

Ventilation of the northern Indian Ocean from the Last Glacial Maximum to the Holocene

A Thesis submitted in partial fulfillment for the Degree of

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By

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DECLARATION

I, **Kumari Nisha**, hereby declare that this thesis titled “Ventilation of the northern Indian Ocean from the Last Glacial Maximum to the Holocene”, represents the work which has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

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CERTIFICATE

I hereby certify that the above Declaration of the candidate, **Ms. Kumari Nisha**, is true and the work was carried out under my supervision.

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*This thesis is dedicated to my parents;
to my loving papa Mr. Dina Nath Padar,
who was (and still is) a source of inspiration & courage to me,
and to my beloved maa Mrs. Girija Devi,
who has always motivated me to strive higher*



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Kumari Nisha

*“The climate is an angry beast
and we are poking at it with sticks”*

~Prof. Wallace Smith Broecker

Preface

Chapter 1 consist of the general introduction to the research objective and significance of the ocean circulation changes. The chapter starts with a general introduction of global warming and its effect on ocean circulation. With the increase in the anthropogenic CO₂, there will be more uptake of CO₂ by the deeper ocean, hence effecting the ocean circulation in the future. This chapter provides a detailed explanation to study the ventilation changes in the northern Indian Ocean and brief background on various oceanographic proxies such as radiocarbon ages, stable carbon and oxygen isotopes, porosity of benthic foraminifera and geochemical analysis. Objectives in undertaking this work are listed in this chapter.

Chapter 2 includes a literature review of the ventilation records from all the world oceans during the glacial-interglacial cycle. There is a consensus that ¹⁴C-depleted deep water mass existing in the abyssal of the Southern Ocean during the last glacial, dissipated during the Heinrich Stadial 1 (HS1; 17.5-14.5 kyr) and the Younger Dryas (YD; 12.8- 11.2 kyr) and hence, resulted in a drop in atmospheric radiocarbon activity. Numerous ventilation changes records have been reported from the Atlantic and Pacific Ocean, whereas the Indian Ocean remains scantily studied. Hence it is extremely important to have sufficient data on the ventilation aspect from specific locations in the Indian Ocean.

Chapter 3 emphasis on geological setting and hydrography of the northern Indian Ocean. This chapter begins with an introduction of the Indian Ocean. It includes the geological setting and the terrigenous inputs in the northern Indian Ocean. This chapter, however, mainly deals with the surface and deep water circulation in the northern Indian Ocean.

Chapter 4 deals with the material and methods used to address the research objectives. This chapter gives a detail of the two sediment cores, deep water core SSD-044/GC-01 and intermediate water core AAS-9/21 used in this study. This chapter addresses techniques used for the reconstruction of the past ventilation record using the radiocarbon ages of the foraminifera, the epifaunal benthic foraminifera *Cibicidoides wuellerstorfi* used for the stable carbon and oxygen isotope and for the porosity calculations, fragmentation index, size index. Finely ground sediment sample were used for total inorganic carbon and geochemical analysis. In this section, details of sample pre-treatment techniques, protocols followed, size fraction and chemicals used for the fulfilment of the Ph.D. work have been

discussed.

Chapter 5 describes the ventilation changes in the deep water of the northern Indian Ocean during the last 25 kyr. The ventilation age, stable carbon and oxygen, calcium carbonate and coarse fraction percentage record from the core SSD-044/GC-01 indicates that during the last glacial there was more penetration of the poorly-ventilated southern sourced AABW into the northern Indian Ocean. There was rapid decrease in the ventilation ages at the core site during the B-A indicating resumption of inflow of better-ventilated water from the North Atlantic. It also reveals that the northern Indian Ocean was part of the glacially aged carbon pool.

Chapter 6 investigates the variability in the ventilation in Eastern Arabian Sea (EAS) during the last glacial-interglacial cycle. The core AAS-9/21 is mainly ventilated by North Indian Deep Water (NIDW). The ventilation changes in EAS was due to the changes in the contribution of the NADW in the formation of NIDW. This chapter also includes comparison of the ventilation ages record from different depths and location (Western Arabian Sea = 870 m; EAS = 1800 m; equatorial Indian Ocean = 3160 m). The core retrieved from the EAS shows a different trend during the last deglaciation when compared to the Western Arabian Sea.

Chapter 7 addresses the third objective of the thesis. In this, the carbonate ion concentration of the core SSD-044/GC-01 has been used to deduce the bottom water conditions in the northern Indian Ocean over the past 25 kyr. In order to do so, proxies like calcium carbonate, foraminiferal fragmentation percentage and size index has been used. It also investigates bottom water oxygenation condition in the northern Indian Ocean using porosity of the epifaunal benthic foraminifera and concentration of redox-sensitive element uranium in the sediment. This results suggest that there existed O₂-poor and CO₂-rich deep water mass in the northern Indian Ocean from the period ~24 kyr to ~15 kyr. There was incursion of O₂-rich and CO₂-poor deep water from ~15 kyr onwards.

Chapter 8 discusses the inferences and conclusions from this research. This section states that there was poorly ventilated water in the deep water of the northern Indian Ocean during the last glaciation. This poorly-ventilated water existed until ~15 kyr in the northern Indian Ocean. After ~ 15 kyr, this poorly-ventilated water was replaced by better-ventilated water.

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Chapter 1

Introduction

1.1 Carbon dioxide in seawater

The long-term shift in the temperature and weather pattern is one of the major challenges that we are facing today. This global rise in the Earth's temperature is termed as 'global warming'. Global warming is due to the presence of greenhouse gases like water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) in the atmosphere. These gases absorb the infrared radiation emitted by the Earth's surface, preventing it from escaping back into space and thereby leading to the warming of the surface of the planet. Among these gases, CO_2 is the most significant greenhouse gas. It is the second most abundant greenhouse gas and contributes 20% to the Earth's greenhouse effect. The carbon concentration and the heat content of the atmosphere have an inextricable link. The increase of CO_2 in the atmosphere causes warming of the Earth's atmosphere, resulting in global warming. Since the Industrial Revolution, the anthropogenic carbon dioxide content is steadily increasing in the present atmosphere as a result of human activities such as the burning of fossil fuels like coal, oil, and gas. The present August 2024 monthly mean concentration of this gas in the atmosphere recorded at the Mauna Loa Observatory (MLO) has exceeded 422.99 parts per million (<https://gml.noaa.gov/ccgg/trends/>; Fig. 1.1). These increasing levels of CO_2 lead to changes in global climate (IPCC, 2021; 2023).

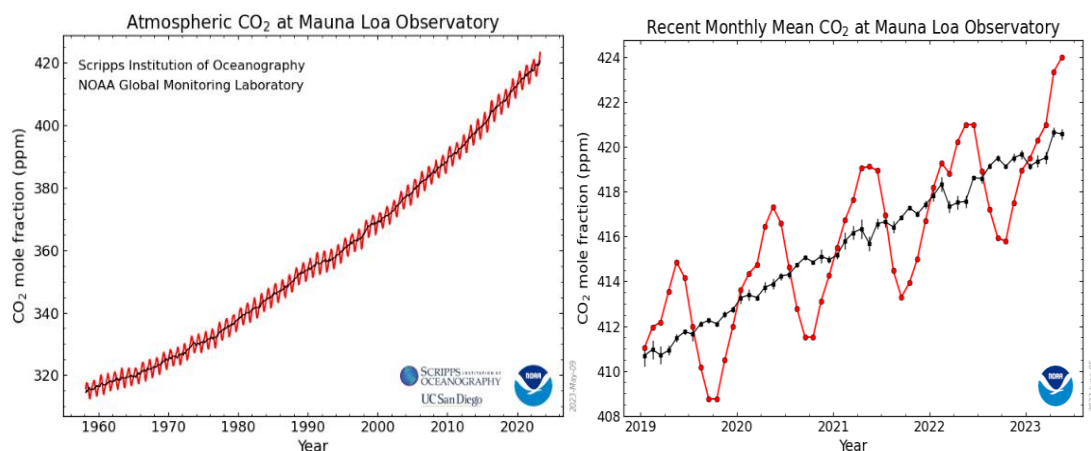
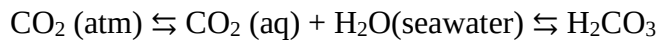
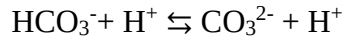
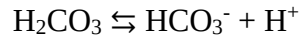


Fig. 1.1: Carbon dioxide levels measured at NOAA's Mauna Loa Atmospheric Baseline Observatory (source: National Oceanographic and Atmospheric Administration).

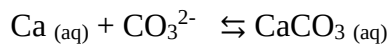
The ocean is the largest reservoir of CO₂ and plays a critical role in the chemical balance of the atmospheric CO₂ levels. It balances the atmospheric CO₂ levels by serving as a major sink and source of the atmospheric CO₂. Even a small change in oceanic CO₂ content can cause profound changes in the radiation balance of the atmosphere (Sundquist and Broecker, 1985). Carbon dioxide from the atmosphere is taken up by the surface seawater by two primary process: biological pumping and chemical process. The biological pump has a first-order impact on the CO₂ concentration of the atmosphere. In the oceanic biological pumping, CO₂ from the atmosphere is fixed into the organic matter via photosynthesis and then it is transported into the deep ocean. In the chemical process, as the atmospheric CO₂ enters the seawater, it reacts with the water to form carbonic acid (H₂CO₃).



This carbonic acid is unstable, and thus it rapidly dissociates into bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). In this process, free hydrogen ions (H⁺) are produced. The free H⁺ ions lower the pH of seawater. Therefore, it can be concluded that the addition of dissolved CO₂ in seawater lowers its pH.



Marine organisms like corals, foraminifera and coccolithophores, having calcareous tests or exoskeletons, use calcium and carbonate ion dissolved in seawater to make up their skeletons. The following reaction describes the precipitation of CaCO₃ from seawater:



The rise in the concentration of anthropogenic CO₂ in the atmosphere will have severe consequences on marine life, particularly the calcifying organisms. Around 2.9 ± 0.4 GtC year⁻¹ of anthropogenic carbon has been taken up by the ocean in the last decade 2012-2021 (Friedlingstein et al., 2022). The uptake of anthropogenic CO₂ by the ocean causes an increase in dissolved CO₂ and total inorganic carbon concentrations, and thus decreases the ocean pH, leading to dissolution of the calcareous organism (Gattuso and Hansson, 2011). Investigating the ocean's role in the global CO₂ exchange in the past and the response of marine biota to this will improve projections of future climate change under the rising anthropogenic CO₂ levels.

1.2 Glacial to interglacial carbon cycle variability

The gas bubbles trapped in ice-sheets provide an extraordinarily valuable record of the variability in the concentration of atmospheric CO₂. Ice cores have been drilled from Antarctica and Greenland and have been examined for variations in the air trapped in the bubbles within these ice cores. Analysis of these trapped gas bubbles has revealed that the CO₂ in the atmosphere varied from ~80-100 ppm over the past 800 kyr (Petit et al., 1999; Lüthi et al., 2008) (Fig. 1.2). The atmospheric CO₂ was high during the interglacial (warm) intervals and considerably lower during the glacial (cold) intervals. Studies of the last glacial and interglacial cycle suggest that there was a sudden increase in the concentration of CO₂ in the atmosphere during the last glacial termination (~18-11 kyr BP; Monnin et al., 2001; Marcott et al., 2014). Since the ocean is the largest reservoir of carbon at the Earth's surface, it is assumed to have played an important role in the atmospheric CO₂ variability (Broecker et al., 1982; Broecker and Denton, 1990). There are number of hypothesis put forth for this glacial-interglacial changes in the concentration of CO₂ in the atmosphere (Sigman and Boyle, 2000), but the exact mechanisms still remains unclear. The overarching goal of this research study is to gain a better understanding of the glacial–interglacial carbon cycle variability and the possible mechanisms behind it. In order to understand the changes in the fluxes of heat and freshwater between the ocean and the atmosphere, it is important to reconstruct changes in ocean circulation in the past.

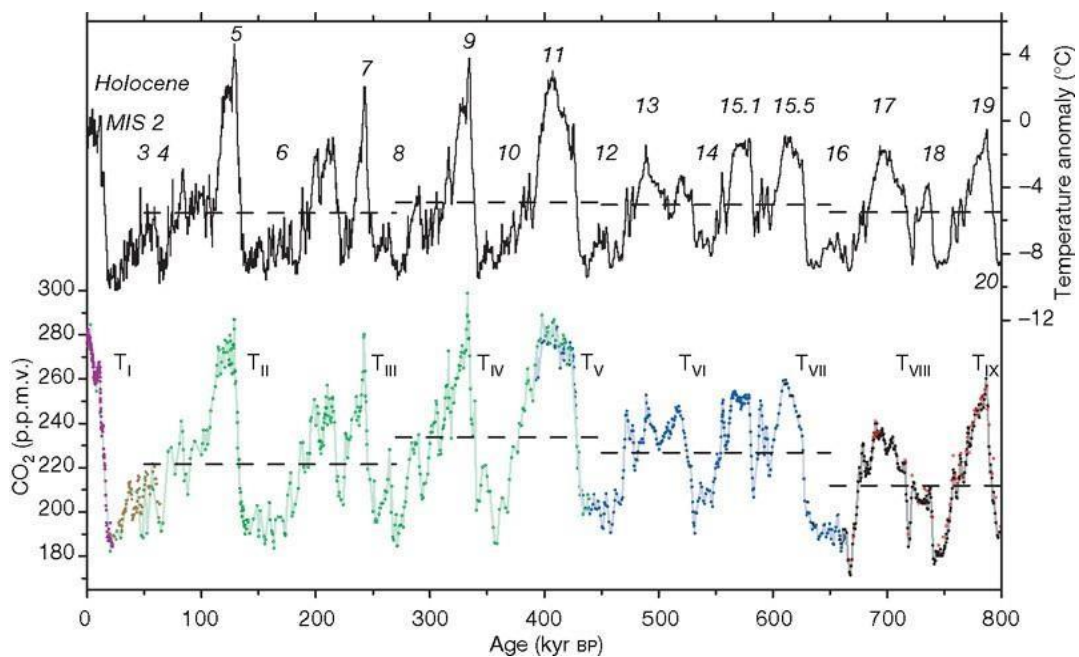


Fig. 1.2: Atmospheric CO₂ and air temperature recorded from air trapped in Antarctic ice cores for the last 800 kyr (Lüthi et al., 2008).

1.3 Thermohaline circulation

Thermohaline circulation is a global belt of moving water masses driven by heat and density contrasts in the world's oceans (Fig. 1.3). It distributes heat, CO₂, oxygen, and nutrients in the global ocean and thereby regulates the global climate (Rahmstorf, 2006). In the Atlantic Ocean, the water masses in the upper 1000 m carry heat from the equator to the northern pole. As this water mass moves northwards, it loses its heat to the overlying water and to the atmosphere. As a result, the northward-moving water becomes cool and dense (thereby increasing salinity) and sinks to the bottom of the ocean at the poles. After sinking, this saline water flows towards south, forming the lower limb of the conveyor belt. At the Antarctic continental margin, primarily in the Weddell and Ross Seas, sea-ice formation results in salt expulsion from the ice, producing brine which causes the water to sink and form cold dense water mass. Thus, deep waters are also formed along the margins of the Antarctic continent. These deep water masses flow towards south as either Bottom Waters or Deep Waters, depending on their relative density. Today, most of the deepest section of the world's ocean is filled by the North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW) (Talley, 2008). Antarctic Bottom Waters are formed due to sea-ice formation adjacent to the Antarctic continent, whereas NADW is formed in the Norwegian Sea and in the Greenland Sea (Kellogg, 1987; Hay, 1993). These deep water masses are transported to all the three major oceans. At present, in the Pacific Ocean, the salt content of the surface water is low which prevents the sinking of the surface water to the bottom, whereas in the Indian Ocean, surface waters are too warm to form deep waters. Hence, there is no reported deep water formation from sinking of surface waters in the northern Pacific and northern Indian Oceans (Piotrowski et al., 2009; Bullister et al., 2013; Kawasaki et al., 2022). The deep water masses are overlain by Intermediate Waters. Intermediate waters have lower salinity and/or higher temperature than the deep waters. There are several intermediate water masses, out of which the Antarctic Intermediate Water (AAIW) is the most dominant in all the oceans. After reaching the lower latitudes, deep water gradually rises to the surface through upwelling. The surface water of the conveyor belt returns the warm waters from the Indian and Pacific Oceans to the Atlantic Ocean.

Changes in the deep water circulation are important for paleoclimatology because this circulation regulates the Earth's climate through heat redistribution and biogeochemical cycling of nutrients, specifically carbon around the globe and finally outsourcing it back to the atmosphere during upwelling. Therefore, reconstruction of past changes in global

thermohaline circulation is important for understanding the global and regional paleoclimatic and paleoceanographic changes.

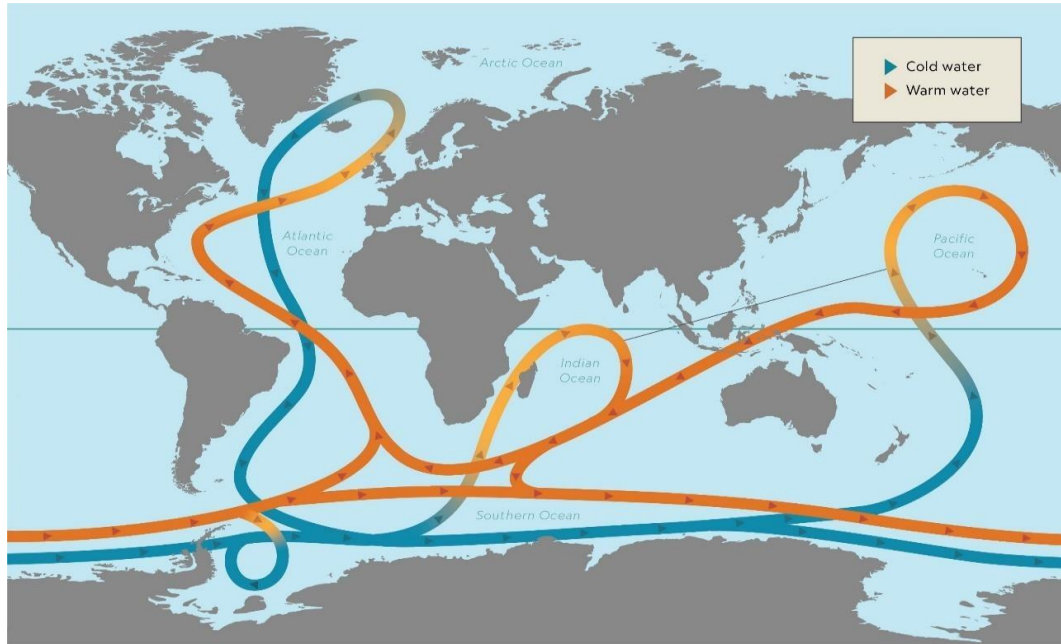


Fig. 1.3: Thermohaline circulation (source: National Geographic Society).

1.4 Proxies

There are various proxies that could be used to reconstruct the past oceanic changes in the northern Indian Ocean. The following section includes the proxies that have been used in this study.

1.4.1 Foraminifera

Foraminifera are a large group of marine “amoeboid” protists. They existed and diversified since Cambrian times. They are single-celled, preferentially marine microorganisms. Though they are primarily marine organisms, some species are found in brackish or freshwater. The soft part of the organism is enclosed in a test, also called as a test, which is made up of either calcium carbonate secreted by the cells or agglutinated sand particles of various sizes. Calcareous foraminifera secrete their test using calcium and carbonate ions from the seawater. The test contains a series of chambers that increase in number as they grow. They may have either one or multiple chambers. They have a wide variety of shapes, and their size ranges from 63 μm to $\sim 120 \mu\text{m}$. As the organisms die, they sink to the bottom of the sea, and their test gets preserved in sediments for thousands of

years. Foraminiferal test dissolution starts from the lysocline depth, where the dissolution of CaCO_3 begins and increases dramatically (Peterson and Prell, 1985), and the foraminiferal carbonate test gets completely dissolved below the Carbonate Compensation Depth (CCD; depth at which the rate of carbonate supply is equal to the carbonate dissolution rate) (Van Andel, 1975). However, the agglutinated foraminifera are found deeper than the CCD (Murray, 2006). The lysocline is generally few meters above the CCD. The CCD ranges from ~4.6- 5.1 km (Broecker and Peng, 1982), where the CCD in the equatorial Indian Ocean is the deepest (Kolla et al., 1976). The foraminiferal lysocline depth in the equatorial Indian Ocean lies at 3800 m (Cullen and Prell, 1984), whereas the CCD is around ~4600 m (Banakar et al., 1998).

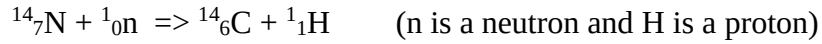
Foraminifera exhibits both planktic and benthic modes of life. Planktic foraminifera are free-floating surface-dwelling foraminifera. They are most abundant in the upper 100-150 m of the water column as the solar light penetration is maximum at these depths. The *Globigerinoides* species inhabits shallow waters while few species (*Globigerina bulloides*, *Hastigerina pelagica*, *Orbulina universa*) live in intermediate water at 50-100 m depths (Saraswati, 2021). Species such as *Globorotalia menardii*, *Sphaeroidinella dehiscens* and *Neogloboquadrina pachyderma* live below 100 m (Saraswati, 2021). Planktic foraminiferal tests are globular-shaped (to provide buoyancy), highly perforated with a large aperture. Benthic foraminifera are bottom-dwelling foraminifera, majorly found in shallow waters. The benthic foraminiferal distribution patterns are intricately linked to the flux of particulate organic matter from the upper ocean to the ocean floor (Van der Zwaan et al., 1990, Gooday, 1993, den Dulk et al., 2000). Benthic foraminifera living on the surface of the sediment are the epifaunal species and are characterized by planoconvex, biconvex, rounded trochospiral and spherical test shapes (species like *Cibicides*, *Discorbis* and *Planulina*) (Kaiho, 1994; Murray, 2006, Murray, 2014). Benthic foraminifera living in the few centimeters of the upper sediments are classified as infaunal species and are mostly porous, flat or elongated-tapered forms (species like *Bulimina*, *Bolivina*, *Trifarina*, *Reusella*, *Nodosoria*, *Virgulina* and *Cassidulina*) (Kaiho, 1994; Murray, 2006, Murray, 2014). Benthic foraminifera in marine sediments are considered as a "tracer" of deep water conditions. Benthic foraminifera are abundant in coastal waters, whereas the planktic foraminifera live in open ocean environments, usually away from the coast (Saraswati, 2021). Both benthic as well as planktic foraminifera are found in the oceanic regions deeper than ~75-100 m but above the CCD. Planktic to benthic ratio increases with the increase in water depth, more precisely,

with increasing distance from the coast (Murray, 1976; Berger and Diester-Haass, 1988; Van der Zwaan et al., 1990; Murray, 2014).

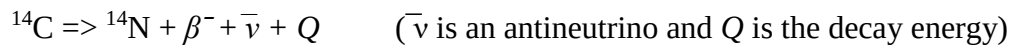
Foraminifera have stratigraphic significance, occur in a wide range of environments, are extremely sensitive to the ambient environment, and are well preserved; hence it makes them a valuable proxy for paleoceanographic reconstructions. There are mainly two methods for paleoceanographic reconstructions using foraminifera: non-destructive and destructive. The non-destructive methods include observing the physical properties of the foraminifera without breaking the test like, species abundance, species assemblages, benthic/planktic ratio, benthic foraminiferal number, coarse fraction percentage, total foraminiferal number, test weight, pore size (Arrhenius, 1952; Berger, 1968; Berger, 1973; Berger et al., 1982; Kaiho, 1991; Naidu, 1991; Lohmann, 1995; Naidu and Malmgren, 1996; Broecker and Clark, 1999; Naik and Naidu, 2007, 2010, 2014; Naik et al., 2014a). Planktic foraminiferal assemblages are used in studies of paleobiogeography and ocean circulation. The benthic/planktic foraminifera ratio is based on the fact that benthic foraminifera are more resistant to dissolution than planktic foraminifera (Arrhenius, 1952). Proxies like coarse fraction percentage (Broecker and Clark, 2001a, b, c), ratio of foraminifera fragments to whole tests (Peterson and Prell, 1985, Wu and Berger, 1989), shell weight (Lohmann, 1995), and size index (Broecker and Clark, 1999) provide a measure of the extent of dissolution. The destructive techniques involve geochemical analysis of tests to determine their isotopic and elemental compositions. They include radiocarbon ages, Mg/Ca, carbon and oxygen isotopes, boron isotopes, Cd/Ca, B/Ca, Zn/Ca (Shackleton, 1967; Shackleton, 1977; Boyle, 1981; Broecker, 1982; Duplessy et al., 1984; Curry et al., 1988). The radiocarbon age difference between the concurrent benthic and planktic foraminifera gives the ventilation age of the water (Broecker, 1982; Skinner et al., 2010; Skinner and Bard, 2022). The ratio of Mg/Ca is a valuable proxy for paleotemperature (Rosenthal et al., 1997; Skinner and Elderfield, 2005; Elderfield et al., 2006; Yu and Elderfield, 2008). The stable isotopes of oxygen and carbon of planktic foraminifera are used to reconstruct the temperature, salinity and productivity of the upper water column (Duplessy et al., 1984; Curry et al., 1988; Sijinkumar et al., 2016; Singh et al., 2021). For the reconstruction of temperature, salinity and productivity of deeper water, stable isotopes of oxygen and carbon in benthic foraminifera can be used. The Cd/Ca in benthic foraminifera carries the imprint of nutrient content of deep waters (Boyle, 1981). The B/Ca ratio is used in the reconstruction of carbonate ion of seawater (Yu and Elderfield, 2007; Naik et al., 2023). The Zn/Ca ratio is also used as a proxy to quantify carbonate ion concentrations (Marchitto et al., 2000).

1.4.1.1 Radiocarbon

Carbon has three naturally occurring isotopes. Carbon-12 (^{12}C) and carbon-13 (^{13}C) are the stable isotopes, whereas the carbon-14 (^{14}C) is a radioactive isotope of carbon. Radiocarbon (^{14}C) makes up about one part per trillion of carbon (0.00000000010%) on the Earth. It has a half-life of 5730 ± 30 years (Godwin, 1962). Radiocarbon is continuously produced in the upper atmosphere by the collision of cosmic ray neutrons with atmospheric nitrogen.



The radiocarbon formed by this collision rapidly oxidizes to form $^{14}\text{CO}_2$ and enters the global carbon cycle through photosynthesis and respiration. Plants and animals assimilate ^{14}C into their body. When they are alive, there is continuous exchange of ^{14}C between the organism and atmosphere i.e. the old decayed ^{14}C in the organism is exchanged with the new ^{14}C from the surrounding. However, when the organism dies, this exchange of ^{14}C ceases, and no further exchange of ^{14}C occurs between the organism and its surrounding. The ^{14}C decays back to stable ^{14}N and emits a β -particle with an energy of 156 keV.



The rate of generation of radiocarbon is not constant in the atmosphere and has varied in the past, mainly influenced by variations in cosmic ray intensity, and the magnetic field of Earth's geomagnetic field intensity (Lal and Peters, 1967; Brehm et al., 2021). But for radiocarbon dating procedure, it is assumed that the atmospheric radiocarbon has remained constant.

Radiocarbon dating can be done by proportional gas counters, liquid scintillation, or by Accelerator Mass Spectrometer (AMS). The raw radiocarbon ages are expressed in terms of radiocarbon ages or radiocarbon years, and are not directly comparable to calendar ages. This is because of the variation in ^{14}C content in the atmosphere due to factors like changes in the Earth's magnetic field, fluctuations in solar activity, and also due to anthropogenic ^{14}C that had been added to the atmosphere by bomb-produced radiocarbon. The calculation of the conventional ^{14}C age depends on the assumptions that the initial ^{14}C content of the sample is known and that its value equals that of the preindustrial atmosphere (1890 wood, with $^{14}\text{C}/^{12}\text{C}$ ratio equivalent to 0.95 times the OX-I standard). The $^{14}\text{C}/^{12}\text{C}$ ratio of the sample, if it is smaller than that of the preindustrial atmosphere, gives an estimate of the time elapsed since the system was closed to exchange of ^{14}C with the atmosphere. Hence,

the conventional ^{14}C age is not equivalent to the calendar ages and thus, the radiocarbon ages need to be calibrated to calendar ages. The radiocarbon ages of a sample are converted to calendar age using calibration curves like IntCal20 (Reimer et al., 2020), SHCal20 (Hogg et al., 2020), and Marine20 (Heaton et al., 2020). These calibration curves are constructed using known age samples, such as tree rings, corals, and marine calcareous tests. IntCal20 and SHCal20 are atmospheric-based calibration curves used for calibrating the radiocarbon dates of the northern hemisphere and southern hemisphere, respectively. Radiocarbon dates of samples from marine environments are calibrated using a marine-specific calibration curve like Marine20 (Heaton et al., 2020). Since techniques are being constantly improved to calibrate the radiocarbon ages to calendar ages, the dating results are standardized to record values in radiocarbon ages instead of calendar ages.

The atmospheric ^{14}C enters the ocean by air-sea $^{14}\text{CO}_2$ exchange. Oceanic ^{14}C is generally reported as $\Delta^{14}\text{C}$. The $\Delta^{14}\text{C}$ is defined as the per mil deviation of the ^{14}C to ^{12}C ratio in a sample from a standard, normalized to $\delta^{13}\text{C} = -25\text{‰}$ to correct for isotopic fractionation (Stuiver and Polach, 1977). The radiocarbon content differs between the atmosphere and the ocean. The surface water partially equilibrates with the atmosphere and its radiocarbon concentration is less than the atmosphere due to relatively long time required for carbon isotopic equilibrium between the surface ocean and the atmosphere. The $\Delta^{14}\text{C}$ of the surface water begins to decline as soon as it sinks to form intermediate or deep water mass. Since the deep water doesn't remain in contact with the atmosphere because of the overlying water, the ^{14}C content in it decreases as a result of continuous decay of ^{14}C . Ocean circulation brings these ^{14}C depleted waters to the surface through upwelling, therefore we can say that nowhere on Earth's surface does the sea surface is in isotopic equilibrium with the atmosphere (Broecker and Peng, 1982). Consequently, the apparent age of the surface water varies geographically. The apparent age of the surface water at lower latitude varies by ~ 400 ^{14}C years ($\Delta^{14}\text{C} \sim -45\text{‰}$).

At higher latitude, the apparent age will be larger (~ 1000 ^{14}C years in Southern Ocean) as the old deep water upwells there (Bard 1988; Reimer and Reimer 2001; Key et al., 2004; Heaton et al., 2020). Near Antarctica, reservoir ages can be in excess of 1200 ^{14}C years ($\Delta^{14}\text{C} \sim -125\text{‰}$). The high reservoir age at the Southern Ocean is because of the ^{14}C -depleted water upwells from the deep ocean, which was once at the sea surface. This causes the ^{14}C gradient between atmosphere and ocean to be larger than caused by the limited gas exchange alone (Franke et al., 2008). The difference between the ^{14}C concentration of

surface water and deep ocean water signifies the CO₂ ventilation rate of the deep water. This ventilation age can be calculated by comparing the radiocarbon ages of coexisting bottom water dwelling benthic and surface water dwelling planktic foraminifera in marine sediment (referred as B-P ventilation age; Broecker et al., 1984). The planktic foraminifera dwelling on the surface water will incorporate the ¹⁴C of the surface water during their test calcification. Since the surface water is relatively in equilibrium with the atmosphere and continuous exchange of ¹⁴C takes place between them, their age is almost similar to the contemporaneous atmospheric age. Therefore, when the radiocarbon dating of planktic foraminifera is carried out, the ages are closer to the contemporaneous atmospheric age. The benthic foraminifera living at the sea bottom take up the ¹⁴C from the bottom water for their calcareous test formation. Deep water being isolated from the atmosphere is ¹⁴C-depleted because of continuous decay of radiocarbon. As a result, the radiocarbon dates of benthic foraminifera show older ages than the contemporaneous atmosphere. This difference between the radiocarbon ages of the coexisting benthic and planktic foraminifera gives the ventilation age (Broecker et al., 1984; Broecker et al., 2007; Keigwin and Schlegel, 2002; Skinner and Shackleton, 2004; Skinner et al., 2010; Gottschalk et al., 2020; Bharti et al., 2022; Nisha et al., 2023). Lower ventilation age indicates mixing of deep and surface water and hence exchange of ¹⁴C between these water masses (Fig. 1.4a). Whereas, the higher ventilation ages indicate stratified water and no mixing of deep and surface water (Fig. 1.4b).

Another method that has been used for the ventilation age calculation is the difference between the radiocarbon age of benthic foraminifera and the contemporaneous atmosphere (Siegenthaler et al., 1980; Soulet et al., 2016). The benthic foraminifera will reflect the radiocarbon activity of the bottom water at the time it was living. When compared to the contemporary atmosphere, (ideally) there will be a radiocarbon offset between the deep water and the atmosphere at that time (Skinner et al., 2010; Skinner et al., 2017; Skinner et al., 2023). As mentioned earlier, the reason for this offset is isolation of deep water from the atmosphere. This radiocarbon gradient gives the deep-water reservoir age.

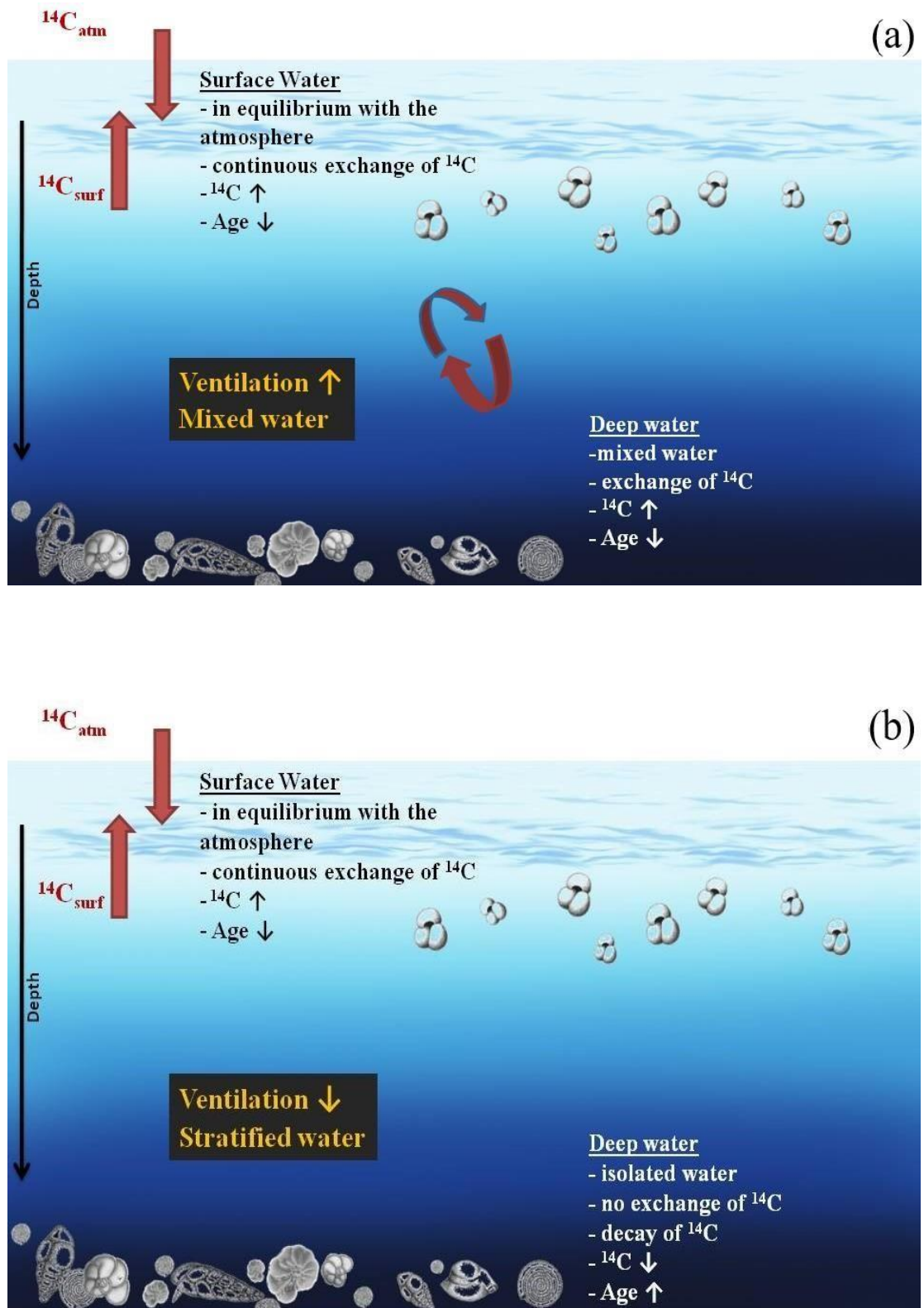


Fig. 1.4: Illustration representing the condition of (a) mixed water and (b) stratified water.

1.4.1.2 Stable isotopes of carbon

Carbon-12 with 6 protons and 6 neutrons is the most abundant isotope of carbon. It contributes to 98.89 % of the natural carbon whereas carbon-13 with 6 protons and 7 neutrons represents 1.11 % of the natural carbon on Earth. In the ocean, $\delta^{13}\text{C}$ (the ^{13}C to ^{12}C ratio relative to a standard) is predominantly controlled by the mass-dependent fractionation. The phytoplankton living on the sea surface takes up the lighter isotope ^{12}C than the heavier stable isotope ^{13}C during their photosynthesis. This preferential uptake of stable isotopes of carbon leads to high ^{12}C concentration in the organic matter and hence leaves the surface seawater dissolved inorganic carbon (DIC) enriched in the ^{13}C concentration. When the organisms die, they sink to the bottom of the ocean and are decomposed to release CO_2 and nutrients. The CO_2 released during the oxidation of this organic matter is rich in ^{12}C and thus dilutes the ^{13}C concentration in seawater DIC (Kroopick, 1985). This biological pump in the ocean results in relative enrichment of $\delta^{13}\text{C}$ of surface seawater DIC to the $\delta^{13}\text{C}$ of the deeper depths (Kroopnick, 1985). Apart from the biological cycling, the ^{13}C of surface ocean is also controlled by the air-sea CO_2 exchange (Lynch-Stieglitz et al., 1995). The carbon isotopic composition is expressed using the following equation:

$$\delta^{13}\text{C} (\text{‰}) = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000$$

where, the standard material for the carbonate sample is Pee Dee Belemnite (PDB). The $\delta^{13}\text{C}$ values are calibrated against the PDB reference scale using National Bureau of Standards (NBS).

Different water masses have distinct $\delta^{13}\text{C}$ values due to varying degrees of nutrient utilization. Deep waters formed at high latitudes by sinking of surface water due to physical processes have high $\delta^{13}\text{C}$ values. As the water mass sinks, phytoplankton strips ^{12}C and nutrients from the water, enriching it in ^{13}C . The $\delta^{13}\text{C}$ of the bottom water changes only through two processes: remineralization of organic matter and mixing of water masses with different isotopic compositions (Curry et al., 1988). The $\delta^{13}\text{C}$ of the ocean is reliably recorded by foraminifera and are preserved in the sediment. Foraminifer's calcareous tests reflect the seawater DIC in which they grew, nutrients, organic matter respiration and air-sea CO_2 exchange. Hence, they are used for tracing past distributions of water masses and their properties (Duplessy et al., 1984; Curry et al., 1988, Kallel et al., 1988; Naqvi 1993; Ahmad et al., 2008, Raza et al., 2014). The $\delta^{13}\text{C}$ of benthic foraminifera carries the imprint

of the nutrient content of the deep water (Shackleton, 1977). Thus, $\delta^{13}\text{C}$ of benthic foraminifera are used to reconstruct the past changes in the deep water circulation and its residence time. Also, stable carbon isotope gradient ($\Delta\delta^{13}\text{C}$) between the epifaunal and the infaunal benthic foraminiferal species are used for determining the past oxygen concentrations in the ocean (Schmiedl and Mackensen, 2006; Hoogakker et al., 2015; Gottschalk et al., 2016). Redox conditions in marine sediments typically indicate changes in organic carbon respiration influenced by the downward diffusion of oxygen from bottom waters and/or the supply of organic carbon to the sea floor. Aerobic degradation of organic matter is the most efficient method for respiration of organic carbon, which mainly occurs above the sedimentary anoxic boundary. At this boundary, the diffusion of oxygen from the bottom water matches the rate of oxygen consumption due to aerobic respiration in the subsurface sediment, resulting in depletion of oxygen. The release of ^{13}C -depleted carbon during organic matter degradation significantly affects the $\delta^{13}\text{C}$ gradient in marine subsurface pore waters. Consequently, the total amount of aerobic sedimentary organic carbon respiration depends on bottom-water oxygen and is reflected in the $\delta^{13}\text{C}$ difference between bottom waters and pore waters at the zero-oxygen boundary (Gottschalk et al., 2016).

1.4.1.3 Stable isotopes of oxygen

Oxygen isotopes are one of the most significant proxy used for the reconstruction of past climatic and ocean circulation changes. Natural oxygen has three common isotopes: oxygen-16, oxygen-17 and oxygen-18, of which “light” oxygen (^{16}O) with 8 protons and 8 neutrons and “heavy” oxygen (^{18}O) with 8 protons and 10 neutrons. Light oxygen (^{16}O) is the most common isotope of oxygen and constitutes 99.7% of the Earth’s oxygen whereas ^{18}O constitutes 0.2%. Both of these oxygen isotopes have distinct physical properties. Because of difference in the atomic weight of the two isotopes, ^{16}O being lighter, it evaporates more readily from the seawater, while ^{18}O being heavier precipitates first than the ^{16}O . The seawater remaining after evaporation will have higher concentration of heavy oxygen (^{18}O) compared to the universal standard, and the ice sheets after precipitation will have a higher concentration of lighter oxygen (^{16}O). As the temperature increases, melting of the ice sheet leads to return of ^{16}O back to the seawater. Thus, the isotopic ratio ($\delta^{18}\text{O}$) of these two isotopes depends upon the climatic changes. Higher $\delta^{18}\text{O}$ values indicates cooler temperature and low $\delta^{18}\text{O}$ values indicates warmer temperature. The $\delta^{18}\text{O}$ are determined

using Isotope Ratio Mass Spectrometer (IRMS) and are expressed using the following equation:

$$\delta^{18}\text{O} (\text{‰}) = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \times 1000$$

The calcareous test of foraminifera incorporates this isotopic signatures into their tests and hence, reveals the information about the past ocean temperature and isotopic composition of the seawater. The foraminiferal test grown during colder periods will incorporate more ^{18}O during their test formation and hence, will have higher $\delta^{18}\text{O}$ values. Conversely, foraminifera test grown during warm period, will incorporate more ^{16}O and will hence have lower $\delta^{18}\text{O}$ values. Hence, the isotopic composition of calcium carbonate formed by the foraminifera can be linked to the temperature at the time of deposition. Oxygen isotope of planktic foraminifera is also related to the salinity of the surface water. Any alterations in salinity resulting from large-scale dilution effects, such as ice sheet melting, or from local shifts in the precipitation-evaporation balance, will also be reflected in the oxygen isotope of foraminifera that are influenced by these changes. Evaporation leads to increase in salinity of the water. During evaporation, the ^{16}O isotope being lighter, evaporates faster, leaving the surface water enriched in ^{18}O . Therefore, with the increase in salinity, the $\delta^{18}\text{O}$ of surface water increases. On the other hand, $\delta^{18}\text{O}$ of surface water decreases with decrease in salinity due to precipitation as well as the influx of continental runoff. The $\delta^{18}\text{O}$ changes captured by the foraminifera test reflects these salinity changes. Hence, the isotopic oxygen composition of planktic foraminifera can also be used to estimate salinity changes at the sea surface.

1.4.1.4 Porosity

Foraminifera have pores over their entire test or portions of it that are used for gas exchange between the test and the ambient environment (Glock et al., 2011; Kuhnt et al., 2013). Pores of benthic foraminifera are sensitive to the bottom water oxygen condition. The pores present on the test surface of the benthic foraminifera take up the oxygen from bottom water mass, and are used by the mitochondria to produce energy and then releases metabolic CO_2 (Hottinger and Dreher, 1974; Berthold, 1976; Leutenegger and Hansen, 1979; Bernhard et al., 2010). It is inversely related to ambient bottom water oxygen concentrations. The porosity (the mean percentage of the surface area covered by the pores) of the test from oxygen-poor bottom water tends to be higher than those of the test from

well-oxygenated bottom waters, and vice versa. This is because, benthic foraminifera living in low oxygen bottom water will adjust their pore size and volume (i.e. porosity) in order to obtain sufficient oxygen, whereas in oxygenated bottom water, they mainly respire through the aperture instead of using pores. An increase in the number of pores and pore size (or porosity) on the surface of benthic foraminifera increases its ability to take up the oxygen. As a result of this, a cluster of mitochondria can be seen around the pores of such species, whereas the mitochondria are more uniformly distributed on benthic species of well oxygenated water (Leutenegger and Hansen, 1979; Bernhard et al., 2010).

Porosity of epifaunal benthic foraminifera (which lives at the sediment-water interface or attached to hard substrates) gives the true representation of bottom water oxygen condition as they are in direct contact with the overlying bottom waters. Unlike the infaunal benthic species, epifaunal species do not migrate to anoxic waters deeper in the sediments and, hence, do not use nitrate for respiration. Another reason for why epifaunal benthic foraminifera are used for bottom water oxygen conditions is because they are not influenced by oxygen gradients within seafloor sediments.

1.4.1.5 Foraminiferal fragmentation index

Foraminiferal fragmentation index has the potential to serve as a dissolution proxy (Le and Shackleton, 1992). It is defined as the number of foraminiferal fragments per whole test, where more than $2/3^{\text{rd}}$ portion of the original test is considered as a whole test and portion less than $2/3^{\text{rd}}$ of the original test are considered as fragments (Berger et al., 1982). The rate of foraminiferal fragmentation depends upon the dissolved CO_2 and carbonate ion in the seawater. When the seawater is rich in CO_2 , dissolution of foraminiferal test takes place, which leads to a high fragmentation rate. Fragments of foraminiferal test increase where the dissolution susceptibility increases due to shoaling of lysocline or CCD. Preservation of foraminiferal test on the sea-floor also depends upon the physico-chemical conditions of the sediment, such as pore-water chemistry. Undersaturated pore-water, caused by the degradation of organic matter will lead to higher fragmentation. Also, high-energy conditions (increased turbidity) results in increased breakage of the foraminiferal tests, whereas less proportion of fragments are present in low-energy conditions. Thus, foraminiferal fragmentation index is used as a proxy to infer the concentration of dissolved CO_2 and carbonate ions of the seawater as well as the turbidity of the currents (Berger et al., 1982; Peterson and Prell, 1985; Chen et al., 1997).

1.4.1.6 Size Index

Size index is another proxy used to determine the carbonate ion concentration of the seawater. It is the percentage of the ratio of coarse carbonate to total carbonate in marine sediments (Broecker and Clark, 1999). As the foraminifera tests dominate the $>63\ \mu\text{m}$ fraction and the fractions $<63\ \mu\text{m}$ majorly contains coccoliths, juvenile foraminifera and foraminiferal fragments, this size index is mainly the ratio of CaCO_3 contained in whole foraminifera tests to CaCO_3 contained in total sediments. This ratio has been successfully used to measure the CO_3^{2-} content in deep tropical oceans. Broecker and Clark (1999) have shown that in today's tropical ocean, the CaCO_3 percentage contained in grains $>63\ \mu\text{m}$ in size is closely related to the pressure-normalized carbonate ion of water bathing the sea floor. Later Naik and Naidu, 2010 noted that size index is also altered by the terrigenous input. The terrigenous inputs dilute the CaCO_3 content in the sediment and thus decreases its size index.

1.4.2 Sediment sample

1.4.2.1 Elemental analysis

The concentrations of minor and trace elements in the marine sediments have been largely used as a tool to assess the provenance changes, paleo-productivity and oxygenation conditions of the bottom waters. These concentrations are regulated by factors like terrestrial influx, biological processes, in-situ precipitation and hydrothermal activities occurring within the water column. Elements intrude into the ocean through rivers, atmosphere and hydrothermal activities, and then a series of chemical and biological reaction takes place. After undergoing various reactions, they either dissolve or precipitate and get deposited in sediments and remain preserved for several years. For example, records of redox sensitive elements (vanadium, chromium, cobalt, nickel, copper, manganese, molybdenum, uranium and thorium) can provide information on oxygenation conditions of the bottom water (Pattan and Pearce, 2009). Some of these elements precipitate where free dissolved sulphide is present without any change in their valency, whereas other elements undergo valency changes in oxic/anoxic conditions (Calvert and Pedersen, 1993). Ratio of aluminium and titanium content in the marine sediments are used to trace the terrigenous inputs (Nath et al., 1989; Pattan et al., 2003). Concentration of barium in the marine sediments are used as a geochemical indicator of biogenic productivity (Schmitz, 1987).

1.4.2.2 Calcium carbonate

The calcareous skeletal material of planktons like foraminifera and coccolithophores are the primary contributors of the calcium carbonate (CaCO_3) in the open-ocean sediment. The calcareous skeleton can be made up of either calcite or aragonite, which are polymorphs of CaCO_3 . The CaCO_3 content in marine sediments is controlled majorly by three factors: dilution by non-carbonate material, carbonate dissolution, and biological productivity (Damuth, 1975; Volat et al., 1980). These variations in the CaCO_3 content of the sediment can be correlated to the glacial-interglacial cycles. Input of non-carbonate material such as biogenous silica and terrigenous matter dilute the CaCO_3 content of the sediment (Naidu, 1991). Dissolution of the calcareous matter also takes place during its journey through the water column as well as on the seafloor. The rate of dissolution increases when the concentration of dissolved CO_2 in seawater increases as it decreases the pH of seawater (Le and Shackleton, 1992). The hydrostatic pressure also plays role in dissolution of CaCO_3 . Increase in hydrostatic pressure with the increase in water depth, increases the rate of solubility of carbonate which led to dissolution. Fluctuations in biological productivity are also responsible for variations in the CaCO_3 content (Arrhenius, 1952; 1988; Archer, 1991; Naidu and Malmgren, 1999). The higher biological productivity would increase the flux of organic carbon to deep water. Oxidation of this material would give off CO_2 to bottom waters, which would intensify carbonate dissolution leading to decrease in CaCO_3 content (Arrhenius, 1952). Berger (1977) points out that low biological productivity would induce better preservation of calcareous tests.

1.5 Study Hypothesis

During the last deglaciation, there was an abrupt increase in the concentration of CO_2 in the atmosphere. The concentration was increased by ~50% in two pulses that coincided with the timing of the Heinrich Stadial 1 (HS1) and Younger Dryas (YD) (Broecker W. S., 1998). The mechanisms responsible for such an abrupt rise in atmospheric CO_2 at the last glacial termination (23,000 to 9,000 years ago) are still unclear (Petit et al., 1999; Sigman and Boyle, 2000; Shakun et al., 2012). Since the deep ocean is the largest reservoir of carbon, redistribution of carbon between atmosphere and the ocean is considered as the most valid reason for this rise in atmospheric CO_2 (Archer et al., 2000; Sigman and Boyle, 2000). The ocean can act as the source and sink for the CO_2 through its physical and biological pump (Sundquist and Broecker, 1985).

The rising atmospheric CO₂ during the deglaciation coincided with decrease in the radiocarbon content of the atmosphere (Broecker W. S., 1998; Hughen et al., 2004). There was a 190 ‰ drop in atmospheric $\Delta^{14}\text{C}$ during the Mystery Interval (~17.5-14.5 kyr) (Broecker and Barker, 2007). During the period HS1 (~17.5-14.5 kyr), the mountain glaciers in the Alps underwent significant retreat, reflecting considerable warming (Denton et al., 1999). However, the ratios of ²³¹Pa to ²³⁰Th indicate that the export of deep water from the Atlantic to the Southern Ocean largely ceased during this period, resulting in unusually cold temperatures in the northern Atlantic and western Mediterranean (McManus et al., 2004). Hence this period is also referred to as the Mystery Interval. During the Younger Dryas (~12.8-11.5 kyr), the ¹⁴C content of the atmosphere also steadily declined (Hughen et al., 1998). One of the reasons put forth to explain this drop in the atmospheric ¹⁴C is the change in the production of radiocarbon. During the last glacial period, the Earth's magnetic field was weak, which resulted in increased production of ¹⁴C. Data from paleomagnetic record (Laj, 2002) and marine sediment ¹⁰Be (Frank et al., 1997) indicate a slight decrease in production of ¹⁴C during the deglaciation. Therefore, changes in production of ¹⁴C cannot entirely explain such huge decline in atmospheric ¹⁴CO₂ during these two intervals. Another major leading hypothesis is the release of sequestered CO₂ from the radiocarbon depleted oceanic abyssal reservoir that had been isolated from the atmosphere (Marchitto et al., 2007). The Southern Ocean is the region where deep water makes its first contact with the sea surface and atmosphere (Primeau, 2005), and ventilates much of the respired carbon to the atmosphere and hence it is considered to have played a major role in release of sequestered CO₂. According to this hypothesis, prior to the deglaciation there existed poorly ventilated deep water in the Southern Ocean that was isolated from the upper water because of density stratification (Schmittner and Galbraith, 2008) or sea ice cover (Stephen and Keeling, 2000; Skinner et al., 2010). This isolation of deep water leads to the continuous decay of radiocarbon, thus making the water ¹⁴C-depleted. During the deglaciation (HS1 and YD), enhanced wind-driven upwelling in the Southern Ocean exposed these ¹⁴C-depleted deep waters to the atmosphere (Anderson et al., 2009). The deep water was mixed back into the upper ocean and then exposed to the atmosphere. Marchitto et al. (2007) suggests that ¹⁴C-depleted waters upwelled to the surface in the Southern Ocean and were transported northward into the Pacific as intermediate waters.

Numerous studies investigating the changes in radiocarbon content in intermediate and deep water since the LGM have been carried out in the Atlantic and Pacific. Previous deep- water studies from the Atlantic and Pacific have suggested that glacial deep waters

were ^{14}C depleted (i.e. poorly ventilated) (Skinner and Shackleton, 2004; Broecker et al., 2007; Galbraith et al., 2007; Barker et al., 2010; Skinner et al., 2014; Bharti et al., 2022). Studies from intermediate water depths have shown an existence of poorly ventilated water in the Southern Ocean during the LGM, which was transported to the other oceans via the AAIW (Marchitto et al., 2007; Bryan et al., 2010; Siani et al., 2013; Freeman et al., 2015; Ma et al., 2019). However, there are few studies that do not support this hypothesis and have no records showing significant changes in the ventilation age since the last glacial period (Broecker et al., 2008; De Pol-Holz et al., 2010; Lund et al., 2011).

Evidences from the Indian Ocean providing the Southern Ocean's role in atmospheric $^{14}\text{CO}_2$ fluctuations are few (Bryan et al., 2010; Ma et al., 2019; Gottschalk et al., 2020; Bharti et al., 2022). These studies suggest that the intermediate water was influenced by the incursion of ^{14}C -depleted AAIW in the Indian Ocean during the deglaciation. This ^{14}C depletion in AAIW was because of the mixing of old isolated abyssal water in the south of the subantarctic frontal zone. Records from Bharti et al. (2022) has shown extensive incursion of poorly ventilated AABW into the northern Indian Ocean during the HS1 and YD. My Ph.D. research aims to understand the ventilation of the Indian Ocean during glacial- interglacial cycle, which involves changes in deep water carbon storage in the Indian Ocean. Even though immense work has been done in the Atlantic and Pacific Ocean in reconstructing the deep water ventilation, yet the Indian Ocean remains unexplored. By investigating the role of Indian Ocean in the degassing of CO_2 and its link to climatic changes in the past, we can prognosticate the future climate changes under the rising anthropogenic CO_2 levels.

1.6 Objectives

In view of the above discussions, my thesis is aimed to address the following objectives:

1. To determine the ventilation age of intermediate and deep water mass in the northern Indian Ocean during the last 30 kyr.
2. To assess and compare the degree of intermediate and deep ocean-atmosphere ^{14}C disequilibrium during the last glacial period.
3. To determine the changes in deep water carbonate ion concentrations during the last 30 kyr.

Chapter 2

Literature Review

Atmospheric carbon dioxide (CO₂) concentrations are known to be regulated by the oceans, as the ocean can act as a source or sink for CO₂ through its physical and biological pump (Sundquist and Broecker, 1985). The oceans soak up almost one-third of CO₂ released into the air as a result of human activities (Sabine et al., 2004). The present-day atmospheric CO₂ concentrations have risen to >400 ppm as a result of anthropogenic activities since the industrial era. This rise was steep, from 280 ppm before the beginning of the industrial era to the present, which occurred within a short span of 200 years and led to an ocean storage of ~120 Pg C (Sabine and Tanhua, 2010). As is well documented, high CO₂ levels in the atmosphere leads to ‘global warming’ along with changes in ocean water temperature, ocean acidification, and deoxygenation.

For the last 800 kyr, glacial-interglacial CO₂ variations were within bounds of 180 to 280 ppm (Lüthi et al., 2008). This increase in atmospheric CO₂ from the glacial to interglacial was not gradual throughout. Especially during the last deglaciation (~17.5–11.2 kyr), there was a two-step jump in atmospheric CO₂ (Fig. 2.1a; Monnin et al., 2001). Moreover, this rapid increase in the atmospheric CO₂ was accompanied with a decrease in radiocarbon activity (Fig 2.1b; Reimer et al., 2020). The forcing factor behind these changes is still uncertain, though a large amount of studies have shown a link between the Southern Ocean circulation and the atmospheric CO₂ changes (Broecker and Barker, 2007; Marchitto et al., 2007; Anderson et al., 2009; Skinner et al., 2010; Barker et al., 2011; Burke and Robinson et al., 2012; Siani et al., 2013; Menviel et al., 2018; Galbraith and Skinner, 2020; Gottschalk et al., 2020; Bharti et al., 2022). This jump in atmospheric CO₂ was thought to be facilitated by a large release of CO₂ stored deep in the ocean during glacial times (Marchitto et al., 2007; Skinner et al., 2010). This process of CO₂ release is supposed to have mainly occurred through enhanced upwelling of isolated deep waters in the Southern Ocean and subsequent incorporation of these ¹⁴C-depleted waters into the thermocline and intermediate water masses (especially the Antarctic Intermediate Water; AAIW) which spread northward into the Pacific, Indian and Atlantic Ocean basins (Marchitto et al., 2007; Bryan et al., 2010; Skinner et al., 2010; 2014; Ma et al., 2019, 2020; Shao et al., 2019).

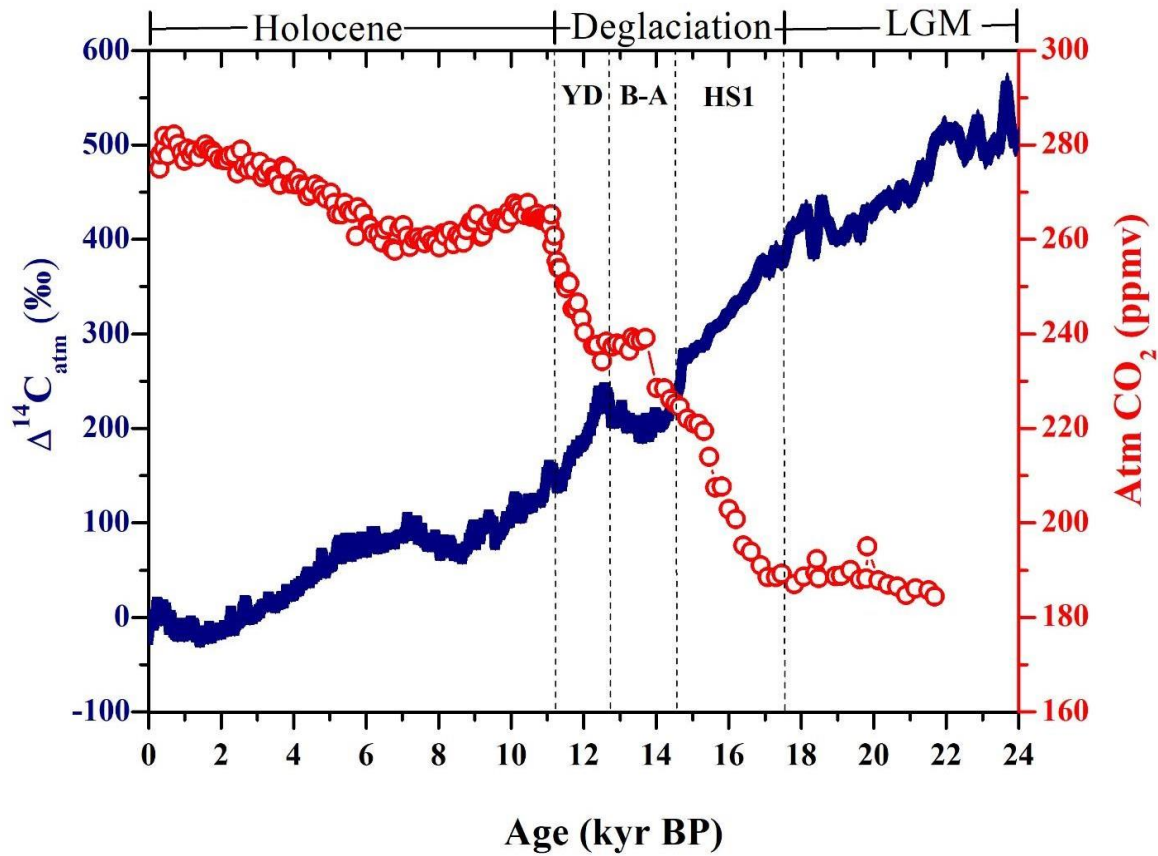


Fig. 2.1 (a) Atmospheric CO₂ record from the Antarctica Dome (red circles, Monnin et al., 2001), and (b) atmospheric $\Delta^{14}\text{C}$ (dark blue line, Reimer et al., 2020).

Skinner et al. (2010) showed that deep waters of the Southern Atlantic which were thought to be ^{14}C depleted during the glacial, upwelled into intermediate waters, thus decreasing the ^{14}C of intermediate waters (Fig. 2.2 and 2.3a). Similar results were seen at many locations throughout the world oceans and therefore this mechanism was widely accepted.

A lot of studies were carried out from various parts of the world's oceans to reconstruct the past marine ventilation (i.e., exchange of gases between the atmosphere and the ocean interior) changes. Initially, the marine radiocarbon ventilation was estimated by the benthic-planktic foraminifera radiocarbon age offset (B-P; Broecker et al., 1984, Broecker et al., 2007; Keigwin and Schlegel, 2002; Keigwin et al., 2004; Skinner and Shackleton, 2004; Skinner et al., 2010; Gottschalk et al., 2020; Bharti et al., 2022; Nisha et al., 2023). Later, the radiocarbon age offset between the benthic foraminifera and the contemporary atmosphere was used for the ventilation reconstructions (B-Atm; Skinner et al., 2010; Freeman et al., 2016; Skinner et al., 2017; Ronge et al., 2020; Skinner et al., 2023). Ventilation records have also been derived from cold-water corals (Adkins et al., 1998;

Robinson et al., 2005; Burke and Robinson, 2012; Chen et al., 2015; Hines et al., 2015; Raddatz et al., 2023), and dated tephra (Sikes et al., 2000; Siani et al., 2001, 2013; Skinner et al., 2015). Some studies have used “plateau tuning” i.e., fluctuations in planktonic radiocarbon time-series aligned with assumed equivalents in the atmospheric records for the ventilation age calculation (Sarnthein et al., 2007, 2013; 2020; Ausín et al., 2021).

Majority of the studies showed that there was an aged water mass existing in the abyssal ocean during the last glacial, which dissipated during the Heinrich Stadial 1 (HS1; 17.5-14.5 kyr) and the Younger Dryas (YD; 12.8-11.2 kyr, cold event) (Marchitto et al., 2007; Bryan et al., 2010; Skinner et al., 2010; Galbraith and Skinner, 2020; Bharti et al., 2022). During the HS1/YD, the Southern Ocean warmed as a result of the ‘bipolar seesaw’. This led to a significant reduction in Antarctic sea-ice and deep water masses (Antarctic Bottom Water; AABW) were drawn upward and mixed into the Circumpolar Deep Water (CDW) through which the ^{14}C -depleted CO_2 was eventually released to the atmosphere at the sea surface (Skinner et al., 2010; Skinner and Bard, 2022). Hence, we observe lower ^{14}C , greater ventilation ages and larger B-P (benthic– planktic) offsets in intermediate depth cores during the HS1/YD. During the Bølling–Allerød (B-A; 14.5-12.8 kyr, a warm climatic stage in the North Atlantic, coinciding with the Antarctic Cold Reversal; ACR, a cold stage) the Southern Ocean cooled as a result of the bipolar seesaw and the sea ice extent increased. Mixing of ^{14}C -depleted AABW into the CDW ceased, which is seen in higher ^{14}C of intermediate waters, decrease in ventilation age, and smaller B-P offsets (Skinner et al., 2010). Thus, ocean circulation drives climate variability at timescales ranging from seasonal to glacial–interglacial timescales. It is important to understand the mechanisms for the similarity in observations at several locations of the world ocean, in order to understand the future response of oceans to increasing atmospheric CO_2 .

Numerous studies were undertaken on unravelling the deglacial ventilation of intermediate and deep waters in the Atlantic and Pacific (Fig. 2.2, Murayama, 1992; Skinner and Shackleton, 2004; Marchitto et al., 2007; Barker et al., 2010; Basak et al., 2010; Skinner et al., 2010; Siani et al., 2013; Skinner et al., 2015; 2017; Dai et al., 2021). The deep water ventilation records from the Atlantic (Skinner and Shackleton, 2004; Barker et al., 2010; Skinner et al., 2010; Burke and Robinson, 2012; Skinner et al., 2017) and Pacific Ocean (Sikes et al., 2000; Galbraith et al., 2007; de la Fuente et al., 2014; Keigwin and Lehman, 2015; Dai et al., 2021) support the existence of a significantly aged deep water mass in the ocean interior during the LGM. Studies from the southern sector of the Indian Ocean (Ronge

et al., 2020; Gottschalk et al., 2020) have also supported the presence of a radiocarbon-depleted deep water mass during the LGM. Furthermore, a deep water ventilation record by Bharti et al. (2022) has shown poorly ventilated deep water advection into the northern Indian Ocean.

Table 2.1: Details of all cores shown in Fig. 2.2 and discussed in text.

Sr. No.	Core	Location	Latitude	Longitude	Water Depth(m)	Reference
1	MD99-2334K	North Atlantic	37.80° N	10.17° W	3146	Skinner and Shackleton (2004)
2	MD07-3076 CQ	South Atlantic	44.07° S	14.21° W	3770	Skinner et al. (2010)
3	TNO57-21	South Atlantic	41.1° S	7.8° E	4981	Barker et al. (2010)
4	RC27-23 RC27-14	Arabian Sea	18° N 18.3° N	57.6° E 57.6° E	820 596	Bryan et al. (2010)
5	MD77176	Bay of Bengal	4.50° N	93.12° E	1375	Ma et al. (2019)
6	MV99-MC19/ GC31/ PC08	North Pacific	23.5° N	111.6° W	705	Marchitto et al. (2007)
7	MD07-3088	South Pacific	46° S	75° W	1536	Siani et al. (2013)
8	MD97-2121	South Pacific	40.38° S	177.99° E	2314	Skinner et al. (2015)

Ventilation records from the intermediate waters of the Atlantic (Robinson et al., 2005; Chen et al., 2015; Skinner et al., 2021) and Pacific Ocean (Marchitto et al., 2007; Ronge et al., 2016; Rafter et al., 2018; Ronge et al., 2019) suggest the existence of radiocarbon depleted waters during the deglaciation. Relatively, the Indian Ocean studies on radiocarbon were almost non-existing, only when Bryan et al. (2010) showed a significant aging of intermediate waters in the Arabian Sea during the HS1 and, to a lesser extent, during the YD (Fig. 2.3b). The timing and magnitude of ^{14}C depletion in the Arabian Sea during the HS1 is very similar to that previously observed in the eastern North Pacific near Baja California (Marchitto et al., 2007), indicating that similar mechanisms were involved in controlling $\Delta^{14}\text{C}$ (radiocarbon activity) at these two sites. Recent work using $^{230}\text{Th}/\text{U}$ and ^{14}C derived from cold-water corals has shown radiocarbon-depleted thermocline waters in the northern Indian

Ocean because of its mixing with extremely ^{14}C -depleted abyssal waters during the LGM (Raddatz et al., 2023). Interestingly, there are few studies in the Arabian Sea which show outgassing of CO_2 during the deglaciation, all the studies use boron isotopes from planktic foraminifera (Palmer et al., 2010; Naik et al., 2015; Tarique et al., 2023). Naik et al. (2015) found an outgassing of CO_2 during the deglaciation and thought it may be related to increased monsoon upwelling of high CO_2 waters which are advected from elsewhere (Fig. 2.3c). Palmer et al. (2010) also show pCO_2 was high during the 11-17 kyr period and linked it to the Asian monsoon. These studies point out to the northern Indian Ocean as a location for CO_2 outgassing along with the several other locations in the Atlantic and the Pacific. For example, the surface waters at sub-Antarctic Atlantic and the eastern equatorial Pacific, both, which partly derive from deep water upwelled in the Southern Ocean became a significant source of carbon to the atmosphere during the last deglaciation (Martinez-Boti et al., 2015; Shao et al., 2019; Shuttleworth et al., 2021). A point to make here is that the timing of CO_2 degassing and the ventilation of deep oceans from different regions of the world oceans was well-timed and happened during the deglaciation. However, the mechanism of how the outgassing occurred at the same time over distant locations is not known.

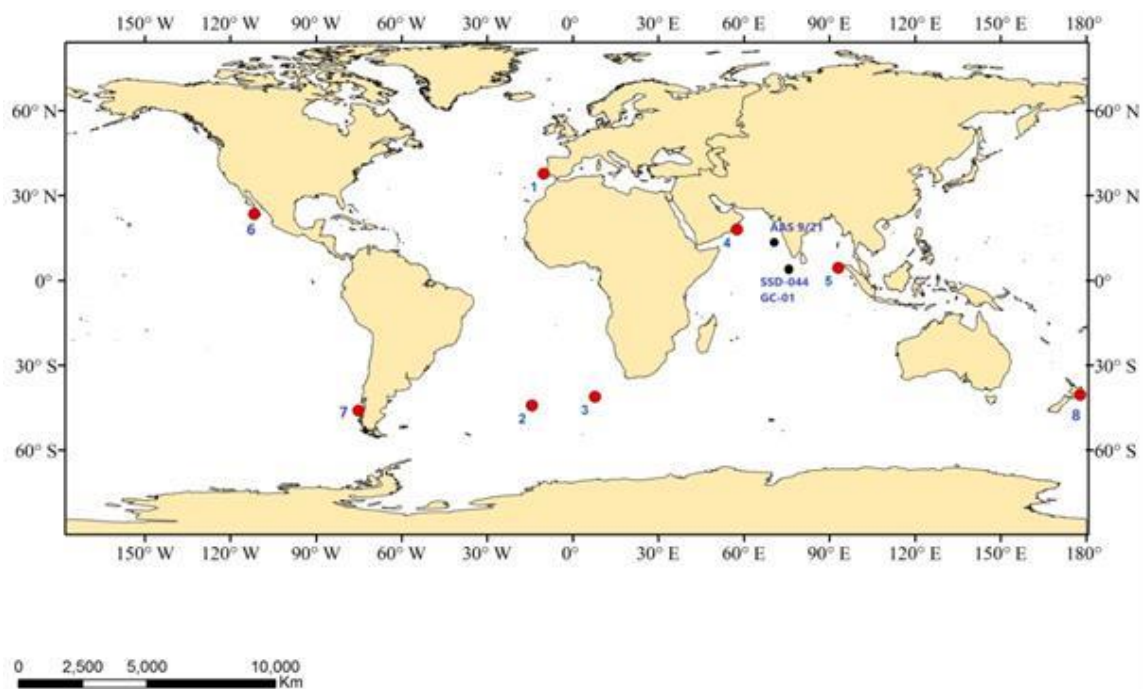


Fig. 2.2: Map showing the location of sediment cores in all the major oceans used in understanding ventilation changes and discussed in the text. (1) Skinner and Shackleton, 2004, (2) Skinner et al., 2010, (3) Barker et al., 2010, (4) Bryan et al., 2010, (5) Ma et al., 2019, (6) Marchitto et al., 2007, (7) Siani et al., 2013, and (8) Skinner et al., 2015.

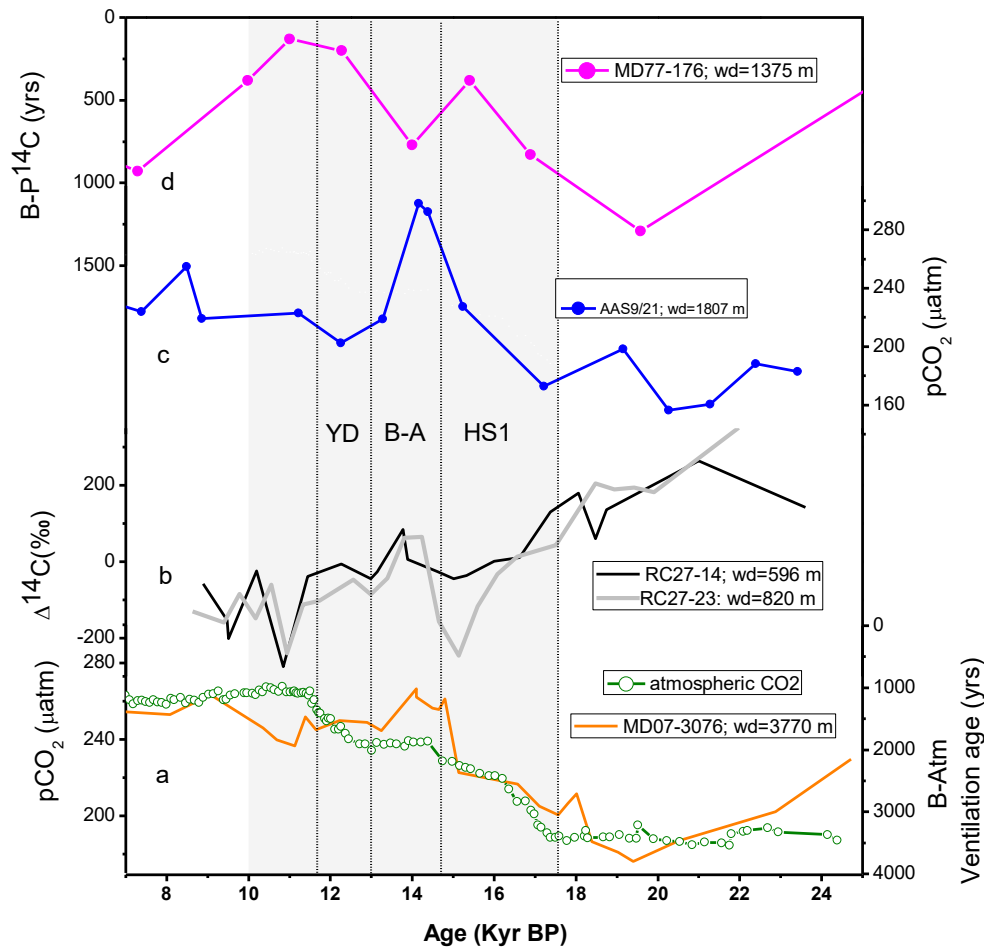


Fig. 2.3: (a) Benthic-Atmosphere ventilation age from the Southern Ocean (Skinner et al., 2010) plotted along with atmospheric CO_2 concentrations (Monnin et al., 2001, Lemieux-Dudon et al., 2010, Schmitt et al., 2012), (b) $\Delta^{14}\text{C}$ from sediment cores of the western Arabian Sea (Bryan et al., 2010), (c) pCO_2 from the eastern Arabian Sea (Naik et al., 2015) and (d) benthic-planktic ^{14}C age from the Bay of Bengal (Ma et al., 2019). The grey shaded area marks the entire deglacial period. The dotted lines mark the Heinrich Stadial 1, HS1, Bølling–Allerød, B-A, and the Younger Dryas, YD, respectively.

In contrast to the Arabian Sea, the Bay of Bengal, which is the eastern basin shows decreased ventilation during the B-A relative to HS1 and the YD (Fig. 2.3d, Ma et al., 2019). This is an intriguing finding as the Arabian Sea and Bay of Bengal cores are from intermediate depth and we could expect the same mechanism operates in both these regions on either side

of the Indian landmass, since AAIW (source of low ^{14}C) penetrates into both these regions (Böning and Bard, 2009; Yu et al., 2018). Such contrast between the eastern and western Ocean was also noted in the Pacific, while the reason why this occurs was not understood (De Pol-Holz et al., 2010). One possible explanation could be the pathway that the southern sourced waters follow into the Indian Ocean. The study location by Bryan et al., 2010, is in the pathway of the Deep Western Boundary Current, and hence, the southern sourced water could influence the study area directly. However, the study location by Ma et al. (2019), located in the Bay of Bengal is extreme north. The distal location of their core site along with increased stratification as a result of freshwater input due to proximity to the major river system (Ganges-Brahmaputra), which may have increased during the B-A (Govil and Naidu, 2011), and led to reduced mixing and decreased ventilation there.

The deglacial radiocarbon ages does show contradictory results in some regions (Murayama, 1992; Broecker et al., 2008; De Pol-Holz et al., 2010; Lund et al., 2011; Siani et al., 2013). These contradictory results could be a cause of regionally confined phenomena. At least for the northern Indian Ocean, it is extremely important to have sufficient data on the ventilation aspect from specific locations chosen to be in the pathway of the deep water circulation branch directing southern sourced waters up north. Subsequently, the focus should be on unravelling the mechanisms responsible for ventilation changes and whether these ventilation changes are timed and linked globally.

Chapter 3

Study Area

3.1 Physiography

The Indian Ocean is the most complex among all the major oceans. It is connected to the other oceans through the Antarctic Circumpolar Current in the Southern Ocean, and being in the mid-way of the thermohaline circulation, it connects the Atlantic and Pacific Oceans (Talley, 2008; 2011). The Indian Ocean extends only up to 25° N, which is bounded by Africa in the West, the Eurasian continent in the North, Indonesia and Australia in the East and Antarctica in the South.

The northern Indian Ocean has two major embayments: Arabian Sea and Bay of Bengal. The Arabian Sea covers an area of 3,863,000 km², whereas the area covered by the Bay of Bengal is 2,173,000 km². They are separated by the Indian peninsula. The Arabian Sea is bounded by the Arabian Peninsula to the West, Iran and Pakistan to the North and the Indian Peninsula to the East. Indus, Narmada and Tapti are the major rivers which discharge freshwater and huge amount of sediment to the Arabian Sea along with aeolian dust from deserts of Oman, Africa and western India (Milliman and Meade, 1983). The Bay of Bengal, located in the northeastern Indian Ocean is bordered by Sri Lanka and India to the West, Bangladesh to the North, Burma and the northern Malay Peninsula to the East. Sediments of the Bay of Bengal are mainly fed by the Ganges-Brahmaputra, Indo-Burman, the Irrawaddy, and several Indian peninsular rivers (Curry and Moore, 1971).

The northern Indian Ocean has two major submarine fans: the Bengal Fan in the Bay of Bengal and the Indus Fan in the Arabian Sea. The Bengal Fan, covering an area of $\sim 3 \times 10^6$ km², is one of the largest deep-sea fans in the world's oceans (Curry and Moore, 1971; Curry et al., 1982). The sediments of the Bengal fan are largely of the Himalayan provenance, which gets transported by the Ganges- Brahmaputra River system. The sediments in the Indus Fan are mainly brought by the rivers Indus, Narmada and Tapti (Milliman and Meade, 1983). The Indus Fan covers an area of $1.1\text{--}1.25 \times 10^6$ km² (Clift et al., 2002).

3.2 Geological setting

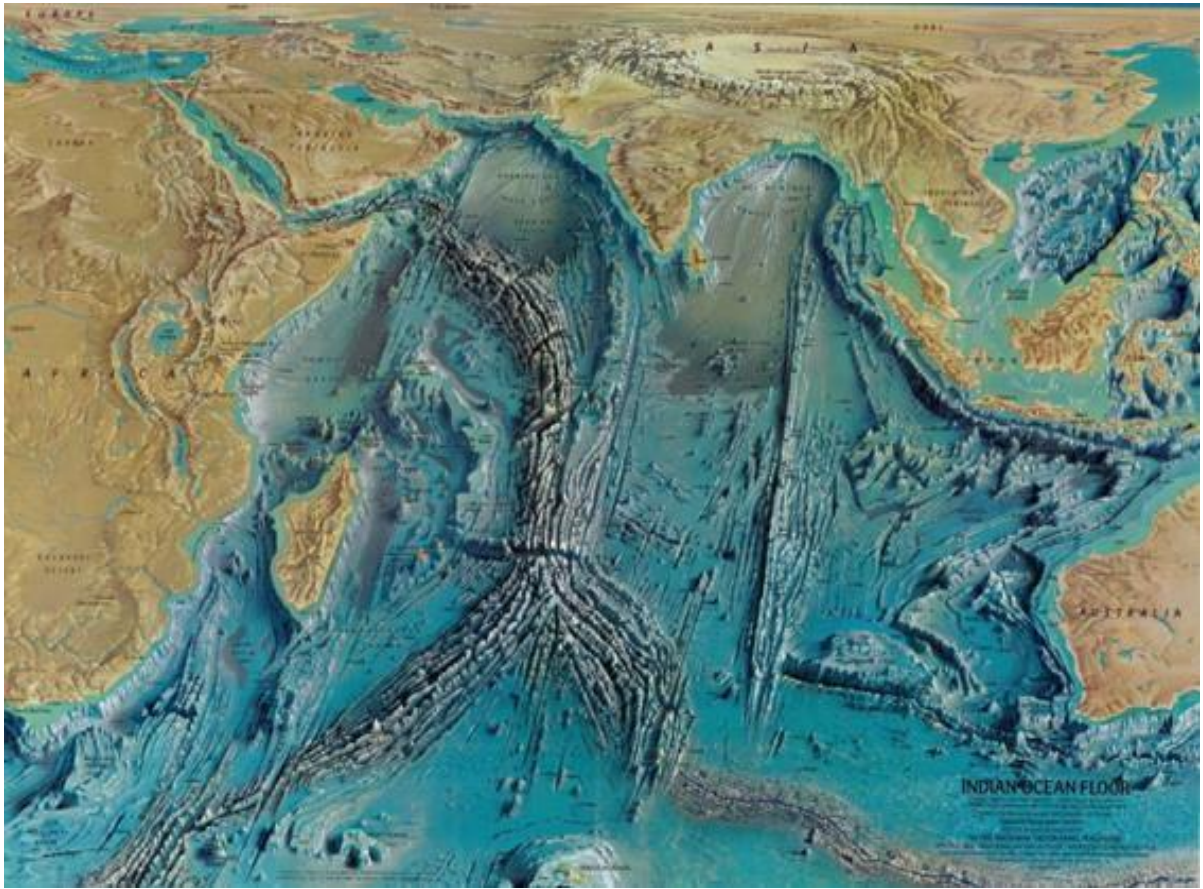


Fig. 3.1: Bottom Topography of the Indian Ocean.

(<https://www.lib.uchicago.edu/collex/exhibits/marie-tharp-pioneering-oceanographer/1967-indian-ocean-map/>)

The sea floor topography of the Indian Ocean is much more geographically complex than the Atlantic and Pacific Oceans. It comprises of a chain of volcanically active ridges, namely Carlsberg Ridge (CR), Central Indian Ridge (CIR), which bifurcates into Southwest Indian Ridge (SWIR) and Southeast Indian Ridge (SEIR) in an inverted Y shape, along with passive ridges like the Chagos-Laccadive Ridge, Maldives Ridge, Laxmi Ridge, and Ninety-East Ridge (Fig. 3.1) (Fisher et al., 1971; Schlich, 1982; Hazra et al., 2021). The active ridges extend from the western Arabian Sea to the central Indian Ocean, and are further connected with other major mid-ocean ridges on either side. The Carlsberg and Central Indian Ridge divides the Arabian Basin and the Somali Basin (Schlich, 1982). The seismically and volcanically inactive Chagos-Laccadive Ridge extends from the Chagos Archipelago in the central Indian Ocean (10° S) to the Laccadive Islands of the southwestern coast of India ($\sim 14^{\circ}$ N) (Fisher et al., 1971; McKenzie and Sclater, 1971). The Maldives Ridge is also a part

of the Chagos-Laccadive Ridge (Bhattacharya and Chaubey, 2001). The region around the Maldiva Ridge is seismically active due to tectonic processes. The Laxmi Ridge is characterized by isolated seamounts (Krishna et al., 2006). The Ninety-East Ridge runs roughly parallel to the eastern coast of India, approximately to 90° E longitude. It stretches linearly in a north- south direction for about 3,100 miles (Stein and Okal, 1978). It is a seismically inactive ridge.

3.3 Surface hydrography

Modern sea surface circulation in the northern Indian Ocean reverses seasonally under the influence of the Indian monsoon wind (McCreary et al., 1993; Shankar et al., 2002). It experiences a unique climate throughout the year with a semi-annual reversal of surface currents during the summer monsoon (June-August) and winter monsoon (November-January). Currents developed during these seasons run in exactly opposite directions to each other (Shankar et al., 2002).

During the summer monsoon (Fig. 3.2), the south-westerly wind blows parallel to the Indian coast, which causes Ekman transport and results in strong upwelling off Somalia and Oman, bringing cold and nutrient-rich water to the surface (Wyrski, 1973a; Lachkar et al., 2018). The Somali Basin exhibits relatively high productivity because of the intense upwelling occurring between 10° N and 5° N. This intense upwelling in the western Arabian Sea (WAS creates one of the most productive coastal upwelling ecosystems globally) (Ryther and Menzel, 1965). These strong winds blowing from the ocean towards land are generally associated with heavy precipitation (1600 cm³) in the eastern Arabian Sea (EAS). Freshwater input in the EAS brings considerable changes in its surface salinity (Banse, 1959, 1968; Johannessen et al., 1987; Shetye et al., 1990).

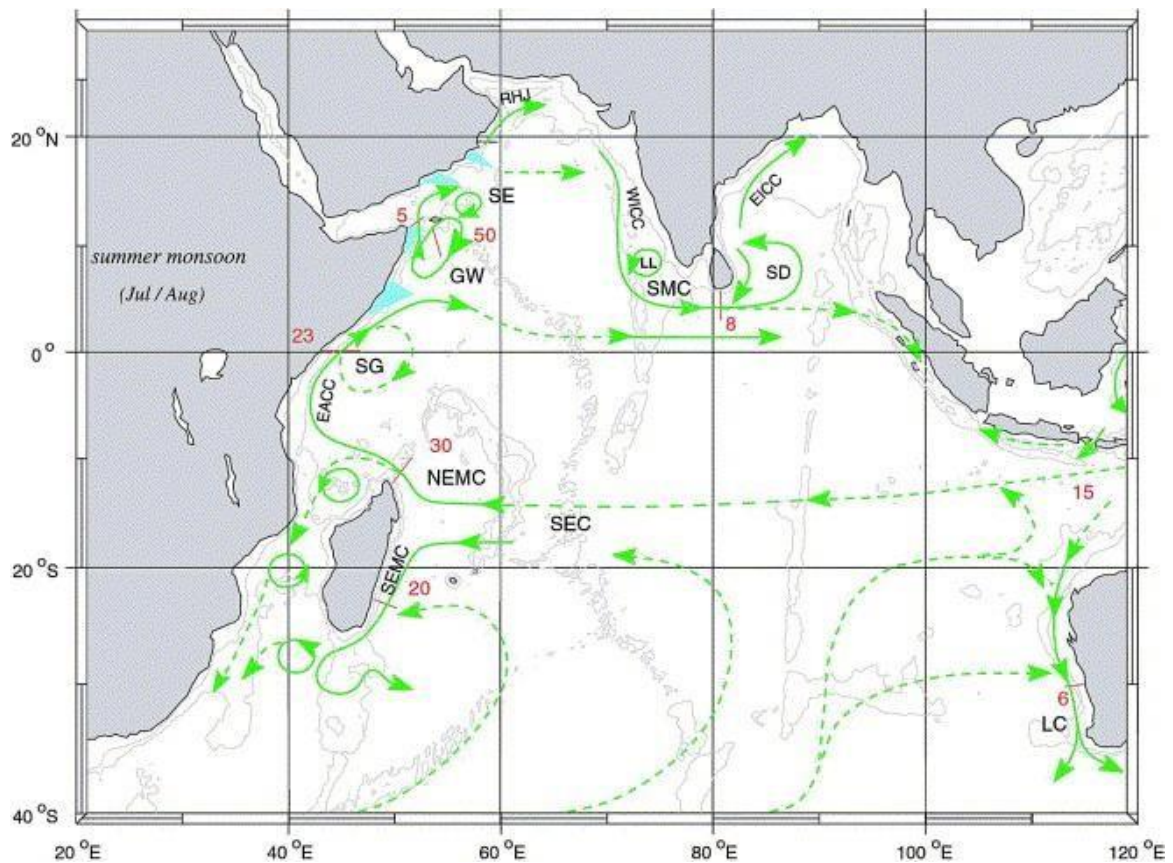


Fig. 3.2: A schematic representation of identified current flow during south-west monsoon. Current branches marked on the map are East Indian Coast Current (EICC), West Indian Coast Current (WICC), Southwest Monsoon Current (SMC), Northeast and Southeast Madagascar Current (NEMC and SEMC), Leeuwin Current (LC), South Equatorial Current (SEC), East African Coastal Current (EACC), Laccadive Low (LL), Ras al Hadd Jet (RHJ), Socotra Eddy (SE) Southern Gyre (SG), Great Whirl (GW) and associated upwelling wedges (adopted from Schott and McCreary, 2001).

During the north-east monsoon (Fig. 3.3), wind direction reverses and cold wind blows from northeast direction, which causes an onshore Ekman transport of surface waters. This reversal in wind direction suppresses upwelling and lowers productivity in the western and southern Arabian Sea. In addition, these dry cold winds cause cooling and convective mixing (Madhupratap et al., 1996; Reichart et al., 1998). This convective mixing brings the subsurface cold and nutrient-rich water to the euphotic zone leading to higher productivity in the EAS (Yentsch, 1993; Banse and English, 1993; Lachkar et al., 2018), which later also contributes to the extensive Oxygen Minimum Zone (OMZ) development.

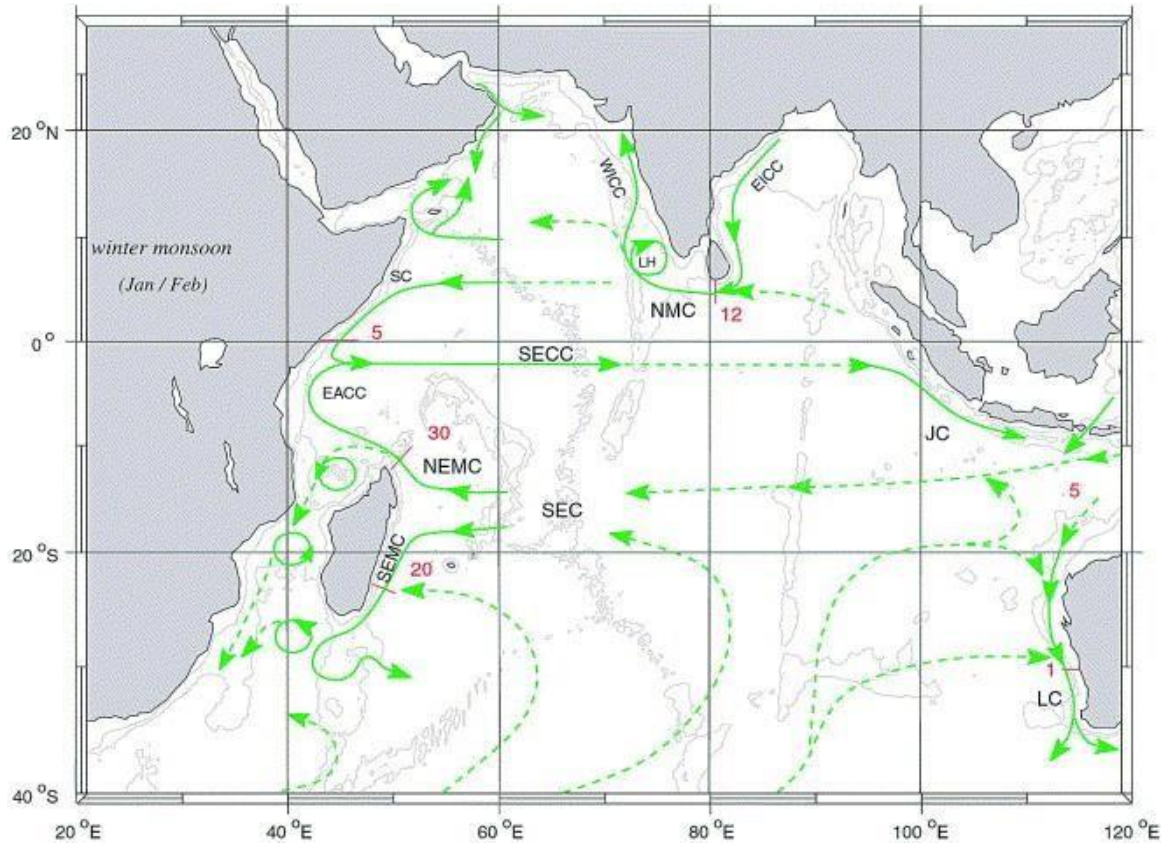


Fig. 3.3: A schematic representation of identified current flow during NE monsoon. Current branches marked on the map are Northeast Monsoon Current (NMC), West Indian Coast Current (WICC), East Indian Coast Current (EICC), South Equatorial Counter Current (SECC), South Equatorial Current (SEC), Northeast and Southeast Madagascar Current (NEMC and SEMC), South Java Current (JC), East African Coastal Current (EACC), Leeuwin Current (LC), Laccadive High (LH) (adopted from Schott and McCreary, 2001).

Oxygen Minimum Zone occurs due to the reduced supply of O_2 while there is an intense demand for oxygen. The dissolved O_2 in the OMZ is $<20 \mu\text{mol/kg}$. The OMZ of the Arabian Sea lies between the depths of 150–1250 m depth (Wyrski, 1973a). Denitrification in the OMZ typically takes place within the depth range of 200–800 m, where the oxygen levels are $<10 \mu\text{mol/kg}$. During this process, nitrate undergoes reduction to nitrite. The OMZ region in the northern Arabian Sea covers an area of $1.37 \times 10^6 \text{ km}^2$ (Naqvi, 2022).

Due to higher river input in the Bay of Bengal, the surface water above the depth of 100 m is the low saline Bay of Bengal surface water (BoBSW) (Talley et al., 2011). The average salinity of the BoBSW is ~ 31 psu. The southeastern Arabian Sea receives low saline water from the Bay of Bengal through the West Indian Coastal Current (WICC) during the north-east monsoon.

3.4 Deep-water hydrography

The intermediate water masses in the northern Indian Ocean majorly comprises of the Arabian Sea High Saline Water (ASHSW), Persian Gulf Water (PGW), Red Sea Water (RSW), and the Antarctic Intermediate Water (AAIW) (Wyrcki, 1973a; Rochford, 1964; Kumar and Li, 1996; You, 1998; 2000; Talley, 2008; Talley et al., 2011). The intermediate water masses of the northern Indian Ocean are majorly sourced from the south, with a small contribution from the PGW, RSW, and Pacific water through the Indonesian Sea (Talley et al., 2011).

The Arabian Sea High Saline Water comprises the ~150 m of top surface water of the Arabian Sea (Talley et al., 2011). It forms during the northeast monsoon as the result of cooling of the surface water by the continental winds (Shetye et al., 1994). It has a salinity of 35.3-36.7 psu and a temperature of 24-28° C (Shetye et al., 1994; Kumar and Prasad, 1999). The ASHSW moves southwards and is bounded by the North Equatorial Current (NEC). Its extent to the East is limited to 67° E and it finally intrudes below the low saline water of the Bay of Bengal (Tomczak and Godfrey, 2003; Talley et al., 2011).

The Persian Gulf Water is a highly saline water which enters the Arabian Sea through the Strait of Hormuz (Prasad et al., 2001). The high salinity of around >36.2 psu is due to excess of evaporation over precipitation (Prasad et al., 2001). The dissolved oxygen concentration of PGW is ~3.5 mL/L, and has temperature of ~17° C (Wyrcki et al., 1971). The PSW has been traced between depths of 200- 300 m in the Arabian Sea (Prasad et al., 2001). The water mass progressively deepens, whereas the salinity decreases as it moves southwards.

The RSW occupies a depth of 500-800 m in the Arabian Sea (Wyrcki, 1973a; Beal et al. 2003). It is a warm and high saline water having a salinity of 35.1-35.6 psu (Kumar and Prasad, 1999). It enters the Arabian Sea through the Strait of Bab-el-Mandeb. The dissolved oxygen and the temperature of RSW is ~2.5 mL/L and 9-11° C respectively (Grasshoff 1969; Kumar and Prasad, 1999). The water mass RSW deepens as it moves towards the equator.

The intermediate water of the northern Indian Ocean is dominantly occupied by the AAIW (core density of 27.1–27.3 kg/m³). It is a global intermediate water mass found in all the three major oceans and can be traced only up to 5° N in the Indian Ocean (You, 1998; Talley et al., 2011). This low saline water (~34.39 psu) occupies a depth of 1000-1500 m in

the northern Indian Ocean and contributes 10-20 % of its water into the Indian Ocean (Tomczak and Godfrey, 2003; Talley et al., 2011).

The Indonesian Intermediate Water, also known as the Indonesian Throughflow (ITF), originates from the Pacific Central Water (You and Tomczak, 1993). This low saline water (34.8 psu) is part of the global thermohaline circulation connecting the Pacific Ocean to the Indian Ocean (Tomczak and Godfrey, 2003). Initially, it exhibits high salinity, but as it flows over various sills of the Indonesian passages, the salinity decreases due to the intense vertical mixing. It flows zonally westwards, contributing 50-60% of its water into the Bay of Bengal, and reaches up to 15° N in the Arabian Sea (You, 1998). It is also known as Banda Sea Water or as Australian Mediterranean Water (AAMW) in the Indian Ocean.

The North Indian Intermediate Water (NIIW) is the mixture of all intermediate waters. It is mixture of aged AAIW, Subantarctic Mode Water (SAMW), and IIW, advected from the South through the Somali current (Morrison et al., 1999).

There is no deep water formation from the surface water within the Indian Ocean, and therefore the deep waters are sourced from the South. North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW) are the major deep water masses in the Indian Ocean (Reid, 2003; Piotrowski et al., 2009; Talley et al., 2011). The North Atlantic Deep Water originates from the Norwegian Sea and Labrador Sea in the North Atlantic (Talley, 2008). The NADW is characterized by enrichment in $\delta^{13}\text{C}$ and is poor in nutrients and CO_2 . The AABW originates from the Antarctic Basin and are CO_2 and nutrient-enriched, and are depleted in $\delta^{13}\text{C}$ (Talley et al., 2011). It is high saline and has a high dissolved oxygen content. The Circumpolar Deep Water (CDW) is mixture of these two i.e., NADW and AABW. Circumpolar Deep Water is further classified as Upper Circumpolar Deep Water (UCDW) and Lower Circumpolar Deep Water (LCDW). Upper Circumpolar Deep Water is the upper limb of CDW and has a major component of the NADW (McCave et al., 2005). The Lower Circumpolar Deep Water is the lower limb of the CDW and has AABW as the dominant component. Below ~4 km water depth, the abyssal basin is occupied by the AABW (Wyrski, 1973a; Reid, 2003; Tomczak and Godfrey, 2003). The UCDW and LCDW flow in the Central Indian Basin by traversing regions adjacent to the Broken Plateau and via deep trenches along the Ninety-East Ridge, respectively (Kumar and Li, 1996; Mantyla and Reid, 1995; Piotrowski et al., 2009). The Circumpolar Deep Water enters the northern Indian Ocean from the Southern Ocean by three pathways (Mantyla and Reid, 1995; You, 2000; Piotrowski et al., 2009; Fig. 3.4). The first path is through the Crozet Basin-Madagascar

Basin-Somali Basin to the Arabian Sea. The second route traverses the Central Indian Ocean Basin, reaching the Equatorial Indian Ocean. Lastly, the third pathway is through the South Australian Basin- western Australian Basin, ultimately leading to the southern Bay of Bengal (Piotrowski et al., 2009).

The CDW enters the northern Indian Ocean, upwells and mixes with the intermediate water AAIW, PGW, and RSW to form the North Indian Deep Water (NIDW) (You and Tomczak, 1993; Tomczak and Godfrey, 2003). The NIDW, also refer to as the Modified North Atlantic Deep Water (MNADW; Shetye et al., 1994) and High Salinity Deep Water (HSDW; Kumar and Li, 1996) is a southward flowing water mass in the northern Indian Ocean and is traced between 1100- 2200 m in the northern Indian Ocean (Beal et al. 2003). Due to its mixing with the intermediate waters, it exhibits low oxygen and high salinity. The dissolved oxygen concentration of this water at the depth of its occurrence is ~ 2 mL/L.

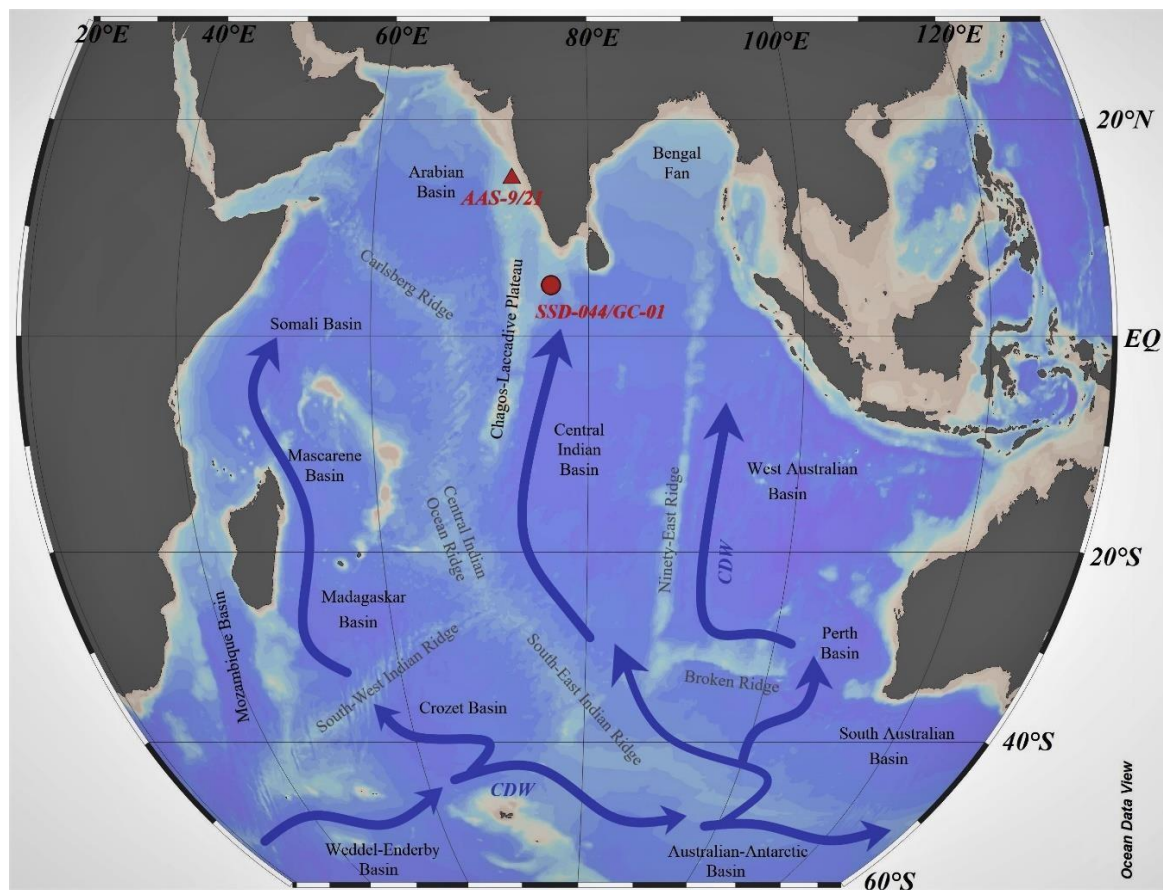


Fig. 3.4: Schematic map showing the deep water circulation of the Indian Ocean. Location of the studied core has been marked by red circles (modified after You, 2000).

3.5 Terrigenous input

The terrigenous input in the northern Indian Ocean is sourced from fluvial as well as aeolian sources. The fluvial sources include discharge of terrigenous sediment by the Rivers (Ganga, Brahmaputra, Indus, Sabarmati, Shetrunji, Narmada, Tapi) to the Ocean as a weathering product. The aeolian sediments are mostly sourced from the Arabian and Thar Desert (Manjunatha and Shankar, 1992). The sediments in the WAS are mainly aeolian sourced (Shimmield et al., 1990), whereas the sediments in the EAS are mainly fluvial sourced (Paropkari, 1990). The terrigenous material in the EAS is mostly derived from numerous peninsular rivers originating in the Western Ghats. Before the construction of barrages and dams, more than 400 million tonnes of the suspended sediments were transported by the Indus River to the Arabian Sea annually (Milliman et al., 1984), whereas about 60 million tonnes of the suspended matter is contributed by Narmada and Tapi Rivers. The southern part of the Arabian Sea has low sedimentation accumulation than the northern part of the Arabian Sea because of the low concentration of suspended particles coming from the rivers. Every year, more than 80-115 million tonnes of dust derived from the Arabian and Somali regions is delivered to the Arabian Sea by monsoonal winds (Sirocko and Sarin, 1989; Ramaswamy et al., 1991).

The Bay of Bengal sediments are mainly terrigenous material with little contribution of volcanic and biological (such as calcareous) materials. Most of its fluvial deposition are eroded materials from the Tibetan Plateau and Himalaya Mountains (Colin et al., 1999; Galy et al., 2007). The major rivers transporting the fluvial sediments are Ganga and Brahmaputra along with Indian peninsular rivers like Godavari, Krishna, and Mahanadi (Sarin and Krishnaswami, 1984; Sengupta et al., 2006).

Chapter 4

Material and Methods

4.1 Sediment cores

Two sediment cores were selected from intermediate and deep water masses of the northern Indian Ocean to meet the objectives of this research work. The details of the sediment cores and the study area map along with the core locations are given in Table 4.1 and Fig. 4.1, respectively.

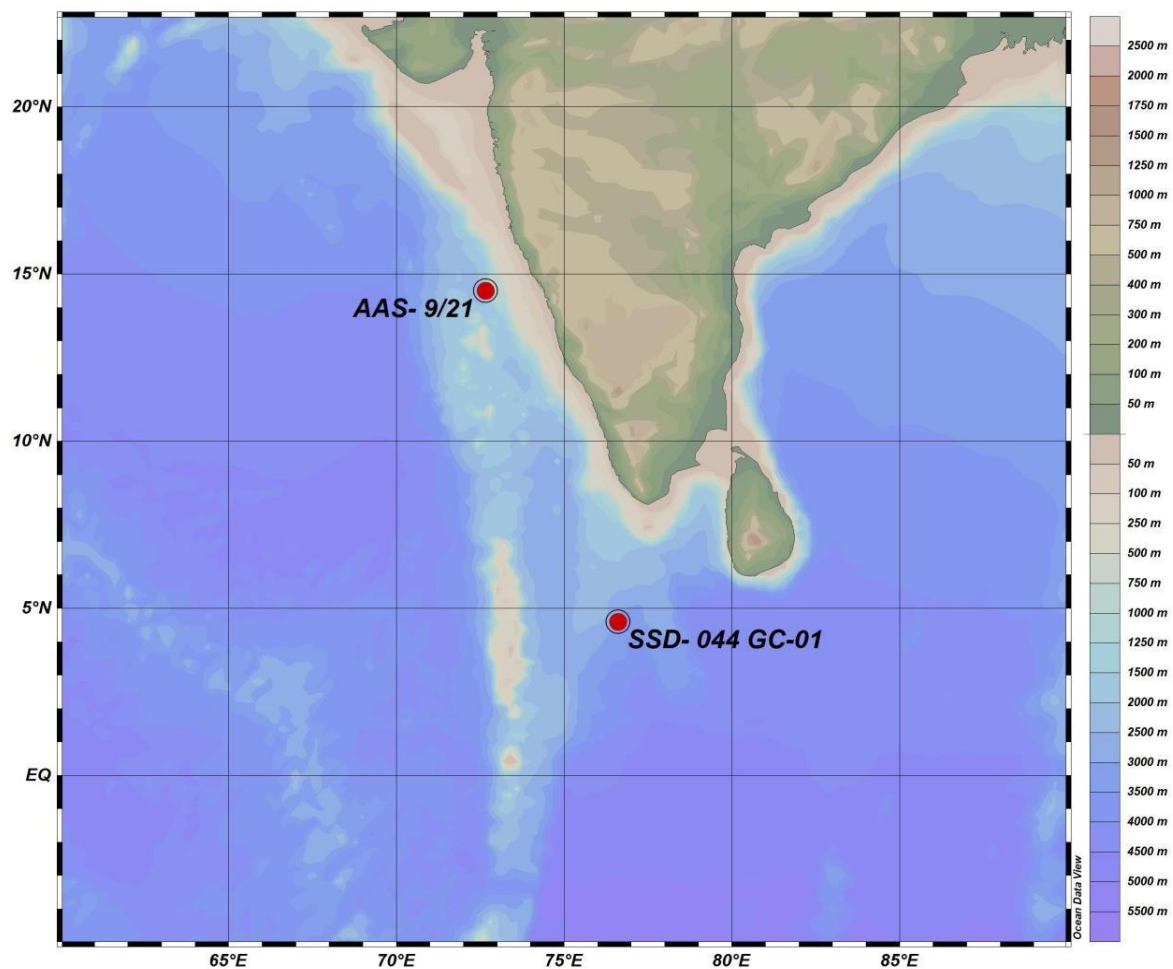


Fig. 4.1: Location map of sediment cores SSD-044/GC-01 and AAS-9/21 used in the present study.

Gravity core SSD-044/GC-01 (Lat: 4° 35' 56" N; Long: 76° 35' 56" E) was collected from a water depth of 3160 m from the northern Indian Ocean during *RV Sindhu Sadhana*

cruise number 44. Total core recovery was ~5.4 m. The top 100 cm of the core was used for this study. The core location lies in the equatorial Indian Ocean, bounded by the Chagos-Laccadive ridge to the West, Indian Peninsula to the North, and Sri Lanka to the East. To the South of the core lies the open Indian Ocean. The source of sediment to the core site can be fluvial as well as Aeolian, and the primary source of sediment is from the Indian Peninsula. This core is ventilated by water primarily sourced from the northward circulating Upper Circumpolar Deep Water (UCDW), which has a greater component of the North-Atlantic Deep Water (NADW) (Piotrowski et al., 2009). The region is affected by the seasonal reversal of boundary currents.

Another core AAS-9/21 (Lat: 14° 30' 0" N; Long: 72° 39' 0" E) was retrieved from the Eastern Arabian Sea, from a water depth of 1800 m (below the present-day Oxygen Minimum Zone (OMZ)) during A. A. *Sidorenko* cruise number 9. The total core recovery was ~4.2 m. The core lies above the present day lysocline depth (~3800 m; Peterson and Prell, 1985). The sedimentary sequence comprises of a mixture of terrigenous and biogenous material. Core AAS-9/21 is bathed by North Indian Deep Water (NIDW) (Naik and Naik, 2022).

Table 4.1: Sediment cores used in the present study.

Sr. No.	Sediment cores	Latitude	Longitude	Water depth (m)
1	SSD-044/GC-01	4° 35' 56" N	76° 35'56" E	3160
2	AAS-9/21	14° 30' 0" N	72° 39' 0" E	1800

4.2 Age model of the sediment cores

The age model for the top 100 cm of the core SSD-044/GC-01 was established using Accelerator mass spectrometry (AMS) ^{14}C dates of planktonic foraminifera (*Globigerinoides ruber*, *Globigerinoides quadrilobatus*, *Neoglobobulimina dutertrei* + *Globorotalia menardii*) picked from a size fraction of $>250\ \mu\text{m}$. An age-depth modelling routine named *Undatable* was used, which is developed in MATLAB and uses Bayesian radiocarbon (^{14}C) calibration software (MatCal) (Lougheed and Obrochta, 2019). These ^{14}C based age models were updated using IntCal20 calibration data. Downcore median ages, confidence intervals, and a density cloud that displays the most likely regions of age-depth probability were calculated by linearly interpolating all *nsim* number of unique age-depth

(Lougheed and Obrochta, 2019) runs to 1 depth unit resolution (e.g., cm), and then computing the 1st to 99th percentiles of the ages corresponding to each depth unit. Darker regions of the density cloud are closer to the 50th percentile (Fig. 4.2a). A reservoir correction of $\Delta R = -91 \pm 25$ years was used (Dutta et al., 2001; Southon et al., 2002). The radiocarbon and the calendar ages for the core SSD-044/GC- 01 are given in Table 4.2. The average sedimentation rate of the core is ~ 3.5 cm/kyr.

The age model for the core AAS-9/21 is based on the AMS ^{14}C dates of planktonic foraminifera (*G. ruber*) of a size fraction of $>250 \mu\text{m}$. Few AMS ^{14}C dates were adopted from Govil and Naidu, 2010, and Naik and Naik, 2022. The radiocarbon ages were calibrated to calendar ages using Calib 8.20 (Stuiver and Reimer, 1993) with the Marine20 calibration curve (Heaton et al., 2020) and were corrected with reservoir age correction of $\Delta R = 11 \pm 69$ years (Southon et al., 2002). The radiocarbon and the calendar ages for the core AAS-9/21 are given in Table 4.3. The average sedimentation rate of the core is ~ 14 cm/kyr, where the sedimentation rate for each interval is calculated by assuming a constant sedimentation rate between dated depths. The age versus depth graph for the core AAS-9/21 is given in Fig. 4.2b.

Table 4.2: Calendar ages and sedimentation rate for the core SSD-044/GC-01.

Sr. No	Sample Interval (cm)	Sample ID	Species	^{14}C age (yr BP)	^{14}C error ($\pm$)	Cal age (yr BP)	Sedimentation rate (cm/kyr)
1	*0-1	D-044 GC-01 0-1cm(PF)	<i>G. ruber</i> + <i>G. sacculifer</i> + <i>N. dutertrei</i> + <i>G. menardii</i>	2195	22	1934	3.4
2	13-14	SD-044 GC-01 13-14cm(PF)	<i>G. ruber</i> + <i>G. quadrilobatus</i>	5008	30	5706	2.2
3	23-24	SD-044 GC-01 23-24cm(PF)	<i>G. ruber</i>	9284	38	10237	3.0
4	27-28	SD-044 GC-01 27-28cm(PF)	<i>G. ruber</i>	10235	42	11580	2.6

5	29-30	SD-044 GC-01 29-30cm(PF)	<i>G. ruber</i>	10733	41	12351	4.7
6	31-32	SD-044 GC-01 31-32cm(PF)	<i>G. ruber</i>	11509	42	12775	3.4
7	35-36	SD-044 GC-01 35-36cm(PF)	<i>G. ruber</i>	12272	47	13946	4.8
8	37-38	SD-044 GC-01 37-38cm(PF)	<i>G. ruber</i>	12603	50	14360	3.8
9	39-40	SD-044 GC-01 39-40cm(PF)	<i>G. ruber</i>	12786	43	14890	3.5
10	41-42	SD-044 GC-01 41-42cm(PF)	<i>G. ruber</i>	13194	44	15462	5.3
11	45-46	SD-044 GC-01 45-46cm(PF)	<i>G. ruber</i>	13619	57	16220	3.2
12	57-58	SD-044 GC-01 57-58cm(PF)	<i>G. ruber</i>	16777	61	19955	4.2
13	73-74	SD-044 GC-01 73-74cm(PF)	<i>G. ruber</i> + <i>G. quadrilobatus</i>	19837	81	23741	3.2
14	*99-100	SD-044 GC-01 99-100cm(PF)	<i>G. ruber</i> + <i>G. sacculifer</i> + <i>N. dutertrei</i> + <i>G. menardii</i>	28160	270	31799	

*AMS ^{14}C dates adopted from Yadav et al., 2021.

Table 4.3: Calendar ages and sedimentation rate for the core AAS-9/21.

Sr. No.	Sample Interval	Species	¹⁴ C age (yr BP)	¹⁴ C error (±)	Calendar age (yr BP)	Sedimentation rate (cm/kyr)
1	*0-3	<i>G. ruber</i>	850	25	302	5.4
2	39-43	<i>G. ruber</i>	7460	28	7729	4.7
	47-50	<i>G. ruber</i>	8752	39	9224	5.9
3	*53-56	<i>G. ruber</i>	9540	80	10229	38.7
	79-85	<i>G. ruber</i>	10087	47	10978	2.2
4	85-90	<i>G. ruber</i>	11912	36	13222	18.8
5	90-96	<i>G. ruber</i>	12216	37	13545	30.0
6	***96-99	<i>G. ruber</i> + <i>G. sacculifer</i>	12301	33	13642	20.9
7	102-108	<i>G. ruber</i>	12630	37	14072	20.8
8	*110-113	<i>G. ruber</i>	12770	80	14316	6.9
9	**116-119	<i>G. ruber</i> + <i>G. sacculifer</i>	13326	36	15197	8.3
10	128-130	<i>G. ruber</i> + <i>G. quadrilobatus</i>	14342	46	16521	12.2
11	**136-139	<i>G. ruber</i> + <i>G. sacculifer</i>	14953	39	17256	8.5
12	*148-150	<i>G. ruber</i>	16070	115	18546	18.3
	179-182	<i>G. ruber</i>	17554	68	20282	7.9
13	*213-216	<i>G. ruber</i>	21290	180	24582	

*AMS ¹⁴C dates adopted from Govil and Naidu, 2010.

**AMS ¹⁴C dates adopted from Naik and Naik, 2022.

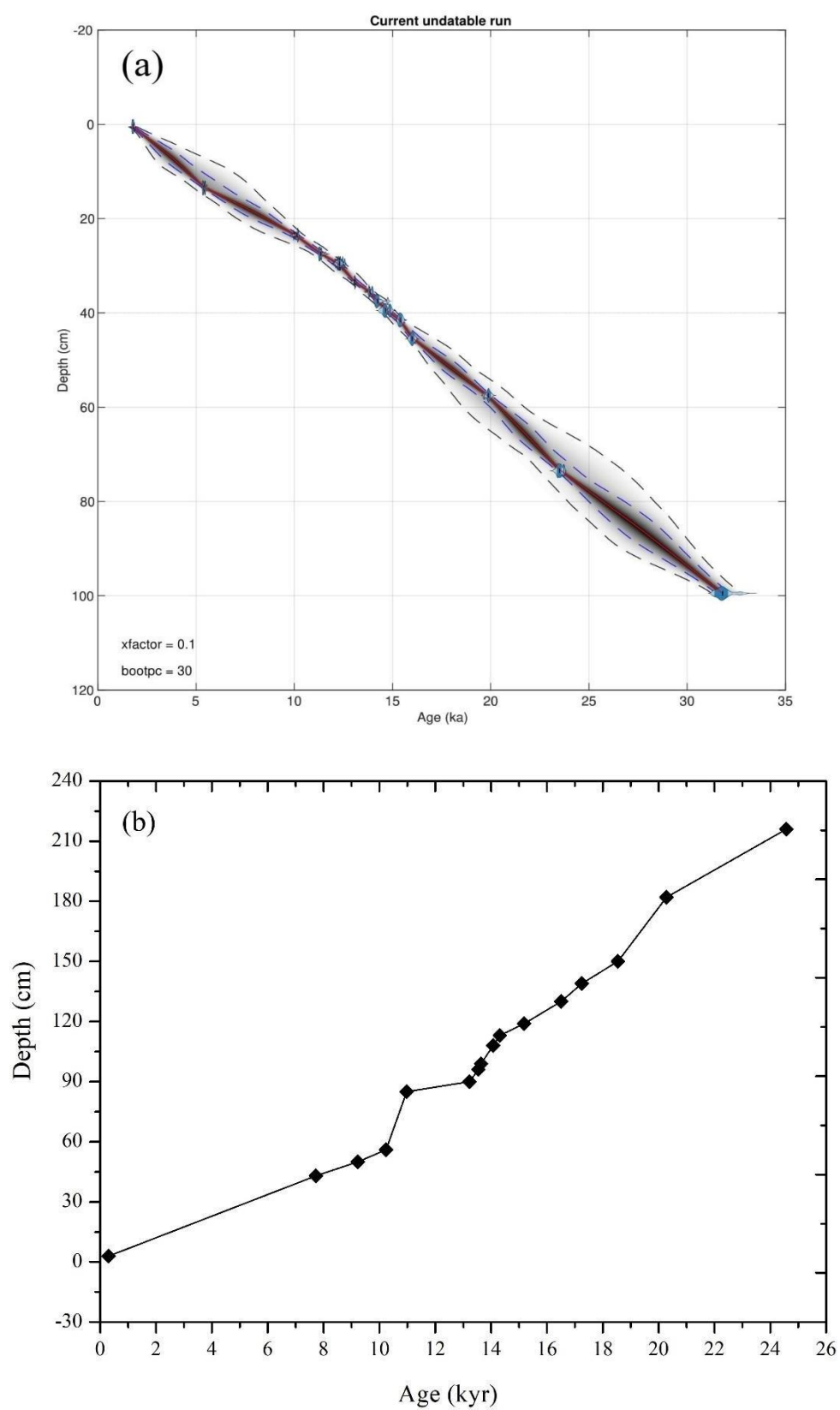


Fig. 4.2: Age versus depth profile for the cores (a) SSD-044/GC-01 and (b) AAS-9/21.

4.3 Processing of sediment samples

Sediment cores were sub-sampled, and approximately half of the total wet sample was processed in the Paleoceanography Laboratory. The wet sample from each interval was oven dried for 24 hrs at a temperature of 50-60° C. Weight of the dried sample was measured and then it was soaked in a 100 mL beaker for 24 hrs in water for the samples to disintegrate. Properly disintegrated sample was then wet sieved through a >63 µm mesh in order to remove clay particles. Washing of the sample was done carefully to avoid any breakage of foraminifera. Size fraction of >63µm was collected in 100 mL beakers and kept in an oven at 60° C for drying. The dried coarse fraction was collected in 10 mL vials. The coarse fraction was used for picking foraminifer for various analyses.

4.4 Ventilation age

4.4.1 Radiocarbon measurement for core SSD-044/GC-01

For the core SSD-044/GC-01, 24 samples (12 samples containing planktic foraminifera and 12 samples containing benthic foraminifera) were used for radiocarbon dating. The picked sample was analyzed at the Inter- University Accelerator Centre, Delhi, India, for AMS radiocarbon dating.

4.4.1.1 Picking of planktic foraminifera for AMS radiocarbon dating

A representative aliquot of the coarse fraction was used for picking. The coarse fraction was dry sieved through a mesh of >250 µm. A fraction of the sieved sample was spread on the picking tray. Surface dwelling planktic foraminifera *G. ruber* was identified and picked up using stereo-zoom binocular microscope Meiji Techno EMZ-5. Only the intact and clay-free tests were picked. The weight of every sample was ~13mg; wherever there was insufficient weight of *G. ruber*, *G. quadrilobatus* was also picked.

4.4.1.2 Picking of benthic foraminifera for AMS radiocarbon dating

A representative aliquot of the coarse fraction was obtained for picking, with the help of a splitter. The representative coarse fraction aliquot was dry-sieved through a mesh of >250 µm. A fraction of the sieved sample was spread on the picking tray. Mixed benthic foraminifera (Fig. 4.3) was picked up using a stereo-zoom binocular microscope Meiji Techno EMZ-5. In some samples, the weight was less than 13 mg; in such cases two adjacent

sample sections were combined. In some samples size fraction 150-250 μm were also used to get the required weight.

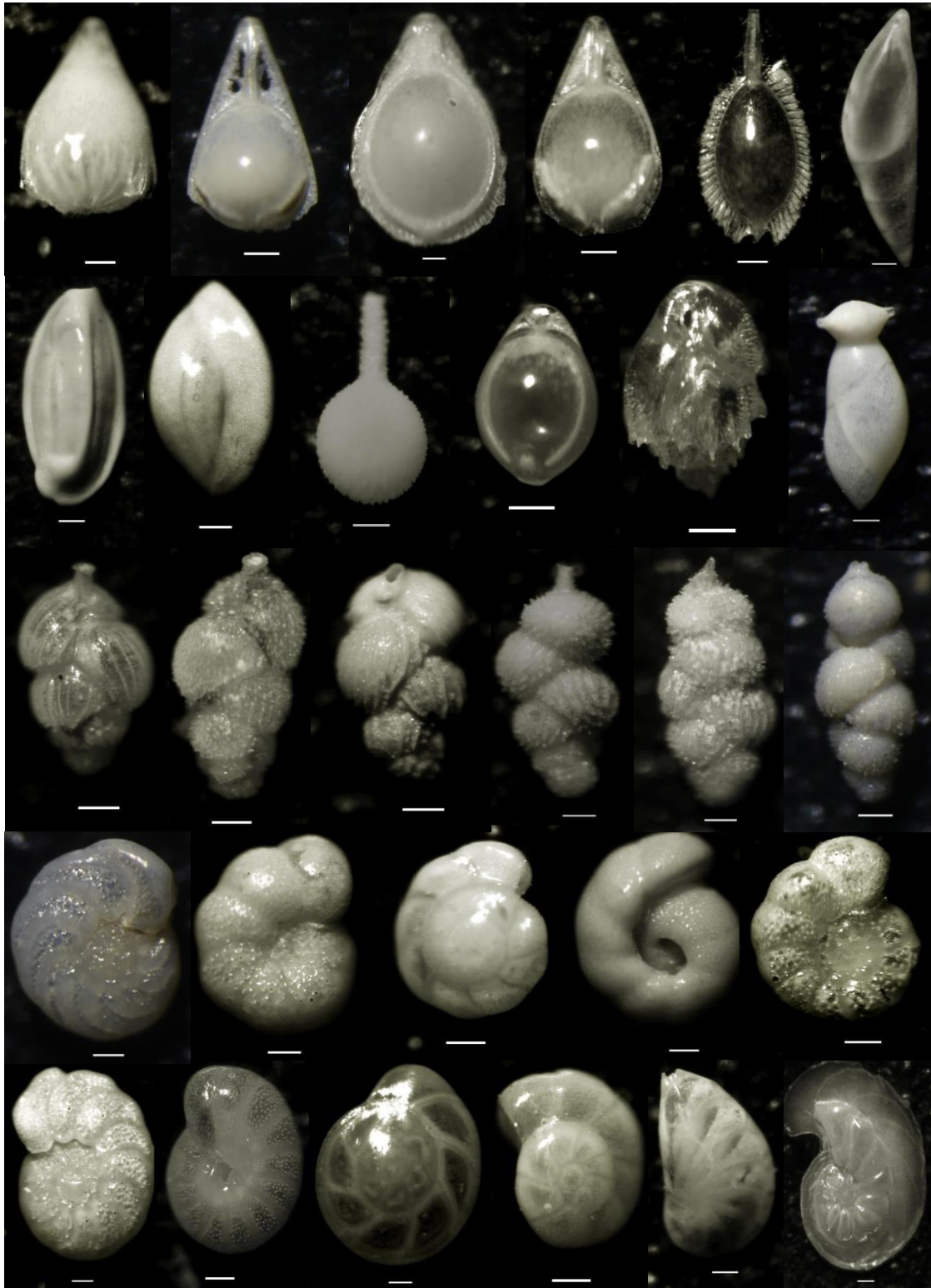


Fig. 4.3: Mixed benthic foraminifera picked from core SSD-044/GC-01. Nikon DS-Ri2 binocular microscope was used to photograph all the foraminifers. Scale bar at the bottom of each picture is of 100 μm .

4.4.2 Radiocarbon measurement for core AAS-9/21

22 Radiocarbon dates were obtained using 13 samples of mixed-species of benthic foraminifera (excluding pyrgo and agglutinated species) and 9 coexisting mono-species of planktic foraminifera (*G. ruber*). Four ^{14}C dates on planktic foraminifera obtained previously were also used. AMS ^{14}C dates were measured at the Inter-University Accelerator Centre (IUAC), Delhi, India. For 7 samples, AMS radiocarbon dating was carried out at the Physical Research Laboratory (PRL) in Gujarat, India.

A representative aliquot of the $>250\text{ }\mu\text{m}$ dried coarse fraction of the core was taken after splitting and was uniformly spread on a tray for picking. Planktic foraminifera *G. ruber* was identified and picked up using stereo-zoom binocular microscope Meiji Techno EMZ-5. Only the well-preserved, intact tests were picked for AMS dating. The weight of the picked sample was $\sim 13\text{mg}$. Mixed benthic foraminifera ($>250\text{ }\mu\text{m}$) were also picked from the respective intervals. Wherever the samples weight was less than 13 mg, foraminifera from the adjacent intervals were picked.

4.4.3 Ventilation age calculation

The difference between the deep water (measured on benthic foraminifera) and surface water (measured on planktic foraminifera) radiocarbon concentration provides the deep water circulation changes in the past (Broecker et al., 1988). Benthic foraminifera record the radiocarbon concentration of the deep water in which it calcified, while the planktic foraminifera will reflect the radiocarbon content of the surface water. To calculate the ventilation age, ^{14}C to C ratios of coexisting planktonic and benthic foraminifera are measured. The $\Delta^{14}\text{C}$ of the water masses will help us get a picture of global radiocarbon distribution through the last 30 kyr (Broecker et al., 2008). Another method to calculate the ventilation age is B-Atm which is the age offset between the ^{14}C age of benthic foraminifera and the contemporaneous atmosphere.

4.5 Stable carbon and oxygen isotopes

For the stable carbon and oxygen isotope of benthic foraminifera, 2-5 specimens of well-preserved foraminifera *Cibicidoides wuellerstorfi* were picked from a size fraction of $>250\text{ }\mu\text{m}$ within a section of 1 cm thickness and interval of 1 cm between sections. *Cibicidoides wuellerstorfi* are epifaunal benthic foraminifera and, therefore record the bottom-water conditions above the sediment-water interface within their calcium carbonate

tests. The tests of *C. wuellerstorfi* are plano-convex consisting of 8-12 chambers in their final whorl.

The analysis for stable carbon and oxygen was carried out at CSIR- National Geophysical Research Institute (NGRI), Hyderabad, India. The isotopic measurement was performed on a Thermo Finnigan Gas Bench II, equipped with a CTC auto-sampler and coupled to a Delta Plus XP Mass Spectrometer with a precision better than $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.08\text{‰}$ $\delta^{18}\text{O}$. Calibration was carried out against VPDB (Vienna Pee Dee Belemnite) standard using an in-house dolomite standard subsequent to linearity correction that has been calibrated against NBS-18 and NBS-19 reference standards.

4.6 Total Inorganic Carbon (TIC)

Determination of calcium carbonate content in the sediment was carried out using an UIC CM5015 Coulometer in the Wet-chemistry Laboratory at GOD, CSIR-NIO. 10 ml of 1N HCl was used to evolve CO_2 from the sediment sample, which then goes into the coulometer cell. Total Inorganic Carbon present in the sediment sample was detected and displayed on a digital screen in terms of micrograms.

4.6.1 Sample Preparation

Analysis of CaCO_3 involves a systemic procedure for sample preparation which includes drying, grinding, and weighing. An adequate amount of wet sediment sample is taken into a petri dish and is kept in an oven at 60°C for drying. The dried sample was then transferred to a mortar and pestle for grinding. The samples were ground to fine particles in order to get homogeneous size, structure, and purity. The ground samples were then weighed and secured in vials for carrying out the inorganic carbon analysis.

4.6.2 Setting up of Acidification module

The acidification module consists of an acid dispenser, a pre-scrubber (potassium hydroxide), and post- scrubber (potassium iodide).

4.6.2.1 Acid dispenser

An acid reacts with the carbonate-containing samples and hence CO_2 was liberated as the inorganic carbon gets dissolved. A variety of acids can be used for the dissolution of the carbonates. Here 1N hydrochloric acid (HCl) was filled in the container, and 10

mL was pumped into the reaction vessel by the acid dispenser.

4.6.2.2 Pre-scrubber (Potassium Hydroxide)

Potassium hydroxide (KOH) solution was used as a pre-scrubber, which removes CO₂ from the carrier gas before it enters the reaction vessel. For its preparation, 11.25g KOH was weighed out and diluted in 25ml distilled water. 15ml of this solution was filled in the pre-scrubber assembly of the acidification module. Potassium hydroxide solution was changed either on daily bases or when it becomes foamy.

4.6.2.3 Post-scrubber (Potassium Iodide)

After the reaction of acid and sediment samples, many other gases, such as H₂S, SO₂ are evolved along with CO₂. A post-scrubber was used to remove such unwanted gases from entering the coulometer cell. Post-scrubber consists of potassium iodide (KI) solution, which was prepared by diluting 12.5g KI in 12.5 ml distilled water. Out of this 25ml prepared solution, 12.5 ml solution was transferred to the post-scrubber. 2-3 drops of glacial acetic acid (CH₃COOH) were added to acidify it to approximately a pH of 3. Fresh KI solution was prepared daily before starting the analysis.

4.6.2.4 Cell Preparation

A clean and dry coulometer cell was used for analyses. A teflon-coated magnetic stirrer was placed at the bottom of the large chamber of the coulometer cell and was filled with cathode solution. The cell top with the coiled platinum electrode was inserted into the cell. In the side arm of the cell (anode compartment), a small amount of KI was added and filled with anode solution. A cell top with the silver electrode (which should submerge in the solution) was used to cover the anode compartment. The outer surface of the cell was cleaned again to avoid any grease, fingerprints, water spots, etc., which might affect transparency (and thus %T). The assembled cell was then placed into a coulometer cell such that a maximum cell current was obtained.

4.6.3 Analysis Procedure

For the measurement of TIC, before starting with the samples, a few blanks were run initially to verify the performance of the instrument. Blanks were run in empty sample tubes filled with 10 ml HCl, and acceptable blank values were obtained. Blanks were followed by measurement of known standard CaCO₃, whose value was ~11.8- 12.0 % of

carbon. An in-house standard (SSD-044/GC-01 14-15 cm) of a known TIC value (7.18 %) was also used as reference material. Approximately 10-12 mg of finely ground sediment sample was taken into a clean and dry sample reaction flask and 10 ml of 1N HCl was pumped into the reaction flask through an acid dispenser. Once the titration completes, display on the coulometer becomes stable and the value of % carbon was recorded. After every 10 samples, 2 duplicate and 1 in-house standard were analyzed. Replicate analysis on ten samples yielded a repeatability of $\pm 2\%$.

4.6.4 Calculation

The calculation for TIC is as follows:

$$\% \text{ TIC} = \{(\mu\text{g C [display value]} - \text{per minute } \mu\text{g C [blank value]}) / \mu\text{g sample weight}\} \times 100$$

The CaCO_3 content in the sediment sample was calculated by multiplying TIC with a conversion factor of 8.333, where the conversion factor is:

$$\text{Molecular weight of } \text{CaCO}_3 / \text{atomic weight of C} = 100/12 = 8.333$$

(Ca = 40, C = 12 and O = 16 x 3; $\text{CaCO}_3 = 100$)

4.7 Trace element analysis

4.7.1 Sample Preparation

For elemental analysis of sediment samples, an adequate amount of wet sample was oven dried at 60°C. The dried sample was then ground to fine particles using mortar and pestle. The ground samples were then transferred to air-tight vials.

4.7.2 Acid Digestion

The sediment sample was homogeneously ground for the redox-sensitive elemental analysis. Sediment sample weighing accurately 50 mg was digested using an acid mixture of HF, HNO_3 , and HClO_4 in the ratio 7:3:1. The digested solution was evaporated to near dryness before the residue was taken into solution in 50 mL of 2 % HNO_3 . Rhodium was used as an internal standard in the final solution. Marine mud sediment standard (MAG-1) and National Research Council Canada standard (NRCC PACS-3) were used as reference standards. Blanks and duplicate samples were also analyzed along with the samples.

4.7.3 Analysis

Trace element analysis was carried out using High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP MS). Concentrations for trace element uranium was obtained for all samples. The accuracy of the analytical results is better than $\pm 4\%$ and the average relative standard deviation (%RSD) obtained from the multiple repetitions of samples lies within 6%. The recovery percentage for uranium is 96%.

4.8 Pore Size and Pore Density

Benthic foraminiferal surface porosity is used as a proxy for the past bottom water oxygenation. The coarse fraction ($>63\ \mu\text{m}$) from the core SSD-044/GC-01 was subsequently dry-sieved over a $>125\ \mu\text{m}$ sieve for pore size analysis. In this study, epifaunal benthic foraminifera *C. wuellerstorfi* with size ranged from 125-350 μm was picked for the pore measurements. For each interval, 2-4 well-preserved foraminiferal species were picked. A total of 43 specimen in 15 samples were picked. For each specimen two images were taken: one image of the dorsal side of the entire specimen (90x magnification) and one close-up image of the penultimate chamber (300x magnification). Photomicrographs of the pores on the dorsal side of the test were taken using a Scanning Electron Microscope (SEM) 6360 LV, JEOL instrument. The surface porosity of the benthic foraminifera was calculated based on Petersen et al. (2016). Since the last chamber is often damaged or broken, the chamber next to the last chamber, i.e. penultimate chamber of the foraminiferal test is used for the pore measurements. Specific frame was manually positioned on each SEM using a macro, developed by Petersen et al. (2016) in ImageJ software to calculate the pores in the penultimate chamber. A frame of size 300 x 150 pixel, covering an area of 4869 μm^2 was positioned on the middle, flat portion of the chamber to avoid any distortion because of the round edge of the specimens. The porosity was calculated based on the grayscale threshold applied to specific frames. The porosity for each interval was calculated as the average porosity of 2-3 specimen in the respective interval.

4.9 Foraminiferal Fragmentation Index

Foraminiferal fragments for the core SSD-044/GC-01 were counted for the 50 samples with an interval of 1cm each. For foraminiferal fragmentation index, a representative sample of coarse fraction ($>63\ \mu\text{m}$) was split with the help of a splitter and

was then sieved through a size fraction of $>125\ \mu\text{m}$. tests with more than two-thirds portion of the original test size were counted as whole test, whereas tests with less than two-thirds of the original test are considered as fragments. The foraminiferal fragments were calculated using the method by Le and Shackleton (1992), where it is assumed that a foraminiferal test breaks into 8 fragments.

The foraminiferal fragmentation index is calculated as:-

$$\text{FF (\%)} = \frac{(\text{Foraminiferal fragments}/8)}{[(\text{Foraminiferal fragments}/8) + \text{whole tests}]} \times 100$$

4.10 Size Index

Size index is used to estimate the carbonate ion saturation state of the bottom water (Broecker and Clark, 1999). Here, the size index is calculated as the ratio of CaCO_3 in $>63\ \mu\text{m}$ to that in total CaCO_3 % in bulk sediments multiplied by 100 (Broecker and Clark, 1999). An aliquot of bulk sediment was wet sieved through a $63\ \mu\text{m}$ sieve. The material that was retained in the sieve, was oven dried and then weighed. This measured weight is the CaCO_3 in $>63\ \mu\text{m}$. The non-carbonate contaminant in the sediment was sufficiently small and can be neglected. For total CaCO_3 % in bulk sediments, an aliquot of the bulk sediment sample was weighed and then analysed using UIC CM5015 Coulometer in Wet-chemistry Laboratory, GOD, CSIR- NIO.

$$\text{Size index (SI \%)} = \frac{\text{CaCO}_3 \text{ in } >63\ \mu\text{m} \text{ fraction}}{\text{Total CaCO}_3 \text{ in the bulk sediment}} \times 100$$

4.11 Coarse Fraction

The coarse fraction content in all the samples was calculated as the weight of the dried coarse fraction ($>63\ \mu\text{m}$) divided by the total weight of the dry sediment multiplied by hundred.

Chapter 5

Radiocarbon evidence for reduced deep water ventilation of the northern Indian Ocean during the last glacial maxima and early deglaciation

5.1 Summary

Enhanced outgassing of sequestered carbon to the atmosphere by upwelling of deep water in the Southern Ocean during the last deglaciation is assumed to be the main factor that modulated changes in atmospheric CO₂ and atmospheric radiocarbon activity; however, the exact mechanism behind this deglacial CO₂ release still remains unclear. In this study, we have investigated ventilation changes in the deep waters of the northern Indian Ocean over the past 25 kyr BP using paired benthic and planktic foraminiferal radiocarbon, along with stable carbon and oxygen isotopes of benthic foraminifera, sedimentary CaCO₃ content and coarse fraction from the gravity core SSD-044/GC-01(3160 m water depth) collected from Central Equatorial Indian Ocean. The results indicate greater proportion of southern sourced CO₂-rich, poorly-ventilated Antarctic Bottom Water (AABW) during the Last Glacial Maximum (LGM) and Heinrich Stadial (HS1), in the northern Indian Ocean. The observed poor ventilation during the last glaciation show that the northern Indian Ocean was a part of the glacial ocean aged carbon pool. Improved ventilation during the Bølling-Allerød (B-A) is consistent with rapid resumption of Atlantic overturning circulation and inflow of North Atlantic Deep Water (NADW) into the northern Indian Ocean at the onset of the B-A, which caused flushing of the deep-carbon pool with evidence of degassing from the northern Indian Ocean. This study thus supports the role of Southern Ocean in modulating atmospheric CO₂ variations during the last deglaciation.

5.2 Introduction

Deep-water being the largest reservoir of carbon at the Earth's surface, plays a very important role in modulating and regulating Earth's climate as it redistributes heat and influences the ocean-atmosphere CO₂ cycle (Sigman and Boyle, 2000). The Southern Ocean is considered to have played a crucial role in past atmospheric CO₂ fluctuations. It is known that during the northern hemispheric stadials: Heinrich Stadial 1(HS1) and Younger Dryas (YD), there was an abrupt increase in atmospheric CO₂ (Monnin et al., 2001). Along with this increase in atmospheric CO₂, there was a sudden drop in atmospheric radiocarbon activity ($\Delta^{14}\text{C}$; Hughen et al., 2006; Reimer et al., 2020).

The mechanism for such atmospheric changes still remains uncertain. One of the possible sources for this drop in atmospheric $\Delta^{14}\text{C}$ is assumed to be enhanced upwelling of ¹⁴C depleted CO₂-rich water from the Southern Ocean during the last deglaciation (Marchitto et al., 2007; Anderson et al., 2009; Skinner et al., 2010; Burke and Robinson, 2012; Skinner et al., 2015). According to this so-called 'Southern Ocean upwelling' hypothesis, during the last glaciation, the air-sea exchange in the Southern Ocean decreased, which led to the isolation of deep water from the upper ocean and resulted in greater carbon storage in the glacial deep waters (Skinner et al., 2010; Burke and Robinson, 2012; Skinner et al., 2015; Ronge et al., 2016; Sikes et al., 2016). Continuous decay of radiocarbon due to restricted interaction with the atmosphere caused ¹⁴C depletion in these isolated waters. Retreat of Antarctic sea-ice and southwardly shift of polar westerlies (Toggweiler et al., 2006) during the deglaciation led to enhanced upwelling of these old, carbon-rich deep waters and released the ¹⁴C depleted CO₂ into the atmosphere (Anderson et al., 2009; Skinner et al., 2010).

Previous deep-water studies from the Atlantic and Pacific have suggested that glacial deep waters were ¹⁴C depleted (i.e. poorly ventilated) (Skinner and Shackleton, 2004; Galbraith et al., 2007; Barker et al., 2010; Burke and Robinson, 2012; Skinner et al., 2014). Studies from the intermediate water depths have shown an existence of poorly ventilated water mass in the Southern Ocean during the LGM, which was transported to the other oceans via the Antarctic Intermediate water mass (Marchitto et al., 2007; Bryan et al., 2010; Siani et al., 2013; Freeman et al., 2015; Ma et al., 2019). Such evidences from the Indian Ocean providing the Southern Ocean's role in atmospheric ¹⁴CO₂ fluctuations are few (Naik and Nisha, 2020). The Indian Ocean being solely ventilated from the south because of no deep-water formation, could be a suitable location to deduce the role of the Southern Ocean

on past atmospheric CO₂ variability.

The intermediate waters from the Indian Ocean (Bryan et al., 2010; Ma et al., 2019) studies suggest the incursion of ¹⁴C-depleted Antarctic Intermediate Water (AAIW) in the Indian Ocean during the deglaciation (HS1 and YD). This ¹⁴C depletion in AAIW was because of mixing of old isolated abyssal water in south of the sub-Antarctic frontal zone. Interestingly, Naik et al. (2015) have reported outgassing of CO₂ during the last deglaciation, possibly indicating release of sequestered carbon from intermediate water to the surface. Studies from the Indian sector of the Southern Ocean have shown that the Indian Ocean was part of a glacial aged carbon pool and suggested these ¹⁴C depleted, CO₂-rich waters from the southernmost Indian Ocean contributed to atmospheric CO₂ rise during the deglaciation (Ronge et al., 2020; Gottschalk et al., 2020) albeit differing on the timing of CO₂ release within the last deglaciation. Though some studies have been carried out for deep water paleoceanographic changes in the northern Indian Ocean using stable isotope and geochemical tracers as a proxy (Kallel et al., 1988; Naqvi et al., 1994; Piotrowski et al., 2009; Ahmad et al., 2012; Singh et al., 2012; Chandana et al., 2017; Lathika et al., 2021; Bang et al., 2021), studies on radiocarbon changes in the deep water of Indian Ocean are limited (Naik and Nisha, 2020; Bharti et al., 2022). In this study, we have reconstructed ventilation changes in deep water of the northern Indian Ocean for the last 25 kyr using radiocarbon measurements from core SSD-044/GC-01.

5.3 Methodology

5.3.1 Core location

Core location (Fig. 5.1a and b) has been discussed in section 4.1, and the method of sediment core processing is provided in section 4.3.

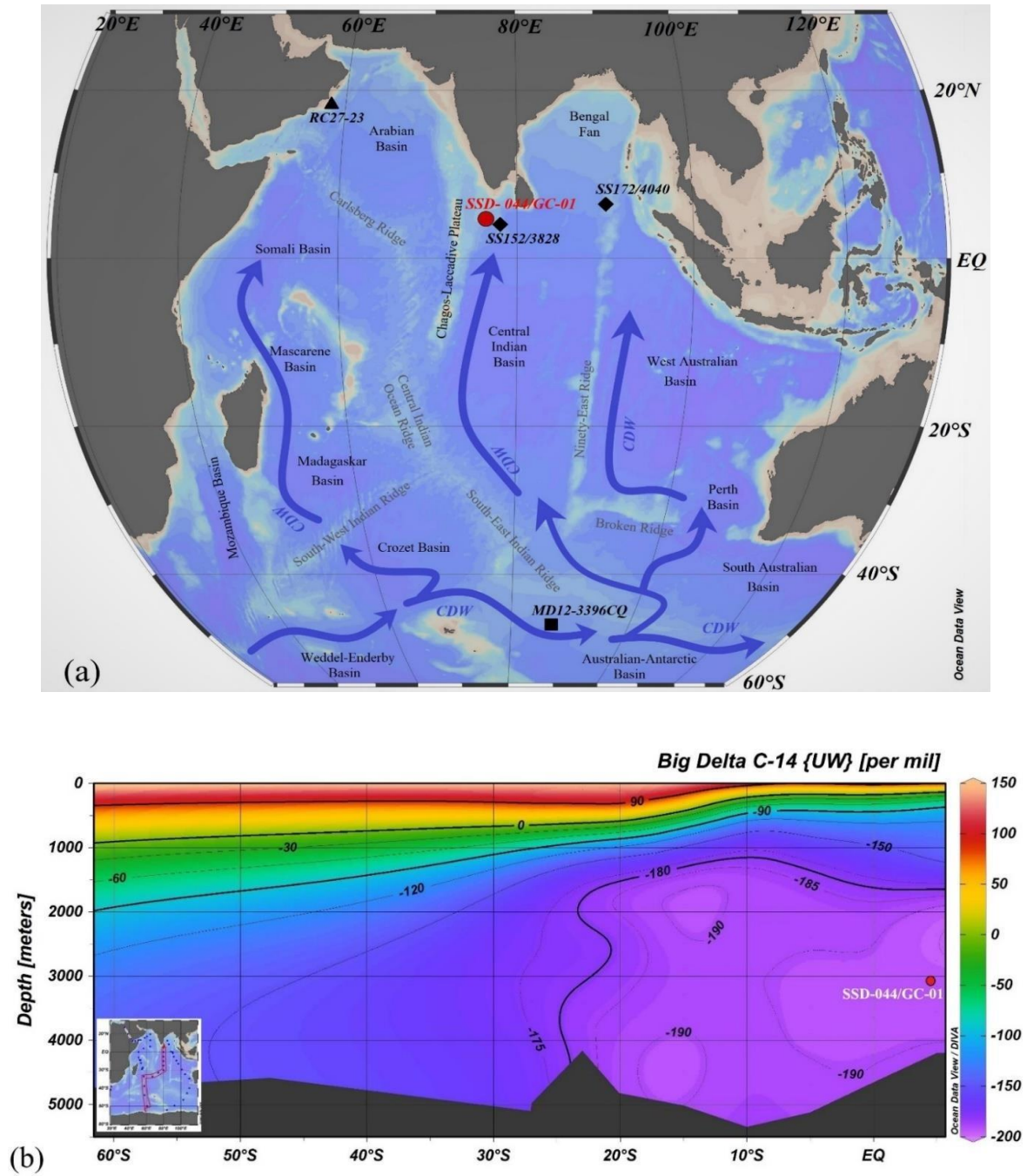


Fig. 5.1: Core location (a) Map showing location of core SSD-044/GC-01 (CEIO; 4.99° N; 76.99° E; water depth = 3160 m) along with four other cores discussed in this study (RC27-23-Bryan et al., 2020; SS152/3828 and SS172/4040-Bharti et al., 2022; MD12-3396CQ-Gottschalk et al., 2020). The deep water circulation of the northern Indian Ocean is shown with blue arrows. (b) a cross-section of the Indian Ocean with core location showing modern $\Delta^{14}\text{C}$ (GLODAPv2; Key et al., 2015; Lauvset et al., 2016). Both the plots were prepared using Ocean Data View (Schlitzer, 2021).

5.3.2 Radiocarbon measurements for age model and ventilation ages

The radiocarbon measurements are discussed in section 4.4 and within subsections of 4.4.1. Radiocarbon ages for the core SSD-044/GC-01 are summarized in Table 4.2 (Section 4.2; Fig. 5.2). Here the ventilation ages of deep water are reported as radiocarbon age which is the difference between paired bottom-dwelling benthic foraminifera and surface-dwelling planktic foraminifera (B-P) based on Broecker et al. (1984) which represents sub-surface radiocarbon age offset.

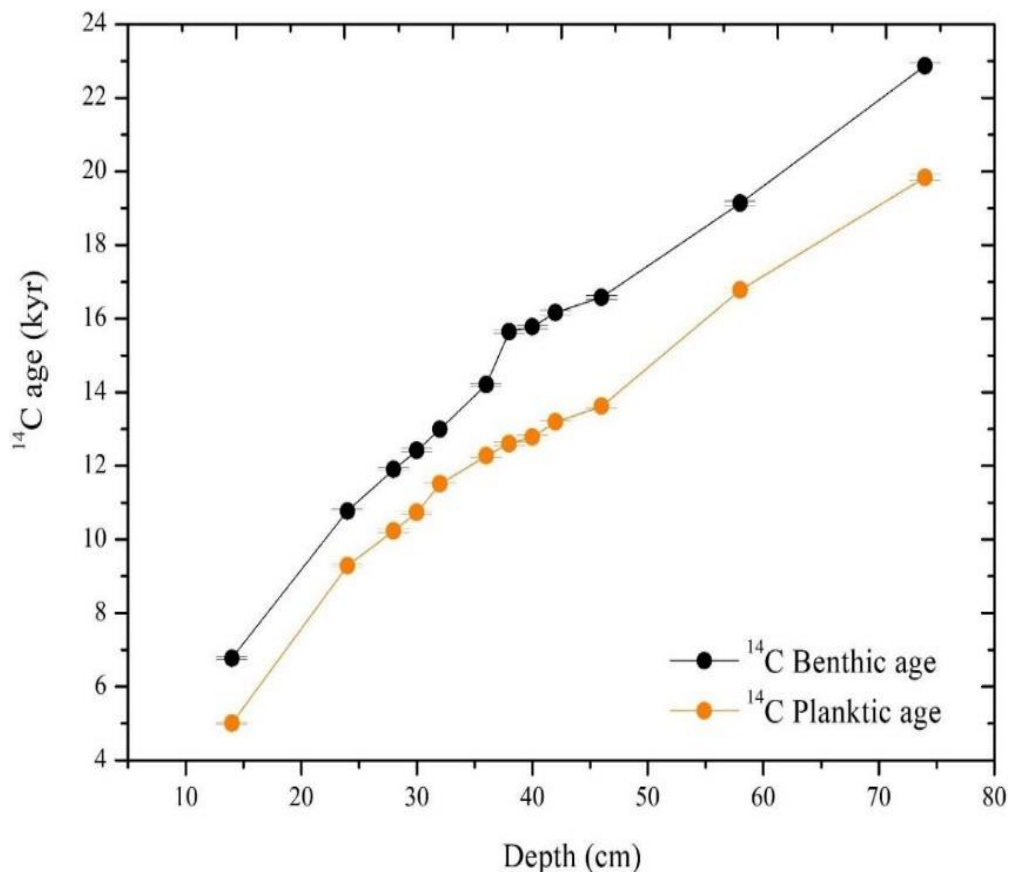


Fig. 5.2: Measured radiocarbon ages of paired benthic and planktic foraminifera versus depth in the core SSD-044/GC-01. ^{14}C age of benthic foraminifera (black circles), ^{14}C age of planktic foraminifera (orange circles).

5.3.3 Age Model

Age model for the top 100 cm of the core has been discussed in section 4.2. Fig. 5.3 shows the sedimentation rate of the core SSD-044/GC-01.

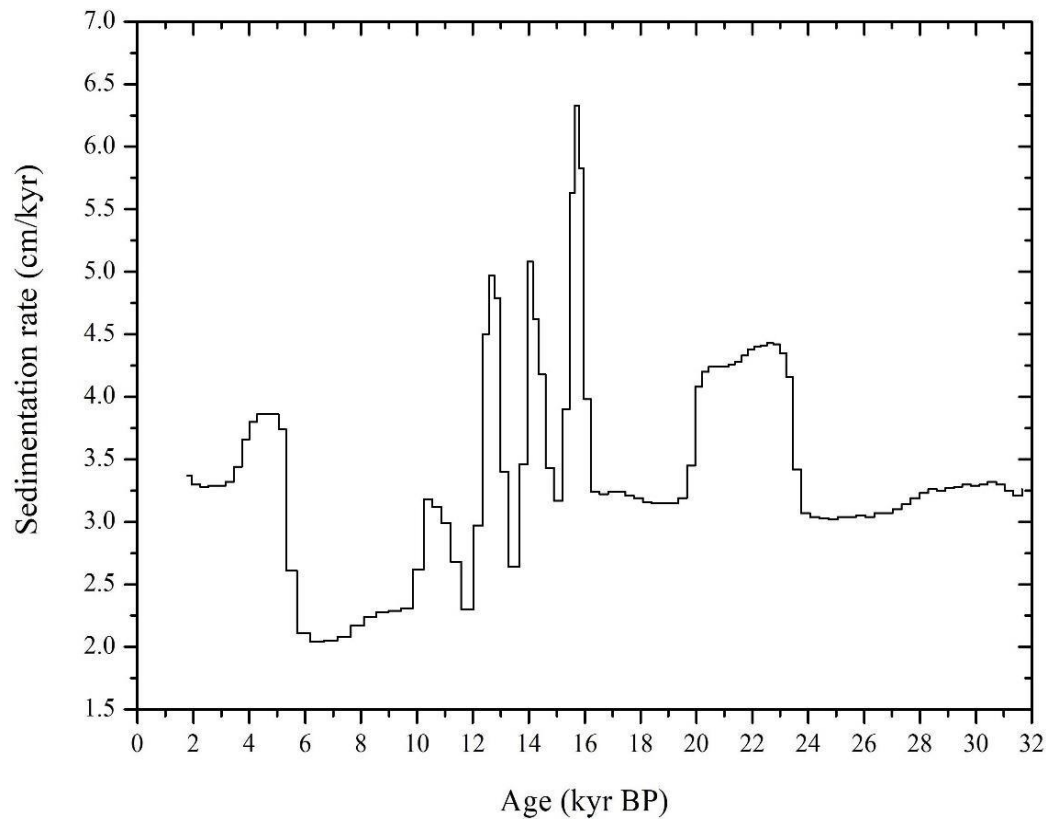


Fig. 5.3: Sediment accumulation rate (cm/kyr) plotted versus age in kyr BP.

5.3.4 Total Inorganic Carbon (TIC)

The TIC determination method is discussed in section 4.6.

5.3.5 Stable Carbon and Oxygen Isotope

The method for determination of carbon and oxygen stable isotopes is discussed in section 4.5.

5.3.6 Coarse Fraction

The method for determination of coarse fraction is discussed in section 4.11.

5.4 Results

The reconstructed ventilation ages for deep waters suggest that there have been significant changes in deep-water ventilation during the last 25 kyr (Fig. 5.4). The apparent age difference between coexisting benthic and planktic foraminifera was ~ 2500 to 3000 ^{14}C

years during the LGM (~24 -17.5 kyr) indicating poorly ventilated water at the core location. The ventilation age remained high during the HS1 (~17.5-14.5 kyr) and was around 3000 ^{14}C years, indicating lowered radiocarbon activity of deep water. At the start of the Bølling-Allerød (B-A; ~14.5-12.8 kyr), there was an abrupt reversal in the ventilation age of deep water. The ventilation age significantly decreased to as low as ~1500 ^{14}C years indicating better ventilated deep water at that time. During the YD (~12.8-11.5 kyr) there was a small increase of ~300 ^{14}C years in the ventilation age, which further showed a decrease during the Holocene and was ~1500 ^{14}C years, indicating relatively better ventilation of water.

The B-Atm ventilation age show similar trend to the B-P ventilation age. The ventilation age at the core site ranged from 1600- 3300 years. During the LGM, the difference between the radiocarbon activity of the benthic foraminifera and the atmosphere was ~2944 years. The B-Atm ventilation age reached maximum during the HS1. At the onset of B-A, there was decrease in the ventilation ages. The B-Atm continued to decrease from ~14.5 kyr onwards with the lowest value during the Holocene. Since both B-P and B-Atm ventilation age shows a similar trend, only the B-P ventilation age is taken for further discussion.

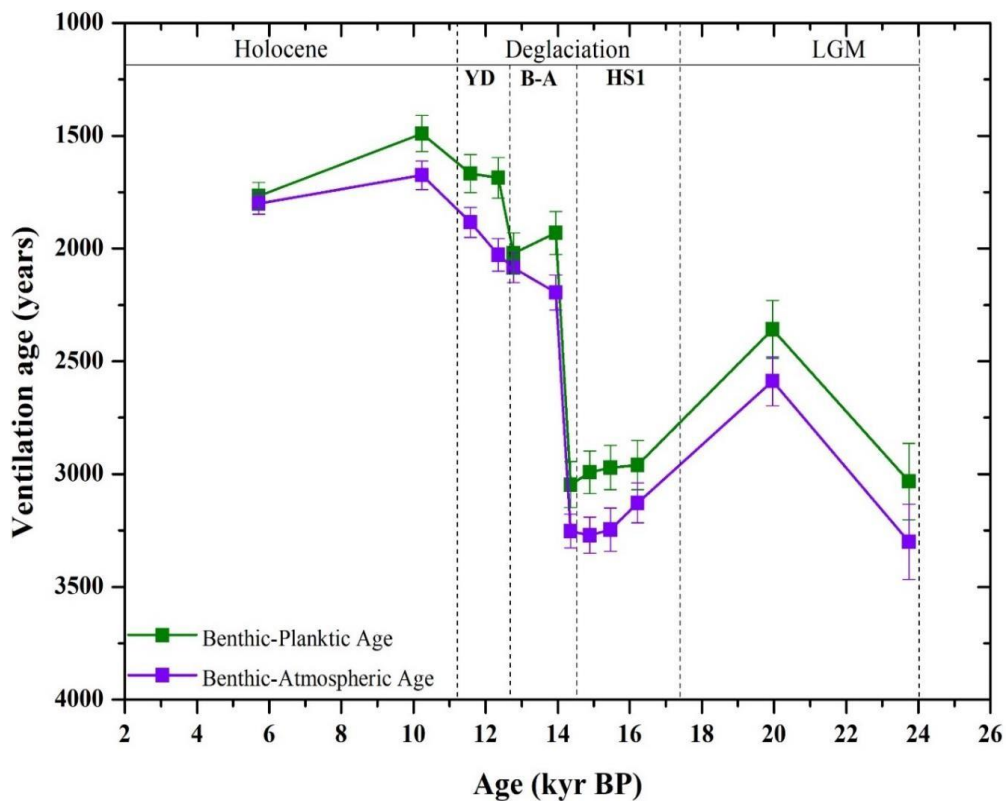


Fig. 5.4: Graph showing changes in ventilation ages for the core SSD-044/GC-01 in the equatorial Indian Ocean during the last 26 kyr. Ventilation ages are plotted as benthic-planktic foraminifera radiocarbon age difference (B-P; green square) and benthic-

contemporaneous atmosphere radiocarbon age difference (B-Atm; purple square). The vertical error bars for B-P and B-Atm ventilation ages are the sum of the $\pm$ error of the planktic and benthic foraminifera and the sum of the $\pm$ error of the contemporaneous atmospheric and benthic foraminifera respectively. Climatic events such as LGM, deglaciation (HS1, B-A, YD) and Holocene are marked.

Calcium carbonate content of sediment complements the radiocarbon data (Fig. 5.5b). In glacial sediments, the average CaCO_3 was $\sim 53\%$, showing lower values at the beginning of LGM and an increase towards the end of it. At the beginning of deglaciation, CaCO_3 began to decline, reducing to $\sim 54\%$ during the HS1. During the B-A, there was a sudden increase in CaCO_3 content, which further reached up to $\sim 62\%$ at ~ 12 kyr. Thereafter CaCO_3 content declined into the Holocene with an increase during the late Holocene.

Stable carbon isotopic ($\delta^{13}\text{C}$) records of benthic foraminifera *Cibicidoides wuellerstorfi* showed an increasing trend from the LGM to the Holocene (Fig. 5.5c). Stable carbon isotopic values range from -0.6‰ to 0.4‰ for the last 25 kyr. The $\delta^{13}\text{C}$ values remained low at $\sim -0.4\text{‰}$ during the LGM and HS1. There was a gradual rise in $\delta^{13}\text{C}$ values through the B-A and YD. This was followed by a short drop and then an increase during the Holocene with values reaching up to $\sim 0.4\text{‰}$ at 4 kyr, followed by a slight drop in the late Holocene. The oxygen isotopic ($\delta^{18}\text{O}$) values showed a decreasing trend from the LGM to the Holocene (Fig. 5.5d). The $\delta^{18}\text{O}$ values fluctuated between 4.4‰ and 2.6‰ for the last 25 kyr. Maximum $\delta^{18}\text{O}$ values were recorded during LGM and HS1. The $\delta^{18}\text{O}$ values decreased at the B-A, decreased further at the YD and then gradually decreased through the Holocene.

The percentage of CF ranged from $\sim 12\text{--}24\%$ (Fig. 5.5e). The major component of the coarse fraction was biogenous remains with almost no lithogenous fraction for the last 25 kyr. The CF % was low during the LGM and HS1. Coarse fraction started to increase from the B- A into the YD, and showed a gradual decrease during the Holocene.

5.5 Discussion

5.5.1 Deep water ventilation changes in the northern Indian Ocean

Reconstruction of deep water ^{14}C ventilation age along with benthic stable carbon and oxygen isotope, CaCO_3 , and coarse fraction data from the core SSD-044/GC-01 imply changes in deep water ventilation/source for the last 25 kyr. The difference between benthic-planktic ^{14}C age was higher ($\sim 2500\text{--}3000$ ^{14}C years) during the LGM than in the modern ocean (Fig. 5.5a). These high ventilation ages during the LGM indicate a strong stratification between the upper and deep water masses, and hence poor ventilation existing during that time. We suspect that this poorly ventilated water at our core site originated from a glacially isolated deep-water mass. Studies from the Indian Ocean have suggested that during the LGM, the export of northern sourced water into the Indian Ocean was reduced and was compensated by an increased flow of southern sourced water (Curry et al., 1988). Neodymium (Nd) isotope and ventilation age records of deep water masses in the northern Indian Ocean have also shown a reduced flow of NADW and an increased penetration of nutrient and CO_2 -rich southern sourced water during the LGM (Piotrowski et al., 2009; Lathika 2021; Bang et al., 2021; Bharti et al., 2022). Results from a modelling study suggests the LGM ocean circulation state was characterized by a weak (10–15 Sv) and relatively shallow (2000–2500 m) NADW cell, and a reduced AABW transport (Menviel et al., 2017). A weaker AABW formation rate at the LGM could result from the presence of grounded ice over today's main AABW formation regions such as the Ross and Weddell Seas, and/or weakened or equatorward shifted Southern Hemispheric Westerlies (Menviel et al., 2017). The overall reduced oceanic ventilation at the LGM thus enhanced the efficiency of the oceanic biological pump by enhancing the storage of respired carbon in the ocean interior without causing anoxia (Galbraith and Jaccard, 2015; Menviel et al., 2017). Therefore, reduced deep ocean ventilation during the glaciation would contribute to lowering atmospheric CO_2 , with important implications for past carbon cycle and climate changes (Skinner et al., 2017). Zhang et al. (2022) state that the persistent northward inflow of CDW with corrosive Pacific waters contribution must have been responsible for the ventilation of the deep Indian Ocean during the glacial. Thus majority studies infer presence of CO_2 -rich, poorly-ventilated deep-water mass during the glacial, which probably filled the deeper parts of the Indian Ocean.

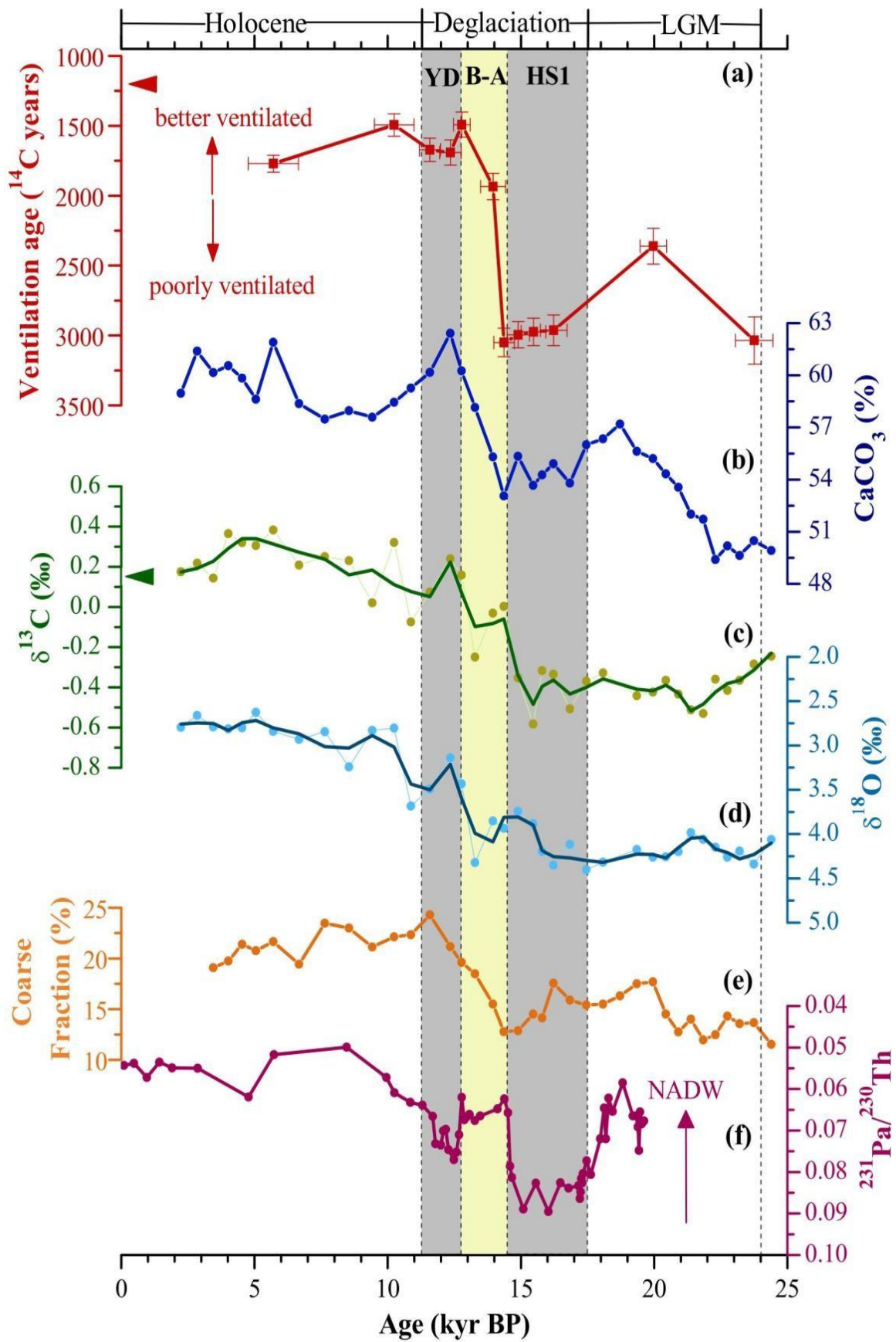


Fig. 5.5: Graph showing changes in deep water circulation in the northern Indian Ocean during the last 25 kyr. (a) Ventilation ages (red square) which are plotted as benthic-planktic

foraminifera radiocarbon age difference from core SSD-044/GC-01. The vertical error bars are the sum of the $\pm$ error of the planktic and benthic foraminifera. The horizontal error bars signify the 1σ depth errors. The red arrow indicates the modern ventilation age. (b) Calcium carbonate content in the sediment core SSD-044/GC-01. (c) Stable carbon isotopic data. The green arrow indicates the modern $\delta^{13}C_{DIC}$. (d) stable oxygen isotopic data of benthic foraminifera *Cibicidoides wuellerstorfi* from core SSD-044/GC-01. (e) Coarse fraction % ($>63 \mu m$) in core SSD-044/GC-01, and (f) sedimentary $^{231}Pa/^{230}Th$ in core GGC5 (McManus et al., 2004). Climatic events such as Last Glacial Maxima (LGM), Heinrich Stadial 1 (HS1), Bølling-Allerød (B-A) and Younger Dryas (YD) events are marked by dashed black lines and are shaded.

Variations in $CaCO_3$ content complement our radiocarbon data (Fig. 5.5b). Low values of $CaCO_3$ are recorded during the LGM, which could either be because of low surface productivity, dilution by terrigenous influx, or dissolution at the sea floor. Yadav et al. (2021) have reported high surface productivity during the LGM from the same core, and hence low $CaCO_3$ content at the core site is not driven by productivity. Dilution can be a factor for this low $CaCO_3$, but the low sedimentation rate during the LGM does not support dilution as an important factor (Fig. 5.5c). Calcium carbonate data is consistent with the coarse fraction record from the same core (Fig. 5.5e). Low coarse fraction along with low $CaCO_3$ during the LGM indicates decreased preservation and increased dissolution, implying low bottom-water CO_3^{2-} concentration and hence CO_2 -enriched water prevailing at that time. Thus high ventilation age and low $CaCO_3$ suggest less ventilated (as compared to the modern ocean), CO_2 -rich glacial water prevailed in the northern Indian Ocean.

The $\delta^{13}C$ values of benthic foraminifera can be used as a tracer of deep water circulation, complementary to ^{14}C ventilation ages. Benthic foraminifer's carbon isotopic records from the northern Indian Ocean have shown significant changes in deep water chemical characteristics since the last glaciation (Kallel et al., 1988; Ahmad et al., 2012). During the LGM, low $\delta^{13}C$ values of ~ -0.4 ‰ were recorded in our core (Fig. 5.5c), indicating incursion of nutrient-rich and poorly ventilated water. This low $\delta^{13}C$ is consistent with previously published records from the northern Indian Ocean which have been interpreted as reduced export of NADW, which was compensated by increased export of nutrient-rich southern sourced water in the Indian Ocean (Duplessy et al., 1984; Naqvi et al., 1994; Ahmad et al., 2012; Raza et al., 2014). The glacial-interglacial $\delta^{18}O$ shift of ~ 1.4 ‰ (difference

between the $\delta^{18}\text{O}$ average of LGM and early Holocene) exceeds the ice volume change by 0.4‰, which indicates cooler deep waters during the LGM (Fig. 5.5d). Hence, high $\delta^{18}\text{O}$ values during the LGM can be linked to an increased inflow of cold southern sourced deep water masses into the northern Indian Ocean. Thus lowered $\delta^{13}\text{C}$ and high $\delta^{18}\text{O}$ support the reduced flow of northern-sourced deep waters, countervailed by glacial-aged southern sourced ^{14}C depleted waters at the core site. There is also a mismatch between the trend in ventilation ages and $\delta^{13}\text{C}$, at ~ 20 kyr (Fig. 5.5a and c). Though we see a drop in ventilation age of ~ 500 yrs, the $\delta^{13}\text{C}$ remain almost unchanged. This could occur due to increasing air-sea disequilibrium of carbon isotopes with lowered $p\text{CO}_2$. Under low atmospheric $p\text{CO}_2$ conditions of the glacials, $\Delta^{14}\text{C}$ is known to increase, and surface reservoir age to increase by ~ 250 yrs throughout the world ocean (Galbraith et al., 2015).

Poorer ventilation (high ventilation ages) of deep waters during the last glaciation in comparison to the modern, has been noted by other studies in the Indian Ocean (Gottschalk et al., 2020; Bharti et al., 2022), the Atlantic (Barker et al., 2010; Skinner et al., 2010) and Pacific Ocean (Galbraith et al., 2007; Rafter et al., 2022). High ventilation ages of the Indian Ocean along with the records from the other oceans suggest significant aging of Southern Ocean deep water (hence, ^{14}C depleted) during the glacial time. This ^{14}C depletion could be possibly the result of a decrease in the exchange of gases between the atmosphere and deep water during the LGM which led to continuous decay of ^{14}C (Skinner et al., 2010).

Similar to the LGM, deep-water ventilation in the northern Indian Ocean during the HS1 remained poor (Fig. 5.5a). This period is associated with the melting of icebergs in the North Atlantic. Massive discharge of glacial ice and more freshwater input led to the reduced formation and shoaling of the NADW and hence resulted in the weakening of AMOC at this time (Elliot et al., 2002; McManus et al., 2004). These changes in the production of NADW led to decreased export of NADW into the Atlantic (Skinner and Shackleton, 2004; Freeman et al., 2015) and Pacific Ocean (Galbraith et al., 2007). In the Indian Ocean, stable isotopic and geochemical studies suggest a decrease in the export of northern sourced water (Piotrowski et al., 2009; Ahmad et al., 2012; Bharti et al., 2022). Intermediate water studies from the Indian Ocean have pointed to an increased export of southern-sourced water into the Indian Ocean (Jung et al., 2009; Ma et al., 2019; Ma et al., 2020). Direct evidence of increased penetration of southern sourced AAIW due to reduced inflow of northern-sourced water have been reported using ^{14}C (Bryan et al., 2010) and ϵ_{Nd} (Yu et al., 2018) proxies.

Therefore, the increased ventilation ages at our core site during the HS1 suggests a reduced export of NADW into the northern Indian Ocean. This strongly suggests a greater proportion of southern sourced poorly ventilated AABW inflow as a result of NADW shoaling. The high ventilation ages are very well correlated with CaCO_3 and $\delta^{13}\text{C}$ values.

Studies from the Atlantic Ocean (Skinner and Shackleton, 2004; Robinson et al., 2005; Barker et al., 2010; Skinner et al., 2010) and Pacific Ocean (Galbraith et al., 2007; Marchitto et al., 2007) have reflected increased penetration of NADW during the B-A, since the resumption of AMOC led to extensive formation of NADW at this time (McManus et al., 2004; Böhm et al., 2015). Stable isotope data from the Indian Ocean have also shown an increase in northerly sourced better ventilated water during the B-A (Ahmad et al., 2012; Raza et al., 2014; Ma et al., 2019). In addition, Nd isotopic record points to an expansion of the NADW in the Indian Ocean (Piotrowski et al., 2009). In our study, the HS1 was followed by an abrupt decrease in deep water ventilation age (better ventilation) during the B-A (Fig. 5.5a), suggesting a major shift in deep water circulation. We suspect that this low ventilation age could be the result of intensified penetration of better ventilated northern sourced deep water at the core site. A shift in CaCO_3 to higher values was observed in the B-A with a peak in the YD, indicating better preservation of CaCO_3 suggests incursion of better ventilated water during this period (Fig. 5.5b). This is also supported by an increase in coarse fraction % beginning from the B-A (Fig. 5.5e). A marked positive shift in $\delta^{13}\text{C}$ from B-A onwards, indicates a progressive influx of nutrient-depleted and better ventilated NADW at the core site.

This increase in ventilation was followed by a short-term reduction in deep water ventilation during the YD. The ventilation age increased by ~ 300 ^{14}C years during this cold stadial. This time coincides with the partial weakening of the AMOC (McManus et al., 2004). The reduction in NADW formation was less intense compared to that during the HS1, which is why the decrease in ventilation during YD was less pronounced than HS1 at the core site. Low ventilation age along with high CaCO_3 and $\delta^{13}\text{C}$ during the Holocene indicate that the deep waters were well ventilated as compared to the LGM. Combined results of ventilation age, CaCO_3 , $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data suggest an increased export of NADW during the Holocene and less dominance of southern sourced deep water in the UCDW.

5.5.2 Redistribution of ^{14}C depleted water from the Southern Ocean

The benthic-planktic ventilation age variations seen in the Indian Oceans studies; cores SSD-044/GC-01 (this study), RC27-23 (Bryan et al., 2010), SS152/3828 and SS172/4040 (Bharti et al., 2022) are consistent with the increase in atmospheric CO_2 and atmospheric $\Delta^{14}\text{C}$ decline during the deglaciation (Fig. 5.6). Atmospheric CO_2 rose in two steps during the deglaciation, during the HS1 and the YD (Monnin et al., 2001). Rising deglacial atmospheric CO_2 levels are related to the upwelling of deep, CO_2 -rich water masses to the surface of the Southern Ocean (Broecker and Barker, 2007; Anderson et al., 2009). Vertical mixing in the Southern Ocean is a result of interference of Antarctic Circumpolar Current (ACC) with local bathymetry. At the onset of HS1, deep-ocean ^{14}C ventilation increased until 16.3 kyr, signaling a net loss of remineralized carbon from the deep ocean during that time interval as a result of reinvigorated vertical mixing (Core MD12-3396CQ; Gottschalk et al., 2020 and references therein). However, our core record does not have sufficient number of data points during the LGM and early HS1 to understand if the Southern Ocean signal was transmitted into the northern Indian Ocean. Later to ~ 16.3 kyr, ventilation age records from south of 40°S show a return to glacial-like condition, which relates to a ventilation decrease, a unique feature of the deep South Indian Ocean due to inter-basin differences (Gottschalk et al., 2020). Our ventilation ages are highest at ~ 3000 years during the HS1. This inter-basin heterogeneity abruptly dissipated at the end of HS1, when the ventilation age and oxygen characteristics of deep waters in the different ocean basins rapidly approached prebomb values for the first time throughout the deglaciation (Gottschalk et al., 2020). We find a sharp decrease in ventilation ages beginning at ~ 14.6 kyr as observed in the Southern Indian Ocean core MD12-3396CQ and deep-se corals from the Drake Passage (Southern Ocean; Burke and Robinson, 2012). The fast increase in ^{14}C and O_2 ventilation in the South Indian Ocean at the end of HS1, at ~ 14.6 kyr, is linked to a rapid resumption of Atlantic overturning at the onset of the B-A warm period, which caused homogenization of the entire South Indian water column, laterally and vertically (Gottschalk et al., 2020). The ventilation age records from the northern Indian Ocean along with atmospheric $\Delta^{14}\text{C}$ (Reimer et al., 2020) relate well to the Southern Ocean upwelling indices (Fig. 5.6d) pointing towards the Southern Ocean as the source for redistribution of aged carbon to the other oceans, and to the atmosphere (Anderson et al., 2009).

During the YD, we find a slight increase in ventilation age (poorer ventilation) in core SSD-044/GC-01 (Fig. 5.5a). In line with our observation, the South Indian Ocean was a

moderate source of carbon to the atmosphere during the YD and did not significantly contribute to the late deglacial $\text{CO}_{2,\text{atm}}$ increase (Gottschalk et al., 2020). At the end of YD, however, there was a rapid loss of carbon from the South Indian Ocean mediated by stronger Atlantic overturning and wind-driven Ekman pumping (Gottschalk et al., 2020). These authors call attention to spatial differences in timing of CO_2 release from the Southern Ocean, possibly due to lateral variations in the mode and rate of AABW formation and/or the efficiency of air-sea gas equilibration. Coinciding with the low ventilation ages in the deep waters of the Southern Ocean, aged ^{14}C has been observed in the intermediate waters of the western Arabian Sea during the HS1 and YD (Bryan et al., 2010; Fig. 5.6c). The explanation provided was the release of ^{14}C -depleted carbon from the deep ocean by renewal of upwelling and mixing in the Southern Ocean and further incorporation into thermocline and intermediate water masses of the Southern Ocean, and spread northward into the Pacific, Indian and Atlantic Ocean basins (Bryan et al., 2010). However, an outgassing of CO_2 at $\sim 14.4\text{-}14.2$ kyr concomitant to the CO_2 increase of 12 ± 1 ppm of the atmosphere has been reported from the surface water of the eastern Arabian Sea, which was reasoned to be indicative of the upwelling of a nutrient-enriched water mass of Southern Ocean origin (Naik et al., 2015; Fig. 5.6e). This observation of CO_2 outgassing during the B-A is in agreement with the increase in ^{14}C and O_2 ventilation in the South Indian Ocean linked to a rapid resumption of Atlantic overturning (Gottschalk et al., 2020). The possible link between near-identical timing of CO_2 outgassing from the eastern Arabian Sea during the B-A, the improved ventilation of deep-waters of the northern Indian Ocean during the B-A (present study), and the increase in ^{14}C and O_2 ventilation in the South.

Indian Ocean seems to be the flushing of the deep-ocean carbon pool, not only limited to the Southern Ocean, but with a wider impact, in the northern Indian Ocean. Hence our data supports the hypothesis that the Southern Ocean upwelling had a vital role in atmospheric CO_2 variation during the deglaciation (Anderson et al., 2009; Skinner et al., 2010). Furthermore, our data suggests that the northern Indian Ocean could have also contributed to the atmospheric CO_2 rise during the deglaciation (specifically the B-A).

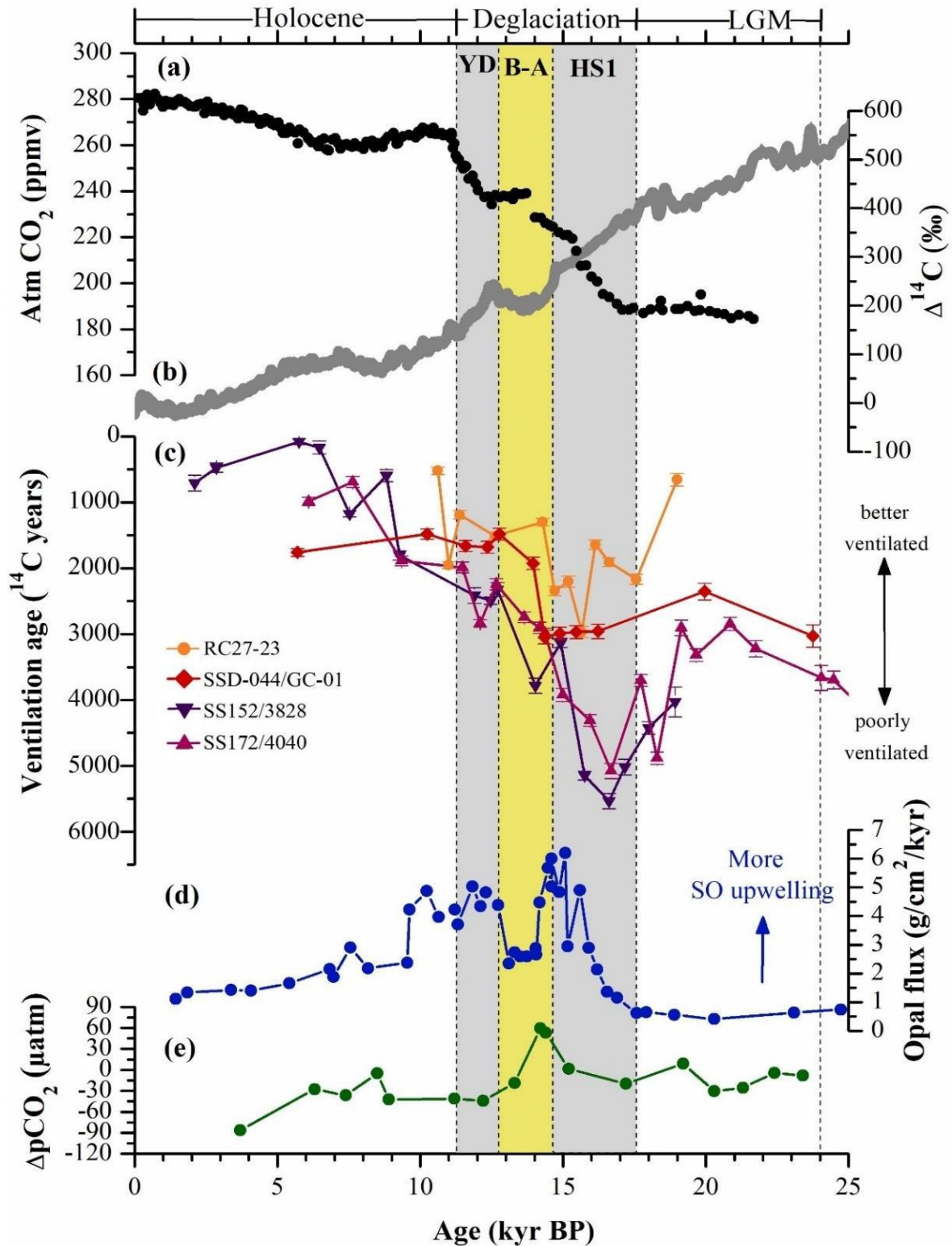


Fig. 5.6: Comparison of ventilation ages of the northern Indian Ocean to atmospheric CO_2 , atmospheric $\Delta^{14}\text{C}$, and the Southern Ocean upwelling record during the last 25 kyr. (a) Atmospheric CO_2 record (black circles; Monnin et al., 2001). (b) Atmospheric $\Delta^{14}\text{C}$ is the IntCal20 calibration curve (grey line; Reimer et al., 2020). (c) The ventilation ages of the core SSD-044/GC-01 (red diamonds), core RC27-23 (orange circles; Bryan et al.,

2020), core SS152/3828 (violet inverted triangles; Bharti et al., 2022), and core SS172/4040 (purple triangles; Bharti et al., 2022). These ventilation ages are plotted as benthic-planktic radiocarbon age differences. The vertical error bars are the sum of the $\pm$ error of the planktic and benthic foraminifera. (d) Southern Ocean opal flux indicates upwelling in the Southern Ocean (Anderson et al., 2009). (e) Outgassing of CO₂ from the surface water of the Arabian Sea (Naik et al., 2015). Climatic events Last Glacial Maxima (LGM), Henrich Stadial 1(HS1), Bølling-Allerød (B-A), and Younger Dryas (YD) events are marked by dashed black lines and are shaded.

5.6 Conclusions

The ventilation data from core SSD-044/GC-01 illustrates changes in northern Indian Ocean deep water circulation and its relation to climatic changes across the last 25 kyr. The results indicate that during the LGM and the HS1, poorly-ventilated CO₂-rich glacial water prevailed in the northern Indian Ocean. This suggests a greater proportion of southern sourced poorly ventilated AABW filled up majority of the oceans, which could be due to shoaling of the NADW. A sharp decrease in ventilation ages noticed during the B-A coincides with a rapid resumption of Atlantic overturning at the onset of the B-A warm period and an abrupt increase in well-ventilated, high-¹³C NADW flow into the Indian Ocean. Furthermore, changes in deep water ventilation are consistent with changes in atmospheric $\Delta^{14}\text{C}$ which implicates changes in carbon exchange between the deep water and atmosphere. Our results thus demonstrate the Southern Ocean's role in ventilation changes of deep waters and hence its control over the exchange of ¹⁴C between the ocean and atmosphere.

Chapter 6

Reconstruction of intermediate-water ventilation from the Eastern Arabian Sea for the last 25 kyr

6.1 Summary

Ventilation ages determined by marine radiocarbon ages are widely used to trace the past ocean circulation. The past changes in the deep ocean ventilation have been considered as a primary cause for the atmospheric carbon dioxide (CO₂) variations during the last glacial-interglacial cycle. Records of ventilation ages from the Indian Ocean have shown that the Indian Ocean was a part of a glacially aged carbon pool, yet the paths of deglacial CO₂ release are still under debate. There have been records from the equatorial Indian Ocean, Western Arabian Sea (WAS) and Bay of Bengal to support this. However, ventilation records from the Eastern Arabian Sea (EAS) are still missing. Here we have used a gravity core retrieved from the EAS (water depth 1800 m) to reconstruct ventilation changes in the intermediate waters of the northern Indian Ocean for over the last 25 kyr. The ventilation age was reconstructed from the radiocarbon age difference between the coexisting benthic and planktic foraminifera. This ventilation age along with B/Ca and $\delta^{13}\text{C}$ records of foraminiferal *Cibicidoides wuellerstorfi*; and CaCO₃ % obtained from the same core show not so well-ventilated water existed during the last glacial period. Such poor-ventilation in the EAS can be partly explained by decreased production of North Atlantic Deep Water under glacial conditions and inflow of southern-sourced water in the EAS. The ventilation improved in the EAS during and post deglaciation.

6.2 Introduction

The thermohaline circulation plays a vital role in the distribution of heat, carbon dioxide (CO₂), oxygen (O₂), and nutrients in the global ocean and thereby regulates the global climate. Nutrient-based proxy reconstructions suggest that there have been repeated changes in the North Atlantic Deep Water (NADW) flow during the glacial-interglacial cycle (Lynch-

Stieglitz et al., 2007; Curry and Oppo, 2005). During the Last Glacial Maximum (LGM; ~ 24-18 kyr), there was a weakening of the Atlantic Meridional Overturning Circulation (AMOC), which resulted in the reduction in formation of the NADW (McManus et al., 2004). The last glacial termination was marked by the resumption of AMOC. This was followed by abrupt changes in the AMOC during the last deglaciation. During northern hemispheric stadials: Heinrich Stadial (HS1; 17.5-14.5 kyr) and Younger Dryas (YD; 12.8-11.2 kyr), large freshwater fluxes into the North Atlantic interrupted the AMOC and resulted in a decrease in the production of NADW (Elloit et al., 2002; McManus et al., 2004).

These changes in the thermohaline circulation were accompanied by variations in the atmospheric CO₂ during the last glacial-interglacial period. It is known from studies that Southern Ocean had played a major role in these atmospheric variations during the last deglaciation as it is highly recognized that the deep-water of the Southern Ocean plays a major role in modulating the atmospheric carbon dioxide (Marchitto et al., 2007; Anderson et al., 2009; Barker et al., 2010; Skinner et al., 2010; Burke and Robinson, 2012; Skinner et al., 2015; Skinner et al., 2017; Nisha et al., 2023). During the last glaciation, there was an extensive sea-ice cover and density stratification in the Antarctic, which caused the isolation of the Southern Ocean deep water from the atmosphere (Stephens and Keeling, 2000; Fischer et al., 2007; Schmittner and Galbraith, 2008). The intensity of upwelling of the deep waters of the Southern Ocean also depends upon the position of the Southern Hemisphere westerly winds. During the last glaciation, there was a northward shift of these westerly winds (Toggweiler et al., 2006). All these factors led to a carbon-rich and radiocarbon-depleted deep-water mass. Upwelling of this isolated deep-water with depleted radiocarbon has been suggested as a potential reason for the enhanced release of CO₂ and decrease in atmospheric radiocarbon activity.

Notably, a lot of studies have been carried out from the Atlantic, Pacific and Southern Oceans to understand the last glacial-interglacial circulation changes in the ocean. Ventilation records from the Indian Ocean are largely missing even though it plays an important role in the thermohaline circulation in terms of deep water ventilation. Previous stable isotopes and geochemical tracer records have reported changes in deep-water circulation in the northern Indian Ocean (Kallel et al., 1988; Naqvi et al., 1994; Piotrowski et al., 2009; Ahmad et al., 2012; Chandana et al., 2017; Naik and Naik, 2022). Neodymium isotope (ϵ_{Nd}) records of deep water masses in the Indian Ocean from previous studies have also shown changes in the

NADW export (Piotrowski et al., 2009; Naik et al., 2019; Lathika et al., 2021; Bang et al., 2021). Recent boron-to-calcium ratios (B/Ca) have suggested the existence of stored CO₂ in deep waters of the Eastern Arabian Sea (EAS) during the last glaciation. Intermediate water studies using ¹⁴C (Bryan et al., 2010; Ma et al., 2019) and ϵ_{Nd} (Jung et al., 2009; Yu et al., 2018; Ma et al., 2019) give direct evidence of increased penetration of southern-sourced Antarctic Intermediate Water (AAIW) into the Indian Ocean. Limited studies have been done from the northern Indian Ocean to reconstruct the past ventilation ages using radiocarbon dates (Bryan et al., 2010; Ma et al., 2019; Bharti et al., 2022; Nisha et al., 2023; Raddatz et al., 2023), with a lesser focus on the Arabian Sea. The Arabian Sea is landlocked to the north, and the intermediate and deep water is mainly sourced from the south, apart from the Persian Gulf and the Red Sea, making it a suitable site for the study of ventilation changes. There has been a record from the Western Arabian Sea (WAS; Bryan et al., 2010), but there is no such radiocarbon-based ventilation record from the EAS up until now. To improve our understanding of the circulation changes in the Indian Ocean, in this study we have investigated the ventilation dynamics for the last 25 kyr in a sediment core collected from the EAS.

6.3 Methodology

6.3.1 Core location

The core location (Fig. 6.1) has been discussed in section 4.1.

6.3.2 Age Model

The age model is discussed in section 4.2. Fig 6.2 shows the age-depth model and sedimentation rate of the core AAS-9/21.

6.3.3 Ventilation age

Here, the ventilation age for the sediment core is calculated by two methods. In one of the methods, the ventilation age is calculated as the difference between the Accelerator Mass Spectrometry (AMS) radiocarbon ages of coexisting planktonic and benthic foraminifera (Broecker et al., 1984). Discussed in section 4.4 and subsection 4.4.2.

In the other method, the reconstructed ventilation age is the difference between the radiocarbon age of the benthic foraminifera and the contemporaneous atmosphere.

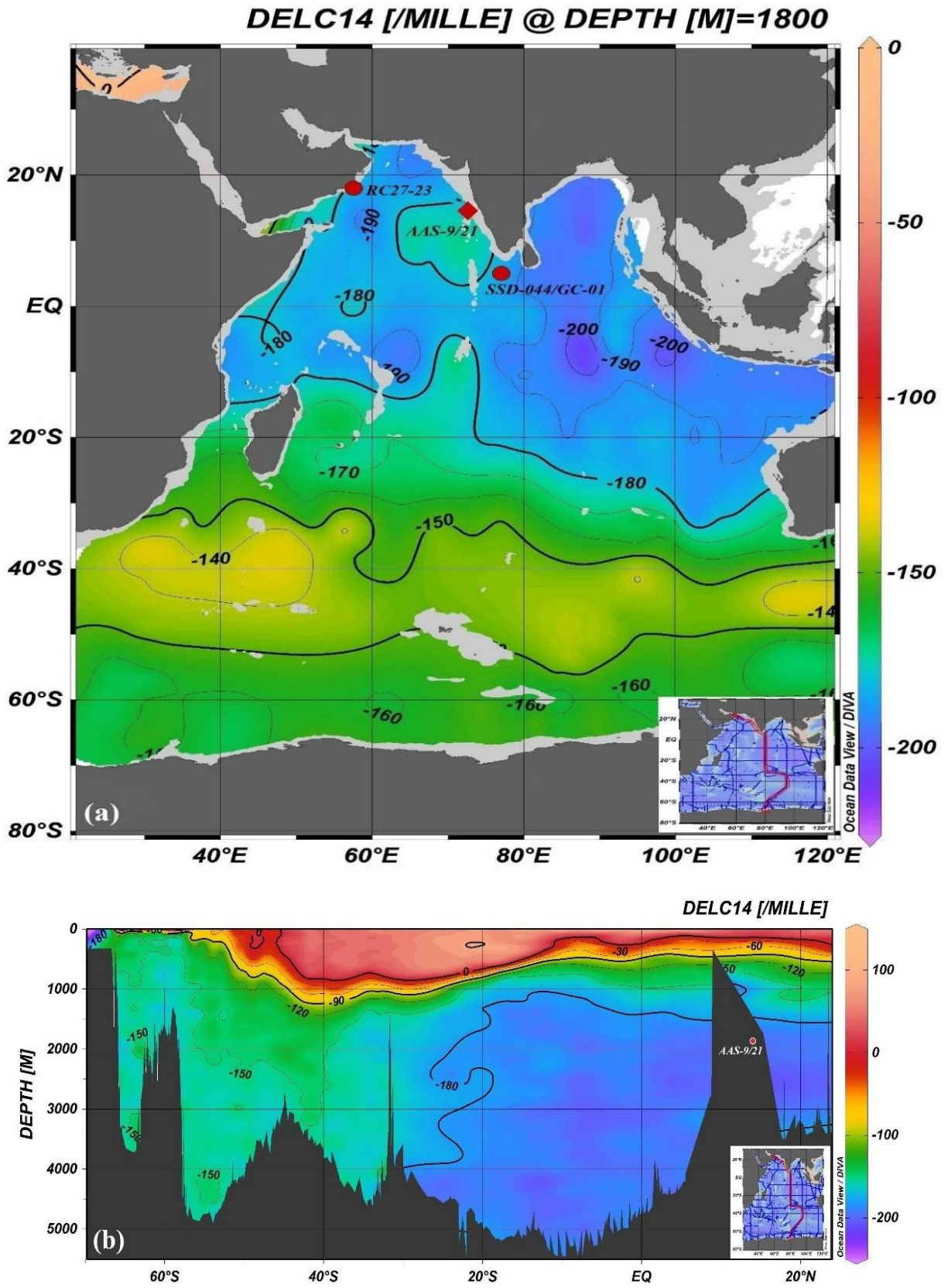


Fig. 6.1: Core location (a) Map showing location of the studied core AAS-9/21 (EAS; 14° 30' N; 72° 39' E; water depth = 1800 m) along with two other cores discussed in this study (RC27-

23-Bryan *et al.*, 2010; SSD-044/GC-01- Nisha *et al.*, 2023) along with the $\Delta^{14}\text{C}$ in the northern Indian Ocean at a depth of 1800 m. (b) A cross-section of the Indian Ocean with core location showing modern $\Delta^{14}\text{C}$ (GLODAPv2; Key *et al.*, 2015; Lauvset *et al.*, 2016). Both the plots were prepared using Ocean Data View (Schlitzer, 2021).

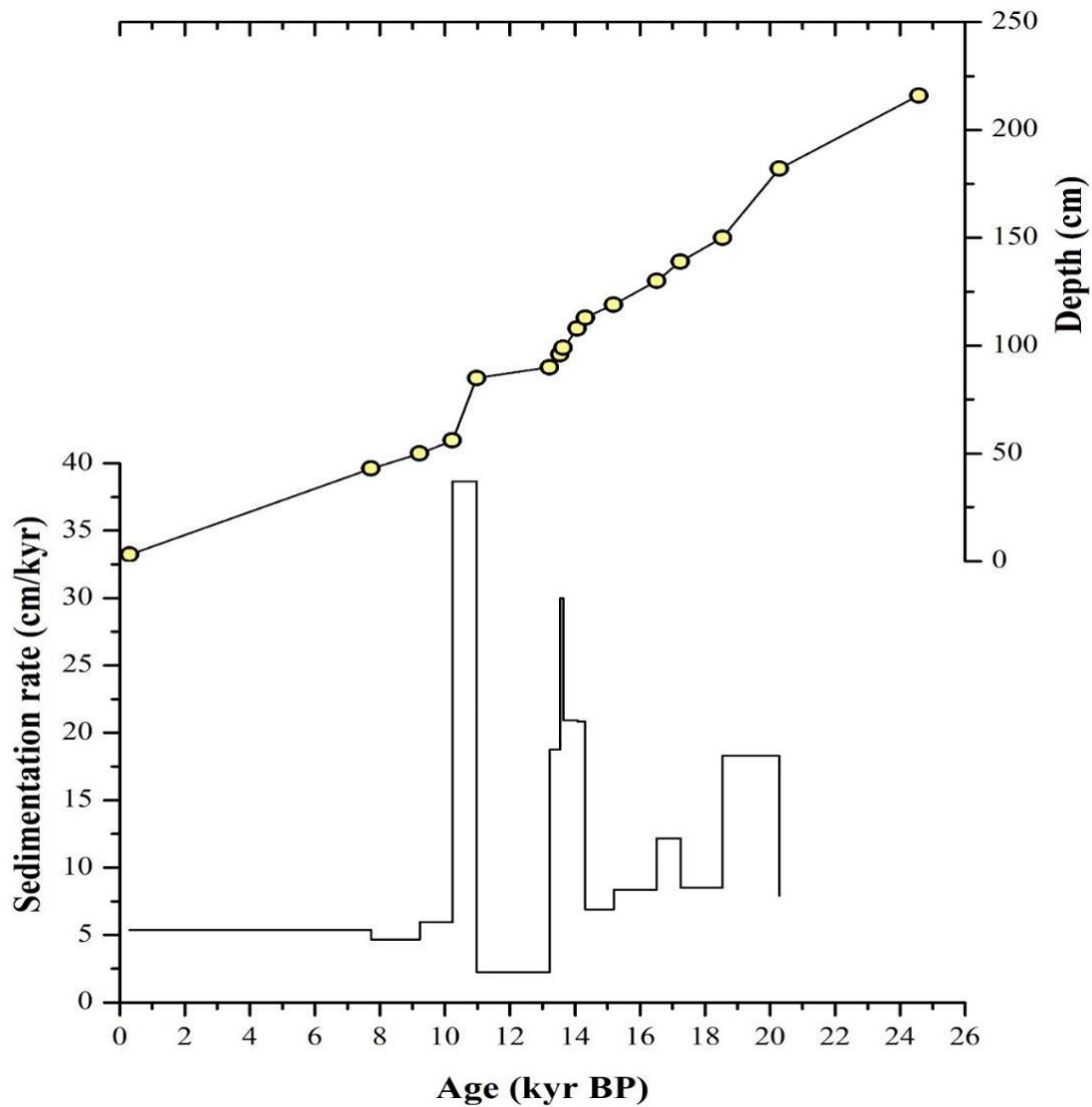


Fig. 6.2: (a) Age-depth model of core AAS-9/21. (b) Sedimentation rate (in cm/kyr) versus age (kyr BP).

6.4 Result

The apparent ventilation age (expressed as ^{14}C years) of core AAS-9/21 from the EAS has been estimated using two methods, one with the difference between the paired benthic and planktic foraminifera radiocarbon ages (B-P; Broecker et al., 1984), and another using radiocarbon age offsets between the benthic foraminifera and the contemporaneous atmosphere (B-Atm; Soulet et al., 2016). As shown in the Fig. 6.3a and b, the maximum offset between the radiocarbon ages of the coexisting benthic and planktic foraminifera was during the LGM, reaching an average of ~ 1400 years. The reconstructed B-P ventilation age decreased from ~ 1400 years to ~ 980 years between the LGM and the start of deglaciation. The radiocarbon age difference between the paired benthic-planktic foraminifera fluctuated around ~ 200 years throughout the deglaciation. During the Holocene, the ventilation age decreased to 400 years. The B-Atm ventilation age was also high during the last glaciation, with a maximum offset of ~ 2500 years between the benthic foraminifer and contemporaneous atmosphere. Consistent with our B-P ventilation age, the B-Atm ventilation age decreased by the end of the last glaciation and a low ventilation age (~ 1550 years) was recorded throughout the deglaciation. During the Holocene, lower values (as low as ~ 890 years) of B-Atm were observed at the core site. Qualitatively, there is not much difference between the two methods used here (i.e., B-P and B-Atm ventilation age) for the ventilation age reconstruction. Both methods indicate a high ventilation age during the last glaciation, followed by a rapid decrease in the ventilation ages during the deglaciation, and subsequently better-ventilated water during the Holocene. Therefore, only the B-P ventilation age is considered for further discussion.

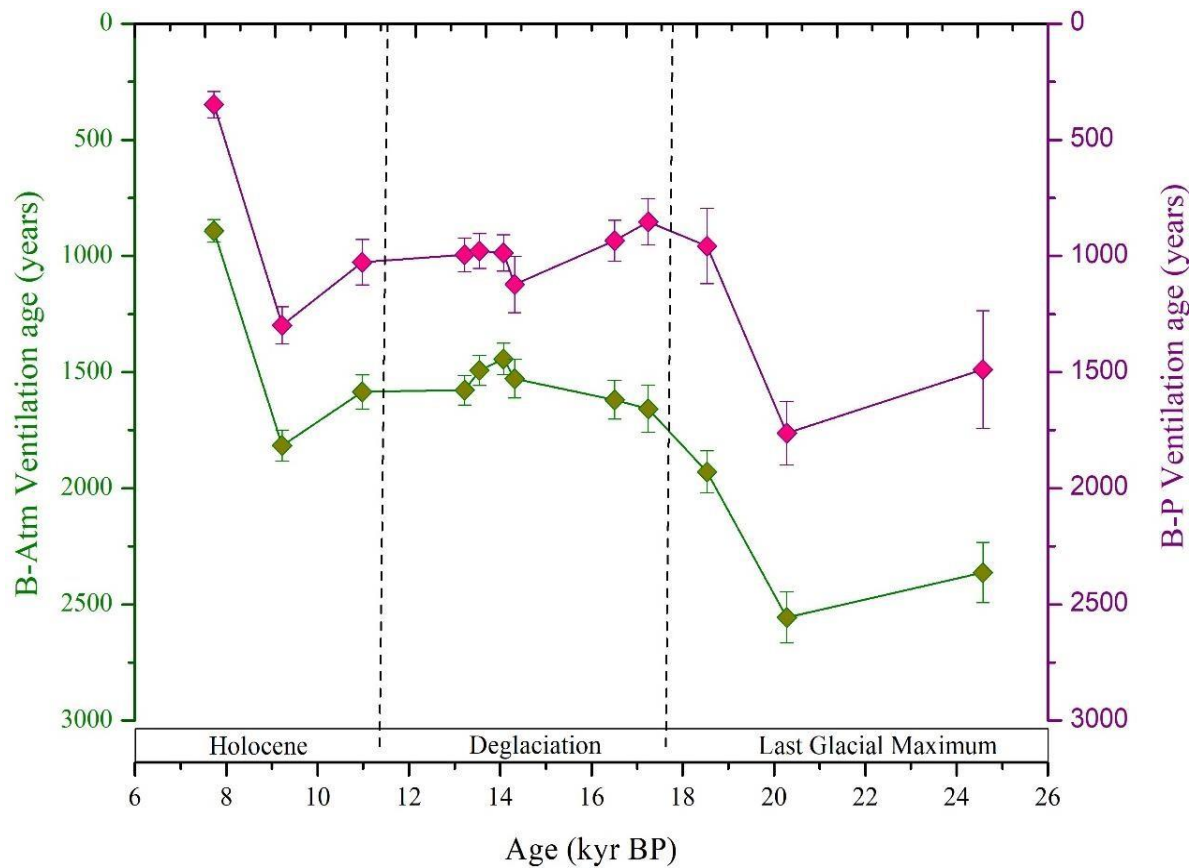


Fig. 6.3: Graph showing changes in ventilation ages for the core AAS-9/21 in the Eastern Arabian Sea during the last 25 kyr. Ventilation ages are plotted as (a) benthic-planktic foraminifera radiocarbon age difference (B-P; pink diamonds). The vertical error bars are the sum of the $\pm$ errors of the planktic and benthic foraminifera; (b) benthic-contemporaneous atmospheric radiocarbon age difference (B-Atm; green diamonds) for the core AAS-9/21. The vertical error bars are the sum of the $\pm$ error of the contemporaneous atmospheric and benthic foraminifera. Climatic events such as LGM, deglaciation and Holocene are marked.

6.5 Discussion

6.5.1 Last glacial to interglacial variations in the intermediate water ventilation

Reduced ventilation during the LGM

The ventilation record of the core AAS-9/21 indicates that the maximum offset between coexisting benthic and planktic foraminifera radiocarbon age was during the last glaciation (Fig. 6.4a). This high apparent age difference between the radiocarbon age of

benthic and coexisting planktic foraminifera indicates that the water in the EAS was not so well-ventilated during the last glaciation compared to today. The B-P ventilation age at the core site is around ~ 1500 ^{14}C years, however, in comparison studies at > 2000 m depth from the northern Indian Ocean show a B-P offset of 3000 ^{14}C years or greater (Bharti et al., 2022; Nisha et al., 2023). Therefore, the deeper cores show poor ventilation compared to the studied core site. During the same interval, the carbonate ion concentration ($[\text{CO}_3^{2-}]$; Naik et al., 2023; Fig. 6.4b); calcium carbonate (CaCO_3 ; Godad et al., 2017; Fig. 6.4c) and stable carbon isotope ($\delta^{13}\text{C}$; Naik and Naik, 2022; Fig. 6.4d) were also low as per the previous studies from the same core. The $[\text{CO}_3^{2-}]$ was around ~ 70 $\mu\text{mol/kg}$ during the last glaciation, with CaCO_3 content of ~ 30 %. The lowest $\delta^{13}\text{C}$ value which was around -0.27 ‰ was observed during the LGM. This low $[\text{CO}_3^{2-}]$, CaCO_3 and $\delta^{13}\text{C}$ indicate that the water in the EAS contained stored CO_2 during the LGM (Naik et al., 2023).

The studied core AAS-9/21 is presently ventilated by the NIDW, which is a southward flowing water mass in the northern Indian Ocean. Different authors also refer to it as Modified North Atlantic Deep Water (MNADW; Shetye et al., 1994) and High Salinity Deep Water (HSDW; Kumar and Li, 1996). It is formed from a mixture of upwelled CDW, AAIW, RSW, and PGW, where CDW is a mixture of NADW and AABW. The NIDW is characterised by better ventilated, high $[\text{CO}_3^{2-}]$ and has significant proportion of NADW. Therefore, changes in NADW production would in principle lead to the changes in ventilation state at the core site. Several studies have supported the reduced formation and export of NADW during the last glaciation (McManus et al., 2004; Robinson et al., 2005). This period is associated with the weakened Atlantic Meridional Ocean Circulation (AMOC). AMOC weakened because of decreased production and shoaling of NADW (Elliot et al., 2002). These changes in production of NADW were detected in the Atlantic, Pacific as well as in the Indian Ocean. Previous studies from the northern Indian Ocean reported that during the LGM, there was a reduction in the NADW flow in the northern Indian Ocean (Ahmad et al., 2008; Chandana et al., 2017; Lathika et al., 2021; Naik et al., 2023). This reduced inflow of NADW was compensated by the enhanced northward flow of southern sourced water in the Indian Ocean during this period (Kallel et al., 1988; Piotrowski et al., 2009; Bharti et al., 2022; Nisha et al., 2023). During the LGM, the extensive sea-ice coverage over Antarctica (Stephens and Keeling, 2000; Fischer et al., 2007), density-stratification between the surface and deep water (Schmittner and Galbraith, 2008), and/or northwardly shift of westerly winds (Toggweiler et al., 2006) led to a reduction in the upwelling of the deep water and resulted in isolation of

deep water in the Southern Ocean. This isolation of the deep water lead to decay of ^{14}C , making the water poorly ventilated. Therefore, the southern sourced water was depleted in ^{14}C during the last glaciation. Several water-mass tracers have indicated that during the LGM, water below ~ 2 km depth was dominantly occupied by the southern sourced water, which had properties similar to the Antarctic Bottom Water i.e. old radiocarbon, depleted in $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}$ (Keigwin, 2004; Curry and Oppo, 2005; Howe et al., 2016). The studied core AAS-9/21 lies at the transition between the intermediate and deep water in the northern Indian Ocean, reduced production of NADW may have led to an increased contribution of southern sourced poorly ventilated deep water in the NIIDW. This increase in the ^{14}C -depleted southern sourced deep water and upward mixing of these deep waters with the overlying intermediate waters of the Indian Ocean during their pathway must, therefore, be the primary cause of the high ventilation age observed at the core site as compared to the last deglaciation and Holocene. These deep waters shoaled as they flowed northward. On their pathway to the EAS, these ^{14}C -depleted deep waters got mixed with the intermediate waters, which decreased the ^{14}C of intermediate waters. But, in comparison to the deep waters, the ventilation age of the intermediate waters remained lower during the LGM.

Boron to calcium ratio is a proxy to quantify the $[\text{CO}_3^{2-}]$ in the respective water masses. During the last glaciation, isolated glacial deep water in the Southern Ocean accommodated respired carbon through decreased upwelling and ocean-atmosphere CO_2 exchange. Study from the northern Indian Ocean have reported this stored CO_2 deep water during the LGM (Nisha et al., 2023). At the same time, a low CaCO_3 % was recorded at the core site. The low $[\text{CO}_3^{2-}]$ and CaCO_3 during the LGM (Fig. 6.4b) supports the enhanced storage of CO_2 at the core site. The high ventilation age is supported by low $[\text{CO}_3^{2-}]$ and indicates incursion of radiocarbon-depleted and CO_2 -rich deep water, leading to the lowering of $[\text{CO}_3^{2-}]$ concentration at the core site. The $\delta^{13}\text{C}$ serves as a tracer of ocean circulation, as well as to determine the nutrient content of the deep water masses. The NADW is characterised by enriched- $\delta^{13}\text{C}$ whereas the southern sourced waters are depleted in $\delta^{13}\text{C}$. The depleted $\delta^{13}\text{C}$ -values during the LGM in the core AAS-9/21 (Fig. 6.4d) indicates high organic carbon and nutrient-enriched southern sourced water. During the last glaciation, the southern sourced deep water was enriched in organic carbon due to enhanced biological pump during the LGM (Muglia et al., 2018). Also, due to the isolation of deep water at the Southern Ocean, there was an accumulation of remineralized carbon in the deep water. This resulted in low- $\delta^{13}\text{C}$ values in the deep Southern Ocean (Ninnemann et al., 2002). This $\delta^{13}\text{C}$ -depleted and

CO₂-enriched water was transferred to the other oceans, including the northern Indian Ocean (Duplessy et al., 1984; Curry et al., 1988; Piotrowski et al., 2009; Naik et al., 2023). Previous studies based on benthic foraminifer's stable carbon isotopic from the northern Indian Ocean have also shown reduced incursion of NADW during the LGM (Ahmad et al., 2012; Raza et al., 2014; Ma et al., 2019; Naik and Naik, 2022). Ventilation ages combined with [CO₃²⁻], CaCO₃, and $\delta^{13}\text{C}$, tend to show that southern-sourced water is contributing to the changes in the ventilation of the EAS due to reduced export of NADW.

Ventilation during the last deglaciation

The early deglaciation (~ 18 kyr) was documented by the retreat of sea ice and southward shift of westerly winds, permitting the upwelling of isolated deep water (Skinner et al., 2010). This was followed by the resumption of NADW and the strengthening of AMOC during the deglaciation. At ~ 16.3 kyr, massive discharge of glacial ice and more freshwater input in the higher latitudes of the North Atlantic led to the reduced formation and shoaling of the NADW, leading to a glacial-like condition in the Southern Indian Ocean (Gottschalk et al., 2020). During the interval 12.8-11.2 kyr, there was again a decrease in the export of NADW into the Indian Ocean, but it was not as intense as during the ~ 16.3 kyr event (Nisha et al., 2023). In between these intervals, there was a period (~ 14.6 kyr) when there was an increased inflow of NADW in the Indian Ocean.

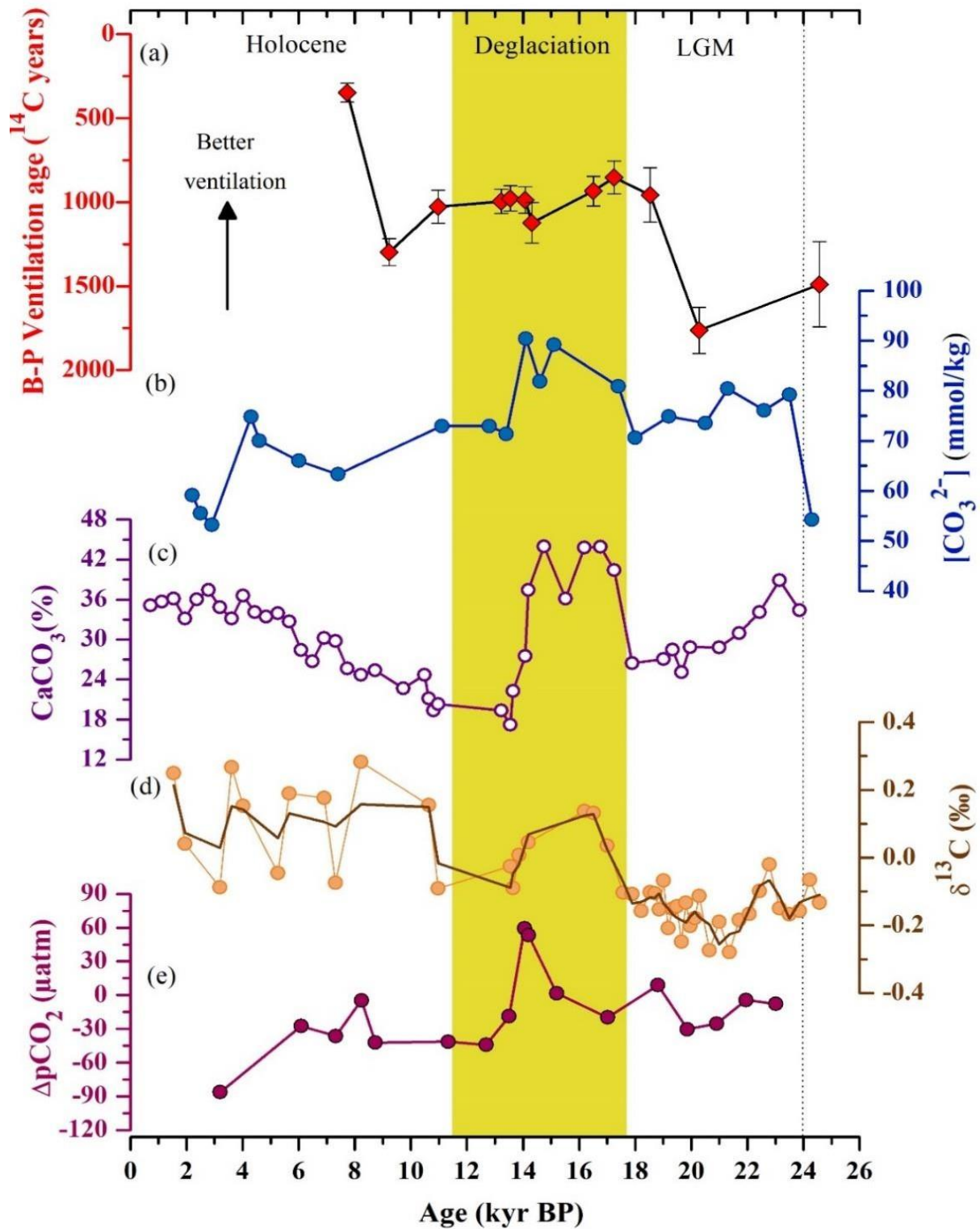


Fig. 6.4: Graph showing changes in intermediate water circulation in the EAS during the last 25 kyr (a) Ventilation ages (in years; red diamond) which are plotted as benthic-planktic foraminifera radiocarbon age difference from the core AAS-9/21. The vertical error bars are the sum of the $\pm$ error of the planktic and benthic foraminifera; (b) $[\text{CO}_3^{2-}]$ (in $\mu\text{mol/kg}$; Naik et al., 2023; (c) CaCO_3 (%; Godad et al., 2017) record from the core AAS-9/21; (d) stable

carbon isotope of benthic foraminifera *Cibicidoides wuellerstorfi* (‰) from the core AAS-9/21 (Naik and Naik, 2022); (e) Outgassing of CO₂ from the surface water of the Arabian Sea (µatm; Naik et al., 2015). Climatic events such as LGM, deglaciation and Holocene are marked.

The ventilation age recorded at the core site decreased by the end of the last glaciation and as well as during the deglaciation (Fig. 6.4a). This could be attributed to gradual decrease of poorly-ventilated water influx and inflow of better-ventilated water into the EAS, which could probably be related to the strengthening of AMOC during the deglaciation. The expelling of stored carbon was marked by a significant *p*CO₂ peak from the same core during the B-A (Naik et al., 2015; Fig. 6.4e). Another boron (δ¹¹B) based study by Tarique et al. (2023) have shown degassing of CO₂ from the EAS during the HS1 and YD. This implies flushing out the stored CO₂ by upwelling of CO₂-rich southern sourced deep-waters via surface water to the atmosphere during this interval. This outgassing of CO₂ was associated with increase in [CO₃²⁻] and CaCO₃ at the beginning of the deglaciation (Fig. 6.4b and c). The rise in CaCO₃ % at our core site supports the reported spike in the carbonate preservation in the northern Indian Ocean during the same interval (Naik and Naidu, 2016), indicating an increased proportion of CO₃²⁻-rich water, which could be possibly due to changes in the ocean circulation (Naik et al., 2023). Also, the water is characterized by enrichment of δ¹³C during the early deglaciation as compared to the LGM, suggesting change in the source of water mass. This has been interpreted as the resumption of the inflow of NADW into the EAS. Previous multi-proxy records have shown an inflow of NADW in the northern Indian Ocean during the deglaciation (Ahmad et al., 2008; Piotrowski et al., 2009; Ahmad et al., 2012, Raza et al., 2014; Chandana et al., 2017; Ma et al., 2019). The [CO₃²⁻], CaCO₃, and δ¹³C record, well aligned with the reconstructed ventilation age at the start of deglaciation, provide a strong evidence of increased contribution of shoaled NADW to the NIIDW.

Ventilation during the Holocene

The ventilation age shift from the LGM to Holocene is about ~500 ¹⁴C years (Fig. 6.4a). These lower values of ventilation age have been interpreted as enhanced incursion of well-ventilated water masses at the core site. The result is consistent with previous ventilation records from the northern Indian Ocean (Bryan et al., 2010; Ma et al., 2019; Bharti et al., 2022; Nisha et al., 2023). Previous studies from the northern Indian Ocean confirm the intensified penetration of NADW during the Holocene (Chandana et al., 2017; Lathika et al.,

2021; Bharti et al., 2022; Nisha et al., 2023). The calcium carbonate content also gradually increased during the Holocene. The stable isotopes of carbon also show a shift to positive $\delta^{13}\text{C}$ values during this period. This supports the ventilation age record, indicating $\delta^{13}\text{C}$ –rich and nutrient-poor water mass like NADW into the northern Indian Ocean. Previous stable carbon isotope (Ahmad et al., 2008; Piotrowski et al., 2009; Naik and Naik, 2022) and ϵ_{Nd} (Piotrowski et al., 2009; Lathika et al., 2021) based studies have suggested NADW influx in the northern Indian Ocean during the Holocene. This increased flux of NADW led to a higher contribution of NADW in the NIIDW, making it better-ventilated.

The $[\text{CO}_3^{2-}]$ is in contrast to the ventilation, CaCO_3 and $\delta^{13}\text{C}$ record during the Holocene (Fig. 6.4b). During the early Holocene, a decline trend in the $[\text{CO}_3^{2-}]$ could be seen in the core. As suggested by Naik et al. (2023) this was the result of the shifting of the locus of dissolution of calcium carbonate from the Atlantic Ocean basin to the Indo-Pacific Ocean basin.

6.5.2 Factors affecting ventilation age of the EAS

In order to examine the ventilation changes in the northern Indian Ocean during the last 25 kyr, we have compared the ventilation ages of Western Arabian Sea (WAS; core RC27-23; water depth: 820 m; Bryan et al., 2010), EAS (core AAS-9/21; water depth: 1800 m; this study) and the equatorial Indian Ocean (core SSD-044/GC-01; water depth: 3160 m; Nisha et al., 2023). These studies have been used for comparison because the same species were used for reconstructing the ventilation ages i.e., *G. ruber* (except for a few intervals where the required weight for AMS ^{14}C dating was less, species such as *G. quadrilobatus*, *G. menardii* and *N. dutertrei* were also used along with *G. ruber*) for planktic foraminifera radiocarbon ages and mixed species for benthic foraminifera radiocarbon ages. To calculate the ventilation age during a specific time interval (LGM, HS1, B-A and Holocene), the average of the ventilation ages for that period have been used for each core. The average ventilation ages are plotted against the different depths (Fig. 6.5). Ventilation age for YD has not been plotted because of no available data points in the core AAS-9/21.

The radiocarbon-based ventilation age records from the northern Indian Ocean at different depths during the LGM show higher ventilation ages as compared to the Holocene (Fig. 6.5a and d). However, the ventilation age of the deep-water (core SSD-044/GC-01) is quite higher (~ 1000 ^{14}C years) than the intermediate water masses. This difference in the

ventilation ages shows a clear stratification between the intermediate and deep water masses in the northern Indian Ocean during the LGM (Fig. 6.5a). This stratification indicates significant aged water in the deeper interior of the Indian Ocean than the intermediate depths. This could be notably because of the injection of poorly ventilated southern sourced water at deeper depths in the northern Indian Ocean during the LGM, while the intermediate waters were comparatively better ventilated. A well-stratified water masses below ~1800 m can be seen in the northern Indian Ocean during the LGM. A study from the Atlantic Ocean have shown less radiocarbon depleted intermediate water (< 200 m) than the deep water suggesting significant aging of water > 2000 m depth (Chen et al., 2020). This is in support with the hydrographic divide at ~2000 m water depth during the LGM as reported by a few studies (Kallel et al., 1988; Marchitto and Broecker, 2006; Skinner et al., 2017; Skinner and Bard, 2022). Kallel et al. (1988) using stable carbon and oxygen isotope demonstrated the presence of stratified and isolated deep waters in the Arabian Sea during the LGM. The intermediate water was warmer and $\delta^{13}\text{C}$ -rich while the deep-water was weakly ventilated and cooler. The difference in the ventilation record of intermediate and deep water further supports this hydrochemical front as the intermediate waters less than ~2000 m are well-ventilated whereas the deep waters are poorly-ventilated and depleted in ^{14}C .

During the deglaciation, the ventilation age record of the core AAS-9/21 shows a decrease in the benthic-planktic radiocarbon age offset. This EAS ventilation record shows a different pattern to that of the previously published records RC27-23 (Bryan et al., 2010) from the WAS and SSD-044/GC-01 (Nisha et al., 2023) from the equatorial Indian Ocean (Fig. 6.5b). The ventilation age of the EAS decreased by the end of LGM and showed a clear separation between lower-depth (RC27-23) and deep-water ventilation ages (SSD-044/GC-01). The deep core SSD-044/GC-01 remained poorly ventilated during the beginning of deglaciation (HS1). Unlike seen in the WAS (Bryan et al., 2010), where the ventilation age during the mystery interval (HS1; 17.5-14.5 kyr) was more than the LGM, no such ‘old-water mass’ was noted at the studied core site during the HS1 and YD. To explain these differences in the east-west ventilation gradient in the Arabian Sea, we have evaluated the following possible mechanisms, which include (a) monsoon upwelling (b) bioturbation (c) the influence of resumption of PGW and RSW (d) the core lies near to the hydrological front (e) depth difference between the two cores (f) changes in the circulation.

(a) In the method used for the ventilation age determination in this study, it is assumed that the radiocarbon ages of the shallow sub-surface water in which the planktic foraminifera lived

remained more or less in equilibrium with the contemporary atmosphere. However, the planktic ages may get altered due to various factors, including the upwelling of deeper sub-surface water. During the monsoon, the upwelling of the deeper sub-surface water brings the low- $\Delta^{14}\text{C}$ water to the surface, which leads to a decrease in the radiocarbon age of the planktic foraminifera. Major upwelling in the Arabian Sea takes place in the WAS, making it as a constant source of CO_2 to the atmosphere (Palmer et al., 2010), whereas the EAS acts as a sink for the atmospheric CO_2 (Naik et al., 2015). However, a spike in $p\text{CO}_2$ was seen from the surface water of the EAS during the last deglaciation indicating EAS was source of CO_2 during that period (Naik et al., 2015). During early deglaciation, the strong southwest monsoon enhanced the upwelling, which may have led to substantial mixing of the deeper sub-surface water with the surface water and could have resulted in decrease in benthic-planktic radiocarbon age offsets. This can be ruled out by the B-Atm ventilation age record from the same core. Both the ventilation record, i.e. B-P and B-Atm shows a similar trend (Fig 6.3), which indicates that the monsoonal upwelling did not affect the planktic foraminifera radiocarbon ages.

(b) Bioturbation could be one of the factors hampering the radiocarbon ages of the foraminifera. Mixing at the upper surface layer of the sediment by the burrowing of benthic organisms, increases the age-heterogeneity (Guinasso and Schink, 1975; Peng and Broecker, 1984; Boudreau, 1998). This happens mostly due to low sedimentation rates. The core site shows a relatively high sedimentation during the deglaciation, limiting the bioturbation and lateral mixing at the core site.

(c) Another factor could be resumption of the PGW and RSW flow during the deglaciation. During the LGM, the sea level was lowered by ~ 120 m, which resulted in the shutdown of PGW and a limited supply of RSW to the Arabian Sea intermediate water masses. During interglacial, the rise in sea level led to the opening of the semi-enclosed basin of the Red Sea and Persian Gulf. The inflow of PGW-RSW and its mixing with southern sourced water to form the Indian Deep Water might have affected the foraminiferal radiocarbon ages (and hence the ventilation age) of the EAS. However, this reason could be ruled out because in this case the ventilation ages of the WAS core would have been lower than that of the EAS core. Therefore, initiation of PGW and RGW flow during the deglaciation will have minimal effect on the ventilation ages.

(d) Kallel et al. (1988) had reported a deep chemical front separating intermediate and deep water masses in northern Indian Ocean during the LGM using stable carbon and oxygen

isotopes. The core AAS-9/21 lying near the chemical front, vertical mixing of the ^{14}C -rich NADW from the deeper waters may have led to decreased ventilation ages. This factor is not well accepted, as from the previous studies (Bharti et al., 2022; Nisha et al., 2023) it was noted that during the early deglaciation, the deeper water masses of the northern Indian Ocean were dominantly ^{14}C -depleted. Upward mixing of these poorly ventilated waters at the core site will further increase the ventilation ages during the deglaciation.

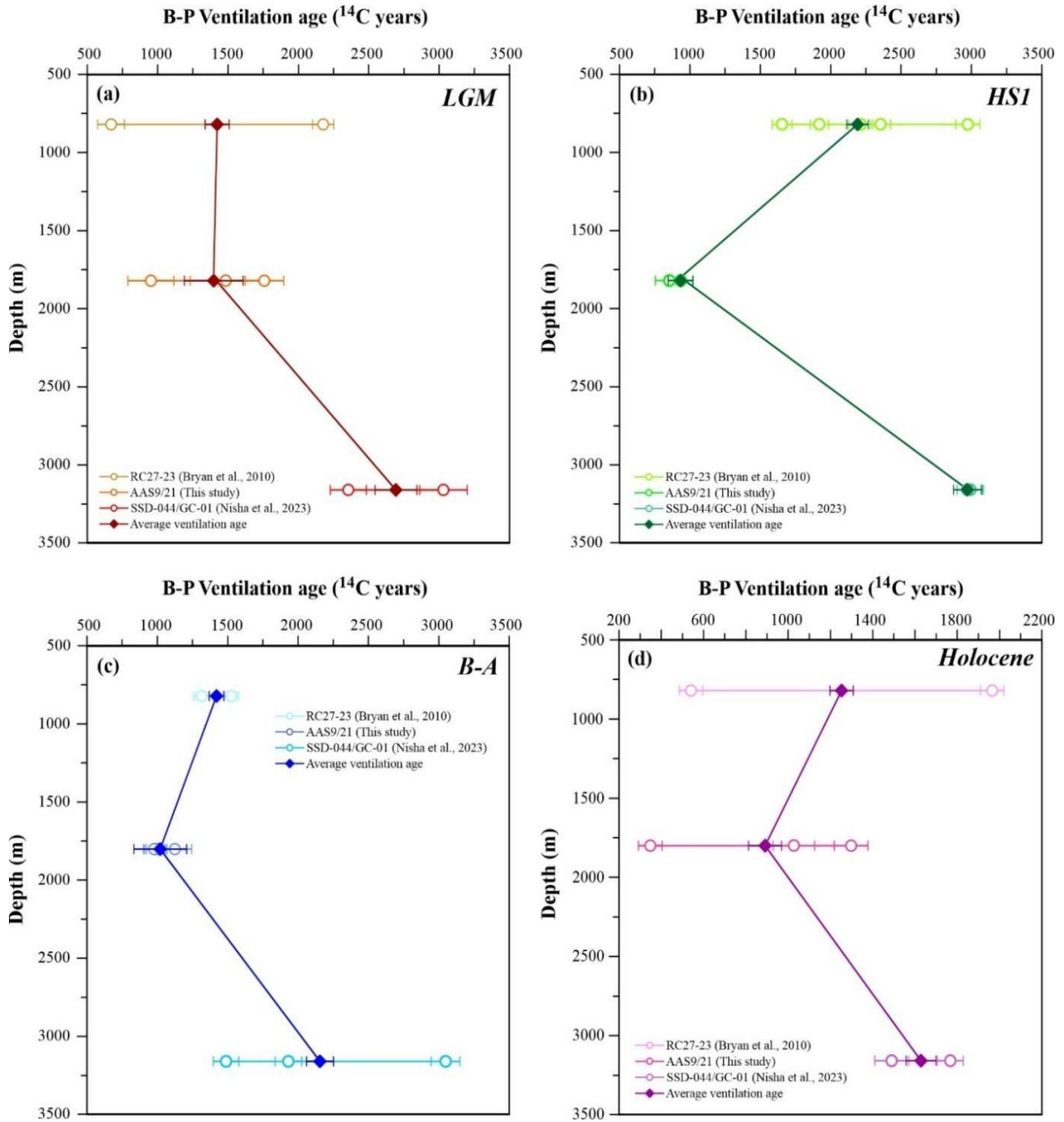


Fig. 6.5: Average ventilation age of the cores from the northern Indian Ocean at different depths i.e. RC27-23 (WAS; water depth: 820 m; Bryan et al., 2010), EAS (AAS-9/21; water depth: 1800 m; this study) and (SSD-044/GC-01 (EIO; water depth: 3160 m; Nisha et al., 2023) for the selected time interval (LGM, HSI, B-A, YD, Holocene).

(e) The WAS core lies at a water depth of 820 m and is mainly influenced by water masses AAIW and SAMW (Bryan et al., 2010). In contrast, the EAS core lies at a deeper depth, i.e., 1800 m and is occupied by the NIDW, which is controlled by the relative contribution of NADW (major fraction) and AAIW (minor fraction). During the HS1, there was an increased proportion of AAIW injection into the northern Indian Ocean (Jung et al., 2009; Bryan et al., 2010; Yu et al., 2018; Ma et al., 2020). This southern-sourced AAIW carried ^{14}C -depleted intermediated water to the rest of the oceans during the HS1 and YD (Marchitto et al., 2007; Bryan et al., 2010). However, the AAIW in the Arabian Sea is found from water depths of 200-1000 m; hence, there is comparatively less contribution of the AAIW in the NIDW formation. Since the core AAS-9/21 lies below the AAIW flow, the influence of poorly-ventilated AAIW on the ventilation ages is unlikely.

(f) The Atlantic overturning resumed during the early deglaciation with an increased flow of NADW. During the early deglaciation, the NADW was not fully halted, it was shallow. This resumption and shallowing of NADW during the early deglaciation lead to its increased contribution to NIDW formation. This NADW was better ventilated (hence ^{14}C -rich), rich in $[\text{CO}_3^{2-}]$ and $\delta^{13}\text{C}$. Therefore, it can be assumed that the changes in water circulation were the major reason for the ventilation variations in the Arabian Sea. The average ventilation age of all the cores improved during the B-A (Fig. 6.5c). This decrease in the ventilation ages suggest propagation of well-ventilated NADW into the northern Indian Ocean.

The ventilation ages during the Holocene shows lower values, indicating better ventilated water in the northern Indian Ocean (Fig. 6.5d). However, the ventilation ages of EAS shows lower values compared to the cores from the WAS and EIO, this could be possibly due to enhanced penetration of well-ventilated NADW at this depth.

6.5.3 Mechanism of intermediate water ventilation

A lot of studies were carried out to reconstruct the AMOC changes during the last glacial-interglacial cycle, however, no clear picture is established (Elliot et al., 2002; McManus et al., 2004; Menviel et al., 2017; Muglia et al., 2018; Menviel et al., 2020; Muglia et al., 2021), especially, the Indian Ocean circulation is least understood. The cores AAS-9/21 and SSD-044/GC-01 are ideal to understand the changes in NADW production and inflow, as the ventilation of both the core sites are dependent on the NADW penetration in the northern Indian Ocean. The intermediate water core AAS-9/21 (1800 m), is ventilated by the

NIDW which has major fraction of the NADW. The deep water core occupied by the UCDW is a mixture of NADW and AABW. The high ventilation age records in the northern Indian Ocean during the LGM have been attributed to reduced flow of NADW. This decrease export of NADW was accompanied by an increased contribution of ^{14}C -depleted AABW (Bharti et al., 2022; Nisha et al., 2023). A study has shown that during the LGM, the AABW penetrated further north and to shallower depths (Muglia and Schmittner, 2021). In the Indian Ocean, as this deep water moved northward, it mixes with the overlying intermediate waters and transfers the low- ^{14}C to it. In comparison to the deep waters, the better ventilated intermediate waters (Fig. 6.6) suggests an active but shoaled NADW during the LGM. This is in agreement with other studies suggesting a shallow AMOC during this time (Menviel et al., 2017; Muglia et al., 2018; Menviel et al., 2020; Muglia et al., 2021). A recent study by Liu et al. (2023) has shown that there was shallowing of NADW by approximately 600 m during the LGM, and the water mass below ~ 2000 m was dominated by the low- ^{14}C AABW as seen in core SSD-044/GC01.

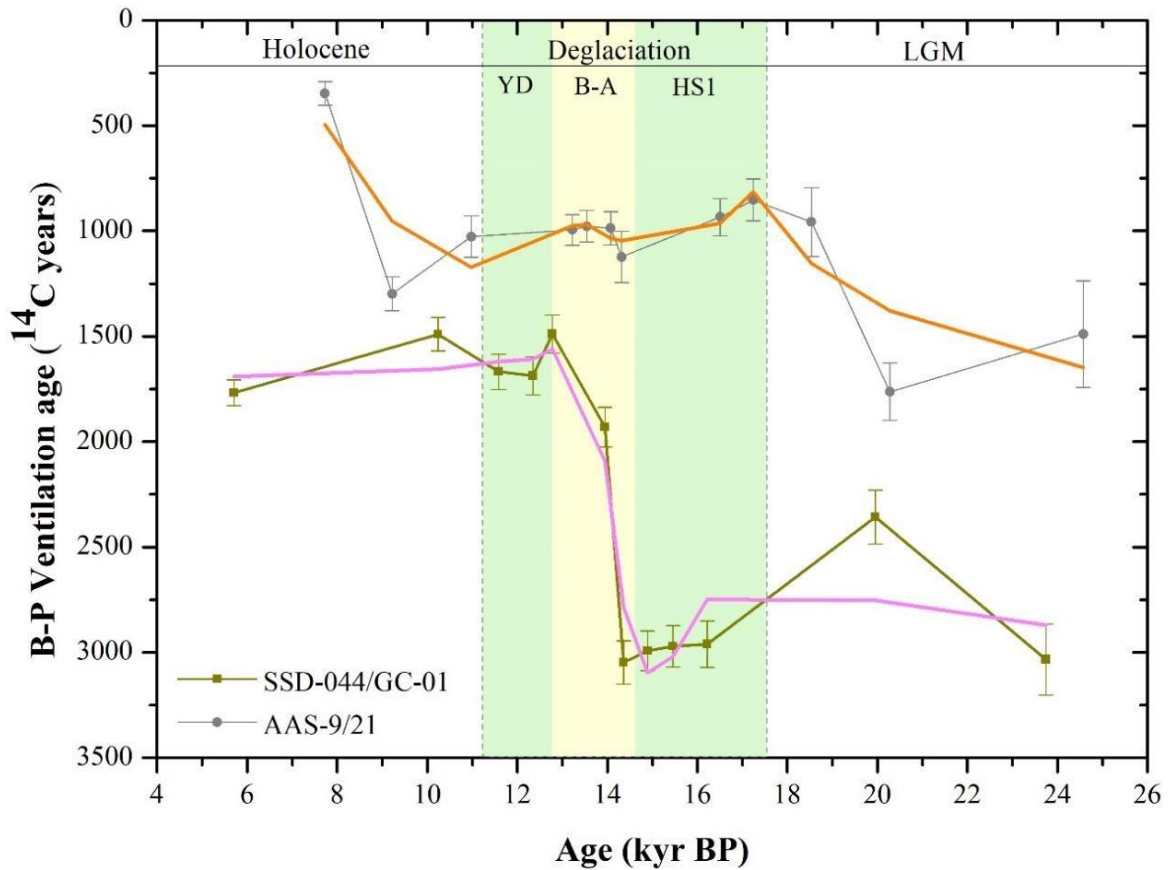


Fig. 6.6: The ventilation ages of the core AAS-9/21 (grey circles) and core SSD-044/GC-01 (green squares). These ventilation ages are plotted as benthic-planktic radiocarbon age

differences. The vertical error bars are the sum of the $\pm$ error of the planktic and benthic foraminifera. Climatic events- LGM, deglaciation, HS1, B-A, YD and Holocene are marked.

During the deglaciation, studies have reported weakening to complete collapse of the AMOC (during the HS1) due to outburst of meltwater from the northern ice sheets (Rahmstorf, 2002; McManus et al., 2004; Gherardi et al., 2005; Bradtmiller et al., 2014). However, recent studies have shown that there was an active but weak AMOC reaching up to 3000 m water depth in the subtropics (Oppo et al., 2015; Repschläger et al., 2021). A shift in the ventilation record of AAS-9/21 could be seen during the late LGM indicating an active NADW flow in the northern Indian Ocean. We acknowledge that our intermediate-water core does not have a sufficient number of data points for a clear explanation of small variations in the ventilation record during the deglaciation. Considering the deeper core, the high ventilation age continued during the HS1 suggesting a decreased export of NADW in the deeper waters. At the onset of B-A, there was proper resumption and overshoot of AMOC. This was noticed as a rapid decrease in the ventilation age in core SSD-044/GC-01.

6.6 Conclusion

Our results reflect that there have been variations in the EAS ventilation during the last 25 kyr due to the changes in the NADW formation. The ventilation record from the northern Indian Ocean indicates a strong stratification at ~2000 m water depth with better-ventilated water at water depths < 2000 m, and poorly-ventilated water at depths of > 2000 m during the LGM. The present studied ventilation record suggests that during the LGM, the >1800 m water depth of EAS was dominated by the southern-sourced water which was old and depleted in ^{14}C , and contained a large amount of CO_2 . This ^{14}C -depleted water as it moved northward it upwelled and mixed with the intermediate water of the EAS. The ^{14}C -depleted CO_2 from the deep water was transferred to the intermediate which lead to high ventilation age and CO_2 in the EAS. However, the ventilation age at AAS-9/21 was not as high as the deep core SSD-044/GC-01. The condition changed to better-ventilated water during the deglaciation than the LGM, indicating increased contribution of NADW to the NADW formation during the deglaciation. The stored CO_2 in the water from the LGM period was released during this period. This was further supported by $[\text{CO}_3^{2-}]$, CaCO_3 % and $\delta^{13}\text{C}$ records from the same core. The ventilation age at the core site further decreased during the Holocene.

Chapter 7

Reduced bottom-water oxygenation in the northern Indian Ocean during the Last Glacial Maximum

7.1 Summary

Understanding changes in the past bottom water oxygenation of the oceans is crucial in improving our understanding of the current global ocean deoxygenation and respired carbon storage. Changes in the deep water circulation plays a major role in controlling the bottom water oxygenation conditions. In this study, we track changes in bottom water deoxygenation for the past 25 kyr using a multi-proxy record of surface porosity of epifaunal benthic foraminifera *Cibicidoides wuellerstorfi*, foraminiferal fragmentation percentage, size index, and uranium concentration in sediments, from a core SSD-044/GC-01 raised from a water depth of 3160 m from the northern Indian Ocean. Our results suggest that from the period ~24 kyr to ~15 kyr there existed a low O₂ and CO₂-rich deep water mass in the northern Indian Ocean. This was probably the result of an increased proportion of southern sourced Antarctic Bottom Water (AABW) at the core location as a replacement for the reduced export of North Atlantic Deep Water (NADW). During the deglaciation, there was an incursion of O₂-rich and CO₂-poor NADW. Furthermore, a well-oxygenated deep water prevailed in the northern Indian Ocean during the Holocene.

7.2 Introduction

A decrease in dissolved oxygen in the ocean water is expected in the near future as a result of climate change, and will have a major impact on the marine ecosystems as dissolved oxygen concentration in the ocean is one of the main factors modulating the abundance and diversity of organisms. Understanding the past bottom water oxygenation conditions related to climate change will better inform us of the dynamics of the oxygen-deficient zones in the future. The bottom-water oxygenation mainly depend on two factors, increased oxygen demand for enhanced organic carbon supply and its degradation, and deep

water circulation (Wyrski, 1962). Based on the presence or absence of oxygen at the sediment-water interface, the bottom water oxygen conditions can be classified as oxic (8.0-2.0 ml/1 O₂), dysoxic (2.0-0.2 ml/1), suboxic (0.2-0.0 ml/1) and anoxic (0.0 ml/1) (Tyson and Pearson, 1991). A range of proxies have been proposed to understand the bottom-water oxygenation in the past. In several previous studies, geochemical proxies like redox-sensitive trace elemental (such as V, Mo, U, Mn) concentration in the bulk sediment have been used to trace the changes in the bottom water oxygen conditions of the northern Indian Ocean (Sarkar et al., 1993; Pattan and Pearce, 2009; Naik et al., 2014b; Chandana et al., 2017; Godad et al., 2017; Nambir et al., 2022). Organic carbon preserved in sediments was also utilized to document the bottom water oxygenation conditions (Sarnthein, 1988; Sarkar et al., 1992). Also, the foraminifera due to their rapid response to ecological and environmental changes, serve as valuable bio indicators for the changes in past oxygenation conditions (Murray et al., 2006). The stable carbon isotope gradient ($\Delta\delta^{13}\text{C}$) between the epifaunal and the infaunal benthic foraminiferal species has also been used as a tool to assess the past oxygen concentrations in the ocean (Hoogakker et al., 2015). Studies have also used benthic foraminiferal distribution, and abundance in order to understand paleo-redox conditions (Tetard et al., 2017a; Ma et al., 2019; 2020; Tetard et al., 2021; Verma et al., 2021), and more lately have utilized I/Ca in benthic foraminiferal tests (Glock et al., 2014; Lu et al., 2020; Lu et al., 2021). Porosity in benthic foraminifera is another important proxy of past bottom water oxygen concentrations (Glock et al., 2011; Glock et al., 2012; Kuhnt et al., 2013; Petersen et al., 2016; Tetrad et al., 2017b; Rathburn et al., 2018; Richirt et al., 2019; Lu et al., 2021).

Calcareous benthic foraminifera have the potential to decipher the past changes in the bottom water oxygenation, and are reflected by: (1) changes in species abundance i.e. epifaunal to infaunal species record the bottom water conditions (Corliss and Chen, 1988). Infaunal species are mostly (highly) porous, flat, or elongated-tapered forms which are present in low oxygen conditions, whereas the high abundance of epifaunal species indicates the oxic conditions and are characterized by planoconvex, biconvex, rounded trochoidal, and spherical test shapes (Bernhard, 1986; Kaiho, 1994), (2) changes in test size (Sen Gupta and Machain- Castillo, 1993)- oxygen-poor environments tend to have relatively smaller foraminiferal species in assemblages (Koho and Pina-Ochoa, 2012), (3) changes in test morphology (Perez- Cruz and Machain-Castillo, 1990)- foraminifera from oxygen-depleted habitats tend to have thinner, more porous, and less ornamented tests

(Bernhard, 1986). Pores of benthic foraminifera are related to the gas exchange (specifically oxygen) between the organism and the environment (Glock et al., 2011; Kuhnt et al., 2013). Field and laboratory observations have shown that the pores present on the test surface of benthic foraminifera take up oxygen from the overlying waters, and are used by the mitochondria to produce energy, and then release metabolic CO₂ (Hottinger and Dreher, 1974; Berthold, 1976; Leutenegger and Hansen, 1979; Bernhard et al., 2010).

A recent study has shown a greater proportion of southern sourced CO₂-rich, poorly- ventilated Antarctic Bottom Water (AABW) in the northern Indian Ocean during the Last Glacial Maximum (LGM) and Heinrich Stadial (HS1) (Nisha et al., 2023). However, the ventilation improved during the Bølling-Allerød (B-A) with an inflow of better oxygenated North Atlantic Deep Water (NADW), which caused flushing of the deep-carbon pool (Nisha et al., 2023). The aim of this study is to test the relationship between the porosity of the epifaunal benthic foraminifera *C. wuellerstorfi*, a proxy rarely used in the northern Indian Ocean, and the bottom water oxygen conditions, and hence understand the bottom water oxygenation variations from the LGM to the Holocene in line with the changing deep water sources. We also employ other supporting proxies such as uranium concentration, foraminiferal fragmentation percentage, and size index.

7.3 Methodology

7.3.1 Sediment core SSD-044/GC-01

The sediment core location is discussed in section 4.1.

7.3.2 Age Model

The age model for the core is given in Table 4.2 and discussed in section 4.2.

7.3.3 Porosity

The method of porosity measurement is discussed in section 4.8.

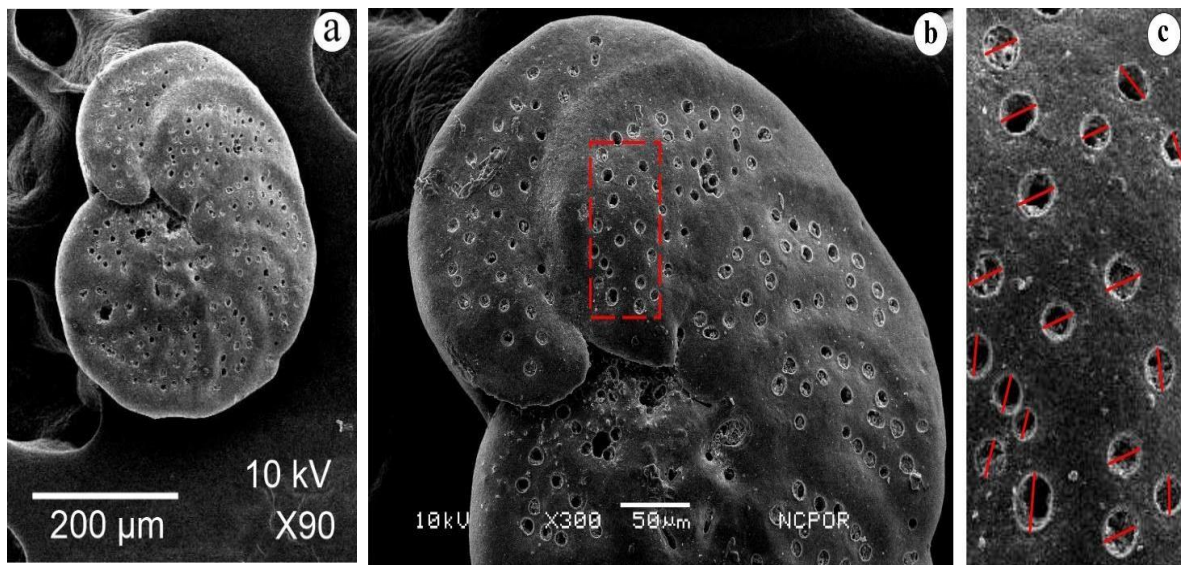


Fig. 7.1: Scanning electron micrographs of epifaunal benthic foraminifera *Cibicidoides wuellerstorfi* from the core SSD-044/GC-01 (a) SEM image of the entire specimen with a magnification of 90x (Scale bars are 200 µm); (b) SEM image of the penultimate chamber with 300x magnification (Scale bars are 50 µm); (c) Pore measurement within the frame 300 x 150 pixel.

7.3.4 Uranium concentration

The geochemical analysis is discussed in section 4.7 and within subsections.

7.3.5 Foraminifera Fragmentation Percentage

The method for determination of foraminifera fragmentation is discussed in section 4.9.

7.3.6 Size Index

The method for the determination of size index is discussed in section 4.10.

7.4 Results

The dorsal side of the *C. wuellerstorfi* gets exposed to the bottom waters, and thus was considered for the porosity calculations. A large variation was observed in the porosity of *C. wuellerstorfi* throughout the last 25 kyr and the average porosity was 1.94 % (Fig. 7.2a). The average porosity of *C. wuellerstorfi* during the LGM (17.5-24 ka) was 2.20 %. During the deglaciation, average value of porosity decreased to 2.00 %, and further decreased to 1.46 % during the Holocene.

The FF (%) varied from ~6 to ~50 throughout the last 25 kyr (Fig. 7.2b). The foraminiferal fragmentation index was high during the early and late LGM, it decreased during the deglaciation and again slowly increased during the Holocene.

The size index ranged from ~20 % to ~40 % throughout the last 25 kyr with values of < 31% before ~15 kyr (Fig. 7.2c). Size index value was low during the LGM and increased abruptly after 15 kyr and showed a gradual decrease through the Holocene.

The uranium (U) concentration ranged from 0.5-10 ppm throughout the last 25 kyr and showed a decreasing trend from the LGM to Holocene (Fig. 7.2d). The concentration of U was extremely high during the LGM (~8 ppm), and further it decreased to ~2 ppm during the deglaciation. The concentration of U got depleted during the Holocene, reaching to ~1ppm.

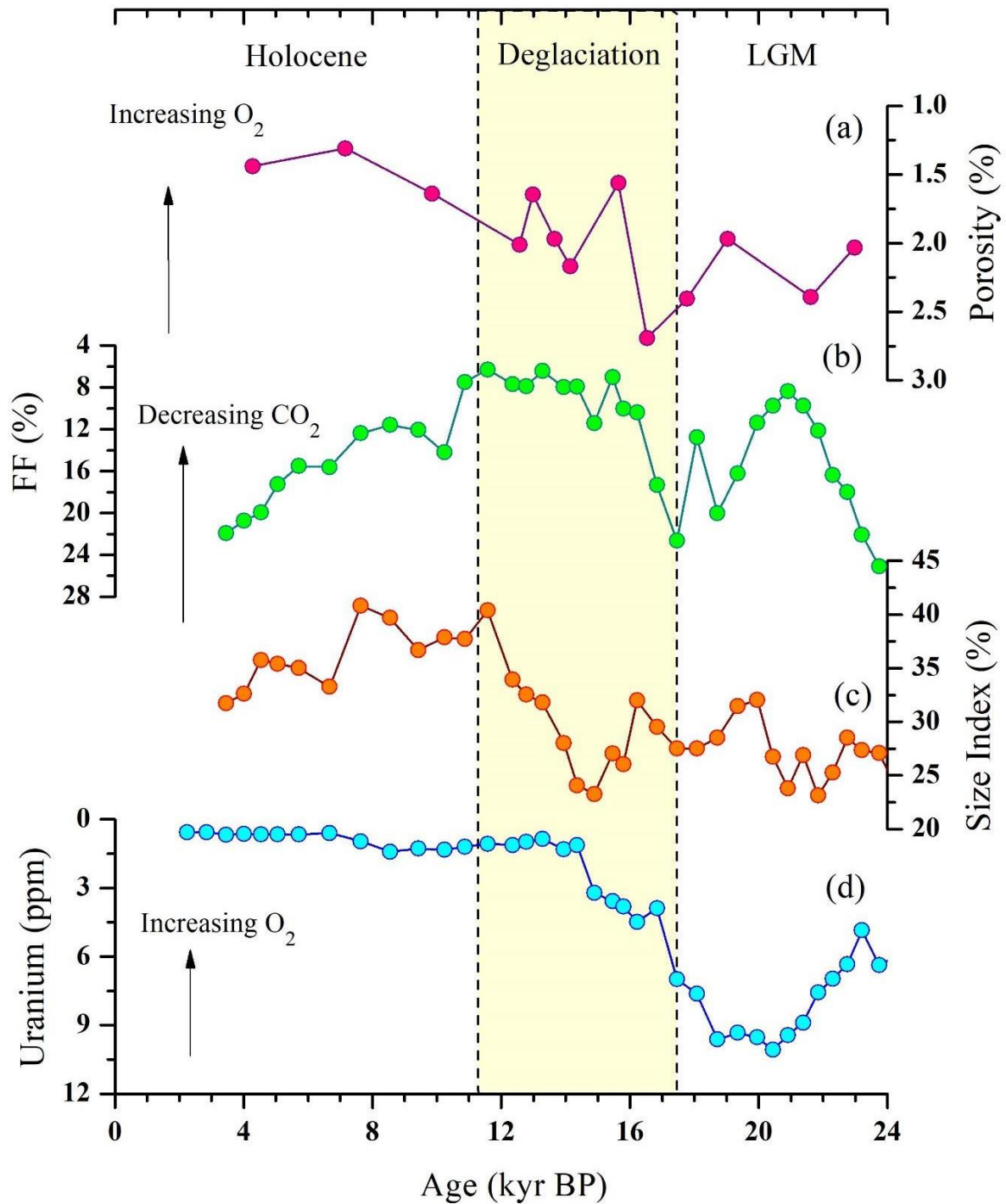


Fig. 7.2: Graph showing changes in deep water circulation in the northern Indian Ocean during the last 24 kyr. (a) Porosity of benthic foraminifera *Cibicidoides wuellerstorfi*; (b) foraminiferal fragmentation percentage; (c) size index; (d) uranium concentration for the core SSD-044/GC-01. Climatic events such as Last Glacial Maxima (LGM), deglaciation and Holocene are marked.

7.5 Discussion

7.5.1 Porosity of benthic foraminifera

Calcareous foraminifera have pores over their entire test or portions of it, that are used for gas exchange between the test and the environment. The pore size and the pore density (number of pores per surface area of the frame) are interdependent variables while porosity (the mean percentage of the surface area covered by the pores) accounts for both the former variables. Hence, porosity better represents an individual foraminifera's oxygen accessibility than pore size and pore density (Rathburn et al., 2018). *Cibicidoides wuellerstorfi* is an epifaunal foraminifera with a plano-convex-shaped test and has 8-12 chambers in the final whorl. They are abundant in well-oxygenated bottom water as well as in low-oxygen bottom water masses (Rathburn et al., 2018). Pores on the dorsal surface of *C. wuellerstorfi* are used for pore analysis as the dorsal side is exposed to the overlying bottom water, and the ventral side pores are used for adhering to the hard substrates (Rathburn et al., 2018). Pore analyses on the entire test or on the entire chamber of the foraminifera were avoided as the rounded edge of the specimen distorts the SEM image. The middle, flat part of the last few chambers of the specimen is sufficient to represent the porosity of the whole test. Since the last chamber is very thin, and is often damaged or broken, therefore chamber next to the last chamber i.e. penultimate chamber of the foraminiferal test is used for the pore measurements in this study.

There have been limited down-core studies based on the porosity of *C. wuellerstorfi* (Rathburn et al., 2018; Lu et al., 2021; Lu et al., 2022), thus robustness of this species of foraminifera as a proxy for bottom water paleo-oxygen conditions has not been fully established, and hence it needs further investigation. In this study, the variation in the porosity of *C. wuellerstorfi* shows major changes in the bottom water oxygen concentration since the LGM. Consistently high porosity was observed during the LGM with a subsequent marginal increase during the early deglaciation, and gradually declining from the deglaciation to the Holocene (Fig. 7.2a). The porosity of the benthic foraminifera is consistent with the uranium (U) concentration in the sediment (Fig. 7.2a & d). Accumulation of U in the sediment takes place in oxygen-depleted deep waters. In oxygenated water, U is present as soluble U (VI) which is chemically unreactive (Calvert and Pedersen, 1993). Under reducing conditions U (VI) is reduced to U (IV) which is less soluble and gets adsorbed or precipitates in the sediment (Morford and Emerson, 1999; Pattan and Pearce, 2009). Records from previous studies from the northern Indian Ocean

have reported low-oxygenated deep water during the LGM (Pattan and Pearce, 2009; Chandana et al., 2017). High porosity *C. wuellerstorfi* and high U concentration in the sediment during the LGM must have resulted from low-oxygenated deep waters at the core location. The porosity and the U concentration decreased during the deglaciation suggesting a shift from low-oxygenated to better-oxygenated deep waters at that time. A rapid decrease in porosity and U concentration during the Holocene corresponds to the presence of oxygenated deep waters compared to the LGM and deglaciation.

7.5.2 Changes in bottom-water conditions

The bottom water oxygenation condition is mainly influenced by two factors: consumption rate of oxygen for the remineralization of the organic matter and deep water circulation (Wyrski, 1962; Pattan and Pearce, 2009; Pattan et al., 2013). The organic matter content in the sediment depends upon the surface productivity, sedimentation rate, and the dissolved oxygen content in the bottom water & pore water (Emerson et al., 1985). Increased surface productivity leads to high organic matter deposition in the sediment. The preservation of organic matter also depends upon the presence or absence of the oxygen. In the presence of oxygen, decomposition of the organic matter will be more efficient, leading to its oxidation. However, it gets preserved in the absence of oxygen. The sediment depositional rate is also one of the factors that influences the preservation of organic matter (Canfield, 1994). At lower depositional rates, the organic matter preservation is reduced since it is exposed to the oxygenated water for a longer duration and hence, which allows a longer exposure time for the decomposition to occur. It is known that the sediments having higher organic matter content result in greater utilization of oxygen from the water column for the decomposition of organic matter. Therefore, high organic matter content in the sediment have been associated with low oxygenated bottom water and vice versa (DeMaison and Moore, 1980). The preservation of organic matter further depends upon the depositional depth and the rate of degradation of the organic matter decreases exponentially with the water depth (Berner, 1980). It was noted that in Core SSD-044/GC-01 the organic carbon (C-org) content was high during the LGM and gradually decreased from the deglaciation to the Holocene (Yadav et al., 2021; Fig. 7.3a). During the LGM, there was a weakened southwest monsoon which resulted in low sediment deposition. Therefore, the high C-org during the LGM indicates either enhanced overhead productivity or the prevalence of oxygen-depleted deep water masses. However, surface ocean productivity was moderate at the core location during the LGM (Yadav et al., 2021). Also, the sediment core was collected from the open ocean from

a water depth of >3000 m, a depth wherein most of the sub-surface organic matter gets remineralized before deposition and only ~10 % of it reaches the ocean floor (Berner, 1980; Hedges and Keil, 1995). A study by Chandana et al. (2017) has shown the high C-org observed in the equatorial Indian Ocean sediment during the LGM was a result of good preservation of organic matter under anoxic conditions. In this study, the U concentration in sediment was high during the LGM. From the C-org record (Yadav et al., 2021), the redox-sensitive element U concentration record (this study, Fig. 7.3f), and previous studies from a nearby site (Chandana et al., 2017), it can be inferred that the changes in deep water circulation is the major controlling factor than the productivity-related organic matter flux to the ocean floor, for the low bottom water oxygen during the LGM. The insufficient oxygen in deep water originating from the poorly ventilated (low O₂ and CO₂-rich) deep waters led to high C-org content in the sediment. Previous studies have also suggested the bottom water present in the northern Indian Ocean during the LGM was poorly ventilated and nutrient-enriched (Duplessy et al., 1988; Naqvi et al., 1994; Ahmad et al., 2008; Piotrowski et al., 2009; Bharti et al., 2022; Nisha et al., 2023).

The calcium carbonate (CaCO₃) content in marine sediment is controlled by three factors: surface ocean productivity, dilution by non-carbonate material (terrigenous input), and carbonate dissolution (Volat et al., 1980). The coarse fractions (>63 µm) majorly contained foraminifera and foraminiferal fragments and were devoid of any sand-sized particles, indicating insignificant terrigenous input at the core site (Yadav et al., 2022), and the surface ocean productivity was also moderate during the LGM (Yadav et al., 2021). Hence, dissolution seems to be the primary factor controlling the CaCO₃ in this core. In this study, FF (%), size index, along with CaCO₃ are used as dissolution proxies (Fig. 7.3b, c & d). The rate of foraminiferal fragmentation depends upon the dissolved CO₂ and carbonate ion concentration in seawater. When seawater is rich in CO₂, dissolution of the foraminiferal test takes place which leads to a higher fragmentation of the tests. The high value of FF (%) during the early LGM are indicative of CO₂-rich deep water, which led to an increase in the fragmentation of the tests (Fig. 7.3b). However, the high fragmentation values were not consistently observed throughout the interval. A drop in the FF (%) was recorded around ~22 kyr. This decreased values could probably be the result of intensified dissolution. Under intensified dissolution, the fine fragments get completely dissolved leaving behind the coarser fragments and hence, overall reduced number of broken fragments. The size index is used to determine the carbonate ion saturation state of the deep-water (Broecker and

Clark, 1999). Broecker and Clark (1999) have shown that in today's tropical ocean the CaCO_3 percentage contained in grains $>63\ \mu\text{m}$ in size is closely related to the pressure-normalized carbonate ion of water bathing the sea floor. The size index and CaCO_3 follow a similar trend (Fig. 7.3c and d). Thus, low size index and CaCO_3 values, and high foraminiferal fragmentation percentage suggest the dissolution of calcareous material during the LGM. This signifies increased proportion of poorly-ventilated CO_2 -rich deep water existed in the northern Indian Ocean during this period. The porosity of benthic foraminifera was also low during the LGM supporting the case for prevalence of low O_2 water in the northern Indian Ocean (Fig. 7.3e). The FF%, size index, CaCO_3 , and porosity of benthic foraminifera are further supported by the ventilation age record from the same core (Nisha et al., 2023; Fig. 7.3g). The ventilation ages indicate that the bottom water was poorly ventilated during the LGM as compared to the modern ocean. All these proxies point towards an increased proportion of low O_2 and CO_2 -rich, poorly ventilated AABW in the northern Indian Ocean. This poor ventilation of AABW was the result of isolation of deep waters due to factors like extensive sea-ice coverage over Antarctica (Stephens and Keeling, 2000; Fischer et al., 2007), density-stratification (Schmittner and Galbraith, 2008), and northward shift of westerly winds (Toggweiler et al., 2006). Our results are also supported by previous studies suggesting enhanced incursion of poorly-ventilated AABW in the Indian Ocean during the LGM (Ahmad et al., 2008; Piotrowski et al., 2009; Chandana et al., 2017; Lathika et al., 2021; Bharti et al., 2022; Nisha et al., 2023). During the same period, there was weakening of the Atlantic Meridional Overturning Circulation (AMOC) and shallowing of the NADW (McManus et al., 2024). This shallowing of NADW lead to its decreased export in the northern Indian Ocean compensated by an increased influx of AABW.

The values of FF (%) dropped abruptly after the LGM suggesting a decreased export of CO_2 -poor deep water in the northern Indian Ocean (Fig. 7.3b). A sharp increase in size index and CaCO_3 after 14.5 kyr indicates better calcium carbonate preservation (Fig. 7.3c & d). The porosity of foraminifera decreased as well, suggesting oxygenated deep waters at the core site (Fig. 7.3e). Decrease in the values of FF (%), porosity, ventilation, and increase in size index and CaCO_3 could be related to the inflow of O_2 -rich and CO_2 -poor NADW after the resumption of AMOC. Strengthening of AMOC during the ~14.5 kyr resulted in progressive influx of NADW and a decreased export of AABW into the northern Indian Ocean, making the bottom waters of the northern Indian Ocean oxygen-

enriched. Degassing of CO₂ (Naik et al., 2015; Fig. 7.3h) during this period could be possibly associated with the upwelling of CO₂-enriched deep water to the upper water column and its release to the atmosphere. This release of CO₂ from the deep water resulted in better preservation of calcium carbonate.

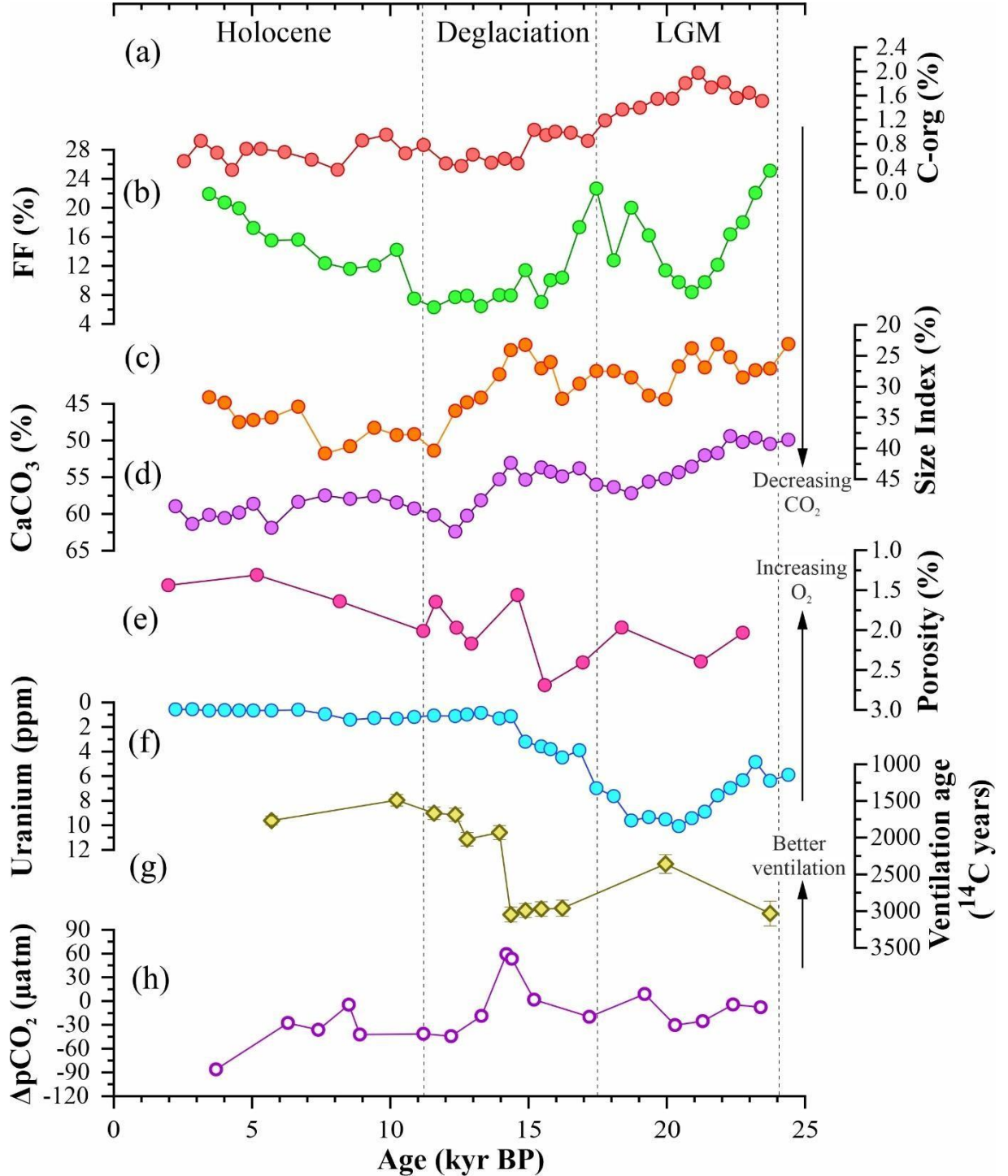


Fig. 7.3: Down-core variations in the core SSD-044/GC-01 during the last 25 kyr (a) organic carbon (Yadav et al., 2021); (b) foraminiferal fragmentation percentage; (c) size index; (d) calcium carbonate (Nisha et al., 2023); (e) porosity of benthic foraminifera *Cibicoides*

wuellerstorfi; (f) uranium concentration; (g) ventilation age for the core SSD-044/GC-01 (Nisha et al., 2023); (h) outgassing of CO₂ from the surface water of the Arabian Sea (Naik et al., 2015). Climatic events such as LGM, deglaciation and Holocene are marked.

The high value of size index and CaCO₃ content along with the low ventilation age at the studied site during the Holocene indicates a progressive inflow of the well-ventilated bottom water (Fig. 7.3c, d and g). Furthermore, the porosity as well as the uranium concentration remained low suggesting presence of oxygenated bottom water (Fig. 7.3e and f). All these proxies indicate intensified penetration of NADW in the northern Indian Ocean during this time interval. Previous studies have also observed enhanced contribution of NADW in to the northern Indian Ocean (Yu et al., 2018; Ma et al., 2019; 2020; Nisha et al., 2023). However, the FF (%) doesn't follow the trend of the other dissolution based proxies for the Holocene period. A gradual increase in the FF (%) from the mid-Holocene was observed, where the value reaches as high as glacial values (Fig. 7.3b). The major factor responsible for this value possibly be dissolution. But this cannot be expected under the influence of enhanced well-ventilated NADW. Another study using the same sediment core showed a that the gradual increase in FF (%) could be probably result of undersaturated pore water caused by degradation of organic matter under oxygenated deep water conditions (Yadav et al., 2022). The oxidation of organic matter which reaches the sediment surface releases CO₂ as a byproduct, thereby causing dissolution of calcium carbonate (Emerson and Bender, 1981). Studies have shown that change in the bottom/pore water chemistry will affect the porosity of the foraminifera (Sen Gupta and Machain-Castillo, 1993; Glock et al., 2011; Lu et al., 2022). However, the porosity at the core site remained low during the Holocene along with high size index and CaCO₃ content in the sediment. Hence, the high fragmentation doesn't appear to be driven by dissolution. Another factor for the high fragmentation could possibly be the high energy conditions, which is not supported by the lower sedimentation rate during the Holocene. Looking at the above factors, the foraminiferal fragmentation index of the core top doesn't seem to be properly capture the dissolution trend during the Holocene as compared to the other dissolution parameters used and is likely to be anomalous. Hence, our multi-proxy data showing high size index and CaCO₃ along with low porosity, U concentration and ventilation age during the Holocene suggests an inflow of well-ventilated water at the core site during the Holocene.

7.6 Conclusions

The down-core porosity record of the epifaunal benthic foraminifera *C. wuellerstorfi*, FF (%), size index, and U concentration in the sediment from the core SSD-044/GC-01 illustrates changes in deep water source over the last 25 kyr. Foraminifera porosity record and concentration of U in the sediment indicate that an oxygen-depleted deep water mass was present in the Indian Ocean during the LGM. The LGM witnessed an increased flow of low O₂ and CO₂-rich southern sourced AABW at the core location. During the same period, dissolution indices support the dissolution of calcium carbonate. Bottom water oxygen content at the core site increased from deglaciation onwards to the Holocene. Oxygen-rich deep water and better preservation of calcium carbonate after ~15 kyr, may have resulted from the increased inflow of O₂-rich and CO₂-poor NADW, after the resumption of the AMOC. Oxygenated deep water at the core site during the Holocene suggests an increased propagation of NADW compared to the LGM. Furthermore, the progressive inflow of the well-ventilated bottom water continued during the Holocene.

Chapter 8

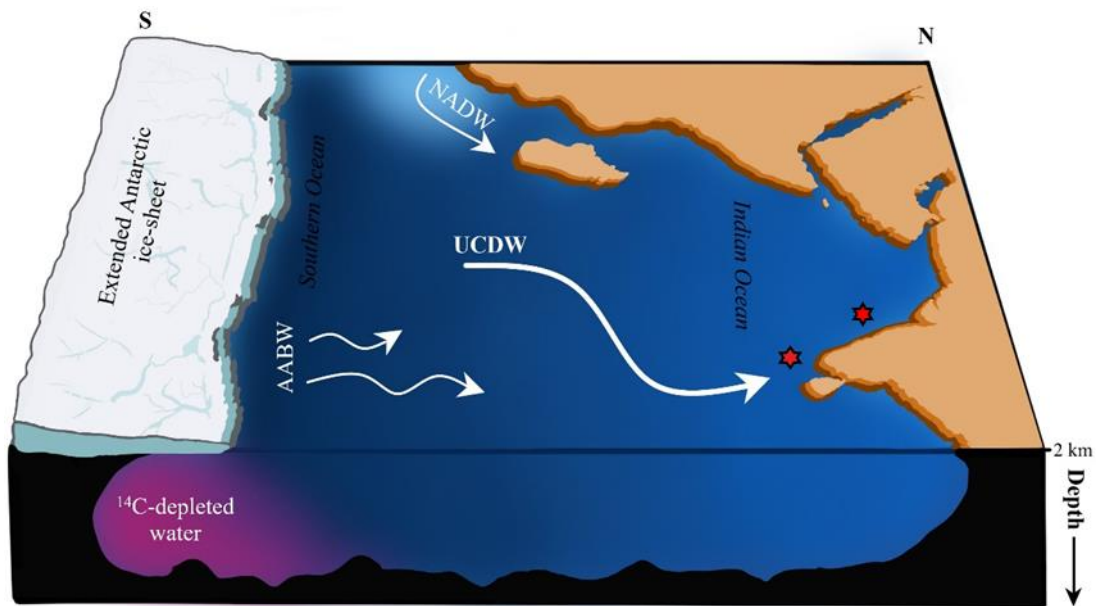
Summary and Conclusions

The main objective of this research was to reconstruct the changes in the intermediate and deep water circulation in the northern Indian Ocean from the LGM to the Holocene. In this study an intermediate water core AAS-9/21 (1800 m water depth) from Arabian Sea and a deep water core SSD-044/GC-01 (3160 m water depth) from the equatorial Indian Ocean, were used. To carry out this research, we have measured radiocarbon ages of benthic and planktic foraminifera to reconstruct the ventilation record, stable isotopes (carbon and oxygen) and porosity of benthic foraminifera *Cibicidoides wuellerstorfi*, fragmentation percentage, size index, calcium carbonate content as well as geochemical analysis of sediment. From this study, it is known that there have been major ventilation changes in the intermediate and deeper water of the northern Indian Ocean from the LGM to the Holocene.

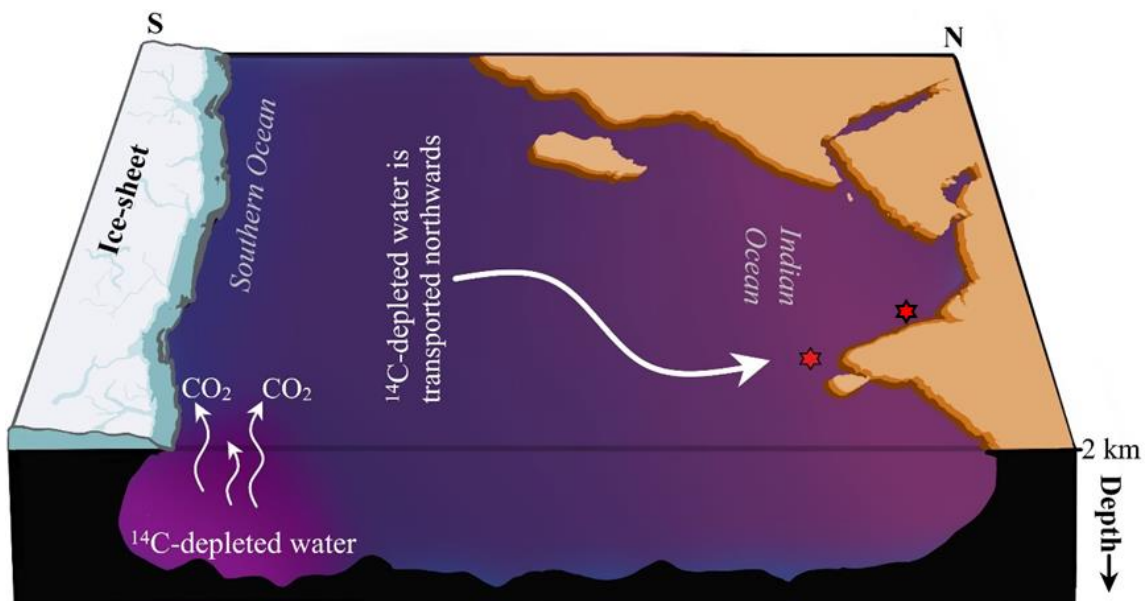
During the LGM, the ventilation age of the deep water core SSD-044/GC-01 was quite high (~3000 ^{14}C years). The deep water core is ventilated by the Upper Circumpolar Water (UCDW), which has a major proportion of NADW and minor fraction of AABW. During the LGM, slowdown of the AMOC led to reduced production of NADW. This decreased inflow of NADW led to advection of southern-sourced water - AABW into the northern Indian Ocean (Fig. 8.1). The Indian Ocean was majorly filled with the southern-sourced deep water during this period. This southern-sourced water was isolated from the atmosphere, contained high amounts of CO_2 and was depleted in ^{14}C . During the HS1, with the sea-ice retreat, there was an upwelling of the deep waters in the Southern Ocean. Some of the ^{14}C -depleted CO_2 was released to the atmosphere leading to a drop in atmospheric radiocarbon and some of this was transported to the rest of the oceans. The high-ventilation ages during the HS1 at the core SSD-044/GC-01 site are indicative of the presence of ^{14}C -depleted deep water. The effective inflow of NADW resumed in the deep waters of the Indian Ocean with the overshoot of AMOC during the B-A. As the ventilation improved in the Indian Ocean, the stored CO_2 was flushed from the deep water to the atmosphere during the B-A.

The ventilation age of the intermediate water core AAS-9/21 suggests active but shallow NADW flow in the northern Indian Ocean during the LGM. On comparison of ventilation

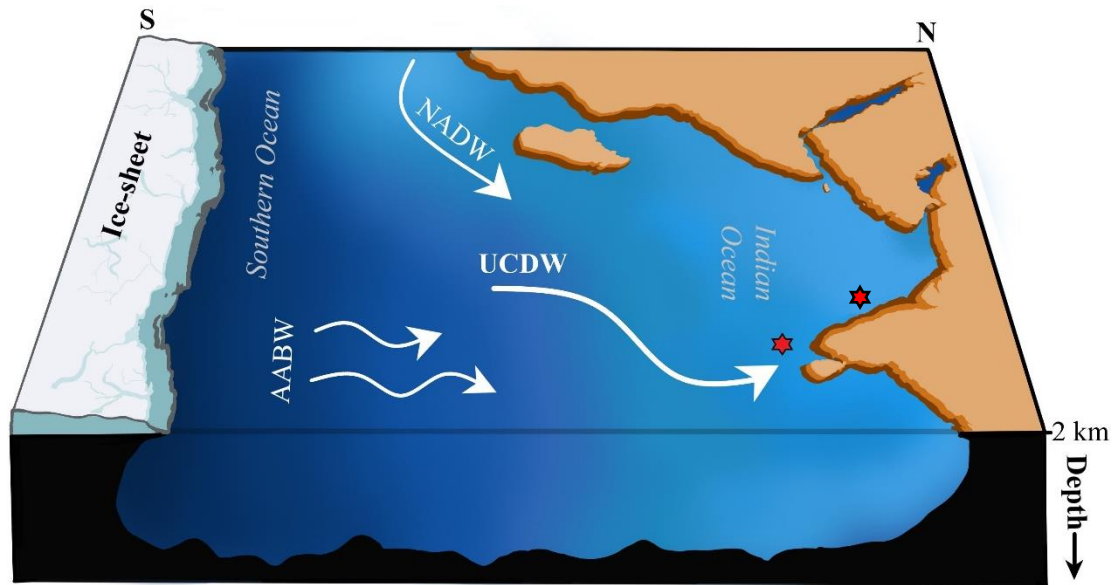
records from the northern Indian Ocean, a strong stratification at ~ 2000 m water depth was observed during the LGM. The water below 2000m shows a significantly aged deep water that was CO_2 -rich, whereas the intermediate water from < 2000 m depth was better ventilated. – The comparatively higher ventilation age (~ 1500 ^{14}C years) observed in the core AAS-9/21 during the LGM than the last deglaciation and the Holocene could possibly be due to the influence of these poorly ventilated southern sourced deep waters.



(a) Last Glacial Maximum



(b) Heinrich Stadial 1



(c) Bolling-Alleroid



Fig. 8.1: Schematic illustration of changes in deep water circulation (from below 2 km depth) and ventilation of the northern Indian Ocean. Shaded colour indicates ^{14}C ventilation. The core location is indicated by a red star. White arrows indicate water masses flow. UCDW is mixture of AABW and NADW with variable proportions (a) LGM: less export of NADW in the northern Indian Ocean because of an extended ice-sheet. UCDW flow in the northern Indian Ocean with AABW as a dominant component and less fraction of NADW. The purplish pink colour represent ^{14}C -depleted isolated deep water; (b) HS1 and YD: melting of ice-sheet and release of ^{14}C -depleted CO_2 into the atmosphere. Weakening of the AMOC and shoaling of the NADW led to intensive penetration of poorly ventilated AABW at the core site; and (c) B-A: resumption of NADW formation and inflow of better ventilated water in the northern Indian Ocean.

To understand the deep water oxygenation and carbonate dissolution conditions since the LGM, proxies like porosity of benthic foraminifera & uranium concentration in the sediment and dissolution proxies have been used from core SSD-044/GC-01. These proxies were in support with the ventilation age record and suggest the deep water was poorly- oxygenated and CO₂-rich before ~ 14.5 kyr. After ~14.5 kyr, which coincides with the onset of B-A and resumption of AMOC, an oxygenated and CO₂-poor NADW prevailed.

This study gives us a better understanding of the changes in the intermediate and deep water ventilation, and ocean circulation in the Indian Ocean. However, numerous questions remained unanswered regarding the pathways of deglacial CO₂ release from the deep water to the atmosphere. In order to fully elucidate the ventilation changes in the northern Indian Ocean, and its role to the past climate and carbon cycle change, more sediment cores from the northern Indian Ocean, and covering shallow to deeper water depths need to be studied.

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List of Publications

1. **Nisha, K.**, Naik, S.S., Kumar, P., Banerjee, B., Murty, P.R., 2023. Radiocarbon evidence for reduced deep water ventilation of the northern Indian Ocean during the last glacial maxima and early deglaciation. *Earth and Planetary Science Letters*, 607, 118067 (**IF: 5.3**).
2. Naik, S.S., **Nisha, K.**, 2020. Increased ventilation of the Northern Indian Ocean during the last deglaciation. *Journal of the Geological Society of India*, 96, 148-150 (**IF: 1.3**).
3. **Nisha, K.**, Naik, S.S. Reduced bottom-water oxygenation condition in the Northern Indian Ocean during the Last Glacial Maximum. *Marine Geology (Under review, IF: 2.9)*.
4. **Nisha, K.**, Naik, S.S., Kumar, P. Poorly ventilated water in the Eastern Arabian Sea during the last glacial maximum (*In preparation*).

List of Conferences

1. **Nisha, K.**, and Naik, S. S., (2023), “Northern Indian Ocean bottom water condition for the last glacial-interglacial cycle: Evidence from redox-sensitive elements” at Goldschmidt- 2023 during 9th- 14th July 2023 (**Oral Presentation**).
2. **Nisha, K.**, Naik, S. S., and Kumar, P., (2022), “Ventilation changes in the intermediate waters of Arabian Sea from the Last Glacial Maximum to the Holocene” at International Indian Ocean Science Conference (IIOSC)-2022 during 14th- 18th March 2022 (**Oral Presentation**).
3. **Nisha, K.**, Naik, S. S., and Kumar, P., (2022), “Deep water ventilation changes in the equatorial Indian Ocean during the last deglaciation” at the Ocean Sciences Meeting (OSM)-2022 held on 24th Feb- 4th March 2022 (**Oral Presentation**).
4. **Nisha, K.**, Naik, S. S., and Kumar, P., (2022), “Radiocarbon evidence for reduced ventilation in the northern Indian Ocean at the onset of deglaciation” at the XXVIII Indian Colloquium on Micropaleontology and Stratigraphy-2022 held on 4th Feb- 6th May 2022 (**Poster Presentation**).
5. **Nisha, K.**, Naik, S. S., and Banerjee, B., (2022), Changes in deep-water circulation in the equatorial Indian Ocean during the last 25 ka BP: Evidence from carbon and oxygen isotope of benthic foraminifera at the 1st Indian Quaternary Congress (IQC) held on 19th - 21st January 2022 (**Oral Presentation**).

List of Webinar/ Workshop(s)

1. Attended two-day National Webinar on '*Indian Ocean Paleoceanography: Late Glacial-Holocene Period (IOPLG-HP)*' from 29th -30th December-2021 organized by Department of Marine Science, Bharathidasan University, Tiruchirappalli, Tamil Nadu.
2. International Conference on '*Paleoclimate Changes (ICPC 2020)*' held during 9-10 July, 2020 on virtual platform organized by School of Civil Engineering, VIT Chennai
3. Attended an e-Training on '*Micropalaentology and C14 dating*' from 21st -31st July 2020 organized by Geological Survey of India, Regional Training Division, Northern Region, Lucknow
4. Participated in a 3 day '*National Workshop on Isotopes in Earth, Ocean & Atmospheric Sciences*' jointly organized by IUAC-New Delhi & CSIR-NIO and hosted by CSIR-NIO, Goa during 18th -20th February, 2019.

Appendix I

Table 1: Calendar age for the core SSD-044/GC-01.

Sr. No	Depth (cm)	Sample ID	Species	¹⁴ C age (yr BP)	Error (±)
1	0-1	SSD-044 GC-01 0-1cm(PF)	<i>G. ruber</i> + <i>G. sacculifer</i> + <i>N. dutertrei</i> + <i>G. menardii</i>	2195	22
2	13-14	SSD-044 GC-01 13-14cm(PF)	<i>G. ruber</i> + <i>G. quadrilobatus</i>	5008	30
3	23-24	SSD-044 GC-01 23-24cm(PF)	<i>G. ruber</i>	9284	38
4	27-28	SSD-044 GC-01 27-28cm(PF)	<i>G. ruber</i>	10235	42
5	29-30	SSD-044 GC-01 29-30cm(PF)	<i>G. ruber</i>	10733	41
6	31-32	SSD-044 GC-01 31-32cm(PF)	<i>G. ruber</i>	11509	42
7	35-36	SSD-044 GC-01 35- 36cm(PF)	<i>G. ruber</i>	12272	47
8	37-38	SSD-044 GC-01 37-38cm(PF)	<i>G. ruber</i>	12603	50
9	39-40	SSD-044 GC-01 39-40cm(PF)	<i>G. ruber</i>	12786	43
10	41-42	SSD-044 GC-01 41- 42cm(PF)	<i>G. ruber</i>	13194	44
11	45-46	SSD-044 GC-01 45-46cm(PF)	<i>G. ruber</i>	13619	57
12	57-58	SSD-044 GC-01 57-58cm(PF)	<i>G. ruber</i>	16777	61
13	73-74	SSD-044 GC-01 73- 74cm(PF)	<i>G. ruber</i> + <i>G. quadrilobatus</i>	19837	81
14	99-100	SSD-044 GC-01 99- 100cm(PF)	<i>G. ruber</i> + <i>G. sacculifer</i> + <i>N. dutertrei</i> + <i>G. menardii</i>	28160	270

Table 2: Ventilation ages of the core SSD-044/GC-01.

Sr. No.	Depth (cm)	Cal Age (kyr BP)	Sample ID	Species	AMS ¹⁴ C age (yr BP)	¹⁴ C age error (± yr)	Sample ID	Species	AMS ¹⁴ C age (yr BP)	¹⁴ C age error (± yr)	B-P offset (¹⁴ C yr BP)	B-P error (± yr)
1	13-14	5.7	SSD-044 GC-01 13-14cm (PF)	<i>G. ruber</i> + <i>G. quadrilobatus</i>	5008	30	SSD-044 GC-01 12-14cm (BF)	Mixed Benthic Foraminifera	6775	31	1767	61
2	23-24	10.2	SSD-044 GC-01 23-24cm (PF)	<i>G. ruber</i>	9284	38	SSD-044 GC-01 22-24cm (BF)	Mixed Benthic Foraminifera	10774	42	1490	80
3	27-28	11.6	SSD-044 GC-01 27-28cm (PF)	<i>G. ruber</i>	10235	42	SSD-044 GC-01 27-28cm (BF)	Mixed Benthic Foraminifera	11903	42	1668	84
4	29-30	12.4	SSD-044 GC-01 29-30cm (PF)	<i>G. ruber</i>	10733	41	SSD-044 GC-01 29-30cm (BF)	Mixed Benthic Foraminifera	12420	49	1687	90
5	31-32	12.8	SSD-044 GC-01 31-32cm (PF)	<i>G. ruber</i>	11509	42	SSD-044 GC-01 31-32cm (BF)	Mixed Benthic Foraminifera	12997	48	1488	90
6	35-36	13.9	SSD-044 GC-01 35-36cm (PF)	<i>G. ruber</i>	12272	47	SSD-044 GC-01 34-36cm (BF)	Mixed Benthic Foraminifera	14203	48	1931	95
7	37-38	14.4	SSD-044 GC-01 37-38cm (PF)	<i>G. ruber</i>	12603	50	SSD-044 GC-01 36-38cm (BF)	Mixed Benthic Foraminifera	15650	52	3047	102
8	39-40	14.9	SSD-044 GC-01 39-40cm (PF)	<i>G. ruber</i>	12786	43	SSD-044 GC-01 38-40cm (BF)	Mixed Benthic Foraminifera	15778	51	2992	94
9	41-42	15.5	SSD-044 GC-01 41-42cm (PF)	<i>G. ruber</i>	13194	44	SSD-044 GC-01 40-42cm (BF)	Mixed Benthic Foraminifera	16165	54	2971	98
10	45-46	16.2	SSD-044 GC-01 45-46cm (PF)	<i>G. ruber</i>	13619	57	SSD-044 GC-01 44-46cm (BF)	Mixed Benthic Foraminifera	16579	53	2960	110
11	57-58	20.0	SSD-044 GC-01 57-58cm (PF)	<i>G. ruber</i>	16777	61	SSD-044 GC-01 57-58cm (BF)	Mixed Benthic Foraminifera	19135	67	2358	128
12	73-74	23.7	SSD-044 GC-01 73-74cm (PF)	<i>G. ruber</i> + <i>G. quadrilobatus</i>	19837	81	SSD-044 GC-01 73-74cm (BF)	Mixed Benthic Foraminifera	22870	88	3033	169

*PF: planktic foraminifera; BF: benthic foraminifera.

*Calendar ages derived from AMS ¹⁴C age of planktic foraminifera *Ventilation ages are calculated as the difference between the radiocarbon age of benthic foraminifera and planktic foraminifera (B-P) based on Broecker et al., 1984.

*Ventilation age errors are the sum of the ± σ error of the planktic and benthic foraminifera.

Table 3: Stable carbon and oxygen isotopic data of benthic foraminifera *Cibicidoides wuellerstorfi*.

Sr. No.	Depth (cm)	Age (kyr)	Sample ID	$\delta^{13}\text{C}$ ‰ vs. PDB	$\delta^{18}\text{O}$ ‰ vs. PDB
1	2	2.2	SSD-044/GC-01 (1-2cm)	0.17	2.8
2	4	2.8	SSD-044/GC-01 (3-4cm)	0.22	2.66
3	6	3.5	SSD-044/GC-01 (5-6cm)	0.14	2.79
4	8	4.0	SSD-044/GC-01 (7-8cm)	0.36	2.81
5	10	4.5	SSD-044/GC-01 (9-10cm)	0.32	2.8
6	12	5.1	SSD-044/GC-01 (11-12cm)	0.31	2.63
7	14	5.7	SSD-044/GC-01 (13-14cm)	0.38	2.84
8	16	6.7	SSD-044/GC-01 (15-16cm)	0.21	2.93
9	18	7.6	SSD-044/GC-01 (17-18cm)	0.25	2.85
10	20	8.5	SSD-044/GC-01 (19-20cm)	0.23	3.24
11	22	9.4	SSD-044/GC-01 (21-22cm)	0.02	2.83
12	24	10.2	SSD-044/GC-01 (23-24cm)	0.32	2.8
13	26	10.9	SSD-044/GC-01 (25-26cm)	-0.07	3.68
14	28	11.6	SSD-044/GC-01 (27-28cm)	0.07	3.49
15	30	12.4	SSD-044/GC-01 (29-30cm)	0.24	3.14
16	32	12.8	SSD-044/GC-01 (31-32cm)	0.16	3.43
17	34	13.3	SSD-044/GC-01 (33-34cm)	-0.25	4.32
18	36	13.9	SSD-044/GC-01 (35-36cm)	-0.03	3.85
19	38	14.4	SSD-044/GC-01 (37-38cm)	0.00	3.93
20	40	14.9	SSD-044/GC-01 (39-40cm)	-0.35	3.74
21	42	15.5	SSD-044/GC-01 (41-42cm)	-0.58	3.88
22	44	15.8	SSD-044/GC-01 (43-44cm)	-0.32	4.2
23	46	16.2	SSD-044/GC-01 (45-46cm)	-0.33	4.35
24	48	16.8	SSD-044/GC-01 (47-48cm)	-0.51	4.12
25	50	17.5	SSD-044/GC-01 (49-50cm)	-0.37	4.4
26	52	18.1	SSD-044/GC-01 (51-52cm)	-0.33	4.32
27	56	19.4	SSD-044/GC-01 (55-56cm)	-0.44	4.17
28	58	20.0	SSD-044/GC-01 (57-58cm)	-0.42	4.26
29	60	20.4	SSD-044/GC-01 (59-60cm)	-0.36	4.26
30	62	20.9	SSD-044/GC-01 (61-62cm)	-0.43	4.2
31	64	21.4	SSD-044/GC-01 (63-64cm)	-0.51	3.98
32	66	21.8	SSD-044/GC-01 (65-66cm)	-0.53	4.06
33	68	22.3	SSD-044/GC-01 (67-68cm)	-0.36	4.15
34	70	22.8	SSD-044/GC-01 (69-70cm)	-0.42	4.26
35	72	23.2	SSD-044/GC-01 (71-72cm)	-0.37	4.19
36	74	23.7	SSD-044/GC-01 (73-74cm)	-0.28	4.34
37	76	24.4	SSD-044/GC-01 (75-76cm)	-0.25	4.06

Table 4: Calcium carbonate and coarse fraction % in the sediment core SSC-044/GC-01.

Sr. No.	Depth (cm)	Age (kyr)	Sample ID	CaCO ₃ (%)	Coarse Fraction (%)
1	2	2.2	SSD-044/GC-01 (1-2cm)	58.96	--
2	4	2.8	SSD-044/GC-01 (3-4cm)	61.39	--
3	6	3.5	SSD-044/GC-01 (5-6cm)	60.16	19.09
4	8	4.0	SSD-044/GC-01 (7-8cm)	60.56	19.75
5	10	4.5	SSD-044/GC-01 (9-10cm)	59.83	21.4
6	12	5.1	SSD-044/GC-01 (11-12cm)	58.62	20.76
7	14	5.7	SSD-044/GC-01 (13-14cm)	61.9	21.66
8	16	6.7	SSD-044/GC-01 (15-16cm)	58.38	19.42
9	18	7.6	SSD-044/GC-01 (17-18cm)	57.48	23.47
10	20	8.5	SSD-044/GC-01 (19-20cm)	57.96	23
11	22	9.4	SSD-044/GC-01 (21-22cm)	57.59	21.13
12	24	10.2	SSD-044/GC-01 (23-24cm)	58.45	22.13
13	26	10.9	SSD-044/GC-01 (25-26cm)	59.26	22.34
14	28	11.6	SSD-044/GC-01 (27-28cm)	60.17	24.3
15	30	12.4	SSD-044/GC-01 (29-30cm)	62.41	21.17
16	32	12.8	SSD-044/GC-01 (31-32cm)	60.25	19.62
17	34	13.3	SSD-044/GC-01 (33-34cm)	58.15	18.49
18	36	13.9	SSD-044/GC-01 (35-36cm)	55.31	15.49
19	38	14.4	SSD-044/GC-01 (37-38cm)	53.06	12.78
20	40	14.9	SSD-044/GC-01 (39-40cm)	55.34	12.87
21	42	15.5	SSD-044/GC-01 (41-42cm)	53.67	14.52
22	44	15.8	SSD-044/GC-01 (43-44cm)	54.27	14.13
23	46	16.2	SSD-044/GC-01 (45-46cm)	54.91	17.56
24	48	16.8	SSD-044/GC-01 (47-48cm)	53.8	15.89
25	50	17.5	SSD-044/GC-01 (49-50cm)	56.01	15.4
26	52	18.1	SSD-044/GC-01 (51-52cm)	56.34	15.49
27	54	18.7	SSD-044/GC-01 (53-54cm)	57.2	16.31
28	56	19.4	SSD-044/GC-01 (55-56cm)	55.63	17.49
29	58	20.0	SSD-044/GC-01 (57-58cm)	55.21	17.69
30	60	20.4	SSD-044/GC-01 (59-60cm)	54.32	14.52
31	62	20.9	SSD-044/GC-01 (61-62cm)	53.56	12.76
32	64	21.4	SSD-044/GC-01 (63-64cm)	52.01	14
33	66	21.8	SSD-044/GC-01 (65-66cm)	51.72	11.97
34	68	22.3	SSD-044/GC-01 (67-68cm)	49.4	12.47
35	70	22.8	SSD-044/GC-01 (69-70cm)	50.19	14.31
36	72	23.2	SSD-044/GC-01 (71-72cm)	49.63	13.57
37	74	23.7	SSD-044/GC-01 (73-74cm)	50.48	13.67
38	76	24.4	SSD-044/GC-01 (75-76cm)	49.91	11.53

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Radiocarbon evidence for reduced deep water ventilation of the northern Indian Ocean during the last glacial maxima and early deglaciation

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ABSTRACT

Enhanced outgassing of sequestered carbon to the atmosphere by upwelling of deep water in the Southern Ocean during the last deglaciation is assumed to be the main factor that modulated changes in atmospheric CO₂ and atmospheric radiocarbon activity; however, the exact mechanism behind this deglacial CO₂ release still remains unclear. In this study, we have investigated ventilation changes in the deep waters of the northern Indian Ocean over the past 25 kyr BP using paired benthic and planktic foraminiferal radiocarbon, along with stable carbon and oxygen isotopes of benthic foraminifera, sedimentary CaCO₃ content, and coarse fraction from the gravity core SSD-044/GC-01 (3160 m water depth) collected from Central Equatorial Indian Ocean. The results indicate a greater proportion of southern sourced CO₂-rich, poorly-ventilated Antarctic Bottom Water (AABW) during the Last Glacial Maximum (LGM) and Heinrich Stadial (HS1), in the northern Indian Ocean. The observed poor ventilation during the last glaciation shows that the northern Indian Ocean was a part of the glacial ocean aged carbon pool. Improved ventilation during the Bølling-Allerød (B-A) is consistent with the rapid resumption of Atlantic overturning circulation and inflow of North Atlantic Deep Water (NADW) into the northern Indian Ocean at the onset of the B-A, which caused flushing of the deep-carbon pool with evidence of degassing from the northern Indian Ocean. This study thus supports the role of Southern Ocean in modulating atmospheric CO₂ variations during the last deglaciation.

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1. Introduction

Deep-water being the largest reservoir of carbon at the Earth's surface, plays a very important role in modulating and regulating Earth's climate as it redistributes heat and influences the ocean-atmosphere CO₂ cycle (Sigman and Boyle, 2000). Deep waters formed at high latitudes of the North Atlantic are then exported southwards where they mix and upwell in the Southern Ocean. The Southern Ocean is the region where deep water makes its first contact with the sea surface and the atmosphere (Primeau, 2005) and ventilates much of the respired carbon to the atmosphere. Hence, the Southern Ocean is considered to have played a crucial

role in past atmospheric CO₂ fluctuations. It is known that during the northern hemispheric stadials: Heinrich Stadial 1 (HS1) and Younger Dryas (YD), there was an abrupt increase in atmospheric CO₂ (Monnin et al., 2001). Along with this increase in atmospheric CO₂, there was a sudden drop in atmospheric radiocarbon activity ($\Delta^{14}\text{C}$; Hughen et al., 2006; Reimer et al., 2020).

The mechanism for such atmospheric changes still remains uncertain. One of the possible sources for this drop in atmospheric $\Delta^{14}\text{C}$ is assumed to be enhanced upwelling of ¹⁴C-depleted CO₂-rich water from the Southern Ocean during the last deglaciation (Marchitto et al., 2007; Anderson et al., 2009; Skinner et al., 2010; Burke and Robinson, 2012; Skinner et al., 2015). According to this so-called 'Southern Ocean upwelling' hypothesis, during the last glaciation, the air-sea exchange in the Southern Ocean decreased due to factors like sea-ice cover (Stephens and Keeling, 2000), density stratification, and displacement of westerly winds (Toggweiler

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et al., 2006), which led to the isolation of deep water from the upper ocean and resulted in greater carbon storage in the glacial deep waters (Skinner et al., 2010; Burke and Robinson, 2012; Skinner et al., 2015; Ronge et al., 2016; Sikes et al., 2016). Continuous decay of radiocarbon due to restricted interaction with the atmosphere caused ^{14}C depletion in these isolated waters. Retreat of Antarctic sea-ice and southwardly shift of polar westerlies (Toggweiler et al., 2006) during the deglaciation led to enhanced upwelling of these old, carbon-rich deep waters and released the ^{14}C depleted CO_2 into the atmosphere (Anderson et al., 2009; Skinner et al., 2010).

One possible way of testing the 'Southern Ocean upwelling' hypothesis is to reconstruct past ocean ventilation changes, i.e. the rate at which atmosphere and oceanic interior exchange gases, which can be directly estimated from its radiocarbon content. The difference between the ^{14}C age of paired bottom-dwelling benthic and surface-dwelling planktic foraminifera provides the past changes in ventilation rate (Broecker et al., 1984, 1990). It also indicates the extent of mixing of the deep water with surface water. When there is lesser mixing between deep and surface water, the radiocarbon (and therefore CO_2) exchange between these water masses also decreases, which will result in a longer carbon sequestration time in the deep waters, making it radiocarbon depleted and hence the ventilation ages (the difference between ^{14}C ages of benthic and planktic foraminifera) will be high, and vice versa. Similarly, the difference between the radiocarbon of deep water and the atmosphere provides an insight into carbon exchange between the atmosphere and the marine carbon pool. Thus, ventilation changes can be used as markers for past ocean circulation and climatic changes.

Numerous studies have been carried out in the Atlantic and Pacific Ocean, which investigated changes in intermediate and deep-water radiocarbon content since the Last Glacial Maximum (LGM). Previous deep-water studies from the Atlantic and Pacific have suggested that glacial deep waters were ^{14}C depleted (i.e. poorly ventilated) (Skinner and Shackleton, 2004; Galbraith et al., 2007; Barker et al., 2010; Burke and Robinson, 2012; Skinner et al., 2014). Studies from the intermediate water depths have shown an existence of poorly ventilated water mass in the Southern Ocean during the LGM, which was transported to the other oceans via the Antarctic Intermediate water mass (Marchitto et al., 2007; Bryan et al., 2010; Siani et al., 2013; Freeman et al., 2015; Ma et al., 2019). Such evidences from the Indian Ocean providing the Southern Ocean's role in atmospheric $^{14}\text{CO}_2$ fluctuations are few. The Indian Ocean being solely ventilated from the south because of no deep-water formation, could be a suitable location to deduce the role of the Southern Ocean on past atmospheric CO_2 variability.

There have been limited studies from the Indian Ocean that attempted to reconstruct the changes in radiocarbon distribution from intermediate waters (Bryan et al., 2010; Ma et al., 2019). These studies suggest the incursion of ^{14}C -depleted Antarctic Intermediate Water (AAIW) in the Indian Ocean during the deglaciation (HS1 and YD). This ^{14}C depletion in AAIW was because of the mixing of old isolated abyssal water to the south of the sub-Antarctic frontal zone. Interestingly, Naik et al. (2015) have reported outgassing of CO_2 during the last deglaciation, possibly indicating release of sequestered carbon from intermediate water to the surface. Studies from the Indian sector of the Southern Ocean have shown that the Indian Ocean was part of a glacial aged carbon pool and suggested these ^{14}C -depleted, CO_2 -rich waters from the southernmost Indian Ocean contributed to atmospheric CO_2 rise during the deglaciation (Ronge et al., 2020; Gottschalk et al., 2020) albeit differing on the timing of CO_2 release within the last deglaciation. Though some studies have been carried out for deep water paleoceanographic changes in the northern Indian Ocean using stable isotope and geochemical tracers as a proxy (Kallel et al., 1988; Naqvi et al., 1994; Piotrowski et al., 2009; Ahmad et al., 2012;

Singh et al., 2012; Chandana et al., 2017; Lathika et al., 2021; Bang et al., 2021), studies on radiocarbon changes in the deep water of Indian Ocean are limited (Naik and Nisha, 2020; Bharti et al., 2022). In this study, we have reconstructed ventilation changes in the deep water of the northern Indian Ocean for the last 25 kyr using radiocarbon measurements from core SSD-044/GC-01. Results show evidence for reduced ventilation in the Indian Ocean during the LGM and beginning of deglaciation (HS1) compared to the modern ocean, and enhanced ventilation after ~ 14 kyr. Our results clearly support the role of the Southern Ocean in atmospheric CO_2 variation during the last deglaciation.

2. Material and methods

2.1. Study area

The hydrography of the Indian Ocean is quite unique and different from the rest of the oceans. Surface hydrography is driven by the seasonal reversal of wind circulation during the monsoon. During summer monsoon (June–September) winds blow in the south-west (SW) direction whereas during winter monsoon winds blow in the north-east (NE) direction (Schott and McCreary, 2001). In response to wind, the surface water circulation also changes in the northern Indian Ocean. The surface water up to 150 m is comprised of a mixture of Arabian Sea High Saline Water (ASHSW) and low saline Bay of Bengal surface water. The intermediate depth of the northern Indian Ocean is occupied by northern sourced high saline Red Sea-Persian Gulf Water. Red Sea Water is found at depths of 600–800 m, whereas Persian Gulf Water is found at about 250–300 m. This northward flow of Red Sea-Persian Gulf Water is compensated by southern sourced AAIW, which is the dominant intermediate water mass in the Indian Ocean and is found up to 1500 m. Indian Indonesian Water from the Pacific Ocean enters the Indian Ocean at depths of 500–1500 m. Under modern conditions, deep water in the Indian Ocean is ventilated by southern sourced Circumpolar Deep Water (CDW), which is a mixture of well-ventilated, high- ^{13}C , nutrient-poor North Atlantic Deep Water (NADW), and poorly ventilated, CO_2 and nutrient-rich Antarctic Bottom Water (AABW) (You, 2000). The northward flowing CDW after entering the Indian Ocean flows through three different paths; the western pathway - Deep Western Boundary Current (DWBC), the central pathway, and one along the ninety-east ridge (Piotrowski et al., 2009). The Upper Circumpolar Deep Water (UCDW) is mainly composed of NADW and a lesser fraction of AABW. It flows between a water depth of 2–3.8 km. Below 3.8 km is the Lower Circumpolar Deep Water (LCDW), which has AABW as a major component and a small proportion of NADW.

The gravity core SSD-044/GC-01 was raised from a water depth of 3160 m during the RV Sindhu Sadhana cruise No. 44 from the northern Indian Ocean (4.99°N ; 76.99°E) (Fig. 1a and b), within the Central Indian Basin. At present, the core is ventilated by a water mass primarily sourced from the northward circulating UCDW, which has a greater component of NADW (Piotrowski et al., 2009). The region is affected by the seasonal reversal of boundary currents. The sediment core was sub-sampled at a 1 cm interval to a length of 100 cm. The samples were oven dried for 24 hrs at a temperature of 50–60 $^\circ\text{C}$. The weight of the dried samples was measured and then were soaked for 24 hrs in 100 mL distilled water for the samples to disintegrate. The disintegrated samples were wet sieved through a 63 μm mesh in order to remove clay particles. Washing of the samples was done carefully to avoid breakage of foraminifera. The retained coarse fraction ($>63 \mu\text{m}$) was collected in a beaker and kept in an oven at 60 $^\circ\text{C}$ for drying. The dried coarse fraction was then collected in 10 mL vials.

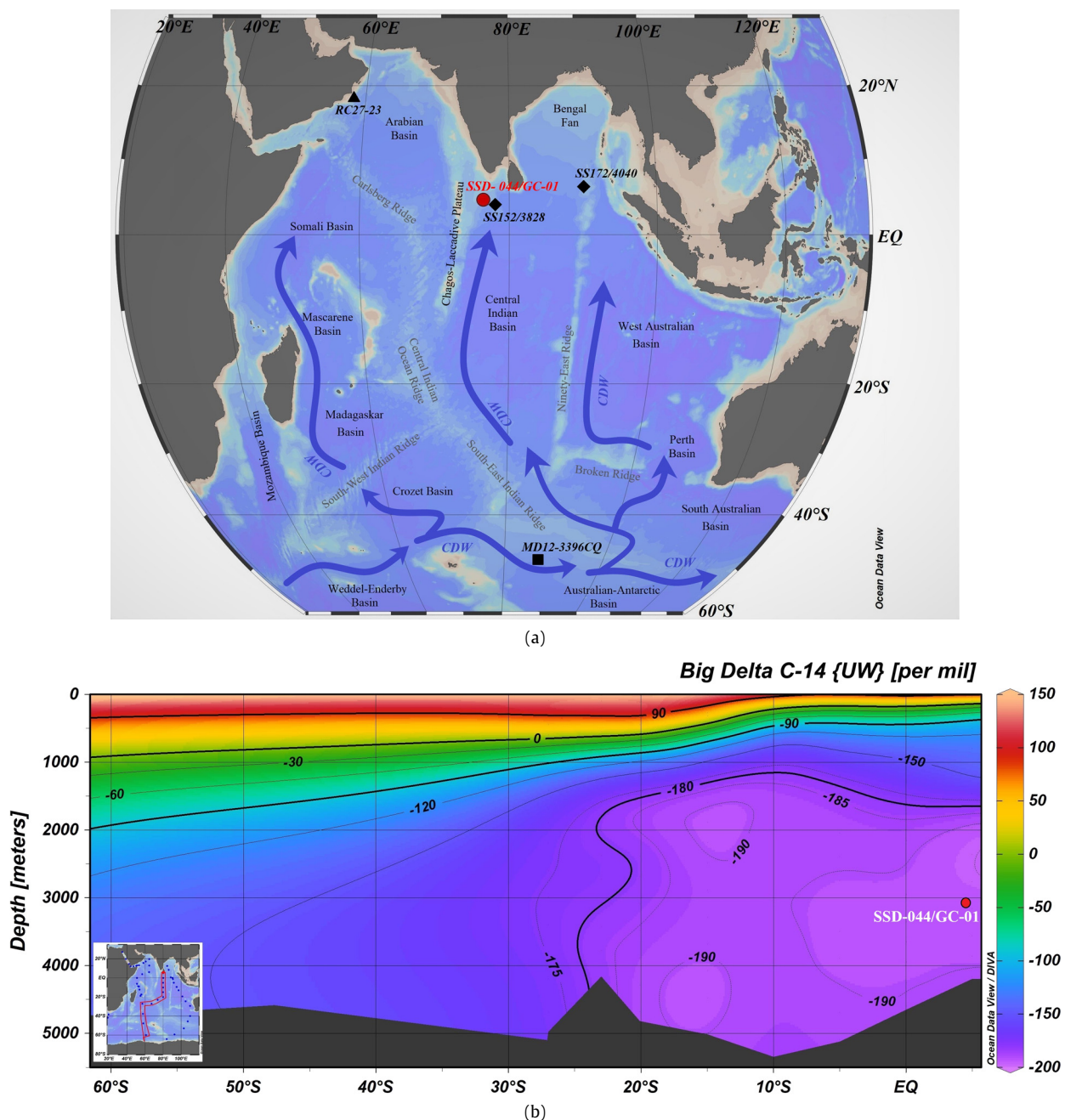


Fig. 1. Core location (a) Map showing location of core SSD-044/GC-01 (CEIO; 4.99°N; 76.99°E; water depth = 3160 m) along with four other cores discussed in this study (RC27-23-Bryan et al., 2010; SS152/3828 and SS172/4040-Bharti et al., 2022; MD12-3396CQ-Gottschalk et al., 2020). The deep water circulation of the northern Indian Ocean is shown with blue arrows. (b) A cross-section of the Indian Ocean with core location showing modern $\Delta^{14}\text{C}$ (GLODAPv2; Key et al., 2015; Lauvset et al., 2016). Both the plots were prepared using Ocean Data View (Schlitzer, 2021).

2.2. Radiocarbon measurements for age model and ventilation ages

Radiocarbon dates were obtained using paired samples of mixed-species of benthic foraminifera (excluding pyrgo and agglutinated species), and planktic foraminifera (*Globigerinoides ruber*). In a few cases, planktic foraminifera *Globigerinoides quadrilobatus* was also picked to obtain the required weight for AMS analysis (~13 mg). For radiocarbon measurement, a representative aliquot of the coarse fraction was dry-sieved through a >250 μm sieve, from which paired intact benthic and planktic foraminifera were handpicked using a stereozoom microscope, and wherever the picked sample weight was <13 mg, foraminifera from size fraction 150–250 μm were also picked. For some benthic samples, specimens from two adjoining intervals were combined to attain suffi-

cient weight for AMS dating. AMS ^{14}C dates were measured at the Inter-University Accelerator Centre (IUAC), New-Delhi, India. Radiocarbon ages for the core SSD-044/GC-01 are summarized in supplementary data (Table 1 and 2, supplementary material; Fig. 2a). Here the ventilation ages of deep water are reported as radiocarbon age which is the difference between paired bottom-dwelling benthic foraminifera and surface-dwelling planktic foraminifera (B-P) based on Broecker et al. (1984), which represents sub-surface radiocarbon age offset.

2.3. Age model

The age model for the top 100 cm of the core was established from the AMS ^{14}C dates derived from planktonic foraminifera from

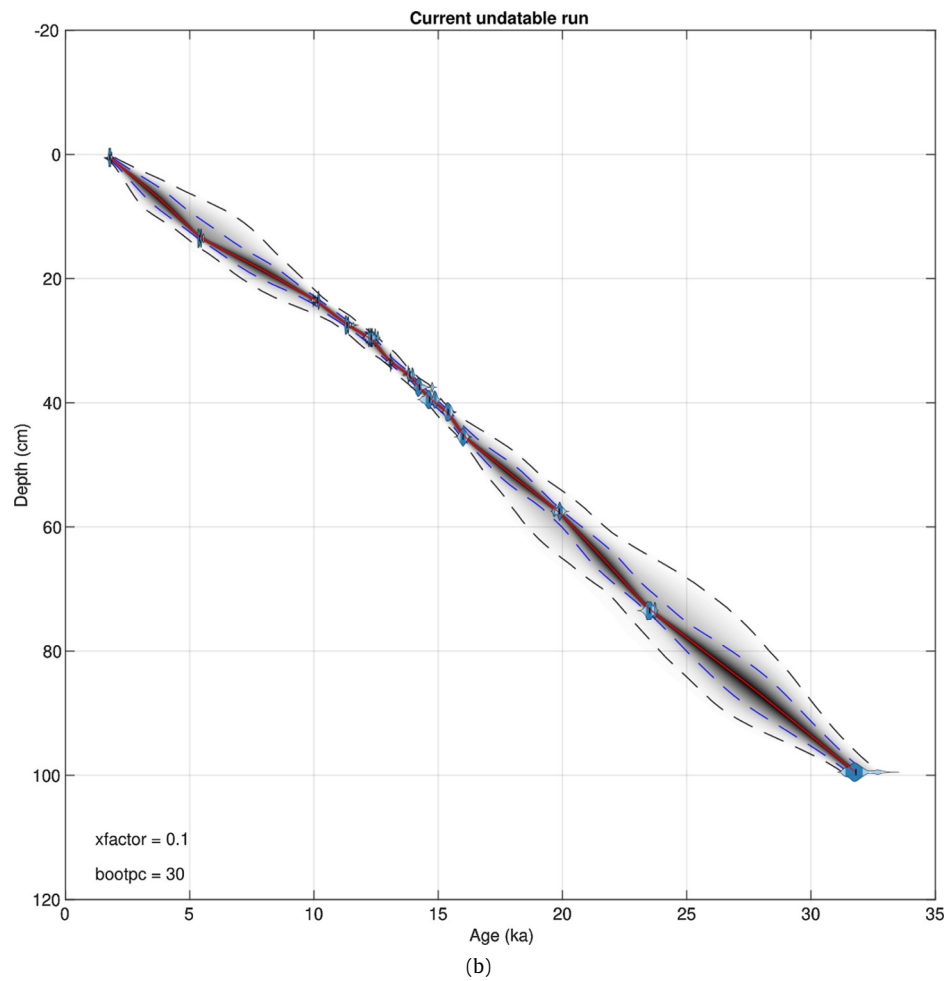
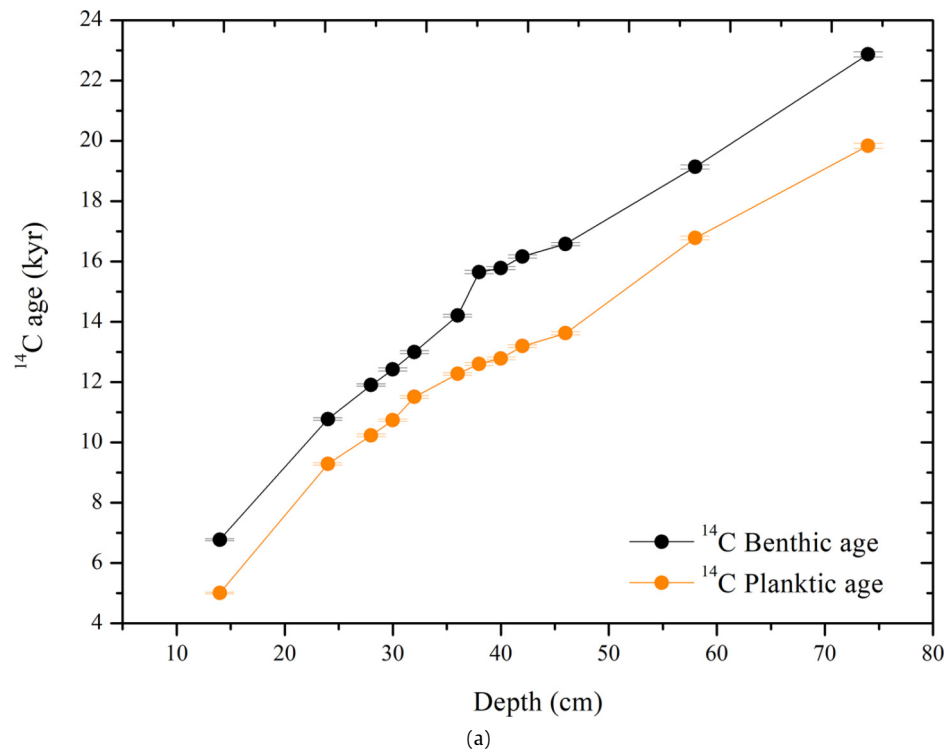


Fig. 2. (a) Measured radiocarbon ages of paired benthic and planktic foraminifera versus depth in the core SSD-044/GC-01. ^{14}C age of benthic foraminifera (black circles), ^{14}C age of planktic foraminifera (orange circles). (b) Undatable age-depth model for the core SSD-044/GC-01. The red line is median, and the blue and black broken lines represent 1σ and 2σ confidence intervals, respectively. The model output of calibrated age (mean and median) at each cm interval along with the uncertainties and sediment accumulation rate (SAR) is provided in supplementary material. (c) Sediment accumulation rate (cm/kyr) plotted versus age in kyr BP.

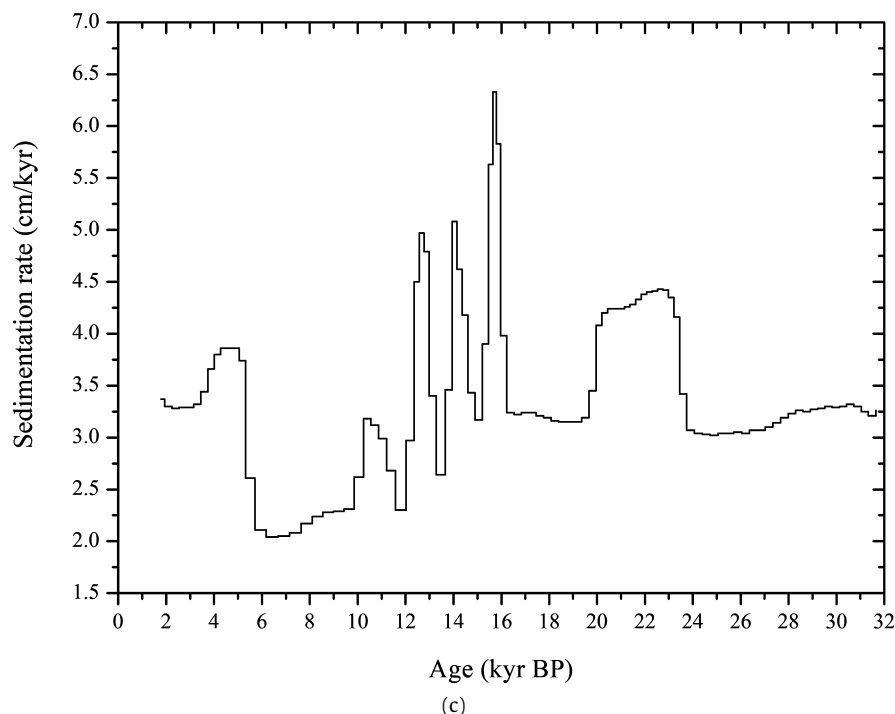


Fig. 2. (continued)

a size fraction of $>250\ \mu\text{m}$ (Table 1, supplementary material). We have used an age-depth modelling routine named *Undatable*, which is developed in MATLAB and uses Bayesian radiocarbon (^{14}C) calibration software (MatCal) (Lougheed and Obrochta, 2019). These ^{14}C ages based age models were calibrated using IntCal20 calibration data. Downcore median ages, confidence intervals, and a density cloud that displays the most likely regions of age-depth probability were calculated by linearly interpolating all *nsim* number of unique age-depth (Lougheed and Obrochta, 2019) runs to 1 depth unit resolution (e.g., cm), and then computing the 1st to 99th percentiles of the ages corresponding to each depth unit. Darker regions of the density cloud are closer to the 50th percentile (Fig. 2b). A reservoir correction of $\Delta R = -91 \pm 25$ years was used (Dutta et al., 2001; Southon et al., 2002). A few of the AMS ^{14}C dates were adopted from Yadav et al. (2021), and re-calibrated using the above procedure. The average sedimentation rate of the core is ~ 3.5 cm/year (Fig. 2c).

2.4. Total Inorganic Carbon (TIC)

Total Inorganic Carbon analysis was done on 10–12 mg of finely ground sediment samples using UIC CM5015 Coulometer. The values are reported as percentage of CaCO_3 . Replicate analysis on ten samples yielded a repeatability of $\pm 2\%$.

2.5. Stable carbon and oxygen isotope

Stable carbon and oxygen isotopes were generated using epifaunal benthic foraminifera *Cibicidoides wuellerstorfi*. For each interval, 3–5 well-preserved foraminifera ($>250\ \mu\text{m}$), with no apparent dissolution, were picked. Isotopic measurement was performed on a Thermo Finnigan Gas Bench II, equipped with a CTC auto-sampler and coupled to a Delta Plus XP Mass Spectrometer with a precision better than $\pm 0.06\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.08\text{‰}$ $\delta^{18}\text{O}$. Calibration was carried out against V-PDB (Vienna Pee Dee Belemnite) standard using an in-house dolomite standard, subsequent to linearity correction that has been calibrated against NBS-18 and NBS-19 reference standards.

2.6. Coarse fraction

The coarse fraction content in all the samples was calculated as the weight of the dried coarse fraction ($>63\ \mu\text{m}$) divided by the total weight of the dry sediment multiplied by hundred.

3. Results

The reconstructed benthic-planktic (B-P) ventilation ages for deep waters suggest that there have been significant changes in deep-water ventilation during the last 25 kyr (Fig. 3a). The apparent age difference between coexisting benthic and planktic foraminifera was ~ 2500 to $3000\ ^{14}\text{C}$ years during the LGM (~ 24 – 17.5 kyr BP) indicating poorly ventilated water at the core location. The ventilation age remained high during the HS1 (~ 17.5 – 14.5 kyr BP) and was around $3000\ ^{14}\text{C}$ years, indicating lowered radiocarbon activity of deep water. At the start of the Bølling-Allerød (B-A; ~ 14.5 – 12.8 kyr BP), there was an abrupt reversal in the ventilation age of deep water. The ventilation age significantly decreased to as low as $\sim 1500\ ^{14}\text{C}$ years indicating better ventilated deep water at that time. During the YD (~ 12.8 – 11.5 kyr BP) there was a small increase of $\sim 300\ ^{14}\text{C}$ years in the ventilation age, which further showed a decrease during the Holocene and was $\sim 1500\ ^{14}\text{C}$ years, indicating relatively better ventilation of water.

Calcium carbonate content of the sediment complements the radiocarbon data (Fig. 3b). In glacial sediments, the average CaCO_3 was $\sim 53\%$, showing lower values at the beginning of LGM and an increase towards the end of it. At the beginning of deglaciation, CaCO_3 began to decline, reducing to $\sim 54\%$ during the HS1. During the B-A, there was a sudden increase in CaCO_3 content, which further reached up to $\sim 62\%$ at ~ 12 kyr BP. Thereafter CaCO_3 content declined into the Holocene with an increase during the late Holocene.

Stable carbon isotopic ($\delta^{13}\text{C}$) records of benthic foraminifera *Cibicidoides wuellerstorfi* showed an increasing trend from the LGM to the Holocene (Fig. 3c). Stable carbon isotopic values range from -0.6‰ to 0.4‰ for the last 25 kyr BP. The $\delta^{13}\text{C}$ values remained low at $\sim -0.4\text{‰}$ during the LGM and HS1. There was a gradual

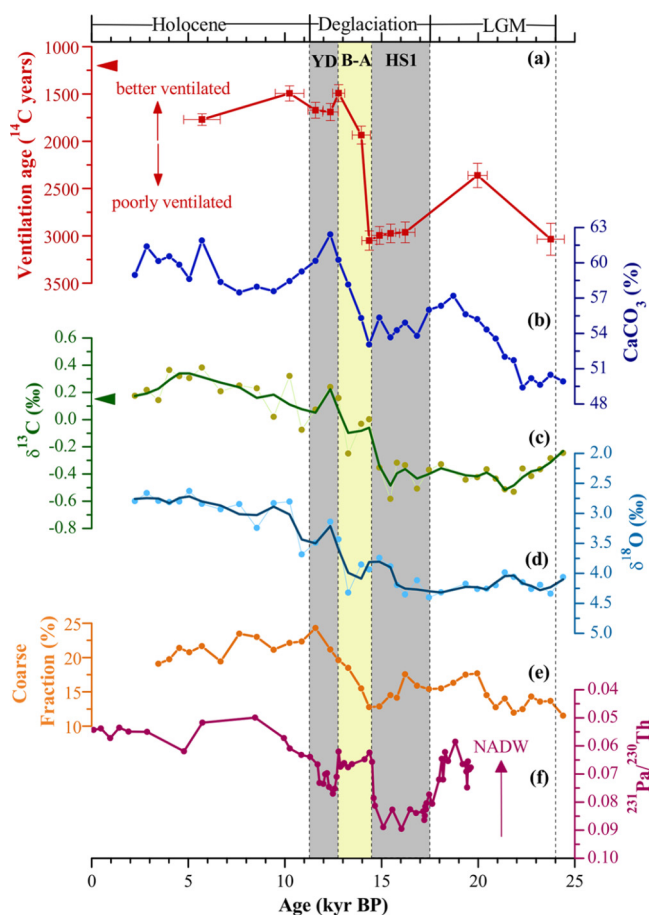


Fig. 3. Graph showing changes in deep water circulation in the northern Indian Ocean during the last 25 kyr. (a) Ventilation ages (red square) which are plotted as benthic-planktic foraminifera radiocarbon age difference from core SSD-044/GC-01. The vertical error bars are the sum of the $\pm$ error of the planktic and benthic foraminifera. The horizontal error bars signify the 1σ depth errors. The red arrow indicates the modern ventilation age. (b) Calcium carbonate content in the sediment core SSD-044/GC-01. (c) Stable carbon isotopic data from core SSD-044/GC-01. The green arrow indicates the modern $\delta^{13}\text{C}_{\text{DIC}}$. (d) Stable oxygen isotopic data of benthic foraminifera *Cibicides wuellerstorfi* from core SSD-044/GC-01. (e) Coarse fraction % ($>63\ \mu\text{m}$) in core SSD-044/GC-01, and (f) sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ in core GGC5 (McManus et al., 2004). Climatic events such as Last Glacial Maxima (LGM), Heinrich Stadial 1 (HS1), Bølling-Allerød (B-A) and Younger Dryas (YD) events are marked by dashed black lines and are shaded.

rise in $\delta^{13}\text{C}$ values through the B-A and YD. This was followed by a short drop and then an increase during the Holocene with values reaching up to $\sim 0.4\text{‰}$ at 4 kyr BP, followed by a slight drop in the late Holocene. The oxygen isotopic ($\delta^{18}\text{O}$) values showed a decreasing trend from the LGM to the Holocene (Fig. 3d). The $\delta^{18}\text{O}$ values fluctuated between 4.4‰ and 2.6‰ for the last 25 kyr BP. Maximum $\delta^{18}\text{O}$ values were recorded during LGM and HS1. The $\delta^{18}\text{O}$ values decreased at the B-A, decreased further at the YD, and then gradually decreased through the Holocene.

The percentage of CF ranged from $\sim 12\text{--}24\%$ (Fig. 3e). The major component of the coarse fraction was biogenous remains with almost no lithogenous fraction for the last 25 kyr BP. The CF % was low during the LGM and HS1. Coarse fraction started to increase from the B-A into the YD, and showed a gradual decrease during the Holocene.

4. Discussion

4.1. Deep water ventilation changes in the northern Indian Ocean

Reconstruction of deep water ^{14}C ventilation age along with benthic stable carbon and oxygen isotope, CaCO_3 , and coarse frac-

tion data from the core SSD-044/GC-01 imply changes in deep water ventilation/source for the last 25 kyr. The difference between benthic- planktic ^{14}C age was higher ($\sim 2500\text{--}3000$ ^{14}C years) during the LGM than in the modern ocean (Fig. 3a). These high ventilation ages during the LGM indicate a strong stratification between the upper and deep water masses and hence poor ventilation existing during that time. We suspect that this poorly ventilated water at our core site originated from a glacially isolated deep-water mass. Studies from the Indian Ocean have suggested that during the LGM, the export of northern sourced water into the Indian Ocean was reduced and was compensated by an increased flow of southern sourced water (Curry et al., 1988). Neodymium (Nd) isotope and ventilation age records of deep water masses in the northern Indian Ocean have also shown a reduced flow of NADW and an increased penetration of nutrient and CO_2 -rich southern sourced water during the LGM (Piotrowski et al., 2009; Lathika et al., 2021; Bang et al., 2021; Bharti et al., 2022). Results from a modelling study suggest the LGM ocean circulation state was characterized by a weak ($10\text{--}15$ Sv) and relatively shallow ($2000\text{--}2500$ m) NADW cell, and a reduced AABW transport (Menviel et al., 2017). A weaker AABW formation rate at the LGM could result from the presence of grounded ice over today's main AABW formation regions such as the Ross and Weddell Seas, and/or weakened or equatorward shifted Southern Hemispheric Westerlies (Menviel et al., 2017). The overall reduced oceanic ventilation at the LGM thus enhanced the efficiency of the oceanic biological pump by enhancing the storage of respired carbon in the ocean interior without causing anoxia (Galbraith and Jaccard, 2015; Menviel et al., 2017). Therefore, reduced deep ocean ventilation during the glaciation would contribute to lowering atmospheric CO_2 , with important implications for past carbon cycle and climate changes (Skinner et al., 2017). Zhang et al., 2022 state that the persistent northward inflow of CDW with corrosive Pacific waters contribution must have been responsible for the ventilation of the deep Indian Ocean during the glacial. Thus majority of studies infer the presence of CO_2 -rich, poorly-ventilated deep-water mass during the glacial, which probably filled the deeper parts of the Indian Ocean.

Variations in CaCO_3 content complement our radiocarbon data (Fig. 3b). Low values of CaCO_3 are recorded during the LGM, which could either be because of low surface productivity, dilution by terrigenous influx, or dissolution at the sea floor. Yadav et al. (2021) have reported high surface productivity during the LGM from the same core, and hence low CaCO_3 content at the core site is not driven by productivity. Dilution can be a factor for this low CaCO_3 , but the low sedimentation rate during the LGM does not support dilution as an important factor (Fig. 2c). Calcium carbonate data is consistent with the coarse fraction record from the same core (Fig. 3e). Low coarse fraction along with low CaCO_3 during the LGM indicates decreased preservation and increased dissolution, implying low bottom-water CO_3^{2-} concentration and hence CO_2 enriched water prevailing at that time. Thus high ventilation age and low CaCO_3 suggest less-ventilated (as compared to the modern ocean), CO_2 -rich glacial water prevailed in the northern Indian Ocean.

The $\delta^{13}\text{C}$ values of benthic foraminifera can be used as a tracer of deep water circulation, complementary to ^{14}C ventilation ages. Benthic foraminifera's carbon isotopic records from the northern Indian Ocean have shown significant changes in deep water chemical characteristics since the last glaciation (Kallel et al., 1988; Ahmad et al., 2012). During the LGM, low $\delta^{13}\text{C}$ values of $\sim -0.4\text{‰}$ were recorded in our core (Fig. 3c), indicating incursion of nutrient-rich and poorly ventilated water. This low $\delta^{13}\text{C}$ is consistent with previously published records from the northern Indian Ocean which have been interpreted as reduced export of NADW, which was compensated by increased export of nutrient-

rich southern sourced water in the Indian Ocean (Duplessy et al., 1984; Naqvi et al., 1994; Ahmad et al., 2012; Raza et al., 2014). The glacial-interglacial $\delta^{18}\text{O}$ shift of $\sim 1.4\text{‰}$ (difference between the $\delta^{18}\text{O}$ average of LGM and early Holocene) exceeds the ice volume change by 0.4‰ , which indicates cooler deep waters during the LGM (Fig. 3d). Hence, high $\delta^{18}\text{O}$ values during the LGM can be linked to an increased inflow of cold southern sourced deep water masses into the northern Indian Ocean. Thus lowered $\delta^{13}\text{C}$ and high $\delta^{18}\text{O}$ support the reduced flow of northern-sourced deep waters, counterbalanced by glacial-aged southern sourced ^{14}C depleted waters at the core site. There is also a mismatch between the trend in ventilation ages and $\delta^{13}\text{C}$, at ~ 20 kyr (Fig. 3a and c). Though we see a drop in ventilation age of ~ 500 yrs, the $\delta^{13}\text{C}$ remains almost unchanged. This could occur due to increasing air-sea disequilibrium of carbon isotopes with lowered $p\text{CO}_2$. Under low atmospheric $p\text{CO}_2$ conditions of the glacials, $\Delta^{14}\text{C}$ is known to increase, and surface reservoir age to increase by ~ 250 yrs throughout the world ocean (Galbraith et al., 2015).

Poorer ventilation (high ventilation ages) of deep waters during the last glaciation in comparison to the modern, has been noted by other studies in the Indian Ocean (Gottschalk et al., 2020; Bharti et al., 2022), the Atlantic (Barker et al., 2010; Skinner et al., 2010) and Pacific Ocean (Galbraith et al., 2007; Rafter et al., 2022). High ventilation ages of the Indian Ocean along with the records from the other oceans suggest significant aging of Southern Ocean deep water (hence, ^{14}C depleted) during the glacial time. This ^{14}C depletion could possibly be the result of a decrease in the exchange of gases between the atmosphere and deep water during the LGM, which led to continuous decay of ^{14}C (Skinner et al., 2010).

Similar to the LGM, deep-water ventilation in the northern Indian Ocean during the HS1 remained poor (Fig. 3a). This period is associated with the melting of icebergs in the North Atlantic. Massive discharge of glacial ice and more freshwater input led to the reduced formation and shoaling of the NADW, and hence resulted in the weakening of AMOC at this time (Elliot et al., 2002; McManus et al., 2004). These changes in the production of NADW led to decreased export of NADW into the Atlantic (Skinner and Shackleton, 2004; Freeman et al., 2015) and the Pacific Ocean (Galbraith et al., 2007). In the Indian Ocean, stable isotopic and geochemical studies suggest a decrease in the export of northern sourced water (Piotrowski et al., 2009; Ahmad et al., 2012; Bharti et al., 2022). Intermediate water studies from the Indian Ocean have pointed to an increased export of southern sourced water into the Indian Ocean (Jung et al., 2009; Ma et al., 2019, 2020). Direct evidence of increased penetration of southern sourced AAIW due to reduced inflow of northern sourced water has been reported using ^{14}C (Bryan et al., 2010) and ε_{Nd} (Yu et al., 2018) proxies. Therefore, the increased ventilation ages at our core site during the HS1 suggest a reduced export of NADW into the northern Indian Ocean. This strongly suggests a greater proportion of southern sourced poorly ventilated AABW inflow as a result of NADW shoaling. The high ventilation ages are very well correlated with CaCO_3 and $\delta^{13}\text{C}$ values.

Studies from the Atlantic Ocean (Skinner and Shackleton, 2004; Robinson et al., 2005; Barker et al., 2010; Skinner et al., 2010) and Pacific Ocean (Galbraith et al., 2007; Marchitto et al., 2007) have reflected increased penetration of NADW during the B-A, since the resumption of AMOC led to extensive formation of NADW at this time (McManus et al., 2004; Böhm et al., 2015). Stable isotope data from the Indian Ocean have also shown an increase in northerly sourced better ventilated water during the B-A (Ahmad et al., 2012; Raza et al., 2014; Ma et al., 2019). In addition, Nd isotopic record points to an expansion of the NADW in the Indian Ocean (Piotrowski et al., 2009). In our study, the HS1 was followed by an abrupt decrease in deep water ventilation age (better ventilation) during the B-A (Fig. 3a), suggesting a major shift

in deep water circulation. We suspect that this low ventilation age could be the result of intensified penetration of better ventilated northern sourced deep water at the core site. A shift in CaCO_3 to higher values was observed in the B-A with a peak in the YD, indicating better preservation of CaCO_3 , which suggests incursion of better ventilated water during this period (Fig. 3b). This is also supported by an increase in coarse fraction % beginning from the B-A (Fig. 3e). A marked positive shift in $\delta^{13}\text{C}$ from B-A onwards, indicates a progressive influx of nutrient-depleted and better ventilated NADW at the core site.

This increase in ventilation was followed by a short-term reduction in deep water ventilation during the YD. The ventilation age increased by ~ 300 ^{14}C years during this cold stadial. This time coincides with the partial weakening of the AMOC (McManus et al., 2004). The reduction in NADW formation was less intense compared to that during the HS1, which is why the decrease in ventilation during YD was less pronounced than HS1 at the core site. Low ventilation age along with high CaCO_3 and $\delta^{13}\text{C}$ during the Holocene indicate that the deep waters were well ventilated as compared to the LGM. Combined results of ventilation age, CaCO_3 , $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ data suggest an increased export of NADW during the Holocene and less dominance of southern sourced deep water in the UCDW.

4.2. Redistribution of ^{14}C depleted water from the Southern Ocean

The benthic-planktic ventilation age variations seen in the Indian Oceans studies; cores SSD-044/GC-01 (this study), RC27-23 (Bryan et al., 2010), SS152/3828 and SS172/4040 (Bharti et al., 2022) are consistent with the increase in atmospheric CO_2 and atmospheric $\Delta^{14}\text{C}$ decline during the deglaciation (Fig. 4). Atmospheric CO_2 rose in two steps during the deglaciation, during the HS1 and the YD (Monnin et al., 2001). Rising deglacial atmospheric CO_2 levels are related to the upwelling of deep, CO_2 -rich water masses to the surface of the Southern Ocean (Broecker and Barker, 2007; Anderson et al., 2009). Vertical mixing in the Southern Ocean is a result of interference of the Antarctic Circumpolar Current (ACC) with local bathymetry. At the onset of HS1, deep-ocean ^{14}C ventilation increased until 16.3 kyr BP, signalling a net loss of remineralized carbon from the deep ocean during that time interval as a result of reinvigorated vertical mixing (Core MD12-3396CQ; Gottschalk et al., 2020 and references therein). However, our core record does not have a sufficient number of data points during the LGM and early HS1 to understand if the Southern Ocean signal was transmitted into the northern Indian Ocean. Later to ~ 16.3 kyr BP, ventilation age records from south of 40° S show a return to glacial-like condition, which relates to a ventilation decrease, a unique feature of the deep South Indian Ocean due to inter-basin differences (Gottschalk et al., 2020). Our ventilation ages are highest at ~ 3000 years during the HS1. This inter-basin heterogeneity abruptly dissipated at the end of HS1, when the ventilation age and oxygen characteristics of deep waters in the different ocean basins rapidly approached prebomb values for the first time throughout the deglaciation (Gottschalk et al., 2020). We find a sharp decrease in ventilation ages beginning at ~ 14.6 kyr as observed in the Southern Indian Ocean core MD12-3396CQ and deep-sea corals from the Drake Passage (Southern Ocean; Burke and Robinson, 2012). The fast increase in ^{14}C and O_2 ventilation in the South Indian Ocean at the end of HS1, at ~ 14.6 kyr BP, is linked to a rapid resumption of Atlantic overturning at the onset of the B-A warm period, which caused homogenization of the entire South Indian water column, laterally and vertically (Gottschalk et al., 2020). The ventilation age records from the northern Indian Ocean along with atmospheric $\Delta^{14}\text{C}$ (Reimer et al., 2020) relate well to the Southern Ocean upwelling indices (Fig. 4d) pointing towards the Southern Ocean as the source for redistribution of aged

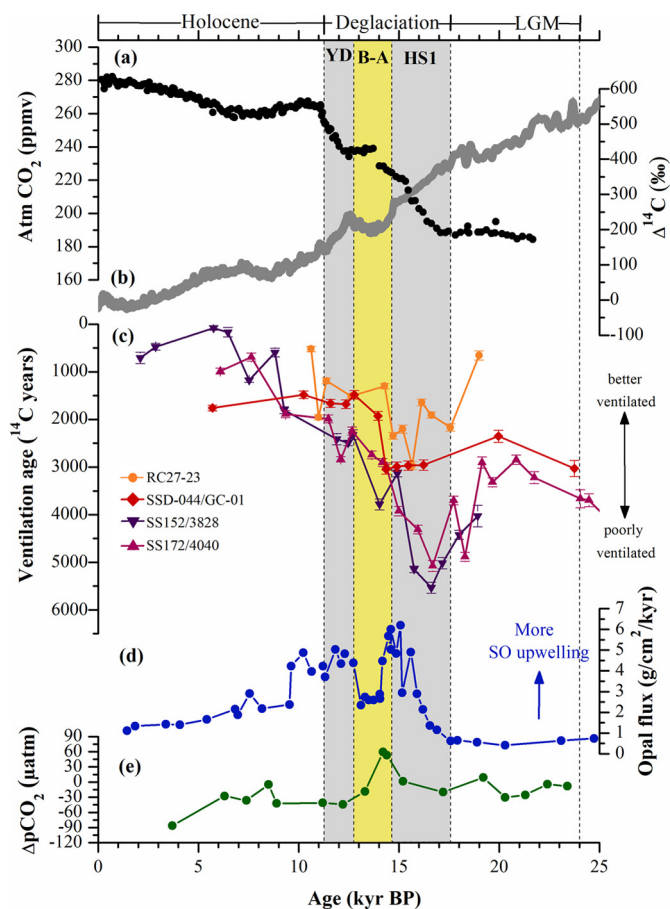


Fig. 4. Comparison of ventilation ages of the northern Indian Ocean to atmospheric CO₂, atmospheric $\Delta^{14}\text{C}$, and the Southern Ocean upwelling record during the last 25 kyr. (a) Atmospheric CO₂ record (black circles; Monnin et al., 2001). (b) Atmospheric $\Delta^{14}\text{C}$ is the IntCal20 calibration curve (grey line; Reimer et al., 2020). (c) The ventilation ages of the core SSD-044/GC-01 (red diamonds), core RC27-23 (orange circles; Bryan et al., 2010), core SS152/3828 (violet inverted triangles; Bharti et al., 2022), and core SS172/4040 (purple triangles; Bharti et al., 2022). These ventilation ages are plotted as benthic-planktic radiocarbon age differences. The vertical error bars are the sum of the $\pm$ error of the planktic and benthic foraminifera. (d) Southern Ocean opal flux indicates upwelling in the Southern Ocean (Anderson et al., 2009). (e) Outgassing of CO₂ from the surface water of the Arabian Sea (Naik et al., 2015). Climatic events Last Glacial Maxima (LGM), Heinrich Stadial 1 (HS1), Bølling-Allerød (B-A), and Younger Dryas (YD) events are marked by dashed black lines and are shaded.

carbon to the other oceans, and to the atmosphere (Anderson et al., 2009).

During the YD, we find a slight increase in ventilation age (poorer ventilation) in core SSD-044/GC-01 (Fig. 3a). In line with our observation, the South Indian Ocean was a moderate source of carbon to the atmosphere during the YD and did not significantly contribute to the late deglacial CO_{2,atm} increase (Gottschalk et al., 2020). At the end of YD, however, there was a rapid loss of carbon from the South Indian Ocean mediated by stronger Atlantic overturning and wind-driven Ekman pumping (Gottschalk et al., 2020). These authors call attention to spatial differences in the timing of CO₂ release from the Southern Ocean, possibly due to lateral variations in the mode and rate of AABW formation and/or the efficiency of air-sea gas equilibration. Coinciding with the low ventilation ages in the deep waters of the Southern Ocean, aged ^{14}C has been observed in the intermediate waters of the western Arabian Sea during the HS1 and YD (Bryan et al., 2010; Fig. 4c). The explanation provided was the release of ^{14}C -depleted carbon from the deep ocean by the renewal of upwelling and mixing in the Southern Ocean and further incorporation into thermocline

and intermediate water masses of the Southern Ocean, and spread northward into the Pacific, Indian and Atlantic Ocean basins (Bryan et al., 2010). However, an outgassing of CO₂ at $\sim 14.4\text{--}14.2$ kyr concomitant to the CO₂ increase of 12 ± 1 ppm of the atmosphere has been reported from the surface water of the eastern Arabian Sea, which was reasoned to be indicative of the upwelling of a nutrient-enriched water mass of Southern Ocean origin (Naik et al., 2015; Fig. 4e). This observation of CO₂ outgassing during the B-A is in agreement with the increase in ^{14}C and O₂ ventilation in the South Indian Ocean linked to a rapid resumption of Atlantic overturning (Gottschalk et al., 2020). The possible link between near-identical timing of CO₂ outgassing from the eastern Arabian Sea during the B-A, the improved ventilation of deep waters of the northern Indian Ocean during the B-A (present study), and the increase in ^{14}C and O₂ ventilation in the South Indian Ocean seem to be the flushing of the deep-ocean carbon pool, not only limited to the Southern Ocean but with a wider impact, in the northern Indian Ocean. Hence our data support the hypothesis that the Southern Ocean upwelling had a vital role in atmospheric CO₂ variation during the deglaciation (Anderson et al., 2009; Skinner et al., 2010). Furthermore, our data suggests that the northern Indian Ocean could have also contributed to the atmospheric CO₂ rise during the deglaciation (specifically the B-A).

5. Conclusions

The ventilation data from core SSD-044/GC-01 illustrates changes in northern Indian Ocean deep water circulation and its relation to climatic changes across the last 25 kyr. The results indicate that during the LGM and the HS1, poorly-ventilated CO₂-rich glacial water prevailed in the northern Indian Ocean. This suggests a greater proportion of southern sourced poorly ventilated AABW filled up majority of the ocean, which could be due to shoaling of the NADW. A sharp decrease in ventilation ages noticed during the B-A coincides with a rapid resumption of Atlantic overturning at the onset of the B-A warm period and an abrupt increase in well-ventilated, high- ^{13}C NADW flow into the Indian Ocean. Furthermore, changes in deep water ventilation are consistent with changes in atmospheric $\Delta^{14}\text{C}$, which implicates changes in carbon exchange between the deep water and atmosphere. Our results thus demonstrate the Southern Ocean's role in ventilation changes of deep waters and hence its control over the exchange of ^{14}C between the ocean and atmosphere.

CRediT authorship contribution statement

Kumari Nisha: Conceptualization, Data curation, Formal analysis, Methodology, Visualization, Writing – original draft. **Sushant Suresh Naik:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Visualization, Writing – review & editing. **Pankaj Kumar:** Formal analysis, Writing – review & editing. **Barnita Banerjee:** Formal analysis, Writing – review & editing. **P.B. Rama Murty:** Formal analysis, Writing – review & editing.

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

All data is provided in supplementary files.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2023.118067>.

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Increased Ventilation of the Northern Indian Ocean during the Last Deglaciation

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ABSTRACT

This paper gives an overview of the deep-water ventilation studies carried out over the world oceans using radiocarbon. There is a consensus that aged water mass existing in the abyssal ocean during the last glacial, dissipated during the Heinrich Stadial 1 (HS1; 17.5-14.7 ka) and the Younger Dryas (YD; 12.9-11.7 Ka, cold event) and hence ventilation increased. The data from the Arabian Sea is in agreement with global records and shows a significant aging of intermediate waters during HS1 and to a lesser extent during the YD and also shows an outgassing of CO₂ centered on the early Bølling Allerød (B-A). Though several studies have been carried out in the Atlantic and Pacific, the Indian Ocean remains scantily studied. Hence it is extremely important to have sufficient data on the ventilation aspect from specific locations in the Indian Ocean chosen to be in the pathway of the deep water circulation branch directing southern sourced waters up north.

INTRODUCTION

Atmospheric CO₂ concentrations are known to be regulated by the oceans, as the ocean can act as a source or sink for CO₂ through its physical and biological pump (Sundquist and Broecker, 1985). The oceans soak up almost one third of CO₂ released into the atmosphere as a result of human activities (Sabine et al., 2004). The present day atmospheric CO₂ concentrations have risen to > 400 ppm as a result of anthropogenic activities since the industrial era. This rise has been steep, from 280 ppm before the beginning of the industrial era to the present, over a short span of 200 years and has led to an ocean storage of ~120 Pg C (Sabine and Tanhuat, 2010). As is well documented, high CO₂ levels in the atmosphere leads to 'global warming' along with changes in ocean water temperature, ocean acidification and deoxygenation.

For the last 800,000 years, the glacial-interglacial CO₂ variations have been within bounds of 180 to 280 ppm (Lüthi et al., 2008). There was an increase in atmospheric CO₂ from glacial to interglacial, but was not gradual throughout. Especially, during the last deglaciation (~ 17.5 – 10 ka) there was a two-step jump in atmospheric CO₂ (Fig. 1a). This has been thought to be facilitated by a large release of CO₂ stored deep in the ocean during glacial times (Broecker and Barker, 2007). This process of CO₂ release is supposed to have mainly occurred through enhanced upwelling of deep waters in the Southern Ocean and subsequent incorporation of these ¹⁴C-depleted waters into the thermocline and intermediate water masses (especially the Antarctic Intermediate Water; AAIW) which spread northward into the Pacific, Indian and Atlantic Ocean basins (Skinner et al., 2010). Skinner et al. (2010) showed that deep waters of the Southern Atlantic which were thought to be ¹⁴C depleted during the glacial, upwelled into intermediate waters, thus decreasing the ¹⁴C of intermediate waters (Fig. 1a and 2). Similar results were reported at many locations throughout the world oceans and therefore this mechanism has come to be widely accepted.

Many studies have shown that during the last glacial there was an aged water mass that existed in the abyssal ocean which dissipated during the Heinrich Stadial 1 (HS1; 17.5-14.7 ka) and the Younger Dryas (YD; 12.9-11.7 ka, cold event) (eg. Marchitto et al., 2007; Skinner et al., 2010). During the HS1/YD, the Southern Ocean warmed as a result of the 'bipolar seesaw'. This led the Antarctic sea ice to reduce significantly from its large extent during the glacial times and deep water masses (Antarctic Bottom Water; AABW) were drawn upward and mixed into the Circumpolar Deep Water (CDW) through which the ¹⁴C depleted CO₂ was eventually released to the atmosphere at the sea surface (Skinner et al., 2010). Hence it is observed that lower ¹⁴C (Fig. 1b), greater ventilation ages (Fig. 1a) and larger B-P (Benthic – Planktic) offsets in many sediment cores at intermediate water depths (see Table 1). During the Bølling Allerød (B-A; 14.7-13 ka, a warm climatic stage in the North Atlantic, coinciding with the Antarctic Cold Reversal; ACR, a cold stage) the Southern Ocean cooled as a result of the bipolar seesaw and the sea ice extent increased (Skinner et al., 2010). Mixing of AABW into the CDW ceased, which is seen in higher ¹⁴C of intermediate waters, decrease in ventilation age and smaller B-P offsets (Skinner et al., 2010). Thus, ocean

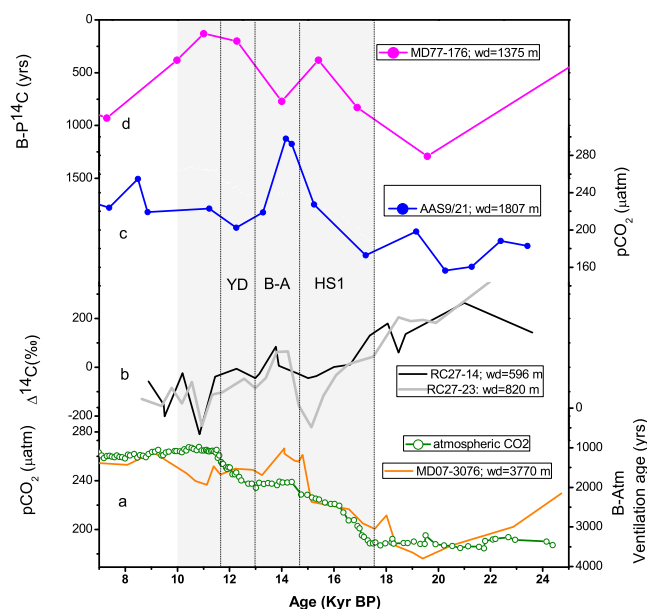


Fig.1. (a) B-Atmosphere ventilation age from the Southern Ocean (Skinner et al., 2010) plotted along with atmospheric CO₂ concentrations (Monnin et al., 2001, Lemieux-Dudon et al., 2010, Schmitt et al., 2012), (b) $\Delta^{14}\text{C}$ from sediment cores of the western Arabian Sea (Bryan et al., 2010), (c) pCO₂ from the eastern Arabian Sea (Naik et al., 2015) and (d) Benthic-Planktic ¹⁴C age from the Bay of Bengal (Ma et al., 2019). The grey shaded area marks the entire deglacial period. The dotted lines mark the Heinrich Stadial 1, HS1; Bølling Allerød, B-A and the Younger Dryas, YD.

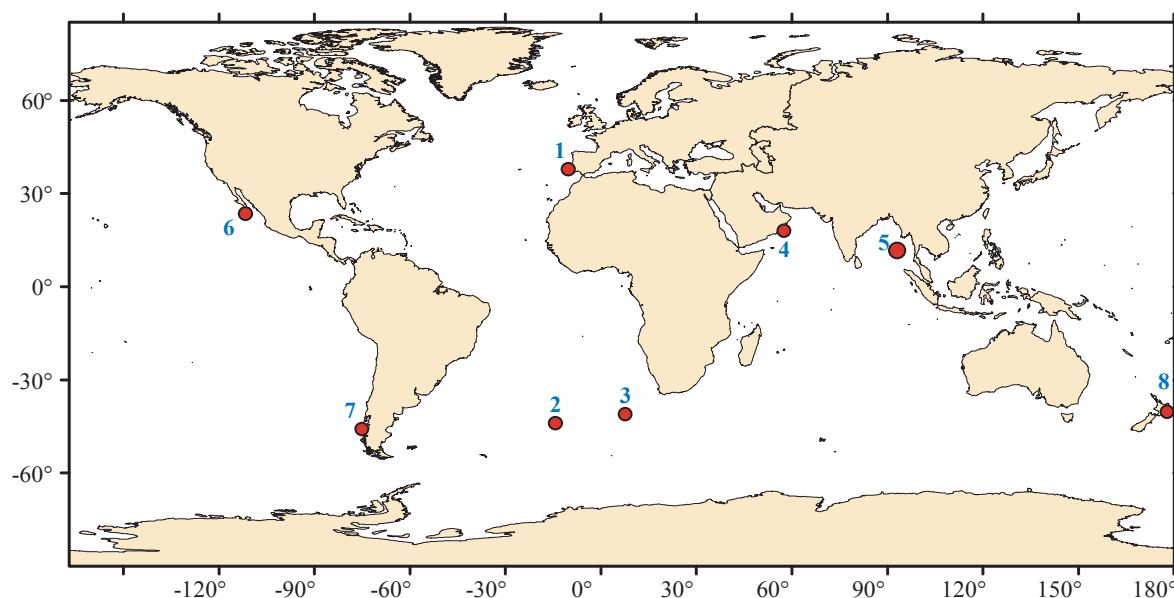


Fig. 2. Map showing the location of sediment cores in all the major oceans used in understanding ventilation changes and discussed in the text. (1) Skinner and Shackleton, 2004, (2) Skinner et al., 2010, (3) Barker et al., 2010, (4) Bryan et al., 2010, (5) Ma et al., 2019, (6) Marchitto et al., 2007, (7) Siani et al., 2013, and (8) Skinner et al., 2015.

circulation can be seen to drive climate variability at timescales ranging from seasonal to glacial–interglacial.

Against the above background, in this paper we have attempted a comparative study of the ventilation history of the deep water masses in two segments of the northern Indian Ocean, the Arabian Sea constituting the western segment and the Bay of Bengal forming the eastern arm. The choice of the study area was dictated by three factors: (a) the northern Indian Ocean is in the pathway of the deep water circulation branch of the global circulation system which directs the southern-sourced waters northwards; (b) the paucity of observations on the deglacial ventilation history of the Indian Ocean compared to such studies in the Atlantic and the Pacific Oceans; and (c) the availability of radiocarbon data from the sediment cores in the Arabian Sea and the Bay of Bengal.

Datasets

Existing data from sediment cores from the two basins of the northern Indian Oceans, viz. $\Delta^{14}\text{C}$ data from the Arabian Sea (RC27-14 and RC27-23 from a water depth of 596 and 820 m respectively; Bryan et al., 2010) and benthic-planktic ^{14}C from the Bay of Bengal (MD77-176 from a water depth of 1375 m; Ma et al., 2019) both covering the last 25 kyr is used. Both the data sets from the Indian Ocean sectors will give an idea on the changes in ventilation of the respective water masses through time. For comparison, published results of similar studies carried out elsewhere in the Atlantic and the Pacific is used (Fig. 2 and Table 1).

DISCUSSION

As mentioned earlier, several studies have been carried out on unravelling the last deglacial ventilation history of deep waters of the Atlantic and Pacific oceans (Fig. 1, Murayama, 1992; Skinner and Shackleton, 2004; Marchitto et al., 2007; Barker et al., 2010; Basak et al., 2010; Skinner et al., 2010; Siani et al., 2013; Skinner et al., 2015). In contrast, similar studies in the Indian Ocean have been non-existent till a decade or so back, when Bryan et al., (2010) showed a significant aging of intermediate waters in the Arabian Sea during HS1 and, to a lesser extent, during the YD (Fig. 1b). The timing and magnitude of ^{14}C depletion in the Arabian Sea during HS1 is very similar to that previously observed in the eastern North Pacific near Baja California (Marchitto et al., 2007), indicating that similar mechanisms were

involved in controlling $\Delta^{14}\text{C}$ (radiocarbon activity) at these two sites. The low $\Delta^{14}\text{C}$ intervals are coincident with increased atmospheric pCO_2 and decreased atmospheric $\Delta^{14}\text{C}$ suggesting the release of ^{14}C -depleted carbon from the deep ocean. Subsequently, there have been two more studies in the Arabian Sea which show outgassing of CO_2 during the deglaciation; both studies use boron isotopes from planktic foraminifera. Palmer et al. (2010) showed that pCO_2 of surface waters was highest during the 11–17 kyr period and linked it to the Asian monsoon. Naik et al. (2015) found an outgassing of CO_2 during the last deglaciation centered on the early B-A and thought it was related to increased monsoon upwelling of high CO_2 waters which were advected from elsewhere (Fig. 1c). These two studies point to the northern Indian Ocean as a location for CO_2 outgassing along with many other locations in the Atlantic and the Pacific. For example, the surface waters at sub-Antarctic Atlantic and the eastern equatorial Pacific, both, which partly derive from deep water upwelled in the

Table 1. Details of all cores shown in Fig. 2 and discussed in text.

Sr. No.	Core	Location	Latitude	Longitude	Water Depth (m)	Reference
1	MD99-2334K	North Atlantic	37.80°N	10.17°W	3146	Skinner and Shackleton (2004)
2	MD07-3076 CQ	South Atlantic	44.07° S	14.21°W	3770	Skinner et al. (2010)
3	TNO57-21	South Atlantic	41.1° S	7.8° E	4981	Barker et al. (2010)
4	RC27-23 RC27-14	Arabian Sea	18°N 18.3°N	57.6°E 57.6°E	820 596	Bryan et al. (2010)
5	MD77-176	Bay of Bengal	4.50°N	93.12°E	1375	Ma et al. (2019)
6	MV99-MC19/ GC31/ PC08	North Pacific	23.5°N	111.6°W	705	Marchitto et al. (2007)
7	MD07-3088	South Pacific	46° S	75° W	1536	Siani et al. (2013)
8	MD97-2121	South Pacific	40.38°S	177.99°E	2314	Skinner et al. (2015)

Southern Ocean became a significant source of carbon to the atmosphere during the last deglaciation (Martinez-Boti et al., 2015). A point to make here is that the timing of CO₂ degassing and the ventilation of deep oceans from different regions of the world oceans were nearly synchronous and happened during the last deglaciation. However the mechanism of how the outgassing occurred at the same time over distant locations is still a matter of debate.

In contrast to the Arabian Sea, the Bay of Bengal sediment core record shows decreased ventilation during the B-A relative to HS1 and the YD (Fig. 1d, Ma et al., 2019). This is an intriguing finding as the AS and BoB cores are from intermediate water depths and we could expect the same mechanism to operate in both these regions on either side of the Indian landmass, and more so since the AAIW (source of low ¹⁴C) has been documented to penetrate into both these regions (Böning and Bard, 2009; Yu et al., 2018). Such a contrast has also been observed between the eastern and western Pacific (De Pol-Holz et al., 2010). A point to note here is that the study location of Ma et al. (2019), in the BoB is further to the north of the study location by Bryan et al. (2010) in the AS. With regard to the study location of Ma et al. (2019) in the northern BoB, it is possible that there was an increase in stratification which started during the Bølling-Allerød, consequent on a freshening of the BoB due to a strengthening phase of SW monsoon and resultant increased freshwater discharge from the Ganges-Brahmaputra river system (Govil and Naidu, 2011).

This increased stratification may not have allowed the sub-surface radiocarbon depleted/aged waters, derived from the Southern Ocean waters, to upwell to the surface, thus leading to a decrease in B-P ¹⁴C yrs. This hypothesis is however, based on the interpretation from a one-off data point from a single sediment core and needs supporting evidence from more studies in the future.

CONCLUSIONS

In agreement with the global records of deep-water ventilation from radiocarbon studies, the lone Arabian Sea record shows aging of intermediate waters during HS1 and the YD. There is a paucity of well-constrained data from the pathway of the deep-water circulation branch which directs the southern-sourced waters northwards in the northern Indian Ocean. The focus should be on unravelling the mechanisms responsible for ventilation changes and whether these ventilation changes are timed and linked globally.

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