The Morphology and Composition of Pyrite in Sandy Podosols in The Swan Coastal Plain

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Abstract
Seventeen very deep peaty sandy podosol profiles containing distinct A, E, B, coffee rock (spodic B horizon) and C horizons were investigated. Some profiles contain buried soils (Palaeopodosols) representing former levels of the water table. Electron microscopy showed that pyrite is present in these podosols. Synchrotron XRD confirmed the presence of pyrite. Two pyrite morphologies were present: discrete submicron single crystals and 10-20 μm framboids. Single crystals of pyrite occurred in all E, B, coffee rock and C horizons examined. X-ray spectra of single crystals and framboids have the pyrite atomic ratio of Fe: S ≈ 1: 2. Framboidal pyrite is present in coffee rock and B horizon. As individual pyrite crystals are very small (≤ 1 μm), they have high specific surface area and are thus potentially very reactive if profiles are aerated.

Key Words
Pyrite, acid sulphate soil, Podosols, Swan Coastal Plain

Introduction
The acid sulphate soils (ASS) contains iron sulphide, especially pyrite. The oxidation of pyrite is the primary cause of acidification of acid sulphate soils. Pyrite is generally stable under reducing conditions (below the watertable), however, when the soil is drained and pyrite exposed to the atmosphere acidity is produced due to pyrite oxidation. The release of oxidation products can affect water quality, aquatic life, agricultural production and causes corrosion of concrete and other infrastructure.
The Swan Coastal Plain comprises of a series of three major sand dunes including Quindalup, Spearwood and Bassendean dunes. The soils on the Swan Coastal Plain consist predominantly of former beach deposits, the highly leached Bassendean Sands with very little clay and no carbonates to provide acid buffering capacity. These very sandy soils are unable to buffer against very low intensity acidifying processes. The acidification of the soils is apparently caused by oxidation of pyrite in peat soils within swampy areas being dewatered for urban development which lower the watertable and exposes of the pyritic soil to oxidation.

Methods
The Swan Coastal Plain, which lies to the west of the Darling Fault, developed over a deep trough filled with sedimentary rocks and consists of a series of geomorphic entities oriented sub-parallel to the coastline. The generalised surface geology is largely reflected in the distribution of soils, and includes the Guildford Clay in the east, the Bassendean Dune System fringing the present coastline (McArthur 2004).
The plain is composed of sedimentary material of Cainozoic and Mesozoic age. Sediments in wetlands are commonly peaty. Seventeen Humic/ Alsilic aquic podosols in swales in the Bassendean Dunes have been investigated. The 85 samples include A horizon rich in decomposing organic matter (14 samples), a light coloured sandy albic E horizon (30 samples), brown B horizon (9 samples) and a dark spodic B horizon (coffee rock, 19 samples) over a sand C horizon (13 samples). Some profiles contain several E and B horizons which may be regarded as remnants of palaeopodosols that formed when the water table was at lower positions.

Soil samples were kept in a wet condition in a cool room until analyzed and novel preparation procedures were employed to limit microbial activity and oxidation. Physico-chemical properties of whole soils were determined. Studies of the fine fraction (non quartz sand fraction) used scanning electron microscopy (SEM; JEOL 6400), transmission electron microscopy (TEM; JEOL 3000) and energy-dispersive X-ray analysis (EDAX). A highly dilute suspension of the fine fraction was prepared in distilled water by dispersion using ultrasonic treatment. For synchrotron X-ray diffraction (XRD), powder samples of the fine fraction were placed in glass capillaries, and analysed over an angular range of 4 - 60° 2Theta. The wavelength was set at ~1.0Å to provide for adequate dispersion/resolution.

Results

Soil morphology and properties

These podosol profiles are ancient and represent an extreme stage of pedogenesis. The substantial annual rainfall (about 800 mm at present) and the very high sand content (>95%) of the parent material has resulted in highly leached podsolised soils. All studied soil profiles show the typical A horizon, bleached E horizon, brown B horizon, strong dark cemented B horizon (coffee rock) and C horizon typical of podosols.

- A horizon: the Ag horizon of all soils is rich in organic matter with sandy texture.
- E horizon: the Ag horizon is underlain by grey quartz sand which becomes increasingly bleached with depth.
- B horizon: below the bleached sand is the illuvial B horizon which is highly porous, (brownish gray to brownish black) but does not contain cemented material.
- coffee rock: coffee rock is the term used to define a material which has a dark colour (yellowish brown to black), high organic matter and is strongly cemented. There appears to be a reduced porosity within the coffee rock due to the precipitation of iron oxyhydroxide, organic matter and aluminosilicate organic complexes.
- C horizon: the pale yellow parent material consisting of dune sand.

The typical soil depth of A, E, coffee rock, B and C horizons is 0-20 cm, 20-200 cm, 200-300 cm, 300-350 cm and 350-400 cm, respectively. Soil texture is sand (A, E and C horizons), with some B and coffee rock horizons having a loamy sand texture due to the high organic matter and allophane contents. The sand grains of the Bassendean Dune System which is a beach dune deposit are characteristically well rounded and are well sorted due to prolonged transport and sorting by water and wind. Soil pH in 1:5 H_2O varies between pH 3.2 - pH 8.8 for the A horizon, pH 4.0 - pH 6.9 for E horizon, pH 4.2 - pH 6.0 for the B horizon, pH 3.7 - pH 6.6 for coffee rock and pH 4.1 - pH 6.4 for the C horizon. The pH of soil in pH 5.5 H_2O_2 solution is in the range pH 1.8 - pH 6.0. Delta pH (pH H_2O-pH H_2O_2) ranges from 0.01-4.39 units, high values being indicative of the presence of sulphide (Soil Survey Staff 2006). The organic carbon content is mostly low in the E and C horizons ranging between 0.02-1.2%. The organic carbon content of A, B, and coffee rock horizons is high (ranging from 0.05-3.6%). Some soil profiles have distinct deep sub-soil horizons (2E horizon and 2coffee rock) which indicate buried palaeopodosols. These wetlands on the Swan Coastal Plain are commonly peaty and the subsoils contain pyrite (Appleyard *et al*. 2006). The podosols are classified as Humic/ Alsilic aquic podosols and Typic Endoaquods respectively in the Australian (Isbell RF 2002) and US (Soil Survey Staff 2006) soil classifications.

Mineral properties

Synchrotron XRD patterns of fine fractions extracted from podosol horizons show that quartz is the dominant mineral of the fine fraction with minor amounts of feldspar, kaolin and in some samples gibbsite and lepidocrocite. Resistant mineral, including anatase and ilmenite are present in some horizons. Pyrite is present in most E, B and coffee rock horizons and elemental sulphur is a minor constituent in most samples and occurs in all horizons (Figure 4).

Morphology and composition of pyrite

The reducing chemical environment within saturated horizons of very sandy humus podosols on the Swan Coastal Plain provides a favorable condition for pyrite (FeS_2) formation. Pyrite is the only sulphide mineral present. Pyrite single crystals (0.5-1 μm diameter) are abundant in all horizons except for the A horizon (Figure 1), however pyrite framboids (10-20 μm diameter) only occur within organic rich soil materials (coffee rock and B horizons) (Figure 2). Thus this study indicates a close association between organic matter and framboidal pyrite. Framboid formation may have formed from the spherical grains of sulphur present in these podosols, which correspond in shape and size to framboids (Figure 3) (Graham and Ohmoto 1994). The abundance of iron, sulphur and organic material evidently play important roles in the formation of pyrite framboids in these soils. Several authors have concluded that the formation of framboids can be explained by sulphidation of metastable spherical grains of sulphur either in an inorganic way by oxidation of hydrogen sulphide (abiogenic activity), or in a metabolic way, by the action of microorganisms (biogenic activity) (Kribek 1975; Kortenski and Kostova 1996). Gong *et al*. 2008 reported that pyrite framboids are the pyritized remains of microbial colonies (probably sulphate-reducing bateria). On the other hand various morphological types of single crystals of pyrite e.g. euhedral cubic and octahedral and anhedral pyrite are generated in the sedimentary matrix due to chemical reactions (abiogenic activity) (Dharmasri *et al*. 2004). SEM and TEM of fine fractions of these sandy podosols show that the iron to sulphur ratio of single crystal and framboidal pyrite is always 1: 2 which is consistent with pyrite and not other iron sulphides (Figures 1 and 2).

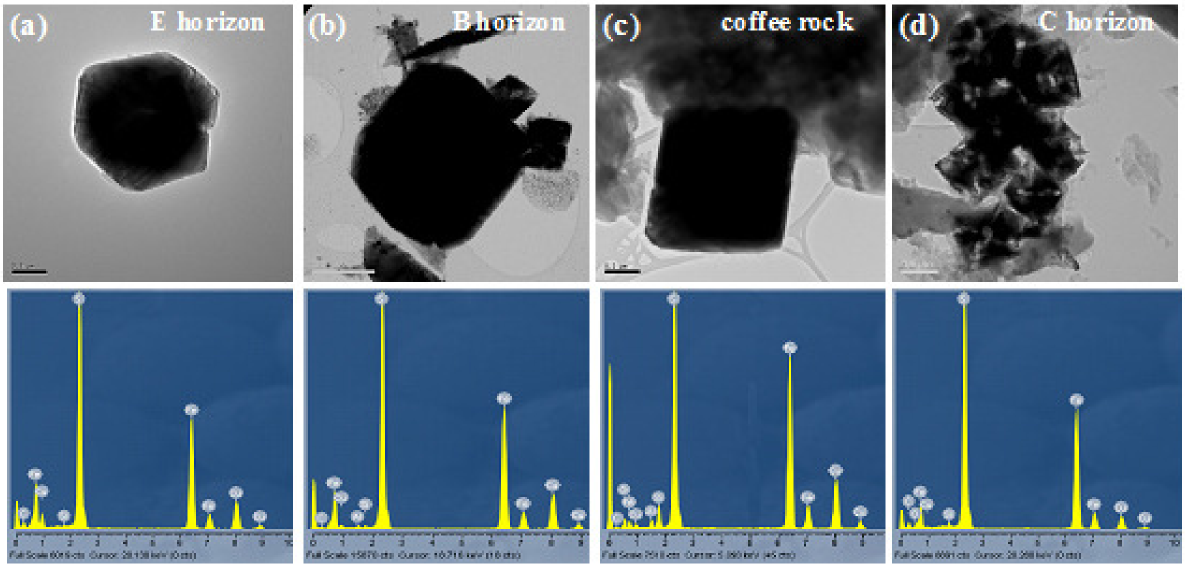

Figure 1. Transmission electron micrograph and x-ray spectra of pyrite crystals of diverse morphology from (a) E horizon (175-350 cm), (b) B horizon (350-600 cm), (c) coffee rock (225-400 cm) and (d) C horizon (250-350 cm); the atomic ratio of all particles is Fe: S ≈ 1: 2.

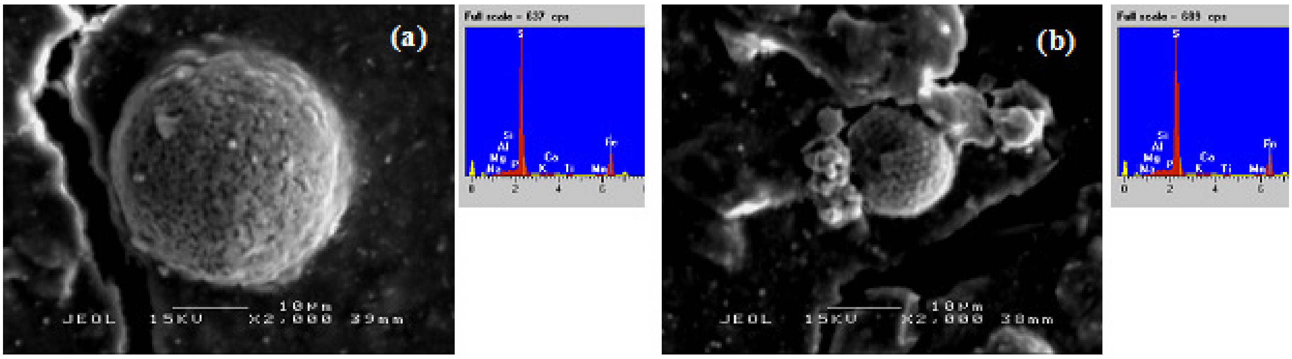

Figure 2 Backscattered electron image and x-ray spectra of pyrite particles in the fine fraction of (a) coffee rock (500-600 cm) and (b) B horizon (325-400 cm) deposited on a metal stub; the atomic ratio of all particles is Fe: S ≈ 1: 2.

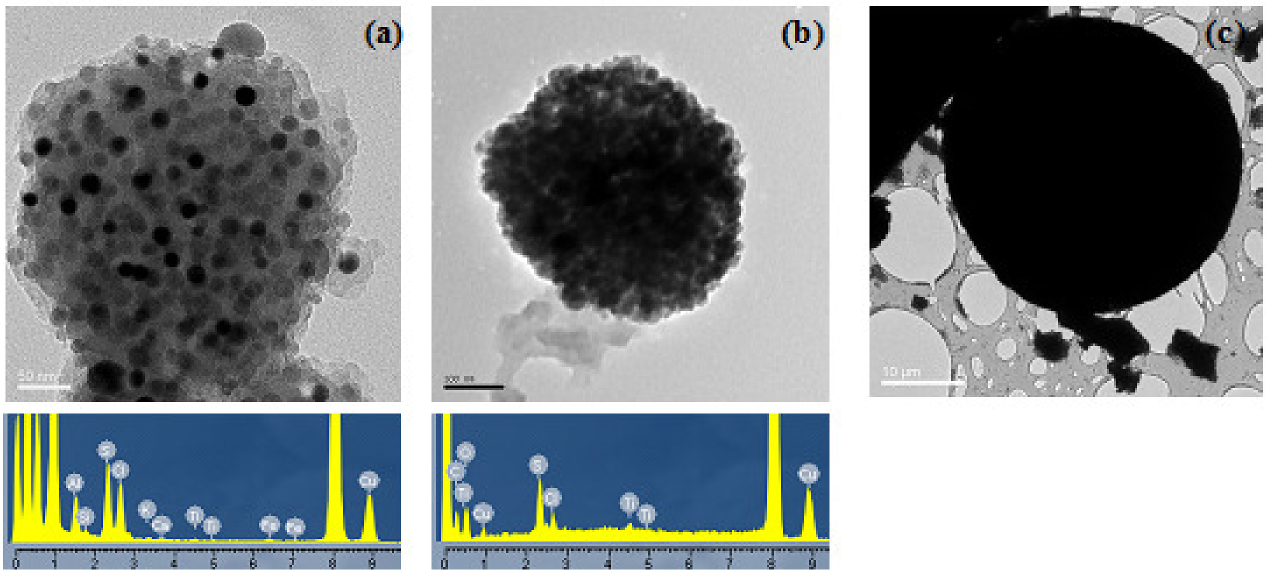

Figure 3 Transmission electron micrograph and X-ray spectra of (a, b) subspherical grains of sulphur from the B horizon (300-500 cm) and (c) framboidal pyrite from coffee rock (160-250 cm).

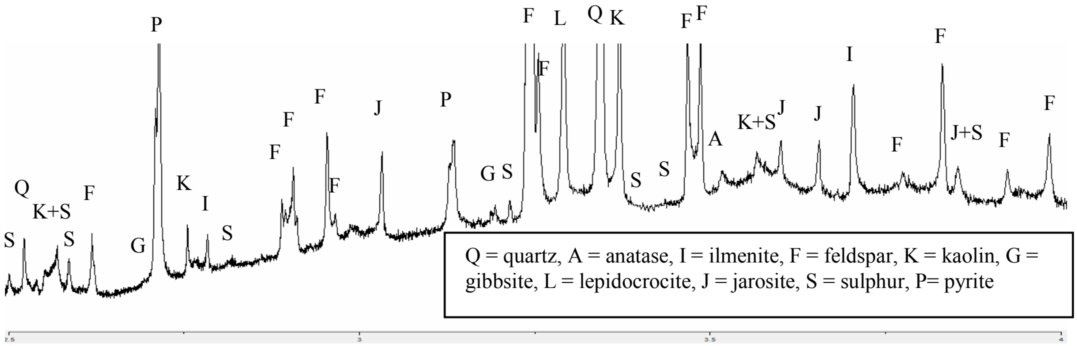

Figure 4. Synchrotron XRD pattern of the fine fraction of the E horizon of a podosol (200-325 cm) showing that pyrite and sulphur are present.

Conclusion

This research investigated 17 sandy podosols (85 samples) including A, E, B, coffee rock and C horizons from the Swan Coastal Plain. Some profiles contain palaeopodosols representing former levels of the water table. The studied soils are classified as Humic/ Alsilic aquic podosols (Australian Soil Classification, Isbell 2002) or Typic Endoaquods (Soil Survey Staff 2006). The studied acid sulphate soils on the Swan Coastal Plain are characterised by dark brown materials and pale leached sand which contains very little clay and no carbonate and is thus is unable to buffer changes in pH. The micrographs and XRD results provide unambiguous evidence for the occurrence of pyrite in these sandy podosols. Two pyrite morphologies occur: discrete submicron single euhedral crystals and 10-20 µm framboids. Single crystals of pyrite were present in all E, B, coffee rock and C horizons examined. Framboidal pyrite is present in coffee rock and B horizon materials. X-ray spectra of single crystals and framboids conform to the atomic ratio of pyrite Fe: S ≈ 1: 2. The grain size distribution and grain morphology of pyrite (euhedral single crystal or framboidal aggregate) provide information about the reactive pyrite surface area which affects oxidation rate and thus management. The rapid population growth of Perth with large numbers of developments requiring dewatering, and a prolonged period of low winter rainfall continue to induce acidification of groundwater.

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