CHAPTER 5
OMZ Variability in the Eastern Arabian Sea: Implications of Productivity

1. Introduction

The Arabian Sea is unique in terms of seasonal reversals of winds during the south-west (SW) and north-east (NE) monsoon due to seasonal variations in heating of the southern Asian continent. Associated with the seasonal reversal of winds is the reversal of surface-water circulation. Strong winds blowing from the SW generate upwelling of nutrient-rich waters in the Western Arabian Sea (WAS), off Somalia/Oman leading to very high primary production, and weak and sporadic upwelling along the coasts off India and Pakistan (Eastern Arabian Sea (EAS) (Fig.5.1). The EAS receives more precipitation compared to the WAS during the SW monsoon. Most of the SW monsoon precipitation on the Western Ghats drains into the Arabian Sea through numerous rivers and streams. During the NE monsoon winds from the NE evaporate and cool the surface water which deepens the mixed-layer and leads to input of nutrients to the surface in the Northern basin and also increases the primary productivity (Madhupratap et al., 1996). The organic production in the Arabian Sea is however significantly higher during the SW monsoon in comparison to the NE monsoon and decreases in the inter monsoonal seasons.

The Arabian Sea is amongst the highest seasonal productivity zones in the world (Qasim, 1977). The high biological productivity prevailing during the south-west monsoon is a source of large amounts of organic matter which subsequently sinks to deeper depths (Nair et al., 1989). At intermediate depths, the oxidation of organic matter consumes dissolved oxygen and therefore the entire Arabian Sea is characterized by a permanent, intense Oxygen Minimum Zone (OMZ) between depths of 150-1200m (Wyrtki, 1971; Von Stackelberg, 1972). In the OMZ, bacterial degradation of organic matter takes place, which reduces NO$_3^-$ and produces N$_2$ and N$_2$O in the water-column by a chain of processes known as denitrification (Deuser et al., 1978; Naqvi, 1991). OMZs are important due to their climatic interactions and impacts on ecosystems for eg., their contribution to major greenhouse gases such as
CO₂ and N₂O (Resplandy et al., 2012). Modern observations suggest that the volume of OMZs' suboxic waters has increased over the past decades (Stramma et al., 2008) and could further expand due to ocean warming and climate change (Sarmiento et al., 1998; Keeling et al., 2010). Therefore, improving our understanding of OMZs is of primary importance when considering the future evolution and impacts of OMZs (Resplandy et al., 2012). Several studies were carried out to understand variations in productivity/denitrification and OMZ intensity in the EAS focused on glacial-interglacial or longer timescales (Schulz et al., 1998; Reichart et al., 1998; Schulte et al., 1999; von Rad et al., 1999a; Ganeshram et al., 2000; Agnihotri et al., 2002; Reichart et al., 2004; Pichevin et al., 2007; Böning and Bard, 2009) and few studies covering shorter timescales in the EAS (Von Rad et al., 1999b; Agnihotri et al., 2003; Agnihotri et al., 2008). The OMZ is known to be intense during the Holocene, in particular during the Late Holocene (Gupta et al., 2011) controlled by the supply of oxygen depleted intermediate waters combined with elevated monsoon-controlled oxygen demand (Böning and Bard, 2009).

Our understanding on the dissolution/preservation of calcite in response to varying intensity of the OMZ is very little. In the present study two cores were examined from the EAS with high sedimentation rates. Core AAS9/19 which covers the Holocene was studied in order to address the changes in productivity, denitrification, and oxygenation of bottom waters and to understand the influence of OMZ on the dissolution/preservation of calcite. Core AAS9/21 was examined to understand denitrification changes and oxygenation of bottom waters for the last 70 kyr.
Fig. 5.1. Composite SeaWiFS chlorophyll-a concentrations (mg/m$^3$) image (source: http://gdatal.sci.gsfc.nasa.gov/), for south-west monsoon (June-September; 2008) in the Arabian Sea. A distinct difference between the western and eastern Arabian Sea is noticed with the western side showing higher chlorophyll concentrations and hence more productive. Likewise the west coast of India shows higher chlorophyll concentrations. Thick circles indicate core locations of Core AAS9/19, AAS 9/21, RC-27-14, RC-27-23, 3268G5 and SK17.

2. Chronology

Fig. 5.2a Depth versus Age derived from the AMS $^{14}$C dates for the Core AAS-9/19.
3. Results and Discussion

3.1. Early to Late Holocene contrast in productivity, denitrification, OMZ intensity and calcite dissolution.

The CaCO$_3$ content varied from 38 to 72% with higher values encountered during early Holocene (from ~12 to 7 kyr) (Fig. 5.2a). The Organic Carbon (OC) content varied from 0.8 to 5% with low OC values during the early Holocene and a gradual increase beginning from ~7 kyr (Fig. 5.3b). The core top values are within the range of OC values obtained from the continental margin sediments (Paropkari et al., 1992). N content varied from 0.1 to 0.7% with variations similar to that of OC ($r^2 = 0.87$, n=36) (Fig. 5.3d). C/N values range from 3.7 to 14.5 units (Fig. 5.3e), which are generally within those reported for marine sedimentary organic matter $8 \pm 2$ (Reichart et al., 1997; Bhushan et al., 2001). Higher values during the early Holocene could be due to contribution from terrestrial organic matter. $\delta^{13}$C$_{org}$ values range from -21 to -22 ‰ (Fig. 3f). A cross plot of $\delta^{13}$C$_{org}$ versus C/N ratios shows all values in the range of marine organic matter (Meyers, 1994) (Fig. 5.4) indicating that deposition of organic matter at this site has been predominantly of marine origin throughout the Holocene. $\delta^{15}$N values range from 3.4 to 7 ‰ with lower values during the early Holocene and gradually increasing towards the Late Holocene (Fig. 3c). The $\delta^{15}$N
values of the top sections of the present core are in the range observed for the EAS (Agnihotri et al., 2003). The $\delta^{13}$C of *G. ruber* varied from 0.86 to 1.59‰ (Fig. 2g). Molybdenum concentrations varied from 1.3 to 9.7 ppm and Chromium concentrations varied from 137 to 214 ppm. Higher concentrations of Mo and Cr were noted during ~7-0 kyr. Ti showed a decreasing trend through the Holocene period with concentrations varying from 0.3 to 0.8 wt% (Fig. 5.3h) and are positively correlated to CaCO$_3$ ($r^2 = 0.36$, $n=36$) suggesting that terrigenous dilution is not the cause for CaCO$_3$ variations. The shell weights of *Globigerinoides ruber* range from 13 to 19 μg (Fig. 5.3m). Higher shell weights were noticed during Younger Dryas (YD) and early Holocene and then a decrease in shell weights was noticed throughout the Holocene period. On an average the ~12-7 kyr shells weighed ~17 μg and the 7-0 kyr shells weighed ~14 μg, a ~3μg decrease in shell weights during the Late Holocene. Scanning Electron Micrographs (SEM) were taken on a 6360 LV, JEOL instrument.

3.2. Changes in surface productivity, denitrification and bottom-water oxygenation intensity

Organic matter (OM) input is either generated by primary production in the photic zone or through transport of terrestrial OM to the marine realm. The organic carbon (OC) content of sediments depends upon various factors such as sedimentation rates; oxygen exposure times and organic matter composition (amount of refractory and non-refractory components) (see Zonneveld et al., 2010). Studies on the OC distribution in surficial sediments collected along the western continental margin of India suggest that primary productivity is the major controlling factor (Calvert et al., 1995). The AAS 9/19 sediment core is located on the continental slope, characterized by the presence of fine material, high sedimentation rates, presence of OMZ and therefore high organic carbon content. The OC content shows higher values during the Late Holocene and appears to reflect surface water productivity variations.

The $\delta^{13}$C of planktonic foraminifera can vary in response to productivity changes, carbonate chemistry of seawater and upwelling processes (Peeters et al., 2002). In the EAS, the processes of upwelling and winter convective mixing aid in bringing $^{13}$C depleted subsurface waters to the surface, eventually depleting $\delta^{13}$C of
the surface waters. Planktonic foraminifera calcifying in these waters record lower $\delta^{13}C$ in their shells. On the other hand an increase in surface productivity increases the $\delta^{13}C$ of surface seawater. Increasing productivity is also linked to upwelling of nutrient-rich subsurface waters, foraminifera taking in $^{12}C$ preferentially over $^{13}C$ and hence the organic matter gets enriched in $^{12}C$.

Therefore the $\delta^{13}C$ in shells is a net result of whichever process dominates. We observe lower values of $\delta^{13}C_{\text{Gruber}}$ and $\delta^{13}C_{\text{org}}$ beginning from $\sim$7 kyr and a positive relationship between the two parameters which also advocates the increase in productivity during this period. In summary, the Late Holocene period from $\sim$7 to 0 kyr is dominated by higher productivity as seen from the high OC %, low $\delta^{13}C_{\text{org}}$ and low $\delta^{13}C$ of planktic foraminifera as a result of increase in intensity of upwelling/winter convective mixing.

Productivity increase is linked to an increase in denitrification. Arabian Sea is one of the most important regions wherein water-column denitrification occurs. Denitrification results in enrichment of $^{15}N$ in residual NO$_3^-$, and the lighter isotope ($^{14}N$) is consumed relatively faster due to kinetics. The heavier NO$_3^-$ is then supplied to the ocean surface via upwelling and gets incorporated in newly formed particulate organic matter. Thus, the nitrogen isotopic composition ($\delta^{15}N$) of particulate organic matter depositing in sediments has been used as a proxy for the intensity of water-column denitrification in the past (Altabet et al., 1995; 1999; Ganeshram et al., 1995). However, certain processes affect this proxy such as mixing with isotopically lighter terrestrial organic matter, organic matter alteration in water column and sediments, incomplete nitrate utilisation, variability in nitrogen fixation, etc. (See Ganeshram et al., 2000). We observed that organic matter deposited at this site is of marine origin and therefore temporal variations in $\delta^{15}N$ are not a result of mixing or dilution due to terrestrial organic matter. Furthermore, lack of correlation between $\delta^{13}C_{\text{org}}$ and $\delta^{15}N$ suggests that spatial variations in $\delta^{15}N$ are not due to mixing of terrestrial and marine organic matter (Peters et al., 1978). Significant positive relationships between $\delta^{15}N$ - OC and $\delta^{15}N$ - N ($r^2 = 0.86$, n=36) rule out any early diagenetic effect of organic matter degradation on the $\delta^{15}N$ signal (Agnihotri et al., 2003). Incomplete nitrate utilisation, i.e. preferential uptake of $^{14}N_{\text{NO}_3}$ by phytoplankton leading to increase in $^{15}N$ in the remaining nitrate pool, and lowering of $^{15}N$ in the sinking OM, is a process which is not of importance in the eastern Arabian Sea, due to near-complete
utilization of available nutrients (Altabet et al., 1999). Enhancement of nitrogen fixation by cyanobacteria can produce isotopically lighter $\delta^{15}$N as they mostly use atmospheric nitrogen with very little fractionation (See Ganeshram et al., 2000). However, in the eastern Arabian Sea, nitrogen fixation does not have much effect on $^{15}$N${\text{NO}}_3^-$ (Altabet et al., 1999). $\delta^{15}$N values in AAS9/19 are significantly correlated with OC content ($r^2 = 0.8$, $n=36$) which suggests that subsurface denitrification is controlled by the extent of biological productivity. Thus, we infer that present core location has experienced intense denitrification during Late Holocene from ~7 to 0 kyr.

Variations in surface productivity are expected to induce changes in oxygen level of bottom waters/sediment-water interface due to organic matter degradation. Redox conditions of bottom waters/sedimentary column strongly influence the distribution of some of the trace elements, such as Mo and Cr amongst others. In anoxic basins, Cr (VI) appears to be rapidly reduced to the Cr (III) state and removed from solution. Mo lacks chemical reactivity under oxic conditions but is enriched to a great extent in anoxic conditions (see Calvert and Pedersen, 1993). In modern anoxic environments, Mo shows a strong positive correlation to OC (Algeo and Lyons, 2006) as seen in the present core ($r^2 = 0.48$, $n=36$). Down core variations of Mo and Cr, normalized to Al or Ti, are often used to infer paleo-redox conditions at the sediment-water interface at the time of deposition. Ti in marine sediment is mostly of continental origin and supplied through eolian and fluvial pathways. Cr/Ti and Mo/Ti both show higher values during the Late Holocene (Fig. 5.3i and 5.3j) which suggests prevalence of sub-oxic waters during the Late Holocene. Continuous rise in denitrification and OMZ intensity through the Holocene was proposed to be due to the sluggish circulation of the Red Sea and Persian Gulf waters, which reached its present state at around 6 kyr and this, prevented the oxygen-rich southern water masses to the northern Arabian Sea enabling a continuous build-up of oxygen deficiency (Pichevin et al., 2007).
Fig. 5.3. Downcore variations from the Core AAS 9/19 in (a) CaCO3%,(b) organic carbon %, (c) $\delta^{15}N$ (%), (d) nitrogen %, (e) C/N ratios, (f) $\delta^{13}C_{org}$ (%), (g) $\delta^{13}C$ (%) of Globigerinoides ruber (values are in greyscale and the black line denotes 5-point adjacent averaging ), (h) Ti (ppm), (i) Cr/Ti, (j) Mo/Ti ratios, (k) pteropod numbers, (l)aragonite content and (m) shell weights of G. ruber.
3.3. Calcite dissolution due to variations in bottom-water oxygenation

Geochemical proxies such as OC, N, C/N, δ^{15}N, δ^{13}C_{org}, and δ^{13}C_{G.ruber} from core AAS 9/19 suggest that in comparison to the early Holocene, surface productivity increased during middle to Late Holocene and so did the intensity of denitrification. Increased denitrification must have also lead to a better preservation of OC during the Late Holocene. Moreover, Cr/Ti and Mo/Ti from the same core do suggest that bottom-waters were suboxic, which means that the OMZ intensity increased during this period. Oxygenated bottom-water conditions prevailed during the early Holocene and YD wherein sediments were rich in carbonate, aragonite and pteropods and low in OC and redox sensitive elements (von Rad et al., 1999a). There is also a strong anti-correlation between CaCO_{3} and δ^{15}N (r^2 = 0.74, n=36) which suggest that during the Late Holocene CaCO_{3} dissolution was a result of increased OMZ intensity. This implies that denitrification and calcite preservation are intimately linked and reflect OMZ intensity variations. We also rule out that CaCO_{3} content decrease during the Late Holocene was not a result of dilution by terrigenous material, by examining the...
Ti variations from this core which is a proxy for terrigenous dilution. The decrease in Ti concentrations through the Holocene, observed in AAS 9/19 is reliable as such a decreasing trend was seen in another core from the EAS, 3268G5. Higher Ti during the early Holocene was probably due to increased dust supply because of stronger winds (Agnihotri et al., 2003).

OMZs have been also termed as a Carbon Maximum Zones (CMZ) since they have high dissolved inorganic carbon (DIC) concentrations and are local sources of CO₂ (Paulmier et al., 2011). They could therefore induce a positive feedback for atmospheric CO₂ (Paulmier et al., 2011) and lead to dissolution of CaCO₃ on the seafloor. Aragonite is a metastable polymorph of CaCO₃ and more soluble in water than calcite (Morse et al., 1980). Low aragonite content and absence of pteropods during the Late Holocene from a nearby core SK 17 resulted from an increase in OMZ intensity (Fig. 1, 2k and 2l; Singh et al., 2007). It is also observed in Core SK 17 that Aragonite content was high during YD (Singh, 2007) due to inflow of oxygenated Subantarctic Mode and Antarctic Intermediate Water (SAMW-AAIW) (Böning and Bard, 2009). However the YD event is not well demarcated in all the proxies as the response of Arabian Sea to YD event is thought to be weak (Gupta et al., 2011).

Shell weights of *G. ruber* from AAS 9/19 were heavier during the early Holocene and highest during the YD probably due to the inflow of SAMW-AAIW. Lower shell weights during the Late Holocene could be a result of dissolution or due to increasing atmospheric CO₂ concentrations during the Holocene thus reducing the surface-water carbonate ion [CO₃²⁻] concentrations and hence leads to thinner foraminiferal shells (Naik et al., 2010). In order to corroborate calcite dissolution during the Late Holocene, we acquired SEM micrographs of *G. ruber* shells at 3.57 kyr, representative of Late Holocene and 9.9 kyr, representative of early Holocene period (Fig. 5.5a and b). Marked dissolution features were seen on the 3.57 kyr shells, thus providing evidence that shell weight variations are due to dissolution which occurred during the Late Holocene as a result of sub-oxic bottom waters. Based on measurements of gases trapped in Antarctic ice, Indermühle et al. (1999) demonstrate that the CO₂ content of the atmosphere rose by 20 ppm between 8000 BP and the onset of the Little Ice Age. This CO₂ rise is thought to be resultant form different processes such as deposition of shallow water carbonate, carbonate compensation of land uptake during the glacial termination, terrestrial carbon uptake and release during
the Holocene, the response of the ocean-sediment system to marine changes during the termination, etc. (Menviel and Joos, 2012). The CO$_2$ release from calcite dissolution in OMZ regions could be an important process contributing to the Holocene CO$_2$ rise and further studies should be aimed at quantification of CO$_2$ released from major OMZ regions of the world through the Holocene.

![Fig. 5.5a. SEM of Globigerinoides ruber shells at a magnification of 700x at 3.57kyr interval.](image)

3.4. Variations in denitrification, bottom water oxygenation and calcite dissolution during the last 70 kyr.

In core AAS 9/21, the CaCO$_3$ content varied from 15 to 46% through the last 70 kyr. CaCO$_3$ content was observed to be lower during MIS 1 and 3 and comparatively higher during MIS 2 and 4 (Fig. 5.6a). The Early-Holocene values are lower in comparison to the Late-Holocene period and in contrast to the core AAS 9/19. The MIS 2 shows the highest CaCO$_3$ content for the last 70 kyr. The total carbonate content at any given location may fluctuate due to productivity of carbonate secreting organisms, dilution by non-calcareous material and dissolution of calcareous tests during and after deposition. Since Ti in marine sediment is mostly of continental origin and supplied through eolian and fluvial pathways, the Ti variations from core AAS 9/21 were examined to understand whether they indicate the periods of terrigenous influx. Ti varied from 0.3 to 0.9% through the study period (Fig. 5.6b). However, the titanium concentrations did not display systematic variations, as
observed in CaCO$_3$ profile. Further there was no correlation between CaCO$_3$ content and Ti, which signifies that dilution by terrigenous material is not the cause for the CaCO$_3$ variations (Fig. 5.6).

The nitrogen isotopic composition ($\delta^{15}$N) of particulate organic matter depositing in sediments has been used as a proxy for the intensity of water-column denitrification in the past (e.g. Altabet et al., 1995). Therefore to understand the denitrification intensity variations in the past, the $\delta^{15}$N record of core AAS 9/21 was observed. Since the sedimentation rate in core AAS 9/21 is high, the sediments should faithfully record the $\delta^{15}$N of sinking organic matter. $\delta^{15}$N values varied from 5 to 9 $\%$ through the study period. The Holocene section of core AAS 9/21 is similar to that of core AAS 9/19 with higher $\delta^{15}$N values during Late-Holocene and lower during Early-Holocene (Fig. 5.6c). The overall profile displayed higher values during MIS 1 and 3 and lower values during MIS 2 and 4 as also observed by Ganeshram et al., (2000) for the Arabian Sea and the eastern Pacific margins. The $\delta^{15}$N record from AAS 9/21 is also similar to that of cores RC 27-14 and RC 27-23 from the western Arabian Sea (Altabet et al., 2002). They found that the high frequency oscillations in $\delta^{15}$N were similar to Greenland ice-core records of changes in polar climate and that denitrification was high during warm phases of the Dansgaard-Oeschger Events and minimal during the cold phases. Denitrification requires sub-oxic conditions and thus depends on the intensity and extent of subsurface oxygen minimum zone which in turn varies with the local production, downward flux of carbon and ventilation age of Arabian Sea intermediate water sources (Altabet et al., 2002). Changing high-latitude temperature occurred at the same time as altered weather patterns linked to the strength of the summer south Asian Monsoon. Through atmospheric forcing, Northern Hemisphere climate events would have a practically instantaneous expression in the Arabian Sea denitrification record. The $\delta^{15}$N record demonstrates high sensitivity of the Arabian Sea Oxygen Minimum zone to Northern Hemisphere climate change on short timescales (Altabet et al., 2002). A comparison was made between CaCO$_3$ content and $\delta^{15}$N content from core AAS 9/21. A negative correlation was observed between these two parameters ($r^2 = 0.28$, $n=46$) which again advocates that calcite dissolution occurred when the intensity of denitrification increased.

The link between denitrification and sub-oxic conditions in the eastern Arabian Sea is compared through the record of Molybdenum from core AAS 9/21. In the ocean, the concentration of Molybdenum is more or less constant with water depth.
This is thought to be due to the unreactive nature of the dissolved species, namely molybdate ($\text{MoO}_4^{2-}$) in oxygenated sea water. Though unreactive in oxic conditions Mo is highly enriched in anoxic sediments. The behaviour of molybdenum therefore shows great potential as a proxy indicator of deposition under anoxic conditions.

Molybdenum concentrations in core AAS 9/21 varied from 0.5 to 7 ppm (Fig. 5.6d). The core top shows slightly enriched Mo content which then decrease and remains low till around 17 kyr. Thereafter Mo concentration shows a gradual increase. The highest values of Mo are seen during MIS 3 which then decrease during MIS 4.
The Mo variations through the last 70 kyr signifies that sub-oxic condition prevailed during the Late-Holocene, early part of MIS 2 and mainly throughout MIS 3. Furthermore, there is a correlation between Mo and $\delta^{15}$N ($r^2 = 0.3$, n=46). High Mo concentration corresponds to higher $\delta^{15}$N content which signifies that denitrification leads to sub-oxic bottom waters which was significant during MIS1 and 3.

4. Conclusions

Productivity proxies such as OC, $\delta^{13}$C$_{org}$, and $\delta^{13}$C$_{G.ruber}$ in the eastern Arabian Sea sediment cores reveal that productivity was higher during the Late Holocene (~7 to 0 kyr) in comparison to early Holocene. Down core variations in $\delta^{15}$N of sedimentary organic matter appear to be controlled by the extent of surface productivity. Temporal variation in $\delta^{15}$N demonstrates that the intensity of subsurface denitrification has increased from ~7 kyr BP, in response to increasing surface productivity during this period. Redox sensitive elements such as Molybdenum and Chromium indicate that the OMZ intensity also increased simultaneously suggesting a strong coupling between productivity and OMZ intensity in the eastern Arabian Sea. The increase in OMZ intensity further lead to an increase in calcite dissolution as seen in the low CaCO$_3$ content, lower shell weights of planktonic foraminiferal species $G$. $ruberr$ and visible dissolution features on $G$. $ruberr$ shells, during the Late Holocene. This calcite dissolution is probably a result of an increase in DIC in waters of the OMZ releasing $CO_2$ to the atmosphere most likely contributing to the Holocene $CO_2$ rise. Intensified denitrification during MIS 1 and 3 and weak denitrification during MIS 2 and 3 beyond the present day OMZ depth in the Arabian reveals the fluctuation of OMZ depth between glacial and interglacial periods along the eastern Arabian Sea. The increase in sub-oxic conditions also leads to calcite dissolution which was most intense during the Early-Holocene and MIS 3.