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Late Holocene changes in hypoxia off the west coast of India: Micropalaeontological evidences

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A study has been carried out to understand benthic foraminiferal and sedimentary organic matter characteristics under low dissolved oxygen conditions off the central west coast of India. Based on the strong correlation between the present-day abundance of rectilinear bi- and triserial benthic foraminifera (RBF) and low dissolved oxygen conditions in the northeastern Arabian Sea, the geologic extent of low oxygen zone off the central west coast of India, is inferred from a core collected from the shallow water region. Persistently high relative abundance of RBF, large proportion of amorphous organic matter and protoperidinioid dinocysts throughout the time-span covered by the core that goes well beyond the beginning of human intervention, indicate that the eutrophication of coastal water and subsequent development of low dissolved oxygen conditions is a natural phenomenon that has been in existence even before anthropogenic influence.

Keywords: Benthic, dissolved oxygen, foraminifera, hypoxia, organic matter, rectilinear.

OXYGEN is essential for life on both land as well as under water. While the atmospheric concentration of oxygen is

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largely controlled by the altitude, vegetation, anthropogenic activities and shows small seasonal variation over a particular locality, the amount of oxygen dissolved in sea water varies significantly over different seasons. The oxygen concentration in the euphotic zone depends on the presence of oxygenated waters in relation to primary productivity and amount of organic matter decomposed during its transit in the water column¹. Increased supply of nutrients, either by river run-off or upwelling of nutrient-rich deeper water to shallower depth, facilitates biological productivity. The excessive production of organic matter leads to increased consumption of dissolved oxygen for the decay of the former. This increased consumption of dissolved oxygen during the decomposition of organic matter, coupled with restricted circulation leading to limited renewal, results in conditions wherein the amount of dissolved oxygen decreases considerably. Such a considerably low dissolved oxygen condition has often been termed as oxygen minimum zone (OMZ) and has been reported at varying depths from different parts of the world oceans^{2,3}. Interestingly, the development or intensification of shallow-water OMZ has been attributed to the spurt in anthropogenic activities in the coastal regions^{4,5}. The improvised farm practices requiring increased use of fertilizers have been said to result in increased nutrient loading through run-off^{5,6}. Sewage discharge has also been cited as a factor leading to increased amount of nutrients in the coastal regions and ultimately high biological production⁴. The disturbing aspect of increased run-off of nitrogenous fertilizers is the production of nitrous oxide by microorganisms that use anaerobic mechanism for respiration^{4,7}. The suboxic conditions and considerably high organic matter content in the euphotic zone promote the denitrification process^{8,9}. Nitrous oxide is among the gases responsible for the greenhouse effect¹⁰. Thus increased production of nitrous oxide in the coastal regions can contribute significantly to global warming. Additionally, seasonal changes in dissolved oxygen severely affect the marine biota. Therefore, it is necessary to understand the factors leading to the development and intensification of the OMZ. The possible influence of anthropogenic activities on the OMZ also needs to be assessed.

The Arabian Sea is well known as one of the most productive regions in the world ocean¹¹. The primary productivity in terms of organic matter production is substantially higher in summer and fall, than in the winter and spring¹². Intensity of the southwest monsoon promotes the productivity of the Arabian Sea¹³. The oxygen-depleted conditions also occur during or just after summer monsoon¹⁴. The central Arabian Sea is known as one of the largest bodies of oxygen-deficient waters on earth¹⁵. A pronounced OMZ exists between 150 and 1250 m water depth, with the lowest oxygen concentration in the northeastern part of the Arabian Sea². The region off the west coast of India provides a unique

opportunity to study the aspects related to OMZ, as both shallow as well as deeper water OMZ have been reported from this region^{3,4,16}.

Suitable indices or proxies have to be developed in order to track the geologic extent of the OMZ. Temporal variation of intermediate depth OMZ has been reconstructed earlier using various proxies, including benthic foraminiferal characteristics¹⁷⁻¹⁹. However, no such attempt has been made yet to assess the geologic extent of shallow water OMZ in the Arabian Sea. The foraminiferal proxies have also been extensively applied in palaeoclimatic and palaeoceanographic studies²⁰⁻²³. Negligible lateral movement and presence of hard exoskeleton that incorporates the signatures of ambient sea-water characteristics, make benthic foraminifera an efficient tracer for physico-chemical conditions of sea water during geologic past. Further, the presence of OMZ leads to excellent preservation of foraminiferal tests due to minimal bioturbation, as low oxygen conditions result in significant decline in the population of benthic macrofauna.

Since organic matter characterization is the direct measure of productivity-related environmental conditions at the time of deposition in the marine realm, its temporal variations in the sediment column are used as an aid in palaeoenvironmental and hydrographic interpretations²⁴⁻²⁶. While in pre-Quaternary marine sediments, palynofacies analysis allows determination of depositional environments and identification of source rock for petroleum²⁵, in Quaternary marine sediments, changes in the relative abundance of palynofacies are attributed to changes in hydrographic parameters such as distance from shoreline, hydrodynamic energy in the water column, sea surface temperature, salinity, nutrient availability and oxygen regime²⁶. Palynofacies analysis considers organic-walled microfossils or debris as sedimentary particle and each one of them provides information about their origin, transportation and diagenetic evolution²⁷. Therefore, in view of the foregoing, it becomes essential to characterize the organic matter content to assess the productivity related organic matter behaviour pattern.

Thus, in this communication we apply benthic foraminiferal and palynological indices pattern in the sub-subsurface sediments to explore whether the development and intensification of the OMZ along the western continental margin of India, is related to increased human activity or not.

To develop foraminiferal proxy for the OMZ, a total of 103 sediment samples were collected during cruises of *RV Gaveshani* (G-18) and *ORV Sagar Kanya* (SK-117), from the region off the central west coast of India, covering both shallow as well as intermediate to greater water depths (15–3300 m; Figure 1). In order to reconstruct the geologic extent of the shallow water OMZ, benthic foraminiferal and palynological investigations were carried out on subsurface sediment samples in a core (SK 117 SC-06, 15.49°N, 73.44°E, water depth 56 m), collected

Table 1. Rectilinear benthic foraminifera reported in the study area

<i>Bolivina dilatata</i> Reuss	<i>B. gibba</i> Fornasini
<i>B. doniezi</i> Cushman and Wickenden	<i>B. marginata</i> d'Orbigny
<i>B. cf. B. inflata</i> Heron-Allen and Earland	<i>B. mexicana</i> (Cushman)
<i>B. kuriani</i> Seibold	<i>Buliminella cf. B. milletti</i> Cushman
<i>B. lowmani</i> Phleger and Parker	<i>Euuvigerina aculeata</i> (d'Orbigny)
<i>B. marginata</i> Cushman	<i>Neouuvigerina ampullacea</i> (Brady)
<i>B. cf. B. oceanica</i> Cushman	<i>N. interrupta</i> (Brady)
<i>B. ordinaria</i> Phleger and Parker	<i>Siphouuvigerina porrecta</i> (Brady)
<i>B. cf. B. pacifica</i> Cushman and McCulloch	<i>Uvigerina asperula</i> Czjzek
<i>B. persiensis</i> Lutze	<i>U. cf. U. auberiana</i> d'Orbigny
<i>B. pseudoplicata</i> Heron-Allen and Earland	<i>U. bassensis</i> Parr
<i>B. robusta</i> Brady	<i>U. bifurcata</i> d'Orbigny
<i>B. seminuda</i> Cushman	<i>U. brunensis</i> Karrer
<i>B. silvestrina</i> Cushman	<i>U. canariensis</i> d'Orbigny
<i>B. spinata</i> (Cushman)	<i>U. hollicki</i> Thalmann
<i>B. spinescens</i> Cushman	<i>U. mediterranea</i> Hofker
<i>B. variabilis</i> (Williamson)	<i>U. peregrina</i> Cushman
<i>Bolivina</i> sp.	<i>U. proboscidea</i> Schwager
<i>Brizalina difformis</i> (Williamson)	<i>U. vadescens</i> Cushman
<i>B. spathulata</i> (Williamson)	<i>U. schwageri</i> Brady
<i>B. striatula</i> (Cushman)	<i>Uvigerina</i> sp. A
<i>Bolivinella elegans</i> Parr	<i>Uvigerina</i> sp. B
<i>Bolivinella quadrilatera</i> (Schwager)	<i>Trifarina carinata</i> (Cushman)
<i>Stainforthia concava</i> (Hoglund)	<i>Trifarina</i> sp.
<i>Hopkinsinella glabra</i> (Millett)	<i>Reussella laevigata</i> (Cushman)
<i>Loxostomina limbata</i> (Brady)	<i>R. spinulosa</i> (Reuss)
<i>Rectobolivina</i> sp.	<i>Fursenkoina bradyi</i> (Cushman)
<i>Sagrinella convallaria</i> (Millett)	<i>F. complanata</i> (Egger)
<i>S. cf. S. guinai</i> Saidova	<i>F. pontoni</i> (Cushman)
<i>Siphogenerina</i> aff. <i>S. virgula</i> (Brady)	<i>F. cf. F. schreibersiana</i> (Czjzek)
<i>Bulimina aculeata</i> d'Orbigny	<i>F. texturata</i> (Brady)
<i>B. alazanensis</i> Cushman	<i>Sigmavirgulina tortuosa</i> (Brady)
<i>B. biserialis</i> Millett	<i>Virgulina pertusa</i> (Reuss)
<i>B. exilis</i> Brady	<i>Pleurostomella</i> sp.

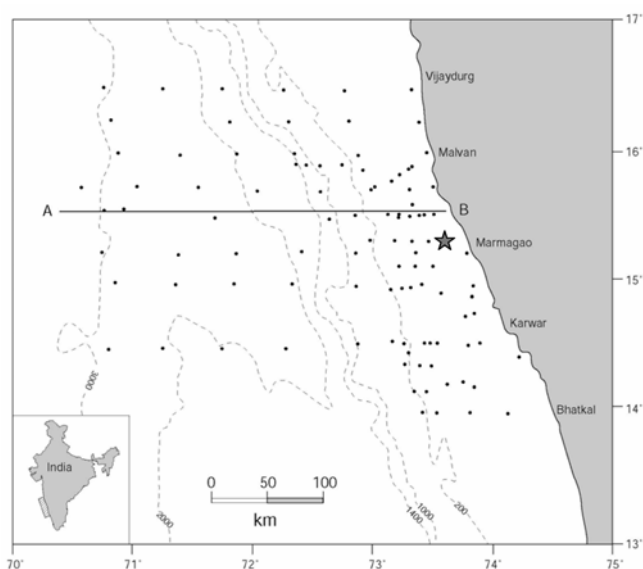


Figure 1. Location of sediment samples. Asterisk shows the location of the core, SK-117 SC-06. The line AB shows the transect along which seawater dissolved oxygen measurements were taken and compared with the relative abundance of rectilinear benthic foraminifera in a previous study³³.

from the region lying under the present-day shallow water OMZ. Radiocarbon and Pb²¹⁰ dating established the time period covered by the core.

The sediment samples were processed for foraminiferal studies according to established procedures. From >63 µm fraction of the processed samples, a minimum of ~300 benthic foraminiferal specimens were picked from each sample. Based on the reported ubiquitous presence of a few rectilinear bi and tri-serial benthic foraminiferal species (RBF) from several OMZs throughout the world oceans²⁸⁻³¹, it was decided to quantify the abundance of all RBF in the sediments collected from the study area (Table 1). For palynofacies analysis, precise quantitative extraction and counting of organic matter debris and microfossil content were made³². Palynofacies analysis involves a study of the changes in the relative abundance of various types of sedimentary organic matter, including dinocysts, palynomorphs, phytoclasts and amorphous organic matter. Various types of allochthonous organic matter – black oxidized (charcoal), degraded brown (woody), cuticle and autochthonous-marine dinocyst, copepod eggshells, zooplanktons, amorphous organic

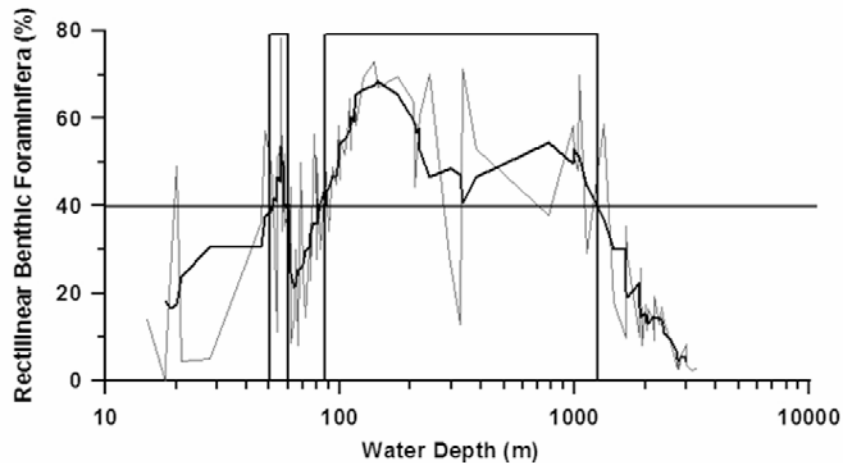


Figure 2. Distribution of rectilinear benthic foraminifera (RBF) against water depth in the study area. Thick line is the five-point average, while the horizontal line shows >40% rectilinear benthic foraminiferal abundance. Water depth is plotted as log-scale. Rectangles mark the increased abundance of RBF in both shallow (~50–60 m) and shallow to intermediate water depth (~90–1100 m) regions.

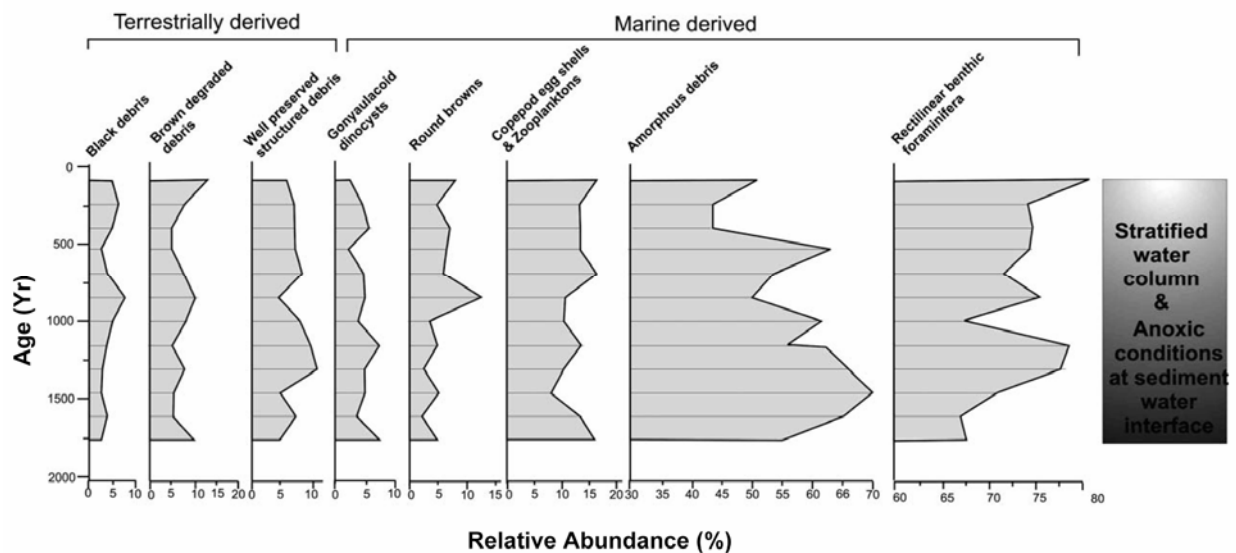


Figure 3. Palynofacies and RBF distribution in the core.

matter were examined and counted. Percentages of gonyaulacoid and peridinioid dinocysts were taken into account to assess the productivity-related changes.

The plot of relative abundance of RBF in surface sediment samples shows increased abundance in both the shallow and intermediate water depth OMZ in the eastern Arabian Sea (Figure 2)³³. The RBF was found to be >40% in the region established as the OMZ based on physico-chemical investigations. The RBF abundance showed an inverse relationship with the amount of dissolved oxygen in an east-west transect in the study area³³. The increased abundance of RBF probably reflects its infaunal nature and its ability to tolerate low oxygen levels in subsurface (upper few centimetres) conditions^{34–36}. The relationship

between RBF abundance and amount of dissolved oxygen was then applied to subsurface sediment samples.

RBF abundance throughout the core remains higher than 40% (Figure 3). Amorphous organic matter also dominates the assemblage, reaching up to 50–70%. Since the source of amorphous organic matter is chiefly marine phytoplankton, its abundance in the sediments signifies high primary productivity. Moreover, large proportions of dinocysts (protoperidinioids and gonyaulacoid), copepods egg shells and zooplanktons further support high primary productivity in the sediments. Presence of a large proportion of dinocysts at various stages of degradation and their conversion into amorphous content has been noted in all the sediment samples. Amorphous organic matter is

known to be highly prone to oxidation. Hence dominance and well-preserved nature of the amorphous organic matter along with specks of hydrogen sulphide in all the sediment samples also points to oxygen-deficient conditions during the last 2460 ± 403 yrs BP, covered by the shallow core. A good number of round, brown, peridinioid dinocysts in the assemblage suggests the prevalence of oxygen-deficient conditions, since they get easily oxidized in the presence of pore-water oxygen at sediment–water interface³⁷. Besides preservation aspects, the peridinioid dinocysts are also indicators of nutrient richness in the euphotic zone³⁸. Continuous occurrence of various types of terrestrially derived organic matter and large proportion of freshwater diatoms throughout the core indicate the influence of shoreline proximity and riverine run-off.

Since amorphous organic matter is a product of phytoplankton decomposition under anoxic conditions, and since the anoxic condition promotes denitrification, the presence of a large amount of amorphous organic matter in the sediments could be logically linked to the denitrification process. Hence, occurrence of a large proportion of amorphous organic matter in the marine sediments could be used to track denitrification that is usually associated with oxygen-depleted conditions in the ocean.

Hence the persistent occurrences of significantly high relative abundance of RBF, large proportion of amorphous organic matter and peridinioid dinocysts in the shallow core in the present study indicate that the eutrophication of coastal water is a natural phenomenon that has been in existence even before human establishment. Such existence of intermediate-depth OMZ from the Arabian Sea, during most of the late Quaternary period because of natural reasons has been previously reported^{17–19}. The variation in geographic extent of the OMZ over the years has also been attributed to the natural sea level or monsoon variations^{17,39}. The palynofacies study also demonstrates that part of the coastal waters off the central west coast of India has remained oxygen depleted for much beyond the last ~1800 yrs BP as a result of natural processes, instead of anthropogenic influence. However, more such studies on subsurface samples will help in identifying the intensification, if any, of the shallow-water OMZ in this region.

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Production of epsom, gypsum and other industrial products from the mill tailings of Jhamarkotra rock phosphate project, India

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At the Jhamarkotra rock phosphate mines, the low-grade Proterozoic rock phosphate containing 14–19% P₂O₅ is beneficiated by froth flotation process to produce beneficiated rock phosphate having 32–34% P₂O₅, to provide raw material for fertilizer plants. The process generates considerable quantity of dolomitic tailings which contain 5–6% P₂O₅, 16–18% MgO and 32–34% CaO, that are potentially useful in agriculture. It is therefore necessary to utilize these products to conserve the diminishing, meagre and non-renewable phosphate resources of India. About 1500–1800 tonnes per day (TPD) of dolomitic tailings is produced through the processing of ~3000 TPD of the ore, which is collected in the tailing ponds. Investigation carried out on final carbonate tails (FCT) of Jhamarkotra rock phosphate froth flotation beneficiation plant revealed that good quality epsom (MgSO₄·7H₂O)/fertilizer-grade magnesium sulphate, gypsum (CaSO₄·2H₂O) and magnesium ammonium phosphate (MAP) can be produced by leaching FCT with dilute sulphuric acid (30%) at 60–80°C and subsequent crystallization through evaporation and cooling. MAP also can be produced, which has citrate solubility of about 96%. MAP has proved to be beneficial for rice crop on acid as well as alkaline soils. Additionally, ammonium carbonate/carbon dioxide, hydrogen fluoride/calcium fluoride can also be produced. This scheme will certainly help reduce the wastage of these resources, mitigation of pollution and will generate additional revenue to the company.

Keywords: Epsom, fertilizer, gypsum, magnesium ammonium phosphate, mill tailing.

IN the present global scenario of ever-increasing pollution, any effort or investigation to mitigate pollution needs to be encouraged. Utilization of waste tailings is the best way to deal with the problem, but till now the tailing utilization is restricted to brick making and as construction material¹. This aspect was unsuccessfully tried for the Jhamarkotra mill tailings too; therefore, a different and better approach was necessary. With this objective, a chemical utilization approach was carried out for the tailings of Jhamarkotra rock phosphate beneficiation plant of

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