



Release of metals during oxidation of pyrite from marine sediments in Malaysia

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Abstract: Pyrite, FeS_2 , extensively accumulates under saline and brackish-water tidal swamp and marsh. Pyrite is stable under waterlogged (reduced) condition. When drainage brings oxygen into this environment, the pyrite is oxidized releasing sulfuric acid. A study was conducted to determine the release of metals when pyritic sediment was oxidized or exposed to the atmospheric conditions. The pyrite content of sediments was 1.67% and 2.58%, respectively, from Sitiawan and Kuala Linggi. The total Fe and Al of both sediments were very high. Zn and Mo contents in sediments from Kuala Linggi were above the accepted level in soils and sediments (Alloway, 1990). Other metals were in normal range found elsewhere in soils and sediments. Large amounts of metals especially Fe and Al were present in the water soluble form indicating that exposing the sediments rich in pyrite to the atmosphere would release Fe and Al into the environment.

INTRODUCTION

Pyrite, FeS_2 , can be found in coal, lignite, or marine sediment. The latter is the extensive place for pyrite formation. The formation of pyrite under coastal areas is best met since these environments can provide the necessary materials such as abundance of organic matter (from mangroves), sulfate (from sea water) and iron (from the sediment itself) under flooded condition (Dent, 1986). The mineral is accumulated in the sediments over the years. When the soils are reclaimed by artificial drainage (example by cultivation) or by natural process as a result of changes in hydrology or relative sea level, the pyrite is exposed to the atmosphere (oxygen) and subsequently oxidized releasing high amounts of acid and acidic solutes into the soils and environment. Several trace elements may accumulate together with Fe during pyrite formation, either substituting for the Fe in the pyrite structure notably by Ni, Mn, Ti or replacing in related sulfides especially by Cu, Zn, As, or Pb. These metals are believed to be released during the oxidation of the pyrite. The objective of this study is to evaluate the release of metals in pyritic sediment exposed to the atmosphere.

MATERIALS AND METHODS

Sediments from Sitiawan, Perak and Kuala Linggi, Melaka, Malaysia, were used in this study. Both places are located in the coastal plains of the West Coast of Peninsular Malaysia. Marine alluvial deposits of Quaternary age cover a large portion of the coastal plain.

Pyritic materials (Cg) from subsoil were taken from the field and packed tightly to prevent oxidation. Upon arrival, the soils were kept under 4°C for 3–4 days. The original soils (unoxidized samples) were oven dried at $60^\circ\text{--}80^\circ\text{C}$ for 48 hours in order to prevent further oxidation. The oven-dried soils were subjected to various methods, namely standard chemical methods for important sediments properties and scanning electron microscopy-energy dispersive X-ray (SEM-EDAX).

Briefly, pH of fresh sediments were determined by inserting the pH electrode into the samples. C, N, S contents were analysed using an automated LECO analyser. The sediments were extracted using aqua regia ($\text{HNO}_3\text{:HCl}$ in 1:3) and metals in the extract were determined using Atomic Absorption Spectrophotometry (AAS) or otherwise using inductively coupled plasma atomic emission

spectrophotometry (ICPAES).

Samples for SEM-EDAX studies were obtained from separate sub-samples of the bulk sediments which had been handled carefully to minimize disturbance to their structure. The samples were oven dried, broken carefully to small fracture (< 2 mm), and glued to SEM stubs. Examinations using SEM instruments was done in gold plated samples.

The oxidative experiment was set up by putting about 300 g (wet basis) of the sediments in a plastic bag (15 x 20 cm). The material in the bag was pressed to form a slab 1 cm thick as recommended by Soil Survey Staff (1992), and the end of the bags were folded but not sealed. The soils are then put under a temperature of 25°C and dark condition. This procedure was followed to approximate slow oxidation in the field without leaching losses of oxidation product (van Bremen, 1976). After a certain time (12 weeks), the sediments were subjected to analysis of several metals using water as an extracting agent at soil to water ratio of 1:5. Metals in the extract were determined using AAS and ICPAES.

RESULTS AND DISCUSSIONS

Table 1 shows the chemical properties of the soils. The pH of fresh pyritic material from Sitiawan is 6.2, while that from Linggi is 3.91, respectively. The pyrite content of sediments is 1.67% and 2.58%, respectively, from Sitiawan and Kuala Linggi. Pyritic materials from Kuala Linggi are clayey with very high contents of organic matter, while the materials from Sitiawan are sandy with moderate amount of organic matter. The total Fe and Al of both sediments are very high. Zinc and Mo content in sediment from Kuala Linggi is above the accepted level in soils and sediments (Alloway, 1990). Other metals are in the normal range found elsewhere in soils and sediments.

Several trace elements notably As, Ni, Co, Mn, Ti, Pb and Zn may accumulate together with Fe during pyrite formation or replacing some of the Fe or S in the pyrite structure (Deer *et al.*, 1966; Viera e Silva *et al.*, 1994; Shamsuddin, *et al.*, 1995). Dudas (1985) found a high content of As (as high as 290 mg As kg⁻¹ compared to an average of 7.2 mg As kg⁻¹ from various world locations) in acid sulfate soils from Alberta, Canada. These soils developed as a result of pyrite oxidation. The accumulation of As in acid sulfate soils are linked with pyrite, since this mineral is a known carrier of As. In the pyrite structure, As can readily substitute for S and accumulate in the mineral as a trace or minor constituent. Recently, Gustafsson and Tin (1994) also found As content between 6–41 mg As kg⁻¹ in acid sulfate soils in Mekong delta, Vietnam.

Table 1. Characteristics of the studied marine sediments.

Characteristics	Sitiawan	Kuala Linggi
Texture	Sandy	Clay
PH	6.2	3.91
C-org (%)	0.79	6.23
Tot.Pot.Acidity (cmol/kg)	29.78	65.38
Tot.S acidity (cmol/kg)	29.78	42.34
Pyrite (%)	1.67	2.58
Metals: (mg/kg)		
Fe	10,315	9,733
Al	8,058	11,708
Mn	224	58
Zn	31.35	107.6
Cu	0.73	4.37
Ni	10.3	14.6
As	trace	19.23
Se	trace	0.53
Cd	trace	0.58
Pb	trace	25.89
Mo	0.57	22.18
B	10.2	14.11
Co	6.76	5.2
Cr	17.26	24.35

Scanning Electron Microscope (SEM) study indicated that the organic matter remnants were roots of mangrove tree. The pyritic material from Sitiawan contains remnants of diatoms and spicules indicating that the material was a shallow marine deposit. However, the materials from Kuala Linggi did not have spicules and diatoms.

Unoxidized as well as oxidized pyrite structure was also studied using SEM/EDAX. The morphological feature for pyrite under (SEM) showed that it occurred as (i) framboid (pyrite crystals in large cluster body) which are mostly embedded in clay and in organic matter (Fig. 1) or (ii) as occasional individual crystals (Fig. 2). In unoxidized samples, pyrite is almost in perfect form of S and Fe having ratio of 2:1 as indicated by EDAX analysis (not presented) indicating that the mineral was almost uncontaminated. Small SEM-EDAX peaks of Al and Si were present (not presented). Silica is known to exist as an impurity within pyrite crystals (Viera e Silva *et al.*, 1994). Meanwhile, studies elsewhere indicated that pyrite crystals can also be contaminated with other trace metals (Deer *et al.*, 1966; Dudas, 1987). However, no peaks of other than those of Al and Si could be observed under EDAX.

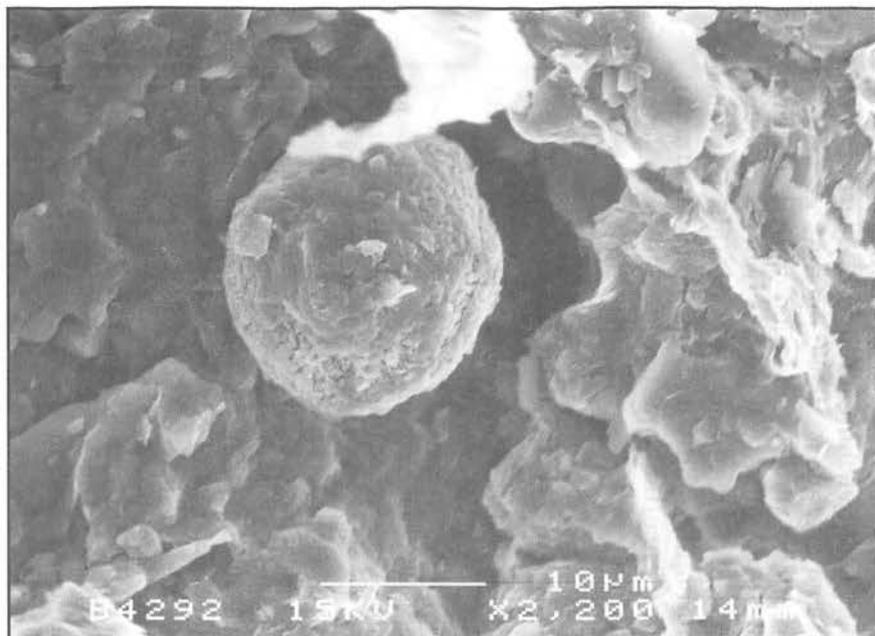


Figure 1. Scanning Electron Micrograph showing pyrite framboid of marine sediments from Sitiawan, Perak, Malaysia.

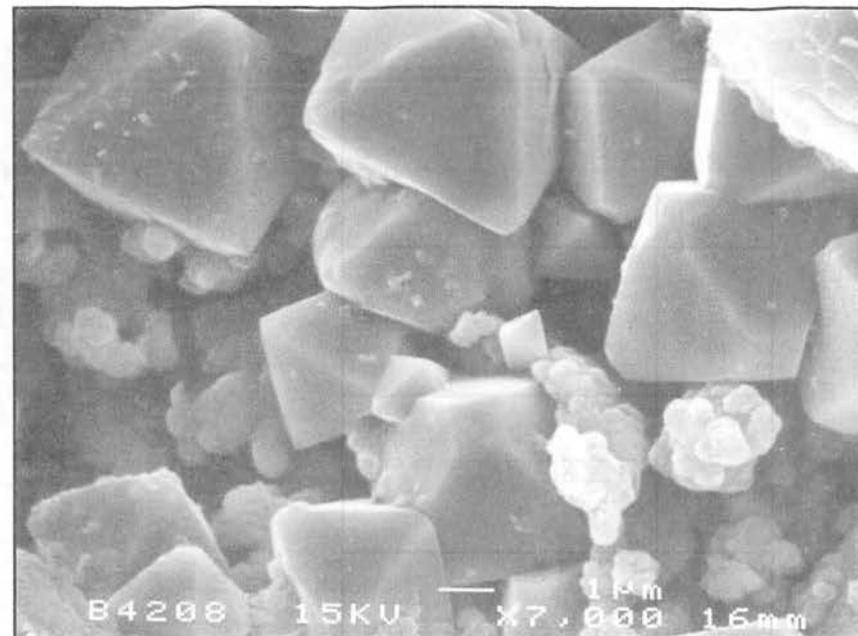


Figure 2. Scanning Electron Micrograph showing well crystalline pyrite found in the marine sediment from Sitiawan, Perak, Malaysia.

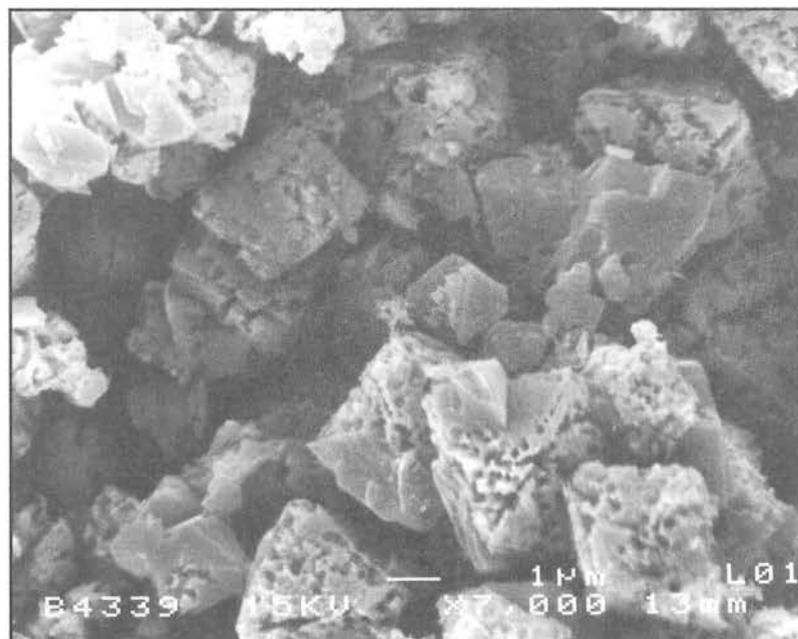


Figure 3. Scanning Electron Micrograph showing pyrite undergoing weathering in the marine sediment from Sitiawan, Perak.

Table 2. Total and water soluble metals concentration after 12 weeks of oxidation in the pyritic sediments from Sitiawan, Perak, Malaysia.

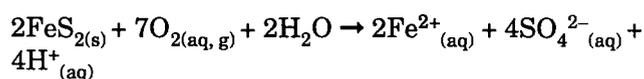
Metals	Total (µg/g)	Water Soluble (µg/g)	% to Total
Fe	10,315	418.35	4.05
Al	8,058	136.5	1.68
Mn	224	100.35	44.6
Zn	31.35	1.03	3.28
Cu	0.73	0	0
Ni	10.3	1.78	17.28
As	trace		
Se	trace		
Cd	trace		
Pb	trace		

Table 3. Total and water soluble metals concentration after 12 weeks of oxidation in the pyritic sediments from Kuala Linggi, Malaysia.

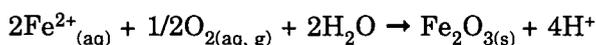
Metals	Total (µg/g)	Water Soluble (µg/g)	% to Total
Fe	9,733	1,256.7	12.9
Al	11,708	596.55	5.09
Mn	58	40.05	68.96
Zn	107.6	16.57	1.54
Cu	4.37	0	0
Ni	14.6	2.44	16.44
As	19.23	0	0
Se	0.53	0	0
Cd	0.58	0.15	25.9
Pb	25.89	0.16	0.61

Several morphological types of disintegration of pyrite were also observed under SEM (Fig. 3). Under high magnification, it was very obvious that the initial stage of pyrite weathering was etching in the surface structure of individual pyrite and at a later stage it become disintegrated. The corroded individual crystals are generally FeS₂. Using EDAX analysis, an excess of Fe over S, and the presence of Al and K were observed indicating that there was oxidation taking place which lead to acidification and liberation of some elements from the clay mineral.

After incubation of 12 weeks, the pH value dropped by more than 1 unit to value of pH = 3.20 and pH = 2.85, respectively for sediment from Sitiawan and Kuala Linggi. The production of high acidity was clearly as a results of pyrite oxidation. The oxidation process takes place according to the following reaction (van Bremen, 1976; van Bremen, 1993):



Further oxidation of Fe(II) to Fe(III) oxide, again produces acidity:



Two mol of pyrite will produce 4 mol of sulfuric acid that of course will lower the pH of the sediments.

Total and water-soluble metals are presented in Table 2 and Table 3. After oxidation for 12 weeks, the percent water soluble Fe to total Fe is about 4.1 in sediment from Sitiawan and at about 12.9 Fe to total Fe in sediment from Kuala Linggi. A high amount of Al was also present in the water soluble from both sediments. Nickel present in water-soluble form was 17.28 and 16.44% to total Ni in the sediment from Jawa and Kuala Linggi,

respectively. While Zn in the water soluble form was 3.28 to its total in sediment from Sitiawan and 1.54% to total Zn in sediment from Kuala Linggi.

Satawathananont (1986) observed a rather high concentration of water-soluble Cu, Zn, Mo, Cd, Pb, Ni and As in an aerated pyritic soil (pH 2.9) from Bangkok plain. Severe acidification on the surface water adjacent to pyrite bearing soils has been reported in Guyana (Dent, 1986), in Indonesia (Klepper *et al.*, 1990), in Finland (Palko and Yli-Halla, 1993) and in Australia (Callinan *et al.*, 1993; Willet *et al.*, 1993). Recently, Minh *et al.* (1997) reported that leaching of pyrite bearing soils released an average of 16,690 kmol Al ha⁻¹ month⁻¹ to surrounding water. Oxidation of pyrite bearing sediments would result in the release of high amounts of Fe, Al and trace metals into the environment. This causes concern among environmentalist because it leads to land degradation.

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