

CHAPTER 1

Introduction

The aim of this thesis is to present an in-depth study of causes and consequences of biogenic sedimentation in the eastern Arabian Sea, in particular, along the western continental margin of India (WCMI). The thesis consists of three papers which have already been published in scientific journals (chapters 2, 3 and 4), one paper in press (chapter 5) and two manuscripts, one under preparation to be submitted (chapter 6) and the other being already submitted (chapter 7). The existing publications were prepared and written in 1992/3 at the National Institute of Oceanography at Dona Paula in India. The remaining papers and manuscripts result from my stay as a visiting scientist at ICBM in Oldenburg as part of the DAAD sandwich program. All analytical data of these later contributions were generated by me using the facilities available at the ICBM, Oldenburg University.

In the following I will present a brief and general introduction into the current state of knowledge on oceanographic, sedimentological and geochemical aspects of the Arabian Sea. This will be followed by a summary of the major conclusions which could be drawn from the individual publications including statements on my own scientific contribution to these multi-authorship papers.

The Arabian Sea is characterized by a biannual current reversal associated with the winter (NE) and summer (SW) monsoons, which bring cold nutrient-rich waters to the surface thus promoting high plankton productivity. This enhanced bio-productivity and a strong upper thermocline limits the exchange of oxygen between surface and sub-surface layers and results in the development of an oxygen minimum zone (OMZ) at intermediate water depths (150-1200 m) where the dissolved oxygen levels are as low as <0.2 ml/l. The presence of such a mid depth OMZ is consistent with the occurrence of widespread denitrification (Deuser et al., 1978; Qasim, 1982; Sengupta and Naqvi, 1984; Somasunder and Naqvi, 1988; Naqvi, 1991), a pronounced Mn maximum in the water column (Saager et al., 1989) and low Mn excess (Mn_{xs}) in trap particles at site EAST (eastern Arabian Sea trap; Bala Krishna Nair et al., 1999). The productivity and OMZ signals should be encoded in the underlying sediments.

In chapter 2 an attempt was made by me and my colleagues to compile all data available to date on the organic carbon (OC) distribution in the Arabian Sea

(Paropkari et al., 1992). We have shown that even though the productivity is three to four times lower at the WCMI, OC is enriched two to four fold when compared to western Arabian Sea sediments. In addition, highest OC concentrations (10-16%) were reported between Ratnagiri and Mangalore, an area where productivity is low (Qasim, 1977). This mis-match between bioproductivity and OC data has lead us to conclude the importance of dissolved oxygen on the preservation of organic matter (OM).

In chapter 3 we tried to further substantiate our interpretation of the OC distribution along the WCMI, which stressed the importance of OM preservation, by providing new data on the quality of the OM deposited in the study area. This was done by Rock Eval analysis and we could demonstrate that the OM is predominantly of marine origin with high hydrogen indices (HI) which was deposited under reducing conditions (Paropkari et al., 1993 a). This study seemed to further prove that our understanding of OM deposition at the WCMI, i.e., the dominance of preservation over production, was valid.

In 1992 Pedersen et al. have proposed that hydrodynamic features, i.e., winnowing and reworking of sedimentary matter provide the primary control on the distribution and preservation of OM on Oman margin sediments and not increased preservation owing to the lack of oxygen in the OMZ. This view contrasted with our findings on OM sedimentation and we subsequently commented (Paropkari et al., 1993 b) on the Pedersen et al. (1992) paper (chapter 4). This discussion on OM accumulation in the Arabian Sea forms the basis for the still ongoing production versus preservation debate.

My main contribution during the above investigations were the literature search for published OC values, the compilation of all OC data available which includes our own and literature values of the above investigations. Together with the co-authors A.L. Paropkari and A. Mascarenhas I participated in completing the spatial OC distribution map of the Arabian Sea and the preparation of the three scientific manuscripts which form chapters 2 to 4 of this thesis.

The following chapters 5 to 7 are based on results obtained during my stay as a DAAD scholar (Sandwich Program) at ICBM, Oldenburg University, from October 1995 to July 1997. Keeping in view the OC distribution and importance of oxygen depleted waters in the eastern Arabian Sea trace metal studies were undertaken to

understand the influence of productivity and OMZ on the enrichment/depletion of trace elements. Earlier studies of Arthur et al. (1987), Brumsack (1980), Brumsack and Thurow (1986), Thurow et al. (1992) and Nijenhuis et al. (1999) have shown the importance of an oxygen depleted water column that is responsible for the accumulation of redox sensitive elements.

The results and discussion of the present investigation are presented as three research papers which in part lead to conclusions not in agreement with our earlier published work. The main logic for the inclusion of earlier work in the present thesis is to show that, when trace metals are analyzed, their spatial distribution and accumulation mechanism shows a mis-match with the earlier published OC distribution. So the combination of earlier and present work will highlight the improvements in knowledge gained by applying a different approach, i.e. the analysis of trace metals, for understanding OM accumulation at the WCMI.

Based on preliminary data I observed a discrepancy between trace metal and OC data along the WCMI. This led to the re-analysis of a larger sample set at the Oldenburg university. The new data significantly deviated from the OC distribution published previously (chapter 2). In the new data set variations in productivity and reported upwelling intensity in different regions of the WCMI are coherent with the spatial OC distribution. Moreover the OC pattern is in agreement with the abundance of *G. bulloides*, a planktonic foraminifera productivity proxy. The problems with respect to the differing data sets could be related to the applied analytical methods for OC determination, i.e., the wet oxidation method as opposed to the CHN and coulometric technique.

The source rocks of the terrigenous detrital material are different in chemical composition along the WCMI. Therefore the enrichment/depletion of trace metals in WCMI sediments can in part be ascribed to the dominating Deccan Trap basaltic in the north or granitic source rocks further south. Cd and Se, two elements whose background concentrations are low in both rock types were chosen along with several major and trace metals to study OM deposition at the WCMI (chapter 6). Less intense oxygen depletion at the SW coast of India, despite of high productivity and OC concentrations, has resulted in regeneration of biogenic elements. Moreover, at a few stations on the upper slope which is overlain by the OMZ, shelf derived material due to winnowing is also recognized. An intense OMZ at the NE margin of India

has resulted in the accumulation of OC, biogenic and redox sensitive elements. Together with Cd and Se, the behavior of P, Cu, Cr and V are discussed. Many of the trace metals were analyzed for the first time in WCMI sediments.

The last manuscript (chapter 7) deals with the element Ba, which is traditionally used as a proxy for productivity. Ba when examined with water depth show partial loss of productivity signal in near shore sediments and in OMZ. Pore water sulfur isotope data (^{34}S) show that Ba is not mobilized due to intense sulfate reduction. Biogenic Ba shows high values in regions of high productivity and vice versa which is in conformity with biogenic Zn and foraminiferal (*G. bulloides*) evidence. Surprisingly the accumulation of Cd, biogenic Cu and V is almost negligible in SW coast of India sediments even though the productivity is high. This infers the regeneration of biogenic elements in the water column or at the sediment/water interface. On the contrary biogenic Cd, Cu, U and V appear to accumulate in NE margin of India sediments due to intense reducing conditions. This fact appears to have resulted in the partial loss of the Ba productivity signal whereas the prevailing more oxygenated conditions in SW coast of India sediments appear to be responsible for the preservation of the Ba productivity signal.

The preservation of OC along the WCMI appears to be mainly due to productivity changes and not an exclusive preservational effect. Even though similar OC values are observed in regions of high and moderate to high productivity the trace metal accumulation show a different pattern. Trace metals are accumulated under suboxic/anoxic conditions whereas they are released due to an oxygenated interface in other regions. The combination of OC and trace metal data, instead of using OC alone, is a powerful tool to obtain a better understanding of the depositional environment of productivity influenced continental margin sediments.

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Chapter No.	Journal	Year	Details
Two	Marine Geology	1992	Vol. 107, pp. 213-226.
Three	Marine Geology	1993	Vol. 111, pp. 7-13.
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CHAPTER 6

INFLUENCE OF THE ARABIAN SEA OXYGEN MINIMUM ZONE ON THE ACCUMULATION AND PRESERVATION OF BIOGENIC AND REDOX SENSITIVE ELEMENTS IN SURFICIAL SEDIMENTS

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Abstract :

P, S, Cd, Se, Cu, V and Cr were analyzed in 112 surficial sediment samples from the western continental margin of India (WCMI) to investigate their spatial distribution and the mechanism responsible for the incorporation of these elements into upper slope sediments from within the oxygen minimum zone (OMZ). In the southern Arabian Sea, especially at the SW coast of India, a less intense OMZ has resulted in low Cd/Al, Se/Al, P/Al, Cu/Al and V/Al ratios due to regeneration processes. Iodine reaches high concentrations (0.17%) and I/OC ratios (200-380) as well. This suggests the presence of an oxygenated sediment seawater interface.

Cd and Se are enriched in upper slope sediments of the NE Arabian Sea when compared to SE Arabian Sea sediments. P, Cd, Se, Cu, V and Cr enrichments and low I/OC ratios (40-70) are coherent with the presence of reducing conditions close to the sediment seawater interface. The suboxic/anoxic sediment seawater interface in this region has led to the preservation of biogenic and redox sensitive elements confirming intense reducing conditions at the interface.

Introduction:

The Arabian Sea is considered as one of the highest productivity zones in the world oceans (Qasim, 1977). It is characterized by the presence of a mid-water depth oxygen minimum zone (OMZ) where dissolved oxygen concentrations approach zero (Wyrski, 1973; De Souza, 1996). The presence of intense oxygen depleted conditions is also evidenced by denitrification in the water column (Naqvi, 1991) and low Mn excess (Mn_{xs}) in trap particles at location EAST (eastern Arabian Sea trap) when compared to WAST (western Arabian Sea trap, Bala Krishnan Nair et al., 1999). Moreover there exists a spatial productivity variation during summer (SW) and winter (NE) monsoon (Bhattathiri et al., 1996; Madhupratap et al., 1996).

Earlier studies of Prakash Babu et al. (1999) on sediments of the western continental margin of India (WCMI) have shown that organic carbon (OC) is enriched in upper slope sediments (2-4%, max. 5.30%) at the SW coast of India where productivity is high ($>1 \text{ g C/m}^2/\text{d}$; Qasim, 1977; Pant, 1992). The OC concentration is lower in the NE Arabian Sea (1-2%) because of moderate to high productivity ($0.50\text{--}1.0 \text{ g C/m}^2/\text{d}$; Qasim, 1977) and/or dilution with material delivered by the major rivers such as the Indus, Narmada and Tapti. OC concentrations are low ($<4\%$) at the central WCMI where the productivity is low ($<0.5 \text{ g C/m}^2/\text{d}$; Qasim, 1977). These variations in OC concentration with productivity have lead Prakash Babu et al. (1999) to infer that the OC distribution in sediments primarily depends on bioproductivity at the WCMI.

The shelf ($<150 \text{ m}$ water depth), lower slope and deep sea sediments ($>1500 \text{ m}$) are well oxygenated (dissolved $O_2 >0.5 \text{ ml/l}$ to 5 ml/l ; Wyrski, 1971), whereas the upper slope sediments in water depths of $150\text{--}1200 \text{ m}$ are overlain by an OMZ.

Brumsack (1980) has earlier observed the accumulation of heavy metals in black shales by factors up to 330 when compared to average shale and concluded that the heavy metals are probably originating from contemporaneous sea water. Similarly Nijenhuis et al. (1999) have demonstrated that trace metal enrichments in Mediterranean sapropels and Cretaceous black shales at the Cenomanian/Turonian Boundary Event (CTBE) are due to scavenging and/or (co-)precipitation from an anoxic water column. These studies have shown the importance of an oxygen depleted water

column for the accumulation of trace metals. As the Arabian Sea is characterized by the presence of an OMZ this study is undertaken to understand the response of redox sensitive elements (Mn, Se, Cr and V) to changing redox conditions in the OMZ. Besides redox sensitive elements a few biogenic elements (P, Cd and Cu) are also selected and studied to check whether these elements are accumulated in high productivity areas. The conclusions drawn from this study will be helpful while studying the long term variations of oxygenation/productivity in the geological record by using geochemical proxies.

Oceanographic setting:

The monsoonal winds are the key to physical forcing in the Arabian Sea. During winter (December to February) the NE monsoon prevails (Carruthers et al., 1959), whereas during summer (June to September; Wyrтки, 1973) the SW monsoon dominates. Monsoonal coupling between atmosphere and ocean is vigorous and the seasonal shift in wind pattern causes complete semi-annual reversal of surface currents in the Arabian Sea. This gives rise to seasonal variations in surface water characteristics.

Recent studies of Madhupratap et al. (1996) have shown that NE winds in the northern Arabian Sea are too weak to produce offshore Ekman transport during winter monsoon. These authors have suggested that surface cooling, densification and reduced solar insolation lead to convective mixing which injects nutrients into the surface layers from the thermocline. The same authors have reported an enhanced water column productivity (335 to 807 mg C/m²/d in February 1995) in the NE and central Arabian Sea (Madhupratap et al., 1996).

During summer monsoon a comparatively weaker upwelling has been noticed off the SW coast of India (Wyrтки, 1973). Pant (1992) has shown that the highest productivity occurs at the SW coast of India (>1 g C/m²/d) during summer monsoon and that its intensity decreases progressively towards north with rates as low as <0.005 g C/m²/d north of 20°N. This spatial variation in productivity is in conformity with the productivity measured during the summer monsoon in July 1995 (Bhattathiri et al., 1996). Shetye et al. (1990) have also observed the occurrence of upwelling up to 15° N whereas around 20° N upwelling is barely noticeable.

Material and Methods:

112 surficial sediment samples collected by a Petersen grab sampler during various cruises of RV Gaveshani and ORV Sagarkanya were selected for the present work (Fig. 1). The water depth range from 25 to 3600 m. Samples were homogenized in an agate mortar and kept in screw top plastic vials until analysis.

Total reduced sulfur was analyzed by coulometric titration (Ströhlein Model 702) following combustion (Lange and Brumsack, 1977). For sulfur the accuracy based on the analysis of an in-house standard (TW-TUC, shale type material) is better than $\pm 10\%$.

The dried and homogenized powdered sediment samples were digested with sub-boiling quality HClO_4 , HF and HNO_3 in closed teflon vessels (Heinrichs et al., 1986). The acids were evaporated on a hotplate and the residue dissolved in 2% HNO_3 and made up to the final volume. These sample solutions were analyzed for Mn by flame AAS (Perkin Elmer 4100). The analytical precision and accuracy is $\pm 5\%$.

The powdered sediment samples were analyzed for major and trace elements by X-ray fluorescence spectrometry (XRF). 600 mg of powdered sediment was mixed with 3600 mg of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$, Spektromelt), pre-oxidized at 500°C with NH_4NO_3 and fused into glass beads. These glass beads were analyzed by XRF (Philips PW 2400). The analytical precision of an in-house standard (TW-TUC), which was analyzed several times during the analysis, for V was $\pm 1\%$, P $\pm 3\%$, Cr $\pm 9\%$ and Zr $\pm 3\%$. The analytical accuracy with respect to international reference material (MAG-1 and SCO-1) for P and Cr was $\pm 3\%$, V $\pm 1\%$ and Zr is $\pm 6\%$. Iodine was analysed by XRF from powder pellets. The analytical accuracy with reference to MAG-1 and GSS-7 was $\pm 3\%$ and $\pm 17\%$ respectively.

Cu and Cd were analyzed from the digested solutions by graphite furnace AAS (UNICAM 939). For Cu the analytical accuracy with regard to SGR-1 was $\pm 2\%$, GSR-6 and MESS-2 $\pm 3\%$ and GSD-11 $\pm 9\%$. For Cd the analytical accuracy with reference to SGR-1 was $\pm 2\%$ and $\pm 10\%$ with respect to PACS-1 and GSD-11. Selenium was analyzed separately by hydride generation AAS (Perkin Elmer 4100) with a flow injection

module (FIAS 200) in 73 samples after digesting the samples with aqua regia. As a carrier and reducing solution 1 M HCl and 0.20% NaBH₄ in 0.05% NaOH were used. The analytical accuracy for Se with reference to SGR-1 and PACS-1 was $\pm 5\%$, MAG-1 and GSS-6 $\pm 10\%$ and GSS-5 $\pm 14\%$.

Sulfur isotope measurements were carried out by combustion-isotope-ratio-monitoring mass spectrometry (C-irm MS, for details see Böttcher et al., 1998). The sediment samples were combusted in an elemental analyzer (Carlo Erba EA 1108) connected to a Finnigan Mat 252 mass spectrometer via a Finnigan MAT Conflo II split interface. ³⁴S/³²S ratios are given in the ‰-notation with respect to the Vienna-Canon-Diablo troilite (V-CDT) standard. The reproducibility is better than $\pm 0.2\%$.

Results:

The calcium carbonate content in the study area varies between 4 and 93%. A ternary plot with SiO₂, -Al₂O₃•5-CaO•2 (Fig. 2) shows different degrees of clay-carbonate dilution for most of the samples. One group of samples which deviates from the average shale - carbonate mixing trend displays higher SiO₂ contents. This increase is due to the presence of quartz in near shore samples.

The spatial variation of absolute element concentrations under this scenario will predominantly reflect differences in carbonate level. To be able to decipher actual enrichments all elements are normalized to Al and only metal/Al ratios will be discussed.

Mn/Al ratios are high ($100-400 \cdot 10^{-4}$; Fig. 3) in shelf sediments of the NE Arabian Sea and off Cochin, but lower ($\text{Mn/Al} < 100 \cdot 10^{-4}$) between Ratnagiri to south of Mangalore. In this low Mn region a small band rich in Mn/Al ($100-400 \cdot 10^{-4}$) is observed between Mangalore and north of Cochin. The entire upper slope sediments between Ratnagiri to Cochin are low in Mn ($\text{Mn/Al} < 100 \cdot 10^{-4}$). Similarly low ratios are also observed in upper slope sediments off Mumbai and Saurashtra. The lower slope and deep sea sediments are rich in Mn ($\text{Mn/Al} 400-700$ and $> 700 \cdot 10^{-4}$).

P/Al ratios are high in shelf sediments ($75-100$ and $> 100 \cdot 10^{-3}$; Fig. 4) from Mumbai to the southern tip of India whereas the lower slope and deep sea sediments are low in P ($\text{P/Al} < 25 \cdot 10^{-3}$). The sediments from the upper slope in the northeastern

Arabian Sea have high P/Al ratios ($25-75 \cdot 10^{-3}$) whereas in the SE Arabian Sea P/Al ratios are generally lower ($<25 \cdot 10^{-3}$).

To our knowledge, this is the first report on the behavior of Cd and Se in WCMI sediments. The shelf and lower slope sediments are low in Cd ($\text{Cd/Al} < 0.15 \cdot 10^{-4}$) except for one lower slope station off Mumbai where a Cd/Al ratio of $0.36 \cdot 10^{-4}$ is observed (Fig. 5). Cd is significantly enriched (factor 2-4) in upper slope sediments when compared to shelf sediments. Among the upper slope sediments the NE Arabian Sea is characterized by high Cd/Al ratios ($0.30-0.45$ and $>0.45 \cdot 10^{-4}$) with a maximum Cd/Al ratio of $0.47 \cdot 10^{-4}$ whereas the SE Arabian Sea upper slope sediments are less enriched in Cd ($<0.15 \cdot 10^{-4}$).

Se/Al ratios are low in the entire shelf and deep sea sediments of the NE Arabian Sea ($<0.50 \cdot 10^{-4}$; Fig. 6). Se is enriched by a factor of two to five in slope sediments when compared to shelf and deep sea sediments. Among the slope sediments upper slope sediments are relatively more enriched in Se than lower slope sediments. Further Se/Al ratios of $0.50-1.25 \cdot 10^{-4}$ occur in a broader band in SE Arabian Sea sediments (Fig. 6).

Cu/Al ratios are high ($10-15 \cdot 10^{-4}$; Fig. 7) in shelf sediments of the NE Arabian Sea in comparison to SE Arabian Sea sediments, especially between Mangalore and the southern tip of India ($<10 \cdot 10^{-4}$; FIG. 7). Cu/Al ratios are elevated in lower slope and deep sea sediments ($10->25 \cdot 10^{-4}$; Fig. 7). In upper slope sediments Cu/Al ratios are comparably low ($10-15 \cdot 10^{-4}$; Fig. 7), except for a few stations in the NE Arabian Sea ($\text{Cu/Al} 20-25 \cdot 10^{-4}$). Such high ratios of Cu/Al are not observed in SE Arabian Sea upper slope sediments ($\text{Cu/Al} < 15 \cdot 10^{-4}$).

V/Al ratios are high in shelf sediments ($>35 \cdot 10^{-4}$; Fig. 8) from off Saurashtra to south of Marmagao, off Mangalore and the southern tip of India. Higher V/Al ratios ($20-25 \cdot 10^{-4}$) are discernible in lower slope sediments between off Saurashtra to north of Ratnagiri whereas in the remaining lower slope and deep sea sediments V/Al ratios are rather low ($<20 \cdot 10^{-4}$). In upper slope sediments V/Al ratios are generally low ($<20 \cdot 10^{-4}$) but V/Al ratios reach high values ($20-25 \cdot 10^{-4}$) at a few stations with maxima of up to $28 \cdot 10^{-4}$ off Saurashtra (Fig. 8).

The shelf sediments from off Mumbai to the southern tip of India have high Cr/Al ratios (25-30 and $>35 \cdot 10^{-4}$; Fig.9). In general the upper and lower slope and deep sea sediments are low in Cr/Al ($20-25 \cdot 10^{-4}$) when compared to shelf sediments. But a few upper slope sediments in the NE and SE Arabian Sea exhibit high Cr/Al ratios ($25-30 \cdot 10^{-4}$) with maxima up to $33 \cdot 10^{-4}$ (Fig. 9). High Cr/Al ratios ($25-30$ and $30-35 \cdot 10^{-4}$) in upper slope sediments between off Mangalore and Cochin occur in a small but continuous band. South of Cochin Cr/Al ratios are low (20-25) in upper slope sediments.

Iodine concentrations are low in the shelf and deep sea sediments (<100 ppm). An increase in Iodine concentrations is observed in the OMZ, varying from 238 to 1737 ppm. But a north-south gradient in upper slope sediments overlain by OMZ is apparent. Iodine concentrations are very high in SE Arabian Sea sediments (378 to 1737 ppm) whereas they are lower in the NE Arabian Sea (238 to 605 ppm).

The metal/Al values of Cu, Cr and V of shelf sediments are significantly influenced by lithogenic characteristics of the weathered and eroded rocks (Figs. 7, 8 and 9), as these values are in general above average shale (Cu: $4.4 \cdot 10^{-4}$, Cr: $11 \cdot 10^{-4}$, V: $15 \cdot 10^{-4}$; Wedepohl, 1971, 1991). The studies of Murty et al. (1978) and Rao et al. (1974,1976) have shown a high lithogenic influence in shelf sediments at the WCMI and the decrease of this effect towards offshore. For this reason all these samples are excluded from the discussion.

Even though the contribution of coarse-grained material decreases offshore a few samples in the upper slope sediments have Zr/Al ratios higher than average shale ($22.5 \cdot 10^{-4}$; Wedepohl, 1971, 1991). Zr represents an index for terrigenous material since Zr is resistant to chemical and physical weathering (Taylor and McLennan, 1985) and may be used as a proxy for high energy environments (Hild, 1997). Furthermore a few samples from the the upper slope, within the OMZ, show very high CaCO_3 contents (70-90%). In such sediments both Al and other terrigenous element concentrations are low. When elements are normalized to Al a large scatter is evident owing to this dilution effect. For this reason slope sediments with Zr/Al values exceeding average shale and high carbonate samples are excluded from the discussion. The same holds true for one sample with a C^{14} age of more than 30 ka and one station off Mumbai (water depth 1700 m) which showed a high concentration of P_2O_5

(2.35%), as phosphorites are rich in trace metals (Price and Calvert, 1978).

The study area is broadly divided into three sub regions as the samples cover a wide latitudinal distance with spatial variation in productivity (Prakash Babu et al., 1999). In brief, area A at the SW coast of India represents a region of high productivity ($>1 \text{ g C/m}^2/\text{d}$; Qasim, 1977; Pant, 1992; Fig. 1). Area B, at the NE margin of India is a region of moderately high productivity ($0.50\text{--}1.0 \text{ g C/m}^2/\text{d}$; Qasim, 1977; Madhupratap et al., 1996; Fig. 1) and area C, at the central margin of India, a region of comparatively low productivity ($<0.50 \text{ g C/m}^2/\text{d}$; Qasim, 1977; Fig. 1). Moreover this division broadly coincides with differing rock types outcropping at the WCMI. In area B the dominating rocks are Deccan Trap basalts (Krishnan, 1968) whereas gneissic rocks of felsic composition form the major rock type in areas A and C (Krishnan, 1968).

Discussion:

From the above results it seems evident that biogenic and redox sensitive elements are enriched in NE compared to SE Arabian Sea sediments owing to very low dissolved oxygen concentrations (Wyrski, 1973; Stackelberg, 1972; De Souza, 1996). In the following we will try to evidence that in the SE Arabian Sea biogenic elements seem to be regenerated to a higher degree due to an oxygenated sediment seawater interface, whereas distinct metals are accumulating in the NE Arabian Sea due to the presence of a more pronounced suboxic/anoxic interface.

To date relatively few investigations exist to understand the behavior of Cd (Klinkhammer 1980; Klinkhammer et al., 1982; Gendron et al., 1986; Gobeil et al., 1987 and 1997; Rosenthal et al., 1995 and Morford and Emerson, 1999) and Se in marine sediments (Sokolova and Pilipchuck, 1973; Tamari, 1978; Belzile and Label, 1988; Thomson et al., 1998; Mercone et al., 1999). For this reason we will briefly review what is known about the behavior of Cd and Se under oxic conditions.

Both Cd and Se are nutrient type elements that are involved in biogeochemical cycles, i.e, they are depleted in surface waters and show increasing concentrations with water depth (Boyle et al., 1976; Measures and Burton, 1980; Cutter and Bruland, 1984; Takayanagi and Wong, 1985). Cd has only one oxidation state (+II) whereas the possible oxidation states for Se are (+VI), (+IV), and (-II, selenide). Se (+VI) is the common oxidation state in oxic waters, whereas selenide (-II) dominates in anoxic

waters.

Both Cd and Se seem to be mainly derived from biogenic material as the spatial distribution of Cd and Se (Figs. 5 and 6) agrees with OC distribution (Prakash Babu et al., 1999). This is also confirmed by positive correlations of Cd/Al and Se/Al with OC/Al in areas A and B (Fig. 10, Table 2). The derivation of Cd chiefly from the biogenic material is in conformity with earlier observations of Bender and Gagner (1976), Boyle et al. (1976), Bruland (1980) and Knauer and Martin (1981). The association of Se with an organic fraction is supported by the mechanism proposed by Cutter and Bruland (1984) and by the sequential leaching experiments of Cutter (1985).

Low concentrations of Cd and Se in shelf and deep sea sediments (Figs. 5 and 6) appear to be due to regeneration when labile organics are consumed under oxic conditions. The release of Cd to pore waters during oxic degradation of organic matter, which results in low Cd concentration in oxic sediments, was shown earlier by Klinkhammer (1980), Klinkhammer et al. (1982), Gobeil et al. (1987) and Lapp and Balzer (1993). Similarly the benthic flux experiments of Westerlund et al. (1986) have also shown the release of Cd, Cu and Ni from sediments during oxic bottom water conditions and have further demonstrated that the release rate of Cd depends on the availability of oxygen in surface sediments. The release of Cd, which is sensitive to the presence of dissolved oxygen concentrations, infers high regeneration rates even though marine plankton is enriched in Cd (avg. 12 ppm; Brumsack, 1989 and references therein). Brumsack (1989) could show that about 90% of the Cd is regenerated and only 10% deposited in OC-rich sediments of the Gulf of California.

As Se is closely related to OC (Fig. 10 c, d; Table 2) it can be assumed that Se is also lost to the pore waters during oxic degradation of organic matter. A sharp rise in pore water Se was observed when Great Marsh sediments were oxidized (Velinsky and Cutter, 1991). Thus the oxidative release of Se from oxic sediments results in low Se concentrations. Moreover Se solubility increases under oxic conditions (Masscheleyn et al., 1991).

High Mn/Al ratios (Fig. 3) above average shale ($100 \cdot 10^{-4}$; Wedepohl, 1971), in shelf, lower slope and deep sea sediments also indicate the presence of an oxygen-

ated water column. It is well known that Mn is enriched in oxic sediments due to dissolution of Mn in the Mn-reduction zone, upward diffusion and precipitation as Mn-(hydr)oxides (Klinkhammer, 1980 and Klinkhammer et al., 1982). The low Mn/Al values in the shelf sediments between Ratnagiri and Cochin may also be ascribed to the dominating rock types of this area, i.e, gneissic rocks which are low in Mn. The mean Mn/Al value of shelf sediments collected within a 10 km radius off Kochi (Cochin, water depth <20 m) is $19 \cdot 10^{-4}$ (Nath et al., 2000). Such low Mn/Al values ($<100 \cdot 10^{-4}$) in the southern WCMI are not exclusively explained by reduction of Mn (IV) to Mn (II) but may also be due to provenance of the terrigenous detrital material.

Evidence for an oxygenated sediment seawater interface in the SE Arabian Sea (area A):

An enrichment of Cd and Se in upper slope sediments when compared to shelf sediments of Area A suggests that reducing conditions do prevail in this environment, which is impinged by the OMZ. The suboxic /anoxic sediments act as a sink for both elements. Low Mn/Al values indicate Mn (IV) to Mn (II) reduction. As the water column at mid depth is severely depleted in dissolved oxygen it can be assumed that Mn escapes into the water column by diffusion. If we compare Mn/Al values of upper slope sediments with those of inner shelf sediments (54 m water depth) in area A, a reduction in Mn/Al ratio by 20-30% seems evident. But if we compare our data with mean Mn/Al values of Nath et al. (2000) which were collected off the Kochi (Cochin) coast (<20 m water depth) the upper slope sediments are generally enriched. This infers relatively less intense reducing conditions.

Low Cd concentrations in area A in comparison to area B along the SW coast of India (Fig. 5) are surprising, despite high OC concentrations (2-5%; Prakash Babu et al., 1999), productivity and sedimentation ($>1 \text{ g C/m}^2/\text{d}$; Qasim, 1977; Pant, 1992; 52 cm/kyr; Sirocko and Lange, 1991). Cd requires only trace levels of H_2S to precipitate as CdS (greenockite; Rosenthal et al., 1995). The low Cd concentrations therefore seem to indicate the regeneration of Cd and the absence of hydrogen sulfide. This is also supported by the non existing correlation between Cd/Al and OC/Al when deep sea samples are excluded (Fig. 10 a; Table 2).

The distribution of Cd and phosphate is similar in the water column (Boyle, 1976 and Bruland, 1980). P appears to be mainly derived from biogenic material as is evidenced by a positive correlation with OC/Al in areas A and B ($r=0.82$ and 0.66 ; Table 2). Relatively low P/Al ratios in the sediments from the OMZ in area A (Fig. 4) suggest the preferential regeneration of P (probably P_{org}). This infers that P_{org} is more labile than OC which is in conformity with the studies of Ingall and van Cappellen (1990). The preferential regeneration of P during oxic decomposition of organic matter was shown earlier by Bishop et al. (1977), Krom and Berner (1981) and Jørgensen (1983). Moreover Jørgensen (1983) has further shown that this release occurs in the upper oxic zone of sediments. Hartmann et al. (1976) have also observed low P_{org} in a high sedimentation area and attributed this to intense diagenesis.

Low concentrations of Se in area A when compared to area B (Fig. 6) indicate a relatively low trapping efficiency for Se accumulation. It appears that the authigenic fraction of Se is being lost by oxidation. As the geochemical behavior of Se and S is rather similar, a positive correlation still is observed between Se/Al and S/Al in these samples ($r=0.65$; Table 2).

Low Cu/Al and V/Al ratios in area A are surprising as an increase in the flux of these elements associated with biogenic material has been observed in the California borderland basins, which are characterized by an oxic water column as well (Shaw et al., 1990). Moreover a strong correlation between V and Cr with organic carbon was observed earlier by Brumsack and Gieskes (1983). Rao et al. (1974) have reported a relatively low Cu concentration in the south Indian margin (off Cochin) in clay fractions of shelf sediments compared to the north and related this finding to the low importance of clay minerals in the adsorption of Cu. Thus Cu seems to be derived from biogenic material in this area. This is also supported by the positive correlation of Cu/Al with Se/Al ratios ($r=0.73$; Table 2) when deeper slope samples are excluded. Low Cu/Al ratios suggest that Cu is regenerated during remineralization of labile organic matter. An increase in pore water Cu relative to the overlying water due to aerobic degradation of organic matter was reported earlier by Klinkhammer (1980) and Klinkhammer et al. (1982). Similarly V seems to be released to pore waters at or close to the sediment seawater interface during degradation of biogenic material and/or

degradation of particles which have scavenged metals from the water column. V release is also supported a negative correlation of V/Al with OC/Al ($r=-0.83$; Table 2). Shaw et al. (1990) have also shown the release of V at oxic sites at California Borderland basin sites.

As both, Cd and Cu, are significantly regenerated a negative correlation is noticed ($r=-0.66$; Table 2) confirming the release of biogenic elements close to the sediment seawater interface. Revesbech et al. (1980) and Sørensen and Jørgensen (1987) have noticed that the oxic decomposition of organic matter occurs very close to the sediment surface.

The enrichment of Cr/Al in upper slope sediments of area A, especially off Cochin (Fig. 9, Table 1), may suggest the early diagenetic or biogenic accumulation of Cr, as observed earlier (Brumsack and Gieskes 1983). But at those stations where Cr is enriched Ti/Al ratios are high as well (0.6-0.7) in comparison to average shale (0.53; Wedepohl, 1971). This indicates that the Cr enrichment may be linked to the downslope movement of material from the shelf. In a similar way high Cr/Al ratios in area C (25-30; Fig. 9), which are noticed in a few upper slope sediments between Mangalore and Cochin also have high OC (3-4%; Prakash Babu et al., 1999) and Ti/Al ratios (0.6-0.8). The association of OC with Cr and Ti in this area suggest the partial derivation of these elements from downslope movement of shelf material.

Iodine/OC ratios (I/OC) which are low in marine plankton ($\sim 1 \cdot 10^{-4}$) are higher in marine sediments during early diagenesis (Price and Calvert, 1977). Iodine is enriched in oxic sediments due to adsorption of the iodate ion by a high molecular weight organic fraction (Francois, 1987) or Fe (hydr)oxides (Kennedy and Elderfield, 1987). High concentrations of Iodine (up to 0.17%) and I/OC ratios ($385 \cdot 10^{-4}$) in this region also support the idea of an oxygenated sediment seawater interface.

Evidence for the presence of a suboxic/anoxic interface in area B:

The low Mn/Al ratios (<100 ; Fig. 2) in upper slope sediments from the OMZ in comparison to oxygenated sediments are due to Mn reduction, which infers reducing conditions at the sediment seawater interface.

The enrichment of Cd in area B by a factor of two to four relative to area A requires an efficient trapping mechanism for Cd accumulation. Cd is most likely fixed as CdS due to the presence of trace amounts of hydrogen sulfide under reducing conditions at the sediment water interface. Gobeil et al. (1997) have shown the drastic increase in Cd concentration in a depth profile which precisely coincides with the increase in acid volatile sulfides. Cd enrichment in this area under reducing conditions is also supported by its positive correlations with OC ($r=0.70$) and S ($r=0.70$; Table 2).

Further an enrichment factor (EF) of P, Cd and U and other trace metals is calculated for two samples each from areas A and B in the NE and SE Arabian Sea sediments. The stations have been selected in such a way that OC concentrations are comparable ($\sim 5\%$). Eventhough OC concentrations are similar, the dissolved oxygen concentrations are low in NE Arabain Sea and higher in SE Arabian Sea (< 0.1 ml/l; ~ 1 ml/l; Stackelberg, 1972 and NIO Data center). The enrichment factor is calculated as follows:

$$\text{Enrichment factor (EF)} = (\text{Metal}/\text{Al}_{\text{sample}}) / \text{Metal}/\text{Al}_{\text{reference material}}$$

After calculating the EF the values are averaged for Areas A and B. Cd, P and U enrichments are clearly visible in the NE compared to the SE Arabian Sea (Fig. 11). Although Cu, V and Cr are above the 1:1 ratio in the NE Arabian Sea, the EF for these elements is not significant due to high background concentrations.

The precipitation of Cd under reducing conditions has been demonstrated by low pore water Cd concentrations relative to overlying waters at anoxic sites, indicating the removal of dissolved Cd from core top sections (Elderfield et al., 1981; Lapp and Balzer, 1993). Similarly benthic flux experiments of Westerlund et al. (1986) have also shown the accumulation of Cd as a sulfide mineral when sulfide was present in the water column. The same was shown by Jacobs et al. (1985) for a stagnant hydrogen sulfide containing water column in an anoxic basin. Pedersen et al. (1989) have observed Cd enrichment in Ucluelet Inlet, British Columbia, and attributed this to the diffusion of Cd from the overlying water column and fixation as a solid sulfide phase at a few millimeters depth. But anoxic conditions in the water column do not appear to be existing in area B.

High P/Al ratios (factor 2-3 higher than average shale) in area B reflect the preservation of biogenic P (P_{org}). The studies of Toth and Lerman (1977), Krom and Berner (1981) and Tromp et al. (1995) have indicated that in anoxic marine sediments there is no evidence for large scale preferential release of P relative to OC.

At the stations where Se/Al ratios are high, OC/Al, Cd/Al and P/Al ratios are elevated as well (Figs. 4 and 5 and Prakash Babu et al., 1999). The close correspondence between the distribution of Se and OC has already been demonstrated by the close correlation between OC/Al and Se/Al ($r=0.95$; Table 2). It appears that Se is finally fixed in the sediments as elemental Se, incorporated into pyrite or as ferroselite ($FeSe_2$), as demonstrated by the correlation between Se/Al and S/Al ($r=0.67$, Table 2).

High ratios of Cu/Al ($20-25 \cdot 10^{-4}$) in upper slope sediments coincide with the decrease in Cu concentrations noticed in the water column with minimum values at 1000 m depth due to adsorption of Cu onto organic material derived from the productive surface waters (Saager, 1994). Thus the relationship between OC and Cu in the sediments and Cu minima in the oxygen depleted waters reflects the accumulation and preservation of this element associated with marine plankton. The positive correlations between Cu/Al and OC/Al as well as Se/Al ($r=0.56, 0.69$; Table 2) also support this assumption regarding biogenic element accumulation in this region.

A high V/Al ratio (max. $28 \cdot 10^{-4}$; Table 1) which is observed at one station indicates strong reducing conditions that are required for V accumulation (Wanty and Goldhaber, 1992). The presence of such intense reducing conditions at this location is also evidenced by enhanced ratios of OC/Al, P/Al, Cd/Al, Se/Al and Cr/Al and a low I/OC ratio ($46 \cdot 10^{-4}$). This close similarity suggests the immobilization of reduced species of redox sensitive and accumulation of biogenic elements.

Vanadium concentrations in the water column are relatively high (1.8 - 2.3 ppb; Collier, 1984 and Jeandel et al., 1987). Probably at few locations in the study area V, which is present as the vanadate anion in oxic seawater may be reduced to the vanadyl cation at the sediment sea water interface (VO^{2+}) in OC-rich sediments (Szalay and Szilagyi, 1967; Brumsack, 1989).

If we compare the Cr enrichment in area B to the riverine particulate matter (Bhaskaran et al., 1984) the following possibilities seem likely: 1) the direct associa-

tion of Cr with organic matter in the sediments 2) the addition of Cr to the sediments in proportion to the amount of organic matter reaching the sea floor and 3) the reduction of Cr (VI) to Cr (III) which is particle reactive in anoxic waters (Emerson et al., 1979). Yamazaki et al. (1980) have shown that Cr (III) forms uncharged and/or negatively charged organic complexes of various molecular weights in the presence of humic substances within the neutral pH range. Udinstev (1975) has reported high concentrations of suspended particulate matter (2.5 to 5 mg/l and >5 mg/l) in the northern Arabian Sea over a wide depth range in the water column (up to 1000 m). Naqvi et al. (1993) have reported, a sharp increase in turbidity in sub-oxic waters of this area within the depth range of 150-500 m. It appears that Cr reduction and incorporation into the sediments by settling particles is an important step in area B. At this moment it is difficult to distinguish the enrichment of Cr between non-lithogenic Cr associated with marine plankton and/or addition of Cr (III). Francois (1988) has also observed a good correlation between Cr/Mg ratio and OC in anoxic sediments of Saanich Inlet sediments.

The association of Cr with biogenic matter is supported by positive correlations with OC/Al ($r=0.88$), Se/Al ($r=0.89$), P/Al ($r=0.80$) and Cd/Al ($r=0.70$, Table 2). This demonstrates the involvement of Cr in the biogeochemical cycle. The enrichment of Cr in upper slope sediments in area B indicates the better preservation of Cr compared to V, in conformity with the studies of Shaw et al. (1990). The relation of Cr with biogenic and redox sensitive elements reflects the importance of organic matter for the development of reducing conditions which in turn are responsible for the reduction of oxygenated species.

Iodide (I^-), the stable form of iodine in anoxic waters, is not adsorbed effectively by high molecular weight organic matter in the sediments (Francois, 1987). This results in low I concentrations and I/OC ratios in suboxic/anoxic sediments. Low I/OC ratios (46-77), which were analyzed in a few upper slope sediments, confirms the presence of a suboxic/anoxic sediment seawater interface in area B.

Comparison with other environments:

From the above discussion it appears that biogenic elements and reduced species of redox sensitive elements appear to accumulate at the the WCMI sediments. The enrichment of trace elements in sediments from the study area is compared with other continental margin and anoxic basins sediments (Fig. 12). For this comparison we only considered samples from within the most reducing portion of the OMZ in the NE Arabian Sea which show enrichments in Cd, Se, V, Cr and U and have low I/OC ratios. The enrichment factors (EF) for Cd, Cu and V in Arabian Sea sediments are rather low when compared to upwelling sediments of Gulf of California and anoxic basins. But the EF for Se in the Arabian Sea sediments is high in comparison to the Gulf of California, which requires further studies. Cr is distinctly enriched in the study area even when anoxic basins are considered (EF is calculated with respect to particulate matter in the study area). It appears that Cr reduction may take place in the suboxic water column. The presence of higher amounts of settling particles (Udinsteve, 1975) and a turbidity layer in the sub-oxic zone augments the incorporation of reduced Cr species into the sediments.

Conclusions:

An oxygenated sediment seawater interface at the southern WCMI upper slope sediments leads to the regeneration of biogenic elements like P, Cd, Se, Cu and V in the water column. High Iodine concentrations and I/OC ratios also seem to evidence the presence of an oxygenated interface. Intense reducing conditions (stronger OMZ) at the northern Indian margin upper slope sediments explain the enrichment of P, Cd and Se. Cu and V enrichments, even though small, are also noticeable. Cr appears to be reduced to Cr (III) due to the presence of suboxic waters at intermediate water depths and incorporated into the sediments. The presence of a suboxic/anoxic interface is also evidenced by low I/OC ratios.

The significant enrichments of Cd and Se serve as a useful tool for tracing paleo oxidation fronts while studying the temporal variations. Cr appears to be a tracer for paleoxygenation levels. But care has to be taken for Cr enrichment owing to provenance of terrigenous detrital material.

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Legend to Figures:

Figure 1. Station location map. Also shown in the figure are three sub-areas based on spatial variations in primary productivity.

Figure 2. Ternary diagram showing the carbonate dilution in the sediment samples of the present investigation

Figure 3. Spatial variation of Mn/Al

Figure 4. Spatial variation of P/Al * 1000

Figure 5. Spatial variation of Cd/Al

Figure 6. Spatial variation of Se/Al

Figure 7. Spatial variation of Cu/Al•10⁻⁴

Figure 8. Spatial variation of V/Al•10⁻⁴

Figure 9. Spatial variation of Cr/Al•10⁻⁴

Figure 10. (a) Relation between Cd/Al and OC/Al in area A. Samples from upper slope (○) and lower slope and deep sea sediments (●) are shown with different symbol. Notice the change from positive to negative correlation after ignoring the samples from deeper parts which are oxygenated

10 (b) Relation between Se/Al and OC/Al in area A. All the samples (●) are shown together.

10 (c) Relation between Cd/Al and OC/Al in area B.

10 (d) Relation between Se/Al and OC/Al in area B.

Figure 11. Enrichment of trace metals in NE Arabian Sea (area B) when compared to SE Arabian Sea (area A). The source rocks are compositionally different along WCMI (see text for details). So the enrichment factor (EF) is calculated with different reference materials as follows:

P and Cd with respect to average shale (Wedepohl, 197, 1991)

U with respect to source rocks (Taylor, 1964)

Cu and Cr in area B with respect to river particulate matter (Bhaskarn et al., 1984)

Cu, V and Cr in area A and V in area B with an inner shelf sediment sample close to the coast.

Figure 12. Enrichment factor (EF) of trace elements along various continental margins. Note the enrichment of Cr in the study area (except for SW African shelf sediments). Data sources Brumsack (1989), Calvert and Pedersen (1993)

Legend to Tables:

Table 1 Metal/Al values for major and minor elements ($\bullet 10^{-4}$) for samples with low terrigenous component (see text for details).

Table 2 Correlation matrix for various elements in the study area. Number of samples (n) in:

Area A = 18 (Normal letters), n = 14 (within brackets). after ignoring deeper slope samples in area A. Area B n = 26 (bold letters). Level of confidence for 18, 14 and 26 samples at 99.9% is 0.68, 0.74, 0.55 and at 99% is 0.56, 0.62 and 0.45.

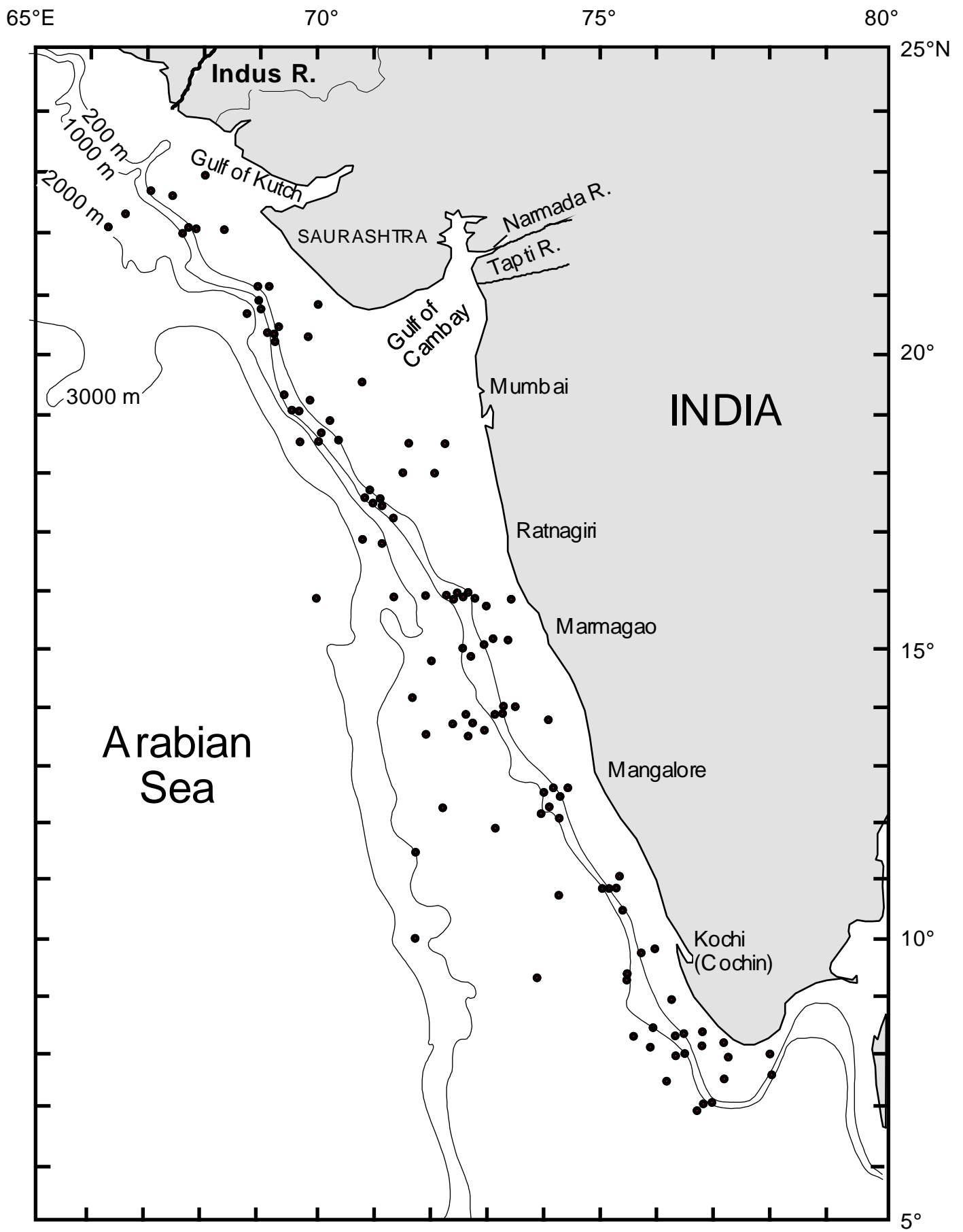


Fig. 1

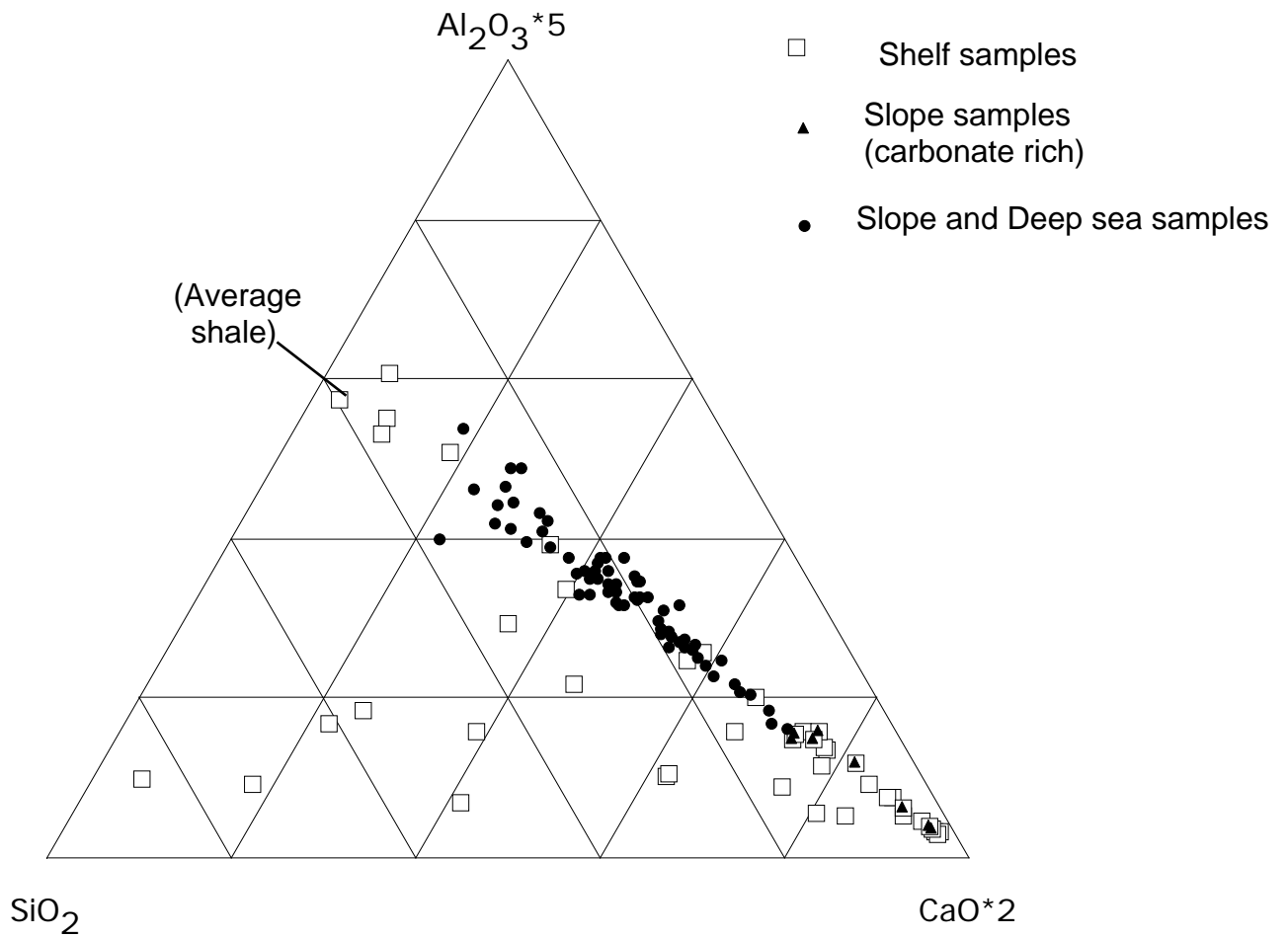


Fig. 2

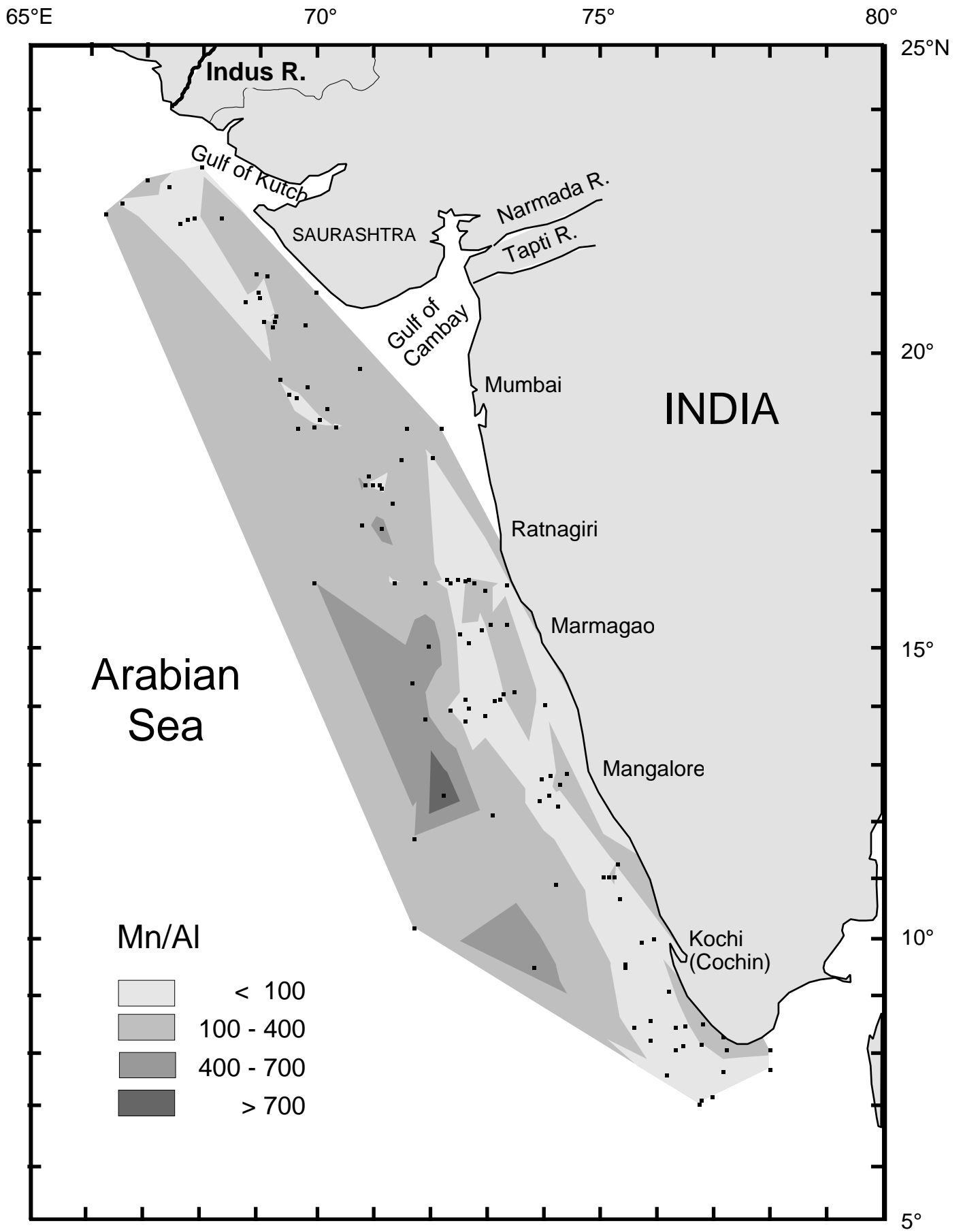


Fig. 3

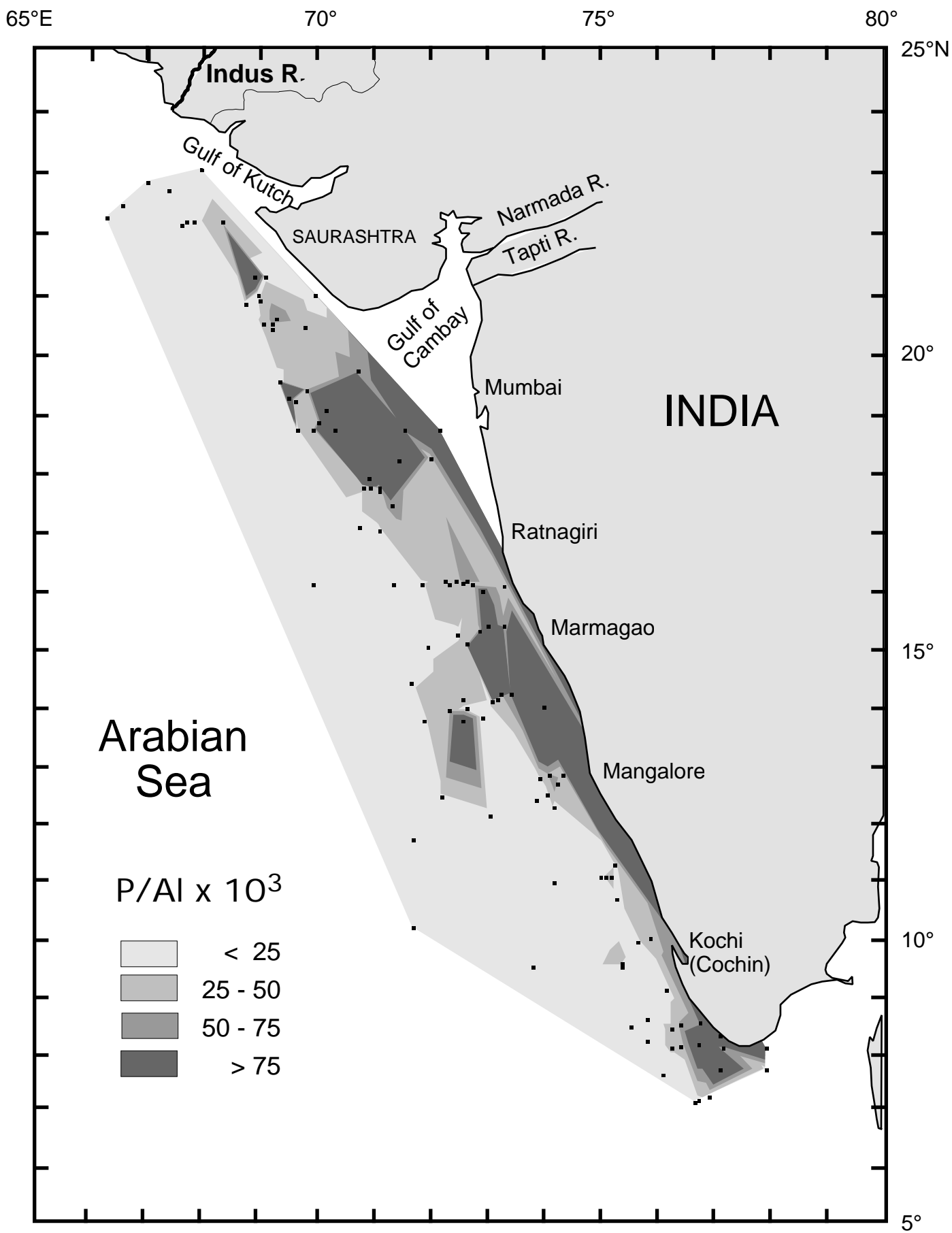


Fig. 4

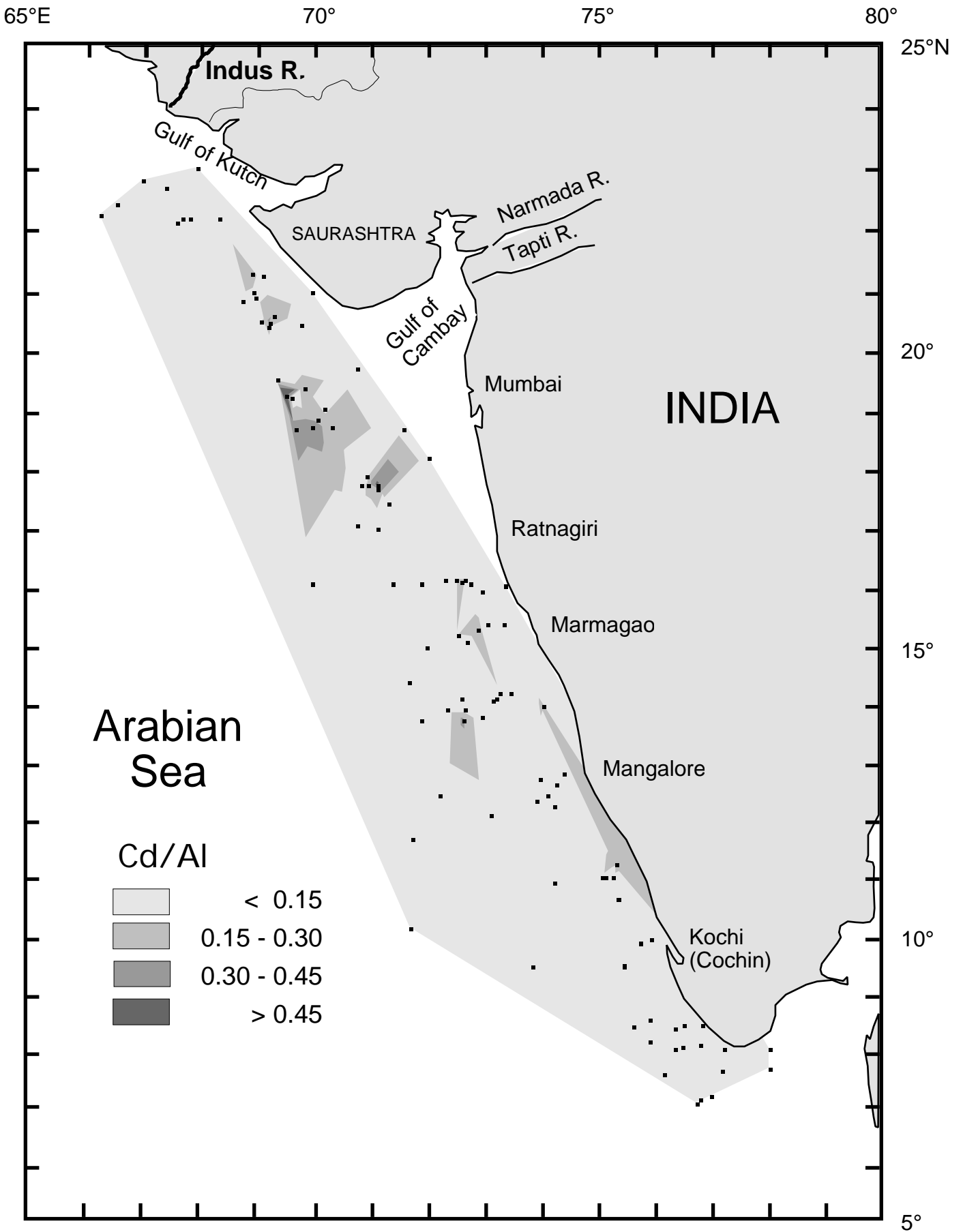


Fig. 5

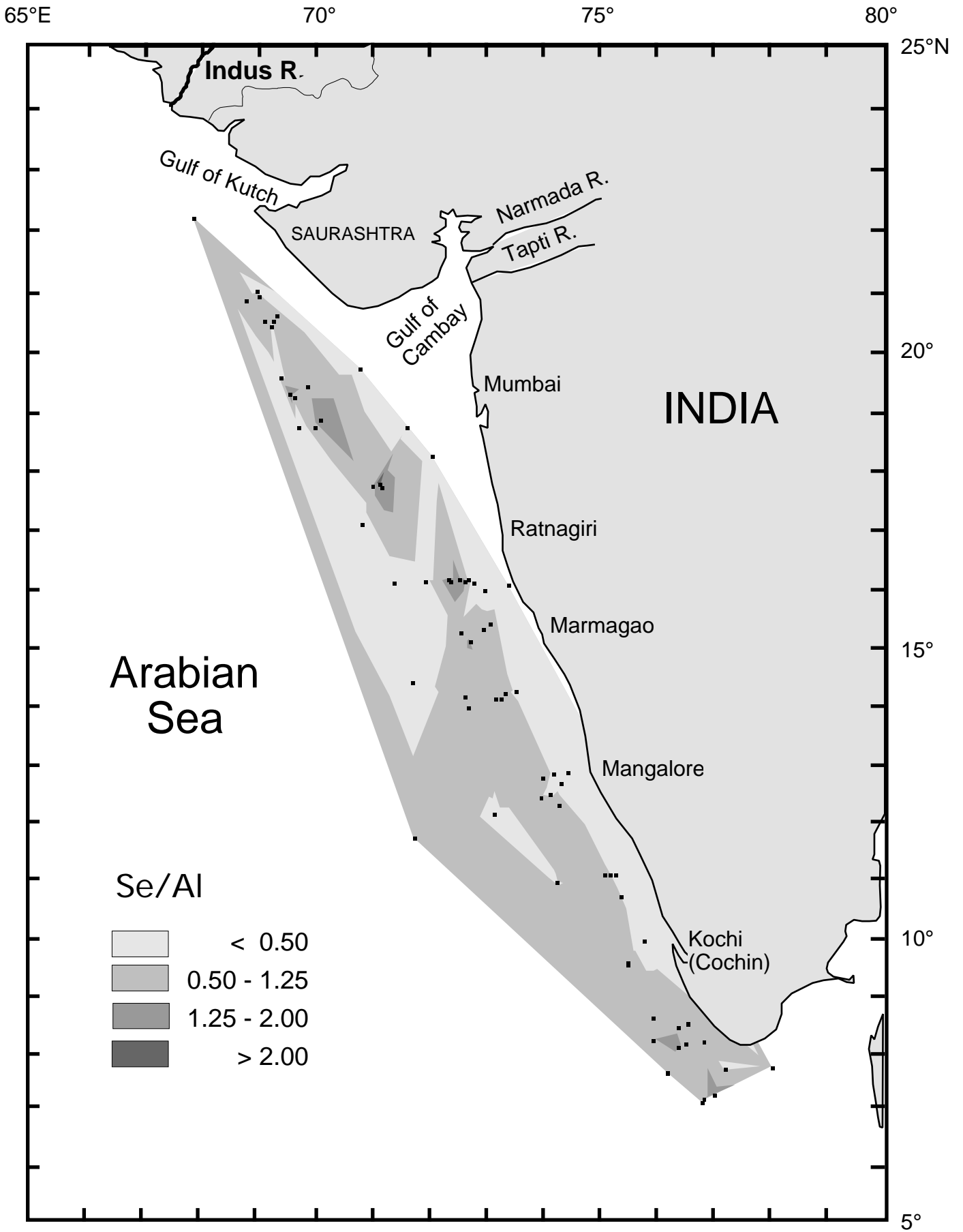


Fig. 6

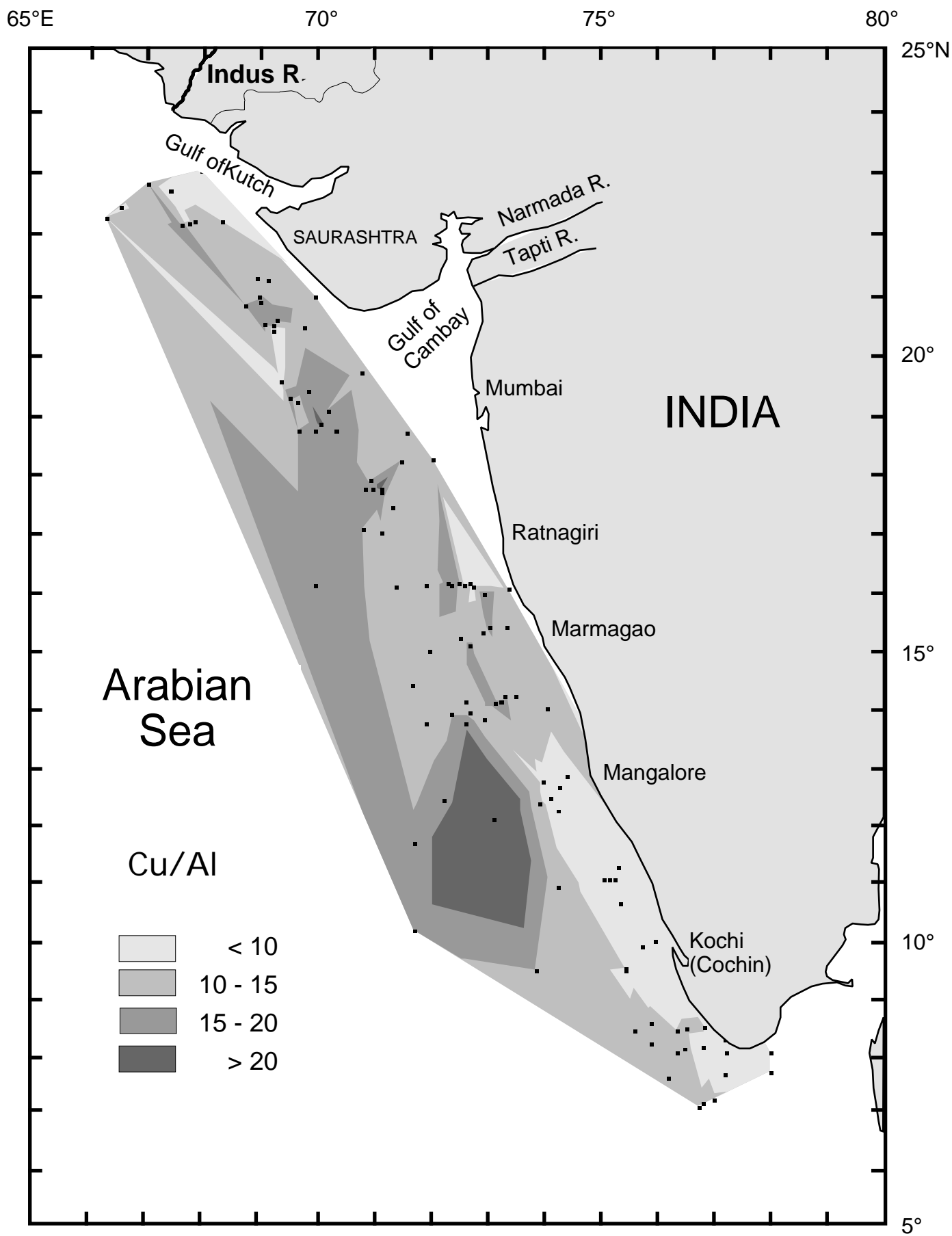


Fig. 7

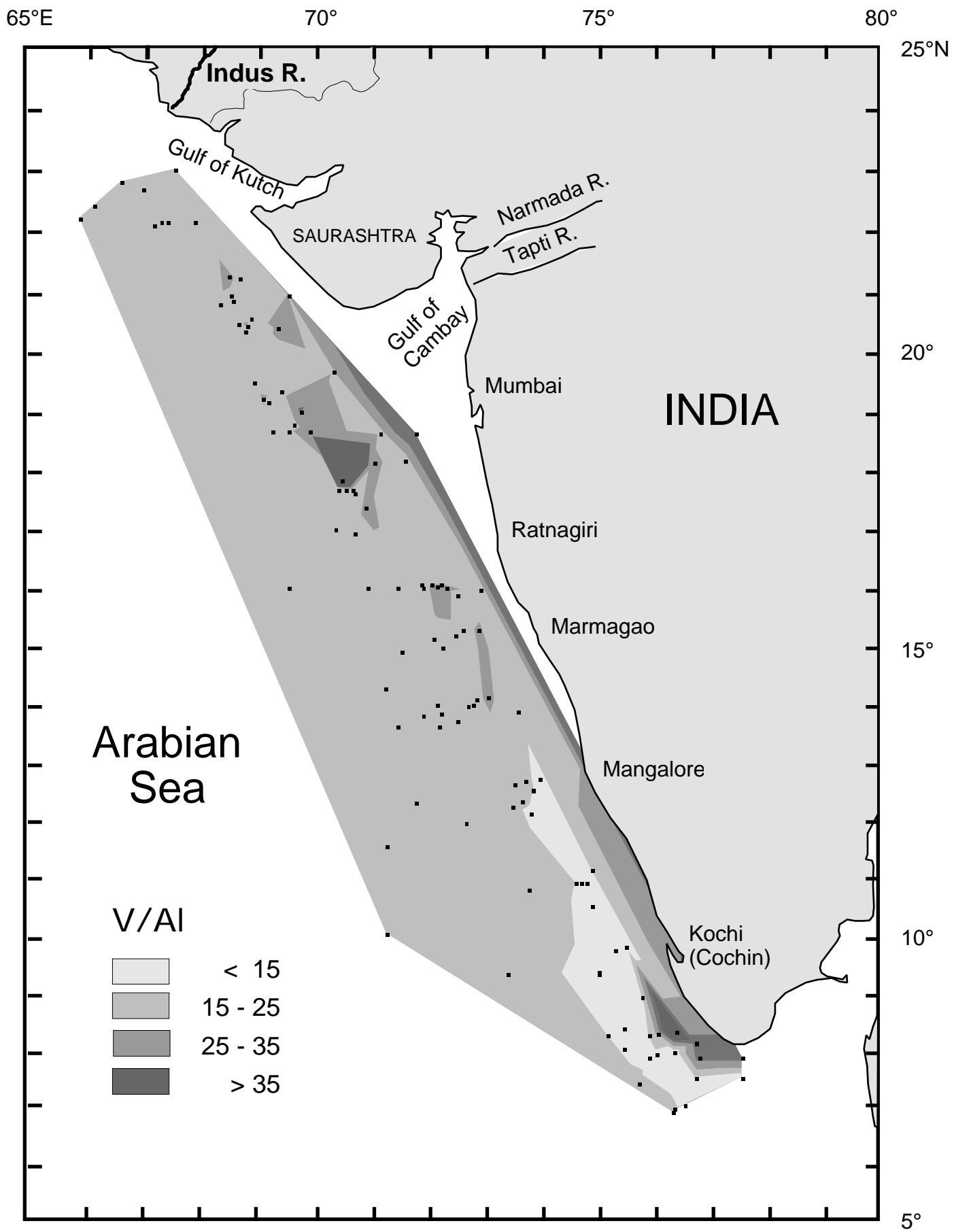


Fig. 8

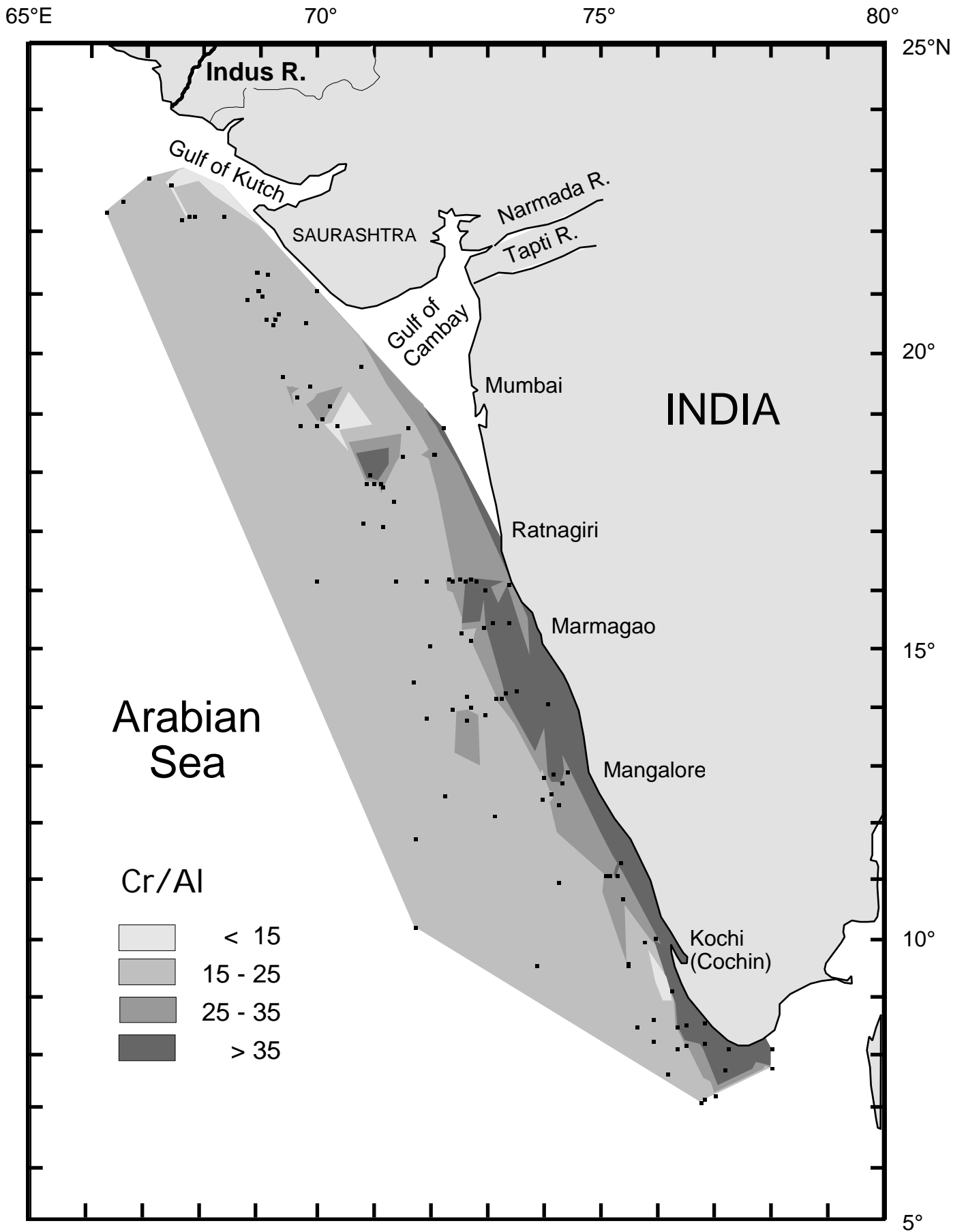
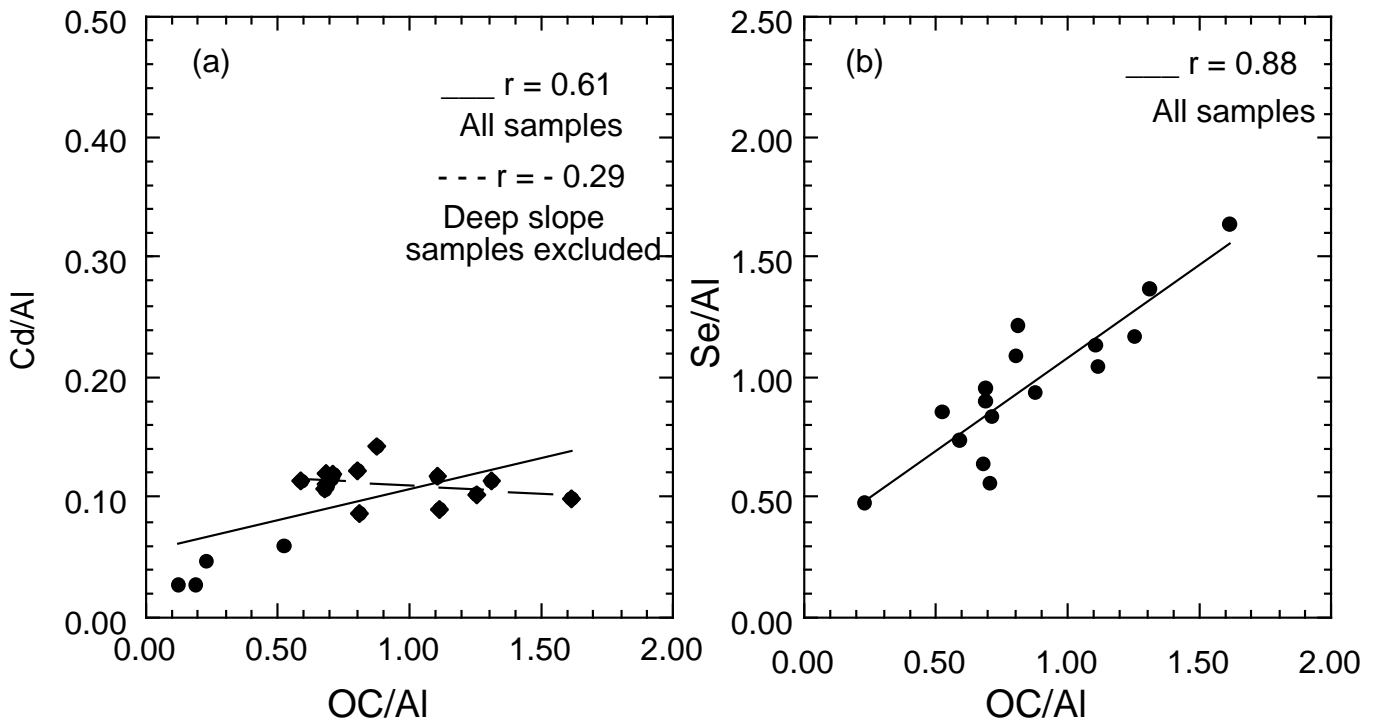


Fig. 9

Area A



Area B

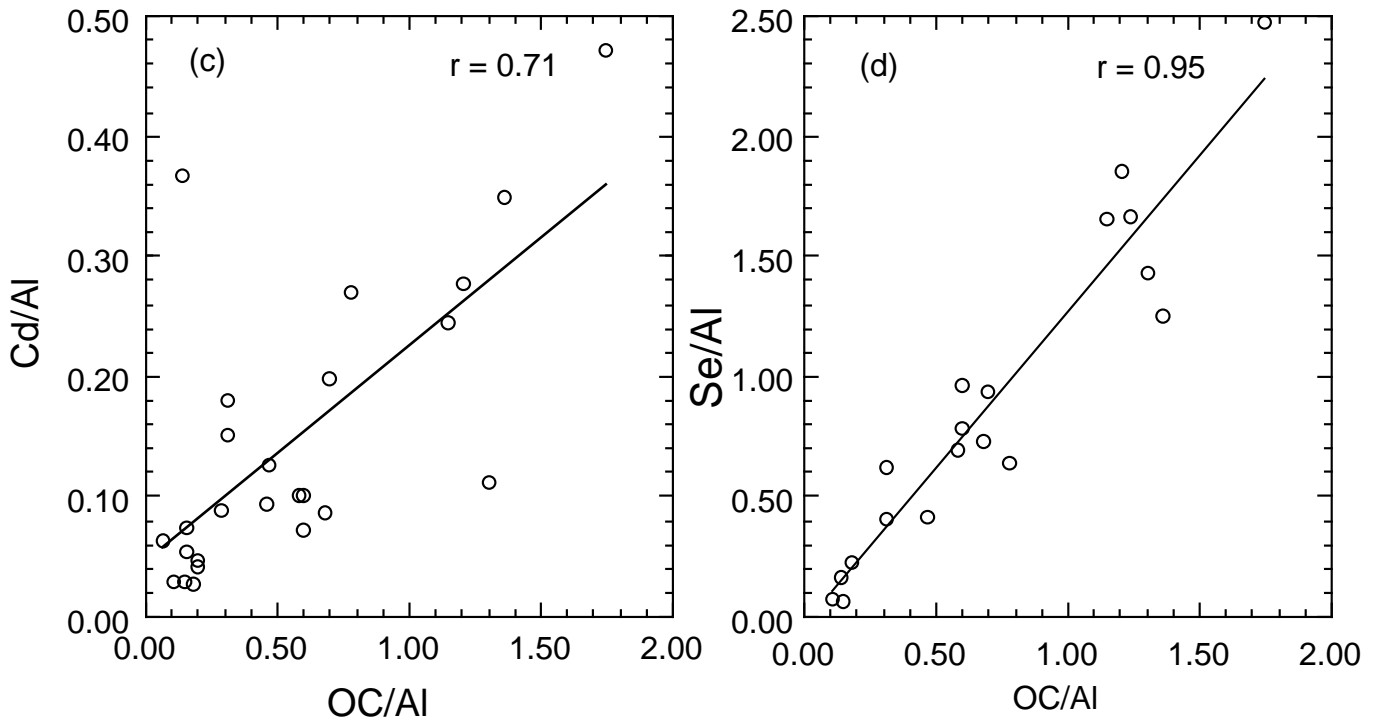


Fig. 10

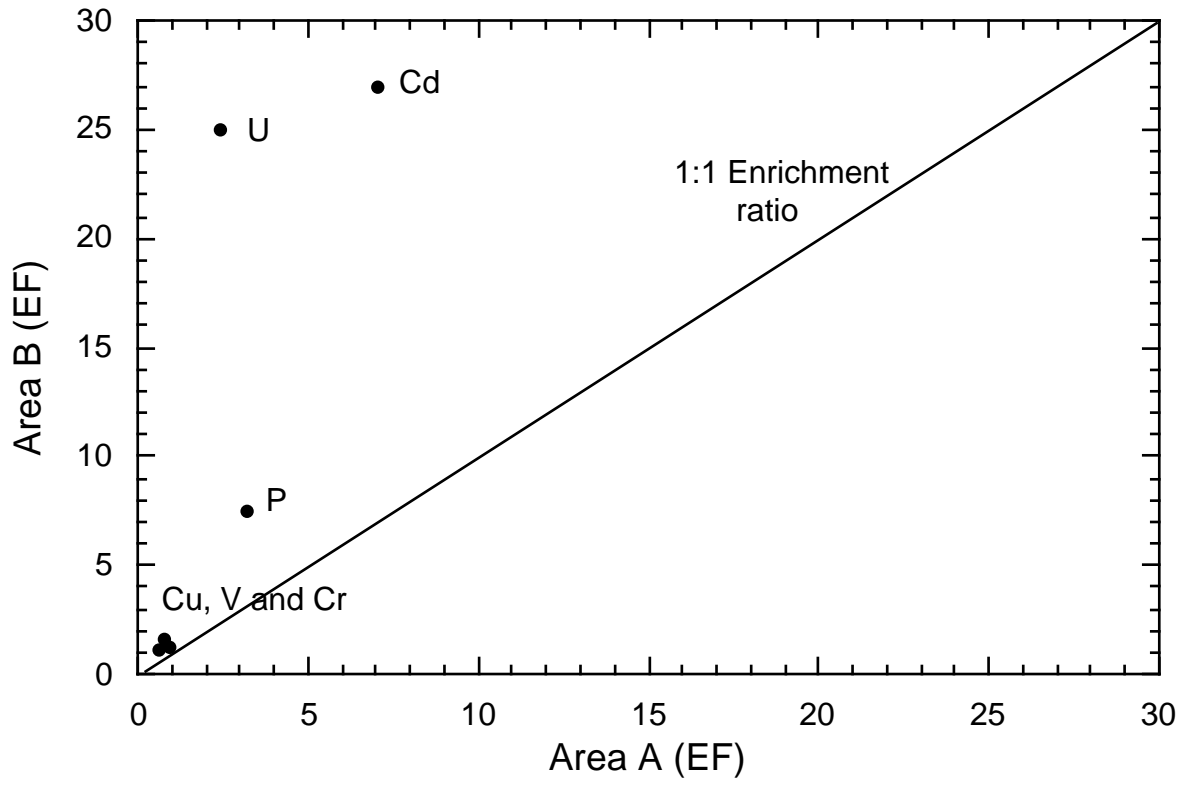


Fig. 11

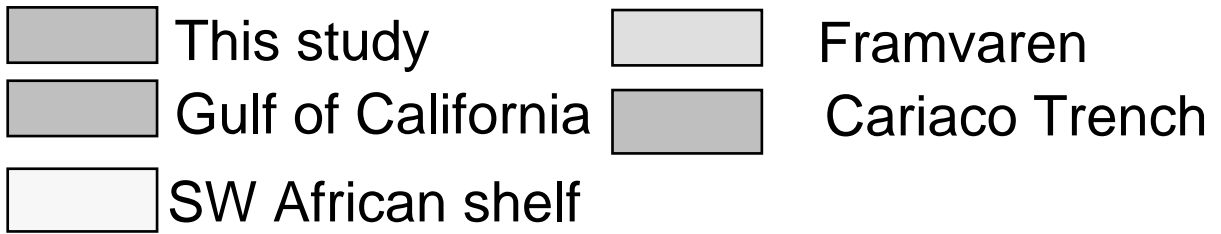
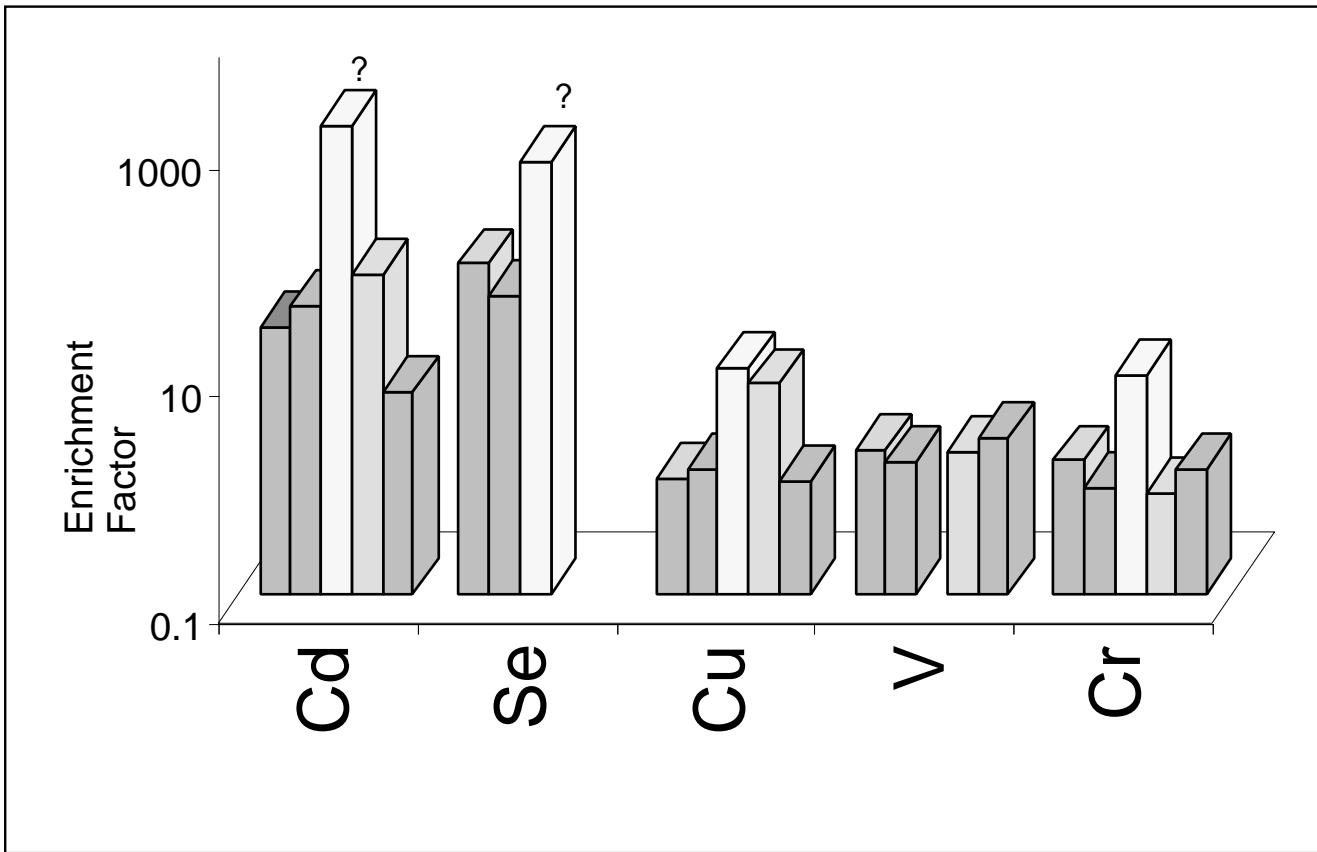


Fig. 12

Table 1

	Area A			Area B			Area C			Average shale *	River Particulate\$	Basalt ^{\$}	Granite ^{\$}
	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.				
Mn/Al	26	526	84	38	509	139	40	977	229	100	136 - 142	171	52
P/Al	0.01	0.03	0.02	0.01	0.07	0.03	0.01	0.05	0.02	0.08	---	160	91
Se/Al	0.48	1.64	0.97	0.07	2.48	0.90	0.18	1.30	0.74	0.011	---	0.006	0.006
Cd/Al	0.03	0.14	0.10	0.03	0.47	0.15	0.01	0.14	0.07	0.015	---	0.02	0.03
Cu/Al	6.01	15.76	11	1.31	23.44	16	5.93	17.21	13	4.4	16 - 22	11.42	5.19
V/Al	11.86	19.07	15	16.88	27.95	21	14.32	25.08	19	14.6	---	28.54	0.26
Cr/Al	16.17	32.70	22	18.61	30.57	22	17.99	28.01	22	10.7	16 - 18	22.83	0.52

* Wedepohl (1971, 1991)

\$ Narmada and Tapti river particulate (Bhaskaran et al., 1984)

\$ Taylor 1964

-- Data not available

Table 2

	OC/Al	Se/Al	S/Al	P/Al	Cd/Al	Cu/Al	V/Al	Mn/Al	Cr/Al
OC/Al	1.00								
Se/Al	0.88 (0.86) 0.95								
S/Al	0.31 (0.53) 0.70	0.37 (0.65) 0.67							
P/Al	0.82 (0.75) 0.66	0.70 (0.62) 0.55	0.03 (0.20) 0.78						
Cd/Al	0.61 (-0.29) 0.70	0.19 (-0.31) 0.62	-0.09 (-0.38) 0.70	0.44 (-0.36) 0.74					
Cu/Al	-0.28 (0.43) 0.56	0.52 (0.73) 0.69	0.08 (0.54) 0.48	-0.18 (0.26) 0.21	-0.66 (-0.22) 0.45				
V/Al	-0.83 (-0.58) 0.16	-0.53 (-0.35) -0.07	-0.40 (0.09) 0.31	-0.81 (-0.77) 0.44	-0.70 (0.34) 0.34	-0.52 (-0.01) -0.14			
Mn/Al	-0.64 -0.49 (-0.52)	-0.49 -0.39 -0.60	-0.27 0.20 -0.22	-0.45 -0.47 -0.30	-0.79 0.27 -0.35	0.68 -0.23 0.08	0.68 0.76 -0.13		
Cr/Al	0.34 (-0.10) 0.88	-0.26 (-0.47) 0.89	0.03 (-0.59) 0.72	0.44 (0.21) 0.80	0.55 (0.11) 0.70	-0.82 (-0.82) 0.43	-0.63 (-0.40) 0.19	-0.44 -0.03 -0.38	

Area A, n = 18 (Normal letters); Area A, n = 14 (within brackets); Area B, n = 26 (bold letters). Level of confidence for respective number of samples at 99.9 is 0.68, 0.74, 0.55 and at 99 is 0.56, 0.62 and 0.45 respectively.

CHAPTER 7

BARIUM AND BIOGENIC ELEMENTS AS PRODUCTIVITY INDICATORS ALONG CONTINENTAL MARGIN SEDIMENTS: A STUDY FROM THE EASTERN ARABIAN SEA

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Abstract :

Barium and several major and trace elements (Si, Al, Cd, Cu, V, Zn and U) were analysed in 112 surficial sediment samples from western continental margin of India (WCMI). Excess Ba and ZN (Ba_{xs} , Zn_{xs}) are higher at the SW margin of India where the productivity is high (0.75 - >1.0 g C/m²/day) and lower in the NE margin of India where the productivity is moderate to high (0.50 - 0.75 g C/m²/day). The spatial variation of Ba_{xs} matches with organic carbon distribution and percentage abundance of *G. bulloides*, a foraminiferal productivity proxy. Furthermore Ba/Al shows a correlation with water depth, Si/Al (possibly opaline silica), CaCO₃, Cu/Al and V/Al in the SW whereas in the NE such correlations are not observed. High organic carbon export coupled with high sedimentation rate and a relatively oxygenated interface, evidenced by regeneration of biogenic Cu and V, appear to result in the accumulation of high concentrations of Ba_{xs} at the SW Indian margin. By contrast, sub-oxic diagenesis in the NE Indian margin results in relatively low Ba_{xs} values and high concentrations of organic carbon, Cd, U and excess Cu and V.

This seems to indicate that although Ba may be partially lost during sub-oxic diagenesis the productivity trend still appears to be reflected by this element along WCMI.

1.0 Introduction:

Goldberg and Arrhenius (1958) proposed the use of barium (Ba) as a proxy for productivity based on its enrichment in sediments along the equatorial Pacific. Since then Ba has been used as a proxy for productivity by several workers (Bishop 1988; Shimmield and Mowbray 1991; Dymond et al., 1992; Francois et al., 1995). Further Dymond et al. (1992) observed a linear relationship between Ba and organic carbon fluxes and concluded that Ba may be used as a productivity indicator. Based on increased concentration of Ba Schmitz (1987) has traced the northward drift of the Indian plate during the Cenozoic and indicated that the Indian plate once was located below the equatorial high productivity belt. Similarly Shimmield and Mowbray (1991) have shown increased Ba concentrations during interglacial periods which they ascribed to enhanced productivity. But certain limitations exist for the use of Ba as a productivity proxy along continental margin sediments.

The first limitation is noticeable particularly in highly productive nearshore sub-oxic and anoxic sediments where Ba remobilization may take place. It was demonstrated by Brumsack and Gieskes (1983) and Brumsack (1989) for the Gulf of California margin sediments that due to extensive bacterial sulfate reduction pore water sulfate approaches zero. Then barite (the usual form of excess Ba) dissolution starts and pore water Ba concentrations increase significantly. The upward diffusing dissolved Ba reprecipitates when it encounters downward diffusing sulfate and may form "barite concretions". Such concretions may be identified by their „heavy“ sulfur isotopic signature (Von Breymann et al., 1990 and Torres et al., 1996).

Along continental margin sediments Ba concentrations are water depth dependent. Von Breymann et al. (1990, 1992) have shown a significant increase in Ba with water depth in Peruvian and northwestern Arabian Sea surficial sediments. Calvert and Price (1983) have also reported high Ba concentrations offshore Namibian shelf sediments. Based on the closer relationship between Ba and water depth Von Breymann et al. (1992) have shown at ODP Site 682 that Miocene upwelling sediments deposited at a shallower depth lack significant Ba enrichment even though organic carbon and opaline silica were enriched. By

contrast, Ba, opaline silica and organic carbon were enriched in the Quaternary sequence which was deposited at a water depth of more than 3000 m. This has lead Von Breymann et al. (1992) to conclude that Ba may be used as a productivity proxy at water depth exceeding 2000 m.

Prakash Babu et al. (1999) have shown a broad similarity between OC concentrations and productivity variations along the western continental margin of India (WCMI). An attempt is made here to understand the spatial distribution of Ba in WCMI sediments and to check if Ba may serve as a productivity proxy in this setting as well.

2.0 Oceanographic setting:

The Arabian Sea is characterized by seasonally changing monsoon winds (Wyrki, 1973). During summer (southwest) monsoon (June to September) the surface circulation is dominated by a strong wind-driven anticyclonic gyre. This summer monsoon is responsible for coastal upwelling at the Somalian, Arabian and SW Indian continental margin. The spatial variability of upwelling along WCMI could be inferred from the water column productivity which in July 1995 at 10°N 75°E was 660 mg Cm⁻² d⁻¹, at 12°N 73°E was 1760 mg Cm⁻² d⁻¹ and at 18°N 70°E was 440 mg Cm⁻² d⁻¹ (Bhattathiri et al., 1996). The upwelling which occurs at the SW coast of India continues up to 15°N but ceased to be noticeable around 20° N (Shetye et al., 1994).

During winter (northeast) monsoon (November - February) the current pattern is counter clockwise and NE winds produce a weak upwelling in the NE Arabian Sea (Carruthers et al., 1959; Fontugne and Duplessy, 1986). However, recent studies have shown that the winds in the northern Arabian Sea are too weak to induce any significant offshore Ekman transport (Madhupratap et al., 1996). These authors observed that the northern Arabian Sea experiences surface cooling and densification due to the cool dry continental air brought by the prevailing NE trade winds as well as by reduced solar insolation. This densification leads to convective mixing which injects nutrients into the surface layers from the thermocline thus enhancing biological productivity. The water column productivity measured during February 1995 at 21°N 67°E was 643 mg Cm⁻² d⁻¹, at 21°N 64°E was 807 mg Cm⁻² d⁻¹ and at 11°N 64°E was 335 mg Cm⁻² d⁻¹, respectively (Madhupratap et al., 1996).

This moderate to high surface productivity coupled with sluggish renewal of intermediate waters has resulted in the development of oxygen depleted conditions. This is also evident from the presence of denitrification in the water column at these latitudes (Naqvi, 1991; 1994). De Souza et al. (1996) have also observed high nitrate deficits in winter particularly in the north. During summer monsoon, in spite of high oxygen contents in intermediate waters, nitrate deficits are observed which indicates that the Arabian Sea experiences denitrification to a variable degree during all seasons (De Souza et al., 1996). At the southern WCMI upwelling and productivity are high during summer but not in winter.

The excess bio productivity in the water column leads to a greater demand for oxygen supply across the lower boundary of the euphotic zone which results in the depletion of dissolved oxygen in waters at intermediate depths of the Arabian Sea. Highly depleted dissolved oxygen concentrations (approaching zero, Wyrski, 1973) are a characteristic feature of the Arabian Sea oxygen minimum zone (OMZ).

3.0 Material and Methods:

112 surficial sediment samples collected by a Peterson grab sampler onboard various cruises of RV Gaveshani and ORV Sagarkanya were selected for the present work (Fig. 1). The water depth ranges between 28-3700 m. The samples were selected in such a way that the sediments are from the shelf, lower slope and deep sea which are oxygenated (< 150 and > 1500 m; dissolved oxygen = > 0.5 to 5 ml/l, Wyrski, 1973) and upper slope sediments overlain by an OMZ (150-1200 m; dissolved oxygen = < 0.2 ml/l, Wyrski, 1973).

The dried and homogenized powdered sediment samples were analyzed for major and trace elements by X-ray fluorescence spectrometry (XRF). For XRF analysis 600 mg of powdered sediment was mixed with 3600 mg of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$, Spektromelt) and pre-oxidized at 500°C with NH_4NO_3 and fused into glass beads. These glass beads were analyzed by a X-ray spectrometer (Philips PW 2400). The analytical precision of an inhouse standard (shale type material), which was analyzed several times during the analysis, for Si, Al and V was $\pm 1\%$, Ba $\pm 2\%$, Zn $\pm 6\%$ and Zr $\pm 3\%$. The analytical accuracy checked with international reference materials (MAG-1 and SCO-1) was as follows: Si and V $\pm 1\%$, Al and Ba $\pm 2\%$, Zn $\pm 5\%$ and Zr $\pm 6\%$.

The sediment samples were digested with sub-boiling quality HClO₄, HF and HNO₃ in closed teflon vessels. Copper and cadmium were analyzed by a Graphite Furnace Atomic Absorption Spectrometer (UNICAM 939). The analytical accuracy for Cu with reference to SGR-1 was ± 2%, GSR-6 and MESS- 2 was ± 3% and GSD-11 was ± 9%. For Cd the analytical accuracy with reference to SGR-1 was ±2% and ±10% with respect to PACS-1 and GSD-11. U was determined in selected samples on separate sample dissolutions with sub-boiling quality HF and H₂SO₄ in closed teflon vessels and analyzed by HR-ICP-MS (Finnigen Mat). The accuracy for the U determinations when compared to international reference material (MAG- 1) was < 10%. A detailed description about the digestion procedure and analytical measurements by ICP-MS is mentioned elsewhere (Schnetger, 1997).

Sulfur isotope measurements are carried out by combustion-isotope-ratio-monitoring mass spectrometry (C-irm MS, for details see Böttcher et al., 1998) and combusted in an elemental analyzer (Carlo Erba Ea 1108) connected to a Finnigan Mat 252 mass spectrometer via a Finnigan MaT Conflo II split interface. ³⁴S/³²S ratios were given in the ‰-notation with respect to the Vienna-Canon-Diablo troilite (V-CDT) standard. The reproducibility was better than ± 0.2‰.

4.0 Results:

The spatial distribution of calcium carbonate (Fig. 2) shows low contents for the inner shelf sediments (< 25%) except near the southern tip of India where CaCO₃ contents of > 70% are observed. The outer shelf sediments of the NE Arabian Sea are very rich in CaCO₃ (80 – 92%). CaCO₃ values, when compared to inner shelf sediments, are high in upper slope (25–50%), lower slope and deep sea sediments (< 60%).

As CaCO₃ contents are highly variable along the WCMI the spatial variation in concentration of biogenic elements is significantly affected by different degrees of dilution from CaCO₃. To remove the influence of carbonate dilution on the spatial distribution of metals the elements are normalized to Al, except for Ba.

Ba_{xs} (Fig. 3; detailed discussion follows) is almost absent in shelf sediments except near the Gulf of Kutch (753 ppm) and off Cochin (162 to 258 ppm); increase towards offshore but a north south gradient is distinct. In the

southern part of the WCMI high Ba_{xs} values are observed (800 to > 1000 ppm) whereas in the northern part such high concentrations are not noticeable.

The WCMI shelf sediments exhibit low Zn/Al ratios ($< 14 \times 10^{-4}$, Fig. 4; average shale 12.9×10^{-4} ; Wedepohl, 1971, 1991) except for a small patch off Cochin. Zn/Al ratios increase offshore. The upper slope sediments are enriched in Zn (Zn/Al $14 - > 26 \times 10^{-4}$) compared to shelf sediments. Again a north south variation is observed. A wide band with higher Zn/Al ratios ($20-26$ and $>26 \times 10^{-4}$) is observed in upper slope sediments between off Mangalore and Cochin with a maximum Zn/Al ratio of 28×10^{-4} at the southern tip of India. In the northern part of the WCMI high Zn/Al ratios ($20-26 \times 10^{-4}$) are observed in a small patch off Mumbai (Bombay). The lower slope and deep sea sediments are in general relatively low in Zn/Al ratio ($14-20 \times 10^{-4}$) when compared to upper slope sediments, except for one station off Cochin where the Zn/Al ratio is 28×10^{-4} similar to the maximum value obtained in upper slope sediments.

The detailed spatial distribution and behavior of Cd will be discussed elsewhere. Since the background concentrations of Cd are low (< 200 ppb; Wedepohl, 1971, 1991) the absolute concentrations, instead of Cd/Al, are discussed. Cd concentrations are low along the entire shelf and lower slope (< 300 ppb), except in the lower slope sediments off Mumbai where Cd concentrations of more than 900 ppb are observed. In upper slope sediments Cd is enriched almost by an order of magnitude (600 - 900 and > 900 ppb) when compared to shelf sediments. Among these upper slope sediments a north south gradient is observed. The NE Arabian Sea is characterised by a relatively larger band rich in Cd (600 - 900 ppb) with concentrations reaching up to ~ 1.5 ppm. In the SW Arabian Sea Cd is relatively less enriched (300 - 600 ppb) with occasional high concentration (600-900 ppb).

The ^{34}S values of pore water sulfate ($n = 8$) retrieved at different depth intervals (between 0-300 cms) in several cores collected at water depth between 250-3500 m along WCMI range between +20 and + 20.5‰ (rel. V-CDT standard).

4.1 Calculation of Ba_{xs} :

Elemental concentrations are usually normalized with reference to average shale to infer an additional metal source other than the aluminosilicate of approximately shale composition. Average shale has 650 ppm of Ba (Wedepohl,

1971, 1991). In the study area the source rocks are different as mentioned earlier. Area B is dominated by Deccan basalts (Krishnan, 1968; except near the river Indus mouth which flows through a terrain of Precambrian metamorphic rocks of the Himalayas of felsic composition) which are low in Ba (< 250 ppm; Najafi et al., 1981; Shukla et al., 1988; Peng et al., 1994). Areas A and C are dominated by felsic rocks (Krishnan, 1968) rich in Ba (600 ppm; Taylor 1964). So average shale may not be appropriate for the calculation of Ba_{xs} especially in area B. Moreover Dymond et al. (1992) have given a wide range of Ba/Al ratios for crustal rocks (0.005 to 0.01) and suggested the proper usage of source material Ba/Al before calculating Ba_{xs} . As mentioned earlier by Von Breymann et al. (1990) and as observed in this study Ba concentrations at continental margin sediments are water depth dependent. To remove any ambiguity with reference to water depth six transects have been carefully chosen in three regions with almost similar depth for calculating Ba_{xs} . The source rock Ba content is taken for calculating Ba_{xs} instead of average shale. Since a wide variation in Ba concentrations is reported at different sections for Deccan basalts (between 50 and 250 ppm, Najafi et al., 1981; Shukla et al., 1988; Peng et al., 1994) choosing the correct average value is difficult. For this reason the average value of Taylor (1964) for basalt (tholeiitic composition) is chosen for calculating Ba_{xs} . Additionally it is assumed that the source rock contribution from one region to the other is negligible. The Ba_{xs} is calculated as follows (equation 1) and the results are given in Table 1.

$$Ba_{xs} = Ba_{total} - (\%Al_{total} \times Ba/Al_{source\ rock}) \text{ -----} > \text{ Eq. (1)}$$

In a similar way Ba_{xs} is calculated for all other stations in the study area and presented in Fig. 3. Negative Ba_{xs} values are ignored.

Another way of calculating the metal excess is by choosing the sample with the lowest Ba/Al ratio in that area. Ba_{ex} calculated by choosing the source rock as well as with a sample having the lowest Ba/Al ratio (these data are not shown in the Table 1) are similar.

The study area has been broadly divided into three units based on the spatial variability of productivity (Fig. 1). Area A, a region of high productivity (0.75 - > 1.0 g C/m²/day, Qasim, 1977; between Mangalore and the southern tip of India), area B with moderate to high productivity (0.5-0.75 g C/m²/day, Qasim, 1977; between offshore Saurashtra and Ratnagiri) and Area C a region with less

productivity ($< 0.50 \text{ g C/m}^2/\text{day}$, Qasim, 1977, central margin of India). The divisions based on productivity are arbitrary since the productivity in the Arabian Sea varies seasonally and annually. This division broadly coincides with the source rocks adjoining the WCMI. The source rocks in area B are Deccan basalts (Krishnan, 1968) whereas gneissic rocks of felsic composition form the source rocks in areas A and C. Around $16^{\circ}30' \text{ N}$ of WCMI the source rocks change in composition from basalts to gneissic rocks of felsic composition (Krishnan, 1968).

5.0 Discussion:

5.1 Spatial distribution of Barium:

The increase in Ba concentrations with water depth suggests partial loss of the Ba_{xs} signal within OMZ of WCMI sediments as is shown in Fig. 5. The increase of Ba with water depth has also been observed at other continental margin sediments (Von Breyman et al., 1990, 1992; Calvert and Price, 1983).

High concentration of Ba_{xs} in the shelf sediments north of the Gulf of Kutch appear to be due to the presence of feldspars and mica, as Ba is rich in these minerals (Rankama and Sahma, 1950; Berlin and Henderson, 1969). Nair et al., (1982) have observed high mica concentrations north of the Gulf of Kutch. The second evidence for detrital Ba is based on Ba/Sc and K/Sc ratio of Indus river particulates. Ba/Sc and K/Sc of the Indus river particulate (Thomas and Martin, 1982) matches with the Ba/Sc (23) and K/Sc ratio (1583×10^{-4} ; unpublished data with the authors) of shelf sediments off the Gulf of Kutch. Similarly elevated concentrations of Ba_{xs} in the shelf sediments off Cochin appear to be due to the presence of relict terrigenous sands. Very high Si (total) contents at these stations (32 and 42%) support this assumption. Calvert and Price (1983) have also observed slightly higher Ba values for near shore sediments off Namibia and ascribed it to the presence of feldspars.

Ba_{xs} at a given depth interval is highest in area A (high productivity) and relatively low in area B (moderate to high productivity). Lowest Ba_{xs} values are observed in area C (low productivity). Thus it seems justified to state that Ba_{xs} distribution is broadly in accordance with the observed regional variations in productivity.

Prakash Babu et al. (1999) have shown that organic carbon (OC) is enriched in upper slope sediments (2-4%) along the SW coast of India (area A). In area B,

OC is less enriched in upper slope sediments (1-2%), except for isolated patches (2-4%). These low values of OC may be ascribed to relatively moderate to high productivity and/or dilution by fluvial material from the Indus, Narmada and Tapti rivers. In area C relatively low concentrations of OC (< 4%) are observed where the productivity is low. Thus a similarity is noticeable between the spatial distribution of Ba and OC.

Further evidence for enhanced upwelling and productivity variations comes from the planktonic foraminifera species *G. bulloides*, a productivity proxy (Prell and Curry, 1981; Divakar Naidu et al., 1992). Divakar Naidu et al. (1992) have noticed high percentage abundances of *G. bulloides* (30-40%) at the SW margin of India (area A) and in a small patch off the Saurashtra coast. Lower abundances of *G. bulloides* (20-30%) are noticed in the north (area B) whereas the abundance is low (< 20%) along the central margin of India (area C; Divakar Naidu 1990). This distribution of *G. bulloides* is in accordance with the Ba_{xs} variation. Hermilin and Shimmiel (1995) have also observed a coherence between OC, Ba and *G. bulloides* during oxygen isotope stage 3 (between 45- 50 kyr and 30 kyr) in the western Arabian Sea. The study of Reichart et al. (1997) have shown a similar result and according to their interpretation higher interglacial Ba/Al ratios and percentage abundances of *G. bulloides* reflect an increase in upwelling intensity.

5.1.1 Relationship between Ba and biogenic elements:

Marine plankton is enriched in trace metals. Moreover Brumsack (1983) has shown that the excess of trace metals in sediments from upwelling regions can be explained by a simple mixing model using average shale and marine plankton as end members when the different degree of regeneration in the water column is taken into consideration. The relations of $CaCO_3$, Cu, Zn and V are examined in comparison to Ba.

To distinguish the changes that are not caused by carbonate dilution the metals are normalized to Al. The influence of lithogenic material in shelf sediments is high (Murthy et al., 1978; Rao et al., 1974, 1976). Eventhough the terrigenous contribution decreases offshore few samples in the upper slope sediments have Zr/Al ratios higher than average shale ($22.5 \cdot 10^{-4}$; Wedepohl, 1971, 1991). Zr is resistant against physical and chemical weathering (Matthes, 1993 and Taylor and McLennan, 1985) and may be used as a proxy for high energy environments (Hild,

1997). Few samples from the upper slope sediments are rich in CaCO_3 (70-90%). In these samples Al as well as other terrigenous elements concentrations are low and when normalized a big scatter is evident due to carbonate dilution. To avoid this all the shelf and upper slope sediment samples with Zr/Al values higher than average shale and high carbonate content are excluded from the discussion. By this approach the contribution of terrigenous material in the sediment samples is kept at minimum levels and the process controlling the enrichment/depletion of elements can be understood more easily.

Area A:

A positive correlation between Ba/Al and Si/Al ratios ($r = 0.81$; Table 2) in area A indicates the possible association of Ba with biogenic silica. The biogenic silica values for a few samples studied in this area (Divakar Naidu et al., 1992) show a positive relation with Ba/Al ($r = 0.78$; $n = 5$). This relation suggests that the association between Ba and Si is due to siliceous material like diatoms and not to felsic source rocks which are rich in these elements as well. Herguera (1992) and Thiede et al. (1997) have shown that periods of high productivity should be reflected in higher accumulation rates of biogenic opal and the Ba profile in the water column indicates that it is almost entirely involved with the deep regeneration nutrient like silica (Chan et al., 1977). The accumulation of both, Ba and Si in this area thus infers the formation of barite in micro-environment of decaying organic matter and the remains of siliceous organisms (Bishop, 1988) and suggest a possible link between Ba and Si. An alternate possibility is the dissolution of celestite (SrSO_4) and siliceous radiolaria. Celestite tests and spores of acantharia are enriched in Ba relative to Sr in sea water (Bernstein et al., 1992) and celestite dissolves in less than 1000 m water. The dissolution of celestite releases sulfate and barium. When this dissolution occurs in micro environments barite may be precipitated. Another possibility of barite formation is from hydrothermal source (Dymond, 1981). There are no reports of hydrothermal source close the study area ruling out barite derivation from a hydrothermal solution. Biotic source for marine barite in pelagic regions is also reported earlier (Bertram and Cowen, 1997). The samples in the present investigation are from continental margin thereby ruling out the mechanism proposed by Bertram and Cowen (1997).

The vertical distribution of Zn in the oceanic water column is similar to that of the nutrient silica (Bruland et al., 1978). We consider only samples from the OMZ (between water depths of 150-1200 m, low in dissolved oxygen, < 0.2 ml/l; Wyrki, 1973) to compare the metal enrichment in different areas. Deep sea surface sediments (> 1200 m) are enriched in Cu, Ni, Co and Zn due to scavenging by Mn oxides (Klinkhammer, 1982; Schnetger et al., 2000) and therefore are not considered. After adopting this criteria high average Zn/Al ratios are noticed in area A (Table 3). Similarly Zn_{xs} is also high, in conformity with Ba_{xs} values (Table 1). The accumulation of Zn_{xs} due to its association with biogenic material along with Ba and biogenic silica indicates high productivity.

Although total Zn concentrations in area C are comparable to area A low Zn_{xs} and Zn/Al ratios (Table 1 and 3) suggest lower productivity and the dominance of Zn from a terrigenous source by winnowing or down slope movement from the shelf or upper slope. Aluminium concentrations are comparatively high at these stations (5-7%) which further supports the above contention. Relatively low concentrations of CaCO₃ (25-50%; Fig. 2) also confirm the dilution by terrigenous material from the shelf or upper slope.

The involvement of Cu in the biogeochemical cycle (Bruland, 1980) is also supported by positive correlations of Cu/Al ratios with water depth ($r = 0.85$) and Ba/Al ratios (0.87; Table 2). The relation of Cu with water depth and Ba appears to suggest a relatively high productivity even further offshore. Kameswara Rao (1973) has observed high abundances of planktonic foraminifera and *G. bulloides* in the water column and suggested high organic production in the surface waters. Furthermore satellite altimetry studies of Prasanna Kumar et al. (1998) have shown the offshore drift of cold waters during summer monsoon which possibly increased the productivity.

The assumption of an offshore increase in productivity is also supported by CaCO₃ contents which may serve as a productivity indicator along this margin (Divakar Naidu et al., 1992). CaCO₃ show a positive correlation with Ba/Al and Si/Al ratios ($r = 0.66, 0.75$; Table 2).

Even though Cu is likely to be derived from the biogenic material Cu/Al ratios in this area are surprisingly low in comparison to other areas. Moreover excess Cu (Cu_{xs}; calculated with reference to shelf sediments; Table 1) is negligible. It appears

that biogenic Cu is mostly regenerated which seems to be the reason for the poor correlation between CaCO_3 and Cu.

Vanadium is also partly involved in the biogeochemical cycle (Collier, 1984). V/Al ratios, similar to Cu/Al, show positive correlations with water depth ($r = 0.78$) and Ba/Al ratios ($r = 0.78$; Table 2). Excess V (V_{xs}), when calculated in a similar way to Zn and Cu, is also not observed. This suggests that the non-lithogenic V which is associated with the biogenic material is mostly regenerated similar to Cu. Another possibility for not observing excess V is the high concentration of terrigenous V in the shelf sediment which is chosen for calculating excess V.

Area B:

In area B the scenario is contrastingly different when compared to area A. Ba/Al ratios are not correlated with Si/Al ratios ($r = 0.33$; Table 2) and biogenic silica content ($r = 0.26$; $n = 11$; biogenic silica values are taken from Divakar Naidu et al., 1992). Moreover the relation between Si/Al and water depth, as seen in area A, is also not seen ($r = 0.34$; Table 2). Even though the productivity is relatively low in area B during winter, a column productivity of $807 \text{ mg C/m}^2/\text{day}$ was observed at near coastal stations in NE Arabian Sea during winter 1995 (Bhattathiri et al., 1996). As discussed before Ba_{xs} evidences enhanced productivity at the SW margin of India. Despite moderate to high productivity the lack of a correlation between Ba and Si (opaline silica) in area B is unexpected. This indicates that the productivity signal of Ba may be partially lost during sub-oxic diagenesis (see below). Another possibility is dilution by river particulate matter supplied by the Indus, Narmada and Tapti rivers. Alternatively the productivity in this region during winter may be dominated by nitrate rather than silicate. Relatively low Zn_{xs} values and Zn/Al ratios (Table 1 and 3) support this assumption. Calcium carbonate, unlike in area A, shows a poor correlation with Ba/Al and Si/Al ratios in this area (Table 2).

Cu_{xs} is observed in a few upper slope sediments overlain by the OMZ (Table 3). The enhancement of Cu_{xs} at these stations is high even when compared to deep sea stations where Cu is enriched during early diagenesis (Klinkhammer, 1982; Schnetger, 2000). The enrichment of Cu_{xs} in upper slope sediments presumably indicates the Cu fixation in reducing environment as a sulfide mineral. The increase in Cu/Al ratios in mid-depth upper slope sediments is also supported

by non-existent correlation with water depth and Ba/Al ratios ($r = -0.29, -0.14$; Table 2) which is in contrast to area A where a good correlation is noticed between Cu/Al, water depth and Ba/Al (Table 2).

V/Al ratios in area B are higher than in area A (Table 3). V_{xs} is observed only at one station. V requires strongly intense reducing conditions for its accumulation (Shaw et al., 1990). The increase of V in upper slope sediments that are overlain by the OMZ reflects the importance of reducing conditions for the accumulation of biogenic and redox sensitive elements in this region.

A distinct contrast is noticeable between the SE and NE Arabian Sea with respect to the Ba relation with other biogenic elements. Even though the Ba accumulation trend is in agreement with productivity on a broader scale Ba/Al ratios show a relation with biogenic elements in the SE Arabian Sea sediments whereas in the north this is not observed. At present it is not clear whether the low biogenic Ba values in NE Arabian Sea sediments are due to productivity and/or sub-oxic diagenetic conditions which is examined below.

5.2 Interpretation of the Ba record:

The above discussion has shown a broad agreement of Ba accumulation with productivity along the WCMI. In this section we will examine the causes for the observed differences in biogenic Ba accumulation between the southern and northern transects of WCMI sediments.

The pore water sulfate along WCMI is similar to dissolved sulfate in the water column of the Arabian Sea (+ 20.6 ‰, Böttcher et al., in press) that indicates no significant sulfate reduction. Extensive diagenetic mobilization of Ba, as observed in other continental margin sediments (Brumsack, 1989; Von Breyman et al., 1992; Torres et al., 1996) may be lower for the study area. Passier et al. (1997) have also observed low sulfate reduction rates at Oman margin sediments.

In continental margin sediments with high rain rates of organic matter sulfate is the major electron acceptor for the oxidation of organic carbon after oxygen (Jørgensen, 1982). The sulfur isotope data in two surface sediment samples indicate the presence of reduced sulfur species. Two samples from area A and B have ^{34}S values of - 1.0 and +7‰. Lückge et al. (1999) have also shown evidences for sulfate reduction along northeastern Arabian Sea sediments. This indicates sulfate reduction in the upper part of the sediments or reworking of

deeper sediments by bioturbating organisms. Due to re-oxidation, gross sulfate reduction rates have been found to be higher than net sulfate reduction rates (Canfield et al., 1993), which may in part explain that sulfate reducing activity is not reflected in the near-surface pore water sulfate. Direct evidence for sulfate reduction in the form of reduced sulfur species in pore waters and the presence of elemental sulfur has been observed by Passier et al. (1997) in Oman margin sediments.

At continental margin sediments the thickness of the oxidized surface layer varies from a few mm at the inner shelf to more than 1 m in deep sea sediments. At the WCMI Stackelberg (1972) has shown that the thickness of the oxidized surface layer varies from < 1 mm to >150 cms towards the deep sea. The shorter residence time of labile organic compounds and the availability of dissolved oxygen concentrations at near shore sediment induce higher rates of organic carbon oxidation resulting in a thin oxidized surface layer. On the contrary in deep sea sediments labile organic compounds are degraded in the water column itself as they have to settle through deeper waters and are exposed to oxygen for longer time periods. Mostly the resistant phases reach the bottom which ultimately results in a comparatively thick oxidized surficial layer (Lyle, 1983). The decrease in organic carbon oxidation rates roughly coincides with higher oxygen penetration depths and Ba concentrations towards the deep sea. A positive correlation was observed between down core Ba pore water concentrations and the organic carbon oxidation rate for the equatorial Pacific sediments (McManus et al., 1999). This positive relation seems to suggest that high carbon export leads to intense sub-oxic reducing conditions. Under these conditions, as assumed by McManus et al. (1999), the less crystalline barite phase (?) is soluble resulting in increased pore water Ba concentrations and thus lowering Ba preservation rates along WCMI.

An assumption is made here that the Ba signal is partially lost during sub-oxic diagenesis due to sulfate reduction despite the same is not reflected in the pore water sulfur isotope data. For this purpose U and Cd are selected as a geochemical proxy for verifying the sulfate reduction. It is well known that U accumulates at low dissolved oxygen concentrations in sub-oxic and anoxic environments (Klinkhammer and Palmer, 1991; Morford and Emerson, 1999). Cadmium precipitates as CdS even under low concentration of H₂S (Rosenthal et

al., 1995). The idea is that under sulfate reducing conditions, both U and Cd, should accumulate and at the same time Ba concentrations should be low.

A plot between Ba_{xs} and U (Fig. 6 a and b) for the two areas A and B show distinct features. In area A irrespective of the wide variation in Ba_{xs} concentration (~ 274 to 798 ppm) the U range is rather narrow (4 to 6 ppm). The productivity as well as the sedimentation rates are high in this region. Off Kochi (Cochin) a sedimentation rate of 17 cm/kyr is noticed for the Holocene period (Thamban, personal communication). Similarly, Sirocko and Lange (1991) have reported a sedimentation rate of 27 to 51 cm/kyr in this area. Dymond et al. (1992) have proposed that the burial efficiency of Ba varies with the logarithm of the mass accumulation rate (MAR). This means that Ba preservation is expected to increase with MAR as a higher rain rate of Ba would facilitate pore water saturation with respect to barite. Relatively high Ba_{xs} values in the SW Arabian Sea support the observation of Dymond et al. (1992). Alternatively less intense sub-oxic diagenesis due to relatively oxygenated sediment sea water interface also seems to preserve Ba_{xs} .

The negative relation of low Ba_{xs} at high Cd concentrations is distinct in comparison to Ba_{xs} and U in area A (Fig. 6a). Cd show relatively low concentrations in area A, especially in upper slope sediments along the SW coast of India (~ 0.50 ppm) when compared to area B. Low concentrations of Cd indicate high regeneration rates of biogenic elements and the absence of H_2S . This observation is also supported by the regeneration of Cu and V (non-lithogenic). It may be assumed that the relatively oxygenated sediment sea water interface has resulted in better preservation of biogenic Ba along the SW continental margin of India.

The scenario in area B contrasts with area A. High concentrations of U and Cd are noticed at low concentrations of Ba_{xs} and vice versa (Fig. 6 b). Cd reaches maximum concentrations of ~ 1.5 ppm in this region. As discussed above Cu and V also appear to accumulate. This indicates the presence of intense reducing conditions close to the sediment sea water interface. This is also confirmed by the studies of Bala Krishnan Nair et al. (1999) who have observed low Mn_{xs} in trap particles at site EAST (eastern Arabian Sea trap) due to reductive dissolution of Mn oxy/hydroxides in the mid water depth denitrifying layer. Under these sub-oxic diagenetic conditions the Ba productivity signal is partially lost but at the same

biogenic and redox sensitive elements are accumulating, an observation in conformity with the studies of McManus et al. (1999). The negative relation between Ba_{xs} and Cd is very well expressed in area B in comparison to area A due to high Cd concentrations.

The spatial distribution of Ba_{xs} appears to suggest its usefulness, in spite of several constraints, as a qualitative proxy for productivity. It may allow to discriminate whether productivity is high or low, at least along the WCMI.

6.0 CONCLUSIONS :

The spatial variation of Ba_{xs} and Zn_{xs} at the WCMI is in accordance, on a broader scale, with the distribution of OC and planktonic foraminifera productivity proxy *G. bulloides*, despite the partial loss of the Ba productivity signal. High productivity coupled with high sedimentation rate and an oxygenated interface seems to have resulted in relatively high concentrations of Ba and at the same time low accumulation of biogenic elements. Sub-oxic diagenesis leads to the poor preservation of Ba_{xs} and the accumulation of biogenic and redox sensitive elements along the NE continental margin of India. Ba_{xs} in combination with biogenic elements appears to give an indication for productivity variations along Indian margin.

The study of pore waters along with benthic Ba flux experiments will certainly improve the knowledge in understanding the biogeochemical cycling of Ba along WCMI.

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Caption to Figures:

Fig. 1 Station location map. Six transects from area A, B and C where excess Ba, Zinc and Cu (Ba_{xs} , Zn_{xs} and Cu_{xs}) calculated are also shown

Fig. 2 Spatial distribution of Calcium carbonate (wt.%)

Fig. 3 Spatial variation of Ba_{xs} (see text for Ba_{xs} calculations)

Fig. 4 Spatial variation of Zn/Al

Fig. 5 Relationship between Ba_{xs} (ppm) and water depth

Fig. 6 Relation between

(a) Ba_{xs} vs U/Al and Ba_{xs} vs Cd/Al in area A

(b) Ba_{xs} vs U/Al and Ba_{xs} vs Cd/Al in area B.

Ba, U and Cd concentrations (in ppm) of granite and basalt (Taylor, 1964) (source rocks in the study region, Krishnan, 1968) are also shown

Captions to Tables:

Table 1. Ba_{XS} , Zn_{XS} and Cu_{XS} (calculated) along six transects in the study region.

Table 2. Correlation coefficient of biogenic elements in area A and B. Normal letters represent area A and bold letters area B. Correlation coefficients are obtained for the samples with low terrigenous component. See text for details.

Table 3. Metal/Al values of biogenic elements in the oxygen minimum zone (water depth of 150-1200 m).

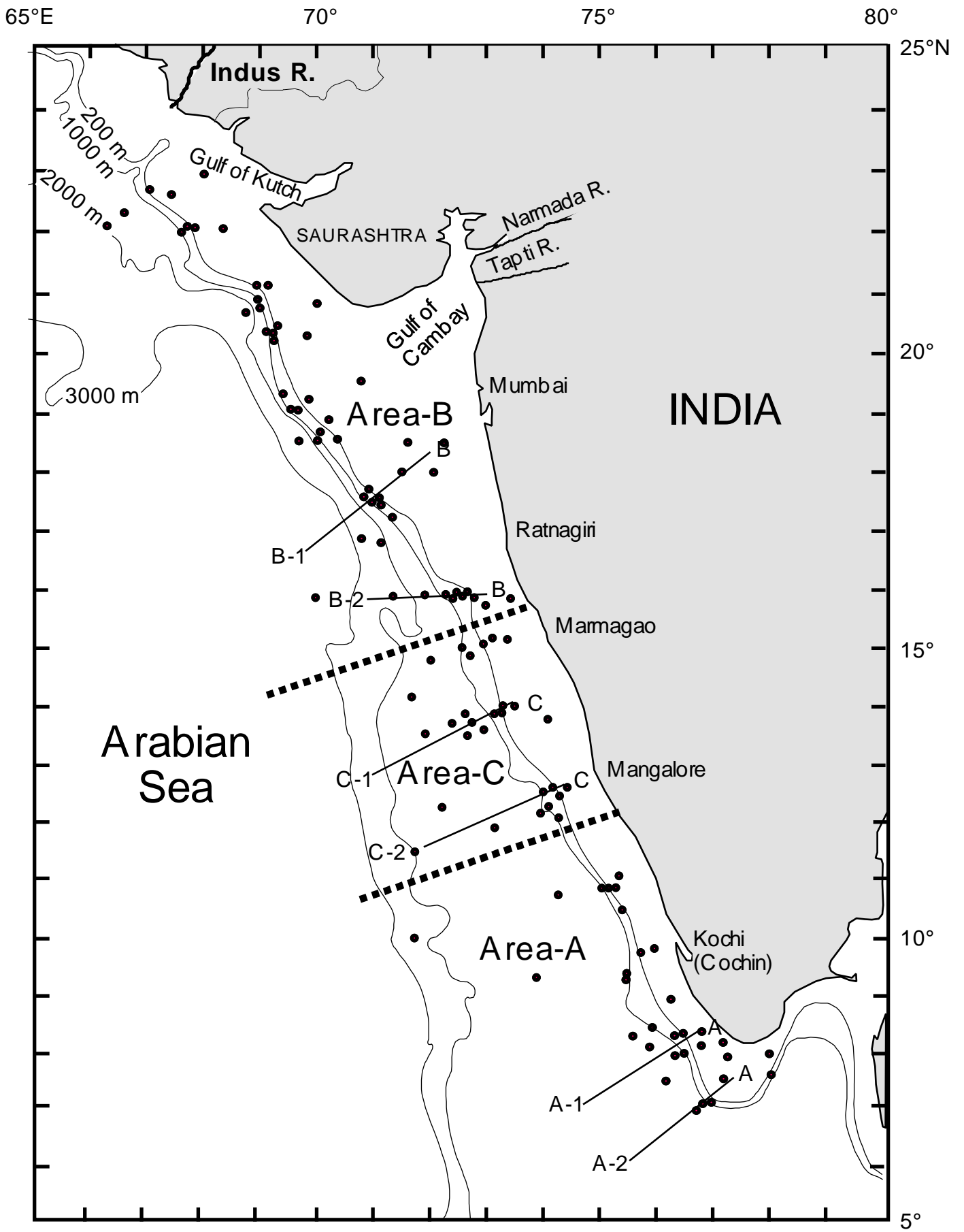


Fig. 1

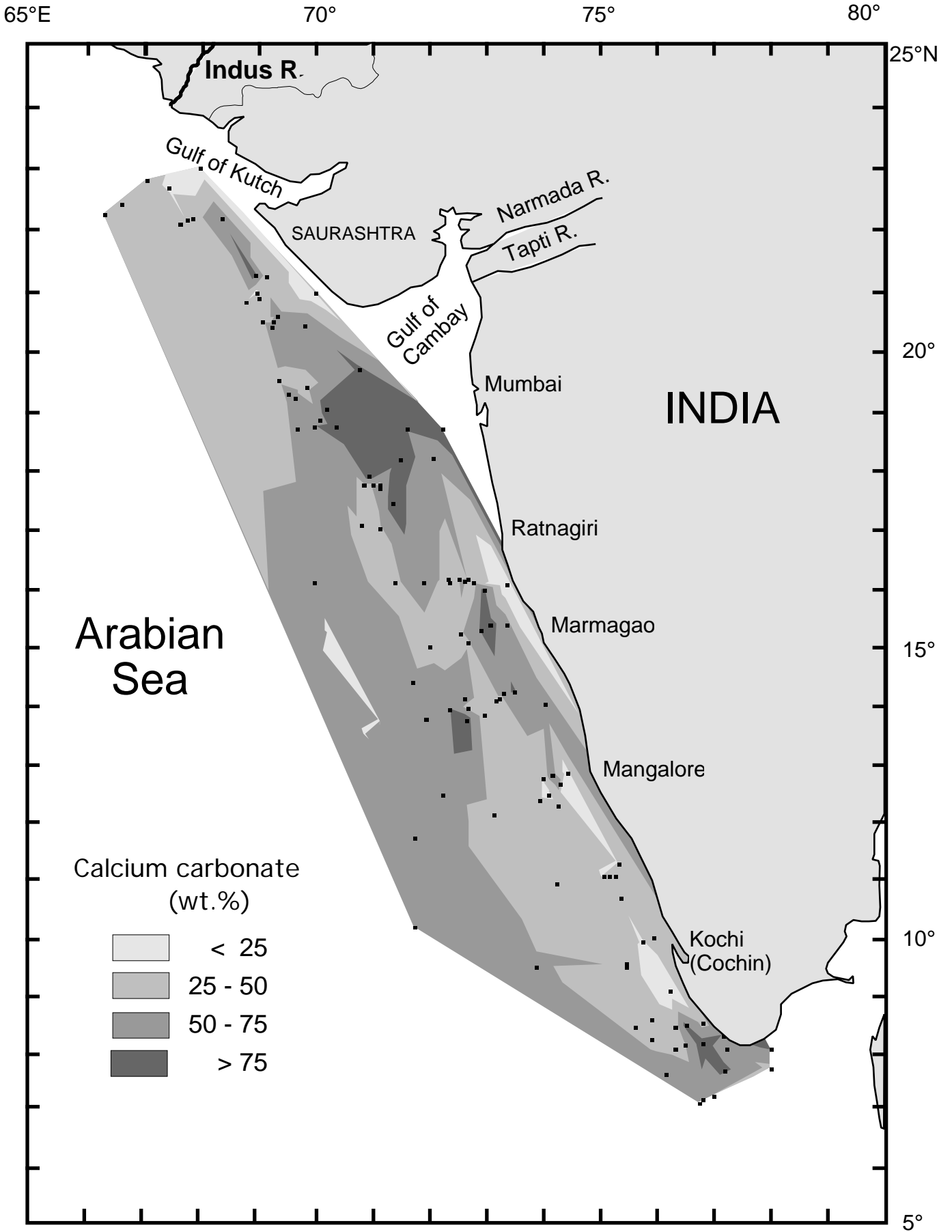


Fig. 2

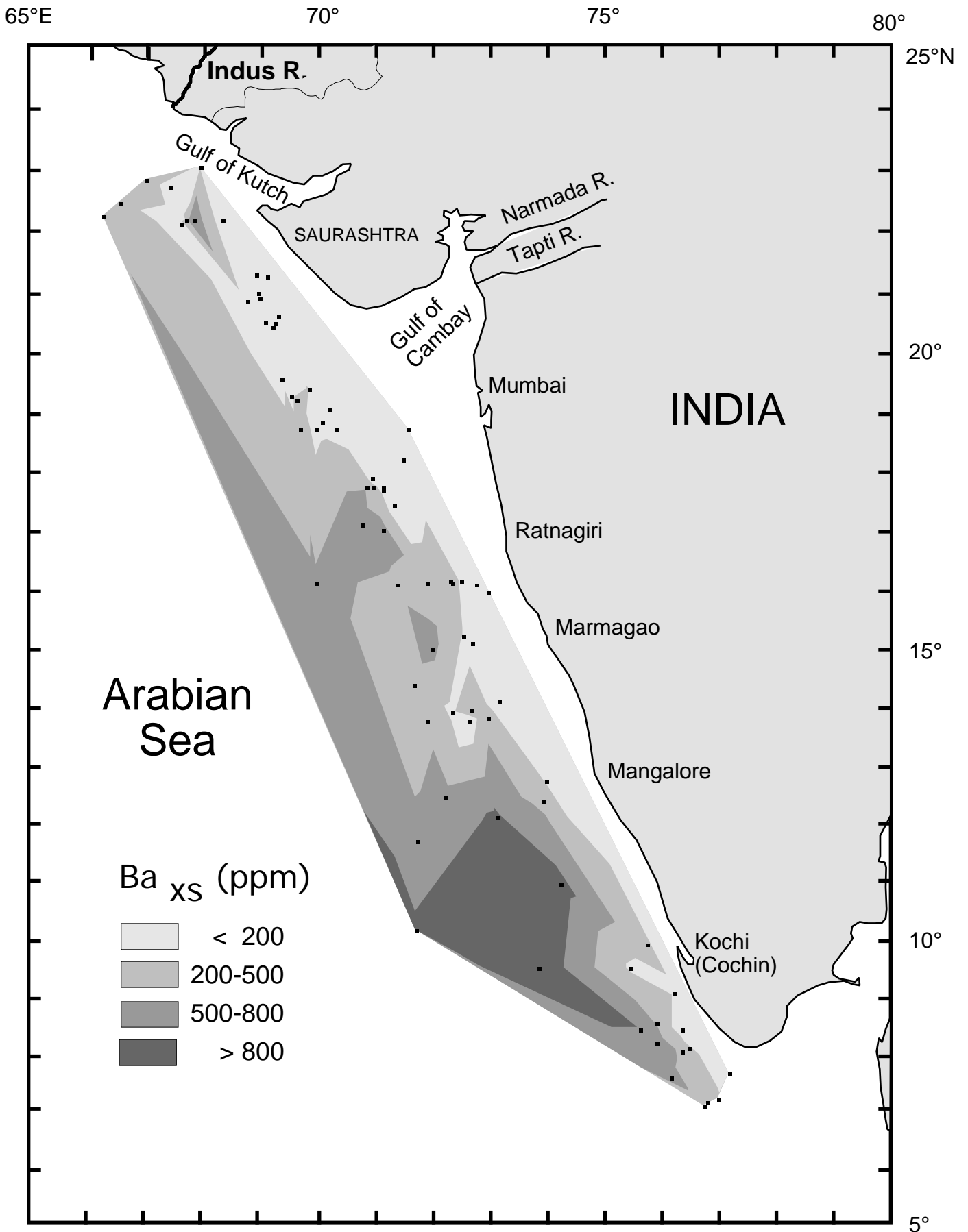


Fig. 3

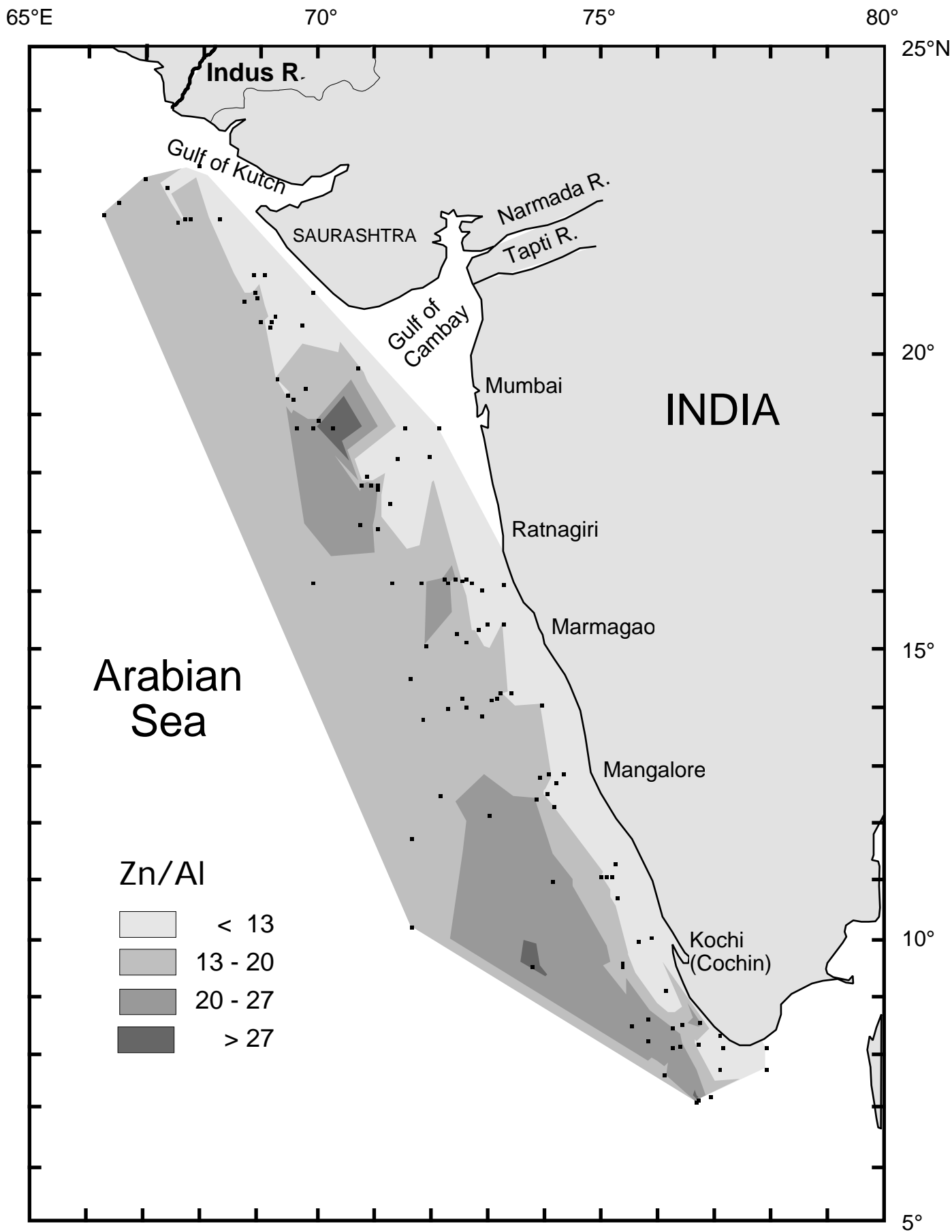


Fig. 4

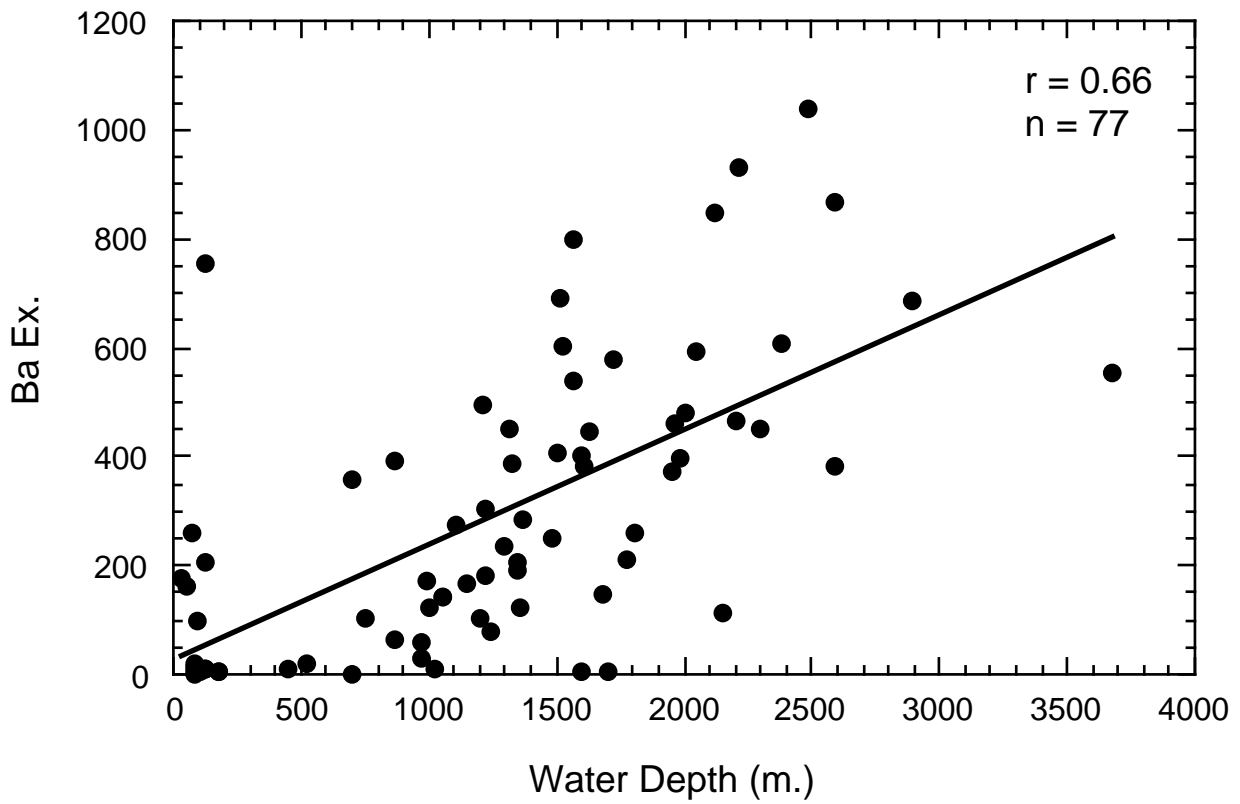
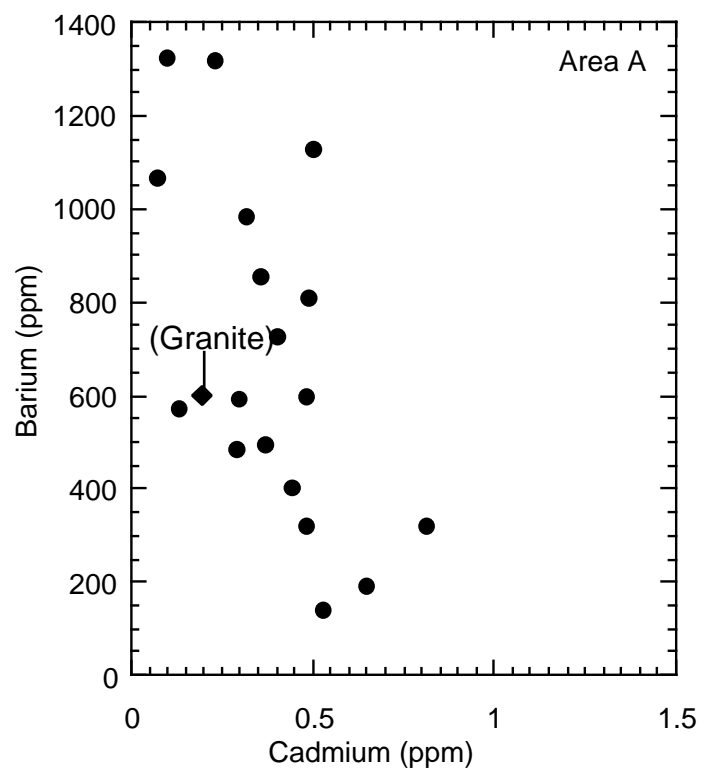
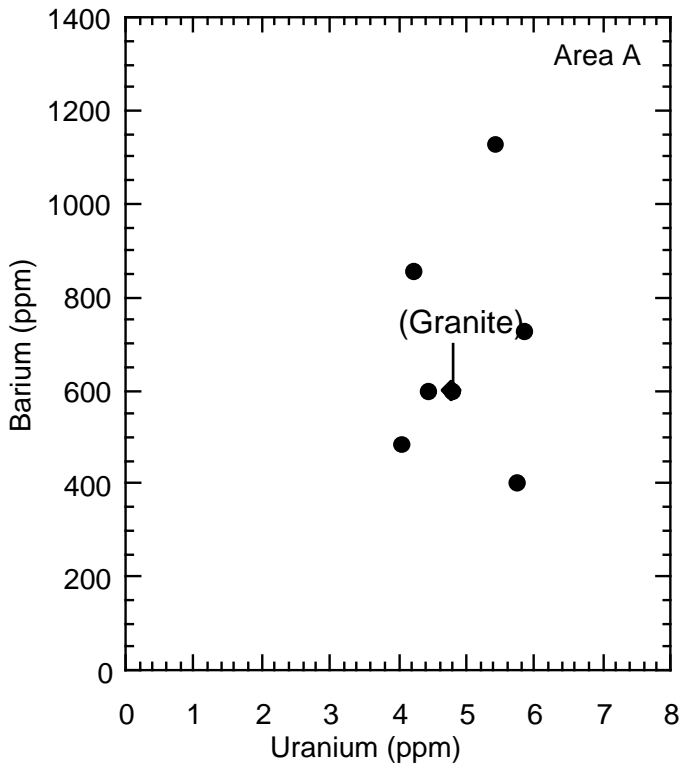


Fig. 5

(a)



(b)

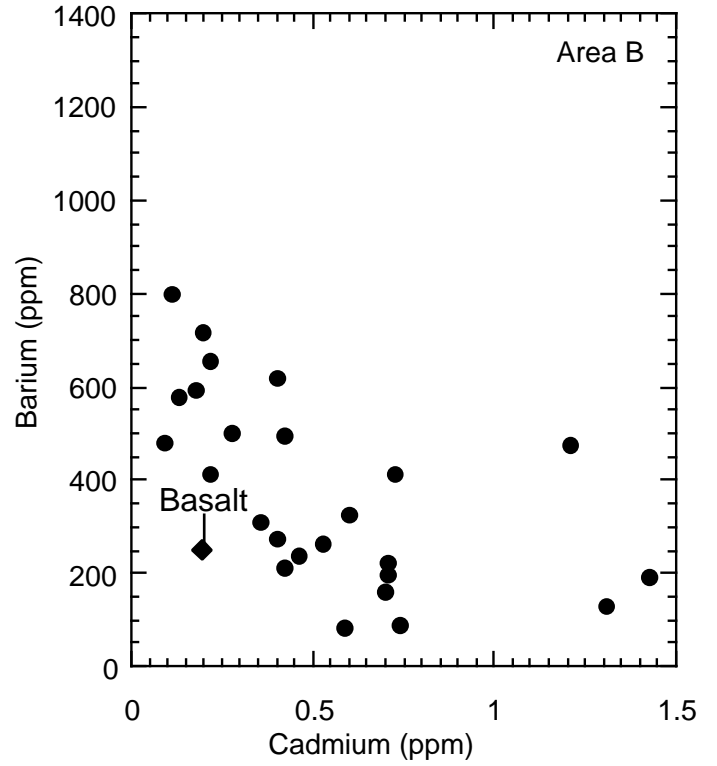
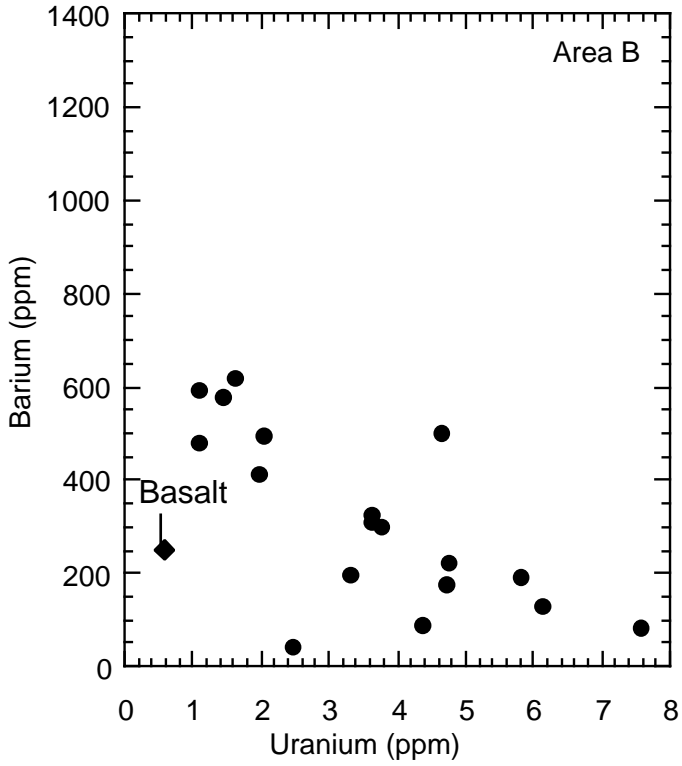


Fig. 6

Table 1

Area	Trans ect	Water Depth (m.)	Excess			Trans ect	Water Depth (m.)	Excess			
			Ba	Zn	Cu			Ba	Zn	Cu	
			----ppm-----						----ppm----		
A	A-A1	85	--	--	--	A-A2	81	--	--	--	
		375	--	--	--		870	395	47	--	
		870	69	47	--		1480	255	27	--	
		1110	279	53	--		1980	398	21	--	
		1320	453	49	--						
		1530	606	33	--						
B	B-B1	100	3	--	--	B-B2	85	2	--	--	
		750	102	9	13		220	--	--	--	
		1060	140	11	--		990	168	13	--	
		1300	235	18	--		1217	304	22	--	
		2000	479	7	5		1610	383	7	--	
C	C-C1	117	--	--	--	C-C2	148	--	--	--	
		190	--	--	--		210	--	9	9	
		1020	13	22	15		610	--	2	2	
		1110	--	10	--		980	--	--	--	
		1630	448	18	--		1220	189	26	--	
		1680	149	14	9		1725	582	19	13	

Ba_{xs} is calculated by assuming that Ba/Al ratio of lithogenous material is represented by the source rocks due to non-availability of particulate Ba/Al values. A Ba/Al value of 0.0079 is taken for areas A and C and 0.00285 for area B (see text for details).

As riverine particulate matter data is not available for area A and C the metal excess values for Zn, Cu and V are calculated with respect to a shelf sediment close to the continent. Care is taken to avoid the provenance/mineralogical effect by comparing K/Al and Ti/Al ratio of the shelf sediment with other sediment samples chosen for calculating metal excess. This approach seems to be appropriate when Zn/Al and Cu/Al of Narmada and Tapi riverine particulate matter in area B ($14-17 \times 10^{-4}$ and $16-17 \times 10^{-4}$) is compared with a shelf sediment having maximum values of Zn/Al and Cu/Al (17 and 19×10^{-4}). The riverine particulate matter and shelf sediment data match within a narrow range. Metal excess is calculated as per equation 1 (see text for details).

--- Negative biogenic values which are ignored

TABLE 2

	CaCO ₃	Ba/Al	Si/Al	Cu/Al	V/Al	Zn/Al
CaCO ₃						
Ba/Al	0.66 0.36					
Si/Al	0.75 0.05	0.81 0.42				
Cu/Al	0.55 0.20	0.87 0.09	0.60 0.26			
V/Al	0.44 - 0.20	0.78 - 0.45	0.81 - 0.19	0.52 - 0.15		
Zn/Al	0.30 0.32	0.53 0.63	0.33 0.28	0.60 0.32	0.22 - 0.66	
Depth	0.48 0.03	0.90 0.77	0.72 0.44	0.85 ---	0.78 - 0.46	0.39 0.39

N = Number of samples; Normal letters n = 18; Bold letters n = 26

Level of confidence (n = 18) 0.56 at 99 level

Level of confidence (n = 26) 0.45 at 99 level

TABALE 3

	Area A			Area B			Area C			River Particu- -late* (x 10 ⁻⁴)	Ave. shale ^{\$} (x 10 ⁻⁴)
	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.		
Cu/Al	6	12	9	1.3	23	17	6	17	8	16-17	4.4
V/Al	12	16	13	18	28	22	14	20	15	n.a	14.6
Zn/Al	11	28	19	9	21	16	12	20	15	14-17	12.9

* Narmada and Tapti river particulate (Bhaskaran et al., 1984)

\$ Wedepohl (1971, 1991)

n.a. Data not available

SUMMARY:

This thesis deals with the eastern Arabian Sea upwelling system, which is caused by biannual current reversals associated with winter (NE) and summer (SW) monsoons. The excess bioproductivity and associated organic matter remineralization enforces consumption of dissolved oxygen and results in the development of an oxygen minimum zone (OMZ) at intermediate water depths (150 -1200 m; dissolved O₂ levels < 0.2 ml/l). The monsoon and OMZ signals are finally preserved in the underlying sediments. Detailed inorganic geochemical studies are carried out on western continental margin of India (WCMI) surface sediments to understand the behavior of biogenic and redox sensitive elements under these oceanographic settings.

While studying the trace metal accumulation/depletion in the OMZ a mismatch was noticed with the organic carbon (OC) distribution published previously. When the sediment samples were re-analyzed for OC by coulometry a large discrepancy was noticed. In view of this fact a new OC spatial distribution map is provided for WCMI sediments.

OC concentrations are high (> 2%) along SW coast of India where the productivity is high (> 1 g C/m²/day). In this band high concentrations of OC(>4%) occur as isolated patches with maximum values reaching up to 5.3%. OC is relatively less enriched (1-2%) at the NE Arabian Sea where the productivity is moderately high (0.75 - 1 g C/m²/day). In this band 2-4% and > 4% of OC occur as isolated patches. Along central margin of India where the productivity is low (<0.50 g C/m²/day) the OC concentrations are less than 4%. Thus a broad similarity is observed between OC distribution and productivity, in conformity with the abundance of *G.bulloides*, a planktonic foraminiferal productivity proxy. Surprisingly, a continuous OC-rich band (>8% or >4%) and high OC contents (up to 12-16%) as reported earlier, could not be confirmed in this new study.

High Mn/Al and low Cd/Al and Se/Al ratios in oxic shelf, lower slope and deep sea sediments infer release (Cd, Se) or fixation (Mn) of metals during aerobic degradation of organic matter. Low Mn/Al and high Cd/Al and Se/Al ratios are, by contrast, observed in sediments from within the OMZ. A north-south gradient is seen which suggests a stronger oxygen depletion in the north. Low P/Al, Cu/Al and V/Al ratios in the SW area support this assumption. High concentrations of Iodine (up to

~0.18%) are in accordance with the above findings and infer intense oxic regeneration and loss of an authigenic fraction of Cd and Se. Intense reducing conditions in NE Arabian Sea upper slope sediments favor the accumulation of Cd and Se besides P ($P_{org.}$), Cu, V and Cr and reductive release of Mn. Low I/OC ratios indicate intense reducing conditions as Iodide is not adsorbed effectively by OC under suboxic/anoxic conditions.

The spatial distribution of Ba is studied, as it may serve as a productivity proxy along with Si, Cd, Cu, V, Zn and U. The WCMI is characterized by Deccan Trap basalts in the north and granitic rocks and gneisses south of 16°N. This differing geological setting besides climate induced weathering has to be considered when interpreting major and minor element data of sediments deposited in this area.

The increase of excess Ba (Ba_{xs}) with water depth suggests its partial loss from sediments overlain by the OMZ. Ba_{xs} and Zn_{xs} distributions are in broad accordance with productivity, OC and *G. bulloides* abundance. At the SW margin of India Ba/Al ratios show a positive correlation with opaline silica, Cu/Al and V/Al ratios. Despite high productivity Cd/Al, Cu/Al, V/Al as well as Cu_{xs} and V_{xs} values are relatively low compared to the NE margin of India, indicating intense regeneration processes at an oxygenated sediment interface.

The lack of a correlation between Ba and opaline silica in NE Arabian Sea sediments suggests the partial loss of the Ba_{xs} signal during suboxic/anoxic conditions. Alternatively the productivity in this region may be dominated by nitrate and not silicate. Low Zn_{xs} values support this assumption. Dilution of opaline silica with quartz derived from major rivers is another possibility. The enrichment of OC, Cd, Cu, V (non-lithogenic) and U in sediments from the OMZ infers the presence of a suboxic/anoxic interface in this region.

It seems that the Ba productivity signal is maintained under oxic conditions. Suboxic/anoxic conditions likely have resulted in poor preservation of biogenic Ba. Although Ba may partially be lost the productivity trend still appears to be reflected by Ba/Al ratios of WCMI sediments, when provenance of the terrigenous detrital material is considered.

Curriculum Vitae:

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Research publications : see attached list

List of publications :

(a) Papers published or submitted

Paropkari, A.L., Iyer, S.D., Chauhan, O.S., Prakash Babu, C., 1991. Depositional environments inferred from variations of CaCO₃, organic carbon and sulfide sulfur: A core from SE Arabian Sea. *Geo-Mar. Lett.* 11, 96-102.

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(b) Internally published Scientific/Technical Reports

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Paropkari, A.L., Mascarenhas, A., Rao, Ch.M, Prakash Babu, C., Murty, P.S.N., 1994. Elemental distributions in sediments and potential offshore mineral

resources from the western continental margin of India. Tech. Report No. NIO/TR-4/94.

(c) Abstracts presented/accepted in organised symposium/conferences etc.,

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Paropkari, A.L., Prakash Babu, C., Rao, Ch.M., Murty, P.S.N., 1991. Geochemistry of the surficial sediments of the western continental margin of India. Abstract presented at International symposium on Oceanography of Indian Ocean, held at National Inst. of Oceanography, Dona paula, Goa. Jan. 14-16, 1991.

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- Prakash Babu, C., Brumsack, H.J., Schnetger, B., Böttcher, M.E., 1998. Distribution of organic carbon and barium along eastern Arabian sea surficial sediments. International symposium on Benthic process in the Deep Arabian Sea 1-3 July, 1998, Edinburgh, Scotland.
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Ich erkläre hiermit, daß ich die Arbeit selbständig verfaßt, andere als die von mir angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzen Werken wörtlich oder inhaltlich entnommenen Stellen als solche gekennzeichnet habe.

Oldenburg, Dezember, 1999.