔR value of -21 ± 26 yr and 400 yr marine reservoir age. Here, we analyzed the upper 2401 cm of the core, covering the last 630 kyr according to our age model. This interval shows an average sedimentation rate of 4.5 cm/kyr.

3.1.2. Core MD96–2052

Sediment core MD96–2052 was retrieved off Madagascar in the Mozambique Channel (SW Indian Ocean, 19°52.7'S, 41°49.9'E, 2627 m water depth) (Fig. 1) during the MOZAPHARE cruise (R/V MD Chen,

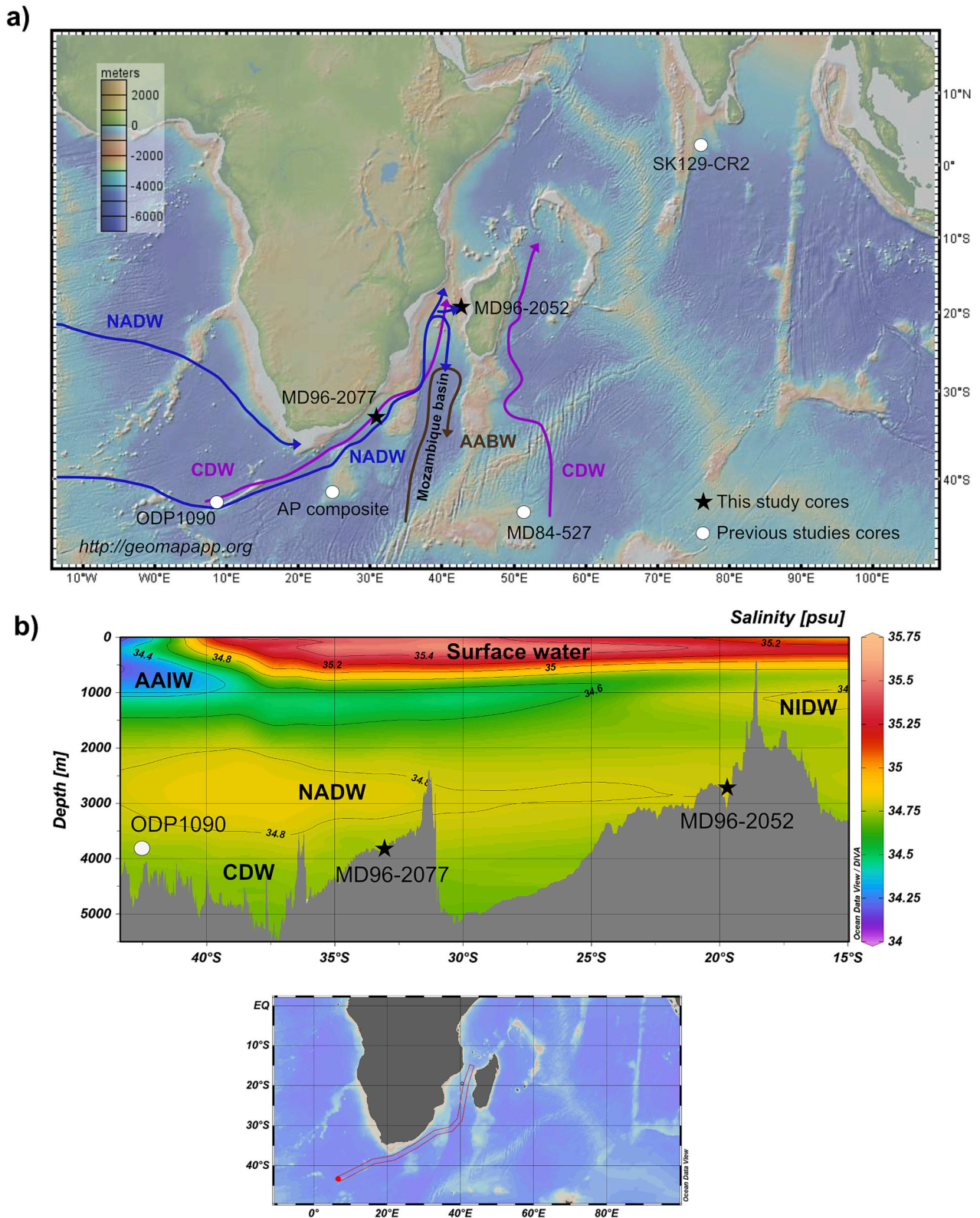


Fig. 1. a) Simplified modern ocean circulation of the study area with the core locations of this study (black stars): MD96–2077 (33°10.1'S, 31°14.8'E, 3781 m water depth), and core MD96–2052 (19°52.7'S, 41°49.9'E, 2627 m water depth); and previous studies cores (white dots): core Agulhas Plateau (AP) composite site (41°19.9'S, 25°49.7'E, 2907 m water depth) (Ziegler et al., 2013; Starr et al., 2021), core MD84–527 (43°49'3S, 51°19'E, 3262 m water depth) (Pichon et al., 1992), core ODP1090 (42°54.82'S, 8°53.98'E, 3702 m water depth) (Hodell et al., 2003) and core SK129–CR2 (3°N, 76°E, 3800 m water depth) (Piotrowski et al., 2009). The colored arrows depict modern flow paths of different water masses: North Atlantic Deep Water (NADW, blue), Circumpolar Deep Water (CDW, purple), and Antarctic Bottom Water (AABW, dark brown). b) SW–NE salinity transect along latitude showing the major water masses: NADW, CDW, AAIW (Antarctic Intermediate Water), NIDW (North Indian Deep Water) and surface water. Symbols as for a). Figures are created with the software Ocean Data View (ODV) (Schlitzer, 2015). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

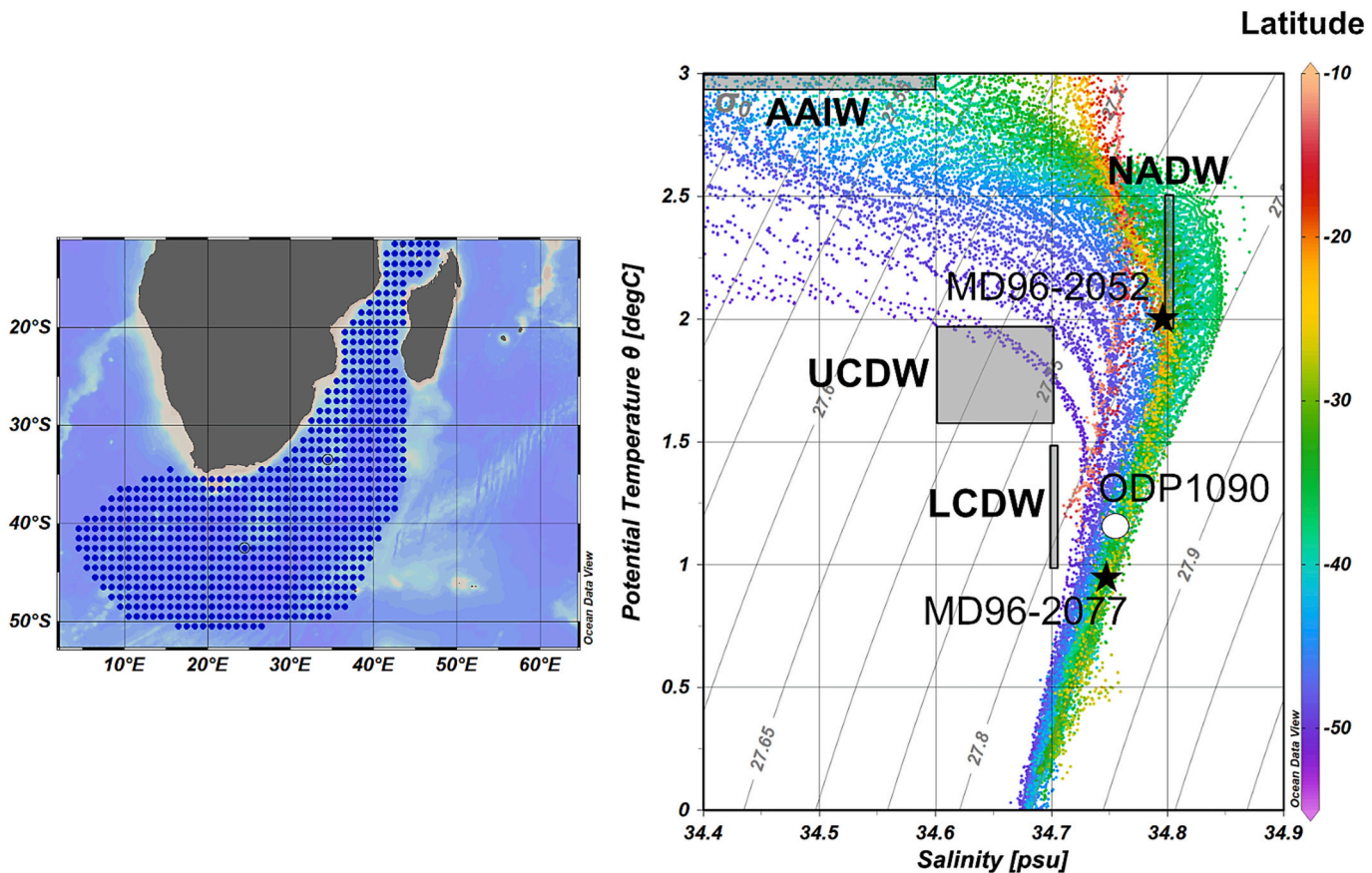


Fig. 2. Potential temperature and salinity diagram of the modern southeastern Atlantic and southwest Indian waters based on Electronic Atlas of WOA Data at cores MD96–2077, MD96–2052 and ODP1090. The grey squares indicate the source water type potential temperature and salinity for NADW, Upper Circumpolar Deep Water (UCDW) and Lower Circumpolar Deep Water (LCDW) (Larqué et al., 1997). Antarctic Bottom Water (AABW) with a negative temperature is not shown in this diagram. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

1996). This 3754-cm-long core consists of biogenic sediments rich in coccoliths and foraminifera (Lancelot and Shipboard Scientific Party, 1997). This core was dated using radiocarbon dating on the planktic foraminifera *Globigerinoides ruber* and tuning the benthic foraminiferal *Cibicides wuellerstorfi* $\delta^{18}\text{O}$ record to the benthic LR04 global stack (Lisiecki and Raymo, 2005) (Figs. A.2 and A.3). The age model was constructed using 28 tie points, 7 ^{14}C dates and 21 benthic $\delta^{18}\text{O}$ tie points (Table B.2). In the uppermost part of the core (0–480 cm) (Fig. A.3), the age model was established with the Bayesian statistics software Bacon v2.3 (Blaauw and Christen, 2011) using the statistical package RStudio v4.1.1. The radiocarbon ages were calibrated using the Marine20 calibration curve (Heaton et al., 2020), with a ΔR value of 108 ± 51 yr and 400 yr marine reservoir age. In the rest of the core (480–3140 cm) (Fig. A.2), the age model is based on linear interpolation using the 21 benthic $\delta^{18}\text{O}$ tie points. The upper 3140 cm of the core, representing the last 575 kyr, were studied. The average sedimentation rate for this interval is 7.7 cm/kyr.

3.2. Methods

3.2.1. Nd isotopes of cleaned mixed planktic foraminifera

Samples for Nd isotopic analyses on mixed planktic foraminifera were selected to cover glacial-interglacial variability on core MD96–2077 (Fig. 3b), with a sampling resolution of 13.8 ka along the studied interval and higher resolution (3.9 ka) during terminations I (MIS 1–2), II (MIS 6–5) and V (MIS 12–11) (Fig. 3b). For core MD96–2052, we focused on terminations I, II and V (Fig. 3b), with a resolution per sample of 3.4 kyr within terminations. Terminations I, II and V were analyzed in detail because they are related to the warmest

interglacials and characterized by large glacial-interglacial amplitudes (Fig. 3a). For the ϵ_{Nd} analyses, 20–50 mg of mixed planktic foraminifera from the size fraction $>250 \mu\text{m}$ were picked. Most of the samples were automatically picked by MiSo (Microfossil Sorter) prototype (26 samples in core MD96–2077, and 29 samples in core MD96–2052), a novel device developed at CEREGE, which images sediment coarse fraction, identifies particles and foraminifera using Convolutional Neural Networks (Marchant et al., 2020), and picks microfossils for subsequent geochemical analyses (patent pending). Additionally, samples were handpicked to complete the picking of selected samples (20 samples in core MD96–2077, and 2 samples in core MD96–2052).

Prior to the measurements of Nd isotopic composition, foraminiferal tests were mechanically cleaned with the established method summarized in Tachikawa et al. (2014). Briefly, foraminiferal chambers were gently crushed using two glass slides under the binocular stereo microscope. Fine particles, including clays, were removed by repeated ultrasonication steps until the water was clear. Carbonate test fragments were dissolved by step-wise addition of 1 M acetic acid. The obtained solution was centrifuged, and the recovered supernatant was evaporated and attacked with concentrated nitric acid. Then, samples were purified by a 2-step column separation using TRU.Spec and Ln.Spec resins to isolate Nd (Pin and Santos Zalduegui, 1997).

Nd isotopic composition was measured using a Thermo Fisher Neptune^{plus} Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at CEREGE. The sample size was around 10 ng of Nd. An Apex Omega Quartz desolvation device was used for sample introduction. To correct instrumental mass bias, $^{143}\text{Nd}/^{144}\text{Nd}$ were firstly normalized internally to a $^{146}\text{Nd}/^{144}\text{Nd}$ of 0.7219 after correcting for any Sm interferences. Secondly, the $^{143}\text{Nd}/^{144}\text{Nd}$ were corrected by

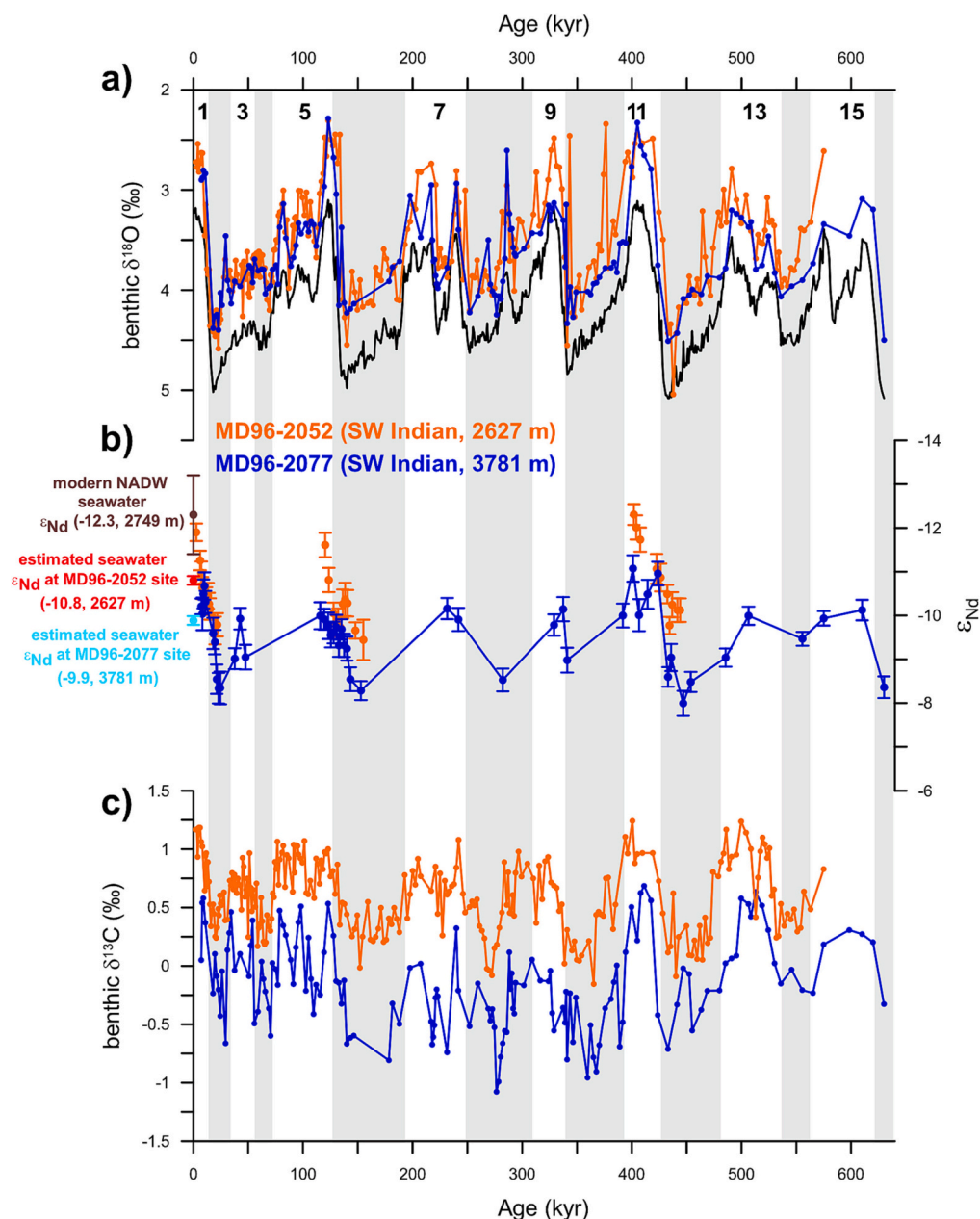


Fig. 3. a) Benthic foraminiferal $\delta^{18}\text{O}$ of MD96-2052 (orange) and MD96-2077 (blue). b) foraminiferal ϵ_{Nd} of MD96-2052 (orange) and MD96-2077 (blue), modern NADW seawater ϵ_{Nd} (dark brown) and estimated seawater ϵ_{Nd} at core sites MD96-2052 (red) and MD96-2077 (sky blue). c) benthic foraminiferal $\delta^{13}\text{C}$ of MD96-2052 (orange) and MD96-2077 (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bracketing every sample with the JNdi-1 isotopic standard solutions obtained from a neodymium oxide reagent ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512115 \pm 0.000007$, Tanaka et al. (2000)). The JNdi-1 standard solutions were analyzed at the same concentrations as the samples. The sample uncertainties reported in Table B.3 were calculated by error propagation of the standard error of the sample and the ones of the bracketing standards (assuming independent variables). It is reported as 2σ . The average uncertainty is 0.3ϵ -unit (Table B.3), in agreement with the external reproducibility (2SD) of the JNdi-1 standard, 0.27ϵ -unit as well as the ones obtained on complete procedural replicate analyses of several samples (see Table B.3). Repeated measurements of the AMES ($^{143}\text{Nd}/^{144}\text{Nd} = 0.511961 \pm 0.000008$) and VWR ($^{143}\text{Nd}/^{144}\text{Nd} = 0.512177 \pm 0.000006$) standard solutions were carried out to check the accuracy of the analyses. Procedural blank values were $<100 \text{ pg}$ and were therefore neglected as they represented $<1\%$ of the Nd analyzed

per sample.

3.2.2. Benthic foraminiferal stable isotope measurements

For benthic oxygen and carbon stable isotope measurements of cores MD96-2077 and MD96-2052, 2–4 shells of the epibenthic foraminifer *C. wuellerstorfi* (250–355 μm size fraction) were picked. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signature of *C. wuellerstorfi* was measured on an IRMS Delta V-Plus (Thermo-Finnigan) equipped with a carbonate preparation device (Carbo-Kiel IV) at CEREGE. The standard NBS19 was used to normalize measured isotopic values. Mean external reproducibility (1SD) was better than 0.07‰ for $\delta^{18}\text{O}$ and 0.03‰ for $\delta^{13}\text{C}$. The resolution per sample was respectively 4.3 kyr and 2.2 kyr for cores MD96-2077 and MD96-2052.

4. Results

4.1. Foraminiferal ϵ_{Nd} records

The foraminiferal core-top ϵ_{Nd} value of core MD96–2077 is -10.2 ± 0.2 at 7.3 ka (Fig. 3b and Table B.3). Since no data on seawater Nd isotopic composition are available at site MD96–2077, we compare the core-top value with the seawater ϵ_{Nd} value estimated by an empirical equation using seawater PO_4 , SiO_2 , salinity, and temperature values from World Ocean Atlas 2018 (WOA18) (Tachikawa et al., 2017; Boyer et al., 2018). The core-top value (-10.2 ± 0.2) is close to the estimated seawater ϵ_{Nd} value of -9.9 . Over the last 630 kyr, the ϵ_{Nd} record of core MD96–2077 ranges from -11.1 ± 0.3 (MIS 11) to -8.0 ± 0.3 (MIS 12), with generally more radiogenic values (i.e. higher) during glacial periods and less radiogenic values (i.e. lower) during interglacial periods (Fig. 3b).

The average core-top ϵ_{Nd} value of core MD96–2052 is -11.9 ± 0.2 at 2.8 ka based on 3 replicate analyses (Fig. 3b and Table B.3). This value is in good agreement with the typical modern NADW seawater ϵ_{Nd} value of -12.3 ± 0.9 in the N Atlantic (Tachikawa et al., 2017) (Fig. 3b). The core-top ϵ_{Nd} value is also similar to the seawater ϵ_{Nd} value of -10.8 estimated at MD96–2052 site using the previously described empirical equation. The ϵ_{Nd} record of this core along terminations I, II, and V ranges from -12.3 ± 0.2 (MIS 11) to -9.4 ± 0.5 (MIS 6), with more radiogenic glacial values and less radiogenic interglacial values (Fig. 3b).

4.2. Benthic foraminiferal $\delta^{18}O$ and $\delta^{13}C$ records

At core MD96–2077, the benthic $\delta^{18}O$ values range from 2.29 (MIS 5) to 4.51‰ (MIS 12), with heavier values during glacial periods and lighter values during interglacial periods (Fig. 3a and Table B.4). In core MD96–2052, the benthic $\delta^{18}O$ record ranges from 2.31 (MIS 5) to 5.04‰ (MIS 12), with heavier glacial values than interglacial values (Fig. 3a and Table B.4). The average benthic $\delta^{18}O$ of core MD96–2077 (3.64 ± 0.46 ‰) is very similar to the average $\delta^{18}O$ value of core MD96–2052 (3.55 ± 0.53 ‰), which is shown by the close correlation of both records (Fig. 3a).

Concerning the benthic $\delta^{13}C$ records, values at core MD96–2077 range from -1.08 (MIS 8) to 0.69 ‰ (MIS 11), with more depleted values during glacial periods (Fig. 3c and Table B.4). A trend towards generally more depleted glacial values from MIS 14 to MIS 10 is observed (Fig. 3c). The benthic $\delta^{13}C$ values at core MD96–2052 range from -0.16 (MIS 10) to 1.24 ‰ (MIS 11 and 13). The average benthic $\delta^{13}C$ value of core MD96–2077 (-0.15 ± 0.39 ‰) is much more depleted than the average $\delta^{13}C$ value (0.60 ± 0.30 ‰) of core MD96–2052.

5. Discussion

Deep-water authigenic foraminiferal ϵ_{Nd} values mostly reflects water mass provenance and mixing; however, local Nd source such as boundary exchange can also modify authigenic ϵ_{Nd} values. We estimated that the influence of unradiogenic ϵ_{Nd} from boundary exchange is negligible at the two sites based on the following reasons. Firstly, as shown in Fig. 3b, the core-top ϵ_{Nd} values of both cores are close to the compiled or expected modern seawater ϵ_{Nd} (Tachikawa et al., 2017 and references therein). Secondly, detrital ϵ_{Nd} values at MD96–2052 and MD96–2077 sites are about -15 and -10 , respectively (Robinson et al., 2021) and the contribution of local Nd sources with these low ϵ_{Nd} (including Limpopo and Zambezi) cannot explain the observed more radiogenic glacial signals. The ϵ_{Nd} difference between the two sites of ~ 1 ϵ -unit (Fig. 3b) can be better explained by the presence of different water masses (NADW in core MD96–2052 and CDW in core MD96–2077) (see Fig. 1b).

The two studied ϵ_{Nd} records indicate clear glacial-interglacial changes. The benthic foraminiferal $\delta^{13}C$ records of the two cores also

show glacial-interglacial cycles with always more depleted values for core MD96–2077, particularly during glacial periods. The higher authigenic ϵ_{Nd} values and lower benthic foraminiferal $\delta^{13}C$ during glacial periods have been interpreted as an enhanced proportion of southern-sourced water represented by glacial CDW with possible contribution of glacial AABW (Starr et al., 2021). To determine which amount of the benthic foraminiferal $\delta^{13}C$ changes can be explained by water mass mixing and what is the amount of additional depletion of $\delta^{13}C$, we focus on the relationship between authigenic ϵ_{Nd} and benthic $\delta^{13}C$ data.

5.1. Accumulation of respired carbon in deep glacial Indian water inferred from ϵ_{Nd} - $\delta^{13}C$ signatures

Since the present-day water masses occupying the core sites MD96–2052 and MD96–2077 are NADW and CDW, respectively, we consider binary mixing between the two water masses, defined by the present-day NADW and CDW endmembers values of ϵ_{Nd} and $\delta^{13}C$ -DIC (Key et al., 2004; Schmittner et al., 2013; Tachikawa et al., 2017) (Fig. 4). If the paired ϵ_{Nd} - $\delta^{13}C$ data of the cores are on the defined mixing envelop, the changes in authigenic foraminiferal ϵ_{Nd} and benthic foraminiferal $\delta^{13}C$ data can be considered to reflect the different mixing proportion between the northern-sourced water (NSW) and southern-sourced water (SSW) without additional accumulation of respired carbon in the water masses. This is the case with Holocene values for the two studied cores as well as ODP Site 1090 (3702 m water depth) in the SE Atlantic Ocean (Hodell et al., 2003; Pena and Goldstein, 2014) and the equatorial Indian core SK129-CR2 (3°N, 76°E, 3800 m water depth) (Piotrowski et al., 2009), located deeper than 2700 m and bathed by the Upper Circumpolar Deep Water (UCDW) (Figs. 1 and 4).

During glacial periods, ϵ_{Nd} - $\delta^{13}C$ values of both NSW and SSW could be different from those of the modern ocean (Fig. 4). The glacial binary mixing is evaluated assuming that the glacial NSW corresponded to the Glacial North Atlantic Intermediate Water (GNAIW), a water mass resulting from the shallowing of NADW during glacial periods, and the glacial SSW was composed of Glacial Pacific Deep Water (GPDW) with potential contribution of Glacial Antarctic Bottom Water (GAABW) (Starr et al., 2021). The properties of these endmembers are estimated by Yu et al. (2020) for the LGM: GNAIW is characterized by ϵ_{Nd} ranging from -13.5 to -10.5 and a $\delta^{13}C$ of $+1.5$ ‰; GPDW has ϵ_{Nd} of -3.5 and $\delta^{13}C$ of -0.4 ‰; GAABW has ϵ_{Nd} of -6.7 and $\delta^{13}C$ of -0.83 ‰ (Yu et al., 2020). Dissolved inorganic carbon and dissolved Nd concentration of each member are also from Yu et al. (2020). We are aware that the estimated glacial endmember values contain uncertainty and the LGM does not represent the whole studied glacial periods. We thus consider the uncertainty of the endmember properties equivalent to the modern values (Fig. 4).

Using the glacial binary mixing line, we observe that glacial benthic $\delta^{13}C$ values of core MD96–2077 (3781 m water depth) are more depleted than the expected values from the glacial binary mixing line (Fig. 4). A closer look at the ϵ_{Nd} - $\delta^{13}C$ relationship of MD96–2077 data reveals the following points: 1) the majority of glacial values from core MD96–2077 are found below the glacial binary mixing line (Fig. 4); and 2) few interglacial values are also below the glacial binary mixing line, but they are evaluated to be influenced by high organic matter fluxes (inferred by high Total Organic Carbon (TOC) and *Globigerina bulloides* abundance) or cold climate substage conditions within interglacial periods, which favored depleted benthic $\delta^{13}C$ (Figs. 4 and A.4). The observed glacial ϵ_{Nd} - $\delta^{13}C$ relationship for cores MD96–2077 and ODP1090 is difficult to explain without accumulation of respired carbon. Only direct mixing between GNAIW and GAABW without GPDW contribution could partly account for the depleted $\delta^{13}C$, but such a mixing is improbable considering the rapid dilution of AABW during northward flow by CDW and the absence of GAABW originated from the Weddell Sea (Huang et al., 2020). The glacial ϵ_{Nd} - $\delta^{13}C$ relationship with low $\delta^{13}C$ for cores MD96–2077 and ODP1090 contrasts well with the

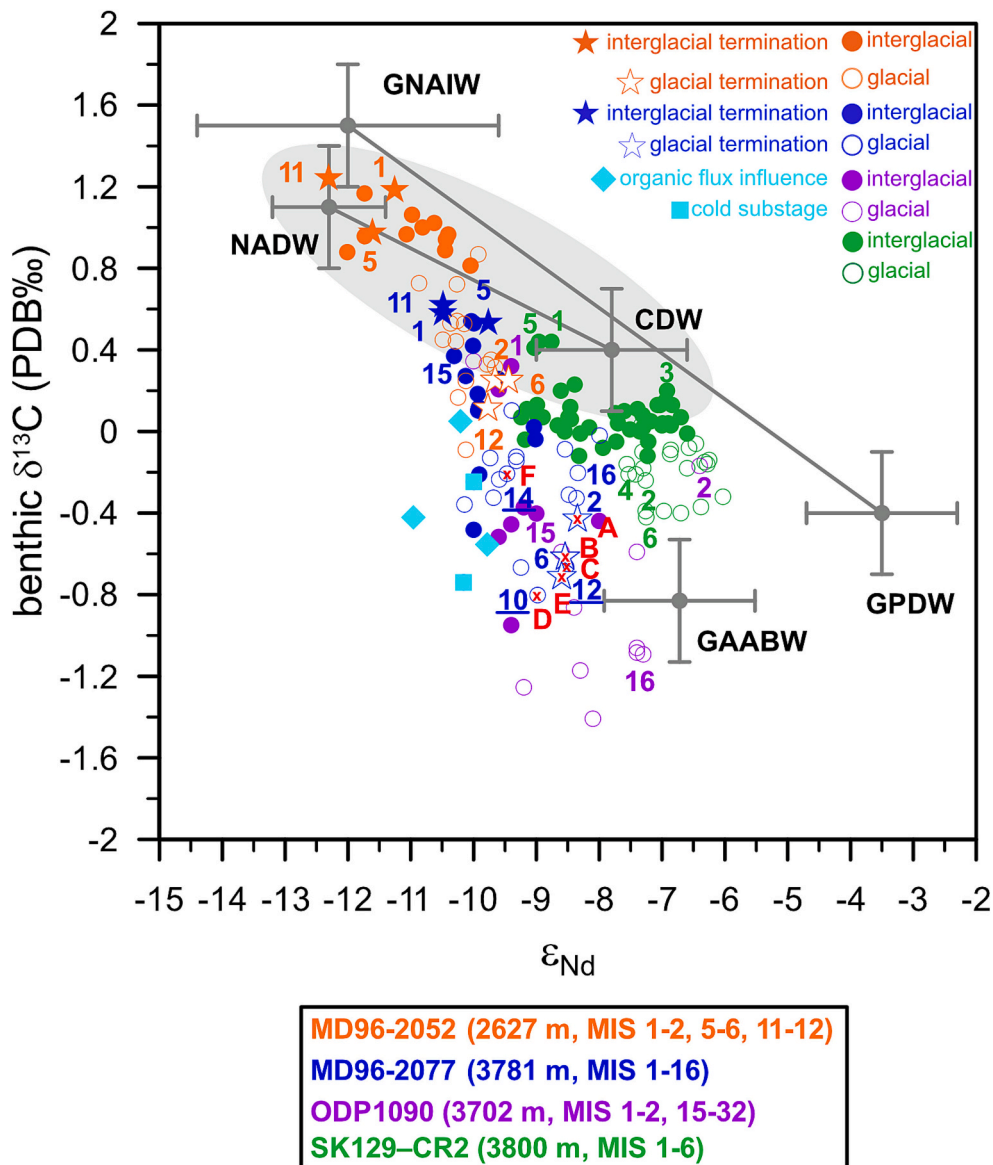


Fig. 4. a) Relationship between benthic $\delta^{13}\text{C}$ and foraminiferal ϵ_{Nd} of MD96–2052 (orange) (this study), MD96–2077 (blue) (this study), ODP1090 (purple) (Hodell et al., 2003; Pena and Goldstein, 2014), and SK129–CR2 (grass green) (Piotrowski et al., 2009). Data influenced by organic fluxes or cold climate substages are colored in light blue. Open symbols are used for glacial periods and closed symbols for interglacial periods. Terminations’ data are indicated with stars. The upper black line is the binary mixing line defined by the present-day NADW and CDW endmembers: for NADW, $\epsilon_{\text{Nd}} = -12.3 \pm 0.9$ (1σ), dissolved Nd concentration = 20.3 ± 3.2 (1σ) pmol/kg, $\delta^{13}\text{C-DIC} = 1.1 \pm 0.3\text{‰}$ (uncertainty is arbitrarily fixed to be 0.3‰) and DIC concentration = 2175 ± 109 mmol/kg (uncertainty is arbitrarily fixed to be 5%), for CDW $\epsilon_{\text{Nd}} = -7.8 \pm 1.2$ (1σ), dissolved Nd concentration = 24.0 ± 4.8 (1σ) pmol/kg, $\delta^{13}\text{C-DIC} = 0.4 \pm 0.3\text{‰}$ (uncertainty is arbitrarily fixed to be 0.3‰) and DIC concentration = 2285 ± 114 mmol/kg (uncertainty is arbitrarily fixed to be 5%). The ϵ_{Nd} and Nd concentration values are derived from Tachikawa et al. (2017). The $\delta^{13}\text{C-DIC}$ and the DIC concentration values are obtained from Schmittner et al. (2013) and Key et al. (2004), respectively. The glacial binary mixing line between Glacial North Atlantic Intermediate Water (GNAIW) and Glacial Pacific Deep Water (GPDW), and the Glacial Antarctic Bottom Water (GAABW) endmember value are based on published values from Yu et al. (2020). Red crosses indicate A-F periods from Fig. 8. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

trend of MD96–2052 and SK129-CR2, more closely located on the glacial binary mixing (Fig. 4).

It is interesting to note that even more depleted epibenthic $\delta^{13}\text{C}$ values relative to the glacial binary mixing were also observed for ODP Site 1090 (3702 m water depth) in the SE Atlantic Ocean (Hodell et al., 2003; Pena and Goldstein, 2014) (Fig. 4), also indicating accumulation of respired carbon in the bottom water in the SE Atlantic (Tachikawa et al., 2021). Thus, as carbon-rich deep waters (i.e. high in respired carbon) were found in both the deep SE Atlantic and SW Indian, we propose a northward extension of carbon-rich southern-sourced deep water into the SW Indian at site MD96–2077, with a vertical boundary between 2700 and 3700 m. In the southernmost sector ($>46^\circ\text{S}$) of the

SW Indian Ocean and the studied MD96–2077 core site (33°S), authigenic uranium concentration data from several cores point towards poorly-ventilated carbon-rich waters below 2500 m (Bard and Rickaby, 2009; Amsler et al., 2022), consistent with our findings. In addition, presence of corrosive deep waters in the SW Indian Ocean during the LGM (Zhang et al., 2022) supports the inferred influence of carbon-rich deep waters below 2700 m in the SW Indian.

5.2. Spatial expansion of glacial carbon-rich deep waters in the SW Indian Ocean

Paired analysis of foraminiferal authigenic ϵ_{Nd} and benthic

foraminiferal $\delta^{13}\text{C}$ fingerprints depleted glacial benthic $\delta^{13}\text{C}$ caused by the accumulation of respired carbon in the deep ocean, which in turn could help to estimate the water volume affected by oceanic carbon storage. Currently, only a limited number of data sets are available for the combined analysis of authigenic ϵ_{Nd} and epibenthic $\delta^{13}\text{C}$ records. Here, we try to evaluate the possible extension of glacial carbon-rich deep waters in the Indian Ocean, following the modern flow path of deep currents in the study area (Fig. 1a) based on a synthesis of benthic $\delta^{13}\text{C}$ records from the South Indian Ocean. Special attention is paid to water depths of cores and benthic $\delta^{13}\text{C}$ values relative to global stacked $\delta^{13}\text{C}$ values (Hoogakker et al., 2006) (Fig. 5). We compare several benthic $\delta^{13}\text{C}$ records from cores retrieved at different water depths in the SW and S Indian Ocean (Figs. 5 and 6), including cores MD96–2077 and MD96–2052 (this study), core Agulhas Plateau (AP) composite site (SW Indian Ocean, $41^{\circ}19.9\text{S}$, $25^{\circ}49.7\text{E}$, 2907 m water depth) (Ziegler et al., 2013; Starr et al., 2021), and core MD84–527 (S Indian Ocean, $43^{\circ}49.3\text{S}$, $51^{\circ}19.1\text{E}$, 3262 m water depth) (Pichon et al., 1992).

The comparison of SW and S Indian benthic $\delta^{13}\text{C}$ records and the stacked benthic $\delta^{13}\text{C}$ curve reveals that the cores from water depths deeper than around 2700 m are characterized by benthic foraminiferal $\delta^{13}\text{C}$ values in the same range of the stacked values only during interglacials (Fig. 5). During glacial periods, benthic $\delta^{13}\text{C}$ values of these deep cores never reach the level of the stacked values. If depleted benthic $\delta^{13}\text{C}$ values during glacials are indicative of carbon-rich waters, then these waters extended to depths deeper than 2700 m between 25°E and 51°E until 33°S along the S coast of Africa in the S Indian Ocean (Figs. 5 and 6). Our interpretation is consistent with previously reported presence of carbon-rich waters below 2500 m in the SW Indian at

latitudes $>46^{\circ}\text{S}$ (Amsler et al., 2022). The equatorial Indian core SK129-CR2 (3°N , 76°E , 3800 m water depth) (Piotrowski et al., 2009) shows glacial $\epsilon_{\text{Nd}}\text{-}\delta^{13}\text{C}$ values, which are closely located on glacial binary mixing line between GNAIW and GPDW (Fig. 4). This reveals that glacial carbon-rich deep waters did not reach the equatorial Indian Ocean (Fig. 6).

We propose a tentative route for the extension of glacial carbon-rich deep waters in the central part of the study area, flowing northward into the Mozambique Channel (Fig. 6). Additional benthic foraminiferal $\delta^{13}\text{C}$ records from deep core sites in the SW Indian Ocean will be helpful to better depict the horizontal extension of these glacial deep waters with high accumulation of respired carbon.

5.3. Processes controlling deep-water carbon storage

To study processes controlling deep-water carbon storage in the South Indian, we at first compare global long-term background fluctuations of $\delta^{13}\text{C}$ and the benthic $\delta^{13}\text{C}$ record from various sites (Fig. 5). We assume that the long-term background $\delta^{13}\text{C}$ changes can be represented by the global stacked benthic $\delta^{13}\text{C}$ values (Hoogakker et al., 2006). As shown in Fig. 5, the stacked $\delta^{13}\text{C}$ has much smaller variability than benthic foraminiferal $\delta^{13}\text{C}$ changes at site MD96–2077. The larger amplitude of benthic $\delta^{13}\text{C}$ reflects the regional/local changes in ventilation, air-sea exchange of CO_2 , and biological organic fluxes to the seafloor.

The $\epsilon_{\text{Nd}}\text{-}\delta^{13}\text{C}$ combination allows distinguishing $\delta^{13}\text{C}$ changes related to water-mass mixing and deep-water carbon storage. Yet, the estimated storage is associated with both biological and physical processes without

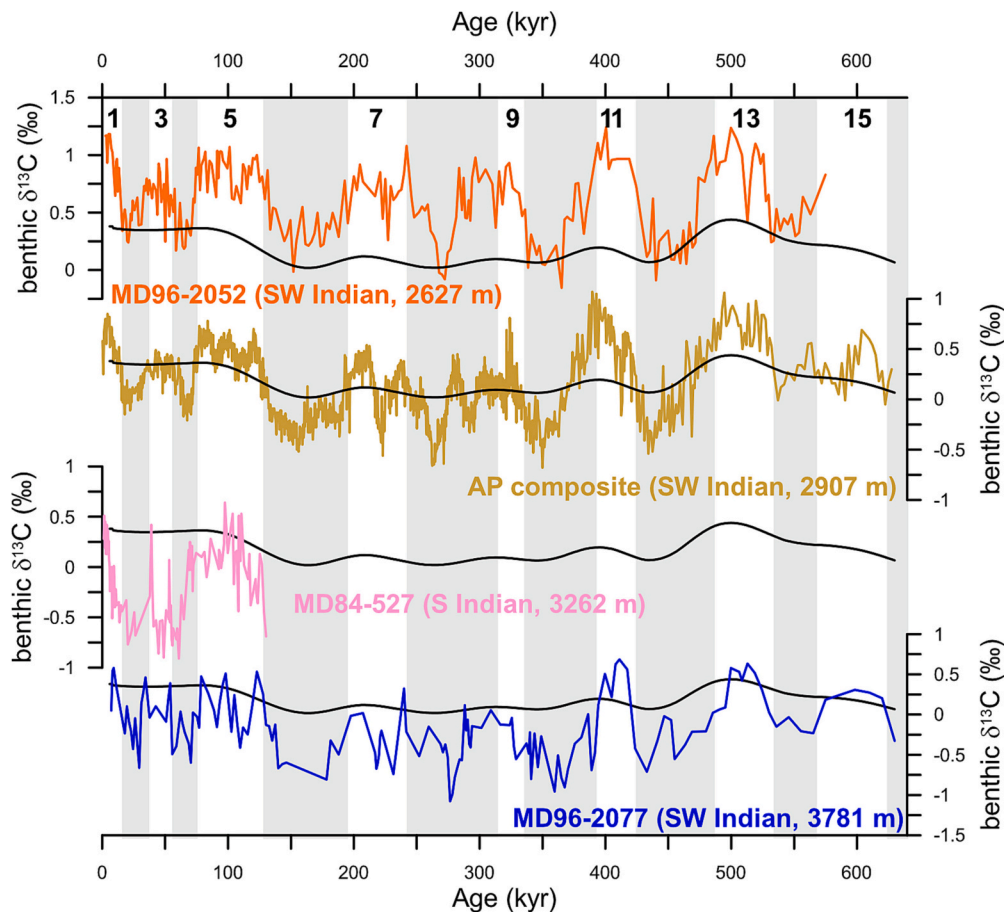


Fig. 5. Benthic foraminiferal $\delta^{13}\text{C}$ of cores MD96–2052 (orange) (this study), AP composite (gold) (Ziegler et al., 2013; Starr et al., 2021), MD84–527 (pink) (Pichon et al., 1992), and MD96–2077 (blue) (this study), compared with the global stacked benthic $\delta^{13}\text{C}$ record (black) (Hoogakker et al., 2006). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

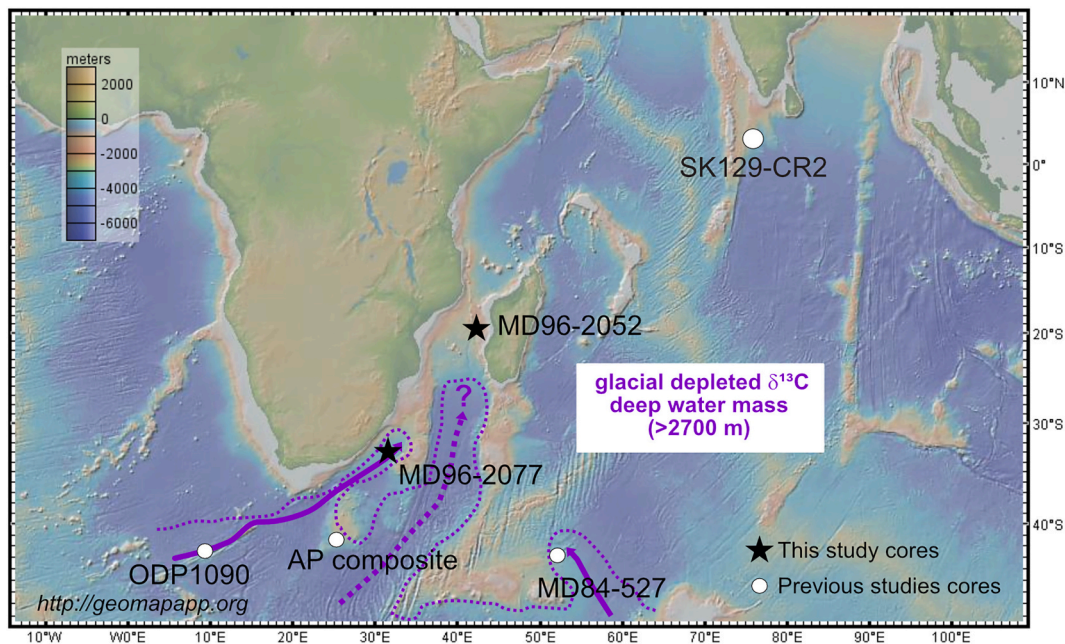


Fig. 6. Map showing the possible extension of glacial depleted $\delta^{13}\text{C}$ deep water masses (>2700 m) into the SW Indian Ocean (dash purple line). A doubtful pathway is indicated by the dash purple arrow. Black stars represent studied cores and white dots previous studies cores. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

any distinction. It was proposed that biological and physical processes contributed to atmospheric CO_2 decline about 50% each (Hain et al., 2010). Thus, glacial carbon storage in the SW Indian resulted from the combination of biological processes (biological pumping) and physical processes (air-sea exchange, water stratification) in addition to higher proportion of carbon-rich SSW relative to the NSW.

The biological and physical processes controlling ocean carbon storage might be modulated by orbital forcing. To evaluate the influence of orbital cycles on carbon storage and related ice-sheets dynamics, spectral and wavelet analyses were performed using the software PAST (Hammer et al., 2001). The corrected benthic $\delta^{13}\text{C}$ record of core MD96-2077 shows significant spectral peaks with periodicities of 100 kyr (eccentricity) and 23 kyr (precession) for the whole studied interval (Fig. 7a). Furthermore, higher carbon storage (lower corrected benthic $\delta^{13}\text{C}$) occurred at times of relatively lower eccentricity and obliquity within glacial periods (see A-F red rectangles in Fig. 8b, c, and d). These findings support that orbital forcing could have influenced the extension and reduction of the nutrient-rich deep waters, and related ocean carbon storage. Orbital forcing governed the waxing and waning of polar ice sheets due to linear response to changes in high-latitude insolation for 41 and 23-kyr cycles and due to nonlinear response of the cryosphere for 100-kyr cycles (Hays et al., 1976; Shackleton, 2000). During glacial periods, more extended Antarctic sea ice was reconstructed by multiproxy records for the last 130 kyr (Crosta et al., 2022 and references therein). The larger sea-ice could restrict air-sea exchange of CO_2 (Mix and Fairbanks, 1985; Sigman and Boyle, 2000; Gebbie, 2014) and similar reduction of air-sea exchange could have occurred during glacial periods of the last 630 kyr. Moreover, stronger density stratification in the Antarctic Zone waters during glacial periods would have also favored the accumulation of respired carbon in the deep ocean (Hasenfratz et al., 2019). Sea-ice expansion promoted higher vertical density stratification through brine rejection during glacial periods. This ocean stratification played a dominant role in increasing CO_2 sequestration during the early stages of glacial cycles (Stein et al., 2020). For example, sea-ice driven stratification fostered higher C storage in the Cape Basin (Southern Ocean) during glacial periods (Hines et al., 2021). A modelling study shows that glacial atmospheric cooling can predict Antarctic bottom water isolation due to reduced air-sea exchange under

larger sea ice and weaker mixing with NADW during LGM, explaining half of the glacial atmospheric CO_2 drawdown (Marzocchi and Jansen, 2019). Finally, glacial enhanced biological pumping, favored by dust-driven iron fertilization, and the equatorward migration of glacial westerlies and/or weaker westerlies would have also contributed to accumulate carbon in the deep ocean (Mix and Fairbanks, 1985; Gebbie, 2014; Sigman et al., 2010, 2021; Toggweiler et al., 2006). All these physical and biological processes might have enhanced the CO_2 sequestration capacity of glacial deep waters.

In addition to orbitally-controlled fluctuations in the ice-sheet and sea ice extension, changes in ocean circulation, including NADW reduction and poorly ventilated SSW, may have also contributed to promoting the extension of glacial carbon-rich waters. More radiogenic ϵ_{Nd} during glacial periods could support both weaker glacial NADW formation and/or relatively active glacial CDW flow compared to glacial NADW, both accounting for a higher influence of carbon-rich deep waters in the SW Indian (Fig. 4). Recently, Starr et al. (2021) suggested that a northward shift in iceberg trajectories during glacial periods led to much more meltwater spreading northward. This mechanism reduced salinity in surface waters flowing towards the North Atlantic and, therefore, weakened AMOC strength and/or favored occupation of shallower water depths, thus reducing the proportion of northern-sourced water in the binary mixing (Fig. 4). This other process might have indirectly promoted the development of glacial carbon-rich deep waters, along with the previously discussed processes.

Assuming that the temporal evolution of carbon storage capacity of the deep S Indian Ocean over the last 630 kyr, including both reduced ventilation and water mass mixing, can be monitored using the corrected benthic $\delta^{13}\text{C}$ curve from core MD96-2077 (Fig. 8d), we compare variations in the main forcing mechanisms such as orbital forcing and related sea-ice cover extension, which may be reconstructed using orbital curves (eccentricity and obliquity), the relative abundance of the diatom species *Fragilariopsis curta* and *F. cylindrus* at core SK200/33 located in the west Indian Ocean sector (Chadwick et al., 2022), and ice-rafted debris mass-accumulation rate (IRD_{MAR}) at Agulhas Plateau (AP) composite site (Figs. 1a and 8). A northward shift of IRD trajectories, indicated by higher IRD_{MAR} at the AP composite site, points to a more extensive sea-ice cover (Starr et al., 2021). The validity of this indirect

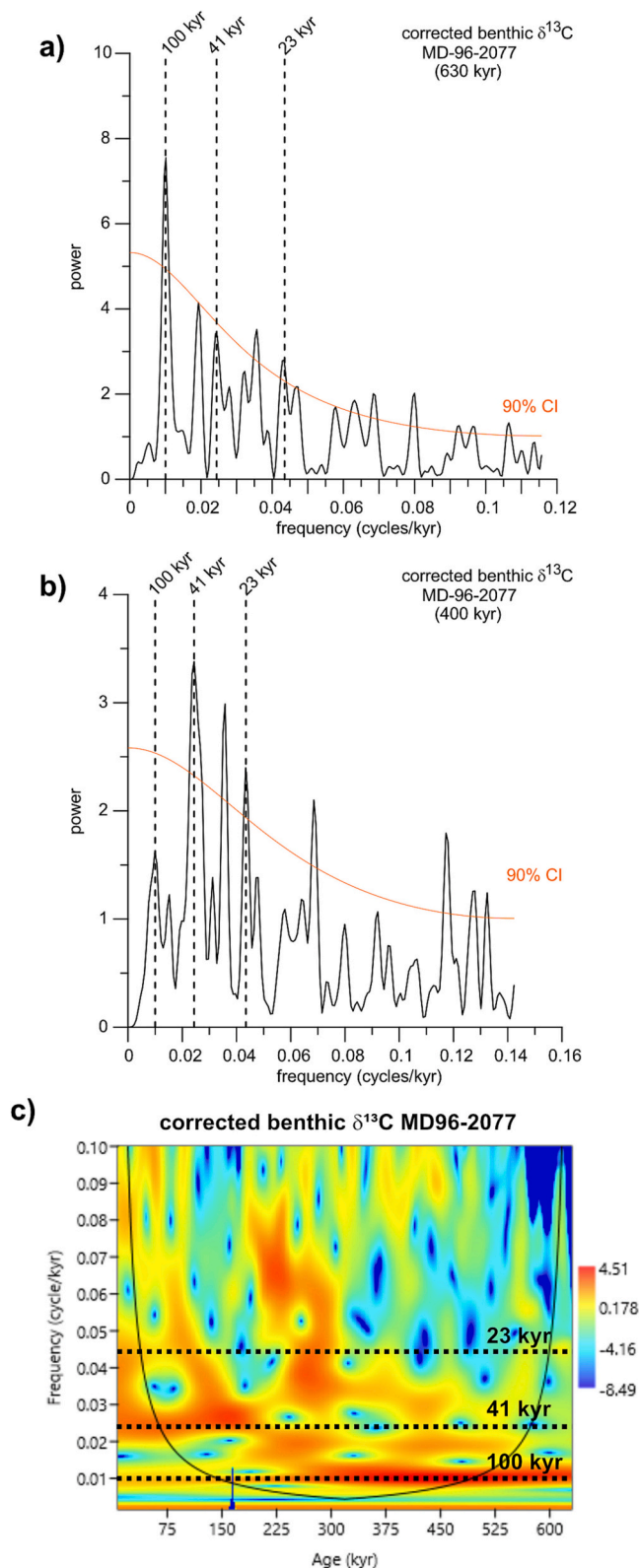


Fig. 7. a) Power spectrum of the corrected benthic $\delta^{13}\text{C}$ of core MD96-2077 (last 630 kyr) with principal orbital periodicities indicated in kiloyears. The 90% confidence interval (CI) is shown. b) Power spectrum of the corrected benthic $\delta^{13}\text{C}$ of core MD96-2077 (last 400 kyr) with major orbital periodicities indicated in kiloyears. The 90% confidence interval (CI) is depicted. c) wavelet power spectrum of the corrected benthic $\delta^{13}\text{C}$ of core MD96-2077 (last 630 kyr). Main orbital cycles are marked with dash lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

proxy for sea-ice cover extension is supported by the positive correlation between higher IRD_{MAR} and higher abundances of the diatom species *F. curta* and *F. cylindrus* from west Indian core SK200/33, which indicate larger sea ice cover (Chadwick et al., 2022) (Fig. 8d). Over the last 630 kyr, the most conspicuous feature is the progressively decreasing of corrected benthic $\delta^{13}\text{C}$ from MIS 14 to MIS 10, suggesting gradually higher C storage capacity (Fig. 8d). The effect of local productivity influences on this trend was estimated to be minor since the highest surface productivity (inferred from *G. bulloides* abundance (Chen, 1996 [dataset])), the related highest organic matter accumulation and preservation (based on TOC and alkenones in bulk sediment) and seafloor oxygen decrease (deduced by authigenic uranium content) (Bard and Rickaby, 2009), occurred at the end of glacial periods (Fig. A.4). In contrast, corrected benthic $\delta^{13}\text{C}$ values decreased across glacial inceptions (Fig. A.4), revealing that carbon-rich deep waters arrived at the SW Indian at the beginning of glacial periods. Interglacial to glacial $\delta^{13}\text{C}$ change was 0.5, 1.3, and 1.6‰ for glacial MIS 14, 12, and 10, respectively. Therefore, carbon storage in the SW Indian Ocean increased gradually until MIS 12 and 10, which show extreme glacial conditions. This gradual higher C storage capacity towards MIS 12 and 10 in the SW Indian Ocean was mainly controlled by progressively larger sea-ice cover related to 100-kyr eccentricity minima (Fig. 8b and d).

After MIS 10, a gradual transition from eccentricity- to obliquity-dominated cycles is observed for corrected benthic $\delta^{13}\text{C}$ in the spectral analyses (Fig. 7a and b), the wavelet power spectrum of corrected benthic $\delta^{13}\text{C}$ (Fig. 7c), and the power of the 100 and 41-kyr corrected benthic $\delta^{13}\text{C}$ cycles (Fig. 8a). As for the corrected benthic $\delta^{13}\text{C}$ record, the 100-kyr cycle of the $\delta^{18}\text{O}$ is less important than the 41-kyr obliquity cycle over the last 400 kyr (Fig. A.5b and A.5c). This replacement of 100-kyr eccentricity cycles by 41-kyr obliquity cycles, governing both sea-ice cover and related C storage changes (Fig. 8a), could be related to changes in the northern and southern hemispheres ice sheet dynamics (Starr et al., 2021). Before MIS 10, Southern Ocean climate was influenced by the complex non-linear 100-kyr response due to the northern hemisphere thick ice sheets established after the Mid-Pleistocene transition (Clark et al., 2006). Obliquity 41-kyr linear response of the Southern Ocean after MIS 10 might be caused by a stronger relationship between southern hemisphere ice sheets and obliquity (Zhang et al., 2013; Fogwill et al., 2015; Starr et al., 2021).

Our results highlight the importance of the SW Indian Ocean as a sink for CO_2 during glacial periods, when highest C storage occurred during relatively lower 100-kyr eccentricity and 41-kyr obliquity conditions, which fostered the largest sea-ice cover and lowest air-sea exchange of CO_2 . In addition, our findings help to better constrain the dimensions of expanded glacial carbon-rich deep waters, which can increase the C storage capacity, with larger global volumes of southern-sourced nutrient-rich waters holding more CO_2 (Skinner, 2009).

6. Conclusions

We investigated the spatial and temporal evolution of glacial carbon-rich deep waters entering the SW Indian over the last 630 kyr based on foraminiferal ϵ_{Nd} and benthic $\delta^{13}\text{C}$ of two cores from the SW Indian Ocean.

Assuming that foraminiferal authigenic ϵ_{Nd} values essentially reflected the relative proportion between the northern- and the southern-sourced water whereas benthic $\delta^{13}\text{C}$ values varied with ventilation state, the comparison of $\epsilon_{\text{Nd}}-\delta^{13}\text{C}$ relationship between the two cores revealed that glacial deep waters with a high accumulation of respired carbon bathed sites deeper than 2700 m. These southern-sourced deep waters could have extended at least until 33°S within the SW Indian Ocean.

Spatial and temporal expansion of glacial carbon-rich deep waters was governed by several forcing physical mechanisms. Periodicity analyses showed eccentricity (100 kyr) and obliquity (41 kyr) cycles in benthic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records from core MD96-2077, where the presence of glacial deep carbon rich waters was inferred. Furthermore,

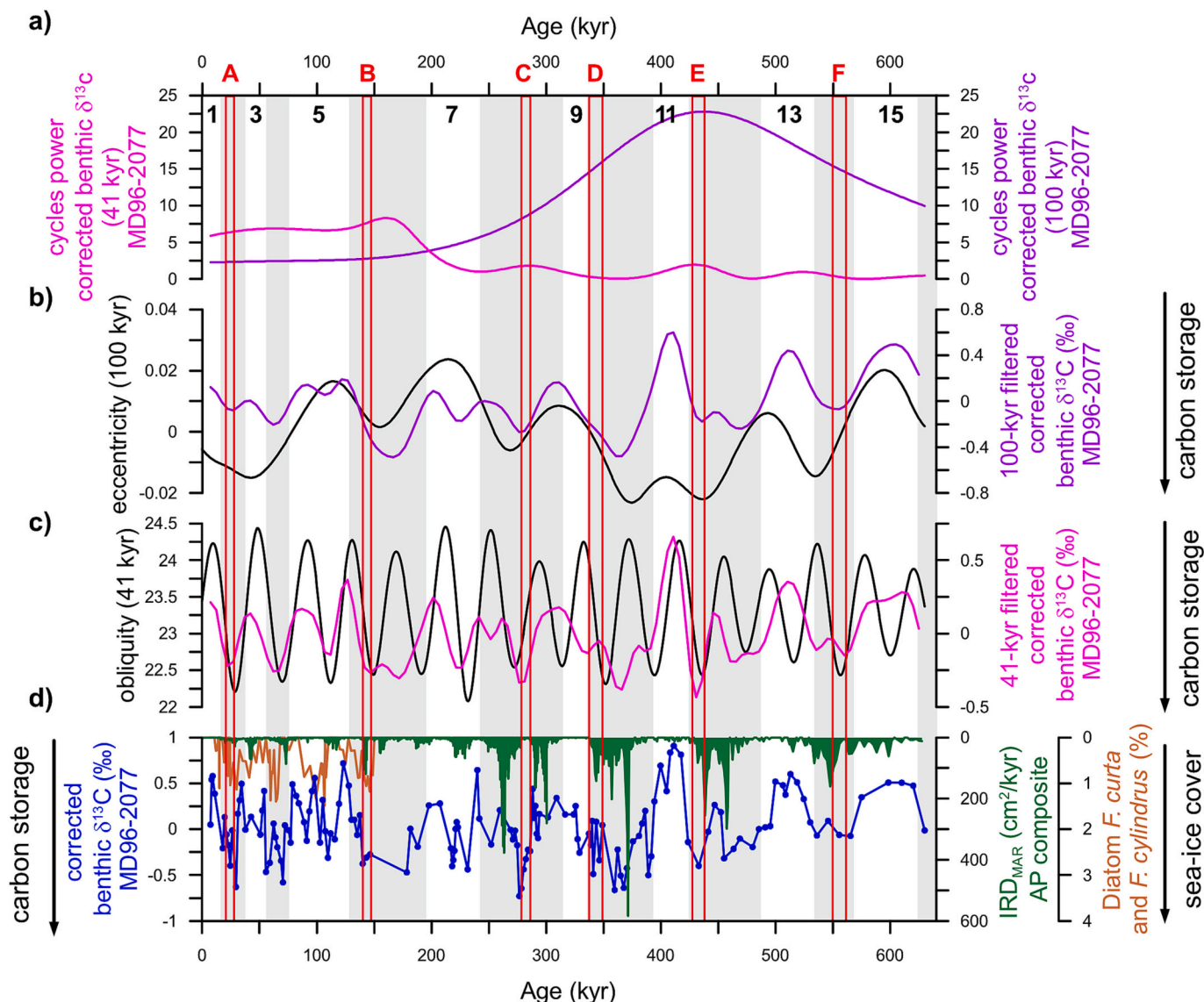


Fig. 8. a) Power of the corrected benthic $\delta^{13}\text{C}$ of core MD96–2077 in the 100-kyr eccentricity (purple) and 41-kyr obliquity (magenta) frequency bands. b) 100-kyr filtered corrected benthic $\delta^{13}\text{C}$ of core MD-96-2077 (purple) and filtered 100-kyr eccentricity (black). c) 41-kyr filtered corrected benthic $\delta^{13}\text{C}$ of core MD-96-2077 (magenta) and filtered 41-kyr obliquity (black). d) Corrected benthic $\delta^{13}\text{C}$ of core MD-96-2077 (blue) (this study), diatom *Fragilariopsis curta* and *F. cylindrus* relative abundances of core SK200/33 (red brown) (Chadwick et al., 2022) and IRD_{MAR} (cm^2/kyr) of AP composite site (forest green) (Starr et al., 2021). Red rectangles show periods (A-F) of more depleted corrected benthic $\delta^{13}\text{C}$ of core MD-96-2077 (higher carbon storage) at times of low eccentricity and obliquity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

higher C storage occurred during glacial periods at times of relatively lower eccentricity and obliquity, showing an increasing trend in C storage from MIS 14 to MIS 10.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data of this study can be found online in the supplemental files and in the database Pangaea (www.pangaea.de).

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