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The ecological significance of sulfur in the energy dynamics of salt marsh and coastal marine sediments*

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Abstract. Sulfur is an important element in the metabolism of salt marshes and subtidal, coastal marine sediments because of its role as an electron acceptor, carrier, and donor. Sulfate is the major electron acceptor for respiration in anoxic marine sediments. Anoxic respiration becomes increasingly important in sediments as total respiration increases, and so sulfate reduction accounts for a higher percentage of total sediment respiration in sediments where total respiration is greater. Thus, sulfate accounts for 25% of total sediment respiration in nearshore sediments (200 m water depth or less) where total respiration rates are 0.1 to 0.3 $g C m^{-1} day^{-1}$, for 50% to 70% in nearshore sediments with higher rates of total respiration (0.3 to 3 $g C m^{-2} day^{-1}$), and for 70% to 90% in salt marsh sediments where total sediment respiration rates are 2.5 to 5.5 $g C m^{-2} day^{-1}$.

During sulfate reduction, large amounts of energy from the respired organic matter are conserved in inorganic reduced sulfur compounds such as soluble sulfides, thiosulfate, elemental sulfur, iron monosulfides, and pyrite. Only a small percentage of the reduced sulfur formed during sulfate reduction is accreted in marine sediments and salt marshes. When these reduced sulfur compounds are oxidized, energy is released. Chemolithoautotrophic bacteria which catalyze these oxidations can use the energy of oxidation with efficiencies (the ratio of energy fixed in organic biomass to energy released in sulfur oxidation) of up to 21–37% to fix CO_2 and produce new organic biomass.

Chemolithoautotrophic bacterial production may represent a significant new formation of organic matter in some marine sediments. In some sediments, chemolithoautotrophic bacterial production may even equal or exceed organoheterotrophic bacterial production. The combined cycle of anaerobic decomposition through sulfate reduction, energy conservation as reduced sulfur compounds, and chemolithoautotrophic production of new organic carbon serves to take relatively low-quality organic matter from throughout the sediments and concentrate the energy as living biomass in a discrete zone near the sediment surface where it can be readily grazed by animals.

Introduction

Sulfur plays two key roles in biotic systems: it is an essential element in living tissues, and it is an important electron carrier in anoxic and partially anoxic ecosystems. Sulfur typically accounts for about 1% of the dry mass of living organisms and is a required component of proteins, sulfo-lipids, and

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sulfate esters. As is discussed elsewhere in this volume, sulfur is scarce enough in some ecosystems to limit primary productivity (Tabatabai, 1984). This is never true in marine ecosystems, however, since sulfate is abundant in seawater. In fact, sulfate is the second most abundant anion in seawater, and full-salinity seawater contains 28 mM sulfate.

In coastal marine ecosystems, sulfur is of interest primarily because of its role as an electron carrier under anoxic or partially anoxic conditions. Sulfate is the major electron acceptor for anaerobic respiration in these systems. Much of the decomposition in near-shore marine sediments and in salt marshes is mediated by sulfate-reducing bacteria (Jørgensen, 1977, 1982a; Howarth and Teal, 1979; Howarth and Giblin, 1983). During dissimilatory sulfate reduction, only a small percentage of the energy of the organic matter which is respired is available to the microbes for growth and maintenance. Most of the energy of the organic matter is transferred and stored as the reduced sulfur products of sulfate reduction (Howarth and Teal, 1980). Reduced sulfur compounds such as hydrogen sulfide then become important carriers of energy and can support bacterial autotrophic fixation of CO_2 either through photosynthesis in the presence of light or through chemolithotrophy in the presence of an oxidizer such as O_2 or nitrate (Cohen et al., 1975; Kuenen, 1975; Pfennig, 1967, 1975; Utkilen, 1976; Timmer-ten Hoor, 1981; Kelly, 1981, 1982; Kuenen and Beudeker, 1982; Nelson and Jannasch, in press). Although chemosynthetic production in deep-sea hydrothermal vents has recently attracted a great deal of interest and attention (Jannasch and Wirsen, 1979; Felbeck, 1981; Rau and Hedges, 1979; Cavanaugh et al., 1981), the magnitude and importance of chemolithotrophy on a global scale may well be much greater in coastal marine ecosystems, as a rough calculation later in this paper demonstrates.

In this paper I review the importance of sulfate reduction in the metabolism of near-shore, marine sediments and salt marshes and discuss the magnitude of energy flow through reduced sulfur compounds. I also speculate on the potential magnitude of chemolithoautotrophic production in these ecosystems by examining the fate of reduced sulfur and by using estimates for the efficiency of chemolithoautotrophy derived from pure-culture studies. I have relied heavily on the work with which I am most familiar: my own and that of colleagues studying the Great Sippewissett Salt Marsh (Falmouth, Massachusetts, U.S.A.) and on the work of Bo Barker Jørgensen and colleagues studying the nearshore coastal sediments of Denmark.

The importance of sulfate reduction to decomposition

Sulfate reduction combined with fermentative reactions which degrade polymeric organic matter and provide the substrates used in sulfate reduction account for a major portion of organic matter decomposition in shallow-water, coastal sediments and salt marshes (Jørgensen, 1982a; Howarth and

Teal, 1979; Howarth and Giblin, 1983; Martens and Klump, in press. Studies with O_2 micro-electrodes have shown that coastal sediments become anoxic within a few mm of the sediment-water interface (Revsbech et al., 1980a; b; Howarth and Jørgensen, in press). Thus, all sediment metabolism below this depth must be anaerobic. Possible electron acceptors other than sulfate include nitrate, iron (III), and CO_2. Although nitrate is energetically preferred to sulfate as an electron acceptor in respiration, the limited rate of supply of nitrate to typical coastal sediments results in relatively minor amounts of nitrate-mediated respiration (denitrification or dissimilatory nitrate reduction to ammonium) relative to sulfate reduction (Sørensen et al., 1979). Iron (III) may serve as an electron acceptor for respiration in sediments (Sørensen, 1982), but the magnitude of iron-based respiration in situ in natural sediments is not known. The arguments of Jørgensen (1982a) suggest that iron-mediated respiration is of less importance than sulfate reduction in shallow-water, coastal sediments. In salt marshes, sulfate reduction is clearly the major form of respiration involved in decomposition processes (Howarth and Teal, 1979; Howarth and Giblin, 1983; Howarth and Hobbie, 1982). Unlike freshwater sediments (Kelly et al., 1984), sulfate rarely becomes depleted in marine sediments since sulfate is such an abundant component of seawater. Thus, methanogenesis is a relatively minor process in most marine sediments and salt marshes (Howarth and Teal, 1979; Martens and Klump (in press).

Jørgensen (1977, 1982a) estimated that for sediments in the coastal waters of Denmark, sulfate reduction accounted for approximately 50% of the respiration in sediments at water depths of 20 m or less with a total community respiration greater than 0.24–0.30 g C m^{-2} day^{-1}. In deeper water of up to 200 m depth where total community respiration ranged from 0.1 to 0.36 g C m^{-2} day^{-1}, sulfate reduction accounted for approximately 25% of respiration. This conclusion was reached by comparing O_2 consumption and sulfate reduction rates in the sediments. Oxygen consumption was typically 4 to 7 times greater than sulfate reduction. The accretion rate of reduced sulfur minerals was only 5 to 20% of the rate of sulfate reduction. Assuming that the rest of the reduced sulfur compounds diffused or were advected to the surface of the sediments where they were oxidized at the expense of molecular O_2, Jørgensen (1977, 1982a) calculated that 25 to 50% of the sediment O_2 consumption was used in oxidizing sulfur compounds. Organoheterotrophic, O_2-mediated respiration was estimated by difference.

Martens and Klump (in press) in their study of Cape Lookout Bight, North Carolina, found that both the rate of sulfate reduction and the flux of CO_2 from the sediments exceeded the rate of sediment O_2 consumption. As in the sediments studied by Jørgensen (1982a), only a small percentage of the reduced sulfur formed in sulfate reduction was accumulating in their sediments. Therefore, Martens and Klump (in press) concluded that the sediment O_2 consumption resulted mainly from the oxidation of reduced sulfur compounds. If so, virtually all of the sediment metabolism was mediated

by anoxic processes. Cape Lookout Bight represents an extremely stagnant and organic-rich coastal marine environment where methanogenesis appears unusually important for carbon cycling. Yet of the annual mean rate of sediment respiration of $1.2\,g\,C\,m^{-2}\,day^{-1}$, 68% is estimated to be mediated by sulfate reduction and only 32% by methanogenesis (Martens and Klump, in press). During summer when metabolism was most intense, the CO_2 flux from the sediments to the overlying water was 1.4 times larger than the O_2 flux to the sediments.

Hargrave and Phillips (1981) measured fluxes of O_2 and CO_2 in a sandy, subtidal sediment in Nova Scotia and found that the molar quantity of CO_2 released from the sediments was 2.7 times greater than the sediment O_2 consumption. The annual mean total sediment metabolism as measured by the CO_2 flux was $0.65\,g\,C\,m^{-2}\,day^{-1}$. Even if all of the O_2 consumption were due to heterotrophic respiration, at least 65% of the respiration in this sediment was clearly anoxic and was probably mediated by sulfate reduction. As in the sediments studied by Jørgensen (1977, 1982a) and Martens and Klump (in press), much of the O_2 consumption was probably due to oxidation of reduced sulfur compounds. Also, it seems unlikely that the total sediment respiration was underestimated since chemolithoautotrophic fixation of CO_2 would have reduced the flux of CO_2. Thus, anoxic respiration, mostly via sulfate reduction, probably made up much more than 65% of the total respiration. Since the CO_2 flux exceeded the O_2 flux, large amounts of the reduced products of sulfate reduction were presumably stored in the sediments.

Sulfate reduction is the major form of microbial respiration in salt marsh sediments as well as in many nearshore sediments. Measured rates of sulfate reduction are similar to estimates of carbon input to these systems (Howarth and Teal, 1979; Howarth and Hobbie, 1982; Howarth and Giblin, 1983). However, it is impossible to estimate with any precision what percentage of respiration is mediated by sulfate reduction since total respiration and aerobic respiration are both poorly known in salt marsh sediments. Our best estimates (derived from comparing sulfate reduction rates with estimates of carbon inputs) are that sulfate reduction accounts for perhaps 70% and 90% of the total microbial respiration in stands of short *Spartina alterniflora* at Sapelo Island, Georgia, and in the Great Sippewissett Marsh, Massachusetts, respectively. That these estimates are higher percentages than those found for many subtidal, coastal sediments is logical since total sediment respiration in salt marshes is higher (Table 1). Since the rate of O_2 supply to a sediment limits the percentage of respiration which is aerobic, more metabolically active sediments should be expected to have a higher percentage of anoxic respiration. Also, in salt marsh sediments, labile carbon is being produced directly in the anoxic sediments by marsh-grass roots and rhizomes.

The estimates on the percentage of total microbial respiration which is

Table 1. Total respiration rates, percents of respiration which are anoxic, and percents of respiration mediated by sulfate reduction for a variety of sediments.

	Total sediment microbial respiration ($g C m^{-2} day^{-1}$)	Percent of microbial respiration which is anoxic	Percent of microbial respiration mediated by sulfate reduction
Danish coastal waters, 20–200 meters depth[a]	0.1–0.36	25%	25%
Danish coastal waters, 0–20 meters depth[a]	0.3–3	50%	50%
Limfjorden[b]	0.43	53%	53%
Nova Scotia coastal waters[c]	0.65	65%	65 (?)
Cape Lookout Bight[d]	1.2	100%	68%
Sapelo Island Salt Marsh[e]	2.4	80%	70%
Sippewissett Salt Marsh[f]	5.5	90%	90%

[a]Jørgensen (1982a); [b]Jørgensen (1977); [c]Hargrave and Phillips (1981); [d]Martens and Klump (in press); [e]Howarth and Giblin (1983); [f]Howarth and Teal (1979).

mediated by sulfate reduction are based on comparing measured rates of sulfate reduction with estimates of inputs and decomposition of organic matter in these marsh sediments (Howarth and Teal, 1979; Howarth and Hobbie, 1982; Howarth and Giblin, 1983). Unfortunately, the inputs of organic carbon to marsh sediments are not easily measured and are not well known. Much of the input occurs from production of grass roots and rhizomes, and despite much effort, this below ground growth and decomposition has proven very difficult to measure (Valiela et al., 1976; Gallagher and Plumley, 1979; Good et al., 1982). The excretion of dissolved organic carbon from living roots and rhizomes may also be a significant input to marsh sediments, but there are few measurements of this (Howarth and Hobbie, 1982). There are also no determinations of bacterial chemolithoautotrophic production in salt marsh sediments.

Fluxes of CO_2 from the sediment are more difficult to use to estimate total microbial respiration in salt marshes since these fluxes include CO_2 produced by the respiration of roots and rhizomes and do not include CO_2 fixed by the grasses, by algae, and by autotrophic bacteria. Also, CO_2 produced in the sediments may leave dissolved in tidal waters as well as by diffusion as a gas across the sediment surface (Howarth and Teal, 1979; Howarth et al., 1983). In addition to problems of internal cycling, it has proven difficult even to get reliable estimates of net gas fluxes for marshes, and estimates for various marshes or even the same marsh vary by more than an order of magnitude (Howarth and Hobbie, 1982).

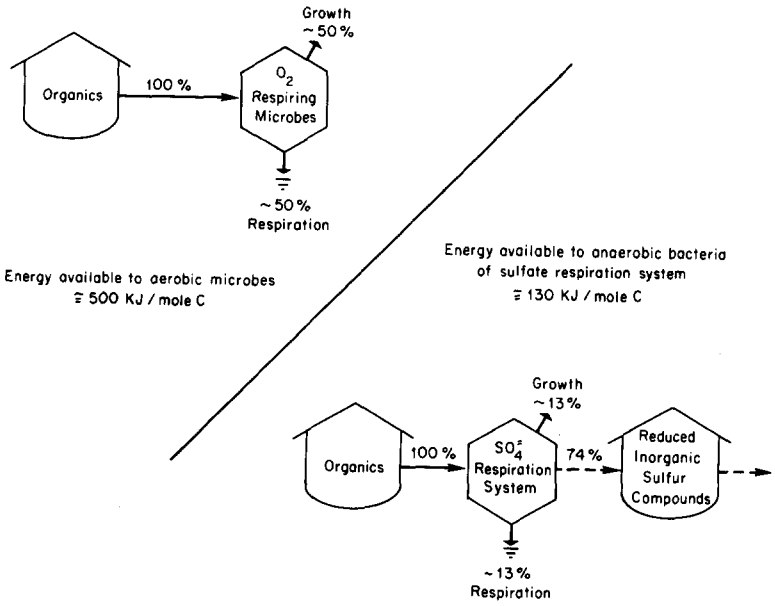

Figure 1. Comparisons of oxygen respiration with sulfate reduction. During sulfate reduction and associated fermentation reactions, there is a decoupling of energy flow from carbon cycling. See text.

Significance and fate of reduced sulfur

The above discussion indicates that in shallow (less than 20 m of water) near-shore sediments and in salt marshes, respiration mediated by sulfate reduction probably accounts for 50% to perhaps 90% of total respiration. Even in sediments underlying deeper water (20–200 m), sulfate reduction can account for 25% of total respiration (Jørgensen, 1982a). This has very interesting ramifications for energy flow in these sediment systems since during sulfate reduction there is a decoupling of energy flow from carbon cycling (Fenchel and Jørgensen, 1977; Howarth and Teal, 1980). During O_2-mediated respiration, all of the free energy of the respired organic matter is available to the respiring organisms or is dissipated to the environment as heat and increases in entropy (Figure 1). During dissimilatory sulfate reduction, on the other hand, only a fraction of the energy of the organic matter is dissipated to the environment or is available to the microbes which are metabolizing the organic matter. Most of the free energy (relative to complete oxidation) is conserved in reduced sulfur compounds. For sulfate-reducing bacteria and related fermentative microbes which metabolize 'typical' polymeric organic matter in sediments, approximately 25% of the free energy of the organic matter is fixed by the microbes in new biomass or dissipated to the environment 75% is transferred and stored as hydrogen

Table 2. Rates of sulfate reduction and rates of accretion of reduced sulfur in several sediments.

	SO_4 reduction (moles m^{-2} $year^{-1}$)	Net rate of sulfur sulfur accretion (moles m^{-2} $year^{-1}$)	% of SO_4 reduction which is accreted
Limfjorden[a]	3.5	0.26	7.5%
Solar Lake[b]	24	0.037	0.15%
Sapelo Island Salt Marsh[c]	40	0.40	1.0%
Sippewissett Salt Marsh[d]	75	0.40	0.53%

[a]Jørgensen (1977); [b]Jørgensen and Cohen (1977); [c]Howarth and Giblin (1983) and unpublished; [d]Howarth and Teal (1979).

sulfide (Figure 1; Howarth and Teal, 1980; Howarth et al., 1983). Thus, in a sediment where 90% of the total respiration is mediated by sulfate reduction, 68% (75% of 90%) of the energy flow through the sediment will be stored as hydrogen sulfied. In sediments where 50% and 25% of total respiration is mediated by sulfate reduction, 38% and 19% respectively of the energy flows through the sediments are stored as hydrogen sulfide.

What is the fate of hydrogen sulfide produced in sediments? Does it move to sediment surfaces where the presence of O_2 or light allows microbes to use its potential energy? In both subtidal sediments and salt marshes, much of the hydrogen sulfide produced during sulfate reduction is very quickly precipitated in iron minerals such as iron monsulfides and pyrite (Jørgensen and Fenchel, 1974; Jørgensen, 1977; Howarth 1979; Howarth and Teal, 1979; Howarth and Giblin, 1983; Howarth and Jørgensen, in press; Howarth and Merkel, 1984). However, the rate of accretion of these sulfide minerals is small compared with the rate of sulfate reduction in all nearshore sediments and marshes studied (Table 2). From 80% to over 99% of the sulfide formed during sulfate reduction in a variety of sediments is reoxidized or otherwise lost from the sediments (Jørgensen and Cohen, 1977; Jørgensen, 1977, 1982a; Howarth and Teal, 1979; Howarth and Giblin, 1983).

For nearshore, subtidal sediments, the reduced sulfur must diffuse or be mixed to the surface layers where O_2 or nitrate are present before it can be oxidized. An enrichment in sulfate relative to the conservative tracer chloride is often observed at or near the surface of near-shore sediments, confirming that an oxidation of reduced sulfur is occurring there (Vosjan, 1974). In highly reducing sediments, O_2 and hydrogen sulfide coexist over a short depth due to diffusion of O_2 into the sediments and diffusion of sulfides up from deeper sediments (Figure 2, and Jørgensen 1982b). In these systems, the diffusion of sulfides upward and oxidation near the sediment surface may be sufficient to account for the loss of reduced sulfur compounds from the sediments. However, more typically in nearshore sediments, O_2 and sulfide are separated by a depth of at least a few centimeters (Jørgensen, 1982b).

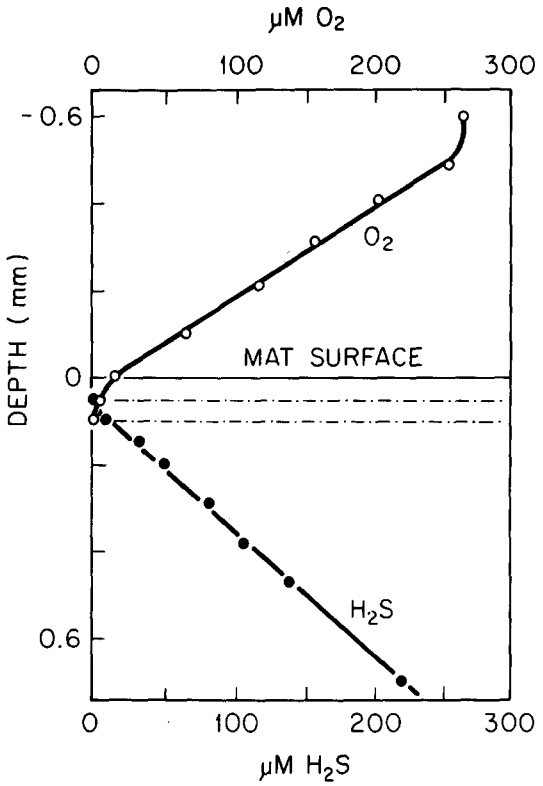

Figure 2. Distribution of oxygen and hydrogen sulfide in a *Beggiatoa* mat growing on a mud surface (after Jørgensen, 1982b).

The mechanism whereby reduced sulfur is lost from these sediments is unknown but is almost certainly oxidation near the sediment surface. This oxidative mechanism may involve a carrier such as iron or manganese which is reduced by sulfide and diffuses upward and is oxidized by O_2 (Jørgensen, 1982b). Bioturbation and resultant mixing of pyrite and elemental sulfur to the oxygenated surface layers may also be important. Elemental sulfur has been shown to be a dynamic chemical species in the surface layers of nearshore sediments (Troelsen and Jørgensen, 1982). Pyrite is the major form of reduced sulfur present in nearshore marine sediments, including the very surface layers (Kaplan et al., 1963; Berner, 1970; Goldhaber et al., 1977; Howarth and Jørgensen, in press). The recent finding that pyrite can form quickly in at least some nearshore sediments suggests that as with elemental sulfur, pyrite may be a dynamic species (Howarth and Jørgensen, in press). Figure 3 presents a hypothetical mechanism wherby pyrite acts as an intermediate in sulfide oxidation in sediments. Hydrogen sulfide diffuses upward and reacts with iron (III) oxides or hydroxides. The sulfides are partially

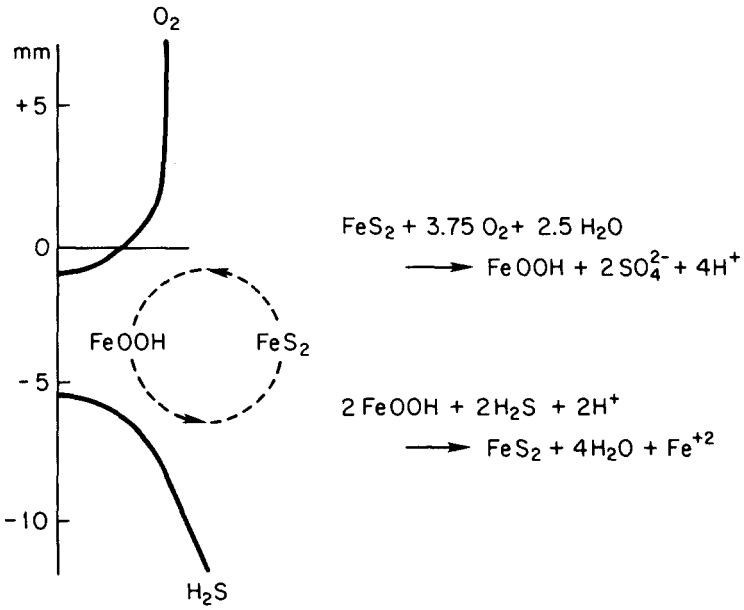

Figure 3. A hypothetical mechanism for pyrite as an intermediate in the oxidation of hydrogen sulfide in sediments where there is no overlap between hydrogen sulfide and oxygen. See text.

oxidized, and pyrite precipitates. Due to sediment mixing through bioturbation, pyrite is mixed to the surface where O_2 is present. The pyrite is oxidized, forming oxidized iron compounds which are mixed downward to the hydrogen-sulfide zone, completing the cycle.

Using the calculations given above, for a sediment where 25% of the total respiration is mediated by sulfate reduction and only 20% of the reduced sulfur is permanently accreted, the energy released by sulfur oxidation near the sediment surface is equivalent to 15% of the energy flow from organic matter decomposition in the benthos. For a sediment where 50% of the total respiration is mediated by sulfate reduction and only 7.5% of the reduced sulfur is permanently accreted, the energy released by sulfur oxidation is equivalent to 35% of the energy flow from organic matter decomposition in the benthos. Thus, for the Limfjorden sediments with a total respiration of $18\,KJ\,m^{-2}\,day^{-1}$ ($0.43\,g\,C\,m^{-2}\,day^{-1}$), the energy released during the oxidation of reduced sulfur compounds if $6.3\,KJ\,m^{-2}\,day^{-1}$.

Forms and fate of reduced sulfur in salt marshes

In salt marsh sediments, much of the sulfide formed in sulfate reduction is very quickly precipitated as pyrite at all depths where sulfate reduction

occurs (Howarth, 1979a; Howarth and Giblin, 1983; Luther et al., 1982; Howarth and Marino, 1984; Howarth and Merkel, 1984). As discussed in more details below, pyrite is the major form of sulfur in marsh sediments. However, pyrite does not just accumulate; rather it is a very dynamic constituent. Most of the pyrite in marsh sediments is present as very small micro-crystals with diameters of 0.2 to 2 μm (Luther et al., 1982). Consequently, the crystals have a high suface to volume ration, and thus the pyrite is probably more reactive and easily oxidized than larger crystals. Pyrite forms throughout the year, but during the summer when the marsh grasses are most active and capable of oxidizing the sediments, there is a net loss of pyrite (Howarth and Teal, 1979). During the fall, winter, and spring when the grasses are less able to oxidize the sediments, there is a net accumulation of pyrite, although the net rate of accumulation may still be less than the gross rate of formation. The mechanism of oxidation is not yet clear but may involve O_2 transport through the internal gas spaces of the marsh grasses or O_2 diffusion or advection through the sediments as they drain. Enzymatic oxidations without direct consumption of molecular O_2 as suggested by Armstrong (1975) for rice plants may also be important. Presumably an organic compound synthesized in the leaves and transported to the rhizosphere could serve as an oxidant. Peracids (Vámos and Köves, 1972) or even glycolate (Howarth, 1979b) are possible oxidizing compounds. Most of the pyrite which is oxidized is transformed all the way to sulfate (Howarth et al., 1983; Giblin and Howarth, 1984; Peterson and Howarth, unpublished data). In this process, tremendous quantities of energy are released. The combined oxidation of reduced sulfur compounds within the sediments of the Great Sippewissett Marsh releases an average of some 151 KJ m^2 day^{-1} (calculated using the sulfate reduction rates reported in Howarth and Teal (1979) and sulfur export estimates reported in Howarth et al., 1983), an amount of energy roughly equivalent to the average rate of production of roots and rhizomes by the marsh grasses belowground (Howarth and Teal, 1979; Valiela et al., 1976). Most if not all of this oxidation may be biologically catalyzed, as Jørgensen (1982b) reports for subtidal sediments. However, this has not been proven and requires further research. The recent finding by McClung et al. (1983) of symbiotic bacteria within the roots of salt marsh grasses suggests that these may be important in oxidizing reduced sulfur compounds, as Cavanaugh et al. (1981) and Cavanaugh (1982) have suggested for the symbiotic bacteria they found in animal tissues. It would be surprising if the marsh grasses or microflora of the grass rhizosphere received no energy benefit from the oxidation of reduced sulfur.

Some of the reduced sulfur compounds formed during sulfate reduction in marsh sediments are exported to creeks or to the surface of the marsh rather than reoxidized to sulfate within the sediments at the grass rhizosphere. Once in creeks or at the marsh surface, the oxidation of these compounds can support chemolithoautotrophic bacterial production or anoxygenic

photosynthetic production, and the resulting bacterial production is readily available to be grazed by animals of the coastal food webs. Reduced sulfur compounds can be exported from the sediments to the creeks and surface of the marsh either by bioturbation or other mixing of pyrite and solid-phase sulfur species or by diffusion or advection of dissolved sulfur species in pore waters. In the Great Sippewissett Salt Marsh, bioturbation is absent in much of the marsh because fiddler crabs do not burrow through the thick peat. Thus, export there is through diffusion or advection of dissolved substances.

In a year-long study of pore-water chemistry of the Great Sippewissett Marsh, Howarth et al. (1983) found that the only soluble reduced sulfur compounds present in abundance were sulfides and thiosulfate. Assuming a net advective exchange of pore water with tidal waters of $131\,m^{-2}\,day^{-1}$, about 2.4 moles $m^{-2}\,day^{-1}$ sulfide and 1.5 moles thiosulfate-S $m^{-2}\,day^{-1}$ are exported from the sediment (Howarth et al., 1983). This is only 5% of the rate of sulfate reduction but represents an average energy export of approximately $6.6\,KJ\,m^{-2}\,day^{-1}$, roughly one third of the average rate of aboveground production in the marsh (Howarth et al., 1983). Although there is much uncertainty in these estimates because of uncertainties in the measurement of pore-water exchange, recent experiments with microcosms where energy export was quantified under carefully controlled hydrologic conditions support these field estimates (Peterson and Howarth, unpublished data).

I speculate that since pyrite precipitates rapidly, it helps keep the concentration of soluble below that which would tend to kill the marsh grasses. Yet the small pyrite crystals are probably easily oxidized, releasing energy and recycling iron from precipitation of pyrite again (Howarth, 1979a; Howarth and Teal, 1979; Luther et al., 1982; Giblin and Howarth, 1984). Thus, pyrite acts both to buffer sulfides at low concentrations and to store energy, analogous to a battery. Pyrite makes up most of the sulfur in salt marsh sediments and accounts for 80% or more of the reduced sulfur compounds (Table 3, and references therein). The data reported for the Sippewissett Marsh are for samples taken in August, when pyrite concentrations tend to be lowest, and winter and spring samples could be 2–3 times higher or more (Howarth and Teal 1979, and unpublished data).

Several scientists working in mangrove sediments, the ecological equivalent of salt marshes for tropical and semi-tropical areas, have concluded that organic sulfur compounds are much more abundant than pyrite (Casagrande et al., 1977; Altschuler et al., 1983). These workers concluded that both sulfate esters and C-S bonded sulfur are more abundant in mangrove sediments than is pyrite. This is in marked contrast to salt marsh sediments (Table 3 and Kaplan et al., 1963; Howarth and Teal, 1979; Luther et al., 1982), brackish swamp sediments in Denmark (Postma, 1982), and mangrove sediments in Malaysia (Diemont and Wijngaarden, 1974; Pons et al., 1982). Perhaps a low iron availability limits the amount of pyrite which can form in the mangrove

Table 3. Concentrations of sulfur in various fractions in mangroves and salt marsh sediments.

	mmoles S per g dry weight					Percent total non-SO_4^{2-} sulfur which is FeS_2
	FeS	FeS_2	SO_4^{2-}	Organic S	Total S	
Florida mangrove peat, 0–5 cm[a]	undetectable	0.01	0.11	0.19	0.31	5%
Florida Mangrove peat, 30–35 cm[a]	undetectable	0.11	0.29	0.28	0.68	28%
Florida Mangrove peat, 0–4 cm[b]	undetectable	0.23	0.11	1.14	1.61	15%
California salt marsh peat, 0–5 cm[c]	0.007	0.29	0.032	0.003	0.34	94%
Massachusetts salt marsh peat in August, 10–15 cm[d]	0.0005	0.32	0.102	0.080	0.50	80%

[a]Altschuler et al., 1983; [b]Casagrande et al., 1977; [c]Kaplan et al., 1973; [d]Howarth and Teal, 1979; Luther et al., 1982, and unpublished data.

sediments studied by Casagrande et al. (1977) and Altschuler et al. (1983), both of which are in Florida. This explanation has been suggested for a cyanobacterial mat in Solar Lake, Sinai (Aizenshtat et al., 1981). In the cyanobacterial mat, rather little pyrite forms and concentrations of soluble polysulfides build up to high concentrations (approximately 1 mM; Cohen, personal communication). The polysulfides react with organic matter to create high concentrations of C–S bonded sulfur (Aizenshat et al., 1981).

A real difference in the abundance of pyrite vs. organic sulfur in the Florida mangrove swamps (Casagrande et al., 1977; Altschulder et al., 1983) as compared with other swamps and marshes (Kaplan et al., 1963; Howarth and Teal, 1979; Luther et al., 1982; Begheijn et al., 1978; Pons et al., 1982; Postma, 1983) would have major ecological implications. The C–S bonded sulfur formed by nucleophillic attach of polysulfides (e.g., forming compounds such as humic and fulvic acids) may be more difficult to oxidize than is pyrite. That is, once formed, this C–S bonded sulfur is more likely to remain permanently accreted rather than by recycled as for most pyrite. However, different investigators have used different analytical methods for measuring pyrite and organic sulfur, and the difference between the systems may not be real but merely reflect these different methods. Altschuler et al. (1983) measured pyrite by the amount of iron which was extracted by 2 N HNO_3 after prior extracter with 5 N HCl. This is a fairly mild treatment, so they may well have underestimated pyrite. If so, they would have overestimated organic sulfur since organic sulfur was determined by difference. Casagrande et al. (1977) measured pyrite by reduction with elemental zinc

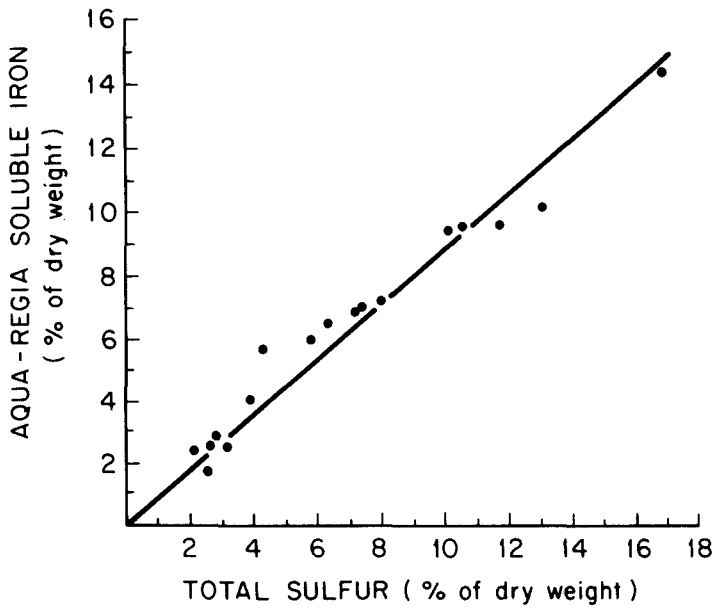

Figure 4. The relation between total sulfur and iron extracted by Aqua Regia oxidation after pre-extraction with HCl for sediments in a brackish swmp in Denmark. The solid line indicates the theoretical ratio for pyrite of 1 mole iron for every 2 moles of sulfur (after Postma, 1982).

in hot acid, a procedure that we have found to yield low and variable recoveries (unpublished data). In contrast, Postma (1982) used an Aqua Regia oxidation to measure pyrite in brackish swamp sediments. He found an excellent correlation between total sulfur and Aqua Regia soluble iron which agreed well with the theoretical ratio of Fe to S in pyrite (Figure 4).

In the Sippewissett Marsh, pyrite has been measured by several different methods with comparable results. Howarth and Teal (1979) measured sulfur oxidized by Aqua Regia oxidation of sediments after first extracting with HCl. As Postma (1982) also found, this approach compared well with estimating pyritic sulfur by measuring the iron released by Aqua Regia oxidation after extraction with hot 6 N HCl (Luther et al., 1982). Scanning electron-microscopy energy dispersive X-ray analysis of the sediments also has demonstrated the abundance of pyrite in a semi-quantitative fashion (Luther et al., 1982). More recently, chromium (II) reduction (Zhabina and Volkov, 1978; Westrich, 1983) has been used as a specific analysis for pyrite in the Sippewissett Marsh sediments, yielding results similar to the earlier assays (Howarth and Merkel, 1974, and unpublished data).

Extent and significance of chemosynthesis

The production of chemolithoautotrophic, sulfur-oxidizing bacteria in deep-sea hydrothermal vents has recently attracted a great deal of interest (Jannasch

and Wirsen, 1979; Felbeck, 1981; Rau and Hedges, 1979; Cavanaugh et al., 1981). Although these bacteria are probably physiologically similar to those found in coastal sediments and marshes, the hydrothermal vents are ecologically different from the near-shore systems. The energy in the reduced sulfur compounds in coastal environments comes from the organic matter dissimilated by sulfate-reducing bacteria, and so chemolithoautotrophic production is secondary production. In the hydrothermal vents, the energy in the reduced sulfur compounds comes from geothermal heat which chemically reduces sulfate. In the vents, therefore, chemolithoautotrophic production is primary production.

The vents are of major interest because chemolithoautotrophic bacterial production is probably the major input of organic matter supporting these ecosystems (Jannasch and Wirsen, 1979; Rau and Hedges, 1979) and because of the presence of chemolithoautotrophic bacteria living symbiotically in animals (Felbeck, 1981; Cavanaugh et al., 1981; Cavanaugh, 1982). However, on a global scale the magnitude of chemolithoautotrophic production is probably much greater in coastal marine ecosystems. An upper limit on the world-wide flux of sulfide from hydrothermal vents can be calculated from the flux estimates of Edmond et al. (1979) and the concentration of sulfide in the hottest vent solutions, those at 350 °C from the East Pacific Rise (approximately 6.5 mM; Edmond et al., 1982). The upper limit calculated from these data is approximately 10^{12} moles $year^{-1}$. Mottl (1983 and personal communication) has since suggested that this estimate is at least 6-fold too high. The maximum likely sulfide flux from hydrothermal vents is therefore probably 0.17×10^{12} moles $year^{-1}$. Let us assume that the data from the Sippewissett and Sapelo Island salt marshes (Tables 1 and 2) are typical of salt marshes worldwide, that the Limfjorden data (Tables 1 and 2) are representative for estuaries worldwide, and that the data collected by Jørgensen (1982a) for sediments at 200-m depth in the North Sea (Table 1) are typical of continental shelf sediments. Then, we can calculate that the world-wide fluxes of reduced sulfur from sediments in marshes, estuaries, and the continental shelf are 19×10^{12} moles $year^{-1}$, 4.5×10^{12} moles $year^{-1}$, and 11×10^{12} moles $year^{-1}$ respectively (using areas estimated by Woodwell et al., 1973 and Whittaker and Likens, 1973). These numbers are obviously very rough estimates which will be refined by further research, but it appears that the potential for chemolithoautotrophic production in coastal ecosystems in some 200-fold greater than in hydrothermal vents.

Reduced sulfur compounds can be oxidized either chemically or biologically, and biologically catalyzed oxidations of reduced sulfur compounds may or may not result in conservation of energy through chemolithoautotrophic fixation of CO_2. Most studies of hydrogen sulfide oxidation and chemolithoautotrophy in natural systems have been performed at the oxic/anoxic interface in stratified water bodies. The oxidation of hydrogen sulfide in some of these systems appears to be purely chemical (Sorokin, 1972), while

Table 4. Comparison of three oxygen-hydrogen sulfide interfaces (after Jørgensen, 1982b).

	Black Sea	Solar lake	*Beggiatoa* mat
Residence time of hydrogen sulfide	5 days	10–20 min	0.6 s
Oxidation rate of hydrogen sulfide per volume (μmol l^{-1} d^{-1})	0.8	250	250 000
Oxidation rate of hydrogen sulfide per area (mmol m^{-2} d^{-1})	10	20–30	12
Percent of hydrogen sulfide oxidation which is microbially catalyzed	0%	30–50%	100%

in others up to 30–50% of the oxidation appears to be microbially catalyzed (Jørgensen et al., 1979).

The oxidation of hydrogen sulfide in *Beggiatoa* mats in sediments has recently been studied by Jørgensen and Revsbech (1983). Unlike the stratified water bodies, the oxidation in these sediments is 100% microbially catalyzed, as indicated by a residence time of hydrogen sulfide (0.6 s), that is much less than probable from chemical oxidation (Table 4; Jørgensen, 1982b). The thickness of the interface of O_2 and hydrogen sulfide in the sediment *Beggiatoa* mats is orders of magnitude less than in the stratified water bodies, and this apparently allows the bacteria to compete favorably with the purely chemical oxidation. There are as yet no measurements of chemolithoautotrophic CO_2 fixation in *Beggiatoa* mats, and so the efficiency of energy conservation is unknown. Until recently, *Beggiatoa* species were thought to be primarily organoheterotrophic in metabolism, oxidizing sulfide for protection against hydrogen peroxide and other such reactive O_2 compounds rather than for energy (Nelson and Castenholz, 1981a, 1981b; Kuenen and Beudeker, 1982). However, Nelson and Jannasch (in press) have recently isolated a marine, chemolithoautotrophic strain of *Beggiatoa*. The energetic efficiency of this strain appears comparable to that found in pure cultures of obligately chemoautotrophic *Thiobacilli* species (Nelson and Jannasch, in press).

Pure-culture studies of a variety of strains of *Thiobacilli* have found growth yields of 0.21 to 0.53 moles organic C per mole of hydrogen sulfide or thiosulfate oxidized when either O_2 or nitrate is the electron acceptor (reviewed by Kelly 1982). These correspond to energetic efficiencies of approximately 21 to 37% (Table 5; calculated from the free energies of reaction for each of the studies reviewed by Kelly, 1982). These efficiencies are 3 to 6 times higher than estimated above for the chemocline of Solar Lake, probably because the pure-culture conditions are more favorable for

Table 5. Calculated efficiencies of chemolithoautotrophic production by pure-cultures of *Thiobacilli* strains. Production values are calculated from the data reviewed by Kelly (1982).

Sulfur source	Electron acceptor	Observed range of production (moles organic C per mol HS^- or $S_2O_3^{2-}$ oxidized)	Approximate energetic efficiency
$S_2O_3^{2-}$	O_2	0.31–0.53	21–35%
$S_2O_3^{2-}$	NO_3^-	0.21–0.37	21–36%
HS^-	NO_3^-	0.24–0.38	24–37%

growth of these microbes than the conditions found in the chemocline of Solar Lake. The conditions for growth of chemolithoautotrophs in sediments are much better than in the chemoclines of stratified water bodies (Jørgensen, 1982b), and so the energetic efficiencies may well approach 21 to 37%.

If it is assumed that chemolithoautotrophic bacteria found in the surface of marine sediments do indeed have energetic efficiencies of 21 to 37%, then we can estimate the magnitude of chemolithoautotrophic production. In Table 6 I have estimated chemolithoautotrophic production for three sediment types: a sediment lying under 20–200 m of water with a respiration rate of 0.2 g C m^{-2} day^{-1} (Jørgensen 1982), Limfjorden sediments with an annual mean respiration of 0.43 g C m^{-2} day^{-1} (Jørgensen, 1977), and Cape Lookout Bight sediments with an annual mean respiration of 1.2 g C m^{-2} day^{-1} (Martens and Klump, in press). As discussed earlier, the energy released during the oxidation of reduced sulfur compounds in these three sediment types would release respectively 1.3, 6.3 and 24.3 KJ m^{-2} day^{-1}. If the chemolithoautotrophs use this energy with an efficiency of 21 to 37%, rates of production would be 0.0065 to 0.011 g C m^{-2} day^{-1} in the deeper water sediment with a respiration rate of 0.2 g C m^{-2} day^{-1}, 0.032 to 0.056 g C m^{-2} day^{-1} in Limfjorden, and 0.12 to 0.21 g C m^{-2} day^{-1} in Cape Lookout Bight. Thus, chemolithoautotrophic production might vary from only 3–6% of the respiration rate in the low-metabolism sediment to perhaps 10–18% of the respiration rate in a system with reasonably high rates of respiration (Table 6). Chemolithoautotrophic production represents an input of new organic carbon to these sediments from CO_2 fixation, but the production is secondary production and not primary production since the energy came orginally from the decomposition of organic matter through sulfate reduction.

The ecological significance of chemolithoautotrophic production in coastal sediments is probably greater than these carbon input estimates might suggest. Most of the chemolithoautotrophic production probably occurs at the oxic-anoxic interface within the top few millimeters of sediment or near the edge of animal burrows. Consequently, this provides a rich and concentrated source of food for the benthic animals. The combined cycle of anaerobic decomposition through sulfate reduction and associated fermentation, energy

Table 6. Estimated rate of chemolithoautotrophic production in three sediments of differing respiration rates. Energetic efficiency of chemolithoautotrophy is assumed to be 21–37%.

†	Sediment respiration ($g C m^{-2} d^{-1}$)	% of respiration mediated by SO_4^{2-} reduction	% Sulfur accreted	Energy released in sulfur oxidation ($KJ m^{-2} d^{-1}$)	Chemolithoautotrophic production ($g c m^{-2} d^{-1}$)	Ratio of chemolithoautotrophy to total respiration
Danish coastal sediments, 20–200 m	0.2	25%	20%	1.3	0.0065–0.011	3–6%
Limfjorden	0.43	53%	7.5%	6.3	0.032–0.056	7–13%
Cape Lookout Bight	1.2	68%	5% (?)	24.3	0.12–0.21	10–18%

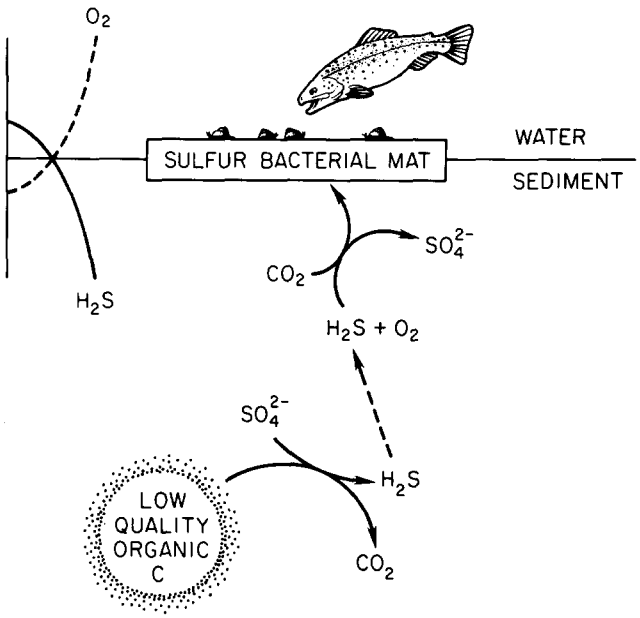

Figure 5. Schematic diagram illustrating the ecological importance of the sulfur cycle in concentrating high-quality food near the sediment-water interface.

conservation as reduced sulfur compounds, and chemolithoautotrophic production of new organic carbon serves to take relatively low-quality organic matter (material which is only slowly decomposed and which is distributed throughout the sediments) and concentrate the energy as living biomass (high quality food for animals) in a discrete zone near the sediment surface and around oxygenated dwelling tubes of bioturbating animals in the sediment (Figure 5).

In at least some sediments, chemolithoautotrophic bacterial production may exceed organoheterotrophic bacterial production. For example, in Cape Lookout Bight where I estimate chemolithoautorophic production might be as much as 0.12 to 0.21 $g\,C\,m^{-2}\ day^{-1}$, total respiration is 1.2 $g\,C\,m^{-2}\ day^{-1}$. Almost all of this respiration is probably anaerobic, mediated either through sulfate reduction or methanogenesis (Martens and Klump, in press). This represents an energy flow through the organoheterotrophic bacterial community of approximately 12 $KJ\,m^{-2}\ day^{-1}$ (calculated using the assumptions of Howarth and Teal (1980) for sulfate reduction and analagous calculations for methanogenesis). Assuming a maximum energetic efficiency for these organoheterotrophic bacteria of 50% (Payne, 1970; Howarth and Teal, 1980), heterotrophic bacterial production is probably no greater than 0.14 $g\,C\,m^{-2}\ day^{-1}$, approximately the same magnitude as my estimate for chemolithoautotrophic bacterial production.

For the sediments of the Sippewissett Salt Marsh, the amount of energy released during the oxidation of reduced sulfur compounds within the sediments at the grass rhizosphere is approximately 150 KJ m^{-2} $year^{-1}$ day^{-1} (as calculated earlier in this paper). If this is catalyzed by chemolithoautotrophic bacteria with energetic efficiencies of 21–37%, than chemolithoautotrophic production would average 0.75 to 1.4 g C m^{-2} day^{-1}. Such an input of carbon would help explain an apparent discrepancy between the rate of production of grass roots and rhizomes and the rate of sulfate reduction (Howarth and Hobbie, 1982). Since the energy export to marsh creeks as reduced sulfur compounds is smaller, chemolithoautotrophic production within the creeks is also presumably smaller. If the export of energy as reduced sulfur compounds is 6.6 KJ m^{-2} day^{-1} (as calculated above) and chemolithoautotrophic production is 21–37% efficient, then chemolithoautotrophic production in creeks and on the marsh surface would average 0.03–0.06 g C m^{-2} day^{-1} (averaged over the entire marsh surface). This is equivalent to perhaps 10% of the aboveground production by marsh grasses. But as with the nearshore, subtidal sediments, this chemolithoautotrophic production may be important as a source of high-quality food for animals which is concentrated in discrete parts of the marsh, the creeks and surface.

The efficiency of chemolithoautotrophic production in natural sediments may be much lower than in pure-culture studies, although one might well argue that the predictable and steep gradients of sulfides and O_2 in sediments offer ideal conditions for these bacteria. Also it should be noted that the efficiency of chemolithoautotrophic production by bacteria in pure-culture studies is different for different species; for example, it is very much lower for *Thiomicrospira denitrificans* than for *Thiobacillus denitrificans* (Timmerten Hoor, 1981). There is clearly a need to measure the coupling of sulfide oxidation to chemolithoautotrophic production and production by photosynthetic bacteria in natural sediments. There is also a need to study the efficiency of chemolithoautotrophic production when substances other than hydrogen sulfide and thiosulfate are the substrates since other compounds such as pyrite may be more important substrates in natural sediments.

In this review, I have speculated on the potential ecological significance of chemolithoautotrophic production. Where light is present at the surface of anoxic sediments, production by photosynthetic bacteria using sulfide as an electron donor may be of greater significance (Pfennig, 1975). Production by mixotrophic bacteria which obtain energy from organic matter as well as from sulfur oxidation or by chemolitho-heterotrophs which use the energy from sulfur oxidations to assimilate organic growth substrates from the environment (Kelly, 1981) may also be greater than production by strict chemolithoautotrophs. However, there are no data on the productivity of any of these in salt marshes or coastal sediments, and to estimate the potential productivity for photosynthetic bacteria, mixotrophs, and chemolitho-heterotrophs is even more difficult than for chemolithoautotrophs. I hope

that the calculations in this manuscript will encourage work on the production of sulfur-oxidizing bacteria in coastal ecosystems.

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