

Organic carbon–sulfur relationships in sediment cores from the western and eastern continental margins of India

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Abstract

Two sediment cores from the western continental margin (WM1, WM2) and one core from the eastern continental margin (EM1) of India have been analysed to determine the relative importance of factors such as oxidizing/reducing environment, mass deposition and terrigenous influx on organic carbon–sulfur relationship. The results indicate that the cores consist of two stratigraphic units: an upper unit of Holocene age and a lower unit of Late Pleistocene age. The upper unit of WM1 and WM2 has C–S relationships similar to those of normal marine (oxic) sediments, whereas in the lower unit the relationship is controlled by mass sedimentation processes and the amount of terrestrial organic matter. In EM1, organic carbon and sulfur do not show any significant correlation since their abundance is mainly controlled by the amount of detrital pyrite. Further, a synthesis of data of all the three cores resulted in delineation of different clusters which reflect the importance of sedimentary processes and the types of organic matter.

1. Introduction

Organic-rich marine sediments usually have high sulfur content, mostly in the form of pyrite and other monosulfides such as mackinawite and greigite which form due to the reaction of hydrogen-sulfide with reactive iron (Berner, 1984). A linear relationship exists between organic carbon and sulfide sulfur in normal marine sediments with the regression line passing through the origin (Goldhaber and Kaplan, 1974; Berner, 1982), whereas the regression line for anoxic sediments has a positive intercept on S-axis (Leventhal, 1983). The carbon–sulfur relationship has been increasingly used in interpretation of paleoenvironments of both modern and ancient sedimentary sequences (Raiswell and Berner, 1985, 1986; Dean and Arthur, 1989; Morse and Emeis, 1990; Lin and Morse, 1991). Here, we present data of three cores from the deep continental margins of India

to evaluate the organic carbon–sulfur relationships with respect to lithologic variations, depositional environment, sedimentary processes and source of sediments.

2. Study area

The northern Indian Ocean is divided into the Arabian Sea and the Bay of Bengal by the Indian sub-continent. The physiography of the eastern Arabian Sea is influenced by the Indian continental margin, bathymetric highs such as Chagos–Laccadive ridge and the Indus fan. The sediments in the WM1 area form a part of the Indus fan. The surface sediments of this area are hemipelagic clays of Holocene age which are underlain by gray, dark gray and gray-green inter bedded sands, silts and muds deposited due to slumping from the western continental margin of India during late

Pleistocene lowered sea levels (Kolla and Coumes, 1987; Rao, 1989). The WM2 area is free of Indus borne sediments as it is separated by the Chagos–Laccadive ridge system from the Indus fan. However, several westward flowing smaller rivers, mostly estuarine in nature, discharged directly onto the slope during the Late Pleistocene lowered sea levels thereby increasing the terrigenous input, whereas this discharge is presently limited to the inner shelf only. The organic carbon content in the surficial sediments of the eastern Arabian Sea is generally less than 1%, with the exception of the continental slope of India where it is more than 4% (Paropkari et al., 1992).

The core EM1 is from the eastern continental margin of India, off Penner River. The margin in this area is narrow, with steep slopes. Most of the rivers flowing into the Bay of Bengal form canyons across the slope. The sediments are influenced by the Ganges in the central Bay of Bengal, whereas near the continental margin the effect of peninsular rivers is high. Low CaCO_3 content in the surficial sediments (< 10%; Siddiquie, 1967) is due to high terrigenous influx.

3. Materials and methods

As a part of geological studies in the seas around India, the National Institute of Oceanography has collected several cores from different geographic locations. For this study, we have selected three cores collected by a gravity corer (Fig. 1; Table 1). All the cores were collected from the deeper regions characterized by oxic bottom waters, beyond the intersection of the oxygen minimum zone. The core from the central western continental margin (WM1) has a hemipelagic upper part and a turbidite-derived lower part representing normal and mass sedimentation processes (Rao, 1989). The core from the southwestern margin (WM2) represents oxic sediments in the upper part and micro-reducing environments in the lower part. The core from the eastern margin (EM1) displays characteristics of river-discharged terrestrial sediments, the influence of which is more in the lower part and less in the upper part. The core lengths are 12.00 m for WM1, 1.25 m for WM2 and 2.63 m for

EM1. In order to have meaningful comparisons with other cores, only the top 3.00 m of sediment column of WM1 has been considered in this study.

Textural analysis was carried out following Folk (1968). The coarse fraction was observed microscopically. Organic carbon content in the subsamples of WM1 was determined with a CHN analyzer (Perkin-Elmer model 240B), while the titration method of El Wakeel and Riley (1957) was adopted for other cores. Calcium carbonate content was determined by EDTA complexometric titration using murexide as indicator (Müller, 1967), and also by a “Karbonat Bombe” (Müller and Gastner, 1971). The difference in the CaCO_3 content from both methods is less than 5%. Reduced sulfur content was determined gravimetrically by digesting the sample in aqua-regia and precipitating as BaSO_4 (Vogel, 1961). To avoid dilution effects, organic carbon and sulfur values are expressed on a carbonate free basis.

4. Results and discussion

Downcore variations of lithology, organic carbon (C), sulfur (S) and calcium carbonate contents and C/S ratios are shown in Fig. 2. The organic carbon and sulfur data are plotted along with the average regression line for normal marine sediments established by Goldhaber and Kaplan (1974) (Figs. 3–6). A comparison of various parameters for individual cores is given in Table 1. The results show that each core can be sub-divided into two units with different sedimentological and geochemical characteristics. Hence, it is of interest to study the C–S relationships in each of the units of these cores.

4.1. Stratigraphic boundaries

A sharp change in colour is noticed at 50 cm depth in WM1, which is associated with a change in chemical composition and coarse fraction content (Fig. 2) indicating a stratigraphic break. Radiocarbon dating of this core yielded sedimentation rates between 3.83 and 4.81 cm/kyr in the upper 50 cm which places the Holocene/Pleistocene boundary at this level. In WM2, the downcore variations of calcium carbonate and organic

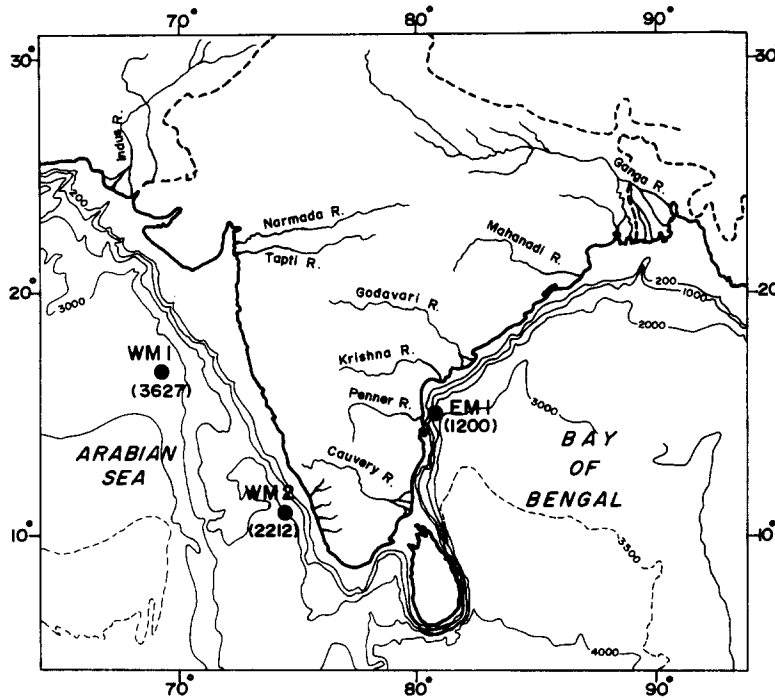


Fig. 1. Location of cores and simplified bathymetry of the continental margins of India. Depth contours are shown in meters. Numbers in brackets denote water depth at the station.

Table 1
Core details and ranges of organic carbon, sulfur, calcium carbonate and C/S ratios

Core	WM1		WM2		EM1	
	Lat. 16°26'N Long. 69°57'E Depth 3627 m		Lat. 10°44.7'N Long. 74°14.5'E Depth 2212 m		Lat. 14°33.9'N Long. 80°35'E Depth 1200 m	
Unit	I	II	I	II	I	II
Length (cm)	0–50	50–300	0–60	60–125	0–94	94–263
No. of samples	9	31	12	13	5	16
C _{org} (wt%)	0.76–1.23	0.50–5.90	1.09–2.22	2.24–3.13	0.89–2.35	2.53–4.26
Sulfur (wt%)	0.28–0.43	0.71–3.56	0.26–0.59	0.31–0.94	0.36–1.94	0.61–3.40
CaCO ₃ (wt%)	47–56	47–86	22–33	22–29	14–16	15–25
C/S ratio	2.11–3.14	0.40–2.95	2.70–5.00	2.70–10.00	0.67–5.00	1.09–7.14

carbon exhibit contrasting trends above 40 cm and below 60 cm, with a transition zone in between (Fig. 2), which represents the boundary between Holocene and Pleistocene. The Holocene sedimentation rates in the WM2 area obtained by the biostratigraphic method (Naidu et al., 1989) and the ¹⁴C method (A.L. Paropkari, unpubl. data, 1993) averaged 3.5 cm/kyr and 4.0 cm/kyr, respec-

tively. These sedimentation rates confirm that the transition zone in this core is the boundary between the Holocene and the Pleistocene. In EM1, textural analysis and microscopic observations reveal that the detrital matter is more abundant in unit II (below 94 cm) than in unit I (Rao et al., 1992). This is due to the fact that river Pennar was discharging directly onto the slope during the Late

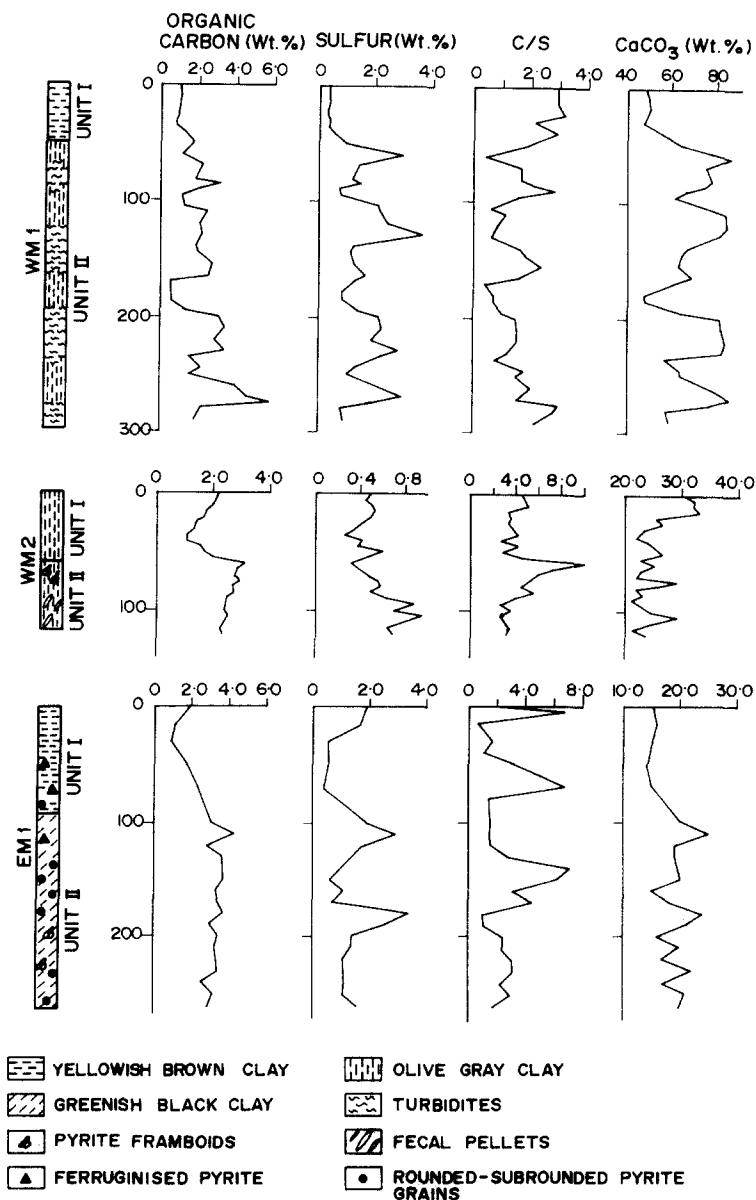


Fig. 2. Down core variations of lithology, organic carbon, sulfur, C/S ratios and calcium carbonate. Core depths in centimeters.

Pleistocene; the low detrital content in unit I resulted from the subsequent rise of sea level during the Holocene and the landward shift of the shoreline. Therefore, the 94 cm level is assigned as the boundary between Pleistocene and Holocene (Rao et al., 1992). The rate of sedimentation is relatively high in EM1 area compared to WM1 and WM2 areas, the former being a part of the

depo-center for the large amount of suspended load carried by the Indian peninsular rivers flowing eastward.

4.2. Carbon–sulfur relationships

The C–S relationship in WM1 (Fig. 3a) shows a significant correlation ($r=0.590$) with a positive

intercept on S-axis (0.49) indicating sulfur enrichment. However, sulfur and organic carbon contents and the C/S ratio (Table 1) do not show excess sulfur in unit I. The relatively high positive correlation ($r=0.678$) between organic carbon and sulfur and the similarity of its regression line with that of the normal marine sediments (Fig. 3b) suggest that the sediments of unit I of WM1 were deposited under oxic conditions similar to that of present day.

The C/S ratios (Fig. 2) and the regression line for unit II of WM1 (positive S-intercept; Fig. 3c) indicate anoxic conditions similar to that of the Black Sea (Leventhal, 1983). Although the Arabian Sea has an oxygen minimum zone between 150 and 1500 m, the waters below are fairly well oxygenated (Spencer et al., 1982). The presence of abundant benthic fauna (Rao, 1989) also indicates that the bottom waters did not contain H_2S during the deposition of these sediments.

Microscope observations and radiocarbon dating revealed that the sedimentation of unit II of WM1 was disrupted by the deposition of turbidites transported from the slope. The slope sediments are characterised by the presence of high organic carbon (more than 4%; Paropkari et al., 1992) and dispersed grains of pyrite. The high organic carbon and sulfur contents and the relatively low C/S ratios in the unit II are the result of sediment transport from the slope to the present site. Therefore, organic carbon and sulfur are poorly correlated (Fig. 3c). The turbidity flows were initiated on the outer shelf and upper slope during the Late Pleistocene lowstands of sea level (Rao et al., 1988; Rao, 1989), and are therefore restricted to unit II only.

In WM2, all the data plotted on the C–S diagram fall below the normal regression line indicating organic carbon enrichment in relation to sulfur (Fig. 4a). Unlike WM1, the intercept on the S-axis is not a true expression of excess sulfur but resulted from the poorly defined slope ($r=0.351$) between organic carbon and sulfur (Fig. 4a). The data points belong to two different populations; one for unit I (0–60 cm) and the other for unit II (60–125 cm). Though the correlation is negligible in the whole core (Fig. 4a), organic carbon and

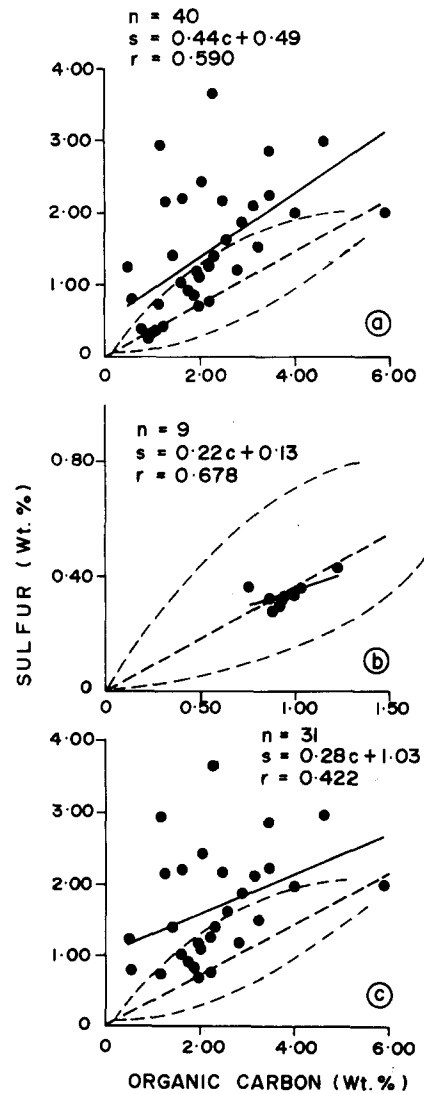


Fig. 3. Correlation between organic carbon and sulfur in WM1; whole core (a), unit I (b) and unit II (c). The points of unit I closely follow the regression line for normal marine sediments (dashed line, Goldhaber and Kaplan, 1974), and fall within the envelope of oxic environment (Berner, 1984; Leventhal, 1983). The distribution of unit II shows excess sulfur.

sulfur show a strong positive correlation ($r=0.634$) in unit I (Fig. 4b) and a strong negative correlation ($r=-0.730$) in unit II (Fig. 4c). The similarity in variations of sulfur and organic carbon (Fig. 2) and the positive correlation between them in the

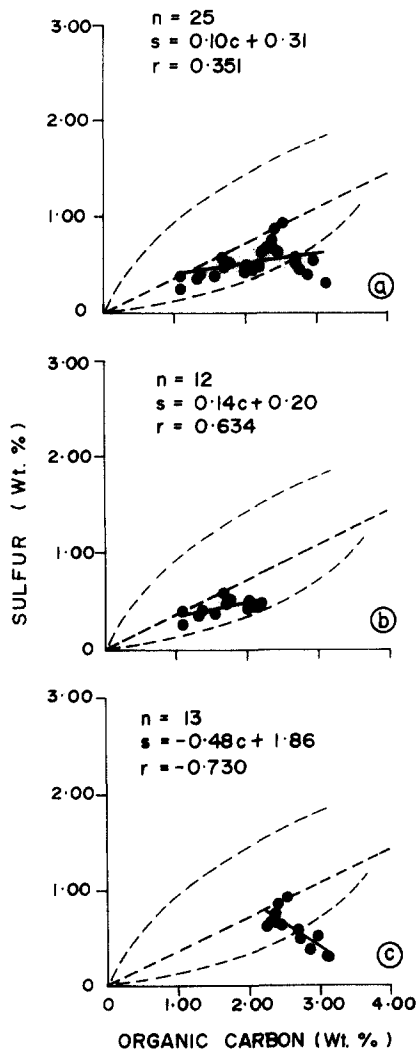


Fig. 4. Correlation between organic carbon and sulfur in WM2; whole core (a), unit I (b) and unit II (c). All the points fall below the regression line for normal marine sediments. Though the correlation is not significant in whole core, unit I shows a strong positive correlation and unit II a strong negative correlation.

sediments of unit I (Fig. 4b) indicate their deposition in an oxidizing environment.

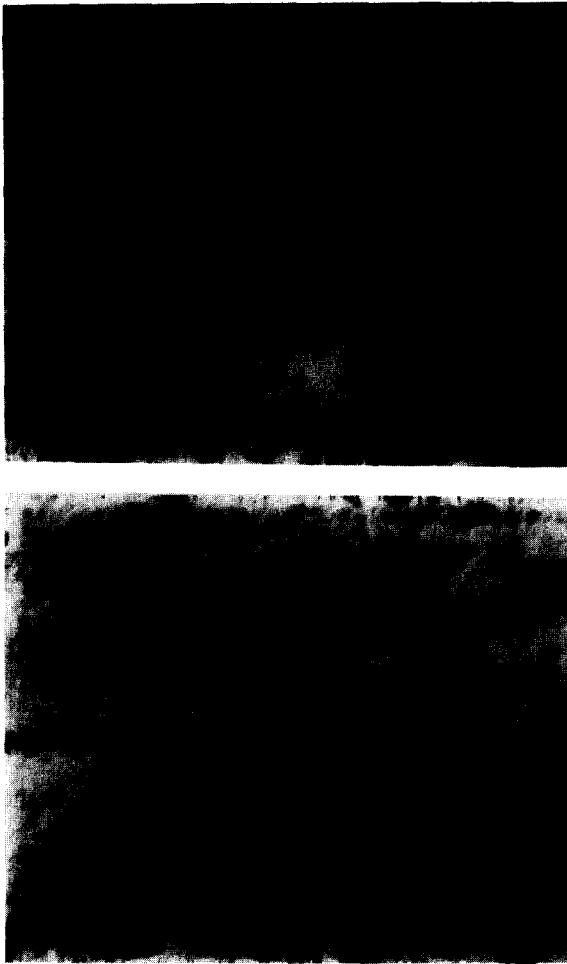
Below 60 cm, a reverse relationship occurs between organic carbon and sulfur. The low calcium carbonate and high organic carbon contents indicate higher terrigenous input as a result of rivers such as Valapattanam discharging directly on the slope during the Late Pleistocene lowered sea levels. Therefore, the availability of

neither iron nor organic carbon are limiting factors for the formation of iron sulfides. However, SEM observations did not reveal any distinct iron sulfide minerals in the sediments (Paropkari et al., 1991). This is due to the fact that the organic matter in the Pleistocene sequence in the area of WM2 is of terrestrial origin, as evidenced by higher C/N ratios in cores collected nearby (Marchig, 1972). Therefore, the organic matter in unit II of WM2 is more resistant resulting in its preferential accumulation. Hence, this unit is characterised by high C/S ratios and the data points fall below the normal regression line with a strong negative correlation in the C–S plot (Fig. 4c). The relatively high S content of unit II compared to unit I (Table 1) is partly due to the presence of framboidal pyrite on the fecal pellets which occur abundantly in the animal burrows (Plate I). The bacterial breakdown of organic matter within the fecal pellets results in the development of micro-reducing environment favouring the formation of framboidal pyrite.

In EM1, the data on C–S plot are widely distributed on either side of the normal regression line (Fig. 5a). In contrast to the other cores, organic carbon and sulfur show no meaningful correlation in the entire core (Fig. 5a) or in individual units (Fig. 5b and c) indicating their independent nature. More than half of the data points on the C–S plot fall above the normal regression line. The downcore variations of C/S ratios (Fig. 2) show sulfur enrichment in some parts of both the units, especially in unit II. The abundance of rounded to subrounded pyrite grains is higher in unit II sediments (Rao et al., 1992) and is responsible for high sulfur values.

4.3. Depositional environment and sedimentation processes

The cores exhibit different C–S relationships that resulted from different environmental settings and depositional processes. When all the data points are plotted on the C–S diagram, three distinct fields are identified (Fig. 6). The field that lies above the normal regression line is occupied by the unit II of WM1 and those points of unit I and unit II of EM1 which are associated with



Pyrite framboids on the surface of a fecal pellet as seen under SEM ($\times 400$). Enlarged micrograph of framboids (bottom) showing pyrite crystals ($\times 2000$).

detrital pyrite grains. This field can therefore be demarcated as an area of excess sulfur. High sulfur content in unit II of WM1 and EM1 is due to the addition of sulfides as a consequence of slumping and terrigenous river deposition. Hence, this field represents areas of mass sedimentation.

The field close to the normal regression line lies within the oxic boundaries defined by Leventhal (1983) and Berner (1984). The points are segregated into two groups. The first group consists of points of unit I (open marks; Fig. 6) and is closer

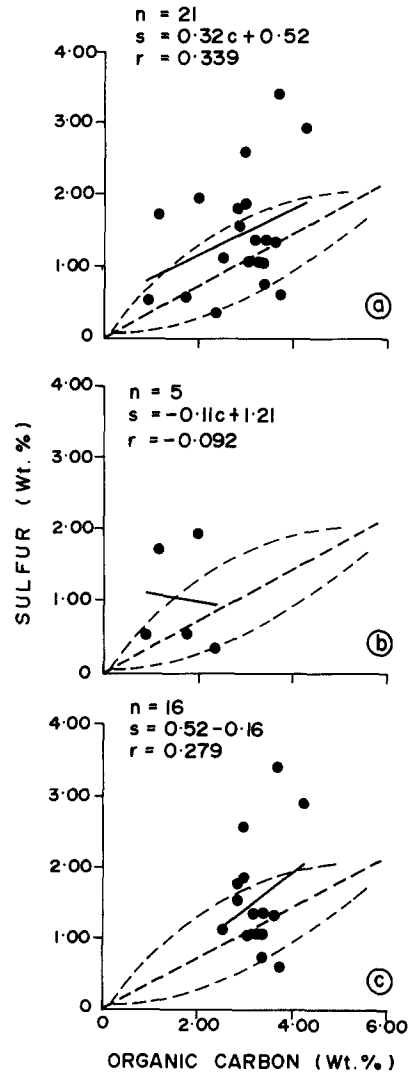


Fig. 5. Correlation between organic carbon and sulfur in EM1; whole core (a), unit I (b) and unit II (c). The points are distributed on either side of the regression line for normal marine sediments. The correlation is significant neither for the whole core nor for individual units.

to the origin (organic carbon less than 2.5%); the second group concerns unit II deposits with high organic carbon and sulfur values (solid marks; Fig. 6). As stated earlier, the unit I of WM1 and WM2 are hemipelagic sediments deposited under normal conditions. The points of unit II that lie in this field belong to core segments interrupted neither by slumping nor by terrigenous influx. Therefore, this field characterizes normal depos-

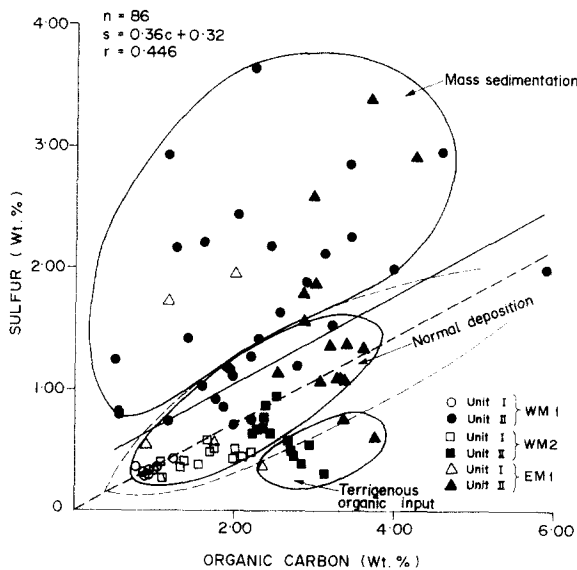


Fig. 6. Plot of organic carbon and sulfur for all cores demarcating the fields of mass sedimentation, normal deposition and terrigenous organic matter input. Regression line of the present study (solid line) runs parallel to that of normal marine sediments (thick dashed line). Also shown is the boundary of oxic environment (thin dashed line) according to Leventhal (1983) and Berner (1984).

ition in an area of oxic environment and supports previous studies (Leventhal, 1983; Berner, 1984).

Below the normal regression line, another field can be identified which shows depletion of sulfur despite of high organic carbon content. This is occupied partly by unit II of WM2 and partly by EM1 which are characterized by terrigenous component. The C/N ratios in the pre-Holocene sediments indicate higher terrestrial organic matter in the southeastern Arabian Sea (Marchig, 1972). The Rock-Eval pyrolysis data show low hydrogen index values ($HI < 100$) for core EM1, indicating that the organic matter belongs to the Type III kerogen and hence is terrestrially derived (Rao et al., 1992). In the terrestrial organic matter nutrients are low, restricting microbial decomposition and H_2S generation, thus inhibiting the pyrite formation. Therefore, this field has high organic carbon and low sulfur contents and reflects an area of terrestrial organic matter deposition.

The processes through which the organic matter and sulfur accumulated in the continental margins

of India have been summarised in Fig. 7. In the western margin, during the Holocene, the organic matter has accumulated through normal settling from the overlying waters and sulfur through diagenetic sulfide formation. During the Late Pleistocene, in addition to normal settling of organic matter and diagenetic sulfide formation, the lowered sea levels resulted in the addition of sulfides and organic matter through slumping in the central western margin and in high terrestrial organic flux in the southwestern margin. In the eastern continental margin, besides normal settling of organic matter and diagenetic sulfide formation, the peninsular rivers contributed substantial amounts of terrigenous organic matter and detrital pyrite during Late Pleistocene. The terrestrial contribution, however, drastically reduced during Holocene due to raised sea level.

5. Conclusions

(1) All the three cores investigated consist of two stratigraphic units of Holocene (unit I) and Late Pleistocene (unit II) ages, which exhibit different C–S relationships.

(2) The C–S relationship in the unit I of the western continental margin cores (WM1 and WM2) suggests that the sediments were deposited through normal sedimentary processes under oxic environment similar to that of present day, whereas the relationship in the unit I of the eastern continental margin sediments is influenced by the terrigenous input.

(3) The C–S relationship of unit II sediments of all the cores shows sulfur enrichment compared to unit I. The relatively higher sulfur content in the unit II sediments of WM1 is due to addition of sulfides issuing from the western continental slope of India through mass sedimentation processes, whereas micro-reducing environments facilitated sulfide accumulation in unit II sediments of the WM2. The high S content in the unit II of EM1 is attributed to higher terrestrial contribution that occurred due to lowered sea levels.

(4) The grouping of data points on the C–S diagram for all cores enables to distinguish three fields, namely high sulfur, normal organic carbon

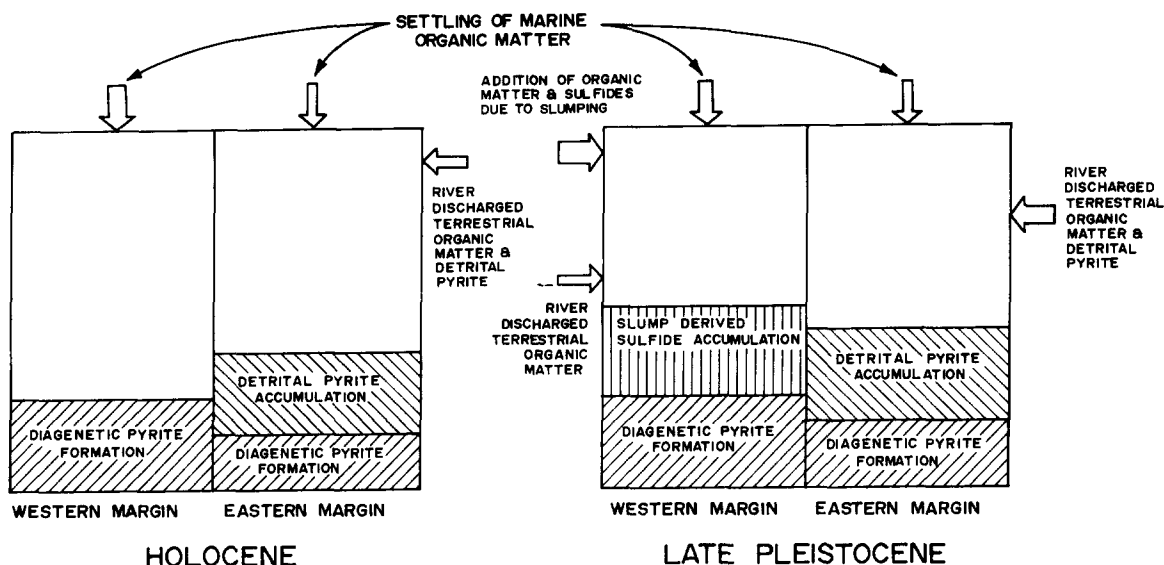


Fig. 7. Schematic presentation of processes through which organic carbon and sulfur accumulated during the Holocene and the Pleistocene.

and sulfur, and high organic carbon–low sulfur. This allows to establish the relative importance of various factors such as slumping, terrestrial input and type of organic matter, responsible for the resulting organic carbon–sulfur relationships.

(5) This study demonstrates that, in addition to the chemical environment, the C–S relationship is also influenced by sedimentary processes. Therefore, a careful evaluation is needed to decipher whether the C–S relationships truly represent in-situ environmental conditions or artifacts determined by the sedimentary inputs.

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