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

Pratima M. Kessarkar1,*, V. Purnachandra Rao1, S. W. A. Naqvi1, Allan R. Chivas2 and T. Saino3
1National Institute of Oceanography, Council of Scientific and Industrial Research, Dona Paula, Goa 403 004, India
2Geo-QuEST Research Centre, School of Earth and Environmental Sciences, University of Wollongong, NSW 2522, Australia
3Hydrospheric Atmospheric Research Center, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

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 India14 (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 Sea1,17 (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.
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 Hydrospheric–Atmospheric Research Center (Institute for Hydrospheric–Atmospheric Science), Nagoya University, Nagoya, Japan. The δ¹⁵N value is 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. at the School of Earth and Environmental Sciences, University of Wollongong, Australia. The isotopic ratios are reported in standard delta notation 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 calibrated using CALIB 4.3 program of Stuiver et al.

Results

Stratigraphy

An age model was obtained by using calibrated ¹⁴C dates 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. 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 top represents 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
Figure 3. Stable oxygen isotope ($\delta^{18}O$) values and content of CaCO$_3$, organic carbon ($C_{org}$), total nitrogen (TN), and nitrogen isotope ($\delta^{15}N$) values; marine isotope stage (MIS). Black arrows show intensified monsoon signatures during MIS 1/2 and grey arrows during MIS 3.

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‰ and 7.3‰. 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‰ is much larger than the combined effect of the global ice volume change (1.2‰) between LGM and Holocene. Some workers have reported small or no sea surface temperature (SST) changes in the Arabian Sea, whereas others have observed $\Delta\delta^{18}O$ of $\sim$2‰ 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.

A significant shift of $\delta^{18}O$ towards a lower value ($\sim$1.1‰) at $\sim$15 ka BP, starting around 22 ka BP may be related to deglacial warming and/or intensification of the southwest monsoon. Tiwari et al. 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. using geochemical and multi-tracer studies and, by Huguet et al. 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. 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 interruption, 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‰) 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. 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. 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, 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...
have been invoked to explain higher
workers\textsuperscript{25,34} reported similar conditions even further
ence of reduced salinity at the study site which could be
\(-19.2\,\text{‰} \) (unpublished data) that are typically marine,
indicating a predominantly marine source of organic mat-
ter. Relatively high \( C_{\text{org}} \) and TN content in sediments
during LGM and MIS 4 suggest elevated productivity
\( (\text{Figure } 3) \). During MIS 2, the southwest monsoon was
weaker\textsuperscript{25} as indicated by higher \( \delta^{18} \text{O} \) values and lower
\( \delta^{18} \text{O} \) 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\textsuperscript{25}. Our
results are supportive of this hypothesis\textsuperscript{6,10}. Several other
workers\textsuperscript{25,34} reported similar conditions even further
south of our study area during LGM. Higher \( \delta^{18} \text{O} \) values and high \( C_{\text{org}} \) 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.

\textit{During MIS 1 and MIS 3}: Increased \( C_{\text{org}}, \text{CaCO}_3 \) and
TN content during MIS 1 and MIS 3 also support higher
productivity which is directly related to strong southwest
monsoon. Low \( C_{\text{org}}, \text{TN and CaCO}_3 \) contents during
MIS 1/2 and mid-MIS 3 \( (40-50 \text{ ka } \text{BP}) \) indicate reduced
productivity. The MIS 1/2 transition, however, coincides
with a strong southwest monsoon \( (11-6 \text{ ka } \text{BP})\textsuperscript{10,25,35} \),
with maximum intensity at \(-11 \text{ ka } \text{BP} \) (ref. 35). Similarly,
increased upwelling has been reported during mid-MIS 3
\( (-50 \text{ ka } \text{BP})\textsuperscript{25} \). Low \( \delta^{18} \text{O} \) and \( \text{CaCO}_3 \) content observed at
\(-40 \text{ and } -50 \text{ ka } \text{BP} \) (Figure 3) further support the preva-
ence 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\textsuperscript{36}, low productivity
during the times of intense monsoon is unexpected and
needs explanation. We speculate that increased freshwa-
ter 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 intensifi-
cation 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 oligotro-
phic conditions were reported in the northeast and south-
west Arabian Sea during MIS 1/2 (ref. 37) and related to
advection of equatorial oligotrophic surface water. Naaqvi
and Fairbanks\textsuperscript{38} have reported a cessation of Red Sea
water during the period of deglacial monsoon intensifica-
ton. 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.

\textbf{Monsoon strength – denitrification variations}

\textit{During MIS 2 and MIS 4}: The \( \delta^{15} \text{N} \) values are lower by
more than 1\% during LGM than the late Holocene, point-
ing to less intense denitrifying conditions in subsurface
waters during LGM. Suppressed denitrification has been
previously reported based on \( \delta^{15} \text{N} \) measurements in cores
collected from various parts of the Arabian Sea\textsuperscript{2,4,7} and
attributed to low productivity during LGM (i.e. related to
weaker southwest monsoon). Implicit in this interpreat-
tion is the assumption that the oxygen concentration in
subsurface waters is dominantly controlled by produc-
tivity.

The sedimentary \( \delta^{15} \text{N} \) record in the present study also
indicates less intense denitrification during LGM, consist-
tent with previous results from elsewhere in the Arabian
Sea, providing further support for the \( \delta^{15} \text{N} \) signal to be
regional. Galbraith \textit{et al.}\textsuperscript{37} have related reduced denitrifi-
cation rates during glacial periods to greater oxygen sup-
ply to thermocline waters. Significantly, at the core site
itself productivity seems to have been higher during gla-
cial 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 \( \delta^{15} \text{N} \) 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 baring
a single-point sharp excursion in \( \delta^{15} \text{N} \) (discussed here),
there is a broad maximum in \( \delta^{18} \text{O} \) that is associated with
decreasing \( C_{\text{org}} \) and TN but increasing \( \text{CaCO}_3 \) before con-
sistent 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\textsuperscript{40}. The sharp minimum in \( \delta^{15} \text{N} \) to 4.8\% around
14 ka BP (Figure 3), associated with the higher \( \delta^{18} \text{O} \) values
suggest a brief period of cooler climate. Similar lower \( \delta^{15} \text{N} \) values have been reported by Suthhof \textit{et al.}\textsuperscript{13}
from the northern Arabian Sea during Heinrich Events
and Younger Dryas and related to the reduced denitrifi-
cation 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\textsuperscript{11-13}. The low \( \delta^{15} \text{N} \) values
and higher \( C_{\text{org}} \) 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 δ15N are more conspicuous during MIS 1. Reduced denitrification rates, represented by lower δ15N values (to 5.4‰), correspond to lower Corg, TN and CaCO3 contents (Figure 3) around 10 ka BP. This period of seemingly weaker denitrification coincides with intensification of the southwest monsoon and increased precipitation. Elsewhere in the Arabian Sea, this period is distinguished by high sedimentary δ15N (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. 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 upwelling, a part of the SW monsoon circulation, prevents the development of suboxic conditions. The lighter δ15N observed during the intensified monsoon, could again be a local feature arising from a more vigorous upwelling 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. Higher denitrification rates since 7 ka BP are suggested by relatively high δ15N 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 δ15N 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. However, large changes in sedimentary δ15N 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) δ15N in the Arabian Sea sediments. In our core, variations in δ15N 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.

References:


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