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SULFATE REDUCTION, DIFFUSION, AND BIOTURBATION IN LONG ISLAND SOUND SEDIMENTS: REPORT OF THE FOAM GROUP

FOAM (Friends of Anoxic Mud)

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ABSTRACT. Sediment gravity and box cores were taken over the course of a 10-month period at a single station in Long Island Sound. A range of pore water and solid phase constituents were measured. Summer pore water profiles exhibit an upper zone from 1 to 8 cm in which concentrations of constituents, such as sulfate and alkalinity, do not change markedly with depth. The actual concentration levels, however, are significantly altered from bottom water values with the transition between bottom water and pore water occurring within the top 1 to 2 cm. The upper 8 cm zone is underlain by a much thicker one in which pore water profiles show trends indicative of progressive diagenesis involving bacterial sulfate reduction (for example, sulfate decrease). Winter pore water profiles do not show an upper zone of constant pore water concentration.

As an aid to interpreting the pore water data, direct measurements were made of sulfate reduction rates by incubating sediment aliquots under anaerobic conditions and following sulfate depletion with time. These rates fall in the range 2 to 77 mM sulfate/l pore water/yr and show a striking decrease with depth in the sediment column.

It is argued that the depth independent pore water profiles in the upper 8 cm of summer sediment arise from irrigation or particle mixing of sediment by macroinfaunal organisms (that is, bioturbation) rather than by lack of sulfate reduction. This conclusion is based on high measured rates of sulfate reduction in the upper 8 cm. Frequent recovery during coring of the deposit-feeding polychaete worm *Nephtys incisa* and presence of abundant iron-sulfide minerals in the upper 8 cm also support this conclusion. The vertical transport of pore water constituents arising from bioturbation during the summer is at least five times more rapid than by ionic diffusion. Such transport does not swamp out all effects of bacterial metabolism, as the latter process is so rapid in the upper 1 cm as to modify the chemistry of solutions passing through this interval. During winter the bioturbating activity of infauna decreases; hence pore water profiles are diffusion controlled.

Below the zone of bioturbation (0-8 cm), mass transport of sulfate is dominated by ionic diffusion and burial. Rates of sulfate reduction over the depth interval 10 to 80 cm were estimated from the sulfate profiles by mathematical modeling using a diffusion coefficient (4.0×10^{-6} cm^2/sec) measured on cores in the study area and a sedimentation rate (0.3 cm/yr) estimated by three independent techniques. Rates so calculated fall in the range 0 to 2 mM/l/yr and are in good agreement with values measured in the laboratory.

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INTRODUCTION

Bacterial sulfate reduction is a biogeochemical process occurring predominately within marine and terrestrial sediments. The consequences of sulfate reduction to long-term cycling of sulfur through the oceans (Holser and Kaplan, 1966; Holland, 1973) as well as short-term cycling of sulfur through the atmosphere (Koyama, Nakai, and Kamata, 1965; Kellogg and others, 1972) have been widely acknowledged. These consequences arise in large part from the ability of sulfate reducing bacteria to facilitate transfer of sulfur from dissolved to solid and gaseous phases. In the marine realm, the major process of this type is the net transfer of sulfur from the sulfate reservoir of seawater to solid phase iron sulfide of the sediment column. The quantitative evaluation of this process requires a detailed understanding of the mechanisms by which sulfur is transported between and within reservoirs and the rate at which it is incorporated into a given reservoir.

We have studied sulfur transport and rates of sulfate reduction in sediments at a single station in Long Island Sound. Sulfur transport is particularly complex near the sediment-water interface because of physical or biological disturbance by waves, currents, and burrowing organisms (Rhoads, Aller, and Goldhaber, 1977; Berner, 1976a). We have studied this upper zone as distinct from deeper sediment where transport is controlled predominately by diffusion. Mathematical modeling of sulfate pore-water profiles (Berner, 1964a, 1972, 1974; Lasaga and Holland, 1976; Tsou, Hammond, and Horowitz, 1973) together with direct measurement of ionic diffusion coefficients for the sediments under study is used to evaluate the relative importance of different transport mechanisms with depth as well as bacterial metabolic rates.

Rates of sulfate reduction are known to be highly variable (Goldhaber and Kaplan, 1975). We have attempted to measure rates of reduction at different levels of the sediment pile by incubating sediment from various depths at close to *in situ* conditions and following progressive chemical changes through time (see, for example, Gunkel and Oppenheimer, 1963; Nakai and Jensen, 1964). No additional substrate was added. Rates of reduction obtained by incubation technique and mathematical modeling are compared.

The study site (hereafter referred to as the Foam site) is located in approximately 9 m of water in Long Island Sound adjacent to the Thimble Islands (fig. 1). This site is readily accessible for repetitive sampling and rapid sample processing on shore. Sulfate removal at this station is complete over a depth interval easily sampled by gravity cores. Sediments at the Foam site are silt-mud characterized by a brown surficial layer 1 to 3 cm thick underlain by gray-green sediment with occasional black mottles. Shell debris is extremely abundant in the upper 50 cm below which it decreases noticeably. The upper ~15 cm of sediment show prominent evidence of bioturbation. Most active burrowing is associated with the errant polychaete worm, *Nephtys incisa;* the dwelling tubes of

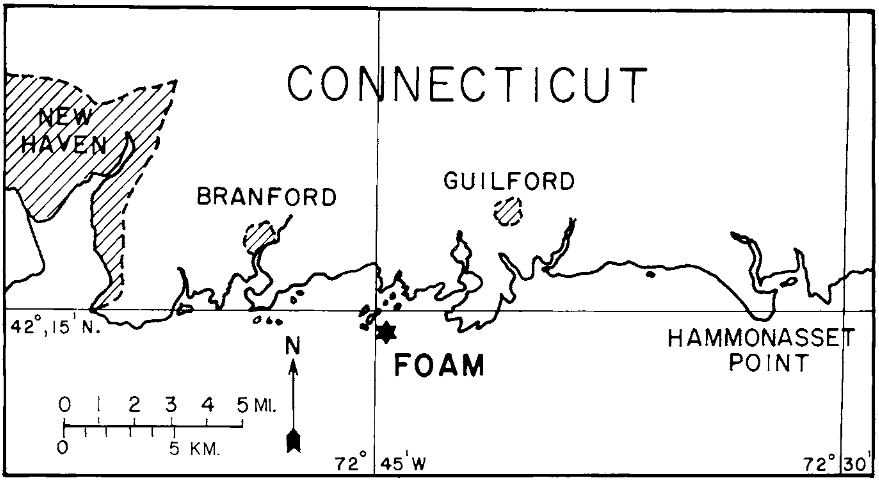

Fig. 1. Location map of FOAM site.

Spiochaetopterus sp. (deep-burrowing polychaete) and *Ampelisca* sp. (near-surface-dwelling amphipod crustacean) are also common. Deposit-feeding protobranch bivalves typical of many soft-bottom areas of the Sound are not abundant at the Foam site.

METHODS

Sample collection.—Several gravity cores were obtained at various times from the Foam site in clear plastic 4.78 cm I.D. core liners. They were returned within 3 to 5 hrs to the laboratory, and pore waters were removed by mechanical squeezing. Two techniques were utilized. The first approach (Kalil and Goldhaber, 1973) entails sectioning the cores in a miter box at 10 cm intervals, removing about 1 cm of sediment from each cut end, and inserting filter paper against the sediment. Mud removed from the core ends was used to estimate water content by drying at 70°C in a vacuum. O-ring-sealed end pistons drilled to allow passage of pore waters are then seated against the filter paper. This procedure is duplicated at the other end of the section, and the whole assembly is placed in a mechanical press. Water is forced out of both ends of the section at pressures <200 psi and passed through in-line millipore filters. Samples are obtained by expansion into plastic syringes, and the first 5 ml are discarded in order to avoid analysis of air contaminated samples. Waters from each end of the core section were analyzed separately. Core 20B was squeezed by a modified Reeburgh (1967) type squeezer using an interlock device (Martens, 1974), so that sample loading could be accomplished in a helium atmosphere. Core 20D was also squeezed in the Reeburgh type squeezer without benefit of the interlock. This latter core was not analyzed for volatile constituents.

To supplement the gravity core data, two closely spaced box cores were obtained by scuba divers at the Foam site during August 1974 and again in March 1975. These cores designed by one of us (Aller) are plexiglas boxes of dimension 7.6 × 30.5 × 25.4 cm and 2.5 × 30.5 × 25.4 cm with a beveled cutting edge along the (open) bottom. A core is taken by a diver who inserts the core gently into the sediment column and then slips a tightly fitting base into position. The base is secured by elastic straps. The smaller cores were X-rayed on a medical X-ray unit, and the larger one analyzed chemically as follows: After removal by aspiration of all supernatant seawater, sediment samples were obtained at successive 1 cm depth increments and packed (under a nitrogen atmosphere in a glove bag) into empty precut and cleaned 10 cm core sections. These sections were then squeezed using the same approach as for cut 10 cm sections of gravity core.

Sediment analysis.—Pore waters from gravity and box cores were analyzed for chloride, alkalinity, sulfate, sulfide, phosphate, and ammonia. Alkalinity was determined potentiometrically on 10 ml samples (1-2 ml in core 20B) using the procedure of Gieskes and Rogers (1973). Sulfate was measured gravimetrically as $BaSO_4$ on 10 ml samples acidified to pH 2-3 and heated to about 80°C to coarsen the precipitate. Frequently the pore water samples became cloudy upon acidification. We take this to indicate formation of organic precipitates or of elemental sulfur from polysulfides which decompose at acid pH. Such samples were refiltered before precipitation of $BaSO_4$. Dissolved sulfide was determined by a modification of the colorimetric methylene blue procedure (Cline, 1969; Goldhaber, 1974). This approach entails collecting about 2 ml of pore water in a plastic syringe containing a known volume of zinc acetate which preserves the sulfide as ZnS. The sample volume is obtained by weighing the syringe before and after water sample collection and applying a density correction to the sample weight. The color is developed by adding the acidic ferric chloride catalyst and diamine reagent sequentially rather than as a mixture. This allows dissolution of ZnS before catalyzed development of the color. Phosphate was determined colorimetrically (Strickland and Parsons, 1968), ammonia by a modification of the phenol hypochlorite method of Solorzano (1969), and chloride by titration with silver nitrate. Precision of the alkalinity, sulfide, phosphate, and ammonia determination is better than ±5 percent, and the sulfate is precise to ±0.5 mM/l. Not all cores were analyzed for the entire range of parameters.

The squeezed cakes of mud enclosed in plastic liners were stored frozen, later thawed, and analyzed for acid volatile sulfides (that is, greigite, mackanawite, amorphous sulfides) by acid evolution of sulfide in a gas train into a silver nitrate trap and weighing of resulting silver sulfide. "Pyrite" sulfur was determined on the sediment residue from this acid treatment by oxidation in boiling bromine plus aqua-regia and precipitation of resulting sulfate as $BaSO_4$. Weights of sulfur from these two procedures are referred to the dry weight of unreacted sediment using the initial wet weight of unreacted sediment taken, together with a separate measurement of the water content of this material made on a subsample dried at 80°C. "Pyrite" sulfur determined in this way actually includes subordinate contributions from elemental sulfur and organically bound sulfur (Kaplan, Emery, and Rittenberg, 1963). Estimates of organic matter were made by weight loss at 475°C on a sample initially dried at 105°C. Some measurements were made of the trace elements Zn and Cu on the combusted material according to the procedure of Thomson, Turekian, and McCaffrey (1975) which involves leaching by hot nitric acid and analysis by atomic absorption spectrophotometry by direct aspiration of the leachate. Calcium carbonate was estimated by weight loss in 1N HCl (Molnia, 1974).

"Jar" experiments.—To have some estimate of the rates at which bacterial metabolism was progressing in the sediment column, four separate suites of experiments were carried out in which sediment was partitioned into a number of containers maintained in the laboratory. Rates of sulfate depletion and ammonia production were estimated by analyzing the containers serially with time.

The first of these series of jar experiments, denoted JJ, was made on sediment obtained by a Van Veen grab at a site near (within 90 m) of the Foam site. The surficial brown zone was visibly present in this material suggesting minimal washout of sediment. We estimate that approximately the upper 10 cm of sediment was sampled. This mud was returned to the laboratory, very completely homogenized in a cleaned 40 gallon plastic trash can, and subdivided into 10 glass chromatographic tanks. These were left open for several hours during which time macrofauna that surfaced were removed. The tanks were then covered with snug fitting glass tops. Pore waters were analyzed at various times by subcoring using a short length of empty core liner, and the sediment squeezed after transfer into a Reeburgh type squeezer. It is likely that some infaunal organisms were unable to escape and were, therefore, entombed with the sediments.

The second suite of experiments (denoted DJ) was made, using Foam site gravity cores, on sediment from the 10 to 20 and 20 to 30 cm intervals. Mud from these horizons was homogenized separately and loaded into a

TABLE 1

Summary of cores analyzed

Core	Date	Length cm
*1A	5/16/74	170
20B	6/4/74	150
20C	6/4/74	125
20D	8/5/74	138
Box-1	8/5/74	24
**20E	9/11/74	
20GG	10/3/74	150
**20H	10/23/74	142
Box-2	3/13/75	12

* Adjacent to Foam site (within 90 m).
** Used primarily for diffusion studies.

series of 30 ml test tubes with tightly fitting tops. Sample handling was carried out under nitrogen in a glove bag. The tubes were stored in a nitrogen flushed, sealed, dissicator further to minimize air oxidation. Sulfate analysis was carried out on the clear supernatant obtained by centrifuging the test tubes. The precision of these analyses is relatively low due to small (2-5 ml) water sample volumes.

The third series (SJ) was made on the (summer) X-ray box core using sediment from the 0 to 2, 3 to 5, 5 to 8, and 11 to 14 cm intervals. This material was prepared, stored, and analyzed in the same manner as for the DJ series.

Finally, a series of experiments (TJ) was made on mud from a coastal salt marsh known from a previous study (Martens and Berner, 1974) to support very rapid sulfate reduction. This was prepared and analyzed in the same manner as for series JJ, except that half the chromatographic tanks were placed in a refrigerator at 2 ± 1°C. All the remaining jars from all experiments were maintained at room temperature.

Rates may, in some cases, be best described as "potential" rates. In particular, there is no *a priori* reason to believe that sediment from the brown "oxidizing" zone 0 to 2 or 3 cm is involved in sulfate reduction at all. The rate of sulfate reduction determined on such material is that which would occur in the absence of oxygen. All sediment for jar experiments was obtained between May and September. Temperature and pressure differences between summer Long Island Sound sediment and the laboratory regime are small (17°-19°C versus 22°C and 2 atm versus 1 atm pressure). Temperature effects can be corrected as discussed in the section on results.

Diffusion procedure.—The diffusion coefficient of sulfate was determined on sediment from Foam gravity cores by a technique adapted from Li and Gregory (1974). This involves joining two cells filled with undisturbed sediment such that one cell contains interstitial sulfate and the other does not. The cells used in the present study were prepared directly from the Foam cores by cutting 5 cm sections near the top and bottom of the core. Sulfate analyses on adjacent (above and below) 5 cm sections were used to bracket the initial sulfate concentrations in the diffusion cells. Additional measurements of $D_{SO_4^{2-}}$ were made on sediment taken from the top and bottom 20 cm of a core. This sediment was homogenized and added to cylindrical lucite cells 5 cm long × 5 cm diameter. Initial sulfate concentrations were determined directly by analyzing an aliquot of the homogenized sediment.

For each experiment the cells were joined, separated only by a filter (Whatman #41 paper or coarse nylon mesh), and sulfate diffusion was allowed to proceed for a measured length of time (<7 days) following which the sediment in each cell was homogenized, and a sample of interstitial water collected by squeezing (Reeburgh squeezer). Sulfate was determined as previously described, and the amount of sulfate that diffused was calculated.

The procedure used to determine $D_{SO_4^{2-}}$ in the present study differs from similar recent studies (Li and Gregory, 1974; Phillips and Brown, 1964) in that (1) tracer ^{35}S was not used, and (2) the natural sulfate gradient in a core was used to establish the sulfate gradient in the diffusion cells. This ensured a counter-gradient of HCO_3^-, thus approximating the conditions under which sulfate diffusion occurs *in situ*. Further, the use of sediment plugs cut from cores minimized disturbance of the sediment, preserving the original tortuosity. Berner (1975) has shown that concentration changes due to diffusion can be affected by gradients in water content in addition to Fick's second law effects. The water content for any two sediment plugs joined together in the present study was 50 ± 5 percent. To check on possible non-diffusive changes in sulfate concentration during the course of an experiment, controls were run by placing an impermeable membrane between the cells. Sulfate

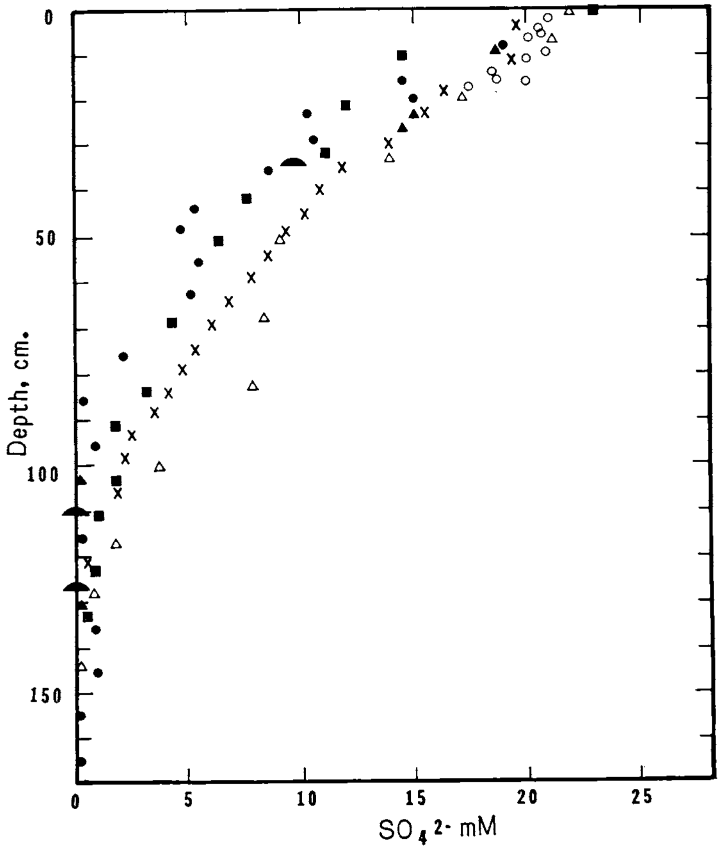

Fig. 2. Pore water sulfate analyses of FOAM site cores. Filled circles, FOAM 1A; open triangles, FOAM 20B; crosses; FOAM 20C; filled squares, FOAM 20D; filled triangles, FOAM 20E; filled ellipse, 20H; open circle, Box-1.

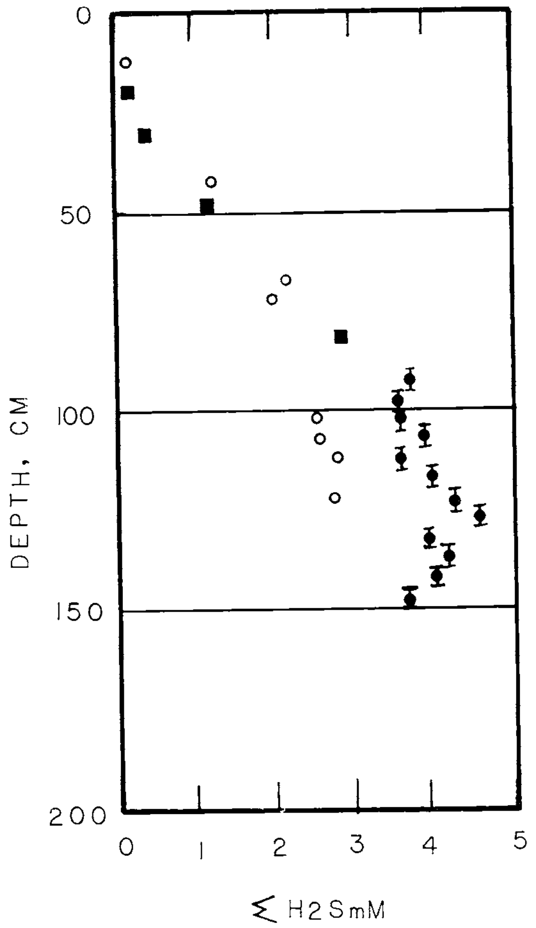

Fig. 3. Dissolved total sulfide ($H_2S + HS^-$) in FOAM gravity core pore waters. Filled squares, FOAM 20B; open circles, FOAM 20C; filled circles, FOAM 20GG.

TABLE 2

Results of analysis of core Foam 20B

Depth cm	SO_4^{2-} mM	ΣH_2S mM	Cl M	NH_4^+ mM	PO_4^{3-} micro-molar	Alkalinity meq/l
0-2	22.0			0.766	130	
2-10	21.3	Tr.?	0.440	0.81	159	7.8
14-22	17.4	0.18	0.440	1.10	214	11.6
27-35	14.0	0.44	0.455	1.36	216	17.5
45-53	9.1	1.11	0.454	1.78	218	23.1
63-71	8.4		0.451	1.97	230	27.3
78-86	7.6	2.80	0.450	1.90	227	34.0
96-105	3.8		0.454	2.29	239	36.0
113-120	1.9		0.452	2.48	250	38.4
126-133	1.1		0.450	2.72	259	41.0
140-148	0.3		0.450	2.54	261	45.4

loss by bacterial reduction during the diffusion experiments was thereby checked.

RESULTS OF SEDIMENT ANALYSES

Pore water chemistry.—The general aspects of trends with depth in pore water chemistry of Foam gravity cores are similar to those that have been observed in previous studies of near-shore organic matter-rich marine sediments sediments (for example, Shiskina, 1964; Sholkovitz, 1973). Sulfate is observed to decrease from near bottom water values in the vicinity of the sediment water interface to essentially zero at depth greater than 150 cm (fig. 2). This decrease is not associated with a decrease in salinity as evidenced by essentially constant Cl^- concentration below 20 cm (table 2). Associated with the sulfate decrease is an increase in the aqueous reaction products of sulfate reduction such as sulfide (fig. 3) and ammonia (fig. 4).

In general, variations between gravity cores taken at different times (over the interval May-September) and different places within the study area are small relative to total changes over the entire depth range. This is best shown for sulfate in figure 2. We take this to indicate that the

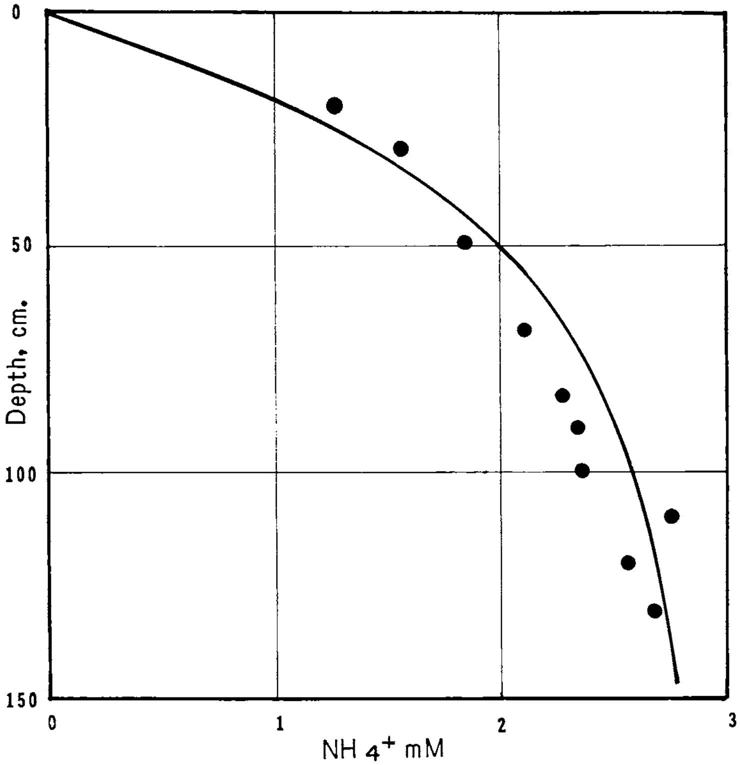

Fig. 4. Dissolved ammonia in pore waters of core FOAM 20D. The curve drawn through the data is an exponential fit as discussed in the text.

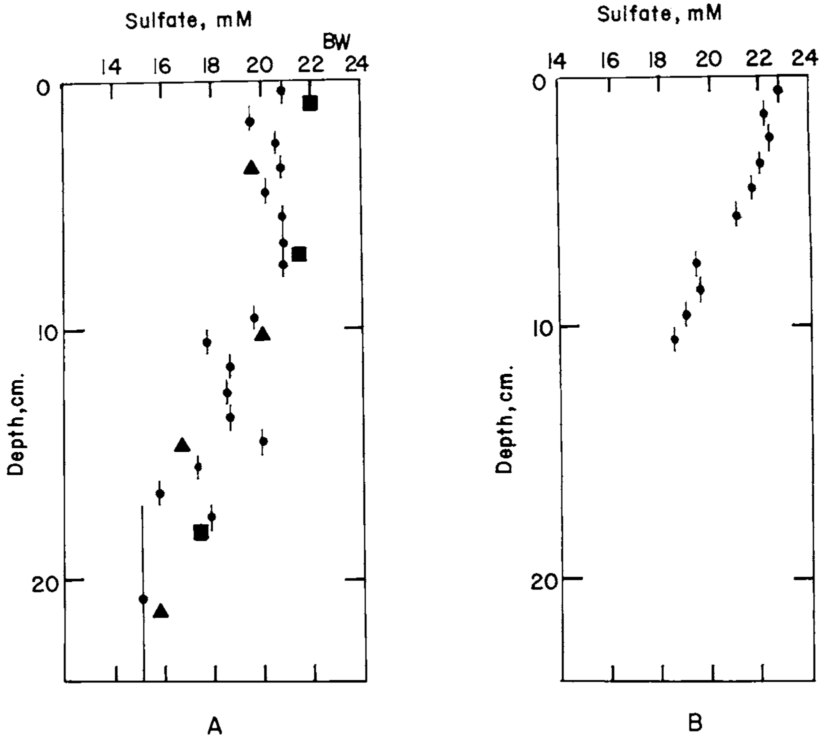

Fig. 5. A. Pore water sulfate data from analysis of the summer box core: (filled circles). Also shown are data from gravity cores 20B (filled squares) and 20C (filled triangles). B W = Bottom Water.

B. Pore water sulfate data from the winter box core.

variability in rates and extent of diagenesis over this time interval is small within the study area, and therefore that conclusions regarding one core may be generalized to the remaining ones. This statement is further substantiated by additional data on several cores taken within 1 km of the Foam site which show sulfate profiles similar to those of figure 2 (Martens and Berner, 1977). In the top few centimeters, however, seasonal variability does clearly exist, the significance of which will be discussed in detail.

The results of pore water analyses on the summer box core are striking in a number of respects. The summer sulfate data are shown on figure 5A. Within the upper 7 to 9 cm, sulfate is essentially constant within experimental uncertainty at a value 2 mM less than that of the overlying LIS water, particularly when box core data alone are considered. Below this depth a great deal of scatter exists, but there is an unmistakable overall decrease in concentration. Also shown on figure 5A are sulfate values from gravity cores 20B and 20C. Note the general agreement between gravity and box core data at comparable depths. This may be taken as further support for between-core similarity. Gravity core 20C

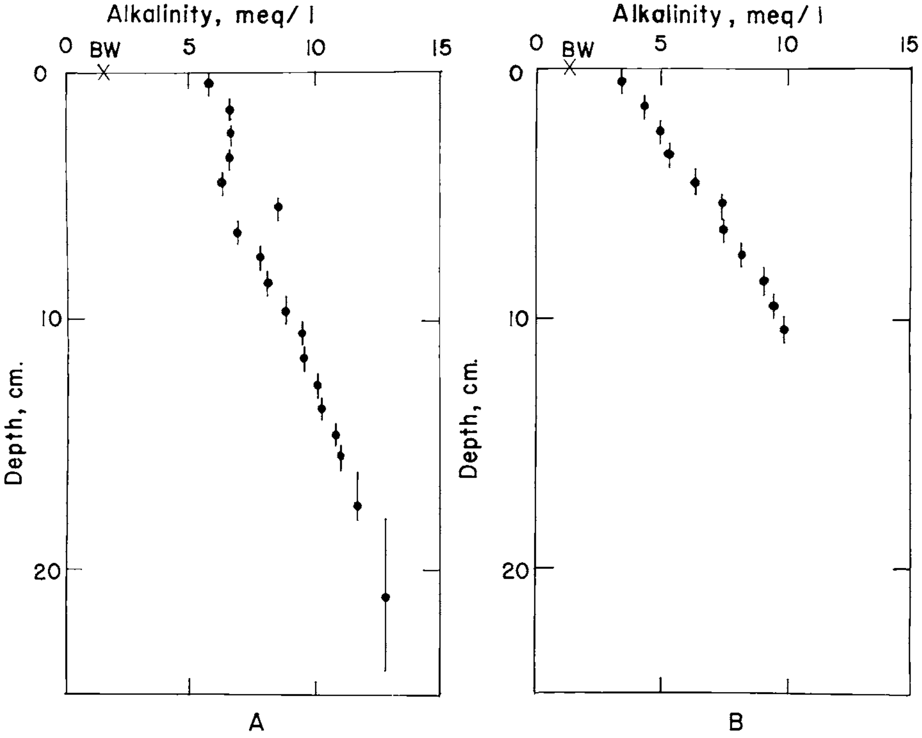

Fig. 6. Pore water titration alkalinity data from the summer (A) and winter (B) box cores. BW = Bottom Water

shows SO_4^{2-} constant in the upper 13 cm in a manner like the box core. Similar gravity core sulfate profiles have been found by Martens and Berner (1976) for Long Island Sound and by Berner (1964b), Sholkovitz (1973), and Goldhaber and Kaplan (1974) for other near-shore marine environments.

Alkalinity measurements on the summer box core (fig. 6A) show less scatter than sulfate data. A very rapid rise occurs in the upper 2 cm from bottom water values to a constant concentration of between 6 to 7 meq/l. As for sulfate, a break in the profile occurs at about 7 to 8 cm with a steeper slope below 8 cm.

Dissolved sulfide (fig. 7) is undetectable in the summer box core until 7 to 8 cm at which depth it begins to accumulate. The coincidence of the depth of initial appearance of sulfide with that of breaks in sulfate and alkalinity profiles suggests a process in common among all three parameters. Also plotted on figure 7 are sulfide values from gravity core 20C. Again, excellent correspondence between gravity and box core data is evident. Furthermore, this agreement demonstrates that sample handling involved in sampling the box core did not lead to substantial loss of volatile constituents by outgassing or air oxidation.

Summer phosphate data (fig. 8A) are characterized by an extremely rapid rise in concentration within the first cm (as was found for alkalinity) followed by a gradual decrease down to at least 7 cm and a second more gradual increase. This second increase continues to at least 1.5 m depth based on data from core 20B (table 2).

Pore water data from the upper 7 to 8 cm of the winter (March) box core are in striking contrast to the summer data. Alkalinity, for example, figure 6B, shows a systematic increase rather than constant values over this depth interval. Sulfate (fig. 5B) systematically decreases with depth. The winter box core has lower near-interface phosphate values which increase gradually and continuously with depth. Below 7 to 8 cm, summer and winter box core sulfate and alkalinity data are in good agreement.

Solid phases.—Solid phases in upper layers of Foam site sediments are characterized by high contents of organic matter (percent ignition wt

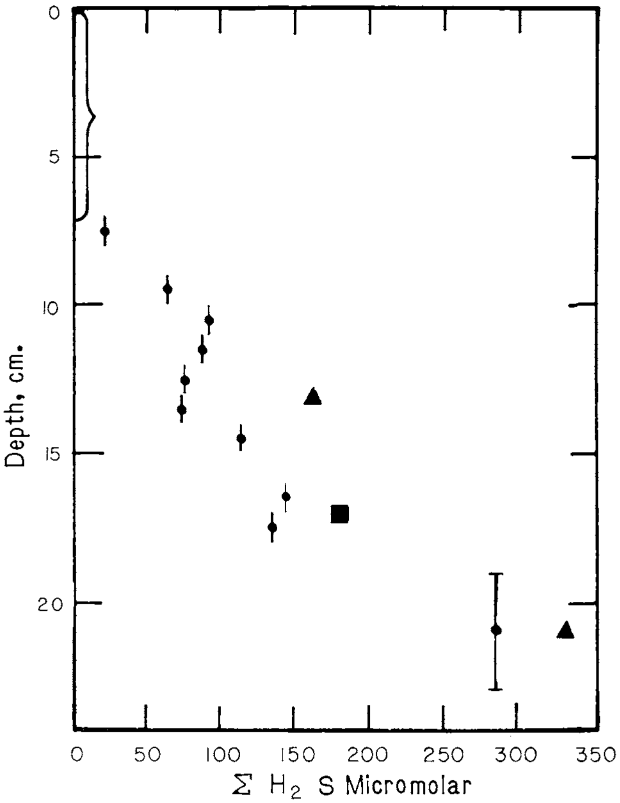

Fig. 7. Pore water sulfide data from the summer box core (closed circles). Also shown for comparison are data from gravity cores 20B (filled squares) and 20C (fillled triangles). The brackets indicate depths at which sulfide is less than the detection limit of the analytical procedure.

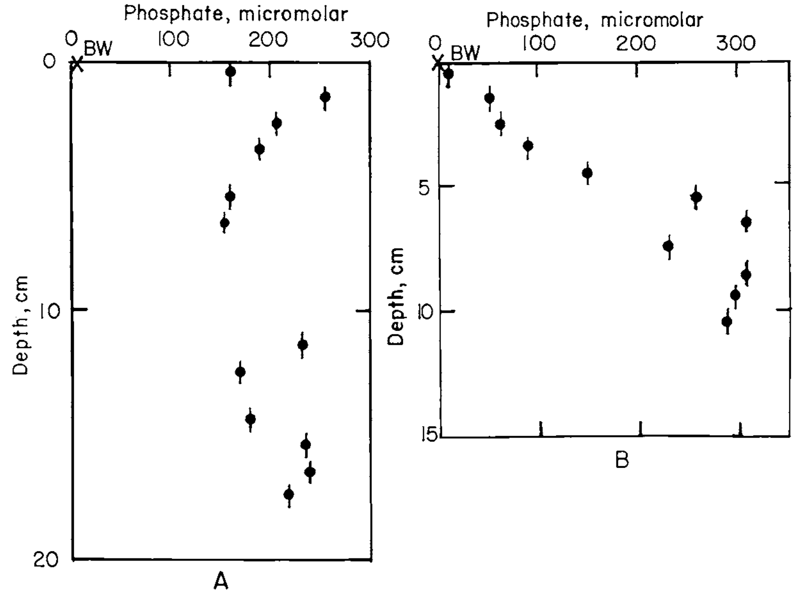

Fig. 8. Pore water phosphate data from the summer (A) and winter (B) box cores.

TABLE 3

Results of analysis of core Foam 20C

Depth cm	SO_4^{2-} mM	ΣH_2S mM	Pyrite S % dry wt	Organic matter % dry wt	Cu microgram/ gram
0-7	19.5	0	0.47		
8-12	19.7	0.16	0.67	6.4	
12-17	16.7		0.89	5.4	
18-25	15.7	0.34	1.20	7.5	
25-30	14.1		0.84		
30-35	12.0	0.42	0.66	5.3	10.6
35-40	11.0		0.60		
40-45	10.3	1.20	0.71	5.1	8.6
45-50	9.5		0.77	3.2	10.0
50-55	8.6		0.79	4.4	
55-60	8.1		0.62		
60-65	7.0		0.70	4.6	9.5
65-70	6.1	2.13	0.83	4.1	8.3
70-75	5.6		0.86		
75-80	4.9		0.86		
80-85	4.3		0.90	4.2	8.7
85-90	3.4		0.98		9.0
90-95	2.6		0.94		
95-100	2.4		0.92		
100-110	1.9		0.82	4.7	9.8*
115-125	0.6		0.95	5.1	10.5**

* 100 to 105 cm
**115 to 120 cm

loss) exceeding 4 percent (tables 3, 5). A systematic decrease of this parameter occurs in the upper 9 cm. This decrease is underlain by a maximum in concentration located at 15 to 17 cm (table 3). These trends are not artifacts of dilution by $CaCO_3$ which is itself highly variable, ranging between 10 to 30 percent in the upper 25cm (table 5).

Acid volatile sulfur (table 5, fig. 9) is present at relatively low levels not exceeding 0.08 percent S (or 0.094 percent S on a carbonate free basis). A maximum was found at around 5 cm.

Pyrite sulfur initially increases in the upper 3 cm and is then essentially constant down to 12 cm where a second increase takes place to a maximum at about 16 cm (fig. 10). This latter depth coincides with the organic matter maximum. A positive correlation in marine sediments between organic carbon and pyrite sulfur was described previously (Berner, 1970; Sweeney, ms) and is attributed to a control on the amount of sulfate reduced by metabolism of a reactive component of organic matter rapidly consumed near the sediment water interface. Also shown on figure 10 are gravity core data for core 20C. As for the pore water constituents, excellent agreement between cores is noted. An interesting feature of the box core pyrite data is that the upper brown zone (0-2 cm) contains considerable pyrite sulfur, the origin of which will be discussed below.

The copper and zinc contents of the nitric acid-soluble sediment fraction are presented in table 5, and Cu is shown in figure 11 (on a carbonate free basis). Also plotted on figure 11 are the data of Thomson, Turekian, and McCaffrey (1975) for central Long Island Sound. Their data have not been recalculated carbonate-free, but the carbonate content of the central Sound is considerably less than the Foam site (about 3-9 percent). Note that at both localities trace metals are considerably enriched in surface LIS sediments compared to deeper levels.

RESULTS OF LABORATORY EXPERIMENTS

Jar experiments.—Results of sulfate analyses on jar experiments are shown in figures 12 to 18. Before these rates can be discussed and inter-

TABLE 4

Results of analysis of core Foam 20D

Depth cm	SO_4^{2-} mM	NH_4^+ mM	PO_4^{3-} Micromolar
8-13	14.6		
18-23	12.1	1.13	229
28-33	11.2	1.43	252
38-43	7.7		
48-53	6.7	1.68	254
65-71	4.3	1.93	261
78-88	3.2	2.08	282
88-93	2.0	2.12	290
98-107	1.9	2.16	295
108-113	1.2	2.52	320
118-123	0.7	2.36	318
128-136	0.6	2.47	318

Table 5
Core box 1

Depth cm	Alkalinity mg/l	SO_4^{2-} millimolar	ΣH_2S micromolar	Cu* microgram/gram	Zn* microgram/gram	$CaCO_3$ percent dry wt	Organic matter percent* dry wt	Pyrite sulfur* percent dry wt	Acid volatile sulfur percent
0-1	5.8	20.9		64.5(72.2)	113(127)	10.3	4.17(4.67)	0.29(0.32)	0.024
1-2	6.6	19.6		65.7(74.2)	117(132)	11.1	3.87(4.37)	0.36(0.41)	0.035
2-3	6.7	20.6		74.0(90.3)	123(150)	17.8	3.46(4.22)	0.57(0.70)	0.026
3-4	6.6	26.8		96.2(107.7)	121(138)	12.5	3.44(3.92)	0.65(0.74)	0.040
4-5	6.3	20.2		88.9(99.6)	112(125)	10.8	3.22(3.61)	0.62(0.69)	0.075
5-6	8.5	20.9		45.9(67.0)	77(112)	31.6	3.24(4.73)	0.55(0.80)	0.064
6-7	6.9	20.9		—	—	(30)	3.39(4.75)	0.57(0.80)	0.058
7-8	7.9	20.9	22	—	—	22.2	2.79(3.60)	0.54(0.70)	0.041
8-9	8.2	(13.9)		39.3(55.4)	79(111)	29.0	2.62(3.69)	0.57(0.80)	0.034
9-10	8.9	19.7	63	31.3(45.7)	66(96)	31.5	2.57(3.79)	0.57(0.83)	0.038
10-11	9.5	17.7	91	—	—	27.4	3.05(4.21)	—	0.035
11-12	9.6	18.7	87	29.4(41.5)	63(89)	29.1	3.28(4.62)	(0.53)(0.75)	0.023
12-13	10.2	18.6	75	—	—	25.2	3.07(4.11)	0.68(0.91)	0.027
13-14	10.3	18.7	73	17.2(23.4)	37(50)	26.3	3.10(4.22)	0.84(1.14)	0.021
14-15	10.0	20.0	131	20.0(26.2)	42(55)	23.4	3.25(4.26)	0.98(1.28)	0.023
15-16	11.0	17.4		24.0(29.8)	42(59)	19.6	4.78(5.93)	1.10(1.36)	0.033
16-17	11.7	15.8	143	27.6(32.3)	62(78)	14.4	4.89(5.72)	1.22(1.43)	0.033
17-18	11.7	17.9	134	13.6(15.5)	54(62)	12.4	3.66(4.17)	1.07(1.22)	0.032
19-20	12.8	15.2	287	11.7(13.0)	52(58)	9.6	3.53(3.92)	1.09(1.21)	0.024

* Parentheses indicate carbonate free basis.

preted the origin of the "initial" behavior during the experiments must be considered. In several cases there appears to be a rapid initial decrease in sulfate with time followed by a change in slope to a somewhat slower long term rate. This effect is particularly noticeable in series JJ but may also be inferred in SJ 2-5, 5-8, 11-14, and DJ 20. Alternative explanations may be advanced to explain this behavior. Previous investigators (Nakai and Jenson, 1964) have ascribed rapid initial rates to a kinetic mechanism which is first order in sulfate concentration. However, extensive research on the metabolism of sulfate reducers indicates that reduction rate is independent of sulfate concentration at values greater than 10 mM (Rees, 1973; Ramm and Bella, 1974; Postgate, 1951; Harrison

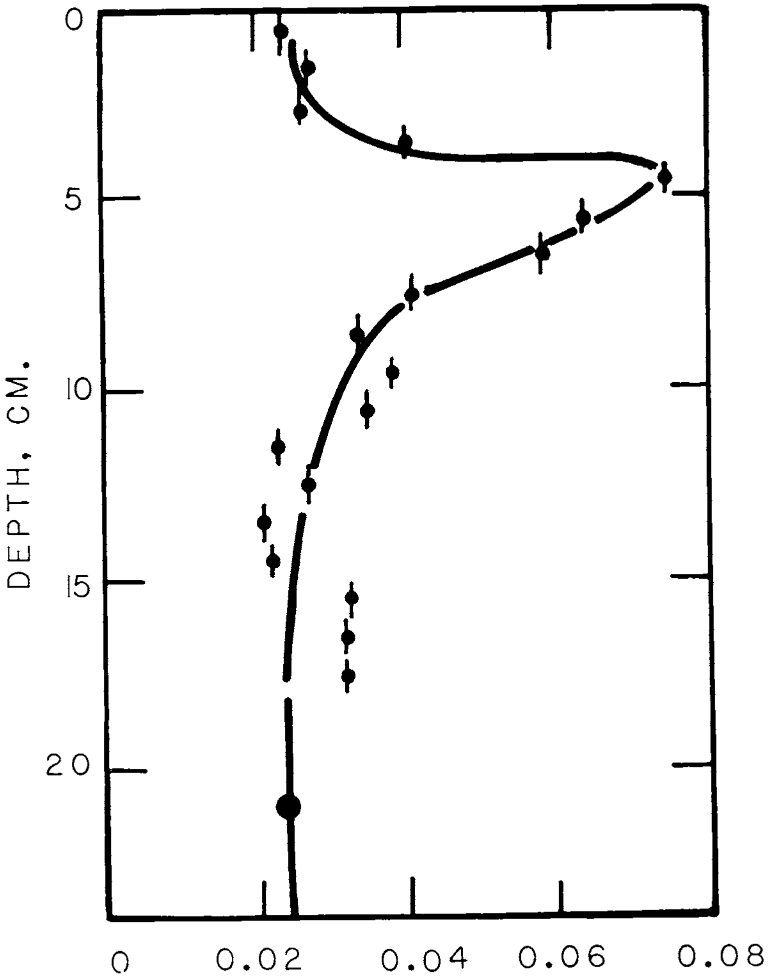

Fig. 9. Acid volatile sulfide (that is, greigite, mackinawite, amorphous sulfides) in the summer box core of FOAM Box-1. Acid volatile S % dry wt.

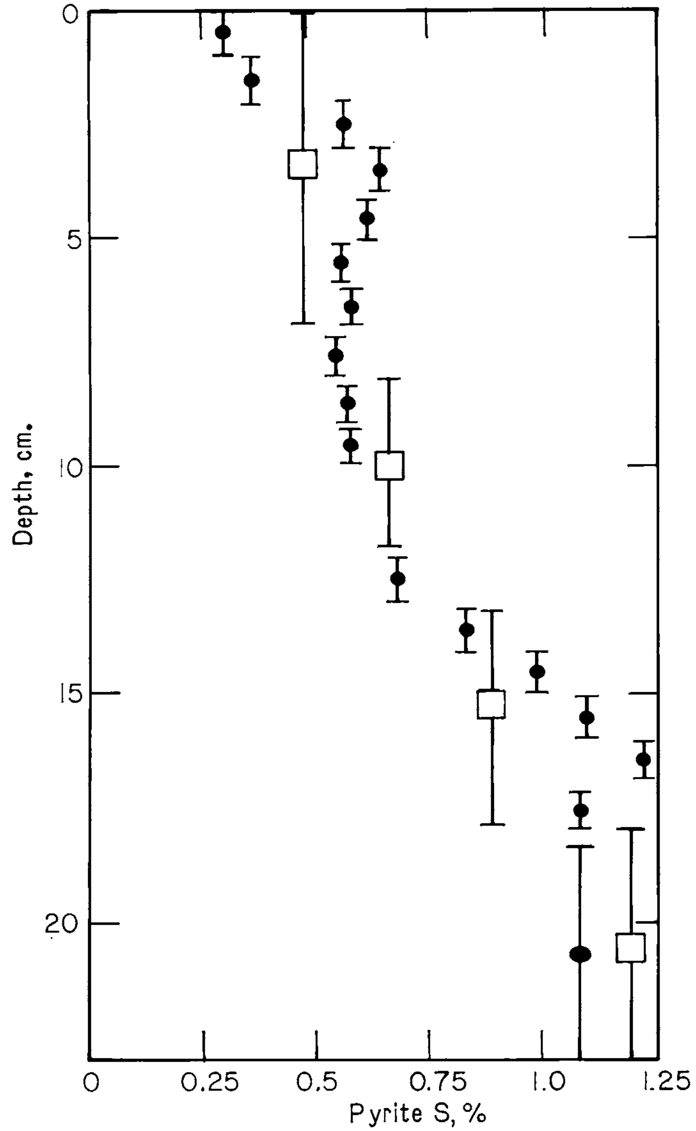

Fig. 10. Results of "pyrite" sulfur analysis of core FOAM Box-1 (closed circles). Also shown for comparison are results from core 20C (open squares).

and Thode, 1958; Kaplan and Rittenberg, 1964). A more likely explanation involves the possible presence of a relatively small component of readily metabolized organic matter which could arise by death and decay of entombed macro-and meiobenthos. Such an explanation is particularly attractive in the case of series JJ where as noted above macro-organisms are thought to have been trapped in this manner. To some extent such processes must take place *in situ,* but they are considered largely experimental artifacts. By way of contrast, the source of highly reactive organic matter might have been present *in situ* owing to the production of fecal material by macro-organisms. Fecal pellets are known to support high

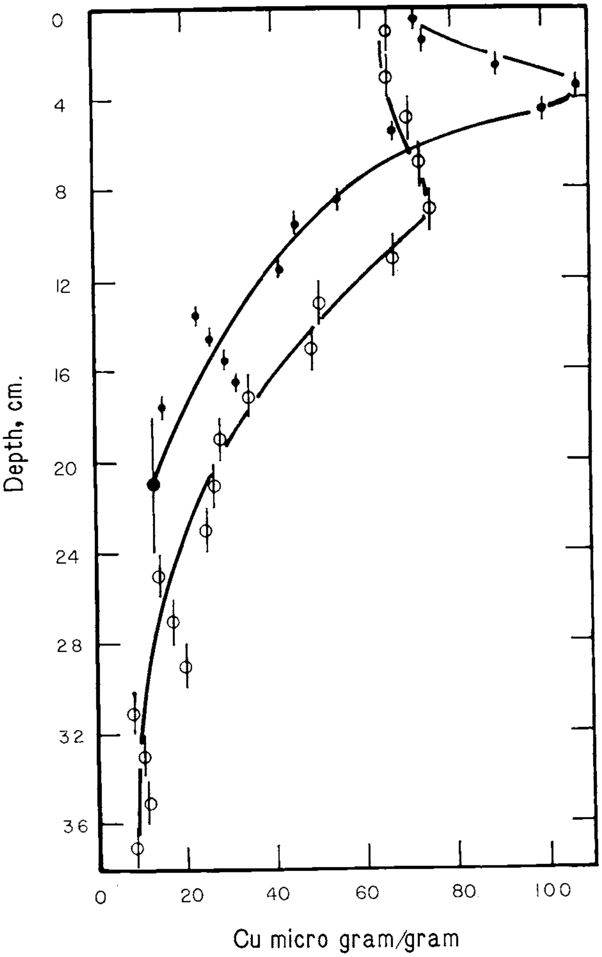

Fig. 11. Copper analyses (carbonate-free basis) on the solid phase of the summer box core (closed circles). Also shown are data of Thomson, Turekian, and McCaffrey (1975) for central Long Island Sound (open circles).

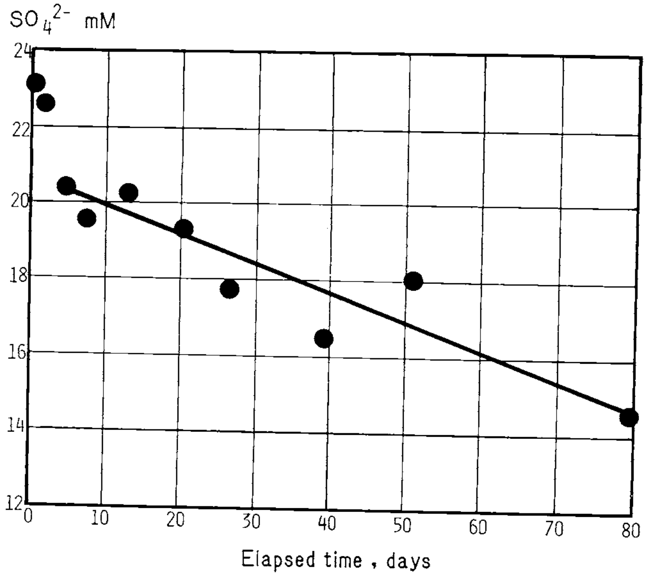

Fig. 12. Plot of jar experiment results from series JJ showing sulfate decrease with time. Note the initial more rapid decrease in sulfate over the first 5 days. Calculated rates are 25 to 38 mM/l/yr when the initial two points are respectively excluded and included in the calculation.

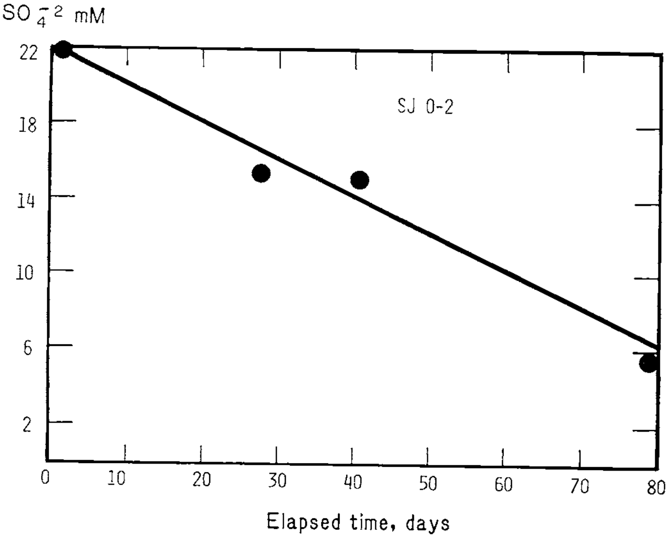

Fig. 13. Plot of jar experiment results from series SJ (O-2 cm) showing sulfate decrease with time. Calculated rate is 77 mM/l/yr.

levels of bacterial metabolism (Hargrave, 1972). Some organisms secrete mucous during burrowing or for cementation of tubes, and its presence as a rich organic substrate might lead to rapid anaerobic metabolism. In fact field observations (by Aller) reveal that most recent sedimentary burrow structures are surrounded by intensely jet black (sulfide rich) sediment probably arising from such a mechanism. If such processes are occurring *in situ* the "initial rate" may actually be closer to the *in situ* rate (R. Wollast, personal commun.). This possibility seems less likely for deeper experiments (DJ series) than for shallower ones owing to the lack of an obvious mechanism for continuously supplying reactive substrate. It should be kept in mind, therefore, that the reported rates may to some extent underestimate *in situ* values. This possibility would not affect our conclusions.

Increased temperature and decreased pressure from *in situ* Foam conditions were used in the laboratory, and these are known to enhance metabolic activity of bacteria. This might cause an initial growth phase (corresponding to the initial rapid rate), while the bacterial population adjusts to the laboratory conditions. The pressure difference, however, between field and laboratory conditions is not large for the situation

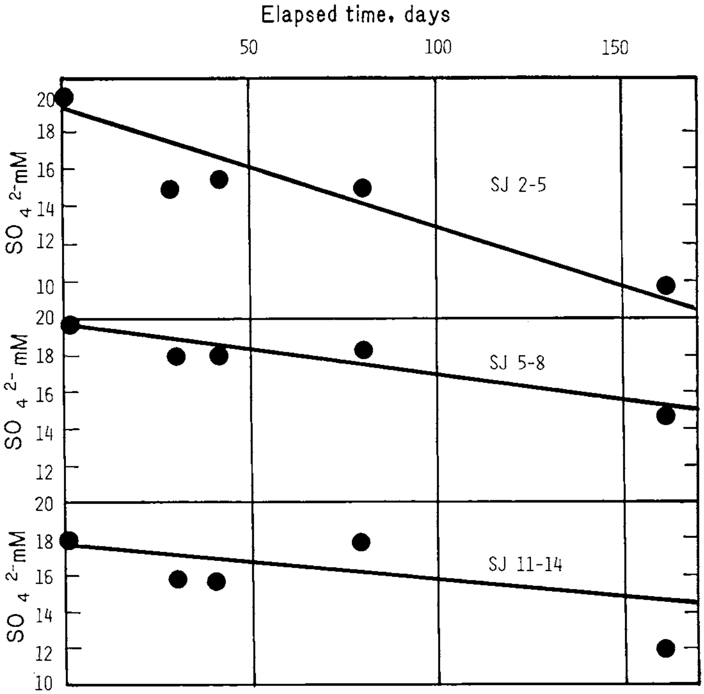

Fig. 14. Plot of jar experiment results from series SJ at depths of 2 to 5 cm, 5 to 8 cm, and 11 to 14 cm. Calculated rates are 13 to 21, 6 to 7, and 2 to 8 mM/l/yr respectively.

under consideration (2 atm versus 1 atm). It is expected that the temperature difference between summer *in situ* and laboratory conditions of at most 5°C will exert some influence on the rate.

The temperature experiment (TJ) at 2°C showed a lag or induction period over the first 20 days during which time no sulfate was reduced. This effect may reflect thermal shock to the bacterial population due to a sudden temperature change.

Because of the existence of these various initial behaviors and their uncertain origin, the results of individual jar experiments are expressed as a range in which the initial data points are alternatively included and excluded from consideration (fig. 18). It is explicitly assumed that sulfate reduction is zero order with respect to sulfate down to low sulfate concentration (<5 mM).

The rates of sulfate reduction measured in this study are not dissimilar from others reported previously from the nearshore marine environment (for example, Gunkel and Oppenheimer, 1963; Ivanov, 1968; Berner, 1972). The spread in Foam site values is quite large, however, ranging well over an order of magnitude from 77 mM/l/hr (SJ 0-2) down to about 2 mM/l/yr (DJ 30). A striking exponential decrease is shown when the data are plotted against the depth in the sediment column from which the sediment was obtained (fig. 18). This localization of rapid metabolic rates in the vicinity of the sediment water interface has been demonstrated previously (Sorokin, 1962). It has also been shown that numbers of culturable bacteria including sulfate reducers fall off ex-

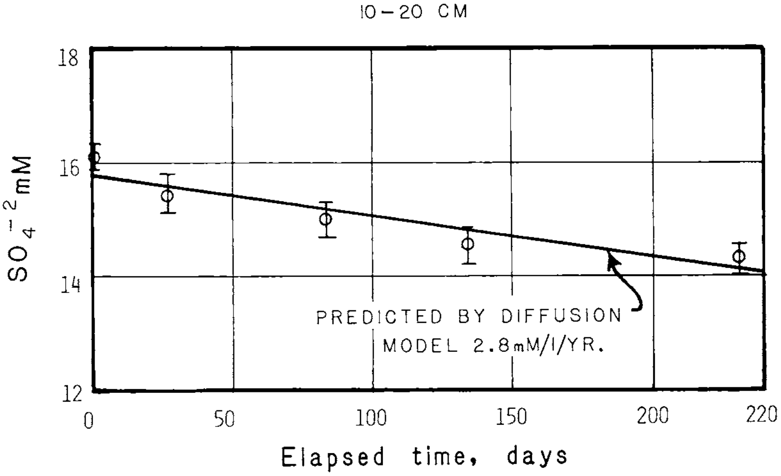

Fig. 15. Plot of jar experiment results from series DJ (10-20 cm) showing sulfate decrease with time. The line drawn through the data is the rate predicted by a diffusion model discussed in the text. Note that the calculated *in situ* values (table 8) have been increased to account for the increased temperature of laboratory conditions under which the jar experiment was run. The basis for this increase is the "activation energy" derived from the TJ jar experiments.

TABLE 6
Core box 2

Depth cm	SO$_4^{2-}$ millimolar	Alkalinity meq/l	NH$_3$ millimolar	PO$_4^{\equiv}$ millimolar	Percent* water
0-1	22.8	3.5	0.071	0.012	56.4
1-2	22.2	4.3	0.124	0.052	50.2
2-3	22.4	5.0	0.181	0.065	49.8
3-4	22.1	5.2	0.245	0.091	50.9
4-5	21.7	6.3	0.322	0.151	54.7
5-6	21.1	7.4	0.361	0.258	53.9
6-7	—	7.4	0.442	0.309	39.6
7-8	19.5	8.2	0.453	0.231	38.5
8-9	19.7	9.0	0.542	0.308	37.5
9-10	19.1	9.5	0.590	0.294	38.7
10-11	18.6	10.0	0.631	0.288	36.9

*Wet wt basis

ponentially with depth in the sediment column (Zobell and Feltham, 1942; Oppenheimer, 1960; Sorokin, 1962). Extremely rapid sulfate reduction rates in a near surface zone have been inferred by Berner (1970) and Sweeney (ms) on the basis of the distribution of iron sulfides within the sediment column, while Orr and Gaines (1973) and Jorgensen and Fenchel (1974) have shown that the ability of anaerobic bacteria to maintain rapid rates of oxidation of organic matter may not be strikingly different than that of aerobic microorganisms.

The results of the temperature jar experiment may be used to obtain the sensitivity of bacterial rates to temperature changes. A difference of about a factor of 16 exists between 20° and 2°C rate data for splits of the same sediment (fig. 17). This corresponds to a factor of 4 difference per 10°C change in temperature or approximately a factor of 0.67 in the rate between summer *in situ* and laboratory conditions. Vosjan (1974) has demonstrated that the temperature dependence of sulfate reduction rates

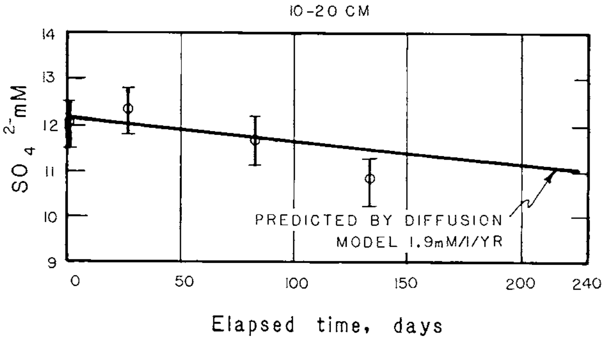

Fig. 16. Plot of jar experiment results from series DJ (20-30 cm) showing sulfate decrease with time. The line drawn through the data is the calculated rate predicted by a diffusion model as discussed in the text. The calculated rate has been increased to account for the increased temperature of laboratory conditions under which the jar experiment was run.

in natural Wadden Sea sediments may be fit to a function of the form of the Arrhenius rate law and calculates an "activation energy" of 22 kcal/mol from his data. Although the activation energy concept is only strictly valid for a single elementary reaction, if we assume that our data may likewise be parameterized as an exponential function, we calculate an "activation energy" of 25 kcal/mol from the rates at 2° and 20°C. This value is used to adjust rates of sulfate reduction to temperatures other than those at which rates were measured. The gross similarity between the activation energies just cited suggests that the assumption of an exponential form to the temperature dependence of our data is reasonable.

Diffusion results.—If the amount of sulfate that has diffused from one cell to the other and the length of time diffusion has proceeded are known, the diffusion coefficient can be calculated from:

$$D = \frac{h^2 f^2 \pi}{t} \tag{1}$$

where

h = length of one cell (5 cm)
f = fraction of initial sulfate which has diffused
t = time for diffusion (sec)

A detailed development of eq 1 as well as restrictions on its use are given in the appendix (see also Phillips and Brown, 1964). D calculated by eq 1

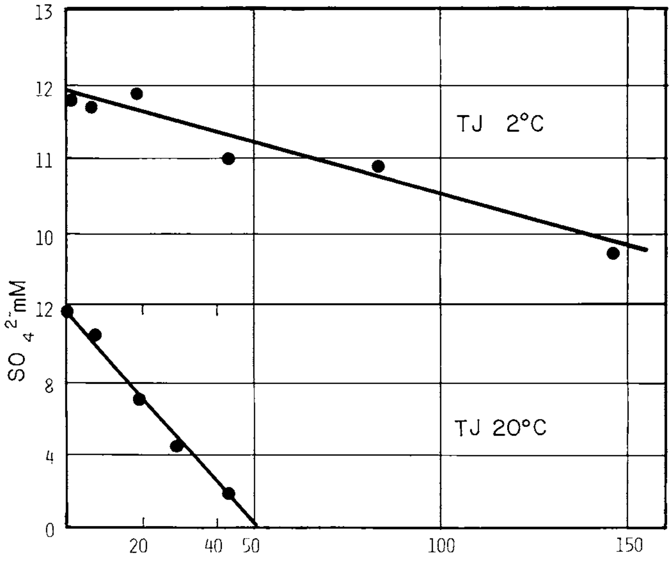

Fig. 17. Plot of jar experiment results from series TJ showing sulfate decrease with time for splits of the same sediment maintained at two different temperatures.

includes the effect of tortuosity only, since adsorption or ion exchange, is negligible for SO_4^{2-} (Li and Gregory, 1974).

Table 7 gives the values of $D_{SO_4}{}^{2-}$ determined on sediment obtained from Foam gravity cores 20H and 20E. Four determinations were made at room temperature, and in those runs a control indicated that a non-diffusive decrease in sulfate concentration occurred, which amounted to about 10 percent of the total decrease. In general the rate of sulfate reduction in these sediments (as determined by the jar experiments) is sufficiently slow to be negligible on the time scale of the diffusion experiments. However, a rapid initial rate of reduction was noted in some of the jar experiments, and we attribute the sulfate decrease in the diffusion controls to this phenomenon as well. The values of D have been corrected accordingly by assuming that none of the sulfate lost by reduction would have diffused.

The effect of the membrane separating the cells is seen to be small by comparing the results for 20H-a and b. Experiment a was run using filter paper, and b used coarse nylon mesh. The similarity in the values of D calculated suggests that no correction for a "cell constant" need be incorporated as eq 1 as is the case for (steady state) diffusion in aqueous solution (Ben-Yaakov, 1972).

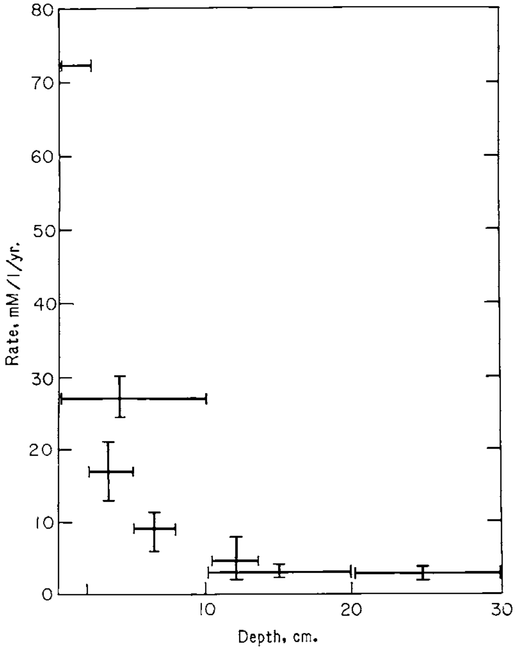

Fig. 18. Summary plot of sulfate reduction rates obtained from jar experiments against depth in the sediment column from which the sediment was obtained. Vertical bars represent the range of values calculated when the initial data points are either included or excluded from the calculated values.

There is a 25 percent range in the values of D determined at 20°C, but the scatter appears to be random and may be due to inhomogeneities such as shell fragments in the sediment. The mean and standard deviation of the 20°C runs is $4.0 \pm 0.7 \times 10^{-6}$ cm^2/sec, which agrees quite well with earlier studies (Berner, 1964a; Li and Gregory, 1974) and with the results for similar experiments in kaolinite/artificial seawater mixtures (see app). The temperature dependence of D for Foam sediment is also comparable to that of kaolinite, corresponding to an activation energy for sulfate diffusion of 6 to 8 kcal/mol, a value in general agreement with other studies of diffusion (Lai and Mortland, 1961).

DISCUSSION

Diagenesis within the zone of bioturbation.—Judging from the complicated depth and time dependence of pore water composition, chemical, biological, and physical processes in the upper 10 cm at the Foam site are complex. We believe, however, that two (seasonally variable) effects are largely responsible for generating observed pore water profiles over this depth interval. The first is bioturbation; the second is bacterial sulfate reduction. We first discuss these processes separately and then their interrelationships as they occur at the Foam site.

The presence of macroinfauna at the Foam site is well established. Virtually all gravity cores were observed to contain either filled or open burrow structures. The filled burrows were brown in contrast to the surrounding gray-green sediment. Two gravity cores were observed to contain the polychaete worm, *Nephtys incisa,* at depths between 5 to 10 cm. A box core also contained open burrows as well as the same species of polychaete worm at near surface (0-2 cm) and 5 cm depths. An X-radiograph of a second box core was largely obscured by the abundant shell debris but did reveal two essentially vertical burrows of approximately 12 cm depth. A Van Veen grab sampler which intercepts a surface area of about 200 cm^2 and 10 cm depth contained a minimum of 10 polychaete worms. A previous study (Sanders, 1956) reported large numbers (~100/m^2) of the same organism in an area adjacent to the Foam site. It is, therefore, worthwhile to consider the potential effects that this and other species might exert upon early diagenesis. These processes that come

TABLE 7

$D_{SO_4^{2-}}$ in Foam sediment

Core	Horizons	Method	f	t ($\times 10^4$ sec)	$D_{SO_4^{2-}}$ ($\times 10^{-6}$ cm^2/sec)	Temperature
20E-a	(0-18 cm)-(124-144 cm)	Homogenized	0.139	42.5	3.6	20°C
20E-b	(18-23 cm)-(119-124 cm)	Core	0.134	45.1	3.1	20°C
20H-a	(20-25 cm)-(112-117 cm)	Core	0.174	54.1	4.4	20°C
20H-b	(25-30 cm)-(117-122 cm)	Core	0.180	54.1	4.7	20°C
20H-c	(0-20 cm)-(122-142 cm)	Homogenized	0.134	58.3	2.4	6°C

Method: Homogenized = sediment mixed and packed into cells; Core = sediment plugs cut from gravity core.

under the general heading of bioturbation may be further divided into two categories: those that dominantly affect pore water chemistry and solid phases, respectively.

An important control on pore water chemistry occurs when an infaunal organism pumps overlying seawater through its burrow in order to replenish its oxygen or food supply. This activity is termed irrigation. In the case of a deposit or scavenger feeder such as *Nephtys incisa* (Sanders, 1956), the former need is dominant and arises from oxygen uptake to both the organism and the sediment. Rates of irrigation for marine polychaetes can be quite high — ranging from 100 to 1000 ml/animal/day (Wells, 1949; Dales, 1961, Mangum, 1964). The net effect of irrigation is to decease concentration differences between solutions contained within the burrow and the overlying seawater. For closely spaced burrows, this may in turn potentially affect overall sediment pore water chemistry due to diffusional exchange driven by concentration differences between the burrow and non-burrow pore solutions. Additionally, the activities of vagile polychaete worms such as *Nephtys* can serve to "ventilate" large volumes of sediment during their feeding or burrowing activities in a manner analogous to the ventilation of soil by earthworms. This second process will be identified below as mixing. Observations made on box cores studied in the laboratory demonstrate that *Nephtys incisa* is capable of moving through sediment at rates exceeding 10 cm/hr.

In studying processes in a hetrogeneous system such as burrowed sediment, it is necessary that the analyses be obtained on a sufficiently large sample to integrate over the various chemically distinct environments (Hanor and Marshal, 1971). This criteria is best met by the box core that samples a surface area of 232 cm^2. It is in the summer box core pore water data that evidence of the effect of irrigation is most evident. The sharp breaks in sulfate, phosphate, alkalinity, and sulfide profiles at about 8 cm correspond approximately to the maximum depth at which *Nephtys incisa* was observed, and these breaks are attributed to the average maximum depth at which summer Foam site pore water chemistry is markedly affected by bioturbation.

It is evident that rate of bottom water supply into the sediments by irrigation or mixing is not completely dominant over concentration changes arising from bacterial metabolism over the upper 8 cm. If irrigation were dominant, one might reasonably suppose that pore water profiles would be constant at precisely the bottom water values. Deviations from bottom water values are, in fact, observed. Nevertheless, most of the concentration change between bottom and pore water in the upper zone occurs *within* the uppermost 1 to 2 cm (see below). The general constancy of pore water profiles between 1 and 8 cm strongly implies an effect due to the presence of macroinfauna. An alternative hypothesis, that the sediment between 1 and 8 cm is biochemically incapable of supporting active metabolism of organic matter, is refuted by the results of jar experiments. These data indicate that this sediment is potentially capable of rapidly reducing sulfate and, therefore, producing alkalinity, phosphate, and sulfide.

It is possible that, because of O_2 addition from bioturbation, sulfate reduction, which might otherwise occur, is inhibited in the 1 to 8 cm depth zone (sulfate reducing bacteria are obligate anaerobes). This is suggested by unmeasurably low concentrations of dissolved sulfide in this zone (fig. 7). However, evidence that sulfate reduction does in fact take place *in situ* is given by the acid volatile and pyrite sulfur analyses. Because iron sulfides are not common detrital phases (Kaplan, Emery, and Rittenberg, 1963), their presence may be taken as direct evidence for *in situ* production of sulfide. In particular, the maximum content of acid volatile sulfur is realized between 4 and 6 cm (fig. 10) which falls within the zone of bioturbation. Virtual absence of dissolved sulfide can be attributed to complete precipitation to form iron sulfides. The iron sulfide minerals that correspond to this fraction are extremely sensitive to oxidation — they are transformed to iron oxides plus elemental sulfur in a matter of minutes to hours in the presence of oxygen. Furthermore, they turn over rapidly — being converted to pyrite on a relatively rapid time scale. Their existence within the bioturbated zone, therefore, suggests the presence of environments, such as the centers of fecal pellets, which are sufficiently protected from oxygenated burrows to allow sulfate reduction to proceed. The presence of 0.08 percent sulfur tied up in the acid volatile form requires that about 25 mM of sulfate per liter of pore water was reduced (at the measured water content of 50 percent) to provide the necessary sulfide sulfur. This predicted concentration decrease does not take into account possible oxidation and loss of sulfide and is, therefore, a minimum estimate. It may be compared to the observed depletion in the upper 8 cm of about 2 mM with respect to bottom water values (or 3 mM in the case of gravity core 20C). This discrepancy between calculated and observed SO_4^{2-} depletion is further evidence for advective interaction between bottom water and pore water. Because of the lack of a summer sulfate concentration gradient in the interval 1 to 8 cm, molecular diffusion cannot make up this discrepancy. The winter core does show a sulfate concentration gradient, and some diffusion will occur (see below). We cannot, however, estimate with available data the winter contribution to reduced sulfur compounds, although because of low winter sulfate reduction rates, it is unlikely to be the dominant contribution. Note that significant "pyrite" concentrations also exist in the upper few centimeters, and the reduced sulfur contained in "pyrite" (minus the contribution of sulfide remineralized from organic matter) must also be added to the total sulfate reduced.

Because infaunal activity is temperature dependent, sulfate reduction rates and the influence of bioturbation on pore water exchange decrease during the winter. As shown by the winter box core data, during the coldwater period a number of subtle but important changes in the near interface pore water profiles occur. The discontinuity between pore and seawater concentrations of $SO_4^=$, $PO_4^{\equiv}$, and alkalinity seen near the interface in the summer box core is considerably reduced (figs. 5B, 6B, 8B). This change is consistent with a lowering of bacterial metabolic rates and a replenishment of $SO_4^=$ and loss of $PO_4^{\equiv}$ and HCO_3^- in the upper zone. Because of an associated decrease in macrofauna activity (Aller and Cochran, 1976), pore water profiles are probably not altered by bioturbation at a rate significantly greater than diffusion during the winter. The lack of any sharp breaks in concentration trends supports this assumption. We attribute the winter profiles observed to diffusion alteration of warm-weather profiles. In the absence of substantial biogenic production or consumption terms of pore water nutrients, inorganic reactions (for example, absorption, sulfide oxidation) may also influence pore water profiles to a greater extent during the winter. Seasonal changes of this type occur at several additional stations in Long Island Sound and are repeatable from year to year both at the Foam site and other stations (Aller, in preparation).

In contrast to the relative lack of variation in the pore water constituents between 1 to 8 cm, the initial concentration gradient within the uppermost 1 cm is quite dramatic for sulfate, alkalinity, and phosphate.[1] These trends are all of the type expected for anaerobic metabolic pathways: such as bacterial sulfate or nitrate reduction; sulfate decrease, alkalinity increase, phosphate increase, rather than aerobic metabolism sulfate constant or increase, alkalinity constant or decrease, phosphate increase. It should be noted that an alternative explanation for the changes observed in the upper 1 cm could be postulated. The sulfate "decrease" might simply reflect seasonally low salinity in the overlying water column (Riley, 1956). One might then call upon $CaCO_3$ dissolution to provide the increase in alkalinity and reduction of iron oxide to release adsorbed phosphate. We consider this explanation to be less likely than anaerobic metabolism to account for observed changes. First, the phosphate release from iron oxides would have to occur *within* the brown oxidized zone. Second, measured changes in water column sulfate values in the vicinity of the Foam site measured over the course of the year (Martens and Berner, 1977) are not large enough to account for the observed decrease in pore water sulfate values. High ammonia concentrations are associated with sulfate depletion and phosphate enrichment in the upper 2 cm of pore waters (table 2). There is no immediately evident non-biological mechanism for producing elevated ammonia concentrations as can be suggested for phosphate.

Sulfate reduction occurring in the upper 1 to 2 cm would be somewhat surprising, as this interval was characterized as the brown "oxidized" zone. There is, in fact, experimental evidence that this zone in LIS sediments requires rapid physical addition of oxygen by organisms or bottom currents to maintain its brown color over a thickness any greater than

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[1] Although phosphate does vary somewhat between 1 to 8 cm, the major variation still occurs in the interval 0 to 1.

a few mm (Rhoads, 1974). Evidently aerobic and anaerobic metabolism can coexist in separate microenvironments within this upper zone, or else the two metabolic pathways are sequential with sulfate reduction following episodic addition and removal of oxygen. The upper 2 cm at the Foam site are granular owing to an abundance of fecal pellets. Such material is rich in nutrients and could constitute the microenvironment just postulated.

The steep pore water concentration gradients in the upper 1 cm are maintained despite the presence of active bioturbation and probably current stirring (Vanderborght, Wollast, and Billen, 1976) as well. From this observation alone one would conclude that rates of bacterial metabolism must be exceedingly rapid within this zone. This inference is verified by jar experiment results, which show that by far the highest potential sulfate reduction rates are near the interface (fig. 18). It is this high rate that acts as a sort of "filter" for altering pore water composition (from that found in the overlying water), while the water is being rapidly mixed downward by bioturbation during the summer. In other words, the water mixed into the 1 to 8 cm depth zone can be thought of as consisting of two hypothetical components: (1) the more remotely overlying seawater of normal sulfate composition, and (2) the directly overlying 0 to 2 cm pore water which, in the absence of bioturbation, would be highly depleted in sulfate.

In addition to transport of aqueous fluids, organisms are also known to redistribute rapidly particles within the sediment column of LIS (Aller and Cochran, 1976). The net sediment transport vector is dependent upon the particular faunal association present. For some organisms described by Rhoads (1974) as "vertical conveyer belt species" the transport vector is directed toward the sediment water interface and arises from feeding at depth and deposition of fecal material at the sediment surface. Transport from the surface to depth can occur as well, resulting from mechanisms such as collapse of sediment into unfilled burrows or by stochastic mixing of sediment particles due to the passage of organisms. Sedimentological and geochemical consequences of such processes have been demonstrated (for example, Calvert, 1964; Rhoads, 1967; Glass, 1969; Schink, Guinasso, and Fanning, 1975). In the present context, one could postulate that the pyrite increase with depth in the upper 3 cm could be generated by transfer of "high" FeS_2 sediment from depths greater than 3 cm to the surface followed by partial oxidation of this material. Thus, it is possible that pyrite in the upper sediment layers does not reflect sulfate reduction in these layers. Although no definitive conclusion is possible with the present data, some tentative evidence exists that such particle transport is not a dominant feature of Foam site sediments. (1) The predominant organisms at the Foam site *during this study* were not of the "conveyor belt" type. (2) Summer pore water profiles in the upper 2 cm strongly indicate rapid sulfate reduction in the interval, and it is reasonable to suppose that the contained iron sulfides are at least in part a result of the process. (3) A preliminary experiment was performed in which 280 g of Foam site sediment (from 11-16 cm depth) were suspended in 2 l of continuously aerated LIS seawater. The supernatant solution was periodically analyzed for SO_4^{2-} and showed only a minor increase over the time scales of 2 weeks. This would seem to argue against extremely rapid oxidation of initially high FeS_2 sediment as the mechanism for producing lowered FeS_2 contents in the upper 3 cm. On the basis of these considerations we feel that the trends exhibited by iron sulfides are in large part indicative of progressive diagenesis with depth rather than particle redistribution effects.

The assumption of progressive addition of iron sulfides with depth (time) affords the possibility of direct comparison of measured trends in these compounds with calculated distributions derived from the jar experiment data. These calculations proceed as follows: The *in situ* rate of sulfate reduction, R, (units of mM/l/yr) in the upper 10 cm is assumed to be given by the jar experiment results, which in turn can be described by an exponentially decreasing function of depth (eq 2).

$$R = R^\circ \exp(-\alpha x) \tag{2}$$

Where R° refers to the sediment water interface, x is depth (cm) measured positively downward, and α is a decay constant with units cm^{-1}. The decay constant and initial rate may be determined as the slope and intercept respectively of the plot of ln R versus x. Although some scatter exists in this plot, the data approximate

$$R = 81 \exp(-0.24\ x) \tag{3}$$

A somewhat different approach to obtaining R° can be applied assuming that the JJ jar experiment gives an average rate, denoted R_{avg} over the upper 10 cm. This average value (~28 mM/l/yr) is given by

$$R_{avg} = \frac{\int_0^{10} R^\circ \exp(-\alpha x)\, dx}{\int_0^{10} dx} \tag{4}$$

or integrating

$$R_{avg} = \frac{R^\circ}{\alpha \cdot 10} [1 - \exp(-\alpha \cdot 10)] \tag{5}$$

Substitution of $\alpha = 0.24\ cm^{-1}$ and solving for R° by iteration yields $R^\circ = 74$ mM/l/yr in reasonable agreement with the previous estimate. The value of the attenuation coefficient calculated above may be used as an aid in comparing laboratory rates with *in situ* iron sulfide production. If steady state diagenesis is assumed, the total sulfate reduced (ΣS, mM/l) is given by the integral of the rate (eq 2).

$$\Sigma S = \frac{1}{\omega} \int_0^X R dx \qquad (6)$$

where (R(x) is an exponential function of depth (eq 2), and ω is the sedimentation rate. Substituting (2) into (6) and integrating:

$$\Sigma S = \frac{R^\circ}{\alpha\omega} \left[1 - \exp\left(-\alpha \cdot 10\right)\right] \qquad (7)$$

for $\alpha = 0.3 \text{ cm}^{-1}$, $R^\circ = 52$ mM/l/yr (77 mM/l/yr corrected to the summer Foam site temperature), $\omega = 0.3$ cm/yr (see below), ΣS is calculated as 550 mM/l. Assuming an average water content of about 45 percent (wet wt, table 6), this corresponds to 1.4 percent solid phase sulfur. This latter figure would hold only if all sulfide produced were fixed in the sediment column and the summer temperature were characteristic of year-round conditions. This calculated abundance may be compared to the analytically determined sum of solid phase sulfur constituents of about 0.6 percent S at 10 cm (see table 7). Lack of correspondence between calculated and measured sulfur contents suggests possible loss of sulfide sulfur from the sediment column. Such loss would be consistent with the lack of dissolved sulfide in the interval 0 to 7 cm despite strong evidence for sulfide production in the interval as discussed above. Alternatively, low winter temperature may in part account for the discrepancy. Note that sulfide loss need not be exclusively by oxidation but could occur as well by water exchange due to irrigation. Based upon evidence cited previously, any sulfide oxidation occurs predominantly at the expense of sulfide species (for example, H_2S, FeS) other than sedimentary pyrite.

Some idea of the role of bioturbation in transport of pore water constituents may be gained by a simple flux constraint; the transport of matter across any plane in the sediment must be continuous. Let this plane be located at 8 cm, which is the depth associated with a sharp (assumed discontinuous) break in sulfate concentration. For purposes of this crude calculation we neglect burial of sulfate within the accumulating sediments. Then the continuity of flux across the plane may be expressed by eq 8.

$$-\phi D_S \left(\frac{\partial S}{\partial X}\right)_{x>8} = -\phi D_M \left(\frac{\partial S}{\partial X}\right)_{x<8} \qquad (8)$$

where

ϕ = porosity, assumed constant across plane
D_S = ionic diffusion coefficient of sulfate

$\left(\frac{\partial S}{\partial X}\right)$ = concentration gradient of sulfate ion immediately above (X<8) or below (X>8) 8 cm

D_M = stochastic coefficient describing the transport of sulfate by mixing (bioturbation) processes.

Rearranging eq 8 and cancelling ϕ gives

$$D_M = \frac{D_S \left(\frac{\partial S}{\partial X}\right)_{x>8}}{\left(\frac{\partial S}{\partial X}\right)_{x<8}} \tag{9}$$

Our formulation assumes that mass transport arising from the activities of organisms can be described by a stochastic coefficient, D_m, which when taken over a sufficiently large surface area relates the net flux to a concentration gradient. This approach has yielded reasonable results in describing the transport of particles due to bioturbation (Schink, Guinasso, and Fanning, 1975) as well as transport of pore water constituents due to wave and current stirring (Vanderborght, Wollast, and Billen, 1976).

The quantity $(\partial s/\partial x) \times < 8$ in eq 9 is for all practical purposes equal to 0 (that is, the sulfate profile is vertical). However, we have forced a line of slope 7×10^{-8} mol/cm^3/cm through the data using as a basis the assumed imprecision of ± 10 percent. Below 8 cm the slope equals 4.7×10^{-7} mol/cm^3/cm. Because of our acceptance of the maximum slope above 8 cm, the following inequality holds:

$$D_M > \frac{4.7 \times 10^{-7}}{7 \times 10^{-8}} D_S = 7 D_S \tag{10}$$

Therefore, the stochastic coefficient at 8 cm is at least 5 times greater than that associated with ionic diffusion.

If our physical picture of the effect of bioturbation on pore water constituents is correct, one could, in principle, construct a diffusion–advection–reaction model (ignoring compaction) which describes pore water chemistry in the zone of bioturbation. It is:

$$\partial \left(\frac{D_M \frac{\partial s}{\partial x}}{\partial x} \right) - \omega \frac{\partial s}{\partial x} - R\,(x,t) = \frac{ds}{dt} \tag{11}$$

where

S = sulfate concentration
t = time

For several reasons we feel that it is as yet inappropriate to take this approach: (1) D_M is likely to be depth dependent, but its functionality is probably complex. If for example, mixing effects are concentrated at a characteristic "feeding depth" which the organisms prefer, the corresponding D_M for this depth might be larger than D_M for shallower depths where organisms are spending less time. (2) The pore water profiles are clearly time dependent as evidenced by summer and winter box core data. We believe that D_M is strongly time dependent as well as depth dependent, but again we cannot as yet define the nature of this dependence. We wish to restress, however, that pore water profiles within the zone of bioturbation result from a competition between rates of physical and chemical addition and removal of dissolved constituents and, therefore, that curvature in such pore water profiles is to be expected in some cases and is in fact observed in summer Foam pore water concentrations.

Rate of sedimentation.—Three arguments are presented here from which estimates of the average rate of sedimentation at the Foam site can be made. It must be emphasized that the derived rates are averages for the top meter of sediment. Deposition is probably episodic and may be very rapid over a scale of centimeters. Even erosion may occur. However, a meaningful average value is decipherable as demonstrated by the Pb^{210} measurements of Thomson, Turekian, and McCaffrey (1975).

The first argument is based on the depth distribution of copper in the solid phase as shown in figure 11. The increased values in the upper levels of the sediment in the central sound have been ascribed by Thomson, Turekian, and McCaffrey to post-industrialization anthropogenic input of metals to Long Island Sound. The increase above baseline (in the central sound) has been dated by ^{210}Pb geochronology by Thomson, Turekian, and McCaffrey to have occurred 70 yrs ago. This was obtained from a core whose overall rate of sedimentation was 0.45 cm/yr. A comparable increase at about 20 cm depth at the Foam site may be taken as a tentative indication that the average sedimentation rate there is 20 cm in 70 yrs or about 0.3 cm/yr (2/3 × 0.45 cm/yr). Note that Cu concentrations from deeper levels at the Foam site (table 3) confirm that base levels there and in the central sound are comparable. A similar sedimentation rate would be calculated from the Zn distribution (table 5).

The relationship between sedimentation rate and sulfide pore water profiles has recently been studied by Goldhaber and Kaplan (1975). It was pointed out that below the depth of complete removal (about 150 cm at the Foam site) sulfide is no longer produced, but sulfide removal to form iron sulfides still occurs. This gives rise to a maximum in the dissolved sulfide concentration. This sulfide maximum has been shown to be related to total sediment accumulation rate (fig. 19). Based upon this relationship and the maximum observed sulfide concentration at the Foam site (fig. 3), an average sediment accumulation rate of about 0.3 ± 0.1 cm/yr is predicted. The sulfide values shown in figure 6 do not show a clear maximum; however, the value where sulfate goes to zero at ~ 120 cm must represent a maximum (assuming steady state diagenesis), since no sulfate is available for sulfide formation below this depth. The sedimentation rate calculated in this way is in good agreement with that based upon the Cu and Zn distribution.

A third argument is based on the depth distribution of ammonia below the zone of bioturbation and its rate of production in jar experiments. Ammonia production in anoxic sediments, if one assumes steady state and ignores bioturbation, can be described by the equation (Berner, 1974):

$$D \frac{\partial^2 c}{\partial x^2} - (1+K)\, \omega \frac{\partial c}{\partial x} + R(x) = 0 \tag{12}$$

Where

c = concentration of total NH_3 (NH_3 + NH_4^+) in the pore water
x = depth in the sediment
$R(x)$ = rate of ammonia production (as measured by jar experiments)
D = ionic diffusion coefficient in the pore water
K = adsorption distribution coefficient
ω = rate of sedimentation

Rearranging equation (12) and solving for ω:

$$\omega = \frac{D \frac{\partial^2 c}{\partial x^2} + R(x)}{(1 + K) \frac{\partial c}{\partial x}}$$

Values of $\partial c/\partial x$ and $\partial^2 c/\partial x^2$ at a depth of 20 cm can be taken from figure 4 (assuming an exponential fit to the data) and combined with the jar sulfate reduction rate at 20 cm and the $R_{SO_4^{--}}/R_{NH_4^+}$ jar data of Rosenfeld (unpub.). Reasonable estimates, good to a factor of 2, of D and K can be obtained from the results of Berner (1974) and the preliminary adsorption results of Rosenfeld. They are: $D = 95$ cm²/yr (3×10^{-6} cm²/sec), $K = 2.5$. Combining these values with $\partial c/\partial x$ (20 cm) $= 4.25 \times 10^{-2}$ mM/cm⁴; $\partial^2 c/\partial x^2$ (20 cm) $= -1.06 \times 10^{-3}$ mM/cm⁵, $R_{SO_4} = 1.8$ mM/cm³/yr, $R_{SO_4^{--}}/R_{NH_4^+} = 13$ one obtains (for 20 cm depth):

$$\omega = 0.25 \text{ cm/yr}$$

Although this value represents a small difference between nearly equal numbers and is therefore highly sensitive to errors in the data used, there is good agreement with the value derived from the (Cu + Zn) and sulfide arguments, thus, the value $\omega = 0.3$ cm/yr will be used for the average depositional rate at the Foam site.

Diagenesis within the diffusion zone.—Below the zone of bioturbation, the major process for the migration of dissolved species is molecular diffusion. In order to calculate sulfate reduction rates diffusion must be considered. For sulfate, the steady state diagenetic equation (Berner, 1964a, 1972, 1975) is:

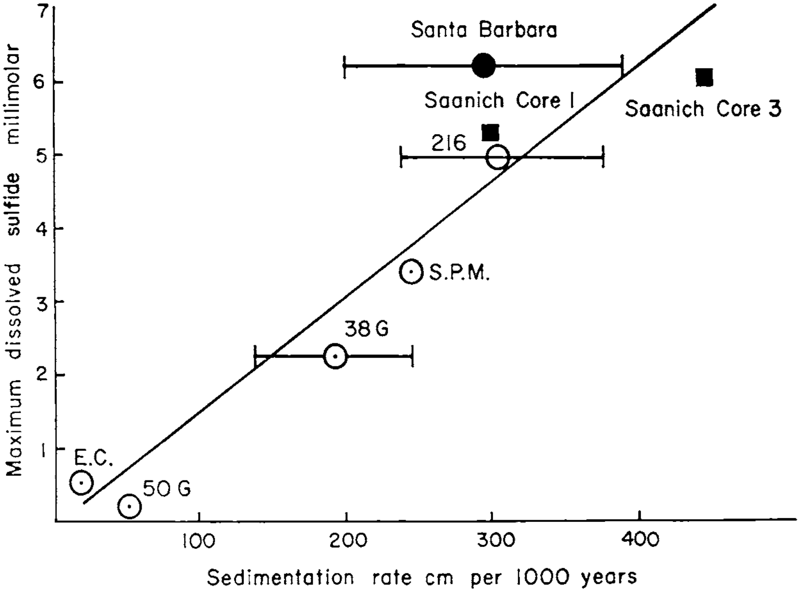

Fig. 19. Plot of maximum dissolved sulfide for cores in which sulfate is essentially completely removed versus sedimentation rate (after Goldhaber and Kaplan, 1975).

Saanich Inlet is in British Columbia; Santa Barbara Basin and Wast Cortes Basin, Southern California borderland; Sal Si Puedes Basin, Carmen Basin, Pescadero Basin, and San Pedro Martir Basin are in Gulf of California.

$$D\frac{\partial^2 s}{\partial x^2} - \omega \frac{\partial s}{\partial x} - R(x) = 0 \tag{14}$$

s = sulfate concentration
D = ionic diffusion coefficient in the sediment
ω = sedimentation rate
R = depth dependent rate of sulfate reduction
x = depth, measured positive-downward below the base of the zone of bioturbation.

For the present calculation the base of the bioturbated zone is taken at 10 cm.

Eq (14) is a special case of a more general one in which such effects as change in porosity with depth and reversible interaction of solutes with sediment particles can be explicitly incorporated (Berner, 1976b; Imboden, 1975; Lerman, 1977). Sulfate, however, interacts only weakly with clay particles in an anion exchange mechanism (Barrow, 1967, 1969), and solute-particle interaction is neglected here. Furthermore, the variation of water content and porosity at the Foam site is sufficiently small to be unimportant in the present context. Eq (14) implies that the sulfate depth profile results from three competing rates (1) transport of matter by diffusion (first term on left) (2) burial of sulfate ion by the accumulating sediment column (middle term), and (3) rate of removal of sulfate by reduction to sulfide. Steady state is assumed. Rather than solving eq 14 analytically, as has been the approach previously, we have employed a simple numerical technique to estimate sulfate reduction rates. The smooth sulfate data (for depths greater than 10 cm) from Foam 20 C were fitted to a higher order polynomial by a least squares routine on an IBM system 370 computer. The resulting polynomial could then be differentiated to obtain expressions for the first and second derivative of sulfate concentration as a function of depth. These were multiplied by the sedimentation rate and diffusion coefficient respectively and then combined as indicated by eq (14) to obtain the rate, R, at various depths. The diffusion coefficient was taken to be 4×10^{-6} cm²/sec, as measured in the present study (the *in situ* sediment temperature was close to 20°C), and the sedimentation rate as 9.6×10^{-9} cm/sec (0.3 cm/yr) as calculated above. This approach has the advantage that it introduces no assumptions on the form of the depth dependence of the sulfate reduction rate (for example, exponentially decreasing with depth) or alternately, its dependence on some other parameter (for example, organic carbon).

Figure 20 is a plot of the sulfate data together with the fitted fourth order polynomial curve;

$$S(x) = 1.95 \times 10^{-5} - 4.72 \times 10^{-7} x + 8.37 \times 10^{-9} x^2 - 9.54 \times 10^{-11} x^3 + 4.06 \times 10^{-13} x^4 \quad (15)$$

It was determined that a fourth order polynomial gave the best fit using as a criterion the sum of the squared deviations of calculated from observed values. Rates of sulfate reduction as a function of depth are contained in table 8, recalculated to units of mM/l/yr. Below 70 cm (model depth) the calculated values become erratic, because errors due to truncation of the polynomial become appreciable. Above 20 cm it is seen that the burial term is less than 10 percent as large as the diffusion term so that the calculated rate at these depths is balanced mainly by diffusion.

The maximum estimated sulfate reduction rate is on the order of 2 mM/l/yr and drops off exponentially with depth. Direct comparison of these calculated values may be made with those obtained in the laboratory. The relevant experiments are DJ 10-20, 20-30, and SJ 11-14, for which rates of 2.2 to 3.2, 2.0 to 3.6, and 2 to 8 mM/l/yr respectively were obtained. Applying the previously discussed temperature coefficient to

TABLE 8

Calculated rates assuming $D = 4.0\times10^{-6}$cm²/sec and $\omega = 0.3$ cm/yr

X;cm*	Rate m mole/l/yr
0	2.2
10	1.5
20	1.0
40	0.25
50	0.08
60	0.03

* Model depth = actual depth − 10 cm

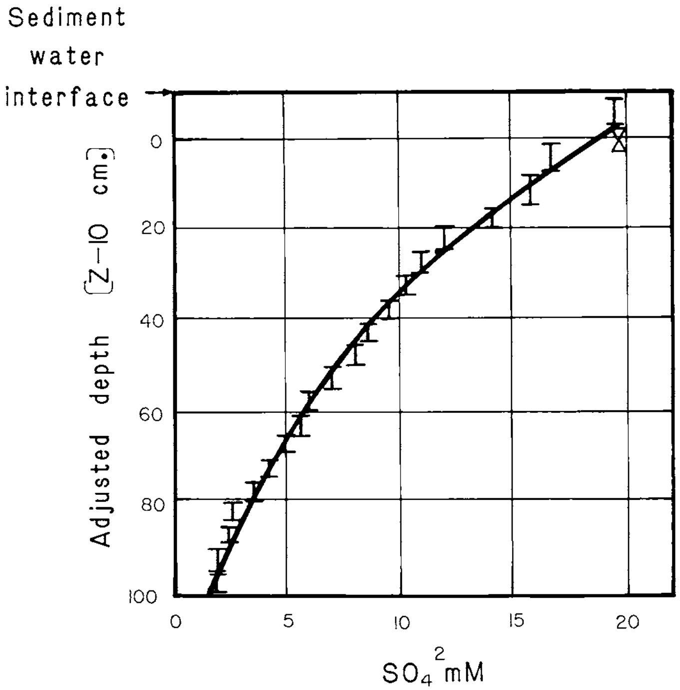

Fig. 20. Pore water sulfate analyses of core 20C. The curve drawn through the data is the fourth order polynomial given by eq 15.

these data, the values become 1.5 to 2.1, 1.3 to 2.4, and 1.3 to 5.4 mM/l/yr respectively. The agreement between predicted and observed rates is quite good particularly considering uncertainties in the jar experiment results (especially SJ 11-14) and the numerous assumptions built into eq (14). The comparison between calculated and measured rates is shown graphically in figures 15 and 16.

The agreement between predicted and observed sulfate reduction rates suggests that: (1) steady state diagenesis is a reasonable assumption at the Foam site; (2) rates of sulfate reduction in sediments can be studied with reasonable accuracy by means of jar experiments; and (3) there is unappreciable bioturbation below 10 cm at the Foam site and that transport of sulfate, relative to surrounding sediment grains, occurs solely by molecular diffusion. Measurements of pore water sulfate profiles at the Foam site are continuing in order to test the steady state assumption.

Summary and conclusions.—Pore water profiles of biogeochemically active constituents in the upper 10 cm of the "Foam" site in Long Island Sound were shown to have a complex time and depth dependent behavior. During the summer months, the following features were observed: (1) A thin zone (upper 1 or 2 cm) of rapid transition between bottom water values of SO_4^{2-}, HCO_3^-, and PO_4^{3-} and those more typical of pore fluid.

The direction of these changes suggest that they are brought about by anaerobic metabolism. (2) A second zone, between 1 to 8 cm in which these pore water constituents, although modified from bottom water concentrations, do not change markedly with depth. (3) The absence of dissolved sulfide from depths shallower than 8 cm. Winter pore water profiles from the upper 10 cm are distinct from summer ones in that they show smooth gradients qualitatively similar, for example, to those reported by Sholkovitz (1973) from the central deep of Santa Barbara basin (a low oxygen, benthos-inhibiting environment). Below 8 cm, the pore water constituents measured show distributions consistent with progressive diagenesis involving sulfate reduction (for example, SO_4^{2-} decrease, NH_4^+ and alkalinity increase).

The above pore water features were interpreted with the aid of "jar" experiment data, designed to yield information on rates of bacterial sulfate reduction. These results demonstrate that sulfate reduction rates are quite rapid near the sediment surface (77 mM SO_4^{2-}/l/yr at room temperature) but drop off exponentially with depth to values near 2 mM/l/yr at a depth of around 10 cm. In particular, though, the rate data demonstrate that sulfate reduction ought to occur quite rapidly in the interval 1 to 8 cm in which no decrease in sulfate concentration is observed for summer profiles. This discrepancy is reconciled if sulfate and/or oxygen can be supplied from overlying water into sediments via the activities of macroinfaunal organisms. Such organisms were observed in large numbers at the FOAM site and are dominated by the deposit-feeding polychaete worm *Nephtys incisa*. Infauna may affect pore water chemistry by irrigation of burrows or by mixing of sediment-pore water during feeding. By invoking a simple flux constraint, it is possible to demonstrate that summer transport of sulfate by such processes is at least five times more rapid than ionic diffusion. Even as rapid as this transport appears to be, bacterial metabolic rates in the upper 1 to 2 cm are sufficiently vigorous that water passing through this interval is chemically modified from that present in overlying seawater. In addition to transport of solutions, organisms also affect the transport of particles. Tentative evidence is advanced, however, that at the FOAM site, particle transport is not quantitatively important. If this is so, it is possible to show by comparison of observed abundances of solid phase sulfur to the integrated rate of sulfate reduction that sulfide sulfur is lost from the sediment column. During the winter, the activities of macroinfauna and microorganism decrease. Under these conditions, upper layer pore water profiles assume shapes indicating that diffusion is the dominant transport mechanism rather than bioturbation.

In order to treat quantitatively the deeper (than 8 cm) sulfate profiles, it was necessary to have data on the sedimentation rate at the FOAM site as well as the ionic diffusion coefficient of sulfate. Sedimentation rate was estimated using arguments regarding the timing of anthropogenic metal input, rate of pore water ammonia generation, and maximum concentration of dissolved sulfide. All three approaches are consistent with a value of 0.3 ± 0.1 cm/yr. Direct measurements of the sulfate ion diffusion coefficient were made under conditions very closely approximating *in situ* conditions. Two plugs of FOAM sediment, one cut from near surface and one cut from a deeper layer, were juxtaposed, and the ions allowed to diffuse against each other, thus allowing counter diffusion of HCO_3^- and SO_4^{2-}. Measured values fall in the range 2.4 to 4.5×10^{-6} cm²/sec over the temperature range 6° to 20°C respectively. Using the above sedimentation rate and diffusion coefficients, sulfate reduction rates were calculated from pore water sulfate profiles using a numerical technique. These rates decrease with depth and are in the range 2.2 to 0.03 mM/l/yr. Measured results from jar experiments are in reasonable accord with the calculated values at comparable depths. This agreement suggests that mathematical modeling is a valid approach to calculation of rates of diagenetic reactions involving pore water constituents.

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APPENDIX

Sulfate diffusion in sediment

The purpose of this section is to discuss in greater detail the theoretical basis for the experimental measurement of sulfate diffusion coefficients and the applicability of such measurements to natural sediments. Determination of the diffusion coefficient of sulfate in sediment pore water can be made based on measurements of the concentration of SO_4^{2-} in a system consisting of two cylindrical cells filled with sediment and joined together such that the following initial conditions prevail:

$$\begin{aligned} C &= C_0,\ x < 0,\ t = 0 \\ C &= 0\ ,\ x > 0,\ t = 0 \end{aligned} \tag{A1}$$

where C = concentration of dissolved sulfate in terms of mass per unit volume of pore water
x = distance from the interface (x = 0) between the cells
t = time

Diffusion proceeds from the cell containing sulfate (x < 0) to that without sulfate (x > 0) according to Fick's second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{A2}$$

where D = whole sediment diffusion coefficient for sulfate, which includes the effects of tortuosity. This equation applies only when simple diffusion occurs without equilibrium adsorption (Duursma and Hoede, 1967). This is reasonable for SO_4^{2-}, which does not readily adsorb to clay minerals (Li and Gregory, 1974). For the boundary conditions:

$$\begin{aligned} C &= C_0, \; x = -\infty \\ C &= 0, \; x = +\infty \end{aligned} \tag{A3}$$

the solution to eq A2 is (Crank, 1956, p. 14):

$$C(x,t) = \tfrac{1}{2}C_0 \operatorname{erfc}\,(x/2\sqrt{D\,t}) \tag{A4}$$

where erfc is the error function complement.

An expression for experimentally determining D results from eq A4 evaluated according to Fick's first law. For sediments (Berner, 1976b),

$$J_{x=0} = -D\,\phi\left(\frac{\partial c}{\partial x}\right)_{x=0}$$

where $J_{x=0}$ = flux of sulfate across the interface between the cells.
ϕ = sediment porosity

Now from eq A4,

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{-C_0}{2\sqrt{\pi D t}}$$

$$J_{x=0} = \frac{C_0\,\phi\,\sqrt{D}}{2\sqrt{\pi\,t}}$$

The total amount of sulfate that has diffused from one cell to the other, M_2, is given by the flux integrated over the length of time diffusion has taken place:

$$\begin{aligned} M_2 &= \int_0^t \alpha\, J_{x=0}\, dt \\ &= \alpha\,\phi\,C_0\sqrt{\frac{Dt}{\pi}} \end{aligned} \tag{A5}$$

where α = cross-sectional area of a cell.

For the initial conditions of eq A1 the amount of interstitial sulfate originally present in the system, M_1, is

$$M_1 = h\,\alpha\,C_0\,\phi \tag{A6}$$

where h = length of one cell.

Thus the fraction of sulfate that has diffused from one cell to the other is:

$$f = \frac{M_2}{M_1} = \frac{\sqrt{Dt}}{h\sqrt{\pi}}$$

and

$$D = \frac{h^2\,f^2\,\pi}{t} \tag{A7}$$

In practice, for a cell of finite length, h, eq A7 is still valid if the boundary conditions

$$\begin{aligned} C &= C_0, \; x = -h \\ C &= c_0, \; x = +h \end{aligned} \tag{A8}$$

with $c_0 << C_0$ are satisfied throughout the course of an experiment.

The validity of eqs A4 and A7 for determining the diffusion coefficient of sulfate in the interstital water of sediment was checked by using artificial sediment consisting of a mixture of kaolinite and a small amount (5 percent) of clean quartz sand with sulfate and sulfate-free solutions mixed to a water content of 50 percent by weight. The sediment-solution mixtures were each put into cylindrical lucite cells 5 cm long and 5 cm in diameter, and the cells were joined with a piece of filter paper between them to prevent physical mixing of sediment. Several experimental situations were considered:

1. SO_4^{2-} —HCO_3^- counter-diffusion: NaCl solution with an ionic strength similar to that of seawater and containing 28 mM Na_2SO_4 was mixed with kaolinite and paired with a similar NaCl solution containing sufficient $NaHCO_3$ to equal the excess negative charge of sulfate in the other solution.

2. Na^+—SO_4^{2-} codiffusion: The SO_4^{2-} solution from situation (1) was used. Na^+ and SO_4^{2-} gradients were created by mixing kaolinite with sulfate-free solution and pairing the two sediment-solution mixtures.

3. Ca^{2+},SO_4^{2-} — NH_4^+, HCO_3^- counter-diffusion: Gradients in Ca^{2+} and SO_4^{2-} were matched with counter gradients in NH_4^+ and HCO_3^- to simulate the effects of sulfate reduction, calcium precipitation, and ammonia formation in anoxic sediments. The SO_4^{2-} and NH_4^+ concentrations (in NaCl solution) were chosen to be typical of those found near the surface and at depth, respectively, in anoxic sediment pore water. The HCO_3^- and Ca^{2+} concentrations initially equalled the excess charge due to SO_4^{2-} and NH_4^+ respectively.

Figure A1 shows the interstitial SO_4^{2-} profile in kaolinite for SO_4^{2-}—HCO_3^- counter-diffusion allowed to proceed for 3 weeks in 15 cm long cells. The data are well fit by the error function expression of eq A4 with $D = 3.6 \times 10^{-6}$ cm²/sec. The validity of the diffusion coefficients calculated from eq A7 depends partly on whether the boundary conditions of eq A8 hold throughout an experiment. Eq A7 implies (for constant D) that f should vary linearly with respect to $t^{1/2}$. Figure A2 plots f versus $t^{1/2}$ for a series of SO_4^{2-}—HCO_3^- counter-diffusion experiments run at 19°C in 5 cm long cells. A linear f versus $t^{1/2}$ relationship obtains for $t \leqq 7$ days and $f < 0.18$ at 19°C.

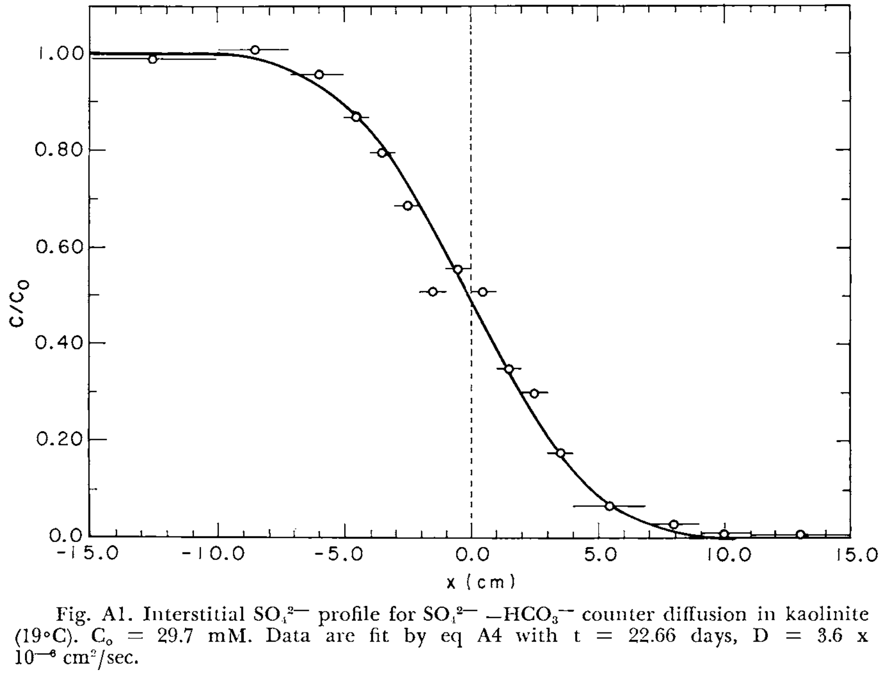

Fig. A1. Interstitial SO_4^{2-} profile for SO_4^{2-} —HCO_3^- counter diffusion in kaolinite (19°C). C_o = 29.7 mM. Data are fit by eq A4 with t = 22.66 days, D = 3.6 x 10^{-6} cm²/sec.

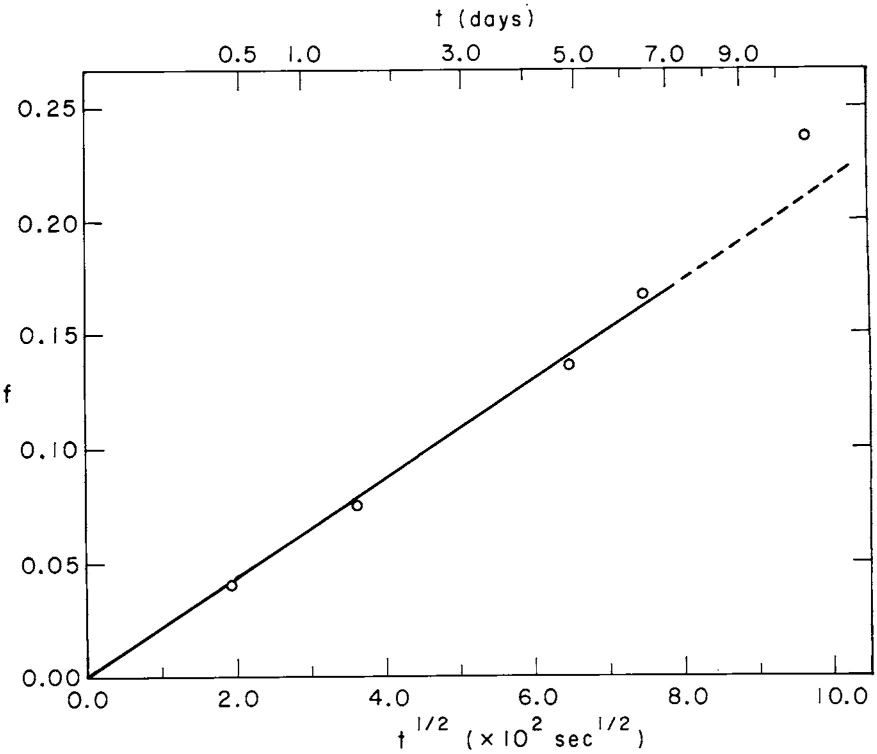

Fig. A2. Fraction of sulfate diffused (f) versus $t^{1/2}$ for a series of SO_4^{2-} $-HCO_3^-$ counter diffusion experiments in kaolinite (19°C). Solid line corresponds to D = 3.7 x 10^{-6} cm^2/sec.

Table A1 gives the results of sulfate diffusion experiments under the various conditions considered. Although there is a suggestion that the SO_4^{2-}—HCO_3^- counter diffusion coefficient is slightly less than that for the other two cases, on the whole relatively little variation is observed between the three situations. This indicates that, at the level of accuracy of the present study (and most other sediment studies), estimates of the sulfate ion diffusion coefficient are not dependent upon a detailed consideration of the codiffusing or counter-diffusing ions as maintained by Ben-Yaakov (1972).

TABLE A1

Sulfate diffusion in kaolinite (50 percent water)

		t (x10^4 sec)	f	D (x10^{-6} cm^2/sec)
SO_4^{2-}—HCO_3^- counter-diffusion				
	7°C	102	0.158	2.01
	19°C	42.1	0.137	3.66
SO_4^{2-}—Na^+ codiffusion				
	7°C	57.0	0.142	2.77
	19°C	13.1	0.079	3.90
(SO_4^{2-}, Ca^{2+})—(NH_4^+, HCO_3^-) counter-diffusion				
	7°C	37.4	0.116	2.70
	19°C	52.5	0.161	3.86

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