

## **Controls on organic matter distribution in oxygen minimum zone sediments from the continental slope off western India**

**Siby Kurian\*<sup>§</sup>, Pratima M. Kessarkar\*, V. Purnachandra Rao\*\*<sup>\*</sup>, K. Reshma\*, Amit Sarkar\*, J.N. Pattan\* and S.W.A Naqvi\***

\*CSIR-National Institute of Oceanography, Dona Paula-403 004, Goa, India

\*\*Department of Civil Engineering, Vignana's University, Vadlamudi-522213, A.P., India

<sup>§</sup>Corresponding author: Siby Kurian; E-mail address: siby@nio.org

### **Abstract**

The causes of organic-rich sediments in contact with the perennial oxygen minimum zone (OMZ) on the continental slope off western India have been debated extensively, largely in relation to two main controlling factors: high productivity in the water column and enhanced preservation due to oxygen deficiency in bottom waters. In order to better understand the causes for organic-richness in sediments, three sediment cores recovered from the upper OMZ (UOMZ) at 500 m, middle OMZ (MOMZ) at 812 m and lower OMZ (LOMZ) at 1168 m water depths from the continental slope off Ratnagiri (west coast of India) were investigated for their organic matter (OM) and their stable isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ), geochemical and rock magnetic parameters. The bottom water dissolved oxygen (DO) concentrations were 0.4  $\mu\text{M}$ , 5.8  $\mu\text{M}$  and 25  $\mu\text{M}$  at UOMZ, MOMZ and LOMZ core locations respectively. Maximum age of the sediments recorded in these cores was 4500 yrs BP. Sedimentation rates in the upper sections of the UOMZ and MOMZ cores were lower (5 to 7 cm/kyr) than that in the LOMZ core (20 cm/kyr). Organic carbon ( $C_{\text{org}}$ ) content was highest (upto 7.9 %) in the UOMZ core than in other cores (upto 4.9 %). Enriched  $\delta^{13}\text{C}_{\text{org}}$  values (-18.6 to -16.8 ‰) in the MOMZ core were indicative of reworked organic matter in the lower section. The  $\delta^{15}\text{N}$  values ranged from 4 to 7.4 ‰, however, with lower values for the reworked sediments at MOMZ site. The parameters representing productivity and redox conditions increased towards core top in all the cores, whereas terrigenous parameters decreased towards core top in the MOMZ and LOMZ cores. Despite the MOMZ core was always in OMZ in the lower section, very low  $C_{\text{org}}$  content coinciding with high terrigenous and reworked OM were deposited in the sediments prior to 1700 years BP. Rock magnetic properties indicate that the degree of diagenetic conditions varied in different sections of the cores and also among the cores within OMZ. Authigenic magnetite and authigenic uranium occurred in the lower sections of UOMZ and LOMZ cores and, authigenic magnetite in the upper sections of MOMZ core. These results suggest that productivity played an important role in organic-richness of the sediments and bottom water oxygen concentration has little effect on the preservation of OM. Besides, sedimentation rates, reworked organic matter, and topography at the core site indeed contribute on the distribution of organic matter in the Late Holocene sediments.

**Keywords:** organic matter, OMZ, productivity, diagenesis, continental slope, western India.

## 1. Introduction

The oxygen minimum zone in the Arabian Sea is one of the three OMZ regions in the World Ocean contributing one third to the global water column denitrification (Naqvi 1987). OMZ impinges on the western continental margin of India at water depths between 150 m and 1200 m, with DO concentrations reaching to near zero close to the sediment-water interface. Though upwelling induced productivity is higher in the western Arabian Sea the eastward location of the OMZ still needs to be fully understood. The south west coast of India experiences moderate upwelling during the southwest monsoon (SWM) which is also remotely forced by local winds. The upwelling of nutrient-rich, sub-surface waters ensure high surface biological productivity in the euphotic zone and high rain of organic matter to the bottom sediments (Naqvi et al., 2006). In addition, the central and south west coast of India receives heavy precipitation (~300 cm/yr) during the SWM resulting in inflow of the freshwater and terrigenous material into the Arabian Sea. On the other hand, the northeast monsoon (NEM) with high biological productivity is active on the northeastern Arabian Sea, especially off Pakistan and Gujarat (Madhupratap et al., 1996). The sediment trap studies carried out extensively in the Arabian Sea indicated large export fluxes of organic matter from the euphotic zone, despite seasonal and spatial variations, reflecting water column productivity (Nair et al., 1989; Haake et al., 1993; Rixen et al., 1996). Organic-rich sediments deposited under the perennial OMZ within the Arabian Sea have been investigated extensively (Cowie et al., 2014 and references therein) for the past few decades to understand the factors controlling organic carbon enrichment.

While several investigators reported low oxygen concentrations in bottom waters to be the most significant factor for organic-richness in the sediments (Demaison and Moore, 1980; Bralower and Thierstein, 1987; Paropkari et al., 1992; van der Weijden et al., 1999), others have attributed this to the high organic matter fluxes to the seabed (Calvert, 1987; Pedersen and Calvert, 1990; Pedersen et al., 1992). Calvert et al. (1995) reported that  $C_{org}$  maximum (proxy for the OM) on the continental slope of the eastern Arabian Sea extends over a large depth range than the OMZ and there is no evidence for preferential preservation of OM within the OMZ, suggesting no direct relation between  $C_{org}$  maximum and oxygen minimum zone. Other factors that could influence  $C_{org}$  enrichment include bio-turbation, water depth, variations in supply, sedimentation rates, cross-shelf transport, quality of organic matter, dilution by other sedimentary components and hydrodynamic conditions (Shimmiel et al., 1990; Pedersen et al., 1992; Calvert et al., 1995; Thamban et al., 1997; Rao and Veerayya, 2000; Cowie, 2005; Kessarkar and Rao, 2007 and references therein). Ingole et al. (2010) and Hunter et al. (2012) emphasized bio-turbation, especially by macrofaunal assemblages to greatly influence the organic matter cycling in low oxygen sediments thus playing a crucial role in OM distribution. Further,

Cowie et al. (2014) have indicated the role of grain size and hydrodynamic conditions in the preservation of organic matter in OMZ sediments of the eastern Arabian Sea. The organic-richness within the OMZ sediments from other continental margins (e.g. the Oman and Pakistan) has also been reported. For example, Pedersen et al. (1992) suggested that the bottom water oxygen concentration has little effect in governing either the distribution or the degree of preservation of organic matter in the Oman margin. Cowie et al. (2009) studied sediments from the Pakistan margin and reported high OM content in the upper slope and suggested that the %C<sub>org</sub> maxima and minima across the OMZ were not simply related to the trends in DO concentration. Therefore, the bottom water DO concentration alone does not seem to be the controlling factor for the preservation of OM in the sediments across the Indian, Oman and Pakistan margins.

In the present study, we have investigated three short sediment cores, in close proximity to each other, recovered from the OMZ of the continental slope off Ratnagiri, for their sedimentological, geochemical and stable isotope parameters to better understand the controls on organic matter distribution during the late Holocene. Here we explore whether downcore records in these cores with varying bottom water DO concentrations can reveal new insights on the factors controlling OM preservation and diagenetic conditions at the core site in sediments deposited for the past 4000 years.

## 2. Materials and methods

Three sediment cores were recovered within the OMZ of the north eastern Arabian Sea during the cruise onboard *RV Yokosuka*, using the manned submersible 'Shinkai 6500'. One core each was recovered from the UOMZ, MOMZ and LOMZ sites as shown in Fig. 1. The bottom water DO concentrations were measured using a sensor attached to the CTD. The length of the sediment cores ranged from 21 to 30 cm. The sediments were homogenous and dominantly silty clays. The cores were sectioned at 1-cm intervals, dried at <40°C and preserved for further analysis.

**2.1. Chronology and sedimentation rates:** The planktonic foraminifer, *Globigerina ruber* was carefully separated from the coarse fraction of sediments in each core, thoroughly cleaned and radiocarbon dated, using Accelerator Mass Spectrometer (AMS) at the Woods Hole Oceanographic Institution, USA. Calibration to calendar year ages was performed using 'Fairbanks0107' programme (Fairbanks et al., 2005) and an age-depth model (Table 1) was constructed through linear interpolation between the measured ages. As we obtained only a few number of ages in each core, we are aware that there could be some uncertainties in the derived sedimentation rates.

**2.2. Inorganic and organic carbon and total nitrogen contents and their isotopes:** Using a coulometer (UIC Inc. Model 5014) with an acidification module attached, calcium carbonate (CaCO<sub>3</sub>)

content was calculated. Accuracy and precision of the results were within  $\pm 2\%$ . The total carbon (TC) content was analyzed, using elemental analyzer, and  $C_{org}$  was calculated as 'TC – IC'. Total nitrogen (TN) and  $\delta^{15}N$  were measured on the bulk samples, whereas  $\delta^{13}C_{org}$  was measured on the decalcified samples, using Isotope Ratio Mass Spectrometer (IRMS Delta V Plus, Thermo) coupled with an Elemental Analyzer in a continuous flow mode. Calibration was done using international and in-house laboratory standards (n-Caprioic acid,  $C_6H_{15}NO_2$ ), as explained in Agnihotri et al. (2008). Analytical precision achieved was  $<2\%$  for the  $C_{org}$  and TN contents and  $<0.2\%$  for  $\delta^{13}C_{org}$  and  $\delta^{15}N$  measurements.

**2.3. Major and trace metals:** The subsamples of dried sediments were ground to fine size, made salt free and again dried and homogenized. Weighed sediment samples (50mg) were taken in teflon beakers and subjected to open-acid digestion with supra pure acid mixture (HF:HNO<sub>3</sub>:HClO<sub>4</sub> in 7:3:1 ratio) on a hot plate at  $\sim 190^\circ C$ . After achieving complete digestion, 4 ml of 50 % HNO<sub>3</sub>, followed by 100  $\mu$ l of Rhodium (Rh, 1 ppm in 2 % HNO<sub>3</sub>) were added and the final volume of sample solution was made to 100 ml. The digested samples were analyzed for trace metals, using Inductively-coupled Plasma Mass Spectrometer (ICP-MS). For the analysis of major elements, sediment samples were decalcified, made organic free, washed and dried. Powdered sample of 0.55 g was mixed with 5.5 g of flux A1000 di-lithiumtetraborate with 0.07 % lithium bromide in a platinum cup and heated at  $1100^\circ C$ . The molten material was quickly transferred to platinum plate to cool down into glass beads. These fused glass beads were analysed on Axio-PAN analytical XRF for major elements. Certified reference standards MAG-1 (Marine mud, United States Geological Survey) and SGR-1 (Green River Shale, United States Geological Survey) were also processed along with the samples and run to test the analytical and instrumental accuracy for ICP-MS and XRF. The repeatability was found to be better than 1 % for the major elements and 10 % for the minor and trace elements.

#### 2.4. Magnetic parameters

For magnetic measurements subsamples of sediments were slightly crushed, weighed and packed in cling wrap and placed in plastic vials. Magnetic susceptibility was measured on a Barrington MS-2 magnetometer that was linked to a MS2B dual frequency sensor. Each sample was measured for low-frequency magnetic susceptibility ( $\chi_{lf}$ ) at 0.47 kHz frequency at least 3 times and the mean values were presented with respect to the weight of the sample as  $10^{-8} m^3 kg^{-1}$ . Anhysteretic remnant magnetization (ARM) was given as anhysteretic susceptibility ( $\chi_{ARM}$ ), which is determined as mass specific ARM /strength of the biasing field. Each sample was applied to a magnetic field with forward value up to 1000 mT, using the Molspin Pulse magnetizer. The Isothermal Remnant Magnetization (IRM) acquired by the sample was measured using Molspin spinner magnetometer. IRM at 1000 mT was

taken as Saturation Isothermal Remnant Magnetization (SIRM) and later samples were subjected to reverse field. Further, magnetic grain size parameters ( $\chi_{ARM}/SIRM$  and  $\chi_{ARM}/\chi_{lf}$ ) and S-ratio ( $((1-IRM_{300mT}/IRM_{1000mT})/2)*100$ ) of the samples were calculated, following Bloemendal et al. (1988) and Walden et al. (1999).

### 3. Results

**3.1 Bottom water dissolved oxygen concentrations:** The bottom water DO concentrations measured with a DO sensor were 0.4  $\mu$ M, 5.8  $\mu$ M and 25  $\mu$ M at the core locations UOMZ, MOMZ and LOMZ respectively.

**3.2. Sedimentation rates:** The age of the sediments at the core top varied between 581 and 817 yrs BP, higher than the mean ocean reservoir age of 400 yrs (Bard, 1988). The maximum age recorded in these cores was 4500 yrs BP (Table 1). Sedimentation rates were calculated based on the derived calendar ages. As indicated earlier, some uncertainties may have been involved due to limited radiocarbon dates of sediments in each core. Nonetheless, the derived sedimentation rates provide insights on the major changes, if any, during deposition. Sedimentation rates were low (5 to 5.6 cm/kyr) in the upper sections of the UOMZ and MOMZ cores, but high (16-20 cm/kyr) for the LOMZ core. However, the sedimentation rates were 7 cm/kyr, 5.7 cm/kyr and 8.08 cm/kyr for the lower sections of the UOMZ, MOMZ and LOMZ cores, respectively.

**3.3. Inorganic and organic carbon and total nitrogen contents and their isotopes:** Organic carbon and  $CaCO_3$  contents in the UOMZ core were high, ranging from 2.2 to 7.9 % and from 30 to 80 %, respectively and were negatively correlated to each other (Fig. 2). The  $C_{org}$  content was high at the core bottom, decreased up core with the lowest value corresponding to 1800 yrs BP and then increased towards core top. The TN content varied between 0.35 and 0.65 % and  $C_{org}/TN$  ratio between 15 and 8, with higher ratios in the lower section of the core and gradually decreasing ratios in the upper section. The  $\delta^{13}C_{org}$  values ranged from -21.1 to -20.3 ‰, with higher values between 1500 and 2500 yrs BP. The  $\delta^{15}N$  values varied between 5.8 and 7.2 ‰, with gradually increasing values up core until 1500 yrs BP and thereafter decreased towards core top.

The  $C_{org}$  and  $CaCO_3$  contents in the MOMZ core varied from 0.4 to 5.2 % and 25 to 55 %, respectively (Fig. 3). They were uniformly low between 4500 and 2000 yrs BP, increased gradually between 2000 and 1500 yrs BP and maintained steady high values (~4.8 % and ~55 %, respectively) for the last 1500 yrs BP. The down core profiles of  $C_{org}$  and TN were similar. Ratios of  $C_{org}/TN$  varied from 10 to 8.8 between 4400 and 2000 yrs BP, and then maintained a value of 8.5 for the last 1500 yrs BP. The  $\delta^{13}C_{org}$  values were more positive (-18.6 to -16.8 ‰) in the lower core sections and more

negative (-20.3 ‰) in the upper sections. In contrast,  $\delta^{15}\text{N}$  values were lower (~5 ‰) in the lower sections than in upper sections of the core (6 -7 ‰).

The  $\text{C}_{\text{org}}$  and  $\text{CaCO}_3$  contents in the LOMZ core ranged from 3.6 to 4.9 % and 48 to 56 %, respectively (Fig. 4). They were negatively correlated and, gradually increasing  $\text{C}_{\text{org}}$  content corresponds to decreasing  $\text{CaCO}_3$  content in the upper section. TN content ranged from 0.4 to 0.55 % and its down core profile resembled that of  $\text{C}_{\text{org}}$ . Ratios of  $\text{C}_{\text{org}}/\text{TN}$  were high (~9.5) in the lower sections but decreased up core. The  $\delta^{13}\text{C}_{\text{org}}$  values varied in a narrow range (-20.2±0.3 ‰) throughout the core. The  $\delta^{15}\text{N}$  values decreased from 6.5 to 6.0 ‰ with intermittent peak high values (7.0 and 7.4 ‰) both in the lower and upper sections of the core.

**3.4. Metal/aluminum (M/Al) ratios in sediment cores:** Aluminum (Al) and titanium (Ti) are resistant to diagenesis in most sedimentary deposits and considered as indicators of aluminosilicate fraction (Calvert and Pedersen, 1993; Tribovillard et al., 2006 and references therein). Generally, the trace element concentrations are normalized to Al or Ti contents to compare their proportions in samples with variable carbonate and opal contents (e.g., Calvert and Pedersen, 1993). Coastal sediments are normally enriched with rutile (titanium mineral) apart from Al-silicate fraction and errors may arise if normalized to Ti. Therefore, we normalized elemental concentrations with Al and the down core variations of M/Al ratios are viewed with respect to the productivity, terrigenous and redox-sensitive proxy parameters.

The  $\text{C}_{\text{org}}$  content and M/Al ratios of Cu and Ni (other productivity parameters) in the UOMZ core showed high ratios at the core bottom (~3000 yrs BP) but decreased gradually up core until 1800 yrs BP and then increased towards the core top (Fig. 2). However, the Ba/Al ratio showed no significant down core variation. The down core variations in the M/Al ratios of terrigenous metals (Sc, Rb, Th and Ti) resembled each other and were also high at the core bottom and decreased gradually up core until 1800 yrs BP and then increased towards the core top (Fig. 5). Among the redox-sensitive elements, the M/Al ratios of Mn and Cd showed no significant variations down core (figure not shown). Uranium concentrations and U/Al ratios were high between 4000 and 3000 yrs BP but decreased gradually up core and maintained steadily low ratios for the last 1800 yrs BP (Fig. 8).

The MOMZ core showed distinct change in geochemical parameters. The M/Al ratios of Ba, Cu, Ni, Pb, Cr and Cd were low and uniform in the lower section but increased gradually and then maintained uniformly high values for the last 1500 years (Fig. 3). The M/Al ratios of Rb, Sc, Th, Ti and Zr were higher in the lower section but decreased gradually up core. Peak high M/Al ratios of Ti and Zr occur around 4000 yrs BP and 2800 yrs BP. Fe/Al ratio increased marginally towards the core

top (Fig. 6). U/Al ratios were low in the lower section and high in the upper section of the core (Fig. 8).

The LOMZ core showed higher M/Al ratios of Ba, Cu, Ni, Pb, Cr and Sc than in average shale. The ratios showed no significant change throughout the core (Fig. 4). The M/Al ratios of Cd, Mn, Zr, Rb and Th were, however, lower than in average shale (Fig. 7) and more uniform, except Mn increased and Cd decreased marginally during the last 1100 yrs BP (figure not shown). U/Al ratios were high at the core bottom and decreased gradually up core with steady values for the last 750 yrs BP (Fig. 8).

### 3.5. Rock magnetic properties

Magnetic concentration, grain size and mineralogy parameters of the sediments in cores are shown in Fig. 9 (A-C). The magnetic susceptibility ( $\chi_{lf}$ ) values were highest (300 to  $100 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ ) for the core from UOMZ and lowest (33 to  $17 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ ) for the LOMZ core. The  $\chi_{lf}$  values ranged from 140 to  $30 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$  in the MOMZ core. Magnetic concentration parameters in the UOMZ core were high at the core bottom but decreased gradually up core to the lowest value at ~1800 yrs BP and then increased towards core top (Fig. 9A). Magnetic grain size parameters ( $\chi_{ARM}/\chi_{lf}$  and  $\chi_{ARM}/\text{SIRM}$ ) increased and, low magnetic concentration parameters correspond to high magnetic grain size at ~1800 yrs BP. Thereafter, the increased magnetic concentration parameters coincided with decreasing grain size parameters towards core top. The MOMZ core showed high and uniform magnetic concentration parameters corresponding to very low grain size parameters in the lower part and vice versa in the upper part (Fig. 9B). This steep change occurred at ~2000-1700 yrs BP. The core from the LOMZ showed extremely low values of magnetic concentration and grain size parameters at the core bottom (Fig. 9C). The values of magnetic concentration parameters increased gradually towards core top, whereas the grain size parameters showed dome-shaped pattern with gradually increasing and high values towards the middle portions of the core and then decreasing values towards core top. S-ratio of all the cores varied between 96 and 99.

## 4. Discussion

### 4.1. Controls on organic matter distribution

The  $C_{org}$  content of the sediments in the UOMZ core (2.2 - 7.9 %) is higher than in MOMZ (0.4 - 5.2 %) and LOMZ (3.9 - 5 %) cores and, much higher than on the continental margins (0.5 %; Romankevich, 1984). Organic carbon on the continental margins can have terrigenous sources as well. However, the  $C_{org}/\text{TN}$  ratios of all cores (range: 6 to 14.6) investigated here are comparable to that of the marine organic matter (6.6; Redfield, 1958). Similarly, the narrow range of  $\delta^{13}C_{org}$  values (-20.0 to -21.1 ‰) in cores from the UOMZ (Fig. 2) and LOMZ (Fig. 4) are within the range of values

reported for marine organic matter ( $-20.12 \pm 2 \%$ ; Hoefs, 1980). However, the core at MOMZ showed contrasting results for the sediments deposited before 1800 yrs BP as detailed later in this section.

Several workers debated the origin of organic-rich sediments on the margins of the Arabian Sea and focused on the relative importance of high productivity and oxygen depletion in bottom waters (Demaison and Moore, 1980; Calvert 1987; Pedersen and Calvert, 1990; Pedersen et al., 1992; Paropkari et al., 1992; van der Weijden et al., 1999). The organic matter content in the sediments is a function of both supply and preservation. Organic matter gets oxidized in oxygenated bottom waters but preserved under sub-oxic and anoxic bottom waters. Therefore, the changes in DO concentration in the bottom waters could affect the  $C_{org}$  content of the sediments. The  $C_{org}$  content is high in all core top sediments (4.4 to 5.2 %, Fig. 2, 3 & 4) and exhibits no significant relationship with bottom water DO concentrations, which ranged from 0.4 to 25  $\mu\text{M}$ . For example, high  $C_{org}$  is associated with low DO (0.4  $\mu\text{M}$ ) in a core from the UOMZ and also with high DO (25  $\mu\text{M}$ ) in a core from LOMZ. In general, the  $C_{org}$  content is higher towards core top than in lower sections, but stabilizes after initial upward rise. Moreover, the  $C_{org}$  contents show no linear relationship with rates of sedimentation (Figs. 2, 3 and 4). Further, the  $C_{org}$  and  $\text{CaCO}_3$  contents are negatively correlated in cores at UOMZ (Fig. 2,  $R^2 = -0.94$ ) and LOMZ (Fig. 4;  $R^2 = -0.52$ ) implying a constant  $C_{org}$  input, which is effectively diluted by increasing  $\text{CaCO}_3$  input. However, the positive correlation between the two in the core at MOMZ (Fig. 3,  $R^2 = 0.95$ ) indicates increased input of  $C_{org}$  occurs in excess of any dilution effect of increased  $\text{CaCO}_3$  input. The core at MOMZ has always been located in the OMZ over the period of study (Naik et al., 2014), but it showed significant down core variations in  $C_{org}$  content (0.5 to  $\sim 5 \%$ ; Fig. 3). This implies that the oxygen depletion alone cannot explain the variations in  $C_{org}$  distribution in the sediments of the Indian margin. Based on surficial sediments of the eastern Arabian Sea, Calvert et al. (1995) reported organic carbon maximum extends over a large depth range than the oxygen minimum and thus showed no evidence for preferential preservation of organic matter within the OMZ. They suggested no direct relationship exist between  $C_{org}$  maximum and oxygen depletion of bottom waters. Although we have studied sediment cores within the OMZ, our findings confirm that of Calvert et al. (1995) - that oxygen depletion alone is not the controlling factor and  $C_{org}$  content can differ dramatically between sites within short distances, despite very similar dissolved oxygen concentrations.

The down core profile of  $C_{org}$  shows dramatic change in a core at MOMZ (Fig. 3) as compared to UOMZ (Fig. 2) and LOMZ (Fig. 4) cores, despite uniform sedimentation rates throughout the core. This core is located on steeper slope adjacent to wider shelf compared to the other cores (UOMZ and LOMZ). The site-specific factors like steep slope favor extensive reworking and/or winnowing of OM



from the slope and, wider shelf favors in dilution of near shore, organic-poor terrestrial clays. High  $\delta^{13}\text{C}_{\text{org}}$  values (-16.8 to -18.6 ‰) associated with low  $\text{C}_{\text{org}}$  (~0.5 %) and high  $\text{C}_{\text{org}}/\text{TN}$  ratios (Fig. 3) along with peaks of high Zr/Al, Ti/Al, Rb/Al and Sc/Al ratios (Fig. 6) in the lower section of the MOMZ core suggest more terrigenous material in this part of the core. Admixing of terrigenous OM with marine OM may lead to more negative  $\delta^{13}\text{C}$  values. The  $\delta^{13}\text{C}$  values in this core, however, are more positive than marine OM implying the presence of reworked organic matter. Reworking increases the  $\text{C}_{\text{org}}/\text{TN}$  ratio of organic fraction by re-exposing previously buried OM to renewed microbial degradation where bacterial populations are higher near the sediment-water interface (Shimmield et al., 1990). Thus, the high  $\text{C}_{\text{org}}/\text{TN}$  ratios in this core represent most degraded OM, and low ratios represent better preservation. Several researchers reported high  $\text{C}_{\text{org}}/\text{TN}$  ratios (Pedersen et al., 1992; Thamban et al., 1997) and more positive  $\delta^{13}\text{C}$  values than marine organic matter suggesting the presence of reworked and winnowed organic matter. In addition, peaks of high Zr/Al, Ti/Al, Rb/Al and Sc/Al ratios indicate events of high terrigenous material supply, most probably transported from the upper slope (as the slope is steep, refer Fig 1). It may be that the clays and fine silts from the upper continental slope are reworked to the lower slope in active regions of bottom currents. In other words, winnowing and associated reworking primarily controlled the distribution and degree of preservation of organic matter at this site (MOMZ). It is also possible that the sediments in lower section of this core (before 2000 yrs) represent a mass deposition event and in the upper section represent deposition in recent period. However, uniform sedimentation rates throughout the core do not support the mass deposition event. Another plausible explanation for more positive  $\delta^{13}\text{C}$  values could be due to high organic matter contribution from C4 plants (-14 ‰) than from C3 (-27 ‰) plants. Dahl et al. (2005) studied plant waxes in the Arabian Sea sediments and showed 75 % of the waxes derived from Africa and Asia are from C4 plants, whereas the waxes derived from the Mesopotamian region largely represent C3 vegetation and are delivered to the site by northwesterly winds.

High  $\text{C}_{\text{org}}/\text{TN}$  ratios (~14) in the lower section (3000 - 4000 yrs BP) of the UOMZ core are consistent with  $\text{C}_{\text{org}}$  profile (Fig. 2) indicating preferential mineralization of organic nitrogen during passage through water column and during early diagenesis (Cowie, 2005; Meyers, 1994). The core exhibits authigenic magnetite formation at the boundary of upper/lower sections (Fig. 9A) suggesting reductive diagenesis at a few cm from sediment surface, supporting mineralization of organic matter at this depth. The high  $\text{C}_{\text{org}}/\text{TN}$  ratios in the lower section are also associated with peaks of high Ti/Al, Rb/Al and Sc/Al ratios (Fig. 5) indicating more terrigenous material supply. However, the  $\delta^{13}\text{C}$  values do not support this possibility (Fig. 2). We therefore infer that the core from the UOMZ experiences reductive diagenesis at a few cm from sediment surface. The narrow range of  $\text{C}_{\text{org}}/\text{TN}$  ratios (8.2 to

9.5) and  $\delta^{13}\text{C}_{\text{org}}$  values (-20.0 to -20.6‰) in the core from LOMZ (Fig. 4) indicate deposition of marine organic matter in these sediments. Our results from the present study suggest that the organic matter is largely reworked type in the lower section of the MOMZ core and marine at the UOMZ and LOMZ cores. Moreover, topography of sea bed at core locations seemed to play a role on the OM distribution by allowing winnowing of sediments and/or transportation and deposition of organic-poor clays from the slope.

Nitrate accounts for most of the fixed nitrogen in the ocean and the global average  $\delta^{15}\text{N}$  value for the deep-ocean nitrate is  $5.7 \pm 0.7\%$  (Liu and Kaplan, 1989). The water column denitrification in the OMZ leads to preferential removal of  $^{14}\text{N}$  leaving residual  $\text{NO}_3^-$  enriched with  $^{15}\text{N}$  (Liu and Kaplan, 1989; Brandes et al., 1998; Altabet et al., 1999; Agnihotri et al., 2006). The  $\delta^{15}\text{N}$  of sediments is determined by the  $\delta^{15}\text{N}$  of surface waters, which may have been influenced by upwelling of  $^{15}\text{N}$ -enriched nitrate from sub-surface to surface waters. In addition, the  $\delta^{15}\text{N}$  of sediments is potentially affected by various processes such as mixing with isotopically lighter terrestrial OM, alteration of OM in water column and sediments, incomplete nitrate utilization, etc. (Ganeshram et al., 2000). The relatively high and consistent  $\square^{15}\text{N}$  values in the lower sections and decreasing trend of values towards core top in the UOMZ core (Fig. 2) are within the range of values in the OMZs of typical upwelling margins (Altabet et al., 1995; Ganeshram et al., 2000). Similar trend was also observed in a core from the LOMZ (Fig. 4). Rasiq et al. (2016) reported similar  $\square^{15}\text{N}$  values (6 to 7.5 ‰) at the study site with a decreasing trend of  $\square^{15}\text{N}$  towards the core top. Higher  $\square^{15}\text{N}$  values (6.5 - 8.5 ‰; Cowie et al., 2009) of sediments from the Pakistan margin than from the eastern Arabian Sea (Rasiq et al., 2016 and present study) were attributed to  $^{14}\text{N}$ -depleted nitrate pool created by pelagic denitrification.

The low  $\square^{15}\text{N}$  values in the lower section (deposited prior to 2000 yrs BP) and gradually increased and consistently high values in the upper sections are characteristic of the MOMZ core (Fig. 3). Low TN content in the lower section could be due to diagenetic effect (Altabet et al., 1999), but early diagenesis increases  $\square^{15}\text{N}$  values. Hence, the low  $\square^{15}\text{N}$  values in the present study may not be due to diagenetic effect. It is likely that the intermediate waters were oxygenated at MOMZ (probably through the under current) with the pulse of intensified monsoon (Kessarkar et al., 2010; 2013; 2018) and thus the low  $\square^{15}\text{N}$  could be due to site-specific or dilution of organic-poor, terrigenous sediments to the site. This increased pulse of monsoon increases the supply of terrigenous material as indicated by the peaks of high Zr/Al, Ti/Al, Rb/Al and Sc/Al ratios (Fig. 6). The higher  $\square^{15}\text{N}$  values in the upper sections of this core (MOMZ) are consistent with the isotopic values of other cores from the UOMZ and LOMZ. Overall,  $\square^{15}\text{N}$  values in the cores were within the range of values in the OMZs of typical upwelling margins, however, with lower values for the reworked sediments in the core at MOMZ.

## 4.2 Sedimentary conditions in the cores through geochemical proxies

In addition to  $C_{org}$ , elements like Cu and Ni act as micronutrients and are commonly used as productivity proxies (Calvert and Pedersen, 1993). The ratios of Cu/Al and Ni/Al showed consistent increase with increasing  $C_{org}$  content for last 1800 years BP for the UOMZ (Fig. 2) and MOMZ (Fig. 3) cores indicating increased productivity. Despite high concentrations, the Cu/Al and Ni/Al ratios do not show significant variation in the LOMZ core possibly because of very high sedimentation rates in the upper section (16-20 cm/kyr) and/or varied sources of sediments and OM at this core site. As this core is located in the lower slope, high sedimentation rates at the core site might have caused by winnowing of sediments from the upper slope.

The MOMZ core showed high  $C_{org}$  and M/Al ratios of productivity parameters (Fig. 3) coinciding with low M/Al ratios of terrigenous parameters (Fig. 6) in sediments for the last 1500 years, despite uniform sedimentation rates throughout the core. Rasiq et al. (2016), however, have not observed similar  $C_{org}$  variations in their core at 800 m water depth from a nearby site. This indicates that the accumulation of organic carbon is site-specific and controlled by several factors. As indicated earlier, the lower section of the core at MOMZ contains reworked OM and upper section contains normal marine OM. This also points out that each core is unique, and factors controlling OM are site-specific. Sediment focusing and winnowing of sediments from the site might have changed the OM type.

The U/Al ratios along with Mo/Al ratios, have been used as marine palaeo-redox indicators (Tribovillard et al., 2006 and references therein). Conditions for the reduction of U (VI) to U (IV) are similar to that of the reduction from Fe (III) to Fe (II), followed by precipitation in the sediments (Morford and Emerson, 1999). Despite variations in depth, the cores at UOMZ and LOMZ behaved similarly with respect to U distribution. Higher U/Al ratios in lower sections of the UOMZ and LOMZ cores are associated with 7 cm/kyr and 8.08 cm/kyr sedimentation rates, respectively (Fig. 8). This indicates authigenic U accumulation, most probably diffused from the overlying sediments in reducing conditions. The decreasing U/Al ratios towards core top despite high organic carbon indicate that the reduced U may have diffused to the sediment-water interface during early diagenesis of organic matter. Rock magnetic properties showed stage 2 diagenesis i.e., dissolution of fine-grained magnetite in the sediments (Fig. 9A and C). Tribovillard et al. (2006) suggested that the oxygen penetration depth and sedimentation rates play significant roles in U enrichment. Low and near similar sedimentation rates at these cores allowed more time for diffusion of uranyl ions from the water column into the sediment (Crusius and Thomson, 2000, Tribovillard et al., 2006). Moreover, U can be remobilized within the sediments if oxygen penetrates to a depth where authigenic U accumulates (Morford et al.,

2001). On the other hand, the core at MOMZ exhibits low U/Al ratios and relatively high U/Al ratios associated with lower and upper sections (Fig. 8), despite near similar sedimentation rates. This could be due to varied sediment types in these sections. Uranium must have been lost in reworked sediments deposited in the lower sections and marginally increased because of productivity associated organic-rich sediments and subsequent early diagenesis in the upper sections. This implies that the type of organic matter played an important role in the accumulation of uranium.

### 4.3. Early diagenesis in sediment cores through rock magnetic properties

Rock magnetic parameters respond to environmental changes in the sediments and have been used to address provenance and early diagenetic changes in various settings (Karlin, 1990; Vigliotti et al., 1999). The dissolution of detrital magnetite and/or formation of authigenic magnetic minerals depend on the redox state and availability of metals in the sediments (Liu et al., 2004; Rey et al., 2005; Hayashida et al., 2007; Rao et al., 2010). All cores in the present study lie within the OMZ. High magnetic concentrations in the UOMZ core may be due to its proximity to the coast. High values of  $C_{org}$ , magnetic concentration parameters (Fig. 9A) and high M/Al ratios of terrigenous elements (Fig. 5) in the core correspond to low magnetic grain size ratios at the core bottom (3800 yrs BP). This indicates that the site experienced early diagenetic conditions, wherein detrital fine-grained magnetites get dissolved. Thereafter, the gradual decrease in  $C_{org}$ , magnetic concentration parameters and M/Al ratios of terrigenous elements corresponding to increase in magnetic grain size ratios imply the increase in ferrimagnetites may be because of the formation of diagenetic magnetites such as gregite or pyrrhotite between 3200 and 1700 yrs BP. Further, the gradual increase in  $C_{org}$ , magnetic concentration and terrigenous parameters corresponding to decrease in magnetic grain size ratios suggest the influence of early diagenesis on the dissolution of fine-grained magnetites in the top 1800 yr sediments (Fig. 9A).

Although the  $\chi_{lf}$  values in the LOMZ core are 10 times lower than in the UOMZ core, down core variations in magnetic properties are similar. For a given low  $C_{org}$  concentrations, magnetic concentration and grain size ratios increase up core in the lower portions indicating increase in the formation of fine-grained magnetites (Fig. 9C). The increase in  $C_{org}$  and magnetic concentrations corresponding to decrease in magnetic grain size ratios in the upper portions of the core implies influence of early diagenesis and selective dissolution of fine-grained magnetite, even at high sedimentation rates (16-20 cm/kyr).

The MOMZ core located within the OMZ showed contrasting results to those found in the other cores (Fig. 9B). Despite uniform sedimentation rates, the core exhibits high magnetic concentrations

associated with very low magnetic grain size ratios and  $C_{org}$  content in the lower sections, suggesting selective dissolution of magnetites. On the other hand, very low magnetic concentrations with high grain size ratios and high  $C_{org}$  content in the upper sections imply formation of ferrimagnetic minerals such as greigite or pyrrhotite (Roberts et al., 1996; Rey et al., 2005). Our results indicate that early diagenesis is evident even at low and high sedimentation rates. Authigenic magnetic mineral formation occurs in the lower sections of the UOMZ and LOMZ cores and at or close to the sediment-water interface in the MOMZ core. In other words, the degree of diagenesis varied in different sections of the cores and among the cores within the OMZ.

## **Conclusion**

Three sediment cores that are in contact with varying bottom water DO concentrations from the eastern Arabian Sea were investigated for their age, rock magnetic properties,  $C_{org}$ , TN content and their isotopes and other geochemical properties to understand the controls on organic matter distribution. The maximum age recorded in these cores was 4500 yrs BP and high sedimentation rates prevailed at LOMZ site. The  $C_{org}$  content and magnetic concentrations were much higher in the UOMZ core than in the other two cores. The  $C_{org}/TN$  ratios and stable isotopes of  $C_{org}$  indicate that OM is largely marine in all cores, except the sediments in the lower section of the MOMZ core, where it was reworked type. Rock magnetic properties showed the formation of authigenic magnetic minerals in the lower sections of cores from UOMZ and LOMZ and in upper sections in a core from the MOMZ implying varied diagenetic conditions at different depth intervals in the core and among the cores. Authigenic U occurs in the lower portions of the UOMZ and LOMZ cores, but mostly diffused to the sediment-water interface in the upper portions. Our results show that bottom water DO concentration played a minimal role in the preservation of OM. Moreover, increase in productivity parameters indicates productivity is probably the primary factor for organic-richness in the sediments. Topography at the core site and winnowing of sediments to the deeper portions also played important roles in  $C_{org}$  distribution. Our results suggest that apart from productivity and OMZ conditions, sedimentation rates, winnowing and type of OM (reworked) controlled organic matter distribution in the late Holocene sediments.

## **Acknowledgements**

The authors wish to thank the Director, CSIR-NIO for his support and encouragement. We are also thankful to the anonymous reviewers for their suggestions in improving the manuscript. Dr. Anil Pratihary is acknowledged for his help in sample collection onboard *Yokosuka*. Authors also wish to thank Dr.H. Kitazato, Chief scientist of the cruise and all the crew members of *Yokosuka* for their logistic support. Mrs. S. Karapurkar is acknowledged for her help in IRMS analysis for generating C

and N isotopic data. This study was funded by the Council of Scientific and Industrial Research and by the Ministry of Earth Sciences (SIBER-INDIA). This is NIO Contribution no.

### References:

- Agnihotri, R., Altabet, M.A., Herbert, T.D. 2006. Influence of marine denitrification on atmospheric N<sub>2</sub>O variability during the Holocene. *Geophys. Res. Lett.* 33, L13704, doi:10.1029/2006GL025864
- Agnihotri, R., Kurian, S., Fernandes, M., Reshma, K., D'Souza, W., Naqvi, S.W.A., 2008. Variability of subsurface denitrification and surface productivity in the coastal eastern Arabian Sea over the past seven centuries. *The Holocene* 18, 755-764.
- Altabet, M. A., Francois, R., Murray, D. W., Prell, W. L. 1995. Climate related variations in denitrification in the Arabian Sea from sediment <sup>15</sup>N/<sup>14</sup>N ratios, *Nature*, 373, 506–509
- Altabet, M.A., Murray, D.W., Prell, W.L., 1999. Climatically linked oscillations in Arabian Sea denitrification over the past 1 m.y.: Implications for the marine N cycle. *Paleoceanogr.* 14, 732-743.
- Bard, E., 1988. Correction of accelerator mass spectrometry <sup>14</sup>C ages measured in planktonic foraminifera: paleoceanographic implications. *Paleoceanogr.* 3, 635-645.
- Bloemendal, J., Lamb, B., King, K. W., 1988. Paleoenvironmental implications of rock-magnetic properties of late Quaternary sediment cores from the eastern equatorial Atlantic. *Paleoceanogr.* 3, 61–87.
- Bralower, T.J. Thierstein, H.R., 1987. Organic carbon and metal accumulation rates in Holocene and mid-Cretaceous sediments: palaeoceanographic significance. In: J. Brooks and A.J. Fleet (Eds.), *Marine Petroleum Source Rocks*. *Geol. Soc. Spec. Publ.* 26, 345-369.
- Brandes, J.A., Devol, A. H., Yoshinari, T., Jayakumar, D.A., Naqvi, S.W.A. 1998. Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles. *Limnol. Oceanogr.* 43, 1680-1689.
- Calvert, S.E., 1987. Oceanographic controls on the accumulation of organic matter in marine sediments. In: J. Brooks and A.J. Fleet (Eds.), *Marine Petroleum Source Rocks*. *Geol. Soc. Spec. Publ.*, 26, 137-151.
- Calvert, S.E., Pedersen, T.F., 1993. Geochemistry of recent oxic and anoxic sediments: implications for the geological record. *Mar. Geol.* 113, 67-88.
- Calvert S.E., Pedersen, T.F., Naidu., P.D., Von Stackelberg, U., 1995. On the organic carbon maximum on the continental slope of the eastern Arabian Sea, *Jr. of Mar. Res.*, 53, 269-296.
- Cowie, G., 2005. The biogeochemistry of Arabian Sea surficial sediments: A review of recent studies. *Progr. Oceanogr.*, 65, 260-289.
- Cowie, G., Mowbray, S., Kurian, S., Sarkar, A., White, C., Anderson, A., Vergnaud, B., Johnstone, G., Brear, S. and Woulds, C., 2014. Comparative organic geochemistry of Indian margin (Arabian Sea) sediments: estuary to continental slope. *Biogeosci.*, 11, 6683-6696.

- Cowie, G.L., Mowbray, S., Lewis, M., Matheson, H., McKenzie, R., 2009. Carbon and nitrogen elemental and stable isotopic compositions of surficial sediments from the Pakistan margin of the Arabian Sea. *Deep Sea Res. II*, 56, 271-282.
- Crusius, J., Thomson, J., 2000. Comparative behavior of authigenic Re, Mo and U during reoxidation and subsequent long-term burial in marine sediments. *Geochim. Cosmochim. Acta* 64, 2233–2243.
- Dahl, K.A., Oppo, D.W., Eglinton, T.I., Hughen, K.A., Curry, W.B., Sirocko, F. 2005. Terrigenous plant wax inputs to the Arabian Sea: Implications for the reconstruction of winds associated with the Indian Monsoon. *Geochim. et Cosmochim. Acta* 69 (10), 2547–2558.
- Demaison, G.J., Moore, G.T., 1980. Anoxic environments and oil source bed genesis. *Org. Geochem.* 2, 9-31.
- Fairbanks, R.G., Mortlock, R.A., Chiu, T.C., Cao, Li, Kaplan, A., Guilderson, T.P., Fairbanks, T.W., Bloom, A.L., Grootes, P.M., Nadeau, M.J., 2005. Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  dates on pristine corals. *Quat. Sci. Rev.* 24, 1781–1786.
- Ganeshram, R. S., Pedersen, T. F., Calvert, S. E., McNeill, G. W., Fontugne, M. R. 2000. Glacial-interglacial variability in denitrification in the world's oceans: Causes and consequences. *Paleoceanogr.* 14, 361–376.
- Haake, B., Ittekkot, V., Rixen, T., Ramaswamy, V., Nair, R.R., Curry, W.B., 1993. Seasonality and inter-annual variability of particle fluxes to the Arabian Sea. *Deep Sea Res.* 40, 1323–1344.
- Hayashida, A., Hattori, S., Oda, H., 2007. Diagenetic modification of magnetic properties observed in a piston core (MD01-2407) from the Oki Ridge, Japan. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 247, 65–74
- Hoefs, J., 1980. *Stable Isotope Geochemistry* (2nd ed.): New York (Springer-Verlag).
- Hunter, W.R., Levin, L.A., Kitazato, H., Witte, U., 2012. Macrobenthic assemblage structure and organismal stoichiometry control faunal processing of particulate organic carbon and nitrogen in oxygen minimum zone sediments. *Biogeosci.*, 9(3), 993-1006.
- Ingole, B.S., Sautya, S., Sivadas, S., Singh, R., Nanajkar, M., 2010. Macrofaunal community structure in the western Indian continental margin including the oxygen minimum zone. *Mar. Ecol.* 31, 148-166.
- Karlin, R., 1990. Magnetite diagenesis in marine sediments from Oregon continental margin. *J. Geophys. Res.*, 95, 4405–4419.
- Kessarkar, P.M., Rao, V.P., 2007. Organic carbon in sediments of the southwestern margin of India: Influence of productivity and monsoon variability during the Late Quaternary. *J. Geol. Soc. India*, 69, 42-52.
- Kessarkar, P.M., Rao, V.P., Naqvi, S.W.A., Chivas, A.R., Saino, T., 2010. Fluctuations in productivity and denitrification in the southeastern Arabian Sea during the Late Quaternary, *Curr. Sci.*, 99, 485-491.

- Kessarkar, P.M., Rao, V.P., Naqvi, S.W.A., Karapurkar, S.G., 2013. Variation in the Indian summer monsoon intensity during the Bolling-Allerod and Holocene, *Paleoceanogr.*, 28, 413-425.
- Kessarkar, P.M., Naqvi, S.W.A., Thamban, M., Fernandes, L.L., Siebert, C., Rao, V.P., Kawahata, H., Ittekkot, V. and Frank, M., 2018. Variations in denitrification and ventilation within the Arabian Sea oxygen minimum zone during the Holocene. *Geochem. Geophys. Geosys.*, 19, 2179–2193.
- Liu, J., Zhu, R., Roberts, A.P., Li, S., Chang, J.H., 2004. High-resolution analysis of early diagenetic effects on magnetic minerals in post-middle-Holocene continental shelf sediments from the Korea Strait. *J. Geophys. Res.* 109 (B03103), 1–15
- Liu, K.K., Kaplan, I.R. 1989. The eastern tropical Pacific as a source of  $^{15}\text{N}$  enriched nitrate in seawater off southern California. *Limnol. Oceanogr.* 5, 820-830.
- Madhupratap, M., Prasanna Kumar, S., Bhattathiri, P. M. A., Kumar, M. D., Raghukumar, S., Nair, K. K. C., Ramaiah, N., 1996. Mechanism of the biological response to winter cooling in the northeastern Arabian Sea. *Nature*, 384(6609), 549–552, doi:10.1038/384549a0.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 144, 289–302.
- Morford, J.L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in sediments. *Geochim. Cosmochim. Acta* 63, 1735–1750.
- Morford, J.L., Russell, A.D., Emerson, S., 2001. Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediments, Saanich Inlet, BC. *Mar. Geol.* 174, 355-369.
- Naik, S.S., Godad, S.P., Naidu, P.D., Tiwari, M., Paropkari, A.L., 2014. Early- to late-Holocene contrast in productivity, OMZ intensity and calcite dissolution in the eastern Arabian Sea. *Holocene*, 24, 749-755.
- Nair, R.R., Ittekkot, V., Manganini, S.J., Ramaswamy, V., Haake, B., Degens, E.T., Desai, B.N., Honjo, S., 1989. Increased particle fluxes to the oceans related to the monsoons. *Nature*, 338, 749–751.
- Naqvi, S.W.A., 1987. Some aspects of the oxygen-deficient conditions and denitrification in the Arabian Sea. *Journal of Marine Research* 45, 1049–1072.
- Naqvi, S.W.A., Naik, H., Pratihary, A., D'Souza, W., Narvekar, P.V., Jayakumar, D. A., Devol, A.H., Yoshinari, T., Saino, T., 2006. Coastal versus open-ocean denitrification in the Arabian Sea. *Biogeosci.*, 3, 621–633.
- Paropkari, A.L., PrakashBabu, C., Mascarenhas, A., 1992. A critical evaluation of depositional parameters controlling the variability of organic carbon in Arabian Sea sediments. *Mar. Geol.* 107, 213-226
- Pedersen, T.F., Calvert, S.E., 1990. Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks? *Am. Assoc. Pet. Geol.* 74, 454-466.
- Pedersen, T.F., Shimmiel, G.B., Price N.B., 1992. Lack of enhanced preservation of organic matter in sediments under the oxygen minimum zone on the Oman margin. *Geochim. et Cosmochim.*



Acta 56, 545-551.

- Rao, B.R., Veerayya, M., 2000. Influence of marginal highs on the accumulation of organic carbon along the continental slope of western India. *Deep-Sea Res. II* 47, 303-327.
- Rao, V.P., Kessarkar, P.M., Thamban, M., Patil, S.K., 2010. Paleoclimatic and diagenetic history of the Late Quaternary sediments in a core from the Southeastern Arabian Sea: geochemical and magnetic signals. *J. Oceanogr.* 66,133–146
- Rasiq, K.T., Kurian, S., Karapurkar, S.G., Naqvi, S.W.A., 2016. Sedimentary pigments and nature of organic matter within the oxygen minimum zone (OMZ) of the Eastern Arabian Sea (Indian margin). *Estuar. Coast. Shelf Sci.* doi: 10.1016/j.ecss.2016.04.013.
- Rixen, T., Haake, B., Ittekkot, V., Guptha, M.V.S., Nair, R.R., Schlussel, P., 1996. Coupling between SW monsoon-related surface and deep ocean processes as discerned from continuous particle flux measurements and correlated satellite data. *Jr. of Geophys. Res.* 101, 28569–28582.
- Redfield, A.C., 1958. The biological control of chemical factors in the environment. *Am. Sci.* 46, 205–222.
- Rey, D., Mohamed, K.J., Bernabeu, A., Rubio, B., Vilas, F., 2005. Early diagenesis of magnetic minerals in marine transitional environments: geochemical signatures of hydrodynamic forcing. *Mar. Geol.* 215, 215–236
- Roberts, A. P., Reynolds, R. L., Verosub, K. L., Adam, D. P. 1996. Environmental magnetic implications of greigite (Fe<sub>3</sub>S<sub>4</sub>) formation in a 3 m.y. lake sediment record from Butte Valley, northern California. *Geophys. Res. Lett.*, 23, 2859–2862.
- Romankevich, E.A. 1984. *Geochemistry of organic matter in the oceans*. Springer-Verlag, Berlin, pp. 334.
- Shimmiel, G.B., Price, N.B., Pedersen, T.F 1990. The influence of hydrography, bathymetry, and productivity on sediment type and composition of the Oman Margin and in the northwest Arabian Sea. In: Robertson A.H.F, Searle, M.P., Ries, A.C (Eds.) *The Geology and Tectonics of the Oman Region*, *Geol. Soc. Spec. Publ.* 49, pp. 759-769.
- Thamban, M., Rao, V.P., Raju, S.V., 1997. Controls on organic carbon distribution in sediments from the eastern Arabian Sea margin, *Geo-Mar. Lett.*, 17(3), 220-227.
- Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.* 232, 12-32.
- van der Weijden, C.H., Reichart, G.J., Visser, H.J., 1999. Enhanced preservation of organic matter in sediments deposited within the oxygen minimum zone in the northeastern Arabian Sea. *Deep Sea Res. I*, 46, 807–830.
- Vigliotti, L., Capotondi, L., Toril, M., 1999. Magnetic properties of sediments deposited in suboxic–anoxic environments: relationships with biological and geochemical proxies. *Paleomagnetism and diagenesis in sediments*. *Geol. Soc. Lond. Spec. Publ.* 151, 71–83
- Walden, J., Oldfield, F., Smith, J., 1999. *Environmental magnetism. A Practical Guide*. No.6. *Quat. Res. Asso.*, London, pp. 243.

**Table 1.** Accelerator Mass spectrometer (AMS) ages of sediment intervals dated in the cores from UOMZ, MOMZ and LOMZ. (yrs BP- years before present ie,1950).

Water depth (m)	Sample ID (WHOI)	Mean depth (cm)	Radiocarbon age			Calibrated Age (Fairbanks 0107)	
			<sup>14</sup> C AMS Age	Age Error	Age-400	Calendar age yrs BP	1 std dev
500	83703	1.5	1500	35	1100	996	39
	83704	10.5	2890	30	2490	2599	88
	83705	20.5	4090	30	3690	4022	49
812	83667	1.5	985	25	585	581	35
	83668	9.5	2570	30	2170	2178	66
	83669	22.5	4400	30	4000	4459	37
1168	83666	1.5	1010	25	610	598	33
	83663	4.5	1280	30	880	784	46
	83664	11.5	1610	30	1210	1132	48
	83665	29.5	3530	35	3130	3357	30

## Figure Captions

Figure 1. Map showing core locations at 500m (UOMZ), 812m (MOMZ) and 1168m (LOMZ) water depths in the eastern Arabian Sea.

Figure 2. Down core variations in the productivity parameters in the UOMZ core;  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  are expressed as ‰. Vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 3. Down core variations in the productivity parameters in the MOMZ core;  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  are expressed as ‰. Vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 4. Down core variations in the productivity parameters in the LOMZ core;  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  are expressed as ‰. Vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 5. Down core variations in the terrigenous parameters in the UOMZ core. Vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 6. Down core variations in the terrigenous parameters in the MOMZ core. Vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 7. Down core variations in the terrigenous parameters in the LOMZ core. Vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 8. Down core variations in U/Al ratios in the UOMZ core (A), MOMZ core (B) and LOMZ core (C). Small vertical dashed line is the Al- normalized ratio of the Post-Archean Australian Shale (PAAS).

Figure 9. Down core variations in the  $C_{\text{org}}\%$  and rock magnetic concentration, grain size and mineralogy parameters in the UOMZ core (9A), MOMZ core (9B) and LOMZ core (9C)

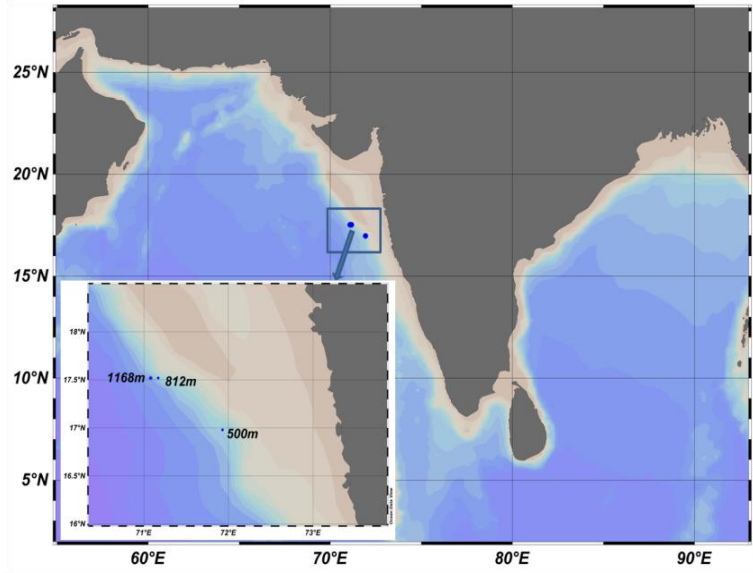


Figure 1

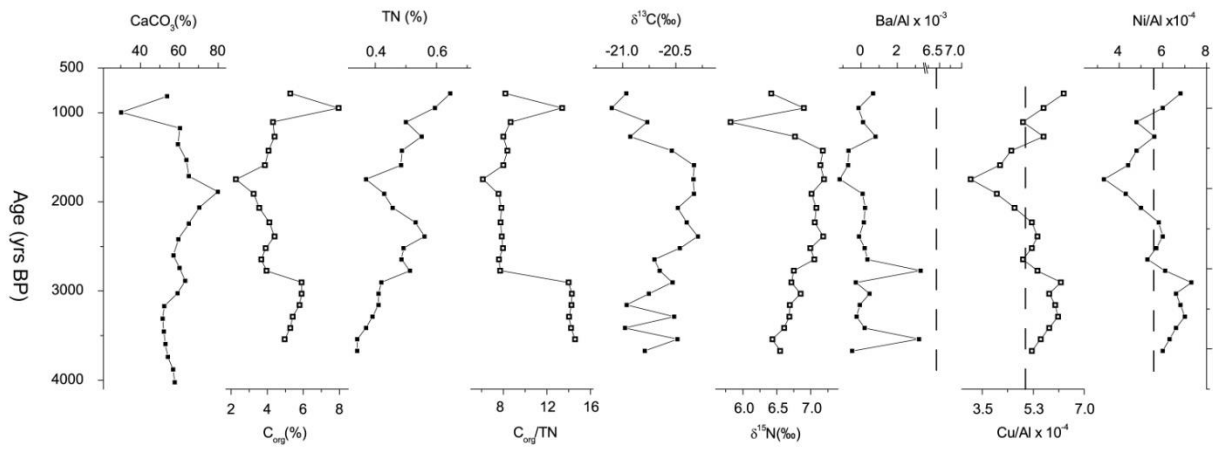


Figure 2

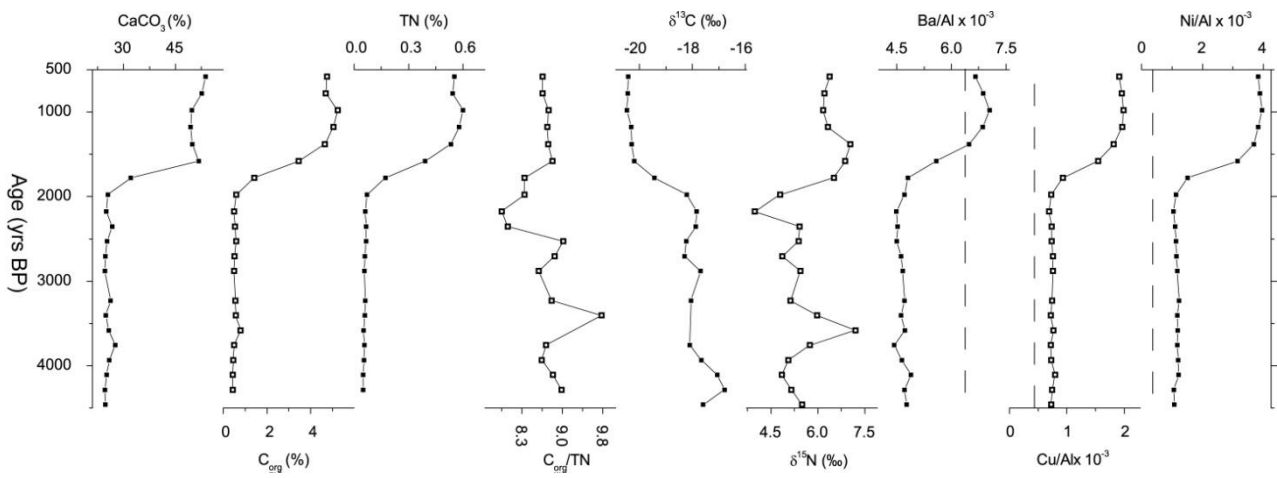


Figure 3

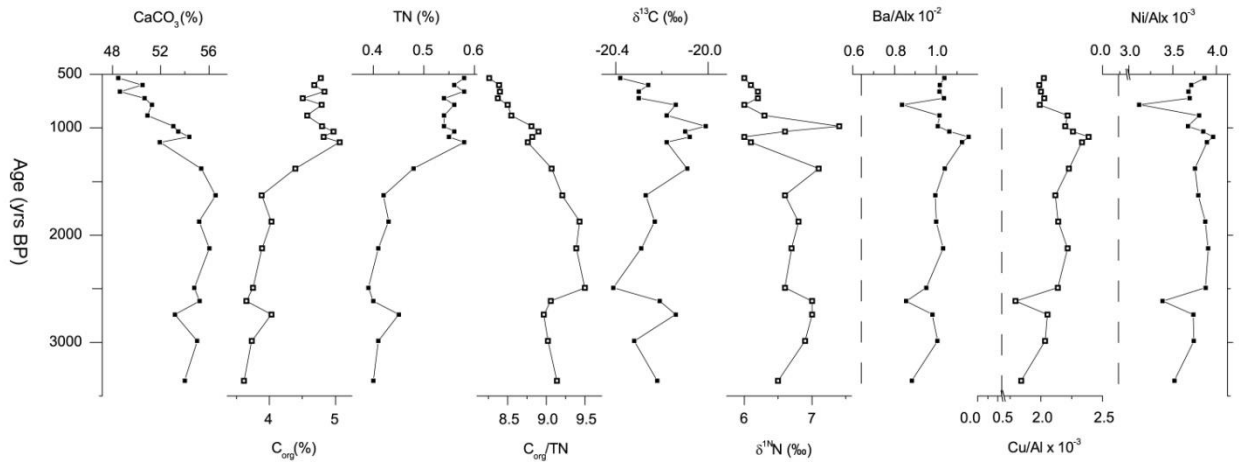


Figure 4

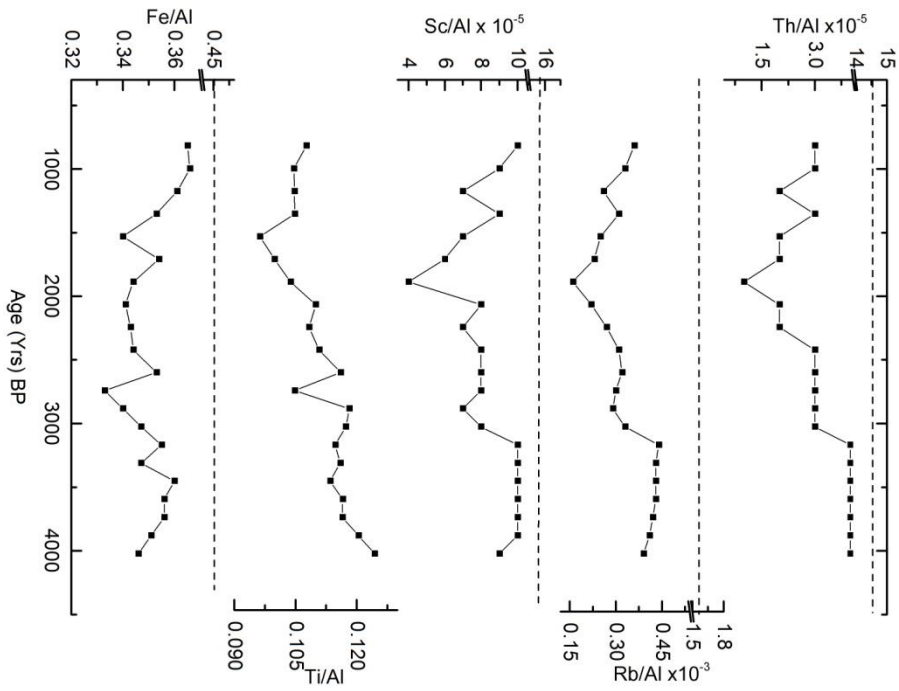


Figure 5

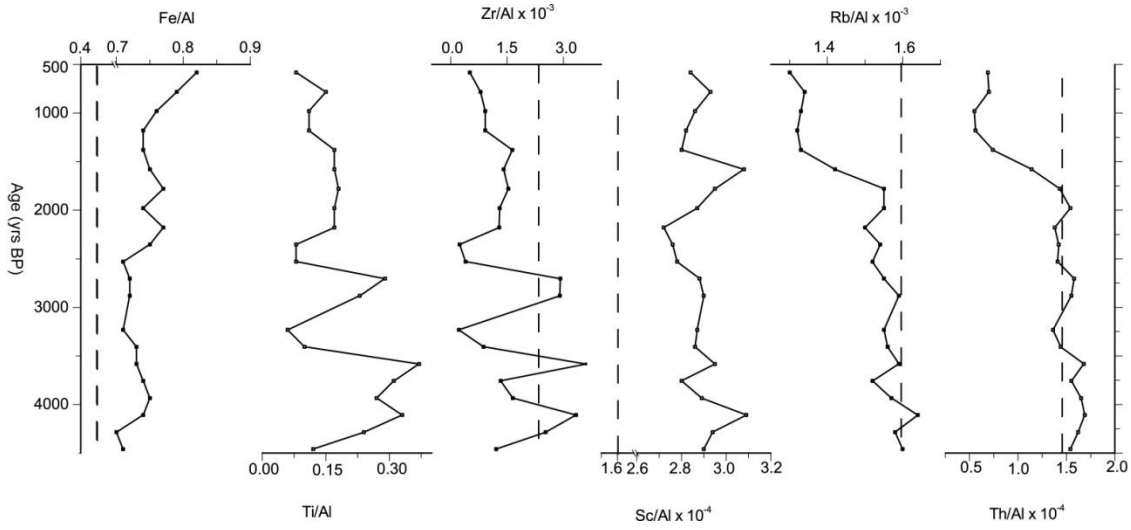


Figure 6

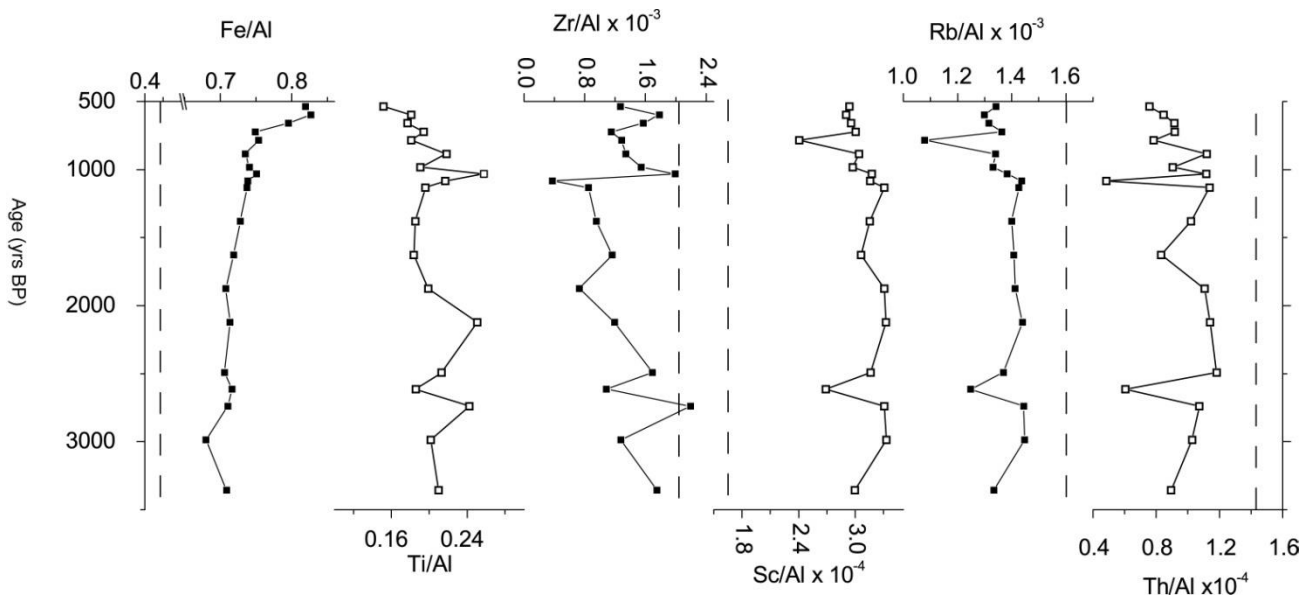


Figure 7

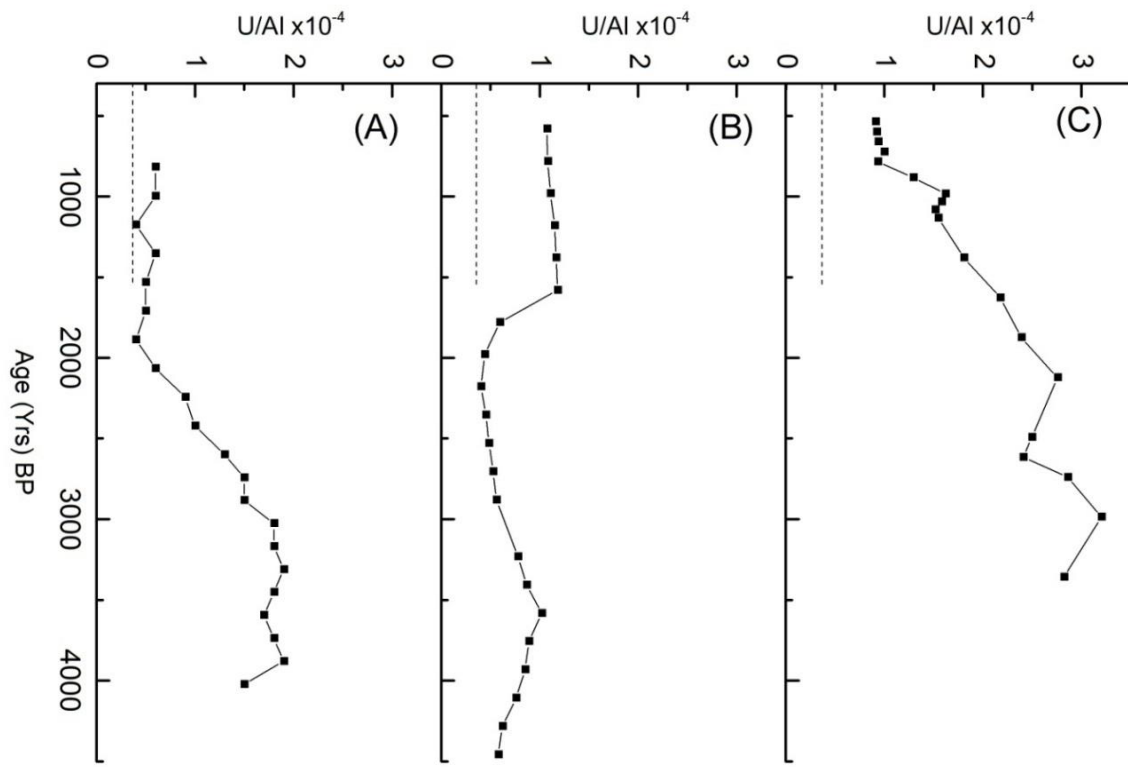


Figure 8



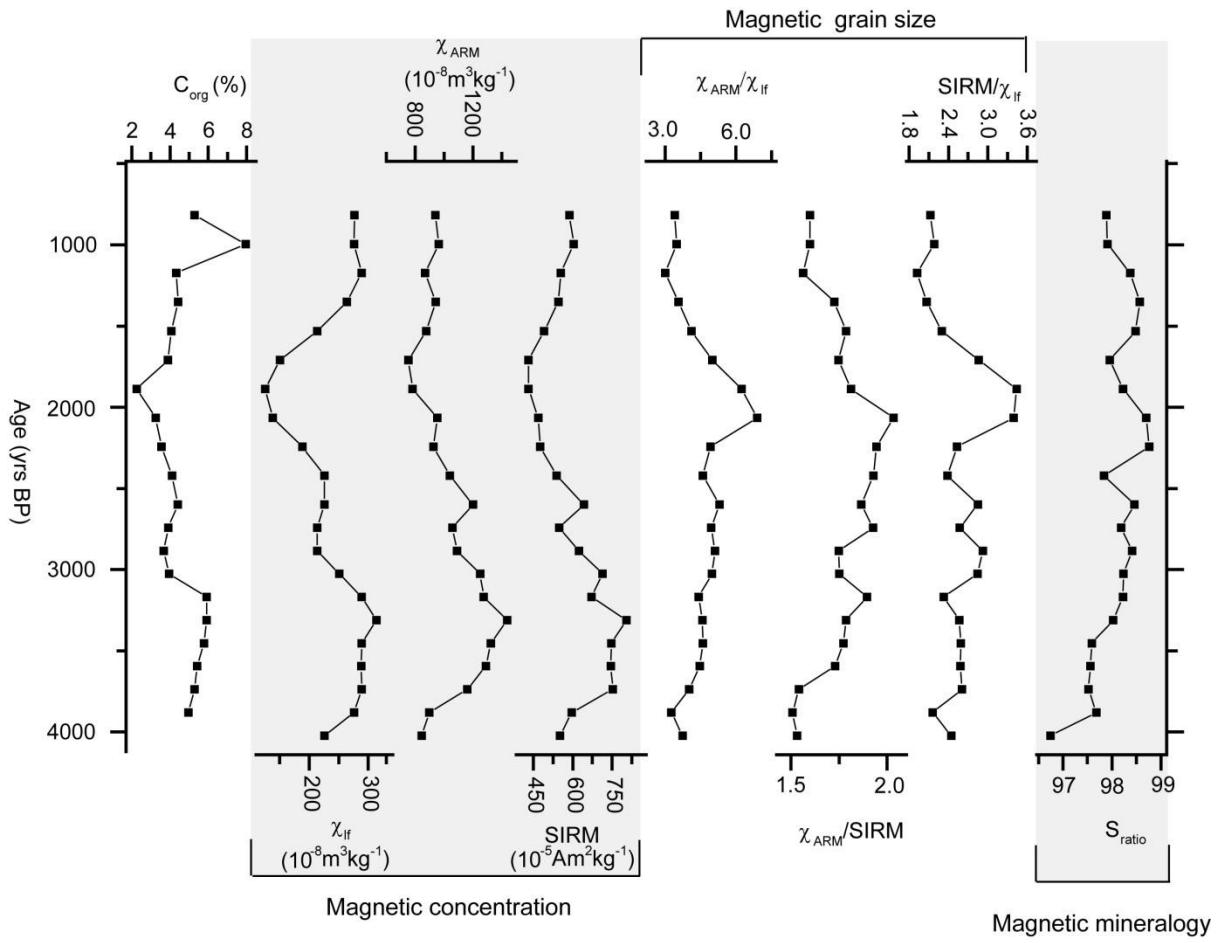


Figure 9A

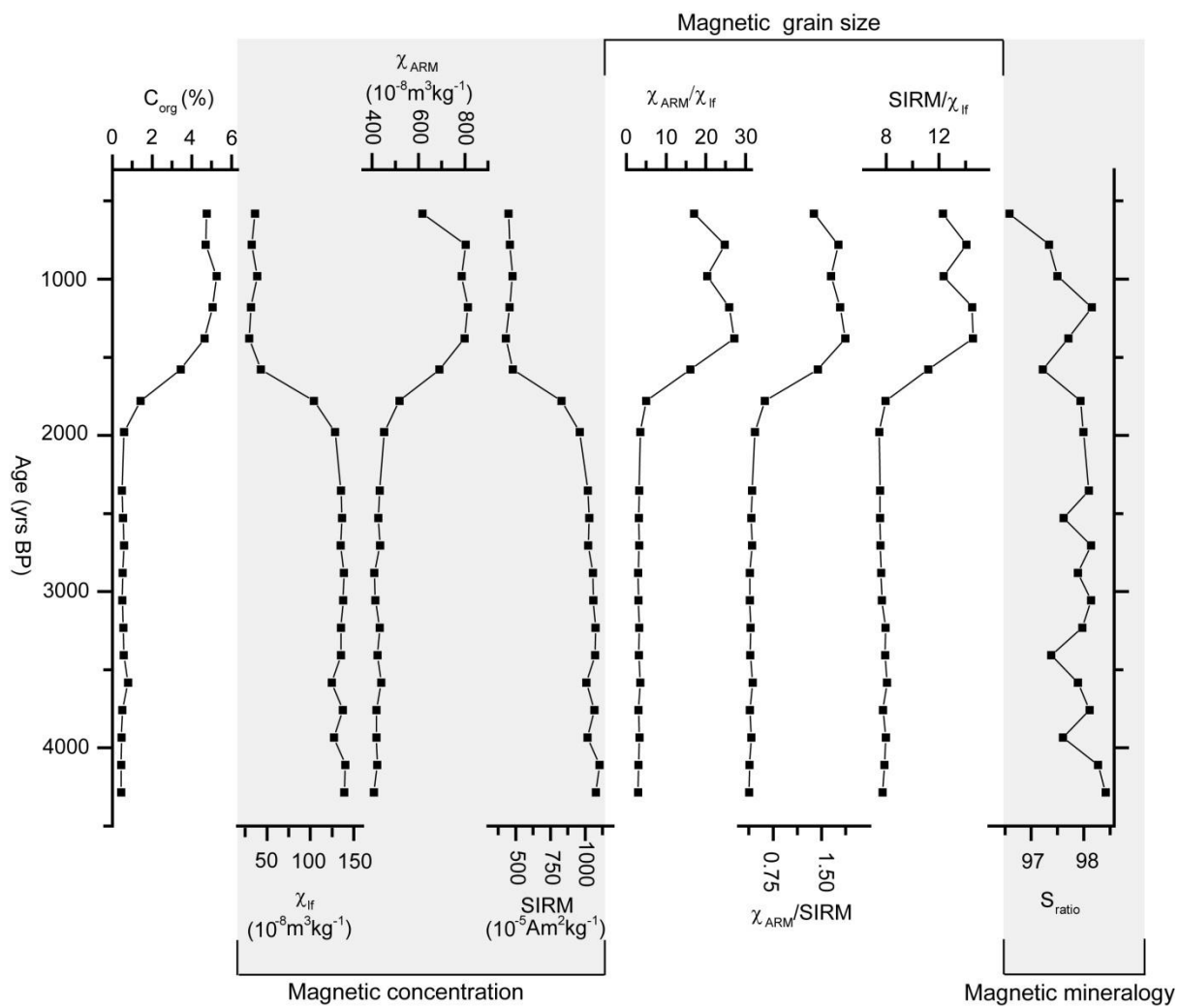


Figure 9B

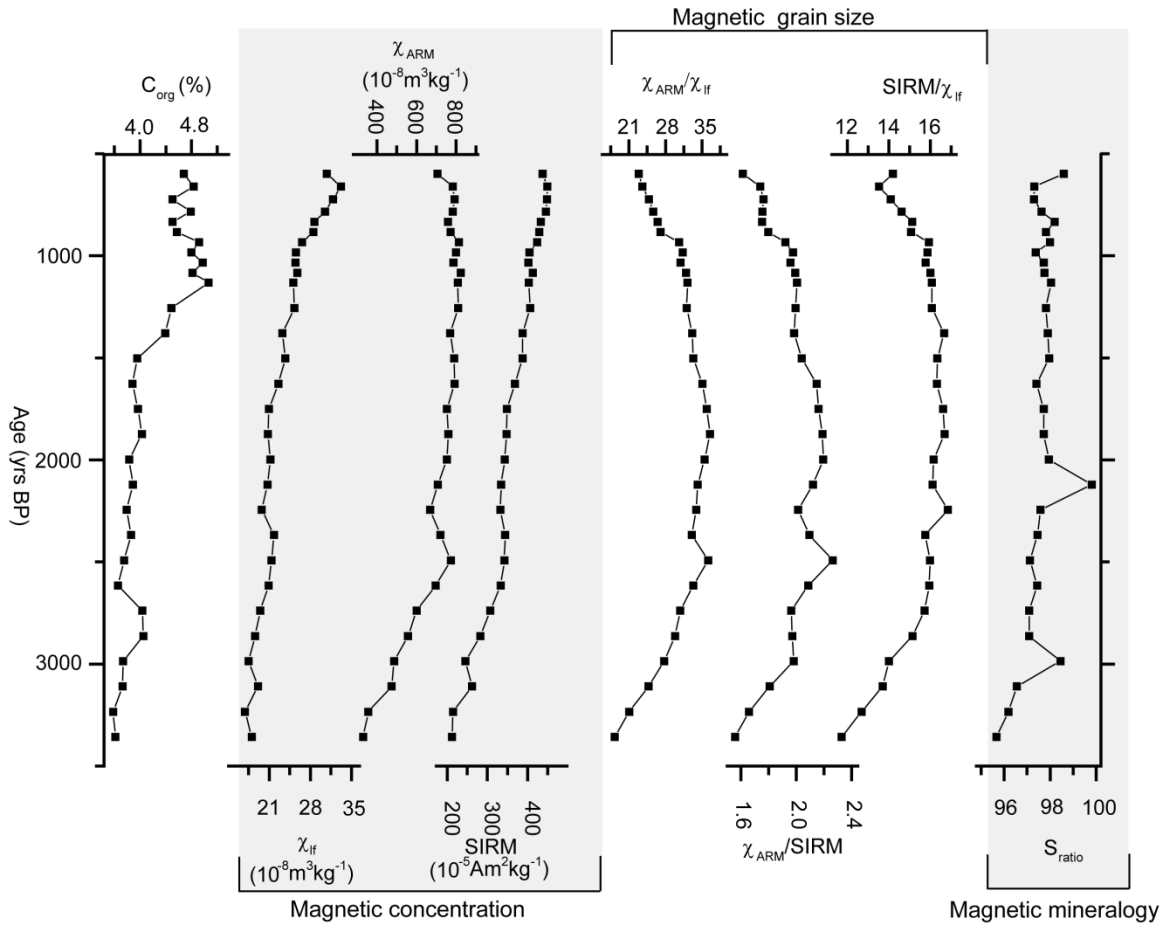


Figure 9C