Advances in GeoEcology 30, 227-240 Reiskirchen 1997

# Iron Oxyhydroxides, Sulfides and Oxyhydroxysulfates as Indicators of Acid Sulfate Weathering Environments

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## Abstract

Iron oxyhydroxides, oxyhydroxysulfates and sulfides are important indicators of weathering environments. The relative proportions of these various secondary iron minerals are critically dependant on soil chemistry; in particular, Eh, pH and ionic concentrations. In addition, colour, form, crystallite size and the concentration of substituted cations in iron minerals can be used as quantifiable, pedogenic indicators. We report on the occurrence, genesis and properties of the wide range of iron minerals formed in soil profiles and associated ochreous precipitates from a variety of acid sulfate surface weathering environments in Australia. Specifically, the environments studied are mangrove swamp soils, non-tidal marsh soils and mine-spoil soils. These soils were chosen because they represent the range of weathering situations from stable (mangrove swamp soils) to non-stable rapid weathering (mine-spoil soils).

In undisturbed mangrove swamp soils the dominant Fe mineral is pyrite in the form of framboids and iron oxyhydroxide minerals seldom precipitate. This is indicative of strongly reducing conditions. In disturbed mangrove swamp soils iron oxyhydroxide minerals crystallise as thick precipitates.

In both undisturbed and disturbed mine-spoil soils, a wide variety of iron oxyhydroxides occur as prominent precipitates in bands of highly-variable colour ranging from bright-yellow to dark-reddish-brown. In addition to the "common" Fe minerals such as goethite, lepidocrocite, ferrihydrite and jarosite, the newly validated oxyhydroxysulfate mineral, schwertmannite, is found in mine-spoil soils. Schwertmannite is indicative of a weathering environment with solutions having a pH in the range 3 to 4 and sulfate concentrations between 1000 and 3000 µg/mL.

The non-tidal marsh soils occur in landscapes affected by seepage of sulfate and iron containing ground water and show properties intermediate between those of the mangrove swamp soils and mine-spoil soils. In these affected landscapes a small amount of pyrite is found in the reduced subsoil. At and near the soil surface a

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ISBN 3-923381-41-7

K. Auerswald, H.Stanjek & J.M. Bigham (Editors): Soils and Environment

variety of Fe oxyhydroxides are found in both undisturbed and disturbed soils. The dominant Fe oxyhydroxide is ferrihydrite containing appreciable amounts of Si. Examination shows that the ferrihydrite is often embedded or encrusted in sheath-like structures of Fe-oxidising bacteria, mainly *Gallionella* and *Leptothrix*. In the topsoil, Fe oxyhydroxides can be found in 2 distinct forms: (i) brown, gel-like precipitates floating in water, (ii) dark-reddish-brown, rusty, friable crusts caked on the banks of water courses or on soil surfaces, with various iron mineral accumulations coating and weakly cementing sand grains. Very-thin, lath-shaped, poorly-crystalline particles of lepidocrocite and goethite are often found embedded in the ferrihydrite. Schwertmannite is also found in the crusts. The occurrence of these minerals can be used as indicators of the prevailing environmental conditions.

## 1 Introduction

The conditions for formation and the properties, in particular colour, of Fe oxyhydroxides, sulfides and oxyhydroxysulfates (Schwertmann, 1993; Schwertmann and Fitzpatrick, 1992; Bigham et al., 1990; 1992; 1994; Fanning et al., 1993; Schwertmann et al., 1995) make them useful *in-situ* indicators of soil processes and conditions. In this paper we bring together the results from several studies of Australian acid-sulfate weathering environments and outline how the properties of Fe minerals can be used as diagnostic indicators for a variety of these environments. The environments studied are tidal mangrove swamp environments from St Kilda, South Australia (SA) and Darwin, Northern Territory (NT), non-tidal inland environments from Cooke Plains, SA, and the Mt. Lofty Ranges, SA (Herrmanns sub-catchment and Gutheries sub-catchment), and mine-spoil soils from Jabiru, NT, and Brukunga, SA.

## 2 Materials and methods

Soil profiles and ochreous precipitates were sampled from representative undisturbed and disturbed tidal mangrove swamps, non-tidal inland marshes and minesites in South Australia and the Northern Territory. Most of these samples have been described, classified according to Soil Taxonomy (Soil Survey Staff, 1994) and characterised elsewhere (Table 1; Fitzpatrick et al., 1992; 1993; 1996; Milnes et al., 1992). Where samples have not been described elsewhere the relevant data are presented in this paper. In most cases, the loose suspensions or thin crusts of ochreous precipitates were collected from the surfaces of soils, sides of ditches or streams.

| Location | Soil Type | Horizon | Depth cm | pH wet | pH oxidised | Organic carbon % | Total S % | ESP* | n-value | EC 1:5 Soil: $H_2O$ dS/m |
|---|---|---|---|---|---|---|---|---|---|---|
| **Tidal mangrove swamp soils** | | | | | | | | | | |
| St. Kilda[1] | Terric Sulfisaprist | Oa1 | 0-12 | 7.2 | 2.2 | 16.1 | 0.9 | 49 | 0.7-1.0 | 15.2 |
| | | Oa2 | 12-32 | 5.5 | 1.9 | 19.8 | 1.2 | 39 | 1.9-2.0 | 13.1 |
| | | Oa3 | 32-48 | 7.0 | 1.9 | 17.1 | 1.1 | 31 | 1.4-2.0 | 18.5 |
| | | Oa4 | 48-55 | 7.2 | 2.0 | 15.5 | 0.9 | 25 | 1.4-2.0 | 20.1 |
| Darwin Harbour | | C | 55+ | 8.0 | 6.5 | 7.8 | 0.3 | 55 | 1.4-2.0 | 23.9 |
| | Typic Sulfihemist | A1 | 0-5 | 8.0 | 8.1 | 6.6 | 0.3 | - | 0.7-1.0 | 3.19 |
| | | Oe1 | 5-90 | 8.5 | 4.8 | 10.8 | 2.0 | - | 1.0-1.4 | 2.67 |
| | | Oe2 | 90-95 | 8.0 | 2.7 | 9.7 | 7.0 | - | 1.4-2.0 | 4.58 |
| | | C2 | 180-270 | 7.9 | 3.9 | 2.3 | 3.0 | - | 1.4-2.0 | 3.47 |
| **Non-tidal inland soils** | | | | | | | | | | |
| Cooke Plains | Petrocalcic Salic Sulfaquent[1] | A | 0-15 | 8.3 | 3.9 | 0.9 | 0.7 | 23 | 1.0-1.4 | 3.68 |
| | | E | 15-30 | 7.8 | 7.2 | 0.5 | 0.1 | 19 | 1.0-1.4 | 1.20 |
| | | Btn1 | 30-45 | 8.5 | 8.1 | 0.1 | 0.2 | 18 | <0.7 | 1.30 |
| | | Ckm | 45+ | | | | | | | |
| Herrmanns Catchment | Alfic Sodic Sulfaquent[1] | A | 0-15 | 7.9 | 2.9 | 4.2 | 0.6 | 17 | 1.4-2.0 | 4.08 |
| | | E | 15-30 | 6.9 | 3.8 | 1.7 | 0.4 | 11 | 1.4-2.0 | 1.17 |
| | | Btn1 | 30-45 | 5.5 | 4.2 | 0.3 | 0.2 | 5 | <0.7 | 0.42 |
| | | Btn2 | 45-60 | 5.9 | 5.0 | 0.2 | 0.1 | 6 | <0.7 | 0.40 |
| Gutheries Catchment | Alfic Sodic Sulfaquent[1] | A | 0-5 | 3.70 | 3.45 | 2.6 | 2.4 | 18 | <0.7 | 7.2 |
| | | E | 5-15 | 3.85 | 3.70 | 1.5 | 2.3 | 16 | 0.7-1.0 | 6.0 |
| | | Bt1 | 15-20 | 3.96 | 3.95 | 0.4 | 0.5 | 17 | <0.7 | 6.7 |
| | | Btn2 | 20-45 | 4.50 | 4.10 | 0.3 | 0.7 | 19 | <0.7 | 5.8 |
| **Mine-spoil soils** | | | | | | | | | | |
| Jabiru[2] | Aeric Tropic Fluvaquent | A1 | 0-1 | 4.6 | 4.2 | 0.96 | 0.04 | 8.3 | 0.7-1.0 | 0.23 |
| | | A2 | 1-7 | 5.3 | 4.0 | 2.85 | 0.13 | 2.8 | 0.7-1.0 | 0.58 |
| | | B2 | 7-25 | 5.4 | 5.2 | 0.89 | 0.02 | 5.9 | 1.0-1.4 | 0.09 |
| Brukunga | Waste rock | A1 | 0-15 | 3.4 | 3.4 | 0.34 | 3.4 | 3.1 | <0.7 | 0.27 |
| | Bench cut | A1 | 0-15 | 3.4 | 3.4 | 0.54 | 3.8 | 2.7 | <0.7 | 0.95 |

[1] See Fitzpatrick et al. (1993) where these new classes (subgroups) were proposed for the subgroup classification in Soil Taxonomy and additional soil hydrological data is given in Fitzpatrick et al. (1992, 1996).

[2] From Milnes et al. (1992).

* ESP = Exchangeable sodium percentage.

*Tab. 1: Selected chemical and physical data of a variety of Australian acid sulfate environments.*

Soils from the acid-sulfate weathering environments were characterised by a variety of methods (for details see Fitzpatrick et al., 1992). These methods included x-ray diffractometry (XRD), x-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both SEM and TEM were used in conjunction with energy-dispersive x-ray spectroscopy (EDX). Analytical techniques to measure Eh, pH, electrical conductivity (EC), exchangeable sodium percentage (ESP), n-value, organic carbon content and sulphur content were carried out in the laboratory and, where appropriate, *in-situ* (Fitzpatrick et al., 1992; 1996).

## 3 Results

### 3.1 Tidal mangrove swamp soils

The soils from coastal mangrove swamps used for this study (i.e. St. Kilda and Darwin Harbour) are described by Fitzpatrick et al. (1993). The St. Kilda soil is formed in modern intertidal and mangrove swamp deposits and is underlain by unconsolidated Holocene coastal marine sediments (St. Kilda Formation) consisting of saturated, light grey, shelly and often silty or clayey sands. The Darwin Harbour mangrove swamp soil is underlain by dense estuarine sediments overlying a buried, strongly-weathered, former upland soil. The properties of the soils are shown in Table 1.

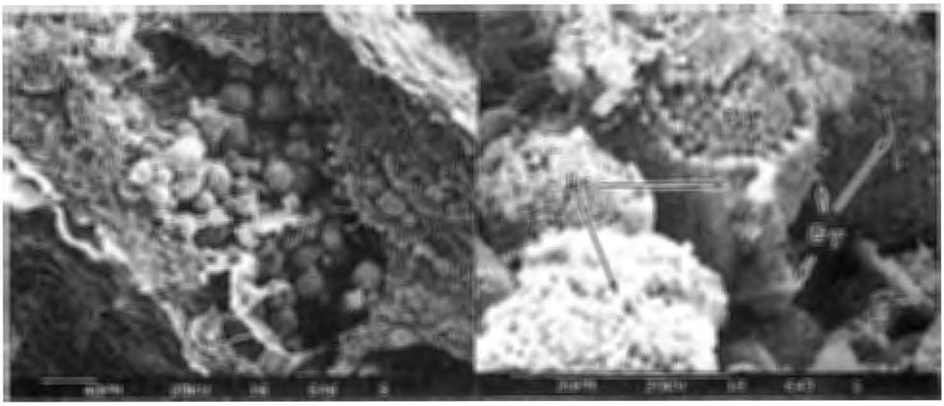
Although the soils from St. Kilda and Darwin Harbour are both Histosols there are significant differences in their properties. The soil from Darwin Harbour extends to a greater depth and contains more S than the soil from St. Kilda. Despite this the St. Kilda soil dries (oxidises) to a lower pH than the Darwin Harbour soil. The organic carbon content of the St. Kilda soil is higher than that from Darwin Harbour. At St. Kilda the organic matter is sapric (highly decomposed) material while that from Darwin Harbour is hemic (partially decomposed) material. Consequently, the St. Kilda soil classifies (Soil Survey Staff, 1994) as a Terric Sulfisaprist and the Darwin Harbour soil as a Typic Sulfihemist.

The Fe mineralogy of the as-sampled mangrove swamp soils is dominated by pyrite framboids (Table 2). The dark colour of the pyrite framboids means that they are not visually discernible in the black, organic-rich soil matrix. On drying (oxidising) or when the soil is disturbed (drained) the framboids as shown in Fig. 1 convert to jarosite and goethite giving rise to bright-yellow streaks along root channels in the original black-grey matrix.

| | Tidal environment | | | | Non-tidal inland sulfate seepage environment | | | Mine-spoil environment | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Soil (sulfidic material) | Surface precipitates | Soil (sulfuric horizon) | Surface precipitates | Soil | Soil | Surface precipitates | Soil | Soil | Surface precipitates |
| **Condition**[1] | UW | UW | DD | DD | UW | UD, DD | UW, UD, DD | UW | UD, DD | UW, UD, DD |
| **Morphological features** | Black; few grey mottles | - | Bright yellow streaks | Bright yellow and red-brown precipitates | Black; many grey mottles | Dark reddish-brown stains | Red-brown gelatinous precipitate | Brown-black; many grey mottles | Dark reddish-brown stains | Red-brown gelatinous precipitate |
| **n-value** | >1 | - | 0.7 - 1.0 | - | 1 - 2 | <1 | - | 1.0 - 1.4 | <1.0 | - |
| **pH 1:5 soil:$H_2O$** | 7.5 - 8.5 | - | <3 | 2.5 - 5.0 | 6.5 - 8.5 | 3.8 - 5.5 | 4.5 - 7.0 | 6 - 7 | 3 - 5 | 4.0 - 6.5 |
| **Organic carbon %** | 5 - 20 | - | 5 - 20 | 2 - 15 | 2 - 10 | 2 - 10 | - | <2 | <2 | - |
| **Sulphur %** | 1 - 8 | - | 1 - 8 | - | 0.2 - 1.0 | 0.1 - 1.0 | - | <0.5 | <0.5 | - |
| **EC 1:5 soil:$H_2O$ (dS/m)** | 3 - 16 | - | 3 - 16 | 10 - 20 | 1 - 10 | 5 - 15 | - | <1 | <1 | - |
| **Eh (mV)** | -200 to 0 | - | - | - | -100 to 50 | - | - | 0 to 100 | - | - |
| **Minerals (in order of abundance)** | Pyrite framboids | Rare: Bacterial sulphur | Jarosite<br>Goethite | Jarosite<br>Ferrihydrite<br>Goethite | Pyrite framboids<br>Ferrihydrite | Ferrihydrite<br>Goethite<br>Schwertmannite | Ferrihydrite<br>Lepidocrocite<br>Goethite<br>Schwertmannite | Poorly cryst. Fe-sulfides<br>Ferrihydrite | Jarosite<br>Ferrihydrite | Ferrihydrite<br>Schwertmannite<br>Goethite<br>Lepidocrocite |
| **Dominant Processes** | Sulfidization | None | Sulfuricization | Sulfuricization<br>Ferritization | Sulfidization | Sulfuricization<br>Ferritization | Sulfuricization<br>Ferritization | Sulfidization | Sulfuricization<br>Ferritization | Sulfuricization<br>Ferritization |
| **Development of processes** | Strong | None | Strong | Strong | Medium | Medium | Strong | Weak | Weak | Strong |

[1] Key: UW = Undisturbed wet condition, UD = Undisturbed dry condition and DD = Disturbed (e.g. drained or eroded) dry condition.

*Tab. 2: Comparison of morphological features, physico-chemical and mineralogical properties for undisturbed and disturbed acid sulfate soils in tidal, non-tidal and mine-spoil environments.*



(a) (b)

*Fig.1: Scanning electron micrographs (backscattered electron mode) of sulfidic material from Darwin Harbour (Oe1 horizon) after aging for 8 weeks following sampling. (a) Clusters of pyrite framboids (spherical particles) embedded in a mixture of organic matter and clay. (b) Close up of pyrite framboids showing an oxidised weathering rind containing jarosite (Jr) surrounding unoxidised pyrite (py) crystals. Gypsum (Gy) crystals can also be seen.*

## 3.2 Non-tidal marsh soils

### 3.2.1 Cooke Plains

The soil at Cooke Plains is derived from limestone that was reworked and deposited from a marine environment during the early Pleistocene. These calcareous materials were further reworked during the subsequent Pleistocene and Holocene. The soil contains authigenic pyrite, sea-derived sulfates, as well as other stored salts. The soil has acquired saline sulfide characteristics in recent times because of rising, saline ground water and seasonal water logging caused by land clearing since European settlement (circa 120 years ago).

Black materials occur in sandy A horizons that are considered to be typical of potential acid sulfate soil materials (Fitzpatrick et al., 1993), with high water content, n-values greater than 0.7, very-high soluble salt contents and high ESP values (Table 1). Once dissolved sulfate from the saline ground water (originally stored in Quaternary deposits) percolates to the surface horizons of the soil, it may transform to sulfide-containing minerals (i.e. very-fine-grained iron sulfides including pyrite). Sufficient organic matter is present (Table 1) for microorganisms to facilitate transformation of sulfate to sulfide so that, in the presence of reduced iron derived from the weathering of ilmenite grains in the soil, iron sulfide forms. During the summer months, these iron sulfides oxidise and react with dissolved calcium to form hydrated calcium sulfate (gypsum). Excess sodium in a chloride saturated solution precipitates to form halite.

The sulfides and organic matter in the A horizon cause this horizon to have a very dark colour (similar to that of the tidal soils). By providing a neutral-coloured background, the sandy nature of the soil helps accentuate the dark colour derived from the sulfides and organic matter. In horizons below the A horizon the soil is a light colour and contains high amounts of calcrete. During the summer months the colour of the surface soil is dominated by the white salt efflorescences ($EC_{1:1}$ of 60dS/m). For this reason, Fitzpatrick et al. (1993) have proposed Petrocalcic Salic Sulfaquent as a new subgroup in Soil Taxonomy.

### 3.2.2 Mt. Lofty Ranges

In high rainfall (> 600mm pa) areas of South Australia, detailed toposequence studies (Fritsch and Fitzpatrick, 1994) show the stepwise transformation of inland Natraqualfs to saline sulphidic marsh soils (Sulfaquents) under a regime of increasing dry land salinisation due to rising water tables associated with land clearing (Fitzpatrick et al., 1994; 1996). Chemical and physical properties of the soil horizons are shown in Table 1. This unique type of salting encompasses not only the usual processes of $Na^+$ and $Cl^-$ ions concentrating in soils, but also highly reactive soil processes involving the mobilisation and biomineralization of sulphur and iron, which rapidly transform productive soils into highly degraded saline sulphidic soils (Fitzpatrick et al., 1992; 1994). Our studies have concentrated on two sites; the Herrmanns and the Gutheries sub-catchments.

### 3.2.3 Herrmanns and Gutheries sub-catchments

Soils in Herrmanns and Gutheries sub-catchments are derived from fractured, metamorphosed rocks that are mainly micaceous schists containing pyrite-rich bands (Fitzpatrick *et al.*, 1996). They are part of catenary toposequences on hill slopes where the dominant soils are Typic Palexeralfs in upslope and midslope positions, grading towards wetter Aquic Palexeralfs, Mollic Natraqualfs and Alfic Sodic Sulfaquents in lower-lying topographic positions with more strongly gleyed argillic horizons. In the natric horizons (Btn) of these soils, distinct yellow-coloured ferruginous mottles occur with grey, prismatic structure, and with increasing depth the dominant chroma in the soil matrices is 2 or less than 2. Conceptual models have been developed that combine the soil and hydrogeological properties to explain the soil processes occurring in these sub-catchments (Fritsch and Fitzpatrick, 1994; Fitzpatrick et al., 1996). These models are applicable throughout the Mt Lofty Ranges and to many other sites where dryland salinity occurs.

The following three saline sulfidic features occur both within the soil profile and on the soil surface: (i) black sulfidic materials, (ii) iron-rich gelatinous precipitates and (iii) iron and salt rich crusts. Based on the abundance of each feature and their distribution relative to each other, Fitzpatrick et al. (1996) established a chronological order in which the features formed. For each saline sulfidic feature, specific minerals (e.g. pyrite framboids, ferrihydrite and schwertmannite) were identified and their conditions of formation (e.g. Eh and pH) established. The development of the saline sulfidic features is closely associated with rising saline sulfatic groundwater tables following land clearing since European settlement and contemporary weathering of pyrite lenses in the underlying rock. The chemical and physical properties of the soil horizons are shown in Table 1.

The black materials in the A1 horizons have properties that are indicative of sulfidic materials and, although pyrite was not detected by XRD, some pyrite framboids were detected by SEM (Fitzpatrick et al., 1992; 1996). The primary origin of sulfate and iron in these sub-catchments is locally rising ground waters, via semi-confined aquifers that dissolve these elements from the pyrite in the fractured, porous, partly-weathered mica schists. The dissolved sulfate percolates through vertical polygonal cracks in the natric horizon of the Mollic Natraqualfs to the A and E horizons where the sulfate is transformed into very-fine-grained pyrite by sulfate-reducing bacteria in the presence of soil organic matter (Fitzpatrick et al., 1992; 1996).

A striking feature is the presence of highly-conspicuous, red, gelatinous precipitates in the water filled pores and ponds on the soil surface of the Herrmanns sub-catchment soil. These precipitates consist of ferrihydrite (with minor amounts of goethite) formed by rapid chemical and bacterial (mainly Gallionella and *Leptothrix*) oxidation of the $Fe^{2+}$ (Fitzpatrick et al., 1992). In the dry summer months the precipitates desiccate and form thin iron-rich reddish crusts on the soil surface. These crusts contain mainly goethite, ferrihydrite and the recently described iron oxyhydroxysulfate schwertmannite (Bigham et al., 1990).

### 3.3 Mine-spoil soils

Selected mine-spoil soils are discussed together with the associated coloured precipitates developed in acid drainage water from mine spoil near Jabiru (Northern Territory) (Fitzpatrick et al., 1993; Milnes et al., 1988) and at the Brukunga abandoned pyrite mine (South Australia).

### 3.3.1 Jabiru

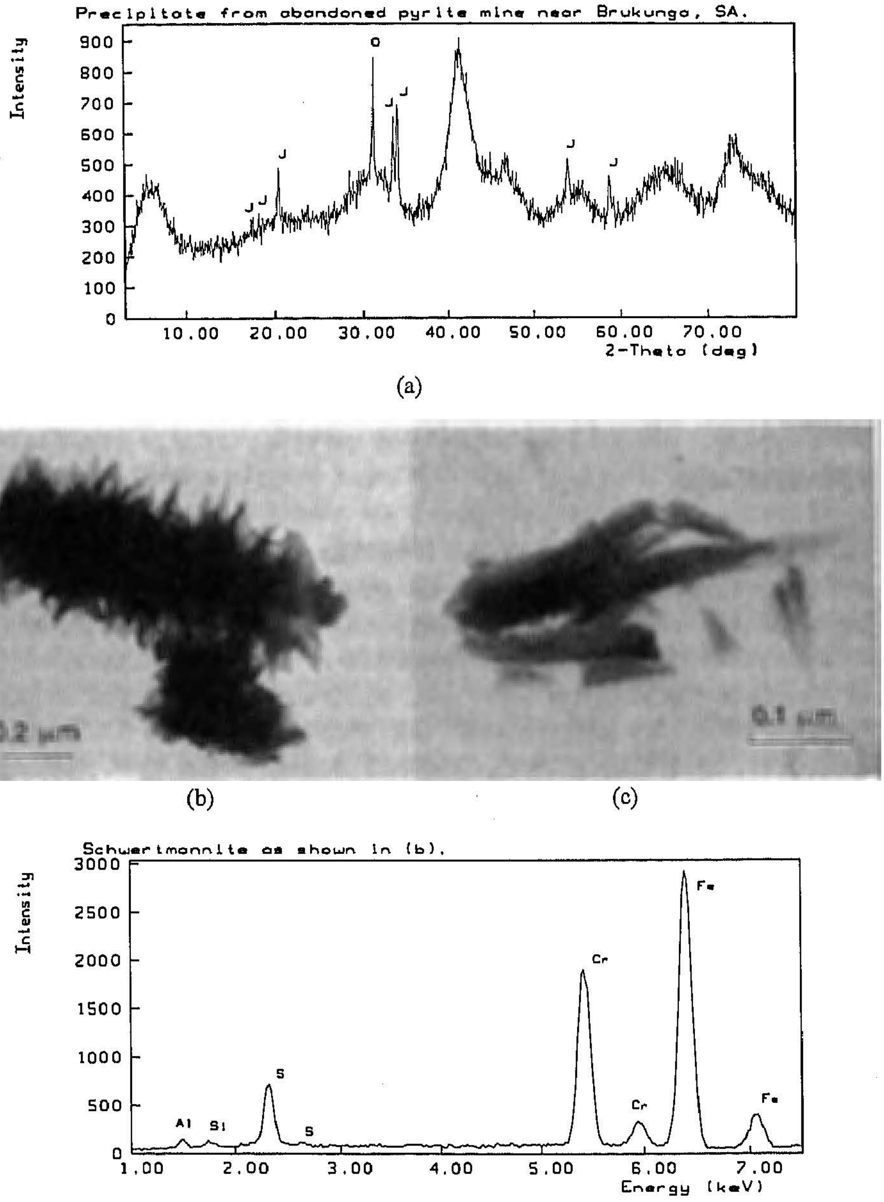
Selected properties of a mine-spoil soil near Jabiru (Milnes et al., 1992) are given in Table 1. An interesting property of this soil is that the pH remains relatively constant in both wet and dry conditions. This means that the soil does not qualify as having sulfidic material as defined by Soil Taxonomy (Soil Survey Staff, 1994) and that sulfides are not being formed at a sufficiently high rate to allow their accumulation. The occurrence of red-brown gelatinous precipitates in the surface horizons of these mine-spoil soils and in waters originating from waste-rock dumps is indicative of an oxidising environment. These gelatinous precipitates contain a mixture of iron minerals such as ferrihydrite, lepidocrocite and goethite (Milnes et al., 1992).

### 3.3.2 Brukunga

Selected properties of mine-spoil soils at the abandoned pyrite mine near Brukunga (Mt. Lofty Ranges, South Australia) are presented in Table 1. These soils are giving rise to extensive problems through acid mine drainage seeping into local surface waters. The underlying and mined bedrock is Cambrian Kanmantoo Group Metasediments consisting of interbedded micaceous sandstones and schists with numerous sulfide-rich lenses or bands (e.g. pyrite, chalcopyrite) (Campana, 1958; Daily et al., 1976; Oliver, 1986). The acid drainage water seeping through the rehabilitated pyrite-rich tailings dam and waste-rock dumps carry a range of bright red, yellow and orange coloured precipitates containing schwertmannite (Fig. 2), jarosite, goethite and gypsum.

### 3.3.3 Comparison between Jabiru and Brukunga

The two saline mine-spoil soils depict extremes in terms of total S and organic carbon levels (Table 1). Brukunga mine-spoil soils contain considerably more S than Jabiru mine-spoil soils. In contrast, organic matter content in the Jabiru mine-spoil soils is about 2 to 8 times higher than in the Brukunga mine-spoil soils. The different mineral constituents identified in the effluent precipitates at Brukunga and Jabiru are directly reflected in the concentration of S in the mine-spoil soils and mine rock. Jarosite and schwertmannite were identified in drainage waters at Brukunga because the concentration of $SO_4^{2-}$ was >3000 µg/mL and the pH between 3.5 to 4.5. According to Bigham et al. (1992), jarosite was rarely detected in their mine drainage sediments when $SO_4^{2-}$ concentrations in associated waters were less than 3000 µg/mL. They also conclude that schwertmannite forms most readily within a narrow pH range of 3.0 to 4.0. The absence of jarosite and



(a)

(b) (c)

(d)

*Fig. 2 Fe-rich surface precipitate from abandoned pyrite mine, Brukunga, SA. (a) XRD (Co Kα radiation) showing quartz (Q), jarosite (J) and schwertmannite (see Bigham et al., 1992). (b) and (c) Transmission electron micrographs of schwertmannite from the surface precipitate. (d) Energy-dispersive x-ray spectrum of schwertmannite particle shown in (b). The dominant elements are Fe and S. Elements lighter than F cannot be detected and the Cr is from the specimen chamber and not the specimen itself.*

schwertmannite in the mine drainage water at Jabiru is because of the low $SO_4^{2-}$ concentrations and high pH (Milnes et al., 1992). It is important to note that acidophilic bacteria also play an active role in the oxidation of Fe. The iron mineralogy is indicative of rapidly changing local environments and variations in the rate of Fe and S mineralisation processes. The rapidity of weathering is also associated with the small particle size of the iron minerals giving broad XRD peaks (e.g. Milnes et al., 1992).

## 4 Discussion

Information from several studies has been presented so that the results from these studies can be integrated and generalisations made about the importance of iron in diverse acid sulfate geochemical environments. Accordingly, a comparison is made in Table 2 between the properties of undisturbed and disturbed (i.e. drained or eroded) soils and associated surface gelatinous precipitates in the three acid sulfate geochemical environments. Properties recorded in Table 2 highlight the commonalities as well as the differences in these environments. The most striking differences between these three environments are the variations in iron mineralogy and soil type (e.g. macro-morphology and associated physico-chemical conditions).

Undisturbed tidal soils have strongly developed sulfidic materials (as defined by Soil Survey Staff, 1994) and have high n-values (Table 2). Iron oxyhydroxide minerals seldom crystallise as thick precipitates in or on these soils and so the soil colour is black with some grey mottles. The dominant process is sulfidization (Fanning and Fanning, 1989), that is, the build up of sulfidic material because of negative Eh and high S, Fe and organic matter contents in a tidal flushing environment.

In contrast, conditions in mine-spoil soils at Jabiru and Brukunga are not ideal for secondary pyrite to form because of a combination of low organic matter content and positive values of Eh (Table 2; Milnes et al., 1992). Furthermore, weathering environments associated with mine-spoil soils are more oxidising compared to natural undisturbed acid sulfate soils. Thus sulfidization only occurs in local pockets in mine-spoil soils. The relatively more oxidising conditions in mine-spoil soils are more favourable to the formation on or near the soil surface of minerals such as ferrihydrite, lepidocrocite, goethite, jarosite and schwertmannite. Schwertmannite was originally called the "mine drainage mineral" (Bigham *et al.*, 1990). The formation of this unique mixture of iron minerals is indicative of rapidly changing local environments and variations in the rate of Fe and S mineralisation processes. The processes leading to the formation of oxyhydroxides and oxyhydroxysulfates have been collectively termed ferritization by Nahon (1991) and are generally characterised by bright ochreous colours in soils and associated run-off waters. Conversion of sulfides to sulfates and accompanying mineral transformation, which also occurs at the surface and in dried soil, has been termed sulfuricization by Fanning and Fanning (1989).

Undisturbed non-tidal (inland) acid sulfate soils have properties intermediate between those of the undisturbed tidal and mine-spoil soils (Table 2). The processes occurring in non-tidal soils are seasonal with moderate development of sulfidic materials during wet periods and strong development of iron oxyhydroxide precipitates during drier times. Iron oxyhydroxide precipitates occur at the surface of undisturbed non-tidal acid sulfate soils throughout the year (Table 2). These soils show a full range of colours from black to strong red and orange.

As with undisturbed soils, the characteristics of disturbed (i.e. drained or dried) acid sulfate soils are dependant on environment and are diagnostic of the soil forming environment. The highly developed sulfidic materials in tidal soils can cause strong acidity when the soils are drained (Table 2). The oxidation of sulfides to sulfates and development of acid conditions favour the formation of jarosite and goethite giving rise to bright-yellow streaking along root channels and pores in the soil. These minerals, together with ferrihydrite, are also seen as precipitates on surfaces of the disturbed soils. The lesser development of sulfidization processes in non-tidal soils and mine-spoil soils means that there is less sulfidic material and therefore less acidification on drying. Consequently, the conditions in disturbed non-tidal soils and mine-spoil soils favour ferritization processes. That is, the conditions favour the formation of ferrihydrite, lepidocrocite, goethite and schwertmannite. This in turn is reflected in the colour of the dried soils (Table 2).

## 5 Conclusions

Tidal (mangrove swamp), non-tidal (inland) and mine-spoil acid sulfate weathering environments (i.e. soil profile and gelatinous precipitate) can be compared because they represent the range of weathering situations from relatively stable (mangrove swamp soils) to non-stable, rapid weathering (mine-spoil soils). Each acid sulfate weathering environment contains a different suite of poorly-crystalline iron oxyhydroxide and oxyhydroxysulfate minerals.

The origin of the primary forms of iron and sulphur are considered to be different for tidal, non-tidal (inland) and minesite soils. In coastal swamp soils, tidal flushing is the main mechanism of sulphur accumulation. In the two examples given for the inland soils, the presence of the sulfate is caused by locally rising ground water in tree-cleared landscapes due to: (i) sulfate in the ground water which originates from the weathering of iron sulfide bands in fractured rock and (ii) a rising regional ground water bringing to surface horizons ancient atmospheric salt stored in the landscape. Weathering environments associated with mine-spoil soils are more oxidising than in the naturally occurring undisturbed tidal and non-tidal acid sulfate soils.

Colours of acid sulfate soils and associated gelatinous precipitates are strongly related to specific types of iron oxyhydroxide and oxyhydroxysulfate minerals. The relative proportions of the various iron oxyhydroxides and oxyhydroxysulfates are critically dependant on the pedo-geochemistry (in particular, Eh, pH and ionic concentrations) and hence can be used as quantifiable indicators of weathering environments. Although we have presented data on a range of environments and, from these data, delineated some trends and correlations, clearly more research is needed to fully understand the significance of iron oxyhydroxides and oxyhydroxysulfates as indicators of various acid sulfate environments.

## Acknowledgments

The authors thank Dr. Greg Bowman (CSIRO Division of Soils), Prof. Wayne Hudnall (Louisiana Agricultural Experimental Station-LSU, USA), Dr. Ravi Naidu (CSIRO Division of Soils) and Dr. Emmanual Fritsch (ORSTOM) for valuable discussions. CSIRO staff who contributed substantially to these studies include Stuart McClure (SEM), Adrian Beech and Damian Mowat (chemical analyses).

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