Fluctuations in productivity and denitrification in the southeastern Arabian Sea during the Late Quaternary

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Sedimentological and stable isotopic characteristics of sediments have been studied in a core from the southeastern Arabian Sea containing records of the past 70 ka. Palaeoproductivity proxies such as organic carbon (Corg), total nitrogen (TN) and calcium carbonate (CaCO3) contents, show high values at the core top and during the Last Glacial Maximum (LGM) and marine isotope stage (MIS) 4, suggesting high productivity, whereas low Corg and CaCO3 contents are associated with the MIS 1/2 and mid-MIS 3, indicating reduced productivity. The δ18O values in planktonic foraminifera range between −2.7‰ and −0.1‰, with a large glacial-interglacial amplitude Δδ18O of ~2.6‰, suggesting changes related to monsoonal precipitation/runoff. The δ15N values fluctuate between 5.4‰ and 7.3‰, signifying variation in denitrification intensity. The δ15N indicates an overall increase in denitrification intensity during MIS 1 and MIS 3 and, reduced intensity during MIS 1/2, LGM and mid-MIS 3. Higher primary productivity and reduced denitrification intensity during LGM and MIS 4 might be due to convective winter mixing and more oxygenated subsurface waters. Reduced primary productivity during MIS 1/2 and mid-MIS 3 might be the effect of enhanced precipitation associated with the intensified southwest monsoon fortifying near-surface stratification.

Keywords: Arabian Sea, denitrification, productivity, stable isotopes.

The Arabian Sea is one of the most productive regions of the world ocean, marked by large-scale water-column denitrification, which also occurs in the eastern tropical North and South Pacific. Denitrification is considered to be a major sink for oceanic fixed nitrogen that controls the oceanic nitrate inventory, in turn influencing global primary productivity and CO2 sequestration by the biological pump. The Arabian Sea also serves as an important source of N2O, a potent greenhouse gas. It is well accepted that the high δ15N values in intermediate waters and particulate organic matter in this region are the result of denitrification linked to the intensity of the summer monsoon and associated upwelling and productivity. The basin-wide homogenization of the δ15N signal is related to the circulation pattern in the Arabian Sea. Temporal changes in the intensity of denitrification in the Arabian Sea have been linked to fluctuations in atmospheric N2O on glacial-interglacial scales. The organic carbon (Corg) accumulation in the sediments has been used as a productivity proxy driven by the intensity of the southwest monsoon in the past. Several workers have reported Corg variations during glacial and interglacial times in the Arabian Sea and related them to changes in water masses, productivity and climate, both on regional and global scales. Past variations in monsoon-induced denitrification intensity suggest a link between the climates of the Arabian Sea and the North Atlantic. Reduced denitrification as a result of better ventilation of mid-water during the Younger Dryas and Heinrich events is related to oceanic teleconnection with water masses advecting from the south. Most of the studies in the Arabian Sea have been concentrated in its northern and western regions, where high productivity occurs during both the northeast and southwest monsoons (see Figure 1). We have chosen a core (SK126/39) from the southeastern Arabian Sea that experiences upwelling-induced productivity only during the southwest monsoon, and is located close to the boundary of the perennial denitrification zone (Figure 1). This is one of the most suitable sites to track variations in the southwest monsoon-related productivity and intensity of denitrification. The purpose of this article is to understand fluctuations in marine productivity and intensity of denitrification during the Late Quaternary and Holocene.

Oceanographic conditions in the study area

The Arabian Sea experiences reversals in atmospheric and surface oceanic circulation associated with the
southwest and northeast monsoons. Winds and surface currents during the southwest monsoon are conducive for upwelling of nutrient-rich subsurface waters, giving rise to high productivity off Arabia, Somalia and southwestern India$^{4}$ (Figure 1a). Increased productivity is also observed during the northeast monsoon due to convective mixing north of about 15°N (Figure 1b). These phenomena make the Arabian Sea one of the most productive areas of the world ocean. The subsurface water renewal in the Indian Ocean mostly occurs through advection of waters from the south and locally formed intermediate waters (outflows from the Persian Gulf and Red Sea) in the northwestern region. As the renewal rate of water is moderate and productivity is high, a pronounced perennial oxygen minimum zone (OMZ) with dissolved O$_2$ < 0.5 ml l$^{-1}$ (~22 µM) has developed in the Arabian Sea at water depths between 150 and 1200 m (refs 15 and 16). The acute oxygen deficiency leads to large scale denitrification in the water column within a zone that extends from the continental margin off Gujarat to the central Arabian Sea$^{1,7}$ (see Figure 1). Core SK126/39 lies within the high productivity area but at the boundary of this zone (Figure 1). The nitrate profile taken close to the study area exhibits a slight minimum at 100 m depth (Figure 1c) presumably due to denitrification, whereas further south (e.g. at 7°S), high nitrate concentrations persist throughout the subsurface water column (Figure 1c), suggesting an absence of denitrifying conditions.

Figure 1. a and b, Core location (marked in pink circle) on satellite imagers of the Arabian Sea indicating distribution of chlorophyll $a$. Red colour indicates high productivity during (a) southwest monsoon and (b) northeast monsoon. c, Water column profiles of NO$_3$ content. d, Location of the gravity cores with respect to the denitrification zone (marked in grey dotted line) and high productivity area with grey shade (modified after Naqvi$^{1}$; Quasim$^{15}$, and Naqvi et al.$^{15}$).
Methods

We have analysed a 70 k year record of southwest monsoon variability from 490 cm long gravity core collected during the 126th cruise of ORV Sagar Kanya (SK126/39). The core SK126/39 was recovered from 12.63°N, 73.33°E, 1940 m water depth in the southeastern Arabian Sea (Figure 1). Sub-sampling of the core was done onboard at 2 cm intervals in the top 20 cm and 5 cm intervals in the rest of the core. The calcium carbonate (CaCO₃) content of the bulk sediments was determined by rapid gasometric technique, with reproducibility better than ±5%. Corg and total nitrogen (TN) contents were determined using an elemental analyser (NCS 2500), with reproducibility of ±1% for Corg. Nitrogen isotopic analysis was carried out on carbonate-free samples in a Carlo Erba NA2500NC elemental analyser coupled to a Finnigan MAT 252 isotope ratio mass spectrometer at the Hydropheric–Atmospheric Research Center (Institute for Hydropheric–Atmospheric Science), Nagoya University, Nagoya, Japan. The δ¹⁵N value expressed in per mille (%) relative to atmospheric N₂. The analytical precision based on replicates of laboratory standards was about ±0.2‰ for δ¹⁵N. About 15–20 tests of Globigerinoides ruber in the size range of 250–350 μm were hand picked under a binocular microscope from each level and analysed for oxygen isotopes using a MultiPrep (acid on individual carbonate at 90°C) unit attached to a PRISM III mass spectrometer calibrated against the NBS 18 and NBS 19 standards with analytical conditions as described by Chivas et al. [18], at the School of Earth and Environmental Sciences, University of Wollongong, Australia. The isotopic ratios are reported in standard delta notations with respect to Vienna Pee Dee Belemnite (V-PDB). Repeated analysis of standards indicated internal reproducibility of <0.1‰. The average sampling resolution for the oxygen isotopes is about 0.9 kilo annum (ka) for marine isotope stage (MIS) 1 and 2, and 1.6 ka for MIS 3 and 4.

Chronostratigraphy for each core is based on three radiocarbon measurements on G. ruber at the Leibniz-Labor of University of Kiel, Germany, using accelerator mass spectrometry (AMS) and, two bulk sample measurements by conventional radiocarbon method at the Birbal Sahni Institute of Palaeobotany, Lucknow, India. The bulk carbonate ages are generally higher due to the presence of old carbonates. The measured ages are after Kessarkar [19] calibrated using CALIB 4.3 program of Stuiver et al. [20].

Results

Stratigraphy

An age model was obtained by using calibrated ¹⁴C dates [19] as control points and linearly interpolating the ages between the control points. The ages of sediment layers older than the ¹⁴C ages were obtained by assigning tie points by correlating δ¹⁸O curves with the stacked SPECMAP δ¹⁸O curve [21,22]. We have linearly interpolated ages between these tie points and used these to calculate sedimentation rates (Figure 2). The core records for the past 70 ka going back to MIS 4, with the interpolated sedimentation rates varied between 6 and 8 cm/ka.

Variations in δ¹⁸O

The δ¹⁸O values of G. ruber in the core vary between −2.7‰ and −0.1‰ (Figure 3). The core tops the Holocene, marked by lower δ¹⁸O values of −2.5‰ whereas higher δ¹⁸O values are found ~22 ka before present (BP). The glacial-interglacial amplitude, Δδ¹⁸O (the difference between peak glacial and interglacial δ¹⁸O values) is ~2.6‰, with residual Δδ¹⁸O (Δδ¹⁸O after subtracting combined global ice volume effect and regional deglacial warming) of ~0.9‰. The δ¹⁸O values are lower during interglacials and higher during glacial intervals. Low δ¹⁸O values (~1.4‰ to ~0.2‰) occur during MIS 3 with maximum depletion at ~40 ka BP (~1.3‰) and ~50 ka BP (~1.4‰). The δ¹⁸O of ~−0.7‰ is the highest value observed during MIS 4.

CaCO₃, Corg and TN

The CaCO₃ content ranges between 16% and 30% with overall lowest during MIS 2 and MIS 4 and highest during MIS 1 and MIS 3 (Figure 3). Prominent low CaCO₃ contents occur at the MIS 1/2 boundary (~11 to 9 ka BP) and mid-MIS 3 (~40 and ~50 ka BP). The Corg content varies between 0.8% and 2.4% and TN from 0.02% to 0.15%. High concentrations of Corg and TN occur at the core
top and during MIS 2 and MIS 4, whereas low C$_{org}$ content characterizes the MIS 1/2 and mid-MIS 3 (Figure 3).

Variations in $\delta^{15}N$

The $\delta^{15}N$ values of organic matter range between 4.8%o and 7.3%o. The lower $\delta^{15}N$ values are associated with Last Glacial Maximum (LGM), MIS 4, at the MIS 1/2 boundary and mid-MIS 3; higher values distinguish MIS 1 and MIS 3. Generally lower $\delta^{15}N$ values correspond to lower $\delta^{18}O$ values and lower C$_{org}$ and CaCO$_3$ contents (Figure 3), but lower $\delta^{15}N$ is associated with higher $\delta^{18}O$, higher C$_{org}$ and lower CaCO$_3$ during LGM and MIS 4.

Discussion

$\delta^{18}O$ record and monsoonal strength

The glacial–interglacial $\Delta$$\delta^{18}O$ amplitude of 2.6%o is much larger than the combined effect of the global ice volume change (1.2%o) between LGM and Holocene, and regional deglacial warming (0.5%o). The $\Delta$$\delta^{18}O$ amplitude of 2.6%o and residual $\Delta$$\delta^{18}O$ of $\sim$0.9%o observed in the present study are the highest so far reported in the southeastern Arabian Sea$^{24}$. Some workers have reported small or no sea surface temperature (SST) changes in the Arabian Sea$^{21}$, whereas others have observed $\Delta$$\delta^{18}O$ of $\sim$2%o (refs 10 and 24) in the eastern Arabian Sea and related it to local changes in temperature and salinity. The higher $\Delta$$\delta^{18}O$ observed in this area may be because of the core location being closer to the continental margin and the associated increased amount of fresh water due to precipitation and land runoff$^{25}$.

A significant shift of $\delta^{18}O$ towards a lower value ($\sim$1.1%o) at $\sim$15 ka BP, starting around 22 ka BP may be related to glacial warming and/or intensification of the southwest monsoon$^{26}$. Tiwari et al.$^{27}$ reported lower planktonic $\delta^{18}O$ values $\sim$18 ka BP in the equatorial Indian ocean and ascribed it to the intensification of the northeast monsoon. However, an intensification of the southwest monsoon during this period has been reported by Sirocko et al.$^{28}$ using geochemical and multi-tracer studies and by Huguet et al.$^{29}$ using organic proxies. The shift in $\delta^{18}O$ towards higher values around 14 ka BP (Figure 3) may be related to a reduced intensity of the southwest monsoon. Tiwari et al.$^{30}$ reported similarly higher $\delta^{18}O$ values and attributed it to weakened southwest monsoon during the Older Dryas and connection with the North Atlantic climate. Another interval, marked with uniform $\delta^{18}O$ values around 12 ka BP (Figure 3) suggests the Younger Dryas colder event. Although the present data have limitations in terms of sedimentation rates and temporal resolution, significant shift towards lower values ($\sim$2.4%o) around 10 ka BP (starting from 14 ka BP) suggests further strengthening of the southwest monsoon. Intensification of the monsoon has been reported to occur in two phases at 11.5 and 9.7 ka BP in the northern Arabian Sea$^{31}$. Due to limited number of data points, the two events are not well constrained in the core.

The MIS 3 was the time of increased insolation when the South Asian summer monsoon strengthened after MIS 4$^{31}$. The lower $\delta^{18}O$ values at MIS 3 suggest warmer climate with increased precipitation. Within MIS 3 lower $\delta^{18}O$ values at $\sim$40 and 50 ka BP, most probably correspond to periods of the most intense southwest monsoon. Signatures of intensified monsoon during MIS 3 have been reported in the northeastern Arabian Sea using upwelling indicators$^{32}$, but not documented in oxygen isotope data or other palaeomonsoon proxies. The heavier $\delta^{18}O$ values during MIS 4 suggest cooler climate.

Relations between monsoon strength and past productivity variations

During MIS 2 and 4: The C$_{org}$ and TN in marine sediments are derived from the water column and serve as
proxy for the surface primary productivity. However, a part of C组织 can also be contributed by land. The present core exhibits δ13C values of C组织 between −20.8‰ and −19.2‰ (unpublished data) that are typically marine, indicating a predominantly marine source of organic matter. Relatively high C组织 and TN content in sediments during LGM and MIS 4 suggest elevated productivity (Figure 3). During MIS 2, the southwest monsoon was weaker as indicated by higher δ18O values and lower SST. High productivity in the study region during LGM was attributed to lower SST that might have induced convective mixing and injection of nutrients to the euphotic zone. Cooler surface temperatures and higher salinities have been invoked to explain higher δ18O values during MIS 2, which would also favour convection in the upper water column. It is most likely that the northward-flowing low-salinity West India Coastal Current, which presently prevents convective mixing over large parts of the western Indian shelf, weakened during LGM. Our results are supportive of this hypothesis. Several other workers reported similar conditions even further south of our study area during LGM. Higher δ18O values and high C组织 content during MIS 4 suggest that such conditions (convective mixing and high productivity) might have occurred during other glacial stages as well in the southeastern Arabian Sea.

During MIS 1 and MIS 3: Increased C组织, CaCO3 and TN content during MIS 1 and MIS 3 also support higher productivity which is directly related to strong southwest monsoon. Low C组织, TN and CaCO3 contents during MIS 1/2 and mid-MIS 3 (40–50 ka BP) indicate reduced productivity. The MIS 1/2 transition, however, coincides with a strong southwest monsoon (11–6 ka BP) with maximum upwelling at ~11 ka BP (ref. 35). Similarly, increased upwelling has been reported during mid-MIS 3 (~50 ka BP). Low δ18O and CaCO3 content observed at ~40 and ~50 ka BP (Figure 3) further support the prevalence of reduced salinity at the study site which could be due to increased precipitation/runoff. As the core is from a monsoon-induced upwelling area, low productivity during the times of intense monsoon is unexpected and needs explanation. We speculate that increased freshwater inputs during these periods could have led to a much stronger stratification and a thicker fresher-water lens than exists today, thus dominating the expected intensification of coastal upwelling. Strong winds associated with the monsoon might not be able to break the stratification (barrier layer effect), as happens in the Bay of Bengal today, resulting in lower productivity. Similar oligotrophic conditions were reported in the northeast and southwest Arabian Sea during MIS 1/2 (ref. 37) and related to advection of equatorial oligotrophic surface water. Naqvi and Fairbanks have reported a cessation of Red Sea water during the period of deglacial monsoon intensification. It is thus likely that a large part of the Arabian Sea received more inputs of freshwater during this period and the salinity was generally lower.

Monsoon strength – denitrification variations

During MIS 2 and MIS 4: The δ15N values are lower by more than 1% during LGM than the late Holocene, pointing to less intense denitrifying conditions in subsurface waters during LGM. Suppressed denitrification has been previously reported based on δ15N measurements in cores collected from various parts of the Arabian Sea and attributed to low productivity during LGM (i.e. related to weaker southwest monsoon). Implicit in this interpretation is the assumption that the oxygen concentration in subsurface waters is dominantly controlled by productivity.

The sedimentary δ15N record in the present study also indicates less intense denitrification during LGM, consistent with previous results from elsewhere in the Arabian Sea, providing further support for the δ15N signal to be regional. Galbraith et al. have related reduced denitrification rates during glacial periods to greater oxygen supply to thermocline waters. Significantly, at the core site itself productivity seems to have been higher during glacial times. The likely cause for this is mentioned here – a more intense convective mixing during winter would also keep the mesopelagic layer more oxygenated, thereby suppressing denitrification. The increase in δ15N values to over 7‰ from 17 to 15 ka BP (Figure 3) suggests an increase in denitrification rate. This implies a reduction of oxygen content of subsurface waters. Note that barring a single-point sharp excursion in δ15N (discussed here), there is a broad maximum in δ18O that is associated with decreasing C组织 and TN but increasing CaCO3 before consistent minima in all proxies are observed around the transition from MIS 2 to MIS 1. A local intensification of the oxygen minimum during deglaciation might arise from a relaxation of convective mixing as a consequence of warming and/or change in circulation (intensification of the northward West Indian Coastal Current). Sediment cores from the southwestern Indian margin and terrestrial records do indicate warming of the climate during this period. The sharp minimum in δ15N to 4.8‰ around 14 ka BP (Figure 3), associated with the higher δ18O values suggest a brief period of cooler climate. Similar lower δ15N values have been reported by Suthof et al. from the northern Arabian Sea during Heinrich Events and Younger Dryas and related to the reduced denitrification and productivity. A relaxation in denitrification has been postulated to occur during each such event due to advection of more oxygenated water masses from the south into the Arabian Sea OMZ. The low δ15N values and higher C組織 during MIS 4 suggest suppressed denitrification as a result of deep convective mixing, similar to MIS 2.
During MIS 1 and MIS 3: The fluctuations in $\delta^{15}$N are more conspicuous during MIS 1. Reduced denitrification rates, represented by lower $\delta^{15}$N values (to 5.4%), correspond to lower $C_{O_{2}}$, TN and CaCO$_3$ contents (Figure 3) around 10 ka BP. This period of seemingly weaker denitrification coincides with intensification of the southwest monsoon$^3$ and increased precipitation$^1$. Elsewhere in the Arabian Sea, this period is distinguished by high sedimentary $\delta^{15}$N (refs 7 and 13). At present, the southeastern Arabian Sea is characterized by complex hydrography and biogeochemistry. Coastal upwelling stimulates phytoplankton growth and the ensuing increase in subsurface oxygen demand leads to the development of anoxic conditions over the inner- and mid-shelf regions during the late southwest monsoon$^3$. This process is helped by the existence of strong near-surface stratification, as the cold, saline upwelled waters are overlain by a thin (5–10 m) warm, low-salinity cap. However, off the continental margin of India, the presence of the undercurrent, a part of the SW monsoon circulation, prevents the development of suboxic conditions. The lighter $\delta^{15}$N observed during the intensified monsoon$^3$, could again be a local feature arising from a more vigorous undercurrent during the southwest monsoon. At the same time, it is also possible that there was greater intrusion of nutrient-poor, surface water from the south as proposed by Rixen et al.$^{42}$.

Higher denitrification rates since 7 ka BP are suggested by relatively high $\delta^{15}$N values (~6.7‰) and are largely similar to that of the present day, except at ~4, ~2.5 and ~1 ka BP (Figure 3). Overall, there does not seem to have been any major fluctuation in subsurface oxygen distribution. Lower $\delta^{15}$N value around 4 ka BP indicates reduced denitrification that seems to be associated with a weaker southwest monsoon. However, it must be pointed out that the core examined here exhibits relatively low sedimentation rates that could have dampened the signal and prevented resolution of high frequency changes. Cores along the continental shelf-upper slope of India with higher sedimentation rates may provide a better insight into these variations.

As indicated earlier, MIS 3 was a time of generally higher insolation, and strengthened SW monsoon$^3$. However, large changes in sedimentary $\delta^{15}$N values have been reported during this stage that seem to relate well to climate variability in the North Atlantic as recorded in the sediments and Greenland ice cores with warm (cold) events in the North Atlantic corresponding to high (low) $\delta^{15}$N in the Arabian Sea sediments$^{11,12}$. In our core, variations in $\delta^{15}$N values during MIS 3 are smaller compared to MIS 1, but this could well be due to coarser temporal resolution. Nevertheless, denitrification seems to have been weaker around 40 and 50 ka BP, again associated with the intensification of SW monsoon within MIS 3.


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