

Sulfate reduction and oxic respiration in marine sediments: implications for organic carbon preservation in euxinic environments

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Abstract—Compilations have been made of sulfate reduction rates and oxic respiration rates over the entire range of marine sedimentation rates, and sedimentary environments, including several euxinic sites. These data show, consistent with the findings of JØRGENSEN (1982, *Nature*, **296**, 643–645), that sulfate reduction and oxic respiration oxidize equal amounts of organic carbon in nearshore sediments. As sedimentation rates decrease, oxic respiration becomes progressively more important, and in deep-sea sediments 100–1000 times more organic carbon is oxidized by oxic respiration than by sulfate reduction. By contrast, nearly as much organic carbon is oxidized by sulfate reduction in euxinic sediments as is oxidized by the sum of sulfate reduction and oxic respiration in normal marine sediments of similar deposition rate.

This observation appears at odds with the enhanced preservation of organic carbon observed in euxinic sediments. However, only small reductions in (depth-integrated) organic carbon decomposition rates (compared to normal marine) are required to give both high organic carbon concentrations and enhanced carbon preservation in euxinic sediments. Lower rates of organic carbon decomposition (if only by subtle amounts) are explained by the diminished ability of anaerobic bacteria to oxidize the full suite of sedimentary organic compounds.

INTRODUCTION

IN marine sediments, various populations of microorganisms compete for sedimenting organic matter, with the energy derived from the oxidation of organic carbon used for growth and maintenance. The success of organisms in competing for the organic substrate is dictated, in part, by the availability of the oxidant they best use in oxidizing the organic matter. Also important is the redox state of the sediments, which determines whether a given organic matter oxidation reaction can occur. This study will focus on the rates of the two most important reactions responsible for organic matter oxidation: sulfate reduction and oxygen respiration.

Data have been compiled from the literature for sulfate reduction rates and sediment oxygen uptake rates over a wide range of marine sedimentation rates. Included in this compilation are sulfate reduction rates calculated from about 200 DSDP pore water sulfate profiles. Also included are sulfate reduction rate data from several euxinic sediments (sediments overlain by sulfide-rich bottom water; e.g. the Black Sea). Taken together, the data allow comparison of the degree to which sulfate reduction and oxic respiration oxidize organic carbon over the whole range of marine sedimentary environments. Also, and importantly, the data can be used to compare total rates of organic carbon oxidation in sediments overlain by both well-oxygenated water and sulfide-rich

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water. Such a comparison allows the effects of bottom water anoxia on organic carbon preservation to be explored.

METHODS

Several methods have been used to determine sulfate reduction rates in marine sediments. These include modeling of pore water sulfate profiles (BERNER, 1964; GOLDBABER *et al.*, 1977; FILIPEK and OWEN, 1980; CHANTON *et al.*, 1987), estimating the burial rate of reduced sulfur (KAPLAN *et al.*, 1963), "tube" or "jar" incubations (ALLER, 1977; GOLDBABER *et al.*, 1977; CRILL and MARTENS, 1987) and radiotracer measurements using $^{35}\text{S-SO}_4$ (e.g. SOROKIN, 1962; JØRGENSEN, 1977; HINES *et al.*, 1982; WESTRICH, 1983; AHMED *et al.*, 1984). Of these techniques, the radiotracer method generally is considered the most reliable (JØRGENSEN, 1978) and is the one most commonly used at present. From the studies of several investigators (JØRGENSEN, 1978; WESTRICH, 1983; CHANTON *et al.*, 1987; CRILL and MARTENS, 1987) it is clear that if carefully applied, the radiotracer technique will give a reasonably accurate measure of sulfate reduction rates. There are, however, a few caveats in interpreting data obtained by this method.

First, in many cases sulfate reduction rates are not seasonally averaged, but measured only at a single time during the year. Because seasonal changes in sediment temperature are not accounted for (JØRGENSEN, 1977; WESTRICH, 1983), sulfate reduction rates may be high or low (compared to a seasonal average) depending on the time of year the rates were measured. Second, any radiolabeled sulfide that rapidly forms into pyrite (HOWARTH, 1979; HOWARTH and JØRGENSEN, 1984) is generally not accounted for with the sulfide distillation techniques commonly in use. The importance of rapid pyrite formation in sequestering radiolabeled sulfide is still not clear, but from the results of WESTRICH (1983) and HOWARTH and JØRGENSEN (1984) rates, in some cases, may be underestimated by as much as 10–20%.

For the data presented here, rates of sulfate reduction are expressed as depth-integrated rates, with units of $\text{mmol cm}^{-2} \text{y}^{-1}$:

$$\text{rate} = \phi \int_0^{\infty} R(x) dx, \quad (1)$$

where ϕ is the sediment porosity, and $R(x)$ is the depth distribution of sulfate reduction expressed as mmol cm^{-3} (of pore fluid) y^{-1} . This gives the total amount of sulfate reduced per year, within a given area of sediment. These are useful units for inter-site comparison and for comparing integrated sulfate reduction rates to other important sediment properties such as organic carbon flux.

For pelagic sediments, rates of sulfate reduction have been determined using DSDP pore water sulfate data. In using this data, integrated rates of sulfate reduction are assumed to equal the net flux of dissolved sulfate into the sediment, as reflected in pore water sulfate profiles (an explanation of the calculation procedure is given in the Appendix). This implies that the sulfate profiles are at a steady state. The use of this method to obtain sulfate reduction rates in deep-sea sediments is possible because, as noted by JØRGENSEN (1982), sulfate reduction does not begin until relatively deep in the sediment column; at a depth below where pore water gradients can be affected by bioturbation. In fact, the obscuring of pore water profiles by bioturbation and irrigation makes diffusion modelling of sulfate reduction in nearshore sediments impractical in most cases. For a few euxinic sites (Cariaco Trench and Baltic Sea) sulfate reduction

rates have also been obtained from pore water modelling. These sites will not be affected by bioturbation.

Oxygen uptake data compiled from the literature have been obtained using several different methods. Most rate measurements have been made using bell-jar experiments of the type described by PAMATMAT and BANSE (1969) and SMITH and HINGA (1983). Oxygen uptake rates obtained in this manner are a direct measure of benthic oxygen respiration if major reduced species, of which sulfide is probably the most important, are not oxidized by oxygen (JØRGENSEN, 1977, 1982). Oxygen uptake by sulfide is not a major concern in pelagic sediments, and for the continental margin data compiled here, the effects have been corrected for [see JØRGENSEN (1977, 1982) for a complete discussion].

In a few cases (e.g. MURRAY and GRUNDMANIS, 1980; REIMERS *et al.*, 1984; EMERSON *et al.*, 1985), oxygen uptake rates are calculated from sediment oxygen profiles. In the studies of BENDER and HEGGIE (1984) and EMERSON *et al.* (1985), rates of oxygen consumption have been calculated from modelling pore water nitrate profiles and from the sediment distributions of solid phase organic carbon. In the study of SILVERBERG *et al.* (1987) oxygen uptake has been estimated from a detailed carbon budget which includes measured (by sediment trap) carbon fluxes to the sediment, coupled with carbon oxidation by sulfate reduction and carbon burial rates.

All rate measurements are compared to sediment accumulation fluxes expressed as $\text{g cm}^{-2} \text{y}^{-1}$. At a sediment porosity of 60%, sedimentation rates in these units are identical to rates expressed in the more familiar units of cm y^{-1} . At a porosity of 80%, $1 \text{ g cm}^{-2} \text{y}^{-1}$ is equivalent to 2 cm y^{-1} . For the continental margin sites, sedimentation rates are usually determined from the depth distributions of natural (^{14}C , ^{210}Pb) or anthropogenic (^{137}Cs) radionuclides. For the DSDP sites and the Black Sea, sediment accumulation rates are based on calibrated biostratigraphy. In a few cases, sedimentation rates have been obtained from particle accumulation rates measured in sediment trap experiments. Some justification for this approach is found in the results of HEATH (1983) and SILVERBERG *et al.* (1986), who report excellent agreement between the accumulation rates of detrital particles measured from sediment traps and the sediment distribution of radioisotopes. It should be cautioned though, that in other studies the agreement is not as good (e.g. HEGGIE *et al.*, 1987).

RESULTS

The complete set of sulfate reduction rates is presented (vs sediment accumulation rate) in Fig. 1, with the data from radiolabeled $^{35}\text{S-SO}_4$ measurements summarized in Table 1. Due to space limitations, data from sulfate modelling (and the associated references) could not be included in the text, but are available from the author on request. It should be mentioned that in plotting the DSDP data, only sites with modern sediment accumulation, and free of major hiatus horizons have been used. For the data in Fig. 1, normal marine sediments have been defined as those permanently overlain by oxygenated bottom water, and euxinic sediments are those permanently overlain by sulfide-rich bottom water. Some sediments, such as those in Saanich Inlet, British Columbia, Skan Bay, Alaska, some deep basins in the Baltic Sea, and the "Black Hole" in Long Island Sound, are intermittently normal marine and euxinic. These sediment sites have been termed "semi-euxinic" and have been designated separately from the other two sediment types.

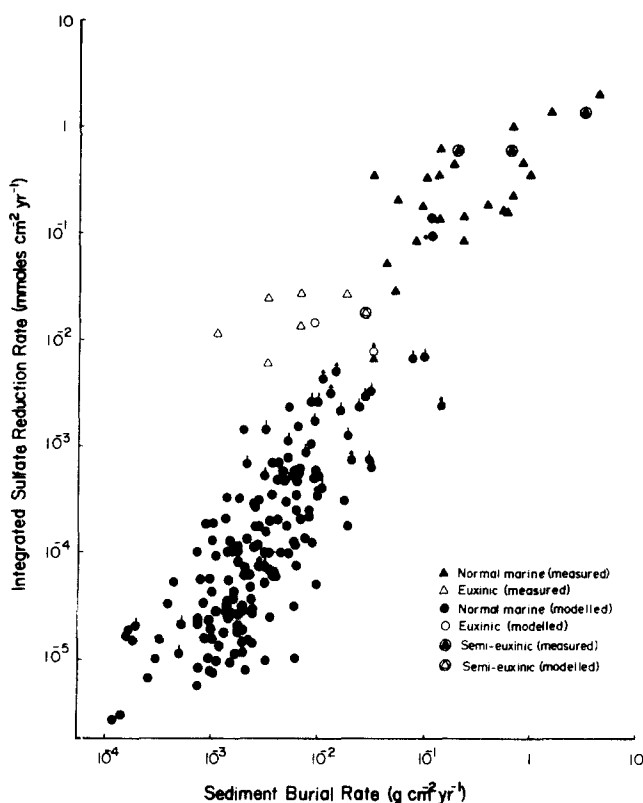


Fig. 1. Rates of sulfate reduction are plotted as a function of sediment burial rate. In some instances, for modelled rates, sulfate gradients are not well defined and a small bar has been added to the point, showing that the value may be higher or lower than that used (with the bar giving the most probable direction of error). Also, a bar has been used for sites where sulphate reduction rates are high (steep gradients) and some sulfate reduction may have occurred within the bioturbation zone. An arrow designates data points where it is certain that sulfate gradients (or sedimentation rate data) are giving only minimum or maximum sulfate reduction rates (or sedimentation rates).

Oxygen consumption rates are presented in Fig. 2 and results tabulated in Table 2. Unfortunately, at many locations where oxygen uptake has been measured, sedimentation rates are unknown, thus precluding the use of many collected data. In some cases, sedimentation rates are known for sediments near to the locations where oxygen uptake measurements were made, and these rates have been used. Though not ideal, the use of "approximate" sedimentation rates for some sites likely does not affect the overall trends in Fig. 2.

DISCUSSION

Sulphate reduction and oxic respiration rates vs sediment deposition rate

Focusing on the "normal marine" data points in Fig. 1, sulfate reduction rates are positively correlated with sediment deposition rate. Such a relationship is not surprising as TOTH and LERMAN (1977) found a positive correlation between the reaction rate

Table 1. Measured sulfate reduction rates and sediment burial rates

Location	Sediment burial rate (g cm ⁻² y ⁻¹)	Sulf. red. rate (mmol cm ⁻² y ⁻¹)	Data references
North Carolina coast			
Cape Lookout Bight	4.13	1.98	1,2
Danish coast			
Limfjorden	0.125	0.35	3
Mississippi Delta			
Sta. 18	1.50	1.30	4
Sta. 19	0.80	0.45	5,4
Long Island Sound			
FOAM	0.088	0.17	6,7
Sachem	0.94	0.36	8,7
Black Hole*	3.13	1.30	7
NWC	0.053	0.21	9,7
S.W. Brit. Columbia			
Saanich Inlet*	0.20	0.61	10,11,12
Danish coast			
Sta. C	0.18	0.45	13
Sta. B	0.10	0.33	13
Sta. A	0.031	0.34	13
Washington coast			
Sta. 2	0.55	0.16	14,15
Sta. 3	0.55	0.16	14,15
Great Bay N.H.			
JEL	0.13	0.60	16
Squam	0.13	0.13	16
Alaska			
Skan Bay*	0.63	0.60	17
Peru coast			
Sta. C3,120	0.63	0.18	18,19
Sta. C1,60	0.63	0.99	18,19
Sta. C5,245	0.38	0.22	18,19
Gulf St. Lawrence			
Sta. 17	0.029	0.0062	20
Sta. 23	0.077	0.047	20
Saguenay Fjord			
Sta. S1	0.22	0.084	20
Black Sea (normal marine)			
Sta. 559	0.219	0.141	21
Sta. 598	0.046	0.050	21
Sta. 568	0.048	0.057	21
Black Sea (euxinic)			
Sta. 580	0.017	0.027	21
Sta. 601	0.0031	0.0062	21
Sta. 571	0.0011	0.0118	21
Sta. 545	0.0062	0.0129	21
Sta. 584	0.0031	0.0251	21
Sta. 582	0.0062	0.0278	22,21

* "Semi-euxinic" sites.

1, CHANTON *et al.* (1983); 2, CRILL and MARTENS (1987); 3, JØRGENSEN (1977); 4, this study; 5, SHOKES (1976); 6, KRISHNASWAMI *et al.* (1984); 7, WESTRICH (1983); KROM and BENNETT (1985); 9, BENOIT *et al.* (1979); 10, MURRAY *et al.* (1978); 11, AHMED *et al.* (1984); 12, DEVOL *et al.* (1984); 13, IVERSON and JØRGENSEN (1985); 14, CHRISTENSEN *et al.* (1984); 15, NITTRouer *et al.* (1979); 16, HINES and JONES (1985); 17, ALPERIN and REEBURGH (1985); 18, HENRICHs and FARRINGTON (1984); 19, ROWE and HOWARTH (1985); 20, EDENBORN *et al.* (1987); 21, VAYNSHTEYN *et al.* (1985); 22, ROSS *et al.* (1970).

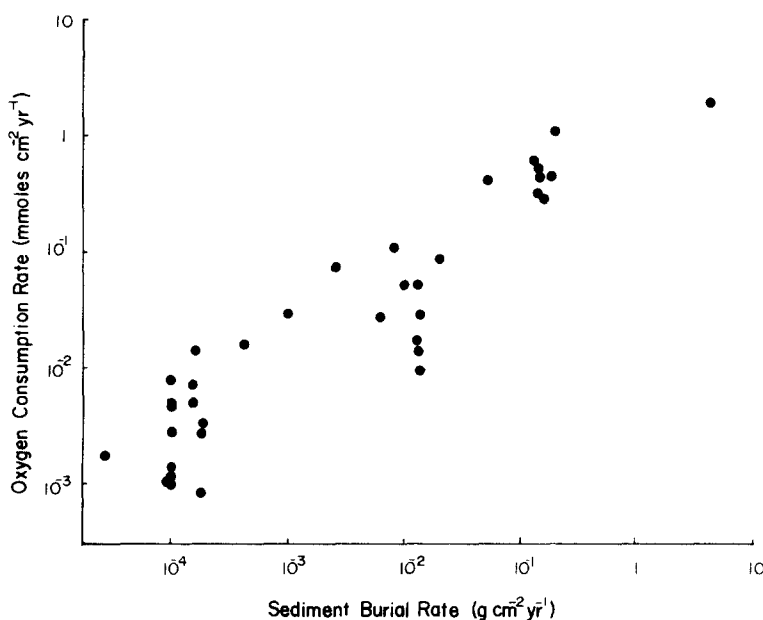


Fig. 2. Rates of oxygen consumption in marine sediments plotted as a function of sediment burial rate. For a list of data see Table 2.

constant (k) for sulfate reduction and sedimentation rate, and BERNER (1978) found that the steepness of the sulfate gradient in marine sediments is proportional to the rate of sediment deposition. Also, JØRGENSEN (1982, 1983) documented that sulfate reduction rates decrease with increasing water depth, which should on average be inversely correlated with the rate of sedimentation.

Figure 1 shows rates of sulfate reduction to be proportional to sediment deposition rate raised to roughly the 5/3 power; TOTH and LERMAN (1977) found the rate constant (k) for sulfate reduction to vary as sedimentation rate squared. These apparently similar results, however, are not quite comparable. Importantly, rates presented here are depth-integrated rates, whereas the rate constant k reflects the rate of sulfate reduction per unit volume of sediment. To be comparable, k values would need to be multiplied by the concentration of reactive organic carbon, and this product integrated over the depth of sulfate reduction.

The sulfate reduction rates calculated here are, in fact, more comparable to (though not exactly the same as) the flux of sulfate across the sediment-water interface as determined by TOTH and LERMAN (1977, their Fig. 9), which was found to vary linearly with sedimentation rate. The difference between the trend of TOTH and LERMAN (1977) and the one in Fig. 1 is attributed to the larger data set used here and to the use of measured and not modelled sulfate reduction rates for nearshore environments. As already mentioned, sulfate gradients in nearshore sediments may be severely affected by bioturbation and irrigation.

Sulfate reduction rates in euxinic sediments are considerably higher than those for normal marine sediments of similar deposition rate. The most likely explanation is that the organic matter settling onto euxinic sediments is decomposed mainly by sulfate-

Table 2. Oxygen consumption and sediment burial rates

Location	Sediment burial rate (g cm ⁻² y ⁻¹)	Oxygen cons. rate × 10 ⁻³ (mmol cm ⁻² y ⁻¹)	Data references
Baltic Sea			
Stas 17-23	1.6 × 10 ⁻¹	290	1
Stas 23-17	1.5 × 10 ⁻¹	450	1
Stas 27-29	1.5 × 10 ⁻¹	505	1
Central Pacific			
MANOP M	4.0 × 10 ⁻⁴	15.9,11.8	2,3,4
MANOP H	1.5 × 10 ⁻⁴	14.0,11.9	2,3,4
MANOP C	9.6 × 10 ⁻⁴	27.0,20.0	2,3,4
MANOP S	2.4 × 10 ⁻⁴	8.2,1.8	2,3,4
North Carolina coast			
Cape Lookout Bight	4.13	2050	5,6
Northwest Atlantic			
Sta. 77DE	1.0 × 10 ⁻²	51	7,8
Sta. DWD	1.4 × 10 ⁻²	18	7,8
Sta. ADS	1.3 × 10 ⁻²	13.7	9,8
Sta. HH	1.3 × 10 ⁻²	17.1	9,8
Sta. DOS-2	1.3 × 10 ⁻²	9.0	9,8
Sta. NN	1.7 × 10 ⁻⁴	2.8	10,8
Sta. MM	1.7 × 10 ⁻⁴	0.8	18,8
Straits of Florida			
Sta. 77FG	8.0 × 10 ⁻³	116	7,8
Gulf of Mexico			
Sta. 76B	6.0 × 10 ⁻³	27	11,8
Northern Pacific			
Sta. SCB	2.0 × 10 ⁻²	89	12,13,14
Sta. C	1.0 × 10 ⁻²	80	15,14
Sta. G	1.5 × 10 ⁻⁴	7.3	16,14
Sta. CNP	1.5 × 10 ⁻⁴	4.7	16,14
Danish coast			
Limfjorden	1.3 × 10 ⁻¹	599	17
California borderland			
San Diego Trough	1.3 × 10 ⁻²	51	12,18
San Nicolis Basin	1.3 × 10 ⁻²	26	12,19
Long Island Sound			
NWC	5.3 × 10 ⁻²	400	20,21,22
Northwest Washington			
Puget Sound	1.2 × 10 ⁻¹	296	23,24
Cape Cod			
Buzzards Bay	1.9 × 10 ⁻¹	1100	25,26
Laurentian Trough	1.7 × 10 ⁻¹	422	27
Western Pacific			
Sta. A	1.0 × 10 ⁻⁴	1.2	28,16
Sta. E	1.0 × 10 ⁻⁴	4.7	28,16
Sta. F	1.0 × 10 ⁻⁴	0.95	28,16
Sta. G	1.0 × 10 ⁻⁴	0.88	28,16
Sta. H	1.0 × 10 ⁻⁴	2.7	28,16
Sta. I	1.0 × 10 ⁻⁴	4.5	28,16
Sta. J	1.0 × 10 ⁻⁴	4.9	28,16
Sta. K	1.0 × 10 ⁻⁴	7.9	28,16
Sta. P	1.0 × 10 ⁻⁴	1.4	28,16

1, BALZER *et al.* (1986); 2, combined carbon burial rate data from BENDER and HEGGIE (1984) with carbon concentrations from EMERSON *et al.* (1985); 3, EMERSON *et al.* (1985); 4, BENDER and HEGGIE (1984); 5, CHANTON *et al.* (1983); 6, CHANTON *et al.* (1987); 7, HINGA *et al.* (1979) and ROWE and GARDNER (1979); 8, SMITH and HINGA (1983); 9, proximity to DSDP site 106; 10, proximity to DSDP site 387; 11, proximity to DSDP site 96; 12, EMERY (1960); 13, SMITH *et al.* (1987); 14, proximity to DSDP site 468; 15, proximity to DSDP site 468; 16, KU *et al.* (1968); JØRGENSEN (1977); 18, SMITH (1974); 19, BERELSON *et al.* (1987); 20, BENOIT *et al.* (1979); 21, CAREY (1967); 22, WESTRICH (1983); 23, CARPENTER *et al.* (1985); 24, PAMATMAT and BANSE (1969), average of seven sites in region of site 52 of CARPENTER *et al.* (1985); 25, FARRINGTON *et al.* (1977); 26, SMITH and TEAL (1973), take total oxygen consumption and divide by two after JØRGENSEN (1977); 27, SILVERBERG *et al.* (1987); 28, MURRAY and GRUNDMANIS (1980); 29, KU *et al.* (1968).

reducing bacteria. This is in contrast to pelagic normal marine sediments, where oxic decomposition during sedimentation and burial results in the removal of labile organic matter. Hence, only the more refractory (as well as a smaller concentration of) organic carbon becomes available for sulfate reduction at depth (BENDER and HEGGIE, 1984; HENRICHS and REEBURGH, 1987), leading to reduced rates.

From Fig. 2, oxic respiration rates vary with sediment deposition rate raised to approximately the $2/3$ power. This relationship shows that at low sedimentation rates, oxygen is responsible for proportionally more organic carbon decomposition (relative to sediment deposition rate) than at high sedimentation rates. This could reflect a higher organic vs total particle flux to slowly depositing deep-sea sediments, or result from the more efficient decomposition of organic matter at slower sediment deposition rates (HENRICHS and REEBURGH, 1987). Another possibility (to be considered in more detail shortly) is that at low sedimentation rates, a higher proportion of the total organic matter is oxidized by oxygen-respiring bacteria, when compared to higher sedimentation rates.

A further observation is that both sulfate reduction and oxic decomposition rates may vary by an order of magnitude at a given rate of sediment deposition. Much of this variability may be real and reflect natural variability in the flux of metabolizable organic carbon at a given rate of sediment deposition. However, some of the variability could be due to poorly documented sedimentation rates, particularly for the oxic decomposition rates.

Oxic vs anoxic organic matter degradation

In order to compare directly sulfate reduction and oxic respiration rates, the data from Figs 1 and 2 are combined in Fig. 3, with both data sets having been recalculated to rates of organic carbon oxidation (depth-integrated as for the sulfate reduction and oxic respiration rate data). For sedimentation rates above about $0.1 \text{ g cm}^{-2} \text{ y}^{-1}$ ($\sim 0.1 \text{ cm y}^{-1}$) sulfate reduction and oxic respiration are equally important in oxidizing organic matter (Fig. 3). This is consistent with the results of JØRGENSEN (1977, 1982), who reported similar findings for shallow water stations off the coast of Denmark. The present comparison shows that this relationship holds for sediments collected from all over the world.

Between sediment accumulation rates of 0.01 and $0.1 \text{ cm}^{-2} \text{ y}^{-1}$ (~ 0.01 – 0.1 cm y^{-1}) sulfate reduction becomes less important in oxidizing organic carbon. Consistent with these findings, JØRGENSEN (1982) found oxic respiration to dominate over sulfate reduction in progressing from shallow to deeper water continental shelf sediments. At sedimentation rates below about $10^{-3} \text{ g cm}^{-2} \text{ y}^{-1}$ ($\sim 1 \text{ cm } 1000 \text{ y}^{-1}$), oxic respiration decomposes about 100–1000 times more organic carbon than sulfate reduction. In line with this, BENDER and HEGGIE (1984) showed that an insignificant amount of organic carbon is oxidized by sulfate reduction at MANOP site M and in pelagic sediment from the eastern equatorial Atlantic Ocean.

Sulfate reduction in nearshore sediments competes with oxic decomposition because oxic decomposition of organic matter takes place only very near the sediment surface (REVSBECH *et al.*, 1980; SØRENSEN and JØRGENSEN, 1987), and rapid sediment burial ensures that labile (easily metabolizable) organic matter will be available for sulfate reduction. As sedimentation rate decreases, organic matter spends progressively more time near the sediment–water interface, the zone of oxic decomposition. This results in

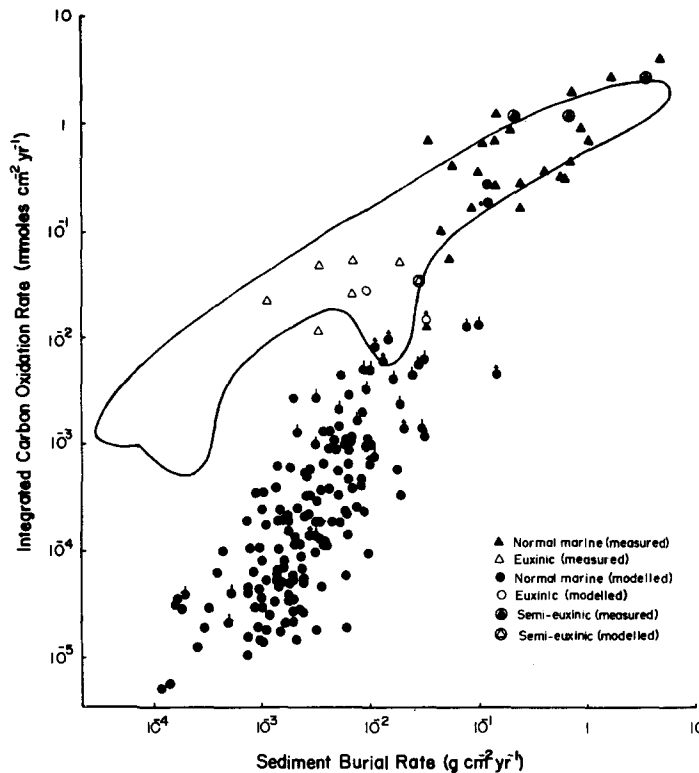


Fig. 3. Data from Figs 1 and 2 have been converted to depth-integrated rates of organic carbon oxidation. Rates of organic carbon oxidation by sulfate reduction have been plotted as individual points. Rates of organic carbon oxidation by oxic respiration are given as the outlined area (from Fig. 2) and are superimposed over the organic carbon oxidation rates by sulfate reduction.

less organic matter (both in concentration and reactivity; see WESTRICH, 1983) for the sulfate-reducing bacteria. The situation is somewhat more complicated because in continental margin sediments bioturbation may enhance the transfer of organic matter into the zone of sulfate reduction, in effect increasing the rate of sediment advection within the upper sediment layers (BERNER and WESTRICH, 1985; BOUDREAU, 1986; RICE, 1986). It may be that enhanced sediment advection by bioturbation allows sulfate reduction to keep pace with oxic respiration over a sedimentation rate range of nearly two orders of magnitude (Fig. 3). This contrasts with deep-sea sediments where sulfate reduction begins well below a reasonable depth for bioturbation (JØRGENSEN, 1982). In fact, bioturbation in deep-sea sediments may retard organic carbon decomposition (EMERSON *et al.*, 1985). In any event, at sedimentation rates less than about 0.01–0.1 $\text{g cm}^{-2} \text{y}^{-1}$ metabolizable organic matter becomes progressively less available to sulfate-reducing bacteria.

As a last consideration, organic carbon oxidation rates by sulfate reduction in euxinic and semi-euxinic sediments (Fig. 3) are not significantly different from rates of organic carbon oxidation by oxic respiration in normal marine sediments of similar deposition rate. However, it is more informative to compare total organic carbon oxidation rates. For euxinic sediments, total oxidation rates are very nearly described by rates of sulfate

reduction (methane fermentation is likely much less important; see HENRICHS and REEBURGH, 1987). For semi-euxinic sediments both oxic respiration and sulfate reduction will decompose organic carbon. However, sulfate reduction may be the most important oxidation pathway because these sediments are overlain by sulfide-rich water in the summer months, when the most vigorous consumption of sedimentary organic carbon occurs (WESTRICH, 1983). An exception is the Gotland Deep in the Baltic Sea whose water-column oxic/anoxic cycles alternate on a time scale of years (GRASSHOFF, 1976). For the semi-euxinic sediments, total rates of organic carbon decomposition are calculated from sulfate reduction rates only, recognizing that these are minimum values.

In normal marine sediments, oxic respiration, nitrate reduction, iron and manganese reduction, methane production and sulfate reduction all contribute to organic carbon oxidation. Despite these numerous oxidation pathways, sulfate reduction and oxic respiration are responsible for most of the organic carbon oxidation in all normal marine sedimentary environments (BENDER and HEGGIE, 1984; HENRICHS and REEBURGH, 1987). So, the sum of oxic respiration and sulfate reduction is considered a good measure of total organic carbon decomposition rates. To calculate total decomposition rates for normal marine sediments the lowest rates of sulfate reduction and oxic respiration are summed (Figs 1 and 2), and then the highest rates, to give upper and lower boundaries for total oxidation rates.

The results for all sediment types are compared in Fig. 4. With the limited available data set, total rates of organic carbon decomposition in euxinic and semi-euxinic sediments are very similar to the rates found in normal marine sediments of the same

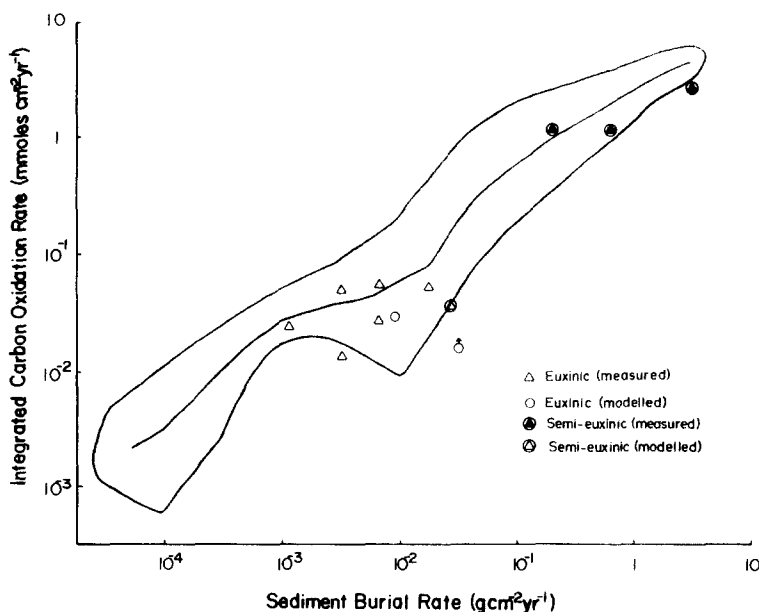


Fig. 4. Total (depth-integrated) rates of organic carbon oxidation in normal marine sediments are compared to total rates in euxinic and semi-euxinic sediments. Rates of organic carbon oxidation in normal marine sediments are enclosed by the outlined area, with the dark line designating the center of the field. Euxinic data include sites from the Black Sea, and the Cariaco Trench. The semi-euxinic data is from the Gotland Deep in the Baltic Sea, the Black Hole in Long Island Sound, Skan Bay, Alaska, and Saanich Inlet, British Columbia.

sedimentation rate. These observations are consistent with the laboratory results of several researchers who have found sulfate reduction to be nearly as efficient as oxic respiration in oxidizing organic matter (FOREE and McCARTY, 1970; OTSUKI and HANGA, 1972a,b; WESTRICH and BERNER, 1984; KRISTENSEN and BLACKBURN, 1987). However, on the time scale of laboratory experiments, fresh organic matter is the most often and most easily studied. The present comparison is from field measurements, and considers naturally decomposing organic matter. This includes not only fresh organic matter, but also highly degraded organic compounds that are present in marine sediments. It is clear that over a wide range of organic matter predecomposition [during settling to the sea floor (e.g. SUESS, 1980) and sediment burial], the ability of aerobic and anaerobic microorganisms to decompose organic matter is very similar.

An implicit assumption is that the rain rate of organic carbon to the sediment surface is similar in both normal marine and euxinic sediments of the same deposition rate. This implies that primary productivities and organic matter water-column decay rates are similar in both environments. For the Black Sea, the range in rates of primary production (SHIMKUS and TRIMONIS, 1974) are similar to those for the oceans (KOBLENTZ-MISHKE *et al.*, 1970). Also, many studies, including those in the Black Sea, have demonstrated that appreciable organic matter decomposition may occur by sulfate reduction (up to 50% or more of the primary productivity) in anoxic water columns (SOROKIN, 1964; SMITH and OREMLAND, 1987; INDREBO *et al.*, 1979; JENSEN and ANDERSON, 1987). To the author's knowledge, the study of SOROKIN (1964) in the southeast Black Sea is the only one where sulfate reduction rates have been measured in a deep anoxic water column. There, organic matter decomposition rates by sulfate reduction are rapid, and in fact exceed rates of primary carbon production (including chemosynthesis; SOROKIN, 1964), suggesting that the measured sulfate reduction rates may be too high. More data would allow better comparison of water-column organic matter decomposition rates in oxic and euxinic environments. However, it is certain that anoxic decomposition is appreciable, and the assumption of similar organic matter delivery rates to euxinic and normal marine sediments (of the same deposition rate) is not unreasonable.

Organic matter preservation in euxinic sediments

An important issue related to the diagenesis of sedimentary organic matter is the processes that control its preservation. Several recent studies and review articles (ALLER and MACKIN, 1984; PRATT, 1984; EMERSON, 1985; CALVERT, 1987; HENRICHS and REEBURGH, 1987) have addressed this problem by discussing how factors such as sediment burial rate, organic vs total particle flux, bioturbation rate, organic carbon source (terrestrial vs marine) and levels of bottom water oxygen potentially affect the concentrations and preservation of sedimentary organic carbon. The present discussion attempts to link many of these considerations by comparing organic carbon preservation in euxinic (and semi-euxinic) and normal marine sediments over a wide range of sediment burial rates.

Following HENRICHS and REEBURGH (1987), organic carbon preservation is quantified for the euxinic and semi-euxinic sites reported here by calculating organic carbon burial efficiencies. Burial efficiency is defined as the percent organic carbon delivered to the sediment surface that escapes oxidation and becomes buried. The calculation begins by combining sediment organic carbon concentrations with sediment deposition rates to give the organic carbon burial flux. The delivery flux is calculated by

combining the organic carbon burial flux with the depth-integrated rates of organic carbon oxidation by sulfate reduction. This calculation assumes that sulfate reduction is the most important process responsible for organic carbon oxidation. The data used for the calculation are summarized in Table 3 and plotted in Fig. 5.

Also plotted in Fig. 5 is an envelope of organic carbon burial efficiencies that encloses all of the normal marine data points compiled by HENRICHS and REEBURGH (1987). Clearly, at lower sedimentation rates burial efficiencies are higher for euxinic sediments, which means that organic carbon preservation is enhanced. This conclusion is different from that reached by HENRICHS and REEBURGH (1987); the difference being attributed to the inclusion of additional euxinic sediment sites. At higher sedimentation rates only data from semi-euxinic sediments are available. Because some of the organic carbon can decompose by other than anoxic pathways, these are maximum values. However, in the absence of "true" euxinic data, it appears that at high rates of sedimentation, the burial efficiency (and preservation) of organic carbon in euxinic and normal marine sediments is similar.

It is intriguing that the enhanced preservation of organic carbon in euxinic sediments of slower (and probably more geologically meaningful) sedimentation rates seems to contradict the observation of similar (depth-integrated) carbon oxidation rates in normal marine and euxinic sediments (Fig. 4). An example from the MANOP sites will show how these two results may be consistent. From MANOP site M (BENDER and HEGGIE, 1984; EMERSON *et al.*, 1985), the burial flux of organic carbon is calculated to be about 3% of the organic carbon flux to the sediment surface, with most of the carbon oxidation resulting from oxic respiration. The concentration of buried organic carbon is about 1 wt%. Assume that MANOP site M becomes euxinic with the same flux of organic carbon to the sediment surface. If depth-integrated rates of sulphate reduction are assumed to be half those for oxic respiration, then about 50% of the organic flux will be buried, resulting in an organic carbon concentration of about 15 wt%—a sapropelic mud.

Table 3. Calculation of burial efficiencies for euxinic and semi-euxinic sediments

Site	Sediment burial rate		wt% C*	Carbon consumed by sulf. red. (g cm ⁻² y ⁻¹)	Burial efficiency (%)
	(g cm ⁻² y ⁻¹)	(cm y ⁻¹)			
Black Sea					
580	0.017	0.027	4.0	6.43×10^{-4}	51
601	0.0031	0.005	4.4	1.49×10^{-4}	48
571	0.0011	0.0017	3.8†	2.83×10^{-4}	13
584	0.0031	0.005	8.8	6.02×10^{-4}	31
Cariaco Trench					
Core 2‡	0.0263	0.035	4.0	4.1×10^{-4}	72
Baltic Sea					
31§	0.0086	0.023	4.5	3.6×10^{-4}	52
Saanich Inlet	0.20	1.05	3.2	1.5×10^{-2}	27
Skan Bay	0.63	1.00	4.0	1.4×10^{-2}	64
Long Is. Sound					
Black Hole	3.13	5.0	3.5	3.1×10^{-2}	78

* Carbon concentrations at base of sulfate reduction zone.

† Carbon concentration at base of euxinic sediment, above the low carbon lake sediments (CALVERT *et al.*, 1987).

‡ Data from LASAGA and HOLLAND (unpublished manuscript).

§ Data from BOESEN and POSTMA (1988).

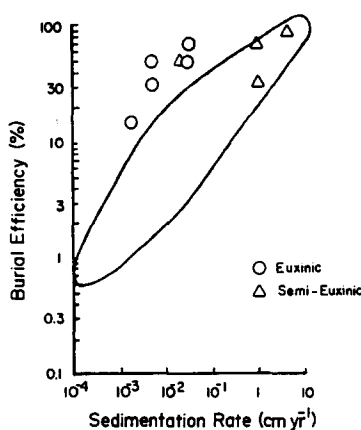


Fig. 5. The burial efficiency of organic carbon in euxinic and semi-euxinic sediments is compared to the burial efficiency of organic carbon in normal marine sediments. The data for normal marine sediments is obtained from HENRICHS and REEBURGH (1987) with all of their data enclosed by the outlined area. See Table 3 and text for details of burial efficiency calculation.

If it is assumed that rates of sulfate reduction are 80% as high as oxic respiration rates, then the concentration of buried organic carbon is still high, at about 7 wt%. A similar calculation for MANOP site C shows that reducing depth-integrated carbon oxidation rates by 50% would increase the concentration of buried organic carbon from 0.2 wt% to about 10 wt%.

This shows that for pelagic sediments, where organic matter decomposition is very efficient, changing the depth-integrated organic carbon decomposition rates by subtle amounts (20–50%) can dramatically affect the concentration of buried organic carbon. Enhanced organic carbon preservation in euxinic sediments, however, requires that depth-integrated decomposition rates by sulfate reduction are lower than for oxic decomposition, even if only by a modest amount. Somewhat lower rates are not inconsistent with the data in Fig. 4.

Possible mechanisms for organic carbon preservation

What then are the likely mechanisms responsible for lower (if only slightly) decomposition rates and increased carbon preservation in euxinic sediments? DEMAISSON and MOORE (1980) suggested that the limited availability of oxidants in euxinic sediments is an important factor. They argued that in euxinic basins bioturbation and irrigation are unavailable to enhance the transport of oxidants (SO_4 in this case) into the sediment, and organic matter oxidation becomes oxidant limited. However, sulfate does not necessarily become depleted in euxinic (and semi-euxinic) sediment pore waters, despite an abundance of organic carbon (3–5 wt%). This is seen in sediment cores from the Black Sea (VAYNSHTEYN *et al.*, 1985), the Gotland Deep in the Baltic Sea (BOESEN and POSTMA, 1988) and the Cariaco Trench (LASAGA and HOLLAND, unpublished manuscript). These observations make the argument of oxidant limitation less compelling.

The most important factor affecting organic carbon preservation is likely the diminished ability of anaerobic bacteria to decompose the complete suite of organic compounds that make up the organic fraction of marine sediments. For example, as discussed

by FENCHEL and BLACKBURN (1979) and KIRK (1984), the *efficient* decomposition of complex aromatic compounds such as found in lignin, requires the presence of oxygen-respiring fungi and bacteria. Recent laboratory experiments have shown that *limited* anaerobic decomposition of simple aromatic compounds (YOUNG, 1984), as well as lignin (COLBERG and YOUNG, 1982; BENNER *et al.*, 1984) can occur. However, in the case of lignin, rates are very slow, and experimental results may measure the decomposition of only the most easily degradable lignin fraction. Clearly more work is required to determine the extent of lignin decomposition by anaerobes in nature.

An argument favoring the preservation of aromatic compounds in euxinic environments is found in the results of PELET and DEBYSER (1977), who reported the ratio of nonaromatic to aromatic hydrocarbons to be about four times higher in Black Sea "unit 3" sediments [sediments deposited under a well-oxygenated water column; DEGENS and ROSS (1974) for classification] compared to euxinic "unit 2" sediments. These authors attributed the difference to early diagenetic processes, and not to a fundamental difference in organic carbon input (e.g. terrestrial vs marine). This view is strengthened by the lack of studies reporting on the anaerobic degradation of polyaromatic hydrocarbons (L. Y. YOUNG, personal communication, 1987).

From another view, the organic matter preserved in modern and ancient euxinic sediments is commonly observed to be more hydrogen-rich than organic matter from normal marine sediments, reflecting a lesser extent of degradation (PELET and DEBYSER, 1977; DEMAISON and MOORE, 1980; PRATT, 1984). Of particular interest is the study of PRATT (1984), who looked in detail at the sedimentology and organic geochemistry of finely laminated to macroburrowed sediments from the Cretaceous mid-continental seaway. Important findings include the close association of high organic carbon content and hydrogen-rich organic matter with laminated sediments (no bottom water oxygen) and low organic content and a low hydrogen index with macroburrowed sediments. These results suggest that organic carbon preservation is closely correlated to the presence or absence of bottom water oxygen.

In summary, several lines of evidence point to the enhanced preservation of organic matter in euxinic sediments as resulting from the reduced efficiency of the anoxic organic matter decomposition process. However, when compared to oxic decomposition, the difference in efficiency is not dramatic, though the result, that is the enhanced preservation (and high concentrations) of carbon may be.

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APPENDIX

Sulfate reduction rates are obtained from sulfate profiles using the following formulation:

$$\text{rate} = \phi D_s dC/dx + \phi_o w C_o - \phi_b w C_b,$$

where ϕ is the average sediment porosity in the zone of sulfate reduction (which may extend 100 m or more), C is the concentration of sulfate and C_o and C_b are, respectively, the concentrations of sulfate at the sediment–water interface and at the base of the sulfate reduction zone (where sulfate no longer changes with depth). Similarly, ϕ_o and ϕ_b are sediment porosities at the sediment surface, and at the base of the sulfate reduction zone, x is sediment depth, D_s is the diffusion coefficient for sulfate at 4°C (LI and GREGORY, 1974), corrected for tortuosity (BERNER, 1980), and w (cm y^{-1}) is the average rate of sediment deposition in the zone of sulfate reduction. This expression states that the integrated rate of sulfate reduction is equivalent to the diffusional and advective fluxes of sulfate into the sediment, minus the advective flux out of the zone where sulfate reduction is complete ($dC/dx = 0$).