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**Variability of subsurface denitrification and surface productivity in the coastal eastern Arabian Sea over the past seven centuries**

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## **Abstract**

Temporal variations over the last ~700 years in surface productivity and subsurface denitrification in the coastal eastern Arabian Sea (off Goa), a hydrographically unique environment that experiences seasonal near-bottom anoxia, have been investigated using multiple geochemical and isotopic proxies. The results suggest that surface productivity was much lower than it is today during all major solar minima during this period, but subsurface denitrification appears to have weakened substantially only during ~1650 to 1750 AD, within the period of the Little Ice Age (LIA; from ~1500 to 1750 AD), most probably due to a less vigorous upwelling associated with a decreased southwest monsoon strength. The proxy data indicate that the productivity during the last ~150 years (the Anthropocene) has been higher than ever before in the past 700 years, and water column measurements demonstrate that the region currently experiences extremely intense denitrification; yet, the nitrogen isotopic ratio in sedimentary organic matter ( $\delta^{15}\text{N}$ ) exhibits a moderately declining trend during the Anthropocene. This is ascribed to dilution by terrestrial sources and/or to small isotopic effect associated with vigorous denitrification that removes all nitrate with possibly additional inputs of light nitrogen through fixation by the diazotrophs that is probably tightly coupled to denitrification. Thus, our results reveal limitation of sedimentary  $\delta^{15}\text{N}$  as a proxy for paleo-denitrification despite excellent preservation of organic matter in coastal sediments.

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**Keywords:** Arabian Sea, Indian shelf, Biological productivity, Denitrification, Anthropogenic impact, Little Ice Age

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## 1. Introduction

The Arabian Sea, eastern tropical North Pacific (ETNP) and eastern tropical South Pacific (ETSP) are three major regions in the open ocean having suboxic (=denitrifying) intermediate waters as a combined consequence of poor reoxygenation and high downward flux of organic matter (OM) (Codispoti et al., 2005). Water column denitrification [(heterotrophic conversion of nitrate ( $\text{NO}_3^-$ ) to elemental nitrogen ( $\text{N}_2$ )] in these oxygen deficient zones (ODZs) produces large N isotope fractionation ( $\epsilon \sim 20\text{-}30\text{‰}$ ), preferentially channeling  $^{14}\text{N}$  into  $\text{N}_2$  and leaving the residual  $\text{NO}_3^-$  enriched with  $^{15}\text{N}$  (Liu and Kaplan, 1989; Brandes et al., 1998; Altabet et al., 1999; Voss et al., 2001). As the isotopically heavier  $\text{NO}_3^-$  is brought up to the surface through upwelling and vertical entrainment through mixing, and assimilated by the phytoplankton, the OM produced is characterized by a higher  $^{15}\text{N}/^{14}\text{N}$  ratio than in areas that do not have pronounced ODZs. Under conditions of complete surface  $\text{NO}_3^-$  utilization, the OM undergoing sedimentation ultimately affixes this enriched  $^{15}\text{N}$  signature on the underlying sediments (Altabet et al., 1995). The available data sets on  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in water column and of organic nitrogen in suspended particulate matter (Montoya and Voss 2006), sinking particles and surficial sediments (Schäfer and Ittekkot, 1995) confirm that this phenomenon occurs on a regional scale. Accordingly, sedimentary  $\delta^{15}\text{N}$  has thus been widely used as a tool to track past changes in subsurface denitrification (Altabet et al., 1995, 1999, 2002; Ganeshram et al., 2000; Suthhof et al., 2001; Agnihotri et al., 2003a).

Due to its potential to greatly and rather rapidly alter the oceanic combined N inventory (Codispoti et al., 2001; Altabet, 2006), denitrification in the ODZs of the Arabian Sea, ETNP and ETSP may play an important role in modulating climatic changes through controls on biological productivity and associated atmospheric carbon dioxide sequestration on the millennial or higher time scales (Altabet et al., 1995, 1999, 2002; Ganeshram et al., 1995; 2000). Moreover, high-resolution sedimentary  $\delta^{15}\text{N}$  data from Peru margin (ETSP) and the Arabian Sea suggest that the centennial to millennial scale natural variability in subsurface denitrification in these regions might have influenced global inventory of atmospheric  $\text{N}_2\text{O}$  (a potent greenhouse gas) during recent geological past (Suthhof et al., 2001; Agnihotri et al., 2006).

In addition to the above-mentioned naturally-formed, perennial ODZs, human activities are causing the emergence of new oxygen-depleted systems in shallow coastal areas

and intensification of naturally existed ones through eutrophication and/or modification of coastal hydrography and subsurface circulation (Rabalais and Turner, 2001; Grantham et al., 2004). The most important shallow ODZ of the latter category is found in the northern Indian Ocean. This is because this region contains about 2/3 of the global continental margin area in contact with bottom waters having oxygen contents  $< 0.2 \text{ mL L}^{-1}$  ( $9 \mu\text{M}$ ) (Helly and Levin, 2004). Seasonal oxygen-deficiency over the western Indian continental shelf has been known for nearly half a century (Banse, 1959; Carruthers et al., 1959). However, recent observations, especially the recurrence of previously unrecorded sulphate reduction every year since 1998 over the inner shelf off Goa, have been taken to argue for an intensification of the shallow ODZ in response to enhanced fertilizer loading from land (Naqvi et al., 2000; 2006a,b). Nevertheless, the possibility that the observed change might be a part of the natural variability on decadal/centennial time scales, related to subtle shifts in hydrography and circulation (upwelling and/or stratification), cannot be ruled out. Several high resolution records have been published recently from various upwelling zones of the northern as well as southern hemisphere showing significant decadal to centennial scale climate oscillations; these are believed to have been induced by solar irradiance variability (von Rad et al. 1999; Agnihotri et al., 2002; Gupta et al., 2003; Agnihotri et al., in review). Using specific biomarkers and other conventional productivity indices (e.g.  $C_{\text{org}}$  and  $\text{CaCO}_3$ ) in a shallow sediment core raised from the western continental shelf of India Kurian et al. (submitted) found that surface productivity has indeed varied in unison with solar irradiance during the last seven centuries and appears to be currently at its all time maximum. The exact physical mechanism involved in the observed coupling between solar irradiance changes at the top of the atmosphere and upwelling stimulated surface productivity in coastal waters is still not absolutely clear; however, solar influence on seasonal migration of ITCZ from its mean latitudinal position, coupled with changes in regional evaporation-precipitation balance, is a possible explanation (Agnihotri and Dutta, 2003; Higginson et al., 2004; Agnihotri et al., in review). Stratospheric modulation of upwelling in the equatorial troposphere, which produces a north-south seesaw of convective activity during seasonal migration of ITCZ from northern to southern hemisphere, is another plausible process (Kodera, 2004).

In this communication, we address the issue of how the subsurface redox environment/ denitrification intensity over the Indian shelf has varied during the past few centuries. This question is of considerable importance in the context of future evolution of the coastal biogeochemical environment and ecosystems in response to the impending global

warming, given its potentially large impact on both socio-economics of coastal communities (e.g. effect on fisheries – Naqvi et al., 2006a) and on climate [possible positive feedback through enhanced production of nitrous oxide (N<sub>2</sub>O) – Naqvi et al., 2000].

## 2. Study site, Chronology, Material and Methods

The gravity core CR-2 was raised from the inner shelf region off Goa (Lat. 14.9°N, Long. 74° E; water depth ~45 m) in the eastern Arabian Sea (Figure 1). Coastal circulation in the region, as in other parts of the northern Indian Ocean, undergoes a complete biannual reversal (in April and October) associated with the monsoons (Shetye and Gouveia, 1998; Naqvi et al., 2006a,c). In winter (northeast monsoon), the West India Coastal Current (WICC) flows poleward causing downwelling off the west coast of India and well-oxygenated water column over the shelf. In contrast, circulation in summer (southwest monsoon) is typical of an eastern boundary – an equatorward flowing WICC, a poleward undercurrent and coastal upwelling. What makes this region unique, apart from the seasonally reversing WICC, is that it receives enormous rainfall (~300 cm in just four months in Goa). The resultant large freshwater input creates a warm, low-salinity lens that often caps the upwelled water leading to strong near-surface thermohaline stratification, as exemplified by the vertical profiles of salinity and temperature at the coring site (Figure 3). Due to the high nutrient concentrations in the freshly upwelled water, the productivity is still quite high despite the stratification (Naqvi et al., 2006c). The consequently high oxygen demand for respiration of the copious organic matter produced by phytoplankton leads to the development of very intense oxygen deficiency very close to the surface (Figure 3). As the sub-pycnocline water loses all of its dissolved oxygen by August, denitrification sets in, and once the dissolved NO<sub>3</sub><sup>-</sup> is also exhausted, sulphate reduction takes over in the inner and mid-shelf regions. The low NO<sub>3</sub><sup>-</sup> concentrations together with moderately high nitrite levels in the sub-pycnocline layer are indicators of intense denitrification at the time the core was collected.

Core CR-2 is of 1-m length in which the top layer was apparently well-preserved (i.e. the overlying water was clear and did not have unusually high ammonium concentration that happens if the upper layer gets resuspended). It was immediately sub-sampled into 2-cm long slices that were freeze-dried for various geochemical and isotopic analyses. Specific biomarkers (dinosterol, phytol, stigmasterol and β-sitosterol) were measured in this core (Kurian et al., submitted). The core was first dated by the <sup>210</sup>Pb<sub>xs</sub> method (eg. Sharma et al.,

1994). A systematic decrease of normalized excess  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{xs}}/\text{Al}$ ) with depth was found between core top to 20-22 cm depth-interval, yielding a linear sedimentation rate of 1.5 mm/yr. Assuming the core top to correspond to the year of collection (2005 AD) and using a linear sedimentation rate of 1.5 mm/yr, an age-depth model was constructed for the last ~150 years. If one extends this age-depth model to the entire core length, the time period covered would be ~660 years with an average sampling resolution of ~13 years. AMS  $^{14}\text{C}$  dating of bulk organic matter from the 97-99 cm level yielded an age of  $900 \pm 66$  ( $1\sigma$ ) Cal yr BP (Figure 1, inset). Given the uncertainties involved in both techniques, two ages are quite close.

An excellent covariance was found between the downcore records of the major biomarkers especially dinosterol, and other organic proxies (based on  $^{210}\text{Pb}$  derived age model), and the Sunspot number time-series during the last ~250 years [adapted from [www.ncdc.noaa.gov/paleo/forcing.html](http://www.ncdc.noaa.gov/paleo/forcing.html)] (see Figure 2, adapted from Kurian et al. submitted). In addition, at deeper levels, beyond the range of  $^{210}\text{Pb}$  dating (last ~150 years), the dinosterol record is remarkably similar to that of reconstructed Total Solar Irradiance (TSI) (Bard et al., 2000) except that the extrema in the former appear to be a little younger. We therefore revised the  $^{210}\text{Pb}$ -derived age model by matching the extrema in two records and assigning the TSI-based ages to the major dinosterol extrema. Using a binomial best-fit ( $r^2 = 0.98$ ) to the depth vs TSI-derived age, ages were recalculated for the entire core (Figure 1, inset). The estimated age of the deepest sample was thus found to be ~720 yr, which is intermediate of the  $^{210}\text{Pb}$  and  $^{14}\text{C}$  based ages, providing further confidence in our tuned age-depth model.

The freeze-dried sediment was powdered using an agate mortar for chemical and isotopic studies. Measurements of  $\text{CaCO}_3$  were carried out using a coulometer (Bhushan et al., 2001) with a precision better than <2%. For measurements of  $\text{C}_{\text{org}}$  and N contents and the C/N (wt/wt) ratio in sedimentary organic fraction, sediment samples were treated with 1N HCl to remove carbonate, washed thoroughly with deionized water and dried. The  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  were measured together with  $\text{C}_{\text{org}}$  and N contents and the C/N ratio using an isotope ratio mass-spectrometer (Delta V plus; ®Thermo) coupled with an Elemental Analyzer (EA) in a continuous flow mode. About 8-12 mg of decalcified dried sediment samples were packed in tin cups and then flash combusted in EA at 1050°C. Evolved  $\text{CO}_2$  and  $\text{NO}_x$  were then passed over a reduction column containing reduced Cu at 670°C and were finally purified and separated with a GC at 50°C before being introduced to the mass-spec. Calibrations for  $\text{C}_{\text{org}}$  and N contents and their isotopes were carried out using a laboratory

standard (n-Caprioic acid, C<sub>6</sub>H<sub>15</sub>NO<sub>2</sub>; ACA) following Higginson and Altabet (2004). Analytical precision of  $\leq 2\%$  for C<sub>org</sub> and N contents was achieved using several international and in-house lab standards throughout the analyses. The overall uncertainties involved in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  measurements (including sample preparation and analysis) were better than 0.2‰. Carbon and nitrogen isotopic ratios of sedimentary organic matter are expressed as  $\delta$  values ( $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$ ) with reference to V-PDB and atmospheric N<sub>2</sub> respectively.

$$\delta^{13}\text{C}_{\text{org}} \text{ and } \delta^{15}\text{N} = ((R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}) \times 1000 \text{ -----(1)}$$

where R = <sup>13</sup>C/<sup>12</sup>C and <sup>15</sup>N/<sup>14</sup>N

For analyses of major and trace elements, bulk sediments (~100 mg) were microwave digested in an acid mixture of HNO<sub>3</sub>, HF and HCl and final solutions were made in 1N HCl and measured using an Inductively-coupled atomic emission spectrometer (ICP-AES, Liberty Plasma II, ®Varian), while Cu was measured using an atomic absorption spectrophotometer (AAS, Perkin-Elmer). Accuracy and precision were checked using several USGS standards (eg. MAG-1, SDO-1 and SCo-1). Uncertainties involved for the measured elements are 2-5%.

### 3. Results and discussion

Data on established proxies of productivity and stable isotope ratios in core CR-2 are presented in Table 1, while major and trace element data are listed in Table 2. The  $\delta^{13}\text{C}_{\text{org}}$  values vary within a narrow range, from  $-21.4$  to  $-20.5$  ‰, while  $\delta^{15}\text{N}$  values range from  $-6$  to  $7.8$ ‰. C<sub>org</sub> and N contents vary from 2.32 to 3.4%, and from 0.24 to 0.40%, respectively. C/N ratios are between 8.5 and 10.5, well within the reported range for marine sedimentary organic matter in the northeastern Arabian Sea ( $8 \pm 2$ ; Reichart, 1997; Bhushan et al., 2001). Changes in inorganic productivity were inferred from CaCO<sub>3</sub> content that varies from  $\sim 4$  to 13.5%. Since the abundances of most of trace elements are controlled by both biogenic and detrital components, in order to investigate changes that are not caused by variations in detritus supply, concentrations of these elements are normalized with that of Al (Calvert and Pedersen, 1993; Reichart, 1997; Agnihotri et al., 2003a).

#### 3.1 Surface productivity during the last ~700 years

Figure 4 shows downcore records of the productivity-related variables, *viz.* C<sub>org</sub>, N, and CaCO<sub>3</sub> contents along with nutrient type elements (Cu and Ni), with the depth scale

transformed to the scale of time of sediment deposition (year AD) using the tuned age-depth model described above. Using major bulk productivity indicators ( $C_{org}$  and  $CaCO_3$ ) along with specific biomarker of marine origin, it has been shown that surface productivity, supported by monsoon upwelling, varied in unison with the Sunspot activity/solar irradiance forcing during the last ~700 years (Figure 2; Kurian et al, submitted). Downcore changes in  $CaCO_3$  closely follow those in  $C_{org}$  and N (Figure 4a,b,c) suggesting a close covariance of the organic and inorganic (calcareous) productivity in the region during the deposition period. Both records display prominent minima during ~1650-1750 AD within the time span of the LIA (~ from 1500 to 1750 AD). We do not have porosity data for the core for computing the accumulation rates. As our tuned age model provides almost linear sedimentation rate (Figure 1) and  $CaCO_3$  content varies with a narrow range ( $8 \pm 2$  % with a maximum of 13%), the dry bulk density derived from the sedimentary  $CaCO_3$  content (Snoeckx & Rea, 1994) yields similar depthwise distribution patterns of accumulation rates of major proxies such as  $C_{org}$  and N as observed for their concentrations. Moreover, there has been no large change in the nature (source) of detritus during the entire deposition period (~700 years) as inferred from narrow ranges observed in Fe/Al ( $0.78 \pm 0.04$ ) or Mg/Al ( $0.32 \pm 0.02$ ) (data not shown). Therefore, sedimentary concentrations of  $C_{org}$  and N can be taken to reflect surface productivity changes (Agnihotri et al., 2002).

In addition to aforementioned conventional productivity indicators ( $C_{org}$ , N, and  $CaCO_3$ ), non-detrital components of trace elements *viz.* Cu and Ni can also be used as productivity proxies. These elements act as micronutrients which are removed from surface waters during plankton growth and liberated from settling organic debris in the sub-surface waters (Calvert and Pedersen, 1993). In anoxic (sulphidic) sedimentary conditions these elements also precipitate as their respective sulphides (Sirocko et al., 2000). In core CR-2, however, Cu and Ni do not show any significant excesses over their detrital components (Figure 4e,f). This may be because the free sulphide concentrations in pore waters in the inner shelf off Goa are surprisingly low (S.W.A. Naqvi, unpublished data). Nevertheless, some accumulation of these nutrient-like elements in sediments should be expected during periods of high productivity such as the last ~150 years. The Cu record does provide some evidence for this phenomenon (Figure 4e). In order to investigate changes in the non-detrital component of phosphorus (P), a major macronutrient, we normalized the P content with Al. In core CR-2, P/Al ratio (by weight) varies from 205 to  $249 \times 10^{-4}$  consistently higher than its average shale value ( $\sim 88 \times 10^{-4}$ ; Turekian and Wedepohl, 1961) thereby suggesting dominant



presence of non detrital P. A visual covariance can be seen in P/Al and C<sub>org</sub> records of CR-2 (Figure 4d).

### 3.2 Variations in sub-surface denitrification and redox conditions

Figure 5 shows depth-profiles of paleo- redox-variables, viz.  $\delta^{15}\text{N}$  (an index for sub-surface denitrification) and non-detrital components of redox-sensitive elements viz. Mn, Cr, and V. Downcore records of  $\delta^{13}\text{C}_{\text{org}}$  and C/N (wt. ratio) were used to look for changes, if any, in the nature of sedimentary organic matter. The  $\delta^{15}\text{N}$  of sedimentary OM is a well-tested tool for tracking past changes in water column denitrification, especially in the rapidly accumulating sediments that experience high surface productivity (Altabet et al., 1999, 2002; Ganeshram et al., 2000; Suthhof et al., 2001; Agnihotri et al., 2003a, 2006). The  $\delta^{15}\text{N}$  of particulate organic matter (POM) is a function of the  $\delta^{15}\text{N}$  of source  $\text{NO}_3^-$  and fractionation that occurs during its uptake by phytoplankton (when  $\text{NO}_3^-$  is not fully utilized). The  $\delta^{15}\text{N}$  of dissolved  $\text{NO}_3^-$  in the seawater is on an average  $\sim 5\text{‰}$  (Altabet, 2006), but in the perennial suboxic zone of the central Arabian Sea ( $\sim 150\text{-}600\text{ m}$ ; Naqvi, 1987), denitrification results in  $\delta^{15}\text{N}$  values as high as  $15\text{-}18\text{‰}$  (Brandes et al., 1998; Altabet et al., 1999). As most of the new nitrogen fuelling primary production in the euphotic zone is derived from the subsurface layers (Naqvi et al., 2007), the suspended and sinking organic matter as well as surficial sediments are characterized by elevated  $\delta^{15}\text{N}$  values all over the Arabian Sea where the upwelled  $\text{NO}_3^-$  is fully consumed on an annual basis (Schäfer and Ittekkot, 1995; Gaye-Haake et al., 2005; Montoya and Voss, 2006). Variations in  $\delta^{15}\text{N}$  in numerous cores raised from the continental slope, seamounts and abyssal plain in the Arabian Sea have revealed that large enrichment of  $\delta^{15}\text{N}$  in sediments has been prevalent not only throughout the Holocene, but also during all interglacial periods over the past 1 Ma. In contrast, lighter isotopic values ( $\sim 5\text{-}6\text{‰}$ ), comparable to those found in non-reducing environments today, characterize sediments that accumulated during the glacial stages indicating that denitrification weakened or was absent during such periods (Altabet et al., 1995, 1999, 2002; Ganeshram et al., 1995, 2000; Suthhof et al., 2001). Higher resolution records indicate variations on an even shorter (millennial) time scale, closely linked with the climatic changes recorded by the Greenland ice cores (Suthhof et al., 2001; Altabet et al., 2002). For example, the  $\delta^{15}\text{N}$  records in two sediment cores from the Oman Margin generated by Altabet et al. (2002) show oscillations that are remarkably similar in structure and timing to the Dansgaard/Oeschger events

recorded in the Greenland (GISP2) ice cores. High resolution records of the Holocene, such as those recently analyzed by Altabet (2006) are not available from the Arabian Sea. Our CR-2 record is, in fact, the first one from the continental shelf anywhere in the Indian Ocean.

As evident from the water column data (Figure 3) the coring site is presently affected by intense denitrification, albeit seasonally; however, this is not reflected in the near core-top  $\delta^{15}\text{N}$  that averages only 6.6‰ in the upper 5 cm (Table 1, Figure 5a). Sedimentary  $\delta^{15}\text{N}$  at this location appears to have decreased slightly but steadily over the 150-200 years (the upper shaded portion in Figure 5). This is inconsistent with the trend exhibited by the productivity proxies e.g.  $C_{\text{org}}$  (Figure 4a), and even more so in dinosterol (Figure 3; Kurian et al., submitted) that suggest an increase in productivity over the same period. There are several possible explanations of this counterintuitive observation: (i) Dilution of the  $\delta^{15}\text{N}$  signal by inputs of terrestrial organic matter containing isotopically lighter nitrogen; (ii) Inputs of lighter inorganic combined nitrogen of anthropogenic origin leading to the production of organic matter with lower  $\delta^{15}\text{N}$ . Note that possibility (i) also requires a decrease in the  $\delta^{13}\text{C}_{\text{org}}$  and an increase in C/N, which are not observed in Figure 5, whereas possibility (ii) only requires a decrease in  $\delta^{15}\text{N}$ . (iii) The sedimentary  $\delta^{15}\text{N}$  may not proportionately reflect the degree of water column denitrification because the isotopic fractionation factor in coastal suboxic zone may be significantly different (lower) than in the perennial suboxic zone of the open ocean (Naqvi et al., 2006b) and/or as denitrification often leads to complete removal of  $\text{NO}_3^-$  from the water column (Naqvi et al., 2000, 2006a,b), the impact of the process on the sedimentary  $\delta^{15}\text{N}$  may not be very large, and (iv) The region is well known for the occurrence of *Trichodesmium* blooms. Fixation of light nitrogen by these and possibly other diazotrophs would compensate for the heavy isotope enrichment by denitrification. It may be pointed out that denitrification and  $\text{N}_2$ -fixation are coupled since the latter produces excess phosphate that is expected to stimulate the growth of diazotrophs (Deutsch et al., 2007; Naqvi, 2007); moreover, other limiting elements for  $\text{N}_2$ -fixation (mainly iron) are expected to be present in high concentrations in the coastal waters. The available data sets do not allow us to evaluate the relative importance of these various possibilities.

Despite the above-mentioned complexities, that limit the application of sedimentary  $\delta^{15}\text{N}$  as a reliable paleo-denitrification tool in coastal marine environments, the  $\delta^{15}\text{N}$  record does, nevertheless, show overall similarities with those of the productivity proxies and TSI curve during much of the time period covered by the core barring the Anthropocene. The

most prominent feature of the  $\delta^{15}\text{N}$  record is the conspicuous decrease in  $\delta^{15}\text{N}$  concurrent with a decrease in organic productivity during the period from ~1650 to 1750 AD, corresponding to the time span of the LIA (~1500 to 1750 AD) (Figure 3d). Contemporaneous  $\delta^{13}\text{C}_{\text{org}}$  values vary within narrow range ( $-20.86 \pm 0.23\text{‰}$ ) that is typical of marine sedimentary OM in the Arabian Sea (Fontugne and Duplessy, 1986; Reichart, 1997) and show no obvious decrease. Similarly, the absence of an increase in the C/N ratio (Figure 3f) indicates that the negative  $\delta^{15}\text{N}$  excursion during ~1650 to 1750 AD could not have been due to dilution by terrestrial OM. Taken together these results strongly suggest that denitrification over the Indian shelf substantially weakened, probably due to a less intense upwelling and weaker stratification in response to weaker southwest monsoon, during this period. Significantly, this event is reflected in marked changes in most of the properties examined here (Figures 4 and 5).

Given the plausible weakening of monsoonal winds in the eastern Arabian Sea during the LIA (Agnihotri et al., 2002), it is also possible that water column denitrification in the Arabian Sea as a whole (coastal as well as open ocean) became less vigorous and thus the observed signal could represent a regional decrease in  $\delta^{15}\text{N}$  in  $\text{NO}_3^-$  and ultimately in the sedimentary OM. It may be pointed out that the coastal hypoxic zone only accounts for ~10% of the overall water column denitrification in the region (Naqvi et al., 2007). However, the open ocean and coastal suboxic zones are not contiguous in the region of our study and the upwelled water is derived from the West India Undercurrent that originates in the southeastern Arabian Sea/Laccadive Sea. The oxygen concentrations in the undercurrent water are not low enough for denitrification to occur (Naqvi et al., 2006a,c), and so the effect of open ocean denitrification at our core site is not expected to dominate that of local denitrification.

Another noteworthy feature of Figure 5a is an apparent absence of a long term change in sedimentary  $\delta^{15}\text{N}$ . The above-mentioned uncertainties in the interpretation of the  $\delta^{15}\text{N}$  data notwithstanding, the lack of a long-term trend probably implies a fairly stable balance between the nitrogen input and removal processes over the last seven centuries. This is consistent with the results of Altabet (2006) who also found little secular trends in sedimentary  $\delta^{15}\text{N}$  variations in other areas over the past few millennia; as discussed by him these results have important implications for the N budget that seems to be grossly out of balance in today's oceans (Codispoti et al., 2005).

Downcore records of redox-sensitive elements Mn, Cr, and V normalized to their respective crustal abundances are presented in Figure 5. Mn concentrations vary from 283 to 354  $\mu\text{g g}^{-1}$ , whereas the corresponding ranges for Cr and V are 111-151 and 59-107  $\mu\text{g g}^{-1}$ , respectively (Table 2). The average Mn/Al ratio in the core is  $44 \pm 4 \times 10^{-4}$ , which is less than half of the average shale value ( $\sim 106 \times 10^{-4}$ ; Turekian and Wedepohl, 1961). Observed lower Mn/Al ratios throughout the deposition period of the core (Figure 5d) suggest that Mn is mobilized out of the sedimentary column, a process commonly observed in reducing sediments (Somayajulu et al., 1994). Elements such as Cr and V are known to precipitate out from seawater under reducing conditions (Piper and Isaacs, 1996). The Cr/Al and V/Al ratios remain within very narrow ranges, 16-20 and 8-14  $\times 10^{-4}$ , respectively. The average value for Cr/Al ( $18 \pm 1 \times 10^{-4}$ ) is slightly higher than the average shale value of  $11 \times 10^{-4}$  but the average V/Al ( $12 \pm 1 \times 10^{-4}$ ) is lower than the shale value ( $16 \times 10^{-4}$ ). Thus, the expected enrichment in the solid phase is seen only in case of Cr. There appears a slow long-term increasing trend in both ratios, the reason for which is not clear, with no consistent excursions during the TSI extrema. It would thus appear that the changes in productivity and the redox status of the overlying water had little effect on sedimentary redox cycling – the sedimentary environment continued to remain reducing throughout the deposition period. Evidently, post depositional diagenetic alterations have not been large since such changes would drive Mn/Al and Cr/Al in opposite directions, and an anti-correlation between the downcore records of these ratios is not observed (Figure 5). Under such persistent reducing environment with almost linear sedimentation rate (Figure 1, inset), sedimentary  $C_{\text{org}}$  serves as a reliable proxy for surface productivity and hence monsoon intensity in the region. Similar behavior of these redox sensitive elements have been found in sediments underlying perennial oxygen deficient waters in the eastern Arabian Sea (Agnihotri et al., 2003a).

#### **4. Conclusions and Implications**

The present study provides the first set of sedimentary data on multiple proxies of surface productivity and subsurface denitrification spanning the last  $\sim 700$  years (with nearly decadal time resolution) from a unique marine environment in the eastern Arabian Sea that experiences both upwelling and large freshwater inputs resulting in strong seasonal near-bottom oxygen depletion. Surface productivity appears to have varied in tandem with external solar irradiance forcing. Intensity of subsurface denitrification during the pre-anthropogenic period (from  $\sim 700$  to last 150 years) appears to have been dominantly

controlled by surface productivity, but moderate decreasing trend in  $\delta^{15}\text{N}$  is seen during the Anthropocene despite increasing trend in productivity. This divergence could be due to a dilution of the sedimentary signal by the isotopically lighter nitrogen supply from land. Alternatively, the current rate of denitrification may be so high that it does not leave its heavy isotope imprint on sedimentary nitrogen. A conspicuous decrease in sedimentary  $\delta^{15}\text{N}$  during ~1650-1750 AD, a period corresponding to the LIA, points to a reduction in the intensity of subsurface denitrification coupled with lower productivity most likely induced by a weakened summer monsoon. This appears to have been a major regional event as indicated by marked excursions in most other properties as well. Overall, surface productivity at the core site seems to have remained predominantly of 'marine type' (upwelling stimulated) throughout the deposition period. An important implication of our results is that  $\delta^{15}\text{N}$  may not always serve as a proxy of subsurface denitrification in shallow suboxic zones despite conducive conditions such as rapid accumulation rates and low ambient  $\text{O}_2$  levels.

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## Figure Captions

**Figure 1:** *Location of core CR-2 and its age-depth model (inset).*

**Figure 2:** *Excellent covariance found between the downcore record of dinosterol and the solar proxies eg. Sunspot numbers, spanning last 250 years and TSI variations during the last ~700 years leads us to tune the  $^{210}\text{Pb}_{\text{xs}}$  derived age model (Figure 1 inset) (Figure adapted from Kurian et al., submitted).*

**Figure 3:** *Vertical profiles of (a) salinity and temperature, and (b) dissolved oxygen, nitrate and nitrite at the location of and time the core CR-2 was collected on 30<sup>th</sup> September 2005.*

**Figure 4:** *Temporal variability of major productivity proxies.  $C_{\text{org}}$ , N, and  $\text{CaCO}_3$  appear to vary in tandem with solar irradiance forcing during last ~700 years. P/Al ratios show reasonable covariance with organic productivity. Nutrient type element elements such as Cu and Ni do not show significant excesses over their detrital contributions.*

**Figure 5:** *N and C isotopes of sedimentary organic matter along with C/N wt. ratio in core CR-2. Sedimentary  $\delta^{15}\text{N}$  does not appear to vary in unison with surface organic productivity except during LIA and shows a moderate decreasing trend during the Anthropocene despite increasing surface productivity (Figure 4). Downcore records of selected redox sensitive elements (Mn, Cr and V) show no evidence of post-burial recycling of these elements during the deposition period.*

Figure 1:

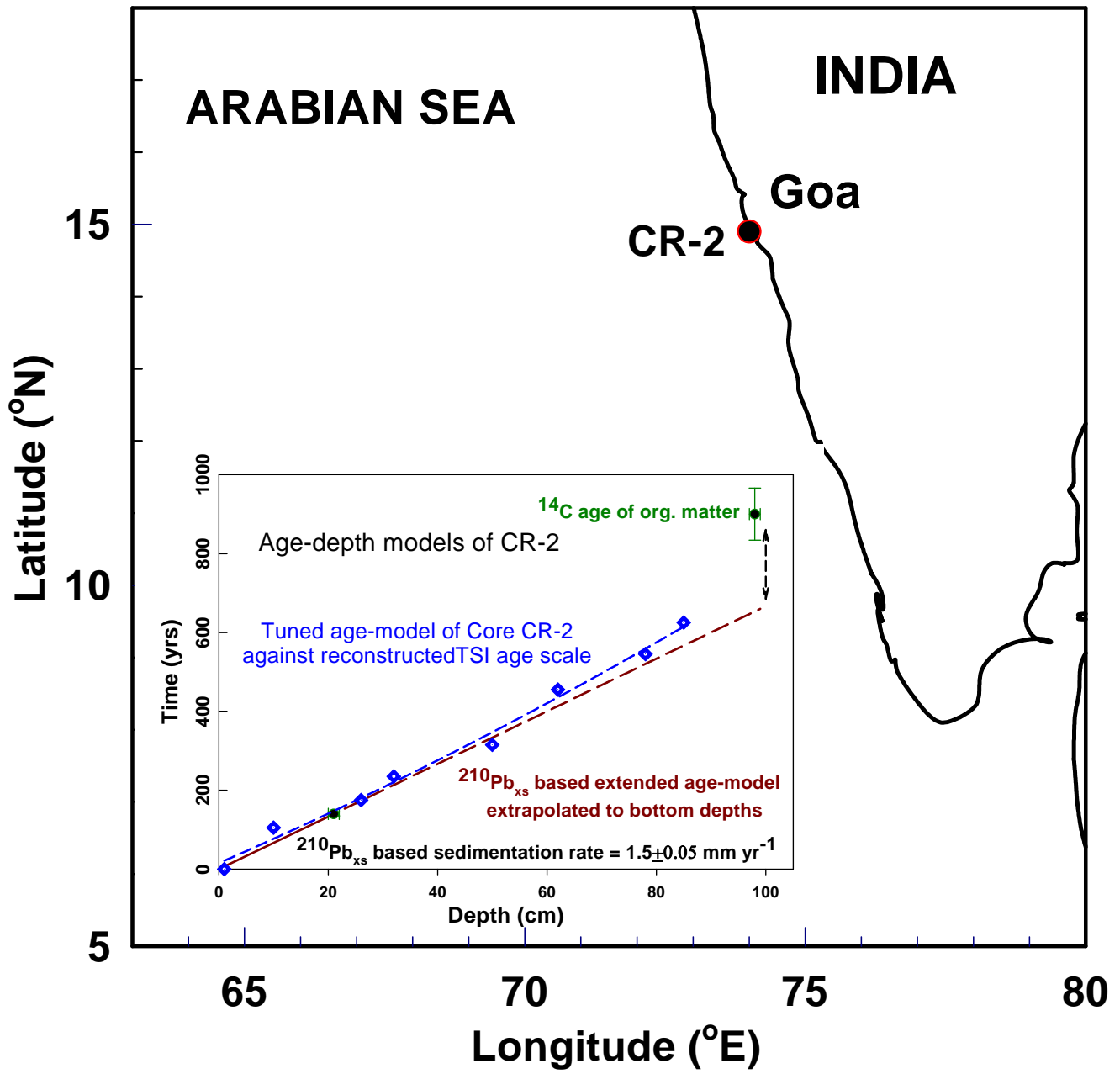


Figure 2:

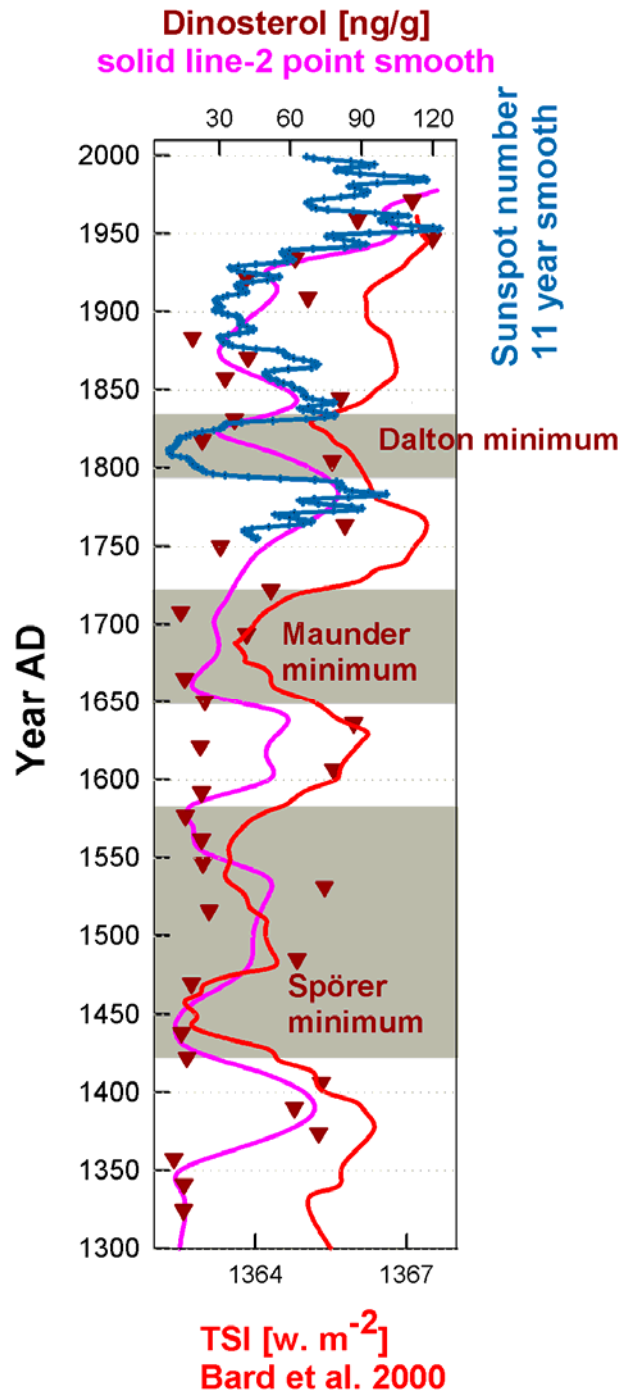


Figure 3

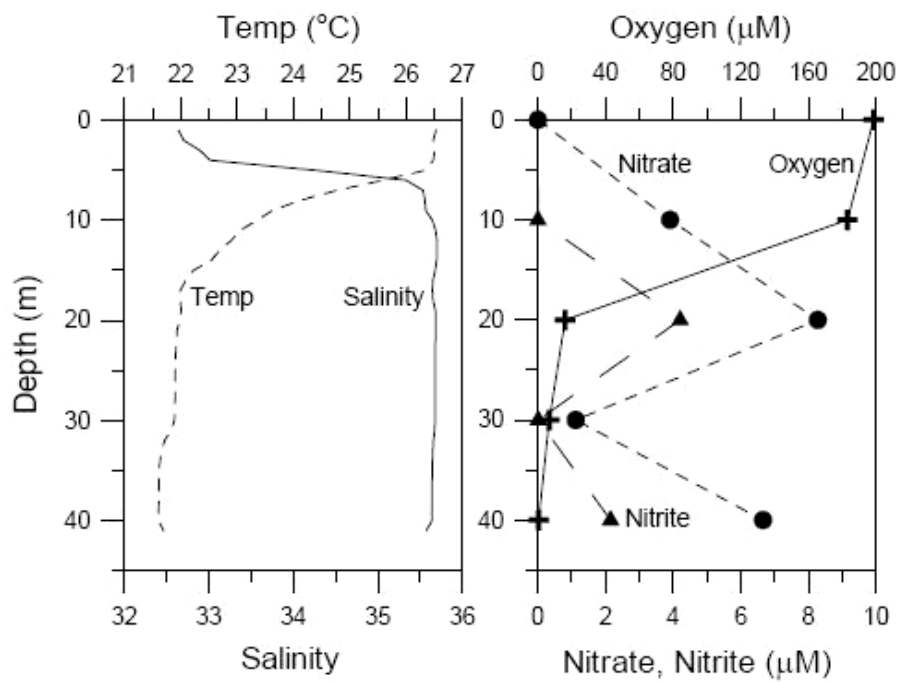


Figure 4:

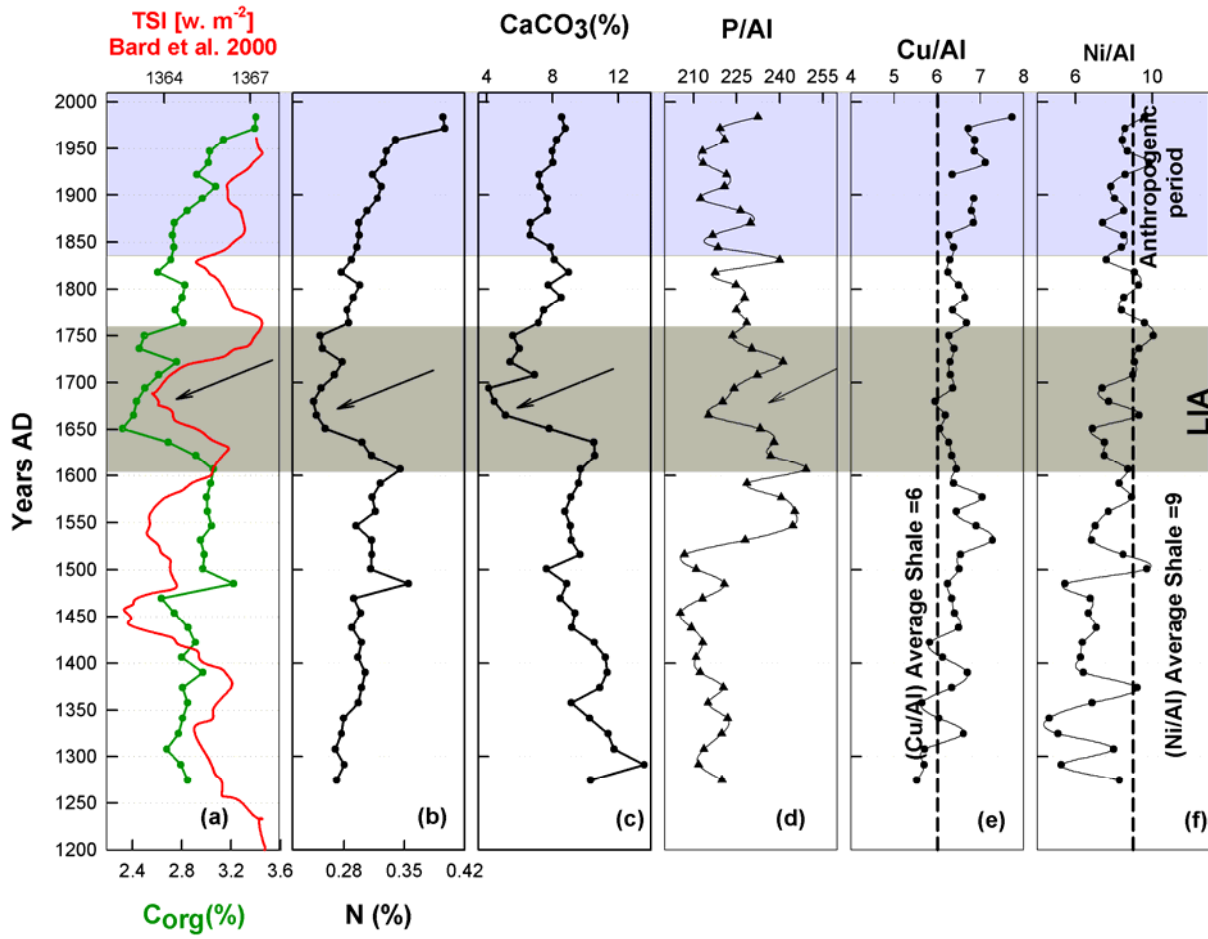


Figure 5:

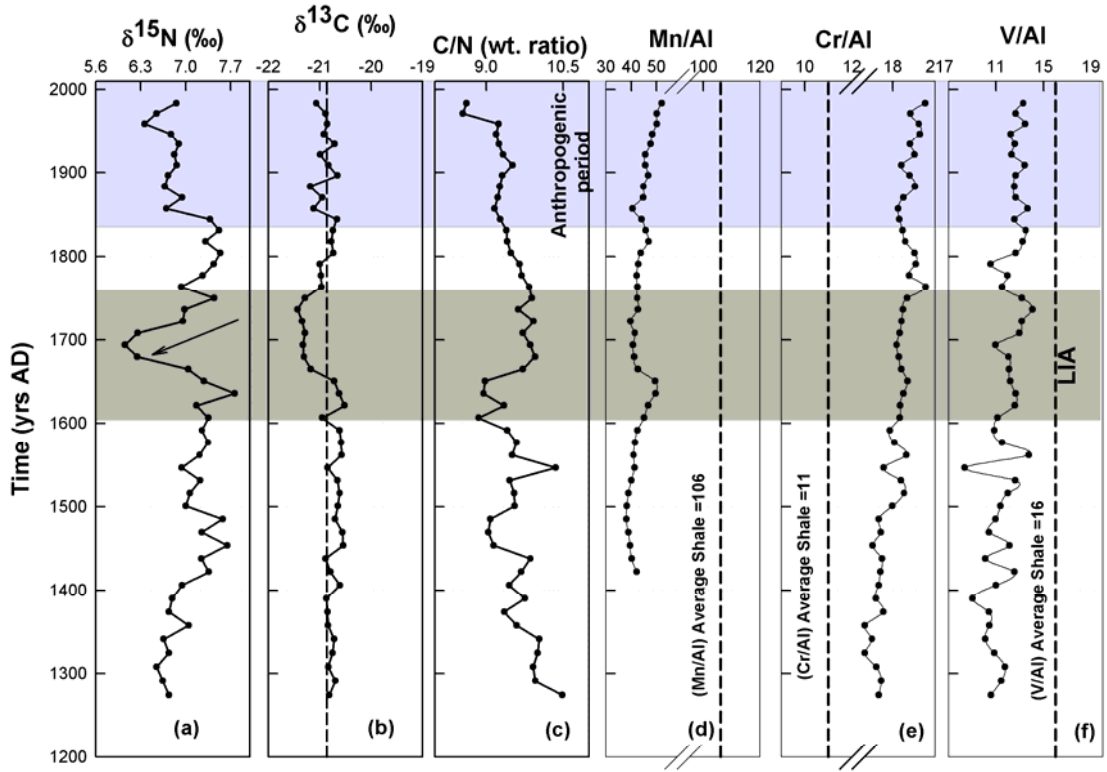


Table 1: Major bulk carriers of productivity measured in Core CR-2 along with C and N isotopes of sedimentary organic matter.

Mean depth	*C <sub>org</sub> %	N %	*CaCO <sub>3</sub> %	δ <sup>13</sup> C(‰)	δ <sup>15</sup> N(‰)	C/N
1	3.4	0.39	8.55	-21.1	6.9	8.6
3	3.39	0.4	8.77	-20.9	6.5	8.5
5	3.14	0.34	8.26	-20.9	6.4	9.2
7	3.03	0.33	7.98	-20.9	6.8	9.2
9	3.02	0.33	8.03	-20.7	6.9	9.3
11	2.92	0.31	7.18	-21.0	6.8	9.3
13	3.07	0.32	7.24	-20.8	6.9	9.5
15	2.97	0.32	7.7	-20.7	6.7	9.3
17	2.84	0.31	7.69	-21.2	6.7	9.3
19	2.74	0.3	6.66	-21.0	6.9	9.2
21	2.72	0.3	6.64	-21.1	6.7	9.2
23	2.74	0.3	7.87	-20.7	7.4	9.3
25	2.71	0.29	8.1	-20.7	7.5	9.4
27	2.6	0.28	8.96	-20.8	7.3	9.4
29	2.83	0.3	7.74	-20.7	7.5	9.5
31	2.8	0.29	8.52	-21.0	7.4	9.6
33	2.75	0.28	7.46	-21.0	7.3	9.7
35	2.81	0.29	7.14	-21.0	6.9	9.8
37	2.5	0.25	5.59	-21.3	7.4	9.9
39	2.45	0.25	5.98	-21.4	7	9.6
41	2.76	0.28	5.42	-21.3	7	9.9
43	2.61	0.27	6.91	-21.3	6.3	9.7
45	2.5	0.25	4.12	-21.3	6.1	9.9
47	2.43	0.24	4.45	-21.3	6.2	10
49	2.41	0.25	5.14	-21.2	7	9.7
51	2.32	0.26	7.79	-20.7	7.3	9
53	2.69	0.3	10.52	-20.6	7.8	8.9
55	2.91	0.31	10.57	-20.5	7.2	9.3
57	3.06	0.35	9.7	-21.0	7.4	8.9
59	3.03	0.32	9.6	-20.6	7.3	9.4
61	3	0.31	9.13	-20.6	7.4	9.6
63	3.01	0.32	8.76	-20.6	7.2	9.5
65	3.04	0.29	9.08	-20.9	6.9	10.4
67	2.95	0.31	9.13	-20.7	7.2	9.5
69	2.98	0.31	9.67	-20.6	7.1	9.5
71	2.97	0.31	7.63	-20.7	7	9.6
73	3.22	0.35	8.85	-20.7	7.6	9.1
75	2.63	0.29	8.47	-20.6	7.2	9
77	2.74	0.3	9.36	-20.5	7.6	9.1
79	2.85	0.29	9.18	-20.9	7.2	9.9
81	2.91	0.3	10.54	-20.8	7.4	9.7
83	2.8	0.3	11.22	-20.6	6.9	9.4
85	2.97	0.3	11.34	-20.9	6.8	9.8
87	2.81	0.3	10.88	-20.8	6.7	9.3
89	2.85	0.3	9.14	-20.8	7	9.6
91	2.8	0.28	10.28	-20.7	6.7	10
93	2.77	0.28	11.37	-20.8	6.7	10
95	2.68	0.27	11.76	-20.8	6.5	9.9
97	2.79	0.28	13.58	-20.7	6.6	10
99	2.85	0.27	10.33	-20.8	6.7	10.5

\*Depth profiles of C<sub>org</sub>, and CaCO<sub>3</sub> have been presented in Kurian et al., submitted



**Table 2:** Major and minor element measured in core CR-2. P and minor element concentrations are presented in µg/g. (na –not analysed)

Mean depth (cm)	Al (%)	P	Mn	Cr	Cu	Ni	V
1	6.41	1489	333	130	50	61	85
3	7.01	1536	351	135	47	60	89
5	6.91	1525	345	137	47	58	93
7	6.99	1489	338	139	48	61	85
9	6.9	1472	329	133	49	68	87
11	7.06	1564	322	138	45	61	87
13	6.95	1534	316	129	47	54	93
15	7.22	1533	337	139	49	58	91
17	7.16	1620	321	140	49	61	90
19	7.17	1648	320	135	49	53	91
21	7.42	1608	301	137	47	63	101
23	7.31	1598	322	135	47	61	92
25	7.35	1763	336	137	46	56	99
27	7.05	1533	330	133	44	64	93
29	6.95	1562	303	136	45	65	88
31	7.23	1646	308	142	48	62	76
33	7.31	1644	308	140	46	61	88
35	7.41	1693	314	151	49	71	85
37	7.71	1724	327	147	48	78	102
39	7.58	1746	323	142	48	71	107
41	7.83	1887	310	146	49	71	103
43	7.76	1802	321	144	49	70	101
45	8.05	1803	327	147	51	59	88
47	8.11	1785	333	149	48	63	98
49	7.89	1699	336	147	49	73	96
51	7.17	1672	354	137	43	49	87
53	6.85	1629	339	128	43	51	87
55	6.85	1622	319	127	43	51	86
57	7.13	1776	321	132	46	62	79
59	7.44	1701	316	133	47	62	81
61	7.4	1779	307	134	52	66	85
63	7.49	1837	306	142	48	58	103
65	7.05	1723	290	122	49	50	59
67	7.06	1609	283	131	51	48	89
69	7.56	1563	294	142	49	64	91
71	7.51	1584	287	135	49	73	85
73	7.78	1717	296	132	49	42	85
75	7.71	1644	299	132	49	52	80
77	7.57	1554	299	126	48	50	92
79	7.71	1613	309	133	50	55	78
81	7.72	1645	325	132	45	49	97
83	7.61	1606	na	130	47	48	84
85	7.44	1579	na	125	50	48	67
87	7.49	1649	na	130	47	69	78
89	7.69	1654	na	123	43	53	80
91	7.44	1651	na	123	45	34	75
93	6.89	1514	na	111	46	35	75
95	7.41	1583	na	125	42	59	87
97	6.97	1475	na	120	40	37	80
99	7.58	1667	na	129	42	63	80