Barron, J., Larsen, B., et al., 1991
Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 119

21. SEDIMENTATION RATE ESTIMATES FROM SULFATE AND AMMONIA GRADIENTS[1]

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ABSTRACT

Data from the Ocean Drilling Program and from other marine studies are used to relate organic carbon flux preserved in the seabed with the uptake of sulfate and production of ammonia in the pore water of the sediment column. Relationships are derived that can be used to estimate recent sedimentation rates to within one order of magnitude, spanning the range from 0.1 to 100,000 m/m.y. The relationships provide a simple rule of thumb to apply to initial observations when an estimate of sedimentation rate is not readily available from biostratigraphic or isotope methods. The sedimentation rates estimated for the Leg 119 sites agree to within a factor of 3 with the biostratigraphic results.

INTRODUCTION

The preservation of organic matter in marine sediments depends on the sedimentation rate, organic carbon concentration, and amount of carbon oxidized by biogeochemical processes (Reimers and Suess, 1983). The sediment becomes anoxic at a depth where the reactive organic carbon flux to the sediment exceeds the oxygen flux into the sediment. In oxic sediments, the more reactive organic matter is efficiently oxidized by oxygen (Froelich et al., 1979). Below the oxic region, less reactive organic matter remains and smaller amounts of oxidizing agents (nitrate, manganese, iron, and sulfate) are available, and thus carbon preservation is more likely. Extensive efforts have been taken to fit diffusion/reaction equations to observed pore-water profiles and in some cases to relate these to the sedimentation rate (e.g., Toth and Lerman, 1977; Berner, 1978; Bender and Heggie, 1984; Val Klump and Martens, 1989). Careful selection of values for porosity, tortuosity, diffusion coefficient, sedimentation rate, and elemental ratio in organic matter allows one to fit pore-water profiles to equations; however, the equations may not be applicable to other areas. This paper presents relationships that can be used to predict recent sedimentation rates to within one order of magnitude.

The flux of carbon to an anoxic zone affects the flux of oxidant into the anoxic zone and the production of oxidation products. A variety of oxidants and oxidation products can be measured in the upper few decimeters to meters of the sediment column (e.g., oxygen and nitrate); however, this region is not adequately studied during Ocean Drilling Program (ODP) operations. Other dissolved chemical species are involved with precipitation and adsorption processes that can provide confusing results (e.g., manganese, iron, bicarbonate, and phosphate). Sulfate is the major oxidant in anoxic sediments and tends to decrease in concentration downcore. Ammonia is a by-product of organic matter oxidation (Henrichs and Reeburgh, 1987), increasing in concentration downcore.

A relationship between sedimentation rate and organic carbon content has often been observed (Heath et al., 1977; Muller and Suess, 1979; Stein, 1986; Henrichs and Reeburgh, 1987). However, this relationship may not apply to some environments. Dilution by organic-poor terrigenous sediment in high-latitude fjords (Syvitski et al., in press) or in deltas (Aller and Mackin, 1984) can produce an inverse relationship between organic matter content and the sedimentation rate.

A relationship between sedimentation rate and sulfate reduction has been reported. The sedimentation rate controls the flux of organic carbon, which controls the thickness of the anoxic layer where dissolved sulfate is present (Berner, 1978; Canfield, 1989). The rate of sulfate reduction can vary due to the quality and quantity of organic matter, ambient temperature, and the amount of bioturbation (Edenborn et al., 1987). Specialized incubation experiments are necessary to determine sulfate reduction rates (Canfield, 1989; Christensen, 1989).

Because such data are not available for ODP operations, a simpler method relating sulfate and ammonia gradients to carbon fluxes will be used to estimate sedimentation rates. There is a constant concentration of sulfate in overlying seawater, whereas ammonia levels are generally below the detection limit. Oxidation of organic matter downcore consumes sulfate and produces ammonia to a depth of hundreds of meters. The rate of sulfate consumption and ammonia production relates to the amount of organic carbon being oxidized, which in turn is related to the amount of organic carbon available. In areas where higher carbon fluxes reach the anoxic sediments, more carbon is present and more sulfate is consumed, and thus the flux of sulfate into the anoxic region is larger. The following discussion will use this steady-state balance to relate sulfate and ammonia gradients to organic carbon concentrations and sedimentation rates.

DATA BASE

Dissolved sulfate and ammonia data, along with solid-phase organic carbon data, are available for some ODP sites. The quality of these results appears to vary for different legs, depending on priorities at each site. Data used in this discussion were selected from ODP *Initial Reports* volumes 112 through 121. Table 1 contains data for sulfate and ammonia concentration-depth gradients for the upper three pore-water samples. Because pore-water samples are normally collected at about 30-m intervals, the gradients represent the upper 100 m of the sediment column. Organic carbon concentrations in dried sediment are averaged for the upper 100 m of the sediment column. Estimates of average sedimentation rates in the upper 100 m at each site are taken from the biostratigraphic results.

Molecular diffusion allows pore-water profiles to re-adjust to present-day conditions at the sediment/water interface. Observed gradients in the upper few tens of meters of the sediment column represent responses to organic carbon fluxes over the past 10,000 yr. Table 2 contains data from other study areas where conventional coring provided sulfate and/or ammonia

[1] Barron, J., Larsen, B., et al., 1991. *Proc. ODP, Sci. Results*, 119: College Station, TX (Ocean Drilling Program).
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Table 1. Redox and carbon flux data (ODP *Initial Reports* volumes 112 through 121).

Site	Sulfate gradient (mM/m)	Organic carbon (%)	Sedimentation rate (m/m.y.)	Ammonia gradient (mM/m)
682	0.60	3.0	26	0.10
683	0.68	3.0	25	0.20
684	0.94	4.0	30	0.17
685	1.4	2.5	100	0.20
686	1.9	2.5	160	0.56
687	0.75	3.0	65	0.12
688	2.0	3.0	100	0.30
689	0.012	0.05	9.0	—
690	0.027	0.08	12	0.0023
698	0.014	0.05	10	—
699	0.020	0.10	13	—
700	0.020	0.05	10	—
701	0.028	0.30	25	—
703	0.005	0.05	6.0	—
704	0.025	0.20	20	—
705	0.010	0.10	8	—
707	0.002	0.05	11	—
708	0.025	0.20	15	—
709	0.003	0.10	11	0.0001
710	0.031	0.05	8.5	0.00043
711	0.010	0.05	5.0	—
713	0.013	0.05	7.0	—
714	0.200	0.50	40	0.0078
715	0.024	0.50	15	—
717	0.62	1.0	260	—
718	0.11	1.0	120	—
719	0.21	0.50	81	—
720	0.36	0.30	54	—
721	0.29	1.0	43	—
722	0.25	0.80	47	—
723	0.56	1.0	170	—
724	0.54	1.0	86	—
725	0.24	0.70	120	—
727	0.47	2.0	110	—
728	0.42	2.0	45	—
730	0.16	2.0	50	—
731	0.17	0.50	38	—
737	0.033	0.30	10	0.002
738	0.005	0.05	2.0	0.00002
739	0.090	0.50	20	0.005
740	0.060	1.0	20	—
741	—	0.20	20	0.001
742	—	0.30	7-30	0.004
743	—	0.30	?	0.004
744	0.005	0.05	5.0	0.00006
745	0.050	0.14	30	0.002
748	0.040	0.05	5.0	—
749	0.009	0.05	1.0	—
751	0.020	0.10	3.0	—
752	0.003	0.05	2.0	—
753	0.001	0.05	0.5	—
754	0.007	0.05	3.0	—
756	0.060	0.05	5.0	—
757	0.060	0.05	10	—
758	0.008	0.05	15	—

gradients, organic carbon concentrations, and information on the sedimentation rate.

DISCUSSION

Sulfate Gradients and Sedimentation Rate

Sulfate concentrations in pore water begin at 28 mM at the sediment/water interface and decrease with depth, because sulfate is consumed as organic matter is oxidized. High sulfate gradients tend to occur where high organic carbon concentrations and high sedimentation rates are found. A linear correlation analysis for the 60 cases listed in Tables 1 and 2 is shown in Table 3. All correlation coefficients are significant at $p < .001$. Included in the analyses is a parameter directly related to the flux of organic carbon to the seafloor. It is the product of the sedimentation rate and organic carbon content. Porosity corrections should be applied; however, water content results were not determined for the samples. It is assumed that porosity and the apparent diffusion coefficient for sulfate in the upper portion of the sediment column are similar, to one significant figure, for all sites. The sulfate gradient correlates extremely well with the carbon flux parameter (r = 0.95) and the sedimentation rate (r = 0.93).

As mentioned in the "Introduction," there are cases where sedimentation rates are very high but organic carbon content is low, and thus the flux of carbon to the seafloor is not exceptionally large. In such cases, the organic carbon flux estimate is a more reliable way to describe the sulfate gradient.

A linear regression equation was calculated using log-transformed data, where the sulfate gradient is the independent variable (−mM/m) and the flux parameter is the dependent variable (organic carbon in percentage multiplied by the sedimentation rate in m/m.y.; Fig. 1):

$$\log(\text{organic carbon} \times \text{sedimentation rate}) = 1.2 \times \log(-\text{sulfate gradient}) + 2.2, \quad (1)$$

$r = -0.95$, $n = 60$. A minus sign is used to convert the sulfate gradient to a positive number in order to carry out the log transformation.

Ammonia Gradients and Sedimentation Rates

Only 19 ODP sites with reliable ammonia profiles were found (Table 1). Ammonia results from an additional nine coring sites were found in the literature (Table 2). Ammonia concentrations tend to increase from detection limit values (<0.01 mM) at the sediment/water interface to values that can exceed 1 mM at depth. Correlation coefficients ($p < .001$) were calculated for these 28 cases (Table 4). Ammonia gradient results correlate with organic carbon (r = 0.87) and with sedimentation rate estimates (r = 0.90). However, ammonia results correlate most strongly with the organic carbon flux estimate (r = 0.97), similar to the previous discussion in which sulfate gradients correlated most strongly with the organic flux. A regression analysis on log-transformed data provides a relationship between organic carbon flux (% × m/m.y.) and the ammonia gradient (mM/m; Fig. 2):

$$\log(\text{organic carbon} \times \text{sedimentation rate}) = 0.93 \times \log(\text{ammonia gradient}) + 3, \quad (2)$$

$r = 0.97$, $n = 28$.

A strong negative correlation between sulfate and ammonia gradients ($r = -0.92$; calculated from Table 1) reflects the close relationship between sulfate reduction and ammonia release from organic matter oxidation. Organic matter composition would suggest that 1 mole of sulfate oxidizes 2 moles of organic carbon and releases 0.3 moles of ammonia (Froelich et al., 1979). Thus, in theory, the ratio between sulfate reduction and ammonia production would be $-1/0.3 = -3.3$. Ammonia diffuses through the sediment column twice as fast as sulfate (Krom and Berner, 1980); thus, the observed gradient ratio should be $2 \times -3.3 = -6.6$. A linear regression equation was determined for sulfate and ammonia gradients in Table 1, where

$$\text{sulfate gradient} = -4.1 \times (\text{ammonia gradient}) - 0.11, \quad (3)$$

$r = -0.92$, $n = 19$. The theoretical ratio and that observed in interstitial pore-water concentrations varies for each area and depends in part on core handling and analytical approaches.

Table 2. Redox and carbon flux data.

Area	Sulfate gradient (mM/m)	Ammonia gradient (mM/m)	Organic carbon (%)	Sedimentation rate (m/m.y.)	Reference[a]
NWC	2	—	1	500	1, 2
FOAM	20	4	1	1,000	1, 2
Sachem	40	10	2	5,000	1, 2
Black Hole	300	—	3	50,000	1, 2
North Carolina	300	80	3	100,000	3
Narragansett Bay	40	10	3	2,000	4
Santa Barbara	20	3	3	2,000	5
G10	0.3	0.02	0.4	100	6, 7, 8
N48	—	0.002	0.1	10	6
N56	—	0.02	0.4	40	6
N60	—	0.01	0.3	30	6

[a] 1 = Westrich (1983); 2 = Rosenfeld (1981); 3 = Val Klump and Martens (1989); 4 = Elderfield et al. (1981); 5 = Sholkovitz (1973); 6 = Buckley and Cranston (1988); 7 = G. DeLange (pers. comm., 1986); 8 = Nozaki et al. (1987).

Table 3. Sulfate correlation.

	Sulfate gradient	Organic carbon	Sedimentation rate	Organic flux
Sulfate gradient	1	0.83	0.93	0.95
Organic carbon	0.83	1	0.74	0.91
Sedimentation rate	0.93	0.74	1	0.96
Organic flux	0.95	0.91	0.96	1

Note: $n = 60$, $p < .001$, $\log_{10}$-transformed data.

Table 4. Ammonia correlation.

	Ammonia gradient	Organic carbon	Sedimentation rate	Organic flux
Ammonia gradient	1	0.87	0.90	0.97
Organic carbon	0.87	1	0.65	0.86
Sedimentation rate	0.90	0.65	1	0.95
Organic flux	0.97	0.86	0.95	1

Note: $n = 28$, $p < .001$, $\log_{10}$-transformed data.

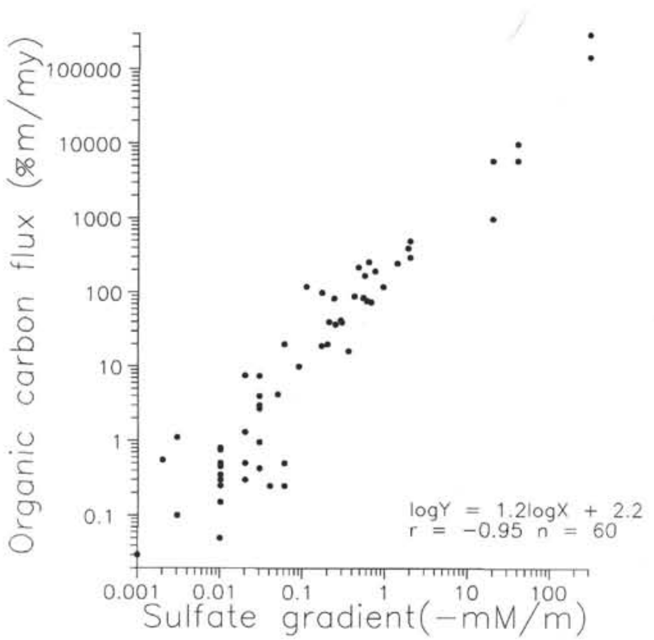

Figure 1. Relationship between organic carbon flux and sulfate gradient.

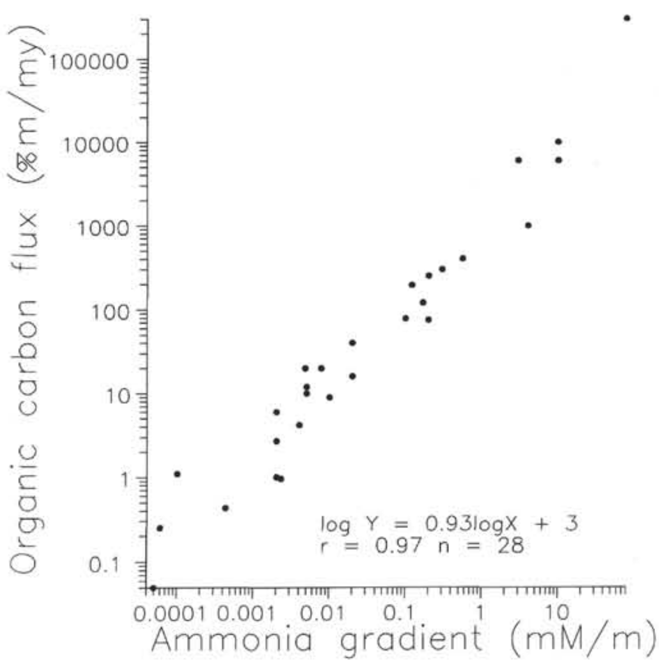

Figure 2. Relationship between organic carbon flux and ammonia gradient.

For example, Aller (1980) found gradient ratios of 7 to 10 in Long Island Sound while Elderfield et al. (1981) found ratios of 4 to 11 in Narragansett Bay.

Estimating Sedimentation Rates

The relationships illustrated in Figures 1 and 2 can be used to provide estimates of recent sedimentation rates, especially in cases where biostratigraphic control was questionable, as for Prydz Bay during ODP Leg 119. Deviations can result from approximations in profiles (e.g., gradients can change seasonally; Val Klump and Martens, 1989), from ammonia adsorption, and from changes in bottom water composition (e.g., anoxic overlying water may be depleted in sulfate and enhanced in ammonia, thus affecting gradients).

Table 5 contains biostratigraphic estimates of sedimentation rates for the Leg 119 sites compared to estimates from the relationships derived in this paper. There is agreement to within a

Table 5. Estimated and observed sedimentation rates for Leg 119 sites.

Site	Sulfate gradient (mM/M)	Ammonia gradient (mM/m)	Organic carbon (%)	Sedimentation rate (m/m.y.) Observed from data[a]	Estimated[b] Equation (1)	Equation (2)
736	[c]0.1	0.008	0.6	50	20	20
737	0.033	0.002	0.3	10	9	10
738	0.005	0.0002	0.05	2	5	1
739	0.09	0.005	0.5	20	20	20
740	0.06	[c]0.008	1	20	5	10
741	[c]0.1	0.001	0.2	20	50	8
742	[c]0.07	0.004	0.3	7–30	20	20
743	[c]0.1	0.004	0.3	?	30	20
744	<0.005	<0.00006	0.05	5	<5	<2
745	0.05	0.002	0.14	30	30	20

[a] Barron, Larsen, et al. (1989).
[b] Equation (1): log (sedimentation rate) = 1.2 × log (sulfate gradient) + 2.2 − log (organic carbon). Equation (2): log (sedimentation rate) = 0.93 × log (ammonia gradient) + 3 − log (organic carbon).
[c] Approximate value due to highly variable interstitial-water data.

factor of 3 in all cases. Biostratigraphic estimates were highly approximate or nonexistent for Prydz Bay Sites 742 and 743, whereas the estimates from the sulfate and ammonia gradients predict that recent sedimentation rates for these two sites are in the range of 20 to 30 m/m.y. This suggests that sulfate and ammonia gradients have adjusted over the last few thousand years to a bulk-sedimentation rate of tens of meters per million years for sediments containing a few tenths of one percent organic carbon. Kvenvolden et al. (this volume) suggested that much of the total organic carbon is actually terrigenous coal dust. If the reactive organic carbon is an order of magnitude lower than reported in Table 5, this would suggest that estimated sedimentation rates for these two sites could be on the order of hundreds of meters per million years.

Both the sulfate and ammonia relationships can generally be used for ODP operations if reasonable quality data are available for the upper 100 m of the sediment column. However, in most other geochemical field programs, recovered cores are not commonly longer than 10 m. For these shorter cores from open-ocean regions, sulfate gradients may not be detected, whereas the ammonia relationship is somewhat more sensitive and may be more useful as a means for estimating sedimentation rates. In coastal systems where organic carbon fluxes are high, sulfate depletion and ammonia production are observed, thus both equations appear to be applicable.

CONCLUSIONS

1. Sulfate and ammonia concentration-depth gradients in pore water correlate closely with an estimate of the flux of organic matter to the sediment column.

2. Relationships between sulfate and ammonia gradients with the sedimentation rate cover a range of sedimentation rates from 0.1 to 100,000 m/m.y.

3. Using simplified relationships derived from ODP sulfate and ammonia gradients, estimates of sedimentation rates for the Leg 119 sites agree to within a factor of 3 in comparison with biostratigraphic estimates.

ACKNOWLEDGMENT

Geological Survey of Canada Contribution no. 45889.

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Date of initial receipt: 6 December 1989
Date of acceptance: 1 August 1990
Ms 119B-172