Distribution of major and trace elements of a sediment core from the eastern Arabian Sea and its environmental significance

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A sediment core recovered from the southeastern Arabian Sea off the Indian subcontinent was analysed to understand the distribution of major (Fe, K, Mg, Al, Ca and Sr) and trace elements (Mn, Ni, Cu and Co) as well as their environmental significance. According to the results, variation of Fe, K, Mg and Al during early Holocene period is reflective of the strengthened southwest monsoon and resulting fluvial input of terrigenous materials to the study region. The concentration profile of Ca, Sr and total organic carbon during late Holocene reveals increased productivity and coastal upwelling during recent periods. The profile of redox-sensitive metals indicates the role of terrigenous sources in the variation of these elements apart from the scavenging-releasing effects of Fe–Mn oxides/hydroxides as well as decrease in oxygen level in sediment–water interface from early Holocene to late Holocene period. The study suggests that two factors are predominantly responsible for observed geochemical variations – terrigenous and biological contribution.

Keywords: Fluvial input, Holocene, major and trace element chemistry, upwelling.

geochemical study of marine sediments provides important insights on the role of environmental processes in controlling sediment distribution, fluctuations in biological productivity, redox state of bottom water, tectonic activity and wind strength. The understandings about the distribution of sedimentological, geochemical and magnetic proxies such as clay minerals, elements and magnetic records from sediments are useful tools in the assessment of status of environmental conditions. Once elements are discharged into the water, they rapidly become associated with particulates and are incorporated in bottom sediments. The elements associated with sediments are, however, not sheltered permanently. Under changing environmental conditions, they may be released to the water column by various processes of remobilization. Also in the marine aquatic systems, sediments may be both a carrier and a possible source of...

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various elements, metals in particular. Especially in the oxygen minimum zone (OMZ), trace elements play a vital role, since OMZ has an important impact on ecosystems in terms of their contribution to greenhouse gases (GHGs) to the atmosphere during decay of organic matter. Here, the trace elements minimize the ecosystem stress by forming complexes and sulphides, which leads to decrease in the release of GHGs. The role of organic matter and other geochemical factors in trace metal accumulation has been studied. There are several studies dealing with geochemistry of Arabian Sea sediments. These are mainly focused on the clay mineralogy and elemental distribution of the Arabian Sea.

The Arabian Sea is characterized by a reversal of monsoonal winds that results in large seasonal variations in upwelling and related primary productivity, which has a large impact on the distribution of elements in the sediment. Of the two monsoons, southwest (SW) and northeast (NE), the former is dominant in the Arabian Sea and surface winds associated with this season (June–September) blow from the SW direction leading to the increase in continental humidity and precipitation over the Indian peninsula. The hinterland of the SE Arabian Sea also receives heavy rainfall (up to a maximum of 3000 mm/yr) and upwelling waters in this region are capped by a thin layer (5–10 m thick) of warm, low-salinity water, which in part forms from local precipitation and in part from run-off from the narrow coastal plain. During the SW monsoon, biological productivity increases and results in a permanent OMZ that impinges the continental margins at depths between 150 and 1200 m (ref. 25). The distinct geochemical compositions of sediment cores from the Arabian Sea reveal the source, weathering mechanism and factors that control their composition. Moreover, the presence of OMZ in the Arabian Sea makes the investigation of geochemical proxy variation significant in this region.

The present study examines the down-core variations in major (Al, K, Fe, Mg, Ca and Sr) and trace element (Co, Cu, Ni and Mn) concentrations in a sediment core from southeastern Arabian Sea in terms of changes in terrigenous flux and biological productivity.

A 180 cm long gravity core was recovered from a water depth of 218 m from the eastern Arabian Sea (72.62°E, 15.99°N) during SK-268 cruise of ORV Sagar Kanya (SK 268/GC 01, Figure 1). The core falls within the modern OMZ. The sediment along the entire length of the core comprises olive-grey clayey silt/silty clay. The core was sub-sampled on-board at an interval of 2 cm.

The subsamples were subjected to detailed visual examination under a binocular microscope. Grain-size analysis was carried out on 10 representative sediments at depth intervals following standard procedures. Samples were treated with 20% hydrogen peroxide to remove the organic matter. Calcareous materials were removed by treating with 1 N hydrochloric acid. Later, the samples were washed and sieved through 63 μm sieve after adding 20% sodium hexametaphosphate. Using this method the weight of sand and clay fraction was determined.

For inorganic elemental chemistry, sediments were dissolved following acid dissolution procedure. The powdered sediment samples (n = 90) were weighed accurately (50 mg), transferred to clean Teflon beakers and subjected to open acid digestion. The sediments were repeatedly digested by treating with a mixture of HF, HNO3 and HClO4 in the ratio 6:3:1. Finally, the extract was brought to a standard volume. Major and minor elements were analysed using AAS (Thermofisher Scientific M Series at National Centre for Antarctic and Ocean Research, Goa). The accuracy and reproducibility were confirmed by repeated measurements of the NIST standards. The accuracy of the analytical method was better than 3% and reproducibility of the measurements for all the elements was better than ±8%. Total organic carbon (TOC) analysis was performed on 19 subsamples from selected depth intervals. Sediment samples were treated with 2 M HCl to remove inorganic fraction, dried in an oven and powdered well. About 100 mg of the treated samples was used for TOC analysis on a TOC-V series SSM-5000A Shimadzu elemental analyser. The analytical accuracy was better than 4% and precision of the TOC analysis exceeded ±5%. For age determination of the core, we adopted the radiocarbon dating results of core AAS9/19 (ref. 29), which is very close to our core location (Table 1). Core AAS9/19 was collected at 73°08.515′E and...
14°30.115’N in the eastern Arabian Sea at water depth of 367 m.

According to the adopted radiocarbon dating results, the studied sediment core represents the Holocene period (9–1 ka). We discuss the down-core geochemical variations with reference to three Holocene periods: (i) early Holocene (9–7 ka), (ii) middle Holocene (7–4 ka) and (iii) late Holocene (4–1 ka). Also, the elements were classified into terrigenous (Fe, K, Mg, Al), biogenic/organic-associated (Ca, TOC, Sr) and redox-sensitive elements (Cu, Ni, Mn, Co) for descriptive purposes.

The down-core variations of grain sizes of the sediment are shown in Figure 2a. The figure indicates that the sediment grain size is mostly dominated by fine-grained sediments. The clay fraction is higher during early Holocene and it shows a decrease in trend towards late Holocene. The highest clay content in this period corresponds with the intensified SW monsoon and resulting freshwater run-off from the rivers.

The geochemical data show that early to middle Holocene sediments comprise higher average concentrations of Fe, K, Al, Mn, Co and Ni (Figure 3a and b). While late Holocene sediments show enrichment of biogenic elements such as Ca and Sr (Figure 3c). These variations of elements are mainly controlled by geological and chemical factors such as provenance, precipitation, oxic/anoxic condition, etc.25

The early Holocene period witnessed relative enrichment in the concentration of Fe, Al and K (Figure 3a). The higher concentration of Al can be related to an increased input of aluminosilicate minerals, which are generally detrital.19 The observed higher concentration of Fe can be attributed to an increased input of smectite clay minerals derived from the Deccan traps in the hinterland.21,30,31 Also, the early Holocene sediments are marked by a higher concentration of redox-sensitive elements, Mn, Ni, Cu and Co (Figure 3b). These elements show a significant positive correlation with Al and Fe (r = 0.92, n = 89, P = 0.05; Table 2). The observed relationship between Fe and the trace elements may be on account of the extent to which the precipitation or dissolution of Fe-oxides/hydroxides occur, since the scavenging or releasing effects of Fe-oxides/hydroxides act as significant ‘sinks’ or ‘sources’ of trace elements. The positive correlation between the trace elements and Al could be related to the abundance of clays.22 Also the higher concentration of Mn during early Holocene period could be due to an oxic sediment deposition environment. While the decrease in concentration of biogenic elements (Figure 3c) could be due to relatively less intense surface productivity during this period. These observations suggest a significant increase in precipitation-derived terrigenous supply during the early Holocene period. Thus, the present study precisely shows the intensification of early Holocene Indian monsoon1,33.

All the major elements in the samples during the middle Holocene period show a decrease in concentration relative to samples of the early Holocene period. The relatively lower concentration of Mg, Fe and Al during the middle Holocene period compared to the early Holocene period indicates the low input of clay minerals from terrigenous sources compared to the early Holocene period. It is reported that the variation of Mg is affected by the substitution of Mg2+ for Fe2+ in Fe-rich minerals.20 Also, the distribution of trace elements during this period depends on the trace element scavenging capacity of clay from sea water23,34. The lower concentration of Ca and TOC could be due to a decreased biological productivity during middle Holocene. The elemental records (Fe, K, Mg and Al) from our studies also reveal a significant weakening of the Indian monsoon during the middle Holocene period35. The archaeological and other land records in the Indian subcontinent also support a substantial weakening of the SW monsoon during this period35.

During the late Holocene period, it is seen that the average concentration of major elements varies in the order: Ca > Mg > Fe > Al > Sr > K. TOC concentration is also relatively high compared to the other two periods. The higher concentration of Ca, Sr and TOC in the late Holocene sediments can be considered as reflective of

<table>
<thead>
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<th>Core depth (cm)</th>
<th>Measured age (yrs BP)</th>
<th>Calibrated age (yrs BP)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>1,680 ± 25</td>
<td>115</td>
</tr>
<tr>
<td>140</td>
<td>7,340 ± 40</td>
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<td>10,795 ± 45</td>
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</tr>
<tr>
<td>275</td>
<td>10,960 ± 45</td>
<td>12,335</td>
</tr>
</tbody>
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Table 1. AMS radiocarbon dates and calibrated ages of core AAS9/19 taken from Naik et al.29

Figure 2. Down-core variation of sand, silt and clay fraction.
increased surface productivity during this period. Since the input of organic matter (TOC) to the marine realm occurs significantly through primary production in the photic zone, variation in TOC profile can indicate the changes in primary productivity during the particular time interval. Also, studies on organic carbon or biogenic element distribution in the sediments from the Arabian Sea suggest that primary productivity is the major controlling factor. The general distribution pattern of CaCO₃ in the Arabian Sea sediments tends to corroborate this argument. Furthermore, the strong covariance exhibited by Ca and Sr \((r = 0.82, n = 89, P = 0.05; \text{Table 2})\) in the present study can also be considered as a supportive of this argument. It is established that Sr is present mainly in the calcareous tests of organisms. Acantharid skeletons made up of celestite (SrSO₄) are also important contributors of Sr to marine sediments. Because the present study area is characterized by strong seasonal upwelling, the inferred higher productivity in the surface waters during late Holocene period can be attributed to a phase of enhanced upwelling. A factor to be considered in the above context is the relative role of detrital carbonates in the observed concentration of Ca and Sr. Microscopic observations of the coarse fraction, however, tend to discount this possibility. The relatively low concentration of K, Fe and Al in the late Holocene sediments compared to the other two periods indicates a phase of reduced terrigenous influx during the times of deposition of late Holocene sediments. Also, the sand and clay fraction is lower in late Holocene period compared to other two periods. It indicates the reduced freshwater run-off during this period attributed to the weakening of monsoon. Therefore, the lower terrigenous input during this period could result in decrease in terrigenous dilution.
The sedimentary record of the concentration distribution of trace elements such as Co, Ni, Cu and Mn is associated with adsorption capacity of Fe-oxides/hydroxides or scavenging capacity of clays. It indicates that the sources of these elements are similar in this region. Factor analyses results support these observations by forming a cluster of these elements (Fe, K, Mg, Al, Mn, Cr, Ni and Cu; Figure 4). From these observations, factor 1 can be assigned to terrigenous input. As already discussed from geochemical data, the factor controlling the Ca distribution is from biogenic sources. From the factor analysis results, it is clear that factor 2 has positive factor loadings with Ca. Also, factor 2 has not shown any significant loadings with Fe, K and Al. Due to the positive factor loading with Ca, factor 2 is considered as biological contribution.

The sedimentary record of the concentration distribution and possible sources of selected major and trace elements, and TOC from the southeastern Arabian Sea reveals the importance of geochemical processes and the productivity can induce changes in oxygen level of sediment–water interface due to organic matter degradation. This productivity-induced oxic condition variation of water column affects the concentration profile of redox-sensitive element such as Mn. Therefore, in the present study area Mn profile is attributed to productivity-induced reduction of oxygen level during the late Holocene period.

For better understanding of the observed geochemical variations of elements, factor analysis was carried out. There are two important factors that can explain the observed variations and distribution of elements in the sediments. The factors with eigen value greater than 1 are considered as significant. The factor 1 explains 71.6% variance of the observations with eigen value 7.877 and factor 2 of 7% of variance with eigen value 1. According to the factor loadings, it is clear that factor 1 has a significant positive factor loading with the elements Fe, K, Al, Co, Ni, Cu and Mn, whereas a negative factor loading is observed with Ca and Sr (Table 3). According to elemental data, the input of Fe, K and Al is significantly through terrigenous sources during early Holocene and middle Holocene periods. Also, the higher concentration of trace elements such as Co, Ni, Cu and Mn is associated with adsorption capacity of Fe-oxides/hydroxides or scavenging capacity of clays. It indicates that the sources of these elements are similar in this region. Factor analyses results support these observations by forming a cluster of these elements (Fe, K, Mg, Al, Mn, Co, Ni and Cu; Figure 4). From these observations, factor 1 can be assigned to terrigenous input. As already discussed from geochemical data, the factor controlling the Ca distribution is from biogenic sources. From the factor analysis results, it is clear that factor 2 has positive factor loadings with Ca. Also, factor 2 has not shown any significant loadings with Fe, K and Al. Due to the positive factor loading with Ca, factor 2 is considered as biological contribution.

The sedimentary record of the concentration distribution and possible sources of selected major and trace elements, and TOC from the southeastern Arabian Sea reveals the importance of geochemical processes and the
possible environmental factors that influence their distribution. The enrichment of Fe, K, Mg and Al during the early Holocene period in the sediment core reflects an enhanced input of terrigenous material to the study area through fluvial sources. Also, reduced concentration of Ca and TOC during this period indicates a decrease in surface productivity during the period of deposition. The gradual decrease in the major elemental concentration in the middle Holocene period suggests a weakening of the SW monsoon relative to early Holocene to middle Holocene. The higher concentration of Ca, Sr and TOC in the late Holocene sediments reveals an enhanced productivity due to upwelling during this time interval. The distribution pattern of redox-sensitive metals (Mn, Ni, Cu and Co) indicates that the terrigenous sources as well as the scavenging or releasing effects of Fe-oxides/hydroxides, and clays have played a major role in the observed variations of these elements. Specifically, the variation of Mn concentration from early Holocene to late Holocene suggests that oxic conditions prevailed during early Holocene period and reduced oxygen level was prevalent during late Holocene. Our study indicates that major factors controlling the biogeochemical cycling of elements in the east coast of the Arabian Sea are fluvial input during monsoonal period and coastal upwelling-related productivity.

Earliest dates and implications of Microlithic industries of Late Pleistocene from Mahadebbera and Kana, Purulia district, West Bengal

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Microlithic industries, a technology associated with modern humans, as defined by the production of microblades have been found in different parts of the Indian subcontinent with the earliest date being 48 ka. The present communication reports on recent archaeological excavations of these industries from a colluvial context located in the pediment surface of Pecambrian hills in Purulia, West Bengal. These are dated to 34–25 ka by optically stimulated luminescence dating and are the earliest dates for microlithic industries in eastern India. To our knowledge such dating does not exist for any prehistoric site in Bengal. The context of the sites – hill-slope colluvium – is also unique and a rarity in the subcontinent. These findings add additional inputs to the knowledge of these industries, providing supporting evidence to their antiquity.

Keywords: Colluvium, excavation, microlithic industries, modern humans.

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