

Pyrite and elemental sulphur cause acidification of drying wetlands on the Swan Coastal Plain, Western Australia

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Introduction

The Swan Coastal Plain (SCP) is on the eastern onshore edge of the Perth Basin, extending between Geraldton in the north and Dunsborough in the south. It is bounded to the west by the Indian Ocean and by the Gingin, Darling and Whicher Scarps to the east. The surficial materials of the Swan Coastal Plain are predominately alluvium and three major sand dunes deposits namely the Quindalup Dunes, Spearwood Dunes and Bassendean Dunes (McArthur, 2004). Common sediments in wetland basins (swales) in the Spearwood Dunes and Bassendean Dunes are peat, diatomite, calcilutite (carbonate mud), and intermediates such as diatomaceous peat, organic enriched diatomite or calcilutite, and carbonate skeletal gravel and sand (all formed by biogenic processes), as well as quartz sand and kaolinite-dominated mud (as terrigenous sediments), and various types of muddy sand formed as mixtures between biogenic mud-sized sediments and quartz sand, or between kaolinitic mud and quartz sand (Semeniuk and Semeniuk, 2004). Acidification of the wetland systems is occurring and is likely to be due to the steadily dropping groundwater table inducing pyrite oxidation, combined with the low buffering capacity of the leached sandy sediments. This paper describes how the source of acidity has been identified as microcrystalline pyrite and elemental sulfur in peaty, very sandy Humic/Alsilic Aquic Podosols (Typic Endoaquods) in Spearwood Dune (leached yellow sand and calcarenite) and Bassendean dunes swales.

Materials and Methods

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

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. TEM and SEM show that pyrite is present in these soils (Figs. 1, 2 and 3). Single crystals of pyrite occurred in all E, B, coffee rock and C horizons examined (Fig. 1), however, framboidal pyrite occurs only in horizons with high organic matter. Some buffering of acidity is provided by the weakly buffering minerals mica, feldspar and kaolinite which occur in these soils together with allophane and organic matter in some instances (Fig. 4). 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, mica and in some samples gibbsite and lepidocrocite. Resistant mineral, including anatase and ilmenite are present in some horizons. Allophane is not evident in these XRD patterns due to the high background originating from the glass capillary tube that contains the samples examined by synchrotron XRD. Pyrite is present in most E, B coffee rock horizons however elemental sulphur is a minor constituent in most samples and may occur in all horizons (Fig. 5). Jarosite was present in some partly oxidised samples.

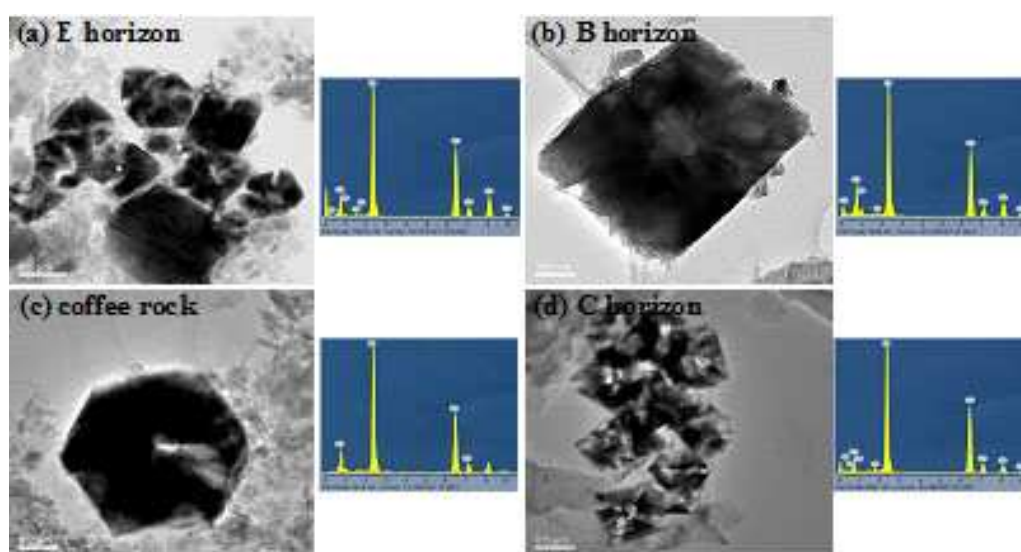


Fig. 1. Transmission electron micrograph and x-ray spectra of pyrite crystals of diverse morphology from (a) E horizon (site 616-02-68, 300-375 cm), (b) B horizon (site 616-02-71; 350-600 cm), (c) coffee rock (site 616-02-82; 500-600 cm) and (d) C horizon (250-350 cm); the atomic ratio of all particles is Fe: S \approx 1: 2.

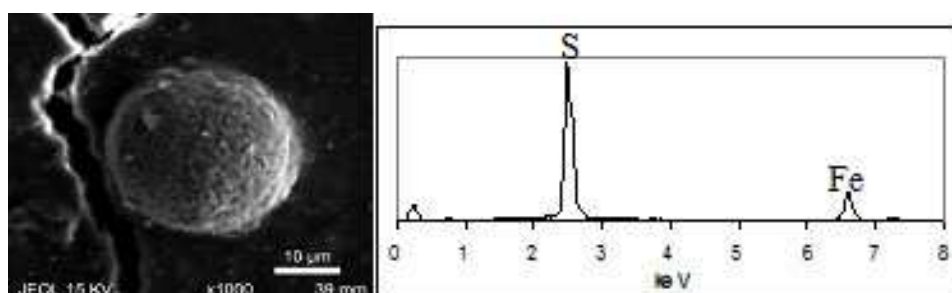


Fig. 2. Backscattered electron image and x-ray spectrum of framboidal pyrite in the fine fraction of coffee rock (site 6161-02-82; 500-600 cm) deposited on a metal stub; the atomic ratio of the particle is Fe: S \approx 1: 2.

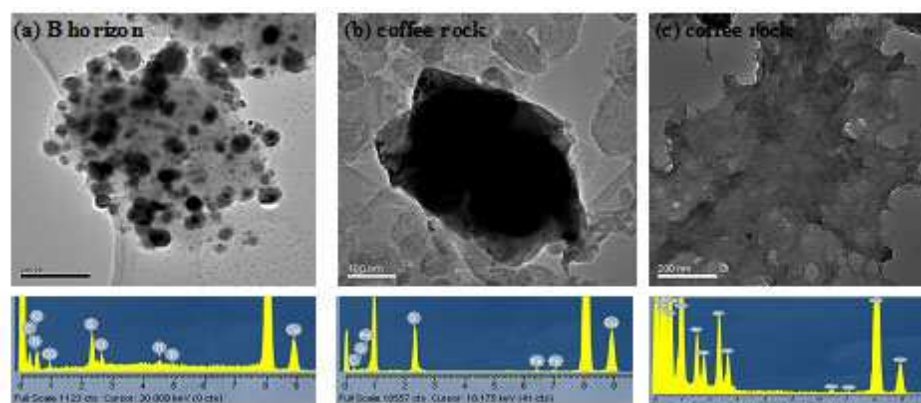


Fig. 3. Transmission electron micrograph and X-ray spectra of (a) subspherical grains of sulphur from the B horizon (site 616-02-58; 300-500 cm), (b) elemental sulfur from coffee rock (site 616-02-82; 525-575 cm) and (c) allophane ($\text{Al, Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$) from coffee rock (site 616-02-58; 300-500 cm); the atomic ratio of allophane is $(\text{Al, Fe}) : \text{Si} \approx 2 : 1$.

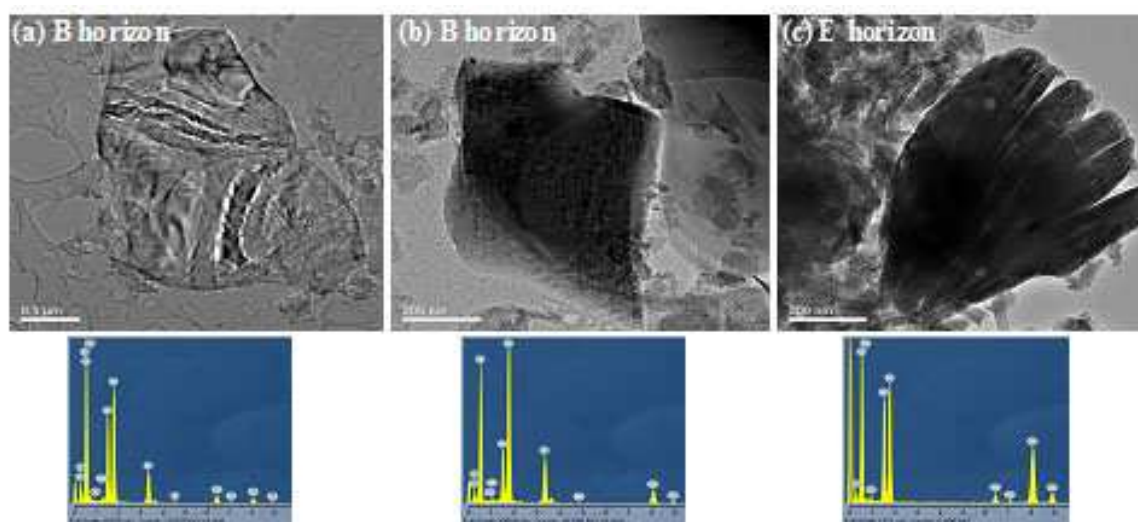


Fig. 4. Transmission electron micrograph and X-ray spectra of (a) mica from the B horizon (site 616-02-58; 300-500 cm), (b) feldspar from the B horizon (site 616-02-71; 350-600 cm) and (c) kaolinite from the E horizon (site 616-02-68; 300-375 cm).

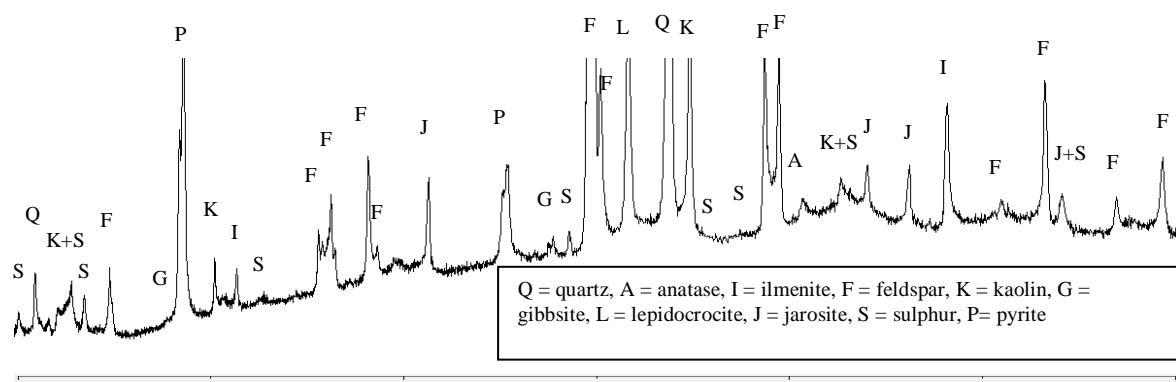


Fig. 5. Synchrotron XRD pattern of the fine fraction of the E horizon of a podosol (200-325 cm) showing that pyrite, sulphur and jarosite are present.

Conclusions

The very sandy soils on the Swan Coastal Plain consist predominantly of former beach deposits deposited as dunes by the wind. The highly leached Bassendean Sands with very little clay and no carbonates provide little acid buffering capacity to resist acidifying processes. The buffering capacity is provided by kaolin, gibbsite, Fe-oxides, allophane and minor primary minerals (feldspar, mica, etc) which are not very effective buffering agents. The acidification of the soils is caused by oxidation of pyrite (and sulfur in peaty materials) and possibly also of humus (OM) –Al complexes within swampy areas being dewatered for urban development which lowers the watertable and exposes of the pyritic soil to oxidation.

Acknowledgments

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