

# The process of pyrite formation in mangrove soils

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## 1 Summary

Undisturbed soil samples were collected from mangrove areas in the west coast of Peninsular Thailand. Soil thin sections were prepared and plant debris was separated from these soil samples. The soil thin sections were observed under a light microscope. Samples of the plant debris were observed under light microscopes and a scanning electron microscope and also were analyzed for pyrite by X-ray diffraction method.

On the basis of the results of these investigations, we proposed a new comprehensive hypothesis of pyrite formation in mangrove soils. That is, pyrite is mainly formed in a boundary zone between the upper more oxidized horizons and the lower strongly reduced horizons. In this zone,  $H_2S$  formed in the lower horizons will react with ferric compounds deposited in the upper horizons.

Most of the ferric compounds are the pseudomorphs of microorganisms including aquatic fungi which grow in the fairly well decomposed plant debris. Within these pseudomorphs pyrite particles substitute for the ferric compounds. When the plant debris is strongly decomposed, pyrite particles may occur free from the plant debris. If pyrite-rich horizons are eroded, plant debris and pyrite particles are transported and sedimented at remote places.

## Résumé

Des échantillons en structure naturelle ont été prélevés de treize Sulfaquents Typiques de mangroves de la région côtière de la Thaïlande péninsulaire (Figure 1) afin d'étudier les processus de la formation de la pyrite.

Les lames minces préparées et les débris des plantes séparés à partir de ces échantillons, ont été examinés au microscope polarisant et au microscope binoculaire. Une partie de débris ont été également examinés au microscope électronique et analysés aux rayons X, en vue de la détermination de la pyrite.

Les observations faites, ont montrés que:

- les cristaux de pyrite sont rares dans les horizons superficiels (20-30 cm), tandis qu'ils sont fréquents dans les horizons plus profonds.
- les cristaux de pyrite se trouvent particulièrement dans les restes de racines en voie de décomposition desquelles elles se détachent, au fur et à mesure, que la décomposition avance.
- un examen détaillé de la pyrite, permet de constater que les cristaux de pyrite sont

groupés en sphères ressemblant aux spongiaires et en colliers ressemblant aux hyphes de certaines fungies aquatiques qui sont responsables de la décomposition des restes des plantes présentes dans les sols mal drainés.

- dans les horizons superficiels où la quantité de pyrite est très faible, les mêmes spongiaires ont une couleur brun rougeâtre à cause des hydroxides de fer qu'ils contiennent.

Basés sur ces observations, les auteurs proposent une nouvelle hypothèse sur la formation de la pyrite dans les sols de mangrove.

En lignes générales dans les sols de mangroves on distingue une zone supérieure plus ou moins oxydée jusqu'à environ 20 à 30 cm avec peu de pyrite et une zone inférieure fortement réduite, avec beaucoup de pyrite.

Dans la zone inférieure le  $H_2S$  se forme à partir de  $SO_4^{2-}$ , en présence de la matière organique et le  $Fe^{2+}$  des certains constituants de  $Fe^{3+}$ , et aussi en présence de la matière organique en voie de décomposition. Dans la zone supérieure, continuellement nourrie avec de la matière organique fraîche, les racines fines sont décomposées par les micro-organismes. Dans un premier stade, cette décomposition contribue à une forte réduction, tandis que dans un deuxième stade, des bactéries autotrophes et fungi aquatiques actionnent dans un milieu oxydé. C'est ainsi que les spongiaires et les hyphes se forment. Le  $Fe^{2+}$ , venant des horizons réduits s'accumule comme hydroxydes ferriques dans ces pseudomorphes. Suit après le  $H_2S$  qui venant de mêmes horizons, réagit avec le  $Fe(OH)_3$  et forme le  $FeS$  et le  $S^0$  (où  $S_n^{2-}$ ) qui s'unissent, donnent le  $FeS_2$ . C'est ainsi qu'on trouve des sphéroides et des filaments de  $FeS_2$  ressemblant aux hyphes de fungies qui ont remplacé le  $Fe^{3+}$ .

Par sédimentation lente, la zone de la formation active de pyrite monte et l'horizon pyritique se développe.

Au fur et à mesure que la décomposition des débris de plantes avance, une partie des sphéroides pyritiques se décompose libérant des cristaux de pyrite 'libres' qui suite à l'érosion arrivent dans les sédiments où ils n'ont aucune relation avec les tissus végétaux.

## 2 Introduction

Unripe reduced soil materials (or sediments) in mangrove areas are famous for their high content of pyrite. It has been widely accepted that active  $H_2S$  formation is responsible for this large accumulation of pyrite. The active  $H_2S$  formation, in turn, is considered to be maintained by abundant supply of  $SO_4^{2-}$  from the sea water and organic matter from the mangrove vegetation (Rickard 1973; Vijarnsorn 1985).

However, the following aspects of pyrite formation cannot readily be understood as a mere result of  $H_2S$  formation:

- Upper horizons (or layers) of about 20-30 cm have a far lower pyrite content than deeper horizons (or layers);
- Pyrite occurs often in spherical or framboid clusters of micro crystalline particles (Rickard 1973; Van Dam and Pons 1973);
- Some pyrite particles are contained in organic debris (mainly plant debris) but others are free from plant debris (Rickard 1973; Van Dam and Pons 1973);
- Pyrite is formed in strongly reduced soil material in which it is expected that  $H_2S$  be formed after complete reduction of ferric compounds (Van Dam and Pons 1973),

resulting in formation of FeS rather than of pyrite. In this report, we will propose a hypothesis which can solve all of the above mentioned problematic aspects of pyrite formation.

### 3 Materials and methods

#### 3.1 Soil

Undisturbed soil samples were collected from 13 sites on tidal flats in mangrove areas on the west coast of peninsular Thailand (Figure 1). All sampled soils are Typic Sulfaquents; a description of a representative soil profile is given in Annex I.

#### 3.2 Preparation of soil thin sections

The moist soil samples were treated with acetone and oven-dried at 60°C for more than two weeks. These dehydrated samples were impregnated with polyester resin solution (polyester: monostyrene = 1:1 v/v) under reduced pressure. The impregnated samples were sectioned and polished according to the method of Stoop (4).

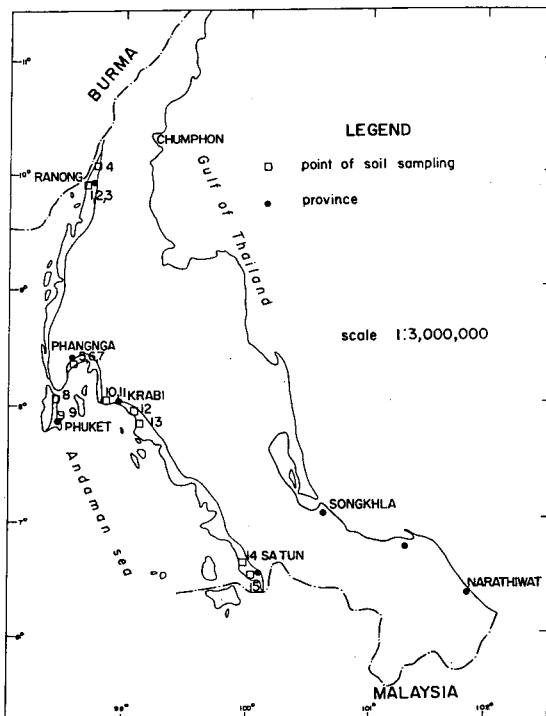


Figure 1 Location of the study area

### 3.3 Separation of plant debris

A few grams of soil samples were placed in a beaker, gently dispersed in water and passed through a 150 mesh screen (Wada and Kanazawa 1970). Plant debris on the screen was collected and preserved in 10% formalin solution.

### 3.4 Observation of soil thin sections and preparations of plant debris

The soil thin sections were examined under a microscope in a usual way. The plant debris was at first placed in a Petri dish and examined under a binocular microscope (6.3-80x) (X-Tr, Olympus, Japan). Some of the plant debris was picked up by forceps, transferred to a slide glass and mounted with lactophenol cotton blue (Wada et al. 1978). This preparation was examined under a microscope equipped with a polarizer and an analyzer (40-1,500x) (BHB, Olympus, Japan). A part of the plant debris was examined with a scanning electron microscope (40-150,000x) (JS-510, Hitachi, Japan) and was also analyzed by X-ray diffraction (Geigerflex 2013, Rigakudenki, Japan).

## 4 Results and discussion

### 4.1 Observation of soil thin sections

In general, pyrite particles were rare in the upper horizons of 20-30 cm deep and abundant in the lower horizons in accordance with the analytical data previously reported (Vijarnsorn 1985).

In the pyrite-rich horizons, pyrite particles are either embedded in plant debris or scattered in the soil matrix. In both cases individual pyrite crystals often form clusters in a wide variation of size and number of particles. The number and population density of the pyrite clusters contained in plant debris tended to increase with the advance of decomposition of the plant debris (Figure 2). The embedment of pyrite in plant tissue becomes obscure where the plant debris is strongly decomposed and there is a gradual transition to areas where pyrite particles seem to be scattered in the soil matrix without any spatial association with plant debris (Figure 2). However, careful examination revealed that these free pyrite particles and clusters are often covered with thin reddish brown halos (Figure 3). These reddish brown halos were considered to be humified organic substances, remnants of plant debris. It was also considered that some plant debris may have been decomposing and disappearing without further accumulation of pyrite particles inside. That is, pyrite formation and decomposition of plant debris are closely related but somewhat independent processes. On the basis of these observations, we proposed a process of pyrite accumulation inside and outside plant debris with the advance of decomposition of plant debris as illustrated in Figure 4.

The above discussion and conclusion only holds for plant debris supplied in situ by the standing mangrove vegetation e.i. autochthonous plant debris. In deep horizons at Ranong, plant debris showed little variation in particle size and degree of decomposition, and the debris particles were oriented parallel to laminae of sedimentation as revealed by mica particles. This fact suggests that this plant debris has been transported

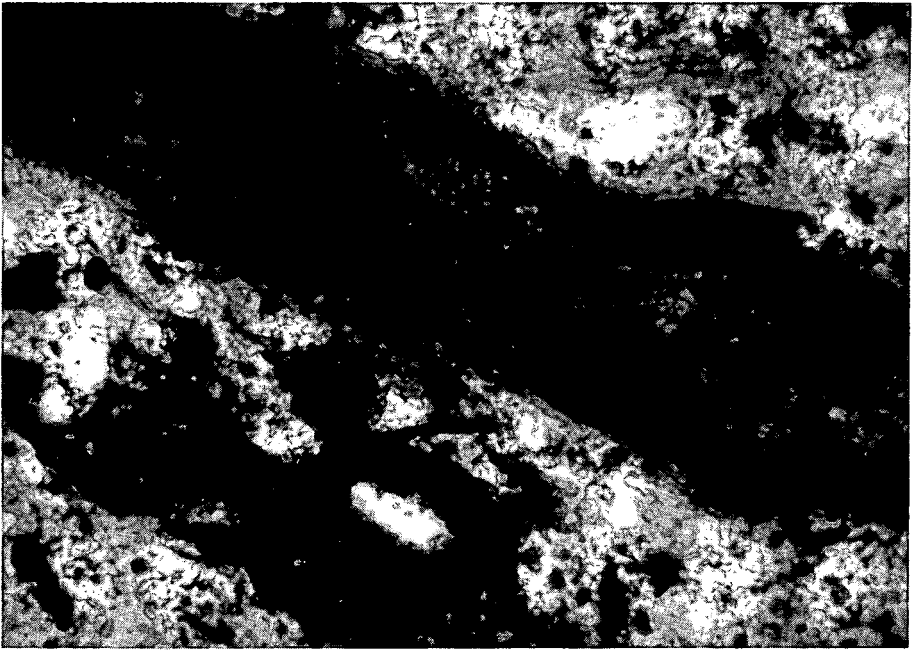


Figure 2 Pyrite particles associated with plant debris. Upper plant debris is rather fresh and contains a few pyrite particles. Lower plant debris is fairly well decomposed and contains a large number of pyrite particles. (Satul Province, 32-50 cm) 100 x

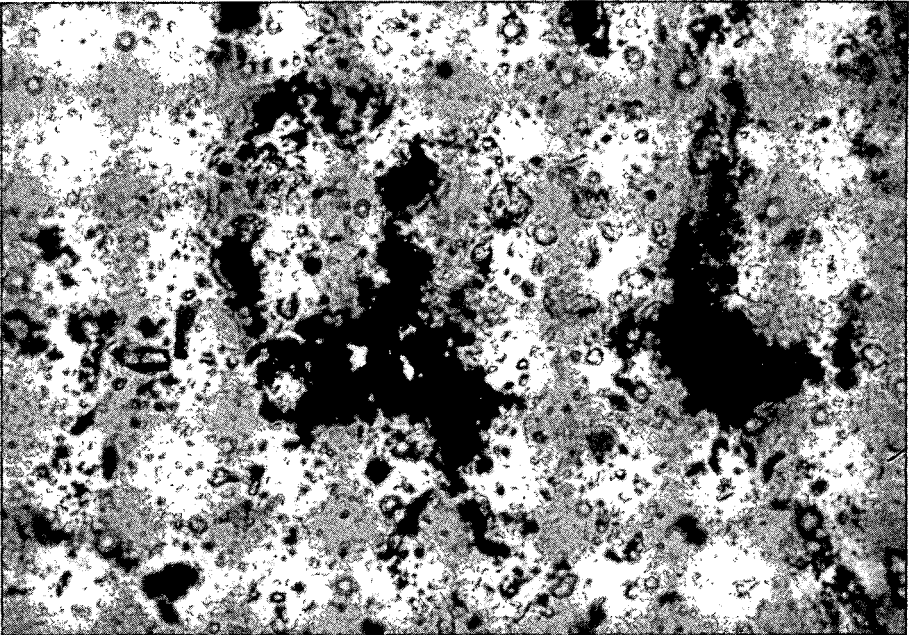


Figure 3 Pyrite particles free from organic debris with reddish brown halo (Phangnga Province, 30-80 cm) 200 x

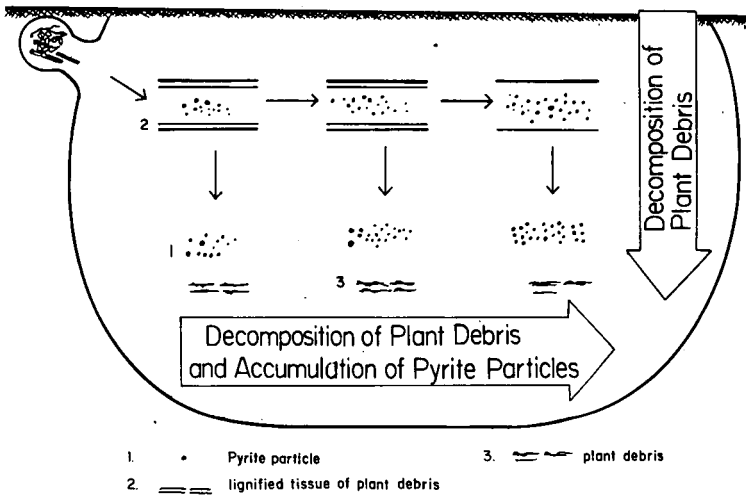


Figure 4 Relation between pyrite particles and plant debris

from a remote place and sedimented along with mineral particles in the deep and clam Ranong Bay, where faunal pedoturbation is not active. This type of plant debris can be called allochthonous (Van Dam and Pons 1973). It is dense and dark brown and not associated with pyrite particles. This indicates that this allochthonous plant debris consists of lignified remnants of the strongly decomposed plant debris. However, Van Dam and Pons (1973) recognized allochthonous plant debris containing pyrite particles. Their allochthonous plant debris appeared to be not strongly decomposed. Apparently there are several types of allochthonous plant debris.

Allochthonous plant debris must be related with autochthonous plant debris, because the former is derived from the latter. If the moderately decomposed plant debris containing pyrite particles, is transported and sedimented without marked disintegration, we can expect that the resulting allochthonous plant debris retain pyrite particles. On the contrary, if material with strongly decomposed autochthonous plant debris with disengaged pyrite particles is transported and sedimented, the resulting allochthonous plant debris will not contain pyrite particles.

The 'free pyrite particles' will be transported separately from the plant debris and sedimented along with mineral particles.

#### 4.2 Observation of plant debris preparations

Most of the plant debris was found to be remains of fine roots of mangrove trees in various stages of decomposition. Even cursory observations at a low magnification sufficed to confirm the relationship between plant debris and pyrite particles, earlier recognized by observing soil thin sections.

In the pyrite-rich horizons, weakly decomposed plant debris contains none or very few pyrite particles while fairly well decomposed plant debris (most of its remnants

of the epidermis of the fine roots taking the shape of transparent tubes) contains numerous pyrite particles. Actually, at a low magnification, pyrite clusters appear as black patches in the plant debris. Some of the fairly well decomposed plant debris is completely black due to a large accumulation of pyrite particles. The plant debris with black patches effervesces with hydrogen peroxide solution. After termination of the effervescence, the black patches had disappeared and the solution become acid. This simple chemical test indicates that these black patches indeed consist of pyrite particles. X-ray diffraction confirmed that the black patches are pure crystals of pyrite.

The configuration and position of the black patches inside plant debris is similar to that of microorganisms growing inside decomposing plant debris in submerged paddy soils (Wada 1980). In fact most of the pyrite particles reside inside the walls of the transparent tubes of root remnants. These observations suggest that pyrite formation is closely related with microbial growth in the decomposing plant debris.

At higher magnifications, the peculiar shapes and the distribution pattern of the pyrite particles were recognized more clearly. Pyrite particles inside the cell structure of plant debris, occur either as framboidal spherical accumulations or as tiny individual cubes (Figures 5, 6). In some of the cells pyrite clusters are interconnected by filaments of small pyrite particles and there filaments even connect clusters in adjacent cells (Figure 7).

The pyrite particles and clusters are easily detached from the plant debris by crushing of samples. After crushing many of the framboidal pyrite clusters had fallen apart into tiny crystals, but often fragments of framboids together with connecting pyrite filaments remained unimpaired (Figure 8).

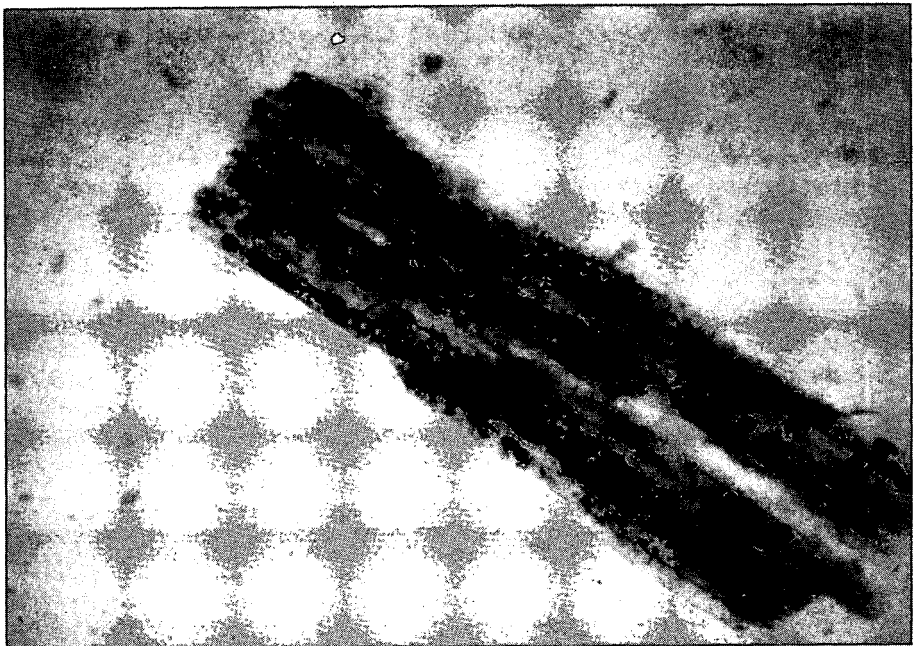


Figure 5 A transparent tube-shaped piece of plant debris containing numerous pyrite particles (Phangnga Province, 50-80 cm) 100 x

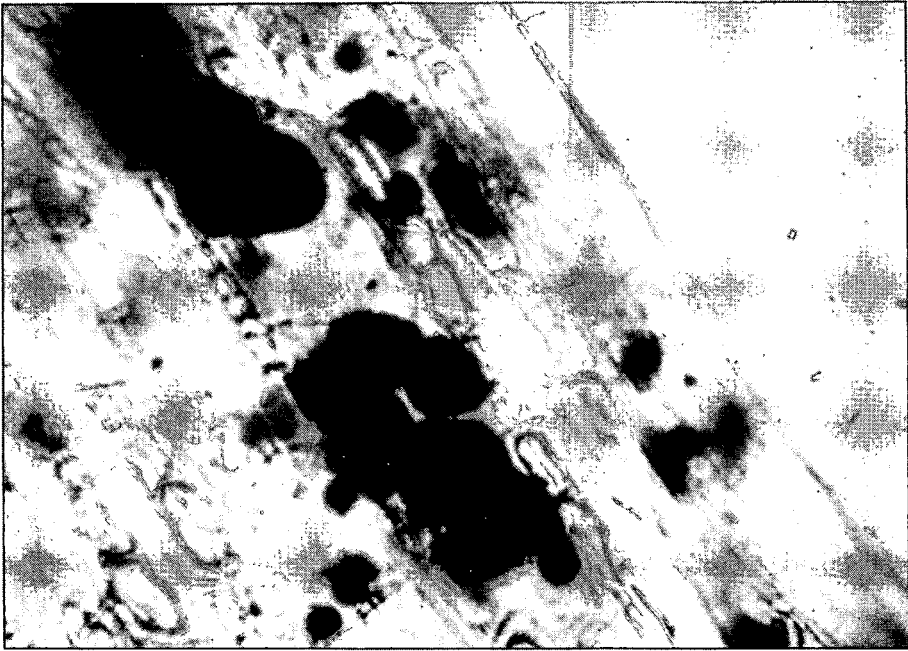


Figure 6 Framboidal pyrite particles inside plant debris (Phangnga Province, 50-80 cm) 400 x

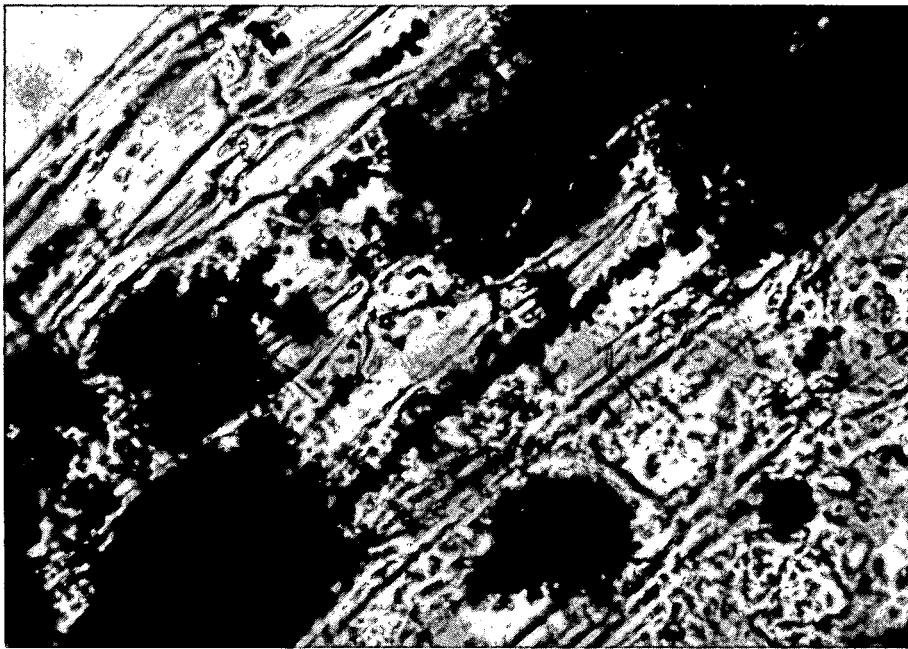


Figure 7 Filaments of pyrite particles connecting clusters of pyrite particles (Phangnga Province, 50-80 cm) 400 x



A few crystals were sometimes found to stick out from the surface of the detached framboids, suggesting that the framboidal spheres might grow by newformation of tiny crystals on their surface.

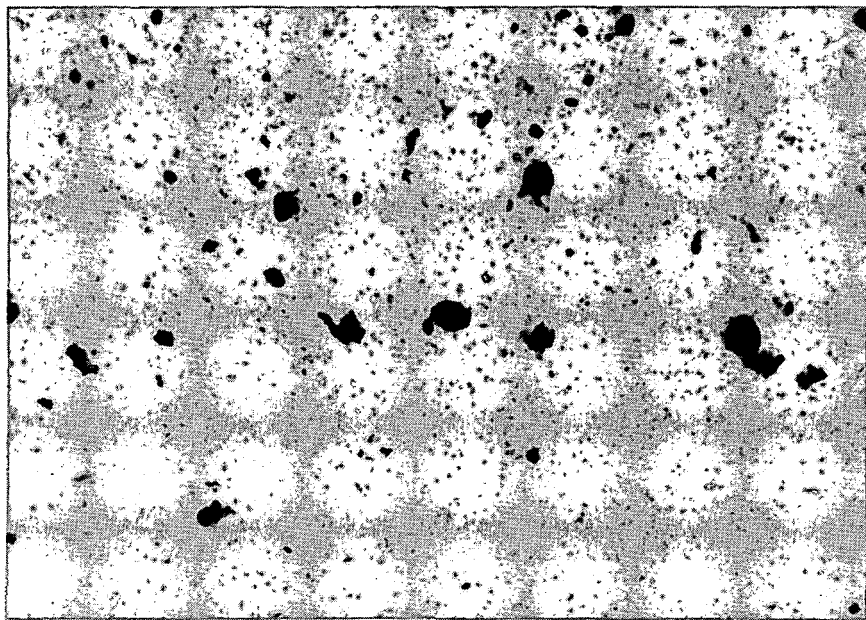
Under a scanning electron microscope, the pyrite clusters were found to be completely composed of tiny cubic crystals of pyrite which in the case of framboids are about the same size and neatly arranged in the convex surface of the spherical clusters (Figure 9). The combination of framboidal spheres and their interconnecting filaments strongly resemble the shape of the sporangia and hyphae of some aquatic fungi that are contributing to the decomposition of plant debris in wet soils (Figure 10). This resemblance intimates the possibility that such fungi be instrumental in the formation of micro crystalline pyrite.

As mentioned above, pyrite particles were rarely found in samples of the upper horizons. Instead, plant debris in these horizons contained reddish or brownish stains of various shapes among which spherical shapes were predominating. When Na-thioglycolate solution was added to the plant debris, at first a purple color developed but then faded out. After this treatment, the reddish or brownish stains had disappeared from the plant debris. This result indicates that the reddish or brownish stains are composed of ferric compounds.

In the upper horizons, some plant debris contained both framboidal pyritic and ferric spheres of similar size. In this plant debris, some of the spherical particles showed intermediate color between pyrite and ferric compounds.

These observations suggest that the spheres of ferric compounds are formed at first which then are converted into pyritic framboidal spheres.

Figure 8 Framboidal pyrite particles with fragments of filaments of pyrite particles (Phananga Province, 50-80 cm) 200 x



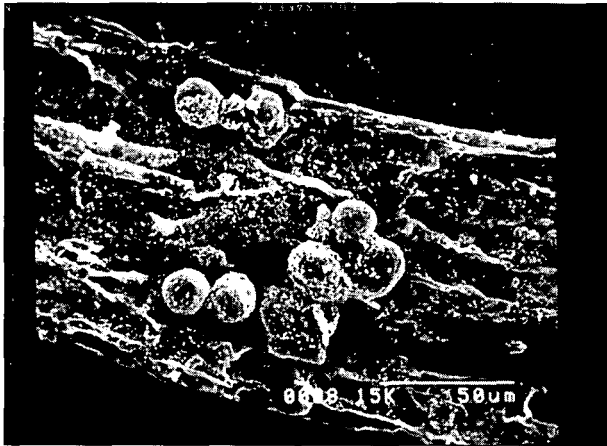


Figure 9a Framboidal pyrite particles inside plant debris (Phangnga Province, 50-80 cm)

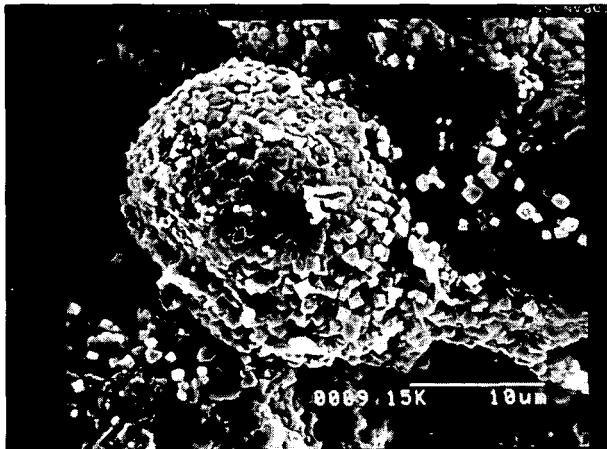


Figure 9b A framboidal pyrite accumulation composed of tiny crystals of pyrite (Phangnga Province, 50-80 cm)

#### 4.3 A hypothesis of pyrite formation in mangrove soils

On the basis of the presented observational results, we can propose the following hypothesis of pyrite formation in mangrove soils.

Upper horizons of mangrove soils are heterogenous in regard to oxidation-reduction state. Tunnels of burrowing animals and young active roots of mangrove trees will supply  $O_2$  to the upper horizons and oxidize their surroundings. Organic debris, especially debris of fine roots, is abundantly supplied to the upper horizons by the standing mangrove trees. When this organic debris is still fresh and rapidly decomposing, it will enhance the reduced state of the soil. However, once the debris is already

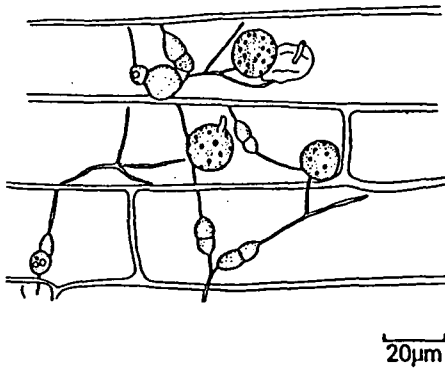


Figure 10 *Cladochytrium replicatum*. Rhizomycelium within the epidermis of an aquatic plant. From Webster, J. 1980. Introduction to Fungi. Cambridge University Press

fairly well decomposed, it will not contribute much more to further the reduced state of the soil. Agents of decomposition of the organic debris are zymogenous bacteria in the initial stage of decomposition and autotrophic bacteria and aquatic fungi in the later stage of decomposition.

In the upper horizons  $\text{Fe}^{2+}$  is formed in the reduced parts of the soil and is deposited as ferric compounds in the oxidized parts of the soil. The dying microorganisms in the well decomposed plant debris are favorable sites for this iron deposition.

In the lower horizons, the soil remains strongly reduced throughout and a part of the  $\text{H}_2\text{S}$  formed in these horizons will rise to the upper horizons.

At the boundary zone between the upper horizons and the lower horizons, the  $\text{H}_2\text{S}$  will react with the ferric compounds of the well decomposed plant debris to form at first  $\text{FeS}$  and  $\text{S}^0$  (or  $\text{S}_n^{2-}$ ). The  $\text{FeS}$  and  $\text{S}^0$  (or  $\text{S}_n^{2-}$ ) thus formed side by side will react to form pyrite. Accordingly, this boundary zone can be called the zone of pyrite formation (Figure 11). Where sedimentation continues slowly, the zone of active pyrite formation will gradually be raised with the surface level of the mangrove soil and the pyritic horizon below built up at the same rate.

The newly formed pyrite crystals occupy predominantly the sites of the microorganisms that have been active in decomposing plant tissue, e.i.: sites inside the cell and tissue structure of the debris. When the plant debris is decomposed further, the pyrite particles become free from the plant debris (Figure 4). When pyritic horizons are eroded; their plant debris and pyrite particles are transported and sedimented separately and give rise in other places to respectively allochthonous plant debris and deposits of 'free pyrite particles'.

With this hypothesis a plausible explanation can be offered for many problematic occurrences of pyrite in mangrove soils. E.g. accumulation of pyrite particles on the surface of cleavage planes free from plant debris (Van Dam and Pons 1973). Probably, at some early period, this soil was drained to form cracks the walls of which became coated with ferric compounds. In a later period,  $\text{H}_2\text{S}$  coming up from lower horizons reacted with the ferric compounds, resulting in pyrite.

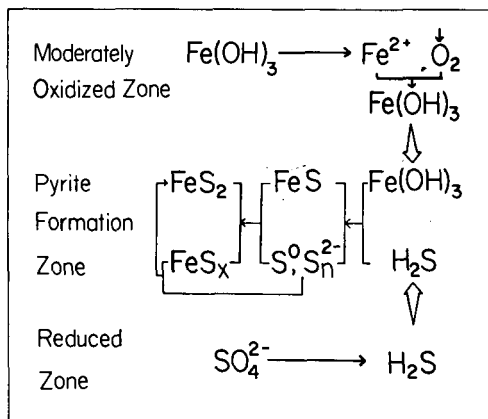


Figure 11 The process of pyrite formation in mangrove soils

The proposed hypothesis takes in the following ideas previously reported:

1. The sulphidation of ferric hydroxides is particularly important because  $\text{S}^0$  is produced spatially near  $\text{FeS}$  (Rickard 1973);
2. Framboidal pyrite accumulations may be pseudomorphs of organic spherules (probably *pyritosphaera barbara*) (Love 1962);
3. Pyrite is mainly formed just below the oxidized layer (Rickard 1973).

## Acknowledgments

We thank Mr. Y. Satoi (Chiba University) for analyzing pyrite by X-ray diffraction. We are also grateful to Mr. Y. He (Institute of Academia Sinica, Ch'eng-tu, China) for taking photographs and to the Cambridge University Press for their kind permission to reproduce Figure 10.

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## Annex I

### Description of representative soil profile

Date	23/4/83
Soil name	Thakua Thung series
Classification	fine-silty, mixed, isohyperthermic Typic Sulfaquents
Latitude	8°20'45"N
Longitude	98°26'50"E
Location	Ban Khao Po, Amphoe Tha Kua Thung, Phang-nga province
Physiographic position	Mangrove swamp on intertidal flat
Topography	Flat
Slope and Aspect	0%
Elevation	< 1 m. MSL
Drainage	Very poorly drained
Vegetation	Mangrove forest: Rhizophora sp, Sylocarpus sp, Avicennia sp.
Parent material	Marine deposit
Sampled by	P. Vijarnsorn W. Sirichuaychoo
Remarks	1. Ground water table level about 20 cm from the soil surface 2. Common mud lobster mounds

Depth (cm)	Horizon	Description
0-10	A <sub>t</sub>	Mixed dark gray (10YR 4/1) and very dark grayish brown (10YR 3/2) clay; common fine distinct brown to dark brown (7.5 YR 4/4) mottles; massive; slightly sticky, slightly plastic; common fine roots; overwash material as polluted in stream by tin mining; moderately alkaline (field pH 8.0)
10-50	C <sub>1g</sub>	Mixed very dark grayish brown (10YR 3/2) and dark gray (10YR 4/1) peaty clay loam; half ripe; common fine distinct yellowish brown (10YR 5/6) mottles; massive; slightly sticky, slightly plastic; many roots and

woody fragments (partially decayed); moderately alkaline (field pH 8.0)

50-100	C <sub>2g</sub>	Mixed dark grayish brown (10YR 4/2) and dark gray (2.5Y 4/0) peaty silt loam; nearly unripe; massive; slightly sticky, slightly plastic; many roots and woody fragments (partially decayed); moderately alkaline (field pH 8.0)
100-150	C <sub>3g</sub>	Mixed dark grayish brown (10YR 4/2) and dark gray (2.5Y 4/0) peaty silt clay loam; nearly unripe; massive; slightly sticky, slightly plastic; common roots and woody fragments (partially decayed); moderately alkaline (field pH 8.0)
150-200	C <sub>3g</sub>	Mixed dark grayish brown (10YR 4/2) and very dark grayish brown (10YR 3/2) silty clay; unripe; massive; slightly sticky, slightly plastic; fine roots and woody fragments (partially decayed); moderately alkaline (field pH 8.0)

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