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On the organic carbon maximum on the continental slope of the eastern Arabian Sea

by S. E. Calvert[1], T. F. Pedersen[1], P. D. Naidu[2] and U. von Stackelberg[3]

ABSTRACT

The sedimentary organic carbon maximum on the continental slope off western India is widely believed to be due to the preferential preservation of deposited organic matter at water depths where the intense oxygen minimum intersects the sea floor. This region is considered to constitute one of the modern analogues for the environment of formation of organic-rich sedimentary facies that are common in the geological record. We critically examine the hypothesis that the oxygen minimum in the eastern Arabian Sea is the site of enhanced organic matter accumulation and preservation using analyses of suites of samples with wide geographical coverage along this margin. Organic carbon and nitrogen reach maximum concentrations between 200 and 1600 m depth, whereas the lowest dissolved oxygen contents in the oxygen minimum lie between 200 and 800 m depth. The $C_{organic}/N$ ratios and the $\delta^{13}C_{organic}$ values show that the organic matter is overwhelmingly marine, and Rock-Eval pyrolysis data demonstrate that the hydrogen indices of the sediments are similar in the sediments accumulating within and outside the oxygen minimum. Thus, the organic carbon maximum extends over a larger depth range than the oxygen minimum (as is also evident on some other slopes), and there is no evidence for preferential preservation of the organic matter within the oxygen minimum.

The distribution of organic matter on the western Indian continental margin is controlled by (1) variations in supply (decreasing westward away from the centers of coastal upwelling and also decreasing with increasing water depth), (2) dilution by other sedimentary components, and (3) the texture of the sediments (coarser-grained sediments having lower carbon contents), which is controlled in turn by sediment supply and reworking. The evidence available suggests that the organic carbon maximum on this slope is not related to the position of the oxygen minimum and, consequently, that oxygen minima cannot be used to explain the distribution of organic carbon at intermediate palaeodepths in the geological record.

1. Introduction

Studies of the distribution of organic carbon in modern marine sediments have shown that concentration maxima are often found at intermediate depths on many continental slopes (Premuzic *et al.,* 1982). Such maxima often, but not always,

1. Department of Oceanography, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Z4.
2. Department of Marine Geology, University of Goteborg, Box 7064, S-402 32 Goteborg, Sweden.
3. Bundesanstalt fur Geowissenschaften un Rohstoffe, Postfach 510153, D-30631 Hannover, Germany.

coincide with the depth where the oxygen minimum intersects the sea floor. This has been used to support the hypothesis that the low bottom water oxygen levels cause preferential preservation of deposited organic matter and are therefore responsible for the existence of the carbon maxima. This hypothesis has been widely accepted following the publication of the seminal papers of Schlanger and Jenkyns (1976) and Thiede and Van Andel (1977) which sought to account for the high organic carbon contents of sediments recovered by the Deep Sea Drilling Program that had accumulated at relatively shallow palaeodepths in the Atlantic and Pacific oceans.

In addition to the high organic carbon concentrations in sediments currently accumulating in some oxygen minima, it is also widely accepted that the organic matter in these areas is better preserved compared with organic matter in sediments from more oxygenated environments (Demaison, 1991). Thus, by analogy with many laminated black shales in the geological record that are considered to have formed in low-oxygen environments, the sediments of anoxic basins and oxygen minima are also thought to have higher Rock-Eval hydrogen indices, which correlate well with the H/C ratios of sedimentary organic matter (Espitalié *et al.,* 1977; Tissot and Welte, 1978), than those accumulating in regions with higher bottom water dissolved oxygen concentrations (Demaison *et al.,* 1984; Demaison, 1991), apparently signifying better preservation of organic matter under low oxygen conditions. Pedersen *et al.* (1992) have recently shown, however, that the hydrogen-richness of the surface sediments on the Oman margin is not related to the bottom water oxygen concentrations, but is controlled by sediment reworking which has had the effect of degrading the organic matter in the sediments to different extents, the degree of degradation being related to, and thus reflecting, the texture (grain size) of the sediment. Moreover, Calvert *et al.* (1992) have shown that the hydrogen index of the modern sediments accumulating in the intense oxygen minimum of the Gulf of California is not significantly different from that in the more oxygenated sediments accumulating above and below the oxygen minimum. Thus, using the Rock-Eval technique as a measure of the state of preservation of sedimentary organic matter, there is no evidence for enhanced preservation of sedimentary organic matter in the oxygen minima of either the Oman Margin or the Gulf of California.

Calvert (1987) has suggested that the locations of organic carbon maxima on continental slopes are not controlled by the bottom water oxygen levels but are probably produced by a combination of factors that control the texture of the sediments, the dilution of organic matter by other sedimentary components and the depth-related settling fluxes of organic carbon to the sea floor. Furthermore, Calvert and Pedersen (1992) have shown that the carbon maxima that occur on the upper slopes of the eastern North Atlantic and the northeastern Pacific either extend over a larger depth range than the respective oxygen minima or do not coincide with the depth where the oxygen minima intersect the sea floor, demonstrating that other factors must be involved in the formation of these facies. Thus, the generally-accepted notion that the absence, or the low concentration, of dissolved oxygen in bottom waters is responsible for the formation of organic-rich sedimentary facies, both in anoxic basins and on continental slopes (Dow, 1978; Arthur, 1979; Arthur and Natland, 1979; Demaison and Moore, 1980; de Graciansky *et al.,* 1984; Demaison *et al.,* 1984; Arthur *et al.,* 1987) requires re-examination.

The presence of a particularly strong carbon concentration maximum on the western slope off India (Schott *et al.,* 1970; Marchig, 1972; von Stackelberg, 1972) was ascribed to the position of the intense oxygen minimum in the water column, and provided strong support for the hypothesis of Schlanger and Jenkyns (1976) and Thiede and Van Andel (1977) that the bottom water oxygen concentration on this margin controls the abundance of organic carbon in the surface sediments. This has been accepted and reiterated by Slater and Kroopnick (1984) and Paropkari *et al.* (1992, 1993). In this paper we present new data and interpretations on the factors controlling the distribution of organic carbon in the sediments accumulating on the continental slope of the eastern Arabian Sea. We critically examine the relationship between the position of the surface sediment organic carbon maximum on the slope and the position of the oxygen minimum, the relationship between the hydrogen richness of the deposits and the position of the oxygen minimum and the relationship between the organic carbon content and the sediment texture to unravel the factors that have produced the wide compositional variability of the sedimentary facies on this margin.

2. Materials and methods

Surface sediment samples (0–2 or 0–5 cm sections) from three core and sample collections have been used in this study (Fig. 1). These included a selection of core top samples collected by the R. V. *Meteor* in 1965 (prefix M- in Table 1) (von Stackelberg, 1972), a set of grab samples (with prefix N-) collected on a cruise of the R. V. *Gaveshani* in the central part of the slope in 1988 (Naidu, 1990), and core and grab samples collected by the National Institute of Oceanography, Goa that were provided by Dr. B. K. L. Somayajulu (prefix S-). From the available information on sedimentation rates on the upper part of the slope (Barole, 1988; Yadav *et al.,* 1992), we estimate that the sample intervals represent sediment that has accumulated over the last few decades in these locations; sedimentation rates probably decrease in deeper water, so that the sample intervals represent correspondingly longer time intervals on the lower part of the slope. All subsamples were dried at 60°C and ground to fine powders in a disc mill. Total carbon and nitrogen were determined by combustion/gas chromatography (CNS analyzer) with precisions of ±1.2 and 3.5% (2σ), respectively. Carbonate carbon was determined by acid liberation of CO_2 followed by coulometry, with a precision of ±3.7%. Organic carbon values were derived from the difference between the total and carbonate carbon values, with a combined precision of ±3.1% (2σ). Organic carbon isotope ratios were determined

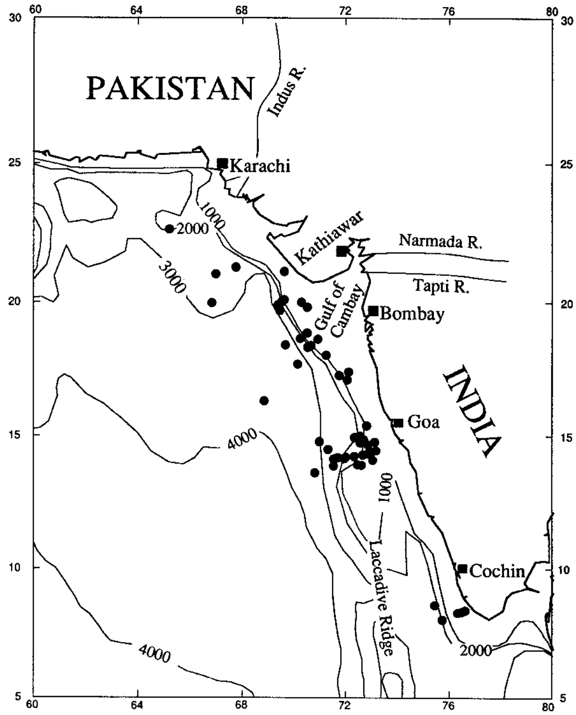

Figure 1. Location of sediment samples in the eastern Arabian Sea. Isobaths in meters.

on decarbonated subsamples using a VG PRISM mass spectrometer with an on-line CHN analyzer as the gas preparation device. Results are reported in the δ notation relative to PDB and the precision of the measurements was ±0.05‰. The concentration of iodine was determined by X-ray fluorescence spectrometry following the method described by Calvert (1990), with a precision better than ±5%. Rock-Eval pyrolysis and total organic carbon (TOC) contents were determined with a Rock-Eval II instrument following procedures described by Espitalié *et al.* (1977). Precision of the HI and TOC values was ±8% and ±4%, respectively. The texture of the N-sample subset was determined using a laser particle size analyzer by GeoSea Consulting Ltd, Cambridge, U.K. Reproducibility of duplicate determinations was ±5% for estimates of the sand/silt/clay ratios and ±3.5% for the determination of the mean grain size.

3. Geological and oceanographic background

The continental shelf off western India ranges in width from 300 km off the Gulf of Cambay to 60 km off Cochin (Fig. 1). The shelf break lies at approximately 140 m depth (Ulrich, 1968; Narain *et al.,* 1968). In the northern half of the area, the continental slope merges smoothly with the Indus Fan, which consists of turbidity

Table 1. Compositional and Textural Data

Sample	North Lat	East Long	Depth (m)	$CaCO_3$ (Wt %)	C_{org} (Wt %)	N (Wt %)	I (ppm)	$\delta^{13}C_{org}$ (PDB)	HI (mg HC/g C_{org})	% <63 μ m
N-1	14.48	71.33	1900	56.42	0.46	0.065	120	−18.43	42	97.7
N-2	14.78	71.01	2050	38.58	0.92	0.134	199	−18.74	121	100.0
N-3	14.94	72.37	1850	47.00	1.05	0.134	253	−18.92	302	98.4
N-4	14.99	72.56	1350	42.00	1.59	0.178	276	−19.42	289	98.5
N-5	15.07	72.93	975	46.33	3.46	0.402	669	−19.56		
N-6	14.85	72.71	325	48.33	6.25	0.724	228	−20.01	354	92.6
N-7	14.83	72.66	1350	46.00	1.82	0.229	437	−19.39	302	92.3
N-8	14.74	72.57	1200	38.42	4.20	0.425	674	−19.53	328	95.2
N-9	14.55	72.41	250	65.17	1.65	0.192	114	−19.56		
N-10	14.67	72.87	1520	56.25	0.71	0.097	192	−18.30	338	99.9
N-11	14.76	73.13	1600	54.33	0.68	0.093	158	−18.83	203	63.8
N-12	14.20	72.02	1700	55.17	0.57	0.076	110	−18.34	166	96.0
N-13	14.17	71.72	1750	56.08	0.52	0.075	102	−18.03	696	99.0
N-14	14.12	71.55	1700	55.17	0.54	0.075	92	−18.48	272	99.8
N-15	13.87	71.56	2050	38.42	1.05	0.149	185	−19.17	444	99.9
N-16	14.14	71.96	2000	37.50	1.24	0.174	278	−19.07	118	98.2
N-17	14.22	72.35	325	54.33	0.42	0.072	96	−18.33	297	100.0
N-18	14.28	72.68	900	42.75	3.48	0.420	699	−19.74	374	100.0
N-19	14.31	72.85	320	61.67	2.85	0.365	277	−19.75	141	99.8
N-20	14.34	72.98	1150	35.25	3.08	0.390	591	−19.64	298	99.8
N-21	14.44	73.18	1100	65.25	1.53	0.205	335	−19.25	309	62.1
N-22	14.08	73.06	2050	42.58	1.14	0.158	219	−19.02	299	100.0
S-1	21.00	67.01	2300	26.83	0.93	0.103	122	−19.53	316	
S-2	21.09	69.65	58	61.00	0.72	0.070	47	−18.95	275	
S-3	20.09	69.65	82	88.75	0.39	0.048	31	−20.06	275	
S-5	19.91	69.39	340	46.92	5.20	0.532	142	−20.10	302	
S-6	18.33	70.55	210	85.33	1.37	0.146	62	−21.93	209	
S-7	18.40	70.68	85	94.75	0.25	0.036	18	−20.87	280	
S-8	18.04	71.27	80	93.83	0.33	0.031	20	−20.70	420	
S-9	17.27	71.78	400	70.17	2.70	0.271	149	−20.49	358	
S-10	17.40	72.13	95	76.92	0.93	0.079	58	−19.87	376	
S-11	15.38	72.83	353	71.00	2.47	0.240	140	−20.53	238	
S-12	19.99	70.32	85	50.00	0.76	0.084	115	−19.50	245	
S-13	19.70	69.47	270	74.17	1.34	0.133	45	−21.12	264	
S-14	19.82	70.54	76	84.83	0.40	0.043	44	−20.31	428	
S-15	18.66	70.27	440	92.83	1.11	0.033	5	−23.86	890	
S-16	18.86	70.54	85	95.92	0.11	0.000	20	−20.93		
S-17	18.64	70.95	84	93.58	0.27	0.030	7	−20.91	800	
S-18	8.39	76.63	78	62.33	0.63	0.060	40	−20.75	431	
S-19	8.33	76.50	375	79.42	1.12	0.123	161	−19.34	250	
S-20	8.29	76.34	870	40.92	5.84	0.638	904	−18.87	245	
S-21	8.58	75.46	1460	60.42	2.87	0.300	400	−19.31	272	
S-22	8.02	75.75	1680	49.25	1.72	0.186	264	−19.45		
S-23	17.10	72.08	29	81.67	0.37	0.043	36	−20.38	875	
M-28	14.42	72.97	973	41.00	3.90	0.390	620	−20.24	223	57.9
M-29	13.60	70.83	2728	58.41	0.38	0.062	69	−18.67	640	71.8
M-30	16.32	68.87	3688	53.75	0.48	0.072	72	−19.86	840	83.5
M-31	17.70	70.17	860	53.33	5.39	0.580	733	−20.13	298	51.1
M-32	18.42	69.68	2793	48.66	0.63	0.095	109	−19.30	375	88.9
M-33	19.97	66.85	2686	34.67	1.13	0.134	138	−19.64	237	97.1
M-34	19.97	66.85	2686	24.25	0.83	0.114	191	−19.35	244	
M-35	21.23	67.78	1218	53.25	2.58	0.288	516	−19.82	267	
M-36	21.23	67.78	1218	52.50	2.51	0.261	339	−20.86	321	58.9
M-37	22.60	65.23	2254	27.67	0.80	0.119	158	−20.92		

current deposits derived from the Indus River. In the southern half of the area, the Laccadive Ridge intersects the slope at an oblique angle and merges with the continental shelf to the south of Bombay (Laughton *et al.*, 1970) so that sediments derived by down-slope movement from the continental side and from the ridge itself are ponded behind this natural barrier.

The coastal region north of the Gulf of Cambay is generally low-lying, whereas south of this area a fairly narrow coastal plain separates the coast from the Western Ghats, a mountain range with elevations up to 1000 m above sea level. Rivers that rise in the Western Ghats are fed by monsoonal rainfall and flow predominantly eastward (Vaithiyanathan *et al.*, 1988). Only small streams drain into the Arabian Sea from the western coast even during the southwest monsoon. Sediment supply to the shelf and slope region off western India and Pakistan is dominated by the Indus River, which drains an extensive area of the Himalayas and Pakistan and flows through a large alluvial plain. The only other rivers of consequence are the Tapti and Narmada which deliver sediment to the Gulf of Cambay. The inner part of the northern shelf, under the influence of the Indus River (before the recent diversion and damming), is covered by quartzose sands which grade into silty clays on the outer shelf (von Stackelberg, 1972; Mattiat *et al.*, 1973). South of the Indus, the inner shelf sediments are carbonate-poor terrigenous muds which grade into calcarenites on the middle and outer shelf (Fig. 2). Much of this coarse carbonate is relict (von Stackelberg, 1972). Laminated, olive grey clays and fine-grained silty clays occur on the upper slope and these grade into somewhat coarser-grained, brown silty clays on the lower slope due to an increase in the content of foraminiferal shells and oxidizing conditions, respectively, with increasing water depth (von Stackelberg, 1972). Preservation of foraminiferal carbonate is very good on the upper part of the slope, whereas siliceous fossils are better preserved in deeper waters (von Stackelberg, 1972). Benthonic faecal pellets are most abundant in the sediments of the upper part of the slope, especially where the organic carbon content is high (von Stackelberg, 1972). This implies that, in spite of the low bottom water oxygen levels at these depths, benthic organisms thrive wherever there is a plentiful food supply.

The sedimentation rate on the slope of the eastern Arabian Sea has been determined by ^{210}Pb dating by Barole (1988) and Yadav *et al.* (1992). The rates based on seven gravity cores lie between 0.8 and 7.2 mm/yr. These values encompass the rate of 1.5 mm/yr determined by (von Stackelberg, 1972) on the basis of lamina counting and the assumption that lamina couplets are varves.

Circulation in the Arabian Sea is controlled by the seasonal reversal of the winds caused by the alternate heating and cooling of the Indian sub-continent. During the winter monsoon, winds blow from the northeast and drive a surface cyclonic circulation (Wyrtki, 1973). In summer, the winds blow strongly from the southwest and this drives an anticyclonic circulation pattern. As a result of the strong surface currents and the orientation of the coastlines, upwelling of deeper water occurs on

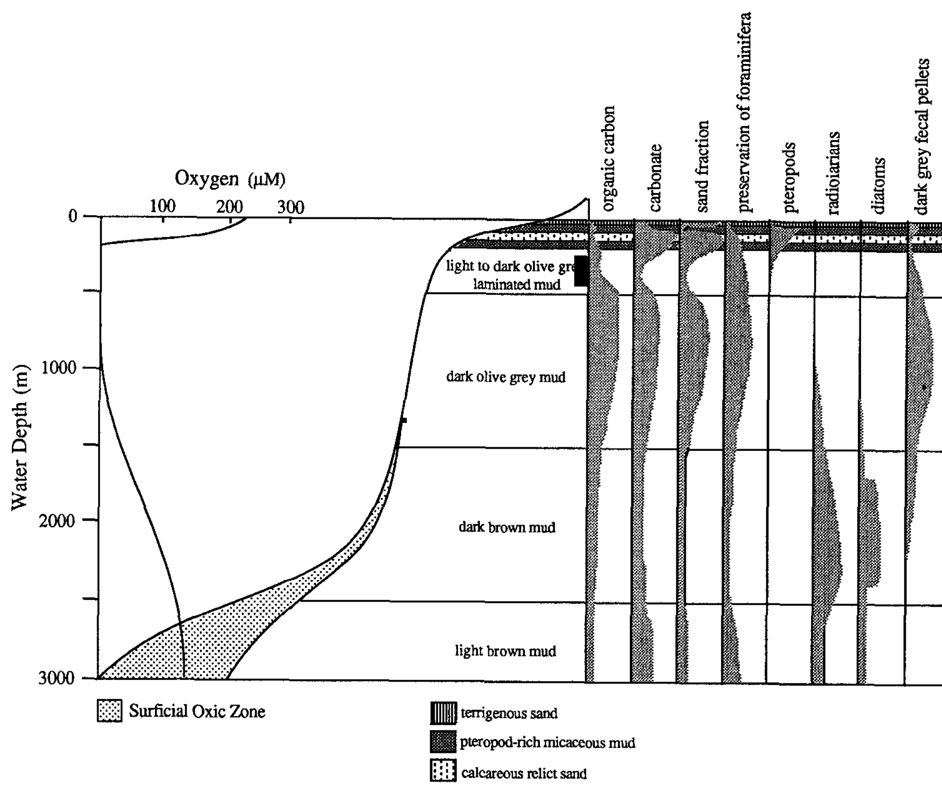

Figure 2. Summary of the principal sedimentological properties of the surface sediments of the western continental margin of India and Pakistan (modified from von Stackelberg, 1972, Fig. 2). Schematic abundances of sediment components increase from left to right in the various panels; the oxygen curve on the left represents a generalized water column profile for the entire margin.

both sides of the Arabian Sea. Off India, upwelling occurs mainly during the summer monsoon, propagating from south to north along the coastline between March and May (Sharma, 1978; Shetye *et al.,* 1990). Cool, nutrient-rich subsurface water is present on the shelf from Cochin to Karachi throughout the summer and extending in some years to mid-December (Banse, 1968). The upwelling is apparently driven by the adjustment of the system to the anticyclonic monsoonal circulation, which causes the isopycnals to slope up toward the coast, and this effect is augmented by the equatorward component of the wind stress blowing surface water offshore (Longhurst and Wooster, 1990). During the northeast monsoon, a coastal current flows northward along the coast against the prevailing winds (Shetye *et al.,* 1991). In this case, the alongshore pressure gradient set up by the circulation overwhelms the effect of the winds, and upwelling occurs only sporadically during the winter months.

An intense oxygen minimum characterizes the entire Arabian Sea at intermediate water depths (Wyrtki, 1971). Although the low oxygen conditions in this layer have previously been ascribed to a combination of the sluggish circulation at intermediate depths due to the presence of a land-mass to the north and to a high rate of oxygen utilization which reflects a relatively high settling flux of organic matter caused by the very high primary production in the region (Wyrtki, 1962; Sen Gupta and Naqvi, 1984), Olson *et al.* (1993) have recently determined that it is due mainly to the initially low concentration of dissolved oxygen in the source waters of the southern Indian Ocean and that the rate of water flow is not abnormally low and oxygen consumption is not exceptionally high within the oxygen minimum itself. The minimum oxygen layer lies between 150 and 900 m depth off Cochin, where the dissolved oxygen levels are 26 ± 3 μM, and is slightly thicker, lying between 150 and 1000 m, off Bombay, where the dissolved oxygen levels are 4 ± 1 μM (Dietrich *et al.*, 1966; Sen Gupta and Naqvi, 1984). Nitrate reduction is prevalent in the central part of the Arabian Sea where the dissolved oxygen levels are particularly low (Sen Gupta *et al.*, 1976a,b; Deuser *et al.*, 1978; Naqvi *et al.*, 1982), and hydrogen sulphide has been detected within the oxygen minimum on some occasions (Ivanenkov and Rozanov, 1961).

The Arabian Sea is known to be an area of high primary productivity (FAO, 1972). This is due to the prevalence of upwelling in the coastal waters caused by the monsoonal circulation, and also by the deep mixing brought about by the strong seasonal winds (Banse and McClain, 1986; Banse, 1987). Values of the annual rate of photosynthetic primary production off the Arabian and the Indian coasts lie in the range observed in eastern boundary currents, for example off Peru and Namibia (Ryther, 1963; Krey and Babenerd, 1976). Surface pigment distributions derived from surface ship observations (Banse, 1987) and from satellite images (Brock and McClain, 1992; Brock *et al.*, 1991) show that the effects of nutrient supply extend farther into the ocean interior on the western side of the Arabian Sea than off India, although pigment concentrations appear to be similar (Krey and Babenerd, 1976). Average values of carbon fixation off the western coasts of India and Pakistan are difficult to obtain from the hourly or daily measurements available, and considerable differences in the distribution of highly and poorly productive areas have been reported (Krey and Babenerd, 1976; Qasim, 1977). However, measurements of the settling flux of organic matter into deep water as measured by moored particle interceptor traps (Nair *et al.*, 1989; Haake *et al.*, 1993), which serve to integrate the surface signals, show that significant amounts of material are transferred to the sea floor in the eastern part of the Arabian Sea during the northeast monsoon. Moreover, the annually-averaged accumulation rate of organic matter in deep water is only 50% higher at the upwelling-dominated western part of the Arabian Sea in spite of the considerably greater rates of primary production off the Arabian peninsula compared to the Indian margin.

4. Results and discussion

The bottom sediments of the western Indian continental margin examined in this study range from sands to muds and comprise mixtures of skeletal and non-skeletal calcite and aragonite, terrigenous aluminosilicates and organic matter. Calcium carbonate concentrations are extremely high in most of the samples from the shelf and the upper part of the slope, ranging up to 96% by weight, whereas the samples from water depths deeper than 800 m have $CaCO_3$ contents ranging from 24 to 60% by weight (Table 1 and Fig. 2a). On the slope, the carbonate occurs as foraminiferal shells, which appear to show little evidence of dissolution (von Stackelberg, 1972; Naidu, 1993), whereas on the shelf it also occurs as reworked, relict macrofaunal shell debris, calcareous algae and oolites (Nair and Hashimi, 1980, 1981).

a. Organic matter. Concentrations of organic carbon are less than 1% by weight on the shelf and increase dramatically at the shelf edge. The maximum on the slope lies between 200 and around 1600 m (Fig. 3a), and values higher than 5% by weight occur only within the depth range 300 to 900 m. The upper boundary of the concentration maximum is quite sharp, whereas the carbon values decrease gradually with increasing water depth at the lower boundary. The distribution of organic carbon with respect to the position of the oxygen minimum (Fig. 3B) shows that although two samples with high carbon contents occur in the core of the oxygen minimum between 200 and 800 m, equally high organic carbon concentrations are also found below the oxygen minimum, and values of 2 to 3% are found at depths where bottom water dissolved oxygen levels are above 50 μM. Hence, the organic carbon maximum occurs over a larger depth range than the oxygen minimum.

Downslope movement of sediment on the western Indian slope, by turbidity flow and by re-suspension and re-settling, causes dilution of the deposited organic matter and foraminiferal shells, especially on the upper part of the slope (von Stackelberg, 1972; Naidu, 1993). This may be augmented by sedimentation from nepheloid layers at the shelf edge (von Stackelberg, 1972). In addition, downslope movement may also carry some organic-rich material to areas deeper than the lower boundary of the oxygen minimum, thereby extending the depth range of the organic-rich sediments. The slope off Cochin, in particular, is especially affected by turbidity flows, and here the organic contents of some deep water sediments described by von Stackelberg (1972) are anomalously high. This process would confound any causal relationship between the organic content of the sediments and the bottom oxygen levels. If this process were a significant factor in redistributing sediment on the western Indian slope, then the fact that surface sediments collected below the lower boundary of the oxygen minimum have high organic carbon contents adds support to the possibility that organic-richness is not related to the oxygen contents of the bottom waters, unless the rapid burial of organic matter in anoxic subsusurface sediments leads to significant preservation of this material. Calvert (1987) has pointed out, however,

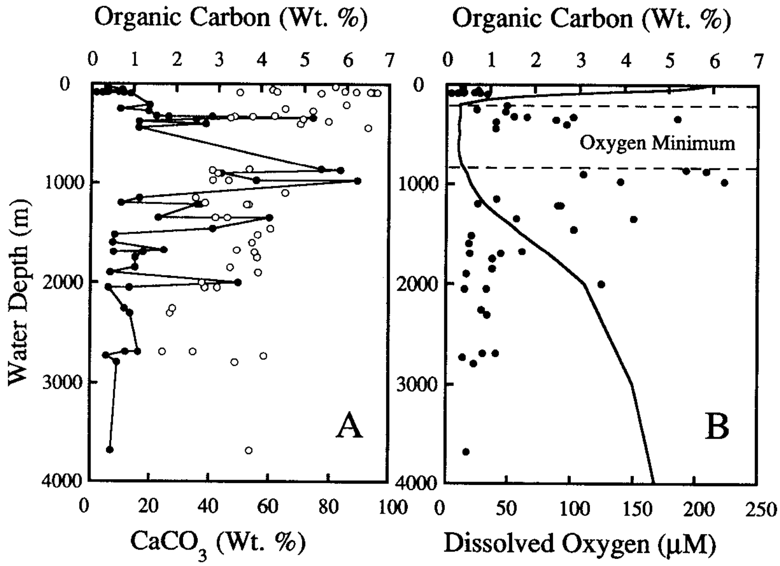

Figure 3. Distribution of (a) surface sediment organic carbon (solid points and line) and $CaCO_3$ concentrations (open circles) with water depth and (b) organic carbon (solid points) and dissolved oxygen content (solid line) of the waters of the western Indian continental margin. The oxygen curve is drawn through the mean of the oxygen values at standard depths from Meteor stations 180 to 229 (Dietrich *et al.,* 1966).

that organic matter is destined to be buried under anoxic conditions in all ocean margin environments, suggesting that there are other factors that control the areal variation in the organic content of surface sediments.

The samples examined in this study cover a latitudinal range of approximately 1,600 km, and, as noted previously, over this area the oxygen minimum varies in thickness and intensity (lowest oxygen concentration). Figure 3, which incorporates data from the entire slope, might therefore obscure the relationship between the positions of the sedimentary carbon maximum and the oxygen minimum at different locations along the slope. We have therefore presented in Figure 4 the depth distribution of organic carbon concentrations and dissolved oxygen along four transects corresponding to the hydrographic profiles determined on the METEOR Expedition of 1965 (Dietrich *et al.,* 1966). This shows that high organic carbon contents are found well below the core of the oxygen minimum on three of the four transects (data are insufficient to make a judgment for the fourth transect) regardless of the thickness and intensity of the oxygen minimum. In other words, organic carbon concentrations at the depth of the oxygen minimum are equally high whether there are comparatively high concentrations of dissolved oxygen within the oxygen minimum, as off Cochin, or whether the dissolved oxygen levels are very low, as off Goa and Bombay. Moreover, organic carbon concentrations reach 2–3 wt. % below the oxygen minimum where dissolved oxygen levels are ca. 50–100 μM. Hence, the

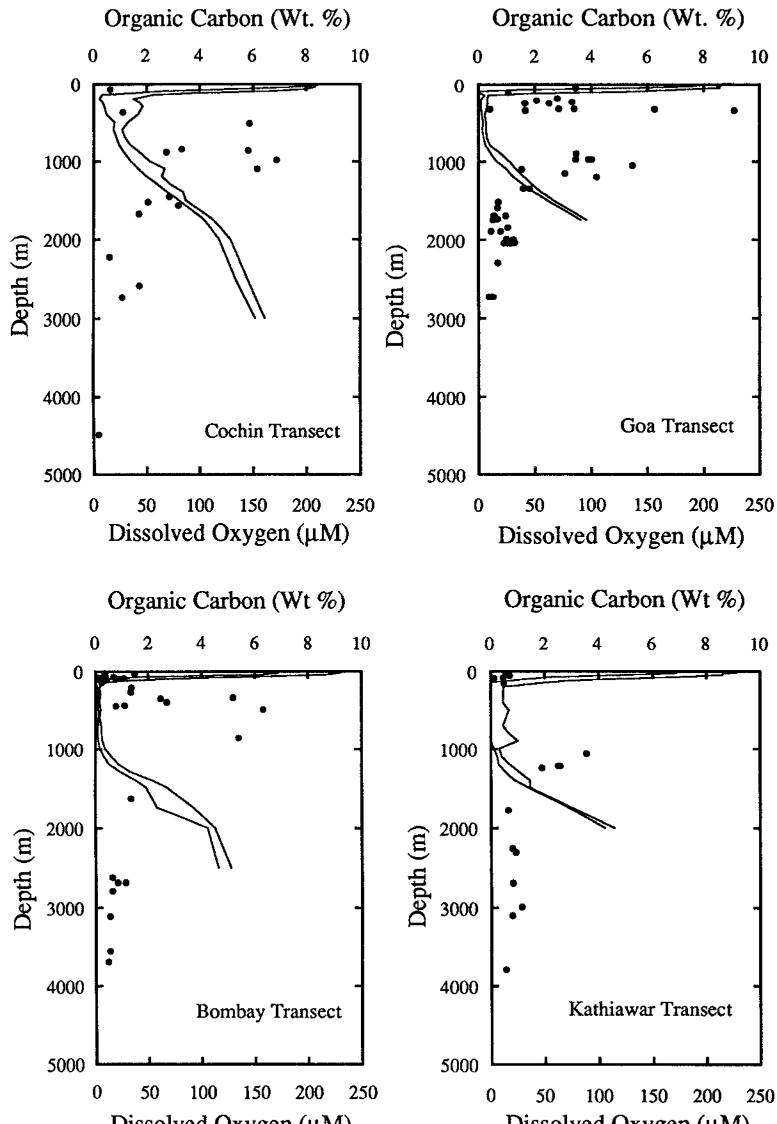

Figure 4. Distribution of sedimentary organic carbon (solid points) and dissolved oxygen content (solid lines representing the mean ± 1σ at standard depths) of the waters along four transects off western India (as represented by the sample groupings in Figure 1). Organic carbon data taken from Table 1 (this paper), von Stackelberg (1972) and Paropkari *et al.* (1993). Oxygen data taken from Dietrich *et al.* (1966).

general conclusions drawn from the examination of Figure 3b appear to be valid for most of the slope off western India.

The source of the organic matter in the surface sediments can be addressed by examining its bulk and stable isotopic composition. Figure 5a shows that the

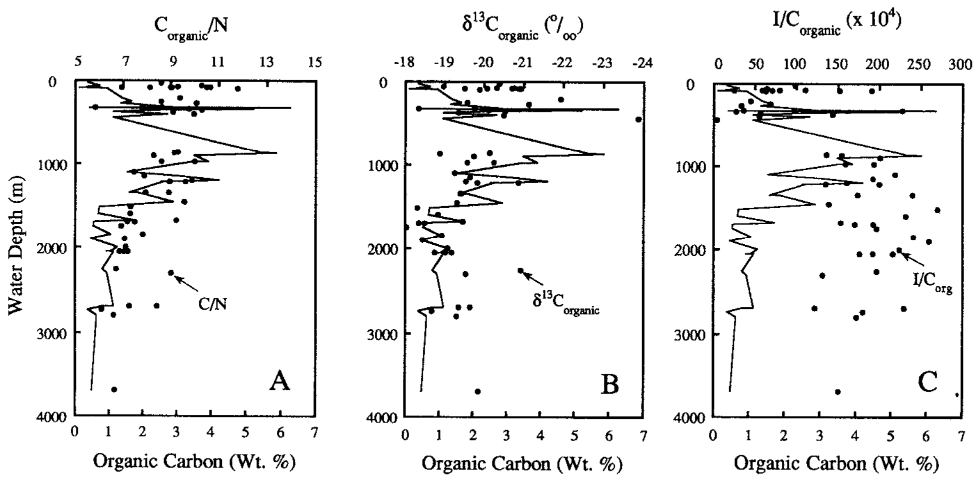

Figure 5. Distribution of (a) $C_{organic}/N_{total}$ and organic carbon (solid line). (b) $\delta^{13}C_{organic}$ and organic carbon (solid line). (c) $I/C_{organic}$ ratios and organic carbon (solid line) with water depth on the western Indian continental margin.

$C_{organic}/N$ ratio decreases with increasing water depth from values of around 10 on the shelf to values of 7–8 at 3000 m depth. This distribution is consistent with the contribution of a small amount of terrestrial organic matter to the shallow-water areas and the overwhelming dominance of planktonic marine organic matter in deeper waters (Emerson and Hedges, 1988). The lower ratios in deep water samples may also be affected by the presence of inorganic fixed nitrogen, which would comprise a significant fraction of the total nitrogen in these relatively organic-poor deposits (Müller, 1977). In addition to the effect of different organic matter sources, a larger degree of sediment reworking in shallower water compared with deeper waters would have the effect of increasing the $C_{organic}/N$ ratio in the shallower samples (Pedersen *et al.,* 1992) because of the preferential degradation of nitrogen relative to carbon in the sediments. That a small proportion of terrigenous organic matter may be present at shallow depths is suggested by the $\delta^{13}C_{organic}$ values (Fig. 5b) which range from -19 to -21‰ on the shelf to -18 to -19‰ in deep water, the lighter values being typical of terrestrial organic matter and the heavier values normally being typical of marine planktonic organic matter (Sackett and Thompson, 1963). Moreover, samples with higher $C_{organic}/N$ ratios also have lower $I/C_{organic}$ ratios (Figs. 5C and 6A), which could reflect the very low I content of terrestrial organic matter compared with planktonic material (Malcolm and Price, 1984).

The relationships between the $C_{organic}/N$ ratio, the isotopic composition of organic carbon and the $I/C_{organic}$ ratio (Fig. 6a and b) could also be caused by a greater degree of reworking of the deposited organic matter in shallower water depths. Thus, samples having higher $C_{organic}/N$ ratios are more depleted in ^{13}C (Fig. 5a and b) and have lower $I/C_{organic}$ ratios (Fig. 6a and b). This could be due to the preferential loss

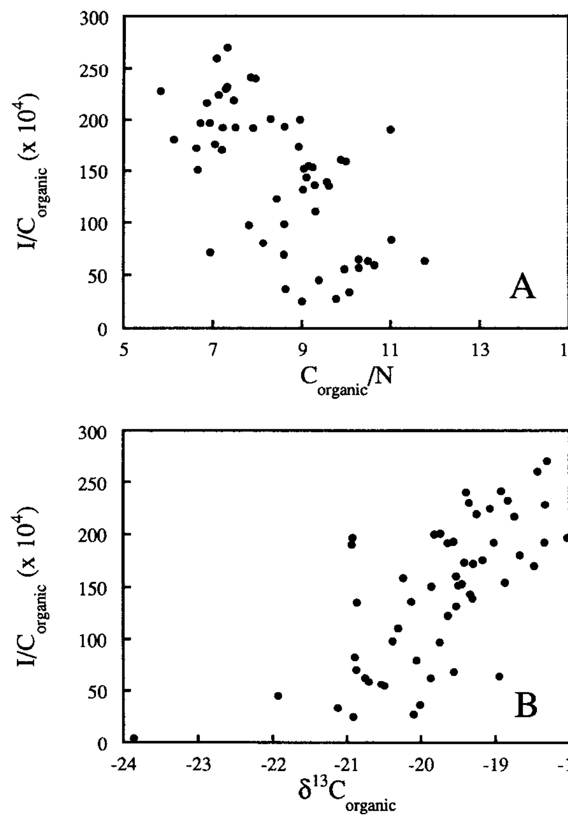

Figure 6. Relationship between (a) $I/C_{organic}$ and $C_{organic}/N_{total}$. (b) $I/C_{organic}$ and $\delta^{13}C_{organic}$ in the sediments of the western Indian continental margin.

of ^{13}C (Spiker and Hatcher, 1984; McArthur *et al.,* 1992), nitrogen (Rosenfeld, 1981) and iodine (Pedersen *et al.,* 1992) from the residual organic matter during diagenesis or reworking. In addition, lighter planktonic carbon isotopic ratios could be produced in areas of intense upwelling closer to the coast because of the increase in PCO_2 at the surface due to the supply of nutrient- and CO_2-rich waters from depth. Under these conditions, the carbon isotopes would be fractionated to a greater extent (Rau *et al.,* 1989), producing more ^{13}C-deficient organic matter. We lack definitive evidence that the variations observed in $\delta^{13}C_{organic}$ are mainly due to source variations or diagenesis.

b. Hydrogen index. There is little correspondence between the distribution of hydrogen index (HI) values and either the organic carbon content (Fig. 7a) or the bottom-water oxygen levels (Fig. 7b) on the slope of the eastern Arabian Sea. Assuming that higher values of the hydrogen index indicate selective preservation of hydrogen-rich organic matter under anoxic or low oxygen conditions (Demaison,

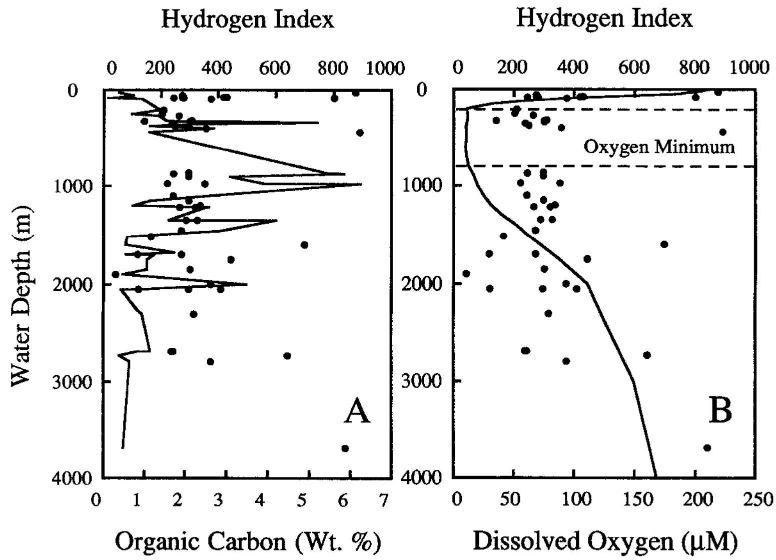

Figure 7. Distribution of (a) surface sediment hydrogen index (HI solid points) and organic carbon (solid line) with water depth. (b) surface sediment HI (solid points) and dissolved oxygen (solid line) on the western Indian continental margin.

1981; 1991; Demaison *et al.*, 1984; Pratt, 1984; Dean and Arthur, 1986), this indicates that the organic matter in these sediments is not preferentially preserved in the organic carbon maximum or the oxygen minimum. The HI values are rather variable due to the inclusion in the sample set of several samples with low organic carbon contents (Table 1) which are known to produce poorly reproducible Rock-Eval results (Katz, 1983). In spite of this variability, the HI values show no significant relationship to the organic carbon contents (Fig. 8a), suggesting that although the concentration of organic carbon covers a range of at least 5% by weight, the organic matter has roughly the same state of preservation regardless of the oxygen content of the bottom water on this slope. Figure 8b shows that the organic matter is predominantly Type II (Tissot and Welte, 1978), with 28% pyrolysable hydrocarbons (Langford and Blanc-Valleron, 1990), and that a single regression line adequately describes the relationship between the size of the S2 peak (hydrocarbons liberated from kerogen during Rock-Eval pyrolysis) and TOC.

Figure 9 shows the distribution of HI and water column dissolved oxygen concentrations along the four transects discussed previously. This shows that there are no consistent trends or differences in HI between the samples collected within and outside the oxygen minimum on three of the four transects. On the Cochin transect, there does appear to be a slight *increase* in HI with depth below the oxygen minimum, that is in increasingly oxygenated waters, but this is not found on any of the other transects. These results suggest that the relationship between HI and water depth

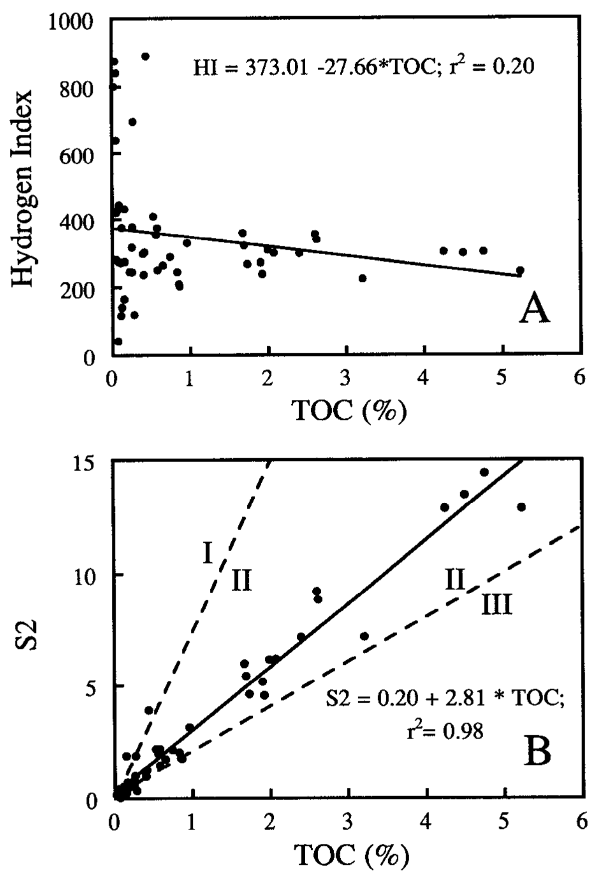

Figure 8. Relationship between (a) HI and TOC and (b) S2 and TOC. The S2 peak on a Rock Eval pyrogram represents the hydrocarbons liberated from kerogen during heating from 250° to 550°C. Solid line in b is the regression through the data points. Dashed lines define the fields for kerogen Types I, II and III on such a plot (after Langford and Blanc-Valleron, 1990).

(position of the oxygen minimum) deduced from Figure 8b, where all data are combined, does apply to the extensive slope sampled off western India.

Paropkari *et al.* (1993) have argued that the depth distribution of HI values on the western slope of India are indeed causally related to the position of the oxygen minimum. However, this interpretation depends critically on the definition of the lower boundary of the oxygen minimum. Although the oxygen minimum in Figure 2 of Paropkari *et al.* (1993) extends over a depth range of ca. 140 to 1000 m, the lower boundary, following von Stackelberg (1972), has been placed at 1500 m by these authors. This choice has caused the inclusion of samples from deeper than 1000 m with high HI values within the group of samples from the oxygen minimum, whereas they are actually from depths where the bottom oxygen contents are significantly

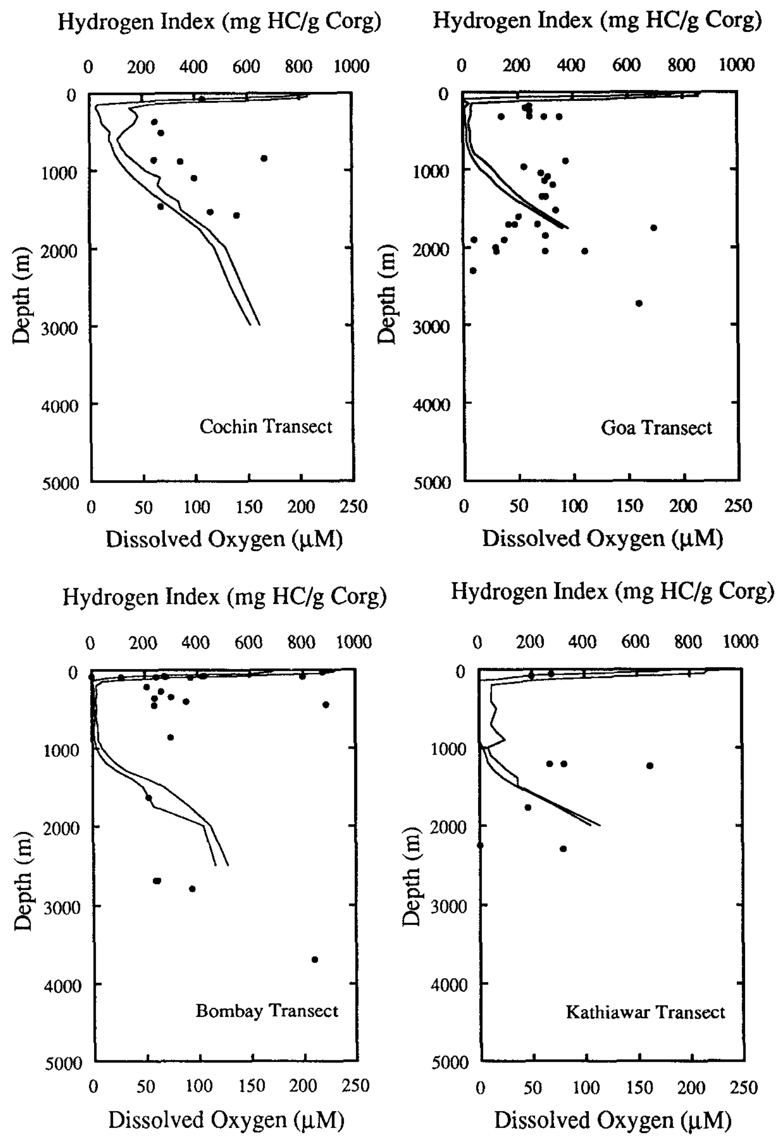

Figure 9. Distribution of the hydrogen index (HI) of the surface sediments (solid points) and dissolved oxygen concentrations (solid lines representing the mean $\pm$ 1σ at standard depths) of the waters along four transects off western India. HI data taken from Table 1 (this paper) and Paropkari *et al.* (1993). Oxygen data taken from Dietrich *et al.* (1966).

higher. If the lower boundary of the oxygen minimum is placed at 1000 m depth, consistent with the depth where dissolved oxygen levels begin to increase with depth below the core of the oxygen minimum (Figs. 3 and 7b), the data of Paropkari *et al.* (1993) show that there is no significant difference in HI between the samples from within and outside the depth of the oxygen minimum ($t = -0.22, p = 0.82$), a result in agreement with that reached in this paper.

c. Relationship between sediment properties and the oxygen minimum. The distribution of organic carbon on the continental slope of the eastern Arabian Sea shown in Figure 3b and by von Stackelberg (1972), Kolla *et al.* (1981) and Slater and Kroopnick (1984) represents the carbon content of sediments that have accumulated over a finite time period depending on the sedimentation rate and the depth of the sampling intervals in the cores. On the other hand, the position of the oxygen minimum is a "snapshot" taken over a much shorter period. It could be argued, therefore, that, if it is accepted that the position of the organic carbon maximum on this slope is causally related to the position of the oxygen minimum, the occurrence of relatively organic-rich sediments at water depths below the core of the present oxygen minimum (Fig. 3b) could have been due to a deeper or an expanded oxygen minimum in the past, possibly related to climate changes. However, the distribution of iodine in the surface sediments effectively rules out this possibility. The geochemical behaviour of iodine in modern marine sediments is controlled exclusively by the organic fraction; it is enriched in oxygenated sediments ($I/C_{organic} > 100 \times 10^{-4}$) and depleted in anoxic deposits ($I/C_{organic} \leq 20 \times 10^{-4}$) (Price and Calvert, 1977). This difference is produced by the adsorption of iodate ion, the stable iodine species in oxygenated seawater (Sillén, 1961), by sedimentary organic matter, whereas iodide, the dominant species in oxygen-free seawater (Wong and Brewer, 1977), is not adsorbed to the same extent (Francois, 1987). The depth distribution of the $I/C_{organic}$ ratios (Fig. 7c) shows that the values are almost all $> 20 \times 10^{-4}$, and that they range between 150 and 250×10^{-4} in samples collected below the oxygen minimum where organic carbon contents lie between 3 and 6%. Thus, the sediment surface here must have remained well-oxygenated for a longer time period than is represented by the oxygen distribution collected during a single expedition (Fig. 3b).

d. Texture and organic carbon. As well as supply and preservation, the organic carbon content of marine sediments is also controlled by sediment texture, finer-grained sediments containing more organic matter than their coarser-grained counterparts (Trask, 1953) because of the hydraulic equivalence of clay and organic particles (Calvert and Pedersen, 1992) and/or a positive association between adsorbed organic matter and the higher surface area of fine-grained particles (Mayer *et al.*, 1985; Keil and Hedges, 1993; Keil *et al.*, 1994; Mayer, 1994). Consequently, the distribution of organic carbon on the eastern margin of the Arabian Sea could be influenced by purely textural parameters which could vary as a result of sediment supply and redistribution (see von Stackelberg, 1972). This aspect was discussed by Calvert and Pedersen (1992), who pointed out on the basis of available information that the shelf sediments off western India are generally coarse-grained and would be

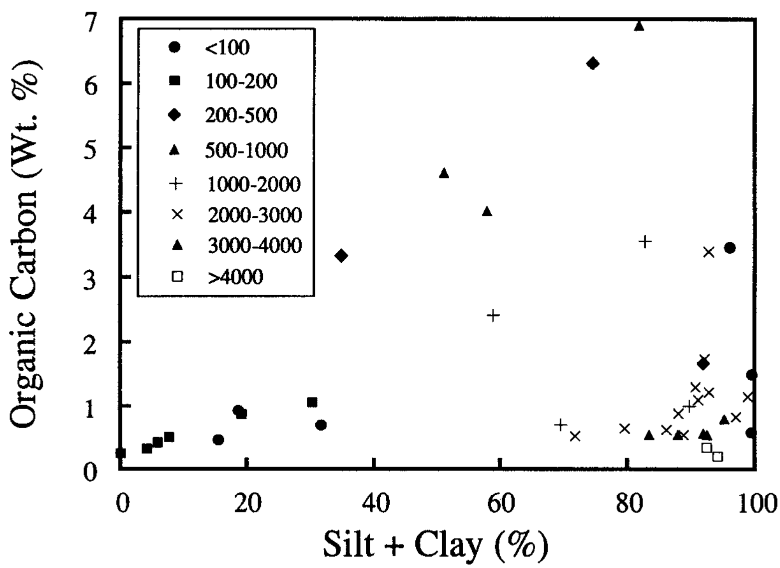

Figure 10. Relationship between organic carbon and mud (silt + clay) concentrations in the surface sediments of the western Indian continental margin (N- and M-samples). Data for the Meteor samples were taken from von Stackelberg (1972). Depth ranges of the samples in meters are indicated in the legend.

expected to have low organic carbon contents compared with the sediments of the slope which are much finer-grained. von Stackelberg (1972) showed that the supply of fine-grained shelf material, low in carbon, to the upper part of the slope dilutes the organic fraction of these sediments, causing the sediments at this depth to have lower organic carbon contents than samples from slightly deeper water. Likewise, Naidu (1993) has ascribed the abundance of planktonic foraminifera shells in the surface sediments of the western Indian margin to the dilution effects of terrigenous sediment from the major rivers of the Indian peninsula.

Figure 10 shows the relationship between organic carbon contents and the abundance of mud (silt + clay) in the METEOR and GAVESHANI samples as a function of water depth. Samples collected at depths shallower than 200 m, with relatively low carbon contents, are either coarse-grained or very fine-grained. The former group of samples characterizes the sandy calcareous sediments, largely relict, of the central and outer shelf, whereas the latter group represents a modern muddy facies of the inner part of the shelf (Nair *et al.*, 1978; Nair and Hashimi, 1980; Paropkari *et al.*, 1987; Paropkari, 1990). The inner shelf sediments probably have low organic matter contents because of the heavy dilution of marine organic material by relatively organic-poor terrestrial clays. Sediment grain size decreases from the outer shelf onto the slope, and organic-rich samples of the upper slope are generally silty clays with less than 40% sand. Grain size continues to decrease into deep water, and below the carbon maximum the sediments are dominantly fine-grained. These relationships reflect the presence of relict, coarse-grained sediments on the outer shelf area, a common occurrence on many continental margins (Curray, 1965), and the decrease in the proportion of coarse-grained material delivered to the sea floor beyond the shelf edge. Organic matter is probably supplied to the shelf at high rates because of the inherently high rate of production in the area of coastal upwelling and the short transit to the sea floor. However, active reworking of the middle and outer shelf sediments prevents the permanent accumulation of much of this deposited material, which, rather, accumulates in quieter water beyond the shelf edge. Cross-shelf transport of water column particulate organic matter (Walsh *et al.*, 1981, 1985) may also contribute to the organic carbon content of the upper slope sediments. The decrease in the concentration of organic carbon with increasing water depth below the oxygen minimum is caused by the offshore decrease in primary production away from the centers of upwelling and the decreasing flux of particulate organic matter to the sea floor with increasing water depth (Suess, 1980). A carbon maximum on the upper slope area is therefore induced by the interplay of these factors; off western India, the upper part of the carbon maximum lies at the same depth as the core of the oxygen minimum, but it extends below the depth of the lower boundary of the oxygen minimum. Carbon maxima on some other continental slopes, such as off northwestern Africa and northeastern and northwestern North America, also do not correspond with the depth of the oxygen minimum, and are evidently related to other factors (Calvert and Pedersen, 1992). Likewise, Keil *et al.* (1994) have concluded that the organic content of the sediments of the Washington continental slope is controlled largely by the surface area, and hence texture, of the sediments and is not directly related to the oxygen content of the bottom waters in this environment.

e. Statistical comparisons. Table 2 presents the results of simple statistical comparisons between the sedimentary parameters of the surface sediments recovered from above, within and below the oxygen minimum off western India. The differences in calcium carbonate, organic carbon and total nitrogen concentrations when the samples within and above, and within and below, the oxygen minimum are compared have been discussed previously. In addition, the results show that iodine is significantly lower above compared to within the oxygen minimum, but no different when the samples from within are compared to those collected below this depth. This is due to the low I contents of the generally coarser-grained sediments of the shelf and upper slope. The carbon isotopic composition of the organic matter at depths below the oxygen minimum is significantly heavier (^{13}C-rich) than samples collected within and above the oxygen minimum, most likely because of the increasing fraction of marine organic matter in the sediments being deposited farther away from the coastal region. Finally, the data show that the HI of samples collected above, within

Table 2. Statistical comparison of sedimentary parameters (from Table 1) in samples collected above (< 200 m), within (200–1,000 m) and below (> 1,000 m) the oxygen minimum on the western Indian slope

Parameter	Above Oxygen Minimum (n = 11)	Within Oxygen Minimum (n = 16)	Below Oxygen Minimum (n = 27)	Above-Within Comparison		Below-Within Comparison	
				Student's t	Probability	Student's t	Probability
$CaCO_3$	80.3 ± 15.9	60.8 ± 16.6	46.4 ± 11.0	3.07	0.006	3.09	0.005
Organic C	0.47 ± 0.25	3.03 ± 1.86	1.33 ± 0.96	−5.45	<0.001	3.41	0.003
Total N	0.048 ± 0.024	0.329 ± 0.212	0.163 ± 0.097	−5.26	<0.001	2.96	0.008
I	39.6 ± 29.1	315 ± 298	244 ± 160	−3.68	0.005	0.88	0.390
$\delta^{13}C_{organic}$	−20.29 ± 0.65	−20.22 ± 1.28	−19.23 ± 0.68	−0.19	0.851	−2.86	0.010
HI	440 ± 221	317 ± 177	322 ± 177	1.46	0.164	−0.07	0.944

and below the oxygen minimum are not significantly different, confirming the conclusions drawn from the examination of Figures 7b and 9.

5. Summary and conclusions

Sedimentary organic carbon concentrations reach a maximum on the upper continental slope off western India. Stable carbon isotope data, $C_{organic}/N_{total}$ ratios and $I/C_{organic}$ ratios all suggest that the organic matter in the sediments of this margin is overwhelmingly planktonic. Moreover, the results of Rock-Eval analyses demonstrate that there is no relationship between the hydrogen-richness (hydrogen index) and the location of the samples with respect to the position of the oxygen minimum or the concentration of organic carbon. Thus, there is little evidence for the preferential or better preservation of organic matter in the sediments underlying the oxygen minimum.

Paropkari *et al.* (1992) have recently carried out an evaluation of the factors controlling the organic carbon content of the sediments of the Arabian Sea. They have concluded that bottom water anoxia in conjunction with a number of depositional parameters, such as sediment texture, sedimentation rates, the width of the shelf, the slope gradient, bottom currents and the adsorption capacity of clay minerals, is the most important factor determining the degree of preservation of sedimentary organic carbon in this area, and that the role of carbon supply (via productivity) is of secondary importance. Our data are consistent with the multiple controls on organic carbon content of marine sediments, as discussed by Calvert (1987), Pedersen and Calvert (1990) and Calvert and Pedersen (1992), but also indicate that the organic material accumulating above, within or below the intense oxygen minimum on this slope sediments cannot be distinguished compositionally. The lack of an exact correspondence between the position of the sedimentary organic carbon maximum and the oxygen minimum may be due partly to the down-slope transfer of sediment on the slope (von Stackelberg, 1972). Hence, a lack of coincidence of the carbon maximum and the oxygen minimum may obscure causal relationships even if there were preferential preservation of organic matter under anoxic conditions. However, the important finding from this study is the fact that there does not appear to be a difference in the degree of preservation of the organic matter under a wide range of oxygenation conditions on the western Indian slope. On any continental margin, the supply of organic material will be spatially variable because of the increase in water depth away from the continent and the contrasting productivities of coastal and oceanic waters. Coupled with the controls on organic matter abundance by the properties of the sediment, principally grain size via the surface area of the particles (Keil *et al.,* 1994; Mayer, 1994), and the fact that organic carbon maxima and oxygen minima do not coincide on other continental margins, this conclusion implies that the bottom-water oxygen concentration cannot be the primary factor determining the organic carbon content of, or its state of preservation in, continental slope sediments.

Dean *et al.* (1994) proposed that bottom-water anoxia was the principal control of the accumulation of organic carbon on the continental slope off northern California, a conclusion diametrically opposed to that presented in this paper. Late Pleistocene horizons of cores recovered from the depth of the oxygen minimum (between roughly 600 and 1200 m depth) on this slope are finely-laminated, enriched in organic carbon and biogenous silica, and have higher hydrogen indices compared with the bioturbated, Holocene sections. Dean *et al.* (1994) interpreted these observations as reflecting the presence of a more intense oxygen minimum that impinged on the slope during the Pleistocene, which led to preferential preservation of organic matter in the sediments. However, these authors also concluded that the low oxygen content of the modern and the Pleistocene oxygen minimum on this margin is directly due to the high rate of primary production in the California Current, and that this has varied on climatic time-scales. Since this is also responsible for a high rate of accumulation of organic matter on the adjacent sea floor, the ultimate control on the organic-richness of the deposits need not necessarily be the oxygen content of the bottom waters. Although Dean *et al.* pointed out correctly that, from an extensive review of the available data, Henrichs and Reeburgh (1987) concluded that anoxia by itself does not result in higher burial of organic matter in marine sediments, they nevertheless contended that anoxic environments are indeed sites where organic matter is preferentially preserved.

Dean *et al.* (1994) maintained that down-core variations in the organic content and its hydrogen richness off California are not due to variations in the type, and hence quality, of organic matter deposited in the slope sediments. In support of this contention, they presented data on two cores from virtually identical water depths (695 and 698 m) within the modern oxygen minimum, and two cores (at 2530 and 3580 m) well below the lower limit (placed at approximately 20 μM) of the oxygen minimum. Close inspection of these data shows that: (a) inexplicably, one of the shallow-water cores has HI values that are higher by a factor of 2 at equivalent organic carbon contents than those in the other shallow-water core; (b) HI values at equivalent organic carbon contents in the core from 2530 m depth lie intermediate between those of the two shallow cores; (c) HI values, again at equivalent organic carbon contents, in the core from 3580 m depth are very similar to those in the shallow core with the lower HI values; (d) the concentration of pyrolyzable hydrocarbons (Langford and Blanc-Valleron, 1990) is identical in the laminated and homogeneous sections of the core with the highest HI values, and lie on the same trend on a plot of S2 vs TOC in the other shallow core; and (e) laminated sediments in one of the shallow cores have significantly heavier $\delta^{13}C_{organic}$ values than the homogeneous sediments, while in the other shallow core, two of the five laminated samples and one of the six homogenous samples also have heavier $\delta^{13}C_{organic}$ values. In addition, as

Dean *et al.* (1994) pointed out, the laminated sections of the two oxygen-minimum cores have higher biogenous silica contents than the homogenous sections. Dean *et al.* suggested that this was a good index of higher production in this continental margin setting. The weight of evidence therefore appears to suggest that on this particular margin, primary production was higher in the late Pleistocene compared with modern conditions, and this led to a higher settling flux of marine organic matter which was also more hydrogen-rich than the material presently being deposited on the slope. The higher organic flux would have caused a larger drawdown of oxygen at the depth of the oxygen minimum, and this would have promoted the preservation of fine-scale sedimentary laminations resulting from changes in the seasonal supply of organic and lithogenous material. Thus, we suggest that, contrary to the conclusions of Dean *et al.* (1994), variations in organic matter supply and its type are the over-riding controls on organic matter accumulation off California, an explanation that strongly supports the main conclusions of this paper.

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