

Occurrence and environmental significance of sideronatrite and other mineral precipitates in Acid Sulfate Soils

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Abstract

This study documents the first occurrence of metavoltine in Australia and the widespread occurrences of sideronatrite and tamarugite in Acid Sulfate Soils (ASS). We interpret the occurrence of these soluble salts to represent changing surface and ground water tables, which are linked to the lowering of water levels in the River Murray and Lower Lakes where capillary action, combined with subsurface evaporation, has concentrated Fe-Al-Na-Mg sulfates, especially in summer or during dry periods. During winter rainfall wet/drying events in the sandy sulfuric materials on exposed beaches, soluble white sulfate-containing evaporite minerals comprising pickeringite-halotrichite, redingtonite, hexahydrite and epsomite precipitate as micron thick layers on the soil surface. Sideronatrite and tamarugite precipitate within yellowish-green friable 2 to 5 mm thick crusts on the soil surface. Sideronatrite (large platelets) is derived from the oxidation and dissolution of the sulfide framboids in sulfuric materials (< pH 2.5). Surrounding some of the crusts where water temporarily leaches and ponds, sideronatrite dissolves and re-precipitates as schwertmannite within orange coloured patches. These mineral precipitates play important roles in the transient storage of components (Fe, Al, Na, Ca, Mg, Cl, Sr and SO₄), which may also dissolve to contribute to the formation of saline monosulfidic black ooze in wetter soils (e.g. adjacent to the lakes). These salts are likely to form if water levels decrease and have the potential to become a problem during re-flooding if not managed properly. Salt efflorescences also have potential for aerial transport and to be dissolved in water. There is a need to prevent stock from ingesting these salts (similar to Epsom salts) because this is likely to lead to scouring in sheep and cattle. Magnesium salts are toxic when ingested in high levels.

Key Words

Sulfuric materials, salt efflorescences, iron oxyhydroxysulfates; sulfate-containing evaporite minerals

Introduction

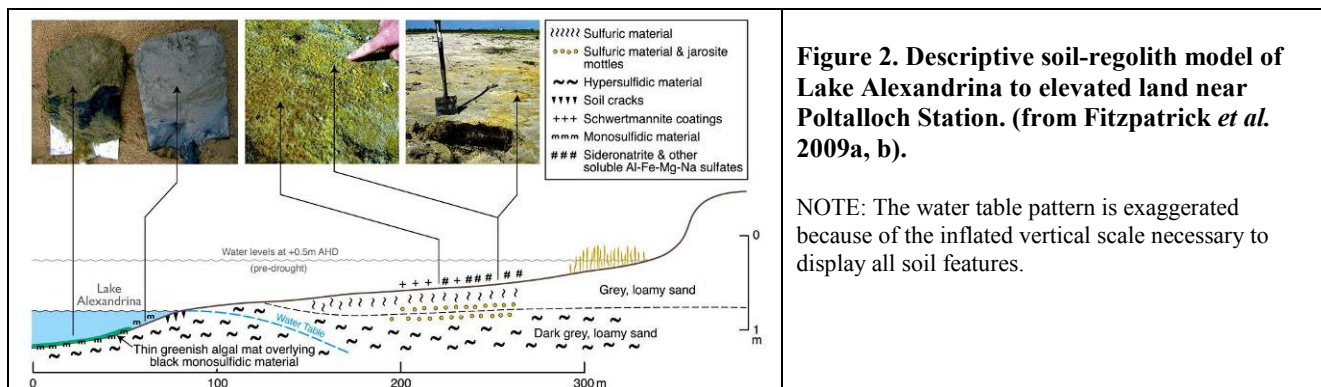
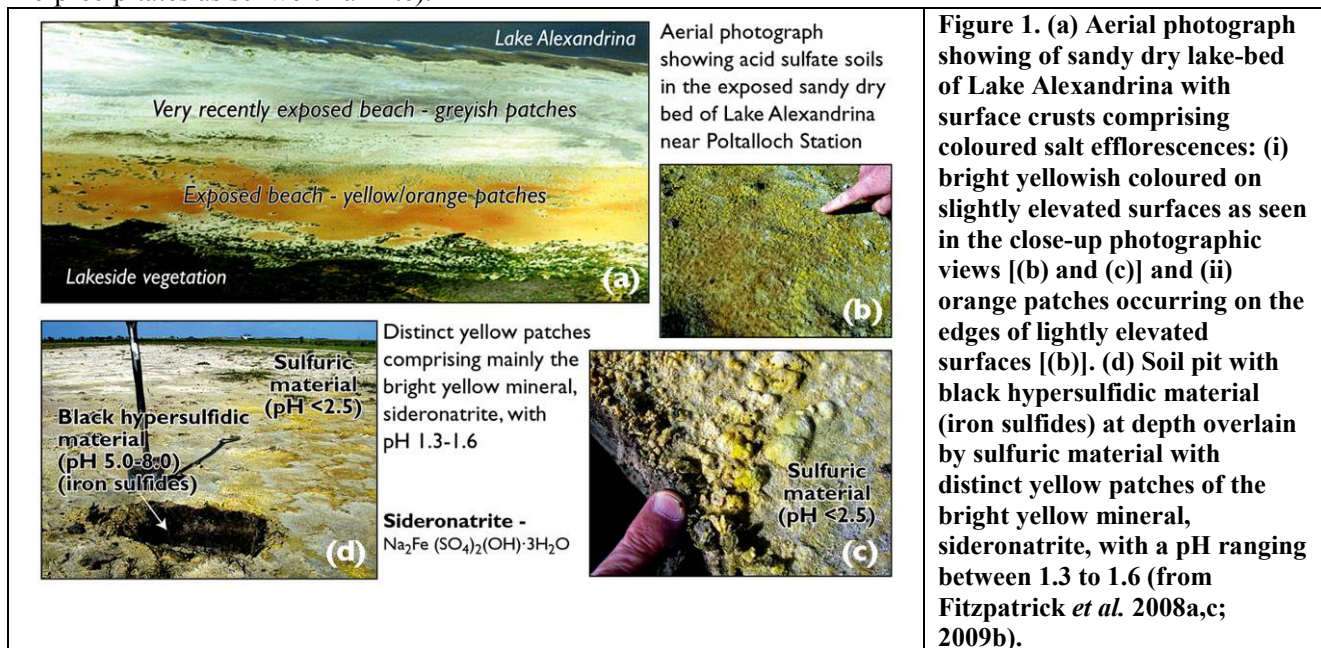
Acidification occurs if the amount of acidity produced exceeds the pH buffering capacity (the overall neutralizing capacity) of the soil. For sulfuric materials, the products of the chemical reactions can: (i) remain as dissolved constituents of soil pore waters, (ii) form a range of secondary minerals in the form of salt efflorescences comprising sulfate-rich salts that accumulate due to evaporation (e.g. epsomite and hexahydrite), (iii) undergo a series of hydrolysis reactions and precipitate new minerals such as iron oxyhydroxides and iron oxyhydroxysulfates (e.g. jarosite, natrojarosite, schwertmannite and sideronatrite) and (iv) accelerate the weathering or dissolution of minerals in soils and sediments. The hydroxysulfate minerals formed are important to recognize because they store acidity and metals that can subsequently generate poor water quality. Several studies have shown that dissolution of salt accumulations along stream banks during a rainstorm temporarily lowers pH and increases metal loads in streams (e.g. Fitzpatrick *et al.* 2009a,b). Such water quality impacts can have damaging effects on aquatic ecosystems and can complicate efforts to remediate acid drainage. Rainfall and rewetting events can also flush salts, leading to pulses of contaminated water flowing into streams or wetlands. Such flushes mean that these various products or minerals may or may not be present at a given site on a given day, depending on weather conditions.

Results and Discussion

Lake Alexandrina, Lake Albert and adjacent tributaries (Finniss River and Currency Creek)

Due to the extreme drought conditions in south-eastern Australia that commenced in about 2006, water levels have declined in Lake Alexandrina, Lake Albert and the River Murray system, especially in the section below Blanchetown (Lock 1) (e.g. Lake Alexandrina shown in Figure 1a; Fitzpatrick *et al.* 2008a; 2009a,b). The reducing hypersulfidic material once covered by water has become exposed to oxygen at the river and lake margins (Figures 1a and 2), and in adjacent wetlands. With continued lowering of water levels, the hypersulfidic material has become progressively oxidised to greater depths in the soil profile (Figure 1).

The spatial variation of the following soil features caused by receding water levels due to current extreme drought conditions is described in Figure 2: (i) monosulfidic material in the subaqueous soils, (ii) the prominent bright yellow mineral, sideronatrite, with a pH ranging between 1.3 to 1.6 on the soil surface, which overlies black hypersulfidic material in the soil pit (see close-up views in Figure 1) and (iii) brownish-orange coatings of the mineral schwertmannite, which forms from sideronatrite (dissolves in rainwater and re-precipitates as schwertmannite).



The widespread occurrences of bright yellowish-green surface efflorescences can be observed at a range of scales from landscape (Figure 1a) to soil profile (Figures 1d & 2) scales and may be present as either finely dispersed powder in sand or as a 2 to 5 mm thick, sandy friable crust (Figure 1c). These surface efflorescences contain mainly precipitates of the minerals sideronatrite ($[\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot \text{OH} \cdot 3\text{H}_2\text{O}]$), tamarugite ($[\text{Na}_2\text{Al}(\text{SO}_4)_2 \cdot \text{OH} \cdot 3\text{H}_2\text{O}]$) and alunogen ($[\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}]$). Sideronatrite occurs as rosettes and platelets (Figure 3) within sulfuric material (pH 0.8 to 1.6) on the soil surface. Sideronatrite is derived from the oxidation and dissolution of pyrite framboids, which occur mainly in the form of spheroidal aggregates of pyrite crystals (Figure 4). Sideronatrite in the yellowish-green crusts dissolves and re-precipitates as schwertmannite (Figure 1 and 2) in immediately adjacent zones where the pH is slightly higher, to display distinct orange patches or areas on the soil surface and diffuse orange mottles to a depth of 2 to 10 cm.

These minerals not only form seasonally during summer heat and high evaporative conditions in soils exposed by drought, but also during: (i) the winter rainfall cyclic wetting and drying events and (ii) the cyclic rewetting of the sulfidic materials due to lake level changes associated with seiching, which is likely to be an important acidity transfer mechanism from ASS to lake water. Seiching has a tidal effect, and occurs when wind blows shallow lake water onshore. Typical water level variations in Lake Alexandrina during seiching can be tens of centimetres according to wind strength and direction, and may advance the waterline many tens of metres inland (i.e. up the beach) due to the shallow bathymetric gradient. The rewetting of sideronatrite by rainwater and seiching causes mineral dissolution and the resultant mobilisation of acid, iron, sulfate and sodium ions to immediately adjacent, temporary ponded areas, where orange coloured

schwertmannite rapidly crystallises. This process has also been simulated in the laboratory by adding rainwater to both natural samples of the sideronatriite-rich crusts and synthetically prepared sideronatriite. A remarkably similar dissolution and precipitation mechanism was previously observed by Fitzpatrick *et al.* (2000) in sandy sulfuric materials in eroded river banks in the Mount Lofty Ranges. This was the first identification of the formation of sideronatriite from oxidation of sulfide framboids in sandy sulfuric materials. They also observed dissolution of sideronatriite (and tamarugite) in sulfuric materials on eroded stream banks and the subsequent formation of schwertmannite in immediately adjacent stream waters.

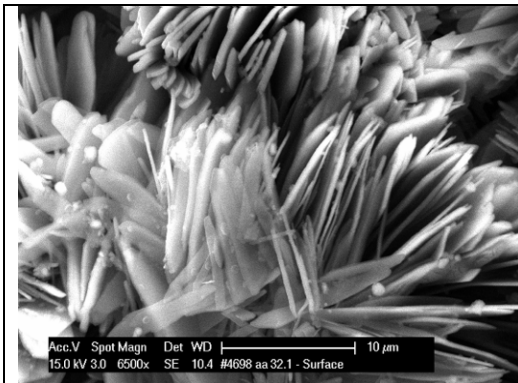


Figure 3. Scanning electron micrograph, of bladed sideronatriite crystals $[\text{Na}_2\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})\cdot 3(\text{H}_2\text{O})]$. Sample as sub-sampled from Lake Alexandrina sample AA 32.1, 0-0.05 cm – from Fitzpatrick *et al.* 2008c). The image was taken in the secondary electron imaging mode, using a Phillips XL30 SEM, at a magnification of 6.50 kX. The approximate composition as analysed by Energy Dispersive X-ray analysis is illustrated in Fitzpatrick *et al.* 2008c.

In addition, a wide range of highly soluble whitish coloured sulfate-containing evaporite minerals in sulfuric materials were identified in Lake Albert and Lake Alexandrina (i.e. pickeringite-halotrichite and redingtonite together with hexahydrite and epsomite – Figure 4) that crystallise in micron thick layers on the exposed sandy soil surfaces during the winter rainfall cyclic wetting and drying events.

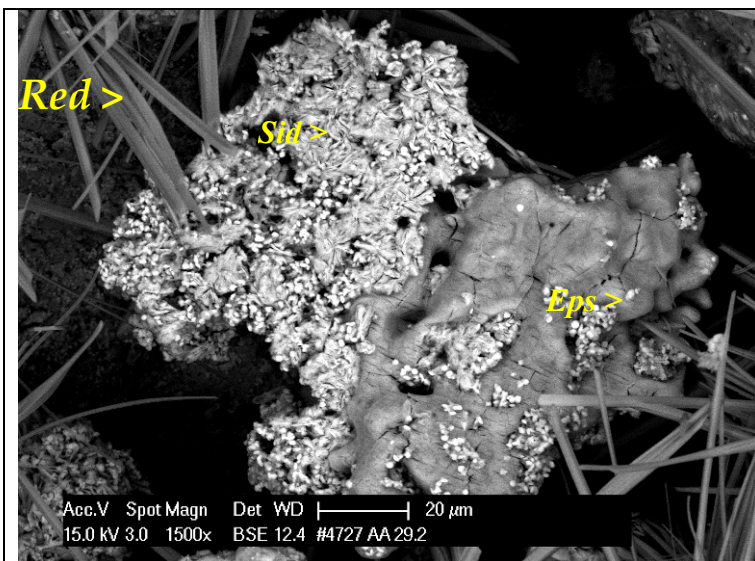


Figure 4. Scanning electron micrograph, of bladed sideronatriite crystals $[\text{Na}_2\text{Fe}^{3+}(\text{SO}_4)_2(\text{OH})\cdot 3\text{H}_2\text{O}]$ mixed with fine grained pyrite crystals (Pyr) $[\text{FeS}_2]$, redingtonite (Red) $[(\text{Fe}^{2+}, \text{Mg}, \text{Ni}) (\text{Cr}, \text{Al})_2(\text{SO}_4)_4\cdot 22\text{H}_2\text{O}]$, and epsomite (Eps) $[\text{MgSO}_4\cdot 7\text{H}_2\text{O}]$ infiltrating the conglomerate. Sample as sub-sampled from Lake Alexandrina; sample AA 29.2, 0-0.2 cm. The image was taken in the BSE imaging mode, using a Phillips XL30 SEM, at a magnification of 1.5kX (from Fitzpatrick *et al.* 2008c).

Main River Channel and adjacent wetlands for River Murray, Loddon River and Burnt Creek (Victoria)

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, which developed after drainage of the soils as watertable levels dropped below 40 cm in June 2007 to below 90 cm in November 2007. In these wetlands, the presence of such key “indicator minerals” proved particularly useful in the field identification of sulfuric materials. In fact, it was these prominent features, which 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). In these surface soils salt efflorescences comprised salts with a yellowish (natrojarosite) or golden mineral determined to be the rare mineral metavoltine $(\text{Na}_6\text{K}_2\text{FeFe}_6(\text{SO}_4)_{12}\text{O}_2\cdot 18\text{H}_2\text{O})$, which 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 $(\text{Al}_2(\text{SO}_4)_3\cdot 17\text{H}_2\text{O})$, hexahydrite and gypsum were also identified, having formed as a result of acidic ($\text{pH} < 2.5$), 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.

Sideronatrinite was also identified in salt efflorescences on surface layers in Lake Bonney (Fitzpatrick *et al.* 2008d) and Nelwart Lagoon (situated close to Renmark in SA Riverland; Shand *et al.* 2009) as they dried out and sulfuric materials gradually formed. These minerals also included natrojarosite and tamarugite 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 and comprised sideronatrinite, which formed as an alteration product of weathered pyrite. In addition, the minerals, hexahydrate, epsomite [MgSO₄.7H₂O], gypsum and halite were also present (Thomas *et al.* 2009).

Conclusions

Soil-surface salt accumulations are unique in the region, which results from a combination of the characteristic Mediterranean type climate, hydrogeology, saline seepages, and salt crusting formed above sulfidic materials. These salt efflorescences are often dominated by the widespread occurrences of sideronatrinite and tamarugite together with a large number of soluble minerals, including halite, gypsum, thenardite (Na₂SO₄), hexahydrate and epsomite, and range in morphology from thin, powdery, very transient efflorescences to thicker, more persistent, soil-cementing crusts. The salt crusts form by the upward wicking of Na, Mg, Cl and SO₄ containing groundwaters and their subsequent surface evaporation. These Fe/Al oxyhydroxysulfate and oxyhydroxide minerals are indicators of very acidic soil conditions (i.e. the presence or former presence of oxidised pyrite), and as such their presence provides important environmental indicators of ASS (e.g. Fitzpatrick and Self 1997).

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