Sedimentary pigments and nature of organic matter within the Oxygen Minimum Zone (OMZ) of the Eastern Arabian Sea (Indian margin)

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Abstract

Sedimentary pigments, carbon and nitrogen content and their stable isotopes were studied in three short cores collected from the oxygen minimum zone (OMZ) of the Eastern Arabian Sea (EAS). Nine pigments including chlorophyll a and their degradation products were quantified using High Performance Liquid Chromatography (HPLC). Astaxanthin followed by canthaxanthin and zeaxanthin were the major carotenoids detected in these cores. The total pigment concentration was high in the core collected from 500m water depth (6.5 µgg⁻¹) followed by 800m (1.7 µgg⁻¹) and 1100m (1.1 µgg⁻¹) depths respectively. The organic carbon did not have considerable control on sedimentary pigments preservation. Pigment degradation was comparatively high in the core collected from the 800m site which depended not only the bottom dissolved oxygen levels, but also on the faunal activity. As reported earlier, the bottom water dissolved oxygen and presence of fauna have good control on the organic carbon accumulation and preservation at Indian margin OMZ sediments. The C/N ratios and δ¹³C values for all the cores conclude the marine origin of organic matter and δ¹⁵N profiles revealed signature of upwelling associated denitrification within the water column.

Key words: sedimentary pigments; organic matter; C/N ratio; oxygen minimum zone; Eastern Arabian Sea.
1-Introduction

Oxygen Minimum Zones (OMZ) are important in terms of organic matter (OM) accumulation, preservation (Schulte et al., 2000) and burial as well as benthic solute fluxes (Berner, 1982; Walsh, 1991; Hedges and Keil, 1995; Woulds and Cowie, 2009). Assessment of organic carbon ($C_{org}$) and nitrogen fluxes in marine sediments are essential for balancing the global carbon budget and quantification of $C_{org}$ burial and nitrogen removal mechanisms. Arabian Sea OMZ sediment is found to be associated with OM rich deposits in the geological records. It is associated with different groups of benthic communities and degrees of bioturbation in terms of OM preservation majorly due to difference in oxygen availability (Cowie, 2005; Cowie et al., 2009; Hunter et al., 2011, 2012). Sedimentary OM derived from various plankton species is the major reservoir of $C_{org}$ in the global carbon cycle. Only 1% of the originally produced OM is estimated to be transferred to the deep biosphere (Middelburg and Meysman, 2007).

Sedimentary pigments can provide historical information on the overall primary production in the overlying surface waters as well as the dominant classes of phytoplankton. It was used as paleo-tracers for algal and bacterial communities (Sanger, 1988; Leavitt and Brown, 1988; Leavitt, 1993; Bianchi et al., 2000; Leavitt and Hodgson, 2001) and as an indicator for the state of decay of OM in sediments (Woulds and Cowie, 2009). Moreover, sedimentary pigment biomarkers reflect long term bloom record in estuarine systems with anoxic, laminated sediments (Bianchi et al., 2002). The comparative lability and source specificity makes them a powerful tool used to investigate many aspects of benthic biogeochemical processes as well as OM source and history (Jeffrey and Vesk, 1997; Boon and Duineveld, 1998). The chlorophyll $a$ profiles could be useful for an estimation of total flux of OM and it can provide an insight into the knowledge of degree of bioturbation in the sediments (Boon and Duineveld, 1998). Specific chlorophyll degradation products, such as the pheopigments and esters have been used as markers for grazing activity of zooplankton through the water column (Chen et al., 2003). The pheopigment/Chl $a$ ratio was used as an index of Chl $a$ decay (Bianchi et al., 2002) and Chl $a$/Pheophytin $a$ ratio could be an indicator of preservation conditions (Reuss et al., 2010). In general, carotenoids in sediments can be diagnostic of phytoplankton OM source (Jeffrey and Vesk, 1997). The redox condition can enhance the preservation of labile pigments in sediments and could be useful for their historical reconstruction.

North Eastern Arabian Sea (NEAS) is characterized by an extremely stable OMZ between 200 and 1200m water depths with dissolved oxygen values reach up to 0-0.5 ml/l and a strong, seasonal and monsoon controlled variability of primary productivity (Schulte et al., 1999; Naqvi et al., 2003). An intense OMZ in the NEAS is associated with laminated and less bioturbated sediments that are
ideally suited for the paleoceanographic reconstruction with fine resolution. It showed strong relationship with oxygen concentration and distribution of organisms, though biological responses to the OMZ varied with the type of organisms (US JGOFS study). Sedimentary pigment concentration in the Arabian Sea were positively correlated with both abundance and biomass of metazoan macrofauna within the OMZ and negatively correlated with species richness and evenness below the OMZ (Cowie, 2005). Benthic communities within the Arabian Sea OMZ mainly composed of surface-feeding polychaetes and crustacea (Levin et al., 2000). In addition, OMZ in the Arabian Sea is one of the three major denitrification sites in the world Ocean with an estimated annual rate of 10-30 Tg N y⁻¹ (Naqvi et al., 1992). Its contribution to total oceanic pelagic denitrification (80-150 Tg N y⁻¹) is substantial and globally significant (Codispoti et al., 2001). Sedimentary denitrification over the Indian continental shelf has yielded rates of 0.4-3.5 Tg N y⁻¹, which are of same order as reported from other areas (Naik., 2002). Geological records reveal the human-induced perturbations of oxygen and carbon budgets which had potential impacts on the biological diversity and chemical fluxes of the Arabian Sea OMZ (Altabet et al., 2002). High primary production and sediment accumulation rates on the Arabian Sea’s margin produce exceptional records of past changes in climatic and oceanographic conditions (Ivanochko, 2004).

Two previous reports on sedimentary pigments from the Arabian Sea were from Oman (Shankle et al., 2002) and Pakistan margin (Woulds and Cowie, 2009) OMZs whereas studies from the Indian margin are not yet been reported. Water depth and bottom DO controlled the chlorin concentration in Oman margin sediments with highly degraded pigment suites, whereas bottom DO and faunal influence played a crucial role in preservation of pigments (less degraded) at Pakistan margin OMZ. We were looking for any similarity or behavioral changes of phytoplankton pigments assemblage in Indian margin compared to other OMZ margins of the Arabian Sea. We have analyzed three short sediment cores from varying water depths (500, 800 and 1100m) within the OMZ of the north eastern Arabian Sea (NEAS). The objectives of the study include 1) the comparison of phytoplankton pigments assemblage and their degree of degradation in three different sediment cores from varying bottom water oxygen concentrations and 2) the study of the source and preservation of organic matter using the bulk productivity signals C_\text{org} and CaCO_3 variation within the OMZ.

2-Materials and Methods:

2.1-sampling

Short sediment cores were collected from three water depths within the oxygen minimum zone (OMZ) of the NEAS during the cruise onboard YOKOSUKA (October, 2008). The locations of the
cores are shown in figure 1 and the bottom water oxygen concentrations in table 1. The core locations were selected based on the intensity of OMZ, as the 500m site experiences severe oxygen deficiency compared to 800m, whereas the 1100m site can be considered outside the intense OMZ. One core from each depth was selected for the analysis. The sediment cores were sectioned at 1 cm interval in dark condition and stored at −20°C until the analysis. Precautions were taken to minimize the degradation of pigments by light and temperature.

2.2-Phytoplankton pigment analysis:

For phytoplankton pigment analyses, ~1g freeze dried and homogenized samples were extracted with 3ml 100% acetone in a glass centrifuge tube covered with aluminium foil. After sonication for 5 minutes in water bath containing ice, the extracts were kept at −20°C over night. The extracts were centrifuged (5 minutes, 3000 rpm, T< 5°C) and filtered using 0.2 μm PTFE syringe filters (Whatmann) and collected in amber coloured vials and kept at −20°C in dark condition. The extract was concentrated near to dryness using nitrogen stream and made up to 500μl with methanol just before HPLC analysis. Sample was analyzed using HPLC (Agilent Technologies) equipped with C-18 column (Supelco, 15cm×4.6mm, 3μm). Elution at a rate of 1.5ml/min was performed using a linear gradient program of 43 minutes as follows: initially, 100% solvent A (80/20, methanol/0.05M ammonium acetate) and switch over to 100% B (80/20, methanol/acetone) within 20 minutes. An isocratic hold of 20 minutes with solvent B for elution of all the major pigments then change to 100% A for 3 minutes. The injection volume was 50 μl. Pigments were detected using diode array detector (DAD) with a scanning range between 300 and 800nm. Absorption chromatograms were extracted for the wavelengths 450nm for quantification of carotenoids and 665nm for quantification of chlorophyll a and pheopigments. Pheophorbides were presented as total pheophorbide. The external standard calibration was done using pigment standards purchased from DHI, Denmark. All the chemicals used were HPLC grade from Merck, Germany.

2.3-CaCO3, carbon and nitrogen content and their isotopic analysis:

The inorganic carbon (CaCO3) was analyzed using Coulometer (UIC Inc. Model 5014) attached with an acidification module following Bhushan et al. (2001). The analytical grade CaCO3 was used as reference standard. Accuracy and precision achieved were within the range of ±2%. The δ13C and δ15N along with organic carbon (Corg) and nitrogen (N) content were measured using Isotopic Ratio Mass Spectrometer (Delta V Plus, Thermo) coupled with an Elemental Analyzer (EA-EUROVECTOR) in a continuous flow mode. Approximately 3mg of decalcified, dried sediment samples were flash combusted in EA at 1050°C. Evolved CO2 and NOx were passed through a
reduction column containing copper at 670°C, and were finally purified and separated with Gas Chromatograph at 50°C before being introduced into the mass spectrometer. Calibration was done using laboratory standard (n-Caprioic acid, C6H15NO2) as explained in Agnihotri et al. (2008). Analytical precision of <2% was achieved using international and in-house lab standards throughout the analysis.

3- Results

3.1-Sedimentary pigments

We have quantified nine pigments including chlorophyll a and its degradation products, pheophytin and pheophorbide. Though we found different allomers of pheophorbide, it was difficult to identify as particular degraded product such as pyropheophorbide a due to lack of standard and LCMS, hence represented as total pheophorbide. Astaxanthin was the major carotenoid followed by canthaxanthin and zeaxanthin. A representative chromatogram from the 500m site is shown in Fig. 2. Chlorophyll b was below detection limit for the top 10cm interval, while its concentration was ~1.5µg/g at 11cm in the core from 500m depth, but it was absent at 800m site. Similarly, β-carotene was absent in the core from 1100m site. Most of the pigments followed similar downcore variation having higher concentration at the surface (Fig. 3). The core from 500m water depth showed the highest concentration of total pigments (TP) with maximum of 16.4 µg/g (Avg: 6.8±1.9µg/g, n=19), followed by the 800m; 2.8 µg/g (1.8±0.6µg/g, n=18), and 1100m; 2.1 µg/g (1.2±0.3µg/g, n=13) sites respectively. The total carotenoids (TC) also showed similar trend with maximum 9.3 µg/g (Avg: 3.9±1.9µg/g, n=19) for the core from 500m followed by 2.1 µg/g (1.3±0.4 µg/g, n=18) and 0.7 µg/g (0.6±0.1 µg/g, n=13) for the 800 and 1100m sites respectively. The relative concentration of each pigment to total pigments showed that astaxanthin was the major contributor of refractory pigments among all the three cores (21±3.5, 27±4.3, and 21±3.2% respectively for 500, 800 and 1100 m sites). Chlorophyll a contribution was <1% for the core from 800m site, whereas other two cores showed ~25% contribution. We have reported chlorophyll a as total chlorophyll including the alteration products.

Total chlorins (chlorophyll a + pheopigments) concentration was high in the core from 500m site (Avg: 2.8±1.5 µg/g), followed by the cores from 1100m (0.64±0.26 µg/g) and 800m (0.53±0.2 µg/g) sites. The Chl a concentration did not show much downcore variation for 500m (Avg: 1.5±0.8µg/g) and 1100m (0.3±0.07µg/g) while nearly zero concentration was observed at 800m site (Fig. 5). The high concentration of pheopigments in sediments reflected the loss of parent Chl a molecule to the decay products. Pheophorbide (reported as total pheophorbide) also showed downcore variation with
higher values at the surface for 500 and 1100m sites, whereas the core from 800m site showed higher values at mid depths. Pheophytin/Pheophorbide ratio was <1 for all the cores except two deeper samples of 1100m site. The increasing downcore ratios were observed for both the 800 (0.4±0.2) and 1100m (0.5±0.3) sites, whereas nearly constant and low values were seen at 500m (0.2±0.1) site (Fig. 6a). The Pheopigments/Chl a ratio, an indicator of state of decay of sedimentary OM, showed similar (range: 0-5) downcore variation for 500 and 1100m sites (except at the surface and bottom depths of 500m site), but high values (range: 0-26) for the 800m site (Fig. 6b). TP showed excellent correlation with all accessory pigments (r>0.9) at both 500 and 800m sites except poor correlation with chlorophyll b at 500m. Whereas at 1100m site, only astaxanthin (r=0.9) and zeaxanthin (r=0.5) showed significant correlation with TP, while poor correlation with alloxanthin and canthaxanthin and significant negative correlation with Chl b (r=-0.6) was observed.

3.2-Carbon, nitrogen contents and their isotopic signatures

The downcore profiles of C\textsubscript{org} at 500m site showed a clear distinction between other two cores (Fig. 7). The highest values were observed at 500m site having the range ~7.8- 9% (Avg: 8.7%, SD: ±0.4) while other two cores showed nearly similar range with ~3.5- 5.3% (Avg: 4.5%, SD: ±0.7) and ~4-4.9% (Avg: 4.7%, SD: ±0.3) for 800 and 1100m sites respectively. All the three cores showed an overall down core decreasing trend, nevertheless significant variation was observed for 800m site (t-test, P<0.05). Nearly similar C\textsubscript{org} values were observed for both 800m and 1100m sites though bottom DO is significantly different. At 500m site, C\textsubscript{org} is inversely correlated with nitrogen (r=>-0.5) but didn’t show any significant correlation with C/N, CaCO\textsubscript{3}, δ\textsuperscript{13}C and δ\textsuperscript{15}N. Whereas, C\textsubscript{org} showed significant inverse relation with C/N, CaCO\textsubscript{3}, δ\textsuperscript{13}C and δ\textsuperscript{15}N (r=>-0.5) for the 800m site. For 1100m, C\textsubscript{org} showed positive correlation with nitrogen (r=0.9) and inverse correlation with CaCO\textsubscript{3} and δ\textsuperscript{15}N (r=>-0.6). The downcore profiles of N followed the same pattern of C\textsubscript{org}, with higher values for the core from 500m site (Avg: 1%, SD: ±0.06) followed by similar values for 800m (0.5%, SD: ±0.09) and 1100m (0.6%, SD: ±0.04) sites with significant downcore variation (t-test, P<0.05; Fig. 7). Nitrogen showed significant inverse correlation with C/N, CaCO\textsubscript{3}, δ\textsuperscript{13}C and δ\textsuperscript{15}N for 800m (r=>-0.5), 500m and 1100m (r= >-0.6) sites respectively. C/N values showed increasing downcore trend for all the three cores with lowest value at the surface but the variation was not much significant (t-test, P>0.05) (Fig. 7).

δ\textsuperscript{13}C values varied in a narrow range for all the three cores with downcore increasing trend (Fig. 8). The highest range of variation (t-test, p<0.05 for each cores) was observed at the 500m site (Avg: -20.7±0.3‰, n=19), followed by 800m (-20.4±0.1‰, n=18) and 1100m sites (-20.3±0.1‰, n=13). Similar values (-20±2‰) were reported for marine organic matter by Cowie et al. (2009) in the
Pakistan margin sediments. The $\delta^{15}$N values showed an increasing downcore variation till ~10-12 cm but not much significant (t-test, $p>0.05$), followed by decrease in values towards the bottom of the core (Fig. 8). The N isotopic values showed an average of 7±0.4‰; 6.8±0.2‰ and 7±0.3‰ at 500m, 800m and 1100m sites respectively. The downcore profiles of CaCO$_3$ showed clear distinction (t-test, $p<0.05$ for each cores) among the three cores (Fig. 8) with an increasing down core profile. The highest percentage was observed at 800m (~55-65%, Avg: 60±3%, $n=18$) followed by 1100m (~45-53%, Avg: 50±3%, $n=13$) and 500m (~35-45%, Avg: 41±2%, $n=20$) sites respectively. The CaCO$_3$ values were lower for the core at 500m site with maximum values at the middle and bottom of the core. Other two cores showed gradual increasing trend towards the bottom of the core.

4 Discussion

4.1-Sedimentary pigments in the oxygen minimum zone

Here we presented the sedimentary pigment data from the oxygen minimum zone of the North Eastern Arabian Sea. Comparatively high pigment concentrations were measured at the core from 500m water depth (very low bottom water DO) followed by 800m and 1100m, suggesting that bottom water oxygen played a great role in preservation of sedimentary pigments. The absence of $\beta$-carotene at 1100m site may be due to its degradation through a sequence of transformation reactions possibly initiated by epoxidation as described by Repeta and Gagosian (1984) from the Peru margin sediments. The decreasing downcore concentration in most of the carotenoids suggests degradation in sediments depending on their individual stabilities (Kusunoki et al., 2012). Astaxanthin and canthaxanthin were the major pigments found in all the cores with varied concentrations and their presence were mainly due to zooplankton, microcrustacean in marine OMZ sediments (Repeta, 1989, Repeta and Simpson, 1991, Burford et al., 1994), however both have similar origin also from green algae as a minor pigment (Jeffrey and Vesk, 1997). Quiblier-Lloberas et al. (1996) reported that canthaxanthin was associated only with zooplankton and totally absent in phytoplankton, whereas it was also used as a marker pigment for colonial and filamentous cyanobacteria (Leavitt and Hodgson, 2001; Kusunoki et al., 2012) with a photoprotective role (Grant and Louda., 2010). Additionally, astaxanthin produced bacterium was isolated from coastal marine sediments of Japan by Matsumoto et al. (2011) and canthaxanthin along with other carotenoids were isolated earlier from gram positive bacteria Micrococcus roseus (Ungers and Cooney, 1968). Though alloxanthin is reported as the principal carotenoid of cryptomonads, their presence in the OMZ sediments needs to be further understood (Repeta and Gogosian, 1987 and references therein). Astaxathin, canthaxanthin and alloxanthin were not degraded through furanoxide intermediate in the OMZ sediments, may be due to their structural stability and selective preservation as observed in the Peru margin (Repeta, 1990).
Variation in zooplankton influx and faunal influences might have led to the downcore variation within and between the cores. This suggests that zooplankton marker pigments were highly preserved in the Arabian Sea OMZ, whereas phytoplankton markers were degraded as also seen in the Peru margin sediments (Repeta, 1990). A combination of diagenesis and depositional changes might have led to their degradation.

Our observation in the sedimentary environment is supported by the water column studies in the EAS (e.g., Goericke et al., 2000; Roy et al., 2015). Matondkar et al. (2006) reported high seasonality and diversity of cyanobacterial species in the EAS (Indian margin) with zeaxanthin and carotene as the major pigments in this region. EAS created an ideal condition for the growth of *Trichodesmium* during NEM and SIM (Naqvi et al., 2003) leading to the preservation of cyanobacterial pigments associated with faunal influence (Levin et al., 2013) in the sediments from this region. A recent study by Ahmed et al. (2016) showed diatoms and dinoflagellates are abundant in the southern region of the Arabian Sea whereas nano- and pico-plankton are dominated in the northern region. It is known that the marker pigments of diatoms and dinoflagellates such as fucoxanthin, diadinoxanthin, peridinin etc. are much more labile and therefore very unstable and rarely preserved especially in oxic sediments (Repeta and Gagosian, 1987; Repeta, 1989; 1990; Bianchi and Findlay, 1991). The concentrations of these phytoplankton pigments were below detection limit in these cores from the NEAS. Though diatoxanthin, a marker pigment of diatoms was present in Peru (Repeta and Gagosian, 1987) and Pakistan margin (Woulds and Cowie, 2009) sediments, its concentration was below detection limit in the present study. However, zeaxanthin was present in all the three cores related to the abundant cyanobacteria in the NEAS (Ahmed et al., 2016) and also due to its selective preservation and molecular stability as explained by Repeta (1990) from the Peru margin.

Benthic study in this area revealed that the highest faunal density and biomass were found at 800m site and both decreased between 800m and 1100m water depths (Hunter et al., 2012). Cirratulids and Oweniids were the two dominant polychaete families between 800 and 1100m sites (Hunter et al., 2012). In addition, the peak in abundance of epi-benthic megafauna (majorly ophiuroids and decapods) was observed at 800m site and lower at higher depths (Hunter et al., 2011). The fishes were the only taxa present at the 500m site and megafauna acted as a control upon the OM availability in this OMZ sediment (Hunter et al., 2011). Our studies clearly showed higher concentration of pigments at 500m site (OMZ core) having no faunal activity, whereas 800m site was associated with highly degraded and less concentration of pigments. Hence it is evident that the faunal activity will adversely affect the pigment preservation.
The comparatively lower total chlorin concentration at 800m site may be due to digestion by fauna (Levin et al., 2013; Hunter et al., 2011; 2012). As mentioned earlier, we could not identify the presence of pyropheophorbide \(a\) due to lack of standard and LC-MS. However, we presume its presence in these OMZ sediments as it is a degradation product of Chl \(a\) and predominantly formed by grazing processes in the water column and sediments (Bianchi et al., 1998; Louda et al., 1998; Szymczak-Żyla et al., 2008). The low concentration of total pheophorbide in 800m and 1100m sites may be due to chlorophyll destruction occurs at an early stage of feeding without pheophorbide as intermediate (Head and Harris, 1996). The downcore decrease of pheophorbide may be due to its further destruction through enzymatic activity as proposed by Louda et al., (1998). Earlier studies showed that pheophorbide \(a\) is produced primarily by metazoan grazing activities and their high concentration in sediments suggest that diatoms were actively grazed by heterotrophs in the water column (Bianchi and Findlay, 1991; Bianchi et al., 2002). The Pheopigments/Chl \(a\) ratio at the 800m site is very high at the top 3cm (range: 17-26) indicating that the material reaching the bottom are highly processed and degree of degradation is highly influenced by faunal activity at this site. The downcore profile of pheophytin/pheophorbide ratio also showed an increasing trend for 800 and 1100m sites indicating the degree of degradation by faunal activity, whereas no considerable downcore variation was observed at 500m site. The pheophytin concentration was nearly constant in all the three cores (<0.5 \(\mu\)g/g) (Fig. 4), may be due to less sensitivity of pheophytin towards bottom DO as evident from a good correlation \((r=0.6)\) with TP (Ming-Yi et al., 1993; Woulds and Cowie, 2009).

Total pigment and refractory pigments showed significant negative correlation with water depth \((r=-0.9)\) and bottom DO concentration \((r=-0.7)\). Asthaxanthin found to be more resistant to degradation and Chl \(b\) was the least as seen from the Pearson’s correlation of TP versus accessory pigments. This may indicate that the preservation and stability among individual pigments strongly depends on the bottom water oxygen availability as well as faunal activity at the OMZ. C
\(_{org}\) is moderately correlated with total pigments \((r=-0.3)\) for both 500 and 1100m sites, whereas poor negative correlation at 800m site indicating poor control of sedimentary pigment distribution by organic matter content, as seen in Pakistan margin sediments (Woulds and Cowie, 2009). Also the poor correlation of nitrogen content with TP at 800m site may indicate that digestion by fauna has considerable role on the removal of nitrogen from sediments. The high pigment concentrations were associated with low bottom DO levels and pigments concentration decreased with increasing water depth. A similar relation with DO was observed earlier in Pakistan (Woulds and Cowie, 2009) and Oman margin (Shankle et al., 2002) sediments. This is supported by the previous studies that low
oxygen concentrations and minimal benthic animal community may enhance the compositional freshness and preservation of sedimentary pigments as seen at the 500m site, the core of the OMZ (Leavitt, 1993; Ming-Yi et al., 1993; King, 1995; Bianchi et al., 2000; Woulds and Cowie, 2009). Hence, the bottom water DO and the presence of fauna played a major role in preservation of sedimentary pigments in the Indian margin sediments.

4.2-Carbon, nitrogen contents and their isotopic signatures

All the three cores showed an overall down core decreasing trend for $C_{\text{org}}$ and nitrogen. Nearly similar values were observed for both 800m and 1100m sites though bottom DO values were significantly different, may be due to differing degree of alteration of OM within the water column or the benthic boundary layer (Jeffrey et al., 2009). A recent report by Cowie et al. (2014) at this site revealed that % silt+clay dominate (50-95%) the sediment and considerable variation of sediment grain size was observed along this transect. That is grain size was generally finer (<61 µm median) from depths below ~400m along the slope which gradually decreased and reached up to 9-14µm median at ~2000m (Cowie et al., 2014). The high value of $C_{\text{org}}$ at 500m site may be related to high surface productivity and also better preservation under core OMZ conditions. Qasim (1982) reported Arabian Sea as one of the zones of highest seasonal productivity in the world. Also changes in macrofaunal assemblage structure influence seafloor OM cycling and faunal activity at this site which have an important control upon C, N cycling in low oxygen sediments (Hunter et al., 2012). The $^{13}$C/$^{15}$N labelled phytodetritus consumption experiment by Levin et al. (2013) showed that capitellid polychaetes and cumaceans were among the major consumers. So benthic communities and the effect of feeding, bioturbation and irrigation by fauna may have an important control on benthic C-cycling and burial in the EAS (Indian margin) OMZ sediments (Jayaraj et al., 2007; Cowie et al., 2009; Ingole et al., 2010, Hunter et al., 2012).

Paropkari et al. (1993) pointed out that the high values of organic carbon in the Arabian Sea sediments depends not only on the productivity but sedimentation rates and the low oxygen concentration are equally important. Previous study by Shetye et al. (2009) reported a maximum of 4.7% $C_{\text{org}}$ (Avg. 3.1%) in a sediment core from the Eastern Arabian Sea (803m water depth) and concluded that $C_{\text{org}}$ distribution is influenced by either productivity or preservation or both rather than surface water productivity alone. The nearly similar $C_{\text{org}}$ at the 800 and 1100m sites associated with high difference in bottom DO may conclude that production of organic matter in the surface water is more likely in determining the concentration of $C_{\text{org}}$ in these sediments. The considerable inverse relation found between the bottom water oxygen concentration and organic matter preservation revealed high preservation trend of organic matter at lower oxygen conditions. This
result is in concurrence with Lehmann et al. (2002) that oxygenation conditions have a direct effect on the preservation of OM with enhanced preservation under anoxic conditions. So it is possible that the faunal influence at 800m site may decrease their actual C_{org} concentration and hence effect of fauna and water depth may have a control on OM preservation at Indian margin sediments. This conclusion is in agreement with Hartnett et al. (1998), who stated that “the heart of the preservation controversy of OM in sediments lies in the fact that no single factor seems to control preservation under all conditions”.

The comparative heavier values of δ^{13}C at the 800 and 1100m sites were associated with the lower C_{org} and higher bottom DO concentrations. Similarly, more depleted values were observed at the 500m site, where the highest C_{org} and lowest bottom DO values were observed. This variation trend could be associated with differing degrees of OM degradation states. But occurrence of low values within the OMZ core without having much difference in C/N values, may suggest a chemosynthetic bacterial imprint on C_{org} isotopic composition as reported in Pakistan margin (Cowie et al., 2009). Additionally, similar values of organic matter were derived from phytoplankton by both photosynthetic process and by subsequent diagenetic alteration (Cowie et al., 2009).

The δ^{15}N values in these cores were within the range of typical upwelling margins at OMZs and may be attributed to the pelagic nitrate pool caused by denitrification within the OMZ (Altabet et al., 1995; 2002; Ganeshram, 1996; Ganeshram et al., 2000). The downcore variation of δ^{15}N is comparatively higher for OMZ core and minimum at 800m site where highly degraded pigment suite was reported. This observation is in well accordence with Sachs and Repeta (1999) that the N-isotopic alteration during OM degradation is minimal under anoxic conditions and the severity of the ^{15}N-enrichment during OM decay is proportional to the bottom water oxygen conditions. And the comparatively higher δ^{15}N values at the EAS OMZs may be due to the result of differential nutrient utilization and reflection of sluggish eastern boundary circulation (Ivanochko, 2004). Also the progressive decrease of oxygen from west to east suggests that more intense denitrification is occurring on the eastern margin, which is actually resulting in the comparative record of heavier δ^{15}N values (Naqvi, 1991; Naqvi et al., 1998; Schulte et al., 1999). The C/N values of all the three cores were in the range of 7.9-9.1 showing the dominant origin of organic matter from marine inputs. Most of the studies from the eastern Arabian Sea revealed that majority of organic matter in the sediment has marine origin (C/N ~8±2) (Bhushan et al., 2001; Agnihotri et al., 2008; Cowie et al., 2009; Kurian et al., 2013) except signals from the coastal heavy monsoonal precipitation/ run-off along the west coast of India.
CaCO$_3$ content varied from 35 to 65% in the present study. The high values of CaCO$_3$ may be due to the past surface water productivity as suggested by Shetye et al. (2009) in the EAS sediments. This conclusion is well accordance with the sediment trap study in the Arabian Sea by Nair et al. (1989), who reported that carbonate was the main component in the total flux (~65%) and suggested that productivity is the main factor which controls CaCO$_3$ fluctuations in the Arabian Sea. In addition, earlier study by Naidu (1991) concluded that calcium carbonate fluctuations in the Arabian Sea during glacial and interglacial periods are mainly controlled by the productivity variations due to intensities of SW and NE monsoons and their associated oceanic circulations. Strong negative correlation was observed for CaCO$_3$ vs. TP at 500 ($r=-0.6$) and 1100m ($r=-0.9$) sites, whereas these were not correlated at 800m site, suggesting a considerable role of CaCO$_3$ in degradation and preservation of pigments at Indian margin OMZ. Strong correlation was observed for C$_{org}$ vs. CaCO$_3$ at 800m ($r=-0.9$) and 1100m ($r=-0.6$) sites but these were poorly correlated at 500m site, suggests that faunal influence and their activity has great control on CaCO$_3$ variation in this OMZ.

4.3-Comparison of pigment data of Eastern Arabian Sea (Indian margin) with Pakistan and Oman margin sediments

The total pigment concentrations in the present study (EAS-Indian margin) were comparatively less than Pakistan margin sediments, but intact pigment quality was comparable. Qualitatively nine pigments were observed at the OMZ of Indian margin while nearly similar diversity of accessory pigments were reported at Pakistan margin (Woulds and Cowie., 2009), but only Chlorins degradation was studied at Oman margin sediments (Shankle et al., 2002). Total chlorins (chlorophyll $a$ + pheopigments) concentrations were lower at Indian margin sediments compared to Oman and Pakistan margins. This may be due to less plankton productivity being recorded in the EAS. Chlorins degradation at Indian margin is mainly controlled by bottom DO concentration and faunal activity similar to Pakistan margin sediments, but in Oman margin it was mainly controlled by grazing activity in the water column and sediment mixing by macrofauna (Shankle et al., 2002). The bottom water dissolved oxygen played a vital role over the OM preservation at Indian margin sediments as seen in Pakistan margin (Woulds and Cowie, 2009), whereas water depth has secondary importance at Indian margin OMZ. A strong inverse relation was observed between sedimentary pigments and water depth at Indian and Oman margins (where water depth were used as a proxy for chlorins fluxes to the sediments) however, it was absent in Pakistan margin sediments. The low bottom DO and minimal faunal activity resulted the comparative freshness and greater preservation of sedimentary pigments at both Indian and Pakistan margins compared to Oman margin sediments.
5-Conclusion

A predominance of the putative microcrustacean zooplankton marker pigments astaxanthin and canthaxanthin and the influence of faunal activity was concluded from sedimentary pigment and carbonate analyses at the Indian margin OMZ. The degradation patterns of sedimentary pigments are either controlled by bottom water DO and faunal activity. Preservation of sedimentary pigments and OM is greatly controlled by bottom water DO, sediment grain size and effect of fauna (mainly by macrofauna) at the Indian margin OMZ sediments. The poor correlation between TP and C_{org} conclude that C_{org} did not have considerable control over sedimentary pigment preservation at Indian margin OMZ. Qualitatively, sediments from present study (EAS) showed fresh and labile OM as observed previously for the Pakistan margin sediments. The C/N and δ^{13}C values concluded the marine origin of organic matter. The δ^{15}N values revealed good signals of upwelling associated denitrification in the water column and/or sediment. A strong inverse relation between CaCO_3 and sedimentary pigments suggest a considerable role of foraminifera in the heterotrophic decrease of pigment preservation.

6-Acknowledgment

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References


**Figure 1**: Study site showing core locations in the North Eastern Arabian Sea (NEAS).
Figure 2: A representative chromatogram for the surface sample of 500m core (at 450nm and 665nm).
Figure 3: Downcore profiles of sedimentary pigments in the cores from 500, 800 and 1100m water depths.

Figure 4: Downcore profiles of Total Pigments (TP) and Total Carotenoids (TC) in three cores.
Figure 5: Downcore profiles of Chlorophyll $a$ and Pheopigments of the cores from 500m, 800m and 1100m sites

Figure 6: a) Downcore profile of Pheophytin/Pheophorbide ratios and b) Pheopigments /Chl $a$ ratios of three cores
Figure 7: Downcore profiles of $C_{org}$ %, N% and C/N ratios in three cores

Figure 8: Downcore profiles of CaCO$_3$%, $\delta^{13}C$ ‰ and $\delta^{15}N$ ‰ in three cores
**Table 1:** Details of the sediment cores and respective bottom water dissolved oxygen (DO) at the sampling sites

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<th>Sr. No</th>
<th>Latitude (°N)</th>
<th>Longitude (°E)</th>
<th>Water depth (m)</th>
<th>Sediment core length (cm)</th>
<th>Bottom water DO (μM)</th>
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