Assessment and behaviour of secondary iron(III) minerals in acid sulphate soil materials

Chamindra Lakmali Vithana

Southern Cross University

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Assessment and behaviour of secondary iron(III) minerals in acid sulfate soil materials

Chamindra Lakmali Vithana (MSc)

A thesis submitted in fulfilment of the requirements of the degree of

Doctor of Philosophy

Southern Cross Geoscience, Southern Cross University,
Lismore, NSW, Australia
March 2014
Thesis Declaration

I certify that the work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text, and that the material has not been submitted, either in whole or in part, for a degree at this or any other university.

I acknowledge that I have read and understood the University's rules, requirements, procedures and policy relating to my higher degree research award and to my thesis. I certify that I have complied with the rules, requirements, procedures and policy of the University.

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Abstract

This study examines two aspects of important acidity generating secondary Fe(III) minerals (i.e., schwertmannite and jarosite) in acid sulfate soils (ASS) environments: i) accurate identification and quantification of schwertmannite and jarosite, and ii) improving our understanding of their behaviour in ASS. Both minerals liberate substantial acidity during their formation and hydrolysis and are involved in controlling trace metal mobility in ASS environments. As such, accurate identification and knowledge of their behaviour are crucial in developing appropriate techniques for the management of ASS environments.

Net Acid Soluble Sulfur (S\textsubscript{NAS}) and Residual Acid Soluble Sulfur (S\textsubscript{RAS}) are two routine laboratory analyses used for the estimation of the Retained Acidity (RA) fraction in the Acid Base Accounting (ABA) approach. A systematic evaluation of both S\textsubscript{NAS} and S\textsubscript{RAS} techniques was conducted by estimating the spiked (synthetic or natural) schwertmannite and/or jarosite content in soil and quartz. S\textsubscript{NAS} was unable to reliably estimate the quantity of schwertmannite spiked in soil/quartz (in which only schwertmannite was present). Schwertmannite interfered with the determination of Actual Acidity (AA) by liberating both acidity and sulfate during the initial 1 M KCl extraction step in the S\textsubscript{NAS} analysis. Approximately 50-60% of jarosite spiked in soil/quartz (in which only jarosite was present) was recovered as S\textsubscript{NAS}. The S\textsubscript{RAS} technique was unable to quantify either schwertmannite or jarosite spiked in soil/quartz. These minerals contributed to the peroxide oxidisable sulfur (S\textsubscript{POS}) fraction during the peroxide oxidation step in S\textsubscript{RAS} determination indicating a possible interference in the determination of potential sulfidic acidity (PSA) through peroxide oxidation.

The utility of 15 min AAO extraction (in the dark) for the identification and quantification of schwertmannite spiked in soil/quartz and the lower detection limit of schwertmannite content in soils using differential X-ray diffraction (DXRD) were both examined. Schwertmannite contents of < 5% could not be identified through the Fe/S molar ratio of the AAO extract. The data indicated that minerals other than schwertmannite also dissolved during the 15 min extraction. As a result, the Fe content in the AAO extract did not offer a reliable measure of schwertmannite content spiked in
soil/quartz. DXRD data also showed that it was not be possible to detect schwertmannite in soil if the schwertmannite content was < 5%. These studies showed that the lower detection limit of schwertmannite in soils by AAO extraction and DXRD techniques was 5%.

An alternative three-step sequential extraction technique was evaluated for the quantification of jarosite spiked in soil/quartz. The steps involve: 1) anoxic water extraction, 2) roasting at 550ºC for 1 h, and 3) 4 M HCl extraction. Jarosite spiked in soil/quartz was largely underestimated by the recovered S content using this technique. This lower recovery was partially attributed to the retention of jarosite by the Teflon filter membrane used in the anoxic water extraction. By replacing the Teflon filter membrane with a Cellulose Acetate filter membrane, the recovery of S from jarosite spiked soil improved appreciably. Overall, the data indicated that a correction factor of 2 was applicable for the jarosite used in this study. However confirmation of the broader applicability of this correction factor would require further experimentation on jarosites sourced from a wide range of different ASS environments.

Mineral transformation of schwertmannite and jarosite involves generation of acidity. Transformation of these minerals was monitored in two environmental settings (i.e. aerobic-acidic water column and anaerobic-reducing sediments) typical for coastal acid sulfate soils (CASS) for 12 months. Schwertmannite incubated in both settings almost completely transformed to goethite by the end of the year. Jarosite partially transformed to goethite, at a much slower rate in the water column than in sediment. The rate of transformation of both minerals was strongly affected by surficial hydrology and the seasonality of the weather. Microbial reductive dissolution and Fe$^{2+}$ catalysed transformation were considered to play key roles in controlling the rate of transformation of both minerals.

Other key factors to affect mineral transformations are organic matter and metal contaminants. The effect of fulvic acid (FA) on the liberation of arsenic (As) and acidity from arsenic substituted schwertmannite was investigated at two pH values (i.e. 4.5 and 6.5) typical for oxidised ASS. The results showed that acidity liberation from schwertmannite was controlled by both pH and FA. Acidity liberation was greater in As-schwertmannite compared to pure-schwertmannite under all
conditions. Under acidic conditions (i.e. pH 4.5), all FA concentrations (i.e. 1, 10 and 25 mg L\(^{-1}\)) impeded the liberation of acidity from schwertmannite. Under neutral conditions (i.e. pH 6.5), all FA concentrations impeded the liberation of acidity from schwertmannite from 9 h onwards. At the same neutral pH, liberation of acidity was enhanced in the first 9 h in samples containing low to moderate FA concentrations. The presence of low concentrations of FA enhanced the liberation of As from schwertmannite, largely at neutral pH.
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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thesis Declaration</td>
<td>ii</td>
</tr>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vi</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>ix</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xv</td>
</tr>
<tr>
<td>Chapter 1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Background</td>
<td>2</td>
</tr>
<tr>
<td>1.2 Aims and Objectives</td>
<td>8</td>
</tr>
<tr>
<td>1.3 Thesis Organisation</td>
<td>9</td>
</tr>
<tr>
<td>Chapter 2 A review on ASS, acidity retained in schwertmannite</td>
<td>14</td>
</tr>
<tr>
<td>and jarosite, their assessment and behaviour</td>
<td></td>
</tr>
<tr>
<td>2.1 Acid Sulfate Soils (ASS)</td>
<td>15</td>
</tr>
<tr>
<td>2.2 Global Distribution of ASS</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Impacts of ASS</td>
<td>22</td>
</tr>
<tr>
<td>2.4 Management of ASS</td>
<td>33</td>
</tr>
<tr>
<td>2.5 Major forms of Retained Acidity (RA) Minerals</td>
<td>43</td>
</tr>
<tr>
<td>in ASS-Schwertmannite and Jarosite</td>
<td></td>
</tr>
<tr>
<td>2.6 Relationship between Natural Organic Matter (NOM), Arsenic (As)</td>
<td>55</td>
</tr>
<tr>
<td>and Schwertmannite in ASS</td>
<td></td>
</tr>
<tr>
<td>2.7 Key Knowledge Gaps</td>
<td>60</td>
</tr>
<tr>
<td>Chapter 3 Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$)</td>
<td>62</td>
</tr>
<tr>
<td>for the assessment of the acidity liberated from schwertmannite and jarosite</td>
<td></td>
</tr>
<tr>
<td>Chapter</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>3</td>
<td>Abstract</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
</tr>
<tr>
<td></td>
<td>Materials and Methods</td>
</tr>
<tr>
<td></td>
<td>Results and Discussion</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
</tr>
<tr>
<td></td>
<td>Acknowledgements</td>
</tr>
<tr>
<td><strong>Chapter 4</strong></td>
<td>Examination of the acidified ammonium oxalate method and differential x-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
</tr>
<tr>
<td></td>
<td>Materials and Methods</td>
</tr>
<tr>
<td></td>
<td>Results and Discussion</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
</tr>
<tr>
<td></td>
<td>Acknowledgements</td>
</tr>
<tr>
<td><strong>Chapter 5</strong></td>
<td>Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
</tr>
<tr>
<td></td>
<td>Materials and Methods</td>
</tr>
<tr>
<td></td>
<td>Results</td>
</tr>
<tr>
<td></td>
<td>Discussion</td>
</tr>
<tr>
<td></td>
<td>Conclusions</td>
</tr>
<tr>
<td></td>
<td>Acknowledgements</td>
</tr>
<tr>
<td>Chapter</td>
<td>Title</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments</td>
</tr>
<tr>
<td>6.1</td>
<td>Abstract</td>
</tr>
<tr>
<td>6.2</td>
<td>Introduction</td>
</tr>
<tr>
<td>6.3</td>
<td>Materials and Methods</td>
</tr>
<tr>
<td>6.4</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>6.5</td>
<td>Conclusions</td>
</tr>
<tr>
<td>6.6</td>
<td>Acknowledgements</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>Acidity and arsenic liberation from schwertmannite effect of fulvic acid</td>
</tr>
<tr>
<td>7.1</td>
<td>Abstract</td>
</tr>
<tr>
<td>7.2</td>
<td>Introduction</td>
</tr>
<tr>
<td>7.3</td>
<td>Materials and Methods</td>
</tr>
<tr>
<td>7.4</td>
<td>Results</td>
</tr>
<tr>
<td>7.5</td>
<td>Discussion</td>
</tr>
<tr>
<td>7.6</td>
<td>Conclusion and Environmental Implications</td>
</tr>
<tr>
<td>7.7</td>
<td>Acknowledgements</td>
</tr>
<tr>
<td>Chapter 8</td>
<td>Conclusions</td>
</tr>
<tr>
<td>8.1</td>
<td>Evaluation of Identification/Quantification Techniques...</td>
</tr>
<tr>
<td>8.2</td>
<td>Investigation of the Behaviour of Schwertmannite and Jarosite</td>
</tr>
<tr>
<td>8.3</td>
<td>Futures Studies</td>
</tr>
<tr>
<td>Chapter 9</td>
<td>References</td>
</tr>
<tr>
<td>Appendix</td>
<td></td>
</tr>
<tr>
<td>A1-1</td>
<td>List of abstracts presented at conferences and forums...</td>
</tr>
</tbody>
</table>
A1-2  Signed author statements........................................ iv
A1-3  Published papers.................................................... vii
List of Tables

Table 3.1 Acronyms used in the text and their descriptions................................................. 66
Table 3.2 Characteristics of soils collected from two sites.................................................... 72
Table 3.3 Weight percentages of the elements and Fe:S/K:Fe:S ratios of synthetic/natural schwertmannite/jarosite determined from aqua-regia digestion method and SEM-EDXA..................................................................................................................... 75
Table 3.4 $S_{POS}$ (%) measured in soils and quartz samples spiked with synthetic and natural schwertmannite.......................................................................................................................... 85
Table 3.5 $S_{POS}$ (%) measured in soils and quartz samples spiked with synthetic and natural jarosite................................................................................................................................. 87
Table 4.1 Selected chemical properties of soil samples, synthetic and natural schwertmannite.. 101
Table 4.2 Amount of synthetic/natural schwertmannite and soils/quartz mixed to obtain obtain various schwertmannite spiking rates................................................................. 106
Table 4.3 Schwertmannite additions in soil and quartz examined through the DXRD approach 107
Table 5.1 Amount of synthetic/natural jarosite and soils/quartz mixed to obtain various jarosite spiking rates............................................................................................................. 127
Table 5.2 Some of the chemical properties of soils, synthetic and natural jarosite samples..... 131
Table 5.3 Percentage of synthetic jarosite retained by the Teflon filter membrane after anoxic water extraction of quartz samples spiked with various additions of synthetic jarosite.......................................................................................................................... 134
Table 6.1 Mean and the range concentrations of major cations/anions in the surface and pore waters in the Tuckean Drain........................................................... 166
Table 6.2 Mean and the range concentrations of trace metals and metalloids in the surface and pore waters in the Tuckean Drain during the sampling period.......................... 166
Table 6.3 Comparison of rate of schwertmannite transformation in present study with other
Table 6.4  Comparison of the rates of dissolution of jarosite in the present study with previous studies.

Table 7.1  Elemental composition and the molar ratios of synthesised Pure and As-schwertmannite.

Table 7.2  Total amount of acidity released from Pure and As-schwertmannite by the end of 48 h titration (a) pH 4.5 (b) pH 6.5.
# List of Figures

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Global distribution of ASS in coastal regions</td>
<td>22</td>
</tr>
<tr>
<td>2.2</td>
<td>Highly acidic drain in the Tuckean Swamp, northern NSW, Australia</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Mullet affected by red-spot disease due to acidification</td>
<td>25</td>
</tr>
<tr>
<td>2.4</td>
<td>Degradation of concrete bridge pylons in the Pimpama River, south-eastern Queensland, by sulfuric acid produced by the ASS</td>
<td>26</td>
</tr>
<tr>
<td>2.5</td>
<td>Soil scalding caused by drainage in ASS affected wetland</td>
<td>32</td>
</tr>
<tr>
<td>2.6</td>
<td>Schwertmannite and jarosite in disturbed ASS in Tuckean Swamp, northern NSW, Australia</td>
<td>44</td>
</tr>
<tr>
<td>3.1</td>
<td>TAA generated as a percentage of theoretical actual acidity contained within the added synthetic/natural schwertmannite and jarosite</td>
<td>77</td>
</tr>
<tr>
<td>3.2</td>
<td>Percentage of S\textsubscript{NAS} recovered with respect to added synthetic/natural schwertmannite and jarosite</td>
<td>79</td>
</tr>
<tr>
<td>3.3</td>
<td>XRD pattern of synthetic/natural schwertmannite before and after 1M KCl extraction and TAA titration and peroxide oxidation and TPA titration</td>
<td>82</td>
</tr>
<tr>
<td>3.4</td>
<td>Change in pH\textsubscript{ox} in relation to added synthetic/natural schwertmannite and jarosite</td>
<td>84</td>
</tr>
<tr>
<td>3.5</td>
<td>Percentage of S\textsubscript{RAS} recovered in added synthetic/natural schwertmannite and jarosite</td>
<td>86</td>
</tr>
<tr>
<td>3.6</td>
<td>SEM images of synthetic schwertmannite and jarosite before and after peroxide oxidation</td>
<td>89</td>
</tr>
<tr>
<td>4.1</td>
<td>XRD patterns of untreated samples of synthetic and natural schwertmannite</td>
<td>104</td>
</tr>
<tr>
<td>4.2</td>
<td>Micromorphology of synthetic schwertmannite and natural schwertmannite</td>
<td>109</td>
</tr>
<tr>
<td>4.3</td>
<td>XRD patterns of natural schwertmannite before and after AAO extraction and the DXRD</td>
<td>110</td>
</tr>
<tr>
<td>4.4</td>
<td>Raw X-ray diffraction (XRD) and differential X-ray diffraction (DXRD) of synthetic schwertmannite spiked at different concentrations in Richmond, Clarence soils and quartz</td>
<td>111</td>
</tr>
</tbody>
</table>
Fig. 4.5  Time sequence AAO extraction data of synthetic schwertmannite and natural schwertmannites……………………………………………………………………………… 113

Fig. 4.6  Recovery of Fe from synthetic and natural schwertmannites spiked soil and quartz samples after 15 min AAO extraction in the dark…………………………………………………… 114

Fig. 4.7  Fe/S molar ratio of synthetic/natural schwertmannite spiked soil or quartz samples, calculated from 15 min AAO extraction…………… 115

Fig. 4.8  Dissolved Fe and S percentages in the AAO extract after 15 min extraction of synthetic/natural schwertmannite spiked soil/quartz samples………………………………………………………… 116

Fig. 5.1  Morphology of synthetic jarosite and natural jarosite……………………………………………………………………………………………………………………………………… 132

Fig. 5.2  S recoveries from jarosite spiked in Richmond and Clarence soil materials and Quartz after roasting at 550°C for 1 h followed by 4 M HCl extraction ………………………………… 133

Fig. 5.3  Comparison of S recovery from 5% synthetic/natural jarosite spiked soil/quartz samples roasted at 550°C using Teflon filter membrane and Cellulose Acetate filter membranes … 135

Fig. 5.4  Thermal decomposition of jarosite…………………………………………………………………………………………………………………………………………………………………… 137

Fig. 5.5  Change in mineralogy during roasting………………………………………………………………………………………………………………………………………………………………… 139

Fig. 5.6  Time-sequence 4 M HCl extraction of unroasted and roasted, synthetic and natural jarosite………………………………………………………………………………………………………… 140

Fig. 5.7  Recovery of Fe, S and K from 5% synthetic and natural jarosite spiked quartz samples…. 142

Fig. 6.1  Location of the study site in the Tuckean Swamp, NSW, Australia……………………………… 156

Fig. 6.2  Morphology of schwertmannite and jarosite before the experiment and after 12 months…………………………………………………………………………………………………… 163

Fig. 6.3  Water column and sediment parameters in Tuckean Swamp a) pH b) Eh……………………………… 165

Fig. 6.4  Plot of Fe$^{3+}$ against pH of the surface water from Tuckean Drain with solubility lines for schwertmannite, jarosite and goethite………………………………………………………… 167

Fig. 6.5  Change in the mineralogy of schwertmannite samples inserted into the Tuckean Swamp a) sediments b) water column……………………………………………………………… 168
Fig. 6.6  Variation of Fe/S ratio of the schwertmannite samples inserted in the sediment and in the water column displaying the dominant mineral phases……………………………… 169

Fig. 6.7  Change in the mineralogy of jarosite inserted into the Tuckean Swamp a) sediment b) water column……………………………………………………………………………… 176

Fig. 6.8  Variation in elemental ratios of jarosite kept in sulfidic sediments and in the water column, and the pH in both systems over 12 months……………………………………… 176

Fig. 7.1  XRD and SEM images of untreated Pure and As-schwertmannite samples……………… 193

Fig. 7.2  Variation in pH over 48 h period in Pure and As-schwertmannite suspensions at pH 4.5 and at pH 6.5……………………………………………………………………………………… 195

Fig. 7.3  Released acidity at different time intervals and cumulative acidity generation over 48 h titration at pH 4.5 from Pure and As-schwertmannite……………………………………… 196

Fig. 7.4  Released acidity at different time intervals and cumulative acidity generation over 48 h titration at pH 6.5 from Pure and As-schwertmannite……………………………………… 197

Fig. 7.5  Variation in the released As by the end of 48 h titration period with different fulvic acid concentrations……………………………………………………………………… 198

Fig. 7.6  Variation in released sulfate from Pure and As-schwertmannite by the end of 48 h titration period with different fulvic acid concentrations…………………………………… 199

Fig. 7.7  XRD of Pure and As-schwertmannite titrated to pH 4.5 in the presence of different FA concentrations……………………………………………………………………………… 200

Fig. 7.8  XRD of Pure and As-schwertmannite titrated to pH 6.5 in the presence of different FA concentrations……………………………………………………………………………… 200
Chapter 1: Introduction
Chapter 1: Introduction

1.1 Background

1.1.1 Acid sulfate soils issues

Acid sulfate soils (ASS) contain iron sulfides and/or oxidised products of iron sulfides (secondary Fe(III) minerals) (Pons, 1973; Bloomfield and Coulter, 1974; Dent, 1986; Dent and Pons, 1995). These secondary minerals strongly influence soil characteristics (i.e. decreases soil pH < 2) due to their potential to liberate acidity (van Breeman, 1973; Dent, 1986; Dent and Pons, 1995). Acidity from sulfidic and secondary Fe(III) minerals in ASS is a major threat to ecological systems, agriculture and infrastructure (Dent, 1986; Dent and Pons, 1995; Powell and Martens, 2005; Sullivan et al., 2006a; Boman et al., 2008; Ljung et al., 2009; Ljung et al., 2010). Acidification and mobilization of metals cause the best known impacts on the environment (Dent and Pons, 1995; Åström and Björklund, 1997; Fitzpatrick, 2003; Ljung et al., 2009; Ljung et al., 2010; Sullivan et al., 2012). Acidification and increased metal concentrations in aquatic systems result in mortality of fish and other aquatic fauna and can also increase the risk of diseases among aquatic fauna (Simpson et al., 1983; Dent, 1986; Dent and Pons, 1995; Sammut and Lines-Kelly, 2000; Stephens and Ingram, 2006; Powell and Martens, 2005). Furthermore, soil scalding, poor growth and shortening of the life span of vegetation can also occur as a result of severe acidification in terrestrial environments (Dent, 1986; Dent and Pons 1995; Sammut et al., 1996; Sammut and Lines-Kelly, 2000; Rosicky et al., 2004a,b).

Another problem caused by acidic drainage waters is corrosion of steel and concrete structures which in turn significantly affect the construction industry (Sammut and Lines-Kelly, 2000; Ljung et al., 2009 and references therein). Besides acidity liberated from both iron sulfides and secondary Fe(III) minerals can also mobilize metals in soils (Åström and Björklund, 1995; Åström and Åström, 1997; Åström, 2001). For example, metals such as Al which are toxic to plants and animals are released in excessive amounts due to dissolution of Al-containing clays under acidic conditions (Dent, 1986; Sammut et al., 1996).
The direct impacts of ASS on human health are poorly understood. Trace metals such as arsenic can be liberated due to oxidation of arsenopyrite and dissolution of arsenic sorbed-secondary Fe(III) minerals with concurrent release of acidity (Smedley and Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a). The implications of exposure to these contaminants are well established, nevertheless, only a few studies have considered the direct role of ASS via such contaminants in human health issues (Appleyard et al., 2006; Hinwood et al., 2006; Ljung et al., 2009). The health issues are mainly mental impairment, problems in skin and general poor health (e.g. Ljung et al., 2009). The impacts on animal health and specifically the economic impacts on agriculture, aquaculture, fisheries and livestock can be very significant (e.g. Dent, 1986; Buschmann et al., 2008; Ljung et al., 2009).

Given the potential impact ASS can have on the environment, economy and human health, proper management of such soils is of paramount importance (Baldwin and Fraser, 2009). While many management approaches focused on preventing or minimizing acidity production and subsequent discharge from already identified ASS, initial identification of ASS is a challenging and important task (Fitzpatrick, 2003; Ahern et al., 2004). This initial step involves the identification and quantification of acidity liberating minerals (i.e. iron sulfides and secondary Fe(III) minerals, Al hydroxy sulfate minerals) as accurately as possible. These quantification results can then be used in predicting the acidity amount that can be discharged (Ahern et al., 2004).

1.1.2 Oxidation and acidification

Acidity in ASS can be present in either a potential or existing form (Ahern et al., 2004). Minerals that have formed and accumulated under anoxic conditions (e.g. in waterlogged soils) and low redox state elements, such as pyrite (FeS₂), gregite (Fe₃S₄), mackinawite (FeS) contribute to the pool of potential soil acidity (Dent, 1986; Fanning, 2002; Ahern et al., 2004). Potential acidity is released and becomes problematic when soils are disturbed by various factors such as prolonged drought and agricultural
and construction activities, enabling the reduced minerals to oxidise (Dent, 1986; Ritsema et al., 1992).

Disturbance and oxidation of iron sulfides results in the formation of a variety of partially oxidised secondary Fe(III) minerals. Acidity existing in those partially oxidised soils are mainly composed of both acidity retained in secondary Fe(III) minerals and Al hydroxy sulfate minerals, and acidity in readily available forms including soluble and exchangeable species (Ahern et al., 2004). The secondary Fe(III) minerals are generally poorly crystalline, partially soluble and metastable, and transform over time to more stable Fe(III) minerals such as goethite by releasing retained acidity (Fanning, 2002; Ahern et al., 2004). Schwertmannite and jarosite are the two main secondary Fe(III) minerals formed from the oxidation of iron sulfides and incomplete hydrolysis of Fe(III), and are known to contain a substantial amount of retained acidity (McElnea et al., 2002a,b; Sullivan and Bush, 2004; Fitzpatrick et al., 2009). Many of these secondary Fe(III) minerals (such as schwertmannite and jarosite) and their transformed products (i.e. goethite) are ochreous in colour, and therefore are indicative of previous and future acidity discharge in ASS. Therefore, their accurate identification and quantification is essential in managing ASS. Furthermore, understanding their behaviour in natural ASS and the factors that affect their stability would be highly useful in developing more appropriate management techniques.

1.1.3 Methods to quantify and assess ASS

Assessment methods developed for ASS have used the acid base accounting (ABA) approach which estimates net acidity generation. In the ABA approach, the potential, retained and soluble/exchangeable acidity forms are determined by separate methods (Ahern et al., 2004). Net acidity generation is then estimated by balancing total acidity with the acid neutralization capacity of the soil (Ahern et al., 2004).
Based on the ABA concept, Ahern et al. (2004) introduced a new set of guidelines for the management of ASS in Australia. Two new methods were developed specifically to estimate the net acidity generation in ASS. These methods are now widely used in Australian commercial laboratories. The two methods are “Net Acid Soluble Sulfur (S_{NAS})” and “Residual Acid Soluble Sulfur” (S_{RAS}), and together they capture the major forms of acidity in ASS. Both methods estimate the retained acidity by selectively extracting the sulfur content in terms of S_{NAS} or S_{RAS}. Although the retained acidity fraction is composed of acidity derived from secondary Fe(III) minerals such as schwertmannite, jarosite and Al hydroxy sulfate minerals such as basaluminite, both S_{NAS} and S_{RAS} techniques appear to have been developed focusing primarily on jarosite (as discussed in Chapter 2). Therefore, a systematic evaluation on the utility of both techniques for the accurate quantification of retained acidity fraction (i.e. schwertmannite and jarosite) is required.

Acidified ammonium oxalate (AAO) extraction in the dark is another selective dissolution technique that is widely used in identifying and quantifying poorly crystalline iron mineral phases (such as schwertmannite, ferrihydrite and poorly formed goethite) in mining impacted environments (Bigham et al., 1990; Childs et al., 1998; Webster et al., 1998; Sing et al., 1999; Dold, 2003a,b; Fukushi et al., 2003a; Gagliano et al., 2004; Regenspurg et al., 2004; Scroth and Parnell, 2005; Kumpulainen et al., 2007, 2008a; Peretyazhko et al., 2009; Caraballo et al., 2009). Extraction time periods used in many AAO extraction studies range from 15 min to 4 h (Bigham et al., 1990; Singh et al., 1999; Dold, 2003a; Regenspurg et al., 2004; Caraballo et al., 2009; Peretyazhko et al., 2009). Furthermore, differential X-ray diffraction (DXRD) has been used in conjunction with selective dissolution techniques to identify dissolved poorly crystalline iron minerals after a selective dissolution (Schulz, 1981, 1986). A complete dissolution of schwertmannite in mineral precipitates collected from acid mine drainage (AMD) environments within 15 min AAO extraction was observed by Bigham et al. (1990). Dold (2003a) reported that the extraction with AAO for 15 min was sufficient to identify the dissolved schwertmannite in mineral precipitates of AMD environments through the DXRD approach. However, the AAO extraction approach has not been applied to identify/quantify schwertmannite in
Chapter 1: Introduction

ASS, where it is present in lesser amounts compared to AMD. Furthermore, the DXRD detection limit for schwertmannite in soils has not been examined previously. An evaluation of both AAO and DXRD techniques for schwertmannite identification/quantification in soils would be highly useful in developing techniques for management of ASS.

In 2007, Li et al. proposed a sequential extraction method for the quantification of jarosite. This method recovers jarosite from a mixture of mine wastes containing pyrite and soluble Fe(II) sulfate minerals (Li et al., 2007). The sequential extraction involves initial removal of soluble Fe(II) minerals followed by roasting at 550° C (1 h) and a final 4 M HCl (30 min) extraction step (Li et al., 2007). However, the applicability of this sequential extraction procedure for jarosite in ASS has not been examined.

1.1.4 Acidic Fe(III) minerals: Schwertmannite and jarosite

Both schwertmannite (Fe₈O₈(SO₄)(OH)₆) and jarosite (KFe₃(SO₄)₂(OH)₆) transform to goethite (α-FeOOH) with concurrent release of acidity (i.e. retained acidity). According to previous research, the rate of schwertmannite transformation to goethite is strongly dependent on oxic/anoxic status and the pH of its coexisting environment. Thus the time frame of the transformation can range from a few hours to years (Bigham et al., 1996a; Regenspurg et al., 2004; Jönsson et al., 2005; Schwertmann and Carlson, 2005; Acero et al., 2006; Burton et al., 2007, 2008b; Knorr and Blodau, 2007). Apart from the oxic/anoxic status and pH, other physio-chemical factors including temperature, dissolved organic matter (humic and fulvic acids), dissolved silica, anions (AsO₄³⁻, Cr₂O₇²⁻, SeO₄²⁻, SO₄²⁻) and cations (Fe³⁺, Cu²⁺) have also been found to strongly influence the stability of schwertmannite (Waychunas et al., 1995; Fukushi et al., 2003a,b, 2004; Regenspurg and Peiffer, 2005; Scroth and Parnell, 2005; Acero et al., 2006; Blodau and Gatzek, 2006; Jönsson et al., 2006; Kumpulainen et al., 2008b; Jones et al., 2009; Nagano et al., 2011; Antelo et al., 2012, 2013; Burton et al., 2007, 2009, 2010, 2013a; Burton and Johnston, 2012). While many studies have focused on schwertmannite in AMD sites and related environments such as construction wetlands, very few studies discuss schwertmannite in ASS
Jarosite is more stable than schwertmannite, however, the stability of jarosite is also affected by pH, dissolved organic matter, anions and cations (Chu et al., 2006; Smith et al., 2006; Welch et al., 2007, 2008; Zhu et al., 2008; Kendall et al., 2013). Although, the dissolution kinetics (Baron and Palmer, 1996; Gasharova et al., 2005; Smith et al., 2006; Elwood Madden et al., 2012) and thermo-chemistry (Drouet and Navrotsky, 2003; Frost et al., 2005; Xu et al., 2010; Vummidi Lakshman et al., 2014) of jarosite have been studied separately and extensively, only a handful of studies have focused on their in-situ behaviour and long term stability in ASS (Welch et al., 2007, 2008; Keene et al., 2010; Johnston et al., 2011a, 2012).

1.1.5 Role of dynamic redox conditions

ASS can be subjected to prolonged drought and flooding periods due to seasonal weather changes (Sammut et al., 1994; White et al., 1997; Johnston et al., 2004). Therefore, sudden fluctuations in soil and water geochemistry (i.e. lowering of the water table and run-off that is rich in organic debris) could strongly affect the stability of schwertmannite and jarosite in those landscapes. In such situations, schwertmannite and jarosite could behave in a manner (in terms of the rate and the fate of the transformation) different to those predicted in previous research, most of which were conducted in laboratories under controlled conditions. Therefore, detailed information on the in-situ behaviour of both schwertmannite and jarosite in ASS environments would expand current understanding of both minerals.

Arsenic (As) is a common environmental contaminant (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006a,b,c). It has been found that As adsorbs strongly to iron hydro(oxides) minerals such as schwertmannite, ferrihydrite, goethite and hematite under acidic conditions (Smedley and Kinniburgh, 2002; Bauer and Blodau, 2006). It is also known that As incorporates into the structure of
Chapter 1: Introduction

schwertmannite when it precipitates (Fukushi et al., 2003a; Regenspurg and Peiffer, 2005). Therefore, these iron minerals (i.e. schwertmannite, ferrihydrite, goethite and hematite) are important in controlling the As mobilization in aquatic environments. In aquatic environments, dissolved organic matter (DOM) is ubiquitous and is largely composed of fulvic and humic acids (FA and HA) (Diallo et al., 2005; Weng et al., 2009). Both FA and HA compete with As for the adsorption sites in iron minerals, and they therefore regulate the mobility of As in such environments (Ritter et al., 2006; Weng et al., 2009). However, FA is likely to be the active component of DOM in ASS landscapes due to their prevailing acidic conditions and the solubility of FA in a wider pH range (Sharma et al., 2011). Therefore, FA likely plays a key role in the liberation of acidity and As from schwertmannite under acidic conditions in ASS. A detailed investigation therefore, is required to understand how FA affects the stability of schwertmannite (including liberation of arsenic), especially under conditions relevant to ASS. Such knowledge would be useful to develop new strategies to minimize the risk of As contamination in aquatic environments. ASS research would also benefit by gaining new knowledge about the role of FA on acidity liberation from schwertmannite, leading the way to development of better management strategies.

1.2 Aims and Objectives

The thesis aims to resolve two main issues related to schwertmannite and jarosite. Firstly, a systematic evaluation of techniques available for the identification and quantification of both minerals was conducted (Chapters 3-5). In this evaluation, two techniques routinely used in Australian laboratories were assessed. Another two techniques that are currently used in acid mine drainage/waste research and management were also tested for their utility for ASS research and management. Secondly, two studies were conducted to understand the behaviour of schwertmannite and jarosite (Chapter 6-7). The first of these behavioural studies examined the in-situ transformation behaviour and long-term stability of both minerals in a natural ASS environment. The second study investigated the effects of arsenic and natural organic matter on schwertmannite.
The broad objective was to evaluate the applicability of available techniques for quantification of retained acidity in ASS and to gain greater insight on the behaviour of the secondary Fe(III) minerals which contribute to the retained acidity fraction.

1.2.1 Specific aims

i. Quantification of schwertmannite and jarosite in ASS using two routine laboratory techniques ($S_{NAS}$ and $S_{RAS}$) from the Australian ASS guidelines and thereby to estimate the retained acidity fraction (Chapter 3).

ii. Determine the suitability of a selective dissolution technique to estimate the schwertmannite content in ASS (Chapter 4).

iii. Determine the suitability of a three-step sequential extraction technique for the estimation of jarosite in ASS (Chapter 5).

iv. Determine the in-situ transformation behaviour and the long-term stability of both schwertmannite and jarosite in natural ASS environments subject to fluctuations in geochemical regimes due to seasonal weather changes (Chapter 6).

v. Examine how fulvic acid (FA), the active component of dissolved organic matter in ASS, influences the behaviour of schwertmannite under acidic and near-neutral and oxic conditions in ASS environments (Chapter 7).

1.3 Thesis Organization

This thesis is comprised of two peer-reviewed journal publications (Chapter 3 and Chapter 7), two manuscripts which are currently under review (Chapters 4 and Chapter 6) and a manuscript at the submitted stage (Chapter 5). All papers were derived from the primary PhD research programme. The contents in all papers are included in Chapters 3-7 and are formatted according to the guidelines set
for the specific PhD thesis requirements (i.e. PhD thesis by incorporating publications) at Southern Cross University.

Appendix – contains the published journal articles in their published format

The breakdown of author contributions for each chapter is provided at the beginning of chapters 3-7. The format and references of the published paper and four manuscripts were standardised to be consistent across the thesis. The following is a brief outline of each chapter.

Chapter 1: Introduction

This chapter describes the research background, overall objective and specific aims. It also outlines the thesis structure.

Chapter 2: A review on ASS, acidity retained in schwertmannite and jarosite, their assessment and behaviour

In this chapter, a review of literature related to the research scope is included. This review examines literature related to ASS, methods used to estimate retained acidity fraction, schwertmannite, jarosite, and the relationship between arsenic, iron oxides and natural organic matter.

Chapter 3: Evaluation of two routine techniques (S\text{NAS} and S\text{RAS}) for the assessment of the acidity liberated from schwertmannite and jarosite (Published).

Schwertmannite and jarosite are two secondary Fe(III) minerals with acidity retained in them. Therefore, their accurate quantification is important to estimate net acidity generation in ASS. This chapter discusses the suitability of two routine ASS soil assessment techniques (S\text{NAS} and S\text{RAS}) used in Australian laboratories for the assessment of schwertmannite and jarosite in ASS.

Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils (Under Review).

Schwertmannite is a poorly crystalline mineral and is known to dissolve selectively in acidified ammonium oxalate in the dark. This selective dissolution followed by DXRD has been used to identify and quantify schwertmannite in mineral precipitates in AMD environments. This study discusses the utility of this selective dissolution and DXRD approach for the identification and quantification of schwertmannite in soil materials.


Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils (Submitted).

Jarosite admixed with pyrite in an acid mine waste sample was recovered using a three-step sequential extraction technique. In this method, the initial anoxic water extraction followed by roasting at 550°C removes soluble Fe(II) minerals and pyrites respectively. This sequential approach was tested in order to recover jarosite in soil materials and is discussed in this chapter.

Submitted manuscript: Vithana, C.L., Sullivan, L.A., Bush, R.T., Burton, E.D. Jarosite quantification in soils: An improved rapid sequential extraction procedure
Chapter 1: Introduction

Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments (Under Review).

Seasonal changes in weather can affect the geochemistry in acidic waters in ASS landscapes. This study discusses the changes in behaviour of schwertmannite and jarosite kept in ASS landscape over a period of one year.

Manuscript currently being reviewed: Vithana, C.L., Sullivan, L.A., Burton, E.D., Bush, R.T.
Stability of schwertmannite and jarosite in an acidic landscape: prolonged field incubation

Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid (Published)

Arsenic is a toxic metalloid found in the natural environment and has a strong affinity towards schwertmannite under acidic conditions. Fulvic acid, the likely active component of natural organic matter in ASS environments, could strongly influence the relationship between arsenic and schwertmannite. Also, schwertmannite is a source of acidity in ASS. In this chapter, the influence of fulvic acid on acidity and arsenic liberation from schwertmannite under oxic conditions at acidic and neutral pHs is also discussed.


Chapter 8: Conclusions

This chapter summarises the findings of each preceding chapter and derives the overall conclusions of this research programme.

Chapter 9: References

References in published and unpublished papers have been removed and included in this chapter.
Appendix: This appendix contains a list of conference abstracts associated with the work of this PhD project, the published articles and signed author contribution statements.
Chapter 2: A Review on ASS, Acidity Retained in Schwertmannite and Jarosite, Their Assessment and Behaviour
This literature review consists of two parts:

1) An introduction to acid sulfate soils (ASS) including its formation, impacts and management approaches followed by a detailed review on techniques used in assessment of different acidity pools in ASS in Australia (Section 2.1-2.4).

2) A detailed review of two of the most important, main secondary Fe(III) minerals, schwertmannite and jarosite, in ASS. Topics covered are their formation, chemical and physical characteristics, structure, and analysis, and factors influencing their stability and behaviour in natural environments (Section 2.5-2.6).

2.1 Acid Sulfate Soils (ASS)

Acid sulfate soils (ASS) are soil materials containing reduced inorganic sulfur and their oxidised products. They occur in coastal and inland environments (Pons, 1973; Bloomfield and Coulter, 1974; van Breeman, 1973, 1976, 1982). ASS are either acidic, or have the potential to become acidic. Acidification results when the inherent acid neutralizing substances are not sufficient to neutralize any acidity generated in those soil materials (Pons, 1973; van Breeman, 1973, 1976, 1982; Fanning, 2002; Fanning et al., 2002).

ASS materials were first described over 200 years ago in coastal landscapes such as estuaries, reclaimed mangrove swamps, and backswamps. The sulfidic sediments in these coastal environments were generally deposited at the end of the last sea level rise that occurred between 6,500-10,000 years ago (i.e. the early Holocene period) (Pons, 1973; van Breeman, 1973, 1976; Pons et al., 1982; Dent, 1986). Sediments started to accumulate after the sea level stabilized and sedimentation slowed (van Breeman, 1973, 1976; Pons et al., 1982; Dent, 1986). Some sulfidic sediments are also found in older marine and estuarine sediments (belonging to Cretaceous or Tertiary time periods) in the north coast of eastern USA (Daniels and Orndorff, 2003; Fanning et al., 2004). Inland ASS are found in upland saline seepage areas, wetlands, rivers, stream channels, and lakes (Fitzpatrick et al., 1998; Fitzpatrick
Sulfidic sediments in inland landscapes developed mainly as a result of rising groundwater and localised salinization in seeps following forest clearing for agriculture (Fitzpatrick and Shand, 2008; Fitzpatrick et al., 2009).

ASS materials pose a severe environmental threat with the potential to liberate substantial amounts of acidity when they are drained and exposed to the atmosphere (Pons, 1973; Dent, 1986; Dent and Pons, 1995). Based on the potential to become acidic, ASS materials can be divided into two sub-classes: *actual acid sulfate soil (AASS)* materials or sulfuric horizons, and *potential acid sulfate soil (PASS)* materials or sulfidic materials (Pons, 1973; van Breeman, 1973, 1976; Pons et al., 1982; Dent, 1986). Both PASS and AASS materials can exist in the same profile with AASS materials overlying the PASS materials (Pons, 1973; van Breeman, 1973, 1976; Pons et al., 1982; Dent, 1986).

### 2.1.1 Potential acid sulfate soils (PASS) materials

PASS materials are typically waterlogged and anoxic. They contain iron minerals such as iron monosulfides (e.g. amorphous iron monosulfides, mackinawite, gregite) and iron disulfides (pyrite and marcasite). Although pyrite is the most common iron sulfides mineral in acid sulfate soil materials, other iron sulfides too can be appreciable (Burton et al., 2006d; Keene et al., 2011). Iron sulfide minerals in PASS materials are stable under anoxic conditions and acidity is not an issue until the soils are disturbed and these minerals become exposed to air (Ritsema et al., 1992).

#### 2.1.1.1 Formation of PASS materials

Two key processes involved in iron sulfide formation are the reduction of dissolved $\text{SO}_4^{2-}$ and decomposition of organic matter (Berner, 1970; Dent, 1986). Organic matter, $\text{SO}_4^{2-}$ and Fe are essential for iron sulfide formation (Berner, 1970; Howarth, 1979; Dent, 1986). Under waterlogged conditions, the decomposition of organic matter leads to anoxic-reducing conditions which favour sulfate reducing bacteria (SRB) (Dent, 1986; Golez, 1995; Cook et al., 2004). In strictly anoxic conditions, which are highly reducing environments, sulfate reduction by bacteria is the key process
of sulfide formation. The oxidation of organic matter by SRB liberates electrons which eventually lead to the production of H₂S (Equation 2.1). This process is known as dissimilatory sulfate reduction (Berner, 1970; Dent, 1986; Dent and Pons, 1995).

\[ SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \]  

(2.1)

The subsequent reaction of H₂S with Fe²⁺ that is derived from parallel microbial Fe reductive dissolution of Fe oxyhydroxides forms iron monosulfides (Equation 2.2 and 2.3) (Berner, 1970; Dent and Pons, 1995). Iron monosulfide formation consumes acidity and generates alkalinity which helps to improve water quality in contemporary acidified environments (Smith and Melville, 2004; Burton et al., 2005).

\[ 4FeOOH + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 7H_2O \]  

(2.2)

\[ Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \]  

(2.3)

Three common iron monosulfide minerals are: amorphous iron monosulfides (FeS_{amorphous}), mackinawite (FeS_{0.94}) and greigite (Fe₃S₄). They are highly reactive and oxidise within hours when exposed to the air (Skinner et al, 1964; Bush and Sullivan, 1997; Fanning et al., 2002; Sullivan et al., 2002; Bush et al., 2004b; Rickard and Morse, 2005). Iron monosulfides are the major component of organic enriched black coloured surface deposits in drains, and are also known as monosulfidic black ooze (MBO) (Bush and Sullivan, 2002a; Bush et al., 2004a,b).

Pyrite (FeS₂) is a Fe(II) disulfide (Rickard and Morse, 2005 references there in). Many researchers suggested that iron monosulfides transform to pyrite over time, and hence are precursors of pyrite (Berner, 1970; Wang and Morse, 1996). However, according to Rickard and Morse (2005), pyrite is not a direct transformed product of mackinawite or greigite, but is rather derived by reacting dissolved FeS with dissolved sulfide (Equation 2.4) or with elemental S in the aqueous phase (Equation 2.5) (Marnette et al., 1993; Gagnon et al., 1995; Postma and Jackobson, 1996; Fanning et al., 2002;
Rickard and Morse, 2005). Elemental S can be formed by the oxidation of $\text{H}_2\text{S}$, thus both reactions 2.4 and 2.5 are coupled (Thamdrup et al., 1993; Böttcher et al., 2001).

\[
\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + 2\text{H}^+ \quad (2.4)
\]

\[
\text{FeS} + \text{S} \rightarrow \text{FeS}_2 \quad (2.5)
\]

### 2.1.2 Actual acid sulfate soils (AASS) materials

AASS are oxidised ASS materials and mainly composed of relatively non-reactive minerals such as quartz, feldspar, mica, and clay. However, the distinctive minerals are the secondary iron minerals (e.g. jarosite and schwertmannite), hydrolysed products of secondary Fe(III) minerals (e.g. goethite) and poorly soluble Al hydroxy sulfate minerals (e.g. basaluminite) (Ahern et al., 2004). These soil materials could also contain minor amounts of iron sulfide minerals (Fitzpatrick et al., 1998). The secondary iron minerals are generally formed due to oxidation and partial hydrolysis of iron sulfides when they are exposed to the atmosphere (Nordstrom, 1982; Ritsema et al., 1992; Fanning et al., 2002). Both the formation of secondary iron minerals and the subsequent hydrolysis of formed secondary Fe and Al hydroxy sulfate minerals generate a substantial amount of acidity (i.e. sulfuric acid) (Fitzpatrick et al., 1998; Fanning, 2002; Ahern et al., 2004). Highly acidic (< pH 4) AASS materials are formed when the neutralization capacity in soil is insufficient to neutralize the acidity liberated from both processes (Pons, 1973; van Breeman, 1973, 1976; Pons et al., 1982; Dent, 1986; Ahern et al., 2004). Therefore, AASS materials can be considered as a store of acidity that can be released over time (Ahern et al., 2004).

#### 2.1.2.1 Formation of AASS materials

PASS materials become AASS materials when iron sulfides oxidise and acidity that is liberated exceeds the soil’s acid neutralization capacity (Dent, 1986; Ritsema et al., 1992; Dent and Pons, 1995; Macdonald et al., 2002; Sullivan et al., 2009). Pyrite oxidation occurs through a series of steps which
involve oxygen, Fe$^{3+}$ and iron/sulfur oxidising microorganisms (Nordstrom, 1982; Dent, 1986). Initially, pyrite is oxidised producing SO$_4^{2-}$, Fe$^{2+}$ and acidity (H$^+$) (Equation 2.6) (van Breeman, 1982; Stumm and Morgan, 1996).

\[ FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \] (2.6)

In natural ASS landscapes, the resulting Fe$^{2+}$, SO$_4^{2-}$ and acidity are transported to surrounding non-ASS landscapes or waterways through run-off which causes acidification in those systems too (Cook et al., 2004; Sammut et al., 1996). Therefore, in some instances, further oxidation of the produced Fe$^{2+}$ occurs in locations distant from where pyrite was originally located. The chemical oxidation of Fe$^{2+}$ to Fe$^{3+}$ by oxygen is an extremely slow process with a half-life of ~1,000 days. In natural systems, this process is catalysed by iron/sulfur oxidising microorganisms such as Acidithiobacillus ferroxidans (Equation 2.7) (Nordstrom, 1982; van Breeman, 1982; Dent, 1986; Cook et al., 2004).

\[ Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \] (2.7)

The fate of Fe$^{3+}$ in reaction (Equation 2.7), depends on the pH in the aqueous phase. If the pH $<$ 4, Fe$^{3+}$ remains in the aqueous phase as soluble Fe$^{3+}$, whereas if the pH $>$ 4, Fe$^{3+}$ is precipitated as ferric hydroxides (Fe(OH)$_3$), liberating more acidity (Equation 2.8) (van Breeman, 1982; Stumm and Morgan, 1996; Ahern et al., 2004). Hydrolysis of Fe$^{3+}$ forms a variety of secondary minerals such as jarosite, schwertmannite, akaganeite, ferrhydrite, sideronatrite, tamarugite, copiapite, halite, and gypsum which are precipitated depending on the pH (Fitzpatrick and Shand, 2008; Ahern et al., 2004). Most of these secondary minerals liberate acidity upon dissolution (Fitzpatrick and Shand, 2008).

\[ Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \] (2.8)
Under acidic conditions (i.e. pH < 4), the presence of Fe$^{3+}$ in the aqueous phase further aggravates the acidity hazard by stimulating pyrite oxidation (Equation 2.9) (Ahern et al., 2004; Cook et al., 2004).

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$ (2.9)

Liberated Fe$^{2+}$ and H$^+$ may drive reactions 2.7 and 2.8 (if they are not transported away from the pyrite source) and continue pyrite oxidation until all oxygen is consumed (Nordstrom, 1982; Cook et al., 2004).

Oxidation of 1 mole of pyrite liberates 4 moles of acidity, (Equation 2.10) (Dent, 1986; Ahern et al., 2004).

$$FeS_2 + {15 \over 4}O_2 + {7 \over 2}H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$ (2.10)

2.1.2.2 Formation of key secondary Fe(III) minerals in AASS materials

A range of secondary minerals precipitate during pyrite oxidation, and are followed by Fe$^{3+}$ hydrolysis (Nordstrom, 1982; Bigham and Nordstrom, 2000; Fitzpatrick and Shand, 2008). Schwertmannite (Fe$_8$O$_8$$(SO_4)_2$$(OH)_6$) and jarosite (KFe$_3$$(SO_4)_2$$(OH)_6$) are two key secondary iron minerals found in AASS materials (van Breeman, 1982; Dent, 1986; Bigham et al., 1996a; Bigham and Nordstrom, 2000; Fitzpatrick and Shand, 2008). The precipitation of both schwertmannite and jarosite liberates a substantial amount of acidity as shown in equations 2.11 and 2.12 respectively (Bigham and Nordstrom, 2000). These minerals are meta-stable and thus hydrolyse to more stable mineral phases over time, liberating a considerable amount of acidity (Equations 2.13 and 2.14) (Regenspurg, 2002; Ahern et al., 2004; Sullivan et al., 2012). These two minerals are a distinctive feature of disturbed ASS landscapes, and also pose an acidity hazard in the event of rainfall. A detailed discussion on the structure, stability, behaviour and the acidity hazard of both minerals is included in Section 2.5.

$$8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(SO_4)_2(OH)_6 + 22H^+$$ (2.11)
Chapter 2: A Review on ASS, Acidity Retained in Schwertmannite and Jarosite, Their Assessment and Behaviour

\[ 3Fe^{3+} + 2SO_4^{2-} + K^+ + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \]  \hspace{1cm} (2.12)

\[ 2H_2O + Fe_8O_6(OH)_6(SO_4) \rightarrow 8FeOOH + SO_4^{2-} + 2H^+ \]  \hspace{1cm} (2.13)

\[ 3H_2O + KFe_3(SO_4)_2(OH)_6 \rightarrow 3Fe(OH)_3 + 2SO_4^{2-} + 3H^+ + K^+ \]  \hspace{1cm} (2.14)

2.2 Global Distribution of ASS

Worldwide distribution of ASS is estimated to be over 500,000 km\(^2\), occurring across climatic regions that range from temperate to tropical (Sullivan et al., 2012). Fig. 2.1 shows the global distribution of coastal ASS (CASS) (Ljung et al., 2009). In Australia, the total land cover affected by ASS is 215,000 km\(^2\), of which 58,000 km\(^2\) are located in coastal regions (Fitzpatrick et al., 2008, 2010). Apart from Australia, ASS are found in the Niger Delta (Senegal), Mekong Delta (Vietnam), Kalimantan (Indonesia), Bangkok Plain (Thailand), Mississippi Deltaic Plain (USA), Malaysia, Kenya, Finland, Sweden, Venezuela, and across all continents (Pons et al., 1982; Dent, 1986; Ljung et al., 2009; Österholm et al., 2010). A geochemistry similar to ASS occurs in acid mine drainage (AMD) (Bigham and Nordstrom, 2000; Johnson and Hallberg, 2005) and acid rock drainage (ARD) environments (Bigham and Nordstrom, 2000). However, unlike those environments, CASS environments are highly enriched with labile organic matter due to surrounding vegetation (Smith and Melville, 2004; Johnston et al., 2005a; Burton et al., 2006c).
Fig. 2.1. Global distribution of ASS in coastal regions (Taken from Ljung et al., 2009)

2.3. Impacts of ASS

Major hazards of ASS materials are acidification and Al toxicity, Fe$^{2+}$ mobilization and precipitation of secondary iron minerals, mobilization of heavy metals and metalloids, deoxygenation, soil scalding and the emission of noxious sulfur gases (Sullivan et al., 2012). These hazards can originate due to various anthropogenic and natural activities and have adversely affected the environment and economy of many countries. Rapid urban development, agricultural practices, engineering works and tourism are the key anthropogenic activities that contribute to drainage in ASS (Dent, 1986; Lin and Melville, 1994; Dent and Pons, 1995; Powell and Martens, 2005; Sullivan et al., 2006a; Boman et al., 2008; Fitzpatrick et al., 2009; Ljung et al., 2010). Prolonged drought, flooding, changes in sea level and episodic rainfall events are natural activities that contribute to trigger hazards in ASS (Dent, 1986; Roach, 1997; Hinwood et al., 2006; Nordmyre et al., 2006; Boman et al., 2010). Numerous undesirable effects caused by these hazards on the aquatic and terrestrial ecosystems, agriculture, and the construction industries have been reported and well documented (e.g. Dent, 1986; Dent and Pons, 1995; Cook et al., 2000; Fitzpatrick et al., 2009). Adverse effects of ASS on human health have also been recently reported (e.g. Powell and Martens, 2005; Hinwood et al., 2006; Ljung et al., 2009).
2.3.1 Acidification and the Al toxicity

Acidification (Fig. 2.2), one of the main hazards of ASS materials, is caused by the oxidation of pyrite and subsequent hydrolysis of secondary minerals (Dent, 1986). Acidity in turn can dissolve clay minerals and thereby mobilize metals such as Al, Fe, Si, trace metals and metalloids. These mobilised metals are then leached into groundwater and also discharged to waterways by surface run-off (Åström and Björklund, 1997). Drainage or leaching of acidic water to waterways and to groundwater not only results in acidification but also strongly influences the soil/water chemistry in those systems (Sammut et al., 1996; Åström and Björklund, 1997).

Fig. 2.2. Highly acidic drain in the Tuckean Swamp, northern NSW, Australia (photo-C.Vithana)

Acidification of waterways can impact aquatic fauna and flora, ultimately resulting in their disappearance from the aquatic system. Most aquatic species prefer neutral pH (i.e. 6) and the stress caused by a decrease in pH to 3-4 may result in their death (Sammut and Lines-Kelly, 2000). Several
incidents of fish and benthic organisms being killed due to severe acidification and deoxygenation of waterways have been reported in ASS affected areas around the world (Lin and Melville, 1994; Åström and Björklund, 1995; Cook et al., 2000; Bush et al., 2004a,b; Powell and Martens, 2005; Baldwin and Fraser, 2009; Toivonen and Österholm, 2011). For example, acidity caused degradation in shells of Sydney rock oysters (*Saccostrea glomerata*) in the Manning River estuary, eastern Australia, resulting in mass mortality of these oysters (Dove et al., 2007). In tropical countries, low productivity in fisheries and aquaculture industries have been observed due to the toxicity caused by both acidification and Al leached from surrounding ASS (Simpson et al., 1983; Stephens and Ingram, 2006). Furthermore, acidic discharges rich in organic matter and soluble Fe(III) are reported to have stimulated the development of toxic algal blooms in waterways in Queensland, Australia (Cook et al., 2000; Powell and Martens, 2005; Ahern et al., 2006). Aquatic food chains can be severely affected due to the toxicity of acidic discharges as has been shown by effects on *Daphnia sp.*, (Liu et al., 2009).

While acidification can decimate acid-sensitive plants in the waterways, it makes way for invasive acid tolerant aquatic plants such as water lilies. These aquatic plants not only invade the aquatic system but also readily absorb the nutrients in the water body, thereby decreasing nutrients available to other aquatic plants (Sammut et al., 1994, 1996).

One of the main impacts of acidification on agricultural production systems is reduced crop yields caused by poor growth, nutrient deficiency and death of crops (Dent, 1986). Acidification makes soils less fertile (due to low pH and high metals) for most major agricultural crops (Sammut and Lines-Kelly, 2000). These less fertile conditions have reportedly caused stunted growth (due to reduced photosynthesis), arrested root development and nutrient deficiencies (i.e. P and N) in vegetation growing in those soils (van Breeman, 1976; Dent, 1986; Sammut and Lines-Kelly, 2000; Liu et al., 2009). Production in agricultural crops such as rice was largely reduced due to poor growth and mortality (van Breeman, 1976; Dent, 1986; Moor and Patrick, 1991). Toxicity caused by Al on crops
such as rice grown in ASS landscapes have been well documented (van Breeman, 1976; Dent, 1986; Minh et al., 1997).

Chronic exposure to acidic water is known to cause damage to skin and gills, lead to diseases such as “red-spot” and reduced growth and breeding rates among aquatic organisms (Fig. 2.3) (Sammut et al., 1996; Cook et al., 2000; Sammut and Lines-Kelly, 2000; Powells and Martens, 2005). Habitat destruction, including spawning and breeding grounds of fish, prawns and oysters, due to prolonged acidification and toxicity by metals has been reported in Finland and in areas of the Great Barrier Reef, Australia that receive acidic discharge from ASS (Åström and Björklund, 1995; Cook et al., 2000; Sammut and Lines-Kelly, 2000; Powells and Martens, 2005). In addition, reduced migration of fish due to acidity barriers, decrease in fish reproduction, and loss of acidity sensitive flora and fauna resulting in decreases in species diversity have been identified as long term negative effects of acidification (Sammut et al., 1996; Cook et al., 2000; Sammut and Lines-Kelly, 2000).

![Mullet affected by red-spot disease due to acidification](http://www.environment.nsw.gov.au/acidsulfatesoil/effects.htm)
The acidity from ASS also causes negative impacts on infrastructure. Essential components in the building industry such as cement, calcium carbonate and metal structures are strongly affected by the acidity produced from ASS. As a result, corrosion among concrete and steel structures occur in infrastructure (i.e. bridges, concrete slabs, pipes, tunnels, foundations of roads and building) in areas affected by disturbed ASS (Fig. 2.4) (Sammut and Line-Kelly, 2000; Ljung et al., 2009 and references therein). Also, the bearing capacity is known to be severely affected due to the oxidation of buried sulfidic sediments causing strong negative impacts on built structures (e.g. Ljung et al., 2009 and references therein). Thus, it has been estimated that the damage caused by ASS on the construction industry could be worth millions of dollars mainly due to the rapid deterioration of built structures and also due to the risk of sudden collapse.

Fig. 2.4. Degradation of concrete bridge pylons in the Pimpama River, south-eastern Queensland, by sulfuric acid produced by the ASS (photo- http://www.ozcoasts.gov.au/indicators/econ_cons_acid_sulfate_soils.jsp)
2.3.2 Iron mobilization and formation of secondary iron precipitates

Mobilization of Fe\(^{2+}\) and the precipitation of secondary iron minerals have been identified as a key hazard of ASS environments (Sullivan et al., 2012). Fe\(^{2+}\) produced via the oxidation of pyrite and subsequent oxidation of Fe\(^{2+}\), not only liberate acidity but also may lead to the precipitation of secondary iron minerals such as schwertmannite and jarosite (Dent, 1986). The presence of these secondary iron minerals that have characteristic ochreous colours indicate the weathering environment in those soils (Dent, 1986; Fanning, 2002; Fanning et al., 2002). Schwertmannite and jarosite are the two key secondary iron precipitates found in oxidised ASS. In coastal ASS environments, these secondary iron precipitates are often found in surface environments such as coatings on organic litter (schwertmannite) (Sullivan and Bush, 2004) and along drain edges, root channels, and on ped surfaces (jarosite) (Dent, 1986; Johnston et al., 2009c). Both minerals may weather over time releasing substantial amounts of acidity and thereby exert strong influence on soil and water geochemistry in the surrounding environments (Dent, 1986; Bigham and Nordstrom, 2000; Sullivan and Bush, 2004).

van Breeman (1976) reported that incomplete hydrolysis of jarosite liberates 2 moles of H\(^+\) for every Fe\(^{3+}\) whereas that of schwertmannite liberates 2.6 moles of H\(^+\) for every mole of Fe\(^{3+}\) (Piene et al. 2000). The amount of acidity that can be liberated from schwertmannite present in coastal ASS environment was estimated as 1,900-2,580 mol H\(^+\)/t by Sullivan and Bush (2004). In natural environments the stability of both of these minerals is strongly regulated by the activities of microorganisms as well as physio-chemical factors such as pH, Eh, cations, anions, organic matter and Si (Knorr and Blodau, 2007; Welch et al., 2007, 2008).

Iron flocs forms when iron rich, acidic water mixes with neutral/alkaline water. The formation of iron flocs causes numerous problems in water bodies and among aquatic fauna and flora (Sammut et al, 1996; Sammut and Lines-Kelly, 2000). These iron flocs smother benthic communities, leading to their death, affect the gills in fish and also impact infrastructure by blocking pumps and staining concrete (Sammut et al, 1996; Sammut and Lines-Kelly, 2000).
2.3.3 Mobilization of metals, heavy metals and metalloids

Another key hazard of ASS is the mobilization of previously immobile heavy metals and metalloids (Åström and Björklund, 1995; Åström and Corin, 2000; Macdonald et al., 2004a; Burton et al., 2008a). Metals associated with sulfide minerals are mobilized due to oxidation and dissolution reactions that are largely controlled by the pH and Eh of the surrounding environments (Burton et al., 2008a).

Trace metals in sulfidic minerals such as galena (PbS), covellite, (CuS) and arsenopyrite (AsS) may be mobilised during the oxidation of these minerals and may subsequently leach into the surrounding soil and adjoining waterways (Åström, 2001). Furthermore, the low pH caused by the acidification dissolves minerals and clays thereby increasing the mobility of metals (e.g. Al) (Åström and Corin, 2000) and trace metals (Cd, Ni, Co, Mn, Zn) (Sohlenius and Öborn, 2004). These metals then leach into groundwater or wash to nearby waterways through run-off (Appleyard et al., 2004; Hinwood et al., 2006). Elevated concentrations of Al, Cd, Co, Cu, Mn, Zn and Ni were observed in sub surface and surface estuarine sediments in Finland indicating leaching from surrounding ASS landscapes (Åström and Björklund, 1995, 1997; Åström and Åström, 1997; Sundström et al., 2002; Nordmyr et al., 2008a,b). According to Sundström et al., (2002), the concentration of metals (Al, Cd, Ni, Co, Mn, Zn) discharged to the waterways from nearby ASS was greater than that was discharged by all industrial factories in Finland.

Although most metals are largely immobile under neutral pHs, some elements such as Fe and As can occur in species that become more mobile under neutral conditions (Burton et al., 2008a). In ASS, anoxic environments with neutral pHs develop during prolonged inundation periods as a result of overbank flooding or tidal events. Arsenic scavenged by secondary iron minerals such as schwertmannite is liberated under such conditions due to the microbial reductive dissolution of those secondary iron minerals (Burton et al., 2007, 2008a). While microbial reductive dissolution of secondary iron minerals increases the mobilization of metals/metalloids such as Fe$^{2+}$ and As,
generated alkalinity decreases the solubility of metals such as Al (Burton et al., 2008a). Fe$^{2+}$ generated from the microbial reductive dissolution of secondary iron minerals has been found to promote Fe$^{2+}$ catalysed transformation of these poorly crystalline secondary iron mineral phases to more crystalline phases such as goethite (Burton et al., 2007, 2008b). The impact of this Fe$^{2+}$ catalysed transformation on the mobilization of metals has not been examined in detail. However, it has been found that during Fe$^{2+}$ catalysed transformation, scavenged As is retained in the solid phase (Burton et al., 2009).

The impact of elevated concentrations of metals, heavy metals and metalloids in aquatic and terrestrial environments has been widely studied (Dent, 1986; Palko, 1986; Sammut et al., 1996; Wilson et al., 1999; Appleyard et al. 2006; Hinwood et al., 2006; Stephens and Ingram, 2006; Dove et al., 2007; Buschmann et al. 2008). Accumulation of some of these trace metals (i.e. Ni, Cr, Mn, Fe and Co) above the accepted levels has been found in Timothy grass and oats grown in ASS landscapes in Finland (Palko, 1986; and Palko and Yli-Halla, 1987). These accumulated metals were found to accumulate in cow-milk as a consequence of grazing on those plants rich in metals (Fältmarsch et al., 2008). Al toxicity on agricultural crops (Dent, 1986) and aquatic fauna (fish, shrimp, oysters) (Simpson et al., 1983; Stephens and Ingram, 2006; Dove et al., 2007) have also been discussed in detail. Al toxicity in fish is mainly attributable to the polymerization of Al on fish gills (Stephens and Ingram, 2006). Contamination of fresh and groundwater sources by acidic and metal rich drainage from ASS have not only limited the availability of unpolluted water for human consumption but also significantly impacted on human health. For example, Appleyard et al. (2006) and Hinwood et al. (2006) reported elevated concentrations of heavy metals (Fe, Cd, Pb, As, Se) and metals (Al) in groundwater in certain areas in Western Australia. This was attributed to the prolonged drought and rapid urban development of low-lying areas that caused a decline in the water table and subsequent exposure of sulfidic sediments (Appleyard et al., 2006; Hinwood et al., 2006). As a consequence, serious concerns have been raised on potential health issues due to prolonged consumption of contaminated groundwater and potential accumulation of metals in crops grown in such landscapes.
using contaminated groundwater. Likewise, Buschmann et al. (2008) also reported high concentrations of As and Mn in water used for drinking purposes in the Mekong Delta which was mainly attributable to the reductive dissolution of secondary iron minerals.

2.3.4 Deoxygenation of aquatic systems

Deoxygenation in ASS environments has acute and devastating impacts. Deoxygenation, or hypoxic conditions, develops in water bodies when oxygen is removed by various factors (i.e. organic matter decomposition, rapid oxidation of monosulfidic black ooze (MBO) at a rate faster than it is replenished (Sullivan et al., 2012). According to the ANZECC (2000) guidelines, most freshwater aquatic species survive at $O_2$ concentrations above 5 mg L$^{-1}$ (~80% saturation), but are subject to stress when the concentration falls below this limit. In ASS, deoxygenation is mainly caused by “blackwater” events and resuspension of MBO in drains.

ASS backswamps areas are prone to prolonged inundation during heavy rainfall periods, and hypoxic conditions can easily develop due to the decomposition of flood intolerant vegetation (Sullivan et al., 2002; Johnston et al., 2003b; Lin et al., 2004; Wong et al., 2010). The development of “blackwater” during the recession period of flooding is a well-known phenomenon in ASS backswamps (Johnston et al., 2003b). Blackwater is rich in dissolved organic carbon (DOC) which gives it the black/dark brown colour and also contains substantially higher amounts of Fe$^{2+}$, Mn$^{2+}$ and S$^{2-}$ (Johnston et al., 2003b). It is also deficient in oxygen due to rapid decomposition of inundated vegetation and therefore shows a higher chemical oxygen demand (COD) (Johnston et al., 2003b).

This “blackwater” can cause rapid deoxygenation when it enters rivers and estuaries resulting in massive fish kills and death of other aquatic species such as shrimps, crabs and oysters (Johnston et al., 2003b; King et al., 2012). In 2001 and 2008, massive scale death in fish and other aquatic species caused by blackwater events occurred in Clarence River and Richmond River estuaries, Australia respectively (Johnston et al., 2003b; Wong et al., 2010).
Mobilization and redistribution of MBO in acidic drains by flooding, run-off and bioturbation can cause their rapid oxidation resulting in deoxygenation in such waterways (Sullivan et al., 2002; Bush et al., 2004a,b; Morgan et al., 2012). As reported by Burton et al. (2006c), resuspension of MBO not only causes rapid deoxygenation but also leads to subsequent severe acidification and liberation of metals. They reported that one of the immediate impacts of resuspension and associated MBO oxidation is the production of elemental S ($S_8$), which may be used to predict imminent acidification.

### 2.3.5 Soil Scalding

Soil scalding, is an extreme form of land degradation found in ASS landscapes. Scalds result from the accumulation of acidity and toxic metals (i.e. Al and Fe) on the surface of soils (Rosicky et al., 2002). Scalded soils are unproductive and unable to sustain vegetation (Fig. 2.5) (Lin et al., 2001; Rosicky et al., 2002, 2004a,b). Scalding is generally found in low lying coastal backswamps underlying sulfidic sediments. In north-east NSW, Australia, scalding affected landscapes are found ranging from small (i.e. 5 ha) to large areas (i.e. 200 ha) (Lin et al., 2001; Rosicky et al., 2002). Drainage is the primary factor that initiates the scalding process by completely drying and shrinking of the soil profile (Rosicky et al., 2002, 2004a). The gradual accumulation of acidity, secondary Fe(III) minerals, evaporative salts such as gypsum and barite and other metals (to the level of toxic concentrations) occurs closer to the surface, kills off the vegetation, and eventually forms a bare land (Rosicky et al., 2004a,b). Schwertmannite and jarosite are key secondary Fe(III) minerals found in these surface accumulations on scalded soils (Rosicky et al., 2004a,b). Apart from higher acidity (pH < 3) and metals such as Al and Fe (accumulated to toxic levels), these scalded sites are rich in soluble Cl$^-$ and SO$_4^{2-}$, Mn, Zn, salinity and also deficient in organic matter and soluble P compared to those in adjacent non-scalded sites (Lin et al., 2001; Rosicky et al., 2004b) The other contributing factors to soil scalding are flooding, peat fires, overgrazing, surface soil removal, frost and rapid change in vegetation types during wet and dry seasons (Rosicky et al., 2002, 2004b).
The use of persistent revegetation is the standard management approach to remediate scalding affected landscapes (Rosicky et al., 2002, 2004b). This mainly helps to minimise build up of toxic metals closer to the surface and prevents transport of accumulated toxic metals to nearby waterways (Rosicky et al., 2002). Addition of organic matter, fertilizers, liming, formation of ridges and furrows are also useful management techniques to promote revegetation (Rosicky et al., 2002; Sullivan et al., 2012).

![Fig. 2.5. Soil scalding caused by drainage in ASS affected wetland (photo-M. Rosicky)](image)

2.3.6 Emission of noxious sulfur gases

While H$_2$S formation in ASS has been known for a considerable period of time (Bloomfield and Coulter, 1974; Dent, 1986), the emission of SO$_2$ from ASS has only been discovered recently (Macdonald et al., 2004b; Kinsela et al., 2007, 2011a). While H$_2$S is known to be more toxic than SO$_2$, both gases affect negatively on the respiratory and nervous systems of humans (Manahan, 2006). Concentrations of both gases above acceptable limit cause detrimental effects on plants either by
destroying their immune system or by killing tissues in plants (Manahan, 2006). In addition, SO₂ is an air pollutant that largely contributes to “Acid Rain” a global environmental hazard (Galloway, 1995).

Apart from anthropogenic sources such as fossil fuel burning and vehicle emissions, the main contributors to atmospheric SO₂ and H₂S are volcanoes and fumaroles (Charlson et al., 1987). The potential emission of SO₂ from oxidised/drained ASS was first suggested by van Breeman (1976). He proposed that some of the unneutralized acidity generated from the oxidation of pyrite can be liberated as SO₂ which is formed from the SO₃²⁻, an intermediate product of pyrite oxidation. Later on, a study conducted by Macdonald et al. (2004b) confirmed the liberation of SO₂ from drained coastal ASS and estimated the global SO₂ emission from ASS as 3Tg/year. A field based experiment conducted by Kinsela et al. (2011a) also indicated emission of SO₂ from drained agricultural ASS.

Under reducing, anoxic conditions which generally occur during prolonged inundation periods, H₂S is formed by the activities of sulfate reducing bacteria (Bloomfield and Coulter, 1974; Dent, 1986). Microbial decomposition of organic-sulfur compounds also contributes to H₂S formation (Manahan, 2006). However, the emission of H₂S produced in ASS can be hindered due to the presence of oxidants such as iron and manganese oxyhydroxides and O₂ in the surrounding environments (Bloomfield and Coulter, 1974; Burton et al., 2006b).

Given the range of undesirable effects caused by ASS, their sustainable management is essential to avoid future problems as well as to mitigate current issues.

2.4 Management of ASS

Managing ASS generally requires neutralization (e.g. addition of lime), leaching, and removal of pyritic materials (Ward, 2004; Baldwin and Fraser, 2009). The foremost task in ASS management is the proper assessment of the acidity hazard in ASS which includes the identification of acidity generating minerals and accurate estimation of the acidity hazard (Sullivan et al., 1999; Ahern et al., 1998, 2004). In this primary task, the presence of sulfidic (i.e. iron monosulfides, pyrite) and sulfuric
(secondary Fe(III)/Al minerals) materials in PASS and AASS respectively need to be identified and quantified. The following section is a brief review of the approaches taken for the assessment of ASS materials (mainly in Australia).

2.4.1 Review of laboratory assessment techniques of ASS

One of the earliest approaches used to assess the potential for acidification was to investigate the decrease in pH in a moist sediment sample by allowing it to oxidise slowly for up to 3 months (Dent, 1986, Lin et al., 1996). In this incubation experiment the natural acidification process is simulated by allowing the oxidation of sulfidic materials in the sample. However, the target pH drop and the duration of the incubation period in this approach ranged from 3.5-4.0 and a few weeks to a year respectively (Andriesse, 1993). Later on, both Australian Soil Classification (Isbell, 1996) and the USDA Soil Taxonomy (Soil Survey Staff, 2003) standardized the target pH drop and the duration of the incubation. In both of the classifications, identification of sulfidic materials is defined as the drop in pH by at least 0.5 units to 4 or less when a 10 mm thickness layer is incubated for 8 weeks. In addition, in the definition given in USDA Soil Taxonomy, room temperature is suggested as the incubation temperature. Nevertheless, one of the problems of this approach is the potential build up of oxidized products which are generally absent in natural environments (van Breeman, 1973). In addition, Ward. (2004a,b) demonstrated that the incubation time frame (i.e. 8 weeks) was not enough to observe the suggested pH drop in 10 mm thick gel-like clayey pyritic soil materials. Therefore, Sullivan et al. (2009) proposed two new improvements to the definition; (i) incubation of 2 mm thick slabs instead of 10 mm slabs (ii) change in the incubation time period from 8 weeks to until a stable pH is reached after at least of 8 weeks of incubation.
Acidity hazard in ASS was initially expressed as a combination of two operationally defined acidity pools: Potential Acidity and Actual Acidity.

1.) Potential Acidity is a combination of Actual Acidity (i.e. readily available-total amount of acidity in soil at present) and the acidity present in a totally or partially reduced soil sample that can be derived from oxidation of soil with 30% H\textsubscript{2}O\textsubscript{2} and subsequent titration (to pH 5.5) with neutral extractants such as 1 M KCl or 1 M NaCl (Konsten et al., 1986; Ahern et al., 1998).

2.) Actual Acidity is acidity that is readily available (and that can be determined by extraction with 1 M KCl (to pH 5.5). (Ahern et al., 1998). This acidity fraction was previously defined as a combination of Soluble Acidity, Exchangeable Acidity and Retained Acidity (Lin et al., 2000; McElnea et al., 2002b).

In practice, the acidity hazard in ASS is assessed through two approaches, namely, the “Acidity Trail” and the “Sulfur Trail” (McElnea et al., 2002a,b; Ward et al., 2002b; Ahern et al., 2004). Acidity Trail is a direct approach of determining acidity by titration (Ahern et al., 1998, 2004). The Sulfur Trail is an indirect approach that is used to predict the Potential Acidity (Ahern et al., 1998). In this approach, combination of the sulfur content and the stoichiometry is used to predict the acidity risk. However, the acidity hazard predicted from the Sulfur Trail can be affected by minerals that contain sulfur but are not acidity-producing (i.e. gypsum), by minerals that produce different amount of acidity per mole of sulfur (i.e. pyrite, jarosite, schwertmannite) and by the effect of acid neutralizing agents (Ahern et al., 1998, 2004).

Potential Acidity is commonly determined through the peroxide oxidation methods following both Acidity and Sulfur Trails (Konsten et al., 1986; O’shay et al., 1990; Lin and Melville, 1993; Dent and Bowman, 1996; Ahern et al., 1998, 2000, McElnea et al., 2002a,b). Konsten et al. (1986) used both Acidity and Sulfur Trails to determine the pyrite content and the Potential Acidity in a range of ASS.
samples. In their study, the Sulfidic Acidity was calculated from the Potential Acidity measured by oxidising the NaCl extract of the sample with H$_2$O$_2$ and the pyrite content was measured by using the approach suggested by Begheijn et al. (1978). They found that the predicted Sulfidic Acidity was poorly related to the measured pyrite content. They observed that the discrepancy between the pyrite content and the Sulfidic Acidity could be due to a variety of reasons such as oxidation of other acidity producing substances such as organic matter, evolution of SO$_2$ during oxidation, neutralizing effect by buffering agents and incomplete oxidation of all pyrite present in the sample.

Lin and Melville (1993) followed the Sulfur Trail to predict the Sulfidic Acidity in estuarine ASS, and the acidity determined was termed as Peroxide Oxidisable Sulfuric Acidity (POSA). They calculated the Sulfidic Acidity by subtracting the soluble sulfate content in a water extract of the sample (soil:water 1:5) from the sulfate content determined by oxidising the sample with 30% H$_2$O$_2$. However, in agreement with Konsten et al. (1986), both Clark et al. (1996) and Lin et al. (1996) further confirmed that the Sulfidic Acidity calculated from the Potential Acidity and that predicted from the POSA, misinterpret the theoretical acidity that could be derived from pyrite.

In Australia, (at least up until 1998), there was a lack of compatibility between the methodologies used in analytical laboratories for the assessment of ASS (Ahern et al., 1998). This inconsistency was observed in relation to the soil solution ratio, duration of peroxide oxidation, the type of unbuffered salt extractant and titration end point (Ahern et al., 1998).

Taking this into account, Ahern et al. (1998) introduced a standardised set of methods to assess the Actual and Potential acidity (and the Sulfidic Acidity) in ASS. Ahern et al. (1998) introduced a new method called Peroxide Oxidisable Combined Acidity and Sulfate (POCAS) as the standard method to assess the acidity generation risk in ASS in Australia. The POCAS method was developed by combining the POSA method (Sulfur Trail) and the method developed by Dent and Bowman (1996) which measures the Total Actual Acidity and the Total Potential Acidity (Acidity Trail). Hence, one of the characteristic features of the POCAS method was that it allowed conducting of both “Acidity”
and “Sulfur” Trails in the same solution unlike previous methods where the Acidity and Sulfur Trails had to be done separately. This was a significant development of the methodology, and as a consequence identification of false results and errors became easier with respect to the previous methods. The POCAS method has three main steps. In the first step the soluble and exchangeable sulfur and the Total Actual Acidity are determined by extracting the sample with 1 M KCl and then titrating the acidity. The second step involves oxidation of the soil residue (after 1 M KCl extraction) and the subsequent determination of Total Potential Acidity (by titrating the acidity generated during the oxidation) and the total peroxide sulfur content in the peroxide digest. In the third step, the peroxide oxidisable sulfur content (a measure of reduced inorganic sulfur-RIS content) and Total Sulfidic Acidity are determined by taking the difference of sulfur and acidity values obtained in the first and second steps.

However, the POCAS method was subjected to considerable debate, especially about the reliability of the measured Total Potential Acidity (and also the calculated Total Sulfidic Acidity), and peroxide oxidisable sulfur values (Sullivan et al., 1999; Ward et al., 2002a, b). Sullivan et al. (1999) compared the RIS content determined as the peroxide oxidisable sulfur content by POCAS versus that determined from the chromium reducible-sulfur method. They reported that the peroxide oxidisable sulfur content determined from POCAS method was considerably influenced by the presence of higher amounts of organic matter and other sulfate minerals such as gypsum. In contrast, the RIS content determined through the chromium reducible-sulfur method was found to be hardly affected by either factor (Sullivan et al., 1999). This chromium reducible-sulfur method was further modified by Sullivan et al. (2000) and Burton et al. (2008c) and the modified method of Sullivan et al. (2000) is now recommended nationally for the estimation of RIS (pyrite, iron monosulfides and inorganic sulfur) in ASS in Australia (Ahern et al, 2004).

Ward et al. (2002a,b) further evaluated the POCAS method and the modified POCAS method (POCASm) (Ahern et al., 2000) and concluded that neither method is reliable or suitable to measure
peroxide oxidisable sulfur (which is a measure of RIS content) or to predict Total Sulfidic Acidity. In their study, they compared the peroxide oxidisable sulfur content and the Sulfidic Acidity determined from POCAS with those determined from the chromium reducible-sulfur method. Further, they also compared the Total Potential Acidity measured from the POCAS with the Net Acidity determined from the acid base accounting approach (ABA). Ward et al. (2002a,b) argued that those two methods were based on the ideal stoichiometric equation 2.15 of pyrite oxidation which is highly unlikely to occur in the natural environment.

\[
\text{FeS}_2 + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{H}_2\text{SO}_4 \tag{2.15}
\]

According to Ward et al. (2002a,b), the observed underestimation in peroxide oxidisable sulfur content and the predicted Sulfidic Acidity with respect to those determined from the chromium reducible-sulfur method was due to precipitation of jarosite, the dissolution of clay minerals consuming the acidity and also due to the possible atmospheric loss of S as SO\(_2\) during peroxide oxidation.

McElnea et al. (2002a) improved the peroxide oxidation technique (POCAS and POCASm) by increasing the soil:solution ratio to 1:40 (from the previous 1:20 ratio), reducing the duration of peroxide oxidation, increasing the titration end point to 6.5 from 5.5, and by using a soil suspension for the peroxide digest instead of a soil extract. As a result of the improvements made to the peroxide technique, the problems (such as jarosite precipitation, influence from organic matter and the atmospheric loss of S as SO\(_2\)) reported by Ward et al. (2002a,b) and other authors of previous peroxide studies were considered to have been overcome (McElnea et al., 2002b). The peroxide oxidisable sulfur content in 9 ASS samples obtained from this modified approach was highly correlated to the corresponding values obtained from the chromium-reducible sulfur method. The Total Sulfidic Acidity determined from the improved peroxide oxidation technique was also comparable to that predicted from the chromium reducible sulfur method (McElnea et al., 2002b).
calculated total sulfur budget from this approach also clearly indicated the negligible loss of sulfur during peroxide oxidation (McElnea et al., 2002a). In this modified peroxide oxidation approach, the Net Acidity was determined by taking the Acid Neutralization Capacity into consideration (McElnea et al., 2002a,b).

According to the initial definition given at the beginning of this section, the Actual Acidity in ASS is comprised of Soluble (titratable), Exchangeable and Retained Acidity forms (Lin et al., 2000; McElnea et al., 2002b). Soluble Acidity is in readily available form and can be exported in the event of rainfall while the Exchangeable Acidity cannot be unless displacement occurs. Similar to the Potential Acidity, Actual Acidity has also been determined by using both Acidity and Sulfur Trails. In the Sulfur Trail, the dominant sulfur fractions in ASS, such as pyrite-sulfur, soluble and adsorbed sulfur and sulfur in jarosite were extracted with various chemicals. For example, in earlier studies, the soluble and adsorbed sulfate forms in ASS were determined by extracting with EDTA.3Na (Begheijn et al., 1978; Willett and Walker, 1982; Konsten et al., 1986) whereas neutral extractants such as 1 M KCl, 1 M NaCl were used in later studies (Lin et al., 1996; Lin et al., 2000; McElnea et al., 2002b). Sulfur in jarosite was recovered by extracting the soil residue (left after the recovery of soluble and exchangeable sulfur) with strongly acidic extractants such as 4 M HCl (Begheijn et al., 1978; Willett and Walker, 1982; Konsten et al., 1986; McElnea et al., 2002a).

Soluble Acidity has also been directly measured by titrating a 1:5 extract (soil:water) with dilute (0.05 M) NaOH (Lin et al., 2000; McElnea et al., 2002b). Over the last few years, extractants such as 1 M KCl (Lin et al., 1996; Lin et al., 2000; McElnea et al., 2002b), 1 M NaCl (Konsten et al., 1986; Lin et al., 2000; McElnea et al., 2002b), 0.5 M BaCl₂ (Lin et al., 2000; McElnea et al., 2002b) and 0.5 M MgCl₂ (McElnea et al., 2002b) have been used for the extraction of both Soluble and Exchangeable Acidity. Although Lin et al. (2000) proposed that 0.5 M BaCl₂ can also be used to extract the acidity from variably charged basic sulfate minerals such as jarosite, a study conducted by McElnea et al. (2002b) disagreed with this finding.
McElnea et al. (2002a,b) highlighted the importance of quantifying the acidity stored in secondary Fe(III) minerals such as schwertmannite, jarosite and secondary Al minerals such as hydrobasaluminite and basaluminite commonly found in oxidised ASS. Acidity stored in these minerals, called “Retained Acidity” (Ahern et al., 2004), is one of the acidity pools in the previously defined Actual Acidity fraction. According to McElnea et al. (2002a,b), the rate of liberation of acidity from these minerals is controlled by soil and climatic conditions. Their studies clearly showed that extractants such as 1 M KCl, 1 M NaCl, 0.5 M BaCl$_2$ and 30% H$_2$O$_2$ were unable to extract the acidity and the sulfur fraction in those minerals (except basaluminite). Therefore, McElnea et al. (2002a,b) argued that the Actual Acidity fraction determined from the existing methods is incomplete without an accurate quantification of the Retained Acidity fraction. They also recommended further research on the accurate identification and estimation of the Retained Acidity fraction/minerals in ASS (McElnea et al., 2002a,b).

In 2004, Ahern et al. introduced a new set of laboratory guidelines for the assessment of ASS in Australia replacing the existing 1998 guidelines. These new guidelines are an improved version of the guidelines introduced in 1998, and were developed by taking into consideration suggestions made by both McElnea et al. (2002a,b) and Ward et al. (2002a,b). Although this new set of guidelines is not the only set of methods available to assess ASS, they are now being used as the standard routine laboratory analyses for the assessment of ASS in Australia (Ahern et al., 2004).

The introduction of the modified Acid Base Account (ABA) approach applicable to AASS was a salient feature of the 2004 guidelines. The ABA approach is not new, and has been widely used to determine Net Acidity generation in mining impact areas (Equation 2.16) (Jennings and Dollhopf, 1995; Skousen et al., 2002; Schumann et al., 2012) and for acid sulfate soils (e.g. Sullivan et al. 2001).

\[
\text{ABA} = \text{Potential Sulfidic Acidity} - \text{Acid Neutralization Capacity}
\] (2.16)
The modified ABA of Ahern et al. (2004) replaced the term “Actual Acidity” with a new function called “Existing Acidity” which accounted for the sum of Soluble, Exchangeable and Retained Acidity pools in ASS (Equation 2.17). The “Actual Acidity” in this modified ABA approach only refers to the Soluble and Exchangeable Acidity and “Retained Acidity” is estimated separately (Equation 2.18) (Ahern et al., 2004). “Potential Sulfidic Acidity” is the term for acidity that is derived from the oxidation of RIS such as pyrite. As a consequence of this new addition (i.e. Existing Acidity), it is possible to estimate the Net Acidity generation in both PASS and AASS (Ahern et al., 2004). Similar to previous methods, the modified ABA approach is able to conduct both Acidity and Sulfur Trails. The “Net Acidity” generation is determined by accounting the Acid Neutralization Capacity (ANC) in PASS and AASS.

Net Acidity = Potential Sulfidic Acidity (PSA) + Existing Acidity (EA) – Acid Neutralization Capacity (ANC)  

(2.17)

where,

Existing Acidity (EA) = Actual Acidity (AA) + Retained Acidity (RA)  

(2.18)

Each component of the ABA approach is estimated from separate methods (Ahern et al., 2004). In the 2004 guidelines, two techniques called the “Chromium Suite” and the “Suspension Peroxide Combined Acidity Sulfur (SPOCAS) Suite” were introduced to determine the “Net Acidity” and the other components in the ABA approach (Ahern et al., 2004). In both suites, the “Actual Acidity” is determined by extracting the soil sample with 1 M KCl and subsequent titration to pH 6.5. The determination of “Acid Neutralization Capacity” is dependent on the pH of the 1 M KCl extract (only if the pH > 6.5) since the presence of “Existing Acidity” and “Acid Neutralization Capacity” is mutually exclusive (Ahern et al., 2004). While “Potential Sulfidic Acidity” is determined separately in the “Chromium Suite” through the chromium-reducible sulfur method, it is determined by oxidising the sample with 30% H₂O₂ in the “SPOCAS Suite”. Oxidisable sulfur content > 0.03% of S.
(determined from either peroxide oxidation or the chromium reducible sulfur method) suggests the need of proper management of such soils (Dear et al., 2002; Ahern et al., 2004). This limit (i.e. 0.03% of S) is known as the “action criteria” for ASS to be managed (Dear et al., 2002; Ahern et al., 2004).

In these 2004 guidelines, ‘Retained Acidity’ refers to the less available acidity that can be released slowly on hydrolysis of secondary Fe(III) minerals such as schwertmannite and jarosite and secondary Al minerals such as basaluminite (Ahern et al., 2004). Both Chromium and SPOCAS Suites measure the “Retained Acidity” fraction in terms of the “Net Acid Soluble Sulfur” (S_{NAS}) and “Residual Acid Soluble Sulfur” (S_{RAS}), respectively (Ahern et al., 2004). In the Chromium Suite, S_{NAS} accounts for the net value of acid soluble sulfur content in the sample. Therefore, S_{NAS} value is obtained by subtracting the sulfur content in 1 M KCl extract from the sulfur content in 4 M HCl extract whereas in the SPOCAS Suite, the S_{RAS} value expresses the residual sulfur content in the sample after the peroxide oxidation. S_{RAS} is therefore determined by extracting the soil residue (after the peroxide digestion) with 4 M HCl (Ahern et al., 2004). In both techniques it is assumed that secondary Fe(III)/Al sulfate minerals do not dissolve in 1 M KCl and 30% H_{2}O_{2}, but are soluble completely in 4 M HCl.

However, in this modified ABA approach, the determination of RA fraction in terms of S_{NAS} and S_{RAS} has taken specifically into account only one secondary Fe(III) mineral in ASS, i.e., jarosite. This is a drawback of this technique as there are a variety of other secondary minerals such as schwertmannite that co-exist with jarosite in natural environments (Sullivan and Bush, 2004) and also liberate acidity during hydrolysis. In addition, Al hydroxy sulfate minerals found in ASS environments also liberate acidity during their hydrolysis process. Therefore, it is important to test the utility of this approach for the estimation of acidity generated by RA minerals, especially schwertmannite which is commonly found in acidic, oxidised ASS environments with jarosite. Although both Chromium and SPOCAS suites are widely used in laboratories in Australia for the analysis of ASS, no systematic evaluation has been conducted, especially for the newly included RA fraction in the ABA approach. Such an
evaluation would be highly useful to find out whether the assessment of RA pool minerals interferes with the assessment of the other acidity pools in the ABA approach (i.e. Potential Acidity, Actual Acidity).

2.5 Major forms of Retained Acidity (RA) Minerals in ASS - Schwertmannite and Jarosite

The properties and environmental impact of ASS are largely determined by the minerals present in those soil materials. While the behaviour and quantification of minerals contributing to the “Potential Acidity” and “Actual Acidity” pools in ASS have been studied extensively, those of “Retained Acidity” minerals, especially schwertmannite and jarosite which are abundantly found in ASS, have not been investigated to such an extent. Nevertheless, the acidity stored in these secondary Fe and Al minerals (i.e. Retained Acidity generating minerals) is known to contribute largely to the acidic runoff in ASS environments (McElnea et al., 2004). Schwertmannite has been identified as the dominant mineral form of RA generating iron precipitating minerals in severely acidified landscapes in eastern Australia (Sullivan and Bush, 2004; Burton et al., 2006b; Sullivan et al., 2006b). The presence of jarosite also indicates disturbed ASS with preceded and future acidity liberation and is also commonly found in both coastal and inland acid sulfate soils in Australia (Dent, 1986; Fitzpatrick et al., 2009; Johnston et al., 2009a,c). Therefore, the behaviour of both minerals is crucial to understanding the geochemistry in such environments.

2.5.1 Occurrence and formation of schwertmannite and jarosite

Schwertmannite and jarosite are secondary Fe(III) minerals found in the sulfuric horizon of inland and coastal oxidised ASS and mining impacted environments (Bigham and Norsdtröm, 2000; Fitzpatrick and Shand, 2008; Fitzpatrick et al., 2009). Acid mine/rock drainage (AMD/ARD) impacted environments are other common environments where both minerals are abundantly found (Bigham et al., 1994, 1996a; Baron and Palmer, 1996; Bigham and Norsdtröm, 2000; Dutrizac and Jambor, 2000). In 2004, jarosite was also detected on the surface of Mars (Klingelhöfer et al., 2004). Both
minerals are formed by the oxidation of pyrite and incomplete hydrolysis of the formed Fe(III) (Equations 2.7, 2.11 and 2.12) (Bigham et al., 1994, 1996a; Bigham and Norsstrom, 2000). In some instances, the oxidised products of pyrite such as Fe$^{3+}$ are transported by runoff and therefore, the precipitation of both jarosite and schwertmannite occurs away from the source (i.e. at locations where further oxidation and hydrolysis of oxidised products of pyrite such as Fe$^{3+}$ occur) (Shamshuddin et al., 1995; Kawano and Tomita, 2001).

Schwertmannite in ASS occurs as a brownish yellow or orange coloured precipitate on the surface of soils, along the edges of the drains and surface coatings of organic litter such as leaves (Fig. 2.6) (Sullivan and Bush, 2004; Fitzpatrick and Shand, 2008; Fitzpatrick et al., 2009). Jarosite mottles are straw/pale yellow in colour (Fig. 2.6) and often found as efflorescences on upper soil layers and channel and chamber infillings (Dent, 1986; Fitzpatrick and Shand, 2008; Fitzpatrick et al., 2009; Johnston et al., 2009a,c, 2011a).
2.5.2 Chemical composition and structure of schwertmannite and jarosite

Schwertmannite is a poorly crystalline mineral with variable composition of sulfate and water in its structure (Bigham et al., 1994, 1996a; Yu et al., 1999; Fernandez-Martinez et al., 2010). Therefore, the standard molecular formula of schwertmannite is derived as Fe$_8$O$_8$(OH)$_8$$_{2x}$(SO$_4$)$_x$$_n$H$_2$O where $1.74 \leq x \leq 1.86$ and $8.17 \leq n \leq 8.62$ (Bigham et al., 1990; 1994, 1996a). Schwertmannite is brownish yellow (7.7YR-9.2YR, 5.6-6.5/7.3-9.1) in colour and has a characteristically higher specific surface area (100-200 m$^2$ g$^{-1}$) compared to most of the other iron oxides (except ferrihydrite) which allows it to adsorb trace metals in the natural environment (Bigham et al., 1994; Schwertmann and Cornell, 2000).

The structure of schwertmannite was first described by Bigham et al. (1990) as being similar to akaganeite. The unit cell of akaganeite has a tunnel structure formed by sharing the corners of double chains of iron (FeO$_3$(OH)$_3$) octahedra (Bigham et al., 1994). In akaganeite, each tunnel cavity (diameter around 0.5 nm) in a unit cell is occupied by a chloride ion (0.35 nm). Through infrared studies, it was revealed that sulfate fill these cavities in schwertmannite by forming bridging bidentate complexes with Fe in the octahedra. However, due to the larger size of a sulfate molecule (0.46 nm diameter) (cf. chloride), the tunnel structure in schwertmannite is slightly distorted compared to that of akaganeite (Bigham et al., 1994). In 2004, Loan et al. suggested that the structure of schwertmannite is much more similar to ferrihydrite than akaganeite as previously suggested by Bigham et al. (1990, 1994). However, a later study conducted by Fernandez-Martinez et al. (2010) confirmed that the structure of schwertmannite is akin to akaganeite. A simulation study of X-ray diffraction patterns conducted by Fernandez-Martinez et al. (2010) showed an occurrence of two types of sulfate molecules per unit cell of schwertmannite based on their position in the tunnel structure. These two sulfate molecules are involved in the formation of one outer-sphere complex and one inner-sphere complex in the iron octahedral tunnels (Fernandez-Martinez et al., 2010). The sulfate in schwertmannite can be substituted by other oxy-anions such as selenate (Waychunas et al., 1995),
arsenate (Carlson et al., 2002; Fukushi et al., 2003a,b, 2004; Regenspurg et al., 2002; Regenspurg and Peiffer, 2005; Burton et al., 2009) and chromate (Regenspurg et al., 2002; Regenspurg and Peiffer, 2005) hence, schwertmannite is known as a scavenger for those trace metals and metalloids.

Jarosite is a crystalline mineral compared to schwertmannite and is straw yellow (2.6Y-3.6Y, 7.4-8.0/3.8-6.2) in colour (Scheinost and Schwertmann, 1999). The surface area of jarosite is considerably lower than that of schwertmannite and the reported values for the surface area of synthetic jarosites range from 1.4 to 2.2 m² g⁻¹ (Smith, 2004; Elwood Madden et al., 2012). It is a member of the alunite group with a standard formula of AB₃(SO₄)₂(OH)₆ (Baron and Palmer, 1996; Bigham and Nordstrom, 2000; Dutrizac and Jambor, 2000) where A is a monovalent cation (generally occupied by K⁺, Na⁺, H₃O⁺, NH⁺) and B is a tri-valent cation (such as Fe³⁺ and Al³⁺) (Dutrizac and Kaiman, 1976; Baron and Palmer, 1996; Dutrizac and Jambor, 2000). Similar to schwertmannite, jarosite is also known to act as a scavenger for trace metals such as As, Cd, Cu, Pb and Zn (Dutrizac and Kaiman, 1976; Dutrizac and Jambor, 2000). These elements are incorporated to the structure of jarosite by occupying A and B positions (Dutrizac and Kaiman, 1976; Dutrizac and Jambor, 2000). In natural environments, jarosite exist as a solid solution of K, Na and H₂O jarosites (Dutrizac and Kaiman, 1976).

2.5.3 Characterization of schwertmannite and jarosite

Physical and chemical properties of schwertmannite and jarosite have been examined extensively using wet chemical approaches and by various analytical techniques such as X-ray Diffraction (XRD), Mössbauer, Infrared (IR), Raman, Scanning/Transmission Electron Microscopy (SEM/TEM) and Thermo-gravimetric analysis/ Differential Thermal Calorimetry (TGA/DTA) (Bigham et al., 1994; Bigham and Nordstrom, 2000, Regenspurg, 2002; Drouet and Navrotsky, 2003; Drouet et al., 2004; Majzlan et al., 2004; Smith, 2004; Frost et al., 2005; Chio et al., 2010; Xu et al., 2010; Vummidi Lakshman et al., 2014). Schwertmannite has eight broad peaks in its XRD pattern where the most intense peak is located at 4.88 Å. The peaks of jarosite are sharp indicating its crystalline nature and the most intense peaks are located around 5.09, 3.11 and 3.08 Å (Bigham and Nordstrom, 2000).
morphism of natural schwertmannite is described as pin-cushion, sea urchin or hedgehog shape (200-400 nm- diameter rounded aggregates of acicular crystals) (Bigham et al., 1994, 1996a; Bigham and Nordstrom, 2000; Regenspurg, 2002), whereas natural jarosite are crystals with rhombohedral morphology (< 500 nm) (Fanning, 2002; Fanning et al., 2002; Grishini et al., 1988; Dutrizac and Jambor, 2000). The analytical techniques mentioned earlier in this paragraph also provide comprehensive knowledge on the mineralogy, thermal stability, molecular structure and the magnetic field of both minerals as discussed in detail elsewhere (Bigham et al., 1994; Bigham and Nordstrom, 2000, Regenspurg, 2002; Drouet and Navrotsky, 2003; Drouet et al., 2004; Majzlan et al., 2004; Smith, 2004; Frost et al., 2005; Chio et al., 2010; Xu et al., 2010; Vummidi Lakshman et al., 2014). Although advanced techniques such as Mössbauer, Infrared (IR) and Raman provide accurate information about both minerals, these methods are not always readily available, and hence cannot be used routinely in many situations. Therefore, there is a demand for readily available wet chemical approaches that can be used for the identification and quantification of schwertmannite and jarosite in natural environments.

Selective dissolution and sequential extraction are two widely employed wet chemical techniques for the characterization/identification of schwertmannite and jarosite in mining impacted environments (Murad et al., 1993; Bigham et al., 1994, 1996a; Dold and Fontboté, 2001, 2002; Dold, 2003a,b; Li et al., 2007). The theory behind selective dissolution is to dissolve only the poorly crystalline minerals such as schwertmannite and ferrihydrite from a mixture of minerals using a strong extractant and then to use the Fe and S composition of the extract to determine the dissolved minerals. Extraction with acidified (pH 3) ammonium oxalate (AAO) in dark has been largely used for the identification of poorly crystalline minerals including schwertmannite in AMD sites, mining impacted environments, quaternary volcanic deposits and constructed wetlands (Bigham et al., 1990, 1994, 1996a; Bhatti et al., 1993; Childs et al., 1998; Webster et al., 1998; Singh et al., 1999; Dold, 2003a; Fukushi et al., 2003a; Gagliano et al., 2004; Regenspurg et al., 2004; Jönsson et al., 2005; Scroth and Parnell, 2005;
Kumpulainen et al., 2007, 2008; Caraballo et al., 2009; Peretyazhko et al., 2009). The Fe/S molar ratio in the AAO extract is then used to determine the presence of schwertmannite. While the presence of schwertmannite is indicated by a typical Fe/S molar ratio ranging from 5-8 (Bigham et al., 1994), a very recent study conducted by Caraballo et al. (2013) demonstrated a wider range for the Fe/S molar ratio (i.e. 3.77-15.52) indicative of schwertmannite. The AAO extraction time periods used in previous studies were inconsistent and ranged from 15 min to 4 h. Nevertheless, Bigham et al. (1990) showed complete dissolution of a synthetic schwertmannite sample (having $\text{SO}_4^{2-}$ content > 11%) and schwertmannite in natural precipitates collected from mine sites within a 15 min extraction time.

DXRD is another technique that has been successfully used in combination with selective dissolution to identify schwertmannite (Bhatti et al., 1993; Singh et al., 1999; Dold, 2003; Caraballo et al., 2009). In the DXRD approach, the XRD patterns before and after the dissolutions are obtained and the XRD pattern after the extraction is subtracted from that of before the extraction which results in the XRD pattern of the dissolved minerals (Schulz, 1981, 1986). Dold (2003a) showed that schwertmannite dissolved within 15 min AAO extraction from the mineral precipitates were sufficiently high enough to be identified through the Differential X-ray Diffraction (DXRD) technique. Interestingly, this combined approach has been successfully employed to identify schwertmannite in mining sites and mining impacted environments, but not in ASS where schwertmannite is also present in abundance. Given schwertmannite’s significant contribution towards the acidity and trace metal mobility in ASS, the accurate identification and quantification of schwertmannite is desirable for the management of ASS. Therefore, an evaluation of the 15 min AAO extraction for the identification of schwertmannite in soil materials would be highly useful for the development of appropriate management techniques for ASS. Such management approaches would also be benefitted by knowledge on the applicability of the DXRD approach for detection of schwertmannite in soil materials.
Sequential extraction techniques are convenient, low technology approaches widely used to examine mineral phases in soils and sediments (Tessier et al., 1979). These procedures involve the sequential extraction of metals from water soluble, exchangeable, carbonate bound and amorphous phases, crystalline phases, sulfide and organic bound phases (Tessier et al., 1979; Dold, 2003b; Claff et al., 2010). In these sequential extraction techniques, a variety of extractants such as 4 M to 12 M HCl, acidified AAO (extraction for about 1 h), 0.3 M NaOH and citrate buffer dithionite (CBD) (some of which also require heating the solution up to 80°C-90°C) have been used to dissolve jarosite (Dold, 2003b; Yin and Catalan, 2003; Claff et al., 2010). In 2007, Li et al. proposed a simple effective three-step sequential procedure to recover jarosite in acid mine waste samples. They proposed this procedure as a good alternative jarosite determination method to the SPOCAS method which was specifically designed for determining jarosite content in environments containing little pyrite. This procedure consists of initial anoxic water extraction followed by roasting the residue left after the anoxic water extraction at 550°C for 1 h and finally 4 M HCl extraction of the roasted sample to recover the sulfur content in jarosite. In the first step of this sequential approach, soluble Fe(II) sulfate minerals such as melanterite are extracted with the anoxic water extraction step. In the roasting step, pyrite and other reactive sulfides are completely removed and jarosite is converted to a 4 M HCl extractable mineral called yavapaiite (KFe(SO$_4$)$_2$). Li et al. (2007) reported a 100% recovery of jarosite from 5% jarosite spiked quartz and also from laterite nickel tailing samples. Li et al.’s (2007) conclusion on this sequential extraction procedure was based solely on one type of jarosite (i.e. Na-jarosite), however, the composition of jarosite in natural environments varies widely. As a consequence of the variability in composition as well as in the crystallinity, the thermal stability and the solubility kinetics in those different jarosite types also vary widely (Frost et al., 2005; Xu et al., 2010). Hence, there is a need for a proper evaluation of Li et al.’s (2007) procedure for quantifying common jarosite types in natural environments. Furthermore, the suitability of this sequential procedure has not been evaluated for the extraction of jarosite in ASS materials even though jarosite is one of the most prominent secondary minerals found in such landscapes.
2.5.4 Behaviour of schwertmannite and jarosite

The behaviour of schwertmannite and jarosite has been investigated in terms of the solubility and stability of both minerals under various chemical and physical conditions. In acidic (pH < 4) oxidising environments, schwertmannite and jarosite transform slowly to other mineral phases such as goethite through hydrolysis (van Breeman, 1976; Dent, 1986; Bigham et al., 1994; Bigham and Nordstrom, 2000; Smith, 2004). Under near-neutral (pH 5-6) reducing environments these minerals become highly unstable and can rapidly transform as a result of reductive dissolution and Fe$^{2+}$ catalysed transformation (Bridge and Johnson, 2000; Küsal et al., 2002; Jones et al., 2006; Burton et al., 2007, 2008b; Jones et al., 2009; Johnston et al., 2009a,b, 2010a,b).

Other physiochemical factors such as temperature, presence of cations (Fe$^{2+}$, Cu$^{2+}$) or anions (AsO$_4^{3-}$, CrO$_7^{2-}$), silica and organic matter are known to strongly influence the stability and the rate of transformation of both schwertmannite (Waychunas et al., 1995; Webster et al., 1998; Fukushi et al., 2003a,b, 2004; Regenspurg et al., 2002, 2004; Regenspurg and Peifer, 2005; Schroth and Parnell, 2005; Blodau and Gatzek, 2006; Jönsson et al., 2006; Knorr and Blodau, 2007; Burton et al., 2007, 2008b, 2013b; Kumpulainen et al., 2008b; Jones et al., 2009; Nagano et al., 2011; Paikarary and Peiffer, 2010, 2012; Burgos et al., 2012; Burton and Johnston, 2012; Antelo et al., 2013) and jarosite (Stofregen, 1993; Gasharova et al., 2005; Chu et al., 2006; Smith et al., 2006; Welch et al., 2007, 2008; Zhu et al., 2008; Asta et al., 2009; Keene et al., 2010; Elwood Madden et al., 2012; Johnston et al., 2012; Kendall et al., 2013).

In the case of schwertmannite, complete transformation to goethite varies from hours to months or even years (Bigham et al., 1996a; Jönsson et al., 2005; Schwertmann and Carlson, 2005; Acero et al., 2006; Burton et al., 2007, 2008b) depending on various physio-chemical factors. For example, under acidic-oxic conditions, the transformation of schwertmannite was slow and required several months to complete (Bigham et al., 1996a; Regenspurg et al., 2004; Jönsson et al., 2005; Acero et al., 2006). However, the rate of transformation is accelerated as pH increases (i.e. under near-neutral conditions)
Chapter 2: A Review on ASS, Acidity Retained in Schwertmannite and Jarosite, Their Assessment and Behaviour

(Regenspurg et al., 2004; Jönsson et al., 2005; Schwertmann and Carlson, 2005; Knorr and Blodau, 2007). Under oxidising conditions, both Bigham et al. (1996a) and Acero et al. (2006) observed a complete transformation of synthetic and natural schwertmannite samples kept in contact with acidic water (pH 3-4) within 543 and 323 days respectively. However, Schwertmann and Carlson (2005) observed a much faster transformation of a synthetic schwertmannite sample kept in acidic water (pH 4) which completed within 100 days. They also reported that the transformation rate was doubled at pH 7. Likewise, Jönsson et al. (2005) also reported an increased rate of transformation at pH 9 as opposed to that at pH 6.

Schwertmannite is a good scavenger for oxy-anions of trace metals such as As, Se and Cr in the environment. It has been demonstrated that the adsorption/co-precipitation of trace metal anions such as AsO$_3^{3-}$/AsO$_4^{3-}$, CrO$_7^{2-}$ stabilised the schwertmannite which in turn reduced the mineralogical transformation of schwertmannite to goethite under oxidising conditions (Regenspurg et al., 2002; Fukushi et al., 2003a,b; Regenspurg and Peiffer, 2005; Paikarary and Peiffer, 2010, 2012). Contrastingly, the studies conducted by Schroth and Parnell (2005) and Acero et al. (2006) observed a transformation of trace metal scavenged schwertmannite to goethite under acidic-oxidising conditions. Some of these trace metals were either retained in the newly formed goethite phase or released back to the solution (Schroth and Parnell, 2005; Acero et al., 2006). Knorr and Blodau (2007) also observed a decrease in the rate of transformation of schwertmannite at higher sulfate (20 mM) and higher organic matter (20 mg DOC L$^{-1}$) concentrations at pHs ranging from 3-5 under oxidising conditions.

The stability of jarosite has been largely examined by batch dissolution experiments under acidic and alkaline conditions (Gasharova et al., 2005; Smith et al., 2006; Welch et al., 2008; Elwood Madden et al., 2012; Kendall et al., 2013). These studies found that jarosite dissolves incongruently under both acidic (pH 2-4) and alkali (pH 5.5-8) conditions with the concomitant release of Fe (but only under acidic conditions), K and SO$_4^{2-}$ to the solution (Gasharova et al., 2005; Smith et al., 2006; Welch et al., 2008). The dissolution under alkali conditions was associated with the formation of a surface
coating of goethite which prevented further dissolution (Smith et al., 2006). However, Gasharova et al. (2005), showed that the presence of iron complexing agents such as organic matter (i.e. humic acids) could continue the dissolution process by complexing with Fe\(^{3+}\) in the mineral.

In reducing environments, Fe(III) and SO\(_4\) in iron(III)oxyhydroxy minerals such as goethite, ferrihydrites, schwertmannite and jarosite act as terminal electron acceptors for anaerobic bacteria (Lovely and Phillips, 1986; Lovely, 1997). Therefore, iron(III) and sulfate reductions are the two main redox processes that affect the stability of both minerals in such environments (Peine et al., 2000; Blodau and Gatzak, 2006; Burton et al., 2007, 2008b). Hence, both minerals are subject to reductive dissolution via the microbial degradation of organic matter in reducing, acidic environments (Bridge and Johnson, 2000; Küsal et al., 2002; Jones et al., 2006). This process generates alkalinity, Fe\(^{2+}\), K\(^+\) and sulfate (Jones et al., 2006; Burton et al., 2007; 2008b; Keene et al., 2010; Johnston et al., 2011a,b, 2012). In the reductive dissolution process, the Fe\(^{2+}\) generated is particularly of importance, as it is known to catalyse the transformation of meta-stable iron(III)oxyhydroxy minerals to more stable mineral phases under reducing conditions (Pedersen et al., 2005; Burton et al., 2007, 2008b; Jones et al., 2009). The role of Fe\(^{2+}\) catalysis was highlighted in the study conducted by Burton et al. (2007, 2008b), which reported a complete transformation of schwertmannite to goethite within 3-5 h under conditions where Fe\(^{2+}\) > 5 mM and pH > 6. These increases in pH, alkalinity and Fe\(^{2+}\) concentration favoured sulfate reduction over iron reduction resulting in a change in the geochemical regime from schwertmannite dominant to goethite, iron monosulfide (mackinawite) and siderite dominant (Burton et al., 2007, 2008b).

Silica is commonly found in ASS environments due the dissolution of alumino-silicate minerals by the acidity in those environments (Sammut et al., 1996). In 2009, Jones et al. reported that Fe\(^{2+}\) catalysed transformation of schwertmannite to goethite within 3-5 h under conditions where Fe\(^{2+}\) > 5 mM and pH > 6. These increases in pH, alkalinity and Fe\(^{2+}\) concentration favoured sulfate reduction over iron reduction resulting in a change in the geochemical regime from schwertmannite dominant to goethite, iron monosulfide (mackinawite) and siderite dominant (Burton et al., 2007, 2008b).
to the surface of schwertmannite and thereby prevented direct adsorption of Fe$^{2+}$ that carry out the exchange of Fe$^{3+}$ in the schwertmannite structure with the adsorbed Fe$^{2+}$. Based on the potential surface coverage by silica, organic matter and phosphate and subsequent inhibition of Fe$^{2+}$ catalysis, Jones et al. (2009) and Collins et al. (2010) argued that schwertmannite could remain for longer time periods than reported by previous laboratory studies even in the presence of higher Fe$^{2+}$ concentrations. As a result, they suggested that the implementation of alternative cycles of drying and wetting that promote the Fe$^{2+}$ catalysed transformation will be an ineffective management approach in ASS environments. In 2012, a laboratory experiment conducted by Burton and Johnston further confirmed the inhibition effect of Si on the Fe$^{2+}$ catalysis transformation of schwertmannite under near-neutral conditions. However, this inhibition effect by Si on the Fe$^{2+}$ catalysed transformation was found to be negligible under conditions where microbiually induced reductive dissolution occurs and generates alkalinity and Fe$^{2+}$ (Burton and Johnston, 2012). Other commonly found natural components in ASS environments such as sulfate (100 mM) and organic matter (25-150 mg L$^{-1}$) at higher concentrations were also found to slow down both the reductive dissolution and the Fe$^{2+}$ catalysed schwertmannite transformation (Blodau and Gatzek, 2006; Jones et al., 2009; Burton et al., 2013a).

Reductive dissolution and Fe$^{2+}$ catalysed transformation of jarosite have been discussed by various authors (Jones et al., 2006; Jones et al., 2009; Keene et al., 2010; Johnston et al., 2009a, 2011a,b, 2012). Jones et al. (2009) observed ~74% of jarosite transformation to lepidocrocite in the presence of Fe$^{2+}$. However, they reported an inhibition of this Fe$^{2+}$ catalysis transformation (jarosite transformation was only ~10%-45%) at higher concentrations of Si (10 mM) and organic matter (Suwannee River Fulvic Acid -150 mg L$^{-1}$). Periodic tidal inundation has been proposed as one of the viable approaches to improve the water quality of ASS drainage (Johnston et al., 2005a; Johnston et al., 2009a,b). However, as found during tidal inundation (Johnston et al., 2010a,b, 2012), the reducing conditions that are generated in the sulfuric horizon promote reductive dissolution of jarosite.
liberating not only Fe$^{2+}$ and SO$_4$ but also the scavenged As in jarosite. Under such conditions, microorganisms drive reductive dissolution. Hence, organic matter plays a key role in promoting the reductive dissolution of jarosite (Chu et al., 2006; Zhu et al., 2008). Furthermore, abiotic dissolution of jarosite by dissolved sulfide, a common substance in reducing environments, has also been discussed by Johnston et al. (2012). They reported that dissolved sulfide destabilizes jarosite by promoting reductive dissolution and the formation of mackinawite.

Previous studies have demonstrated that the stability and fate of schwertmannite and jarosite are governed by a large number of physio-chemical factors and result in stabilities for schwertmannite that range from a few hours to years depending on these factors. However, unlike in laboratory experiments, these factors are subject to spatial and temporal variability in natural environments which in turn strongly influence the stability of both minerals in those environments. For example, the geochemistry in ASS environments is highly dynamic and variable due to natural and human induced activities (Sullivan et al., 2006a,b; Burton et al., 2008c; Johnston et al., 2009a,c). In eastern Australia, most of the CASS landscapes are located in low-lying floodplains that are underlaid by sulfidic sediments (Walker, 1972; Lin and Mellville, 1992; Sammut et al., 1996; White et al., 1997). A network of drainage canals developed for flood mitigation and for agricultural purposes are characteristic features of these landscapes (Lin and Mellville, 1992; Sammut et al., 1996; White et al., 1997). As a consequence, drainage plays a key role on the acidity generation and the acidity discharge by CASS which is strongly regulated by the seasonal changes in the weather such as heavy rain fall, prolonged drought and flooding (Sammut et al., 1994; White et al., 1997; Johnston et al., 2004). Seasonal changes and associated factors such as runoff and stream flow could either accelerate or impede the transformation of schwertmannite and jarosite precipitated in such landscapes, thereby controlling the acidity generation and the discharge. However, there is little field research conducted on the in-situ stability and the fate of schwertmannite and jarosite in highly dynamic CASS. For example, is the stability of schwertmannite in field situations likely to be measured over hours or
months or years, as has been the case in various laboratory studies? Such an understanding of the stability of schwertmannite in field CASS environments would be highly useful to allow the development of more appropriate management strategies for ASS landscapes.

2.6 Relationship between Natural Organic Matter (NOM), Arsenic (As) and Schwertmannite in ASS

ASS (Dudas, 1987; Gustafsson and Tin, 1994; Bennett and Dudas, 2003; Burton et al., 2008a; Johnston et al., 2010a; Kinsela et al., 2011b) and AMD (Fukushi et al., 2003a, b; Regenspurg and Peiffer, 2005; Maillot et al., 2013) environments are common localities where As accumulation are found due to the presence of abundant amounts of iron oxide/iron oxyhydroxide mineral species such as schwertmannite, jarosite, goethite, ferrihydrite and hematite.

2.6.1 Arsenic (As) in natural environments

Arsenic is a common trace metal found in natural environments, where it exists in soils, sediments, rocks, water, atmosphere and even within the organisms (Smedley and Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a). One of the main sources of As in natural environment is the weathering of As containing sulfidic minerals such as areseno-pyrite (FeAsS), orpiment (As$_2$S$_3$) and realgar (AsS) (Smedley and Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a). Volcanic emissions and related geothermal activities are the other main contributors of As in the natural environment (Chilvers and Peterson, 1987; Bissen et al., 2003; López et al., 2012). Arsenic concentration in natural environments has greatly increased due to a number of anthropogenic activities, thereby posing severe threat to human and animal health (Smedley and Kinniburgh, 2002). These anthropogenic activities include the application of As-containing pesticides and wood preservatives, mining activities, industrial activities such as metal smelting, cement production and fossil fuel combustion (Matschullat et al., 2000; Smedley and Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a).
According to the World Health Organization (WHO), the maximum level of As that should be present in drinking water is 10 µg L\(^{-1}\) (Smedley and Kinniburgh, 2002; Bissen et al., 2003). However, as a consequence of both anthropogenic and natural activities, many fresh and groundwater sources have As concentration > 10 µg L\(^{-1}\) (Harvey et al., 2002; Smedley and Kinniburgh, 2002; Bissen et al., 2003). Arsenic concentration > 10 µg L\(^{-1}\) contaminates drinking water and long-term exposure to As containing food and water causes As poisoning in humans. Health problems related to As poisoning have been reported all over the world including Bangladesh, Vietnam, West Bengal (India), Chile, Argentina, China, Hungary, Mexico, and the USA (Harvey et al., 2002; Smedley and Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a). Chronic and acute poisoning of As are reported among humans due to the exposure to As (Smedley and Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a). Symptoms of acute poisoning are non-specific and indicated as weight loss, hair loss, weariness, gastritis and colitis. Long term exposure to As affects the cardiovascular, circulatory and nervous systems and has also been found to cause irreparable damages to major organs in the human body such as kidneys and the liver. A large number of such cases due to chronic poisoning have been reported in Bangladesh and West Bengal (Smedley and Kinniburgh, 2002; Bissen et al., 2003).

### 2.6.2 As mobility in natural environment

In natural environments As mobility is regulated by iron, aluminium and manganese oxyhydroxides, clay, sulfidic minerals and natural organic matter (NOM). The key processes involved in regulating the mobility of As in natural environments are the redox reactions, co-precipitation, weathering, adsorption, desorption and dissolution (Smedley and Kinniburgh, 2002; Bennett and Dudas, 2003; Bissen et al., 2003; Pederson et al., 2006; Wang and Mulligan, 2006a; Cheng et al., 2009; Carlo et al., 2013). These processes are strongly influenced by various physico-chemical factors such as pH, redox status, organic ligands and inorganic anions such as Fe\(^{3+}\), Ca\(^{2+}\), PO\(_4^{3-}\), HCO\(_3^{-}\) and silica (Smedley and
Chapter 2: A Review on ASS, Acidity Retained in Schwertmannite and Jarosite, Their Assessment and Behaviour

Kinniburgh, 2002; Bissen et al., 2003; Wang and Mulligan, 2006a; Cheng et al., 2009; Carlo et al., 2013).

Arsenic has a strong affinity towards iron oxides/iron oxyhydroxide minerals such as goethite, lepidocrocite, jarosite, schwertmannite, ferrihydrite and hematite. Iron oxides/iron oxyhydroxide minerals are effective sinks for As in natural environments due to their abundance and characteristic properties such as lower crystallinity, higher surface area and high density of reactive sites at the crystal surface (Bigham et al. 1996a; Stumm and Morgan, 1996; España et al. 2006; Wang and Mulligan, 2006a). In addition to these characteristic properties, minerals such as schwertmannite, lepidocrocite, goethite and ferrihydrite are able to attract arsenic oxy-anions as the surface of these minerals are positively charged (because the point of zero charge of those minerals is > pH 7) under many natural environments (Bissen et al., 2003; Wang and Mulligan, 2006a). Therefore, the presence of these minerals can help to regulate the mobility of As in natural environments.

The relationship between As and different iron oxides such as goethite (Bowell, 1994; Grafe et al., 2001; Asta et al., 2009, 2010; Weng et al., 2009), schwertmannite (Waychunas et al., 1995; Regenspurg et al., 2002; Fukushi et al., 2003a,b, 2004; Regenspurg and Peiffer, 2005; Burton et al. 2009, 2010; Liao et al., 2011; Paikarary et al., 2011, 2012; Burton and Johnston, 2012; Paikarary and Peiffer, 2012; Antelo et al., 2012; Malliot et al., 2013), jarosite (Asta et al., 2009, 2010; Kendall et al., 2013), ferrihydrite (Grafe et al., 2002; Simeoni et al., 2003; Jia et al., 2006; Bhandari et al., 2011; Adra et al., 2013), lepidocrocite (Bowell, 1994), hematite (Bowell, 1994; Redman et al., 2002; Ko et al., 2004) and akagenite (Deliyanni et al., 2003) have been studied extensively.

Schwertmannite is one of the key iron oxyhydroxy minerals that regulates the mobility of As in ASS and AMD environments (Fukushi et al., 2003a,b, 2004; Regenspurg and Peiffer, 2005; Burton et al. 2009, 2010; Burton and Johnston, 2012). The surface complexation and/or the ligand exchange mechanisms (with sulfate) are/is involved in As uptake by schwertmannite (Waychunas et al., 1995; Fukushi et al., 2004; Liao et al., 2011; Paikarary et al., 2011; Antelo et al., 2012). As(V) is known to
adsorb strongly to schwertmannite at acidic to neutral pHs (3-6) under oxidising conditions whereas As(III) preferably adsorbs at higher/alkaline pHs (~9) (Wang and Mulligan, 2006a; Burton et al., 2009; Mamindy-Pajany et al., 2011). However, in contrast to previous studies, adsorption of As(III) to biogenic schwertmannite at acidic pH (pH 3) was observed by both Liao et al. (2011) and Paikarary et al. (2011, 2012). Paikaray et al. (2011) suggested that the formation of As(III)-Fe(III)-sulfate precipitate on the surface of schwertmannite is the key As(III) uptake process rather than the ligand exchange mechanism which was suggested in many previous studies. Many studies have shown that adsorption of both As(III)/As(V) poisoned the growth of schwertmannite and also inhibited the transformation of schwertmannite to goethite (Waychunas et al., 1995; Regenspurg et al., 2002; Fukushi et al., 2003a,b; Paikarary et al., 2012; Paikarary and Peiffer, 2012; Malliot et al., 2013). However, a study conducted by Burton et al. (2010) showed that the sorbed As(III) in schwertmannite was able to inhibit Fe$^{2+}$ transformation only by 24% as opposed to sorbed As(V) which inhibited the transformation by 94%. Although the Fe$^{2+}$ was able to partially transform the As(III) sorbed schwertmannite to goethite, it didn’t help to desorb As(III) from schwertmannite, indicating the retention of As(III) by the goethite that formed (Burton et al., 2010). In contrast to the oxidising conditions, As was found to re-mobilize from iron oxides/iron oxyhydroxides under reducing conditions due to the reductive dissolution of those iron minerals (Harvey et al., 2002; Wang and Mulligan, 2006a) as well as by the competitive desorption by substances like NOM (Bowell, 1994; Grafe et al., 2001, 2002; Redman et al., 2002).

### 2.6.3 Influence of natural organic matter (NOM) on the relationship between arsenic and iron oxides/iron oxyhydroxides

NOM is ubiquitous, composed of partially degraded organic matter and is redox active due to the presence of polyfunctional groups of organic acids (hydroxyl, amino, sulphydryl, carboxyl and phenolic) (Aiken et al., 1985; Gu et al., 1994; Lovely et al., 1996; Wang and Mulligan, 2006a). In natural environments, NOM, therefore, not only act as electron donors but also function as electron
shuttles, influence the mobility of metals by carrying out redox reactions, by complexation and also by competitive adsorption/desorption processes (Lovely et al., 1996; Scott et al., 1998; Redman et al., 2002; Wang and Mulligan, 2006a,b). Therefore, research has also found that once NOM is adsorbed to the mineral surface it can regulate the properties of the mineral such as zeta potential, surface charge and the stability (Gu et al., 1994; Mak and Lo, 2011). The effect of NOM on the relationship between As and iron oxides/iron oxyhydroxides has been investigated extensively (Xu et al., 1991; Bowell, 1994; Gu et al., 1994, 1995, 1996; Kaiser and Guggenberger, 2000; Grafe et al., 2001, 2002; Redman et al., 2002; Chen et al., 2003; Bauer and Blodau, 2006; Wang and Mulligan, 2006a,b; Mladenov et al., 2009; Weng et al., 2009; Sharma et al., 2011). It has been proposed by many authors that NOM bind with iron oxides/iron oxyhydroxide mainly through surface adsorption (Gu et al., 1994, 1995; Redman et al., 2002; Wang and Mulligan, 2006a,b; Weng et al., 2009). These surface adsorption processes are highly dependent on the pH and it has been found that NOM is strongly adsorbed to iron oxide/oxyhydroxide mineral surfaces under acidic to slightly acidic conditions. Accordingly, studies have found a competitive desorption of adsorbed As(V) from iron oxides/iron oxyhydroxides by NOM under acidic to slightly acidic conditions (Redman et al., 2002; Grafe et al., 2001; Bauer and Blodau, 2006; Weng et al., 2006; Weng et al., 2009).

Fulvic and humic acids (FA and HA) are the two main components of dissolved organic matter (Diallo et al., 2005; Weng et al., 2006; Weng et al., 2009). Both FA and HA have different features in terms of particle size, molecular weight, solubility and the charge (Diallo et al., 2005; Weng et al., 2006; Weng et al., 2009). FA are smaller in size and molecular weight and carry lower charge compared to HA (Diallo et al., 2005; Wang and Mulligan, 2006a, Sharma et al., 2011). One of the important distinctions between FA and HA is the difference in solubility, where FA is soluble in a wider pH range (from acidic to alkaline) while HA is only soluble in the alkaline pHs (Diallo et al., 2005; Sharma et al., 2011).
Although, FA are smaller in size, they are stronger competitors for the arsenate adsorbed in goethite than the HA (Weng et al., 2009). Therefore, it can be proposed that FA could play a major role in regulating As mobility, especially in the coastal acid sulfate soils environments where a large proportion of dissolved organic matter (DOM) is comprised of labile organic matter (Sullivan and Bush, 2004; Johnston et al., 2005a). However, the effects of FA on the potential desorption of As adsorbed/coprecipitated to schwertmannite under the conditions relevant to the ASS environments have not been examined previously. Such understanding would provide more insight to the behaviour of schwertmannite in ASS environments.

2.7 Key Knowledge Gaps

Schwertmannite and jarosite contribute significantly to the environmental chemistry of ASS. Their formation and weathering liberate substantial amount of acidity, and as highly reactive iron oxides they are effective scavengers of trace metals. Therefore, their accurate identification and quantification are essential for ASS management. The development of such assessment methods requires a full understanding of their behaviour in natural settings. Summarised below are the key knowledge gaps in ASS research relevant to schwertmannite and jarosite:

- Acid Base Accounting (ABA) is the common approach used to assess the acidity hazard in ASS. RA fraction in the ABA represents the acidity stored in secondary Fe(III) minerals such as schwertmannite, jarosite and other Al hydroxy sulfate minerals. RA fraction is determined as \( S_{NAS} \) and \( S_{RAS} \). Although \( S_{NAS} \) and \( S_{RAS} \) techniques are widely used in routine laboratory analyses, a systematic evaluation of those techniques for the quantification of schwertmannite and jarosite in ASS has not been conducted yet.

- Selectively dissolution with acidified ammonium oxalate (AAO) is generally used in identification and quantification of poorly crystalline mineral such as ferrihydrite and
schwertmannite. Although this technique has been successfully applied in acid mine drainage environments, it has not been evaluated for the identification of schwertmannite in ASS.

- The three-step sequential extraction technique suggested by Li et al. (2007) has successfully recovered jarosite in quartz and laterite nickel tailing samples. In ASS, the environmental conditions are very different to laterite nickel tailings. Thus, a proper assessment of this three-step sequential extraction procedure is required prior to its application on the recovery of jarosite in ASS.

- Much of the current understanding on the behaviour of schwertmannite and jarosite are based on laboratory based experiments. Those studies have demonstrated that the stability of both minerals is strongly governed by physio-chemical factors and by the activity of microorganisms. In CASS landscapes, hydrology and seasonality in weather strongly control the acidity discharge. However, there is a lack of field based studies on understanding the in-situ transformation behaviour of schwertmannite and jarosite in a highly dynamic CASS environment.

- Schwertmannite has a strong affinity towards arsenic. It also known to strongly interact with natural organic matter (NOM). Fulvic acid (FA), being soluble in a wide pH range, is the active component of NOM in ASS environments and is also abundantly found in those landscapes. Therefore, figuring out the impacts of FA on acidity and arsenic mobility in ASS would be highly useful in understanding the behaviour of schwertmannite in ASS landscapes.
Chapter 3: Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$) for the assessment of the acidity liberated from schwertmannite and jarosite
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Sample collection, laboratory analysis and interpretation of data

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Laboratory analysis: Vithana

Interpretation of data: Vithana and Sullivan

Writing the publication

Original draft: Vithana

Proof reading and editing: Sullivan, Bush and Burton

Preparation of computer graphics: Vithana

Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)

See Chapter 9 for references

See Appendix for article published in Soil Research and signed author contribution statements.
3.1 Abstract

In Australia, the assessment of acidity hazard in Acid Sulfate Soils requires the estimation of operationally defined acidity fractions such as Actual Acidity, Potential Sulfidic Acidity and Retained Acidity. Acid Base Accounting approaches in Australia use these acidity fractions to estimate the net acidity of Acid Sulfate Soils materials. Retained Acidity is the acidity stored in the secondary Fe/Al hydroxy sulfate minerals, such as jarosite, natrojarosite, schwertmannite and basaluminite. Retained Acidity is usually measured as either Net Acid Soluble Sulfur (SnAS) or as Residual Acid Soluble Sulfur (SrAS). In the present study, contributions of schwertmannite and jarosite to the Retained Acidity, the Actual Acidity and the Potential Sulfidic Acidity fractions were systematically evaluated using SnAS and SrAS techniques. The data shows that schwertmannite contributed considerably to the Actual Acidity fraction and that it does not contribute solely to the Retained Acidity fraction as has been previously conceptualized. As a consequence, SnAS values greatly underestimated the schwertmannite content. For soil samples in which jarosite is the only mineral present, a better estimate of the added jarosite content can be obtained by using a correction factor of 2 to SnAS values to account for the observed 50-60% recovery. Further work on a broader range of jarosite samples would be needed to determine whether this correction factor has broad applicability. SrAS was unable to reliably quantify either the schwertmannite or jarosite contents and therefore is not suitable for quantification of the Retained Acidity fraction. Potential Sulfidic Acidity in Acid Sulfate Soils is conceptually derived from reduced inorganic sulfur minerals and has been estimated by the peroxide oxidation approach which is used to derive the SrAS values. However, both schwertmannite and jarosite contributed to the peroxide oxidisable sulfur fraction implying a major potential interference by those two minerals to the determination of Potential Sulfidic Acidity in Acid Sulfate Soils through the peroxide oxidation approach.
3.2 Introduction

Over 500,000 km$^2$ of Acid Sulfate Soils (ASS) are found globally, mainly in highly populated coastal plains (Sullivan et al., 2012). In Australia, nearly 215,000 km$^2$ of land are affected by ASS, of which 58,000 km$^2$ are located in coastal areas (Fitzpatrick et al., 2008, 2010).

From a mineralogical perspective, ASS are soils that contain reduced inorganic sulfur (RIS) minerals such as pyrite (Bush and Sullivan, 1999; Ahern et al., 2004), and/or poorly soluble iron sulfide oxidation products, such as Fe/Al hydroxy sulfate minerals (e.g. jarosite-KFe$_3$(OH)$_6$(SO$_4$)$_2$ schwertmannite-Fe$_{16}$O$_{16}$(OH)$_{10}$(SO$_4$)$_3$, and basaluminite-Al$_4$(OH)$_{10}$SO$_4$). In addition, soils with appreciable contents of iron monosulfides (Bush et al., 2004c) and elemental sulfur (Burton et al., 2006b) are also regarded as ASS materials (Ahern et al., 2004). However, according to Pons (1973) and Fanning (2002), a generalized definition for ASS would be: soils in which sulfuric acid may be produced, is being produced, or has been produced in amounts that have a lasting effect on the main soil characteristics.

There are a number of technical terms used in describing the acidity and sulfur fractions present in ASS and in various techniques used in laboratories. For convenience, a list of those acronyms and their definitions are presented in Table 3.1.
### Chapter 3: Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$) for the assessment of the acidity liberated from schwertmannite and jarosite

Table 3.1. Acronyms used in the text and their descriptions

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASS</td>
<td>Acid Sulfate Soils—Soil materials containing reduced inorganic sulfur and/or oxidised products of iron sulfides such as secondary Fe/Al hydroxy sulfate minerals (e.g. schwertmannite, jarosite, basaluminite).</td>
</tr>
<tr>
<td>RIS</td>
<td>Reduced Inorganic Sulfur</td>
</tr>
<tr>
<td>EA</td>
<td>Existing Acidity—Comprised of Actual Acidity and Retained Acidity</td>
</tr>
<tr>
<td>AA</td>
<td>Actual Acidity—This is the soluble and exchangeable acidity in soils which is readily available. This acidity is measured as TAA by titrating 1 M KCl extract of soil with dilute NaOH.</td>
</tr>
<tr>
<td>RA</td>
<td>Retained Acidity—Acidity stored in poorly soluble secondary Fe/Al hydroxy sulfate minerals such as schwertmannite, jarosite and basaluminite. This acidity is not considered to be readily available but considered to release slowly by the hydrolysis of those minerals.</td>
</tr>
<tr>
<td>PSA</td>
<td>Potential Sulfidic Acidity—Acidity that can be generated by the oxidation of Reduced Inorganic Sulfur.</td>
</tr>
<tr>
<td>ABA</td>
<td>Acid Base Accounting—Used to derive the Net Acidity of a soil material. In this approach the different operationally defined acidity fractions such as Actual Acidity, Retained Acidity, Potential Sulfidic Acidity, as well as the Acid Neutralization Capacity (in Equations (3.1) and (3.2) are used to determine the Net Acidity of that soil material.</td>
</tr>
<tr>
<td>$S_{NAS}$</td>
<td>Net Acid Soluble Sulfur—Determined by subtracting $S_{KCl}$ from $S_{HCl}$. It is considered an estimate of the amount of sulfur originated from the poorly soluble secondary Fe/Al hydroxy sulfate minerals and used to quantify the Retained Acidity.</td>
</tr>
<tr>
<td>$S_{KCl}$</td>
<td>1 M KCl extractable sulfur fraction—This is the sulfur in the soluble and exchangeable sulfate and sulfate from soluble sulfate salts such as gypsum.</td>
</tr>
<tr>
<td>$S_{HCl}$</td>
<td>4 M HCl extractable sulfur fraction—This is the sulfate in a 4 M HCl digest and is comprised of the soluble and exchangeable sulfate, sulfate from soluble sulfate salts such as gypsum as well as sulfate liberated from the poorly soluble secondary Fe/Al hydroxy sulfate minerals.</td>
</tr>
<tr>
<td>TAA</td>
<td>Titratable Actual Acidity—Readily available acidity measured by titrating the 1 M KCl soil suspension with dilute NaOH.</td>
</tr>
<tr>
<td>$S_{RAS}$</td>
<td>Residual Acid Soluble Sulfur—The sulfur fraction determined on the residue after the peroxide oxidation. This is considered to be mainly sulfate contained within the poorly soluble secondary Fe/Al hydroxy sulfate minerals, and is used to estimate Retained Acidity.</td>
</tr>
<tr>
<td>$pH_{ox}$</td>
<td>pH of peroxide digested extract after the peroxide oxidation</td>
</tr>
<tr>
<td>TPA</td>
<td>Titratable Peroxide Acidity—An alternative measure of Net Acidity, which is determined after the peroxide oxidation by titrating the digest with dilute NaOH.</td>
</tr>
<tr>
<td>$S_p$</td>
<td>Peroxide Sulfur—Sulfur fraction measured in the peroxide oxidation digest. Considered to be derived from soluble sulfate, exchangeable sulfate, sulfate from soluble minerals such as gypsum, sulfate formed after the oxidation of reduced inorganic sulfur and sulfate released from organic matter during peroxide oxidation.</td>
</tr>
<tr>
<td>$S_{POS}$</td>
<td>Peroxide Oxidisable Sulfur—This is considered to be the sulfate produced from the oxidation of reduced inorganic sulfur during the peroxide oxidation. It is calculated by subtracting the $S_{KCl}$ from $S_p$.</td>
</tr>
</tbody>
</table>
3.2.1 Review of previous work on the Acid Base Accounting approach and on the estimation of Retained Acidity

Acid Base Accounting (ABA) is a commonly used approach to estimate the net acidity generation in mining impacted areas (Jennings and Dollhopf, 1995; Skousen et al., 2002; Schumann et al., 2012). In this particular approach, net acidity generation is calculated by offsetting the Potential Acidity (mainly arising from oxidation of sulfidic materials) by the Neutralization Potential (mainly arising due to dissolution of carbonates) (Jennings and Dollhopf, 1995; Skousen et al., 2002; Schumann et al., 2012).

In 2004, Ahern et al. introduced a modified ABA approach for the assessment of net acidity generation in ASS in Australia (Equation 3.1). In this modified ABA approach, a separate estimation of the acidity contained within poorly soluble Fe/Al hydroxy sulfate minerals, termed Retained Acidity was introduced (Equation 3.2) (Ahern et al., 2004). This modified ABA is one of the most commonly used approaches for assessing the net acidity pool of ASS in Australia (Sullivan et al., 2012).

\[
\text{Net Acidity} = \text{Potential Sulfidic Acidity (PSA)} + \text{Existing Acidity (EA)} - \text{Acid Neutralisation Capacity (ANC)} \tag{3.1}
\]

\[
\text{Existing Acidity (EA)} = \text{Actual Acidity (AA)} + \text{Retained Acidity (RA)} \tag{3.2}
\]

In this modified ABA approach, the capacity of a soil material to generate acidity is comprised of two components:

i. Potential Sulfidic Acidity (PSA)-acidity that can arise from the complete oxidation of RIS minerals.

ii. Existing Acidity (EA)-acidity present in soil at present as:

   a) Actual Acidity (AA)-arising from soluble and exchangeable acidity and
Chapter 3: Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$) for the assessment of the acidity liberated from schwertmannite and jarosite

b) Retained Acidity (RA)-which is conceptualised as the acidity retained in poorly soluble Fe/Al hydroxy sulfate minerals.

PSA is a potential source of acidity which is present in latent form in soils containing RIS. However, when RIS is exposed to air due to various activities such as drainage and excavations, they can oxidise and produce acidity (Equation 3.3) (Dent and Pons, 1995; Ahern et al., 2004; Fanning et al., 2004), as evident for example in pyrite oxidation:

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$  \hspace{1cm} (3.3)

Poorly crystalline secondary Fe/Al hydroxy sulfate minerals such as jarosite, schwertmannite and basaluminite are found in ASS due the favourable conditions in those environments for their precipitation (McElnea et al., 2002b). According to Bigham et al. (1992), schwertmannite is the most common Fe mineral to precipitate directly from acid sulfate waters. These minerals are grouped together in a separate acidity pool called RA and are considered to constitute a store of non-sulfidic latent acidity with the potential for the liberation of acidity (Ahern et al., 2004). Both schwertmannite and jarosite that contribute to RA, exist in highly acidic ASS materials (i.e. pH < 4 as defined for sulfuric materials in accordance with Isbell (2002), and continue to release acidity as they are weathered by hydrolysis (Equation 3.4 and 3.5) (Peine et al., 2000; Burton et al. 2007). Another RA mineral, basaluminite, precipitates at pH values around 5. Basaluminite, schwertmannite and jarosite release acidity as pH rises (Equation 3.6) (Bigham and Nordstrom, 2000; Ahern et al., 2004).

$$KFe_3(OH)_6(SO_4)_2 + 3H_2O \rightarrow 3Fe(OH)_3 + 2SO_4^{2-} + 3H^+ + K^+$$  \hspace{1cm} (3.4)

$$Fe_8O_6(OH)_{8-2y}(SO_4)_y + 2yH_2O \rightarrow 8FeOOH + ySO_4^{2-} + 2yH^+$$  \hspace{1cm} (3.5)

$$Al_4(OH)_{10}SO_4 + 2H_2O \rightarrow 4Al(OH)_3 + SO_4^{2-} + 2H^+$$  \hspace{1cm} (3.6)
Hydrolysis of RA minerals is generally thought to be a slow process under low pH conditions, and the acidity from this fraction is thus considered to be released slowly (Ahern et al., 2004). In contrast, AA is readily released, for example after a rainfall event or due to a flood event (i.e. after removal of blocking banks) (Ahern et al., 2004).

McElnea et al. (2002a,b) demonstrated that neither the acidity nor the sulfate in jarosite was recovered reliably using the standard methods to determine the AA and PSA. They concluded that 1 M KCl, a standard extractant which is used to extract the soluble and exchangeable acidity in soil, was unable to extract the acidity and sulfate in jarosite. Similarly, the peroxide oxidation method, which determines the PSA using the RIS content, was also unable to recover acidity and sulfate from jarosite.

However, McElnea et al. (2002b) reported that synthetic basaluminite released ~ 60% of acidity during 1 M KCl extraction, in contrast to previously held views which reported that 1 M KCl was unable to remove the acidity held in such minerals (Lin et al., 2000).

According to McElnea et al. (2002b), jarosite dissolves in 4 M HCl. Hence, they introduced a separate extraction step with 4 M HCl which would enable the dissolution of jarosite and other relatively insoluble Fe/Al hydroxy sulfate minerals and in turn enable the determination of the RA fraction using the quantity of liberated sulfate. As such, the data of McElnea et al. (2002a,b), were used to derive a new set of guidelines for the assessment of net acidity of ASS (Ahern et al., 2004). These guidelines included the determination of the RA fraction in ASS. However, neither McElnea et al. (2002a,b) nor Ahern et al. (2004) examined the acidity stored in schwertmannite. They assumed that the acidity stored in schwertmannite and most of the Al hydroxy sulfate minerals can be estimated using the method developed for jarosite as described in the ASS laboratory methods guidelines (Ahern et al., 2004).

The RA fraction in ASS is determined by measuring either the net acid soluble sulfur (S_{NAS}) or the residual acid soluble sulfur (S_{RAS}) (Ahern et al., 2004). These two S fractions are determined from an
additional extraction step with 4 M HCl after the standard AA (1 M KCl extraction) or PSA (peroxide oxidation) procedures (Ahern et al., 2004). AA is measured as the titratable actual acidity (TAA) by titrating a 1 M KCl soil suspension (1:40) to pH 6.5. $S_{NAS}$ is determined by subtracting 1 M KCl-extractable sulfur ($S_{KCl}$) from 4 M HCl extractable sulfur ($S_{HCl}$) which was determined by extracting a fresh sample with 4 M HCl. The basic assumption underlying the assessment of $S_{NAS}$ is that both schwertmannite, jarosite, and some Al hydroxy sulfate minerals (except basaluminite) are insoluble in 1 M KCl but completely soluble in 4 M HCl (McElnea et al., 2002a,b; Ahern et al., 2004). $S_{RAS}$ is determined by extracting the residue of the soil sample with 4 M HCl left after the peroxide oxidation which is conducted for the determination of PSA (Ahern et al., 2004). In the $S_{RAS}$ method, it is assumed that schwertmannite, jarosite and other Al hydroxy sulfate minerals are insoluble in peroxide but completely soluble in 4 M HCl (McElnea et al., 2002a,b; Ahern et al., 2004). RA is calculated based on the assumption that the $S_{NAS}$ and $S_{RAS}$ are derived from jarosite, schwertmannite and other Al hydroxy sulfate minerals (McElnea et al. 2002a,b; Ahern et al., 2004). Accordingly, it is assumed that 1 mole of $S_{NAS}$ or $S_{RAS}$ in jarosite, schwertmannite and basaluminite releases 3, 2 and 2 moles of acidity, respectively (Equations 3.4, 3.5 and 3.6) (Ahern et al., 2004).

In the $S_{RAS}$ determination, acidity generated after peroxide oxidation can be determined by titrating the soil suspension to pH 6.5 and is termed titratable peroxide acidity (TPA). TPA has been used as an alternative measure of net acidity for ASS materials (Ahern et al., 2004). Sulfate contained in the peroxide digest of the sample is assumed to have been derived from the soluble and adsorbed sulfate, or from RIS converted to sulfate, or from any organic sulfur released during the oxidation and is termed as peroxide sulfur ($S_P$) (McElnea et al., 2002a; Ahern et al., 2004). The RIS content of the peroxide digested sample is determined as peroxide oxidisable sulfur ($S_{POS}$) by subtracting the $S_{KCl}$ fraction (i.e. the measure of the soluble and exchangeable sulfate) from $S_P$. $S_{POS}$ determined in such a way can be used to calculate the PSA in soils containing minor concentrations of organic matter (McElnea et al., 2002a; Ahern et al., 2004).
Recent advances in ABA for ASS and sediments have involved improvements for estimating the PSA (Sullivan et al., 2000; Burton et al., 2008c) and the AA (McElnea et al., 2002b). However, RA that is generated by the hydrolysis of relatively insoluble Fe/Al hydroxy sulfate minerals (e.g. jarosite, natrojarosite, schwertmannite, basaluminite) can be a significant source of acidity in these soil materials (McElnea et al., 2004). Despite this, few investigations have been conducted on the evaluation of RA generation by jarosite and schwertmannite and their contribution to the AA and PSA fractions. Therefore, the purpose of this study was to evaluate the efficacy of the main laboratory techniques (SnAS and SrAS methods) to quantify the RA produced by the two most common Fe hydroxy sulfate minerals occurring in ASS (i.e schwertmannite and jarosite) (Sullivan et al., 2012), and to assess the contribution of those two minerals towards AA and PSA by spiking soil samples with both natural and synthetic samples of schwertmannite and jarosite.

3.3 Materials and Methods

3.3.1 Sampling

Soil samples were collected from two regions, known from previous studies to not contain sulfuric soil materials (Isbell, 2002), in north-eastern NSW (Tuckean Swamp on the Richmond River catchment (28°58’ 38” S, 153°24′ 15” E) and Shark Creek on the Clarence River catchment (29°31′ 52” S, 153°12′ 35” E). Both these sites have been classified as Sulfidic Oxyaquic Hydrosols (confidence level 2) (Isbell, 2002). The characteristics of the soil materials collected from both sites are shown in Table 3.2. Samples were collected from the 0-30 cm surficial layer and placed into sealed plastic bags. Within 24 h of sampling, the two soil samples were dried in a fan-forced oven at 80°C. Drying was continued for two weeks until a constant weight was reached. Dried soil samples were sieved (< 2 mm) and then ground using a Ring Mill (Rock Labs, New Zealand). A quartz fine sand sample was also used as a soil reference material.
Chapter 3: Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$) for the assessment of the acidity liberated from schwertmannite and jarosite

Table 3.2. Characteristics of soils collected from two sites

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Colour</th>
<th>Texture</th>
<th>pH$_{1:5}$</th>
<th>EC$_{1:5}$ (µS cm$^{-1}$)</th>
<th>TOC</th>
<th>Fe</th>
<th>S</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tuckean Swamp</td>
<td>Dark grey</td>
<td>Peaty clay loam</td>
<td>4.3</td>
<td>298</td>
<td>4.65</td>
<td>2.95</td>
<td>0.06</td>
<td>4.96</td>
</tr>
<tr>
<td>Shark Creek</td>
<td>Brown</td>
<td>Silty clay</td>
<td>4.6</td>
<td>138</td>
<td>1.78</td>
<td>6.27</td>
<td>0.03</td>
<td>3.07</td>
</tr>
</tbody>
</table>

3.3.2 Synthesis of schwertmannite and jarosite

Schwertmannite and jarosite were freshly synthesized following the method of Regenspurg et al. (2004) and Baron and Palmer (1996), respectively.

3.3.3 Natural schwertmannite and natural jarosite rich soil materials

Schwertmannite rich soil materials were collected as grab samples from Fe-rich O horizon of a coastal lowland acid sulfate soil (CLASS) in eastern Australia (29°26’29”S, 153°14’12” E) as described in Burton et al. (2007). Schwertmannite occurred as coatings upto 2 mm in thickness around undecomposed vegetative material (Burton et al., 2007). Jarosite rich soil materials were collected as grab samples from East Trinity sites (145°48’9” E, 16°56’33”S) described in Johnston et al. (2011a). Jarositic segregations occurred in the sulfuric horizon as channel and chamber infillings (Johnston et al., 2011a). Hereafter the soil materials rich in schwertmannite and jarosite are termed as natural schwertmannite and natural jarosite respectively.

3.3.4 Preparation of samples for the analysis of Net acid soluble sulfur ($S_{NAS}$) and Residual acid soluble sulfur ($S_{RAS}$) methods

For all analyses, a constant sample weight of 0.5 g was used, with a sample: reagent ratio of 1:40. The soil material and quartz samples were spiked with 0.5%, 1%, 2% and 5% of synthetic schwertmannite/jarosite and the total weight of each sample was maintained at 0.5 g by adding an
appropriate amount of soil or quartz sand. The samples were thoroughly mixed and were analysed within 1 h for \( S_{\text{NAS}} \) and \( S_{\text{RAS}} \). For each analysis, blank samples containing unadulterated soils and quartz sand were also analysed and the results were corrected using results obtained for these blank samples. In order to determine any mineral and compositional changes that can occur during the 1 M KCl extraction and the peroxide oxidation, pure samples of schwertmannite and jarosite (both natural and synthetic) were also subjected to the \( S_{\text{NAS}} \) and \( S_{\text{RAS}} \) analyses similar to the manner for the treated samples. Each treated sample was analysed in triplicate and the experiment was repeated for 0.5%, 1%, 2% and 5% of natural schwertmannite/jarosite. All reagents were prepared from analytical grade chemicals and using MilliQ deionised water. All the glassware used were acid washed by soaking in 5% HNO\(_3\) for 24 h. pH measurements were made using a pre-calibrated pH meter (WP-81pH meter, TPS). A detailed description of the procedure followed for the determination of \( S_{\text{NAS}} \) and \( S_{\text{RAS}} \) is given in the ASS laboratory methods guidelines of Ahern et al. (2004).

### 3.3.5 Characterization of the synthetic and natural minerals

The chemical composition of the synthetic and natural schwertmannite and jarosite samples was determined after aqua-regia digestion (microwave digestion) (APHA, 2005) followed by inductive coupled plasma-mass spectrometry (ICP-MS) analysis.

The synthetic and natural schwertmannite and jarosite samples were dried at 60°C for 24 h and were examined before and after analysis by XRD to identify the minerals present and remaining. For XRD analysis, the samples were hand ground (< 63 µm) using a porcelain mortar and pestle. Ground powdered samples were homogenised and analysed using a Bruker D4 Diffractometer using Co K\(\alpha\) radiation (Bruker AXS GmbH, Germany). The diffraction patterns were recorded from 5 to 80°2\(\theta\) in steps of 0.05° 2\(\theta\) step size with 2 seconds counting time per step. The XRD patterns were evaluated using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Germany).
The morphology and elemental/atomic composition of synthetic/natural minerals were also examined before and after analysis by using scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX). Samples were mounted on aluminium stubs and coated with carbon followed by gold. SEM images of the samples were taken using a SEM (Stereoscan 440; Leica Cambridge Ltd, UK), (Working Distance (WD)=7 mm, Probe=30 pA, Electron High Tension (EHT)=10 kV). The elemental/atomic composition of the selected areas of the sample surfaces was determined using an ISIS energy dispersive X-ray EDX microanalysis system (EDX; Oxford Link, Pentafet Detector with Beryllium window, PB Quant Software, Oxford Instruments, Buckinghamshire, UK) EDS detector, PBQuant Software, (WD=25 mm, Probe=350 pA, EHT=20 kV), utilising a Peak-to-Background method (Sullivan and Bush, 1997).

3.3.6 Composition of synthetic and natural schwertmannite and jarosite

The weight percentages (Fe, S, K, and Al) determined through the chemical analysis and SEM-EDX and the Fe:S and K:Fe:S ratios of schwertmannite and jarosite respectively are presented in Table 3.3.

The calculated Fe:S molar ratio of synthetic schwertmannite (~ 4) was within the typical range (4-8) reported in the literature (Bigham et al., 1990, 1994, 1996a; Kim and Kim, 2003). The lower Fe:S ratio observed in synthetic schwertmannite samples was likely due to the greater adsorption of sulfate on the surface during the fast oxidative synthesis process (Kim and Kim, 2003).

The synthetic jarosite (K:Fe:S of 1:2.2:2.1 to 1:2.8:2.7) in the present study had lower Fe content, and higher S content than the ‘ideal’ ratio of 1:3:2 (Baron and Palmer, 1996). However, both the Fe and S contents (relative to K) were much higher in the natural jarosite sample (1:7.8:5.2 to 1:5.5:4) compared to those reported elsewhere (e.g. Baron and Palmer, 1996). The higher Fe:S for natural jarosite samples could be due to other cations (e.g. Na) replacing K and/or other Fe and S containing minerals admixed with the natural jarosite.
Chapter 3: Evaluation of two routine techniques (S\textsubscript{NAS} and S\textsubscript{RAS}) for the assessment of the acidity liberated from schwertmannite and jarosite

Table 3.3. Weight percentages of the elements and Fe:S/K:Fe:S ratios of synthetic/natural schwertmannite/jarosite determined from aqua-regia digestion method and SEM-EDXA

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Fe weight (%)</th>
<th>S weight (%)</th>
<th>K weight (%)</th>
<th>Al weight (%)</th>
<th>Fe: S molar ratio</th>
<th>K:Fe:S molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic schwertmannite</td>
<td>43.7</td>
<td>68.78</td>
<td>5.94</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aqua-Regia</td>
<td>5.94</td>
<td>10.38</td>
<td>-</td>
<td>-</td>
<td>1:4.8</td>
<td>1:3:7</td>
</tr>
<tr>
<td>SEM-EDXA</td>
<td>1:7.4</td>
<td>1:7:7</td>
<td>-</td>
<td>-</td>
<td>1:2.2:2.1</td>
<td>1:2.8:2.7</td>
</tr>
<tr>
<td>Natural schwertmannite</td>
<td>18</td>
<td>63.02</td>
<td>1.53</td>
<td>4.38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Synthetic jarosite</td>
<td>27.3</td>
<td>41.62</td>
<td>14.75</td>
<td>22.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aqua-Regia</td>
<td>8.59</td>
<td>10.11</td>
<td>-</td>
<td>-</td>
<td>1:7.8:5.2</td>
<td>1:5.5:4.0</td>
</tr>
<tr>
<td>SEM-EDXA</td>
<td>1:2.2:2.1</td>
<td>1:2.8:2.7</td>
<td>-</td>
<td>-</td>
<td>1:7.8:5.2</td>
<td>1:5.5:4.0</td>
</tr>
<tr>
<td>Natural jarosite</td>
<td>23.6</td>
<td>43.89</td>
<td>9.07</td>
<td>18.36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aqua-Regia</td>
<td>2.12</td>
<td>6.19</td>
<td>0.85</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SEM-EDXA</td>
<td>1:7.8:5.2</td>
<td>1:5.5:4.0</td>
<td>-</td>
<td>-</td>
<td>1:7.8:5.2</td>
<td>1:5.5:4.0</td>
</tr>
</tbody>
</table>
3.4 Results and Discussion

3.4.1 Net acid soluble sulfur (S\textsubscript{NAS})

3.4.1.1 Contribution to Actual Acidity from synthetic and natural schwertmannite

TAA measures soluble and exchangeable acidity and is termed AA in the ABA approach. Both the synthetic and natural schwertmannite examined in this study exhibited appreciable TAA especially at contents above 1% (Fig. 3.1a, b). Hence, it is clear that the AA determined in oxidised ASS could also be attributable to the acidity produced by schwertmannite. The theoretical actual acidity was calculated assuming the complete conversion of schwertmannite to goethite (Equation 3.5). This acidity generation by schwertmannite was accompanied by the release of sulfate. Sulfate release was clearly indicated as an increase in Fe:S molar ratios from 3.8 to 7.0, and 7.7 to 17.8 of pure synthetic and natural schwertmannite samples respectively after the 1M KCl extraction.

The hydrolysis and dissolution of schwertmannite is accompanied by sulfate release (Jönsson et al., 2005; Kumpulainen et al., 2008a; Paikaray and Peiffer, 2010, 2012). Jönsson et al. (2005) reported ~30% of schwertmannite-S is bound to the surface of the mineral as sulfate and this adsorbed sulfate can be released or exchanged with OH\textsuperscript{-} at higher pHS (i.e. > 6.5). Kumpulainen et al. (2008a) suggested that the release of sulfate is associated with the release of acidity as shown in equation 3.7. The presence of two types of sulfate complexes forming inner-sphere and outer-sphere complexes in schwertmannite was recently proposed by Fernandez-Martinez. (2010). According to their study, sulfate in outer-sphere complexes are less energetically stable and therefore can be easily released or exchanged. Therefore, the observed acidity generation and the release of sulfate from schwertmannite in the present study could have originated due to the exchange of protons and sulfate adsorbed to the surface of schwertmannite.

\[
\equiv FeOH^+SO_4^{2−} + H_2O \rightarrow \equiv FeOOH + SO_4^{2−} + 2H^+ \quad (3.7)
\]
Adsorbed sulfate on schwertmannite has likely been exchanged with Cl\textsuperscript{-} in 1 M KCl and/or OH\textsuperscript{-} in the NaOH during the titration. Evidence for this are the XRD diffractograms of synthetic and natural schwertmannite which show no apparent change after the 1 M KCl extraction and TAA titration (section 3.4.1.5 and Fig. 3.3a, b, d and e).

Fig. 3.1. TAA generated as a percentage of theoretical actual acidity contained within the added a) synthetic schwertmannite b) natural schwertmannite c) synthetic jarosite d) natural jarosite
3.4.1.2 Contribution to Retained Acidity by synthetic and natural schwertmannite

The RA determined for two synthetic and natural schwertmannite samples tested here in terms of the $S_{NAS}$ was greatly underestimated (Fig. 3.2a, b). The underestimation of $S_{NAS}$ content could be due to 2 factors: 1) removal of the surface adsorbed sulfate from schwertmannite into the $S_{KCl}$ fraction, or/and, 2) retention of sulfate liberated from schwertmannite during the 4 M HCl extraction by soil.

Ahern et al. (2004) assumed that schwertmannite is not soluble in 1 M KCl. However, the synthetic and natural samples used in this study clearly demonstrated that considerable amount of sulfate and acidity from schwertmannite were extracted by 1 M KCl. As a consequence of the release of sulfate during the 1 M KCl extraction (i.e. $S_{KCl}$), $S_{NAS}$ values (i.e. $S_{HCl} - S_{KCl}$) substantially underestimated the quantity of schwertmannite present in the soil samples.

The solubility of pure synthetic schwertmannite (i.e. not mixed with soil/quartz) in 4 M HCl was found to be ~ 100%. However, when synthetic schwertmannite was mixed with soil, the 4 M HCl extracted S weight percentages (i.e. $S_{HCl}$) were only ~ 65% indicating retention of some of the released sulfate by the soil matrices. Both of these factors resulted in an inconsistent relationship of $S_{NAS}$ to the added schwertmannite content and even resulted in negative $S_{NAS}$ values (Fig. 3.2a, b).
Chapter 3: Evaluation of two routine techniques (S_{NAS} and S_{RAS}) for the assessment of the acidity liberated from schwertmannite and jarosite

Fig. 3.2. Percentage of S_{NAS} recovered with respect to added a) synthetic schwertmannite b) natural schwertmannite c) synthetic jarosite d) natural jarosite
3.4.1.3 Contribution to Actual Acidity by synthetic and natural jarosite

The TAA data confirmed that both synthetic and natural jarosite tested in this study did not generally contain acidity that could be liberated in 1 M KCl, eventhough two of the samples with very low jarosite contents showed TAAs greater than 20% of the theoretical actual acidity. Hence, jarosite can be considered to have contributed only marginally to the measured AA (Fig. 3.1c, d). Additional evidence for jarosite stability during the 1 M KCl extraction can be drawn from Fe:S ratios determined for the residue of jarosite samples after the TAA titration. The Fe:S ratios of the pure synthetic and natural jarosite samples (i.e. not mixed with soil/quartz) remained relatively constant being 1.07 before and 1.08 after titration, and 1.37 before and 1.36 after titration, respectively.

3.4.1.4 Contribution to Retained Acidity by synthetic and natural jarosite

Unlike schwertmannite, the $S_{NAS}$ calculated for jarosite accounted for ~50% of the added natural jarosite recovery and slightly more for the recovery of the synthetic jarosite (Fig. 3.2c, d). The observed ~ 50% $S_{NAS}$ recovery of jarosite could be due to retention of some sulfate released during the 4 M HCl extraction by soil matrices as was experienced for the sulfate released by schwertmannite. The retention of sulfate by soil matrices is indicated by comparing the efficiency of the 4 M HCl extraction for pure mineral samples and those for the mineral/soil mixtures. While ~85% of the sulfur was recovered when pure synthetic jarosite was extracted with 4 M HCl, only ~60% was recovered from the mineral/soil mixtures. For the soil materials used in this study, in which jarosite is the only sulfur containing mineral present, the application of a correction factor of 2 to $S_{NAS}$ values would provide a more accurate estimate of the jarosite content and hence the RA. However, this correction factor could vary depending on the nature of the soil itself and the type and amount of other minerals present in the soil.
3.4.1.5 Effect of the 1 M KCl extraction and the TAA determination on schwertmannite and jarosite

The XRD patterns of both synthetic and natural schwertmannite after the 1 M KCl extraction and the TAA titration were identical to that of the corresponding untreated samples (Fig. 3.3a, b, d and e). SEM analysis (data not shown) also indicates that minimal submicromorphological change has occurred. These data suggest that the release of sulfate during the 1 M KCl extraction and NaOH titration from both synthetic and natural schwertmannite was from surface-bound sulfate rather than structurally held sulfate.

The XRD and SEM data of both synthetic and natural jarosite after the TAA analysis were almost the same as that of the corresponding untreated jarosite samples (data not shown here).
Chapter 3: Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$) for the assessment of the acidity liberated from schwertmannite and jarosite

Fig. 3.3. XRD pattern a) Untreated synthetic schwertmannite b) synthetic schwertmannite after 1 M KCl extraction and TAA titration c) synthetic schwertmannite after peroxide oxidation and TPA titration d) untreated natural schwertmannite e) natural schwertmannite after 1 M KCl extraction and TAA titration f) natural schwertmannite after peroxide oxidation and TPA titration. Where G=goethite
3.4.2 Residual acid soluble sulfur (S\textsubscript{RAS})

3.4.2.1 Contribution to the Potential Sulfidic Acidity by synthetic and natural schwertmannite

Synthetic and natural schwertmannite tested in this study released acidity during peroxide oxidation and was measured as TPA. However, the amount of acidity generated was minor and only noticeable in the quartz sample (Fig. 3.4a, b). This acidity most likely originated from the exchange of protons on the surface of schwertmannite. Interestingly, the acidity released during the peroxide oxidation was accompanied by the release of sulfate from schwertmannite, again most likely to be from sulfate adsorbed to the surface of schwertmannite. The release of sulfate was further confirmed by the Fe:S molar ratios of pure synthetic and natural schwertmannite before and after the peroxide oxidation, which showed an increase from 3.8 to 9.2, and 7.7 to 28.8, respectively after peroxide oxidation.
Chapter 3: Evaluation of two routine techniques (S\textsubscript{NAS} and S\textsubscript{RAS}) for the assessment of the acidity liberated from schwertmannite and jarosite

![Graphs showing pH changes](image)

Fig. 3.4. Change in pH of a peroxide-digested extract after peroxide oxidation (pH\textsubscript{ox}) in relation to added a) synthetic schwertmannite b) natural schwertmannite c) synthetic jarosite d), and natural jarosite

According to Ahern et al. (2004) and McElnea et al. (2002a), the peroxide oxidised extract is a mixture of soluble and exchangeable sulfate, sulfide converted to sulfate, and organic sulfur (which together are termed S\textsubscript{P}). Therefore, the liberation of sulfate by synthetic and natural schwertmannite samples which was observed in the present study (i.e. in terms of either surface adsorbed or as
structural sulfate) during peroxide oxidation is an important finding for the PSA determination. PSA is estimated from peroxide oxidisable sulfur ($S_{POS}$) (i.e. $S_P$-$S_{KCl}$) and generally represents the acidity that can be potentially liberated by the oxidation of RIS (Ahern et al., 2004), whereas $S_{POS}$ is a measure of RIS. According to our study, the data shows that the $S_{POS}$ determination (and hence the estimation of PSA) can be interfered by the presence of schwertmannite (Table 3.4). Given that the RIS action criteria for ASS are as low as 0.03 %S, soil materials containing schwertmannite could be misinterpreted as soils containing RIS when $S_{POS}$ is used to measure the RIS. Such interferences are important as misinterpretation of the nature of the acidity fractions in ASS can lead to the application of inappropriate management techniques.

Table 3.4: $S_{POS}$ (%) measured in soils and quartz samples spiked with synthetic and natural schwertmannite

<table>
<thead>
<tr>
<th>Added (%)</th>
<th>Synthetic Schwertmannite</th>
<th>Natural Schwertmannite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Richmond (%)</td>
<td>Clarence (%)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.045</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>0.065</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0.125</td>
<td>0.000</td>
</tr>
<tr>
<td>5</td>
<td>0.115</td>
<td>0.000</td>
</tr>
</tbody>
</table>

3.4.2 2 Contribution to Retained Acidity by synthetic and natural schwertmannite

Approximately 10-40% of S was recovered as $S_{RAS}$ from synthetic schwertmannite while it was essentially zero for natural schwertmannite (Fig. 3.5a, b). This observed lower $S_{RAS}$ recovery for both synthetic and natural schwertmannite examined in the present study is again likely to be due to a) the partial release of sulfate during peroxide oxidation and b) the retention of some sulfate released during 4 M HCl extraction by soil matrices. The differences observed in the $S_{RAS}$ recovery between synthetic and natural schwertmannite samples tested in this study could be attributable to differences in their composition or solubility.
Chapter 3: Evaluation of two routine techniques (S\textsubscript{NAS} and S\textsubscript{RAS}) for the assessment of the acidity liberated from schwertmannite and jarosite

Fig. 3.5. Percentage of S\textsubscript{RAS} recovered in added a) synthetic schwertmannite b) natural schwertmannite c) synthetic jarosite d) natural jarosite
3.4.2.3 Contribution to the Potential Sulfidic Acidity by synthetic and natural jarosite

Both the synthetic and natural jarosite tested in this study showed a release of some acidity during peroxide oxidation. Similar to schwertmannite, this acidity generation was only noticed in the jarosite/quartz mixtures (Fig. 3.4c, d). Sulfate was released from both synthetic and natural jarosite during peroxide oxidation which was shown as an increase in Fe:S from 1.06 to 1.46, and from 1.37 to 1.52, respectively.

The sulfate released from jarosite to the peroxide extract was measured as $S_P$ and subsequently used to calculate the $S_{POS}$ (%), similar to the manner described for schwertmannite in section 3.4.2.1 (Table 3.5). Most of the $S_{POS}$ determined by both synthetic and natural jarosite in this study was above the action criteria (0.03%$S$). As discussed for schwertmannite, the RIS action criteria for ASS starts at 0.03%$S$. These preliminary results indicate that soil materials containing jarosite could interfere with the determination of RIS using peroxide oxidation, as a result may be misinterpreted as soils containing RIS.

Table 3.5: $S_{POS}$ (%) measured in soils and quartz samples spiked with synthetic and natural jarosite

<table>
<thead>
<tr>
<th>Added (%)</th>
<th>Synthetic Jarosite</th>
<th>Natural Jarosite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Richmond (%)</td>
<td>Clarence (%)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.003</td>
<td>0.036</td>
</tr>
<tr>
<td>1</td>
<td>0.002</td>
<td>0.096</td>
</tr>
<tr>
<td>2</td>
<td>0.000</td>
<td>0.124</td>
</tr>
<tr>
<td>5</td>
<td>0.039</td>
<td>0.150</td>
</tr>
</tbody>
</table>

3.4.2.4 Contribution to Retained Acidity by synthetic and natural jarosite

$S_{RAS}$ determined was greatly underestimated with a maximum of 50% of $S_{RAS}$ being recovered from synthetic and natural jarosite used in the present study (Fig. 3.5c, d). The possible reasons for the observed lower $S_{RAS}$ recovery for jarosite tested here include: a) the release of sulfate from jarosite...
during peroxide oxidation ($S_{POS}$), and b) the retention of the sulfate released during the 4 M HCl extraction by soil matrices. The differences observed in $S_{RAS}$ of synthetic and natural jarosite containing soil/quartz mixtures could be due to the difference in their composition or solubility (Table 3.3). Although some of this “underestimated jarosite content” was accounted for in $S_{POS}$, which in turn was accounted for in the PSA in the ABA, this data indicates that $S_{RAS}$ is a poor measure of jarosite in soil materials.

3.4.2.5 Effect of the peroxide oxidation and the TPA determination on schwertmannite and jarosite

The XRD data shows that the peroxide digestion procedure resulted in the formation of small but detectable amounts of goethite in both the synthetic and natural schwertmannite samples investigated in this study (Fig. 3.3a, c, d and f). In contrast, there was no change in the XRD pattern of both the synthetic and natural jarosite subsequent to the peroxide digestion procedure (data not shown here).

Peroxide oxidation changed the morphology of synthetic schwertmannite and jarosite (Fig. 3.6b, d). The surface of both synthetic schwertmannite and jarosite developed rougher texture. Especially in jarosite, pitting of varying sizes and the formation of a thin coating on the surface evolved (Fig. 3.6d). In contrast, peroxide oxidation appears to cause no change in the morphology of both natural schwertmannite and jarosite.

These differences indicate that natural mineral phases are likely to be more stable during peroxide oxidation extraction. However, further study would be required to understand the specific differences between synthetic and natural materials in the presence of peroxide.
Chapter 3: Evaluation of two routine techniques ($S_{NAS}$ and $S_{RAS}$) for the assessment of the acidity liberated from schwertmannite and jarosite

3.5 Conclusions

1. Two schwertmannite samples (synthetic and natural) tested in the present study liberated acidity and sulfate during the AA determination process. Accordingly, the $S_{NAS}$ determined for both the synthetic and natural schwertmannite samples tested in the present study was greatly underestimated.

Fig. 3.6. SEM images a) synthetic schwertmannite before peroxide oxidation b) schwertmannite after peroxide oxidation c) synthetic jarosite before peroxide oxidation d) jarosite after peroxide oxidation. The bar indicates: (a)–(b) 500 nm, (c)–(d) 1 µm
2. Both synthetic and natural jarosite samples tested in the present study could be estimated using a correction factor of 2 to $S_{NAS}$ values to account for the observed 50-60\% recovery. However, our preliminary data suggests that quantification of jarosite content using $S_{NAS}$ in mixed schwertmannite/jarosite-containing soil materials may suffer from substantial interference from schwertmannite (due to variable recovery as observed from two schwertmannite samples tested here) and also may be from other Al hydroxy sulfate minerals such as basaluminite. Further work on a broader range of jarositic ASS samples would be needed to determine whether this correction factor has broad applicability.

3. $S_{RAS}$ could not reliably quantify either the synthetic/natural schwertmannite or jarosite samples in the present study.

4. Both synthetic/natural schwertmannite and jarosite samples tested in this study released sulfate during peroxide oxidation and accounted for the calculated $S_{POS}$ which is a measure of RIS (and PSA). The contribution to $S_{POS}$ by schwertmannite and jarosite tested in this study indicates the potential interference of those two minerals in the determination of PSA. This interference compromises the utility of the peroxide oxidation approach to ASS materials.

5. $S_{NAS}$ and $S_{RAS}$ are not able to provide reliable estimates of the content of jarosite and schwertmannite and, hence, the RA content in ASS materials.

3.6 Acknowledgements

The natural jarosite sample was kindly provided by Dr. Annabelle Keene. We thank Ms. Michelle Bush and Ms. Maxine Dawes for their assistance provided in XRD and SEM analyses respectively. This project was funded by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment.
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils

Submitted paper


Concept and design of research

Concept: Vithana and Sullivan

Design: Vithana, Sullivan, Bush and Burton

Sample collection, laboratory analysis and interpretation of data

Collection of samples: Vithana and Sullivan

Laboratory analysis: Vithana

Interpretation of data: Vithana and Sullivan

Writing the publication

Original draft: Vithana

Proof reading and editing: Sullivan, Bush and Burton

Preparation of computer graphics: Vithana

Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)

See Chapter 9 for references

See Appendix for signed author contribution statements.
4.1 Abstract

Schwertmannite is an acidity-generating mineral found in acid mine drainage (AMD) and acid sulfate soils (ASS). Acidic discharges from schwertmannite-contaminated environments can seriously diminish water quality and soil health. Managing such environments requires a clear understanding of whether schwertmannite is present and if so in what quantities. Selective extraction techniques, coupled with Differential X-ray diffraction (DXRD), have been used to identify poorly crystalline iron oxide phases in AMD environments. This study has examined the utility of acidified ammonium oxalate (AAO) extraction and Differential X-ray Diffraction (DXRD) techniques in soils spiked with schwertmannite. Our data shows that complete dissolution of schwertmannite may not be possible with AAO extraction for only 15 min. Iron could not be reliably quantitatively recovered from schwertmannite-spiked soils using the AAO extraction, with under-recoveries of up to 20%. Therefore, it was difficult to obtain a reliable estimate of the schwertmannite content based solely on percent recovery of Fe from the AAO extraction. Reliable identification of schwertmannite using the Fe/S ratio of the AAO extract was achieved for schwertmannite spiked in soils at a rate of 5%. The incomplete recovery of Fe and S from synthetic and natural schwertmannite1 spiked in soils using the 15 min AAO extraction precludes the practical use of this technique in detecting and accurately quantifying schwertmannite in natural soils where contents are at or below 5%. The DXRD technique clearly identified schwertmannite in soils spiked with > 5% by weight of this mineral.

1 In the manuscript under revision based on reviewers’ feedback the term “natural organic rich schwertmannitic material” has been used instead.
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils

4.2 Introduction

Schwertmannite is an iron hydroxy-sulfate mineral found in acidic and sulfate-rich environments such as in acid mine drainage sites (Bigham et al., 1994, 1996a; Schwertmann et al., 1995; Yu et al., 1999; Kawamo and Tomita, 2001) and acid sulfate soils (ASS) (Ahern et al., 2004; Sullivan and Bush, 2004; Burton et al., 2008b). Due to the potential of liberation of acidity and mobilization of previously scavenged trace metals, schwertmannite is an important mineral in the research fields of contaminated soil and water.

The formation of schwertmannite is initiated by the oxidation of iron sulfides minerals present in mined materials or in disturbed acid sulfate soils (Equations 4.1, 4.2 and 4.3) (Bigham et al., 1994, 1996a). This oxidation process is generally catalysed by microorganisms such as Acidithiobacillus ferrooxidans (Equation 4.2) (Schwertmann et al., 1995; Bigham and Nordstrom, 2000; Kawamo and Tomita, 2001). The physio-chemical conditions that favour schwertmannite precipitation/formation are acidic pH (3.0–4.5) and have high sulfate concentrations (1000–3000 mg L⁻¹) (Bigham et al., 1994). However, a recent study by Carballo et al. (2013) demonstrated that schwertmannite can be distributed in pH and pe ranges of 1.93-4.71 and 8.5-13.7 respectively.

\[
FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ 
\]  \hspace{1cm} (4.1)

\[
Fe^{2+} + 0.25O_2 (\text{microorganisms}) + H^+ \rightarrow Fe^{3+} + 0.5H_2O 
\]  \hspace{1cm} (4.2)

\[
8Fe^{3+} + SO_4^{2-} + 14H_2O \rightarrow Fe_8O_8(OH)_6(SO_4) + 22H^+ 
\]  \hspace{1cm} (4.3)

The complete equation for the formation of schwertmannite from pyrite can be derived by combining the equations (4.1), (4.2) and (4.3) which is shown in equation (4.4).

\[
8FeS_2 + 30O_2 + 18H_2O \rightarrow Fe_8O_8(OH)_6(SO_4) + 15SO_4^{2-} + 30H^+ 
\]  \hspace{1cm} (4.4)
Schwertmannite is a meta-stable, poorly ordered mineral often associated with other similar Fe(III) minerals such as ferrihydrite, jarosite and goethite (Bigham et al., 1994; Bigham and Nordstrom, 2000; Sullivan and Bush, 2004; Burton et al., 2006b). The X-ray diffractogram (XRD) of schwertmannite is characterised by 8 broad peaks indicating its poor crystallinity (Bigham et al., 1994). The chemical formula of schwertmannite is frequently expressed as $Fe_8O_8(OH)_8(\text{SO}_4)_x (1< x<1.75)$ taking into account its variable sulfate composition (Bigham et al., 1994). The unit cell of schwertmannite is a tunnel, which is made up by sharing the corners of the double chains of iron octahedra ($Fe_3(OH)_3$) (Bigham et al., 1990). The cavity of the tunnel is occupied by sulfate molecules instead of chloride resulting in a slightly distorted structure compared to that of akaganéite (Bigham et al., 1990; Fernandez-Martinez et al., 2010). A recent XRD simulation study by Fernandez-Martinez et al. (2010) reported the presence of two sulfate molecules per unit cell forming two different complexes (i.e. inner sphere and outer sphere) within the tunnel. These sulfate ions can be substituted by a number of other metal and trace metal anions including arsenate, chromate and selenate (Bigham et al., 1990; Waychunas et al., 1995; Regenspurg and Peiffer, 2005; Burton et al., 2009). The chemical and physical properties of schwertmannite have been be analysed using numerous techniques including X-ray Diffraction (XRD), Mössbauer, Infrared (IR), Raman, Scanning/Transmission Electron Microscopy (SEM/TEM) and Thermo-gravimetric analysis/Differential Thermal Calorimetry (TGA/DTA) (Bigham et al., 1994; Schwertmann et al., 1995; Majzlan et al., 2004; Regenspurg et al., 2004; Boily et al., 2010).

In ASS and acid mine drainage (AMD) environments, schwertmannite is a source of acidity during its formation (Equation 4.4) (Bigham and Nordstrom, 2000) and subsequent transformation to goethite (Equation. 4.5) (Sullivan and Bush, 2004). Importantly, the liberation of acidity is often accompanied by the mobilization of previously sorbed trace elements such as As, to toxic environmental concentrations (Chen et al., 2010).

$$2H_2O + Fe_8O_8(OH)_6(\text{SO}_4)_x \rightarrow 8FeO(OH) + SO_4^{2-} + 2H^+$$  (4.5)
Furthermore, Hedrich et al. (2011), using a bacterial culture of *Ferrovum myxofaciens*, speculated that schwertmannite transforms to jarosite as shown in equation 4.6.

\[
3\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6 + 6\text{H}_2\text{O} + 8\text{K}^+ + 13\text{SO}_4^{2-} + 18\text{H}^+ \rightarrow 8\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6
\]  

Wang et al. (2006) also demonstrated transformation of schwertmannite to NH$_4$/H$_3$O-jarosite during aging of schwertmannite. The transformation of schwertmannite to jarosite induced when the concentration of NH$_4$ increased from 11.4 mM to 111.4 mM and when the temperature increased from 36 to 45°C.

Due to the environmental hazards associated with schwertmannite, such as degradation of land, contamination of ground water and disruption of aquatic systems (Sullivan et al., 2012), the identification and quantification of schwertmannite is a desirable step in managing contaminated environments such as AMD and ASS. However, given that schwertmannite is a poorly ordered mineral and it exists with other similar Fe(III) minerals in soil, its accurate identification and quantification is a challenging task.

Extraction with acidified (pH 3) ammonium oxalate (AAO) has been used by many researchers for the identification and the subsequent quantification of poorly crystalline minerals such as schwertmannite and ferrihydrite (Bigham et al., 1990, 1994, 1996a; Gagliano et al., 2004; Regenspurg et al., 2004; Scroth and Parnell, 2005; Burton et al., 2007; Kumpulainen et al., 2007; Peretyazhko et al., 2009). The duration of the AAO extraction procedures used in these studies varied from 15 min to 4 h.

The Fe/S molar ratio in the AAO extract after extraction in the dark has then been used to determine whether schwertmannite is present. The typical range in the Fe/S molar ratio that indicates the presence of schwertmannite in a sample is 5-8 (Bigham et al., 1994, 1996a; Regenspurg et al., 2004). Bigham et al. (1990) further stated that a Fe/S molar ratio > 8 indicates the presence of ferrihydrite. However, Caraballo et al. (2013) expanded the characteristic Fe/S molar ratio range from 5-8 to a much broader range, 3.77-15.52.
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils

The dissolution of Fe by AAO used in literature quantify schwertmannite in sediments (Fukushi et al., 2003a; Gagliano et al., 2004; Peretyazhko et al., 2009). Solid phase mineralogical analyses confirmed that these samples consisted of schwertmannite, goethite, quartz, jarosite, and gypsum but not ferrihydrite. Therefore, the authors assumed that other iron containing components such as goethite and jarosite would not dissolve in AAO extractions but that schwertmannite would dissolve completely. If these assumptions hold true then the amount of Fe dissolved in AAO could be correlated to the schwertmannite content in the sample.

Bigham et al. (1990) showed that schwertmannite in natural sediments was completely dissolved within 15 min in AAO extraction in dark. The $\frac{F_{\text{Fe oxalate, 15 min}}}{F_{\text{Fe oxalate, 120 min}}}$ fraction of four out of five sediments collected from mine drainage sites approached unity suggesting a complete dissolution of oxalate extractable fraction within 15 min (Bigham et al., 1990). Bigham et al. (1990) also conducted a similar dissolution experiment for synthetic schwertmannite samples and observed that $\frac{F_{\text{Fe oxalate, 15 min}}}{F_{\text{Fe oxalate, 120 min}}}$ approached unity only when the sulfate content was > 11% (Bigham et al., 1990). The schwertmannite samples in Bigham et al.’s (1990) experiments were synthesised by hydrolysing FeCl$_3$ and then dialysing the synthesised product for 30 days (Bigham et al., 1990).

In contrast to Bigham et al. (1990), Dold (2003a) reported that it took 60 min in AAO in the dark to completely (i.e. > 94%) dissolve schwertmannite collected from a coal mine drainage site. However, this dissolution procedure also resulted in the dissolution of >85% of 2-line ferrihydrite, and poorly crystalline goethite in a sediment sample. Therefore, schwertmannite and ferrihydrite could not be distinguished using dissolution in AAO for 60 min (Dold, 2003a). According to Dold (2003a), dissolution of natural ferrihydrite during 15 min AAO extraction was >90% while both synthetic 2-line and 6-line ferrihydrite showed only 7-8% dissolution. However, Dold (2003a) demonstrated that 15 min AAO extraction time was sufficient to selectively detect the presence of schwertmannite through the subsequent differential X-ray diffraction (DXRD). Regenspurg et al. (2004) also used
Dold’s (2003a) 15 min AAO extraction method and the Fe/S molar ratio to identify the presence of schwertmannite in sediments collected from seven acid mining lakes (AML) in Germany.

AAO extraction in conjunction with differential X-ray diffraction (DXRD) was used by Singh et al. (1999), Dold and Fontboté (2001), Dold (2003a,b) and Caraballo et al. (2009) to identify schwertmannite in a range of mineral deposits collected from acid mine drainage and coal mine drainage environments, copper sulfides ores and acid mine water passive treatment systems. Bhatti et al. (1993) also used a 15 min AAO dissolution step, followed by the DXRD, to identify minerals such as schwertmannite formed after the biological degradation of a pyrrhotite sample.

The identification of iron oxide minerals (especially poorly crystalline minerals) in soil materials using XRD analysis is difficult due to their presence in low quantities and their typically broad, low intensity diffraction peaks (Schulz, 1981). Detection under such conditions can be improved by DXRD where a sample (after analysis by XRD) is subjected to selective dissolution of iron oxide minerals and a further analysis by XRD. A DXRD is created by subtracting the XRD of the treated sample from the XRD of the untreated sample (Schulz, 1981, 1986). There is an underlying assumption that differences in the X-ray diffraction (XRD) patterns of the sample before and after extraction are solely due to selective dissolution of reactive phases (Schulz, 1981, 1986). For example, schwertmannite has 8 characteristic peaks in the XRD spectrum, however, the peaks are very broad due to the poorly crystalline nature of schwertmannite. As a consequence, the identification of schwertmannite through XRD is difficult particularly when schwertmannite is present only in relatively minor amounts (i.e. < 5%) (Dold, 2003b) and also when other mineral phases such as aluminosilicate clay minerals, jarosite and goethite are present. In such situations, it has been suggested that AAO extraction followed by the DXRD approach could be used to identify schwertmannite (Dold and Fontboté, 2001; Dold 2003a,b). However, Caraballo et al. (2009) suggested that the DXRD approach should be accompanied by other analytical techniques for the examination of very poorly crystalline minerals such as schwertmannite.
In Australia, schwertmannite has been discovered in both inland (Fitzpatrick and Self, 1997) and coastal ASS (Sullivan and Bush, 2004). The presence of schwertmannite not only indicates acidic (pH 3-4) environments in soils and waterways but also indicates the potential of future acidity discharge from those soils and waterways (Dold and Fontboté, 2001; Sullivan and Bush, 2004). For example, hydrolysis of 1 mole of Fe$^{3+}$ in schwertmannite liberates 2.58 moles of H$^+$ (Peine et al., 2000). In coastal ASS, schwertmannite is present on the surface of soils, as coatings on leaf litter, and vegetation in waterways, and therefore, is often in contact with water in waterways such as acidified drains as well as with runoff during flow events (Sullivan and Bush, 2004). Runoff events allow the export of acidity and trace metals/metalloids liberated from schwertmannite to both groundwater and surface waters. The acidity that can be liberated from schwertmannite in CASS is appreciable (1900-2580 mol H$^+$/t) and can exert a strong influence on the quality of water in these waters (Sullivan and Bush, 2004).

The quantification of acidity contained in schwertmannite and related ASS minerals is considered critical for the assessment and appropriate management of ASS materials (Ahern et al., 2004, Sullivan et al., 2012).

Although the AAO extraction procedure has been used for the identification and quantification of schwertmannite collected from mineral deposits in mining impacted environments (Jönsson et al., 2005; Kumpulainen et al., 2008a; Burgos et al., 2012) and in constructed wetlands (Fukushi et al., 2003a; Gagliano et al., 2004), it has not been evaluated for the identification and quantification of schwertmannite in soil materials. In this study, the 15 min AAO extraction is evaluated for the identification and quantification of schwertmannite by extracting soil and quartz samples spiked with known additions of schwertmannite. Furthermore, the minimum detection limit for schwertmannite identification using the DXRD approach is evaluated for spiked soils and quartz samples.

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2 In the manuscript under revision based on reviewers’ feedback the term “quartz sand” has been used instead.
4.3 Materials and Methods

4.3.1 Sampling

Soil samples collected from two locations known from previous studies not to contain sulfuric soil materials (Isbell, 2002), in north-eastern New South Wales (NSW) Australia, are: 1) Tuckean Swamp on the Richmond River catchment (28°58’ 38” S, 153° 24’ 15” E) and; 2) Shark Creek on the Clarence River catchment (29°31’ 52” S, 153°12’ 35” E). Soils in both sites have been classified as Sulfidic Oxyaquic Hydrosols (confidence level 2) (Isbell, 2002). Samples were collected from discrete soil horizons/layers within the top 30 cm of the soil surface and placed into plastic bags, then sealed. Within 24 h of sampling, the two bulk soil samples were placed in a fan-forced oven at 80°C. Drying was continued for two weeks by which time a constant weight was reached. Dried soil samples were sieved (< 2 mm) and then ground using a ring mill (Rock Labs, New Zealand). These ground soils samples were shaken thoroughly by hand to ensure their homogeneity. A fine river pure (washed) quartz (< 64 µm) sample was also used as a soil matrix analogue for spiking purposes. Ground quartz was only used in the differential x-ray diffraction (DXRD) analysis. The chemical characteristics of Richmond and Clarence soil samples are given in Table 4.1.
Table 4.1. Selected chemical properties of soil samples, synthetic and natural schwertmannite.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>pHw</th>
<th>Total organic carbon</th>
<th>Fe$_{\text{total}}$</th>
<th>S$_{\text{total}}$</th>
<th>Fe$_{\text{oxalate}}$</th>
<th>S$_{\text{oxalate}}$</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
<th>Aqua regia Fe$<em>{\text{total}}$:S$</em>{\text{total}}$ (molar)</th>
<th>AAO Fe$<em>{\text{oxalate}}$:S$</em>{\text{oxalate}}$ (molar)</th>
<th>EDXA-SEM Fe$<em>{\text{total}}$:S$</em>{\text{total}}$ (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Richmond</td>
<td>4.50</td>
<td>4.65</td>
<td>2.95</td>
<td>0.06</td>
<td>0.67</td>
<td>0.0170</td>
<td>0.10</td>
<td>0.12</td>
<td>0.17</td>
<td>28.10</td>
<td>75.90</td>
<td>n.d.</td>
</tr>
<tr>
<td>Clarence</td>
<td>4.60</td>
<td>1.78</td>
<td>6.23</td>
<td>0.05</td>
<td>0.33</td>
<td>0.0025</td>
<td>2.60</td>
<td>0.14</td>
<td>0.38</td>
<td>119.40</td>
<td>15.60</td>
<td>n.d.</td>
</tr>
<tr>
<td>Synthetic schwertmannite</td>
<td>2.30</td>
<td>n.d.</td>
<td>43.70</td>
<td>5.30</td>
<td>39.50</td>
<td>4.20</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.80</td>
<td>5.36</td>
<td>3.80</td>
</tr>
<tr>
<td>Natural schwertmannite</td>
<td>3.00</td>
<td>18.87</td>
<td>18.00</td>
<td>1.53</td>
<td>11.30</td>
<td>1.20</td>
<td>0.09</td>
<td>0.23</td>
<td>0.28</td>
<td>6.70</td>
<td>5.45</td>
<td>7.70</td>
</tr>
</tbody>
</table>

n.d. not determined

All values are derived from duplicate analyses.
4.3.2 Synthesis of schwertmannite

Schwertmannite was freshly synthesized following the fast synthesis method described in Regenspurg et al. (2004). French et al. (2013) reported that the mineralogy and the morphology of schwertmannite synthesised by this method was similar to those of natural schwertmannite samples collected from abandoned mining sites and examined by them in 2012 (French et al., 2012). Using this procedure, 273 g of FeSO₄·7H₂O was dissolved in ~30 L of deionised water followed by addition of 150 mL of 30% H₂O₂ to oxidise the Fe²⁺. The solution was thoroughly mixed and the resulting suspension was allowed to settle overnight. The supernatant was removed after overnight standing and the schwertmannite settled in the bottom of the bin was rinsed daily with deionised water for 5 days to remove the soluble ions. The added deionised water was carefully decanted without disturbing the settled schwertmannite. The slurry containing freshly synthesized schwertmannite in the bottom of the bin was then dried at 30°C for a week. Dried schwertmannite was then ground using a mechanical ring mill to obtain a fine powder.

4.3.3 Natural schwertmannite

Schwertmannite segregations used in this study were the same as those used in Burton et al. (2007). These were present as coatings on leaf litter in a coastal lowland acid sulfate soil (CLASS) in Eastern Australia (29°26’29”S, 153°14’12” E). Schwertmannite segregations were collected by hand and within 24 h of sampling were ground to < 2mm and homogenised (Burton et al., 2007). According to Burton et al. (2007), the collected samples were relatively dry with field moisture content of 6%. Hereafter, this soil material rich in schwertmannite is termed ‘natural schwertmannite’. Some of the chemical characteristics of the natural schwertmannite are presented in Table 4.1.
4.3.4 Analytical Methods

The elemental compositions of synthetic and natural schwertmannite material as well as two soil samples are presented in Table 4.1. The samples were subjected to aqua-regia digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) (APHA, 2005). The aqua-regia digestion was performed using the “Hot Block Digester”. Samples were placed in disposable digestion tubes and then digested with the aqua-regia solution at 120°C for 1 h in a pre-heated block digester. The chemical composition of the AAO extracted samples was also determined using ICP-MS. Total organic carbon content (TOC) in natural schwertmannite and the two soil samples was determined using the total inorganic carbon/total organic carbon analyser (Aurora 1030 TIC/TOC analyser).

The mineralogy of both synthetic and in natural schwertmannite was examined using powder X-ray diffraction (XRD) (Bruker D4 Diffractometer using Co Kα radiation, Bruker AXS GmbH, Germany). Samples for analysis were hand ground (< 63 µm) using a porcelain mortar and pestle and homogenised. The diffraction patterns were recorded from 5°-80°2θ in steps of 0.05° 2θ step size with a 2 seconds counting time per step. The XRD patterns were evaluated using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Germany). The mineralogy of the synthetic schwertmannite was verified by XRD which also indicated the absence of detectable other mineral phases (Fig. 4.1a). XRD of the natural schwertmannite also confirmed the presence of schwertmannite (Fig. 4.1b). The presence of minor quantities of other minerals such as goethite and quartz was also indicated by XRD of the natural schwertmannite (Fig. 4.1b).

Micromorphology of ground schwertmannite samples were determined using scanning electron microscopy (SEM) (Stereoscan 440, Leica, Cambridge Ltd, UK). Synthetic and natural schwertmannite were mounted on an aluminium stub and coated with carbon followed by gold. Images of the samples were taken using the settings: working distance (WD)=7 mm, Probe=35 pA and Electron High Tension (EHT)=12 kV. The elemental/atomic composition of selected areas of pure synthetic and natural schwertmannite (coated with carbon) was determined using an ISIS energy
dispersive X-ray EDX0 microanalysis system (Oxford EDS detector, PBQuant Software, WD=25mm, Probe=500pA, EHT=20kV) utilising a Peak-to-Background method (Sullivan and Bush, 1997).

All reagents were prepared from analytical grade chemicals and using MilliQ deionised water. All the glassware used were acid washed by soaking in 5% HNO₃ for 24h.

![XRD patterns of untreated samples](image)

Fig. 4.1. XRD patterns of untreated samples (a) synthetic schwertmannite (b) natural schwertmannite, where S=schwertmannite, G=Goethite Q=Quartz

**4.3.5 Preparation of samples**

**4.3.5.1 Acidified (pH 3) ammonium oxalate (AAO) dissolution**

For all analyses, a constant sample weight of 0.5 g was used. The soil material and quartz samples were spiked with 0.5%, 1%, 2% and 5% of synthetic/natural schwertmannite and the total weight of each sample was maintained at 0.5 g by adding an appropriate amount of soil or quartz (Table 4.2). AAO was prepared by bringing the pH of 0.2 M ammonium oxalate solution to pH 3.00 by adding 0.2 M oxalic acid as per Dold (2003a,b). Samples spiked with schwertmannite were extracted with 25 mL of AAO solution for 15 min at room temperature and under oxic environment in the dark. The volume of AAO (25 mL) for all treatments in this study was selected based on the highest schwertmannite weight (i.e. 0.025 g) spiked in soil/quartz. This soil:extract ratio (i.e. 0.025 g:25 mL) is similar to that
used by Regenspurg et al. (2004). While schwertmannite in natural precipitates reportedly dissolved within the 15 min to 4 h time frames of AAO extraction, selective dissolution of schwertmannite was observed within the 15 min AAO extraction, leaving goethite and jarosite in the solid phase (Bigham et al. 1990; Dold, 2003a; Regenspurg et al. 2004). Therefore, in the present study, 15 min was applied to selectively dissolve the schwertmannite spiked in soils/quartz samples.

During AAO extraction, the samples were shaken end-over-end. The suspensions were filtered using 0.45 µm cellulose acetate filters (Sartorius Stedim Biotech, Germany). Blank samples of non-spiked Richmond, Clarence and quartz samples were also subjected to the same procedure and analysed for oxalate extractable Fe and S after the 15 min AAO extraction. The oxalate extractable Fe and S results of the non-spiked soil and quartz samples were subtracted from those of the spiked (treated) samples for the purpose of calculating Fe and S recoveries from the added synthetic and natural schwertmannite. Pure samples of synthetic and natural schwertmannite (0.025 g) were also subjected to 15 min AAO extraction (with 25 mL of AAO solution) in order to obtain the Fe/S ratio in the absence of soil and quartz. All analyses were conducted in triplicate and the results of treated samples were corrected using those obtained for the blank samples. The dissolution kinetics of pure synthetic schwertmannite and natural schwertmannite in AAO was examined by extracting both schwertmannites with AAO for different extraction time periods. In this particular experiment, pure samples of synthetic and natural schwertmannite (0.025 g) were subjected to 15, 30, 45, 60, 90 and 120 min AAO extraction (with 25 mL of AAO solution) to obtain the percentage Fe recoveries and to calculate the Fe/S ratio in the absence of soil and quartz.
Table 4.2. Amount of synthetic/natural organic schwertmannite and soils/quartz mixed to obtain various schwertmannite spiking rates

<table>
<thead>
<tr>
<th>Schwertmannite spiking rate (%)</th>
<th>Weight of synthetic/natural schwertmannite added (g)</th>
<th>Weight of soil/quartz added (g)</th>
<th>Total weight of the sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0025</td>
<td>0.4975</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>0.0050</td>
<td>0.4950</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.0100</td>
<td>0.4900</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>0.0250</td>
<td>0.4750</td>
<td>0.5</td>
</tr>
</tbody>
</table>

4.3.5.2 Differential X-ray diffraction (DXRD)

DXRD of natural schwertmannite was obtained by subtracting the XRD of the sample after the AAO extraction, from the XRD of the sample before the AAO extraction. For this purpose, 0.05 g of natural schwertmannite was extracted with 50 mL of AAO for 15 min in the dark. The residue after the extraction was dried and then analysed through the XRD. However, the XRD of synthetic schwertmannite sample after the 15 min AAO extraction could not be obtained since there was no residue left after the extraction. The intensity of the XRD of the residue (after the AAO extraction) was greater compared to that of the untreated sample due to the dissolution of both schwertmannite and other mineral phases in natural schwertmannite sample. Therefore, the intensity of the XRD of the residue after the AAO treatment was adjusted by multiplying with a scale factor (< unity) found by iterative subtractions.

In AMD environments, schwertmannite and other secondary Fe(III) hydroxide minerals are often found in relatively minor concentrations (Dold, 2003b). The detection limit of XRD for schwertmannite in AMD environments is 5%, making the identification of minor concentrations of minerals such as schwertmannite in samples from AMD difficult unless these minerals are separated or enriched prior to XRD analysis (Dold, 2003b). The present study was designed to determine the minimum detection limit of schwertmannite spiked in soil and quartz samples that can be identified through the DXRD approach under ideal conditions (i.e. only schwertmannite is dissolved by the
AAO extraction). For this purpose, soil and quartz samples were spiked with 2%, 5%, 10%, 25% and 50% of synthetic schwertmannite and were analysed using the XRD technique (Table 4.3). The two lower spiking rates (i.e. 0.5% and 1%) which were used in AAO treatment were not used in this DXRD experiment as the minimum detection limit of XRD is 5% (Dold, 2003b). In this particular DXRD approach, the mineral addition approach was used, and the XRD patterns of non-spiked soil/quartz and the soil/quartz with various additions of schwertmannite were obtained. The DXRD of schwertmannite was obtained by subtracting the XRD pattern of non-spiked soil/quartz from the XRD pattern of soil/quartz with various additions of schwertmannite. This was done to eliminate possible interactions between the AAO extractant and the non-target minerals in the soil matrix during the AAO extraction.

Table 4.3. Schwertmannite additions in soil and quartz examined through the DXRD approach

<table>
<thead>
<tr>
<th>Synthetic schwertmannite spiking rate (%)</th>
<th>Weight of synthetic schwertmannite added (g)</th>
<th>Weight of soil/quartz added (g)</th>
<th>Total weight of the sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.0100</td>
<td>0.4900</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>0.0250</td>
<td>0.4750</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>0.0500</td>
<td>0.4500</td>
<td>0.5</td>
</tr>
<tr>
<td>25</td>
<td>0.1250</td>
<td>0.3750</td>
<td>0.5</td>
</tr>
<tr>
<td>50</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.5</td>
</tr>
</tbody>
</table>

4.3.6 Calculations

Recovered Fe and S weight percentages (sections 4.4.3 and 4.4.4, Figs. 4.5 and 4.6) after AAO extraction were determined using the amount of Fe and S recovered and the amount of Fe and S initially present in each spiking rate of schwertmannite (i.e. before the AAO extraction).
4.4 Results and Discussion

4.4.1 Characteristic properties of synthetic and natural schwertmannite

Table 4.1 indicates that ~90% of the total Fe in synthetic schwertmannite was oxalate-extractable. The natural schwertmannite was also mainly composed of oxalate-extractable iron mineral phases which accounted for 63% of the total iron. In addition to the presence of other mineral phases, natural schwertmannite contained ~19% total organic carbon (TOC) consistent with its close association with leaf litter (Table 4.1).

The Fe/S molar ratio calculated for synthetic schwertmannite and natural schwertmannite from total digestion (aqua-regia), oxalate extraction and the SEM-EDXA are also shown in Table 4.1. There is a clear discrepancy between the calculated Fe/S molar ratios of synthetic schwertmannite (3.8-5.4) and natural schwertmannite samples (5.5-7.7) determined from the three techniques. According to Hyde et al. (2011), it is not surprising to observe variability between the Fe and S contents of schwertmannite due to its highly hydrated nature. Based on the total Fe and S content (assuming a pure synthetic product and that the “Fe₈O₈” part of the formula is invariant, and using the weight of the synthetic product digested to assign the remainder of the mass to (OH)), the average molecular formula for the synthetic schwertmannite is Fe₈O₈(OH)₄.66 (SO₄)₁.67.

The reported surface area for schwertmannite synthesised through the fast oxidative approach (i.e. in the range of 4-14 m² g⁻¹) elsewhere (Regenspurg et al., 2004) was adopted for our synthetic schwertmannite. The morphology of synthetic schwertmannite was composed of spheroidal particles as described in Regenspurg et al. (2004) however, the size of the particles ranged from about 0.2 to 1 µm (Fig. 4.2a). Natural schwertmannite existed as aggregates of > 500 nm, which were also composed of spheroidal particles (<500 nm) (Fig. 4.2b).
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils

Fig. 4.2. Micromorphology of: (a) synthetic schwertmannite (b) natural schwertmannite. Scale bars (white) are 1 μm.

4.4.2 DXRD of schwertmannite

Fig. 4.3a, b and c show the XRD patterns of the initial untreated natural schwertmannite sample, the natural schwertmannite sample after 15 min extraction with AAO, and the DXRD, respectively. Raw XRD patterns of synthetic schwertmannite mixed with soil or quartz (before the subtraction) and the corresponding DXRD patterns (after the subtraction) are displayed in Fig. 4.4.

It is apparent from the XRD spectra in Fig. 4.3a and b that schwertmannite in the natural sample almost completely dissolved during 15 min extraction with AAO. The dissolved schwertmannite was easily identifiable in the DXRD spectrum (Fig. 4.3c). Furthermore, DXRD also shows the dissolution of goethite as well as some unidentified mineral phases present in the initial sample during the 15 min AAO extraction (Fig. 4.3b). Goethite dissolution during the AAO extraction in the dark and subsequent identification of the dissolved goethite through DXRD have also been used in the past (Singh et al., 1999; Dold, 2003a,b; Caraballo et al., 2009). However, the duration of AAO extraction in these studies varied from 30 min (Dold, 2003a,b; Caraballo et al., 2009) to 4 h (Singh et al., 1999). Burton et al. (2007) considered the dissolution of goethite by AAO was minor (< 3%) under anoxic conditions. Nevertheless, Burton et al. (2007) observed a substantial increase in the dissolution of goethite (~63%) in the presence of 2 mM Fe²⁺ attributable to the catalytic effect of Fe²⁺. Fe bound to
organic matter can be liberated during the AAO extraction (Loeppert and Inskeep, 1996). Therefore, it is likely that organically bound Fe (given ~19% of TOC) liberated from natural schwertmannite samples during the AAO extraction may have catalysed the dissolution of goethite.

Fig. 4.3. XRD patterns of natural schwertmannite (a) natural schwertmannite before AAO extraction (b) after 15 min AAO extraction (c) DXRD pattern, where S=Schwertmannite, G=Goethite Q=Quartz

Fig. 4.4 demonstrates that schwertmannite spiked in soil/quartz can be detected through the DXRD provided its content exceeds 5%, acknowledging the observation applies to ideal conditions (i.e. when effectively, only the schwertmannite mineral fraction would have been disturbed by interaction with AAO). Other factors including incomplete dissolution of schwertmannite, interactions between AAO and non-target soil components (e.g. goethite) would limit the ability of DXRD to identify schwertmannite in natural materials. Furthermore, the observation on schwertmannite detectability under ideal situations places a detection limit of 5% when using the established DXRD/AAO approach for the identification of schwertmannite in natural ASS samples.
Fig. 4.4. Raw X-ray diffraction (XRD) and differential X-ray diffraction (DXRD) of synthetic schwertmannite at different concentrations in the: (a), (d) Richmond soil; (b), (e) Clarence soil, and; (c), (f) quartz, respectively.

4.4.3 Dissolution kinetics of synthetic and natural schwertmannite

The Fe/S molar ratio of synthetic schwertmannite was constant over time (i.e. 4.8-4.9) (Fig. 4.5a), yet only 76% of synthetic schwertmannite was recovered during the 15 min AAO extraction. The recoveries of both Fe and S were still incomplete after 120 min of AAO extraction (Fig. 4.5b).

Similar to synthetic schwertmannite, the extent of natural schwertmannite dissolution increased (as measured by Fe) with time (Fig. 4.5b). The data show only 65% of the total Fe was oxalate extractable after 15 min extraction, however, the recovery increased up to 87% after 120 min extraction (Fig. 4.5b). In contrast, S recovery from the natural schwertmannite sample was constant (i.e. ~ 80%) over time (Fig. 4.5c). As a consequence of these different behaviours, the Fe/S molar...
ratio of the natural schwertmannite sample increased with increasing extraction time (Fig. 4.5a). The increase in the amount of dissolution of natural schwertmannite over time likely indicates the dissolution of other non-schwertmannitic minerals such as goethite in these materials. Complete dissolution of schwertmannite in natural schwertmannite after the 15 min AAO extraction was also confirmed by the DXRD (Fig. 4.3a, c). However, the DXRD also indicated the dissolution of other mineral phases such as goethite during the 15 min AAO extraction (Fig. 4.3a, c).

Although the characteristic Fe/S ratios for schwertmannite (i.e. 5-8) can be achieved by a 15 min AAO extraction, the dissolution of schwertmannite in samples may be incomplete within this timeframe. Incomplete recovery of both synthetic schwertmannite and schwertmannite in natural precipitates was also observed by Dold (2003a) during a 15 min AAO extraction. Dold (2003a) reported a near complete dissolution of schwertmannite (i.e. > 94%) during the 60 min AAO extraction but also accompanied by dissolution of ferrihydrite.

In contrast to the findings of both the present study and that of Dold (2003a), Bigham et al. (1990) observed the complete dissolution of both schwertmannite in sediments and synthetic schwertmannite. Interestingly, although the synthetic schwertmannite used by both Bigham et al. (1990) and Dold (2003a) showed different dissolution behaviours during the 15 min AAO extraction, they both were synthesised using the same slow dialysis approach.
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils

Fig. 4.5. Time sequence AAO extraction data of synthetic schwertmannite and natural schwertmannite. (a) Percentage Fe recovery and Fe/S molar ratio (b) Percentage S recovery and Fe/S molar ratio. Error bars-standard deviation of three replicates.

4.4.4 Recovery of Fe from synthetic and natural schwertmannite spiked in soil and quartz matrices

When spiked in quartz, almost all of the oxalate extractable Fe fraction of the synthetic schwertmannite (i.e. ~90% of the total Fe-Table 4.1) was recovered (Fig. 4.6a). Nevertheless, the recovery of Fe from synthetic schwertmannite was reduced by 10-20% when it was spiked in the two soil matrices (Fig. 4.6a). The decrease in Fe recovery in the presence of soil matrices is likely due to the adsorption of Fe liberated during schwertmannite dissolution (Fig. 4.8a) on soil particles. Fe readily adsorbs and forms complexes with soil particles and organic matter (Sparks, 2003), and this process may explain the variable recoveries at lower spiking rates of both synthetic and natural schwertmannites.
Fig. 4.6. Recovery of Fe in soil and quartz samples after 15 min AAO extraction in the dark a) synthetic schwertmannite b) natural schwertmannite. The calculated Fe recoveries were based on the Fe content in each spiked sample due to addition of schwertmannite, as calculated from the total-Fe content measured by the aqua-regia digestion and subsequent correction using blanks (i.e. Fe recoveries obtained for non-spiked soil and quartz). Error bars-standard deviation of three replicates.

4.4.5 Fe/S molar ratio of synthetic and natural schwertmannite spiked in soil/quartz matrices

Only the Fe/S ratios obtained for higher spiking rates (i.e. 5%) of synthetic schwertmannite and natural schwertmannite after 15 min AAO extraction were reasonably close to the expected Fe/S ratio of pure synthetic (i.e. 5.45) and natural schwertmannite (i.e. 5.36) (Fig. 4.7a, b). The variability in the Fe/S ratios obtained for synthetic and natural schwertmannite spiked soil/quartz samples as opposed to the corresponding expected ratios (i.e. 5.45 and 5.36) was likely due to two main factors. Firstly, as discussed in section 3.3, the dissolution of both schwertmannite materials was incomplete during the 15 min AAO extraction (i.e. ~76% for synthetic schwertmannite and 65% for natural schwertmannite). Secondly, as shown in Fig.4.8, it is apparent that the soil materials (i.e. Richmond...
and Clarence) adsorbed both Fe and S liberated from schwertmannite, but with Fe absorbed preferentially over S. As a consequence, the Fe/S ratios determined for different spiking rates were inconsistent compared to the expected ratio of the pure schwertmannites (Fig. 4.7).

![Graph showing Fe/S molar ratio of schwertmannite in soil or quartz samples calculated from 15 min AAO extraction a) synthetic schwertmannite b) natural schwertmannite. Fe/S ratios of pure synthetic and natural schwertmannite determined from 15 min AAO are also provided on right hand axis. Lack of S in the AAO extract of the Richmond and Quartz samples spiked to 0.5% with natural schwertmannite precluded calculation of Fe/S. Error bars-standard deviation of three replicates.](image-url)

Fig. 4.7. Fe/S molar ratio of schwertmannite in soil or quartz samples calculated from 15 min AAO extraction a) synthetic schwertmannite b) natural schwertmannite. Fe/S ratios of pure synthetic and natural schwertmannite determined from 15 min AAO are also provided on right hand axis. Lack of S in the AAO extract of the Richmond and Quartz samples spiked to 0.5% with natural schwertmannite precluded calculation of Fe/S. Error bars-standard deviation of three replicates.
Fig. 4.8. Dissolved Fe and S percentages in the AAO extract after 15 min extraction (a), (b)-Fe and S dissolved percentages from synthetic schwertmannite spiked soil/quartz (c), (d)-Fe and S dissolved percentages from natural schwertmannite spiked soil/quartz. Expected Fe and S percentages were calculated from the initial Fe and S content in both schwertmannites at each spiking rate. Error bars=standard deviation of three replicates
Chapter 4: Examination of the acidified ammonium oxalate method and differential X-ray diffraction (DXRD) techniques for the identification and quantification of schwertmannite in acid sulfate soils

4.5 Conclusions

The DXRD approach undertaken in this particular study differed from the traditional DXRD approach. Here, instead of analysing the XRD’s of samples before and after selective dissolution, XRDs of samples before and after the addition of synthetic schwertmannite were examined. Under these ideal conditions, the minimum detection limit of schwertmannite spiked in soils and quartz through the DXRD was 5%.

During the 15 min AAO extraction procedure, goethite was dissolved demonstrating dissolution of Fe from forms other than schwertmannite in soil materials during the 15 min AAO extraction method. The presence of higher organic matter (~ 19% of TOC) might also have contributed to the increased dissolution of other Fe mineral phases in the materials examined here.

The dissolution of both synthetic and natural schwertmannite used in this study was incomplete within 15 min of AAO extraction with only ~ 76% and 65% of Fe being recovered after this duration, respectively. Both incomplete dissolution and the adsorption of liberated Fe by soil particles contributed to the observed under recovery of Fe spiked in soils and quartz matrices after 15 min AAO extraction. Therefore, quantification of schwertmannite using the extracted Fe percentage after 15 min AAO extraction will not provide an accurate estimate of the content of schwertmannite.

Incomplete dissolution of schwertmannite during the 15 min AAO extraction and adsorption of Fe liberated during schwertmannite dissolution by soil particle surfaces, limits the practical utility of Fe/S molar ratio for identification of schwertmannite in soil materials at concentrations less than 5%.

Both AAO extraction and the DXRD data obtained in this study indicate that both techniques could only be used to identify the presence of schwertmannite in soil materials when present in concentrations above 5%.
4.6 Acknowledgement

We thank Ms. Michelle Bush and Ms. Maxine Dawes for their assistance provided in XRD and SEM analyses, respectively. This project was funded by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment. We also thank two anonymous reviewers for their constructive comments.
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

Submitted paper


Concept and design of research

Concept: Vithana and Sullivan
Design: Vithana, Sullivan, Bush and Burton

Sample collection, laboratory analysis and interpretation of data

Collection of samples: Vithana and Sullivan
Laboratory analysis: Vithana
Interpretation of data: Vithana and Sullivan

Writing the publication

Original draft: Vithana
Proof reading and editing: Sullivan, Bush and Burton
Preparation of computer graphics: Vithana

Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%) 

See Chapter 9 for references

See Appendix for signed author contribution statements.
5.1 Abstract

A three-step sequential extraction procedure established for the quantification of acidity producing ferric and ferrous sulfate minerals such as melanterite and jarosite in acid mine wastes was evaluated for quantification of jarosite spiked in soils. The procedure involves in sequence anoxic water extraction, roasting the solid residue after anoxic water extraction at 550°C for 1 h, and 4 M HCl extraction of the roasted solid. The recovery of synthetic and natural jarosite spiked in soil and quartz was examined. Less than 50% of the spiked jarosite was recovered. The missing S is partially attributable to the retention of jarosite by the Teflon filter membrane used during the filtration of the anoxic water extract. Further investigations also demonstrated a lower 4 M HCl-S extractability from jarosite samples roasted at 550°C than those roasted at 450°C. S recovery was substantially improved by replacing the Teflon filter membrane with the Cellulose Acetate filter membrane and including this filter paper in the second step roasting. The modified method is demonstrated to be a useful approach for the study of acidic soils.
5.2 Introduction

Jarosite is a secondary Fe(III) mineral commonly found in acid sulfate soils (ASS) (Welch et al., 2007; Johnston et al., 2011a,b) and acid mine drainage (AMD) sites (Bigham et al., 1996b; Norlund et al., 2010). It is a member of the alunite group with the standard molecular formula of $AB_3(SO_4)(OH)_6$, where $A$ is a monovalent cation such as $K^+$, $Na^+$, $H_3O^+$ and $NH_4^+$ and the $B$ position is occupied by trivalent cations like $Fe^{3+}$ and $Al^{3+}$ (Baron and Palmer, 1996; Bigham and Nordstrom, 2000; Smith et al., 2006; Bigham et al., 2010; Desborough et al., 2010).

In natural environments, jarosite forms as a result of partial oxidation of pyrite (which forms a solution rich in $Fe^{2+}$ and $SO_4^{2-}$) (Equation 5.1), a process generally catalysed by iron-oxidising bacteria (Bigham and Nordstrom, 2000) (Equations 5.1-5.3).

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (5.1)$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \quad (5.2)$$

$$3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad (5.3)$$

Jarosite is stable under oxic, acidic (pH 1-3) and $SO_4^{2-}$-rich (> 3000 mg L$^{-1}$) conditions (Bigham and Nordstrom, 2000; Smith et al., 2006). However, in the long term and under less favourable environmental conditions (i.e. reducing, near-neutral conditions), jarosite transforms to other iron minerals such as goethite as shown in equation 5.4 (White and Melville, 1997; Welch et al., 2007).

$$3H_2O + KFe_3(SO_4)_2(OH)_6 \rightarrow 3Fe(OH)_3 + 2SO_4^{2-} + 3H^+ + K^+ \quad (5.4)$$

In oxidised ASS and AMD environments, jarosite exists with other meta-stable secondary Fe(III) minerals such as schwertmannite and discharges acidity to the environment as they hydrolyse (Ahern et al., 2004; Li et al., 2007; Welch et al., 2007; Johnston et al., 2009a,b). In addition to being an important source of acidity, jarosite can scavenge and influence the mobility of trace metals (Smith,
2004; Welch et al., 2007). However, these scavenged trace metals are likely to be re-mobilized as jarosite weathers (Acero et al., 2006; Welch et al., 2007). Therefore, the presence of secondary Fe(III) minerals such as jarosite in ASS is a potential hazard to terrestrial and aquatic environments (Sullivan et al., 2012).

Assessment of acidity is a key aspect tool for managing ASS and AMD landscapes. The challenge lies in quantitatively discriminating the different sources of acidity, particularly the fraction associated with jarosite (Ahern et al., 2004). In 2004, Ahern et al. introduced two measurements termed “Net Acid Soluble Sulfur” (SNAS) and “Residual Acid Soluble Sulfur” (SRAS) that are widely used in Australian analytical laboratories for the assessment of the acidity present in these iron minerals in ASS. Both SNAS and SRAS employ the recovery of S from such minerals and are stoichiometrically able to estimate their content. The jarosite content is therefore estimated based on the “ideal” jarosite composition (e.g. Equation 5.4). However, a recent evaluation (Vithana et al., 2013) revealed that neither measurement provides a reliable estimate of the jarosite content in ASS.

Li et al. (2007) proposed a sequential extraction procedure to quantify jarosite in acid mine wastes. This method consists of three steps:

1) anoxic water extraction (3 min) which removes water soluble Fe(II) sulfate minerals such as melanterite and epsomite,

2) roasting the solid residue left after anoxic water extraction at 550°C for 1 h to remove pyrite and pyrrhotite as SO₂, and

3) 4 M HCl extraction (30 min) of the roasted sample.

Using this method Li et al. (2007) reported a 100% recovery from a mixture of 5% jarosite in quartz, and from lateritic nickel tailing waste of varying jarosite contents.
During the roasting step, jarosite is thermally decomposed to yavapaiite ($KFe(SO_4)_2$) and hematite ($Fe_2O_3$) (Equation 5.5).

$$KFe_3(SO_4)_2(OH)_6 \rightarrow KFe(SO_4)_2 + Fe_2O_3 + 3H_2O$$

(5.5)

Li et al. (2007), emphasised the importance of keeping the roasting temperature strictly at 550°C or below as the formed yavapaiite decomposes at temperatures above 550°C resulting in liberation of S as SO$_3$ (Equation 5.6).

$$2KFe(SO_4)_2 \rightarrow K_2SO_4 + Fe_2O_3 + 3SO_3$$

(5.6)

Jarosite decomposes via several weight loss stages which involves the removal of water (200°C-320°C), crystallisation of yavapaiite (350°C-450°C) (Equation 5.5), and the decompostion of yavapaiite associated with the removal of SO$_3$ (550°C-800°C) (Equation 5.6) (Baron and Palmer, 1996; Drouet and Navrostky, 2003; Smith, 2004; Forray et al., 2005). However, both Frost et al. (2005) and Xu et al. (2010) have reported widely varying temperatures at which these weight loss stages occur depending on either composition or crystallinity.

The roasting of jarosite enhances S recovery in the subsequent 30 min 4 M HCl extraction step (Li et al., 2007). The composition of jarosite is highly variable in natural environments and therefore, their stabilities will also likely vary (Baron and Palmer, 1996; Dutrizac and Jambor, 2000). Hence, the suggested 30 min time frame for the maximum amount of S recovery from the roasted sample through the 4 M HCl extraction may not hold for all jarosite types.

Li et al.’s (2007) study did not examine jarosite from ASS materials which is predominantly K-jarosite (Keene et al., 2010; Johnston et al., 2009a, 2012). These natural types of jarosite are common and known to have a significant impact on the environment, however those K-jarosites have not been systematically examined. It is very likely that both the thermal behaviour and the solubility kinetics of K-jarosite from ASS behave differently from AMD type jarosites after roasting and in subsequent 4 M
HCl extraction. The objective of this study is to systematically evaluate the utility of the three-step sequential extraction procedure of Li et al. (2007) for quantification of jarosite spiked (at already known rates) in soil materials.

5.3. Materials and Methods

5.3.1 Sampling

Soil samples were collected from two regions previously confirmed as non-sulfuric (Isbell, 2002), in north-eastern New South Wales (NSW) Australia: 1) Tuckean Swamp on the Richmond River catchment (28°58’38”S, 153°24’15”E) and; 2) Shark Creek on the Clarence River catchment, Australia (29°31’52”S, 153°12’35”E). Soils in both sites were classified as Sulfidic Oxyaquic Hydrosols (confidence level 2) (Isbell, 2002). Samples were collected from the upper layer (0-30 cm) and placed into plastic bags and then sealed. Within 24 h of sampling, the two soil samples were placed in a fan forced oven at 80°C and dried for two weeks until a constant weight was reached. Dried soil samples were sieved (< 2 mm) and then ground using a ring mill (Rock Labs, New Zealand). A fine river pure (washed) quartz sand (< 64 µm) sample was used as a soil reference material.

5.3.2 Synthesis of jarosite

Jarosite was synthesised by the method of Baron and Palmer (1996). A beaker containing a mixture of 56 g of KOH, 172 g of Fe₂(SO₄)₃.5H₂O and 1000 mL of deionised water was heated at 95°C for 4 h with continuous stirring. After jarosite settled on the bottom of the beaker, it was separated by decanting the supernatant. Jarosite precipitate was then washed thoroughly with deionised water and dried in an oven at 110°C for 24 h.
5.3.3 Natural jarosite rich soil materials

Jarosite rich soil materials were collected from shallow pits (i.e. < 1 m deep) from East Trinity, Australia (16°56’33”S, 145°48’9”E) as described in Johnston et al. (2011a). Jarosite accretions were present in macropores and fissures of the upper sulfuric horizon (to 1 m depth) (Johnston et al., 2011a). These natural jarosite-rich soil segregations are termed as “natural jarosite”.

5.3.4 Analytical methods

The elemental composition of soil samples and jarosite were determined by aqua-regia digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) (APHA, 2005). The composition of the aqueous phase after the anoxic water and 4 M HCl extractions of jarosite sample was determined by the ICP-MS (APHA, 2005). The total organic carbon (TOC) content in soil and natural jarosite samples was determined using the TIC/TOC analyser (Aurora 1030 TIC/TOC analyser).

The mineralogy of synthetic and natural jarosite was examined by powder X-ray diffraction before and after roasting (Bruker D4 Diffractometer using Co Kα radiation, Bruker AXS GmbH, Germany). Samples for analysis were hand ground (< 63 µm) using a porcelain mortar and pestle and homogenised. The diffraction patterns were recorded from 5-80°2θ in steps of 0.05°2θ step size with 2 seconds counting time per step. The XRD patterns were evaluated using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Germany).

The micromorphology of jarosite samples was determined using a scanning electron microscope (SEM) (Stereoscan 440, Leica, Cambridge Ltd, UK). Samples were mounted on an aluminium stub and coated with carbon followed by gold.

Thermal decomposition of the pure synthetic and natural jarosite was determined using the thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques (STAR software,
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

TGA/DSC 1 STAR System Analyser, Mettler-Toledo LLC, Columbus, OH, USA). Jarosite samples were heated from 30°C - 700°C under an air atmosphere (Heating rate-10°C min⁻¹, gas purge rate 100 mL min⁻¹).

All reagents were prepared from analytical grade chemicals and using MilliQ deionised water. All the glassware used was acid washed by soaking in 5% HNO₃ for 24 h.

5.3.5 Preparation of samples

5.3.5.1 Sequential extraction of jarosite containing soil/quartz samples

Soil and quartz samples were spiked with 0.5%, 1%, 2%, and 5% of synthetic or natural jarosite and the S content was recovered using the three-step sequential method of Li et al. (2007). The total mass of the sample was maintained at 0.5 g (±0.0001 g) by adding an appropriate amount of soil or quartz (Table 5.1). Blank samples containing soil/quartz but without jarosite were also subjected to the same extraction procedure and the results of the jarosite spiked soil/quartz samples were corrected using the results of the corresponding blank samples. Each treatment was repeated with three replicates. Recovered S weight percentage was calculated for each spiking rate as described in section 5.3.5.6.

Table 5.1 Amount of synthetic/natural jarosite and soils/quartz mixed to obtain various jarosite spiking rates

<table>
<thead>
<tr>
<th>Jarosite spiking rate (%)</th>
<th>Weight of synthetic/natural jarosite added (g)</th>
<th>Weight of soil/quartz added (g)</th>
<th>Total weight of the sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0025</td>
<td>0.4975</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>0.0050</td>
<td>0.4950</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.0100</td>
<td>0.4900</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>0.0250</td>
<td>0.4750</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

Anoxic water extraction

0.5 g (±0.0001 g) of the soil/quartz sample spiked with synthetic/natural jarosite was mixed with 20 mL of anoxic water and shaken for 3 min in an orbital shaker. Anoxic water was prepared by purging the deionised water with N₂ gas for 2 h. The suspension was filtered using the Teflon filter membrane (Teflon 0.22 µm) and the extract was acidified using concentrated (70%) HNO₃. The elemental composition of the water extract was analysed by ICP-MS. The solid residue on the Teflon filter membrane was washed off with anoxic deionised water and dried in an oven at 120°C for 2 h.

Roasting at 550°C

The dried solid residue was carefully removed from the Teflon filter membrane and was placed in a porcelain crucible and roasted at 550°C for 1 h in air in a muffle furnace (KSL1700X, High temperature muffle furnace, MTI Corporation, CA, USA).

4 M HCl extraction

After cooling to room temperature, the roasted samples were extracted with 20 mL of 4 M HCl for 30 min. The suspension was filtered using polypropylene filter membranes (Polypropylene, 0.22 µm) and the 4 M HCl extract was analysed for its composition.

5.3.5.2 Sequential extraction of jarosite containing soil/quartz samples using Cellulose Acetate filter membrane

The three-step sequential method (Li et al., 2007) was repeated for soil and quartz samples spiked only with 5% of synthetic or natural jarosite using the Cellulose Acetate filter membranes (0.45 µm) instead of Teflon filter membrane to filter the anoxic water extract. Cellulose Acetate filter membrane with 0.45 µm pore size was selected based on a preliminary experiment which showed a negligible amount of jarosite (i.e. both synthetic and natural) passing through the filter membrane. In this particular experiment, the dried solid residue together with the Cellulose Acetate filter membrane was
placed in a porcelain crucible and roasted at 550°C for 1 h in air in a muffle furnace. Examination of Teflon filter membranes after roasting showed that these membranes coalesced into a lump that precluded such extraction with 4 M HCl. Roasted soil residue with the Cellulose Acetate filter membrane was then subjected to the 4 M HCl extraction and the 4 M HCl extract was analysed for its composition. Similar to the manner discussed in section 5.3.5.1, blank samples containing soil/quartz/Cellulose Acetate filter membrane were analysed and the results of the jarosite spiked soil/quartz samples were corrected using the results of the corresponding blank samples. Each treatment was duplicated. Recovered S weight percentage was calculated for each spiking rate as described in section 5.3.5.6.

5.3.5.3 Preparation of samples to investigate the effect of roasting temperature

Pure synthetic/natural jarosite samples were roasted at temperatures of 150°C, 250°C, 350°C, 450°C and 550°C for 1 h in the muffle furnace. The jarosite samples roasted at different temperatures were then analysed for changes in mineralogy using XRD analysis.

5.3.5.4 Preparation of samples to investigate the solubility kinetics of roasted and unroasted jarosite samples

There exists the possibility that solubility kinetics of the jarosites used in this study may vary from Li et al. (2007), due to differences in the composition of jarosites between this study and Li et al. (2007). Therefore, the solubility of pure, unroasted and pure, roasted jarosites in 4 M HCl over time was investigated to understand the solubility kinetics of jarosite used in the present study. 0.2 g of pure, unroasted and pure, roasted (at 550°C) synthetic and natural jarosite samples were extracted with 8 mL of 4 M HCl for time periods of 15, 30, 60, 90, 120, 180 and 240 min, and the recovered Fe, S and K contents were determined by ICP-MS. Recovered Fe/S/K weight percentage at each extracted time period was calculated as described in section 5.3.5.6.
5.3.5.5 Preparation of samples to investigate the effect of roasting temperature on 4 M HCl and aqua-regia extraction

Two sets of 5% synthetic and natural jarosite spiked quartz samples were prepared and roasted at 150°C, 250°C, 350°C, 450°C and 550°C for 1 h in the muffle furnace. Each 5% spiked sample consisted of 0.05 g of synthetic/natural jarosite and 0.95 g of quartz. One sample set was extracted with 40 mL of 4 M HCl (for 30 min) and the other set digested with aqua-regia and the recovered S contents were determined by ICP-MS. Recovered Fe/S/K weight percentage was calculated as described in section 5.3.5.6. The obtained recovered Fe/S/K weight percentage was then corrected for the weight loss that occurred at each temperature as determined using thermogravimetric and differential thermal analyses (TGA/DTA) analysis.

5.3.5.6 Calculations

The recovered Fe/S/K weight percentage was calculated from the Fe/S/K content in the 4 M HCl extract after the extraction and from the initial Fe/S/K content in synthetic/natural jarosite at each spiking rate. Fe/S/K content in the initially spiked synthetic and natural jarosite was calculated from the total-Fe/S/K content determined from aqua-regia digestion.

5.4 Results

5.4.1 Characteristic properties of synthetic and natural jarosite

The mineralogy of synthetic and natural jarosites was confirmed by XRD. Based on the molecular formula of jarosite (i.e. AB$_3$(SO$_4$)$_2$(OH)$_6$), the typical A:B:SO$_4^{2-}$ ratio is 1:3:2. However, the synthetic jarosite deviated appreciably from this ideal composition. The elemental concentration of synthetic and natural jarosites is shown in Table 5.2. The chemical characteristics of soil samples are also presented in Table 5.2. The (K$^+$+H$_3$O$^+$):Fe:SO$_4^{2-}$ ratio of synthetic jarosite was 1:2.1:2, a lower ‘B’ content than the ideal ratio indicating a relative deficiency in Fe. According to Kubiz (1970), this
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

Charge deficiency can be balanced by adding H₂O (which is formed by joining the hydroxyl groups with protons), hence the average molecular formula derived for the synthetic jarosite was \((\text{H}_2\text{O}^+_{0.04})\text{K}_{0.96}\text{Fe}_{2.13}\text{(SO}_4\text{)}_{2.5}(\text{OH})_{3.39}(\text{H}_2\text{O})_{2.61}\). The calculated \((\text{K}+\text{Na}^+ + \text{H}_3\text{O}^+): (\text{Fe}^{3+}\text{+Al}^{3+}):\text{SO}_4^{2-}\) ratio of natural jarosite was closer to the ideal Fe:S ratio of 3:2, resulting in an average molecular formula of \((\text{H}_2\text{O}^+_{0.29})\text{Na}_{0.32}\text{(K}_{0.38}\text{Fe}_{2.96}\text{Al}_{0.04}\text{(SO}_4\text{)}_{2.5}(\text{OH})_{6}\). Unlike the natural jarosite sample used in Li et al. (2007) which was rich in Na \((\text{Na}_{0.88}\text{K}_{0.12}\text{Fe}_{2.96}\text{Al}_{0.04}\text{(SO}_4\text{)}_{2.5}(\text{OH})_{6}\), both synthetic and natural jarosite samples used in the present study were rich in K.

Table 5.2. Some of the chemical properties of soils, synthetic and natural jarosite samples

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Total organic carbon</th>
<th>Fe</th>
<th>S</th>
<th>K</th>
<th>Al</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%)</td>
<td>(mmol g⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic jarosite</td>
<td>0.0</td>
<td>4.9</td>
<td>4.6</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Natural jarosite</td>
<td>1.6</td>
<td>4.2</td>
<td>2.8</td>
<td>0.5</td>
<td>0.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight (%)</th>
<th>Richmond</th>
<th>4.65</th>
<th>2.95</th>
<th>0.06</th>
<th>n.d.</th>
<th>4.96</th>
<th>n.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clarence</td>
<td>1.78</td>
<td>6.27</td>
<td>0.03</td>
<td>n.d.</td>
<td>3.07</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

n.d. not determined

Synthetic jarosite consisted of spheroidal particles while the morphology of natural jarosite was euhedral crystals (Fig. 5.1a, b).
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

5.4.2 Recovery of S

As anticipated, a negligible amount of water-soluble sulfate was recovered during the anoxic water extraction step from both synthetic and natural jarosite spiked soil and quartz samples.

However, the recovery of S from the jarosite spiked soil/quartz samples after roasting at 550°C for 1 h followed by 4 M HCl extraction was substantially lower compared to that obtained by Li et al. (2007). The recovery of S from both synthetic and natural jarosite accounted for only 40-50% of the initially added jarosite content (Fig. 5.2a, b). The experiment was repeated and essentially produced identical results.

Interestingly, the S recovery regardless of which jarosite used was much lower when mixed with quartz than when mixed with soil (Fig. 5.2a, b). This observation starkly contrasts to the observations of Li et al. (2007), who reported a ~ 100% recovery from natural jarosite (5%) spiked in quartz. Several experiments as discussed below were undertaken to investigate this discrepancy.

Fig. 5.1. Morphology of (a) synthetic jarosite and (b) natural jarosite. Bar indicates 1 µm
Fig. 5.2. S recoveries from jarosite spiked in Richmond and Clarence soil materials and Quartz after roasting at 550°C for 1 h followed by 4 M HCl extraction, (a) synthetic jarosite (b) natural jarosite. Error bars indicate the standard deviation of three replicates.

5.4.3 Loss of sample from retention of sample by Teflon filter membrane

Visual inspection of the Teflon filter papers clearly showed a yellow residue after the anoxic water extraction, demonstrating that jarosite was retained in the Teflon filter membrane during this step. The amount of jarosite retained by the Teflon filter membrane accounted for ~30% of the total S in the samples (Table 5.3).
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of
jarosite in acid sulfate soils

Table 5.3 Percentage of synthetic jarosite retained by the Teflon filter membrane after anoxic water
extraction of quartz samples spiked with various additions of synthetic jarosite

<table>
<thead>
<tr>
<th>Quartz + SJ* (g)</th>
<th>Weight of SJ spiked (g)</th>
<th>Percentage of the spiked SJ retained by the filter paper (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.005</td>
<td>4</td>
</tr>
<tr>
<td>0.5</td>
<td>0.010</td>
<td>22</td>
</tr>
<tr>
<td>0.5</td>
<td>0.025</td>
<td>30</td>
</tr>
</tbody>
</table>

*SJ = synthetic jarosite

To further investigate the retention of S on the filter membrane, the experiments were repeated using a
Cellulose Acetate filter membrane (0.45 µm) for soil and quartz samples that were spiked with 5%
synthetic and natural jarosite. Negligible water soluble S was measured in the anoxic water extract.
However, the use of the Cellulose Acetate filter membrane substantially increased the recovery of S
(through 4 M HCl extraction) from the roasted natural and synthetic jarosite spiked quartz samples to
45% and 70%, respectively, as opposed to the only ~5-10 % recovery of S from the corresponding
samples that used the Teflon filter membrane (Fig. 5.3a, b). Furthermore, a slight increase in S
recovery was also observed for the soil samples spiked with 5% synthetic and natural jarosite when
the Cellulose Acetate filter membranes were used compared to when the Teflon filter membranes
were used (Fig. 5.3a, b).
5.4.4 Thermal decomposition of pure synthetic and natural jarosite

In order to understand the thermal behaviour of pure jarosite, both synthetic and natural jarosite were subjected to the TGA/DTA analyses. The mass loss derivative graphs of both pure synthetic and natural jarosite samples show several weight loss stages during the heating from 100°C to 700°C (Fig. 5.4a, c). There were four distinct mass loss stages: 100°C-180°C, 200°C-270°C, 390°C-450°C and
580°C-700°C for synthetic jarosite. However, for the natural jarosite only two main weight loss stages between 280°C-420°C and 580°C-700°C were observed. The two weight loss stages between 100°C-270°C in the synthetic jarosite are attributable to the removal of adsorbed water as indicated by a weak exothermic peak around 230°C in synthetic jarosite (peak 1, Fig. 5.4b). The absence of an exothermic peak for natural jarosite near this temperature indicates the lack of appreciable adsorbed water on the natural jarosite sample. The weight loss stage between 360°C-450°C in both jarosites corresponds to the dehydroxylation of jarosite structure and the formation of yavapaiite (Drouet and Navrotsky, 2003; Smith, 2004). The intense endothermic peak at 430°C in synthetic jarosite (peak 2, Fig. 5.4b) and weak endothermic peak at 400°C in natural jarosite (peak 1, Fig. 5.4d) are indicative of the formation of yavapaiite. The weak exothermic peaks around 450°C in synthetic jarosite (peak 3, Fig. 5.4b) and around 430°C in natural jarosite (peak 2, Fig. 5.4d) represent the crystallization of hematite (Drouet and Navrotsky, 2003; Smith, 2004). The final weight loss stage from 550°C to 700°C in both jarosites is likely due to the removal of S as SO₃ (Drouet and Navrotsky, 2003; Smith, 2004).
5.4.5 Changes in mineralogy upon roasting

Roasting induced a progressive transformation of the jarosite to other mineral phases. During roasting jarosite is slowly transformed to yavapaiite-KFe(SO₄)₂ and hematite-Fe₂O₃. Both the synthetic and the natural jarosite behaved in this manner, being completely decomposed to other phases by 450°C (Fig. 5.5a, b). The transformation to yavapaiite at around 400°C has been reported previously (Dorouet and Navrotsky, 2003; Smith, 2004; Vummidi Lakshman et al., 2014), but never before at the much lower temperatures observed in this study (i.e. around 150°C) (Fig. 5.5a, b). Similar to yavapaiite, hematite also started to form at lower temperatures (i.e. around 350°C) than reported by previous studies (i.e. above 450°C) (Dorouet and Navrotsky, 2003; Smith, 2004; Vummidi Lakshman et al., 2014). The
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

XRD data indicate that the amount of yavapaiite and hematite formed as a result of roasting increased with increasing roasting temperatures (Fig. 5.5a, b).
Fig. 5.5. Change in mineralogy during roasting: a) synthetic jarosite, b) natural jarosite where (a), (b), (c), (d), (e), (f) represent the patterns of pure synthetic and natural jarosite roasted at 150°C, 250°C, 350°C, 450°C and 550°C, respectively.
5.4.6 Solubility kinetics of roasted and unroasted pure synthetic and natural jarosite samples in 4 M HCl

From Fig. 5.6b, c it is evident that the extractable amount of S and K in roasted (i.e. at 550°C) synthetic and natural jarosite is independent from the extraction time and hence complete recovery was possible within 30 min. In contrast, the recovery of both S and K from unroasted synthetic and natural jarosite showed an increase with the increase of extraction time (Fig. 5.6b, c). This observation is in agreement with Li et al. (2007) who reported an increase in the extractability of roasted jarosite compared to unroasted jarosite.

Fig. 5.6. 4 M HCl extracted (a) Fe weight percentage (b) S weight percentage (c) K weight percentage from roasted and unroasted pure synthetic and natural jarosite at different extraction time periods. Where SJ=synthetic jarosite NJ=natural jarosite. Error bars indicate the standard deviation of three replicates.
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

5.4.7 Elemental recovery from jarosite spiked quartz samples roasted at different temperatures through 4 M HCl extraction and aqua-regia digestion

High temperatures yielded the largest extractable S contents by 4 M HCl extraction for synthetic (450°C ~76% S) and natural jarosite (350°C ~79%) (Fig. 5.7b). However, increasing the temperature to above 550°C diminished the extractability of S by 14% when using synthetic jarosite and by 37% for natural jarosite (Fig. 5.7b). The corresponding aqua-regia digested samples also indicated a clear decrease in recovered S content in samples roasted at 550°C compared to those roasted at 450°C (Fig. 5.7b). At 550°C, the recovered S content by aqua-regia digestion decreased by 14% and 23% for synthetic and natural jarosite spiked quartz samples respectively (Fig. 5.7b). Similar to S, the 4 M HCl extractable Fe recovery from both synthetic and jarosite spiked quartz samples also decreased substantially in samples roasted at 550°C compared to those roasted at 450°C (Fig. 5.7a). Aqua-regia digested Fe recovery showed a constant recovery (~95% for synthetic jarosite and ~80% for natural jarosite) over the roasting temperatures up to 350°C and a slight decrease by 11% and 8% above 350°C for synthetic and natural jarosite, respectively (Fig. 5.7a). Unlike both S and Fe, the 4 M HCl extractable K recovery was fairly constant (~70% for synthetic jarosite and ~90% for natural jarosite) over the roasting temperature ranges from 450°C to 550°C (Fig. 5.7c). Aqua-regia digested K recovery also showed a constant recovery over the roasting temperatures from 150°C to 550°C (Fig. 5.7c).
Fig. 5.7. Recovery of Fe, S and K from 5% synthetic and natural jarosite spiked quartz samples: (a) Fe weight percentage (b) S weight percentage (c) K weight percentage. Where SJ-synthetic jarosite NJ-natural jarosite. Error bars indicate the standard deviation of three replicates.

5.5 Discussion

Quantification of jarosite spiked in soils and quartz using the method of Li et al. (2007) is neither accurate nor predictable. In general, less than 50% of jarositic-S was extractable by this method, in contrast to the experience of Li et al. (2007), who reported 100% S recovery.

These lower recoveries are attributable to the retention of some jarosite by Teflon filter membranes used during the initial washing step, and also the potential liberation of S as SO₂/SO₃ and/or the occlusion of S in the hematite that forms during roasting.
5.5.1. Retention of sample by Teflon filter membrane and the increased S recovery by using Cellulose Acetate filter membrane

There was a loss of jarosite spiked in soil and quartz materials during the filtration of the anoxic water extract where jarosite particles have either been trapped within or on the Teflon filter membranes. The proportion of jarosite retained by the filter membrane accounted for ~30% in the 5% spiked jarosite contents (Table 5.3). Accordingly, only 70% of the initial jarosite spike was left for subsequent roasting and recovery by 4 M HCl extraction.

However, this issue of sample retention by the Teflon filter membrane during the filtration step was lessened by replacing it with a Cellulose Acetate filter membrane (Fig. 5.3). As evident from Fig. 5.3, S recovery from jarosite spiked in quartz increased substantially (up to 45-70%) when Cellulose Acetate filter membranes were used, while only a slight increase in S recovery from jarosite spiked soils were observed.

5.5.2 Lower 4 M HCl extractable S availability in 550°C roasted samples

In contrast to the observations made by Li et al. (2007), our investigations on the 4 M HCl extractable S recovery with various roasting temperatures showed the highest S recovery from samples roasted at 450°C and 350° for synthetic jarosite and natural jarosite spiked quartz samples, respectively (Fig. 5.7b). The data show a clear decrease in the 4 M HCl extractable S content in synthetic jarosite spiked quartz from 450°C to 550°C and in natural jarosite spiked quartz samples from 350°C to 550°C (Fig. 5.7b). The decrease in the 4 M HCl extractable S content accounted for 14% and 37% for synthetic and natural jarosite spiked quartz samples, respectively (Fig. 5.7b). Similar to the 4 M HCl extraction, the aqua-regia digestion of the corresponding samples showed a decrease in recovered S content when the samples were roasted at 550°C (Fig. 5.7b). According to the XRD data, both yavapaiite (KFe(SO$_4$)$_2$) and hematite (Fe$_2$O$_3$) were the dominant minerals at both 450°C and 550°C and jarosite was no longer present at both temperatures (Fig. 5.5). Thus, the origin of the recovered S from 4 M
HCl extraction at both temperatures would have been mainly from yavapaiite. Therefore, it is speculated that the observed loss of S (while the recovery of K was being maintained) when roasting the sample above 450°C could be attributable to either the liberation of SO₂/SO₃ through yavapaiite decomposition, or the occlusion of S within the hematite that formed during the roasting. As clearly indicated in Figs. 5.4a,c, there was a slight change in weight before 550°C in the synthetic and natural jarosites which could be attributable to the loss of S as SO₂/SO₃.

Sulfate can be irreversibly sorbed to hematite and this effect is greatest at acidic (~pH 3) conditions (Parfitt and Smart, 1978; Turner and Kramer, 1992). Accordingly, sulfate released from yavapaiite during the extraction could have been sorbed and occluded in the hematite, thus preventing its recovery. Given the partial solubility of hematite during the 30 min 4 M HCl extraction (~50%) it is unlikely to expect the release of all of these occluded sulfate in hematite (Fig. 5.6a). Further, the XRD data indicates an increase in hematite content with the increase in roasting temperature (Fig. 5.5). As a consequence, it is expected that a larger amount of sulfate could have been adsorbed and occluded in hematite at roasting temperatures of 550°C than at 450°C / 350°C. However, roasting at 450°C to enhance the S recovery is not an option as a temperature of at least 550°C is required to ensure the removal of pyrite from samples.

Although it has not been investigated in this study and in Li et al. (2007), it is necessary to further examine the behaviour of pyrite during roasting. As discussed in Hu et al. (2006) and Cheng et al. (2013), thermal decomposition of pyrite in air results in the formation of iron sulfates (i.e. FeSO₄ and Fe₂(SO₄)₃) in addition to hematite and SO₂. Therefore, subsequent 4 M HCl extraction of the roasted sample could extract these sulfates as well as sulfate in yavapaiite (which is produced from thermal decomposition of jarosite). Hence, if pyrite is actually present in the sample and if sulfates are generated during the roasting step, the calculated jarosite content could be overestimated.
Chapter 5: Assessment of three-step sequential extraction procedure for the quantification of jarosite in acid sulfate soils

5.6 Conclusions

Recovery of synthetic and natural jarosite spiked in soil and quartz was attempted using the sequential extraction procedure of Li et al. (2007). The recovered S content from both synthetic and natural jarosite and soil and quartz admixtures was substantially lower (< 50%) than was reported in Li et al.’s (2007) study.

The observed substantially lower S recoveries from both jarosites in the present study were partially explained by the retention of jarosite by the Teflon filter membrane during the filtration of anoxic water extract (which accounted for up to 30% of jarositic-S). The sample retention effect by Teflon filter membrane was overcome by modifying the method via replacement of Teflon filter membranes with Cellulose Acetate filter membranes and the inclusion of the Cellulose Acetate membranes with the samples for roasting. This modification of Li et al.’s (2007) method resulted in a substantial improvement (although still incomplete) in the S recoveries from both jarosite samples.

Our further examinations showed that the highest 4 M HCl extractable S recovery was from samples roasted at 450°C but not from those roasted at 550°C as suggested by Li et al. (2007). We speculate that the observed lower 4 M HCl-S recovery at 550°C is likely to be due to either the liberation of SO₂/SO₃ through yavapaiite decomposition, or the occlusion of S within the hematite that formed during the roasting.

5.7 Acknowledgements

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Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments
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See Appendix for signed author contribution statements.
6.1 Abstract

Schwertmannite and jarosite are two of the main secondary Fe(III) minerals commonly found in acidic, iron and sulfate-rich environments such as acid mine drainage and coastal acid sulfate soils (CASS). Both minerals exert major influence on the water and soil quality in these environments. While there are many studies conducted on the stability of these two minerals under controlled laboratory conditions, the behaviour of schwertmannite and jarosite under field conditions and the factors influencing their behaviour have not been investigated directly. In the present study, we examined the net transformation of introduced schwertmannite and jarosite samples incubated in a typical acidic CASS environment. Pure (synthetic) schwertmannite and jarosite samples were exposed to the two main chemical regimes: 1) aerobic-acidic water column; and 2) anaerobic-neutral sediment in a CASS environment. Changes in mineralogy, micromorphology, and composition of schwertmannite and jarosite samples were monitored over a period of 12 months. Schwertmannite that was suspended either in the water column or buried in sediments transformed to goethite by the end of 12 months but more quickly in anoxic, reducing sediments. However, the schwertmannite incubated in the acidic water column was transformed at a much faster rate than those reported for acidic and aerobic conditions in the laboratory. Jarosite incubated in both water column and sediments also transformed to goethite but at a much slower rate than schwertmannite. Dissimilatory microbial reduction and Fe\(^{3+}\)catalysed transformation likely played a major role in accelerating the transformation of both minerals to goethite in sediments. It appears that the transformation of both minerals incubated in the water column was sensitive to the hydrological conditions and fluctuations in the water column in relation to antecedent rainfall. In comparison, the sediment’s geochemistry was relatively stable and consequently the rate of transformation and dissolution of both schwertmannite and jarosite in this environment did not appear to be appreciably affected by variable hydrology.
Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments

6.2 Introduction

Acid sulfate soils (ASS) cover around 13 million ha of land worldwide and are considered to be a significant problem globally (Mensvoort and Andriesse, 2005; Sullivan et al., 2012). Acid mine drainage (AMD) can display similar geochemistry as the drainage from ASS and is a major global issue in its own right (Bigham and Nordstrom, 2000). Two of the main environmental hazards associated with ASS and AMD are acidity generation and release of trace metals.

In Australia, ~ 58,000 km² of ASS are distributed across the coastal areas (Fitzpatrick et al., 2010). Many of the coastal acid sulfate soils (CASS) in eastern Australia are located in low-lying floodplain areas and are underlain by sulfidic sediments deposited during the last sea level rise (i.e. <10,000 years ago) (Walker, 1972; Lin and Mellville, 1992; Sammut et al., 1996; White et al., 1997). A common feature of CASS landscapes in eastern Australia is the network of artificial drains which has been constructed mainly for flood mitigation and to enable agriculture (Lin and Mellville, 1992; Sammut et al., 1996; White et al., 1997). Acidity generation and discharge by CASS in these low-lying floodplain areas are highly dependent on the floodplain water balance (Sammut et al., 1994; White et al., 1997; Johnston et al., 2004) which is determined largely by rainfall, evapotranspiration, and the inflows and outflows of both surface and groundwaters (Walker, 1972; White et al., 1997; Johnston et al., 2003a,b, 2004, 2005b). The climate in Australia is prone to huge seasonal variations and such dynamic shifts in rainfall and hydrology are mirrored in the dynamics of waterways geochemistry in CASS landscapes (Walker, 1972; White et al., 1997; Johnston et al., 2003a,b, 2004, 2005b).

Schwertmannite (Fe₈O₈(OH)₆(SO₄)₂) and jarosite (KFe₃(SO₄)₂(OH)₆) are the two main secondary Fe(III) minerals commonly found in ASS and AMD. Jarosite has long been identified in various ASS landscapes in Australia (Lin et al., 1998; Fitzpatrick, 2003; Fitzpatrick et al., 2010) while schwertmannite has been located more recently (Sullivan and Bush, 2004). In natural environments, schwertmannite (Equation 6.1) and jarosite (Equation 6.2) are formed as a result of iron sulfide
Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments

oxidation (Bigham and Nordstrom, 2000; Kawano and Tomita, 2001). Schwertmannite is also known to precipitate directly from acidic, sulfate rich waters (Bigham and Nordstrom, 2000). The stability of both minerals is strongly dependent on the redox status, pH, and the Fe$^{3+}$ and SO$_4^{2-}$ concentrations in their contacting water (Yu et al., 1999; Cornell and Schwertmann, 2003; Majzlan et al., 2004; Regenspurg et al., 2004; Keene et al., 2010). Schwertmannite often occurs in oxidised systems where pH ranges from 2.8 to 4.5 and SO$_4^{2-}$ concentrations span the range of 1000-3000 mg L$^{-1}$. Jarosite also exists in oxidised systems, however, at much lower pH (< 3) values and at much higher SO$_4^{2-}$ concentrations (> 3000 mg L$^{-1}$) (Bigham et al., 1996a).

\begin{align*}
8Fe^{3+} + SO_4^{2-} + 14H_2O & \rightarrow Fe_8O_8(OH)_6(SO_4) + 22H^+ \quad \text{(6.1)} \\
3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2O & \rightarrow KFe_3(SO_4)_2(OH)_6 + 6H^+ \quad \text{(6.2)}
\end{align*}

Schwertmannite and jarosite progressively transform to goethite and/or other thermodynamically stable mineral phases, resulting in the release of a substantial amount of acidity and previously held trace metals (Bigham and Nordstrom, 2000; Welch et al., 2007) (Equations 6.3 and 6.4). The release of acidity and mobilization of trace metals can impact on both terrestrial and aquatic environments (Acero et al., 2006; Welch et al., 2008).

\begin{align*}
2H_2O + Fe_8O_8(OH)_6(SO_4) & \rightarrow 8FeOOH + SO_4^{2-} + 2H^+ \quad \text{(6.3)} \\
3H_2O + KFe_3(SO_4)_2(OH)_6 & \rightarrow 3Fe(OH)_3 + 2SO_4^{2-} + 3H^+ + K^+ \quad \text{(6.4)}
\end{align*}

While both minerals are important sources of acidity, these minerals are also known to affect the mobilization of the toxic trace metals in ASS by acting as scavengers. Schwertmannite, because of its characteristically nanoparticulate size and larger surface area, is an efficient sorbent for many trace metals (Webster et al., 1998; Bigham and Nordstrom, 2000). Jarosite has a chemical structure that
allows the substitution of a variety of metals, thereby also acting as an effective scavenger for trace metals (Baron and Palmer, 1996; Dutrizac and Jambor, 2000; Welch et al., 2007).

In natural environments, the stability of schwertmannite and jarosite is influenced by a range of physio-chemical factors including: pH, redox status, temperature, the nature and concentration of cations, and anions, and by the presence of organic matter and silica (Peine et al., 2000; Regenspurg et al., 2002; Gasharova et al., 2005; Smith et al., 2006; Knorr and Blodau, 2007; Davidson et al., 2008) as well as by the activity of microorganisms (Lovley, 1991; Roden and Zachara, 1996).

Decomposition of organic matter by microorganisms often involves dissimilatory Fe(III) reduction (Lovley and Philips, 1986; Lovley, 1997). Poorly crystalline secondary Fe(III) minerals such as schwertmannite and jarosite in the subaqueous sediments in ASS and AMD environments are a good source of terminal electron acceptors for dissimilatory Fe(III) microorganisms (Bridge and Johnson, 2000). Microbial reductive dissolution of such minerals generates alkalinity, SO$_4^{2-}$, Fe$^{2+}$ and often a marked increase in pH ($> 5$) (Peine et al., 2000; Regenspurg et al., 2002; Burton et al., 2007; Keene et al., 2010; Johnston et al., 2011a,b). When pH is $> 5$, sorption of Fe$^{2+}$ derived from microbial reductive dissolution tends to initiate the Fe$^{3+}$ catalysed transformation of schwertmannite to goethite in anoxic environments (Burton et al., 2007, 2008b).

In reductive, anoxic and aerobic, oxic environments, pH is a key parameter that governs the rate of schwertmannite transformation to goethite. There is a positive correlation with pH and the rate of transformation (Regenspurg et al., 2004; Jönsson et al., 2005; Schwertmann and Carlson, 2005; Paikarary and Peiffer, 2010). Temperature also plays a role in regulating the stability of schwertmannite, where, under acidic pH (3-4) conditions, lower temperatures (4-10°C) retard the transformation of schwertmannite to goethite (Jönsson et al., 2005; Knorr and Blodau, 2007). The presence of anions such as AsO$_4^{3-}$ and Cr$_2$O$_7^{2-}$ are also known to stabilize schwertmannite under acidic oxidising conditions (pH 3-4) (Fukushi et al., 2003a,b; Regenspurg and Peiffer, 2005). It is therefore not surprising then that the reported time frames for complete transformation of
schwertmannite to goethite under oxidising conditions varies from a few months to several years (Bigham et al., 1996a; Jönsson et al., 2005; Schwertmann and Carlson, 2005; Acero et al., 2006).

The Fe$^{2+}$ catalysed transformation of schwertmannite/jarosite/ferrihydrite at circumneutral pH (6.5) under reducing conditions was reported to be inhibited by the presence of both Si (with the Si concentrations being equal to or greater than the pore water Fe$^{2+}$ concentrations) and natural organic matter (NOM) (25-150 mg L$^{-1}$) (Jones et al., 2009). However, more recent research by Burton and Johnston (2012) showed that when the Fe$^{2+}$ concentrations greatly exceeded (> 5 mM) those of Si, especially in microbially reducing systems, the effect of Si was minor. Similar to under oxic, acidic conditions, the presence of As (III) and As(V) reportedly inhibited the Fe$^{2+}$ catalysed transformation of schwertmannite under reducing and near neutral pH (6.5) conditions (Burton et al., 2010).

Jarosite, a far more stable mineral than schwertmannite, will also transform to more stable mineral phases in natural environments (Welch et al., 2008). The stability of jarosite is dependent mainly on solution chemistry (e.g. pH, SO$_4^{2-}$, anions, cations, complexing agents) and mineralogy (i.e. the substituting anion/cation in the jarosite structure) (Drouet and Navrotsky, 2003; Welch et al., 2008; Keene et al., 2010). Previous research has found that jarosite dissolution is incongruent under both highly acidic (pH 2-4) and neutral to alkaline (pH 5.5-8) conditions, resulting in the release of K$^+$ and SO$_4^{2-}$ to the aqueous phase (Gasharova et al., 2005; Smith et al., 2006; Welch et al., 2008). Goethite coatings have been observed to form on the surface of jarosite during the initial stages of dissolution under alkaline conditions, physically preventing further jarosite dissolution (Gasharova et al., 2005; Smith et al., 2006). The presence of Fe complexing agents such as humic acids in the vicinity of jarosite can accelerate the rate of jarosite dissolution by inducing Fe detachment, thereby inhibiting the formation of a Fe oxyhydroxide coating on the surface of the jarosite crystals (Gasharova et al., 2005). The importance of NOM for the rapid dissolution of jarosite has also been noted (Chu et al., 2006; Zhu et al., 2008). In addition to microbially-induced reductive dissolution, jarosite is subjected
to appreciable abiotic dissolution by S$^2-$ at pH levels 5-6 in tidally-inundated CASS (Johnston et al., 2012).

CASS landscapes are often subject to alternating cycles of dry and wet conditions due to the seasonality of rainfall. During the dry season, drainage induced oxidation of pyrite in underlying sediments results in the formation of secondary Fe(III) minerals such as schwertmannite and jarosite. Thus, both schwertmannite and jarosite can be abundant in the surface and near-surface sediments in CASS landscapes (Walker, 1972; Willet and Walker, 1982; Sullivan and Bush, 2004; Johnston et al., 2009c). In the subsequent wet season, waterways are acidified by the acidic drainage from the surrounding CASS (Sammut et al., 1996; White et al., 1997; Johnston et al., 2004). Furthermore, the progressive development of anoxic, reducing conditions with prolonged inundation during the wet season promotes the dissolution of secondary Fe(III) minerals (Johnston et al., 2005b).

Much research on CASS landscapes has focused on understanding the effects of drainage, prolonged inundation (due to flooding) and the vegetation cover on the sediment/water geochemistry (Sammut et al., 1996; Johnston et al., 2003a,b, 2004, 2005b, 2009b,c), ground water discharges (Santos and Eyre, 2011) and understanding the sedimentary Fe and S geochemistry of reduced inorganic sulfur minerals in CASS (Burton et al., 2006a,b,d,f, 2007, 2008b; Keene et al., 2011). However, the net transformation of schwertmannite and jarosite in CASS, the effect of fluctuating hydrology and geochemistry and the potential in-situ factors that accelerate/impede mineral transformations in CASS have not been investigated. Understanding the transformed products of schwertmannite and jarosite is important for understanding their interactions between soil and water quality (Bush and Sullivan, 2004; Johnston et al., 2009c). This study was undertaken to improve our understanding of these important minerals by examining the net transformation/dissolution of both schwertmannite and jarosite in 1) the normally acidic and aerobic water column, and 2) the normally neutral and anaerobic sediment, of a chronically acidified natural CASS system over a period of one year.
6.3 Materials and Methods

6.3.1 Study site

The field site of this study is located in the Tuckean Swamp in the coastal flood plain of the lower Richmond River, north-eastern NSW, Australia (28°57’S, 153°23’E) (Fig. 6.1). The Tuckean Swamp is an estuarine backswamp of the Richmond River catchment covering 5000 hectares of land and having a surface elevation of 1 m Australian Height Datum (AHD) (Tulau, 1999). Approximately 34,000 hectares in the Richmond River catchment is underlain by ASS deposited during the Holocene period (Tulau, 1999). More than 75% of the CASS in the Tuckean Swamp are partially oxidised, hence the soil pH is usually < 3.5 (Sammut et al., 1996; Tulau, 1999). A typical soil profile of the Tuckean Swamp comprises a dark organic matter rich surface layer, then a sub-surface layer containing red and orange coloured goethite and hematite segregations overlying estuarine clay with jarosite segregations which overlies a gel-like unoxidised estuarine clay (Tulau, 1999 and references therein).

Before European settlement, the Tuckean Swamp was a tidal brackish estuarine backswamp linked to the Richmond River (Tulau, 1999). This swamp has been greatly impacted by land clearing for agriculture and the excavation of canals that lowered the water table (Tulau, 1999; Taffs et al., 2008; Santos et al., 2013). As a result of the lowered water table, buried sulfidic sediments have been exposed by downward diffusion of air during dry periods, resulting in oxidation of pyrite (Tulau, 1999; Taffs et al., 2008). Acidity generated by the oxidation of pyrite freely discharges to the drains resulting in widespread and chronic waterway acidification (to pH < 3) (Sammut et al., 1996; Tulau, 1999; Taffs et al., 2008). The intrusion of tidal water to the swamp during high tides and the discharge of water from the swamp during low tide are regulated by the Bagotville Barrage constructed a few kilometres above the Tuckean Broadwater (Fig.6.1).
Prior to European settlement, tea-tree (*Melaleuca quinquenervia*) was the dominant vegetation type in the Tuckean Swamp with lesser areas of sedgeland and wet meadows (Sammut et al., 1996; Tulau, 1999). Currently, the dominant vegetation type in the swamp is pasture (Eyre et al., 2006).

The Richmond River catchment is located in a sub-tropical climatic region and experiences two distinct seasons (i.e. dry and wet) (Wong et al., 2010). The wet season occurs in summer (from December to April) with heavy tropical rainfall and major flooding. The dry season occurs in winter with the driest months from August-November (Sammut et al., 1996; Eyre, 1997; Eyre and Twigg, 1997; Tulau, 1999). Accordingly, catchment flows are highly variable (Eyre, 1997; Eyre and Twigg, 1997). The average annual rainfall in the local region ranges from 1300-1800 mm with ~65% of the annual rainfall being received during summer (Eyre and Twigg, 1997; Eyre and Pont, 2003). Major flooding and overbank inundation can result in the almost complete deoxygenation of the lower 60 km of the Richmond River, largely due to the decomposition of flood intolerant vegetation (Eyre et al., 2006; Wong et al., 2010). Major fish kills are also well documented in this region (Eyre et al., 2006; Wong et al., 2010).

Groundwater flow from the flood plain is one of the sources of acidic water inputs to the drains in this study area and is highly variable between dry and wet seasons (dry season 0.09-0.16 m$^3$ s$^{-1}$ and wet season 0.56-0.89 m$^3$ s$^{-1}$ (de Ways et al., 2011; Santos and Eyre, 2011; Santos et al., 2011). The Tuckean Swamp consists of a few drains which connect to the Main Drain (3-5 m deep). The sampling area of this study was located near the Main Drain (Fig. 6.1). The water in the drains in this area of the Tuckean Swamp are generally highly acidic (average pH 3.2-3.5), however, the pH in these drains can vary from 1.8-7.2 which is being controlled by the antecedent rainfall (Tulau, 1999 and references therein).
Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments

Fig. 6.1. Location of the study site in the Tuckean Swamp, NSW, Australia (adapted from Sullivan and Bush, 2004).
6.3.2 Sample preparation

6.3.2.1 Synthesis of schwertmannite

Schwertmannite was synthesized using the method described in Regenspurg et al. (2004). 273 g of FeSO$_4\cdot 7$H$_2$O was dissolved in 30 L of deionised water followed by addition of 150 mL of 30% H$_2$O$_2$ in a 75 L plastic container. The entire solution was mixed thoroughly and left for 24 h for the freshly formed schwertmannite to precipitate. After 24 h, the supernatant was removed and replaced with ~30 L of deionised water twice a day for a week to remove soluble ions. The schwertmannite slurry was then transferred into a shallow plastic tray and dried at 40°C for a week. The resulting dried schwertmannite solid was gently crushed to produce aggregates that were around 2 mm in diameter to avoid loss from the Nylon sachet bags which inserted in the water column and in the sediments (see section 6.3.2.3).

6.3.2.2 Synthesis of jarosite

Jarosite was synthesised according to the method suggested by Baron and Palmer (1996). 172 g of Fe$_2$(SO$_4$)$_3\cdot 5$H$_2$O and 56 g of KOH were dissolved in 1000 mL of deionised water. The beaker containing this mixture was heated on a hot plate with continuous stirring to 95°C at 1 atm for 4 h. After 4 h, the synthesized jarosite was allowed to settle and subsequently washed 4 times with deionised water to remove soluble ions. The washed precipitate was then dried in an oven at 110°C for 24 h. Approximately 100 g of jarosite was synthesized at the end of the synthesis process.

6.3.2.3 Preparation of small mineral bags

Fine meshed nylon (1µm, NITEX nylon mesh) sachet bags containing 0.5000 g (±0.0001) of either the schwertmannite or the jarosite were sealed prior to incubation.
6.3.3 Insertion of schwertmannite and jarosite samples into the sediment and water column

A sachet bag containing the mineral sample was placed into a 10 mL polypropylene vial: three such vials containing the same mineral were placed in a 120 mL polypropylene vial. The walls of both the 10 mL and 120 mL polypropylene vials had been pre-drilled with multiple holes (~ 4 mm in diameter) to allow the free movement of surface and ground waters through the samples when placed into either the sediments or the water column.

The 120 mL vials were inserted to a depth of 30 cm in the sediment adjacent the Tuckean Drain. These 120 mL vials were anchored to plastic star pickets on the shore by nylon monofilament to facilitate later removal. Six 120 mL vials, placed 0.5 m apart in the sediments, were anchored to each star picket. The distance between the anchoring locations was ~ 5 m.

Large securely fastened plastic containers were used to accommodate the 120 mL vials in the water column. Each 120 mL vial was tied to a side wall of the plastic container using nylon cable ties. The plastic container was placed into the water column on the bed of the drain. This container was leaky (from multiple pre-drilled holes ~ 4 mm in diameter in the side and top of the container) to allow free passage of the drain water through the container. The container was anchored to a star picket on the shore. Each container consisted of twelve of the 120 mL vials allowing 12 separate samplings for each mineral.

6.3.4 Sampling and preparation

A total of twelve 120 mL vials were collected every month: six from the sediments (three of schwertmannite and three of jarosite) and six from the water column (three of schwertmannite and three of jarosite).

Each 120 mL vial placed in sediments was carefully pulled out and transferred to a N₂ purged sealed bag. Each 120 mL vial in the plastic container kept in the water column was placed into sealed bag.
The containers holding the water column samples were immediately re-inserted back in the water column. The sealed bags containing 120 mL vials collected from the sediments and the water column were kept at 4°C during transportation to the laboratory. Immediately upon arrival, the 120 mL vials removed from sediment were transferred into an anaerobic chamber. Inside the anaerobic chamber, the sachet bags containing schwertmannite and jarosite were carefully taken out from the vials, opened up and transferred to smaller plastic weighing trays. Schwertmannite and jarosite collected from sediments were allowed to dry in N₂ atmosphere inside the anaerobic chamber. Schwertmannite and jarosite removed from the plastic container in the water column were opened and transferred to plastic weighing trays and left to dry in air. Care was taken to minimise contamination when opening the vials and sachet bags as the walls of vials and bags were usually surrounded by debris. After the mineral samples were dried, they were finely ground and then analysed for mineralogy, micromorphology and elemental composition. Schwertmannite and jarosite samples collected from sediments were always stored inside an anaerobic chamber in closed glass vials (10 mL, 16×100 mm, Serum Vials) until they were analysed.

6.3.5 Aqueous phase properties

Surface waters were sampled and stored in acid-cleaned 15 L polypropylene containers with zero-head space. The pH and redox potential of surface water and the sediments were measured in the field on each sampling occasion. Sediment samples were collected using a push corer and directly transferred to 50 mL polypropylene vials. The vials were completely filled and placed in N₂ purged sealed bag at 4°C until arrival at the laboratory. Sediments pore water samples were extracted within 24 h of sample collection by centrifugation (3000 rpm, 15 min) of the 50 mL polypropylene vials filled with sediments. Surface and pore water samples were acidified with HNO₃ and then filtered using syringe filters (< 0.45 µm).
Fe$^{2+}$ was determined by adding aliquots of pore water to 1,10-phenanthroline buffer solution (APHA, 2005) and subsequent measurement of the absorbance at 510 nm by UV-Visible spectrophotometry (UV-Visible spectrophotometer, HACH).

The concentrations of S, Fe, Ca, K, Mg, Na, Al, Cl, PO$_4^{3-}$ and trace metals (Mn, Se, Pb, Ni, Cu, Zn, Ag, Hg, As, Cd and Cr) in both surface and pore waters were measured using inductively coupled plasma mass spectrometry/optical emission spectrometry (ICP-MS/OES) (APHA, 2005). Dissolved organic carbon (DOC) was determined only for surface water samples using the total inorganic carbon/total organic carbon analyser (Aurora1030, TIC/TOC analyser).

Based on the water chemistry data (i.e. pH, Eh, ion concentrations) in the water column throughout the year, the activities of surface water Fe$^{3+}$, K$^+$ and SO$_4^{2-}$ over the experimental period were determined by Davies’ equation using the PhreeqC software version 2.1. The average activity of log$_a$[SO$_4^{2-}$] = -3.6±0.4 and log$_a$[K$^+$] = -4.5±0.1 were used to calculate solubility lines for schwertmannite and jarosite. The solubility constants (logK$_{sol}$) used for the calculation of solubility lines of schwertmannite, jarosite and goethite are 18, -12.51, and 1.4, respectively, taken from Bigham et al. (1996a). Another solubility line for schwertmannite was calculated using the solubility constant (9.6) presented by Majzlan et al. (2004).

### 6.3.6 Solid phase properties

Elemental and trace metals composition in schwertmannite and jarosite samples were determined by digesting the samples with 1:3 HNO$_3$:HCl (APHA, 2005) followed by ICP-MS analysis. Silica (Si) and chloride (Cl$^-$) in schwertmannite and jarosite samples were analysed using the X-ray fluorescence spectroscopy (XRF) (Epsilon 3-XL, PANalytical).

The mineralogy of schwertmannite and jarosite collected each month was determined using the X-ray diffraction (XRD) method. For XRD analysis, samples were hand ground (< 63 µm) using a porcelain mortar and pestle. Ground powdered samples were homogenised and analysed using a Bruker D4...
Diffractometer using Co Kα radiation (Bruker AXS GmbH, Germany). The diffraction patterns were recorded from 10 to 80°20 in steps of 0.05° 2θ step size with 2 seconds counting time per step. The XRD patterns were evaluated using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Germany). Schwertmannite and jarosite samples collected from the sediments and kept inside the anaerobic chamber were quickly prepared and analysed through the XRD one-by-one to minimise oxidation of the sample.

The morphology and the elemental/atomic composition of schwertmannite and jarosite collected at each month were also examined using SEM-EDXA. Similar to the manner done for XRD analysis, schwertmannite and jarosite samples collected from the sediments and kept inside the anaerobic chamber were quickly prepared and analysed through the SEM-EDXA. Samples were mounted on aluminium stubs and coated with carbon followed by gold. SEM images of the samples were taken using a SEM (LEICA, Stereo Scan 440, Working Distance (WD)=7 mm, Probe=40 pA, Electron High Tension (EHT)=10 kV). The elemental/atomic composition of the selected areas of the sample (only coated with carbon) was determined using an ISIS energy dispersive X-ray EDX0 microanalysis system (Oxford EDS detector, PB Quant Software, WD=25 mm, Probe=500 pA, EHT=20 kV) utilising a Peak-to-Background method (Sullivan and Bush, 1997).

### 6.3.7 General methods

All reagents were prepared from analytical grade chemicals and using MilliQ deionised water. All the glassware used was acid washed by soaking in 5% HNO₃ for 24 h. The pH, redox potential and EC measurements were made in the field using a smartCHEM-CP instrument (TPS). The pH, Eh and EC probes were pre-calibrated using pH 4 and 7, Zobell’s Reagent and standard EC solution (2.76 mS cm⁻¹) respectively.
6.3.8 Calculations

6.3.8.1 The rate of schwertmannite transformation

The rate of schwertmannite transformation was calculated by dividing the transformed percentage of schwertmannite by the corresponding duration of incubation similar to the procedure followed by Burton et al. (2007). The transformed percentage of schwertmannite was calculated using the amount of SO₄²⁻ released from schwertmannite after each incubation period. The schwertmannite used in this study was aggregated (section 6.3.2.1), hence the surface area was assumed to be different to that of the fine particulate schwertmannite (i.e. ~10 m² g⁻¹) synthesised through the same oxidative approach described in the literature (Regenspurg et al., 2004).

6.3.8.2 The rate of jarosite transformation

The rate of jarosite transformation was estimated from the SO₄²⁻ released over the incubation period and expressed as µmol SO₄²⁻ g⁻¹ of jarosite day⁻¹. The liberation of either SO₄²⁻ and/or K⁺ are useful proxies for jarosite dissolution (Zhu et al., 2008; Johnston et al., 2012). Sulfate release rates were then normalized per mole of jarosite, and expressed using a ratio of 1:2.

6.4. Results and Discussion

6.4.1 Initial properties of synthetic schwertmannite and jarosite

The synthetic schwertmannite contained 7.55 mmol g⁻¹ of Fe and 1.59 mmol g⁻¹ of S giving an Fe/S molar ratio of 4.75 and a derived composition of Fe₈O₈(OH)₄.₆₆ (SO₄)₁.₆₇. The SO₄²⁻ content was within in the range for schwertmannite reported by Bigham et al. (1996a).

The molecular formula of the synthetic jarosite was K₀.₈⁷(H₂O⁺)₀.₁₃Fe₁.₉₁(SO₄)₂⁺(OH)₂.₇³(H₂O)₃.₂⁷ obtained by normalizing the SO₄²⁻ content to 2, and then applying the formula presented by Kubisz (1970). Since jarosite synthesized in the present study was deficient in Fe relative to the ideal composition, the remaining positive charge was balanced by adding water (H₂O) molecules to the
Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments

formula. The water molecules were assumed to be formed by the protonation of some of the hydroxyl (OH) groups. The K:Fe:S molar ratio of synthetic jarosite of 1:2.2:2.3 (1.795 mmol g⁻¹ of K, 3.982 mmol g⁻¹ of Fe and 4.188 mmol g⁻¹ of S) was consistent with other reported values (Baron and Palmer, 1996 and references therein; Drouet and Navrotsky, 2003; Gasharova et al., 2005).

Purity of both minerals was confirmed by the XRD. Schwertmannite consisted of platy-structures having ~2 mm in diameter. These platy like structures were composed of aggregates of spheroidal particles (< 300 nm) (Fig. 6.2a). A similar micromorphology was observed for natural schwertmannite samples collected by Kawano and Tomita (2001). The synthetic jarosite samples also consisted of larger aggregations of spheroidal particles (~1-2 µm) (Fig. 6.2b).

![Fig. 6.2. Morphology of schwertmannite ((a), (c) and (e)) and jarosite ((b), (d) and (f)) before the experiment and after 12 months. (a)-(b) untreated, (c)-(d) incubated in the sediment, (e)-(f) incubated in the water column. Scale bars indicate 500 nm in (a), (c), (e) and (d), and 1 µm in (b) and (f).](image-url)
6.4.2 Properties of surface water in the drain and the pore water in sulfidic sediments

The general sediment properties varied little throughout the year with relatively constant pH ~ 6.5 and Eh ~ -250 mV (Fig. 6.3). In contrast, water quality was variable (Fig. 6.3). The surface water in the drain was acidic and below pH 4 for half of the year (except for January, February, March, May and August) (Fig. 6.3). The low pH (< 4) in the surface water was most likely due to the acidic groundwater discharges and the acidic surface run-off caused by small frequent rainfall events (50-150 mm). Previous studies have reported that groundwater and surface runoff regulate water quality in the floodplain drains in the Tuckean Swamp (Sammut et al., 1996; de Ways et al., 2011; Santos and Eyre, 2011; Santos et al., 2011).

A high rainfall period of over 300 mm during January 2012 could have led to an increase in the pH from a near constant value of < 4 to a peak of 6.6 and a decrease in the Eh from values > +500 mV to ~ -150 mV during January-February 2012 as shown in Figs. 6.3a and b. These figures show a potential influence of rainfall on these parameters (i.e. charging the drain with organic-rich floodwaters generated by the heavy rainfall event in January). For example, heavy rainfall in January could be the main cause for the observed spike in the DOC in the Tuckean Drain (16 mg L\(^{-1}\)) which was well above average of 2±0.80 mg L\(^{-1}\) in the preceding five months. During this period, the field site was inundated and therefore the decomposition of pasture would likely have generated reducing conditions (Wong et al., 2010). Therefore, the decomposition of the inundated pasture would also explain the spike in the DOC concentration in surface waters observed at the same time. Hence, although over the year-long sampling period the sediments maintained near neutral and reducing conditions, the water column conditions were varied between predominantly oxic/acidoic, to a defined period of two months of near-neutral and reducing, in response to the heavy rainfall.
Fig. 6.3. Water column and sediment parameters in Tuckean Swamp a) pH b) Eh.

Table 6.1 and Table 6.2 display the mean concentrations and the range of main cations/anions and trace metals respectively in surface and sediment pore waters over the sampling period. The composition of surface water and sediment pore waters in the Tuckean Drain were typical of ASS landscapes (e.g. Sammut et al., 1996; Burton et al., 2006b), but are far lower than reported for AMD sites (Bigham et al., 1996a; Regenspurg et al., 2004). The average Cl:\SO_{4}^{2-} molar ratios of the surface water was 1.3 and sediment pore waters was 2.08, much lower than that for marine waters (19.3) and indicative of sulfide oxidation of pyrite in the floodplain soils and subsequent discharge of acidic groundwater (Mulvey, 1993).

The sediment pore water was dominated by Fe (1.52 mM±0.78), \SO_{4}^{2-} (1.03 mM±0.66), Na (2.77 mM±1.62) and Cl (2.18 mM±0.94). On average ~ 97% of soluble Fe in the pore water was Fe^{2+}.
Table 6.1. Mean concentrations of major cations/anions in the surface and pore waters in the Tuckean Drain. Variation in the metal concentration throughout the year is shown as the range.

| Element | Surface water | | | Pore water* | | | |
|---------|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|         | Average concentration (mM) | Range (mM) | S.D | Average concentration (mM) | Range (mM) | S.D |
| Na      | 0.78          | 0.51-1.85      | 0.34 | 2.76          | 1.02-6.63      | 1.62 |
| K       | 0.03          | 0.02-0.05      | 0.01 | 0.11          | 0.05-0.22      | 0.06 |
| Ca      | 0.11          | 0.06-0.17      | 0.03 | 0.26          | 0.14-0.47      | 0.10 |
| Mg      | 0.22          | 0.12-0.36      | 0.07 | 0.81          | 0.36-1.62      | 0.40 |
| Cl      | 0.63          | 0.00-1.51      | 0.35 | 2.15          | 0.78-3.45      | 0.94 |
| SO₄²⁻   | 0.48          | 0.22-0.96      | 0.21 | 1.03          | 0.44-2.20      | 0.66 |
| Al      | 0.02          | 0.00-0.06      | 0.02 | 0.50          | 0.00-2.49      | 0.94 |
| Fe      | 0.06          | 0.00-0.30      | 0.10 | 1.52          | 0.55-2.92      | 0.78 |

* Pore water of sediments collected at 30 cm
S.D. standard deviation of three replicates

Table 6.2. Mean and the range concentrations of trace metals and metalloids in the surface and pore waters in the Tuckean Drain during the sampling period.

| Element | Surface water | | | Pore water* | | | |
|---------|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|         | Mean Concentration (µM) | Range (µM) | S.D | Mean Concentration (µM) | Range (µM) | S.D |
| As      | b.d.l.         | -             | -   | 0.02          | 0.01-0.03      | 0.01 |
| Cd      | b.d.l.         | -             | -   | 0.00          | 0.00-0.00      | 0.00 |
| Cr      | b.d.l.         | -             | -   | 0.05          | 0.01-0.20      | 0.06 |
| Cu      | 0.22          | 0.00-1.22     | 0.42 | 0.34          | 0.00-1.11      | 0.45 |
| Ni      | 0.19          | 0.00-1.07     | 0.32 | 0.47          | 0.08-1.91      | 0.63 |
| Pb      | b.d.l.         | -             | -   | 0.01          | 0.00-0.02      | 0.01 |
| Se      | b.d.l.         | -             | -   | 0.04          | 0.02-0.08      | 0.02 |
| Zn      | 0.52          | 0.00-2.56     | 0.72 | 1.63          | 0.10-5.44      | 2.09 |
| Hg      | b.d.l.         | -             | -   | 0.00          | 0.00-0.00      | 0.00 |
| Ag      | b.d.l.         | -             | -   | 0.00          | 0.00-0.02      | 0.01 |
| Mn      | 5.00          | 0.00-0.01     | 2.00 | 13.20         | 6.36-25.85     | 6.66 |

* Pore water of sediments collected at 30 cm
b.d.l. below detection limit
S.D. standard deviation of three replicates
6.4.3 Solubility of schwertmannite and jarosite in the Tuckean Drain

The distribution of Fe$^{3+}$ activity against pH of the surface water clearly indicates that the solution chemistry in the drain was undersaturated with regard to all three mineral phases (i.e. schwertmannite, jarosite and goethite) (Fig. 6.4). Two solubility lines for schwertmannite were plotted in Fig. 6.4 using schwertmannite stability constants determined by Bigham et al. (1996a) and Majzalan et al. (2004). Bigham et al. (1996a) geochemically modelled the stability constant (18) for highly acidic AMD affected environments (pH 2.8-3.2) while Majzalan et al. (2004) determined the stability constant (9.6) for a wider pH range (2-8).

Fig. 6.4. Plot of Fe$^{3+}$ against pH of the surface water from Tuckean Drain with solubility lines for schwertmannite (log [Fe$^{3+}$] = $-2.582\text{pH} + 2.996$) (Bigham et al., 1996a), log [Fe$^{3+}$] = $-2.582\text{pH} + 1.946$) (Majzalan et al., 2004), jarosite (log [Fe$^{3+}$] = $-2 \text{pH} - 0.273$), goethite (log [Fe$^{3+}$] = $-3\text{pH} + 1.4$) included.
6.4.4 Behaviour of schwertmannite

A net dissolution/ transformation of schwertmannite incubated in both systems was observed. Schwertmannite from both systems (sediments and the water column) transformed to goethite (see Fig. 6.5a, b). Within the first month of sample insertion in both systems, this transformation was evident and apparently quicker initially in the sediment, and was essentially complete for both systems after 12 months (Fig. 6.5a, b). In both systems, an occurrence of 3 different temporal phases can be distinguished over the 12 month period according to the variation in the corresponding XRD. These 3 phases can be described as “schwertmannite dominant phase” in the first 3 months, “transient phase” from 4-6 months (where both schwertmannite and goethite coexisted) and then a “goethite dominant phase” from 6 months onwards (Fig. 6.5a, b). The trends in the Fe/S ratios of the incubating schwertmannite in both systems (Fig. 6.6), from the initial ratios of 5 to ~25 after 12 months, reflects the mineralogical change to goethite which is evident in the XRD data (Fig. 6.5a, b). The transformation of schwertmannite in both systems indicated a distinct change (accompanying a sharp increase in goethite peaks) from the 4th month to the 5th month (Fig. 6.5a, b) most likely in response to the strong change in the geochemistry in the water column during this period (Fig. 6.3a, b).

Fig. 6.5. Change in the mineralogy of schwertmannite samples inserted into the Tuckean Swamp a) sediments b) water column. S=Schwertmannite and G=goethite. The corresponding duration of incubation is displayed in months on the right side of each spectrum.
Fig.6.6. Variation of Fe/S ratio of schwertmannite samples inserted in the sediment and in the water column displaying the dominant mineral phases, where S= schwertmannite, G=goethite. pH=pH in the water column and in the sediments at the time of each sampling session. The shaded area from 3rd month to 6th month indicates the time period of “transient phase” during which both schwertmannite and goethite were coexisted.

The transformation of schwertmannite incubated in the water column was likely regulated by both biotic and abiotic factors such as dissimilatory microbial reductive dissolution, Fe²⁺ catalysis, and the variable hydrology and geochemistry of the water column. This variability in hydrology and geochemistry of the water column could be due to the rainfall variability experienced at the study site during the incubations. The observed transformation rates of schwertmannite incubated in the water column were orders of magnitude faster compared to those conducted under controlled aerobic conditions (Table 6.3).
Table 6.3. Comparison of rate of schwertmannite transformation in present study with other studies. The rate of schwertmannite transformation was calculated by dividing the percentage of transformed fraction from the corresponding incubation time in hours (Adapted from Knorr and Blodau, 2007 and Burton et al., 2008b).

<table>
<thead>
<tr>
<th>Natural or Synthetic Schwertmannite</th>
<th>Laboratory/Field Study</th>
<th>Schwertmannite transformation rate (% h⁻¹)</th>
<th>Initial $\text{Fe}^{2+}$ (mM)</th>
<th>pH</th>
<th>DOC (mg $\text{L}^{-1}$)</th>
<th>$\text{SO}_4^{2-}$ in the medium (mM)</th>
<th>Temperature ($^\circ\text{C}$)</th>
<th>Eh (mV)</th>
<th>Incubation period (days)</th>
<th>$\text{SO}_4^{2-}$ release Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic (Oxidative)</td>
<td>Field (water column)</td>
<td>0.098-0.263</td>
<td>0</td>
<td>3.3-6.6</td>
<td>4-16</td>
<td>0.22-0.96</td>
<td>10-25</td>
<td>-184 to 504</td>
<td>366</td>
<td>SO$_4^{2-}$ release</td>
<td>Present study</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.041</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>362</td>
<td>SO$_4^{2-}$ release</td>
<td>Regenspurg et al. (2004)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.014</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>362</td>
<td>SO$_4^{2-}$ release</td>
<td>Regenspurg et al. (2004)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.003</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>362</td>
<td>SO$_4^{2-}$ release</td>
<td>Regenspurg et al. (2004)</td>
</tr>
<tr>
<td>Natural</td>
<td>Laboratory</td>
<td>0.004</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>514</td>
<td>H$^+$ release</td>
<td>Jönsson et al. (2005)</td>
</tr>
<tr>
<td>Natural</td>
<td>Laboratory</td>
<td>0.008</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>514</td>
<td>H$^+$ release</td>
<td>Jönsson et al. (2005)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.02</td>
<td>0</td>
<td>7.2</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>95</td>
<td>H$^+$ release</td>
<td>Schwertmann and Carlson (2005)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.013</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>100</td>
<td>H$^+$ release</td>
<td>Schwertmann and Carlson (2005)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
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<td>0.01</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>80</td>
<td>H$^+$ release</td>
<td>Schwertmann and Carlson (2005)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.007</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>b</td>
<td>80</td>
<td>H$^+$ release</td>
<td>Schwertmann and Carlson (2005)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.0008-0.0096</td>
<td>0</td>
<td>3</td>
<td>0-20</td>
<td>1-20</td>
<td>10-20</td>
<td>b</td>
<td>109</td>
<td>H$^+$ release</td>
<td>Knorr and Blodau (2007)</td>
</tr>
<tr>
<td>Synthetic (Dialysis)</td>
<td>Laboratory</td>
<td>0.0092-0.0383</td>
<td>0</td>
<td>5</td>
<td>0-20</td>
<td>1-20</td>
<td>10-20</td>
<td>b</td>
<td>109</td>
<td>H$^+$ release</td>
<td>Knorr and Blodau (2007)</td>
</tr>
</tbody>
</table>
### Table 1: SO$_4^{2-}$ Release in Synthetic (Oxidative) and Field Conditions

<table>
<thead>
<tr>
<th>Synthetic (Oxidative)</th>
<th>Field (sediments)</th>
<th>0.203-0.412</th>
<th>0.55-2.92</th>
<th>5.9-6.8</th>
<th>n.m.</th>
<th>0.44-2.20</th>
<th>10-25</th>
<th>-141 to -326</th>
<th>366</th>
<th>SO$_4^{2-}$ release</th>
<th>Present study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic (Oxidative)</td>
<td>Laboratory</td>
<td>7.8-22.7</td>
<td>1-10</td>
<td>6.5</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>c</td>
<td>0.33</td>
<td>(8 h) SO$_4^{2-}$ release</td>
<td>Burton et al. (2008b)</td>
</tr>
<tr>
<td>Synthetic (Oxidative)</td>
<td>Laboratory</td>
<td>a</td>
<td>0</td>
<td>6.5</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>c</td>
<td>0.33</td>
<td>(8 h) SO$_4^{2-}$ release</td>
<td>Burton et al. (2008b)</td>
</tr>
<tr>
<td>Synthetic (Oxidative)</td>
<td>Laboratory</td>
<td>2.7-25.4</td>
<td>5</td>
<td>5.5-7</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>c</td>
<td>0.33</td>
<td>(8 h) SO$_4^{2-}$ release</td>
<td>Burton et al. (2008b)</td>
</tr>
<tr>
<td>Synthetic (Oxidative)</td>
<td>Laboratory</td>
<td>a</td>
<td>5</td>
<td>4-5</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>c</td>
<td>0.33</td>
<td>(8 h) SO$_4^{2-}$ release</td>
<td>Burton et al. (2008b)</td>
</tr>
<tr>
<td>Synthetic (Oxidative)</td>
<td>Laboratory</td>
<td>a</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>n.a.</td>
<td>25</td>
<td>c</td>
<td>0.33</td>
<td>(8 h) SO$_4^{2-}$ release</td>
<td>Burton et al. (2008b)</td>
</tr>
</tbody>
</table>

*a* = No detectable schwertmannite transformation  
*b* = Assumed fully aerobic/oxic conditions  
*c* = Assumed fully anaerobic/anoxic conditions  
*n.a.* = not available, *n.m.* = not measured
Chapter 6: Understanding the in-situ transformation behaviour of schwertmannite and jarosite in natural acid sulfate soils environments

The drain water column was acidic (< below 4), most likely due to the acidic groundwater discharges (de Weys et al., 2011; Santos and Eyre, 2011), and was in the stability range for schwertmannite (i.e. 3.3-4.0 except for the months of January, February, March, May and August) for most of the year. The hydrological conditions in the water column, such as advection and diffusion, may have enhanced the rate of transformation of the incubated schwertmannite by removing the products of schwertmannite transformation such as $\text{SO}_4^{2-}$ from the vicinity of schwertmannite. Percolation of groundwater within sediments has been found to influence the stability of schwertmannite in acidic lakes affected by acid mine drainage (Blodau and Knorr, 2006; Knorr and Blodau, 2006; Peiffer et al., 2013).

The impact of high rainfall and flooding on the transformation of schwertmannite is shown in Fig. 6.5a, b. A rainfall of > 300 mm in January 2012 (5th month) could have resulted in increased flooding in the field site. Flood waters in turn might have generated anoxic/anaerobic and reducing conditions due to the decomposition of overbank inundation of pasture. These anoxic and reducing conditions could have caused sudden changes in the pH (i.e. an increase in pH from < 4 to ~ 6.6), Eh (i.e. decrease from +500 mV to −150 mV), and the DOC concentration (from average of 2 mg L$^{-1}$ to 16 mg L$^{-1}$) in the water column observed from the 4th month to the 6th month (Fig. 6.3a, b). This abrupt change of the geochemical regime in the water column from oxic, acidic to organic rich, anoxic and reducing conditions likely triggered both dissimilatory microbial reductive dissolution of schwertmannite and $\text{Fe}^{2+}$ catalysis resulting in the formation of goethite (Fig. 6.5a).

The rates of schwertmannite transformation in sediments were approximately two fold faster than in the water column (Table 6.3). Clearly, the sediments would have provided conditions that favoured schwertmannite weathering. The sediments were anoxic and reducing (pH 6-7) throughout the year (Fig. 6.2a, b) and were rich in organic matter (~ 7-16%) (Bush et al., 2004c). Furthermore, ~ 97% of total soluble Fe in the pore water comprised of $\text{Fe}^{2+}$ with average of 1.48±0.77 mM over the duration of this study. Therefore, the two key mechanisms that could have driven the transformation of
schwertmannite in the sediments are the dissimilatory microbial reductive dissolution and the Fe$^{2+}$ catalysis from the beginning of the incubation. However, these rates observed were orders of magnitude less than reported by Burton et al. (2008b) under reducing conditions with greater Fe$^{2+}$ concentrations.

One possible explanation for the difference in the rates for schwertmannite transformation are the limitations in Fe$^{2+}$ transport and reduced interaction with Fe$^{3+}$ normally experienced by schwertmannite in sediments. While the schwertmannite used in the present study was composed of large (1-2 mm diameter) aggregates and after placement were immobile in the reducing sediment environment over the 12 month period, the schwertmannite used in Burton et al. (2008b) was finely powdered and the reaction chambers were continuously shaken at 150 rpm, thus negating the constraints experienced in sediments resulting from the diffusion of Fe$^{2+}$ to the surface of the schwertmannite. CASS sediments are generally rich in macropores (Johnston et al., 2009c), hence the diffusion of O$_2$ and subsequent oxidation of the Fe$^{2+}$ would also explain the observed lower Fe$^{2+}$ catalysed transformation of schwertmannite compared to Burton et al. (2008b).

One of the interesting findings of this study was the considerably higher Si content (~0.6% Si, Si is produced by the dissolution of aluminosilicate clay minerals by the acidic groundwater) measured in schwertmannite that was incubated in sediments for 12 months. Groundwater in the Tuckean Swamp is rich in Si (~0.0017% Si-0.6 mM) (Sammut et al., 1996). Therefore, the near-neutral conditions of the sediments would favour the adsorption of Si on schwertmannite (Burton and Johnston, 2012). While this observation of the transformation of schwertmannite to goethite in the presence of Si is in agreement with the long-term incubation study conducted by Burton and Johnston (2012), it contrasts with the abiotic Fe$^{2+}$ catalysed schwertmannite transformation study conducted by Jones et al. (2009).

Jones et al. (2009) reported that Fe$^{2+}$ catalysed transformation of schwertmannite was completely inhibited by both low (i.e. 0.0028% Si-1 mM) and high (i.e. 0.028% Si-10 mM) concentrations of Si. However, a long-term incubation study conducted by Burton and Johnston (2012) reported that
schwertmannite was rapidly transformed to goethite in the presence of both low (0.0053% Si-1.9 mM) and high (0.0266% Si-9.5 mM) Si concentrations and under microbially-reducing conditions. Burton and Johnston (2012) confirmed that adsorption of Si on schwertmannite can retard Fe\(^{2+}\) catalysed transformation, especially under abiotic conditions and when Si was added prior to Fe\(^{2+}\) to a schwertmannite suspension at a neutral pH (i.e. 6.5). The pre-adsorption of Si on the surface of schwertmannite can block the mineral surface for a subsequent Fe\(^{2+}\) catalysis. However, under microbially-reducing conditions, the increase in Fe\(^{2+}\) concentration due to the reductive dissolution of schwertmannite can overcome the effects of Si, thus triggering the Fe\(^{2+}\) catalysed transformation.

### 6.4.5 Behaviour of jarosite

In this study, jarosite incubated in both sediments and the water column was undergoing transformation to goethite by the end of 12 months (Fig. 6.7a, b). Transformation of jarosite incubated in the sediments was much faster than those incubated in the water column (Table 6.4, Fig. 6.7a, b). Goethite peaks appear in the XRD data of jarosite incubated in both systems after 5 months of incubation. The transformation of jarosite in the sediments not only led to the formation of goethite but also to the formation of lepidocrocite (Fig. 6.7a). In sediments and water column, the transformation of jarosite is indicated by increases in the Fe/S and Fe/K ratios over the 12 months experimental period (Fig. 6.8a, b). Interestingly, appreciable changes in Fe/S and Fe/K ratios were observed even after one month’s incubation, far earlier than mineralogical changes were evident in the XRD data. This may imply that initial changes to elemental ratios were mainly due to the removal of adsorbed SO\(_4^{2-}\) and K, rather than mineralogical changes. Goethite coatings were observed in some of the jarosite aggregates incubated in the water column by 12 months time (Fig. 6.2f) and the trend in the Fe/S and Fe/K ratio variation indicated a decrease from the 9th month onwards (Fig. 6.8a ,b). Previous studies have found that goethite formed as coatings on the surface of jarosite as it transforms impedes the further dissolution of jarosite (Gasharova et al., 2005; Smith et al., 2006; Welch et al., 2008). In contrast to the jarosite incubated in the water column, jarosite incubated in the sediments
was accompanied by substantial changes in morphology, possibly via fragmentation from substantial etching and pitting (Fig. 6.2d) similar to the manner observed in previous studies (Gasharova et al., 2005; Smith et al., 2006; Elwood Madden et al., 2012; Johnston et al., 2012).

Similar to schwertmannite, the transformation of jarosite incubated in both the sediments and the water column also appeared to be affected by dissimilatory microbial reduction, and changes in both hydrology and geochemistry caused by rainfall events such as advective flow. Anoxic and reducing conditions that might have developed in the water column as a result of heavy rainfall and flooding in the 5th month could have triggered the transformation of jarosite (Fig. 6.7b). The key mechanisms likely to have caused this transformation are dissimilatory Fe(III) reduction and Fe$^{2+}$ catalysis.

Biotic and abiotic reductive dissolution, as well as the Fe$^{2+}$ catalysis, were likely responsible for the formation of goethite and a minor amount of lepidocrocite, from jarosite incubated in sediments (Fig. 6.7a). Lepidocrocite formation during the transformation of jarosite under anoxic, reducing conditions has been reported previously (Jones et al., 2009; Johnston et al., 2012). Jones et al. (2009) found that ~74% of jarosite transformed to lepidocrocite in the presence of 1 mM Fe$^{2+}$ at the end of a 7 day incubation period. Interestingly, Si and organic matter diminished the formation of lepidocrocite (Jones et al., 2009). Furthermore, Johnston et al. (2012) observed lepidocrocite formation as an intermediate product during the sulfidization of arsenic-bearing jarosite to mackinawite at both pH 6.5 and 8. However, at pH 6.5, minor amounts of lepidocrocite formation (25-32%) occurred at a much slower rate (~ 6 h) compared to at pH 8 (81-97%) which occurred at much faster rate (< 1 h) (Johnston et al., 2012). Similar to schwertmannite, jarosite incubated in sediments also showed a high amount of Si (~1.4%, which could have been produced by the dissolution of aluminosilicate clay minerals by the acidic groundwater) by the end of 12 months.
Fig. 6.7. Change in the mineralogy of jarosite inserted into the Tuckean Swamp a) sediment b) water column. G=goethite, L=lepidocrocite. The corresponding duration of incubation is displayed in months on the right side of each spectrum.

Fig. 6.8. Variation in elemental ratios of jarosite kept in sulfidic sediments and in the water column, and the pH in both systems over 12 months: a) Fe/S ratio, b) Fe/K ratio.

The average rate of transformation of jarosite is expressed as the rate of release of SO$_4^{2-}$. Jarosite incubated in the water column were relatively closer to corresponding short term rates (12 days) but slightly higher compared to the long term (from 12-350 days) rates of natural jarosite incubated in a variety of inorganic solutions (i.e. water; HCl pH 3; HCl pH 4; H$_2$SO$_4$ pH 3, and; H$_2$SO$_4$ pH 4) observed by Welch et al. (2008) (Table 6.4). The influence of DOC (average of 2 mg L$^{-1}$) in the water column and the dissimilatory microbial reductive dissolution and Fe$^{2+}$ catalysis could explain the
observed higher transformation rates in the water column when compared to other reports (Welch et al., 2008). The greater rate of transformation of jarosite in the sediment, compared to those reported by Welch et al. (2008) and to those incubated in the water column in the present study, is likely attributable to both dissimilatory microbial reductive dissolution and Fe$^{2+}$ catalysed transformation (Jones et al., 2009; Johnston et al., 2011a,b). Furthermore, the presence of higher amounts of organic matter (Chu et al., 2006; Zhu et al., 2008), S^{2-} (Johnston et al., 2012) and other Fe complexing agents such as humic acids (Gasharova et al., 2005) in sediments compared to the water column and compared to the laboratory study conducted by Welch et. (2008) could also have promoted the reductive dissolution of jarosite.

In our study, jarosite incubated in both sediments and water column dissolved at much slower rates than those reported by Smith et al. (2006) at both pH 2 and 8 (Table 6.4). Jarosite dissolution is highly dependent on pH and shows a V-shaped curve when the rate of dissolution is plotted with the pH (Elwood Madden et al., 2012). Hence, it is not unexpected to observe relatively slower dissolution rates in our studies where the pH was ranging from 3.3-6.6 and 5.9-6.8 in water column and sediments respectively throughout the incubation period.
Table 6.4. Comparison of the rates of dissolution of jarosite in the present study with previous studies. The rate of jarosite dissolution was expressed as rate of sulfate released (µmol SO$_4^{2-}$ g$^{-1}$ of jarosite day$^{-1}$) which was calculated based on the amount of sulfate released during the incubation time and/ time taken to reach equilibrium. Sulfate release rates were then normalized per mole of jarosite based on the jarosite: SO$_4^{2-}$ ratio (1:2).

<table>
<thead>
<tr>
<th>Natural or Synthetic Jarosite (Synthesized method)</th>
<th>Laboratory/Field Study</th>
<th>Jarosite transformation rate (µmol of jarosite g$^{-1}$ jarosite day$^{-1}$)</th>
<th>Initial Fe$^{2+}$ (aq) (mM)</th>
<th>Type of Solution</th>
<th>Initial pH / pH range</th>
<th>DOC (mg L$^{-1}$)</th>
<th>Incubation period (days)</th>
<th>Method used to determine the dissolution rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic (Baron and Palmer, 1996)</td>
<td>Field (water column)</td>
<td>0-1.91</td>
<td>0</td>
<td>Tuckean Drain water</td>
<td>3.3-6.6</td>
<td>3.98-15.77</td>
<td>366</td>
<td>SO$_4^{2-}$ release</td>
<td>Present study</td>
</tr>
<tr>
<td>Synthetic (Baron and Palmer, 1996)</td>
<td>Field (sediments)</td>
<td>1.36-4.04</td>
<td>0.55-2.92</td>
<td>Sediment pore water</td>
<td>5.9-6.8</td>
<td>n.m.</td>
<td>366</td>
<td>SO$_4^{2-}$ release</td>
<td>Present study</td>
</tr>
<tr>
<td>Synthetic (Baron and Palmer, 1996)</td>
<td>Laboratory</td>
<td>0.5-2.2</td>
<td>0</td>
<td>Inorganic$^a$</td>
<td>3, 4 and 6.5</td>
<td>0</td>
<td>12</td>
<td>SO$_4^{2-}$ release</td>
<td>Welch et al. (2008)</td>
</tr>
<tr>
<td>Natural</td>
<td>Laboratory</td>
<td>0.05-0.11</td>
<td>0</td>
<td>Inorganic$^a$</td>
<td>3, 4 and 6.6</td>
<td>0</td>
<td>338</td>
<td>SO$_4^{2-}$ release</td>
<td>Welch et al. (2008)</td>
</tr>
<tr>
<td>Synthetic (Baron and Palmer, 1996)</td>
<td>Laboratory</td>
<td>21</td>
<td>0</td>
<td>Ultra pure water</td>
<td>2</td>
<td>0</td>
<td>125(500h)$^b$</td>
<td>SO$_4^{2-}$ release</td>
<td>Smith et al. (2006)</td>
</tr>
<tr>
<td>Synthetic (Baron and Palmer, 1996)</td>
<td>Laboratory</td>
<td>11</td>
<td>0</td>
<td>Ultra pure water</td>
<td>8</td>
<td>0</td>
<td>146(1500h)$^b$</td>
<td>SO$_4^{2-}$ release</td>
<td>Smith et al. (2006)</td>
</tr>
</tbody>
</table>

$^a$ Type of Inorganic solutions: Water, HCl pH 3, HCl pH 4, H$_2$SO$_4$ pH 3 and H$_2$SO$_4$ pH 4

$^b$ Time taken to reach the equilibrium

n.m. = not measured
6.5 Conclusions

This study investigated the net transformation of schwertmannite and jarosite incubated in both a waterway and sediment typical of CASS (i.e. aerobic-acidic water column and anaerobic-neutral sediment) over a 12 month period. The behaviour of schwertmannite and jarosite in terms of transformation rates, changes in their mineralogy and morphology showed different patterns in the water column and the sediment. While the geochemical properties such as pH and Eh varied considerably in the water column over the experimental period, possibly due to weather fluctuations, especially major rainfall events, these properties remained reasonably constant in the sediments.

While schwertmannite that is incubated in both systems tended to transform to goethite by the end of 12 months, jarosite was also in the process of transformation to goethite at much slower rates. The data highlights the importance of hydrological conditions on the rate of mineral transformations of schwertmannite and jarosite in the water column. The geochemical variability in the water column, which could have occurred in response to rainfall, appears to have had a large influence on the behaviour and transformation rates of both minerals. The abrupt and substantial changes in the water column likely triggered dissimilatory microbial reduction and Fe\textsuperscript{2+} catalysis processes that ultimately enhanced the transformation rates of both minerals in the water column.

The instability of schwertmannite and jarosite in the sediment could be mainly attributed to the dissimilatory microbial reduction and the Fe\textsuperscript{2+} catalysed transformation. The data indicates that adsorption of Si on schwertmannite in natural settings has a lesser impact on transformation rate than expected.

The results of this field-based study provide new insights on the field behaviour of both schwertmannite and jarosite in this CASS environment. These observations partially fill the need for real-world data on two very important and reactive minerals. Notably, their behaviour appears to be strongly influenced by both hydrological conditions in the water column and by geochemical
properties which in turn are driven in a highly dynamic fashion by key environmental factors such as rainfall distribution. The results of direct examinations such as this study are required to provide realistic estimates of the stability of schwertmannite and jarosite in the field in order to appropriately manage such landscapes.

6.6 Acknowledgements

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Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid
Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid

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Concept and design of research

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Design: Vithana, Sullivan, Bush and Burton

Sample collection, laboratory analysis and interpretation of data

Collection of samples: Vithana and Sullivan

Laboratory analysis: Vithana

Interpretation of data: Vithana and Sullivan

Writing the publication

Original draft: Vithana

Proof reading and editing: Sullivan, Bush and Burton

Preparation of computer graphics: Vithana

Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)

See Chapter 9 for references

See Appendix for article published in Chemical Geology and signed author contribution statements.
Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid

7.1 Abstract

Schwertmannite is one of the major components that produces acidity in acid mine drainage (AMD) and acid sulfate soils (ASS) and is also known to be an effective scavenger of Arsenic (As) in such environments. Fulvic acid (FA) is an active component of natural organic matter (NOM) and is known to interact strongly with both schwertmannite and As. Two main environmental hazards related to schwertmannite are acidity liberation and potential re-mobilization of adsorbed or coprecipitated As upon hydrolysis. This study focused on understanding the behaviour of As-substituted schwertmannite with regard to the potential of acidity liberation, the effect of FA on acidity liberation from both Pure and As-substituted synthetic schwertmannites, and the effect of FA on arsenic mobilization from As-substituted synthetic schwertmannite. This was investigated by means of short-term (48 h) titrations. The liberation of acidity from As-substituted schwertmannite and the effect of FA were examined at two pH values (i.e. 4.5 and 6.5) typical for ASS environments.

As-substituted schwertmannite liberated a greater amount of acidity in comparison to pure schwertmannite at both pHs. Concentration of FA and pH each showed a strong influence on the liberation of acidity from both Pure and As-schwertmannite. At the acidic pH (4.5), FA inhibited acidity liberation from schwertmannite. At the near neutral pH of 6.5, the concentration of FA played a critical role in affecting the liberation of acidity from schwertmannite. The initial liberation of acidity was enhanced from pure schwertmannite at pH 6.5 by low FA concentration (1 mg L\(^{-1}\)) and from As-schwertmannite by both low (1 mg L\(^{-1}\)) and moderate (10 mg L\(^{-1}\)) FA concentrations. Interestingly, higher FA concentrations (25 mg L\(^{-1}\)) inhibited acidity liberation from both types of schwertmannite in comparison to the control (pure/As-schwertmannite titrated without added FA). FA enhanced the liberation of As from the As-schwertmannite at both pHs under oxidising conditions and the rate of As liberation was greater at the near neutral pH. The present study provides new insights on the effect of As-substitution on acidity liberation from schwertmannite and the role of FA on: a) liberation of acidity, and b) As mobilization, from schwertmannite.
Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid

7.2 Introduction

Schwertmannite is a secondary iron hydroxy sulfate mineral commonly found in acid sulfate soil (ASS) (Sullivan and Bush, 2004) and acid mine drainage (AMD) environments (Bigham and Nordstrom, 2000). Owing to its characteristic properties including metastability and high surface area, schwertmannite is considered an important acidity source and sink for trace metals such as arsenic (As) and chromium (Cr) (Regenspurg and Peiffer, 2005; Burton et al., 2010). Liberation of acidity from schwertmannite during the weathering process (Equation 7.1) causes a severe environmental hazard in ASS and AMD landscapes (e.g. Bigham and Nordstrom, 2000; Sullivan et al., 2012). The potential of simultaneous release of trace metals (e.g. As, Cr), incorporated or adsorbed in schwertmannite, further aggravates the environmental hazard (e.g. Burton et al., 2010; Sullivan et al., 2012).

\[
\text{Fe}_8\text{O}_8(\text{OH})_{8-2y}(\text{SO}_4)_y + 2y\text{H}_2\text{O} \rightarrow 8\text{FeOOH} + y\text{SO}_4^{2-} + 2y\text{H}^+\quad (7.1)
\]

Arsenic (As) is a common trace element found in ASS (Dudas, 1987; Gustafsson and Tin, 1994; Burton et al., 2008a; Johnston et al., 2010a; Kinsela et al., 2011) and AMD (Fukushi et al., 2003a,b; Regenspurg and Peiffer, 2005; Maillot et al., 2013) environments. In such environments, when schwertmannite is being precipitated, As is easily incorporated or adsorbed from acidic water (Fukushi et al., 2003a; Burton et al., 2009; Cheng et al., 2009; Maillot et al., 2013). According to Waychunas et al. (1995), As is incorporated into the structure by forming strong bidentate inner-sphere complexes during the precipitation of schwertmannite. Burton et al. (2009) also reported that As sorption to schwertmannite occurs through the exchange with structural $\text{SO}_4^{2-}$. However, in addition to the co-precipitation, As can be sorbed to the surface of schwertmannite via ligand exchange mechanism (Fukushi et al., 2003a,b). Therefore, the total amount of As in schwertmannite is a result of both mechanisms (Fukushi et al., 2003a). A quantitative study conducted by Antelo et al. (2012) calculated the exchange coefficients for arsenate adsorption on schwertmannite at different pHs. According to their study, only ~25% of arsenate is exchanged with structural $\text{SO}_4^{2-}$ while the
remaining 75% of arsenate is adsorbed to the surface hydroxyl groups on the mineral surface. Studies on the relationship between As and schwertmannite have shown that the absorption of As by schwertmannite slows down the transformation of schwertmannite to goethite (Fukushi et al., 2003a, b; Regenspurg and Peiffer, 2005; Burton et al., 2010). On the other hand, it was also found that the incorporation of As can prevent the crystal growth of schwertmannite (Waychunas et al., 1995; Maillot et al., 2013).

Arsenic contaminated groundwater is a serious issue in many countries (e.g. India, Bangladesh, Vietnam, China and Chile), where large populations consume daily As-contaminated groundwater (> 10 µg As L⁻¹ according to WHO guidelines) resulting in major health issues (Smedley and Kinniburgh, 2002). Elevated concentrations of As in aquatic systems can arise due to natural or anthropogenic sources (Wang and Mulligan, 2006c and references therein; Cheng et al., 2009). One of the anthropogenic sources that contributes to As in groundwater and aquatic water bodies is the prolonged application of As containing pesticides and wood preservatives (Lombi et al., 2000; Wang and Mulligan, 2006c and references therein; Cheng et al., 2009). Arsenic in those chemicals is then leached to groundwater or transported to aquatic water bodies by run-off, thus resulting in an increase in As concentration, often to toxic levels (Lombi et al., 2000; Wang and Mulligan, 2006c and references therein; Cheng et al., 2009). In natural environments, As is mobilized from As-bearing mineral/solid phases due to various reactions such as oxidation of As-containing sulfides, reductive dissolution of As-adsorbed hydro (oxides) minerals, desorption from As-containing Fe/Mn hydro (oxides) due to competitive effects from carbonates, phosphates, silica and natural organic matter (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006c and references therein; Cheng et al., 2009).

Natural organic matter (NOM) interacts strongly with mineral oxides (e.g. goethite, ferrihydrite, schwertmannite, hematite, alumina) and metal contaminants like As (Gu et al., 1994, 1995, 1996; Kaiser and Guggenberger, 2000; Chen et al., 2003). NOM is ubiquitous in nature and is generally
composed of a variety of partially degraded organic matter (Gu et al., 1994; Kaiser and Guggenberger, 2000; Wang and Mulligan, 2006c).

There are two main classes in NOM, i.e. Fulvic acids (FA) and Humic acids (HA) according to their contrasting physio-chemical properties (Weng et al., 2006; Weng et al., 2009). FA is comparatively lighter in weight (molar mass < 1000 Dalton) and soluble in a wider pH range than HA (Diallo et al., 2005). In aquatic systems, a substantial proportion (~30-50%) of dissolved organic matter (DOM) is generally composed of both FA and HA (Diallo et al., 2005).

Due to the presence of organic moieties containing various functional groups such as phenolic, carboxylic and hydroxyl, NOM is capable of carrying out functions such as redox reactions and different binding mechanisms (Gu et al., 1994; Kaiser and Guggenberger, 2000; Wang and Mulligan, 2006c). Accordingly, once NOM is bound to metal oxides, it can alter the characteristic properties of the mineral oxide such as surface charge, zeta potential, and stability (Gu et al., 1994; Mak and Lo, 2011). Hence, it is not surprising to observe a strong relationship between NOM, metal contaminants (such as As and Cr) and iron minerals such as schwertmannite, jarosite, and goethite in ASS and AMD environments.

Many have studied the adsorption of NOM on iron oxides and their subsequent effect on the behaviour of iron oxides such as stability and potential adsorption of trace metals (e.g. Gu et al., 1994, 1995, 1996; Klaus, 2003; Jönsson et al., 2006; Kumpulainen et al., 2008b). The effect of FA on the stability of schwertmannite was studied by Jones et al. (2009) and reported that FA concentrations ranging from 25-150 mg L⁻¹ substantially reduced (by ~50%) the Fe²⁺-catalysed transformation of schwertmannite to goethite under reducing near-neutral (pH 6.5) conditions. The interaction between DOM, iron oxides and trace metals were investigated by Jönsson et al. (2006). They reported that dissolved organic matter (DOM) was preferentially adsorbed to both schwertmannite and goethite at low pH, and the adsorption of Cu²⁺ to goethite was enhanced at slightly acidic pH in the presence of DOM.
Given the strong relationship between As and iron oxides, there are some studies in literature which specifically examined how NOM affects the adsorption and desorption of As on iron oxide minerals. According to Bauer and Blodau (2006), DOM enhanced the mobilization of As which was adsorbed on goethite at neutral pH (6.2). Grafe et al. (2001) observed a decrease in arsenate adsorption on goethite in the presence of peat HA, FA and citric acid in the pH range 3-8. However, a similar study conducted by Grafe et al. (2002) on ferrihydrite found that arsenate adsorption was decreased only in the presence of citric acid.

While all these previous studies provide insights to the interactions between NOM, iron oxide minerals and metal contaminants, little is known about the effect of As-substitution and NOM on liberation of acidity from iron hydroxy sulfate minerals found in ASS/AMD environments. Given the potential for the co-precipitation of As during iron hydroxy sulfate mineral formation in ASS/AMD environments and the ubiquitous nature of NOM, understanding their influence on the liberation of acidity is essential for the management of those landscapes.

Schwertmannite as surface accumulations mixed with organic litter has a wide spatial distribution in coastal acid sulfate soils (CASS) landscapes in eastern Australia (Sullivan and Bush, 2004). These researchers demonstrated that schwertmannite accumulations contained substantial amounts of acidity (up to 2580 mol H⁺/t) that when liberated, had the capacity to acidify nearby waterways. Schwertmannite formed in natural environments often contains impurities such as trace metals and metalloids, organic matter and silica (Regenspurg, 2002). As a result, schwertmannite accumulations act as a source of reactive iron and trace metals as well as acidity in CASS landscapes (Sullivan and Bush, 2004; Burton et al., 2008a). Burton et al. (2008a) observed an increase in As mobilization associated with liberation of Fe(II) from schwertmannite during the initial stages of soil re-flooding in CASS landscapes. Flooding associated with organic rich surface runoff during heavy rainfall events can trigger microbial reductive Fe(III) dissolution which generates substantial alkalinity (i.e. increase in pH near-neutral pHS) (Burton et al., 2008a). In CASS landscapes the liberation of acidity and mobilization of previously held metals (such as As) from schwertmannite is likely to largely be
controlled by environmental factors such as rainfall, advective flow in drains, surface run-off, tidal flushing and flooding due to seasonality of weather (Sammut et al., 1996; Johnston et al., 2005c; Burton et al., 2008a).

Schwertmannite in CASS occurs mainly as surficial accumulations (Sullivan and Bush, 2004; Johnston et al., 2005c), and these two processes (i.e. liberation of acidity and trace metals/metalloids) will also undoubtedly be influenced by the presence of other soil and water constituents such as organic matter, silica (Jones et al., 2009; Burton and Johnston, 2012) and the wide range of possible substitutions in this mineral that occur in natural environments (e.g. As, Ni, Zn, Cu) (Carlson et al., 2002; Fukushi et al., 2003a; Sidenko and Sher riff, 2005; Antelo et al., 2013). The objective of this study was to understand the behaviour of arsenic substituted schwertmannite and the effect of FA on the behaviour of both pure and arsenic substituted schwertmannite. In this context, we examined two important behavioural aspects of schwertmannite, 1) acidity generation and 2) arsenic mobilization, at two different pH levels (pH 6.5 and 4.5). For this study we simulated the two environmental settings (i.e. oxic, acidic-4.5 and oxic, near-neutral-6.5 conditions) that schwertmannite often encounters after its formation in ASS environments (Burton et al., 2006b). Schwertmannite formed in natural environments often contains impurities, so as examining synthetic pure schwertmannite samples we also examined the behaviour of As-schwertmannite samples to examine acidity liberation, As release and the effect of FA. The experiment was conducted in a medium of artificial acidic water having similar but with strictly defined and reproducible composition to that an acidic drain in CASS to simulate natural CASS surficial waters. FA was selected as the NOM source due to its solubility over a wide pH range whereas HA is prone to coagulation at the severely acidic pHs (i.e. < 4) experienced in the sulfuric horizons of acid sulfate soils (e.g. Sullivan et al., 2012).
7.3 Materials and Methods

7.3.1 Sample preparation

7.3.1.1 Synthesis of pure and arsenic-substituted schwertmannite

Pure schwertmannite was synthesised by following the method suggested in Regenspurg et al. (2004). 500 g of FeSO$_4$·7H$_2$O (i.e. containing ~ 273 g of FeSO$_4$) was dissolved in ~ 30 L of deionised water followed by addition of ~150 mL of 30% H$_2$O$_2$. The solution was mixed thoroughly and left overnight to allow the freshly precipitated schwertmannite to settle. The pure schwertmannite synthesis solution reached a constant pH of 2.4 after several hours. After 24 h, the supernatant was removed and replaced with 30 L of deionised water twice a day for a week in order to remove soluble ions. The schwertmannite slurry was then transferred into a shallow plastic tray and dried at 40°C for a week. Dried schwertmannite was then ground using a ring-mill (Rock Labs, New Zealand).

Arsenic substituted schwertmannite was synthesised by following the same method used to synthesise the pure schwertmannite but with an extra step. In order to obtain a solution ratio of 20FeSO$_4$:1AsO$_4^{3-}$, 28.1 g of Na$_2$HAsO$_4$·7H$_2$O was added to the solution mixture of FeSO$_4$·7H$_2$O (Regenspurg, 2002). The schwertmannite synthesis solution containing arsenic reached a constant pH of 2.5 after several hours.

Henceforth, arsenic-substituted schwertmannite and pure schwertmannite will be denoted as As-schwertmannite and as Pure-schwertmannite respectively.

7.3.1.2 Preparation of Artificial Acidic Water (AAW) and the stock solution of Fulvic Acid (FA)

AAW was prepared based on the average of anion/cation concentrations in the acidic Tuckean Drain water that was monitored in a separate study from August 2011 to August 2012. This water was made up of 0.03 mM KCl, 0.12 mM CaCl$_2$, 0.22 mM MgCl$_2$, 0.32 mM Na$_2$SO$_4$ and 0.16 mM H$_2$SO$_4$. A stock solution of 100 mg L$^{-1}$ FA was prepared by dissolving 0.1 g of Suwannee River Fulvic Acid
Standard I (SRFA) (International Humic Substances Society, St. Paul, MN, USA) in 1 L of deionised water.

7.3.1.3 Titration at pH 4.5 and 6.5

1:20 suspensions (20 mL) were prepared by mixing 0.5000±0.0001 g of Pure- or As-schwertmannite with an appropriate volume of AAW in a 250 mL glass titration vessel followed by the addition of an appropriate volume of 100 mg L⁻¹ FA stock solution to obtain the required final concentrations of FA (i.e. 1, 10 and 25 mg L⁻¹).

This 1:20 suspension of Pure- or As-schwertmannite:artificial acidic water (AAW) containing appropriate volumes of FA (added to the suspension just before the titration) was titrated either to pH 4.5 or to pH 6.5 with 0.005 M NaOH for 48 h using a Tiamo potentiometric titrator (Metrohm AG, Switzerland). A period of ~1.3 h and 3 h were required to reach the target pHs of 4.5 and 6.5, respectively. The experiment was pre-programmed (Tiamo Programme version 1.3) to run for 48 h. The programme was designed such that the pH of the suspension was always maintained at the target pH for 48 h. The 48 h experiment comprised of alternative cycles of titration and pH measurements. When the titration was finished (i.e. to pH 4.5 or 6.5) the pH of the suspension was measured over 3 h at 30 min intervals. After 3 h, if the pH was below the target pHs, the suspension was automatically titrated back to the target pH, after which the pH measurement cycle commenced again. The suspension was stirred continuously throughout the experimental period (i.e. 48 h).

Pure/As-schwertmannite samples titrated to target pHs without FA were considered as the “control” samples. A duplicate of each sample was analysed and the experiment was repeated with a blank sample. The total volume of blank samples was also 20 mL, and consisted of AAW and appropriate volumes of FA without additions of Pure- or As-schwertmannite. Blank samples were titrated to the target pHs within a period of 2 min consuming < 2 mL of 0.05 M NaOH. Both the acidity (i.e. determined from the volume of consumed 0.005 M NaOH) and the elemental composition in the
aqueous phase of the actual samples after the completion of the titration were corrected using the corresponding results of the blank samples.

### 7.3.2 Analytical methods

The elemental compositions of freshly synthesised Pure- or As-schwertmannite were determined by aqua-regia digestion (HNO₃:HCl) followed by analysis through inductively coupled plasma mass spectrometry (ICP-MS) (APHA, 2005). After completion of the 48 h experiment, the solution was divided into two portions. The first portion was filtered to < 45 µm and acidified with HNO₃ acid. The elemental composition in the aqueous acidified filtrate was determined using ICP-MS (APHA, 2005). The second portion was used to isolate the solid residue, which was washed with ultrapure water for a couple of times and allowed to air dry.

The mineralogy of freshly synthesised Pure/As-schwertmannite and the dried solid residue was determined by powder X-ray diffraction (XRD). For XRD analysis, samples were first hand ground (< 63 µm) using a porcelain mortar and pestle. The resulting powdered samples were then analysed using a Bruker D4 Diffractometer using Co Kα radiation (Bruker AXS GmbH, Germany). The diffraction patterns were recorded from 10 to 80°2θ in steps of 0.05° 2θ step size with 2 seconds counting time per step. The XRD patterns were evaluated using EVA software (DIFFRAC-plus evaluation package, Bruker AXS, Karlsruhe, Germany).

The micromorphology of freshly synthesised Pure- and As-schwertmannite was examined using scanning electron microscopy (SEM) (Stereoscan 440; Leica Cambridge Ltd, UK). The freshly synthesised samples were mounted on aluminium stubs followed by carbon and gold coatings and analysed through the SEM. The imaging settings were; Working Distance (WD) =14 mm, Probe = 40 pA, Electron High Tension (EHT)=10 kV.
7.4 Results

7.4.1 Properties of synthesized Pure and As-schwertmannite

The elemental composition of synthesised Pure and As-schwertmannite are shown in Table 7.1. Based on the Fe, S and As content, an average stoichiometry of the Pure and As-schwertmannite were derived as Fe$_8$O$_8$(OH)$_{4.3}$(SO$_4$)$_{1.85}$ and Fe$_8$O$_8$(OH)$_{4.28}$(SO$_4$)$_{1.3}$(AsO$_4$)$_{0.55}$ respectively. The As-schwertmannite contained As:Fe at a ratio of 0.07, similar to the ratios reported for arsenic substituted schwertmannite formed in AMD environments (Carlson et al., 2002; Regenspurg and Peiffer, 2005; Maillot et al., 2013). In line with previous studies, the peaks of As-schwertmannite synthesised in this study were broader compared to the Pure- schwertmannite and contained no detectable phase other than schwertmannite (Fig. 7.1a) (Carlson et al., 2002; Regenspurg and Peiffer, 2005). The Pure and As- schwertmannite were mainly composed of spheroids around 500 nm in diameter (Fig. 7.1b, c). In As-schwertmannite, aggregated particles having diameter around ~100 nm were also abundant (Fig. 7.1c).

Table 7.1. Elemental composition and the molar ratios of synthesised Pure and As-schwertmannite

<table>
<thead>
<tr>
<th></th>
<th>Weight (%)</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>S</td>
</tr>
<tr>
<td>Pure-schwertmannite</td>
<td>40.6</td>
<td>5.4</td>
</tr>
<tr>
<td>As-schwertmannite</td>
<td>38.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>
Fig. 7.1. XRD and SEM images of untreated samples (a) XRD patterns of Pure and As-schwertmannite (b) SEM image of Pure-schwertmannite (c) SEM image of As-schwertmannite, bars indicates 500 nm

7.4.2 Effect of arsenic substitution on acidity release at pH 4.5 and 6.5

As-schwertmannite released considerably higher amount of acidity compared to Pure-schwertmannite at both pHs (i.e. 4.5 and 6.5) irrespective of the FA concentration (Table 7.2). From Fig. 7.2a and b, it is clear that As-schwertmannite liberated acidity at greater rate than Pure-schwertmannite as evident from the greater decrease in pH between the titrations. Acidity liberated from As-schwertmannite at all treatments accounted for 17-27% and 56-62% of the total retained acidity at pH 4.5 and 6.5 respectively. It was in the range of 6-10% and 24-27% of the total retained acidity at pH 4.5 and 6.5 respectively for Pure-schwertmannite in all treatments.
Table 7.2. Total amount of acidity released from Pure and As-schwertmannite by the end of 48 h titration (a) pH 4.5 (b) pH 6.5

<table>
<thead>
<tr>
<th>Fulvic acid concentration (mg L⁻¹)</th>
<th>Released acidity (mol H⁺/t)</th>
<th>S.D</th>
<th>Released acidity (mol H⁺/t)</th>
<th>S.D</th>
<th>Released acidity (mol H⁺/t)</th>
<th>S.D</th>
<th>Released acidity (mol H⁺/t)</th>
<th>S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>11</td>
<td>776</td>
<td>11</td>
<td>1634</td>
<td>40</td>
<td>1770</td>
<td>50</td>
</tr>
<tr>
<td>1</td>
<td>411</td>
<td>1</td>
<td>530</td>
<td>2</td>
<td>1658</td>
<td>11</td>
<td>1799</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
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<td>9</td>
<td>499</td>
<td>9</td>
<td>1584</td>
<td>32</td>
<td>1713</td>
<td>53</td>
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<tr>
<td>25</td>
<td>396</td>
<td>6</td>
<td>482</td>
<td>25</td>
<td>1466</td>
<td>22</td>
<td>1620</td>
<td>20</td>
</tr>
</tbody>
</table>
Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid

Fig. 7.2. Variation in pH over 48 h period (a) and (b) Pure and As- schwertmannite at pH 6.5 and (c) and (d) Pure and As- schwertmannite at pH 4.5
7.4.3 Effect of fulvic acid on acidity release at pH 4.5

At pH 4.5, all three concentrations of FA significantly retarded acidity generation (Fig. 7.3) from both Pure and As-schwertmannite compared to the control. Initial acidity generation was reduced by ~40% for both Pure and As-schwertmannite when FA was present. This inhibition effect by FA on the liberation of acidity was clearly noticeable only in the first 9 h in Pure schwertmannite (Fig. 7.3a). In contrast, acidity generation in As-schwertmannite was inhibited by FA for almost the entire 48 h period (Fig. 7.3b).

Fig. 7.3. Released acidity at different time intervals and cumulative acidity generation over 48 h titration at pH 4.5 (a)–(c) Pure-schwertmannite (b)-(d) As-schwertmannite. Error bars are ± S.D
Chapter 7: Acidity and arsenic liberation from schwertmannite: effect of fulvic acid

7.4.4 Effect of fulvic acid on acidity release at pH 6.5

There was an initial (first 9 h) increase in the generation of acidity from both Pure-schwertmannite and As-schwertmannite in the presence of the lowest FA concentration (1 mg L⁻¹) as compared to the control (Fig. 7.4a, c). However, the two higher concentrations of FA (10 mg L⁻¹ and, especially 25 mg L⁻¹) limited the release of acidity considerably from both the Pure-schwertmannite and As-schwertmannites (Fig. 7.4).

Fig. 7.4. Released acidity at different time intervals and cumulative acidity generation over 48 h titration at pH 6.5 (a)–(b) Pure-schwertmannite (c)–(d) As-schwertmannite. Error bars are ± S.D
7.4.5 Release of sulfate and arsenic from Pure and As-schwertmannite

Liberation of As from the As-schwertmannite over the 48 h period was enhanced considerably in the presence of all three FA concentrations at both pH 4.5 and 6.5 (Fig. 7.5). However, the amount of As released at both pHs in the presence of FA only accounted for 0.002-0.003 % of the total-As content in As-schwertmannite. At pH 6.5, the concentration of As liberated by the lowest FA concentrations (1 mg L$^{-1}$) was double the As concentration liberated in the control. Lesser yet still considerable increases in the release of As from the As-schwertmannite over the 48 h period were observed in the presence of all three FA concentrations at pH 4.5 compared to the control. Substantial release in SO$_4^{2-}$ also occurred from both the Pure- and As-schwertmannite at both target pHs in the presence of FA compared to the control (Fig. 7.6a, b).

![Graph showing variation in released As by the end of 48 h titration period with different fulvic acid concentrations. Error bars are ± S.D](image-url)

Fig. 7.5. Variation in the released As by the end of 48 h titration period with different fulvic acid concentrations. Error bars are ± S.D
Fig. 7.6. Variation in released sulfate from Pure and As-schwertmannite by the end of 48 h titration period with different fulvic acid concentrations (a) at pH 6.5 (b) at pH 4.5. Error bars are ± S.D.

7.4.6 XRD of titrated mineral samples

No observable change in the crystallinity of Pure-schwertmannite was observed at the end of all treatments with exception to the appearance of a small goethite peak in the Pure-schwertmannite that was titrated in the presence of FA 10 mg L\(^{-1}\) at pH 4.5 (Figs. 7.7 and 7.8).
7.5 Discussion

7.5.1 Acidity liberation and dissolution of both Pure and As-schwertmannite at both pHs

The mineralogical stability of schwertmannite titrated at both pHs, indicates that measured acidity can be attributable to proton exchange reactions occurring on the surface rather than mineral dissolution. The dissolved Fe contents in the suspensions of all treatments after the 48 h titration were below or closer to the detection limit (i.e. < 1 µg Fe L⁻¹) providing further support for the lack of appreciable dissolution of both schwertmannite samples during the titrations.
7.5.2 Effect of arsenic substitution on the acidity liberating potential of schwertmannite

Fukushi et al. (2003a,b) reported that As can be incorporated as well as adsorbed to schwertmannite during the formation of schwertmannite. Accordingly, schwertmannite synthesised in the present study (from H₂O₂ oxidative synthesis process) could have had both incorporated and adsorbed H₂AsO₄⁻. In the present study we observed a higher release in acidity from As-schwertmannite in comparison to Pure-schwertmannite at both pHs (Table 7.2). Further, Fig. 7.2a and b show that pH dropped from the target pHs at much faster rates in As-schwertmannite.

Different mechanisms can be proposed for the observed higher liberation in acidity from As-schwertmannite at pH 4.5 and 6.5. The presence of abundant smaller particles in the As-schwertmannite would likely result in a much higher surface area and therefore a greater area for acid liberating reactions. Regenspurg et al. (2002) also reported a higher surface area for As incorporated schwertmannite compared to the Pure-schwertmannite. At pH 4.5, the additional protons adsorbed on the surface of As-schwertmannite could also account for the higher liberation in acidity. Both SO₄²⁻ and H⁺ are exchanged with H₂AsO₄⁻ when As-schwertmannite is being formed (Fukushi et al., 2003b). Therefore, it is anticipated that liberated H⁺ and SO₄²⁻ ions would adsorb to the surface of schwertmannite. Liberation of these additional H⁺ adsorbed on the surface during the titration could also account for the observed higher rates of acidity liberation in As-schwertmannite. Further support for this process can be obtained by comparing the liberated SO₄²⁻ concentrations from both types of schwertmannite in control samples (i.e. no FA added). The exchange of these additional SO₄²⁻ adsorbed on the surface with OH⁻ would explain the observed greater SO₄²⁻ concentration in control As-schwertmannite samples (i.e no added FA) at both pHs.

Arsenic (V) exists as a triprotic acid in the aqueous phase and it deprotonates as pH increases (Smedley and Kinniburgh, 2002; Wang and Mulligan, 2006c). The pKa values for As(V) are ; pKa¹, H₂AsO₄⁻ =2.2, pKa², HAsO₄²⁻ =6.9 and pKa³, AsO₄³⁻ =11.5. Hence, the dissociation of surface
adsorbed $\text{H}_2\text{AsO}_4^-$ to $\text{HAsO}_4^{2-}$ as pH increased from initial pH 3 to 6.5 would explain the increased liberation in acidity from As-schwertmannite.

7.5.3 Effect of fulvic acid on the liberation of acidity from Pure- and As-schwertmannite at pH 4.5

At pH 4.5, FA inhibited acidity release from both Pure and As-schwertmannite (Fig. 7.3). Therefore, it is most likely that when FA was added to the acidic schwertmannite suspension (initial pH ~3), it sorbed to the surface of schwertmannite and thus prevented the liberation of acidity from the schwertmannite surface. The preferential adsorption of NOM by iron oxides and the formation of more stable surface complexes have been also reported in literature. Those studies have revealed that, NOM (i.e. HA and FA) strongly adsorbs and tends to form inner-sphere complexes with the surface of iron oxides at acidic and slightly acidic conditions (Filius et al., 2000; Jönsson et al., 2006; Kumpulainen et al., 2008b). This study indicates that FA alone (i.e. out of HA and FA, the two main components of NOM) can bind to the surface of schwertmannite under acidic conditions. This is important as in acid sulfate soil landscapes HA, another main component of NOM, is prone to coagulation by the severely acidic pHs (i.e. < 4) experienced in the sulfuric horizons of acid sulfate soils (e.g. Sullivan et al., 2012), leaving FA as the main component of soluble NOM in the sulfuric layers of these severely acidified (and likely HA coagulating) environments.

The inhibition of acidity liberation by FA continued over the entire 48 h period only in the As-schwertmannite indicates a strong interaction between FA and As-schwertmannite at pH 4.5 (Fig. 7.3c). This observation is in agreement with previous studies, which reported a relatively strong relationship between As and FA at slightly acidic pHs (pH 5.5) (Wang and Mulligan, 2006c).

7.5.4 Effect of fulvic acid on the liberation of acidity from Pure- and As-schwertmannite at pH 6.5

Schwertmannite is known to destabilize as pH increases (Bigham and Nordstrom, 2000). Hence, the amount of acidity liberated at pH 6.5 were greater compared to that at pH 4.5 (Figs. 7.3 and 7.4).
The initial (i.e. first 9 h) liberation of acidity was enhanced in Pure-schwertmannite by low FA concentrations (1 mg L\(^{-1}\)) and by both low (1 mg L\(^{-1}\)) and moderate (10 mg L\(^{-1}\)) FA concentrations in As-schwertmannite compared to the control (Fig. 7.4a, c). In contrast, the initial liberation of acidity was retarded from both types of schwertmannite by higher FA concentrations (25 mg L\(^{-1}\)) compared to the control (Fig. 7.4a, c).

A FA adsorption study conducted by Filius et al. (2000) reported that the FA formed inner-sphere complexes on the surface of goethite at low pHs, whereas outer-sphere complexes with FA formed preferentially at high pHs. The observed initial increase in liberation of acidity from schwertmannite in the presence of low (1 mg L\(^{-1}\)) to moderate FA (10 mg L\(^{-1}\)) concentrations could be attributable to the pH dependent rearrangement of the surface complexes in schwertmannite. Taking Filius et al.’s (2000) observation into account, we propose that the FA added to the acidic schwertmannite suspension (initially at pH 3) initially formed inner-sphere complexes on the surface of schwertmannite which could have later rearranged to outer-sphere complexes as the pH increased to 6.5. According to Filius et al. (2000), outer-sphere complexes out compete inner-sphere complexes and become stable as the pH increases. A pH-dependent inner-sphere/outer-sphere rearrangement of the surface complexes would explain the increased liberation of acidity that only occurred in the initial phase as the pH increased from 3 to 6.5 (Fig. 7.4a, c).

The initial liberation of acidity was inhibited by higher FA concentration (25 mg L\(^{-1}\)) at pH of 6.5 in contrast to when FA was present in low to moderate concentrations (Fig. 7.4a, c). Previous studies have shown that surface negative charge and colloidal stability can be increased in the presence of higher NOM concentrations (10-100 mg L\(^{-1}\) C) (Kumpulainen et al., 2008b and references therein). Accordingly, schwertmannite, in the present study appeared to be far more stable (i.e. as indicated by slower acidity liberation) in the presence of higher FA concentrations (> 25 mg L\(^{-1}\)). Greater stability of schwertmannite in the presence of higher NOM (i.e. HA and FA) concentrations (> 20 mg L\(^{-1}\)) has been also reported elsewhere (Knorr and Blodau, 2007; Jones et al., 2009). For example, Jones et al. (2009) reported up to 50% reduction in the Fe\(^{2+}\) catalysed transformation of schwertmannite in the
presence of 25 mg L\(^{-1}\) and 150 mg L\(^{-1}\) SRFA at pH 6.5. Knorr and Blodau (2007) also reported an inhibition of the transformation of schwertmannite in the presence of 20 mgL\(^{-1}\) DOC concentration at both pH 3 and 5. Both studies considered the inhibition of transformation was due to the adsorption of NOM on the surface of schwertmannite which in turn prevented access of Fe\(^{2+}\) and OH\(^{-}\) to the adsorption sites.

### 7.5.5 Effect of fulvic acid on liberation of As from As-schwertmannite

Mobilization of As from iron oxides (hematite, ferrihydrite and goethite) in the presence of NOM (FA and HA) has been an important topic of intense investigation (Redman et al., 2002; Ko et al., 2004; Bauer and Blodau, 2006; Ritter et al., 2006; Mladenov et al., 2009; Weng et al., 2009; Sharma et al., 2011). This study extends this knowledge by showing that FA enhanced the liberation of As from the iron hydroxy sulfate mineral, schwertmannite at pHs relevant to ASS environments.

The data show that at pH 6.5, the liberation of As was enhanced in the presence of low FA (1 mg L\(^{-1}\)) yet decreased at higher in FA concentrations (10 and 25 mg L\(^{-1}\)) (Fig. 7.5). Although FA inhibited liberation of acidity at pH 4.5, the liberation of As was enhanced by the presence of all FA concentrations. At pH 4.5, the liberated As concentration was nearly constant at all FA concentrations and lower than those observed at pH 6.5 (Fig. 7.5). Although not investigated in this study, some of the arsenate adsorbed on the surface of schwertmannite could have been desorbed by HCO\(_3\^-\) (bicarbonate) formed due to the greater dissolution of atmospheric CO\(_2\) at pH 6.5, resulting in higher As concentrations in the aqueous phase at pH 6.5 compared to pH 4.5 (Smedley and Kinniburgh, 2002).

At pH 4.5, the surface of schwertmannite was positively charged since the point of zero charge (pzc) of schwertmannite is 7.2 (Jönsson et al., 2005). Therefore, H\(_2\)AsO\(_4\^-\) expected to bind strongly on the positively charged surface of schwertmannite at pH 4.5 hence, less likely to be desorbed. FA has strong affinity towards positively charged iron oxide surfaces and arsenate at acidic pHs (Gu et al., 1996; Wang and Mulligan, 2006c). Therefore, at pH 4.5, FA adsorbed strongly to the surface which
was clearly indicated as an apparent decrease in liberation of acidity over the experimental period (Fig. 7.3b). This adsorption of FA clearly desorbed some of the strongly bonded H$_2$AsO$_4^-$.

At pH 6.5, the surface of schwertmannite is less positively charged compared to at pH 4.5 (as the point of zero charge of schwertmannite is 7.2). Therefore, the HAsO$_4^{2-}$ molecules would have been bonded less strongly to surface allowing easier desorption by FA. However, at higher FA concentrations (25 mg L$^{-1}$) the surface of schwertmannite will become more completely covered by FA which in turn will hinder the desorption process. Xu et al. (1988) reported that the amount of surface area of the mineral (sorbent) covered by FA is directly proportional to the FA: sorbent (mineral) ratio. In the present study the FA:schwertmannite concentration ratio at higher FA concentration (25 mg L$^{-1}$) was 0.05 while it was 25 times lower (0.002) at lowest FA concentration (1 mg L$^{-1}$) which indicates possible greater coverage by FA at higher concentrations.

Further evidence for the surface adsorption of FA can be gained from the increases in SO$_4^{2-}$ concentration in the aqueous phase at higher FA concentrations (Fig. 7.6a, b). FA is known as a strong competitor for the adsorption sites on iron oxide minerals (Weng et al., 2009).

Liberation of As from synthetic schwertmannite has been described in the past (Regenspurg et al., 2002; Burton et al., 2008a, 2013a; Burton and Johnston, 2012). Regenspurg et al. (2002) reported that arsenate did not release from As incorporated schwertmannite incubated with Fe(III) reducing bacteria under acidic conditions. In contrast to Regenspurg et al. (2002), mobilization of As was observed at near-neutral pH under reducing conditions by Burton et al. (2008a). According to their study, reflooding of soil can create near-neutral and reducing conditions that favour the reductive dissolution of schwertmannite. The reductive dissolution of schwertmannite in turn resulted in the reduction of As(V) to As(III) which is the more mobile species of As. Likewise, a smaller (compared to the solid phase) but detectable increase in As concentration in the aqueous phase was observed from As-coprecipitated schwertmannite incubated with Fe (III) reducing bacteria by Burton and Johnston (2012). In their study As concentration up to 0.2 µM was liberated from schwertmannite in
the presence of silica concentration of 9.5 mM at near-neutral pH. In the present study, As under acidic pH (4.5) liberated to a magnitude (0.2 µM, Fig. 7.5) similar to that reported by Burton and Johnston (2012) in the presence of FA. However, in the present study the magnitude of As (maximum of 0.4 µM, Fig. 7.5) released at near-neutral pH (6.5), demonstrates that FA can greatly enhance the mobilization of As from schwertmannite under oxidising conditions.

7.6 Conclusion and Environmental Implications

In summary, the present study focused on understanding the effect of FA on the liberation of acidity and mobilization of As from Pure and As-substituted schwertmannite under laboratory conditions. Acidity liberation in the presence of different FA concentrations from both Pure and As-schwertmannite was determined at two different pHs (i.e. 4.5 and 6.5) relevant to most ASS environments. As-schwertmannite synthesized under acidic-oxic conditions showed a greater liberation of acidity at pH 4.5 and 6.5 in comparison to Pure-schwertmannite. The study revealed that both pH and the FA concentrations play significant roles in the liberation of acidity from both types of schwertmannite. Low to higher FA concentrations (1-25 mg L⁻¹) significantly reduced liberation of acidity from schwertmannite at pH 4.5. Although, both low and moderate FA concentrations (1 and 10 mg L⁻¹) promoted liberation of acidity initially as pH increased from initial ~3 to 6.5, they inhibited the liberation of acidity over time. Similar to at pH 4.5, liberation of acidity was significantly reduced at pH 6.5 by higher FA concentrations (> 25 mg L⁻¹). The results showed that FA enhanced mobilization of As at both pHs with the higher mobilization at pH 6.5. At pH 6.5, the highest mobilization of As occurred in the presence of lowest FA concentrations (1 mg L⁻¹).

The results of this study are highly relevant to environmental situations typical of acidic landscapes such as those associated with ASS. Although, As has been shown to be easily scavenged during the precipitation of schwertmannite, the data here shows that the acidity liberation potential from schwertmannite is considerably enhanced by such As substitution. Importantly, this study has highlighted the importance of the FA fraction of NOM in enhancing the mobilisation of As from As-
schwertmannite in acidic environments. Future research is recommended to understand the mechanism by which FA enhances the As liberation from As-schwertmannites.

7.7 Acknowledgements

We would like to thank Ms Michelle Bush and Ms Maxine Dawes for their assistance provided in XRD and SEM analyses, respectively. This research was funded by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment. Thanks to two anonymous reviewers for their constructive comments.
Chapter 8: Conclusions
This thesis explored two important aspects of the key secondary Fe (III) minerals schwertmannite and jarosite that are commonly found in ASS landscapes. They are: i) the identification and quantification, and ii) the behaviour of the two minerals in ASS. The first part of the thesis (Chapters 3-5) presented a systematic evaluation of four techniques (i.e. Net Acid Soluble Sulfur-SNAS, Residual Acid Soluble Sulfur-SRAS, acidified ammonium oxalate extraction for schwertmannite, three-step sequential extraction for jarosite) used for the identification and quantification of the two minerals. The second part described studies conducted to understand the long term, in-situ behaviour of both minerals in natural ASS environments (Chapter 6), and the effect of arsenic and natural organic matter (fulvic acid) on the behaviour of schwertmannite (Chapter7).

8.1 Evaluation of Identification/Quantification Techniques

8.1.1 SNAS and SRAS techniques

Schwertmannite and jarosite are known to contain stored acidity and therefore belong to the Retained Acidity (RA) fraction in Acid Base Accounting procedures (ABA) (Ahern et al., 2004). In Australia, Acid Base Accounting (ABA) is widely used to assess the acidity hazard in ASS. SNAS and SRAS are the common techniques that are routinely used in Australian laboratories for the estimation of the RA fraction in ASS. SNAS and SRAS techniques for estimation of schwertmannite and jarosite in ASS were systematically evaluated. Also, the contribution of these two minerals to other acidity fractions (potential sulfidic acidity-PSA, and actual acidity-AA) in the ABA was examined.

The SNAS and SRAS approaches were separately tested on soil (non-acid sulfate) and quartz samples spiked with synthetic/natural schwertmannite and jarosite samples. Both synthetic and natural schwertmannite spiked in soil/quartz samples were could not be quantified reliably through the SNAS approach. The observed lower SNAS recovery was due to the liberation of both acidity and sulfate during the 1M KCl extraction step which subsequently determines the AA. Acidity and sulfate liberation could be attributed to the exchange of H+ and SO4²⁻ (adsorbed on the surface of schwertmannite) with Cl⁻ and OH⁻ in the solution. The study showed that ~35% of the sulfate
released during the 4M HCl extraction was retained by the soil which could also account for the observed lower $S_{NAS}$ recovery. The liberation of acidity from schwertmannite during the 1M KCl extraction indicates a potential interference from schwertmannite to the AA.

Only 50-60% of synthetic and natural jarosite was recovered from the jarosite spiked soil and quartz samples. Similar to schwertmannite, the study showed retention of sulfate released during 4M HCl extraction by the soil. Therefore, a correction factor of 2 was suggested for the observed recovery for jarosite used in the present study. However, the data showed that the presence of schwertmannite and other poorly soluble Al hydroxy sulfate minerals (e.g. basaluminite) could interfere with the recovery of jarosite. Unlike schwertmannite, both jarosite types did not liberate acidity and sulfate during 1M KCl extraction, and therefore did not contribute to the AA.

Reliable quantification of the two minerals could not be obtained using the $S_{RAS}$ approach. Sulfate was released from both schwertmannite and jarosite during the peroxide oxidation process and was measured as peroxide oxidisable sulfur ($S_{POS}$), which is a measure of the reduced inorganic sulfur (RIS) and the potential sulfidic acidity (PSA). $S_{POS}$ content determined for both schwertmannite and jarosite spiked samples were greater than the action criteria ($> 0.03\%$) for potential ASS. Accordingly, the study showed that the peroxide oxidation of soils containing schwertmannite and jarosite could misinterpret those soils as potential ASS containing RIS.

**8.1.2 Acidified ammonium oxalate (AAO) and differential X-ray diffraction (DXRD)**

AAO extraction in the dark is a commonly used technique for the identification and quantification of poorly crystalline minerals such as ferrihydrite and schwertmannite in acid mine drainage environments. However, the technique has not been evaluated for the identification of schwertmannite in soil materials. In this study, the 15 min AAO extraction in the dark procedure was used to identify and quantify schwertmannite (synthetic and natural schwertmannite) spiked in soil (non-acid sulfate) and quartz. Time sequence extraction of pure synthetic and natural schwertmannite was also conducted to understand the dynamics of schwertmannite extraction by AAO over time. Synthetic
schwertmannite spiked in soils and quartz at different spiking rates was subjected to a modified DXRD approach to determine the lower detection limit of schwertmannite in soils through the DXRD. In this particular modified DXRD approach, instead of analysing the XRDs of samples before and after the selective dissolution, the XRDs of samples before and after the selective addition of schwertmannite were analysed. This simulates the ideal situation when only schwertmannite is dissolved or affected by the AAO procedure. The DXRD data indicated that, even under ideal conditions schwertmannite concentration in soil materials need to be > 5% to be detected using the DXRD approach. Both DXRD and the AAO extraction data confirmed that during the 15 min extraction, minerals other than schwertmannite such as goethite were dissolved from the natural schwertmannite. The time sequence data indicated incomplete dissolution of both synthetic and natural schwertmannite during the 15 min AAO extraction and that the amount recovered accounted for 76% and 65% of Fe, respectively. Nevertheless, the dissolution of natural schwertmannite could be enhanced by increasing the duration of exposure to AAO.

The recovered Fe content from schwertmannite spiked soil and quartz samples was underestimated by up to 20%. The data also showed that the under-recovery of Fe could also be attributed to the adsorption onto soil particles of Fe liberated from schwertmannite dissolution during the extraction. The results did not support the stated ability of the 15 min AAO extraction procedure to reliably quantify schwertmannite contents in soil materials. The results also showed that the Fe/S molar ratio is not a reliable indicator to identify the presence of schwertmannite in soil materials at concentrations less than 5%. The study indicates that the lower limit of detection of schwertmannite in soil materials is 5% in both the 15 min AAO extraction and the DXRD approaches.

8.1.3 Three-step sequential extraction procedure

The three-step sequential extraction procedure suggested by Li et al. (2007) for acid mine wastes was evaluated for the quantification of jarosite in soil materials. This three step-sequential extraction is comprised of an initial anoxic water extraction (for 3 min), roasting of the dried residue at 550°C (for
1 h) and finally, a 4 M HCl extraction of the roasted residue (for 30 min). Non-acid sulfate soils and quartz samples were spiked with synthetic and natural jarosite and subjected to the three-step extraction procedure and the amount of jarosite spiked was calculated from the recovered S content in the 4 M HCl extract. In contrast to Li et al. (2007), the amount of jarosite recovered in this study was substantially lower and accounted for only 40-50% of the initially spiked jarosite content. Further, a much lower S recovery was observed in jarosite spiked quartz compared to jarosite spiked soil samples. The observed lower S recovery was partially attributable to the retention of jarosite by the Teflon filter membrane during the initial anoxic water extraction which accounted for ~30% of the initially spiked synthetic jarosite. Therefore, the initial step was slightly modified by replacing the Teflon filter membrane with a Cellulose Acetate filter membrane that resulted in a substantial increase in the S recovery in both synthetic and natural jarosite samples. This modification resulted in an increase in the S recovery up to 45% and 70% for natural and synthetic jarosite respectively, from 5% jarosite spiked quartz samples. The examination of 4 M HCl extractability of the jarosite roasted at different temperatures demonstrated a highest 4 M HCl extractable S recovery from those roasted at 450°C but not from those roasted at 550°C as suggested by Li et al. (2007). This observed lower 4 M HCl extractable S recovery from jarosite samples roasted at 550°C could be due to the liberation of SO₂/SO₃ through yavapaiite decomposition, and/or the occlusion of S within the hematite that formed during the roasting.

Our study showed that jarosite in soils at a concentration 5% or below may not be quantifiable accurately by following the three-step sequential extraction procedure suggested by Li et al. (2007). The improvement in S recovery by replacing the Teflon filter membrane with a Cellulose Acetate filter membrane indicates a potential application of a correction factor of 2 for the two jarosite samples used in this study. However, further research using a much wider selection of jarosite from ASS would be required to set a universal correction factor (or determine if such a universal correction factor is indeed possible) for jarosite recovery using this approach.
8.2 Investigation of the Behaviour of Schwertmannite and Jarosite

8.2.1 In-situ, long term behaviour of schwertmannite and jarosite in natural ASS

Incubation of synthetic schwertmannite and jarosite in the natural environment (i.e. in an aerobic-acidic water column and an anaerobic-reducing sediment) revealed dynamic transformation pathways for both minerals. Schwertmannite incubated in both the water column and in sediments was transformed to goethite by the end of 12 months. Jarosite incubated in both systems was also in the process of transformation to goethite by the end of 12 months and the rate of transformation was slower in the water column compared to that in sediments. In addition to goethite, minor amount of lepidocrocite was also observed in jarosite incubated in sediments.

During the period of experimentation, the geochemical regime in the water column became anoxic and reducing approximately for two months, from the typical oxic-acidic regime, in response to heavy rainfall followed by flooding. However, the geochemical properties in the sediment remained fairly constant during the same period. The study showed that the transformation of the two minerals incubated in the water column was strongly affected by the hydrology of the water column and the seasonality of the weather in CASS landscapes. The sudden change in geochemistry due to heavy rainfall affected the mineralogy of the two minerals strongly as was indicated by a rapid, distinct change to goethite. Although not confirmed, it appears that both dissimilatory microbial reductive dissolution and Fe$^{2+}$ catalysis accelerated the rate of transformation in both minerals during this period. The transformation of both minerals in the typically oxic-acidic water column was driven by hydrological conditions such as diffusion, and advective flow by removing the transformed products from the vicinity of the minerals. The transformation of both minerals incubated in anoxic-reducing sediments was mainly driven by the dissimilatory microbial reduction and the Fe$^{2+}$ catalysis. A higher amount of Si (~ 0.6-1.4%) was measured in both minerals incubated in sediments by the end of 12 months.
This field based evidence clearly demonstrated that the rate and the fate of the transformation of schwertmannite and jarosite in ASS (formed by the partial oxidation of pyrite) are strongly influenced both by hydrological conditions in the water column, and by geochemical properties that are driven in a highly dynamic fashion by key environmental factors such as rainfall distribution.

8.2.2 Effect of arsenic (As) and natural organic matter (fulvic acid) on schwertmannite

Liberation of acidity and As from both Pure and As-substituted synthetic schwertmannite (As-schwertmannite) was investigated in the presence of three different fulvic acid (FA) concentrations (i.e. 1, 10, 25 mg L\(^{-1}\)) at acidic and neutral pHs (i.e. 4.5 and 6.5) typical of oxidised ASS. Acidity was determined by titrating the suspensions for 48 h. As-schwertmannite liberated a higher amount of acidity under oxic conditions at both pHs compared to Pure schwertmannite. Both pH and FA largely controlled the liberation of acidity from both types of schwertmannites. At acidic pH (i.e. 4.5), all three FA concentrations largely impeded the liberation of acidity as opposed to schwertmannite titrated without FA. Likewise, liberation of acidity was impeded by all three FA at neutral pH (i.e. 6.5) in the long term, except an initial increase by low and moderate FA (i.e. 1 and 10 mg L\(^{-1}\)) concentrations. FA promoted the liberation of As from schwertmannite, largely at neutral pH (i.e. 6.5) and at low FA (1 mg L\(^{-1}\)) concentrations.

This study revealed two important aspects relevant to schwertmannite in ASS. Firstly, though schwertmannite can act as a scavenger for As in natural environments, the resultant As-schwertmannite can liberate a larger amount of acidity to the environment. Secondly, the active natural organic matter component in ASS (i.e. FA) can enhance the liberation of As from schwertmannite even under oxic conditions.
8.3 Futures Studies

The findings of this thesis indicate that routine analytical techniques may provide inaccurate estimations of the quantity of schwertmannite and jarosite present in ASS. Selective dissolution and sequential extraction techniques widely used for the identification and quantification of the two minerals in AMD environments, showed limited applicability for ASS. The study also demonstrated that the behaviour of both minerals in natural ASS environments is strongly influenced by the hydrology and the seasonality of the weather. The study also highlighted the importance of labile organic matter found in ASS that can strongly influence the liberation of acidity and mobilization of previously scavenged metalloids from schwertmannite.

Future research to resolve the important effect of Al hydroxy sulfate minerals (e.g. basaluminite) and organic matter (the two common substances found in ASS) on the recovery of schwertmannite would advance the development of accurate assessment methods for schwertmannite. The present study suggested application of a conversion factor of 2 for the S_{NAS} recovered from jarosite (both synthetic and natural) used in this study. Future work on a range of jarosite samples from different ASS regions would be useful to determine a universal correction factor (or determine if such a universal correction factor is possible). Liberation of sulfur from both schwertmannite (which led the formation of goethite) and jarosite during peroxide oxidation is an important finding of this study, and further investigation of this aspect would improve the assessment of the acidity hazard in ASS through the ABA approach. Further knowledge on the potential occlusion of sulfur liberated from yavapaiite decomposition during the roasting of jarosite would be also important in the development of assessment methods for jarosite in ASS.

While this study has improved our understanding of the in-situ transformation behaviour of schwertmannite and jarosite in ASS environments, the interaction of both minerals with the nitrogen and phosphorus cycles in acidic waterways (especially at acidic and neutral pHs) due to the seasonality of the weather is worthy of further investigation. The new knowledge on the relationship
between labile organic matter, As, and schwertmannite in ASS environments revealed by this study would be further benefitted by understanding the mechanisms of these interactions to a greater extent. In addition to understanding the effect of labile organic matter on As and acidity liberation from schwertmannite, investigation of other potential competitors such as CO$_3^{2-}$ and PO$_4^{3-}$ (that are commonly found in ASS environments) would further enhance the management of environments that contain ASS materials.


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Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)


Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)


Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)


Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)


Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)

I, Edward Burton, co-author on the article listed above, agree with the stated author contributions.

Edward Burton
A1-2 Statement of Author Contributions: Leigh Sullivan


*Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)*


*Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)*


*Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)*


*Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)*


*Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)*

I, Leigh Sullivan, co-author on the article listed above, agree with the stated author contributions.
A1-2 Statement of Author Contributions: Richard Bush


*Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)*


*Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)*


*Vithana (80%), Sullivan (10%), Bush (5%), Burton (5%)*


*Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)*


*Vithana (80%), Sullivan (10%), Burton (5%), Bush (5%)*

I, Richard Bush, co-author on the article listed above, agree with the stated author contributions.

Richard Bush
Acidity fractions in acid sulfate soils and sediments: contributions of schwertmannite and jarosite

Chamindra L. Vithana\textsuperscript{A,B,C}, Leigh A. Sullivan\textsuperscript{A,B}, Richard T. Bush\textsuperscript{A,B}, and Edward D. Burton\textsuperscript{A,B}

\textsuperscript{A}Southern Cross GeoScience, Southern Cross University, Lismore, NSW 2480, Australia.
\textsuperscript{B}CRC CARE, Building X, University of South Australia, Mawson Lakes, SA 5095, Australia.
\textsuperscript{C}Corresponding author. Email: c.vithana.10@student.scu.edu.au

Abstract. In Australia, the assessment of acidity hazard in acid sulfate soils requires the estimation of operationally defined acidity fractions such as actual acidity, potential sulfidic acidity, and retained acidity. Acid–base accounting approaches in Australia use these acidity fractions to estimate the net acidity of acid sulfate soils materials. Retained acidity is the acidity stored in the secondary Fe/Al hydroxy sulfate minerals, such as jarosite, natrojarosite, schwertmannite, and basaluminite. Retained acidity is usually measured as either net acid-soluble sulfur (SNAS) or residual acid soluble sulfur (SRAS). In the present study, contributions of schwertmannite and jarosite to the retained acidity, actual acidity, and potential sulfidic acidity fractions were systematically evaluated using SNAS and SRAS techniques. The data show that schwertmannite contributed considerably to the actual acidity fraction and that it does not contribute solely to the retained acidity fraction as has been previously conceptualised. As a consequence, SNAS values greatly underestimated the schwertmannite content. For soil samples in which jarosite is the only mineral present, a better estimate of the added jarosite content can be obtained by using a correction factor of 2 to SNAS values to account for the observed 50–60% recovery. Further work on a broader range of jarosite samples is needed to determine whether this correction factor has broad applicability. The SRAS was unable to reliably quantify either the schwertmannite or the jarosite content and, therefore, is not suitable for quantification of the retained acidity fraction. Potential sulfidic acidity in acid sulfate soils is conceptually derived from reduced inorganic sulfur minerals and has been estimated by the peroxide oxidation approach, which is used to derive the SRAS values. However, both schwertmannite and jarosite contributed to the peroxide-oxidisable sulfur fraction, implying a major potential interference by those two minerals to the determination of potential sulfidic acidity in acid sulfate soils through the peroxide oxidation approach.

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Liberation of acidity and arsenic from schwertmannite: Effect of fulvic acid

Chamindra L. Vithana *, Leigh A. Sullivan, Edward D. Burton, Richard T. Bush

Southern Cross GeoScience, Southern Cross University, Australia
CRC CARE, Building X, University of South Australia, Mawson Lakes, SA 5095, Australia

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Abstract

Schwertmannite is one of the major components that produces acidity in acid mine drainage (AMD) and acid sulfate soils (ASS) and is also known to be an effective scavenger of Arsenic (As) in such environments. Fulvic acid (FA) is an active component of natural organic matter (NOM) and is known to interact strongly with both schwertmannite and As. Two main environmental hazards related to schwertmannite are acidity liberation and potential re-mobilization of adsorbed or co-precipitated As upon hydrolysis. This study focused on understanding the behaviour of As-substituted schwertmannite with regard to the potential of acidity liberation, the effect of FA on acidity liberation from both pure and As-substituted synthetic schwertmannites, and the effect of FA on arsenic mobilization from As-substituted synthetic schwertmannite. This was investigated by means of short-term (48 h) titrations. The liberation of acidity from As-substituted schwertmannite and the effect of FA were examined at two pH values (i.e. 4.5 and 6.5) typical for ASS environments. As-substituted schwertmannite liberated a greater amount of acidity in comparison to pure schwertmannite at both pHs. Concentration of FA and pH each showed a strong influence on the liberation of acidity from both pure and As-schwertmannite. At the acidic pH (4.5), FA inhibited acidity liberation from schwertmannite. At the near neutral pH of 6.5, the concentration of FA played a critical role in affecting the liberation of acidity from schwertmannite. The initial liberation of acidity was enhanced from pure schwertmannite at pH 6.5 by low FA concentration (1 mg L\(^{-1}\)) and from As-schwertmannite by both low (1 mg L\(^{-1}\)) and moderate (10 mg L\(^{-1}\)) FA concentrations. Interestingly, higher FA concentrations (25 mg L\(^{-1}\)) inhibited acidity liberation from both types of schwertmannite in comparison to the control (pure/As-schwertmannite titrated without added FA). FA enhanced the liberation of As from the As-schwertmannite at both pHs under oxidising conditions and the rate of As liberation was greater at the near neutral pH. The present study provides new insights on the effect of As-substitution on acidity liberation from schwertmannite and the role of FA on: a) liberation of acidity, and b) As mobilization, from schwertmannite.

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