Variations in Denitrification and Ventilation Within the Arabian Sea Oxygen Minimum Zone During the Holocene

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Abstract The continental slope of India is exposed to an intense perennial oxygen minimum zone (OMZ) supporting pelagic denitrification. Sediments that are presently in contact with the lower boundary of the denitrification zone indicate marked changes in the intermediate and bottom waters ventilation of OMZ during the past 9,500 years. The δ15N of sediment suggests that the OMZ waters were less ventilated during the early Holocene (between 9.5 and 8.5 ka BP) resulting in intensified denitrifying conditions with an average δ15N value of 7.8‰, while at the same time stable Mo isotope composition (average δ98Mo of −0.02‰) indicates that the bottom waters that were in contact with the sediments were better oxygenated. By the mid-Holocene OMZ became more oxygenated suppressing denitrification (average δ15N of 6.2‰), while bottom waters gradually became less oxygenated (average δ98Mo of 1.7‰). The mid-Holocene reduction in denitrification coincided with a global decrease in atmospheric N2O as inferred from ice core records, which is consistent with a decreased contribution from the Arabian Sea. Since ~5.5 ka BP OMZ waters have again been undergoing progressive deoxygenation accompanied by increasing denitrification.

1. Introduction

The Arabian Sea is one of the three major oceanic areas where large-scale nitrogen loss occurs within well-defined mesopelagic oxygen minimum zones (OMZs), largely through denitrification (Codispoti et al., 2001; Naqvi, 1987). The OMZ of the Arabian Sea is today located between 100-/150- and 1,200-m depth (dissolved O2 < 0.5 ml/L) and is the thickest of the global ocean (Sen Gupta & Naqvi, 1984; Wyrtki, 1971). In the upper part of the OMZ large deficits of nitrate (NO3−) are observed that are accompanied by accumulation of nitrite (NO2−) and ammonia (NH3) in the bottom waters (Devol et al., 2006). These NO2−-bearing zones extend from the northwestern continental margin of India to the central Arabian Sea (Naqvi, 1991; Naqvi et al., 2003). Nitrate from the surface layer in turn enriches the organic matter with 15N, resulting in characteristic δ15N signatures of the organic matter preserved in the underlying sediments (Altabet et al., 1995, 2002, 1999; Ganeshram et al., 2000). The sedimentary δ15N signatures reflect denitrification changes in intermediate waters (e.g., Altabet et al., 1999; Brandes et al., 1998; Ganeshram et al., 2000; Kessarkar et al., 2010, 2013). Thus, past changes in the OMZ intensity and water column denitrification have been inferred from sedimentary δ15N with higher/lower values qualitatively indicating increases/decreases in denitrification intensity in the intermediate waters. The inferred changes have been related to variations in water mass composition, monsoon intensity, deep convective mixing, upwelling strength, and N2 fixation (Agnihotri et al., 2003; Altabet et al., 1999; Banakar et al., 2005; Ganeshram et al., 2000; Gaye et al., 2018; Kao et al., 2015; Kessarkar et al., 2010, 2013; Pichevin et al., 2007; Reichart et al., 1998; Suthof et al., 2001). These studies have mostly focused on glacial-interglacial time scales, including variations associated with the Dansgaard-Oeschger and Heinrich events in the North Atlantic. Higher-resolution Holocene studies by Agnihotri et al. (2003) and Naik et al. (2014) suggested an increase in denitrification linked to increased productivity from 10 to 2 ka BP and from 7 ka BP to the present, respectively. While these results from the Arabian Sea indicate an intensification of the OMZ during the Holocene (Agnihotri et al., 2003; Naik et al., 2014; Pichevin et al., 2007), rest of the world’s oceans mostly experienced decrease in the extent and intensity of the OMZ (Deutsch et al., 2005). Most of the above studies have described the OMZ as a whole water column zone with the changing intensity related to processes like upwelling, convective mixing, or changes in inflowing water masses. It is not known if the vertical homogeneity of the OMZ varied during
the Holocene, which may be important for the potential relationship between the Holocene denitrification change and global atmospheric N2O. Here we present high-resolution data from the sediment core SK148/55 (17°45′N, 70°52′E, 500-m water depth) located within the present-day OMZ at the lower boundary of the denitrifying zone (Figure 1). The δ15N (indicating ventilation changes of the intermediate waters) and δ98Mo (indicating bottom water oxygenation/anoxia) data document decoupled mesopelagic and bottom water (water in contact with sediment) oxygenation/ventilation changes during the Holocene. Our results show that the OMZ of the Arabian Sea did not always act as a single homogenous zone but that parts of it could have been more oxygenated at times, which may have had implications for global atmospheric N2O content.

2. Study Area

The Arabian Sea is a semienclosed basin that is land locked in the north, east, and west. During the southwest monsoon (June–September) the intertropical convergence zone moves over the eastern Arabian Sea leading to high precipitation and runoff with low salinity surface waters occurring along the west coast of India. Rainfall on the landward side (in Ratnagir district) of core SK148/55 is high (average of 3,400 mm), which mainly occurs from June to September (http://hydro.imd.gov.in). Wind-driven surface currents flow clockwise during the southwest monsoon with upwelling centers observed off Arabia and Somalia and in the southeastern Arabian Sea (Qasim, 1977). The West India coastal current flows toward the south (Figure 1a), at the same time the West India Undercurrent (WIUC) moves northward extending up to 17°N and 200-m water depth with dissolved oxygen (O2) contents in the core of the current being around 25 μM (Naqvi et al., 2006). During the northeast monsoon the surface currents move in anticlockwise direction (Figure 1a) with high productivity induced by convective mixing in the northern part of the basin. The OMZ located below 100-/150-m depth to a maximum of 1,200 m with O2 below 0.5 ml/L (~22 M) that exists throughout the year (Sen Gupta & Naqvi, 1984; Wyrtki, 1971). The core of the OMZ that experiences denitrification consists of a mixture of high salinity water masses originating from the Persian Gulf and the Red Sea (Persian Gulf water and Red Sea Water) and lower salinity intermediate waters flowing in from the south (Sen Gupta & Naqvi, 1984, and references therein). The intermediate waters from the south (Subantarctic Mode Water/Indian Ocean Central Water) enter the Arabian Sea with higher oxygen contents that can be detected up to 17°N (Naqvi et al., 2006). There is also an intrusion of relatively oxygenated water along the western continental margin of India via the undercurrent (WIUC) during the southwest monsoon (Naqvi, 1991; Naqvi et al., 2006; Schott & McCreary, 2001; Shetye et al., 1994). It was believed earlier (Sen Gupta & Naqvi, 1984; Wyrtki, 1973) that the OMZ owes its existence to high productivity supported by upwelling during the southwest monsoon and convective mixing during the northeast monsoon and slow renewal of intermediate waters. However, it is now generally agreed that the ventilation of the OMZ is not sluggish; instead, the waters responsible for renewal have low O2 contents (Naqvi, Yoshinari, Brandes, et al., 1998).

3. Methods

Gravity core SK148/55 was collected from 500-m water depth (Thamban et al., 2007), which is located close to the lower boundary of the perennial denitrification zone. The denitrification zone is characterized by high δ15N of N2O and NO3− (Figure 1) as reflected by seawater data from a nearby site (station SS3201 of Naqvi, Yoshinari, Jayakumar, et al., 1998). Laminations were observed throughout the core, and the chronology is based on seven accelerator mass spectrometry 14C dates on Globigerinoides ruber (Thamban et al., 2007). The sedimentation rate varied from 0.4 to 1.83 mm/year (Figure 2).

The planktonic foraminiferal species G. ruber was selected for measurements of oxygen isotope composition of carbonate (δ18O). G. ruber tests were picked from 95 samples, cleaned ultrasonically, and analyzed for stable oxygen isotopes (18O/16O) on a Micromass IsoPrime Isotope Ratio Mass Spectrometer at the Geological Survey of Japan, Tsukuba. Replicate analysis of NBS-19 and internal laboratory standards revealed an external precision better than ±0.07‰.

Powdered bulk sediment samples (2 g) were treated with 1N HCl for the removal of CaCO3 and were rinsed repeatedly with deionized water until the acid was completely removed and then dried in an oven at 60 °C. Weighed quantities (~20 mg) of dry, powdered samples filled into tin cups were analyzed for stable carbon and nitrogen isotopes using Finnigan Delta Plus isotope ratio mass spectrometer after combustion in a Flash 1112 EA elemental analyzer at the Centre for Marine Tropical Ecology, Bremen, Germany. The carbon and
Figure 1. (a) Figure showing surface currents (black dotted lines); arrows are the direction of the currents: WICC = West Indian Coastal Current; WIUC = West Indian Undercurrent (Schott & McCreary, 2001). (b) Location of gravity cores (marked by solid circles) with respect to the denitrification zone (marked by the gray dotted line at NO₂ / CO₃ = 0.2 μmol/L). The open circle is location SS3201 of the water column profiles; the core locations include SK148/55 (present study), 905P (Ivanochko et al., 2005), MD-04 2876 (Pichevin et al., 2007), 111KL (Suthhof et al., 2001), SK 126/39 (Kessarkar et al., 2010), and SK177/11 (Kao et al., 2015). The gray shaded areas indicate highly productive zones. (c) Water column profiles of O₂, δ¹⁵N(N₂O), δ¹⁵N(NO₃), N₂O, and NO₂ above and within the OMZ; OMZ marked by gray shading; modified after Naqvi, 1991; Naqvi et al., 2003; Qasim, 1977). OMZ = oxygen minimum zone.
Figure 2. Stable oxygen isotope ($\delta^{18}$O$_{C}$) values (black—present study; gray—AAS62/1; Kessarkar et al., 2013), sediment nitrogen isotopes ($\delta^{15}$N), total nitrogen (TN), C$_{org}$, CaCO$_3$, C$_{org}$/TN, $\delta^{13}$C$_{org}$ and linear sedimentation rate: The vertical gray shaded area marks low denitrification.
nitrogen isotope ratios are expressed as per mil (‰) deviations from Pee Dee Belemmitite and atmospheric N₂, respectively. Analytical precision based on duplicate analysis and internal standard measurement after every four samples was ±0.2‰ for δ¹⁵N and ±0.3‰ for δ¹³C. For calibration, the international reference standards IAEA N1 and N2 were used for δ¹⁵N and U.S. Geological Survey (USGS) 24 and NBS 22 for δ¹³C. Two successive data points are separated by time periods ranging from 20 to 80 years.

For trace elemental analysis, samples were treated with 5:2:5:2.5:5-mI mixtures of concentrated HClO₄:HCl:HNO₃:HF and kept overnight on a hotplate at 100 °C. Subsequently, the samples were heated to 140 °C for 2 hr. Upon cooling the samples were treated with 1.5:1.5:3 ml of HCl:HNO₃:HF and again heated overnight at 140 °C. The temperature was increased to 170 °C the next day to dry the samples. This step was repeated until the sample was completely digested. The samples were then dissolved in 100 ml of 1M HNO₃ and the major elements were analyzed using a Seiko SPS 7800 Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thamban et al., 2007). Minor and trace elements were determined using a HP 4500 ICP-MS at the Geological Survey of Japan, Tsukuba. Based on replicate measurements of rock standards of the Geological Survey of Japan (JR2, JA2, JB2, and JB1A), the measurement accuracies are estimated to be better than 5% (1 standard deviation, S.D.) for all trace elements and 1–2% for major elements.

For Mo isotopes, 500 mg of powdered sample was treated with 1M HCl to remove CaCO₃ and was subsequently dried down. Samples were then digested in a 2:2:4 ml HNO₃:HF:HClO₄ mixture at 180 °C overnight. This resulted in clear sample solutions, which were then dried down on the hot plate at 180 °C. To resolve instrument and laboratory mass fractionation of stable Mo isotopes a Mo double spike (¹⁰⁰Mo, ⁹⁷Mo) was added and data reduction subsequent to analysis was carried out following the procedures described in Siebert et al. (2001). Samples for Mo isotope analysis were purified using 2-mI cation exchange resin in 0.5M HCl (Biorad AG50W-X, 200–400 mesh) to remove iron and subsequently passed through 2 ml of anion exchange resin (Biorad AG 1x8, 200–400 mesh) in 4M HCl, and 2M HNO₃ to remove all other elements and to elute Mo. The samples were analyzed using a Nu instruments Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) at GEOMAR, Germany. The data are presented as δ⁹⁶Mo = [(⁹⁶MoSample /⁹⁶MoStandard)] /⁹⁶MoStandard × 1,000. All results are presented relative to the Alfa Aesar ICP standard solution (Specpure® #38791 (lot no. 011895D); for international comparison, NIST 3134 is 0.13‰ heavier than our in-house standard solution and we measured seawater at the established literature δ⁹⁶Mo value of 2.3 (Goldberg et al., 2013; Greber et al., 2012; Nägler et al., 2014). The external reproducibility of the in-house standard measurements was 0.05‰ (2 S.D.) during the measurement period. Reproducibility of USGS shale standard SDO-1 over the course of 2 years yielded a long-term reproducibility of 0.11‰. USGS standard MAG-1, a marine sediment, was digested twice and each digestion was analyzed twice in the course of these measurements yielding an average δ⁹⁶Mo of −0.2. Two samples were digested twice and analyzed in separate measurement sessions resulting in a reproducibility of 0.08‰ and 0.14‰ (2 S.D.), respectively. Total procedural blanks were at or below 3-ng Mo, while the measurements were performed at 100-ng Mo.

4. Results

4.1. Variations in δ¹⁸O

The δ¹⁸O of G. ruber in the core SK148/55 exhibit an average value of −2.02‰ (range −2.7% to −1.5‰; Table S1 in the supporting information) over the past 9.5 ka (0.25 to 9.5 ka BP). The δ¹⁸O for the period of time from 7 to 5.5 ka BP (average −2.3‰, range −2.5‰ to −2.1‰) is overall lighter than from 5.5 to 0.2 ka BP (average −2‰, range −2.7‰ to −1.7‰) and from 9.5 to 7 ka BP (average −1.9‰, range −2.3‰ to −1.5‰). Averaging data for each kiloyear shows that 5 to 6 ka and 6 to 7 ka periods are characterized by lighter δ¹⁸O values of −2.2‰ and −2.5‰, respectively. From 9.5 to 7.5 ka BP the δ¹⁸O fluctuates rapidly between lighter to heavier values, but from 7.5 to 4.7 ka the values show a more steady shift toward lighter and then to heavier values. Relatively light values with an average of −2.3‰ from 7 to 5.5 ka BP are comparable to the decrease in δ¹⁵N. There are three more steady changes observed around 4.3, 3.4, and 2.3 ka BP (Figure 2), but these occur at shorter time scales and/or with heavier values compared to those of 7 to 5.5 ka BP.

4.2. Variations in Corgan Total Nitrogen, Nitrogen, and Carbon Isotopes in the Sediments

The Corgan concentrations range between 0.8% and 5.1%, with an average of 2.2%. The values are relatively low (0.8% to 1%; average of 0.9%) between 9.5 and 8.9 ka BP (early Holocene) and after that show a systematic
increase toward the core top. Total nitrogen (TN) content ranges between 0.08% to 0.59% with an average of 0.25%. Lower values of TN are observed during the early Holocene, while higher values occur toward the core top and exhibiting a trend similar to that of $C_{org}$ (Figure 2). The $C_{org}$/TN ratio ranges between 8.6 and 10.3 (Figure 2), and $C_{org}$ and TN show very high correlation coefficient ($R = 0.997$) with zero intercept of $C_{org}$ on the negative axis of the TN (Figure S1). The $\delta^{15}N$ ranges from 6‰ to 8.4‰. From 9.5 to 7.6 ka BP the $\delta^{15}N$ values exhibit a marked decreasing trend. From 9.5 to 8.4 ka $\delta^{15}N$ exhibit an average value of 7.8‰ and while from 8.4 to 7.6 ka BP with an average value of 7.0‰. Later from 7.6 to 5.4 ka BP $\delta^{15}N$ does not show much variation with the values ranging between 6‰ and 6.7‰ (average of 6.2‰). From 5.4 to 0.2 ka BP $\delta^{15}N$ values again exhibit increasing trend reaching values up to 8.2‰. The $\delta^{15}N$ versus TN graph (Figure S2) does not show any significant correlation ($R = 0.053$).

The $\delta^{13}C_{org}$ ranges between $-21.1$‰ and $-19.9$‰ and does only show small changes. The average values for $\delta^{13}C_{org}$ are $-20.4$‰ (9.5 to 7.6 ka BP), $-20.9$‰ (7.6 to 5.4 ka BP), and $-20.7$‰ (5.4 to 0.2 ka BP), and they are associated, respectively, with decreasing, stable, and increasing $\delta^{15}N$ values.

### 4.3. Elemental Concentrations and Molybdenum Isotopes in Sediments

The average elemental concentrations followed the sequence $\text{Mn} > \text{Ni} > \text{Cr} > \text{Cu} > \text{V} > \text{U} > \text{Mo}$. The metal contents of the sediments are expected to be controlled by a combination of lithogenic inputs, productivity, and the redox environment. At the first glance concentrations of most elements (Table S2) are much lower than the lithogenic background as inferred from Post-Archean Australian Shale (PAAS) values, except Mo, U, and Ni, which are enriched over PAAS in some sections of the core. However, because the sediments consist of $>70\%$ of biogenic carbon ($\text{CaCO}_3 + C_{org}$), lowered elemental concentrations with respect to PAAS are mainly caused by dilution. Elemental data were thus normalized to the Al content of the respective sample. Aluminum is of lithogenic origin, and the normalization would remove the source effect (Tribovillard et al., 2006), as well as dilution with biogenic carbonate. These Al-normalized values are used for further discussion (Figure 3). Al-normalized values of Ni, Cu, V, Cr, and U are much higher than the Al-normalized values of the PAAS elements, whereas Mn and Fe show lower concentrations in some parts of the core (Figure 3). The ratios are higher during the period 9.5–8.5 ka BP (Table S2) than during 7.5 to 5.6 ka BP. Low $\delta^{15}N$ during the period of time from 7.5 to 5.6 ka BP is associated with a decreasing trend of $\text{Mn}/\text{Al}$, $\text{Fe}/\text{Al}$, $\text{Mo}/\text{Al}$, and $\text{U}/\text{Al}$ with not much variation in $\text{Cr}/\text{Al}$. The $\delta^{98}\text{Mo}$ in the core varied between $-0.35‰$ and $1.85‰$ with lighter values averaging $-0.02‰$ ($-0.4‰$ to $0.3‰$) between 9.8 and 8.5 ka BP followed by an increase from $-0.1‰$ to $1.7‰$ between 8.5 to 7.3 ka BP and remaining relatively constant (from $1.55‰$ to $1.85‰$) since 7.3 ka BP.

### 5. Discussion

The observed $\delta^{18}O_C$ values of *G. ruber* varied between $-2.7‰$ and $-1.5‰$ over the past 9.5 kyr (Figure 2) with the difference between the beginning and the end of the record (9.5 and 0.3 ka BP) being $-0.3‰$. This difference is comparable to the value ($0.36‰$) ascribed to sea level change during
5.1. Changes in Denitrification During the Holocene

Considering that sea level rose by only 45 m over the past 9.5 kyr (Fairbanks, 1989), the sediments of our core (collected at 500-m depth) were deposited within the depth range of the OMZ (Figure 1b).

5.1.1. Sedimentary $\delta^{15}N$ and Its Controlling Factors

The $\delta^{15}N$ of organic matter in the core ranges between 6% and 8.4%. The average $\delta^{15}N$ value of $\text{NO}_3^-$ in the open ocean is $-4.7\%$ (Sigman et al., 1997). The $\delta^{15}N$ of NO$_3^-$ is much higher (e.g., $\sim 15\%_o$, Figure 1c) within the denitrification zones such as the Arabian Sea (Altabet et al., 1999; Naqvi, 1991; Suthhof et al., 2001). As this isotopically heavy NO$_3^-$ is brought up from the OMZ into the surface layer by upwelling/vertical mixing, it results in the production of organic matter that is enriched in $^{15}N$ and this signature gets preserved in the underlying sediments through sinking particles. In the Arabian Sea $\delta^{15}N$ values range between 4.7% and 8.8% for the settling particles and 9.2% and 11% for sediments (Schäfer & Ittekkot, 1995; Suthhof et al., 2001). These $\delta^{15}N$ values may partly be lowered by contributions of terrestrial organic matter that has a value of $\sim 2\%_o$ (Peters et al., 1978; Sweeney & Kaplan, 1980). The $\delta^{13}C$ values of organic material in the core range from $-21.1\%_o$ to $-19.4\%_o$, and $\text{Corg}/\text{TN}$ is between 8.6 and 10.3, which is within the general range of marine organic matter in the Arabian Sea. Therefore, the organic matter in the core is dominantly of marine origin and the recorded $\delta^{15}N$ signatures originate from marine organic matter. Early diagenesis in the sediments can lead to elevated $\delta^{15}N$ values by as much as 4%, but this mainly occurs in low organic-poor deep-sea sediments (Altabet & Francois, 1994). Our core is characterized by relatively high $\text{Corg}$ contents (0.8% to 5.1%) of productive continental margin settings where diagenetic shift in $\delta^{15}N$ is small (Altabet et al., 1999; Pride et al., 1999). If influenced by diagenesis, one would expect a continuous increase to higher $\delta^{15}N$ values with depth, associated with low $\text{Corg}$ and $\text{TN}$, which is not observed. However, we cannot rule out the possibility of minor diagenetic effects during the early Holocene (Figure 2) associated with low TN contents. In addition, incomplete utilization of nutrients in the surface waters can also result in higher $\delta^{15}N$ values (Altabet & Francois, 1994), which may be caused by iron (Fe) limitation (Naqvi et al., 2010). Similar $\delta^{15}N$ values of dissolved nitrate, the core top sediments (7.7%o), and sediment trap material (4.7–8.0%o; Schäfer & Ittekkot, 1995) support the suggestion of Altabet et al. (1999) and Suthhof et al. (2001) that on an annual basis $\text{NO}_3^-$ gets completely utilized by the phytoplankton and incomplete utilization would not contribute to the observed $\delta^{15}N$ changes in our core. Enrichment in $\delta^{15}N$ (Figure 2 and Table S1) values can be caused by entrainment into the surface layer of waters enriched in $^{15}\text{NO}_3^-$ from the denitrification zone, which is then taken up by phytoplankton resulting in elevated $\delta^{15}N$ values in the organic matter that is ultimately transported to the sediments (Altabet et al., 1995, 2002, 1999; Ganeshram et al., 2000). Therefore, $\delta^{15}N$ (Figure 2 and Table S1) values ranging between 6% and 8.4% are suggested to be mainly a consequence of changes of denitrification intensity in the intermediate waters.
5.1.2. Changes in Sea Surface Productivity and Denitrification

High δ¹⁵N values (7.7‰, Figure 2) of sediments at ~9.5 ka BP and near the core top sediments indicate intense denitrification within the OMZ. It has been proposed that the δ¹⁵N changes in the Arabian Sea are related to the variability of the summer monsoon, with more intense denitrification occurring during periods of intensified summer monsoon and vice versa (Altabet et al., 1999; Ganeshram et al., 2000). Our δ¹⁵N data show that this relationship is more complex in detail. Low δ¹⁸Oc values are observed during the mid-Holocene (7–5.5 ka BP, Figure 2) suggesting strong summer monsoon intensity that likely resulted in increased freshwater inputs to the eastern Arabian Sea (Kessarkar et al., 2013; Singh et al., 2006). However, the δ¹⁵N values during the mid-Holocene (7.6 to 5.4 ka BP) were low (average of 6.2‰) indicating weaker denitrification (Figure 2). Increase or decrease in denitrification intensity is often attributed to increase or decrease in surface productivity based on Corg (Agnihotri et al., 2003; Naik et al., 2014). However, the fact that only 1–3% of the Corg produced in the surface waters ultimately reaches the bottom sediments calls for caution in the universal use of Corg and CaCO₃ as proxies. The distribution of Corg in the Arabian Sea is influenced by upwelling induced productivity (Calvert et al., 1995) justifying its use as a proxy of productivity (Agnihotri et al., 2003; Naik et al., 2014, and references therein). In our core Corg and CaCO₃ contents do not show significant variations related to the changes in denitrification (Figure 2). Instead, the Corg and TN profiles exhibit systematic increases from 9.5 ka BP to the core top. High values of δ¹⁵N at 9.5 ka BP indicate vigorous denitrification similar to the today (core top). But the high δ¹⁵N at 9.5 ka BP is associated with low Corg contents (Figure 2) unlike the high core top δ¹⁵N values, found with high Corg contents. Moreover, reduced denitrification appears to have been weaker during the mid-Holocene despite the relatively high Corg content (1.7% to 2.5%). Therefore, changes in Corg content that mainly reflected surface productivity cannot always be the only factor driving variations in denitrification intensity in the water column. Presently, the zones of the highest productivity (Figure 1a gray area) are not associated with the most intense denitrifying conditions in the Arabian Sea (Naqvi, 1991).

5.1.3. Southwest Monsoon Strength, Ventilation of Intermediate Water, and Denitrification Intensity

Changes in productivity on shorter time scales inferred from time series sediment trap data from the Arabian Sea have shown that stronger summer monsoon is not always associated with higher productivity (Rixen et al., 1996). Apart from upwelling strong summer monsoon winds also transfer nutrient-poor waters from south of the equator, thus reducing surface productivity in the western Arabian Sea. The sediment trap data from the eastern Arabian Sea also show that highest wind speeds and lowest SSTs are not always associated with increases in the biogenic particle fluxes. Instead, increased amounts of organic material are transferred to the deep sea during summer monsoons of intermediate strength (Rixen et al., 1996). As discussed by Rixen et al. (1996) if nutrient-poor water were reaching the study area, we would expect lower Corg and CaCO₃ contents. However, the lack of a pronounced decrease in Corg and CaCO₃ (Figure 2) between 7.6 and 5.4 ka BP essentially rules out the possibility of enhanced advection of nutrient-poor water. Records of sedimentary δ¹⁵N in the Arabian Sea covering longer periods of time (Altabet et al., 2002, 1999; Reichart et al., 1998; Suthhof et al., 2001) have reported weaker denitrification linked to strong winter monsoon arising from cooling in the North Atlantic region (Reichart et al., 1998). These results suggested that such periods were characterized by deep convective mixing leading to greater ventilation of subsurface waters in the Arabian Sea (Reichart et al., 1998). Suppressed denitrification has also been reported during colder periods (Heinrich events and Younger Dryas in the North Atlantic; Suthhof et al., 2001) and on millennial time scales (Pichevin et al., 2007) likely caused by enhanced advection of more oxygenated Antarctic Intermediate Water into the Arabian Sea. Similar conditions characterized by low δ¹⁵N are inferred in present study, which indicate weaker denitrification during a time of stronger summer monsoons as inferred from low δ¹⁸Oc signals and other published records (Azharuddin et al., 2016; Kessarkar et al., 2013; Saraswat et al., 2016). Weaker denitrification has also been inferred previously for times of stronger summer monsoon based on analysis of cores off Mangalore (Kessarkar et al., 2010, 2013). This was attributed to a more vigorous ventilation of subsurface waters by the poleward flowing undercurrent (WIUC) carrying more oxygenated waters just below the West Indian Coastal Current (Figure 1) along the western margin of India at depths between 100 and 250 m (Naqvi et al., 2006). This undercurrent may have extended to the depth of the present core location at 17°45’N during times of stronger monsoon thereby ventilating the intermediate layers. Although a decrease in δ¹⁵N during the mid-Holocene (Figure 54) has also been observed in cores off the Oman margin (Altabet et al., 2002) and off Pakistan (Reichart et al., 1998; Suthhof et al., 2001), this low in δ¹⁵N was not
discussed in detail in the above studies that focused on changes occurring on the glacial-interglacial time scales or on specific events (e.g., Heinrich events). Pichevin et al. (2007) studied δ15N variability in a core from the eastern Arabian Sea off Pakistan and compared it to the δ15N records from the western Arabian Sea (RC27-23; RC27-14; Altabet et al., 2002; 905; Ivanochko et al., 2005) and showed that the variations in the east and the west were decoupled. However, these authors also did not discuss the low mid-Holocene δ15N observed in the cores off Oman (core RC27-23). A minimum in denitrification intensity during this time has also been reported from the southeastern Arabian Sea (Kessarkar & Rao, 2007) suggesting that a relaxation in denitrification occurred on a large spatial scale during the mid-Holocene in the Arabian Sea. The locations recording minimum δ15N values during the mid-Holocene are found close to the boundary of the present-day denitrification zone (Figure 1b). The denitrification zone most probably contracted during the mid-Holocene probably responding to a more effective oxygenation of the OMZ and has since been undergoing an expansion. It is noted that the mid-Holocene minimum in δ15N is not observed in core MD-04 2876 from 828-m water depth (Pichevin et al., 2007) at the northern boundary of the denitrification zone but more studies at shallower depths off Pakistan are required to confirm the absence of this feature.

The presence of an intense OMZ supporting denitrification makes the Arabian Sea a globally significant source of nitrous oxide (N2O) to the atmosphere (Naqvi et al., 2000) accounting for an estimated 2–35% of the global oceanic source (Bange et al., 2001). Changes in Arabian Sea denitrification have been postulated to have contributed to variations in atmospheric N2O (Agnihotri et al., 2006; Altabet et al., 1995; Pichevin et al., 2007) as recorded in polar ice cores, such as Dome C from Antarctica that revealed decreasing N2O concentrations (Figure S4) during the early Holocene (Flückiger et al., 2002). However, this does not imply a direct cause and effect relationship, but instead that these signals may have had a common origin (e.g., decrease in Northern Hemisphere summer insolation (Berger & Loutre, 1991); Figure S4).

5.2. Differential Changes in the OMZ and Near-Bottom Waters

Core SK148/55 investigated here is located within the present-day core of the Arabian Sea OMZ and close to the lower boundary of the denitrification zone (Figure 1). In order to assess changes in the redox status of bottom waters at the time of sediment deposition during the past 9.5 ka BP, we have investigated the downcore distribution of trace elements and δ98Mo signatures (e.g., Anbar, 2004; Siebert et al., 2003). We observe very high Cu/Al and Ni/Al ratios as compared to PAAS, which has been suggested to reflect high organic matter supply (Tribovillard et al., 2006) given that Ni and Cu behave as micronutrients and form complexes with organic matter (Böning et al., 2015; Tribovillard et al., 2006). Although Ni and Cu can also form authigenic sulfides and enrichment is therefore not necessarily linked to productivity (given that there can be sulfate reducing microenvironments), we argue that, in combination with Corg accumulation rates (Figure S3), these elements indicate high productivity.

Stronger denitrification (high δ15N) during the period between ~9.5 and 8.5 ka BP is associated with more variable and on average elevated Mo/Al, U/Al Fe/Al, and Mn/Al ratios (Cu/Al, Ni/Al, V/Al, and Cr/Al show no overall enrichment or increased variability) as compared to the mid-Holocene (Figure 3). Vanadium, Cr, Mo, U, Mn, and Fe are redox sensitive elements, which display different geochemical behavior depending on the ambient redox state. Vanadium in oxygenated water is adsorbed on Fe-Mn oxyhydroxides, whereas under anoxic condition it is reduced to vanadyl binds to chelating surface groups (e.g., Morford & Emerson, 1999). Chromium in oxygenated water is soluble but under anoxic conditions becomes adsorbed onto Fe-Mn oxhydroxides or forms complexes with humic/fulvic acid and can be released during anaerobic remineralization of organic matter and diffuses into overlying water during sediment compaction (e.g., Tribovillard et al., 2006, and references therein). Molybdenum is adsorbed on Mn-Fe oxhydroxides under oxic conditions, whereas under reducing conditions authigenic enrichment takes place (Morford & Emerson, 1999). U is dissolved [U (IV)] in an oxic environment and does not get scavenged or reduced (e.g., Anderson et al., 1989). Instead, U is removed by diffusion from the water column into the sediment followed by reduction of U (V) to U (IV) that is subsequently precipitated or adsorbed forming authigenic U (Morford & Emerson, 1999; Tribovillard et al., 2006), whereby changes in sedimentation rate and oxygen penetration affect its concentration (Crusius & Thomson, 2000).

The period from 9.5 to 8.5 ka BP is associated with high V/Al, Mo/Al, and U/Al ratios possibly indicating that these elements were enriched under highly reducing conditions. However, high V/Al, Mo/Al, and U/Al ratios...
also coincide with enrichments of Mn and Fe in the same samples, which argues against strongly reducing conditions during deposition. Recently, Scholz et al. (2011, 2017) suggested that under oxic or oxygen depleted, but nonsulfidic bottom water conditions Mo can be enriched in sediments via a Mn and/or Fe shuttle process in specific settings like the Baltic Sea or the OMZ offshore Peru where the transition to anoxic conditions is located relatively close to the sediment-water interface. The early Holocene section of the core exhibits high $C_{\text{org}}$ accumulation rates (though $C_{\text{org}}$ content is relatively low, see below). Anoxic conditions in the sediment caused by decaying organic matter can explain the enrichment of the diffusive U and Cr, while Mo and V are likely dominated by adsorption and transport by Mn-Fe oxyhydroxides. These oxyhydroxides would then release Mo below the sediment-water interface and with Mn and Fe partly diffusing back into the oxygenated bottom water to capture more Mo resulting in the establishment of a shuttle mechanism. In addition, it is likely that the high sedimentation rate (1.27 to 1.87 mm/year; Figure 2) quickly buried these sediments separating them from the biodegradation and also overlying waters. This may explain the apparently contradictory enrichment of Mn and Fe together with Mo, V, U, and Cr.

To test the model for element enrichment and bottom water conditions presented above, Mo isotope ($\delta^{98}$Mo) analyses were carried out. The Mo isotopes show distinctive values for different redox conditions, namely, light (−0.7‰) in oxic, heavy (−1.5‰) in anoxic environments and reach values similar to seawater (−2.3‰) in euxinic settings due to complete removal of Mo from the water column as sulfide (e.g., Arnold et al., 2004; Barling et al., 2001; Goldberg et al., 2012; Neubert et al., 2008; Poulsen-Brucker et al., 2009, 2006; Siebert et al., 2006, 2003). These changes in $\delta^{98}$Mo mainly arise from the following reasons: Mo is a conservative element and is uniformly distributed in the oceans due to a much longer residence time (440 kyr; Miller et al., 2011) than the global ocean mixing time. Present-day oxic sea water has a uniform $\delta^{98}$Mo signature of 2.3‰ (e.g., Siebert et al., 2003). Under oxic conditions light Mo isotopes are preferentially removed by adsorption to Mn oxides. Wasylenki et al. (2011) suggest adsorption of Mo as polymolybdate complex on the surface of Mn minerals indicating that the observed Mo isotope fractionation is caused by a change in coordination between dissolved and adsorbed Mo species. In suboxic to anoxic environments a wide variety of Mo isotopes have been observed, which are known to be dependent on a variety of factors such as availability of Mn and Fe, thiomolybdate formation, Fe speciation, and the operation of a transport shuttle mechanism versus diffusion (e.g., Dahl et al., 2010; Goldberg et al., 2009, 2012; Poulsen-Brucker et al., 2009, Scholz et al., 2017; Siebert et al., 2006; see also above). However, many anoxic settings seem to have converged around an isotope composition around 1.5‰ (e.g., Poulsen-Brucker et al., 2009; Siebert et al., 2006). In general, all sedimentary fluxes of Mo are isotopically light, with Mo sulfides being the lightest (Tossell et al., 2005). Both oxic and anoxic but not sulfidic sinks remove light Mo isotopes from seawater, leaving the remaining seawater heavy (2.3‰). In sulfidic and hydrographically restricted settings, Mo is thought to be scavenged quantitatively resulting in a close to seawater isotope composition in euxinic sediments (e.g., Arnold et al., 2004).

In our core $\delta^{98}$Mo values within the Holocene systematically vary between −0.35‰ and 1.85‰ suggesting that these sediments have been deposited under oxic and suboxic/anoxic water conditions at different time periods. Lithogenic sediments at this site are reported to be mainly derived from the Deccan traps in the hinterland (Kessarkar et al., 2003; Thamban et al., 2007). Suspended particulate matter supplied by the Narmada River that is passing through these formations has an average hinterland (Kessarkar et al., 2003; Thamban et al., 2007). Suspended particulate matter supplied by the Narmada River that is passing through these formations has an average hinterland...
previously published data (e.g., Poulson-Brucker et al., 2009) would suggest a change to anoxic/suboxic environment (Figure 3) of the bottom waters. These conditions stabilized between ~7.6 to 5.4 ka BP at uniform $\delta^{98}$Mo values (1.55–1.75‰). At the same time enrichments of Fe and Mn decline while Mo, V, and U remain highly enriched despite of reduced sedimentation rates (Figures 2 and 3). Although the levels of enrichment of V/Al, Mo/Al, and U/Al indicate anoxic (Calvert & Pedersen, 1993; Tribovillard et al., 2006) or even euxinic conditions in the sediments during the mid-Holocene (Tribovillard et al., 2006 and references therein; Figure 3a), the Mo isotope signal does not indicate strongly reducing bottom water conditions (i.e., does not approach seawater). Scholz et al. (2017) have shown that very high Mo concentrations can be produced via a Fe shuttle mechanism under nonsulfidic conditions and Mo isotope values around 1.5‰ fit that interpretation. In addition, independent data have suggested that the Arabian Sea was low in oxygen but not sulfidic (Banse et al., 2014) during the present day. U becomes enriched in anoxic sediments by diffusion (Tribovillard et al., 2006, and references therein), which is reflected by U/Al far above the lithogenic background (Figure 3). We therefore suggest that bottom waters at the core site were better oxygenated in the early Holocene and changed to anoxic conditions around 7.5 ka BP. Subsequently, bottom waters remained anoxic.

5.3. Implications for the Water Mass Structure in the Arabian Sea During the Holocene

The period from ~9.5 to 8.5 ka BP is associated with lighter sedimentary Mo isotope signatures indicating oxygenated bottom waters, whereas high $\delta^{15}$N indicates intense denitrification in the overlaying anoxic/suboxic water column (Figure 4). Subsequently from ~ 8.5 to 7.5 ka BP a decrease in $\delta^{15}$N (indicating improved ventilation of the water column) was associated with increasing $\delta^{98}$Mo values from ~0.1‰ to 1.6‰ indicating shifting from oxic to anoxic/suboxic conditions. These findings imply that the OMZ as a whole was better oxygenated whereas the bottom waters at the study site were significantly less ventilated (Figure 4). These anoxic/suboxic bottom water conditions stabilized between ~7.6 and 5.4 ka BP supported by uniform $\delta^{98}$Mo values (1.55–1.75‰). The $\delta^{15}$N signature exhibits significantly lower values during the same time (7.6–5.4 ka BP) documenting more oxygenated, better ventilated conditions in the OMZ water column. Changes in organic carbon content and $\delta^{15}$N in the Arabian Sea during early to mid-Holocene time have been related to more oxygenated conditions and reported in previous studies (e.g., Kao et al., 2015; Kessarkar & Rao, 2007; Kessarkar et al., 2010; Thamban et al., 2001). Kao et al. (2015) reported a decrease in $\delta^{15}$N the southern Arabian Sea since 6 ka BP, in response to N$_2$ fixation and proposed that this was a local effect. The inferred weakening of denitrification toward the late Holocene (Ivanochko et al., 2005; Kao...
et al., 2015) is, however, based on analyses of cores (905P and SK177/11; Figure 1a) located at a significant distance from the perennial denitrification zone and so it is possible that these cores may not have recorded the actual denitrification signals from the Arabian Sea during the Holocene period. It is also possible that there was a major reorganization of subsurface water masses in the Arabian Sea during the mid-Holocene in response to a decrease in Northern Hemisphere insolation (from 9 to 6–5 ka BP) that was accompanied by a stabilization of the sea level by 7 ka BP. This is expected to have affected advection of subsurface waters into the Arabian Sea both from outside (e.g., Subantarctic Mode Water) and within (Persian Gulf Water and Red Sea Water) this region. The δ15N data suggest that the OMZ of the Arabian Sea was better ventilated/oxygenated during mid-Holocene (7.6–5.9 ka BP) resulting in a suppression of denitrification and that there has been a steady intensification/expansion of the OMZ since then. Considering the changes in the denitrification the most likely controlling processes are contractions and expansions of the perennial denitrification zone (Kessarkar et al., 2010; Naqvi, 1987, 1991). Changes in denitrification during the Holocene in intermediate waters and decoupled variations in bottom water conditions at present study site indicate variations in the vertical oxygen distribution within the OMZ. However, more detailed studies are required to identify the source of waters responsible for the better oxygenation parts/whole of the Arabian Sea OMZ during the mid-Holocene (Figure 4). Since 5.5 ka BP denitrification has continuously intensified suggesting reduced ventilation of OMZ associated with uniform Mo isotopes (average of 1.7‰) and consequently less oxygenated bottom waters.

6. Conclusions

The results of our study indicate that denitrification intensity in the Arabian Sea during the Holocene has not been controlled by upwelling intensity and productivity alone. During the early Holocene period (between 9.5 and 8 ka), pelagic denitrification was strong, but it probably occurred within a thinner upper layer as bottom waters at our coring site were better oxygenated as evident from light Mo isotope signatures. Denitrification weakened substantially during the mid-Holocene (7.6–5.4 ka BP), most likely in response to better ventilation of the OMZ at that time. This phase of weak denitrification was associated with a stronger summer monsoon and low N2O levels in the atmosphere. We propose that a reorganization of subsurface water mass circulation was probably responsible for the weakening of Arabian Sea denitrification during the mid-Holocene. The bottom waters at the study site turned anoxic by ~7.5 ka BP, whereas the overlying water only changed to a less oxygenated state at ~5.5 ka BP and have since experienced a continuous intensification of denitrification.

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