Spatiotemporal variations of nitrogen isotopic records in the Arabian Sea

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Abstract

Available reports of dissolved oxygen, $\delta^{15}N$ of nitrate ($\delta^{15}N_{NO3}$) and $\delta^{15}N$ of total nitrogen ($\delta^{15}N_{bulk}$) for trap material and surface/downcore sediments from the Arabian Sea (AS) were synthesized to explore its past nitrogen dynamics. Based on 25 μmol kg^{-1} dissolved oxygen isopleth at 150 m deep, we classified all reported data into northern and southern groups. By using $\delta^{15}N_{bulk}$ of the sediments, we obtained geographically distinctive bottom-depth effects for the northern and southern AS at different climate stages. After eliminating the bias caused by bottom depth, the modern day sedimentary $\delta^{15}N_{bulk}$ values largely reflect the $\delta^{15}N_{NO3}$ supply from the bottom of the euphotic zone. For an addition to the dataset, nitrogen and carbon contents versus their isotopic compositions of a sediment core (SK177/11) collected from the most southeastern part of the AS were measured for comparison. We found a one-step increase in $\delta^{15}N_{bulk}$ starting at the deglaciation with a corresponding decrease in $\delta^{13}C_{TOC}$ similar to reports elsewhere revealing a global coherence. By synthesizing and re-analyzing all reported down core $\delta^{15}N_{bulk}$, we derived bottom-depth correction factors at different climate stages respectively for the northern and southern AS. The

diffusive sedimentary $\delta^{15}N_{bulk}$ values in compiled cores became confined after bias correction revealing a more consistent pattern except recent 6 ka. Such high similarity to the global temporal pattern indicates that the nitrogen cycle in the entire AS had responded to open-ocean changes until 6 ka BP. Since 6ka BP further enhanced denitrification (i.e., increase in $\delta^{15}N_{bulk}$) in the northern AS had occurred and likely driven by monsoon; while in the southern we observed a synchronous reduction in $\delta^{15}N_{bulk}$ implying that nitrogen fixation was promoted correspondingly as the intensification of local denitrification at the northern AS basin.

1 Introduction

Biogeochemical processes of nitrogen in the ocean are intimately related to various elemental cycles synergistically modulate atmospheric CO_2 and N_2O concentrations, thus feedback to climate on millennial time scale (Gruber, 2004; Falkowski and Godfrey, 2008; Altabet et al., 2002). Though oxygen deficient zones (ODZs) occupy only ~4% of ocean volume, the denitrification process therein contributes remarkably to the losses of nitrate, leaving excess P in the remaining water mass to stimulate N_2-fixation while entering euphotic zone (Morrison et al., 1998; Deutsch et al., 2007) and thus controlling the budget of bio-available nitrogen in ocean. Denitrification leaves $^{15}NO_3^-$ in residual nitrate (Sigman et al., 2001); whereas, N_2-fixation introduces new bio-available nitrogen with low $\delta^{15}N$ values (Capone et al., 1997) into ocean for compensation. The Arabian Sea (AS), as one of the three largest ODZs in the world ocean with distinctive monsoon driven upwelling, accounts for at least one third of the loss of marine fixed nitrogen (Codispoti and Christensen, 1985) playing an important role in the past climate via regulating atmospheric N_2O concentration (Agnihotri et al., 2006) or nitrogen inventory to modulate CO_2 sequestration through biological pump (Altabet, 2006).

Sedimentary nitrogen isotope, measured as standard δ notation with respect to standards of atmospheric nitrogen, is an important tool to study the past marine nitrogen cycle. Nitrogen isotope compositions of sedimentary organic matter potentially reflect biological processes in water column, such as denitrification (Altabet et al., 1995; Ganeshram et al., 1995, 2000), nitrogen fixation (Haug et al., 1998), and the degree of nitrate utilization by algae (Altabet and Francois, 1994; Holmes et al., 1996; Robinson et al., 2004). However, alteration may occur (through various ways or processes, e.g., diagenesis) before the signal of $\delta^{15}N$ of exported production is buried.

Previous measurements of $\delta^{15}N_{bulk}$ in various cores and surface sediments in the AS showed the following points: 1) near-surface NO_3^- in AS is completely utilized in an annual cycle, resulting in small isotopic fractionation between $\delta^{15}N$ of exported sinking particles and $\delta^{15}N$ of NO_3^- supplied to the euphotic zone (Altabet, 1988; Thunell et al., 2004); 2) monsoon-driven surface productivity and associated oxidant demand are regarded as the main control on water column denitrification in the past (Ganeshram et al., 2000; Ivanochko et al., 2005); 3) sedimentary $\delta^{15}N_{bulk}$ primarily reflects the relative intensity of water column denitrification in this area (Altabet et al., 1995; 1999) ; and 4) oxygen supply at intermediate depth by the Antarctic Intermediate Waters (AAIW) can modulate the denitrification intensity in northern AS (Schulte et al., 1999; Schmittner et al., 2007; Pichevin et al., 2007). Among previous researches, the geographical features in sedimentary $\delta^{15}N_{bulk}$ between north and south basins of AS have not been discussed, particularly on the basis of bottom-depth effect which might be different during glacial and interglacial periods.

In this study, a sediment core (SK177/11) collected from the slope of southeastern AS was measured for organic C and N contents and their stable isotopes. We synthesized previous hydrographical and isotopic data, such as dissolved oxygen (DO), N* ($N^* = NO_3^- - 16 \times PO_4^{3-} + 2.9$; Gruber and Sarmiento, 2002), and $\delta^{15}N$ of nitrate as well as trapped material and surface/downcore sediments, among which surface and downcore sediments may have experienced more intensified diagenetic alteration. Based on the subsurface DO concentration of 25 μmol kg^{-1} isopleth at 150 m, the datasets in the AS were separated into north and south basins by time span (glacial, Holocene and modern) for comparison. We aim to (1) investigate the geographic and glacial-interglacial differences in bottom-depth effect and to (2) retrieve extra information from sedimentary $\delta^{15}N_{bulk}$ by removing basin/climate stage specific bottom-depth effects, thus, better decipher the environmental history of the Arabian Sea.

2 Study area

The Arabian Sea is characterized by seasonal reversal of monsoon winds, resulting in large seasonal physical/hydrographic/biological/chemical variations in water column (Nair et al., 1989). Cold and dry northeasterly winds blow during winter from high-pressure cell of the Tibetan Plateau, whereas heating of the Tibetan Plateau in summer (June to September) reverses the pressure gradient leading to warm and moist southwesterly winds and precipitation maximum. In present day, the SW monsoon is much stronger than its northeastern counterpart.

The spatial distribution of DO at 150 m deep for the AS is shown in Figure 1a (World Ocean Atlas 2009, http://www.nodc.noaa.gov/OC5/WOA09/woa09data.html), which shows a clear southward increasing pattern with DO increased from ~5 to >100 μmol kg^{-1} and the lowest DO value appears at the northeast of the northern basin. As denitrification, the dominant nitrate removal process, generally occurs in the water column where DO concentration ranges 0.7~20 μmol kg^{-1} (Paulmier et al., 2009), the intensity of denitrification was reported to descend gradually, corresponding with the DO spatial pattern from northern to southern parts of AS, and became unobvious at 11 or 12 °N (Naqvi et al., 1982). As indicated by upper 2000 m N-S transect of DO (Fig. 1c), a southward decreasing in ODZ thickness can be observed and the contour line of 5 μmol kg^{-1} extends to around 13 °N. Since the nitrate source is mainly from the bottom of euphotic zone at around 150 m we postulate a geographically distinctive sedimentary $\delta^{15}N_{bulk}$ underneath ODZ. Thus, an isopleth of 25 μmol kg^{-1} DO at 150 m is applied as a geographic boundary to separate the northern from the southern part of AS basin. The interface where DO concentration changed from 20 to 30 μmol kg^{-1} was such a transition zone. On the other hand, the bottom layer of ODZ moves shallower toward south as shown previously by Gouretski and Koltermann (2004). Accordingly, the bottom oxygen content may also be a factor to influence the degree of alteration in sedimentary $\delta^{15}N_{bulk}$.

As mentioned in Introduction, nitrate is removed via denitrification in ODZs resulting in excess P to stimulate N_2-fixation. In Figs. 1d, 1e and 1f, we presented the N-S transect of nitrate and N* (for both the upper 2000 m and 300 m) in January. Even though there contains nitrate in the very surface water (Fig. 1d), as mentioned earlier near-surface NO_3^- in AS is completely utilized in an annual cycle (Altabet, 1988; Thunell et al., 2004). Furthermore, negative N* (P-excess) throughout the water column represents a nitrate deficit and the lowest N* value appears at ~300 m at 18-20 °N, where DO is <1 μmol kg^{-1}. Meanwhile, a gradually southward increase in N* can be observed for upper 100 m (Fig. 1f) and the isopleth of N* of -4 deepens southward with the highest N* (-2) appearing at ~10-12 °N. The volume expansion of high N* water as well as a simultaneous increase in N* strongly indicate an addition of bio-available nitrogen when surface water traveling southward.

3 Material and method

A sediment gravity core, SK177/11 (8.2 °N and 76.47 °E), was collected at water depths of 776 m on the continental slope off southwest coast of India (Kerala) during the 177th cruise of *ORV SagarKanya* on October 2002. Although the core MD77-191 locates further south in the AS (Bassinot et al., 2012), SK177/11 is so far the southernmost core with reference to $\delta^{15}N$ record. The 3.65 m long core was sub-sampled at intervals of 2 cm from top to 100 cm, and 5 cm from 100 cm to the bottom of the core (open circles in Fig. 2a). There is a distinct boundary at ~1.7 m, above which the core contains mainly of brownish grey clayey sediments. Neither distinct laminations nor turbidities can be observed by visual contact immediately after collection or at the time during sub-sampling (Pandarinath et al., 2007). All sub-samples were freeze-dried and ground into powder in an agate mortar with pestle. Sand was almost absent (<1 wt.%) throughout the core.

The calendar chronology for core SK177/11 was based on 7 accelerator mass spectrometry (AMS) radiocarbon (^{14}C) dates of bulk organic matter (Fig. 2a). Calendar years were calculated using calibration CALIB 6.0 with a reservoir age correction of 402 years (Stuiver et al., 1998; Reimer et al., 2009). Details on the ^{14}C age controlling points were presented in Table 1. Given that the AMS ^{14}C dates of SK177/11 were obtained on total organic carbon, we may not be able to avoid the mixture of organics of different ages during transport (Mollenhauer et al., 2005) or interference by pre-aged organics sourced from land (Kao et al., 2008). However, besides the reservoir age correction, higher TOC contents (Range: 2.2~5.5%) of sediments and their marine-sourced organic carbon, as confirmed by stable C isotope data and C/N ratio shown in Figs. 3b and 3e,we are confident that our age model is reliable and less likely affected by age heterogeneity.

Bulk sedimentary nitrogen content and $\delta^{15}N$ analyses were carried out using a Carlo-Erba EA 2100 elemental analyzer connected to a Thermo Finnigan Delta V Advantage isotope ratio mass spectrometer (EA-IRMS). Sediments for total organic carbon (TOC) analyses were acid-treated with 1N HCl for 16 hr, and then centrifuged to remove carbonate. The acid-treated sediments were further dried at 60 ℃ for TOC content and $\delta^{13}C$. The nitrogen isotopic compositions of acidified samples were obtained in the same time for comparison. Carbon and nitrogen isotopic data were presented by standard δ notation with respect to PDB carbon and atmospheric nitrogen. USGS 40, which has certified $\delta^{13}C$ of −26.24‰ and $\delta^{15}N$ of −4.52‰ and acetanilide (Merck) with $\delta^{13}C$ of −29.76‰ and $\delta^{15}N$ of −1.52‰ were used as working standards. The reproducibility of carbon and nitrogen isotopic measurements is better than 0.15‰. The precision of nitrogen and carbon content measurements were better than 0.02% and 0.05%, respectively. Meanwhile, the acidified and non-acidified samples exhibited identical patterns in $\delta^{15}N$ (not shown) with mean deviation of 0.3‰.

4 Results

4.1 Sedimentation rate

The age-depth curve was shown in Fig. 2a, in which age dates were evenly distributed throughout the core though not high resolution. In Mollenhauer et al. (2005), the largest age offset between total organic carbon and co-occurring foraminifera is ~3000 years and mostly <2000 years. Meanwhile, the offset remains more or less constant throughout past 20 ka regardless of the deglacial transition. The youngest date in our core is 3180 cal ka BP at 58 cm. We may expect younger age on the surface. Thus, if our TOC samples contain any pre-aged organics as indicated by Mollenhaure et al. (2005), the offset should not be too large to alter our interpretation for the comparison between glacial and Holocene periods. The linear sedimentation rates derived from 7 date intervals range from 6 to 20 cm ka^{-1} (Fig. 2b), with relatively constant value (~6 cm ka^{-1}) prior to Holocene except the excursion around the last glacial maximum. The linear sedimentation rates started to increase since Holocene and reached 18~20 cm ka^{-1} when the sea level reached modern day level..

4.2 Nitrogen and carbon contents and their isotopes

Values of $\delta^{15}N_{bulk}$ ranged from 4.7‰ to 7.1‰ with significantly lower values during glacial period (Fig. 3a). The $\delta^{15}N$ values increased rapidly since ~19 ka BP, with a peak at ~15 ka BP and then started to decrease gradually toward modern day except the low $\delta^{15}N$ excursion at ~14 ka BP. Figure 3b shows that values of $\delta^{13}C_{TOC}$ (−21.5~−18.5‰) were consistent with the $\delta^{13}C$ of typical marine organic matter end-member (−22~−18‰; Meyers, 1997). An abrupt decrease in $\delta^{13}C$ was observed in concert with the dramatic increase in $\delta^{15}N_{bulk}$ at the start of deglaciation.

Bulk nitrogen content (TN) had a range of 0.23~0.75% (Fig. 3c) and the total organic carbon (TOC) content ranged from 2.2% to 5.5% (Fig. 3d). Both TN and TOC showed similar trend over the last 35 ka BP with relatively constant values prior to Holocene and an afterward elevation till modern day. The upward increasing TOC and TN patterns since Holocene were consistent with the increasing pattern of sedimentation rate, suggesting a higher organic burial flux induced by enhance productivity, which had been reported elsewhere in the AS (Altabet et al., 2002).

As for TOC/TN ratio, higher values appeared during deglacial transition and glacial period (Fig. 3e). The highest value coincides with the $\delta^{13}C_{TOC}$ drop implying there is still some influence from terrestrial organics. However, the terrestrial organics contains less nitrogen (C/N of 20; Meyers, 1997) thus the $\delta^{15}N$ did not drop correspondingly. In the first meter (since ~5 ka), the downward decreasing pattern of TOC and TN can also be attributed to syn-sedimentary degradation, if so a downward increasing in TOC/TN should be evident. However, TOC/TN values varied in a narrow range not revealing a significant increasing trend. Nevertheless, $\delta^{15}N$ and $\delta^{13}C$ did not show concomitant variations with C/N in the first meter or throughout the core, the influence from either organic degradation or changes in terrestrial organic input on isotopic signals is thus limited.

Figure 4 shows the scatter plot of TOC against TN. The slope of the linear regression line for TOC against TN (TOC = (6.67 ± 0.22) × TN + (0.99 ± 0.11), $R^2 = 0.94$, n = 57, $p < 0.0001$) is 6.67 again indicating that organic matter is mainly marine-sourced. Though this slope is slightly higher than the Redfield ratio of 5.68 (wt./wt.), it is lower than that observed on the East China Sea shelf (7.46; Kao et al., 2003). Meanwhile, the intercept of TN is negative when TOC downs to zero implying that inorganic nitrogen can be ignored in our core. Obviously, if we force the regression through the origin point, TOC/TN values for samples during the Holocene will have the lower ratios reflecting even less contribution from terrestrial organics.

5 Discussion

5.1 Downward transfer and transformation of N isotopic signal

As mentioned, the signal of sedimentary $\delta^{15}N$ may be altered under different burial conditions. Altabet and Francois (1994) reported little diagenetic alteration of the near-surface $\delta^{15}N$ in the equatorial Pacific, while apparent +5‰ enrichment relative to sinking particles in the Southern Ocean, south of the polar front. In the Sargasso Sea, sedimentary $\delta^{15}N$ also enriched by 3~6‰ relative to sinking particles (Altabet et al., 2002; Gruber and Galloway, 2008). The degree of alteration was attributed to particle sinking rate and OM preservation (Altabet, 1988). Gaye-Haake et al. (2005) also suggested that low sedimentation rates benefit organic matter decomposition resulting in positive shift in bulk sedimentary $\delta^{15}N$ comparing to sinking particles in South China Sea. Finally, Robinson et al. (2012) concluded that oxygen exposure time at the seafloor is the dominant factor controlling the extent of N isotopic alteration. Thus, it is necessary to follow the track of $\delta^{15}N$ signal to clarify the occurrence of deviation during transfer.

The reported depth profiles of $\delta^{15}N_{NO3}$ in the AS were shown in Fig. 5, in which $\delta^{15}N_{NO3}$ values of water depth deeper than 1200 m range narrowly around 6~7‰, which is slightly higher than the global average of the deep oceans ((4.8 ± 0.2)‰ for > 2500 m, Sigman et al., 2000; (5.7 ± 0.7)‰ for >1500 m, Liu and Kaplan, 1989). Below the euphotic layer, $\delta^{15}N_{NO3}$ increases rapidly peaking at around 200~400 m. The preferential removal of $^{14}NO_3$ by water column denitrification accounts for these subsurface $\delta^{15}N_{NO3}$ highs (Brandes et al., 1998; Altabet et al., 1999; Naqvi et al., 2006). The subsurface $\delta^{15}N_{NO3}$ maximum ranges from 10 to 18‰ for different stations implying a great spatial heterogeneity in water column denitrification intensity. It is worth mentioning that, higher values in general appear in the northeastern AS (15~18‰; Fig. 5) highlighting that the focal area of water column denitrification is prone to northeastern Arabian Sea (Naqvi et al., 1994; Pichevin et al., 2007), also revealed by the DO spatial distribution (Fig. 1a). Contrary to higher denitrification in the northeastern AS, the export production is always higher in the northwestern AS throughout a year (Rixen et al., 1996). Such decoupling between productivity and denitrification was attributed to the oxygen supply by intermediate water exchange besides primary productivity oxygen demand (Pichevin et al., 2007). Note that, the $\delta^{15}N_{NO3}$ values at water depth of 100~150 m, which corresponds to the bottom depth of euphotic zone (Olson et al., 1993), from different stations fall within a narrow range of 7~9‰ despite of wide denitrification intensity underneath. The rapid addition of new nitrogen as mentioned earlier might account for the relatively uniform $\delta^{15}N_{NO3}$ at the bottom of euphotic layer. Unfortunately, there no either $\delta^{15}N_{NO3}$ profiles or sediment trap data from the southern basin for comparison.

Interestingly, reported $\delta^{15}N$ of sinking particles ($\delta^{15}N_{SP}$) collected by five sedimentation traps deployed from 500 m throughout 3200 m deep ranged narrowly from 5.1~8.5‰ (Fig. 6), which is slightly lower but overlaps largely with $\delta^{15}N_{NO3}$ values at 100~150 m. Such similarity in $\delta^{15}N_{NO3}$ at 100~150 m and sinking particles strongly indicated that 1) NO_3^- source for sinking particles was coming from the depth around 100~150 m instead of 200~400 m, the oxygen deficient zones (ODZs) where the maximum $\delta^{15}N_{NO3}$ value occurred (Schäfer and Ittekkot, 1993; Altabet et al., 1999) and 2) little alteration had occurred in $\delta^{15}N_{SP}$ along sinking in the water column as indicated by Altabet (2006). There were only these five trap stations with nitrogen isotope information available in the AS (Gaye-Haaake et al., 2005). The trap locations were in the same area but little south comparing with $\delta^{15}N_{NO3}$ stations (insert map in Fig. 6). The slightly lower $\delta^{15}N$ in sinking particle is attributable to their geographic locations (see below) since incomplete relative utilization of surface nitrate has been documented to have a very limited imprint on the $\delta^{15}N$ signal in the AS (e.g., Schäfer and Ittekkot, 1993).

The uniformly low values of $\delta^{15}N_{NO3}$ at the bottom of euphotic zone should be a consequence resulted from various processes in the euphotic zone, such as remineralizaiton, nitrification and N_2-fixation. Nevertheless, the distribution pattern of N* (Figs. 1e and 1f) illustrates that there must be an addition of $^{14}NO_3$ into the system to cancel out the isotopic enrichment caused by denitrification. Note that the positive offset in $\delta^{15}N_{NO3}$ ($\Delta\delta^{15}N_{NO3}$, 6~12‰) in ODZs caused by various degree of denitrification were narrowed down significantly while nitrate transports upward. This implies that certain degree of addition processes, most likely the N_2-fixation, varied in concert with the intensity of denitrification underneath. Since the upwelling zones distribute at the very north and the west of the AS and the upwelled water travels southward (or outward) on the surface as shown in Fig. 1e, it is reasonable to see the phenomenon of denitrification-induced N_2-fixation to compensate the nitrogen deficiency. Consistent to this notion, Deutsch et al. (2007) discovered the spatial coupling between denitrification in eastern tropical Pacific (upstream) and N_2-fixation in western equatorial Pacific (downstream). Such horizontal nitrogen addition process can also be seen clearly in our background information of N* (Fig. 1f). In fact, fixed N had been proved to account for a significant part of surface nitrate in modern day AS where denitrification is exceptionally intense (Brandes et al., 1998; Capone et al., 1998; Parab et al., 2012).

Comparing with reported $\delta^{15}N$ of surface sediments retrieved from trap locations, a significant positive shift in $\delta^{15}N$ can be seen at the seafloor (Fig. 6). Such positive deviation can be seen elsewhere in previous reports (Altabet, 1988; Brummer et al., 2002; Kienast et al., 2005) due to prolonged oxygen exposure after deposition (Robinsson et al., 2012) associated with sedimentation rate (Pichevin et al., 2007). Although Cowie et al. (2009) found ambiguous relation between contents of sedimentary organic carbon and oxygen in deep water, they also noticed the appearance of maximum organic carbon contents at the lower boundary of ODZ, where oxygen contents were relatively higher. Accordingly, they believed that there existed other factors controlling the preservation of organic carbon, such as the chemical characteristics of organic matter, the interaction between organic matters and minerals, the enrichment and activity of benthic organism, or the physical factor including the screening and water dynamic effect.

5.2 Geographically-distinctive bottom depth effects in modern day

As classified by oxygen content of 25 μmol kg^{-1} at 150 m, documented surface sedimentary $\delta^{15}N_{bulk}$ (Gaye-Haake et al., 2005) were separated into northern and southern groups to examine the geographic difference in bottom-depth effect. Both groups exhibit positive linear relationships between $\delta^{15}N_{bulk}$ and bottom depth (deeper than 200 m) (Fig. 7a). The regression equations were shown in Table 2. Interestingly, the regression differs statistically from each other in general in term of slope and intercept. The slope represents the degree of positive shift of sedimentary $\delta^{15}N$ due to bottom-depth effect. For the southern AS, the slope is (0.76 (± 0.14) $\times 10^{-3}$ km^{-1}), which is close to the correction factor (0.75 $\times 10^{-3}$ km^{-1}) for the world ocean proposed by Robinson et al. (2012) and further applied by Galbraith et al. (2012). By contrast, the slope for the northern AS is significantly lower (0.55 (± 0.08) $\times 10^{-3}$ km^{-1}), implying that the depth-associated alteration in the northern AS is smaller. The correction factor for bottom-depth effect was suggested to vary in different regions such as that in the South China Sea (Gaye et al., 2009). Since the magnitude of oxygen exposure is the primary control of depth effect (Gaye-Haake et al., 2005; Mobius et al., 2011; Robinson et al., 2012), we attributed this lower slope in the northern AS to relatively higher sedimentation rates (not shown) and lower oxygen contents as indicated by previous researches (Olson et al., 1993; Morrison et al., 1999; Brummer et al., 2002).

On the other hand, the intercept for the northern AS regression (8.1 ± 0.2) is significantly higher than that for the southern AS (6.0 ± 0.3). As mentioned above, $\delta^{15}N$ values of sinking particle resembled the $\delta^{15}N$ of nitrate sourced from 100~150 m deep. According to the depth-dependent correction factor we may convert sedimentary $\delta^{15}N_{bulk}$ values at various water depths into their initial condition when the digenetic alteration is minimal to represent the $\delta^{15}N$ of source nitrate. Higher intercept suggests a stronger denitrification had occurred in northern AS surface sediments. The 2.1‰ lower intercept in the southern AS likely reflects the addition of N_2-fixation in the upper water column while it travels southward. The progressive increase of N* toward southern AS supports our speculation although none $\delta^{15}N_{NO3}$ profiles had been published in the southern basin. Future works about $\delta^{15}N_{NO3}$ and $\delta^{15}N_{SP}$ in the southern AS are needed.

In Fig. 7b, we presented corrected $\delta^{15}N_{bulk}$ values along with bottom depth for northern and southern AS surface sediments for comparison. After removing site-specific bias caused by bottom depth effect, the values and distribution ranges of $\delta^{15}N_{bulk}$ for both northern and southern AS became smaller and narrower. For the northern AS, the distribution pattern skewed negatively giving a standard deviation of 0.88‰, exactly falling in the rage of 7~9‰ for $\delta^{15}N_{NO3}$ (7~9‰) at the bottom of euphotic zone. As a result, the corrected nitrogen isotopic signals in sediments more truthfully represent the $\delta^{15}N_{NO3}$ value at the bottom depth of euphotic zone. Meanwhile, the statistically significant difference in $\delta^{15}N_{bulk}$ distribution between the northern and southern AS further confirms the feasibility of our classification by using DO isopleth of 25 μmol kg^{-1} at 150 m.

5.3 Bottom-depth effect during different climate stages

In order to better decipher the history of $\delta^{15}N_{NO3}$ in the bottom euphotic zone of the water column, we synthesized almost all available $\delta^{15}N_{bulk}$ of sediment cores reported for the AS (see Figs. 1a and 1b for locations). Similar to modern surface sediments, northern and southern groups were defined by the contour line of 25 μmol kg^{-1} DO. To keep data consistency in temporal scale, we focused on the last 35 ka (Fig. 8a). Unfortunately, data points were less in 0~6 ka and there were only three sediment cores in southern AS, SK177/11 in this study and NIOP 905 and SO42-74KL in previous studies.

As shown in Fig. 8a, the original $\delta^{15}N_{bulk}$ from the northern (gray dots) and southern AS (green, blue and red curves) are scattering in a wide range from 4.5 to 10.5‰ over entire 35 ka. The pink dots are for the data from core MD-04-2876, which is peculiar since the relatively low $\delta^{15}N_{bulk}$ values deviated from all other reports in the northern AS. Pichevin et al. (2007) excluded the influences from incomplete nitrate utilization and terrestrial input, thus, we still include this core in our statistical analyses. As for the southern cores, the temporal variations of $\delta^{15}N_{bulk}$ in core SK177/11 and NIOP 905 (red and blue) had a very similar trend distributing at the lower bound of whole dataset. The mean $\delta^{15}N_{bulk}$ values for SK177/11 and NIOP 905 during glacial period were almost identical, and the deviation in the Holocene was as small as 0.7‰. By contrast, the temporal pattern for $\delta^{15}N_{bulk}$ of core SO42-74KL (green) resembles that of NIOP 905 yet with an enrichment in ^{15}N by ~2‰ for the entire period. The core

SO42-74KL is retrieved from depth of 3212 m, which the deepest among the three cores in southern AS, the positive offset is apparently caused by the bottom depth effect. Thus inference should be made with caution when compare sediment cores from different depths.

Below we consider two time spans, 0~11 ka (Holocene) and 19~35 ka (glacial), to examine the bottom-depth effect at different climate stages. We ignore transgression period, which is shorter with more variable in $\delta^{15}N_{bulk}$, to avoid bias caused by dating uncertainties in different studies. Also, we will discuss the peculiar patters for 0~6 ka later. The mean and standard deviation of reported $\delta^{15}N_{bulk}$ values for the specific time span were plotted against the corresponding depth of the core. Accordingly, we obtained the correction factors for glacial and early Holocene, respectively, for northern and southern AS (Figs. 8b and 8c). Since only 35 ka was applied in this practice, the long term alteration (Reichart et al., 1998; Altabet et al., 1999) is ignored. The regression curves for modern day (dashed lines) were plotted for comparison.

The difference among regressions of three climate stages in northern AS (Table 2) is not significant (0.55×10^{-3} km^{-1} to 0.70×10^{-3} km^{-1}); however, the regression slopes for northern AS are significantly lower compared with those obtained from the southern AS for all climate states. This might indicate the oxygen content in the northern AS is always lower resulting in a lower degree of alteration of $\delta^{15}N_{bulk}$. On the other hand, we may not exclude the effect by sedimentation rate changes over these two stages, which also affect the oxygen exposure time**;** unfortunately, insufficient sedimentation rate data in the northern AS in previous reports prevents us to implement further analysis.

As for the southern AS, correction factors are always higher than that in northern AS. The overall spatial temporal patterns are in consistent with the oxygen distribution in the Arabian Sea (Olson et al., 1993; Morrison et al., 1999; Pichevin et al., 2007) and agree with the view that DO concentration was the dominant factor for organic matter preservation (Aller, 2001; Zonneveld et al., 2010). Meanwhile, the regression slopes remained high from 0.76×10^{-3} km^{-1} to 1.01×10^{-3} km^{-1} over different climate stages in the southern AS suggesting that environmental situations, thus the correction factor, change less relative to that in the northern AS. For SK177/11, sedimentation rate in Holocene is 2-fold higher comparing to that in glacial period; however, the influence caused by sedimentation rate changes is likely not significant enough to alter the regression slopes for the southern AS basing on the small changes in slope (0.93×10^{-3} km^{-1} and 1.01×10^{-3} km^{-1}) .

5.4 Insights from temporal changes in geographic $\delta^{15}N_{bulk}$ distribution

Based on the earlier comparison among $\delta^{15}N_{NO3}$, sinking particles and surface sediments, we recognized the regression intercept is representative of the nitrogen isotope of nitrate source at depth of 100 m. Therefore, the regression-derived intercepts given in Table 2 can be used to infer the $\delta^{15}N_{NO3}$ source at different climate stages, while the slopes can be used as correction factors to eliminate the positive shift in $\delta^{15}N_{bulk}$ caused by bottom depth; by doing this, we can get the original signal of $\delta^{15}N_{bulk}$ prior to alteration. We applied the correction factor to be equal to ((bottom depth – 100 m) $\times$ slope), ignoring the sea level changes during the different climate stages.

Noticeably, the regression intercepts for both northern and southern AS are higher in the Holocene compared to that in glacial period indicating the intensified isotopic enrichment in $\delta^{15}N_{NO3}$ in entire AS in Holocene. Such increment is almost the same to be ~1.7‰, which is similar to the increase in Eastern Tropical North Pacific but slightly smaller than that in the Eastern Tropical South Pacific (Galbraith et al., 2012). The 120 m sea level increase, which may induce only 0.1‰ offset, cannot be the reason for such a significant increase of average $\delta^{15}N_{bulk}$ during the Holocene. Moreover, deviations between northern and southern AS at respective climate stage are almost identical (0.8‰ for Holocene and 1.0‰ for glacial) indicating a synchronous shift in the relative intensity of denitrification and N_2-fixation over the basin to keep such constant latitudinal gradient of subsurface $\delta^{15}N_{NO3}$.

The intermediate water formation near the polar region controls the oxygen supply to the intermediate water and thus the extent of denitrification on global scale and the stoichiometry of nutrient source to euphotic zone (Galbraith et al., 2004). Lower glacial-stage sea surface temperature may increase oxygen solubility, while stronger winds in high-latitude regions enhance the rate of thermocline ventilation. The resultant colder, rapidly flushed thermocline lessened the spatial extent of denitrification and, consequently, N fixation (Galbraith et al., 2004).Therefore, such a basin wide synchronous increase in $\delta^{15}N_{bulk}$ is likely a global control. The lower intercepts in glacial time (4.3‰ for south and 5.3‰ for north), which are similar to the global mean $\delta^{15}N_{NO3}$ (4.5~5‰, Sigman et al., 1997), illustrates a better ventilation of intermediate water during glacial time in the Arabian Sea (Pichevin et al., 2007). In fact, the AAIW penetrate further northward over 5 °N in present day and even during the late Holocene (You, 1998; Pichevin et al., 2007). Since the $\delta^{13}C$ of autochthonous particulate organic carbon is negatively correlated to [CO_2 (aq)] in euphotic zone (Rau et al., 1991), the sharp decrease of $\delta^{13}C_{TOC}$ in SK177/11 at the start of deglaciation (Fig. 3b) may infer the timing of a rapid accumulation of dissolved inorganic carbon driven by the shrinking of oxygenated intermediate water (Pichevin et al., 2007) or enhanced monsoon-driven upwelling (Ganeshram et al., 2000); both facilitate the promotion of denitrification. Nevertheless, the mirror image between $\delta^{15}N$ and $\delta^{13}C_{TOC}$ profiles revealed their intimate relation; of which, the variability was attributable to the change of physical processes.

The intercepts of the northern AS increase continuously from 5.3 to 8.1 from glacial through modern day indicating the strengthened intensity of denitrification relative to nitrogen fixation in the northern AS (Altabet, 2007). When we take a close look at the temporal pattern of corrected $\delta^{15}N_{bulk}$ for long cores (Fig. 9), we can see an amplified deviation since 6 ka, during which $\delta^{15}N_{bulk}$ increases continuously in the northern AS, whereas it decreases in the southern AS. (Note that the northern most core, MD-04-2876, also followed the increasing trend in recent 6 ka even though its $\delta^{15}N_{bulk}$ values deviated from all other cores.) Such opposite trends indicate that the controlling factors on nitrogen cycle in northern AS were different from that in the southern AS, which means localized enhancement in specific process had occurred.

Besides the oxygen supply to the intermediate water, the intensity of water column denitrification varies with primary productivity (Altabet, 2006; Naqvi et al., 2006). Strong summer monsoon and winter monsoon drive upwelling or convective mixing to enhance the primary productivity, which in turn intensify denitrification (Altabet et al., 2002; Ganeshram et al., 2002). However, it was reported also that primary productivity did not correlate well with water column denitrification underneath during the Holocene in some parts of the northern AS (Banakar et al., 2005 and references therein). Regardless of the declining summer monsoon strength since 5500 ka (Hong et al., 2003), the primary productivity in northern AS seem to be increased. Similar to the patterns observed for TOC and TN in this study, productivity indicators (TOC and Ba/Al ratios) reported by Rao et al. (2010) in the core SK148/4 located nearby our SK177/11 also increased gradually since the Holocene. Incomplete nitrate consumption can hardly explain the decreasing pattern for all three cores in the southern AS where upwelling intensity is much less relative to that in the north. Moreover, lower TOC/TN ratios observed in Holocene in SK177/11 as mentioned earlier rules out the influence from terrestrial organic input. Therefore, a spatial coupling of denitrification-dependent N_2 fixation is the more plausible cause of the decreasing $\delta^{15}N_{bulk}$ pattern (Deutsch et al., 2007).

We suggested that intensified supply of excess phosphorous (phosphorus in stoichiometric excess of fixed nitrogen) toward the southern AS to stimulate N_2 fixation, subsequently responsible for the decreasing $\delta^{15}N_{bulk}$ pattern in the southern basin. The intensification in excess phosphorous supply can be driven by enhanced upwelling or intensified subsurface water column denitrification or both. According to the increasing pattern in $\delta^{15}N_{bulk}$ and primary productivity in the northern AS, synergetic processes are suggested. The upwelled water in northern AS basin brings up low N/P water to surface for non-diazotrophs to uptake. If we assume complete consumption, the remaining excess phosphorous after complete consumption will be transported toward south by clockwise surface circulation and advection, therefore,

N_2-fixation in the southern AS acts as feedback to balance denitrification changes in the northern AS. This phenomenon is similar to the illustration for the spatial coupling of nitrogen inputs and losses in the Pacific Ocean proposed by Deutsch et al. (2007). Why such forcing to expand the N-S deviation had not occurred before 6 ka warrants more studies.

6 Conclusions

The available data showed that values of $\delta^{15}N_{NO3}$ at the bottom of euphotic zone (~150 m) were similar to $\delta^{15}N_{SP}$ implying that the source of nutrients for sinking particulate organic matter was largely derived from the depth at around 150 m. Values of sedimentary $\delta^{15}N_{bulk}$ were obviously higher than $\delta^{15}N_{SP}$ in surrounding areas suggesting such shift of sedimentary $\delta^{15}N_{bulk}$ occurred after deposition. It is necessary to remove site-specific bias of $\delta^{15}N_{bulk}$ values caused by bottom depth to retrieve the original signal before alteration. As a result, the corrected nitrogen isotopic signal in sediments could be representative of the value of $\delta^{15}N_{NO3}$ at the bottom depth of euphotic zone. The bottom-depth effects in the northern AS varies during different climate stages, but the variation is always lower than such effect in the southern AS in general. The modern surface $\delta^{15}N_{bulk}$ values can be separated statistically into northern and southern AS groups reflecting a special coupling of denitrification to the north and N_2-fixation to the south. This phenomenon is supported by the reported modern day N* distribution. As for historical records, the offset in $\delta^{15}N_{bulk}$ between southern and northern AS remained relatively constant (0.8‰ for early Holocene and 1.0‰ for glacial) prior to 6 ka indicating a synchronous shift in the relative intensity of denitrification and N_2-fixation over the basin to keep such constant latitudinal gradient of subsurface $\delta^{15}N_{NO3}$. However, this offset expanded gradually since 6 ka due lilely to more localized intensifications in denitrification and N_2-fixation had occurred, respectively, in the northern and southern Arabian Seas. The spatial coupling of nitrogen inputs and losses in the Arabian Sea was proposed; yet, why the driving force did not expand the N-S deviation before 6 ka warrants more studies.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (NSFC 41176059, 91328207). KS personally thanks the Director, National Center for Antarctic and Ocean Research, Goa and the Secretary, the Department of Ocean Development, New Delhi, for providing the ship time, and also the crew of *ORV Sagar Kanya* for coring operation. KS also thanks V. Yoganandan for onboard help of sub-sampling and the Coordinator, Ocean Science and Technology Cell of Mangalore University, for the kind encouragement.

References

Agnihotri, R., Altabet, M. A., and Herbert, T.: Influence of marine denitrification on atmospheric N_2O variability during the Holocene, Geophysical Research Letters, 33, doi:10.1029/2006GL025864, 2006.

Aller, R. C.: Transport and reactions in the bioirrigated zone, The benthic boundary layer: Transport processes and biogeochemistry, edited by: B. Boudreau, and Jørgensen, B. B., Oxford University Press, Oxford, UK, 269-301, 2001.

Altabet, M.: Variations in nitrogen isotopic composition between sinking and suspended particles: Implications for nitrogen cycling and particle transformation in the open ocean, Deep Sea Research Part A. Oceanographic Research Papers, 35, 535-554, 1988.

Altabet, M., and Francois, R.: Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization, Global Biogeochemical Cycles, 8, 103-116, 1994.

Altabet, M., Francois, R., Murray, D. W., and Prell, W. L.: Climate-related variations in denitrification in the Arabian Sea from sediment $^{15}N/^{14}N$ ratios, Nature, 373, 506-509, 1995.

Altabet, M., Murray, D. W., and Prell, W. L.: Climatically linked oscillations in

Arabian Sea denitrification over the past 1 my: Implications for the marine N cycle, Paleoceanography, 14, 732-743, 1999.

Altabet, M., Higginson, M. J., and Murray, D. W.: The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO_2, Nature, 415, 159-162, 2002.

Altabet, M.: Isotopic tracers of the marine nitrogen cycle: Present and past, in: Marine organic matter: biomarkers, isotopes and DNA, edited by: Volkman, J. K., Springer-Verlag Berlin Heidelberg, 251-293, 2006.

Altabet, M.: Constraints on oceanic N balance/imbalance from sedimentary ^{15}N records, Biogeosciences, 4, 75-86, 2007.

Banakar, V., Oba, T., Chodankar, A., Kuramoto, T., Yamamoto, M., and Minagawa, M.: Monsoon related changes in sea surface productivity and water column denitrification in the Eastern Arabian Sea during the last glacial cycle, Marine Geology, 219, 99-108, 2005.

Bassinot, F., Marzin, C., Braconnot, P., Marti, O., Mathien-Blard, E., Lombard, F., and Bopp, L.: Holocene evolution of summer winds and marine productivity in the tropical Indian Ocean in response to insolation forcing: data-model comparison, Climate of the Past, 7, 815-829, 2011.

Brandes, J. A., Devol, A. H., Yoshinari, T., Jayakumar, D., and Naqvi, S.: Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles, Limnology and Oceanography, 43, 1680-1689, 1998.

Brummer, G., Kloosterhuis, H., and Helder, W.: Monsoon-driven export fluxes and early diagenesis of particulate nitrogen and its $\delta^{15}N$ across the Somalia margin, Geological Society, London, Special Publications, 195, 353-370, 2002.

Capone, D. G., Zehr, J. P., Paerl, H. W., Bergman, B., and Carpenter, E. J.: Trichodesmium, a globally significant marine cyanobacterium, Science, 276, 1221-1229, 1997.

Capone, D. G., Subramaniam, A., Montoya, J. P., Voss, M., Humborg, C., Johansen, A. M., Siefert, R. L., and Carpenter, E. J.: An extensive bloom of the N_2-fixing cyanobacterium Trichodesmium erythraeum in the central Arabian Sea, Marine Ecology-Progress Series, 172, 281-292, 1998.

Codispoti, L., and Christensen, J.: Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean, Marine Chemistry, 16, 277-300, 1985.

Cowie, G. L., Mowbray, S., Lewis, M., Matheson, H., and McKenzie, R.: Carbon and nitrogen elemental and stable isotopic compositions of surficial sediments from the Pakistan margin of the Arabian Sea, Deep Sea Research Part II: Topical Studies in Oceanography, 56, 271-282, 2009.

Deutsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N., and Dunne, J. P.: Spatial coupling of nitrogen inputs and losses in the ocean, Nature, 445, 163-167, 2007.

Falkowski, P. G., and Godfrey, L. V.: Electrons, life and the evolution of Earth's oxygen cycle, Philosophical Transactions of the Royal Society B: Biological Sciences, 363, 2705-2716, 2008.

Galbraith, E. D., Kienast, M., Pedersen, T. F., and Calvert, S. E.: Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O_2 supply to the global thermocline, Paleoceanography, 19, doi:10.1029/2003PA00100, 2004.

Galbraith, E. D., Kienast, M., Albuquerque, A. L., Altabet, M., Batista, F., Bianchi, D., Calvert, S., Quintana, S. C., Crosta, X., Holz, R. D. P., Dubois, N., Etourneau, J., Francois, R., Hsu, T.-C., Ivanochko, T., Jaccard, S., Kao, S.-J., Kiefer, T., Kienast, S., Lehmann, M. F., Martinez, P., McCarthy, M., Meckler, A. N., Mix, A., Möbius, J., Pedersen, T., Pichevin, L., Quan, T. M., Robinson, R. S., Ryabenko, E., Schmittner, A., Schneider, R., Schneider-Mor, A., Shigemitsu, M., Sinclair, D., Somes, C., Studer, A., Tesdal, J. E., Thunell, R., and Yang, J.-Y.: The acceleration of oceanic denitrification during deglacial warming, Nature Geoscience, 5, 151-156, 2012.

Ganeshram, R. S., Pedersen, T. F., Calvert, S. E., and Murray, J. W.: Large changes in oceanic nutrient inventories from glacial to interglacial periods, Nature, 376, 755-758, 1995.

Ganeshram, R. S., Pedersen, T. F., Calvert, S. E., McNeill, G. W., and Fontugne, M. R.: Glacial-interglacial variability in denitrification in the world's oceans: Causes and consequences, Paleoceanography, 15, 361-376, 2000.

Ganeshram, R. S., Pedersen, T. F., Calvert, S., and François, R.: Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories, Nature, 415, 156-159, 2002.

Gaye, B., Wiesner, M., and Lahajnar, N.: Nitrogen sources in the South China Sea, as discerned from stable nitrogen isotopic ratios in rivers, sinking particles, and sediments, Marine Chemistry, 114, 72-85, 2009.

Gaye-Haake, B., Lahajnar, N., Emeis, K. C., Unger, D., Rixen, T., Suthhof, A., Ramaswamy, V., Schulz, H., Paropkari, A., and Guptha, M.: Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean, Marine Chemistry, 96, 243-255, 2005.

Gouretski, V., and Koltermann, K. P.: WOCE global hydrographic climatology, Berichte des BSH, 35, 1-52, 2004.

Gruber, N., and Sarmiento, J. L.: Biogeochemical/physical interactions in elemental cycles, in: The sea: Biological-Physical Interactions in the Oceans, edited by: Robinson, A. R., McCarthy, J. J., and Rothschild, B. J., John Wiley and Sons, New York, 337-399, 2002.

Gruber, N.: The dynamics of the marine nitrogen cycle and its influence on atmospheric CO_2 variations, in: The ocean carbon cycle and climate, edited by: Follows, M., and Oguz, T., Springer Netherlands, 97-148, 2004.

Gruber, N., and Galloway, J. N.: An Earth-system perspective of the global nitrogen cycle, Nature, 451, 293-296, 2008.

Haug, G. H., Pedersen, T. F., Sigman, D. M., Calvert, S. E., Nielsen, B., and Peterson, L. C.: Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr, Paleoceanography, 13, 427-432, 1998.

Holmes, M. E., Schneider, R. R., Müller, P. J., Segl, M., and Wefer, G.: Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary $^{15}N/^{14}N$ ratios, Paleoceanography, 12, 604-614, 1997.

Hong, Y., Hong, B., Lin, Q., Zhu, Y., Shibata, Y., Hirota, M., Uchida, M., Leng, X., Jiang, H., and Xu, H.: Correlation between Indian Ocean summer monsoon and North Atlantic climate during the Holocene, Earth and Planetary Science Letters, 211, 371-380, 2003.

Ivanochko, T. S., Ganeshram, R. S., Brummer, G. J. A., Ganssen, G., Jung, S. J. A., Moreton, S. G., and Kroon, D.: Variations in tropical convection as an amplifier of global climate change at the millennial scale, Earth and Planetary Science Letters, 235, 302-314, 2005.

Kao, S., Lin, F., and Liu, K.: Organic carbon and nitrogen contents and their isotopic compositions in surficial sediments from the East China Sea shelf and the southern Okinawa Trough, Deep Sea Research Part II: Topical Studies in Oceanography, 50, 1203-1217, 2003.

Kao, S., Dai, M., Wei, K., Blair, N., and Lyons, W.: Enhanced supply of fossil organic carbon to the Okinawa Trough since the last deglaciation, Paleoceanography, 23, doi:10.1029/2007PA001440, 2008.

Kienast, M., Higginson, M., Mollenhauer, G., Eglinton, T. I., Chen, M. T., and Calvert, S. E.: On the sedimentological origin of down-core variations of bulk sedimentary nitrogen isotope ratios, Paleoceanography, 20, doi:10.1029/2004PA0018081, 2005.

Liu, K.-K., and Kaplan, I. R.: The eastern tropical Pacific as a source of ^{15}N-enriched nitrate in seawater off southern Califomia, Limnol. Oceanogr, 34, 820-830, 1989.

Meyers, P. A.: Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes, Organic Geochemistry, 27, 213-250, 1997.

Möbius, J., Gaye, B., Lahajnar, N., Bahlmann, E., and Emeis, K.-C.: Influence of diagenesis on sedimentary $\delta^{15}N$ in the Arabian Sea over the last 130kyr, Marine Geology, 284, 127-138, 2011.

Mollenhauer, G., Kienast, M., Lamy, F., Meggers, H., Schneider, R. R., Hayes, J. M., and Eglinton, T. I.: An evaluation of ^{14}C age relationships between co-occurring foraminifera, alkenones, and total organic carbon in continental margin sediments, Paleoceanography, 20, doi:10.1029/2004PA001103, 2005.

Morrison, J., Codispoti, L., Gaurin, S., Jones, B., Manghnani, V., and Zheng, Z.: Seasonal variation of hydrographic and nutrient fields during the US JGOFS Arabian Sea Process Study, Deep-Sea Research Part II, 45, 2053-2101, 1998.

Morrison, J., Codispoti, L., Smith, S. L., Wishner, K., Flagg, C., Gardner, W. D., Gaurin, S., Naqvi, S., Manghnani, V., and Prosperie, L.: The oxygen minimum zone in the Arabian Sea during 1995, Deep Sea Research Part II: Topical Studies in Oceanography, 46, 1903-1931, 1999.

Nair, R., Ittekkot, V., Manganini, S., Ramaswamy, V., Haake, B., Degens, E., Desai, B. t., and Honjo, S.: Increased particle flux to the deep ocean related to monsoons, Nature, 338, 749-751, 1989.

Naqvi, S., Noronha, R. J., and Reddy, C.: Denitrification in the Arabian Sea, Deep Sea Research Part A. Oceanographic Research Papers, 29, 459-469, 1982.

Naqvi, S.: Denitrification processes in the Arabian Sea, Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences, 103, 279-300, 1994.

Naqvi, S., Naik, H., Pratihary, A., D'Souza, W., Narvekar, P., Jayakumar, D., Devol, A., Yoshinari, T., and Saino, T.: Coastal versus open-ocean denitrification in the Arabian Sea, Biogeosciences, 3, 621-633, 2006.

Olson, D. B., Hitchcock, G. L., Fine, R. A., and Warren, B. A.: Maintenance of the low-oxygen layer in the central Arabian Sea, Deep Sea Research Part II: Topical Studies in Oceanography, 40, 673-685, 1993.

Pandarinath, K., Subrahmanya, K., Yadava, M., and Verma, S.: Late Quaternary Sedimentation Records on the Continental Slope Off Southwest Coast of India-Implications for Provenance, Depositional and Paleomonsoonal Conditions, Journal of the Geological Society of India, 69, 1285-1292, 2007.

Parab, S. G., and Matondkar, S.: Primary productivity and nitrogen fixation by *Trichodesmium spp.* in the Arabian Sea, Journal of Marine Systems, 105, 82-95, 2012.

Paulmier, A., and Ruiz-Pino, D.: Oxygen minimum zones (OMZs) in the modern ocean, Progress in Oceanography, 80, 113-128, 2009.

Pichevin, L., Bard, E., Martinez, P., and Billy, I.: Evidence of ventilation changes in the Arabian Sea during the late Quaternary: Implication for denitrification and nitrous oxide emission, Global Biogeochemical Cycles, 21, doi:10.1029/2006GB002852, 2007.

Rao, V. P., Kessarkar, P. M., Thamban, M., and Patil, S. K.: Paleoclimatic and diagenetic history of the late quaternary sediments in a core from the Southeastern Arabian Sea: Geochemical and magnetic signals, Journal of oceanography, 66, 133-146, 2010.

Rau, G., Froelich, P. N., Takahashi, T., and Des Marais, D.: Does sedimentary organic $\delta^{13}C$ record variations in Quaternary ocean [CO_2(aq)], Paleoceanography, 6, 335-347, 1991.

Reichart, G.-J., Lourens, L., and Zachariasse, W.: Temporal variability in the northern Arabian Sea Oxygen Minimum Zone (OMZ) during the last 225,000 years, Paleoceanography, 13, 607-621, 1998.

Reimer, P. J., Baillie, M. G., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E., Burr, G. S., and Edwards, R. L.: IntCal09 and Marine09 radiocarbon age calibration curves, 0-50,000 yeats cal BP, Radiocarbon, 51, 1111-1150, 2009.

Rixen, T., Haake, B., Ittekkot, V., Guptha, M., Nair, R., and Schlüssel, P.: Coupling between SW monsoon-related surface and deep ocean processes as discerned from continuous particle flux measurements and correlated satellite data, Journal of geophysical research, 101, 28569-28528, 1996.

Robinson, R. S., Brunelle, B. G., and Sigman, D. M.: Revisiting nutrient utilization in the glacial Antarctic: Evidence from a new method for diatom-bound N isotopic analysis, Paleoceanography, 19, doi:10.1029/2003PA000996, 2004.

Robinson, R. S., Kienast, M., Luiza Albuquerque, A., Altabet, M., Contreras, S., De Pol Holz, R., Dubois, N., Francois, R., Galbraith, E., and Hsu, T. C.: A review of nitrogen isotopic alteration in marine sediments, Paleoceanography, 27, doi:10.1029/2012PA002321, 2012.

Schäfer, P., and Ittekkot, V.: Seasonal variability of $\delta^{15}N$ in settling particles in the Arabian Sea and its palaeogeochemical significance, Naturwissenschaften, 80, 511-513, 1993.

Schmittner, A., Galbraith, E. D., Hostetler, S. W., Pedersen, T. F., and Zhang, R.: Large fluctuations of dissolved oxygen in the India and Pacific oceans during Dansgaard-Oeschger oscillations caused by variations of North Atlantic Deep Water subduction, Paleoceanography, 22, doi:10.1029/2006PA001384, 2007.

Schubert, C. J., and Calvert, S. E.: Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition, Deep Sea Research Part I: Oceanographic Research Papers, 48, 789-810, 2001.

Schulte, S., Rostek, F., Bard, E., Rullkötter, J., and Marchal, O.: Variations of oxygen-minimum and primary productivity recorded in sediments of the Arabian Sea, Earth and Planetary Science Letters, 173, 205-221, 1999.

Sigman, D., Altabet, M., Michener, R., McCorkle, D., Fry, B., and Holmes, R.:

Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method, Marine Chemistry, 57, 227-242, 1997.

Sigman, D., Altabet, M., McCorkle, D., Francois, R., and Fischer, G.: The $\delta^{15}N$ of nitrate in the Southern Ocean: nitrogen cycling and circulation in the ocean interior, Journal of Geophysical Research: Oceans (1978–2012), 105, 19599-19614, 2000.

Sigman, D. M., Karsh, K. L., and Casciotti, K. L.: Nitrogen Isotopes in the Ocean, in: Encyclopedia of Ocean Sciences, edited by: John, H. S. (Editor-in-Chief), Academic Press, Oxford, 1884-1894, 2001.

Stuiver, M., and Braziunas, T. F.: Anthropogenic and solar components of hemispheric ^{14}C, Geophysical research letters, 25, 329-332, 1998.

Suthhof, A., Ittekkot, V., and Gaye-Haake, B.: Millennial-scale oscillation of denitrification intensity in the Arabian Sea during the late Quaternary and its potential influence on atmospheric N_2O and global climate, Global Biogeochemical Cycles, 15, 637-649, 2001.

Thunell, R. C., Sigman, D. M., Muller-Karger, F., Astor, Y., and Varela, R.: Nitrogen isotope dynamics of the Cariaco Basin, Venezuela, Global Biogeochemical Cycles, 18, doi:10.1029/2003GB002185, 2004.

You, Y.: Intermediate water circulation and ventilation of the Indian Ocean derived from water-mass contributions, Journal of marine research, 56, 1029-1067, 1998.

Zonneveld, K., Versteegh, G., Kasten, S., Eglinton, T. I., Emeis, K. C., Huguet, C., Koch, B., de Lange, G. J., De Leeuw, J., and Middelburg, J. J.: Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record, Biogeosciences, 7, 483-511, 2010.

Table 1. AMS ^{14}C dates of sediment core SK177/11. Radiocarbon ages were calibrated using CALIB 6.0 program (*http://calib.qub.ac.uk/calib/calib.html*, Reimer *et al.*, 2009).

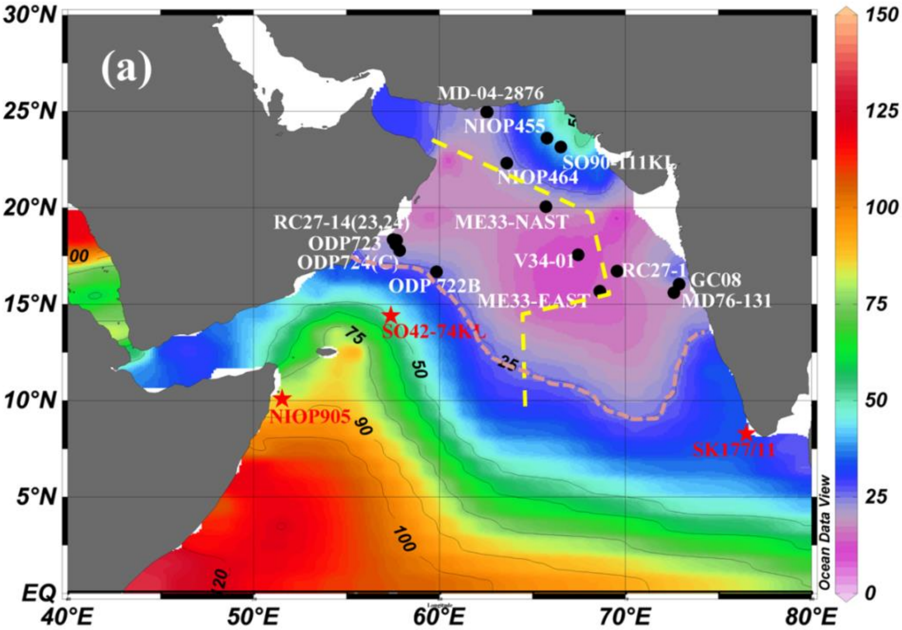
Lab code	**Depth cm**	**Dating materials**	**pMC**	**Raw ^{14}C age (yr BP)**	**Calibrated age (yr BP) (1σ)**	**$\delta^{13}C$ (‰)**
KIA24386	58	OM	65.58 ±0.17	3390 ±20	3186 ±24	−18.55 ±0.04
KIA26327	125	OM	46.65 ±0.20	6125 ±35	6504 ±26	−20.02 ±0.10
KIA24387	155	OM	31.38 ±0.13	9310 ±30	10054 ±104	−19.50 ±0.08
KIA26328	175	OM	21.96 ±0.12	12180 ±45	13618 ±104	−17.71 ±0.18
KIA24388	205	OM	13.94 ±0.11	15830 ±60	18646 ±54	−21.65 ±0.15
KIA24389	275	OM	9.81 ±0.12	18650+100(−90)	21774 ±194	−18.02 ±0.10
KIA26329	355	OM	2.76 ±0.06	28830 ±180	32857 ±207	−19.23 ±0.17

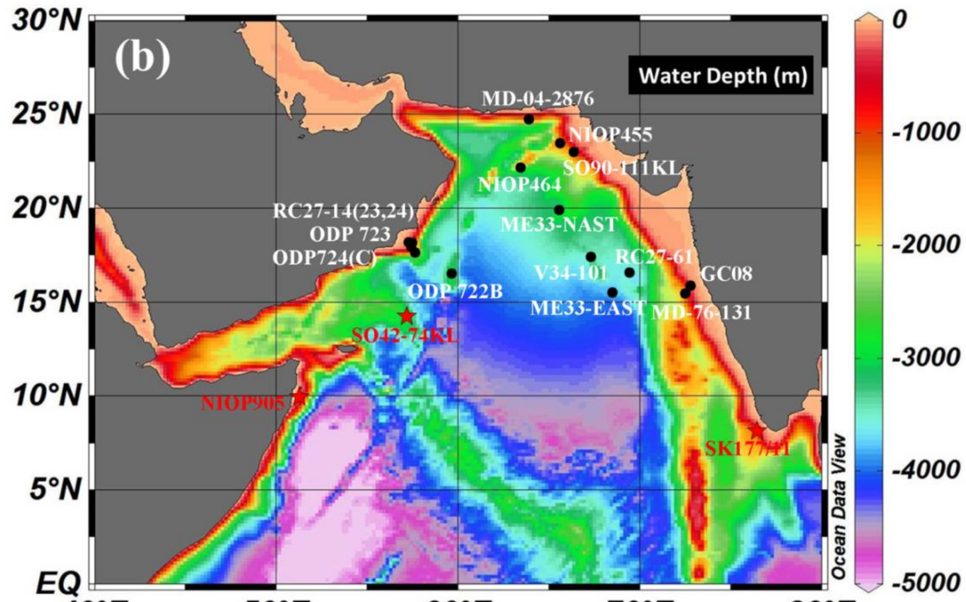
OM-Organic matter; pMC-Percent modern

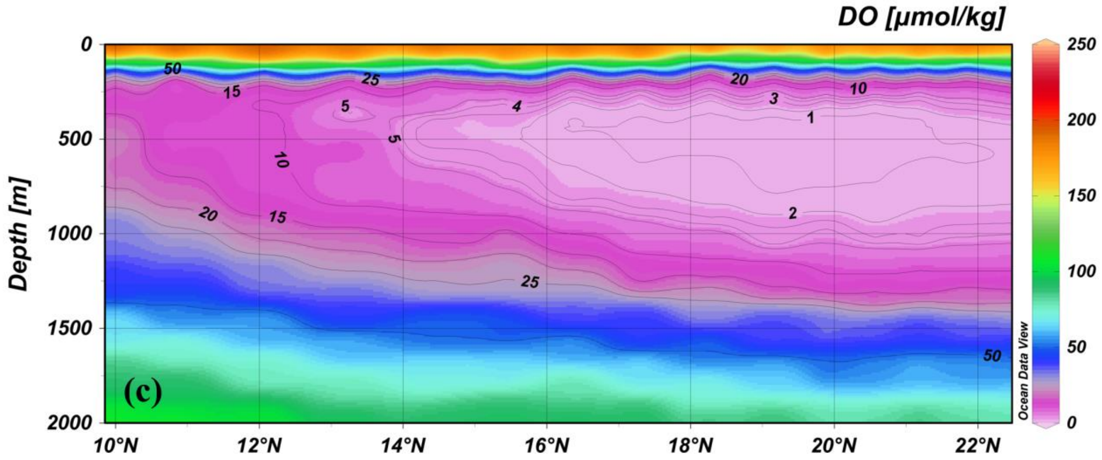
Table 2. Linear equations of bottom-depth effect during different climate stages

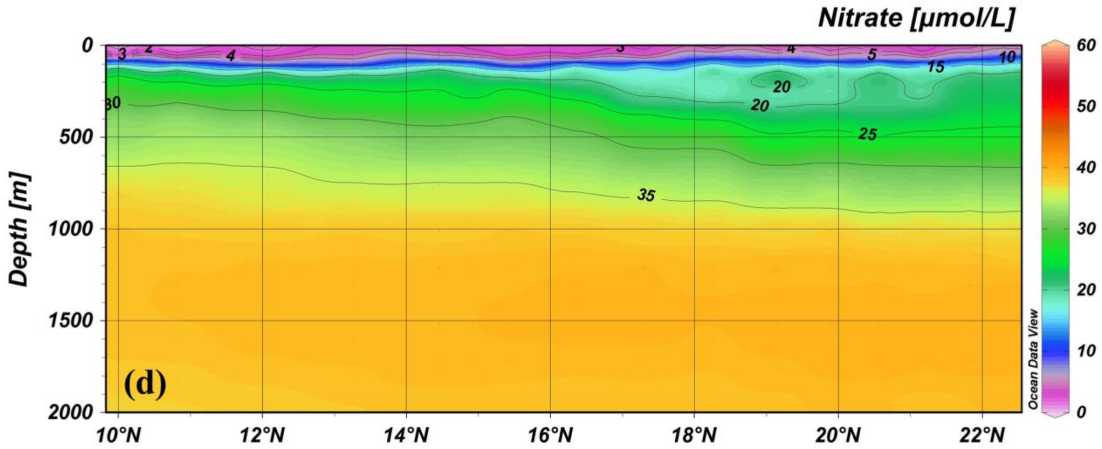
Location	Northern AS	Southern AS
Modern	$\delta^{15}N = 0.55\ (\pm 0.08) \times 10^{-3} \times$ Depth + 8.1 (±0.2) (R^2 = 0.40, n = 78, P <0.0001)	$\delta^{15}N = 0.76\ (\pm 0.14) \times 10^{-3} \times$ Depth + 6.0 (±0.3) (R^2=0.66, n=18, P<0.0001)
Holocene	$\delta^{15}N = 0.70\ (\pm 0.20) \times 10^{-3} \times$ Depth + 6.7 (±0.3) (R^2=0.61, n=16, P=0.0067)	$\delta^{15}N = 0.93\ (\pm 0.06) \times 10^{-3} \times$ Depth + 5.7 (±0.1) (R^2=1.00, n=3, P=0.0152)
Glacial	$\delta^{15}N = 0.64\ (\pm 0.20) \times 10^{-3} \times$ Depth + 5.2 (±0.3) (R^2=0.68, n=16, P=0.0013)	$\delta^{15}N = 1.01\ (\pm 0.31) \times 10^{-3} \times$ Depth + 4.3 (±0.7) (R^2=0.91, n=3, *P=0.1899)

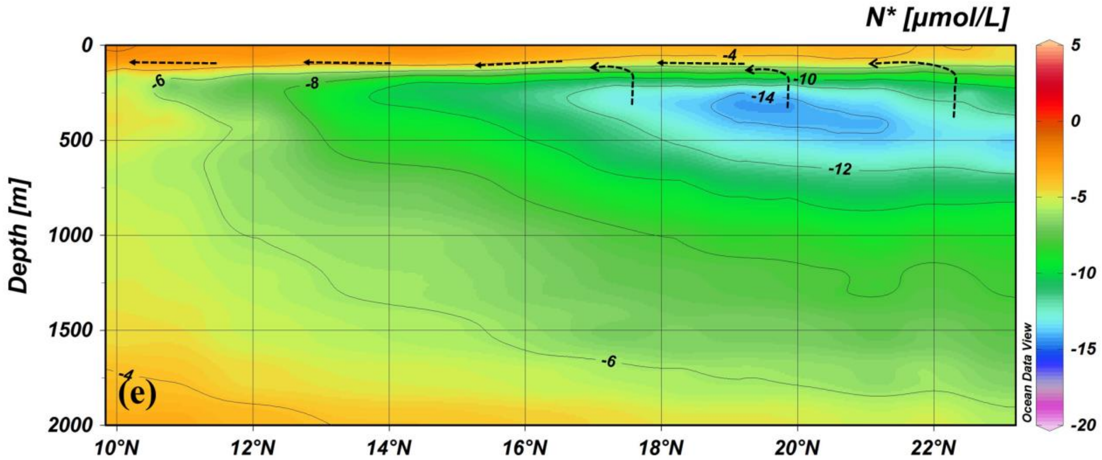
*insignificant by P value


(a)
MD-04-2876
NIOP455
SO90-111KL
NIOP464
ME33-NAST
RC27-14(23,24)
ODP723
ODP724(C)
ODP 722B
V34-01
RC27-1
GC08
MD76-131
ME33-EAST
SO42-74KL
NIOP905
SK177/11
75
50
25
90
100
30°N
25°N
20°N
15°N
10°N
5°N
EQ
40°E
50°E
60°E
70°E
80°E
150
125
100
75
50
25
0
Ocean Data View


(b)
Water Depth (m)
MD-04-2876
NIOP455
SO90-111KL
NIOP464
ME33-NAST
RC27-14(23,24)
ODP 723
ODP724(C)
ODP 722B
V34-101
RC27-61
GC08
ME33-EAST
MD-76-131
SO42-74KL
NIOP905
SK177/11
30°N
25°N
20°N
15°N
10°N
5°N
EQ
40°E
50°E
60°E
70°E
80°E
0
-1000
-2000
-3000
-4000
-5000
Ocean Data View


DO [µmol/kg]
Depth [m]
(c)
Ocean Data View
10°N 12°N 14°N 16°N 18°N 20°N 22°N
1


Nitrate [µmol/L]
Depth [m]
(d)
Ocean Data View
10°N 12°N 14°N 16°N 18°N 20°N 22°N
2


N* [µmol/L]
Depth [m]
(e)
Ocean Data View
10°N 12°N 14°N 16°N 18°N 20°N 22°N
3

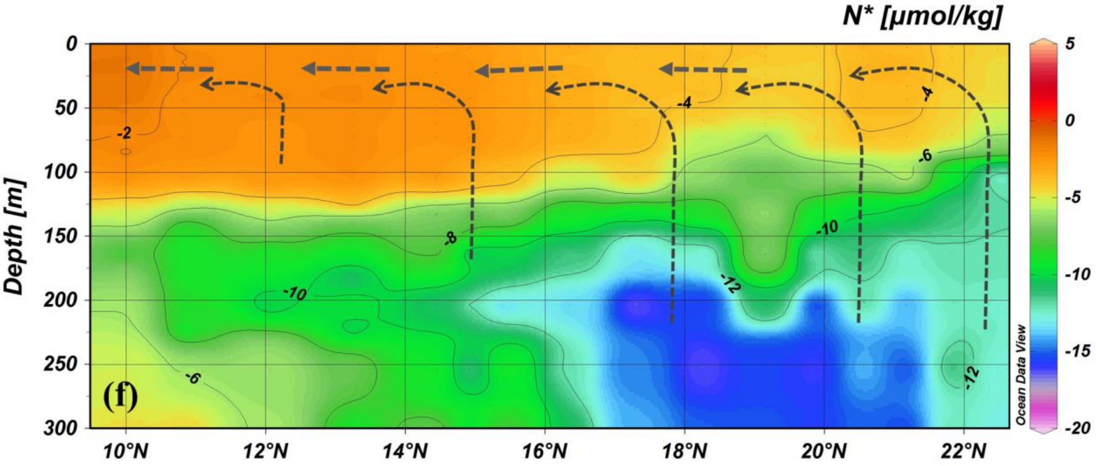


Figure 1. (a) Map of the Arabian Sea. Dissolved oxygen (DO) concentration at 150 m (World Ocean Atlas 09) was shown in color contour. Southern (★) and northern (●) categories of available cores and SK177/11 in this study were defined by DO of 25 µmol kg^{-1} (see text, purple dash curve). (b) Bathymetric map superimposed by core locations; (c), (d) and (e) are DO, nitrate and N* transects (yellow dashed line in (a), online data originated from cruises of JGOFS in 1995), respectively, for upper 2000 m. (f) N* transect for the upper 300m with arrows revealing the flow direction. In (a), the northern cores include core MD-04-2876 (828 m, Pichevin et al., 2007), core NIOP455 vs. NIOP464 (1002 m vs. 1470 m, Reichart et al., 1998), SO90-111KL vs. ME33-NAST(775 m vs. 3170 m, Suthhof et al., 2001), ODP724C vs. ME33-EAST (603 m vs. 3820 m, Möbius et al., 2011), RC27-24 vs. RC27-61 (1416 m vs. 1893 m, Altabet et al., 1995), ODP723, ODP722(B) vs. V34-101 (808 m, 2028 m vs. 3038m, Altabet et al., 1999), RC27-14 vs. RC27-23 (596 m vs. 820 m, Altabet et al., 2002), GC08 (2500 m, Banakar et al., 2005), MD-76-131 (1230 m, Ganeshram et al., 2000); the Southern cores include core SO42-74KL (3212 m, Suthhof et al., 2001), NIOP905 (1586 m, Ivanochko et al., 2005) and SK177/11 (776 m, this study).

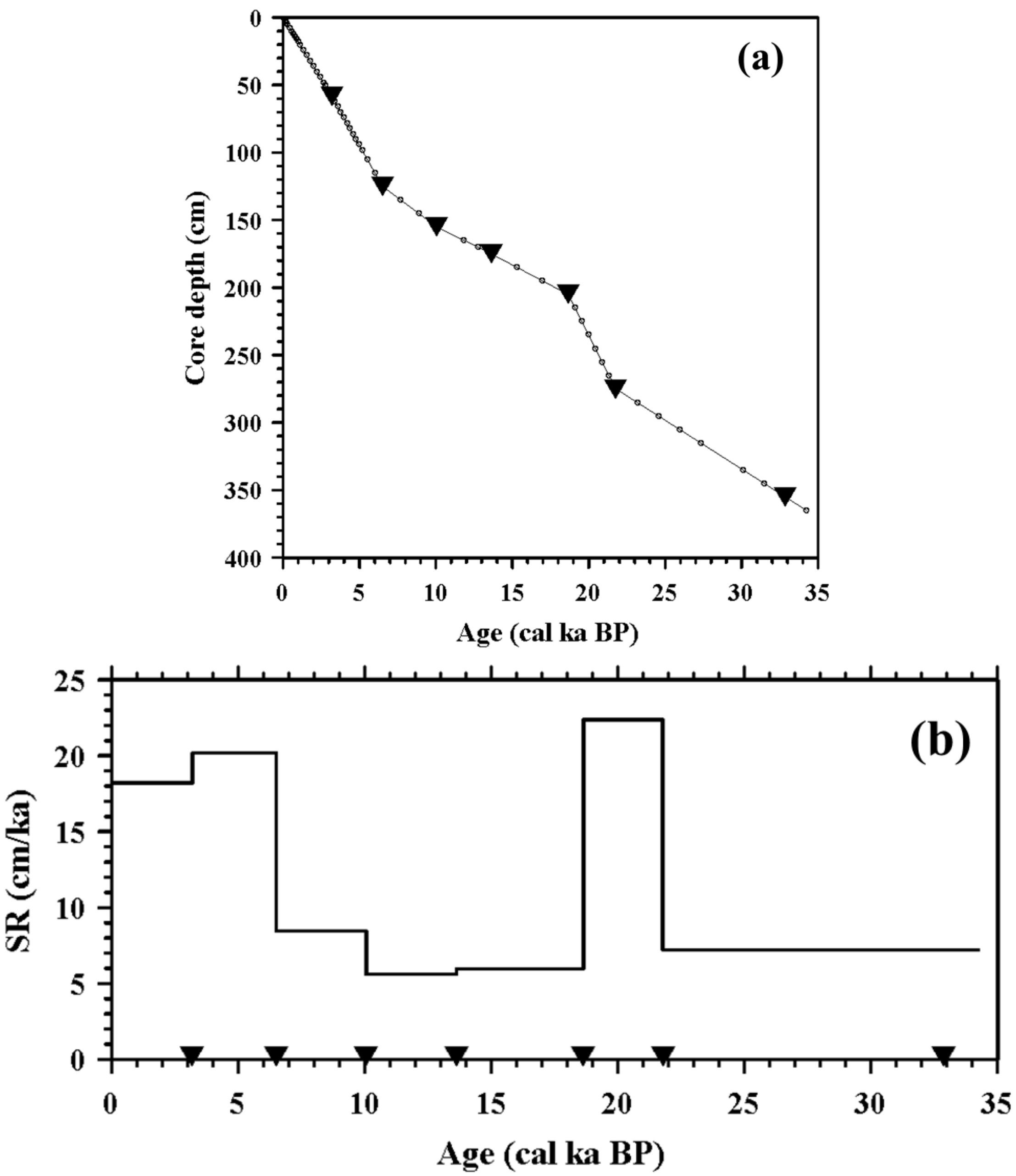


Figure 2. (a) Plot of calendar age against depth; (b) Linear sedimentation rate (▼ indicates the ^{14}C age controlling points).

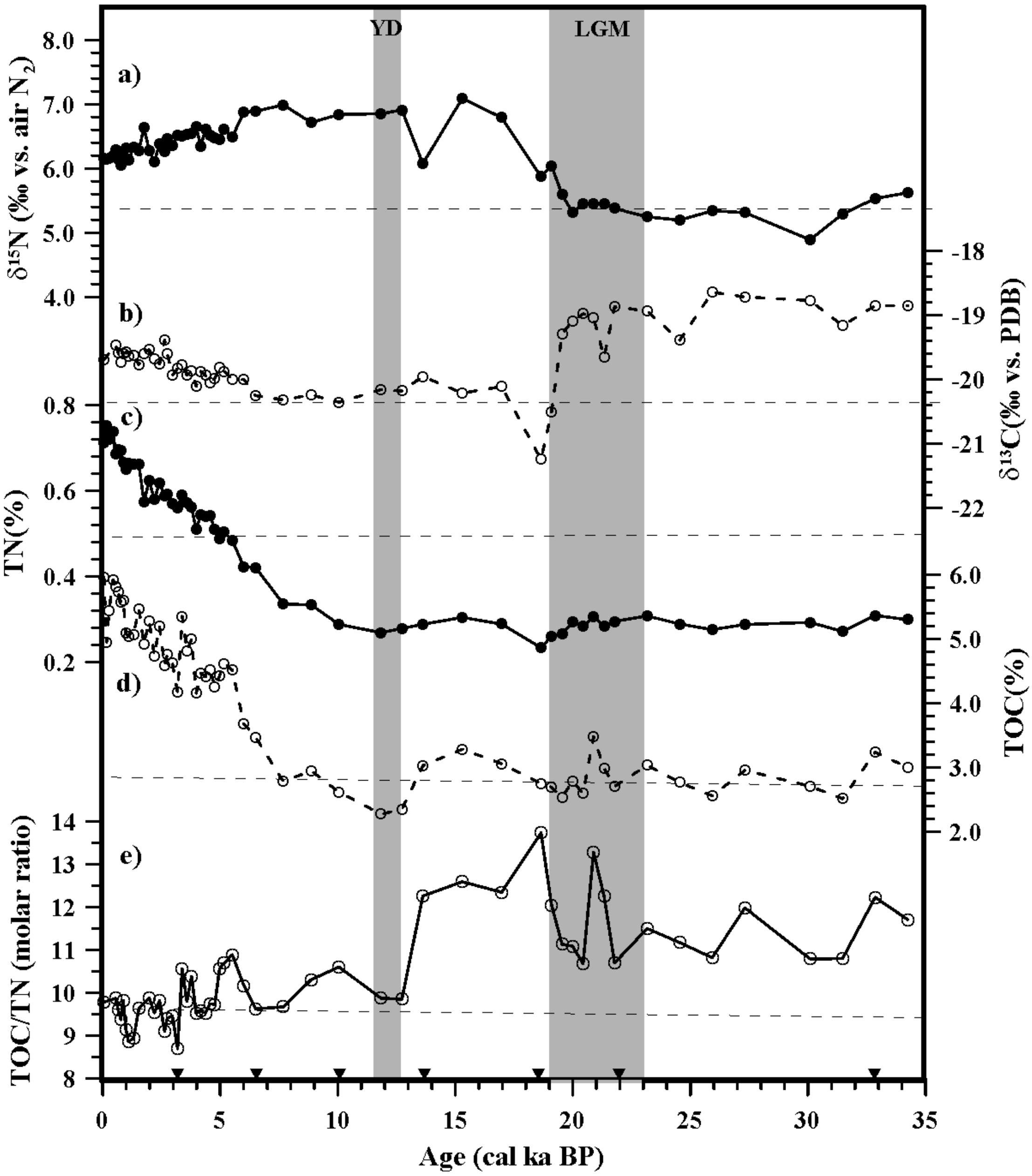


Figure 3. Temporal variations of (a) stable isotopic compositions of bulk nitrogen ($\delta^{15}N$), (b) stable isotopic compositions of TOC ($\delta^{13}C$), (c) contents of total nitrogen, (d) total organic carbon and (e) TOC/TN ratio.. Horizontal dashed lines are references for low value periods.

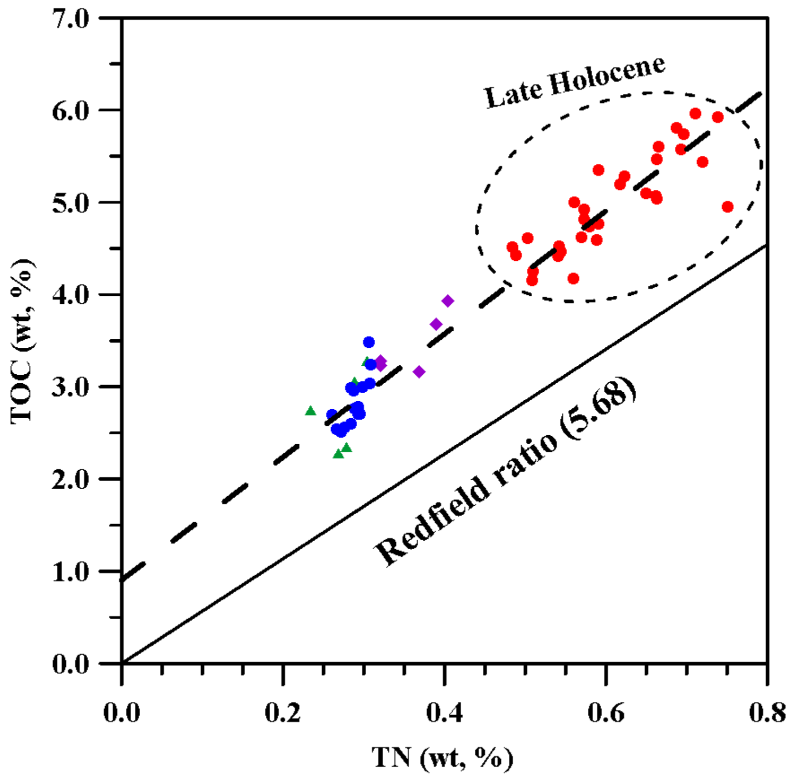


Figure 4. Scatter plot of the total organic carbon content against total nitrogen. Redfield field ratio of 5.68 is shown in line. Bold dashed line stands for regression. Red, purple, green and blue dots represent the late Holocene, early Holocene, deglacial and glacial periods, respectively.

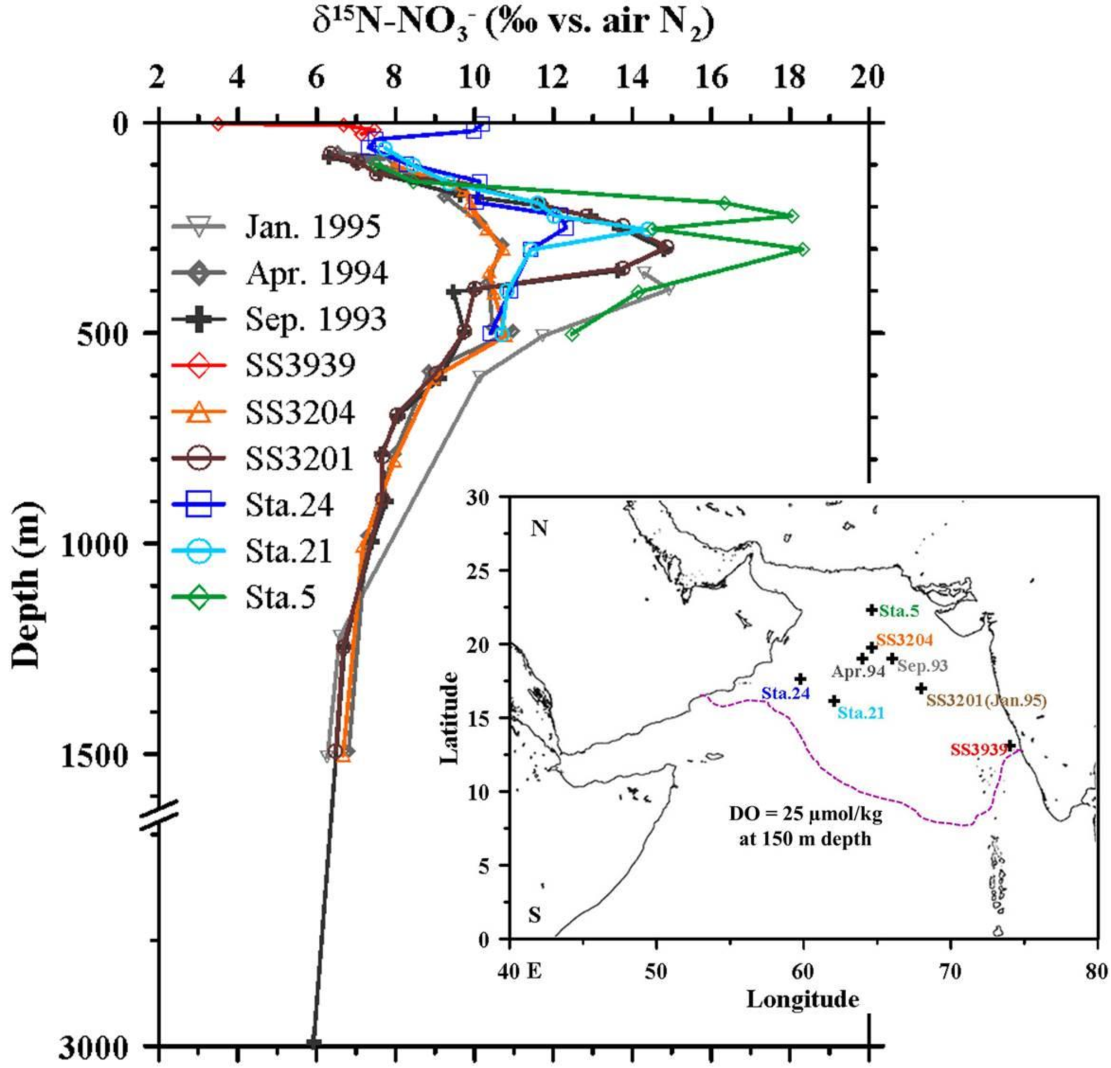


Figure 5. Depth profiles of nitrogen isotope of nitrate ($\delta^{15}N_{NO3}$) in water column (data without months in mark are all from August and Sta. Jan. 1995 overlaps with Sta. SS3201) (Data digitized from Brandes et al., 1998; Altabet et al., 1999; Naqvi et al., 2006).

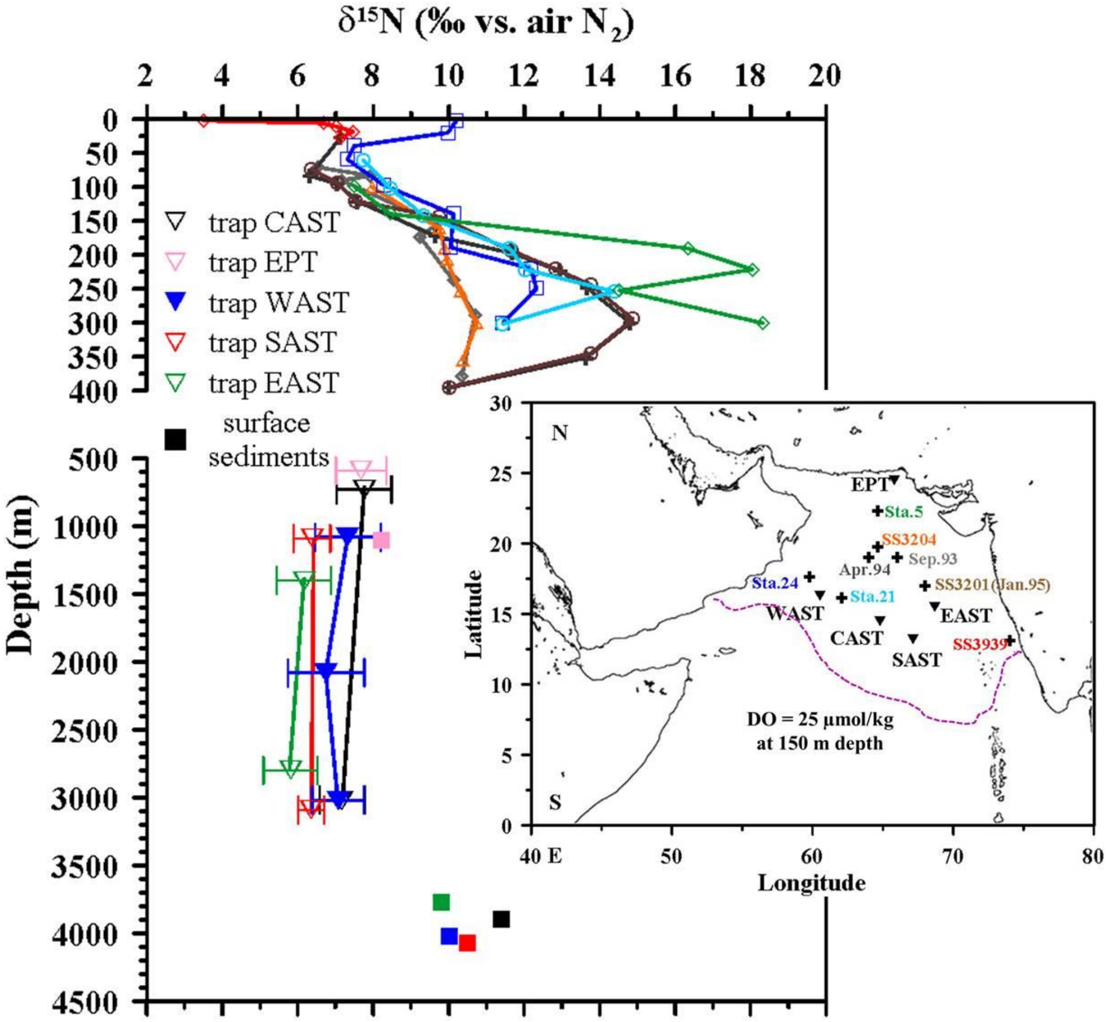


Figure 6. Vertical profiles for nitrogen isotope of nitrate (crosses in inserted map), sinking particles (inverse triangles in map) and trap-corresponding surface sediments. Data for sediment traps and surface sediments are from Gaye-Haake et al. (2005). Depth profile of $\delta^{15}N_{NO3}$ follows that in Figure 5.

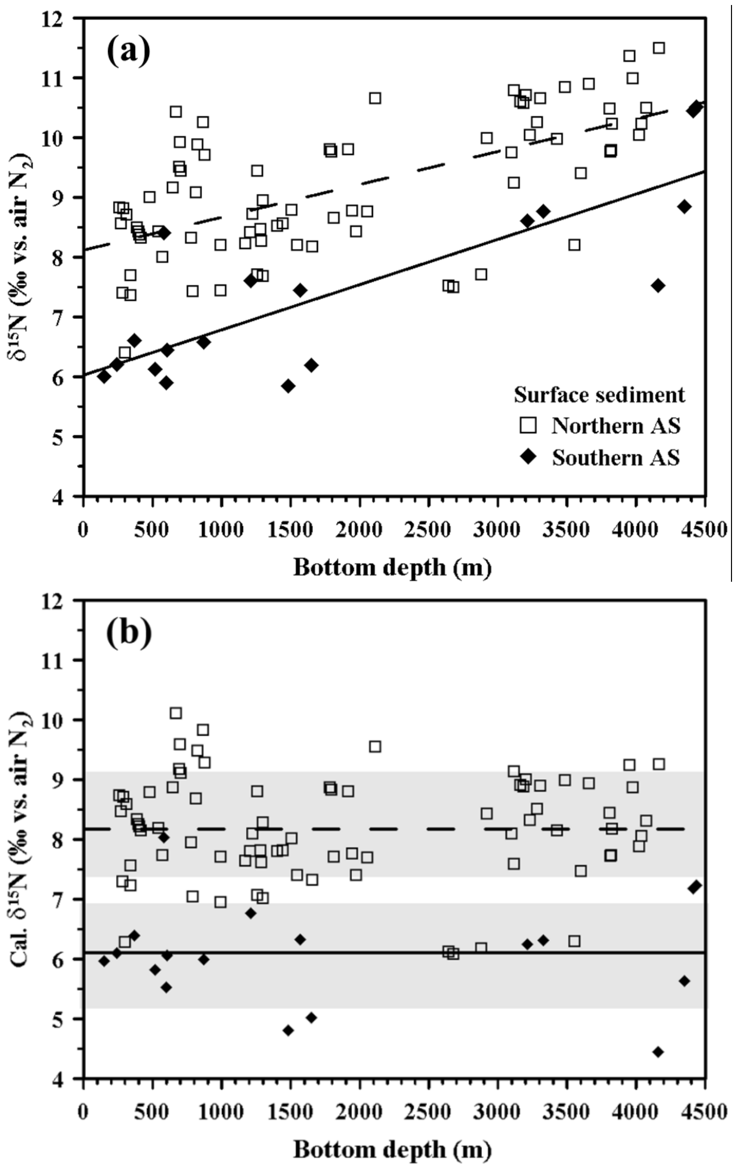


Figure 7. (a) Non-corrected $\delta^{15}N$ values of modern surface sediments against corresponding bottom depth in northern and southern Arabian Sea (see text for N-S boundary). Regression lines were shown in dashed and solid lines, respectively, for northern and southern AS. (b) Corrected surface sedimentary $\delta^{15}N$ values against water depth.

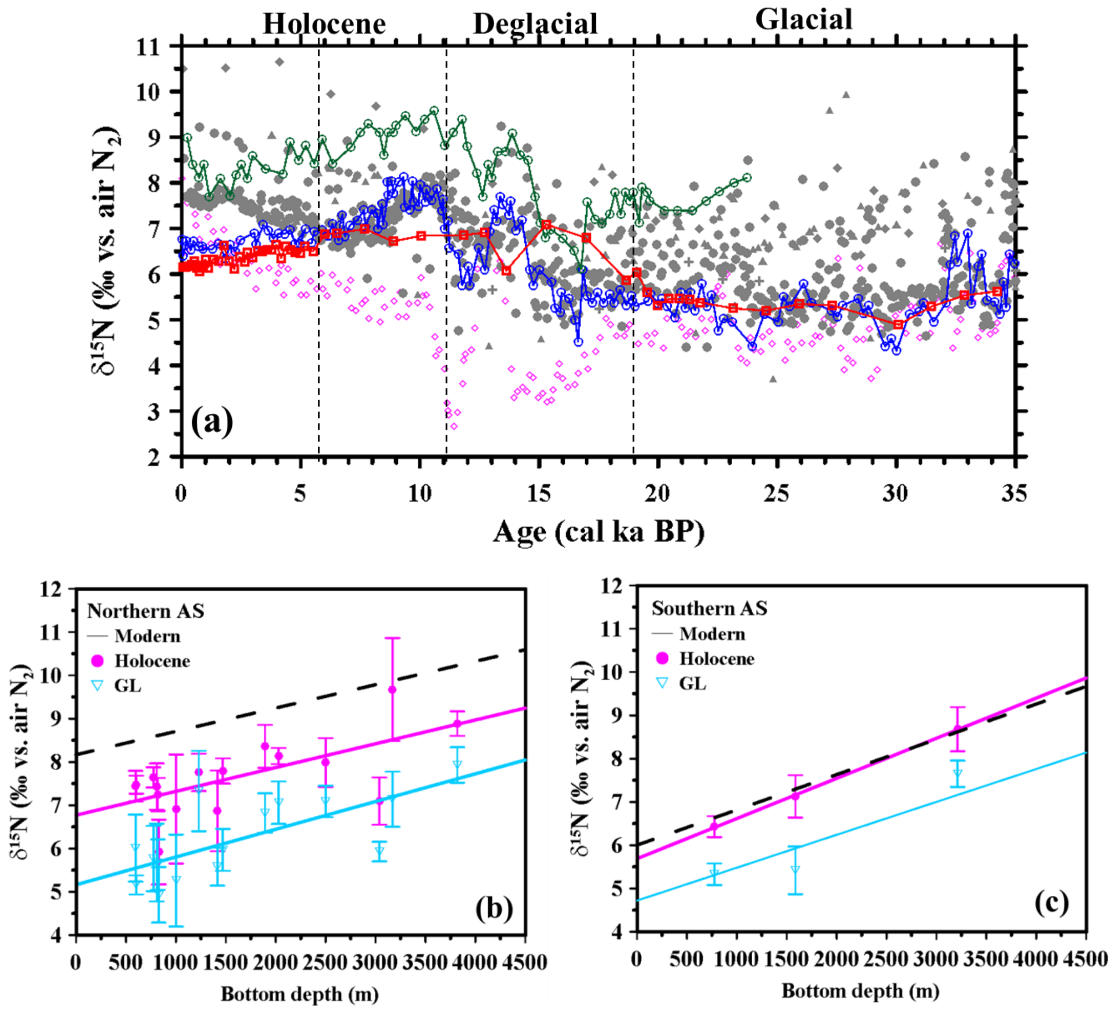


Figure 8. (a) Temporal variations of non-corrected $\delta^{15}N_{bulk}$ values of all reported cores in the AS. Data shown in curves are for cores in the southern Arabian Sea (red for SK177/11, blue for NIOP 905 and green for SO42-74KL), dots in grey are for the northern part (pink dots are for core MD-04-2876). Mean values of $\delta^{15}N$ for fixed periods against corresponding water depths for cores in (b) northern and (c) southern Arabian Sea. Pink and indigo blue are for Holocene and glacial periods, respectively. Error bars represent the standard deviation for mean $\delta^{15}N_{bulk}$.The dashed regression lines for modern surface sediments are shown for reference.

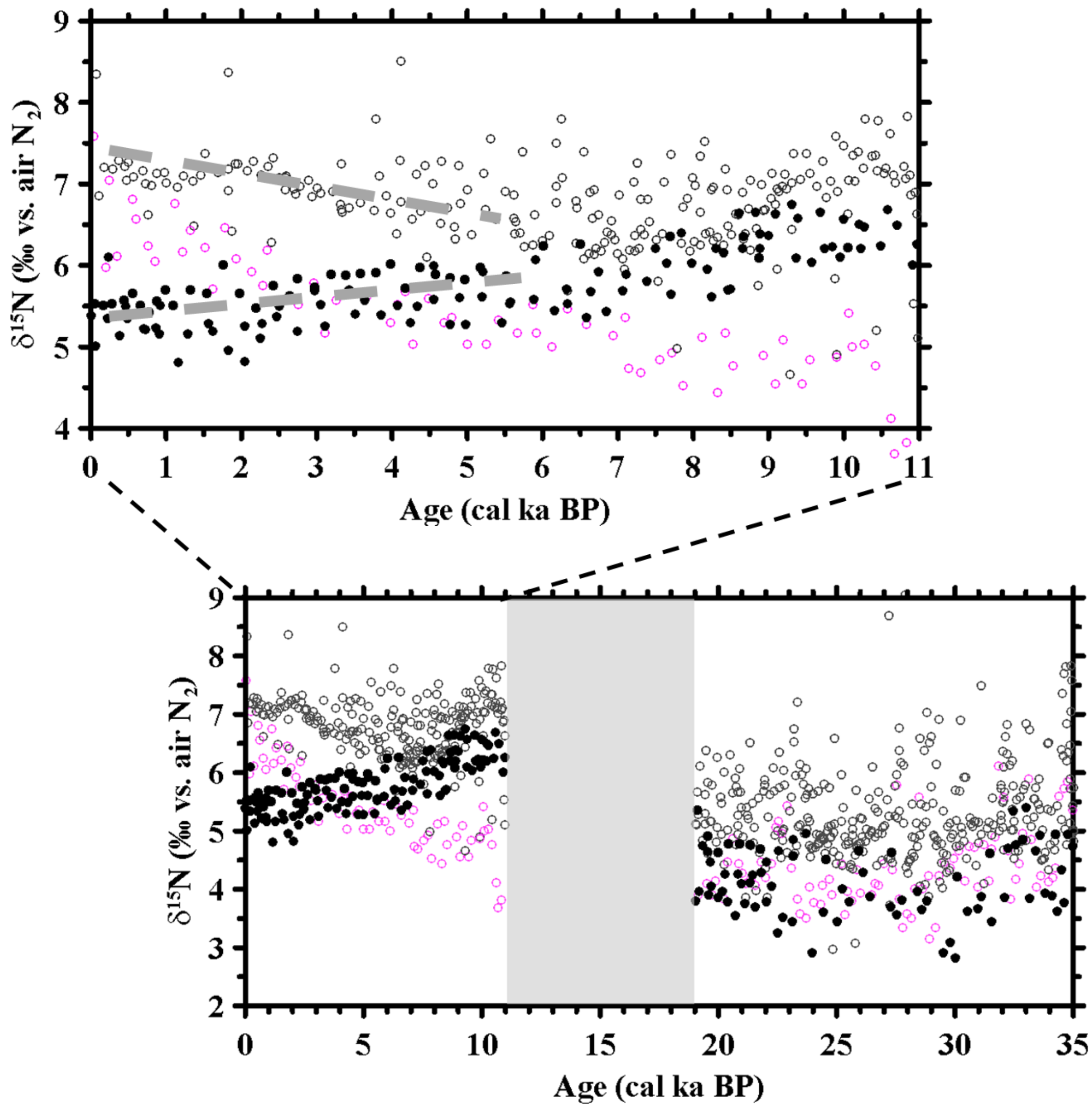


Figure 9. Temporal variations of corrected $\delta^{15}N_{bulk}$ values of all reported cores in the AS. Gray and black dots are for northern and southern AS, respectively. Pink dots are specifically for core MD-04-2876. The deglacial period is in shadow because non proper equations for bottom-depth effect correction. The upper panel is the blow-up for the Holocene period. The intensified deviation trends since 6 ka were marked by bold dashed lines.