

Pyrite Containing Grey Clay Soils and Deep Sands, Swan Coastal Plain, Western Australia

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Abstract

The morphology, chemical and mineralogical properties of contrasting acid sulphate soils in Perth, Western Australia were investigated. The pale coloured deep sand comprising the Bassendean Dune soil has distinct A, E, B and C horizons whereas in some low lying areas clayey soils of the alluvial Guildford Formation occur. Adjacent to rivers estuarine sediments are present. All three types of soil contain subsoil horizons that are saturated and are consequently pyritic. Individual pyrite crystals are present in all horizons except for the A horizon of the deep sands and range in size from 0.07 to 1.5 μm . Single crystals of pyrite in the clayey alluvium range from 0.65-1.2 μm . Framboidal pyrite is present in the B horizon of sands ranges from 5.8-10.0 μm whereas the size of framboidal pyrite in clay soils ranges from 3.3-8.6 μm . An estuarine mud contained calcium carbonate in shell fragments, so that when this material is exposed to the air by a lowering of the water table, acidification caused by oxidation of pyrite may be neutralised by dissolution of calcite. This can not occur in the sandy soils which do not contain carbonate minerals so that soil pH is reduced to very low values when air enters the soil profile.

Key Words

Acid sulphate soil, pyrite, clay, sand, Swan Coastal Plain

Introduction

Acid sulphate soils containing pyrite occurs in many parts of the World. The most favourable conditions for pyrite formation are between mean high water level and mean low water level (Pons and van Breemen, 1982; Diemont et al., 1993) in organic-rich, near-shore, estuarine environments (Goldhaber and Kaplan, 1982). The exposure of acid sulphate soils to air in disturbed land causes acidity with environmental pollution, damaged infrastructure, death of biota, etc. In Perth, Western Australia, prolonged drought, rapid urban growth and intensive use of groundwater on the Swan Coastal Plain have caused the groundwater level to decline (Appleyard et al., 2004), exposing various types of pyritic sediments and soil horizons including organic rich, peat, yellow sand, white sand and mud horizons and inducing formation of actual acid sulphate soil. This study considers three distinctly different pyritic soils within Perth.

Methods

Six soil profiles with aquic characteristics were investigated. These occur in swale locations under a marked Mediterranean climate with a cool wet winter and hot dry summer, with an average rainfall of 890 mm/year (Figure 1a) (McArthur, 2004). The profiles are divided into clayey soils and deep sand profiles (Table 1). Soil profiles were extracted as cores with a vibratory drill and the water saturated cores were sampled into sealed plastic bags and stored in a wet condition in a cool room.

The use of chloroform as a preservative (biocide) for sulphidic soils is a novel preparation procedure which limits microbial activity and oxidation of sulphur minerals during handling; although minor oxidation still occurs during collection and storage of samples. Physico-chemical properties were determined on whole wet soils apart from total organic carbon and nitrogen which were measured on oven-dried (105°C) samples using a Vario Macro elemental analyzer. Soil pH water, pH CaCl₂, pH NaF (adjusted pH 8.5) and EC were measured using a 1:5 solid to solution ratio. The pH H₂O₂ reaction with soil was determined with 4 mL of 30% peroxide solution (adjusted pH 5.5) and 2 g of soil (1:2 soil to solution). The mixture was stirred with a glass rod for 30 min before measuring the pH with a standardized pH meter (National Soil Survey Center, 1996). Cation exchange capacity was determined using 0.01M silver thiourea (AgTU)⁺, this is a standard and robust procedure that is commonly used for analysis of soils in Australia (Rayment and Higginson, 1992). Total chemical composition soils used a fusion/ dissolution method to dissolve finely ground whole dried soils. Elements were measured using inductively coupled plasma optical emission spectrometry (ICP-OES).

The sandy soil materials consisted predominantly (>95%) of quartz sand which was removed by sedimentation to allow the determination of the constituents of the fine fraction. Twenty grams of wet soil was weighed into a 50 mL centrifuge tube, 20 mL of DI water and a few drops of chloroform to suppress microbial activity were added to the tube. The fine fraction (~5 μm) was separated using ultrasonic treatment and centrifugation. The fine fraction was examined by scanning electron microscopy (SEM; JEOL 6400; 15 kV) and transmission electron microscopy (TEM; JEOL 3000; 300 kV) using energy dispersive X-ray analysis (EDAX). Electron micrographs were used for measurement of size and shape of pyrite particles using image analysis software (ImageJ 1.43U). For synchrotron X-ray diffraction (XRD), dried powder samples of the chloroform treated fine fraction were placed in glass capillaries, and analysed over an angular range of 4–60° 2Theta. The wavelength was set at ~1.0 Å to provide adequate dispersion and resolution of reflections. This separation procedure could not be used for the clayey soils which were analysed as whole materials.

Results

Macromorphological properties

Three pale deep sands of the Bassendean dune system were examined (Site 068, 100 and 122). In the eastern side of the study area these sands are not deep and are underlain by clayey alluvial materials of the Guildford Formation (Site 085 and 112), a further site was a soil on estuarine sediment (Site 028). The sampled Bassendean dune soils (Site 068, 100 and 122) are located at low elevations with wet subsoil horizons (Figure 1b). Horizons of these soils are E, Bh and B. The Bh and B horizons occur near the watertable. However Site 100 has peat layer at 80-110 cm and peat/E horizon at 110-200 cm. Accumulation of organic matter occurs at Site 100 because it is at the lowest landscape position [swale]. Sites 085 and 112 are on the Guildford Clay consisting of pale-grey, blue, but predominantly brown silty and slightly sandy clay (Aurousseau and Budge, 1921). The Guildford formation outcrops over much of the eastern Perth region and is essentially a fluvial mud deposit. Site 112 is at the lowest position in the low elevation system therefore it can accumulate organic matter, is commonly flooded and supports a peat layer within the profile. Site 028 has a very deep gray clay profile is an estuarine sediment.

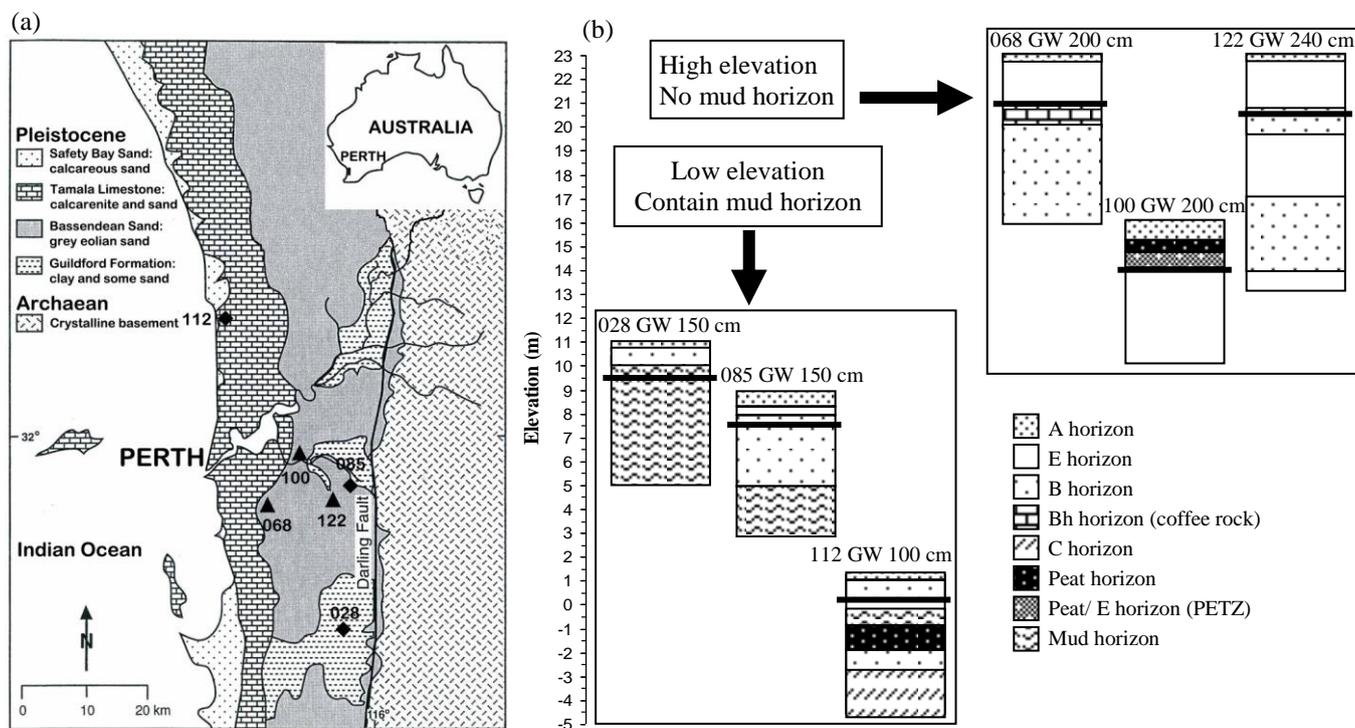


Figure 1 (a) Sampling locations for pyritic soils in Perth Western Australia (◆ = clay soil profile, ▲ = sand soil profile) and (b) the relationship between elevation (m), soil horizons and groundwater level (thick black line).

Chemical properties

Soil pH is higher than oxidized soil pH values by more than 0.5 units. The delta pH is greatest for mud and peat samples. Peat has the highest carbon content (19%). The presence of salt from the influx of seawater has made the estuarine mud line (EC 3174 $\mu\text{S cm}^{-1}$, Na 11 g kg^{-1}) and the base concentration of mud (K and Mg) is also high. Aluminium and iron are associated with clay minerals and sesquioxides so aluminium and iron concentration is highest in mud. Iron and sulphur concentrations in mud are clearly higher than in other materials due to the presence of pyrite. Estuarine mud had the highest calcium content (Ca 102 g kg^{-1}) of all samples because considerable amounts of shell fragments are present in the mud. The acidity generated during oxidation of pyrite is likely to be neutralized by carbonate buffering. Arsenic (<12 mg kg^{-1}) is present in all samples but at concentrations below a hazardous level (20-50 mg kg^{-1}).

Factor analysis and principal component analysis were used to determine elements of similar geochemical behavior and also to group soil samples on the basis of their chemical affinity. Sixty percent of the variation in data for the soils is explained by the first two factors which is a consequence of the diverse nature of these soils (Figure 2). The plot of soil samples illustrated that the clay-rich soil profiles have a high diversity of properties, reflecting their different sediment types (estuarine versus alluvium) whereas the sandy soil profiles form a discrete tight group of samples. Estuarine mud samples from site 112 contain much calcium carbonate (shell fragments) whereas mud samples at sites 028 and 085 have relatively little calcium.

Table 1 Average chemical properties of clay, peat and sand samples.

Horizon	pH H ₂ O	pH H ₂ O ₂	ΔpH	C	N	EC	Si	Al	Na	K	Ca	Mg	Fe	Mn	P	S	As
				(-----%-----)	$\mu\text{S cm}^{-1}$		(-----mg kg ⁻¹ -----)										
A (N=4)	6.24	4.91	1.33	1.05	0.08	102	529145	21844	2888	2864	4018	744	18032	339	518	132	6
E (N=5)	4.99	3.90	1.09	0.08	0.01	71	590512	1171	252	552	53	29	227	5	4	nd	2
B (N=9)	4.84	3.92	0.92	0.29	0.11	486	512847	11531	4364	6555	38333	2915	3331	86	34	1311	3
Bhs (N=1)	3.89	2.36	1.53	0.64	0.02	280	567239	8489	393	2985	336	154	1109	38	nd	129	2
Clay (N=3)	6.09	4.15	1.95	5.54	0.14	3174	286257	40190	11383	8861	102351	7117	30272	502	204	9729	12
Peat (N=3)	5.29	3.03	2.26	19	0.70	618	328835	5383	8484	2061	2675	1648	3887	58	91	2210	10
C (N=1)	8.15	7.60	0.55	3.49	0.02	173	342593	8304	1666	4873	86656	878	2202	150	51	1488	7

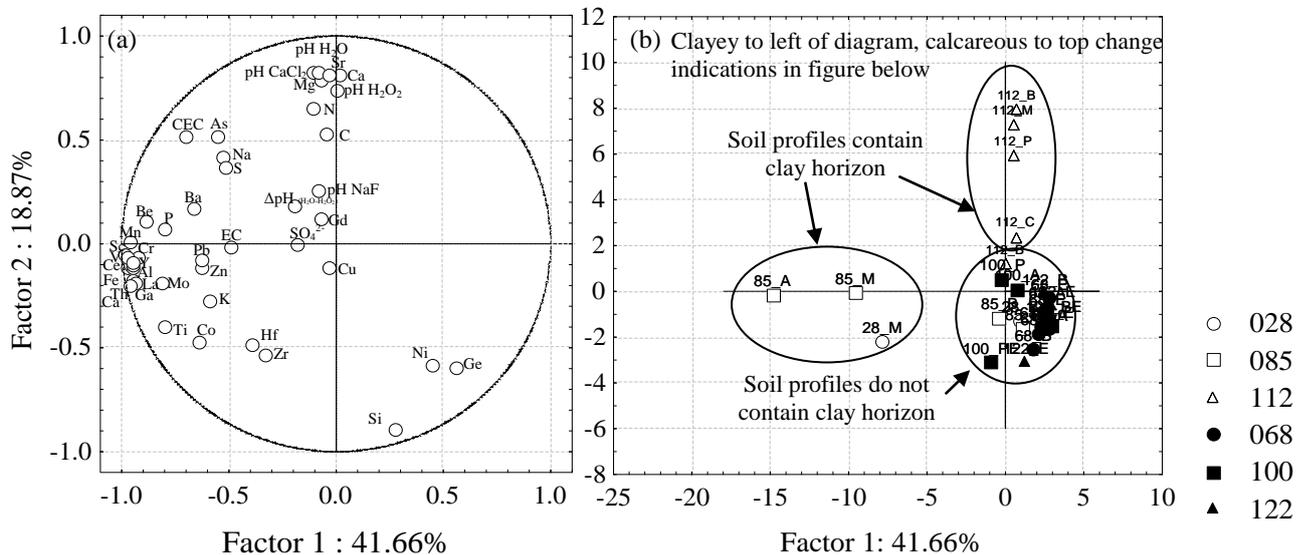


Figure 2 Factor analysis for chemical analyses and other properties of whole soil materials (N = 27) (a) distribution of elements and some soil properties (variables) (b) distribution of soil samples (cases).

Mineralogical properties

Single crystals of pyrite were scattered within the soil matrix of all soil materials (Figure 3) except for the A horizon materials. Some microcrystals of pyrite were partially oxidized. The single crystal pyrites in E, B and C horizons were 0.07 to 1.5 μm whereas the size of individual microcrystal pyrite in mud sample was 0.65-1.2 μm . Framboidal pyrite in B horizon materials ranged from 5.8-10.0 μm in diameter. The size of framboidal pyrite in mud samples ranged from 3.3-8.6 μm .

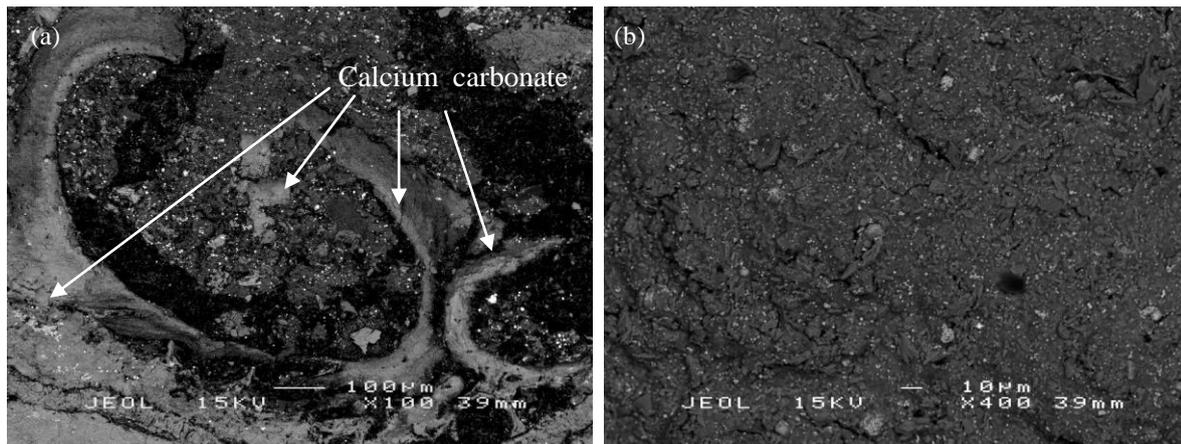


Figure 3 The SEM backscattered electron micrographs of (a) estuarine mud sample (Site 028, 200-250 cm) containing shell fragments and (b) B horizon of deep sand (Site 068, 450 cm). The small white dots seen in both images are single crystals of pyrite.

Conclusion

These wet soils from metropolitan Perth are both sand and clay-rich but all contain pyrite and are potential acid sulphate soils. The pyrite in these soils is present close to the soil surface and as the groundwater level is dropping oxidation produces acidity and possibly the release of toxic elements to groundwater. Estuarine mud has high amounts of calcium carbonate to neutralise the acidity but this not the case for many clayey and all sandy soils. The best way to manage these potential acid sulphate soils is by maintaining high groundwater levels.

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