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Reeburgh, WS

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RATES OF BIOGEOCHEMICAL PROCESSES IN ANOXIC SEDIMENTS

William S. Reeburgh

Institute of Marine Science, University of Alaska, Fairbanks,
Alaska 99701

INTRODUCTION

A new type of study has appeared in the interstitial water literature during the last five years. Guided by microbial ecologists and aided by newly developed analytical techniques from organic geochemistry, direct measurements of a number of remineralization rates have been made in sediments using incubation and stable and radioisotope tracer techniques. These measurements have enormous potential to both confirm and extend the diagenetic models that have been used so successfully during the past decade. These techniques will probably emerge as one of our most effective tools in elucidating the controls on early diagenetic reactions. Since these reaction rate measurements are just beginning, and since the potential is high for great leaps in understanding (as well as misunderstanding), it is important that they be consolidated and presented as an easily compared unit.

This review has several goals. First, since most of these direct rate measurements are scattered throughout the literature of microbial ecology and oceanography, it summarizes and consolidates the measurements so that comparisons between environments and studies can be made conveniently. Second, it compares the results of these direct rate measurements with those predicted by models. Third, it attempts to show the importance of various reactions to total sediment metabolism. Fourth, it presents some perspectives and insights on how future rate measurements should be conducted to insure ready comparison between studies and environments.

The results of the studies summarized here are presented in tables; I have attempted to include the most recent work on sediments. The reported rates

or rate constants have not been extended beyond conversion to uniform units. Since the water contents of most of the sediments considered here are high, no distinctions have been made in results reported in interstitial water and sediment volume units. Studies of the turnover of specific compounds are only included in the tables when they are accompanied by pool size or concentration measurements. Turnover measurements are invaluable in determining reaction pathways and products, but without knowledge of the ambient concentration of the compound studied they give no information on the importance of a transformation to the sediment system. This review does not emphasize a number of important and related subjects, namely, inorganic reactions such as those reviewed recently by Gieskes (1975, 1981) and Manheim & Sayles (1974) for Deep Sea Drilling Project sediments, chronologies (Goldberg & Bruland 1974), sampling methods (Kriukov & Manheim 1982), bioturbation (Aller 1978, Guinasso & Schink 1975), irrigation (Grundmanis & Murray 1977), and studies of bacterial identities, numbers, and physiology (Jørgensen 1978c, Karl 1982).

Studies on the composition of interstitial waters provide a key to many problems in early diagenesis. Interstitial waters are particularly attractive for study because conditions in the interstitial environment, such as limited mixing and circulation, a high surface:volume ratio, and an abundant supply of organic detritus, support large microbial populations, which in turn lead to large chemical composition changes. Studies on interstitial waters from a variety of lacustrine, estuarine, and deep-sea environments are reported in an extensive literature that has been periodically reviewed in chapters and articles (Glasby 1973, Manheim 1976, Gieskes 1981) and in a number of books (Berner 1971, 1980, Kaplan 1974, McCave 1976, Fanning & Manheim 1982). Fenchel & Jørgensen's (1977) review of the role of bacteria in detritus food chains, Fenchel & Blackburn's (1979) book, and Karl's (1982) article are particularly valuable in the context of this review.

ENVIRONMENTS

Since many of the studies summarized here have been conducted in a limited number of coastal environments, some of the important characteristics of the most familiar and frequently cited are summarized in Table 1. It should be noted that the most important parameter in driving the remineralization processes summarized in this paper—the flux of organic carbon—is rarely measured directly; it is usually estimated from budgets and sedimentation rates. This, plus a lack of information on the composition and properties of the organic matter that actually reaches the sediments, is one of our major knowledge gaps.

These environments are not important from a global mass balance

Table 1 Characteristics of frequently studied anoxic sediment environments

Location	Depth (m)	Sedimentation rate (cm yr ⁻¹)	Carbon content (% dry wt)	Temperature (°C)	Water column O ₂	Bioturbation	SO ₄ ⁼ reducing zone thickness (cm)	Carbon flux to sediments (mmole cm ⁻² yr ⁻¹)
Chesapeake Bay (Reeburgh 1969)	30.4 (858-C) 15.2 (858-D)	0.1–1.0	3	4–25	oxic	+	30	—
Santa Barbara Basin (Sholkovitz 1973)	590 (450–475 m sill)	0.4	2–3	6.2–6.4	0.05–0.1 ml L ⁻¹	—	200–300	—
Limfjorden (Jørgensen 1977)	4–12	0.2	1–13	0–20	summer anoxia	+	>140	1.42
Cariaco Trench (Reeburgh 1976)	1300–1400 (150-m sill)	0.05	4	16.7	permanent anoxia	—	45–50	0.1
Long Island Sound (Goldhaber et al 1977, Martens & Berner 1977, Rosenfeld 1981)	9 (FOAM)	0.3	1.5–2	4–28	oxic	+	20	—
Cape Lookout Bight (Martens & Klump 1980, Chanton 1979, Klump 1980)	10	8.4–11.6	3.5–4	5–28	oxic	+ winter — summer	10–20	11.1
Saanich Inlet (Murray et al 1978, Anderson & Devol 1973)	225 (70-m sill)	1.3	3–4	9	anoxic ~8 mo yr ⁻¹	—	20	0.54
Skaneateles Bay (Reeburgh 1980)	65 (10-m sill)	0.7–0.8	2–3	4	intermittent anoxia (late summer)	—	20	0.36

standpoint, but they are important because they represent a range of end-member environments where sulfate reduction and methanogenesis are occurring. Further, because they are convenient to study and since so much is already known about them, they seem logical environments for future studies of the remineralization of organic matter. Even though several environments appear to be nearly isothermal (Santa Barbara Basin, Saanich Inlet), the fact that their sediments are varved indicates that inputs are not uniform in time and that seasonal variations in the organic and inorganic inputs are a characteristic of all of the environments listed. Only a few seasonal studies on sediments have been performed.

REACTION SEQUENCE AND CAPACITY

It is generally recognized that organic matter degradation in sediments proceeds using the available oxidant producing the greatest free energy. Several authors have summarized energy yields and reaction sequences by considering oxidation of glucose (Claypool & Kaplan 1974) or hypothetical compounds such as CH_2O (Berner 1980) and the Redfield molecule, $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$ (Froelich et al 1979, Emerson et al 1980). Organic matter degradation has been observed to follow this sequence of reactions, with each successive reaction starting when the previous oxidant is either exhausted or chemical and biological conditions allow a particular community of organisms to become active.

Portraying the oxidizing capacity of a partially open dynamic system like sediments is difficult, but it can be approached by considering a closed system. The distribution and concentration of species under a range of redox conditions may be shown with log concentration vs $p(e)$ diagrams (Stumm & Morgan 1981, Breck 1974) or with log concentration vs pH + $p(e)$ diagrams (Lindsay 1979), but these tend to become complicated when the commonly encountered oxidants and their products are plotted together. The above approaches imply that we know more about reactions in sediments than we actually do.

Table 2 illustrates the organic matter oxidizing sequence and capacity of marine sediments by summarizing $p(e)$, Eh, and energy yield values from previous references and by also considering a hypothetical sediment that presents dissolved and solid-phase oxidants in comparable concentration units. This sediment has an oxygen-saturated seawater content of 85% and a density of 1.1 g cm^{-3} . Whole sediment concentrations for the hypothetical sediment were obtained using appropriate proportions of the typical dissolved and solid-phase constituents. The oxidation capacity values were derived using Berner's (1980) stoichiometry for CH_2O oxidation. This example is also unrealistic because it considers a closed, homogeneous

Table 2 Sequence and capacity of organic matter oxidation processes important in marine sediments

Reaction	p(e)	Eh (mv)	Energy yield (KJ mole ⁻¹ CH ₂ O ^a)	Typical concentration (mM)	Concentrations in hypothetical sediment (mmole L ⁻¹ sed.)	CH ₂ O oxidizing capacity (mmole L ⁻¹ sed.)	Depth scales in typical environments Low CH ₂ O flux High CH ₂ O flux
O ₂ reduction	12.1-12.5	720-740	-475	0-0.09	0-0.85	0-0.85	0-1 cm
Denitrification	~12	710	-448	0-0.04	0-0.037	0-0.03	15 cm
Mn(IV) → Mn(II)	8.0	470	-349	ΣMn: ≥ 1.5% in deep sea (0.27 mmole g ⁻¹) 0.15% in Skan Bay (0.027 mmole g ⁻¹)	43.2	21.6 (?)	15-30 cm
Fe(III) → Fe(II)	1.0	60	-114	ΣFe: ≥ 4.0% in deep sea (0.7 mmole g ⁻¹) 2.0% in Skan Bay (0.35 mmole g ⁻¹)	4.3	2.2 (?)	≥ 1 m
Sulfate reduction	-3.8	-200	-77	0-30	112	28 (?)	20+ cm
Methanogenesis (fermentation)	-4.2	-250	-58		56	14 (?)	
					0-28.2	56.4 (?)	10+ cm 25+ cm
			Dissolved organic carbon	1-7	0.95-6.5		
			Particulate organic carbon	4% (3.3 mmole g ⁻¹)	528		

^a 1 KJ = 0.239 Kcal.

system, neglects diffusive supply and recycling, and overestimates the concentration of dissolved oxygen and nitrate. Table 2 shows clearly how minor additions of organic matter can overwhelm the oxygen reduction and denitrification capacity. It also shows that sulfate reduction, which is the principal difference between freshwater and marine sediments, is the dominant process because of its large capacity. The comparison of Sørensen et al (1979) experimentally demonstrates the dominant oxidizing capacity of sulfate reduction in marine sediments. The table also points out our poor understanding of the role of Mn and Fe oxides in these sediments. We lack knowledge of how much of the total amount reported is available for redox reactions and whether microbial mediation of Mn and Fe is important in oxidation of organic matter.

The right-hand column of Table 2 shows typical depth scales for this sequence of generalized reactions in two end-member environments; the low organic flux example is the pelagic sediment suboxic diagenesis study of Froelich et al (1979), and the high organic flux example is typical of the environments summarized in Table 1. The depth interval over which sulfate reduction takes place is shown in more detail in Table 1. Bioturbation and irrigation have the effect of increasing rates (Aller 1978, Aller & Yingst 1980) and physically thickening the zones of all reactions preceding sulfate reduction in high organic flux coastal sediments.

MODELS

Two broad classes of models are used in the interpretation of diagenetic processes in interstitial waters: one-dimensional diffusion-advection-reaction models, and analog models that consider decomposition processes in sediments using the rumen (Hungate 1975, Wolin 1979) and sewage digesters (Hobson et al 1974) as model systems. The diagenetic models describe depth distributions of reactants or products without regard to specific reactions or mechanisms, while the analog models draw on a wealth of experience to predict intermediates and products.

The diagenetic models have been developed and extended in a series of papers and books by Berner (1964, 1971, 1974, 1976a, 1980, 1981). These models consider diffusion, advection due to sedimentation, and reaction at steady state in equations similar to the following:

$$\frac{dC}{dt} = \frac{D\partial^2 C}{\partial x^2} - \frac{\omega\partial C}{\partial x} - kC = 0,$$

where C is concentration, t is time, x is distance (positive downward), D is diffusivity, ω is sedimentation rate, and k is a first-order rate constant. Corrections for porosity and sorption are usually applied to the diffusivity.

Values for the diffusivity have been measured for common ionic species (Li & Gregory 1974, Goldhaber et al 1977, Krom & Berner 1980a, Hesslein 1980) and hydrocarbons (Sahores & Witherspoon 1970). Adsorption is incorporated in these models (Berner 1974, 1976b) using a term of the form

$-(1 + K) \frac{\omega \partial C}{\partial x}$, where K is an adsorption coefficient. Adsorption coef-

ficients have been measured experimentally by Rosenfeld (1979), Klump (1980), and Krom & Berner (1980b) and modeled by Murray et al (1978). Sedimentation rates using excess lead-210 (Goldberg & Bruland 1974) have been determined as part of many of the investigations reviewed here. Depth distributions of concentrations are sampled with a variety of squeezing, centrifugation, or equilibration techniques. The ability to measure or readily estimate most of the terms in the diagenetic equation has led to wide use of these mathematical diagenetic models to estimate reaction rates. Variations with depth in diffusivities and reaction rate constants are recognized to be important (Jørgensen 1978b), but are usually not determined.

Since so much is known of the microbial ecology of ruminant digestion and, to a lesser extent, sludge digestion, these systems are convenient analogs in studies of the remineralization of complex organic matter. The range of organic molecules utilized by bacteria that mediate processes like sulfate reduction and methane production is usually limited (Fenchel & Blackburn 1979), so these organisms are dependent on a complex community of fermentative bacteria to supply the necessary substrates. The complex biopolymers present in organic detritus reaching the sediments are initially hydrolyzed to amino acids, simple sugars, and long chain fatty acids. These are in turn converted to volatile fatty acids and eventually to carbon dioxide and methane. The rumen functions with a variety of rations and organisms to maximize microbial biomass and production of volatile fatty acids, which are absorbed by the animal. Digesters are operated to maximize gas production. Microbial communities in sediments appear to operate within narrow environmental and substrate limits, and are probably maximizing their numbers or biomass. Analogies between the rumen, sludge digesters, and sediments break down in several ways, namely (a) our lack of knowledge of the amount and composition of carbon entering the sediments, as well as the extent of reaction, (b) the presence in marine sediments of large quantities of sulfate, which is a relatively minor rumen and sludge component, (c) the high ($\sim 39^\circ\text{C}$) and uniform temperature of the rumen, and (d) the vast differences in substrate concentrations and supply rates, residence times, and mixing rates. Unmetabolized and recalcitrant organic components remain in the sediments, and molecular weight depth distributions (Krom & Sholkovitz 1977, Krom & Westrich

1981) suggest they repolymerize below the sulfate reducing zone to form high-molecular-weight dissolved organic matter and eventually humic and fulvic materials.

One very important aspect of the above microbiological studies is the availability of specific inhibitors for groups of organisms and specific transformations. The ability to experimentally inhibit and manipulate processes is rare in the Earth Sciences, where the scales of processes force us to be passive observers. The use of specific inhibitors combined with models and careful observations provides a powerful approach to understanding the biogeochemistry of sediments.

RATE MEASUREMENTS

The rate measurements summarized in this review represent an attempt to determine the importance of various transformations in total sediment metabolism, and thus have a system rather than an organism or mechanism focus. They deal with complex mixed bacterial populations and multiple substrates, and while they fail to do justice to previous careful work on enzyme and microbial kinetics (Lehninger 1975), they do give a good picture of chemical dynamics in natural systems (Fenchel & Blackburn 1979). The rate measurements reported here fall into two broad categories: time-series incubations in isolated sediments, and turnover rate measurements involving additions of labeled tracer compounds.

The time-series incubations or jar experiments have been used to determine rates of sulfate reduction (Martens & Berner 1974, Goldhaber et al 1977), ammonia production (Rosenfeld 1981), and methane production (Crill 1981). Homogenized sediment from desired depths is sealed in jars and analyzed sequentially for consumption of oxidant or appearance of end products. These experiments are typically conducted over a period of weeks or months.

Experiments involving addition of stable or radioisotope tracers have much greater sensitivity and thus can be conducted with incubation times of minutes to hours. One of the most compelling reasons for using tracer methods is their ability to measure transformation rates of intermediates, which undergo further reactions and do not accumulate in sediments.

All of these rate determinations using tracers fall under the term *turnover rate*; the guidelines of Zilversmit (1955) are used in this review to eliminate confusion in terminology. The turnover rate is the amount of material transformed per unit time and is equivalent to the amount of material entering or leaving a pool. The turnover rate is the product of the in situ pool size or concentration and a fractional turnover rate or first-order rate constant. For a labeled pool, the fractional turnover rate equals $a/A\Delta t$,

where A is the initial pool activity, a is the turned-over activity or the activity of a reaction product, and Δt is the incubation time. Fractional turnover rates determined in tracer experiments are generally referred to as turnover rate constants. Turnover rates are also calculated from experimentally determined first-order rate constants, the slope of a $\ln$ tracer activity vs time plot. Fractional turnover rates give no information on the order of a reaction, but are generally equivalent to first-order rate constants for slow reactions or large pools. Since attention is experimentally restricted to one particular molecule, first-order rate constants in complex systems are very likely pseudo-first-order. The turnover time is the reciprocal of the fractional turnover rate. Since there are large variations with depth for most of the experimentally determined rates, they are often integrated with depth and expressed in flux units, permitting comparisons between environments and reactions.

Since there is ample time for competing reactions to occur, results from jar experiments such as ammonia production and methane production probably yield net rates. Rates determined with isotope tracers are probably nearer to gross rates. Sorption of added tracer has been shown to be a serious complication in turnover rate determinations of volatile fatty acids (Christensen & Blackburn 1982) and amino acids (Christensen & Blackburn 1980). Rate constants for sorption were determined in both of these studies using short-term experiments with high specific activity tracers. The overall turnover rates were corrected for sorption. Many of the turnover rate measurements are correctly identified as "potential" (Sørensen 1978a,b) or "apparent" (Sansone & Martens 1981a,b) and should be regarded as such until we can demonstrate with models and more experiments that the measurements themselves do not perturb the sediment system. Karl (1982) has emphasized the importance of determining exactly what these tracer experiments are measuring.

Jørgensen's (1978a,b) papers on sulfate reduction rate determinations in sediments provide some of the clearest descriptions of how these measurements should be conducted and what precautions should be taken. The technique involves injection of a sediment core with microliter quantities of a $^{35}\text{SO}_4^-$ tracer solution through silicone rubber septa located along a plastic core tube. The core is incubated, killed by freezing, and cut into segments for analysis. The radioactivity of sulfate and sulfide as well as the concentration of sulfate are determined in each segment. Slight modifications involving use of segmented core liners (Reeburgh 1980) or incubation in syringe subcores (Devol & Ahmed 1981) have been reported.

Ideally, the sediment cores should be disturbed as little as possible to preserve zonation and to avoid perturbing the obligate anaerobes present. It is not necessary to homogenize a high specific activity tracer in the

sediment so long as the tracer added and the product formed are retained in the core segment and the form and fate of the tracer are known. Jørgensen (1978a) performed parallel sulfate reduction rate measurements using homogenized and diluted sediment (Sorokin 1962) and reported rates 2 to 30 times lower than those obtained with the core injection technique. Ansbaek & Blackburn (1980) reported a decrease in the acetate turnover rate of 50–75% when the sediment was homogenized. Christensen & Blackburn (1980) obtained similar results for core injection and homogenized tracer experiments with alanine. The effects of concentration increases resulting from use of lower specific activity tracer has been investigated by Christensen & Blackburn (1980) and Ansbaek & Blackburn (1980). Increasing tracer concentrations decreased the acetate and alanine rate constants in both of these studies. The rate measurements summarized here are reported in the same order as their occurrence, proceeding downward in sediments. Since the type of experiment is important in interpreting these sediment rate measurements, as much experimental detail as possible is included in the tables. The rates are tabulated as turnover rates ($\text{mmole liter}^{-1} \text{yr}^{-1}$; mM yr^{-1}) or as depth integrated rates, which are useful in comparing the magnitudes of different processes and have the same units ($\mu\text{mole cm}^{-2} \text{yr}^{-1}$) as fluxes. Results from the amino acid and volatile fatty acid turnover rate measurements are reported in $\mu\text{M hr}^{-1}$.

Oxygen Reduction

Dissolved oxygen is supplied to sediments by mixing or diffusion from overlying waters. Oxygen consumption rates have been measured using cores (Pamatmat 1971), or a variety of diver-operated or free-vehicle benthic respirometers (Smith 1978, Hinga et al 1979). Oxygen consumption rates are often partitioned into community and chemical rates by poisoning with formalin. These rates range over three orders of magnitude with depth (Hinga et al 1979, figure 5), from less than 1 to about $1200 \mu\text{moles cm}^{-2} \text{yr}^{-1}$. Oxygen reduction is probably confined to the uppermost centimeter of anoxic sediments, and oxygen supplied by the overlying water produces these high integrated rates.

Depth distributions of oxygen concentration have been reported in equatorial red clay and calcareous oozes by Murray & Grundmanis (1980). Oxygen was present in concentrations that were never less than $50 \mu\text{M}$ in the upper 50 cm of these low organic carbon flux deep-sea sediments. Detailed depth distributions of dissolved oxygen in the surface portions of high organic content sediments have been measured with microelectrodes (Revsbech et al 1980a,b). These electrodes are so small that they require no stirring; depth distributions are obtained by advancing them into sedi-

ments with micromanipulators. These electrodes may be used to measure detailed oxygen gradients over distances of less than a centimeter.

Denitrification

Table 3 summarizes recent denitrification rate measurements in marine sediments, covering environments ranging from deep-sea to coastal sediments. Denitrification was reviewed recently by Knowles (1982); it is of limited significance in terms of oxidizing capacity (Table 2) because of low nitrate concentrations in sediments. The perspective in most of the studies reported here is of denitrification as a process important in completing the nitrogen cycle, rather than as a source of oxidizing capacity.

Denitrification rates are measured by a wide variety of methods, including direct observation of increases in N_2 (Wilson 1978, Kaplan et al 1979), labeling with $^{15}NO_3^-$, and experiments involving addition of the inhibitor acetylene, which blocks reduction beyond N_2O (Sørensen 1978a). Excluding the N_2 production and model determinations, all methods involve homogenizing depth intervals of the sediment to distribute either inhibitors or tracers. The NO_3^- pool is usually increased to concentrations well above ambient in experiments involving $^{15}NO_3^-$. Oren & Blackburn (1979) determined Michaelis-Menten kinetic parameters on dilutions of the sediment and corrected the "potential" rate measurements obtained at nitrate saturation to in situ levels.

Denitrification is one of a number of nitrogen transformations taking place near the sediment surface. Billen (1978) modeled ammonification, nitrification, and denitrification rates in North Sea sediments and obtained reasonable agreement with observed rates.

Metal Oxide Reduction

Iron and manganese are added to sediments predominantly as oxidized particles and together they have one of the highest capacities for oxidizing organic matter in marine sediments (Table 2). Reduced mineral phases of manganese and particularly iron occur extensively in sediments, so the oxidizing capacity is presumably used in sediments. The role of metal oxides in the oxidation of organic matter is poorly understood and rate measurements comparable to those reviewed here are not available. Depending on their physical availability, these oxides may be reduced inorganically (Stumm & Morgan 1981) and operate by cycling other reduced compounds. Organisms capable of reducing iron and manganese oxides have been cultured from soils and lake sediments. Their activities are summarized by Ehrlich (1981), but their importance in reducing iron and manganese oxides is not clear.

Sørensen (1982) measured Fe(III) reduction in slurries of marine

Table 3 Denitrification rates in sediments

Study/Location	Method	Rate		Comment
		mM yr ⁻¹	μmole cm ⁻² yr ⁻¹	
Bender et al (1977) Guinea Basin	NO ₃ ⁻ profile, model	—	2.5	flux across sediment interface downward flux in sediments
Wilson (1978) Atlantic Ocean	N ₂ excesses	—	0.11 0.5, 0.189 av	
Billen (1978) S. Bight, N. Sea	consumption rate of NO ₃ ⁻ spike	23–205	—	
Sørensen (1978a,b) Randers Fjord (a)	C ₂ H ₂ inhibition	12.7	—	
Limfjorden (b)	¹⁵ NO ₃ ⁻ → N ₂	36–317	—	
Koike & Hattori (1978) Manguko-Ura	¹⁵ NO ₃ ⁻ → N ₂	1.3–96	—	
Kaplan et al (1979) Great Sippewissett Marsh	N ₂ production	—	0.88–1.77	seasonal study
Oren & Blackburn (1979) Kysing Fjord	¹⁵ NO ₃ ⁻ → N ₂ ; corrected w/V _{max} , K _m	0.7–4.5	—	
Koike & Hattori (1979) Bering Sea shelf	¹⁵ NO ₃ ⁻ → N ₂	10.5 (av)	—	

sediment along with denitrification and sulfate reduction. Ferric iron reduction was inhibited by additions of NO_3^- or NO_2^- , but resumed when the additions were depleted. Inhibition of sulfate reduction with molybdate did not affect Fe(III) reduction. Sørensen concluded that iron reduction was associated with facultative nitrate-reducing bacteria and that the process may be important in sediments at low NO_3^- concentrations.

Sulfate Reduction

Sulfate reduction has the largest organic matter oxidizing capacity of any process occurring in marine sediments (Table 2). The presence of large quantities of sulfate in marine systems leads to large differences in the sequences of reactions between marine systems and lakes.

Some of the most recent sulfate reduction rate measurements in marine sediments are summarized in Table 4. Jørgensen & Fenchel (1961) developed methods for the study of a model system and summarized some of the early tracer and incubation determinations of sulfate reduction rates. Goldhaber & Kaplan (1974, 1975) reviewed the sulfur cycle and factors controlling the sulfate reduction rate. Their work reports sulfate reduction rates, largely from model determinations.

Measurements of sulfate reduction rates in sediment have been demonstrated (Jørgensen 1978a,b) to be reliable and are used widely. Since $^{35}\text{SO}_4^-$ can be obtained carrier-free and sulfate pool sizes are generally large in marine sediments, these tracer measurements are true tracer experiments. Sulfate pool sizes can be measured easily in interstitial waters by using gravimetric or titrimetric (Reeburgh & Springer-Young 1983) methods. Adsorption has not been shown to be a problem. The only complication seems to be rapid pyrite formation (Howarth 1979), which occurs in salt marshes and has the effect of lowering the tracer-determined sulfate reduction rate.

Determination of the net sulfate reduction rate requires evaluation of the fate of reduced sulfur compounds. Such compounds may leave the sediments by entering the atmosphere (Hansen et al 1978) or through photosynthetic (Blackburn et al 1975, Jørgensen & Cohen 1977) or inorganic oxidation in the overlying water (Cline & Richards 1969).

Seasonal studies of sulfate reduction rates have been reported in a limited number of environments, namely Limfjorden (Jørgensen 1977), Colne Point salt marsh (Nedwell & Abram 1978), and Cape Lookout Bight (Klump 1980, Crill & Martens 1982). Because of the dominance of sulfate reduction and the ease of the rate determinations, sulfate reduction rates should probably be included as a part of any marine anoxic sediment rate study in the future.

The relationship between sulfate reduction rate and sedimentation rate

Table 4 Recent sulfate reduction rate determinations in marine sediments

Study/Location	Method	Rate (mM yr ⁻¹)	Integrated rate (gross) (mmole cm ⁻² yr ⁻¹)	Comment
Goldhaber et al (1977) Long Island Sound	jar experiment model	77 (surface) 2 (10 cm)	---	(FOAM site)
Jørgensen (1977) Limfjorden	³⁵ SO ₄ ⁼ core injection	9-73 (surface) 0.2 (150 cm)	0.226 (10 cm)	2 yr study, sulfur budget determined
Murray et al (1978) Saanich Inlet	model	$K = 6 \times 10^{-9} \text{ s}^{-1}$	—	
Nedwell & Abram (1978) Colne Point salt marsh	³⁵ SO ₄ ⁼ core injection	—	0.44	1 yr study
Klump (1980), Crill & Martens (1982), Chanton & Martens (1982)	tube incubation ³⁵ SO ₄ ⁼	182-511 (1-4 cm) 0-55 (18-21 cm)	1.7 1.9	
Howarth & Teal (1980) Great Sippewissett Marsh	³⁵ SO ₄ ⁼	—	7.5	
Devol & Ahmed (1981) Saanich Inlet	³⁵ SO ₄ ⁼ core injection	52-78.8 (surface) 0.9 (30 cm)	0.48	max at 15 cm
Reeburgh (1980), Reeburgh & Alperin (unpublished) Skan Bay	³⁵ SO ₄ ⁼ core injection	32 (surface) 9 (30 cm)	1.37 (1979), 0.43 (1980)	one core
Reeburgh & Alperin (unpublished) Chesapeake Bay	³⁵ SO ₄ ⁼ core injection	150 (surface) 10 (55 cm)	2.26	one core

has been studied by Goldhaber & Kaplan (1975), Toth & Lerman (1977), and Berner (1978). Berner (1978) discusses a method for estimating sedimentation rates from the initial sulfate concentration gradient in marine sediments.

Methane Production

Methane production has received attention in rumen studies as a non-utilizable waste product and in digester studies as a desirable product. Methanogenesis has been reviewed by Wolfe (1971), Zeikus (1977), Mah et al (1977), and Bryant (1979). Reliable methane production rates in sediments have largely resulted from modeling, and several problems have emerged that appear to preclude tracer measurements of the methane production rate.

First, although a number of candidate reactions and mechanisms for methane production have been advanced, we still do not know which reaction is the dominant methane producer in marine sediments. Claypool & Kaplan (1974) used stable carbon isotope distributions ($\delta^{13}\text{CO}_2$) and a Rayleigh distillation model to conclude that CO_2 reduction was the most important methane-producing reaction in sediments. Studies in Skan Bay (Shaw et al, unpublished) with $^{14}\text{CO}_2$ as tracer indicate that the CO_2 pool is so large and the resulting specific activity in a tracer experiment so low that unrealistically long incubations are necessary to produce detectable CH_4 . Cappenberg (1974), Winfrey & Zeikus (1979), and Sansone & Martens (1981a) present evidence that acetate is an important precursor for methane. Recent turnover experiments on methionine (Zinder & Brock 1978, Phelps & Zeikus 1980) and methanol (Oremland et al 1982) suggest that both of these compounds may be methane precursors. Pool size measurements were not reported for either of these compounds.

The use of jar experiments to obtain methane production rates is complicated by competition between sulfate reducers and methanogens for hydrogen (Winfrey & Zeikus 1977, Oremland & Taylor 1978, Nedwell & Banat 1981), as well as by anaerobic methane oxidation. Martens & Berner (1974), Crill (1981), and Crill & Martens (1983) have made such measurements and observed no production of methane until sulfate was exhausted. As indicated earlier, these jar experiments are probably measuring net rates of methane production.

One method for determining the dominant reaction and the total amount of methane produced deals with determining a stable carbon isotope budget in sediments. Biogenic methane has a characteristic stable carbon isotope signature, and the carbon pool from which methane was produced should show an isotope "pull" equivalent to the "push" resulting from methane production. Previous work has involved only measurements

of $\delta^{13}\text{CO}_2$ and $\delta^{13}\text{CH}_4$ (Claypool & Kaplan 1974, Doose 1980); by comparing pool sizes and isotope ratios in other carbon reservoirs, namely DOC (dissolved organic carbon), PIC (particulate inorganic carbon), and POC (particulate organic carbon), and by investigating specific classes of compounds the principal reaction can be determined from a stable isotope budget.

Stoessell & Byrne (1982) recently showed that methane does not adsorb in clay slurries. New solubility values for methane in seawater (Yamamoto et al 1976) have made determination of saturation more reliable.

Methane Oxidation

The most important sink for methane was believed until recently to be the atmosphere (Ehhalt 1974), where methane is ultimately oxidized to CO_2 in the troposphere by reaction with the OH radical. Two types of methane oxidation processes, aerobic (Rudd et al 1974, Rudd & Hamilton 1978) and anaerobic (Reeburgh & Heggie 1977, Reeburgh 1982), have been identified recently as important sinks for methane in freshwater systems, such as lakes and wetlands, and in marine sediments. Hanson (1980) and Rudd & Taylor (1980) have reviewed both processes. Water-column methane oxidation rates are summarized in Table 5 and sediment methane oxidation rates are summarized in Table 6.

Aerobic methane oxidation studies have been conducted in the water columns of lakes (Rudd et al 1974, Rudd & Hamilton 1978, Jannasch 1975, Harritts & Hanson 1980) and coastal waters (Sansone & Martens 1978). The rate determinations have involved measuring disappearance of methane in time-series incubations of water samples or labeling with $^{14}\text{CH}_4$ (Rudd et al 1974). These studies show that aerobic methane oxidation is confined to a thin depth interval in the water column by a lack of methane and inorganic nitrogen above and by a lack of oxygen below.

Anaerobic methane oxidation has been controversial ever since its occurrence in sediments was predicted by models (Reeburgh 1976, Barnes & Goldberg 1976, Martens & Berner 1977), but recent tracer experiments (Panganiban et al 1979, Reeburgh 1980, Iversen & Blackburn 1981, Devol, unpublished) and stable carbon isotope models (Reeburgh 1982) agree well with the predicted locations and magnitudes and indicate that the process does occur. Lidstrom (unpublished) has recently observed anaerobic methane oxidation in the anoxic water column of Framvaren fjord. The organisms responsible for anaerobic methane oxidation have not been isolated.

Laboratory evidence favoring (Davis & Yarbrough 1966) and disputing (Sorokin 1957) anaerobic methane oxidation has been presented. There are no known anaerobic organisms capable of using methane as the sole carbon

Table 5 Water-column methane oxidation rates

Study/Location	Method	Oxic/anoxic	Rate ($\mu\text{M yr}^{-1}$)
Rudd et al (1974) Lake 120, ELA	tracer ($^{14}\text{CH}_4$)	oxic	1.4×10^3 (max)
Jannasch (1975) Lake Kivu	time series	oxic	15.6–325 175 av
Reeburgh (1976) Cariaco Trench	model	anoxic	$0.1\text{--}1.5 \times 10^{-2}$
Sansone & Martens (1978) Cape Lookout Bight	time series	oxic	3.6–76.6
Scranton & Brewer (1978) Ocean	apparent CH_4 utilization in dated water masses	oxic	1.5×10^{-4} (<150 yr water)
Panganiban et al (1979) Lake Mendota	tracer ($^{14}\text{CH}_4$)	anoxic	methane oxidation observed
Harrits & Hanson (1980) Lake Mendota	tracer ($^{14}\text{CH}_4$)	oxic	$10.5 \times 10^3\text{--}1.0 \times 10^7$ (max)
Lidstrom (unpublished) Framvaren Fjord	time series	anoxic	methane oxidation observed in 4 experiments from 150 to 177 m

source (Quayle 1972). Zehnder & Brock (1979, 1980) reported simultaneous production and oxidation of methane by nine methanogen strains, but the amounts oxidized (<1%) were too small to produce the net consumption observed in the low methane surface zone of marine sediments. Anaerobic methane oxidation is also confined to a narrow depth interval in sediments; the observed maximum rates lie at the bottom of the sulfate reduction zone, where sulfate is nearly exhausted. Since this process has not been observed in lake sediments and occurs only in a subsurface zone in marine sediments, it is probably connected with sulfate reduction.

These rates can be checked by comparing the integrated methane oxidation rate with the calculated upward flux of methane. These rates are nearly equal in recent Skan Bay work, indicating that methane diffusing upward into the low methane concentration zone undergoes net consumption, confirming the measurements. The integrated methane oxidation rate ranges between 5–20% of the integrated sulfate reduction rate in Skan Bay sediments. Devol & Ahmed (1981) proposed that a subsurface maximum in the sulfate reduction rate in Saanich Inlet was caused by anaerobic methane oxidation.

Table 6 Sediment methane oxidation rates

Study/Location	Method	Oxidation rate (mM yr ⁻¹)	Integrated oxidation rate (μmole cm ⁻² yr ⁻¹)
Reeburgh (1976)	model	E. basin 1.59 (10-cm zone)	15.9
Cariaco Trench		W. basin 0.55 (10-cm zone)	5.48
Barnes & Goldberg (1976)	model	0.232 (46-cm zone)	1.07 × 10 ⁻²
Santa Barbara Basin			
Martens & Berner (1977)	model	0.65 ($K_1 = 8 \times 10^{-9}$ s ⁻¹)	
Long Island Sound			
Kosiur & Warford (1979)	tracer (¹⁴ C-lactate, acetate) flask incubation	0.128 (av)	—
Santa Barbara Basin			
Bernard (1979)	model	($K_1 = 14.4-1.8 \times 10^{-10}$ s ⁻¹)	
Gulf of Mexico			
Reeburgh (1980)	tracer (¹⁴ CH ₄)	3.4 (max)	60 (measured)
Skan Bay	core injection		
Miller (1980)	model	—	8.8
Guinea Basin, Eq. Atlantic	(δ ¹³ CO ₂ distribution)		
Iversen & Blackburn (1981)	tracer (¹⁴ CH ₄)	0.017-0.102	0.12-0.63
Kysing Fjord	core injection		
Whiticar (1978, 1982)	model	sta. 2 0.095 (50-cm zone)	4.76
Eckernfördner Bay		sta. 4 0.046 (25-cm zone)	1.16
Devol (unpublished)	tracer (¹⁴ CH ₄)	6.6-12.4 (max)	25-71 (measured)
Saanich Inlet	core injection		141 (calculated)
Reeburgh & Alperin (unpublished)	tracer (¹⁴ CH ₄)	2 (max)	cores 7, 8, 9 23.6 (measured)
Skan Bay	core injection		23.6 (calculated)
Chesapeake Bay		10 (max)	220-360

Ammonium Production

Ammonium production rate measurements are summarized in Table 7. Ammonium is a product of the decomposition of organic nitrogen compounds in anoxic sediments and accumulates to mM concentrations in interstitial waters. Adsorption of ammonium has been found to be rapid and reversible in anoxic marine sediments (Rosenfeld 1979). Adsorbed ammonium was found to be predominantly associated with organic rather than mineral phases. Adsorption coefficients from several studies seem to be similar.

Although there are few direct measurements of ammonium production rates in marine sediments, two recent studies where measured and modeled rates agree well (Blackburn 1979, Rosenfeld 1981) suggest that the rate measurements and models are approaching the same point. Blackburn's stable isotope dilution method has the added advantage of providing a direct means of obtaining net and gross ammonium production.

Table 7 Ammonium production rates in sediments

Study/Location	Method	Adsorption coefficient	Rate (mM yr ⁻¹)	Comment
Berner (1974) Somes Sound Santa Barbara Basin	model		$K = 3.5 \times 10^{-9} \text{ s}^{-1}$ $K = 1.3 \times 10^{-11} \text{ s}^{-1}$	
Billen (1978) S. Bight, N. Sea	tube incubations		up to 78.8	
Murray et al (1978) Saanich Inlet	model	2	$K = 6.05 \times 10^{-9} \text{ s}^{-1}$ (upper 15 cm) $4.17 \times 10^{-10} \text{ s}^{-1}$ (below 60 cm)	
Blackburn (1979) Limfjorden	¹⁵ NH ₄ ⁺		100. (net, 0–2 cm) 112. (total, 0–2 cm) 0.11 (12–14 cm)	
Klump (1980) Cape Lookout Bight	tube incubations	1.68	36.5 (0–2 cm) 7.3 (28–30)	1.9 mmole m ⁻² yr ⁻¹ over 32 cm
Rosenfeld (1981) Long Island Sound	model	1.6	0.44–0.57 (Sachem) 0.08–0.10 (FOAM)	
	jar expts. (sorption, temperature corrected)		0.65–0.48 (Sachem) 0.26–0.30 (FOAM)	

Table 8 Volatile fatty acid turnover rates in sediments

Study	Experiment type	Tracer	Sp. Act. (mCi/m mole)	Tracer conc. (μM)	Concentration (μM) (method)	Turnover rate constant (hr^{-1})	Turnover rate ($\mu M\ hr^{-1}$)	Comment
Cappenberg & Prins (1974)	flask	U- ^{14}C -L-lactate	45	< ambient	135	2.37	319.9	
Lake Vechten	flask	U- ^{14}C -acetate	57		95 (enzyme methods, Cappenberg 1974)	0.35	33.3	
Winfrey & Zeikus (1979)	tube	U- ^{14}C -acetate	56		2.7-4.5 (g.c. of HAC from porewater)	4.5	16	seasonal average
Lake Mendota								
Ansbaek & Blackburn (1980)	core injection	U- ^{14}C -acetate		10	0.1-5.0 (g.c. of HAC from porewater)	1.6-3.3; 2.1 (av)	6-12	nonexponential uptake suggesting multiple pools.
Limfjorden								Integrated acetate turnover 3 x integrated sulfate reduction
Sansone & Martens (1981a)	tube	1,2- ^{14}C -acetate	53.5	< ambient	SO ₄ zone Jul 91	1.96	180	
Cape Lookout Bight					Jan 150 CH ₄ zone Jul 360 Jan 83	2.19	330	
						0.531	190	
						0.230	19	

Cape Lookout Bight	tube	1- ¹⁴ C-propionate	56.7	SO ₄ zone		
				Jul 5.08	1.40	7.11
				Jan 12.1	0.223	2.70
				CH ₄ zone		
				Jul 13.2	0.462	6.10
				Jan 2.1	0.330	0.70
				(g.c. of methyl ester from whole sediment)		
Lovley & Klug (1982)	syringe core	U- ¹⁴ C-acetate	54	27 Jun 110	3.11	342
Wintergreen Lake	injection			4 Sep 100	1.59	159
		2- ¹⁴ C-propionate	55.7	27 Jun 90	1.86	16.7
				4 Sep 14	1.44	20
		U- ¹⁴ C-lactate	138.6	4 Sep 1	2.76	3
				(Bethge & Lindstrom 1974)		
Christensen & Blackburn (1982)	core	U- ¹⁴ C-acetate	50	10-70	3-7	3-13
Aarhus Bay, Danish coastal sediments	injection			(vacuum distillation, g.c. of HAc from porewater)		exponential for short (8 min) incubations, 4 × ~ 10 × high relative to NH ₄ ⁺ production
Shaw, Alperin & Reeburgh (unpublished)	core	U- ¹⁴ C-acetate	58.6	8-29	0.2	1.6-5.8
Skan Bay	injection			(modified Barcelona et al 1980)		

Volatile Fatty Acid Turnover

Table 8 summarizes the studies of volatile fatty acid turnover rates in sediments. These studies deal principally with acetate, but also include measurements on lactate and propionate. The tracer activities, tracer concentrations, and experimental conditions are reasonably similar for all of the studies summarized. Several authors (Ansbaek & Blackburn 1980, Christensen & Blackburn 1982) have noted that integration of the acetate turnover rates leads to values that are several times larger than the integrated rates of well-understood processes like sulfate reduction and ammonia production. This is unreasonable and requires an explanation.

Given the wide variety of environments and environmental conditions, the measured turnover rate constants for acetate seem to group remarkably well, corresponding to turnover times of about 20 minutes. Similar turnover times are observed for volatile fatty acids in the rumen. The lactate and acetate addition studies of Kosiur & Warford (1979), which were directed at methane production-consumption rates, show what appear to be much slower turnover times ($\sim$ days) and are reported in Table 6 (sediment methane consumption). This close grouping of measured acetate turnover rate constants may be explained in two ways: first, the studies are either correctly measuring the rate of a fundamental process that is relatively immune to environmental differences or second, the experimental conditions are so similar in all of the studies that, right or wrong, the results are the same.

The main source of variation in the turnover rates appears to be the pool size measurements. These determinations were made by a variety of analytical methods on whole sediment and interstitial waters collected by squeezing, centrifugation, and equilibration. The recent work of Christensen & Blackburn (1982) shows that tracer acetate was rapidly adsorbed into two pools, one permanently sorbed and one that can be released with excess acetate. They also presented evidence from gel filtration of interstitial water suggesting that a large portion of interstitial water acetate was complexed and unavailable. Thus the measured acetate pool size may be larger than the active or available pool.

Resolution of the questions about turnover rates of volatile fatty acids will require devising a way to measure or estimate the size of the active or available volatile fatty acid pools in sediments. Christensen & Blackburn (1982) indicate that 75–90% of the measured interstitial water acetate pool may be unavailable. They suggest investigations of availability involving size or other chromatographic separation, studies of the relative rates of remineralization of a tracer and pool constituent, and comparisons with some well-understood rate measurement.

Amino Acid Turnover

The studies of sediment amino acid turnover rates are summarized in Table 9. Two of these studies (Hanson & Gardner 1978, Henrichs et al 1982) were performed in salt marsh sediments. The results of these studies are probably not directly comparable to other sediment systems because of the presence of emergent plant root systems. Other rate measurements were not reported.

Christensen & Blackburn (1980) indicated that the alanine turnover rate in their studies exceeded the ammonium production rate. There are clearly too few comparable amino acid turnover rate measurements to draw firm conclusions, but it does appear that the situation with alanine and probably other amino acids is similar to that for volatile fatty acids—namely, the available pool is a fraction of the measured pool.

SUMMARY AND FUTURE WORK

This review has emphasized and summarized rate measurements of a number of processes important in remineralizing organic matter. It has also emphasized the necessity of showing that the rates of all processes occurring in a given sediment are internally consistent. Sulfate reduction, as indicated by Sørensen et al (1979), is the dominant reaction in anoxic systems in terms of its organic matter oxidizing capacity. The sulfate reduction rate is easily measured and gives results that agree well with diagenetic models. Ammonium production can also be measured reliably, although the analytical instrumentation used by Blackburn (1979) is probably less available. Since we are confident that both of these measurements give realistic results, either should be included in future turnover rate studies in anoxic sediments. These additional measurements allow determination of the importance of a reaction to the sediment system, and provide information that allows independent tests of the measured rates through diagenetic models or budgets. Where possible, detailed depth distributions of both concentrations and rates should be determined to make diagenetic modeling simpler. Determinations of fractional turnover rates or turnover experiments are a useful guide to future studies, but they give no information on system importance unless they are accompanied by pool size measurements.

Future measurements should preserve the integrity of the sediment studied as much as possible by minimizing preincubation manipulation, by adjusting tracer concentrations where possible to minimize perturbations, and by matching incubation temperatures and in situ temperatures. These measurements should also be directed toward determining the effects of

Table 9 Sediment amino acid turnover rates

Study/Location	Experiment type	Amino acid	Tracer conc. (nM)	Concentration (μM) (method)	Turnover rate constant (hr^{-1})	Turnover rate ($\mu\text{M hr}^{-1}$)	Comment
Hanson & Gardner (1978) Georgia salt marsh	tube	alanine	200–250	tall <i>Spartina</i> 30.3	0.11	3.25×10^{-3}	
				mud flat 14.3	0.023	0.33×10^{-3}	
				short <i>Spartina</i> 552	0.015	8.32×10^{-3}	
	tube	aspartic acid	150–200	tall <i>Spartina</i> 3.72	0.05	0.20×10^{-3}	
				mud flat 23.5	0.0094	0.22×10^{-3}	
Christensen & Blackburn (1980) Limfjorden & Aarhus Bay	core injection	alanine	640	short <i>Spartina</i> 65.8 (amino acid analyzer, fluorometric detector, pore water by centrifugation)	0.0040	0.26×10^{-3}	
				0.8	9.60	3.13	in excess of NH_4^+ production
				(HPLC—Lindroth & Mopper 1979 on centrifuged porewater)			
	core injection	proline	750	27–59	0.58	15.6–34.2	
Henrichs et al (1982) Great Sippewissett Marsh	core injection	alanine	1300	2–13	5.0	10–65	
		glutamic acid	900	11–50	2.22–2.85	31.4–142	
				(g.c.—Henrichs & Farrington 1979 on NaNO_3 or NaCl extracts)			

adsorption on pool sizes and rates. Development of methods capable of determining the active or effective pool size of intermediates is critical.

Where possible, seasonal rates and budgets like those available now for Limfjorden and Cape Lookout Bight should be determined to obtain a better understanding of how temperature, carbon input, and reaction rates vary over an annual cycle. This information will allow determination of the net rates of many of the reactions.

The work of Fenchel & Jørgensen (1977) was cited in the introduction of this review. This paper discussed detritus food chains and the role of bacteria, and laid down a broad framework. The Fenchel & Jørgensen paper considered element cycles, the sequence of degradation reactions, and the biomasses of bacteria and protozoans in sediment systems. While the perspective taken in this review is different, it should be pointed out that there are now numbers and rates associated with most of the processes discussed in that paper, and that we are approaching a point of understanding the rates and importance to the whole system of many of the processes responsible for degradation of organic detritus in aquatic sediments. Most of the rate measurements summarized here have been made in the past five years.

What does the future hold? What will future papers similar to Fenchel & Jørgensen (1977) and this one discuss? Analytical capabilities for small samples of organic molecules will improve and become more widespread, so we should be able to obtain agreement in our understanding of small molecules like amino acids and volatile fatty acids. The factors controlling the microbial availability of analytically determined substrates will receive attention. Methods capable of measuring biomass, physiological potential, metabolic activity, growth rate, and cell division rate of microbial populations will be refined and adapted to sediment studies. New organisms will be isolated. Developments in sediment traps will lead to a better understanding of the nature and flux of organic detritus to the sea floor. Studies of stable carbon isotopes in specific carbon pools and in classes of compounds will lead to a better understanding of sediment reactions and their extent. Many of these methods will be applied in hemipelagic and pelagic environments, resulting in a better understanding of denitrification and metal oxide reduction. Collaboration between microbiologists and geochemists in associations like FOAM (Friends of Anoxic Mud), $\text{CH}_4\text{A}\cdot\text{O}_2\text{S}$ (North Carolina), SKUM (Scandinavian Committee for Mud Research), and AARGH (Alaska Anoxic Research Group) should continue to make the study of anoxic mud scientifically exciting and rewarding.

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