

# Sulfidisation processes in a reactive Fe-enriched acid sulfate soil, northeastern Australia

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## Abstract

Solid phase Fe and S fractions were examined in a formerly severely acidified acid sulfate soil (ASS) wetland undergoing remediation via tidal inundation. Considerable diagenetic enrichment of reactive Fe(III) oxides (HCl- and dithionite-extractable) occurred near the soil surface (0–0.05 m depth). Extremely large concentrations of reactive Fe were determined up to 3,590  $\mu\text{mol/g}$  and accounted for ~90% of the total Fe pool. This major source of reactive Fe exerts a substantial influence on sulfidisation processes and the formation, speciation and transformation of reduced inorganic S (RIS) in tidally inundated ASS. Following tidal inundation over the past 5 years, acid volatile sulfide (AVS; up to 57  $\mu\text{mol/g}$ ) and elemental sulfur ( $\text{S}^0$ ; up to 41  $\mu\text{mol/g}$ ) were the dominant fractions of RIS in near surface soils. AVS-S to pyrite-S ratios exceeded 2.9 near the surface, indicating that abundant reactive Fe favoured the accumulation of AVS minerals and  $\text{S}^0$  over pyrite. While the large availability of reactive Fe may limit the transformation of AVS minerals and  $\text{S}^0$  to pyrite during early diagenesis, over longer time scales it can also promote the sequestration of S within pyrite. These findings provide an important understanding of sulfidisation processes occurring in reactive Fe-enriched, tidally inundated ASS landscapes.

## Key Words

Reactive iron, reduced inorganic sulphur, pyritisation, tidally inundated, remediation, East Trinity.

## Introduction

Cycling of Fe and S are key processes in the biogeochemistry of intertidal estuarine sediments (e.g. Canfield 1989; Morse and Rickard 2004). In these sedimentary environments, bioauthigenic pyrite ( $\text{FeS}_2$ ) is a major sink for reduced S and its formation via the process of sulfidisation has been studied extensively (e.g. Berner 1970; Boesen and Postma 1988). Drainage of sulfide-rich, estuarine materials is known to cause rapid oxidation of pyrite, leading to severe acidification and the development of acid sulfate soils (ASS). An innovative approach to remediating ASS landscapes is to restore tidal inundation (Johnston *et al.* 2009a; Powell and Martens 2005). Tidal inundation radically alters the geochemical conditions of soils, promoting microbially-mediated reduction of Fe(III) and  $\text{SO}_4^{2-}$ . Re-establishing tidal inundation in ASS can cause reductive dissolution of these minerals within the soil profile and lead to substantial enrichment of the reactive Fe fraction near the soil surface (Johnston *et al.* 2009b). Reactive Fe is a key component in the formation of iron sulfide minerals, and is defined as that Fe which readily reacts with dissolved sulfides (Berner 1970; Canfield 1989). The abundance of solid phase Fe and its reactivity with sulfides is a major factor influencing the formation of reduced inorganic S (RIS) species, and hence the degree of sulfidisation (DOS) (Boesen and Postma 1988), in coastal marine and estuarine sediments. The exceptional enrichment of reactive Fe in a tidally inundated ASS wetland of far north Queensland provides an ideal opportunity to investigate the composition and transformation of RIS species where Fe is not limiting.

## Methods

### Study site

The study site was located in a Holocene sedimentary coastal plain at East Trinity near Cairns in northeastern Australia (145°48' E, 16°56' S), and covers an area of 940 ha. It experiences a tropical monsoonal climate with summer-dominant rainfall and a maximum tidal range in Trinity Inlet of around 3.2 m. Extensive drainage and clearing of vegetation for agriculture in the early 1970s caused oxidation of pyrite-rich, estuarine sediments and subsequent development of severely acidic soils. Various parts of the site have undergone remediation from 2001, which consisted of the reintroduction of regular tidal inundation to the previously drained ASS (Johnston *et al.* 2009a; Powell and Martens 2005). For this study, sampling sites were located within Firewood Creek sub-catchment and selected to represent an intertidal ASS mudflat, experiencing frequent but attenuated tidal inundation for the preceding 5 years.

### Soil collection and handling

Six duplicate cores were collected within the intertidal ASS mudflat and rapidly sectioned into specified depth intervals. Field measurements of pH ( $\text{pH}_F$ ) and Eh ( $\text{Eh}_F$ ) were undertaken immediately on each undisturbed core by direct probe insertion using calibrated electrodes. Soil samples were bulked and placed into air-tight, sealable polyethylene bags, completely filled with material and stored frozen until analysis.

### Soil chemical analysis

Soil samples were thawed under  $\text{N}_2$  and homogenised for analysis of the solid fraction. Gravimetric moisture content ( $\theta_g$ ) was determined by oven-drying sub-samples at 105 °C. Water-soluble  $\text{SO}_4^{2-}$  was determined turbidimetrically using a spectrophotometer, and water soluble Cl<sup>-</sup> by flow injection analysis (FIA) using a Lachat QuikChem 8000 instrument, in filtered (0.45  $\mu\text{m}$ ), aqueous (1:5 soil to water) extracts. Total C was determined gravimetrically on oven-dry materials using a LECO CNS-2000 Carbon, Nitrogen and Sulfur Analyzer. Near-total Fe and S were determined on oven-dry materials by hot acidic digestion (1:1  $\text{HNO}_3$ :HCl, 1 h, 95°C) in 1:100 soil to solution extracts measured by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Perkin-Elmer ELAN-DRCe instrument.

Operationally-defined solid phase reactive Fe and RIS fractions were extracted sequentially in triplicate from moist 1–2 g soil sub-samples. Poorly crystalline Fe(II) and Fe(III) were extracted with 0.5 M HCl for 1 h. In the remaining soil, crystalline Fe was extracted with citrate-dithionite for 4 h. Fe concentrations were determined by the 1,10-phenanthroline method using spectrophotometry, with the addition of hydroxylammonium chloride for total Fe. The cold, dilute HCl and dithionite extractions are selective for poorly crystalline Fe(III) (oxyhydr)oxides (e.g. ferrihydrite, lepidocrocite) and readily reducible, crystalline Fe(III) oxides (e.g. goethite, hematite), respectively (Kostka and Luther 1994). Together, these extractions provide an estimate of the reactive Fe pool present in the soils. AVS-S was determined by cold diffusion and measured by iodometric titration (Burton *et al.* 2009). In the remaining soil,  $\text{S}^0$ -S was determined by toluene extraction and measured by cold cyanolysis in acetone using spectrophotometry (Burton *et al.* 2009). Subsequently, CRS-S was determined by cold diffusion and measured by iodometric titration (Burton *et al.* 2008). AVS-S provides an estimate of the reactive sulfide pool, and CRS-S is a widely used proxy for pyrite.

## Results and discussion

### General soil characteristics

Soil profile descriptions of the intertidal ASS mudflat revealed a fine-grained, organic soil A horizon (0.0–0.1 m depth, 10YR 2/1), overlying a former sulfuric horizon (0.05–1.1 m depth), which was underlain by reduced, sulfidic materials (1.1–1.5 m depth, 2.5Y 4/1) and comprised predominantly of silty, light clays. Following tidal inundation, these formerly severely acidified ASS were classified as Typic Sulfaquents. Soil pH was circumneutral with a mean  $\text{pH}_F$  range from 6.50 to 7.14, and measured  $\text{Eh}_F$  values were indicative of moderately reducing conditions, with a mean redox potential from +1 to +141 mV in tidally inundated ASS (Table 1). Molar ratios of water-soluble Cl: $\text{SO}_4$  ( $\text{Cl}:\text{SO}_{4W}$ ) reflected the modern supply of marine salts, as indicated by mean EC values ranging from 5.4 to 8.6 dS/m.

**Table 1. General soil characteristics of the tidally inundated ASS profiles examined in this study. Values shown are  $\bar{x}$  of  $n=6$  samples.**

Depth (m)	$\theta_g$ (g/g)	$\text{pH}_F$	$\text{Eh}_F$ (mV; SHE)	$\text{EC}_W$ (dS/m)	Molar Cl: $\text{SO}_{4W}$	Total C ( $\mu\text{mol/g}$ )	Total Fe ( $\mu\text{mol/g}$ )	Total S ( $\mu\text{mol/g}$ )
0.00–0.05	1.20	7.11	1	8.59	11	3867	2545	187
0.05–0.15	0.79	7.14	17	5.34	9	2348	1092	108
0.15–0.25	0.76	7.02	12	5.42	9	1565	630	132
0.25–0.35	0.75	6.87	49	5.95	10	1277	404	145
0.35–0.45	0.83	6.80	74	6.59	10	1360	345	131
0.45–0.55	0.81	6.69	92	6.87	10	1485	298	125
0.55–0.65	0.80	6.65	133	7.76	10	1722	251	116
0.65–0.75	0.82	6.50	141	8.42	10	1801	257	106

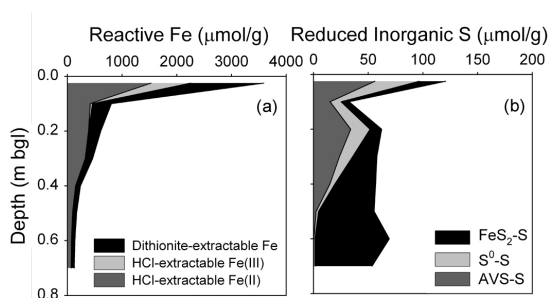
Large concentrations of total C were evident in surface soils (0–0.05 m depth, up to  $4,806 \pm 546 \mu\text{mol/g}$ ), which decreased to a minimum in the former sulfuric horizon (Table 1). Similarly, total Fe (up to  $3,258 \pm 640 \mu\text{mol/g}$ ) and S (up to  $241 \pm 24 \mu\text{mol/g}$ ) contents were greatest in the surface soils. However, the total Fe pool far exceeded the pool of total S throughout the soil profiles of the tidally inundated ASS.

### *Solid phase reactive Fe and RIS fractionation*

Solid phase reactive Fe fractions of soil profiles for tidally inundated ASS are shown in Figure 1a. Of these fractions, HCl-extractable Fe(II) was most abundant in the surface sediments (0–0.05 m depth), with concentrations up to  $1,243 \pm 289 \mu\text{mol/g}$ . These values were considerably greater than HCl-extractable Fe(III) at the same depth interval, with maximum concentrations of  $583 \pm 124 \mu\text{mol/g}$ . Maximum dithionite-extractable Fe concentrations of  $908 \pm 383 \mu\text{mol/g}$  also occurred in the surface sediments (0–0.05 m depth). AVS-Fe represented only a small proportion (generally < 5%) of total Fe in tidally inundated ASS (up to  $57 \mu\text{mol/g}$ ). Pyrite-Fe was also present at relatively small concentrations (7–30  $\mu\text{mol/g}$ ) and consequently comprised a small proportion of total Fe. Amounts of these iron sulfide mineral phases were overshadowed by extraordinarily large concentrations of reactive Fe fractions (HCl- plus dithionite-extractable fractions less AVS-Fe).

The reactivity of iron minerals with sulfide is of major importance for the formation of RIS species. Reactive Fe comprised almost 90% of the total Fe in the upper 0.35 m of tidally inundated ASS, and decreased to 50–80% of total Fe below this depth. The degree of pyritisation (DOP) estimates the amount of Fe available for reaction with sulfide over geologic time (Berner 1970). However, in sediments that contain a significant fraction of AVS, the DOP value can underestimate the availability of reactive Fe during early diagenesis. In these sediments, the effect of reactive Fe availability on sulfide accumulation may be described by the degree of sulfidisation (DOS) (Boesen and Postma 1988): In the tidally inundated ASS, DOS values were small (~3%), indicating that sulfidisation was not limited by the availability of reactive Fe in surface materials.

A large proportion of the total S pool (generally > 40%) was composed of RIS. Solid phase RIS fractions of soil profiles for tidally inundated ASS are shown in Figure 1b. Maximum AVS-S concentrations of  $57 \pm 5 \mu\text{mol/g}$  occurred in the surface soils (0–0.05 m depth), and decreased with depth. Similarly,  $\text{S}^0$ -S was generally most abundant in the surface soils, with concentrations of  $41 \pm 12 \mu\text{mol/g}$ . The formation of  $\text{S}^0$  via  $\text{SO}_4^{2-}$  reduction (Thode-Andersen and Jørgensen 1989) is an important pathway leading to the formation of pyrite and involving FeS clusters (Berner 1970; Morse and Rickard 2004). Pyrite-S contents generally increased with depth from  $14 \pm 6 \mu\text{mol/g}$  (0.05–0.15 m depth) to  $60 \pm 9 \mu\text{mol/g}$  (0.65–0.75 m depth). In most estuarine sedimentary systems, pyrite generally dominates the RIS fractions, with AVS and  $\text{S}^0$  typically comprising only a minor fraction of total RIS (Morse and Rickard 2004). However, AVS-S and  $\text{S}^0$ -S were the dominant forms of RIS in tidally inundated ASS, comprising up to 50% of the total RIS (Figure 1b).



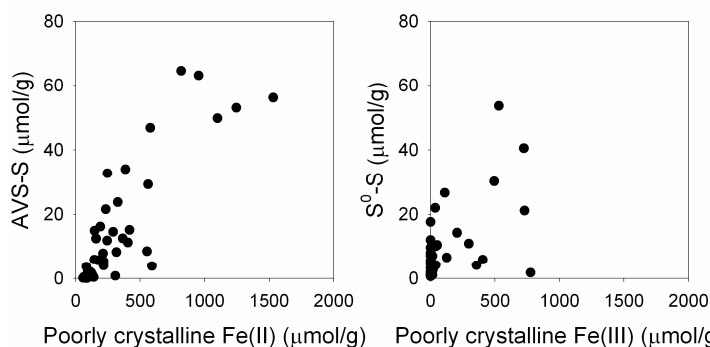
**Figure 1. Speciation of solid phase reactive Fe (a) and RIS (b) in a selected tidally inundated ASS profile.**

Over time, AVS and  $\text{S}^0$  may be progressively transformed to the more geologically stable pyrite, resulting in decreasing AVS-S to pyrite-S ratios (Morse and Rickard 2004). The tidally inundated ASS were characterised by high AVS-S to pyrite-S ratios in the surface soils (up to 2.94), indicating a low degree of conversion of AVS minerals to pyrite. These high ratios are considered anomalous, given conditions were conducive to pyrite formation. A number of biogeochemical parameters may explain the favoured AVS accumulation relative to that of pyrite (e.g. Thode-Andersen and Jørgensen 1989); however, it is most likely that the ratios observed in tidally inundated ASS occur as a result of the abundant reactive Fe favouring S sequestration in FeS (Canfield 1989).

### *Implications of enriched reactive Fe for sulfidisation*

Our results suggest that very large concentrations of reactive Fe in tidally inundated ASS have exerted a substantial influence on sulfidisation processes and RIS speciation in the near surface materials. Strong positive relationships were observed between poorly crystalline Fe and AVS-S ( $r=0.86$ ;  $n=48$ ) and  $\text{S}^0$ -S ( $r=0.59$ ;  $n=48$ ) concentrations, significant at the 0.01 level, and are shown in Figure 2. This is consistent with

abundant reactive Fe favouring the accumulation of AVS minerals and  $S^0$  relative to that of pyrite in these soils. It also suggests that the accumulation of pyrite in tidally inundated ASS may be occurring slowly under the described geochemical conditions. The kinetics of RIS formation and speciation may reflect the relatively short time scale of remediation via tidal inundation ( $\sim 5$  y) at this site. The contemporary situation differs significantly from the adjacent environment (intertidal ASS mudflat cf. mangrove wetland), as there is now a far greater pool of reactive Fe in surface soils. This increase in the availability of reactive Fe has profound consequences for the coupled cycling of Fe and S, and is likely to cause a distinct hysteresis during the short-term accumulation of AVS minerals and  $S^0$  and the reformation of pyrite over the longer term.



**Figure 2. Bivariate relationships of solid phase AVS-S ( $r=0.86$ ) and  $S^0$ -S ( $r=0.59$ ) with poorly crystalline Fe in tidally inundated ASS.**

## Conclusion

Large availability of reactive Fe favoured formation and accumulation of AVS and  $S^0$  relative to pyrite, despite geochemical conditions being conducive to pyrite formation. This appears to be related to the shorter time scale of tidal inundation of ASS and is a consequence of early diagenesis. Reactive RIS fractions in surface soils are likely to oxidise rapidly and cause acidification were tidal inundation ceased. However, enrichment of reactive Fe suggests enhanced S sequestration within pyrite over the longer term.

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