

Letter Section

New evidence for enhanced preservation of organic carbon in contact with oxygen minimum zone on the western continental slope of India

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ABSTRACT

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In order to evaluate the reason for organic enrichment on the western continental slope of India, we provide Rock-Eval pyrolysis data of 25 surficial sediment samples from this area. Results show that the organic matter on the slope is hydrogen-rich Type II kerogen, which suggests that the organic carbon there is mostly marine. The low productivity of overlying waters rules out surface productivity as a possible cause of organic enrichment. The association of higher hydrogen index (*HI*) values (average 306) and higher organic carbon contents (av. 3.28 wt.%) with the sediments of the upper slope in contact with the oxygen minimum zone (OMZ) clearly indicates enhanced preservation under reducing conditions in the anoxic waters of the OMZ. It is suggested that the sediments of the upper slope in contact with the OMZ have excellent hydrocarbon generation potential, and that these slope beds deserve preferential attention for hydrocarbon exploration.

Introduction

The possible causes of organic enrichment in marine sediments have been examined in some detail during the last decade. The results of these studies indicate that the relationship between productivity, oxygen and organic carbon is still perplexing. Some believe that organic enrichment is due to upwelling-induced excessive biological productivity of overlying surface waters resulting in a high flux of biogenic material to the bottom (the production hypothesis; Parrish, 1982; Calvert, 1987; Pedersen and Calvert, 1990; Calvert and Pedersen, 1992), while others believe that the formation of oxygen depleted conditions (anoxia), either in the oxygen minimum zone (OMZ) at intermediate oceanic depths, or in silled basins, is responsible for preservation and consequent enrichment of organic carbon in sediments (the preservation hypothesis; Dow, 1978; Demaison

and Moore, 1980; Bralower and Thierstein, 1987; Summerhayes, 1987). These two discordant views of organic enrichment need serious attention since they have a direct bearing on deciphering the paleo-depositional record and on exploration of hydrocarbons.

The Arabian Sea is characterised by an intense oxygen minimum zone (dissolved $O_2 = < 0.5$ ml/l) at intermediate depths (150–1500 m water depth; Wyrki, 1971; Von Stackelberg, 1972). It also has a very high biological productivity on its western side (> 0.75 gC/m²/day), though not on its eastern margin—the west coast of India (< 0.75 gC/m²/day; Qasim, 1982). This situation provides an excellent opportunity to test the validity of the two contrasting hypotheses of organic enrichment. In this connection, the western continental margin of India can be taken as type example of the preservation hypothesis (Kolla et al., 1981; Slater and Kroopnick, 1984; Paropkari et al., 1987).

Along this margin, the organic carbon content of sediments is low (<4.0%) on the inner shelf, is very low on the outer shelf (<1.0%) and is intermediate (<1.0–2.0%) on the lower slope. But very high organic carbon concentrations (>4.0%) are associated with the sediments of the upper slope between water depths of 150 and 1500 m (Paropkari et al., 1987). Recently, Paropkari et al. (1991, 1992a) indicated that, in the Arabian sea, the organic enrichment occurs only on the slopes of the Arabian Peninsula (Oman margin) and along the slope of the western Indian margin. Furthermore, when compared to that off the Arabian Peninsula, very high concentrations of organic carbon on the western Indian slope (2–4 times) are accompanied by very low productivity (3–4 fold) suggesting that surface productivity does not cause organic enrichment. Paropkari et al. (1991, 1992a) concluded that the oxygen minimum zone is primarily responsible for the preservation of organic carbon on the slope of Oman and the western Indian margin. The sole evidence of organic carbon being enriched by preservation rather than production, off western India, was the juxtaposition of the OMZ with organic enrichment; geochemical proof was lacking.

In this paper, we provide new geochemical data to test the validity of the hypothesis that organic carbon is preferentially preserved under the anoxic waters of the OMZ. For this purpose, we selected 25 surficial sediment samples spread over a wide area and representing a large depth span (85–2297 m water depth) along the western continental margin of India (Fig. 1), thereby covering both the oxic layers above (2 stations) and below the OMZ (8 stations), as well as the OMZ itself (15 stations).

Methods

The surficial sediments were collected using a Petterson grab on board of the research vessels R.V. *Gaveshani* and O.R.V. *Sagar Kanya*, of the National Institute of Oceanography, Goa. The sediments were dried at 60°C and powdered. The organic carbon was determined following the method of El Wakeel and Riley (1957). The samples were also analysed on a Rock-Eval-II instrument to determine the type of kerogen that

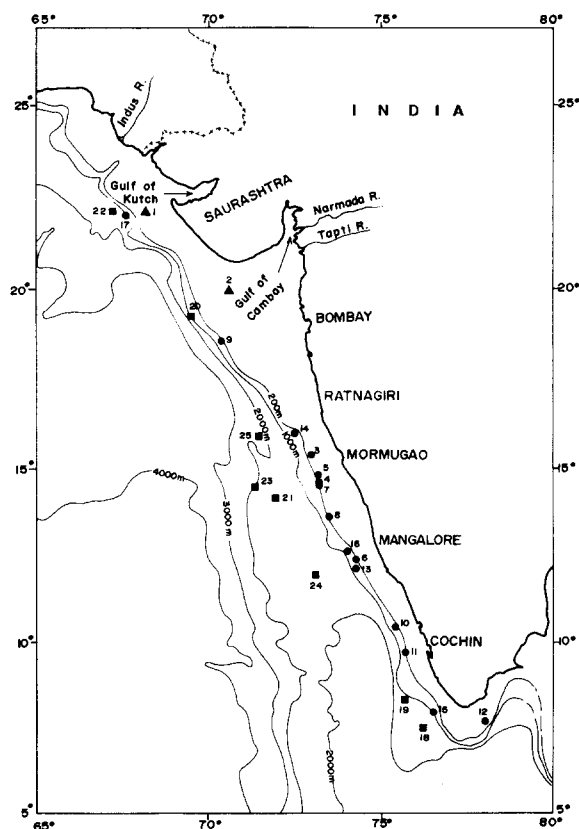


Fig. 1. Station location map. \blacktriangle = shelf sediments; \bullet = upper slope sediments; \blacksquare = lower slope sediments.

constitutes the organic matter. The Rock-Eval pyrolysis method also helps in understanding the source of organic matter, the nature of its preservation, and the hydrocarbon generating potential of sediments (Tissot and Welte, 1978; Espitalie et al., 1985a,b; Peters, 1986; Dean et al., 1986). The pyrolysis hydrocarbon yield (S_2 , mg HC/g sample) represents the hydrocarbon generated from thermal breakdown of kerogen of the sample. The hydrocarbon yield normalized to percent organic carbon gives a hydrogen index (HI) expressed as mg HC/g organic carbon.

Results and discussion

The organic carbon (OC) content varies between 0.14 and 6.18 wt% (Table 1). The depthwise concentration of organic carbon (Fig. 2a) shows that significantly higher values (av. 3.28 wt% OC) are encountered only in the region of the OMZ, with

TABLE 1

Concentrations of organic carbon and results of Rock-Eval pyrolysis of sediments collected on the western continental slope of India

Station number	Depth (m)	Org. carbon (wt. %)	T_{\max} ($^{\circ}\text{C}$)	S_2	PI	HI
1	85	0.14	426	0.28	0.04	200
2	90	1.10	420	1.24	0.02	112
3	186	2.81	417	6.82	0.00	242
4	210	2.07	425	4.74	0.00	229
5	250	2.51	419	6.16	0.00	245
6	285	0.57	493	0.43	0.02	75
7	320	3.40	412	8.33	0.00	245
8	435	4.14	424	10.54	0.00	255
9	445	0.79	433	1.87	0.01	236
10	516	5.88	422	16.16	0.00	275
11	850	3.33	415	22.14	0.00	665
12	890	2.76	409	9.55	0.00	346
13	920	5.06	422	14.87	0.00	294
14	1050	5.47	420	15.52	0.00	284
15	1100	6.18	416	24.60	0.00	398
16	1200	2.33	408	3.73	0.00	160
17	1246	1.90	412	12.31	0.00	648
18	1530	2.07	418	9.51	0.00	459
19	1570	3.21	417	17.99	0.00	560
20	1635	1.35	392	2.87	0.00	213
21	1700	0.98	308	1.86	0.00	190
22	1780	0.66	419	1.22	0.00	185
23	1900	0.79	395	1.20	0.02	152
24	2118	0.59	406	0.92	0.01	156
25	2297	0.69	433	0.25	0.00	36

the carbon maximum coinciding with the core of the OMZ (around 900 m depth); the values are considerably lower in the oxygenated regions of shelf (<150 m water depth, av. 0.62 wt% *OC*) as well as on the lower slope (>1500 m water depth, av. 1.29 wt% *OC*). This clearly indicates that organic matter is enriched in the sediments deposited under reducing conditions developed due to interception of OMZ with the slope. The *PI* (production index, defined as the ratio $S_1/S_1 + S_2$) and T_{\max} (temperature corresponding to the maximum hydrocarbon generation during pyrolysis) values are less than about 0.1 and 435 $^{\circ}$, respectively (Table 1), indicate that the organic matter is immature (Peters, 1986).

The variation of *HI* values (range 36–665, Table 1) with depth (Fig. 2b) shows that the average *HI* is significantly higher in the OMZ (av. 306) compared to *HI* obtained for the sediments

above (av. 156) and below (av. 244) the OMZ. Further, the *HI* maximum lies in the OMZ around 1000–1400 m water depth. Since the *HI* values are indicative of degree of preservation (Dean et al., 1986), the association of higher *HI* values with the sediments in contact with OMZ suggests better preservation. In the diagenetic environment of the OMZ the scarcity of dissolved oxygen leads to more reducing conditions in the sediments and bottom-water mass, thereby enhancing the degree of preservation of organic matter during early diagenesis. The *HI* is a function of the elemental H/C ratio of kerogen and is thought to be a measure of the relative amount of lipid-rich, sapropelic organic matter (Dean et al., 1986). Hence, these higher *HI* values suggest the presence of lipid-rich organic matter in the sediments in contact with the OMZ. Two samples fringing the lower depth level of OMZ, i.e. 1500 m also registered high *HI* values (459 and 560, respectively). These stations marginally exceeded the depth of OMZ by 30 and 70 m which is perhaps not crucial, considering that the lower boundary of OMZ itself is not well defined and may lie deeper than 1500 m at some places (Von Stackelberg, 1972). Alternatively, this enrichment just below the OMZ could also be due to resedimentation of the material from the OMZ due to processes such as gravity flows (Von Stackelberg, 1972; Rao, 1989). In that case, the well preserved organic matter from the OMZ, when transported to the deeper oxygenated environment, will be subjected to greater decomposition; the labile component will be oxidized relatively faster than the kerogen content resulting in higher *HI* values and relatively lower *OC* contents, as observed at these two stations.

Although the *HI* maximum is centered within the OMZ (1200–1400 m depth) it lies slightly deeper than the carbon maximum. Furthermore, an examination of the data on Fig. 2 shows that the higher *HI* values are not necessarily associated with higher organic carbon. This indicates that the correlation between *HI* and *OC* is poor ($r=0.18$). A similar weak correlation was observed in modern sediments of the Gulf of California (Calvert et al., 1992). The data of Pedersen et al. (1992) on the Oman margin seem to indicate an identical pattern. Therefore, a poor correlation between *HI* and *OC*

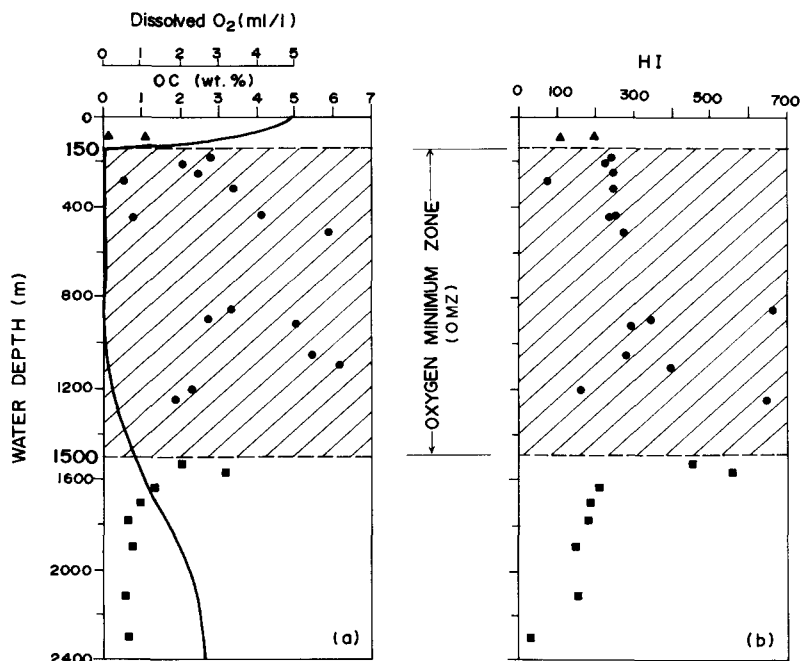


Fig. 2. Vertical distribution of (a) organic carbon (*OC*) and (b) hydrogen indices (*HI*) in sediments from various water depths. The solid line indicates depthwise concentration of dissolved oxygen (ml/l) as presented by Von Stackelberg (1972). The horizontal dashed lines indicate approximate boundaries of oxygen minimum zone (OMZ, dissolved O₂ = < 0.5 ml/l).

may be a common feature in modern immature organic matter. It can be attributed to differential preservation from sample to sample, especially within the OMZ where the preservation of organic matter is also influenced by various depositional parameters (Paropkari et al., 1991, 1992a) which are likely to differ when a vast geographical area and wide depth span is considered, as in this study.

In order to further strengthen understanding of the nature of the organic material, a plot of S_2 vs *OC* is presented (Fig. 3). This plot along with a regression equation is the best method for determining the true average hydrogen indices and the type of kerogen present in order to infer the source of organic matter and petroleum-generation potential of sedimentary organic matter (Langford and Blanc-Valleron, 1990). This figure also includes the boundaries (dashed lines) for Type I–II and Type II–III kerogen (Langford and Blanc-Valleron, 1990).

From the data on Fig. 3, it is evident that two samples from the shallower oxygenated regime occupy the area of Type III kerogen near the origin and have a regression line with very low

slope, lower than the II–III boundary, indicating the organic carbon is either of terrestrial origin or is severely oxidized and degraded marine kerogen, which may have a low hydrogen content due to preferential loss of hydrogenated organic matter during early diagenesis (Pratt, 1984). The petroleum potential of this organic matter is low.

Most of the 13 samples from the OMZ fall between the boundaries of I–II and II–III kerogen and hence the organic matter in these sediments belongs to Type II kerogen. However, 2 samples lie below but very close to the Type II–III boundary. Since the suite has more affinities with Type II rather than Type III kerogen as shown by the slope of the regression line falling between I–II and II–III boundaries, these two samples could be low-hydrocarbon end members of the Type II suite rather than a mixture of Type II and III kerogens. The regression equation shows that these samples liberate 33% pyrolyzable hydrocarbons, following a notion adopted by Langford and Blanc-Valleron (1990). In general, the sediments of the OMZ are characterised by the presence of Type II kerogen suggesting that the organic matter is of marine

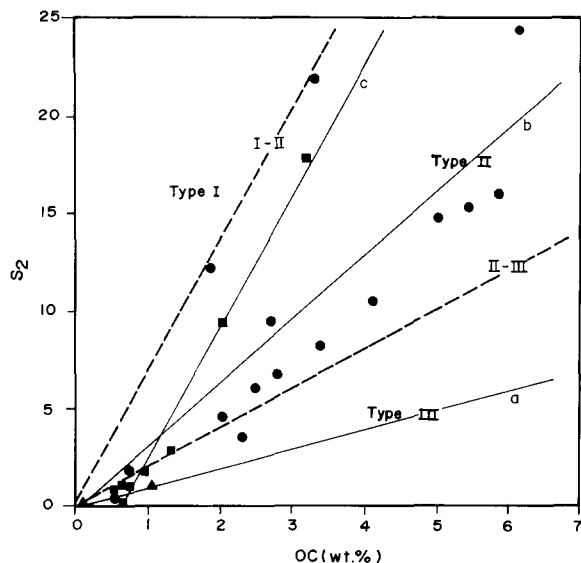


Fig. 3. Relation between pyrolysis hydrocarbon yield (S_2) and organic carbon (OC) for the sediments from the western continental margin of India. (Symbols as in Fig. 1.) The dashed lines indicate the boundaries between kerogen Type I-II and II-III as defined by Langford and Blanc-Valleron (1990). (a) Regression line for shelf sediments ($S_2 = 1OC + 0.14$). (b) Regression line for upper slope sediments ($S_2 = -0.212 + 3.27OC$, $r = 0.80$). (c) Regression line for lower slope sediments ($S_2 = -4.14 + 6.67OC$, $r = 0.99$).

origin. These sediments have a very good oil potential.

Three samples from deeper oxygenated waters fall within the Type II area while another 5 samples fall just below the II-III boundary near the origin. As regards these 5 samples, because of the positive X-intercept of the regression line, these Type II samples may plot below the II-III boundary even though the regression line of the suite has a slope greater than the II-III boundary (Langford and Blanc-Valleron, 1990) and hence belong to Type II. The presence of Type II kerogen in the oxygenated lower slope sediments indicates that organic carbon is mainly of marine origin and has good oil potential. But the hydrocarbon generation potential of these sediments is comparatively less than the sediments from the OMZ, in spite of the regression equation suggesting 67% pyrolyzable hydrocarbons yield, because of lower preservation of organic matter as shown by the lower organic carbon contents and lower average *HI*.

The above discussion clearly suggests that the

organic carbon in the surficial sediments of the western Indian slope is mainly marine. Moreover, this organic carbon is effectively preserved on the upper slope under the reducing conditions developed by the impingement of the OMZ, as is evident from the higher organic content and associated higher *HI* values of sediments and in spite of the relatively low productivity ($< 0.75 \text{ gC/m}^2/\text{day}$; Qasim, 1982) of overlying waters. This observation is consistent with earlier reports (Kolla et al., 1981; Slater and Kroopnick, 1984; Paropkari et al., 1987, 1991, 1992a) concerning the western margin of India. The process of preservation involves the absence of benthonic metazoan life due to oxygen depletion, eventually ceasing bioturbation and ultimately resulting in well preserved hydrogen-rich organic matter (Demaison and Moore, 1980). This preservation aspect is important for interpreting the paleo-depositional environment of older sediments.

Values of *HI* generally correlate well with atomic H/C ratios measured by other methods (Tissot and Welte, 1978; Espitalie et al., 1985a,b) and therefore higher *HI* values of slope sediments indicate hydrogen-rich kerogen. Tissot and Welte (1978) proposed that if surface organic-rich deposits contain hydrogen-rich kerogen, then there is every likelihood of finding oil at greater depths. The organic geochemical studies of Singh et al. (1987) on the northern part of slope (north of Bombay) also revealed that the organic matter is of Type II kerogen and has a good oil generation potential.

According to Biswas (1989), the shelf margin basin across the western continental slope has developed structural features and sedimentary deposits which appear to be attractive targets for oil generation at greater depths. This is particularly important because the geological research revealed that the shelf basin evolved since the Paleocene (Mohan, 1985) and the average sediment thickness of the shelf margin basin across the slope is around 3-4 km (Subramanyam et al., 1991, 1993). The DSDP data on site 219 indicate that the productivity in this region began in the early Eocene and anoxic conditions have been present since the Miocene (Whitmarsh et al., 1974). All the evidence together suggests that the continental slope of western India can act as source beds for petroleum

generation. The areas, especially where the slope gradient is gentler (between Ratnagiri and Mangalore, and south of Cochin) with a wide surficial band of organic-rich sediments (Paropkari et al., 1991, 1992a,b), merit preferential attention as far as petroleum exploration is concerned.

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