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## Research Article

# IMPACTS OF MONSOON VARIABILITY ON THE MAJOR ELEMENT CONCENTRATION OF SEDIMENT CORE OFF COCHIN, SOUTH-EASTERN COAST OF ARABIAN SEA

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### ABSTRACT

This paper reports use of <sup>210</sup>Pb for determination of age of coastal oceanic sediments and determination of the paleo-redox and paleo-productivity proxy by measurement of the concentration of redox sensitive elements. This paper is a synthesis of the use of selected trace elements as proxies for reconstruction of paleo-productivity and paleo-redox conditions. Redox sensitive trace metals tend to be more soluble in water under water in oxidizing conditions while they precipitate under reducing conditions increasing their concentration in authigenic sediments for which these elements can be used as paleo-redox proxies. Significant increase in the amount of Calcium from 1975 to 1980 was observed as a result of high upwelling.

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## INTRODUCTION

Paleoclimatology is a systematic reconstruction of the climatic conditions existed during the geological past and understanding various physical forces that influenced the past climatic cycles. Climate proxies are preserved physical characteristics of the past in various archives providing indirect evidences that stands in for direct measurements of various parameters. Climatic reconstruction can be done with the help of several paleoclimatic “proxies”. The past climatic reconstructions may refer to the past temperature changes, rain-fall amount, humidity, sea level changes, amount of sedimentation, biological productivity, and so on. Study of elemental concentration in the core can help us in reconstructing the paleoenvironmental and palaeoredox condition.

Many trace elements are present in seawater either in soluble form or adsorbed onto particles. Removal of dissolved trace elements from the water column to the sediments results from either biotic or abiotic processes. In suboxic environments, some enrichment may occur through diffusion of dissolved trace elements from the water column across the sediment-water interface or through remobilization and repartitioning along redox gradients within the sediments. The variety of processes results in trace-element enrichments that mirror the specific conditions prevailing by the time of deposition and

early diagenesis. Consequently, trace-element abundances in sediments and sedimentary rocks allow us to reconstruct paleodepositional conditions.

Concentrations of organic matter (OM) in sediments and sedimentary rocks record only a fraction of the total biological productivity in surface waters of the ocean. Export productivity is the part of the phytoplankton biomass that “escapes” from the generally efficient recycling operating in the upper portion of the water column (organic C sinking flux). This material is delivered to the sediment-water interface following additional degradation during passage through the water column. Despite the complications attributable to highly efficient organic recycling, export productivity, delivery to the sediment-water interface and the final burial flux are generally proportional to surface-water productivity.

At the sediment-water interface or within sediments, oxygen-limited conditions and ultimately anoxia may develop when the oxygen demand exceeds the supply. The Arabian Sea is one such such region where oxygen reaches to almost zero at depths between 200-1000 m and generates oxygen minimum zone (OMZ)<sup>1</sup>. Unlike open oceans, coastal areas experience significant changes due to terrestrial contribution from rivers. Any marginal changes in trace element concentration in coastal region can be very detrimental in regulating the coastal

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processes and its ecosystem. Thus, estimation of trace elements in sediments and water in coastal regions is crucial to understand its variation and associated changes in the coastal environment.

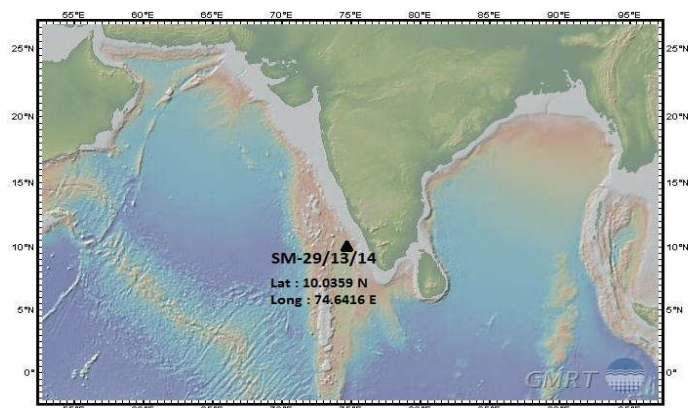
## MATERIALS AND METHODS

The core SM-29/13/14 is collected from Arabian Sea near the western coast where OMZ develops due to increasing productivity after monsoon. During monsoon, upwelling occurs in the Arabian sea due to which nutrient rich deep waters comes up to the surface. In addition to this, numerous streams such as Mandovi, Periyar flowing into the Arabian sea also brings a lot of minerals which acts as nutrients. This increases the productivity and hence aquatic life proliferates which consumes a lot of oxygen leading to seasonal anoxia.

In order to ascertain the elemental distribution in the Oxygen Minimum Zone (OMZ) that persists in the Arabian Sea owing to seasonal anoxia, the sediment core was collected from the Arabian Sea near the western coast of India. The sediment core collected from the Arabian Sea was subsampled at 1 cm interval using a thin perspex knife. The sediment core was assayed for  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  using non-destructive gamma counting technique <sup>2</sup>.



**Figure 1** Process of sediment core retrieval by the gravity corer onboard Sagar Manjusha cruise



**Figure 2** Location of the sediment core SM-29/13/14 collected from the south-eastern Arabian Sea

Nearly 3 gm of dry homogenised samples were sealed in a plastic vial and stored for at least 15 days in order to enable  $^{226}\text{Ra}$  and  $^{222}\text{Rn}$  in each sample to establish radioactive equilibrium. The packed samples were placed in the High Purity Germanium detectors (HPGe) coaxial 16 x 40 mm well type detector (Canberra Industries, CT, USA). The samples were counted for nearly three days to determine the activities of  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$ . The sedimentation rate was determined by applying constant flux: constant sedimentation rate (CF:CS) model of  $^{210}\text{Pb}$  dating

### Sample processing for Major element analysis

The measurement of major and trace elements in sediments is carried out to ascertain variations of various climate indicative proxies. Towards this, samples need to be completely dissolved in solution for their measurements. Prior to the complete dissolution of the sediments, they were dried at 80°C and finely crushed and homogenised with the help of agate mortar in order to avoid any metallic contamination.

Nearly 0.3 gm of bulk, dried crushed sediment samples were subjected to closed digestion (in Microwave digestion system) by treating them with combination of concentrated acids (HCl, HF and HNO<sub>3</sub>) using standard protocol. The digested samples were dried and subjected to open digestion for the removal of silica or organic particles. The dissolved solutions of the sediments were taken in 2 % HNO<sub>3</sub> medium and made up to 50 ml. The sample measurement protocol for relevant elements were calibrated following standard procedure used at PRL, Ahmedabad <sup>3,4</sup>. All the reagents used in the present study were of high purity analytical grade and the contamination from the time of sampling to analysis were minimised by taking due care.

The digested samples were analysed for major elements (Al, Fe, Ca and Mg) by aspirating the sample solutions in the ICP-AES (Jobin Yvon 38S). The reproducibility of the instrument was ascertained by performing duplicate analysis of the samples analysed. The accuracy of analytical procedure was assessed using certified reference standard NOVA, which is deep sea clay sediment collected from Northern Pacific at water depth of 5351 m <sup>5</sup> and MAG which is a fine grained gray-brown clayey mud with low carbonate content, from the Wilkinson Basin of the Gulf of Maine <sup>6</sup>. These reference standards were used as they had similar composition and sample matrix when compared to the samples being analysed as part of this study.

## RESULTS AND DISCUSSION

The  $^{210}\text{Pb}_{(\text{xs})}$  activity was observed up to a depth of 22 cm. The  $^{210}\text{Pb}_{(\text{xs})}$  activity throughout the core ranges between 0.02 to 0.81 dpm/gm (Unpublished work). The core has archived the depositional history since 1966 AD. High sedimentation rate has been observed between 1966–1989 AD (50–20 cm) flowed by a reduction in the sedimentation rates up to the surface i.e. between 1989–1999 AD (20–10 cm) the sediment deposited with a rate of 0.95 cm/yr. which was followed by a sedimentation rate of 0.69 cm/yr during the deposition between 1999–2013 AD (10 cm–surface).

Examination the behaviour of certain elements in coastal sediments will provide valuable information on the chemical state of the environment of deposition of ancient sediments,

provided the characteristic distribution of these elements in the modern ocean is understood. The vertical distribution for most of the trace elements are controlled by production, sinking and deposition of the biogenic particles<sup>7</sup>. Delineating the elements originating from human activities and those from natural weathering is an essential part of geochemical studies. One such technique largely applied is ‘normalization’, where metal concentrations were normalized to a textural or compositional characteristic of sediments. Among reference elements, use of Al to normalise the metal data seems to be most consistent, as it is a major constituent of fine-grained aluminosilicates associated with bulk of the trace metals. It is highly refractory and its concentration is generally not influenced by anthropogenic sources. Various normalising techniques for detrital concentration have been used in past like grain size, total organic carbon, Fe and Al to trace element enhancement over the lithogenic background<sup>8-10</sup>.

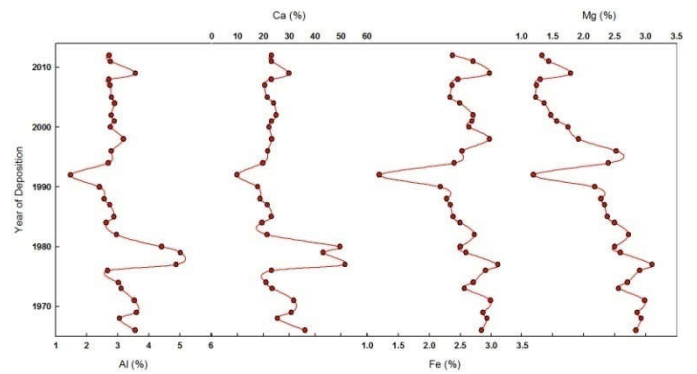


Figure 3 Concentrations of major elements in sediment core SM-29/13/14

Observed high peaks of Ca during 2006-08, 1987-88, 1977-78 which is attributed to strong monsoonal winds. Strong monsoonal winds leads to more upwelling due to which nutrient rich deep waters come up to the surface and hence

Table 1 Depth and year wise distribution of major elements

Depth (cm)	Age	%				Ca/Al	Fe/Al	Mg/Al	
		Al	Ca	Fe	Mg				
0-1	0.5	2012	2.72	23.1	2.37	1.33	8.49	0.87	0.49
1-2	1.5	2011	2.76	23.1	2.71	1.44	8.37	0.98	0.52
2-3	2.5	2009	3.57	29.8	2.97	1.79	8.36	0.83	0.50
3-4	3.5	2008	2.72	23.0	2.46	1.30	8.48	0.91	0.48
4-5	4.5	2007	2.75	20.5	2.37	1.24	7.46	0.86	0.45
5-6	5.5	2005	2.80	21.4	2.33	1.23	7.67	0.83	0.44
6-7	6.5	2004	2.90	23.9	2.49	1.37	8.25	0.86	0.47
7-8	7.5	2002	2.79	24.9	2.71	1.48	8.94	0.97	0.53
8-9	8.5	2001	2.89	23.1	2.69	1.57	8.00	0.93	0.54
9-10	9.5	2000	2.76	22.2	2.64	1.75	8.04	0.96	0.63
11-12	11.5	1998	3.18	23.2	2.97	1.92	7.30	0.93	0.60
13-14	13.5	1996	2.79	21.6	2.53	2.53	7.75	0.91	0.60
15-16	15.5	1994	2.70	19.8	2.40	2.40	7.33	0.89	0.57
17-18	17.5	1992	1.48	9.8	1.19	1.19	6.65	0.81	0.50
19-20	19.5	1990	2.41	17.8	2.18	2.18	7.37	0.91	0.56
21-22	21.5	1988	2.56	18.7	2.28	2.28	7.32	0.89	0.56
23-24	23.5	1987	2.74	21.5	2.34	2.34	7.85	0.85	0.55
25-26	25.5	1985	2.88	23.1	2.38	2.38	8.02	0.83	0.54
27-28	27.5	1984	2.63	19.4	2.50	2.50	7.39	0.95	0.61
29-30	29.5	1982	2.96	21.4	2.73	2.73	7.25	0.92	0.59
31-32	31.5	1980	4.42	49.6	2.50	2.50	11.23	0.57	0.42
33-34	33.5	1979	5.02	43.1	2.59	2.59	8.59	0.52	0.34
35-36	35.5	1977	4.88	51.6	3.11	3.11	10.57	0.64	0.43
37-38	37.5	1976	2.67	23.1	2.90	2.90	8.66	1.09	0.67
39-40	39.5	1974	3.02	21.0	2.71	2.71	6.94	0.90	0.51
41-42	41.5	1973	3.11	23.3	2.56	2.56	7.51	0.82	0.57
43-44	43.5	1971	3.53	31.8	2.99	2.99	8.99	0.85	0.59
45-46	45.5	1969	3.60	30.7	2.86	2.86	8.53	0.80	0.54
47-48	47.5	1968	3.05	25.4	2.93	2.93	8.32	0.96	0.61
49-50	49.5	1966	3.56	36.1	2.84	2.84	10.14	0.80	0.57

Major elements data when plotted against sediment deposition, Al and Ca both shows similar variation (Figure 3; Table 1). While Fe and Mg shows same variation with each other. From 1965-1975, Al and Ca ranged between 3-4 % but post 1975, it increased to almost 5%. But later again it ranged between 2-3 %. This sudden increase during 1975-1982 can be high biological productivity as a result of high rainfall in the area. While both Fe and Mg showed high values from 1965-1990 and later Fe showed same variation but Mg started decreasing. As both this elements are associated with organic carbon productivity, their inverse relation with Al and Ca was expected.

productivity increases. Hence, the concentration of Calcium which gives the measure of productivity also increases.

When any element is normalised by Al, the detrital contribution of that element is removed and whatever trend remains it shows the excess from terrestrial or in-situ production of the element. To investigate whether monsoonal changes during the last 50 years were accompanied with changes in provenance of terrigenous supply, depth-profiles of Fe/Al and Mg/Al (wt. ratios) were analysed (Figure 4). Mg/Al ratios show relatively higher values (0.5) compared to many earlier studies from the region. While Fe/Al mimic the trend of the Mg/Al, showing similar source of both this metals.

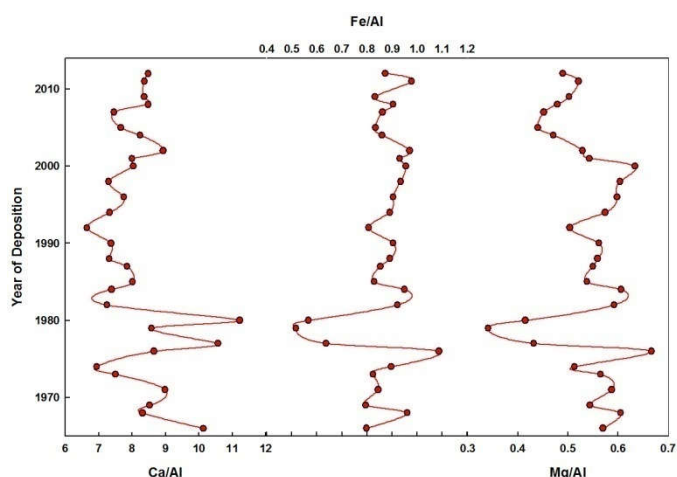


Figure 4 Aluminium normalised major elements ratios in sediment core SM-29/13/14

## CONCLUSION

We observe a significant increase in the amount of Calcium in between 1975 and 1980. This might be possibly due to strong monsoon and high upwelling in that timeframe. Due to upwelling, aquatic life such as foraminifera proliferates whose shell is composed of  $\text{CaCO}_3$ . Once they die, they settle down into the seafloor, thus increasing the amount of Ca in the oceanic sediments. Also, the seasonal streams flowing into the Arabian Sea also deposits Ca into the sea. Due to high rainfall during monsoon, the streams erode more sediments from the continental crust which is rich in Al and then deposits them in the sea. Hence, we see a high peak in Al content during strong monsoon owing to high rainfall.

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