M. Thamban · V. Purnachandra Rao · S. V. Raju Controls on organic carbon distribution in sediments from the eastern Arabian Sea Margin

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Abstract Sediment cores from the upper continental slope of the eastern Arabian Sea have high organic carbon (OC), CaCO₃, and sand content at the top. The values decrease with increasing depth in the Holocene and Upper Pleistocene. Topographic highs show highest OC and lower CaCO₃ in the Holocene clayey sediments and vice versa in the Pleistocene sandy sediments. The OC is immature and marine or a mixture of both marine and terrestrial in the Holocene sediments and is mostly terrestrial and/or reworked marine in the Pleistocene sediments. Productivity is the main controlling factor for the organic carbon enrichment. Texture and reworking also influence the organic carbon variations.

Introduction

The amount and type of organic matter in marine sediments reflect the supply and preservation of organic materials from marine and terrestrial sources (Tissot et al. 1980; Summerhayes 1981). Continental slopes are the sites of accumulation of high concentrations of organic matter. Recent investigations in Quaternary sediments of the Pacific and Atlantic oceans indicate that primary productivity is the principal control for the formation of organic-rich deposits (see Calvert et al. 1992; Calvert and Pedersen 1992). Higher levels of organic carbon (1–4 wt % and up to 16 wt %) occur in the continental slope sediments of the eastern Arabian Sea, Indian Ocean (Paropkari et al. 1987), and the explanation for these levels is still a matter of debate. Some workers consider that anoxia is the most

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S. V. Raju Oil India Limited, Duliajan 786602, Assam, India important deciding factor (Demaison and Moore 1980; Paropkari et al. 1992, 1993), while others (Pedersen and Calvert 1990; Pedersen et al. 1992; Calvert et al. 1995) suggest that productivity in conjuction with factors like sediment characteristics and texture, rather than anoxia, are important for the high organic content. Here, we examine the distribution of organic carbon in the sediment cores retrieved from three physiographic settings on the upper continental slope and discuss the factors responsible for its preservation.

Materials and methods

The Arabian Sea is a classic example of an "anoxic open ocean" (Demaison and Moore 1980). It is a region of intense seasonal upwelling, which induces high productivity (up to $1.0 \text{ gCm}^{-2} \text{ day}^{-1}$) (Qasim 1977), and a permanent oxygen minimum zone (OMZ) (dissolved $O_2 < 0.5 \text{ ml} \text{l}^{-1}$) exists at intermediate depths and impinges the continental slope between 150 and 1200 m water depth (Wyrtki 1971; von Stackelberg 1972). Six gravity cores were collected during the 6th cruise of A. A. Siderenko, from three different physiographic features on the upper continental slope at depths ranging from 280 and 350 m between Goa and Cochin (Fig. 1): three cores are from the continental slope between Goa and Cochin, two from the topographic highs off Goa, and one from the terrace off Cochin. Topographic highs are isolated features on the upper continental slope and raise from about 1200 m depth at the base to 330 m depth on the summit (see inset Fig. 1). All the cores fall within the OMZ. Lengths of the sediment cores range from 3.33 to 4.45 m. Subsampling of the cores was done onboard at 2-cm intervals for the top 20 cm and 5-cm, intervals for the rest of the cores. The color of the sediments was also noted.

Textural studies were carried out on 25–30 representative sediment intervals in each core. The coarse



Fig. 1 Gravity core (GC) locations on the continental slope of the eastern Arabian Margin. (\bigcirc , continental slope cores; \blacklozenge , topographic high cores; \bigstar , continental terrace core). A schematic cross section (off Goa) showing the location of topographic high on the slope is also inserted (transect *x*-*y*); arrows indicate the core locations

fraction (125 to 250 and 250 to 500- μ m sizes) was observed under a binocular microscope. The organic carbon (OC) was determined by a wet oxidation method (El Wakeel and Riley 1957) and CaCO₃ content by the rapid gasometric technique (Hülsemann 1966). Rock-Eval pyrolysis was carried out on 24 representative samples, following the procedures of Espitalié et al. (1985). The parameters of Rock-Eval pyrolysis (HI, T_{max}, S₁, and S₂), useful for understanding the nature of OC (Dean et al. 1994), were measured (Table 1). The reproducibility of these measurements are \pm 5% for OC, \pm 8% for HI, \pm 8% for S₂ values and \pm 1% for T_{max} values. Radiocarbon dates were obtained for three sediment intervals in one core from the slope (Fig. 2).

Results and discussion

The color of the sediments in all cores varied from olive grey in the upper portions to brown black/greyish

black in the lower portions. The texture, OC, $CaCO_3$, and constituents in the coarse fraction of the sediments in all the cores showed distinct differences between the upper portions of the cores and the sediments below. Based on these differences, each core was divided into two units and the boundary between the two may correspond to the position of the Last Glacial Maxima (LGM) (Figs. 2 and 3). For convenience, the sediments above the LGM (18,000 yr BP to present) are referred to here as Holocene and below as Pleistocene sediments. The length of the Holocene sediments varies: it is about 80-100 cm (from the top of the core) in the cores from the slope and terrace and about 50-70 cm in the cores of the topographic highs (Figs. 2 and 3). A few radiocarbon dates obtained for the Holocene sediments (Fig. 2) reasonably justifies the proposed LGM boundary in the cores.

Nature of organic carbon

Organic carbon content varies from 0.94 to 8.7%. OC, hydrogen index (HI) and S₂ values are higher in Holocene than in Pleistocene sediments of all the cores (Table 1). Highest OC, HI, and S₂ values correspond to the sediments of the topographic highs. HI and OC contents show strong positive correlation (r = 0.88, n = 9) with the Holocene and poor correlation (r = 0.22, n = 15) with the Pleistocene sediments of all cores (Fig. 4a). T_{max} values of all samples are low (range: 390–441°C) (Table 1), suggesting that the organic matter is thermally immature. A HI- T_{max} plot (Fig. 5) shows that the Holocene sediments of the slope and terrace fall above and close to the type III boundary, while those of the topographic highs fall close to the type II boundary, suggesting that the OC is a mixture of types II and III in the former and mostly type II in the latter (see Espitalié and Joubert 1987). The Pleistocene sediments of all cores fall below the type III limit (Fig. 5), suggesting that it is either terrestrial (type III) and/or reworked marine (type II). The genetic potential (see Tissot and Welte 1984) is high $(S_1 + S_2 = 2.4-91.2)$ for the Holocene and low (0.4-2.2) for the Pleistocene sediments.

The OC and S_2 of the Holocene sediments show strong positive correlation (r = 0.91, n = 9), and the values fall above and on top of type II–III boundary or just below the boundary line on OC vs. S_2 plot (Fig. 4b). Since these sediments have high HI and a positive x intercept (Fig. 4b), the samples falling below the boundary line may represent low-hydrocarbon end members of Type II kerogen (reworked organic matter) and/or a mixture of type II and III (see Langford and Blanc-Valleron 1990). OC and S_2 of the Pleistocene sediments also show positive correlation (r = 0.65, n = 15) and the values fall below the type II–III boundary (figure not shown), suggesting that the OC is mostly terrestrial and/or reworked marine. The higher x inter-

Table 1 Analytical data on organic carbon, CaCO₃, texture and Rock-Eval pyrolysis parameters for selected samples in different cores

Sample	Core No. and water depth (m) ^a	Sampling depth intervals (cm)	CaCO ₃ (wt%)	Sand content (wt%)	OC (wt%)	Rock-Eval parameters			
						HI (mg HC/g OC)	S_1 (mg HC/g rock)	S_2 (mg HC/g rock)	T _{max} (°C)
1	GC-1 (286)	2–4 ^b	61.3	33	1.31	151	0.41	1.98	423
2	GC-1 (286)	110-115	40.2	7	1.70	55	0.22	0.93	413
3	GC-1 (286)	195-200	44.1	7	1.21	31	0.10	0.38	415
4	GC-1 (286)	260-265	39.2	3	0.94	29	0.09	0.28	395
5	GC-1 (286)	325-330	35.4	2	1.09	38	0.13	0.42	441
6	GC-4 (335)	4-6 ^b	59.7	31	2.76	166	1.07	4.59	419
7	GC-4 (335)	50–55 ^b	47.6	14	2.10	37	0.26	0.77	403
8	GC-4 (335)	210-215	7.1	1	1.45	28	0.20	0.41	396
9	GC-4 (335)	350-355	14.8	1	1.41	34	0.56	0.48	411
10	GC-4 (335)	395–400	15.2	2	1.48	30	0.20	0.44	404
11	GC-5 (280)	0–4 ^b	32.2	13	3.82	198	1.64	7.56	421
12	GC-5 (280)	55–60 ^b	27.5	12	3.10	121	0.85	3.75	415
13	GC-5 (280)	210-215	27.6	13	1.56	33	0.17	0.52	417
14	GC-5 (280)	295-300	23.6	7	1.37	27	0.14	0.37	390
15	GC-5 (280)	325-330	21.7	6	1.48	24	0.14	0.35	392
16	GC-6 (340)	0-2 ^ь	61.7	56	2.38	97	0.65	2.31	411
17	GC-6 (340)	45–50 ^b	57.7	64	1.70	79	0.33	1.35	407
18	GC-6 (340)	100-105	54.0	22	2.50	72	0.41	1.80	413
19	GC-6 (340)	240-245	32.1	10	1.65	89	0.44	1.47	416
20	GC-6 (340)	380–385	23.6	2	1.91	61	0.39	1.16	402
21	GC-2 (323)	2-6 ^b	39.6	4	8.70	445	7.48	38.68	411
22	GC-2 (323)	380-385	67.6	42	0.94	67	0.17	0.63	417
23	GC-3 (355)	0–4 ^b	34.8	3	8.56	892	14.84	76.33	404
24	GC-3 (355)	380-385	67.0	41	1.25	124	0.39	1.55	414

^a GC-1, GC-4, and GC-5 are from the continental slope; GC-2 and GC-3 are from topographic highs; and GC-6 is from continental terrace. ^b Holocene; others are Pleistocene sediments

cept (at 2.0, see Fig. 4b) for Holocene sediments compared to the Pleistocene sediments (at 0.5) indicates the availability of higher amounts of organic materials before the hydrocarbons released by pyrolysis in the Holocene sediments. The high x intercept is mainly due to clayey sediments in the topographic highs. Katz (1983) and Espitalié et al. (1985) suggested that the effect of rock matrix adsorption for clays results in a high x intercept. The y intercepts suggest that the adsorption capacity for 1 g of sample is 16.53 and 0.496 mg of pyrolysable hydrocarbons for the Holocene and Pleistocene sediments, respectively.

Sediment cores from the continental slope

The OC, $CaCO_3$, and sand contents of the Holocene sediments are high in the core tops and gradually decrease with increasing depth (Fig. 2). They show strong positive correlation with each other except in GC-1 (Fig. 6a). The coarse fraction consists of abundant planktic foraminifers, keels, benthic foraminifers such as *Bolivina* sp. and *Uvigerino* sp., and traces of pyrite (as encrustations on skeletals). More shell fragments, echinoderms, and *Orbulina* sp., also occur in

GC-1. Below the LGM, the OC, $CaCO_3$, and sand contents fluctuate in the upper portions (Fig. 2), and then the OC content is uniformly low, inspite of the increase in $CaCO_3$ and sand content at certain levels in the Pleistocene sediments (see GC-5, Fig. 2). Organic carbon shows relatively low or poor correlation with $CaCO_3$ (Fig. 6b) and sand content. The coarse fraction is much smaller in the Pleistocene sediments (Fig. 2) and is composed of shell fragments of shallow-water origin, *Bolivina* sp., *Uvigerina* sp., pteropods, and a few planktic foraminifers in the upper portions and mostly pyritized grains and infillings of benthic organisms and a few planktic foraminifers in the lower portions.

The OC, $CaCO_3$, and sand contents increase progressively from the base of the LGM at 80–100 cm to the top of the cores (Fig. 2) and show strong correlation with each other. Sheu and Huang (1989) and Paropkari et al. (1991) suggested that the direct covariance between OC and CaCO₃ indicate control by primary productivity. Although HI and OC show a positive correlation (Fig. 4a) (discussed below), we propose that low OC at the LGM and its increasing trend towards the surface (Fig. 2) are related to the low and enhanced productivity of the overlying waters during the LGM and in the present interglacial time, respectively. Several workers studied palaeoproductivity fluctuations



Fig. 2 Down core variations in organic carbon (OC), $CaCO_3$, and sand content in the cores from the continental slope

and monsoonal variations in the Arabian Sea and in the adjacent landmass and reported the weakest monsoons and associated low productivity during the LGM and increased monsoonal wind systems and enhanced upwelling induced productivity from 13,000 to 5000 years BP (Street and Grove 1979; Duplessy 1982; Prell 1984; Prell and Kutzbach 1987; Naqvi and Fairbanks 1996). Reducing conditions in the sediments are indicated by the presence of *Bolivina* sp., *Uvigerina* sp., and pyrite encrustations. The weak correlations of OC with CaCO₃ (Fig. 6a) together with abundant shell fragments and benthic fauna in the Holocene part of the core (GC-1) may indicate dilution of OC by reworked material from the shelf.

Fewer planktic foraminifers in the coarse fraction, abundant terrigenous mud (Fig. 2), and relatively low or poor correlation of OC with CaCO₃ (Fig. 6b) and sand contents of the Pleistocene sediments suggest less productivity in the overlying waters and OC derivation from more than one source. Organic carbon is most probably terrestrial. Arid conditions existed during the LGM (Van Campo et al. 1982; Luther et al. 1990). In these conditions, organic carbon in the soils degrades and oxidizes faster and less terrigenous OC would be transported to the marine environment. The cores on the slope are located closer to the shelf break and the deeper sediments accumulated in lowered sea level. Abundant terrigenous mud with broken shell fragments and benthic fauna in the cores suggest their direct deposition and reworking from the shelf sediments on to the slope during the low stands of sea level. Uniform low OC values despite variations in carbonate and sand content (Fig. 2) imply that the supply from these sources is low and shell fragments only diluted the organic carbon content in the sediments. Thus, organic carbon associated with the terrigenous flux, reworked from the adjacent shelf and from less productive overlying waters, is the principle source. The coarse fraction constituents indicate reducing conditions on the continental slope developed either due to the local depletion of the oxidizing agents in oxidizing conditions or due to the impingement of the oxygen minimum zone. Pyritized grains and infillings suggest that part of the OC was used for the pyrite formation and part was consumed by benthic organisms associated with the sediments. Since the OC content itself is less, the role of anoxic conditions in its preservation could not be distinguished in these sediments. The low organic carbon in these sediments is primarily due to the low supply from primary productivity, terrestrial and reworked sediments and dilution by constituents, as suggested by Calvert et al. (1995).



Fig. 3 Down core variations in organic carbon (OC), CaCO₃, and sand content in the cores from the continental terrace and topographic highs

Sediment core from the terrace

The OC content is 2.4% at the surface and also at the LGM. It initially decreases with increasing CaCO₃ and sand contents from the LGM at 95 cm to the top of the core and then increases along with CaCO₃ and decreased sand content in the top 15-20 cm of the core (Fig. 3). It shows poor correlation with $CaCO_3$ (r = -0.22) and sand content (r = 0.31). Although planktic foraminifers, Bolivina sp., Uvigerina sp., brown/black (phosphate/pyrite) infillings and pellets, and pteropods occur throughout the Holocene sediments, keels are abundant in the upper portions and shell fragments in the lower portions. Below the LGM, a broad hump of high OC coincides with a gradual decrease in CaCO₃ and a sharp decrease in sand content (Fig. 3). Uniformly low OC values occur in the lower portions. Organic carbon shows good correlation with CaCO₃ (r = 0.78, n = 18) and sand content (r = 0.54, r = 18). Planktic foraminifers, *Bolivina* sp., Uvigerina sp., pyrite infillings, and shell fragments occur in the upper portions and pyrite moulds and a few planktic foraminifers in the lower portions of the Pleistocene sediments.

The terrace lies seaward of the upper slope. The existence of open ocean conditions may have resulted in the high flux of planktic foraminifers to the bottom sediments. The sediments close to the LGM were accumulated during the initial rise of sea level. Lowest HI values (Table 1) suggest reworking of organic materials (see Pedersen et al. 1992). The negative relationship of OC with CaCO₃ and sand contents (Fig. 3) and abundant shell fragments in the sand content between 95 and 20 cm may indicate that the terrace received sediments from the increased productivity as well as reworked sediments from the adjacent slope. Down-slope movement of sediment on the slope has been reported in this region (von Stackelberg 1972). Therefore, the OC content is diluted by the deposition of reworked sand. The concomitant increase in OC and $CaCO_3$ in the upper portions of the Holocene sediments (Fig. 3) is similar to that in the slope, indicating control by primary productivity and less influence from reworking. The increased mud content in the top 20 cm of the core (Fig. 3) and anoxic conditions may be responsible for more OC preservation. The broad hump of high OC in the sediments below the LGM is associated with increased mud content. This may be due to direct accumulation of sediment during the lowered sea-level and also mass accumulation of finegrained sediments from the adjacent slope. The distribution of OC, CaCO₃, and sand in the lower portions

Fig. 4 a: Relationship between organic carbon (OC) and hydrogen index (HI). b: Relationship between OC and S₂. □, slope samples;
■, topographic high samples;
■, terrace samples





Fig. 5 Relationship between HI and T_{max} . Solid lines are the boundaries for types I, II, and III kerogens. Dashed lines represent the isoreflectance curves

of the Pleistocene sediments is similar to those on the slope.

Sediment cores from the topographic highs

The OC content is highest (7.9-8.7%) at the core tops. It corresponds to the lowest CaCO₃ content and high mud content (Fig. 3). OC shows an inverse relationship

with CaCO₃ (Fig. 6c) and sand content in the Holocene sediments. The sediments are clayey in the upper part and contain mainly keels and a few planktic foraminifers. The sediments between 20–25 cm and LGM at 50–70 cm (Fig. 3) are sandy and contain abundant planktic foraminifers, coiled mollusks, pelecypods, and gastropods. Below the LGM, OC is low (with low HI values) and corresponds to high carbonate (Fig. 6d) and sand content. Although planktic foraminifers dominate in these sediments, otoliths, *Uvigerina* sp., coiled mollusks, pelecypods, gastropods, and shell debris become prominent. Borings on shells and a few cemented foraminiferal aggregates, phosphatized coprolites, and corals encrusted on small gastropods (Rao et al. 1995) occur at certain sediment intervals.

Despite the fact that the lateral distance is only about 50 km between the cores of the slope and topographic highs (see inset in Fig. 1), OC and HI values are signifi cantly higher in the Holocene sediments of the topographic highs (Table 1, Fig. 3). Since oxygen minimum conditions exist at both locations, preservation alone may not account for such high OC and HI values. On the other hand, Pedersen et al. (1992) suggested that hydrogen richness in the surface sediments may not be related to bottom water oxygen content but related to the texture of the sediments. They reported similar HI values for OC deposited under anoxic conditions and oxygenated conditions. Reworking affects the degradation of OC, and the OC in coarser sediments shows low HI values and in finer sediments shows high HI values (Pedersen et al. 1992). Higher HI values in the Holocene clayey sediments and very low HI values in the Pleistocene sandy sediments (Table 1) are in agreement with the above argument. We therefore propose that high HI and OC values mainly reflect fine-grained sediments rather than anoxic conditions. High mud content and type II OC indicate that these highs are probably the sites of low-energy conditions during the Holocene and more marine OC accumulated in the sediments by adsorbing onto clay particles. Abundant

Fig. 6a–d Important scatter plots showing relationship between organic carbon and $CaCO_3$ in the sediment cores from the slope (**a** and **b**) and topographic highs (**c** and **d**)



keels in the sediments indicate intense test dissolution due to upwelling-induced anoxic conditions. Thus, high OC in the sediments is a combined influence of high OC from productivity, the depositional environment, and its preservation in anoxic fine-grained sediments. Calvert et al. (1995) suggested that the OC maximum on the slope of the eastern Arabian Sea sediments is not related to the position of oxygen minima, but varies according to the productivity and a combination of other sedimentological and hydrodynamical factors.

Sediments below 20-25 cm are sandy (see Fig. 3). Sediment constituents indicate mostly oxic open ocean conditions on the topographic highs. Corals encrusted on small gastropod shells also support low sedimentation rates and oxic conditions (Rao et al. 1995). Cemented forminiferal aggregates may indicate their formation similar to conditions in hardgrounds. High sand content suggests winnowing of the fine fraction. Organic carbon is marine but reworked. These findings suggest that, unlike those on the slope and terrace, this part of the sediments of the topographic highs were under oxygenated water column, and current winnowing may be responsible for the low OC content. Thus, the texture and winnowing of bottom sediments under oxidizing conditions were responsible for low OC content. Shimmield et al. (1990) suggested winnowing was responsible for low OC content in the sediments on bank tops. The oxygenated bottom conditions also indicate that the topographic highs were lying above the oxygen minimum zone during the Late Quaternary. The sudden change in lithology of the cores at 20–25 cm (Fig. 3) from sandy sediments below to clayey sediments above may suggest that the topographic highs were subsided during the Late Quaternary. Rao et al. (1996) documented evidence of Late Quaternary neotectonic activity and subsidence along the western margin of India.

Conclusions

The OC content is high in Holocene sediments of all cores. It shows strong positive correlation with $CaCO_3$ and sand content of the sediments of the slope and strong negative correlation with those of the topographic highs. On the terrace, it shows negative correlation in the sediments closer to LGM and then positive correlation at the core tops. The OC content is lower in all the Pleistocene sediments and its relationship with $CaCO_3$ and sand content is also diverse. Several factors such as productivity, anoxic conditions, reworking of the sediments from the adjacent shelf, texture of the sediments, and winnowing in oxidizing conditions are responsible for the OC variations. The influence of these factors vary in each physiographic setting and thus varying OC content results in different depths in the cores. We therefore suggest that the OC in the Holocene sediments is mainly controlled by primary productivity in combination with texture and reworking of sediments rather than anoxic conditions.

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