1

General introduction

1.1 INTRODUCTION

Soils containing iron sulfides or the products of sulfide oxidation are termed as acid sulfate soils (ASS). Pyrite (FeS$_2$) is the most common iron sulfide in ASS, although other sulfide minerals including marcasite (FeS$_2$), mackinawite (FeS$_{0.94}$) and griegite (Fe$_3$S$_4$) have also been observed in small amounts in these soils (Bigham and Nordstrom, 2000; Fanning et al., 2002). Sulfidic sediments accumulate under waterlogged conditions where there is a supply of sulfate (SO$_4^{2-}$), the presence of metabolisable organic matter, and the availability of iron containing minerals (Fitzpatrick, 2008). The prevalence of these conditions from the last major sea level rise during Holocene age resulted in the accumulation of large deposits of sulfidic sediments in coastal floodplains, swamps and wetlands throughout the world (Dent and Pons, 1995). While the presence of sulfidic sediments has largely been associated with the coastal regions, they are increasingly being recognised in saline-inland landscapes in recent years (Hall et al., 2006; Holmer and Storkholm, 2001). There are between $10^7$ and $10^8$ ha sulfidic lowlands in coastal regions around the world, with large deposits identified in the Netherlands, China, Vietnam, Indonesia, South Africa and America (Brinkman, 1981). Although the global extent of inland ASS is not well-known, in Australia, inland ASS make 73% of the total area under ASS, which is approximately $2.2 \times 10^6$ ha (Fitzpatrick et al., 2010). Significant environmental damage due to drainage and changes in land use of ASS has
occurred in Australia and in countries around the world. The major challenge lies in managing sulfide-rich areas that are already drained. The development of an appropriate management scheme for these soils requires an understanding of the accumulation and distribution of sulfidic sediments, the processes leading to their formation and the export of the oxidation products to the environment (White et al. 1997). Inappropriate management of sulfide-rich materials can cause deoxygenation, acidification, and can result in the dissolution of clay minerals and mobilization of heavy metals (Baldwin, 2010; Fitzpatrick and Shand, 2008).

Sulfidic sediments are thermodynamically stable under reducing conditions. The exposure of these sediments to atmosphere, as a result of natural (e.g. drought, sea level fall and tectonic uplift) and/or anthropogenic activities (e.g. drainage works, flood mitigation, and excavation), results in their oxidation (Fanning et al., 2002). Depending on the nature of the sediments or soils (e.g. sands or clays), the oxidation of sulfidic sediments or soils may release copious amounts of sulfuric acid (H$_2$SO$_4$) which could result in a drastic reduction in the solution pH, dissolution of minerals, and a subsequent release of acid (Al$^{3+}$, Fe$^{3+}$) and base (Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$) cations into the soil solution. In addition, many of the ASS systems in the inland regions of Australia are also highly saline. The extremely acidic conditions in conjunction with high levels of salinity (dominated by the presence of NaCl), may be of particular significance.

Phyllosilicates constitute a major group of minerals that dominate in the clay fraction of most soils. Chemical weathering of phyllosilicate minerals is the only process by which acidity can be neutralised on a long-term basis in ASS environments (White and Brantley, 1995). The acid neutralisation capacity of phyllosilicate minerals is dependent on the dissolution rates of these minerals.
The dissolution rates of phyllosilicate minerals have been quantified using both laboratory and field experiments (Brantley, 2007). Field–based dissolution rates of minerals are mostly estimated from solute changes in soil pore waters, groundwater and watershed discharges or from changes in the solid-state regolith compositions (Ganor et al., 2007; White and Brantley, 2003). However, in the field scale determination of dissolution rates there are uncertainties in the estimation of fluid residence times, and fluid flow paths, surface areas of minerals in mineral mixtures and the past variations in the climate and solute composition (White and Brantley, 2003). In laboratory experiments, the dissolution rates of phyllosilicate minerals have been estimated using a variety of experimental methods where solution chemistry is monitored as a function of time. These methods include batch-reactors, flow-through reactors and column-reactors. There are also disadvantages in the experimental dissolution rate determination (such as the extrapolation of laboratory-determined dissolution rates to the field-scale rates), as in these settings freshly prepared mineral surfaces are reacted with the fluid for a relatively short span of time (White and Brantley, 2003). However due to a tight control on the chemical, physical and biological conditions, the effect of individual parameters such as solution composition, temperature and mineral surface area etc. can be accurately measured in the laboratory experiments. In numerous laboratory studies conducted over the past 15–20 years, the dissolution rates of phyllosilicate minerals have been estimated under variable experimental conditions, such as solution chemistry, stirring speed and method. The effects of pre-treatment on the mineral used in experiments have also been investigated (Moore, 2008). In most of the previous studies, the acidic solutions were made using hydrochloric (HCl), perchloric (HClO₄), acetic (CH₃COOH) and nitric (HNO₃) acids (Amram and Ganor, 2005; Cama et al., 2002; Huertas et al., 1999; Zysset and Schindler, 1996). Kaolinite dissolution rate was found to be similar in nitric and perchloric acids (Ganor
et al., 1995; Wieland and Stumm, 1992), and hydrochloric or acetic (Huertas et al., 1999) and perchloric acids (Cama et al., 2002). Smectite dissolution rate was also similar when determined in perchloric or nitric acids (Amram and Ganor, 2005), suggesting that the chlorate (ClO$_4^-$) anion does not affect the smectite dissolution rate. The dissolution rate of smectite remained same between 0.03 and 0.10 M ionic strength; whereas it increased with increasing ionic strength from 0.10 M to 1.0 M (Zysset and Schindler, 1996) in batch reactors. In flow-through reactor experiments, the effect of ionic strength on kaolinite and smectite dissolution rate was found to be insignificant (Amram and Ganor, 2005; Cama et al., 2002). Chlorite dissolved at a faster rate in H$_2$SO$_4$ solutions than in HCl or HNO$_3$ solutions at pH values ≤ 2 (Hamer, 2003). The dissolution rates of gibbsite increased in the presence of SO$_4^{2-}$ in the solution by a factor of 6 to 30 times (pH 2 and 3) (Dietzel and Bohme, 2005; Ridley et al., 1997). An increase in gibbsite dissolution rate due to the presence of SO$_4^{2-}$ ions was suggested to result from the formation of aqueous Al complexes with SO$_4^{2-}$ ions (Mogollon et al., 2000; Ridley et al., 1997). The saline-acid sulfate solution generated from sulfide oxidation in inland ASS can alter the dissolution rates and stoichiometry of commonly occurring phyllosilicate minerals in these soils. To date, no research has been conducted to explain these important aspects.

The release of H$_2$SO$_4$ from iron sulfide oxidation is also accompanied by the precipitation of a wide range of secondary iron minerals. The mineralogy of the precipitates formed on iron sulfide oxidation is dependent on the precipitation conditions (Bigham et al., 1996). The type of secondary iron minerals formed from sulfide oxidation is important, as it governs the amount of acidity released from sulfide oxidation (Dold and Fontboté, 2001). The secondary iron minerals are also important sinks for dissolved trace metals and may significantly reduce
the mobility and bioavailability of metals in the environment through adsorption and/or coprecipitation processes (Burton et al., 2008; Fukushi et al., 2004). Poorly crystalline iron minerals such as ferrihydrite, schwertmannite and akaganéite have large surface areas and a potential for metal adsorption (Gao and Schulze, 2010). Schwertmannite and akaganéite are of particular significance because of their ability to incorporate oxyanions (such as AsO$_4^{3-}$ and CrO$_4^{2-}$) into their square tunnel structures (Regenspurg and Peiffer, 2005).

An incomplete hydrolysis of ferric (Fe(III)) produced from iron sulfide oxidation, results in the precipitation of metastable minerals of Fe, such as schwertmannite and jarosite, which may later transform to the stable minerals (e.g. goethite). The transformation of metastable phases to stable minerals has severe consequences for the surrounding environment as this process releases the additional acidity that was stored on the formation of these minerals (Dold and Fontbote, 2001). Therefore it is important to determine the composition of secondary minerals and the solution and environmental conditions for their formation.

This study was conducted to determine the mineralogy of an inland ASS and to evaluate the dissolution behaviour of clay minerals in these soils which will allow more effective management of these soils.

### 1.2 AIMS

This thesis presents the following aims:

1. To evaluate the dissolution behaviour of kaolinite, illite and montmorillonite in saline-acid solutions with composition similar to inland ASS in Australia.

2. To investigate the dissolution behaviour of a natural polymineralic clay fraction in saline-acid solutions with composition similar to inland ASS in Australia.
3. To determine the mineralogy of oxidised surface precipitates from an inland-acid sulfate soil in New South Wales (NSW), Australia.

1.3 OBJECTIVES

The specific objectives of the work presented in this thesis were:

1. To determine the dissolution rate of illite at an acidic pH range of 1–4 (using H$_2$SO$_4$) and at ionic strengths of 0.01 M and 0.25 M (using NaCl), at 25°C (Chapter 3);
2. To compare the dissolution behaviour of kaolinite, illite and montmorillonite in acidic solutions at pH 1–4 (using H$_2$SO$_4$) and at 0.01 and 0.25 M ionic strengths (Chapter 4);
3. To determine the effects of pH (1–4), ionic strength (0.01 M and 0.25 M) and temperature (25°C, 35°C, 45°C) on the dissolution behaviour of a natural polymineralic clay sample (Chapter 5);
4. Identification and characterisation of minerals formed in the oxidised layer of a saline-ASS in south-western NSW, Australia (Chapter 6).

This thesis starts with the general introduction chapter (Chapter 1), a review of the relevant literature presented in Chapter 2, four main research chapters (Chapters 3–6), followed by a chapter (Chapter 7) that presents a summary of the results presented in research chapters and identifies future research ideas in this field. As the four research chapters (Chapters 3–6) were prepared as manuscripts, for submission to journals for publications, there is some repetition in the introduction, and materials and methods section of these chapters.
1.4 REFERENCES


Chapter 1: General introduction


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Solutions for a Changing World. Published on DVD; http://www.iuss.org; Symposium
WG 3.1 Processes in acid sulfate soil materials, Brisbane, Australia.


Chapter 1: General introduction

