Minerals diagnostic of acid sulfate soils

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Introduction

Acid sulfate soils (ASS) form when sulfides in the soil are oxidised thereby releasing sulphuric acid. ASS formation is associated with lowering of water levels in rivers and lakes. This lowering of water levels exposes sulphide materials (often as pyrite framboids or monosulfides) accumulated in river banks and lake beds to the atmosphere. The recent drought conditions that have persisted over south-east Australia for many years have led to ASS formation and acidification along the length of the River Murray and its tributaries and lakes.

The pH in ASS can be well below 3 leading to the dissolution of clays and other soil minerals. This dissolution causes the release of a range of cations into the soil-water system that, on drying, combine with sulfate to precipitate a variety of minerals. Which particular minerals form on drying is dependant on the conditions (e.g. pH, eH) of the soil-water system. Consequently minerals identified in an ASS are diagnostic of the soil-water conditions in that ASS.

Results

Many of the precipitated minerals associated with ASS are brightly coloured partly because of the high Fe concentrations in ASS. A number of distinctive bright yellow oxyhydroxysulfate minerals have been identified in several wetlands adjacent to the River Murray as a consequence of sulfide oxidation and formation of sulfuric material. These oxyhydroxysulfate minerals developed after drainage of the soils when watertable levels dropped by as much as 50 cm over a 6 month period in 2007. In these wetlands, the presence of coloured “indicator minerals” proved particularly useful in the field identification of sulfuric materials. Sideronatrite ($Na_2Fe(SO_4)_2OH{\cdot}3H_2O$) has been identified in salt efflorescences on surface layers in Lake Bonney South Australia (Fitzpatrick et al. 2008a) and Nelwart Lagoon (situated close to Renmark in SA Riverland; Shand et al. 2009) as they dried and sulfuric materials gradually formed (Fig. 1). These indicator minerals also included natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and tamarugite ($NaAl(SO_4)_2{\cdot}6H_2O$) together with a number of Mg and Na sulfate minerals, particularly where groundwater discharges were present. Bright yellowish green surface efflorescences were also identified in Burnt Creek (upper catchment of the Loddon River, Victoria) and comprised sideronatrite, which formed as an alteration product of weathered pyrite. The minerals, hexahydrite ($MgSO_4{\cdot}6H_2O$), epsomite ($MgSO_4{\cdot}7H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$) and halite (NaCl) were also present (Thomas et al. 2009).

It was the prominent features of oxyhydroxysulfate materials that originally led CSIRO to first discover the presence of sulfuric materials in the Swanport wetland near Murray Bridge in June 2007 (Fitzpatrick et al. 2008b) (Fig. 2). These surface-soils salt efflorescences comprised salts with a yellowish colour (natrojarosite) or a golden-coloured mineral determined to be the rare mineral metavoltine ($Na_6K_2FeFe_6(SO_4)_{12}O_2 \cdot 18H_2O$). Metavoltine formed botryoidal encrustations on the edges of cracks as an alteration product of weathered pyrite. This discovery documented the first occurrence of metavoltine in Australia and possibly the first ever occurrence associated with ASS. White crystals of alunogen ($Al_2(SO_4)_3 \cdot 17H_2O$), hexahydrite and gypsum were also identified, having formed as a result of acidic ($pH < 2.5$), sulfate-bearing solutions that reacted with layer silicates in the soils. These localised solutions were rich in ferrous and ferric iron and also contained dissolved potassium and sodium. Metavoltine and alunogen are the last minerals to form in areas of intense evaporation.

Discussion and Conclusions

By virtue of their chemical composition and conditions of formation the minerals that form in association with ASS are diagnostic of the physico-chemical conditions in the ASS. Sideronatrite forms in strongly-acidic, oxidising conditions. It is most often found in sandy soils where there is little pH buffering from clays and the soil pores are relatively open allowing the flow of oxygen into the soil-water system. Necessarily the formation of sideronatrite requires the soil-water system to be Na-rich. Metavoltine also forms in strongly-acidic, oxidising conditions but unlike sideronatrite, metavoltine requires the presence of both Na and K in the soil-water system. The source of the K in metavoltine is most likely from the dissolution of clays and feldspars under the strongly-acidic conditions. Consequently metavoltine is often found in clay-rich soils. The smaller pores space of these soils (relative to sandy soils) may be an influencing factor in the incomplete oxidation of Fe^{2+} to Fe^{3+} because of the restricted flow of oxygenated water through the soil pores.

The presence of alunogen and tamarugite indicate acidic conditions sufficiently strong to dissolve clays and clay minerals releasing Al into the soil-water system. The formation of tamarugite over alunogen indicates a higher Na content in the soils-water system.

Intermediate acidity regimes (pH from 2.5 to 4) in an oxidising environment can be indicated by the presence of scwhertmannite ($\sim Fe_{16}O_{16}(OH)_{10}(SO_4)_3 \cdot nH_2O$) (Bigham et al., 1990) (Fig. 3).

The diversity of the sulfates minerals formed in association with ASS in terms of both chemical composition and conditions of formation make these minerals useful diagnostic tools for characterising the soil-water conditions in ASS.

References

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Fig. 1. Salt efflorescences and acid water formed as a result of drying at Nelwart Lagoon (Shand et al. 2009).

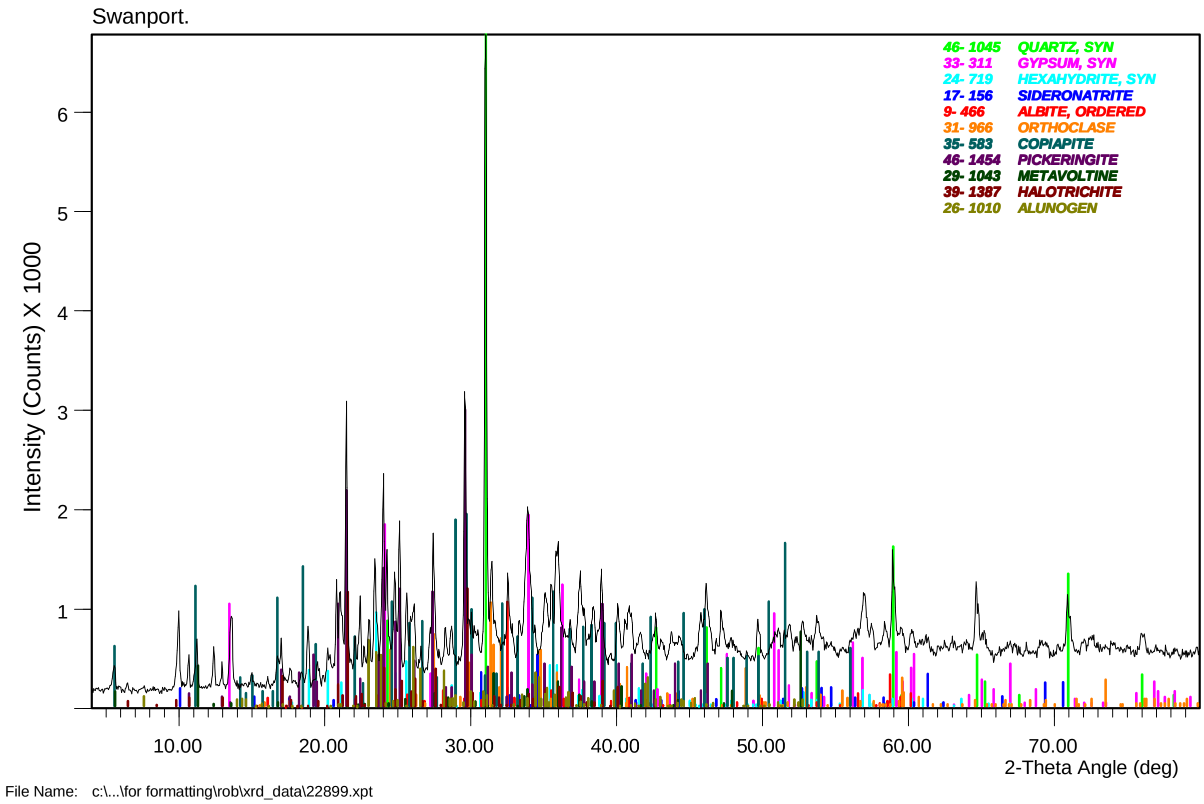

Fig. 2. XRD pattern (Co Kα radiation) of sample collected from an ASS in the lower reaches of the River Murray (Swanport, SA).

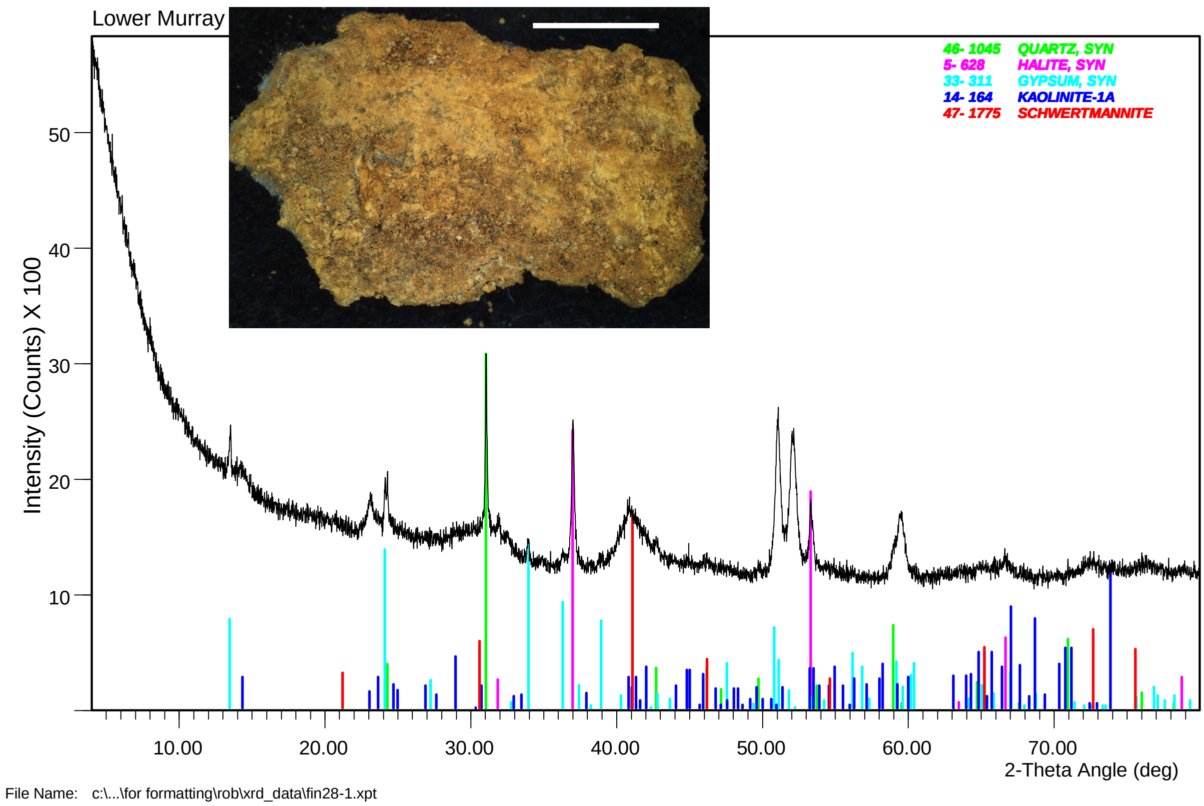

Fig. 3. XRD pattern (Co Kα radiation) and image of a scwhertmannite-rich sample collected from ASS in wetlands adjacent to the Finniss River, SA. Bar in image = 0.5mm.