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CONTROLS ON C/S RATIOS IN HEMIPELAGIC UPWELLING SEDIMENTS

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ABSTRACT. The relationship between organic carbon and reduced sulfur concentrations was investigated in hemipelagic sediments underlying highly productive regions of the ocean and oxic to suboxic waters (the Benguela upwelling area, Peru and Oman margins). At all three sites the degree of pyritization averaged close to 0.4, indicating that reactive iron was probably not limiting for pyrite formation. Complete sulfate reduction occurred in the upper sections of the sediments from the Oman and Peru margins. However, dissolved sulfate never decreased below 5 mM in the Benguela upwelling sediments. We attribute this to more advanced organic matter degradation at the Benguela upwelling site.

C/S ratios increased with increasing organic carbon concentrations at all sites. For sediments with greater than 3 wt percent TOC, the C/S ratio averaged about 1.3 and 1.8 times the normal marine ratio of 2.8 at the Benguela upwelling and Peru margin sites, respectively, but 2.9 times this value in the Oman margin sediments.

We hypothesize that the "quality" of the organic matter undergoing burial and rates of near interfacial transport processes are the dominant controls on sulfur burial in these sediments.

INTRODUCTION

Reduced sulfur is mainly sequestered in marine sediments in the iron sulfide mineral pyrite. For this mineral to form, dissolved sulfate, "reactive" iron minerals, and organic matter for bacterial sulfate reduction must be present (Berner, 1970, 1984). Pyrite formation is ultimately limited by the availability of one or more of these three components.

In "normal" marine sediments (that is, clastic sediments overlain by oxic waters with a salinity typical of most oceanic environments) organic carbon is generally believed to be the limiting factor for pyrite formation (Berner, 1970, 1984). The organic-carbon to reduced-sulfur (C/S) ratio in these sediments averages about 2.8 ± 0.8 (Berner, 1982; Berner and Raiswell, 1983). Dissolved sulfate is generally limiting in freshwater environments where it is at low concentrations. This leads to high (often >10) C/S ratios in the underlying sediments (Berner and Raiswell, 1984). In euxinic environments such as the Black Sea where sulfide is present in bottom waters, pyrite can form in the water column, and H_2S can be supplied to these sediments from overlying waters. This often results in lower than normal C/S ratios in such sediments (Leventhal, 1983; Raiswell and Berner, 1985), and the availability of "reactive" iron may limit pyrite formation (Raiswell, 1982; Raiswell and Berner, 1985;

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Raiswell and others, 1988). These observations on the controls of depositional environment on pyrite formation and the resulting C/S ratio in sediments have led to widespread interest in using sedimentary C/S ratios as paleoenvironmental indicators (Berner, 1982; Leventhal, 1983; Davis, Byers, and Dean, 1988).

A geologically and economically important class of marine sediments-hemipelagic sediments in areas of upwelling has not been systematically studied to determine if they follow these general patterns. These sediments typically have higher organic carbon concentrations than most marine sediments, and the availability of organic carbon may thus not limit sulfide mineral formation, as is the case for most marine sediments. Consequently, C/S ratios in upwelling sediments may deviate from the ratio that is characteristic of other marine sediments.

We selected sediments from three areas where high oceanic productivity results in deposition of organic-rich sediments: the Benguela upwelling area off southwest Africa in the Atlantic Ocean, the area of monsoonal upwelling in the northwest Arabian Sea (Oman margin), and the upwelling region on the Peru margin in the Pacific Ocean. Samples were collected during the Deep Sea Drilling Program (DSDP) and Ocean Drilling Program (ODP) Legs 75, 112, and 117. They cover wide geologic time intervals during which the overall depositional conditions were unchanged but with a wide range of sediment burial rates and TOC (total organic carbon) accumulation rates. Use of DSDP and ODP samples for this investigation is particularly advantageous because a substantial body of information exists on the depositional environments, general sedimentology, and chemical characteristics of the sediments and their pore waters.

STUDY SITES

Only a brief summary will be presented of the most pertinent characteristics of the sediments used for this study, because extensive information is available in the associated DSDP (Hay, Sibuet, and others, 1984) and ODP (Suess, von Huene, and others, 1988; Prell, Niitsuma, and others, 1989) Initial Report volumes.

The sediments studied from beneath the Benguela upwelling area were obtained at Site 532 of DSDP Leg 75 (19°33.61′ S, 10°31.13′E. This site is located on the eastern part of the Walvis Ridge on the Southwest African continental margin at a water depth of 1331 m. The dominant lithology is hemipelagic calcareous and siliceous biogenic ooze which accumulated at rates betwen 25 and 50 m/my and which exhibits pronounced dark-light cyclicity on a scale of meters. From smear-slide analyses, Hay Sibuet, and others, (1984) estimate that bulk biogenic components range from 80 to 90 percent in Pleistocene and Pliocene sediments. Clay-sized clastic material accounts for 10 to 20 percent in the Pleistocene section and increases downhole to 50 percent in the upper Miocene. In the biogenic fraction, nannofossils range from 20 to 50 percent, and diatoms are present in quantities of 10 to 40 percent in

upper Pliocene strata. The opal-rich upper Pliocene sediment is also characterized by a peak in TOC concentrations of up to 8.65 percent. The increase in diatoms and TOC in the upper Pliocene reflects an increase in primary productivity and a strengthening of the Benguela upwelling system (Meyers and others, 1983; Meyers, Brassell, and Huc, 1984). The sediments are thoroughly bioturbated indicating oxic conditions in the overlying water. Samples were selected to cover light-dark cycles in all age units.

Oman margin sediments were collected at Site 723 of ODP Leg 117 (18°03.079'N, 57°36.561'E) which was drilled in water 808 m deep in the Arabian Sea upwelling area. Uppermost Pliocene to Holocene sediments are composed of foraminifer-bearing nannofossil oozes to calcareous clayey silts. Calcium carbonate content ranges from 0 to 60 wt percent; biogenic silica is less than 10 wt percent. The sedimentation rate is high throughout the section (130–240 m/my) and reflects variability in eolian and biogenic input due to changes in the strength of the monsoon (Prell, Niitsuma, and others, 1989). Abundance of TOC and the occurrence of laminations in intervals of latest Pliocene to early Pleistocene age suggest that bottom-water oxygen contents were low and precluded bioturbation; the resulting laminated sequences of less than 1 mm thickness coincide with strata cemented by dolomite during diagenesis and in which biogenic silica was preserved (less than 60 wt percent). Because our primary interest is in normal marine sediments, only bioturbated Pleistocene sediments deposited under oxic conditions are considered in this paper.

The sediments investigated on the Peru margin are from Site 688 of ODP Leg 112 (11°32.26'S, 78°56.57'W) which is located on the lower continental slope at a water depth of 3820 m. The presence of turbidites indicates that at least some of the material was resuspended on the shelf and upper slope and has been redeposited. Organic-carbon-rich diatomaceous oozes and muds accumulated throughout the Pleistocene and Holocene. Calcium carbonate content in these sediments is typically less than 10 wt percent, and biogenic silica is generally less than ~5 wt percent but reaches close to 24 wt percent in some sections. Older sediments (Eocene to Pliocene) are less organic-carbon-rich, contain more clastic components, and are coarser-grained. Because our interest is in organic-rich sediments, we have confined our study to lithologic Unit I (0.0-338.5 mbsf = meters below seafloor) which is of Holocene to Pleistocene age. It is composed of bioturbated diatomaceous mud indicating that the sediments were deposited under oxic conditions.

METHODS

The method for determining abundances of total inorganic reduced sulfur (TRS) is after Zhabina and Volkov (1978), as modified by Canfield and others (1986). In brief, H_2S from reductive decomposition of sulfide by a Cr (II) solution in concentrated HCl is titrated with $PbClO_4^-$, and the end point determined with a silver sulfide reference

electrode. Attempts to measure acid volatile sulfur (AVS) by digestion in cold 6N HCl (Westrich, 1983) failed because AVS was not present above the detection limit of the method (4 μmol g^{-1}), even though we strongly suspect that it was present in some of the fresh samples from the Peru margin. Consequently, we interpret TRS and pyrite-S as being equivalent, recognizing that this may be an overestimate in some cases.

The "reactive" iron fraction is a widely used and often loosely defined term which describes the fraction of total iron that may be available for participation in chemical reactions under diagenetic conditions. It is used in conjunction with pyrite concentrations to obtain the degree of pyrite concentrations to obtain the degree of pyritization (DOP). This is useful in assessing the fraction of the reactive iron converted to pyrite (Berner, 1970) and is given as

$$\mathrm{DOP} = \mathrm{pyrite}_{\mathrm{Fe}}/(\mathrm{pyrite}_{\mathrm{Fe}} + \mathrm{reactive}_{\mathrm{Fe}}),$$

where $\mathrm{pyrite}_{\mathrm{Fe}}$ is generally well approximated as 0.5 TRS (in molar units), based on the molar ratio of iron and sulfur in pyrite.

Leaching procedures using citrate dithionite and HCl solutions of different strengths have been most widely applied to determine reactive iron, but many other methods are also being used. Canfield (ms) conducted a careful study of the behavior of different iron phases, and his results indicate that the citrate dithionite method extracts all the major iron oxide phases, while it removes only minor lattice-bound iron from iron silicate minerals. One exception is the clay mineral nontronite. However, the original hot 12 N HCl method of Berner (1970) is still in common usage (Raiswell and others, 1988).

Huerta-Diaz and Morse (1990) compared the results for iron concentrations measured by both the citrate dithionite method and by leaching with 1N HCl in sediments with varying iron contents. They found remarkably good agreement between the methods. Morse (unpublished data, 1990) compared various methods on a variety of recent sediments (39 different samples) and obtained the following average DOP values: hot 12 N HCl = 0.28; frozen sediment citrate dithionite = 0.35; freeze dried sediment citrate dithionite = 0.27; cold 1 N HCl = 0.42.

We have chosen 1N HCl leachable iron (80–1 solution to solid ratio extracted for 12 hrs) to represent a reasonable and conservative approximation of the "reactive" iron fraction. This was done primarily because many of these samples were analyzed for other "reactive" metals, and the citrate dithionite method interferes with their analysis (see Huerta-Diaz and Morse, 1990). The primary objective of the determination of "reactive" iron was to see if iron was limiting for pyrite formation. As will be discussed later, the DOP values are generally sufficiently low (avg ~0.4) to indicate that iron was not limiting for pyrite formation.

All analyses were performed on freeze dried samples. Information on the techniques used to obtain other chemical parameters, such as organic carbon and dissolved sulfate concentrations are given in the

previously referenced DSDP and ODP volumes. Analytical results are presented in table 1.

Sediment burial rates, where not given in the respective ODP and DSDP volumes, were calculated according to paleontological age models, average porosities, and wet bulk densities for each interval, a density of seawater of 1.025, and average TOC and TRS for each interval.

RESULTS

Organic carbon-sulfate relationships.—The relationship between organic carbon flux to sediments and sulfate reduction rates is largely independent of the availability of reactive iron to form iron sulfide minerals from the H_sS produced as a result of bacterial sulfate reduction. It is reasonable to expect that close to total reduction of sulfate should occur in sediments from beneath highly productive waters receiving a relatively large supply of marine organic matter, as is characteristic of the sediments examined in this investigation.

Figure 1 presents organic carbon and dissolved sulfate concentration profiles for the three sites studied. TOC concentrations are highly variable and range from about 1 to 9 wt percent, with the majority (75 percent) of these concentrations in the range of 2 to 6 wt percent. If we consider sediments with more than 2 wt percent organic carbon as organic-rich, 81 percent of the samples fall into this category. Sediments from the Benguela upwelling area and the margin of Peru had similar average organic carbon concentrations of 3.97 and 3.70 wt percent respectively, and the sediments from the Oman margin averaged slightly lower (2.93 wt percent organic carbon).

Dissolved sulfate exhibited a major decrease in concentration with increasing depth at all three sites. Complete reduction of sulfate occurred in the Peru and Oman margin sediments, by approx 25 and 40 mbsf, respectively. The decrease is dissolved sulfate with depth at Site 532 from the Benguela upwelling area is less rapid than at the other sites. (Note that Gieskes, personal communication, 1990, believes that the dissolved sulfate concentration from the 25 mbsf sample is unreliable, as it probably represents contamination by seawater. It will, therefore, not be considered in subsequent calculations and discussion). Below about 50 mbsf to approx 100 mbsf the concentration of dissolved sulfate decreases in a close to linear manner, below this depth the dissolved sulfate concentration varies irregularly between about 5 to 10 mM over a depth range of close to 200 m. Unlike at the other sites, sulfate is not completely reduced.

Berner (1978) has observed a strong correlation between sulfate concentration gradients and sedimentation rates. The sulfate concentration gradients at the Peru and Oman margin sites are, respectively, about 2 and 3 times higher than the general trend observed by Berner. However, at the Benguela upwelling site the sulfate concentration gradient is only about one third of the typical value for sediments with a similar accumulation rate.

TABLE 1

Analytic results. The average C/S ratio is the ratio of the C and S averages, not the average of the C/S ratios.

Benguela Upwelling

Depth (mbsf)	TOC (wt %)	TRS (wt %)	DOP	C/S
5.70	2.11	0.42	0.32	5.02
14.00	5.09	0.76		6.70
19.70	1.67	0.29		5.76
52.10	5.62	0.94		5.98
53.90	4.46	0.85		5.25
71.00	5.12	1.44	0.44	3.56
71.40	2.93	0.78		3.76
91.70	5.52	0.94		5.87
93.10	3.90	0.63		6.19
93.40	7.43	1.20		6.19
93.50	7.84	1.14		6.88
93.60	8.65	1.26		6.87
93.70	6.43	1.20		5.36
93.70	6.01	1.02		5.89
93.80	8.45	1.13		7.48
116.70	1.94	0.75	0.50	2.59
143.60	2.59	0.56		4.63
143.70	3.96	0.97		4.08
143.80	3.16	0.90		3.51
144.50	3.11	0.74		4.20
179.70	1.99	0.76		2.62
180.30	4.34	1.12	0.47	3.88
180.40	3.99	1.07		3.73
180.50	3.60	0.94	0.38	3.83
194.00	1.61	0.72	0.43	2.24
194.20	2.19	0.85		2.58
194.80	3.85	1.02		3.77
229.00	1.62	0.84	0.47	1.93
229.30	3.07	1.02		3.01
229.40	2.68	0.79	0.44	3.39
229.60	0.70	0.24		2.92
267.10	1.43	0.50	0.33	2.86
Average	3.97	0.87	0.42	4.56
Std. Dev.	2.14	0.28	0.06	

Oman Margin

0.40	5.80	0.30		19.10
1.10	4.80	0.19	0.37	25.70
1.90	2.51	0.20		12.40
4.10	3.50	0.20	0.27	17.30
4.90	1.49	0.43		3.50
5.90	1.80	0.40		4.50
6.40	1.31	0.36		3.60
7.10	2.86	0.28	0.33	10.10
8.20	1.56	0.41		3.80
8.90	2.93	0.38	0.40	7.80
9.70	2.73	0.53		5.10
11.20	3.56	0.60		6.00
10.40	5.05	0.32	0.38	16.00
12.70	2.25	0.45		5.00
14.30	1.68	0.34		5.00
15.80	2.27	0.41		5.60
17.30	4.77	0.36		13.20
17.90	3.59	0.27		13.30
19.40	3.38	0.28		11.90
20.30	4.58	0.37		12.40
20.40	6.83	0.66		10.30
20.90	3.20	0.30		10.50
21.60	3.95	0.21	0.36	18.60
22.40	2.18	0.27		8.20
23.40	0.71	0.49		1.50
23.90	1.23	0.41		3.00
25.40	1.66	0.63		2.60
30.50	1.01	0.47	0.52	2.20
52.30	2.04	0.51		4.00
58.00	4.50	0.40		11.30
56.90	1.82	0.38	0.45	4.80
66.20	3.12	0.19	0.35	16 .70
71.80	1.09	0.53		2.10
77.30	3.85	0.36	0.45	10.80
81.30	2.42	0.29		8.40
93.40	2.27	0.29	0.46	7.80
95.90	1.09	0.70		1.50
119.80	3.49	0.43		8.20
126.80	3.29	0.41		8.10
127.50	2.97	0.29	0.33	10.10
140.90	2.51	0.52		4.80
154.30	2.06	0.53		3.90
177.20	1.76	0.52		3.40
186.70	2.65	0.54		4.90
199.40	2.11	0.50	0.47	4.20
204.40	2.92	0.51	0.53	5.80
212.30	3.04	0.52		5.90
223.40	4.51	0.72		6.30
236.50	4.60	0.47	0.43	9.70
244.50	5.19	0.59	0.46	8.80
Average	2.93	0.41	0.41	7.15
Std. Dev.	1.36	0.13	0.07	

TABLE 1 (continued)

Peru Margin

Depth (mbsf)	TOC (wt %)	TRS (wt %)	DOP	C/S
6.80	3.02	0.66		4.60
8.70	2.77	1.00		2.80
11.70	1.85	0.39		4.80
14.70	1.56	0.56		2.80
17.70	3.73	0.87	0.52	4.30
19.70	3.28	1.16		2.80
22.70	2.72	1.18	0.60	2.30
23.70	1.99	1.14	0.61	1.80
30.70	2.70	0.88		3.10
40.40	1.55	0.84		1.90
48.50	1.91	0.93	0.58	2.00
50.80	2.14	0.81		2.60
65.90	3.67	1.08		3.40
81.90	3.87	1.06		3.70
82.20	4.73	1.34	0.54	3.50
83.40	3.32	0.80		4.20
86.10	3.55	1.32	0.39	2.70
95.60	3.76	0.86		4.40
103.90	4.24	0.68	0.36	6.20
115.00	3.67	0.55	0.26	6.70
121.00	3.56	0.73		4.90
124.70	3.76	0.73	0.25	5.20
130.70	4.08	0.32		12.60
142.90	4.40	0.68	0.32	6.40
148.90	4.87	0.52	0.26	9.30
151.40	3.36	0.79		4.30
158.90	3.53	0.52	0.24	6.80
161.60	4.78	0.67		7.20
170.40	3.71			
174.20	3.24	0.48	0.19	6.70
176.40	2.80	0.90		3.10
189.40	3.53	0.68	0.27	5.20
192.40	3.09	1.00		3.10
192.90	3.41	1.01		3.40
198.50	5.75	0.89		6.40
208.50	3.38	0.69	0.34	4.90
217.80	4.79	1.06		4.50
227.40	8.00	0.95	0.48	8.40
236.60	5.17	0.85	0.73	6.10
246.10	3.24	1.04		3.10
251.70	2.71	1.60	0.66	1.70
255.90	4.99	1.26		4.00
269.70	5.44	1.00		5.50
277.80	4.78	1.14	0.40	4.20
287.40	4.49	0.75		6.00
297.00	3.38	0.95	0.33	3.60
303.70	4.64	0.71		6.60
313.00	4.51	0.27		16.80
332.20	3.75	1.12		3.40
339.90	3.72	1.04	0.47	3.60
Average	3.70	0.87	0.42	4.25
Std. Dev.	1.17	0.27	0.15	

We did not observe a direct relation between either the organic content or the TOC accumulation rates in the depth interval of sulfate reduction of the sediments to their sulfate concentration gradients or extent of sulfate reduction. The Benguela upwelling and Peru margin sediments have similar concentrations of organic carbon but exhibit markedly different dissolved sulfate profiles. In contrast the Oman margin sediments have about 25 percent less organic carbon than the other sites but exhibit a dissolved sulfate profile very similar to that observed in the Peru margin sediments.

Reduced sulfur.—Profiles of TRS, DOP, and the C/S ratio at the study sites are presented in figure 2. TRS concentrations scatter widely

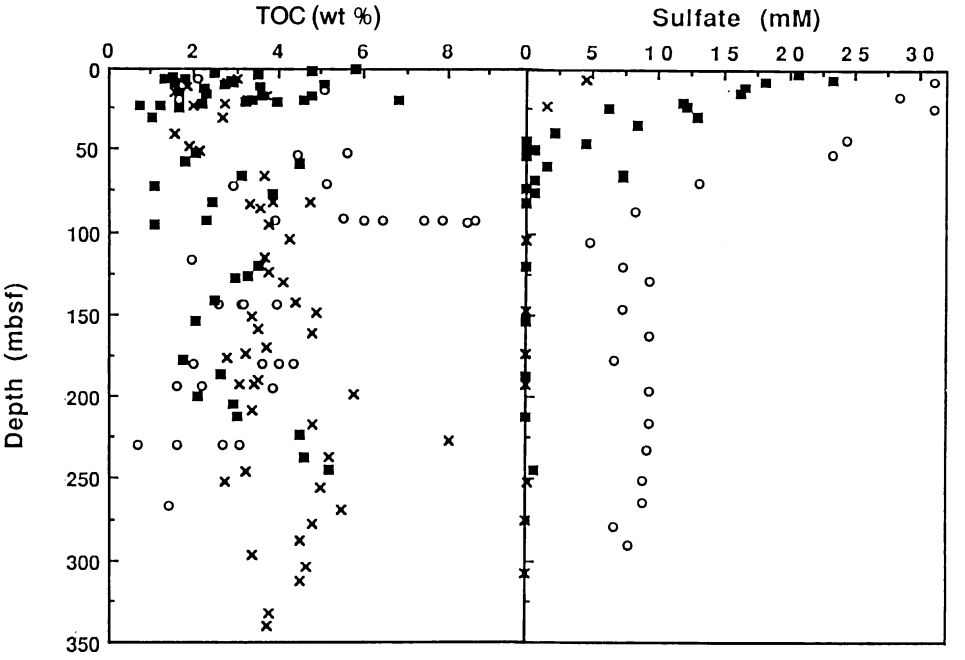

Fig. 1. TOC and dissolved sulfate profiles from the Benguela upwelling (o) and Oman (■) and Peru margins (x). Dissolved sulfate data for these sites were obtained from Gieskes and others (1984), Prell and others (1989), and Suess and others (1988), respectively.

but exhibit no consistent trends with depth at any of the sites. This is consistent with the assumption that pyrite forms mainly in near-surface sediments, as has been found in most marine sediments (Goldhaber and others, 1977), even though sulfate reduction and pyrite formation continue in deeper sediments. Average TRS concentrations are 0.87, 0.41, and 0.87 wt percent respectively, at the Benguela, Oman, and Peru sites.

We were not able to determine DOP on all samples due to limits on sample size. However, DOP was determined throughout most depth intervals. DOP exhibits remarkably similar values and depth trends at all three sites, with maxima occurring at approx 50 and 240 mbsf. Most DOP values fall between 0.2 and 0.6, and DOP never exceeded 0.73. We interpret these results as indicating that reactive iron was *probably* not limiting for pyrite formation in these sediments and will discuss our reasons in more detail below.

C/S ratios in the sediments also exhibit a wide scatter, with particularly high values occurring in the upper 100 mbsf of the samples from the Oman margin. The average C/S ratios (avg C concentration to avg S concentration) for sediments below the zone of apparent active sulfate

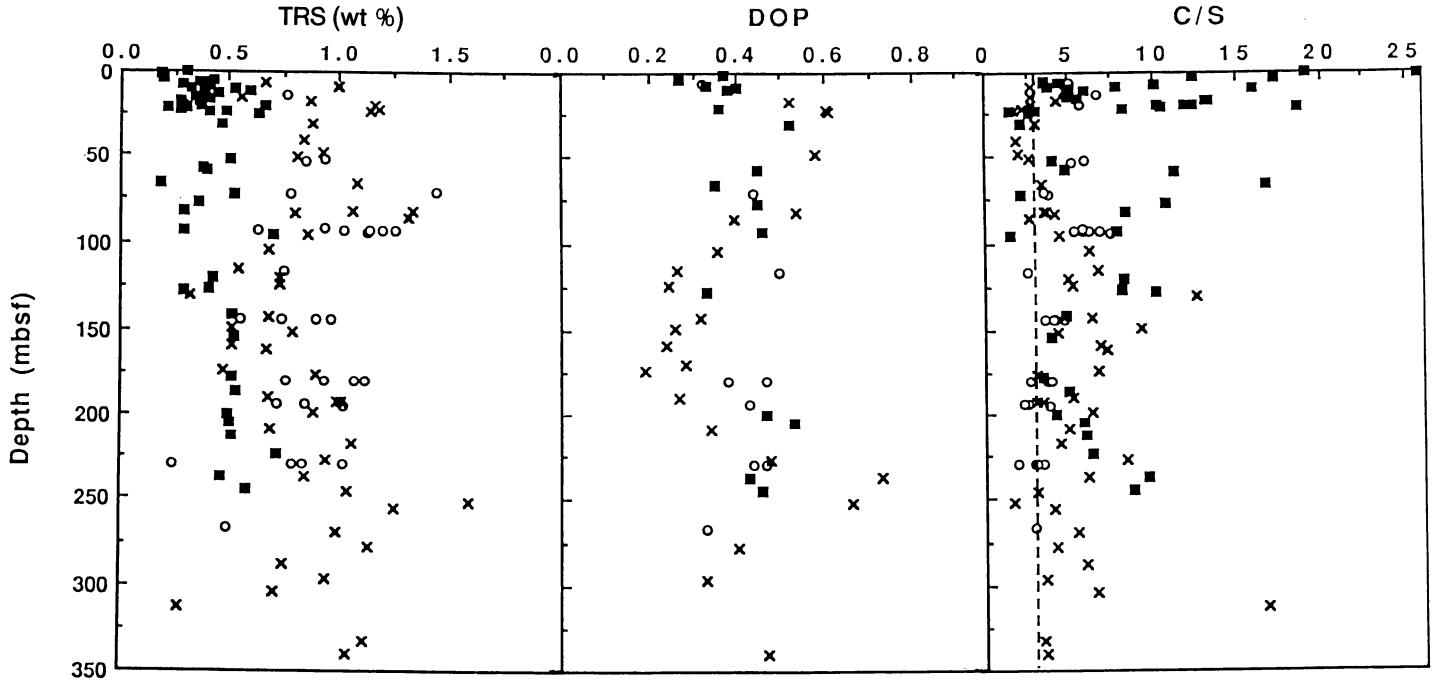

Fig. 2. TRS, DOP, and C/S profiles from the Benguela upwelling (o) and Oman (■) and Peru margins (x). The dashed line in the C/S profile is for the average normal marine C/S ratio of 2.8 ± 0.8.

reduction are 3.3 (±1.6 SD), 6.2 (±2.8), and 4.6 (±1.9) for the Benguela, Oman, and Peru sites, respectively. The average C/S ratios for the Benguela upwelling and Peru margin sites are about 1.2 and 1.6 times, respectively, that of normal marine sediments (2.8 ± 0.8), whereas the average C/S ratio at the Oman margin site is about 2.2 times higher than that generally observed in normal marine sediments. However, the large standard deviations in the data sets result in a significant statistical overlap of the data.

We do not note a strong relationship between TOC and TRS (fig. 3). However, if the sediments at the three sites are grouped according to organic carbon range (<2, 2–3, >3 wt percent) trends in average C/S ratios from beneath the zone of apparent active sulfate reduction are evident (fig. 4). Sediments at the Benguela and Oman sites with "normal" organic contents (<2 wt percent) have an average C/S ratio close to, but slightly below, that of the average for normal marine sediments (no sediments from the Peru margin sites fall into this category). Sediments with moderately high organic contents (2–3 wt percent) are close to the "normal" marine sediment average C/S ratio on the Peru margin and in the Benguela upwelling area and about twice average in sediments from the Oman margin. C/S ratios in highly organic-rich sediments (>3 wt percent organic carbon) from the Benguela upwelling area average about 30 percent higher (C/S = 3.8 ± 0.7) and from the Peru margin about 80 percent (C/S = 5.0 ± 1.9) higher than those of normal marine sediments. The highly organic-rich sediments from the Oman margin have a high average C/S ratio (8.0 ± 2.5) that approaches the range generally characteristic of freshwater environments. Even at these uncharacteristically high C/S ratios for marine sediments DOP is less than 0.4.

DISCUSSION

The results of this study indicate that carbon and reduced sulfur relationships in sediments from three sites in major centers of coastal upwelling exhibit significant differences to normal marine sediments and among themselves. Among the most important are differences in sulfate concentration gradients, average TOC concentrations, and C/S ratios. An examination of possible reasons for these differences is of importance in understanding variability in the carbon-sulfur system of hemipelagic sediments underlying upwelling regions and their general relationship with other types of marine sediments.

Numerous papers have emphasized the general correlation of organic matter accumulation and sulfate reduction rates and accumulation rates of TOC with the rate at which sediments accumulate (Heath, Moore, and Dauphin, 1977; Toth and Lerman, 1977; Berner 1978: Müller and Suess, 1979; Berner and Canfield, 1989; Canfield, 1989). It is, therefore, useful to view the results of this study in the context of these general observations.

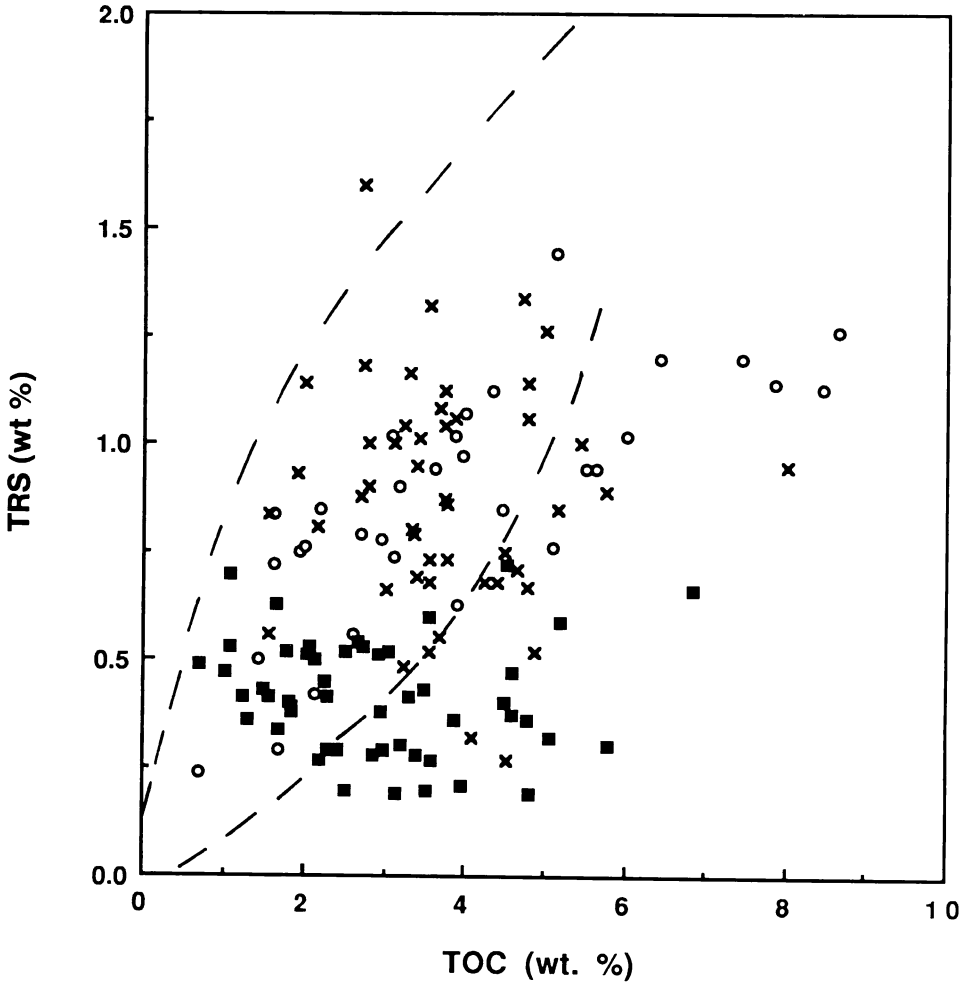

Fig. 3. A plot of TRS versus TOC for sediments from the Benguela upwelling (o) and Oman (■) and Peru margins (x). Dashed lines are data envelope for normal marine sediments of Berner and Raiswell (1983).

The logs of the C and S accumulation rates are plotted against the log of sediment accumulation rate for the results of this study in figure 5 (also see table 2), along with data from other sediments with similar accumulation rates from the summary of Berner and Canfield (1989). In this figure it can be observed that the TOC accumulation rates in the sediments from the Peru and Oman margins are similar to, but slightly higher than, those observed in other sediments and are distinctly higher

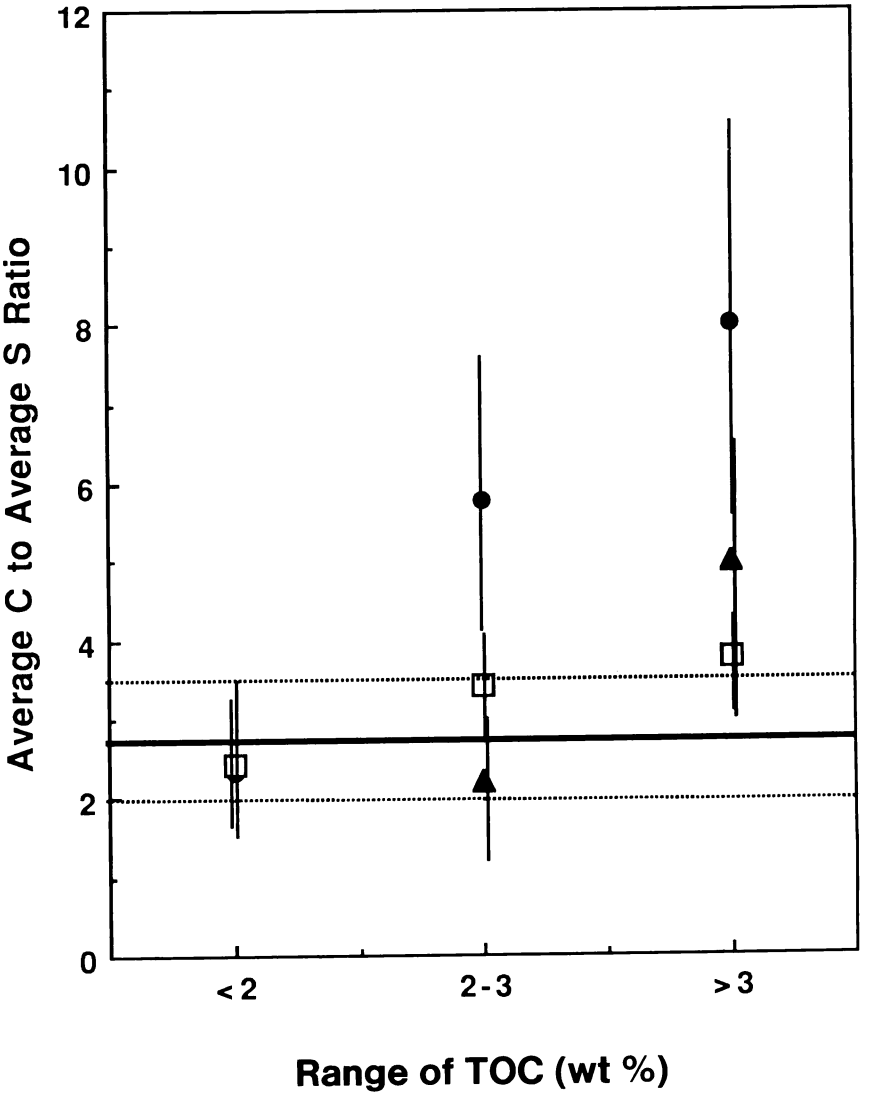

Fig. 4. A plot of the average C/S ratios for 3 different ranges in TOC concentration. Solid horizontal line is average C/S ratio for normal marine sediments, and dotted horizontal line is the standard deviation for these sediments. Solid vertical lines are one standard deviation for C/S ratios. (□) Benguela upwelling area, (▲) Peru margin, (●) Oman margin.

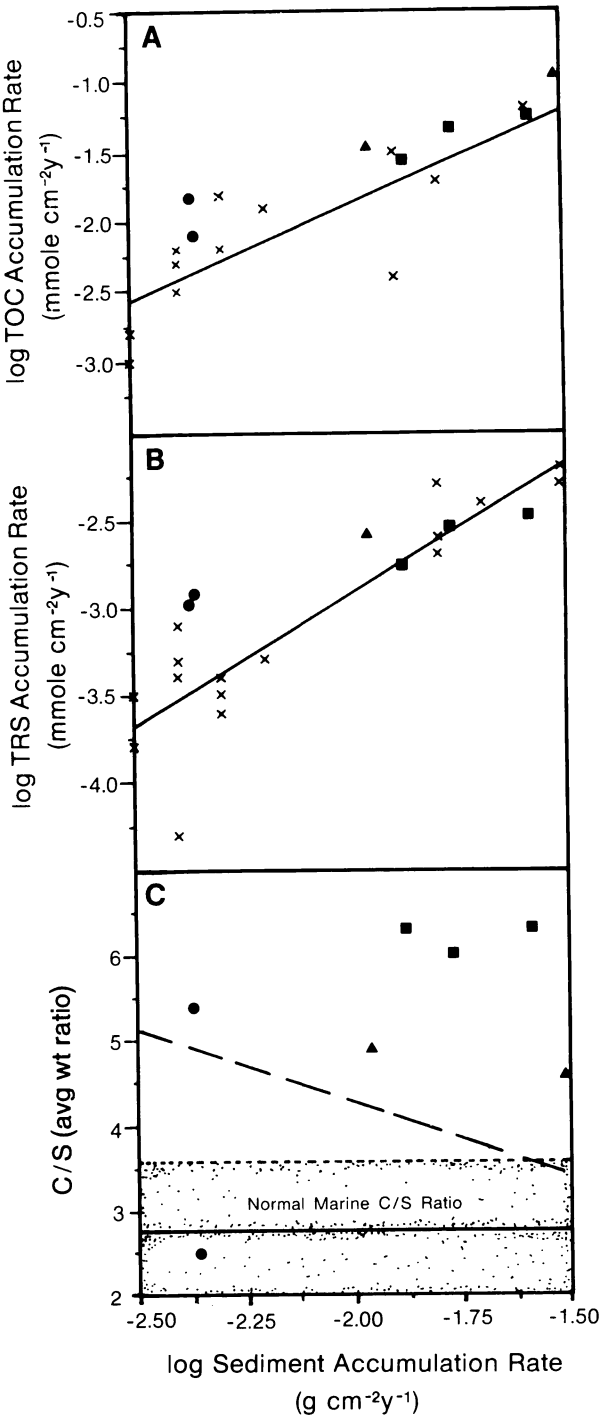

Fig. 5. The relationship of the log of the TOC accumulation rate (A), the log of the TRS accumulation rate (B), and the C/S ratio (C) to the log of the sediment accumulation rate. X's are data of Berner and Canfield (1989), and the solid line in A and B is the least squares fit to their data over the range of sediment accumulation rates presented. In C the dashed line represents the C/S ratio derived from least squares fits in A and B. The stipled area represents ±0.8 about the normal marine C/S ratio of 2.8. (●) Benguela upwelling area, (▲) Peru margin, (■) Oman margin. Only data from below the zone of apparent sulfate reduction are shown.

TABLE 2

Calculated accumulation rates

Site	Depth Interval (mbsf)	Age at Base (m.y.)	Sedimentation Rate (m/m.y.)	Sediment Accumulation Rate (g cm^{-2} y^{-1})	Ave. TOC Accumulation Rate (mmole cm^{-2} y^{-1})	Ave. TRS Accumulation Rate (mmole cm^{-2} y^{-1})	Ave. C/Ave.S (wt. ratio)
532 (Benguela)	0-19.4*	0.45	43	0.0032	0.0103	0.00058	6.6
	19.4-76.6*	1.70	46	0.0036	0.0093	0.00095	3.7
	76.6-94.2*	2.00	59	0.0036	0.0158	0.00120	4.9
	94.2-148.6	3.00	54	0.0042	0.0148	0.00105	5.3
	148.6-256.2	5.80	38	0.0044	0.0079	0.00117	2.5
723 (Oman)	0-35.6*	0.19	187	0.0173	0.0398	0.00204	7.3
	35.6-74.2	0.49	129	0.0133	0.0282	0.00170	6.2
	74.2-153.3	0.82	240	0.0255	0.0575	0.00339	6.3
	153.3-247.6	1.45	150	0.0171	0.0468	0.00288	6.1
688 (Peru)	0-46*	0.49	100	0.0073	0.0148	0.00200	2.8
	46-179	1.45	135	0.0109	0.0347	0.00263	4.9
	179-340	1.90	350	0.0306	0.1122	0.00912	4.6

*Zone of apparent active sulfate reduction.

in the sediments from the Benguela upwelling area. Because the sediments in this study come from beneath highly productive waters, it is not surprising that they have higher than normal TOC accumulations.

The TRS accumulation rates are about the same in the Oman margin sediments, slightly higher in the Peru margin sediments, and distinctly higher in the Benguela upwelling area sediments than those observed in the data of Berner and Canfield for sediments with similar accumulation rates. These differences in TRS accumulation rates roughly reflect those of the TOC accumulation rates.

In figure 5C, C/S ratios have also been plotted versus the log of the sediment accumulation rates. Included in this figure is a line for normal marine sediments derived from the least squares fits of the TOC and TRS data of Berner and Canfield (1989). This relation indicates that C/S ratios in normal marine sediments tend to deviate increasingly from the average C/S ratio for normal marine sediments with decreasing sediment accumulation rate. However, the C/S ratios from our three upwelling sites exhibit little relationship to sediment accumulation rates being, with one exception from Benguela, higher than would be expected.

In the results section, it was noted that the Oman and Peru margin sediments have higher than typical dissolved sulfate concentration gradients with complete sulfate reduction in the upper part of the sediment column, whereas the Benguela site had sediments with a lower than expected dissolved sulfate gradient and incomplete reduction of dissolved sulfate at depth. Westrich and Berner (1984) have demonstrated

that it is not simply the quantity but also the quality of organic matter that determines the pool of metabolizable TOC in sediments. Therefore, a reasonable hypothesis to explain the lower sulfate gradient in the Benguela upwelling sediments is that the organic matter in these sediments is less readily metabolized than that of the other sites. One possible explanation is that degradation is more advanced because the sedimentation rate is substantially lower in Benguela sediments, and organic matter is exposed to microbial attack for longer periods of time. Canfield (1989), for example, has discussed the strong relation between the efficiency of organic matter burial and sedimentation rate (see also Müller and Suess, 1979). Their results indicate that organic matter burial efficiency at the Benguela upwelling sites should be only about a quarter that of the other two sites due to its probable longer exposure to oxic respiration.

Although still somewhat controversial, the organic matter hydrogen index (HI; amount of hydrocarbons released during pyrolysis per gram of TOC) is gaining increased use as at least a qualitative measure of the extent of organic matter degradation (Pratt, Claypool, and King, 1986; Davis, Byers, and Dean, 1988; Dean and Arthur, 1989). Figure 6 summarizes the HI data for the organic matter from these sites. Although there is considerable scatter in the data, it is clear that the HI values from the Benguela upwelling sediments are generally lower than those from the other sites. The averages for Benguela upwelling, Oman and Peru margin sediments (with >2 wt percent TOC) are, respectively, 291, 367, and 381. The increasing trend in the HI of these sites matches their increasing sulfate concentration gradients. In the sediments from below 100 mbsf at the Benguela upwelling site, where the dissolved sulfate concentration does not decrease with increasing sediment depth, the average HI is only 238. In contrast, the Oman and Peru margin sites have HI's excess of 380 over a similar depth interval.

It is possible that the higher-than-normal organic carbon concentration at the Benguela site reflects a residue of extensively degraded organic carbon where the highly productive waters and relatively low clastic sedimentation rates cause the organic to non-organic component input ratios to be high. The coexistence of substantial dissolved sulfate concentrations with relatively high TOC concentrations for millions of years is certainly supportive of our hypothesis that organic matter is relatively low in potential metabolizability.

A major factor that can influence C/S ratios is the "openness" of a system. In shelf sediments where bioturbation and bioirrigation rates are generally high, in excess of 90 percent of the sulfide produced can be lost via transport and reoxidation (Goldhaber and others, 1977, Jørgensen, 1978). There is a general tendency for rates of biologically-mediated transport to decrease with increasing water depth (Berner, 1980). This is a result of both the tendency of deeper sediments to have lower organic matter concentrations and the influences of temperature and pressure on biological processes.

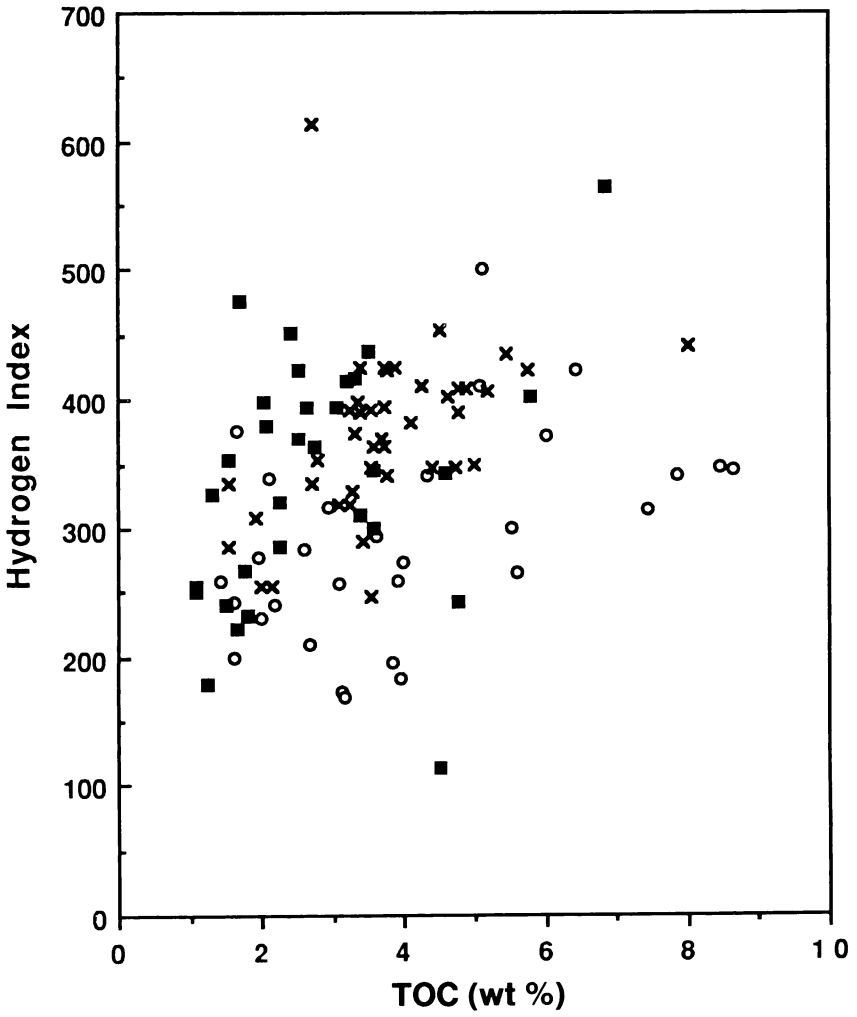

Fig. 6. The relationship between the hydrogen index and TOC in sediments from the Benguela upwelling (o) and Oman (■) and Peru margins (x). Data from Emeis, Morse, and Mays (1990) and Emeis and Morse (1990).

The organic-rich sediments from the Oman margin have anomalously high C/S ratios, even though they have the lowest average TOC concentration, and reactive iron does not appear to be limiting for pyrite formation. This site is the shallowest studied and may, therefore, have the highest rates of bioturbation and bioirrigation. This could possibly

result in the loss of a greater fraction of the reduced sulfur, leading to higher C/S ratios. This explanation for the observed intersite differences in C/S ratios is necessarily highly speculative but could be tested by investigation of processes near the interfacial region of sediments in the different areas studied. It is obvious from a plot (fig. 5) of TRS and TOC accumulation rates, however, that upwelling sediments deviate systematically from other marine sediments.

CONCLUSIONS

The hemipelagic sediments underlying productive oceanic regions from the Benguela upwelling area and Oman and Peru margins have highly variable organic carbon and reduced sulfur concentrations. C/S ratios for sediments containing less than 2 wt percent TOC are close to the average for normal marine sediments. C/S ratios increase with increasing TOC. Sediments with greater than 3 wt percent TOC average about one and a half times that of normal marine sediments for the Benguela upwelling area and Peru margin sediments, whereas sediments with similar TOC concentrations from the Oman margin have C/S ratios approaching those characteristic of freshwater sediments.

The low degree of pyritization in the sediments under investigation indicates that iron is probably not limiting pyrite formation at any site. Rates of sulfate reduction appear to be related more to the quality of the organic matter than to its concentration or water depth. We hypothesize that both the quality of the organic matter that is buried and the openness of the system to exchange of reduced sulfur and oxidants strongly influence C/S ratios in these hemipelagic, organic-rich sediments.

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$^{40}Ar/^{39}Ar$ POLYOROGENIC MINERAL AGE RECORD WITHIN THE SOUTHERN MAURITANIDE OROGEN (M'BOUT-BAKEL REGION) WEST AFRICA

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ABSTRACT. The southern Mauritanide orogen exposed between M'Bout and Bakel is characterized by several internally imbricated, polydeformed, and variably metamorphosed infrastructural allochthons. These include: (1) a calc-alkaline igneous complex (Guidimakha and Débi intrusive units together with eastern portions of the metavolcanic-sedimentary M'Bout Unit); (2) members of a fragmented ophiolitic succession (Hamdallaye and Gabout Units); and (3) continental-margin rift sequences (Diala-Bouanzé Series) which include amphibolite (low-Ti continental-tholeiite dike protoliths), mylonitic quartzite, and micaceous schist. Several structural units with uncertain tectonostratigraphic relations are also exposed in the area. These include low-grade, metasedimentary rocks of the Bakel Unit and western sectors of the M'Bout Unit (low-grade, calc-alkaline metavolcanic and associated metasedimentary sequences). Both tectonic elements may represent suprastructural allochthons structurally overlying infrastructural units.

$^{40}Ar/^{39}Ar$ incremental-release ages recorded by hornblende within undeformed granodiorite of the Guidimakha Complex suggest postmagmatic cooling through appropriate argon closure temperatues at approx 670 Ma. $^{40}Ar/^{39}Ar$ ages recorded by muscovite within lithologic elements of both the Guidimakha Complex and the Diala-Bouanzé Series suggest initial regional metamorphism (associated with Pan-African I orogenesis) was following by cooling through muscovite argon closure temperatures between approx 600 and 620 Ma. Slight rejuvenation of muscovite argon systems occurred locally between approx 325 and 350 Ma.

Muscovite and whole-rock slate/phyllite argon systems within metavolcanic and metavolcaniclastic components of the infrastructural calc-alkaline igneous complex (easternmost sectors of the M'Bout Series) record $^{40}Ar/^{39}Ar$ plateau age of approx 300 to 320 Ma. Muscovite and whole-rock slate/phyllite argon systems within westernmost portions of the study area (western portions of the M'Bout Series) record $^{40}Ar/^{39}Ar$ plateau ages of approx 267 to 312 Ma.

All foreland units within the M'Bout-Bakel area were affected by post-Emsian folding. Effects of this tectonic activity are widespread throughout the parautochthon and western metamorphic sequences. These effects include emplacement of suprastructural (?) allochthons and local reactivation of older thrust faults within infrastructural units.

The early tectonic history recorded within the southern Mauritanide orogen appears to have been related to restricted rifting of a western crustal block from the West African craton and formation of a limited, intervening oceanic domain. Subsequent closure resulted in

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