

Seasonal cycling of Fe in saltmarsh sediments

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Abstract. This study combines an analysis of porewater chemistry with new, solid phase wet chemical extractions to examine the seasonal cycling of Fe in vegetated and unvegetated (cyanobacterial mat) saltmarsh sediments. Saltmarsh sediments are shown to contain more solid phase reactive Fe than other marine sediments studied so far. From the partitioning and speciation of solid Fe, and solid/soluble reduced S analysis in 10 sediment cores, we have observed that a majority of solid Fe in these sediments is cycled rapidly and completely between oxidized reactive Fe and reduced Fe as pyrite. Vegetated porewaters showed a lower pH and much higher Fe(II) concentrations on average than unvegetated porewaters in the top 10 cm, whereas sulfate, alkalinity, and sulfide concentrations were similar in the two environments. The amorphous Fe(III) oxide fraction showed a high negative correlation to solid and soluble reduced S ($r^2 = -0.86$ and -0.71 , respectively) in surface vegetated sediments whereas the crystalline Fe(III) oxide fraction showed a high negative correlation ($r^2 = -0.96$) to sulfide only at depth. Though reactive Fe was observed in unvegetated sediments, no seasonal trend was apparent and the speciation of solid Fe revealed that most of it was reduced. Solid phase and porewater chemistry support the dominant role of the biota (*Spartina alterniflora* and bacteria) in controlling the reactivity of Fe and suggest that the current definition of solid phase, reactive Fe should be expanded to include crystalline Fe(III) minerals which are available for pyrite formation in saltmarsh sediments. In support of previous saltmarsh studies, we present evidence that the redox cycle of solid Fe is controlled by sulfate reduction and sediment oxidation which respond to both annual cycles (light, temperature) and to short-term, episodic effects such as weather and tides.

Introduction

Iron has been shown to undergo a dynamic seasonal cycle in saltmarsh sediments (Giblin & Howarth 1984; Luther & Church 1988; Feijtel et al. 1988; Lord & Church 1983) based upon porewater chemistry and solid phase S data. Its form and speciation are dependent upon precipitation, dissolution, and reduction/oxidation reactions which respond to biological and physical changes in sediments (Berner 1967, 1970). The saltmarsh has an Fe-rich sedimentary environment where exposure to the atmosphere, plant growth, and climate act in concert to cause rapid geochemical cycling (Lord 1980; Hines

et al. 1989). In saltmarshes, Fe could be considered as one of four elements (along with S, O, and organic C) which dominate diagenetic reactions.

The influence of the dominant saltmarsh grass, *Spartina alterniflora* on sediment geochemistry has been documented previously (Howarth 1979; Howarth & Teal 1979; Giblin & Howarth 1984; Hines et al. 1989). Hines et al. (1989) showed that sulfate reduction rates respond quickly to changes in plant physiology. While *S. alterniflora* was growing aboveground, sulfate reduction was stimulated and the sediments were supplied with sufficient oxidants to cause the rapid turnover of sulfide. Hines et al. suggested that DOC from plant roots fuels anaerobic microbial metabolism and that evapotranspiration results in the injection of oxygen and sediment oxidation. Dessication and tidal inundation have also been shown to have large effects on the geochemistry of saltmarsh sediment (Casey & Lasaga 1987; Hines et al. 1989). Most studies of Fe and S geochemistry in sediments have focused on porewaters, and there is a general lack of studies on solid phase Fe despite the previous suggestion by Giblin & Howarth (1984) that changes in porewater Fe represent only a fraction of the Fe turned over during the year in marsh sediments.

Several studies have extracted solid phase reactive Fe in marine sediments (Canfield 1989; Leslie et al. 1990; Oenema 1990; Kostka & Luther 1994), but none of these have concentrated on solid Fe over an annual cycle. Also, though many studies have addressed the geochemistry of vegetated marsh sediments and its interaction with the growth season of *S. alterniflora* (i.e., Howarth 1979; Howarth & Teal 1979; Luther & Church 1988; Hines et al. 1989), comparatively little geochemical data is available concerning unvegetated sediments and no seasonal comparisons have been performed.

Reactive Fe has traditionally been defined as that fraction of marine sediments which reacts with sulfide to form iron sulfides and pyrite (Berner 1970; Lord & Church 1983; Canfield 1989). We have recently reexamined a range of wet chemical extractions in saltmarsh sediments, incorporating chemical principles and careful calibration with standard Fe minerals (Kostka & Luther 1994). The study revealed that because marsh sediment contains a mixture of Fe(II) and Fe(III) minerals, the presence of other minerals may affect the extraction of the mineral in question. Based on previous work, we operationally define 'reactive Fe' as the dithionate-extractable Fe minus the Fe associated with FeS. Our study further indicated that the definition of 'reactive Fe' should be changed to incorporate crystalline Fe(III) minerals and authigenic silicates which may be solubilized during extraction procedures (Kostka & Luther 1994).

A reexamination of the definition of 'reactive Fe' was prompted by recent studies which suggest Fe complexes are important components of the Fe cycle in Delaware saltmarsh sediments. The dissolution of crystalline Fe(III)

minerals may be catalyzed by Fe(II) complexed with organic matter such as carboxylic acids (containing oxygen ligands) produced belowground by plants and bacteria (Luther et al. 1992). In the past year, such Fe complexes associated with DOC were measured in porewaters of the Delaware marsh (Luther et al. 1995). These studies imply that the current operational definition of reactive Fe in marine sediments may lead to an underestimation of crystalline Fe phases which can be rapidly cycled due to reactions with Fe-organic complexes. They also imply that organic ligands must be seriously considered along with dissolved sulfide as reductants of Fe(III) in marine sediments.

The objectives of this study were to: 1) Show the complete partitioning of Fe in the solid phase over an annual cycle, 2) Use cyanobacterial mat sediments adjacent to those with living *Spartina alterniflora* roots as a natural laboratory setting for study of effects of grass roots on sedimentary geochemistry, 3) To address the role of various fractions of solid phase Fe in the formation of pyrite.

Methods

Description of sites

Sediments were sampled in 1990 and 1991 from the saltmarsh near the convergence of Old Mill Creek and the Broadkill River in Great Marsh, Lewes, DE, as described in previous studies (Lord 1980; Luther & Church 1988; Luther et al. 1991). For an annual cycle over all seasons, cores were taken in March, April, June, August, and September of 1990, and in February of 1991. A more detailed description of the vegetation and hydrology of this saltmarsh is given in Dicker (1979). The areas sampled in the saltmarsh are considered mid-marsh sites and were dominated by the short form of saltmarsh cordgrass, *Spartina alterniflora* (Loisel). For each month one core was taken in sediments vegetated by *S. alterniflora* 5 m from the tidal creek and another was taken in unvegetated sediments at the same site and approximately the same distance from the tidal creek. Unvegetated sediments were overlain by a microbial mat and by a saltwater pond for most of the year. The microbial mat was composed mainly of cyanobacteria (including *Oscillatoria* sp., *Microcoleus* sp., *Spirulina* sp., and *Gleocapsa* sp.) and purple sulfur bacteria (such as *Thiocapsa*) were also present (P. Visscher, personal communication). The mat layer of unvegetated sediments was peeled off of the core under strict anoxic conditions and extruded separately from the rest of the solid phase. The mat layer was operationally defined at a depth of 0 cm in the results presented.

Core and porewater sampling

Cores were obtained by driving a cellulose-acetate-butyrate core liner into the sediment with a wooden bat, sealed with butyl rubber stoppers, and transported to the lab within a few hours of sampling. Core samples were acquired and processed under a nitrogen atmosphere in a glove box using a pneumatic squeezer to separate porewaters from the solid phase according to Lord (1980). Porewaters were placed into sealed syringes under nitrogen and, within hours of sampling, were analyzed for pH, alkalinity, sulfate, chloride, Fe(II), Fe(III), and dissolved sulfide. Solid pieces of the squeezed core were sealed in plastic bags under nitrogen and stored frozen.

Porewater analysis

Fe(II) and Fe(III) were measured with ferrozine according to a modification of Stookey (1970) which is described in Kostka & Luther (1994). Chloride and sulfate were analyzed using a Dionex 4000i ion chromatograph. Del sulfate is the sulfate in excess or depleted relative to the standard seawater sulfate/chloride ratio. Total alkalinity was measured via an adaptation of Gieskes & Rogers (1973) by Lord (1980) which involved Gran titration with NaOH after adding an aliquot of the sample to 1 mM HCl solution (pH = 3.0) to remove CO₂ and H₂S. The back titration was performed at the low pH region where organic buffering capacity can be significant. Total alkalinity includes carbonate species and other weak acids such as organic ligands which can complex metal ions. The pH of porewaters was measured by an Accumet pH meter potentiometrically using a Sensorex combination electrode which was calibrated after 15 min. equilibration in standard seawater. Porewater sulfide was measured as described in Luther et al. (1985). Square wave voltammetry was performed at less than 10 μM sulfide and sample DC polarography was used for sulfide measurements at greater than 10 μM concentrations on an EG&G Princeton Applied Research 384B Polarograph.

Solid phase extractions

Frozen sediments were placed immediately into a glove bag under nitrogen. Sediment was thawed and homogenized with a spatula. Triplicate 1 g samples were placed into preweighed vials and dried at 75 °C until a constant mass was reached for calculation of wet-to-dry-weight ratios. Triplicate 0.1 to 0.5 g samples were placed into vials containing each chemical extract (error bars refer to triplicate extractions from each core depth). Solid phase reactive Fe was measured according to an extraction scheme calibrated with standard Fe minerals as described in Kostka & Luther (1994). We operationally define

the amorphous Fe(III) oxide fraction as that leached in ascorbate (pH 8). The total oxidized or total reactive Fe fraction is that Fe leached in dithionite less the Fe associated with acid volatile sulfide (AVS). Crystalline Fe(III) minerals are operationally defined as the difference between the total oxidized Fe and the amorphous Fe(III) fractions.

Acid volatile sulfide and pyrite were measured according to the method of Cutter & Oatts (1987) with modifications to the procedures for trapping and analyzing H₂S (Luther et al. 1991). For AVS, 50–100 mg of wet sediment was added to 20 ml of deaerated 6 N HCl for 30 to 40 min. in a gas-tight reaction flask. Inert gas, nitrogen or argon, was bubbled through the flask and into the trap continuously at the slowest rate possible. One milliliter of concentrated H₂SO₄ and 4 ml of diamine reagent (3–40 μM range as per Cline 1969) were added to the trap which contained 25 ml of 3% Zn acetate. Sulfide was measured as absorbance at 670 nm on a spectrophotometer and compared to a Na₂S standard according to the method of Cline (1969). Sulfide from pyrite was released with acidic Cr(II) solution (Canfield et al. 1986) and the resulting H₂S was trapped and analyzed as above.

Results

Seasonal cycling of solid phase Fe

Total Fe by weight in the sediment was determined for the March, 1990, vegetated core by two methods (Table 1). First, by adding mean pyrite-Fe to the mean dithionite-extractable Fe, and then by measuring the total Fe in sediment extracts treated successively with H₂SO₄, aqua regia, and HF. The additive total is the Cr-reducible fraction which should include most sulfides (Canfield et al. 1986) plus the dithionite-extractable fraction which should include all oxidized forms of Fe except for clay minerals. The extracted total should include all Fe minerals in the sediment including clays. The percentage of the extracted total which was also extractable in dithionite decreased rapidly with depth in March vegetated sediments (Table 1). At 0–2.5 cm depth, additive and extracted total Fe values were similar. Below 2.5 cm, the additive total of reactive plus pyrite-Fe decreased while the total Fe extracted remained relatively constant in the March core. Though we did not measure the extracted total in all cores, the additive total of reactive plus pyrite-Fe was in general lower at 5–7.5 cm and 20–25 cm in all cores studied.

In the top 2.5 cm, amorphous Fe(III) ranged from less than 10 to greater than 250 μmoles Fe/gdwt (Fig. 1a). At depth, lower concentrations of amorphous Fe(III) were observed and no seasonal trend was apparent (Fig. 1b,

Table 1. Total Fe extracted from the March, 1990, vegetated saltmarsh core and the percentage of this total that is reactive Fe.

Depth (cm)	Additive total (%) [*]	Extracted total (%) [@]	% Reactive [#]
0-2.5	2.3	2.6	85
5-7.5	1.4	3.2	42
10-12.5	1.6	2.7	32
20-25	1.2	2.5	23

* Total Fe by weight in sediment calculated by adding mean concentrations of pyrite and dithionite-extractable Fe.

Dithionite-extractable Fe/Total Fe.

@ Total Fe by weight in sediment by successive extraction in H₂SO₄, aqua regia, and HF.

1c). Crystalline Fe(III) ranged from less than 50 to greater than 500 μ moles Fe/gdwt and a seasonal cycle was apparent at all depths to 25 cm (Fig. 1). Solid phase reactive Fe (amorphous + crystalline Fe) and pyrite showed similar/opposite trends at all depths (Figs. 1 and 2).

Evidence of a sedimentary reduction/oxidation cycle was observed throughout the 1990-91 sampling period. At the range of depths shown in Fig. 1, oxidized forms (amorphous Fe(III) and total reactive Fe concentrations) were observed in the highest concentrations in the sediments sampled during the coldest months in March, 1990 and February, 1991. A mid-summer maximum was observed for solid phase, oxidized Fe as well (Figs. 1 and 2). From June to September, decreases in oxidized Fe correspond to increases in pyrite at all depths. The lowest solid phase, oxidized Fe concentrations were observed in September, 1990. This core was sampled after heavy rainfall. The marsh surface was submerged and a layer of black FeS was observed on the top of the sediment. Pyrite values were also highest in September (Fig. 1). With increasing depth in vegetated cores, oxidized Fe accounted for a smaller portion of the extractable Fe and pyrite accounted for a concomitantly larger portion (Fig. 1).

HCl-Fe(II) showed a mid-summer minimum at all depths in September (Fig. 3a). Though larger in scale, these HCl-Fe(II) data parallel in mid-summer minimum observed for AVS (data not shown). Similar seasonal trends were observed for HCl-extractable Fe [Fe(II) at all depths and Fe(III) in surface sediments] as were observed for reactive Fe and amorphous Fe (Figs. 1, 2). HCl-Fe(III) concentrations (Fig. 3b) were nearly identical to those of amorphous Fe(III) (ascorbate-extractable Fe) in all sediments sampled lending support to the assumption that we are indeed extracting oxidized Fe.

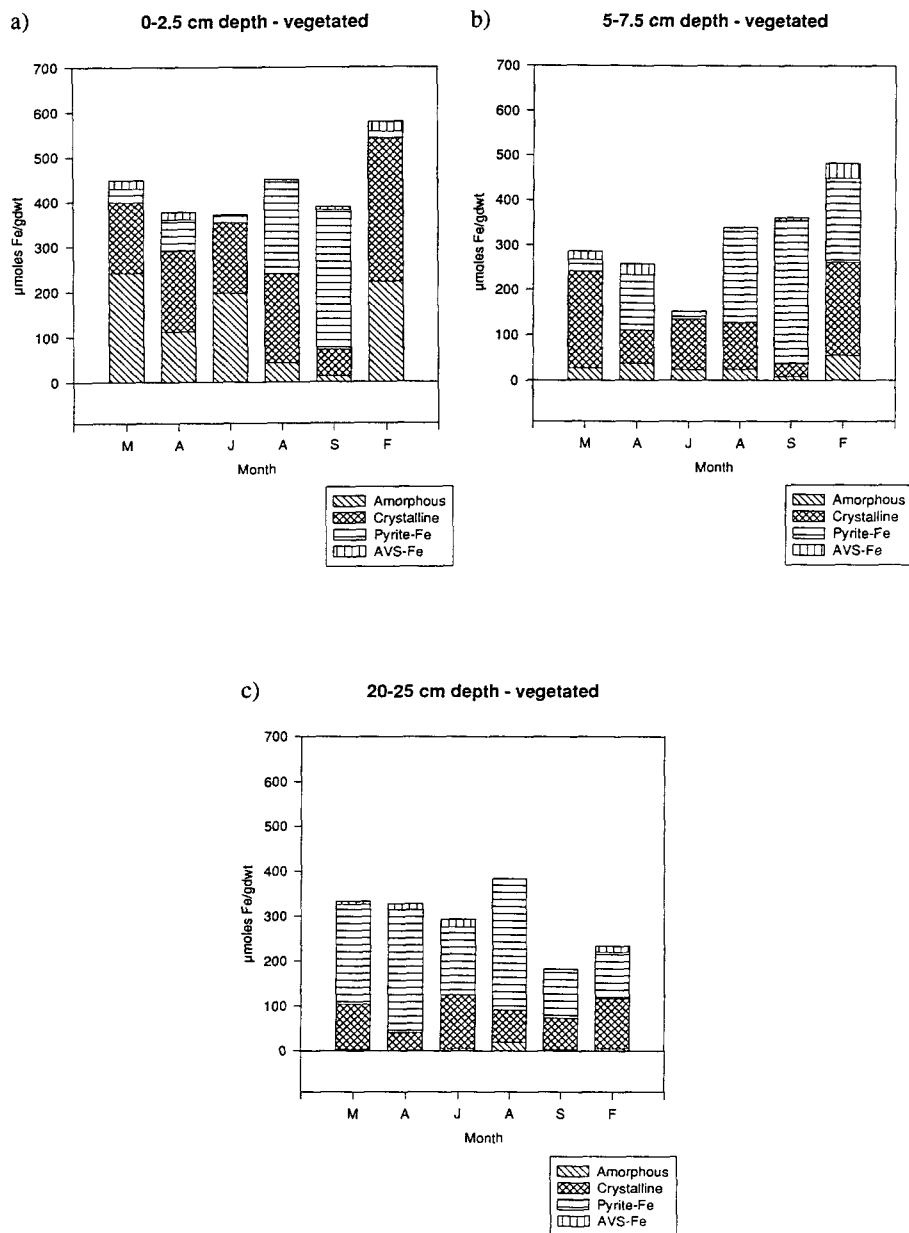


Fig. 1. Partitioning of solid phase Fe extracted from vegetated sediments sampled from 1990 to 1991 in the Delaware saltmarsh: a) 0–2.5 cm depth interval, b) 5–7.5 cm depth interval, c) 20–25 cm depth interval. All extractions were carried out according to Kostka & Luther (1994).

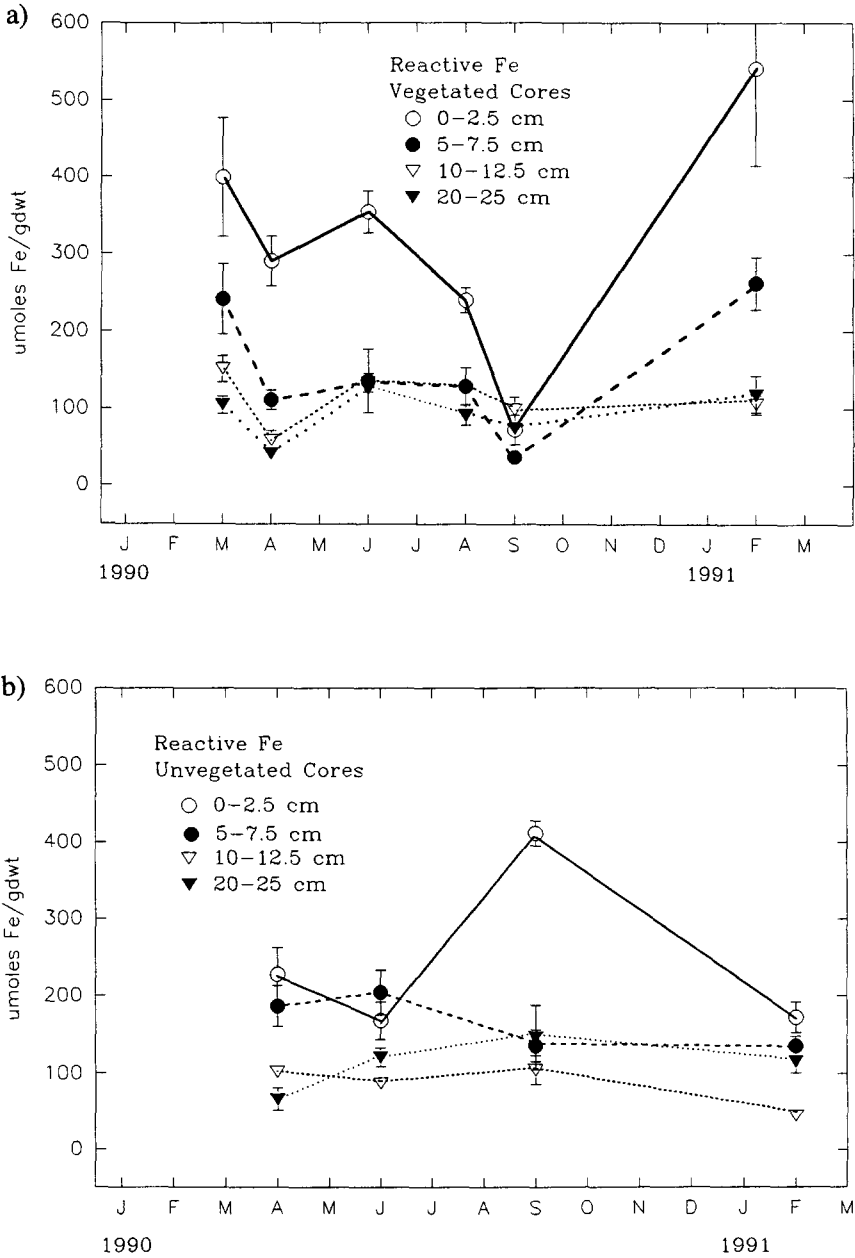


Fig. 2. Reactive Fe extracted from Delaware saltmarsh sediments sampled throughout the 1990-1991 season: a) vegetated sediments, b) unvegetated sediments. Reactive Fe was extracted with dithionite as described in Kostka & Luther (1994).

Large concentrations of solid, oxidized Fe were extracted in HCl at 0–2.5 cm depth, and this solid Fe(III) was rapidly cycled during the 1990–1991 season (Fig. 3b). Much less HCl-Fe(III) was present below 2.5 cm depth and no seasonal trend was observed.

As expected, an abbreviated solid Fe cycle was observed in unvegetated sediments relative to vegetated sediments. Reactive Fe was present at significant concentrations in unvegetated sediments, but no seasonal trend was observed. With the exception of the surface 0–2.5 cm depth sampled in September, reactive Fe changes little over the 1990–1991 sampling period (Fig. 2b), and this maximum in reactive Fe was paralleled by a large increase in HCl-Fe(II) (Fig. 3c). Together, reactive Fe and HCl data suggest that most solid Fe is reduced in unvegetated sediments with FeS or amorphous clay minerals the likely species.

AVS concentrations were small relative to pyrite in vegetated sediments and no seasonal trend was apparent (Kostka 1992). AVS concentrations displayed a large range in unvegetated ($\leq 500 \mu\text{moles Fe/gdwt}$) relative to vegetated marsh sediments ($\leq 35 \mu\text{moles Fe/gdwt}$) (data not shown).

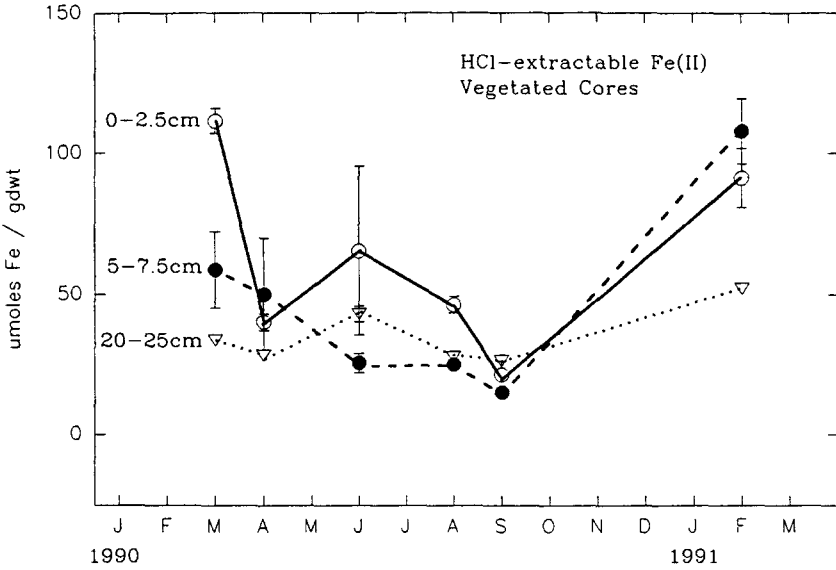
Porewater chemistry

As expected, sulfate concentration decreased with depth to 12.5 cm and alkalinity concomitantly increased (Kostka 1992; Lord & Church 1983). Mean sulfide concentrations showed large increases of 3–4 mM with depth to 12.5 cm in both vegetated and unvegetated environments. Vegetated porewaters (mean pH = 6.5–7.5) displayed an average of 0.5 pH unit lower than unvegetated porewaters (mean pH = 7.0–7.5) throughout all depths in the sediments over the year (Fig. 4; Kostka 1992). Iron (II) displayed a seasonal average of 100–200 μM in vegetated porewaters to 12.5 cm depth, whereas Fe(II) averaged above 10 μM only in the top 5 cm of unvegetated sediments and never reached over 60 μM when averaged over the 1990–1991 season.

Oxygen was never detected polarographically in any of the porewaters sampled during this study and in earlier work (Luther et al. 1991). Oxygen can be detected during the polarographic measurement of porewater sulfide. Using a solid state microelectrode, Brendel & Luther (1995) have since shown that oxygen does not penetrate below 4–5 mm unless there is significant bioturbation or dead plant roots which can pass oxygen through inner open spaces.

A mid-summer maximum in del sulfate (indicative of sulfide oxidation) was observed in the upper depths of vegetated cores (Fig. 4a) which was not observed in the unvegetated cores (Fig. 4b). Del sulfate values remained similar at 20–25 cm depth in vegetated and unvegetated sediments throughout the year (Fig. 4a, b). Total alkalinity values showed an opposite trend to del

a)



b)

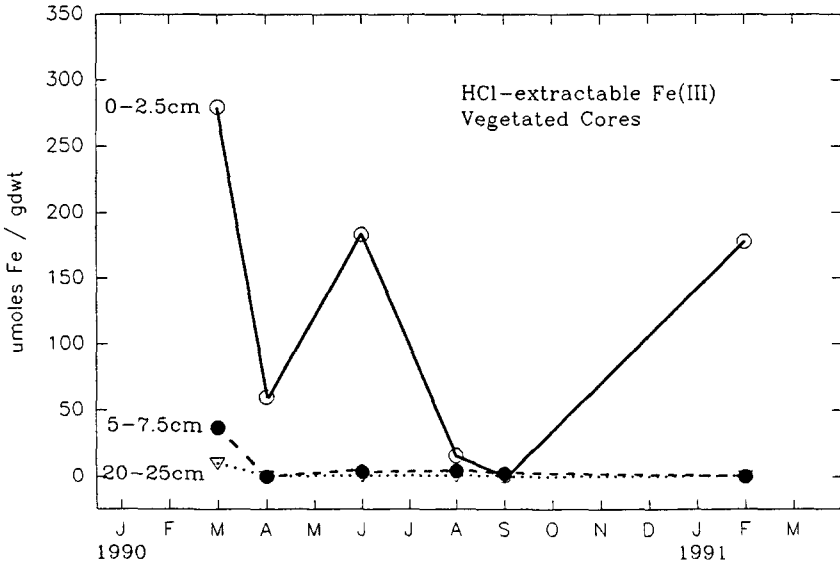


Fig. 3. Solid Fe extracted in HCl from saltmarsh samples collected over the 1990–1991 season: a) Fe(II) in vegetated sediments, b) Fe(III) in vegetated sediments, c) Fe(II) in unvegetated sediments, d) Fe(III) in unvegetated sediments. Note difference in scale between plots of Fe(II) and Fe(III). Oxidation state determination was carried out in 0.5 N HCl according to Kostka & Luther (1994).

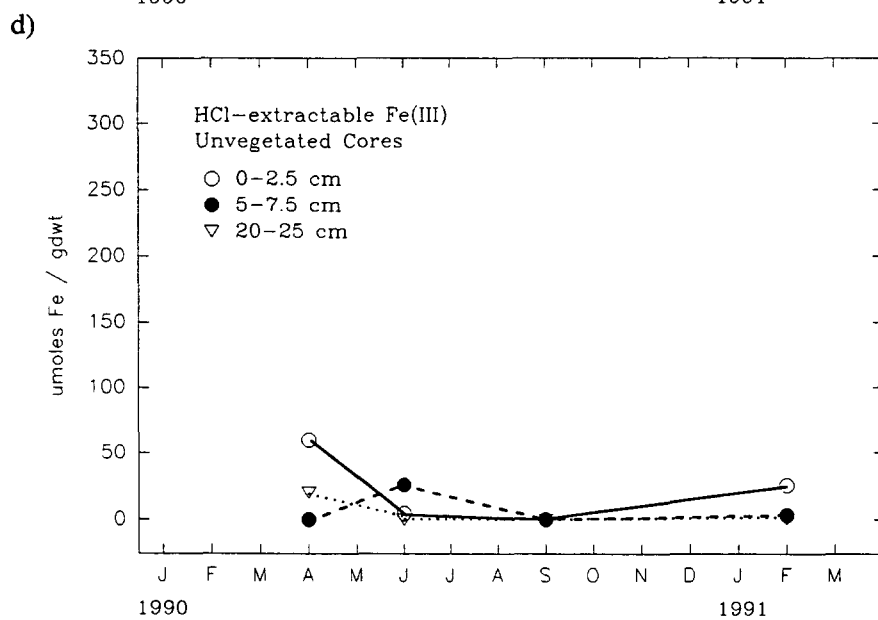
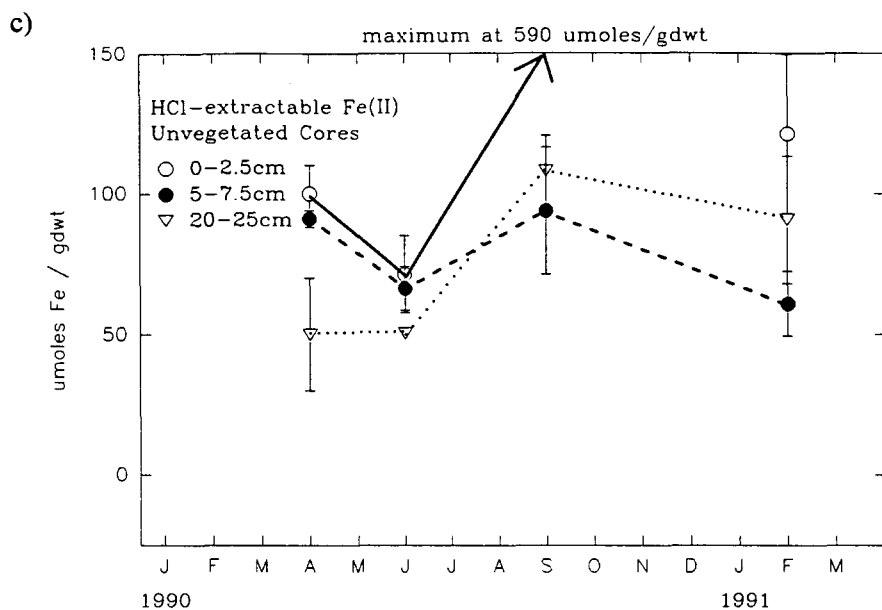


Fig. 3. (Continued).

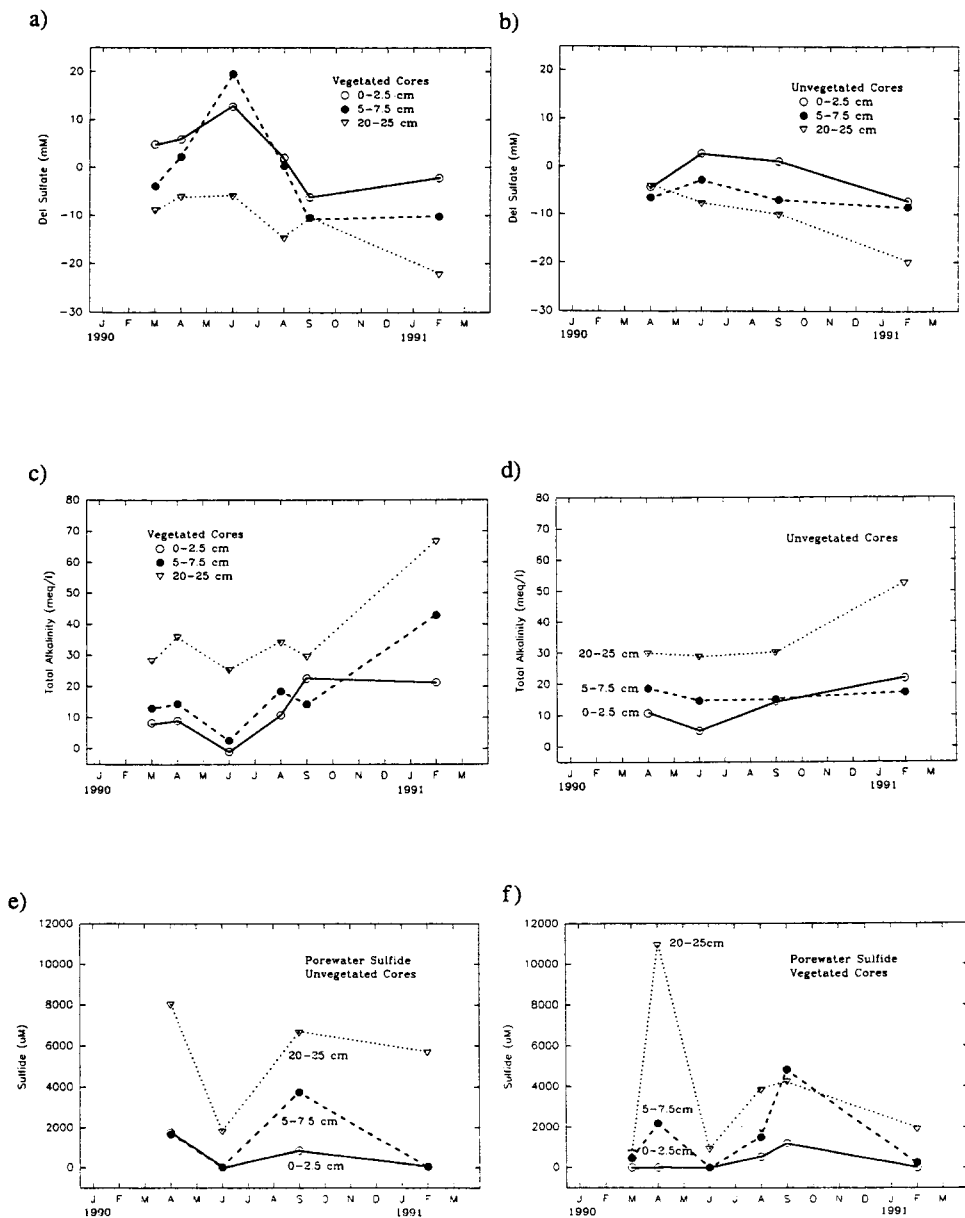


Fig. 4. Porewater chemistry of vegetated and unvegetated sediments sampled over the year of 1990–1991 in the saltmarsh: a) and b) del sulfate, c) and d) total alkalinity, e) and f) sulfide, g) and h) pH, i) and j) Fe(II). Panels on left represent vegetated sediments and panels on right represent unvegetated sediments.

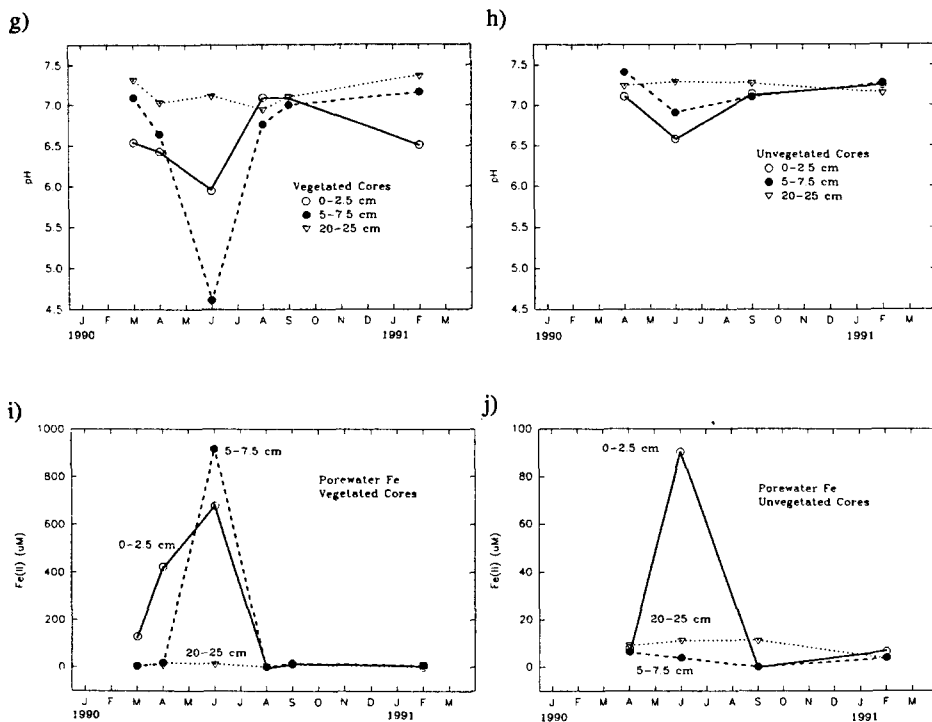


Fig. 4. (Continued).

sulfate at all depths in vegetated and unvegetated cores over the year (Fig. 4c, d).

Porewater sulfide showed a seasonal cycle which persisted at all depths examined (Fig. 4e) with maxima observed in the months of April and September. Dissolved sulfide showed a similar seasonal cycle in unvegetated cores as compared to that of vegetated cores with maxima in April and September (Fig. 4e, f).

Porewater pH exhibited a pronounced mid-summer minimum in vegetated sediments at 0–2.5 cm and 5–7.5 cm depth providing further evidence of sulfide oxidation (Fig. 4g). In the coldest months of the annual cycle, pH was near neutral at all depths in vegetated and unvegetated porewaters (Fig. 4g, h). Porewater pH changed less over the 1990–91 sampling period in unvegetated sediments.

Vegetated sediments showed a release of Fe(II) (Fig. 4i) into the upper porewaters during spring and early summer which corresponded to a large decrease in porewater pH (Fig. 4g) and the beginning of the *Spartina alterni-*

Table 2. Correlation coefficients linking sedimentary Fe concentrations to those of sedimentary sulfides in the Delaware saltmarsh.

	0–2.5 cm depth		20–25 cm depth	
	H ₂ S	FeS ₂	H ₂ S	FeS ₂
Amorphous Fe(III) ^d	–0.71 ^c	–0.86 ^a	–0.03	–0.21
Crystalline Fe(III) ^d	–0.44	–0.40	–0.96 ^a	–0.26
Total reactive Fe ^d	–0.72 ^c	–0.79 ^b	–0.88 ^a	–0.21
HCl Fe(II)	–0.49	–0.59	–0.28	–0.32
HCl Fe(III)	–0.52	–0.67 ^c	No HCl Fe(III)	
Porewater Fe(II)	–0.24	–0.24	–0.004	–0.71 ^c

^a $r_{0.05(2)4} = 0.811$

^b $r_{0.10(2)4} = 0.729$

^c $r_{0.20(2)4} = 0.608$

^d As defined by Kostka & Luther (1994):

Amorphous Fe(III) oxide = ascorbate-extractable Fe (pH 8)

Total reactive Fe(III) = [dithionite-extractable Fe] – [AVS-Fe]

Crystalline Fe(III) = [total reactive Fe] – [amorphous Fe(III)] – [AVS-Fe]

flora growth season (Morgan 1961; Clarke 1978). Similar to the abbreviated cycle of solid Fe, unvegetated sediments showed a depressed cycle of porewater Fe(II) with concentrations exceeding 20 μ M only in June, 1990 (Fig. 4j; note smaller scale). Little Fe(II) was detected in the 20–25 cm depth interval and no seasonal cycle was apparent at this depth in vegetated or unvegetated sediments (Fig. 4i, j).

Linear regressions were calculated to relate sedimentary Fe to sulfides in the six vegetated cores over the year (Table 2). Amorphous Fe(III) oxide in vegetated sediments showed a negative correlation with dissolved sulfide in surface sediments over the year with an $r^2 = -0.71$ (Table 2). Total reactive Fe concentrations (amorphous and crystalline fractions) also negatively correlated with porewater sulfide at all depths with correlation coefficients of –0.72 and –0.88 for the 0–2.5 and 20–25 cm depth intervals respectively (Table 2). The crystalline Fe(III) fraction [$\{\text{dithionite-Fe}\} - \{\text{ascorbate-Fe}\} - \{\text{AVS-Fe}\}$] in vegetated sediments was not highly correlated to dissolved sulfide in the surface, but showed a high negative correlation ($r^2 = -0.96$) at 20–25 cm depth (Table 2). The crystalline Fe(III) (adjusted for amorphous Fe(III) and AVS) was removed from the sediment in April and September, especially at depth which indicates it is a reactive pool which is rapidly cycled. This Fe is likely to be entering the pyrite fraction as maxima were observed in April and September for pyrite (Fig. 1).

Discussion

A wealth of data has been gathered on porewater (Fe, S) and solid phase (mainly S) geochemistry in the Delaware saltmarsh (Lord 1980; Boulegue et al. 1982; Lord & Church 1983; Luther et al. 1986; Cutter & Velinsky 1988; Luther & Church 1988; Schudlark & Church 1989; Ferdelman et al. 1991; Luther et al. 1991; Tsamakis 1991; Luther et al. 1992). Most of the data gathered during previous studies were from cores collected within tens of meters from the sediments described in this study. Our study builds on previous work by using a calibrated extraction scheme (see Kostka & Luther 1994) to partition solid phase Fe and by comparison of porewater/solid phase geochemistry in vegetated and unvegetated cores over a seasonal cycle.

Reactive Fe: definitions, comparisons

Considering the percentage of total Fe that is reactive in the solid phase (Table 1; Kostka & Luther 1994), surficial saltmarsh sediments contain more reactive Fe than any marine sediment studied so far (Canfield 1989, 1993; Aller et al. 1986; Leslie et al. 1990). What drastically differs between marine sediments is the proportion of Fe that is extractable by conventional means and may be considered 'reactive Fe'.

Berner (1970) defined 'reactive Fe' as that which could react to form pyrite. He used 6N HCl to extract the sediments which would have included some Fe in FeS and in silicates. Canfield (1989) used a dithionite extraction in his study and defined 'reactive Fe' as that which would react with sulfides. Our operational definition of 'reactive Fe' is more similar to Canfield's in that we used a dithionite extraction and we partitioned oxidized Fe into amorphous and crystalline fractions. The dithionite extraction we used has been shown to extract a large portion of the Fe contained in crystalline and amorphous Fe(III) oxides, reactive Fe silicates such as smectites, and a smaller portion of FeS (Canfield 1988; Canfield 1989; Kostka 1992; Kostka & Luther 1994). Variability in each of the measures of 'reactive Fe' probably occurs because of differences in crystallinity and mineralogy found in various sediments.

Silicate minerals may cause much of this variability in 'reactive Fe' measured by HCl or dithionite extractions. Canfield (1988) provided an interesting comparison between 6 N HCl and dithionite extractions which is relevant here. The reactive Fe-rich phyllosilicate, nontronite was almost completely extracted overnight in dithionite whereas only 10–15% was extracted in 6 N HCl. In contrast, a larger portion of other Fe silicates (30–40%), such as biotite and chlorite, was extracted in 6 N HCl and not in dithionite. In our laboratory, we have also observed that a small percentage of the structural Fe in smectites is extracted overnight in 6 N HCl (Kostka et al., unpublished

observations). These data imply that dithionite is more effective in selectively extracting reactive silicates than HCl. Therefore, current data suggest that dithionite is a better measure of 'reactive Fe' that is available for chemical or biological cycling on annual scales or less. This conclusion is supported by Canfield et al. (1992), which suggests that HCl digests (reactive iron sensu, Berner 1970), though they may provide some measure of the amount of Fe that is potentially reactive toward sulfide, do not provide accurate information on the actual reactivity of Fe present. This may also explain why Berner (1970) and others usually found low degree of pyritization indices for marine sediment using an HCl extraction while Canfield (1989) found reactive oxide content was lower than 50%.

Previous work has suggested that authigenic silicates may be forming at depth in Delaware saltmarsh sediments (Kostka & Luther 1994). The difference between the additive total Fe and the extracted total Fe (see Fig. 1, Table 1) which becomes larger with depth in our study, could be explained by the formation of less reactive silicates which are extracted in HF (used in extracted total) but not by extractants used to measure pyrite (Cr reduction) or reactive Fe (dithionite).

In coastal marine sediment extracted by Canfield (1989), dithionite-extractable Fe never comprised more than 35% of the total Fe extracted and easily extractable Fe (oxalate Fe-AVS) never reached over 20% of the total Fe extracted. Aller et al. (1986) measured total Fe concentrations of 5% by weight in Amazon sediments but hydroxylamine/HCl and dithionite leaches comprised 14% and 50% of this Fe, respectively. Oenema (1990) reported similar values for oxalate-extractable Fe and dithionite-extractable fractions which comprised half of the total Fe in saltmarsh sediment. In this study, dithionite and HCl-extractable Fe accounted for over 80% of the total Fe in summer, surface sediments (Table 1, Fig. 3) and ascorbate-extractable Fe accounted for up to 50% of the total (Fig. 1, Table 1; Kostka & Luther 1994). Also, reactive Fe(III) was present at deeper depths in our saltmarsh sediments as compared with subtidal marine sediments (Fig. 2; Canfield 1989).

The data show that reactive Fe oxides are present at higher concentrations and are more rapidly cycled in saltmarshes as opposed to marine subtidal sediments. The saltmarsh is an unusual marine sediment in that it is exposed to a constantly renewed supply of organic carbon produced (in the sediment) by grass roots, and oxidant is provided by both the atmosphere and tidal waters. These processes along with episodic weather events produce an extremely reactive sedimentary environment where reactive Fe(III) is rapidly cycled.

Solid Fe(III) in pyrite formation

Saltmarsh Fe that is available for pyrite formation must reside in the solid phase and is only fleetingly cycled through the porewaters. The maximum concentration of porewater Fe(II) observed in our study (1200 μM) would translate into a small fraction of the pyrite or AVS that is present in marsh sediment (0.67 $\mu\text{moles Fe/gdwt}$) at a sediment density of 1.8 g/cm^3 . Further, Fe(II) is only visible in the porewaters of vegetated sediments where the effects of pyrite/sulfide oxidation (porewater pH, alkalinity changes; Figs. 1, 4) are most prevalent (Luther et al. 1991). Amorphous Fe(III) oxides (Fig. 1) and crystalline Fe(III) oxides (Fig. 1) persist in the sediments after the porewater Fe(II) has reacted to form pyrite. For example, a progressive decline in Fe oxides (Figs. 1, 2) is observed from June to September which corresponds to a progressive increase in pyrite (Fig. 1). No porewater Fe is present in August or September so pyrite must be forming ultimately at the expense of the solid phase reactive Fe.

Previous studies suggest that the rapid formation of pyrite from reactive Fe in Delaware saltmarsh sediments extends to 15 cm depth (Cutter & Velinsky 1988) or to 9 cm depth (Lord & Church 1983) primarily because no reactive Fe was thought to be present below these depths. Based on a more precise determination of amorphous and crystalline Fe(III) minerals, our data indicate that the zone where reactive Fe(III) is available extend to at least 20–25 cm depth in the Delaware saltmarsh. Reactive Fe oxides measured in this study ranged from below 40 $\mu\text{moles Fe/gdwt}$ to above 500 $\mu\text{moles Fe/gdwt}$ in the upper 20–25 cm of vegetated sediments (Fig. 2) with over 80% of the reactive Fe pool cycled in 6–8 weeks (June to September, 1990; Fig. 1). Reactive Fe(III) oxide concentrations were highly negatively correlated with sulfides in the 20–25 cm depth interval (Table 2). Also, pyrite was turned over in the 20–25 cm depth interval of this study (Fig. 1).

Crystalline Fe(III) oxides associated with *Spartina* roots have been identified in saltmarsh sediments (e.g., Luther et al. 1982), however previous research has indicated that they were responsible for an insignificant amount of pyrite formation. For example, Lord & Church (1983) incorporated Rickard's (1974) reaction of crystalline Fe(III) oxides with sulfide into their diagenetic model of saltmarsh sediments, and they suggested that crystalline Fe(III) minerals were not reactive on time scales relevant to pyrite formation. Seasonal changes and new data on crystalline Fe(III) minerals (Fig. 1, this study; Kostka & Luther 1994) lead us to suggest that the role of crystalline Fe(III) in pyrite formation has been underestimated in the top 20 cm of saltmarsh sediments, the zone affected most by *Spartina* roots (Gross et al. 1991). Though it is less pronounced, crystalline Fe(III) oxides (Fig. 1) are significantly cycled at all depths and decreases in crystalline Fe(III) oxides

correspond to increases in pyrite (Fig. 1, Table 2). This evidence suggests that a larger Fe(III) pool is available for rapid pyrite formation than has been suggested in the past.

The cycling of reactive Fe(III) is dominated by amorphous Fe(III) minerals in surface sediments and crystalline Fe(III) at depth. The dependence of pyrite formation on amorphous Fe(III) minerals in surface marine sediments was suggested previously (Canfield 1988) based on solid-phase Fe extractions. We support this hypothesis for amorphous Fe(III) by showing the complete cycling of these most reactive Fe oxides in surface sediments, and we suggest the importance of crystalline Fe(III) oxides in rapid pyrite formation over a seasonal cycle.

Both solid (Figs. 2, 3) and porewater Fe (Fig. 4) indicate a lack of reactive Fe(III) at depth in unvegetated sediments. Though solid phase reactive Fe was observed in unvegetated sediments, no seasonal trend was apparent and most of the solid Fe was shown to be reduced (Fig. 3c). Reactive Fe(III) is ultimately cycled at depth in marsh sediments only after it is released via pyrite oxidation and an oxidant is needed to release this Fe (Giblin & Howarth 1984; Luther et al. 1992). Of the reactive Fe that does form, it is dominated by Fe(II) minerals, mainly FeS, which cycle closer to the surface of the sediments.

In general, porewaters of unvegetated sediments showed smaller seasonal changes than those observed for vegetated sediments, and no evidence of pronounced desiccation was observed though unvegetated porewaters did have higher mean chloride concentrations (Kostka 1992). A layer of FeS was commonly observed underneath microbial mats, and elevated AVS concentrations were associated with the surface of unvegetated saltmarsh sediments (Kostka 1992). The presence of elevated AVS in the surface of unvegetated cores seemed to support the hypothesis of Nedwell & Abram (1978) that sulfide was being trapped at the surface as FeS; elevated AVS concentrations may result from the lack of oxidant at depth which prevents pyrite formation (Giblin & Howarth 1984) and subsequent oxidation. Previous studies on the porewaters and solid phase S of sediments overlain by a microbial mat (Jorgensen & Fenchel 1974; Skyring & Johns 1980; Luther & Church 1988; Oenema 1990), though often based on a single core, observed similar characteristics.

Sediment oxidation is clearly related to plant growth since sediments overlain by a microbial mat tended to be more reducing. The mat provides a physical barrier to the diffusion of oxygen to the underlying sediments, and vertical advection has been determined to be of minor importance in these saltmarsh sediments (Luther et al. 1991). Using ^7Be tracers, Casey et al. (1986) observed infiltration of surface waters into unvegetated sediments

which were primarily unsaturated. Delaware saltmarsh sediments in 1990 to 1991 never really exhibited signs of unsaturation on scales similar to those observed by Casey & Lasaga (1987) and Casey et al. (1986). Most likely, the predominant geochemical differences between unvegetated and vegetated sediments can be explained by the passive transport of oxygen to depth along living *Spartina* roots in vegetated sediments. This funneling of oxygen may be supported by tidal inundation which supplies oxygenated water to surface sediments.

Seasonal cycling of solid Fe(III)

This study of solid phase Fe supports the conclusions of previous studies which indicated that the cycling of Fe is controlled by sulfate reduction and sediment oxidation in the saltmarsh (Giblin & Howarth 1984; Giblin 1988; Luther & Church 1988; Casey & Lasaga 1987; Hines et al. 1989). Most of the Fe in saltmarsh sediments is stored in the solid phase, which is cycled rapidly and completely between Fe oxides and pyrite. Sulfate reduction and sulfide oxidation are seasonal phenomena, but the timing and intensity of these processes varies with physical factors and the physiology of grasses. The physiology of *Spartina* has a dominant effect on Fe and S geochemistry via the production of organic matter (Hines et al. 1989; Gardner 1990) and the funneling of oxygen through roots (Dacey & Howes 1984; Howes et al. 1981). Depending upon the interplay of these variables, the cycling of solid Fe(III) is poised between consumption due to reaction with sulfides and production via the oxidation of sulfides.

Sulfate reduction rates determine the net production of sulfides (Howarth & Merkel 1984). Sulfate reduction, mediated by bacteria, depends on C availability which is determined by the physiology of grasses, temperature, and light (Hines et al. 1989). Of these controls, temperature and light will change on an annual scale whereas, *Spartina* physiology may respond episodically to other organisms such as insects (Hines et al. 1989) or to the geochemistry of the sediments in a feedback loop (King et al. 1982).

Sediment oxidation depends upon physical processes such as weather and tidal events. Organisms also have dominant effects on sediment oxidation through the production of reduced S, evapotranspiration, and bioturbation. In the Delaware marsh, bioturbation was determined to be of minimal importance whereas evidence for the infiltration of overlying waters into the sediment was observed (Luther et al. 1991). Dessication was probably less important in our study since surface sediments were always saturated with water. Therefore, sediment oxidation is likely mediated by infiltration, by the passive transport of oxygen through *Spartina* roots, and possibly by evapotranspiration in the Delaware marsh (Dacey & Howes 1984).

We observed that a large amount of control may be exerted on sediment oxidation by episodic rain events. A deluge of rain inundated the marsh in August and September stimulating sulfide production and the storage of pyrite (Fig. 1, 5; Kostka 1992). Black FeS was observed to cover the surface sediment resulting in extreme reducing conditions which were reflected in the porewaters and in solid phase geochemistry. This short-term event (on the scale of a few weeks) caused a nearly complete consumption of the reactive Fe present in the saltmarsh sediments we sampled. Tides must have also played a role in the short-term cycling of Fe but evidence of it is less easily detected. Apparently, annual variables such as climate and the growth of grasses are superimposed by short-term effects such as rainfall and tidal inundation in controlling the geochemical Fe cycle of saltmarsh sediments.

A pronounced seasonal cycle of solid Fe was observed in vegetated sediments of the Delaware marsh (Figs. 1–4) which responds to the controls discussed above. In early spring (March to April), increasing sulfate reduction rates overcame sulfide oxidation to result in net pyrite formation at all depths (Fig. 1). As observed in previous studies (Giblin & Howarth 1984; Luther & Church 1988; Luther et al. 1991), evidence of a pronounced sulfide oxidation event was shown in the porewaters and solid phase of vegetated sediments during late spring/early summer. An increase in porewater Fe indicated that Fe sulfides (pyrite, FeS) were oxidized and a net loss of pyrite was observed (Figs. 1, 4) from April to June. Iron(III) oxides responded dramatically to maxima in porewater sulfide (Figs. 1, 2, 4e) and pyrite (Fig. 1) and were almost completely removed from vegetated sediments from June to September, 1990. Such a cycle was not observed in unvegetated sediments and the concentration of reactive Fe did not change in these sediments throughout the season (Figs. 2–4).

The above controls would explain the fact that the highest Fe(III) oxide concentrations were observed during the coldest months of our study (Fig. 3). Iron(III) oxides may be produced all year through the passive transport of oxygen along roots into the sediment, but they are predominantly cycled or consumed during the summer months when grasses and bacteria are active. Apparently, Fe oxidation reactions outcompeted Fe reduction in colder months as oxidized Fe minerals dominated in these sediments.

With an increase in depth of the sediment, biotic controls and the injection of oxidants diminish. Less Fe is cycled and Fe is stored in more thermodynamically stable forms such as crystalline Fe(III) oxides, pyrite, and Fe silicates. Our study shows that these more stable forms at depth are subject to the same controls as more reactive Fe in surface sediments. Since the amount of extractable Fe decreases with depth (Table 1) when using extraction methods

for pyrite or Fe oxides, we suspect that more solid Fe is stored and cycled as silicates in saltmarsh sediments than was thought previously.

Summary

Nearly all of the Fe(III) extracted from surface sediments in this study must be considered reactive, and more solid phase reactive Fe was observed in this Fe-rich sedimentary environment than in any of the marine subtidal sediments studied previously (Canfield 1988; 1989; Aller et al. 1986). As suggested by Gibling & Howarth (1984), Fe is mainly stored in the solid phase of saltmarsh sediments and is cycled between Fe(III) oxides and pyrite. Amorphous and crystalline Fe(III) oxides both react rapidly to form pyrite in saltmarsh sediments to 20–25 cm depth. In surface sediments, amorphous Fe(III) oxides are primarily responsible for pyrite formation, whereas crystalline Fe(III) oxides are more closely coupled to sulfides at depth. Reactive Fe(III) cycling is governed by the growth of biota (marsh grasses and bacteria) via: sediment oxidation, the production of organic matter, and sulfate reduction. Long-term Fe cycling is governed by climatic variables such as light and temperature on an annual scale; episodic effects such as weather and tidal inundation superimpose and may override the importance of annual variables. Reactive Fe responds to a very different set of conditions in unvegetated sediments, which contain no living roots and therefore no belowground source of oxidant and organic matter. By comparing the geochemistries of adjacent vegetated and unvegetated sediments, we indicate that living *Spartina* roots lead to the production and rapid cycling of solid phase reactive Fe(III).

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