Morphology and genesis of actual acid sulfate soils without Jarosite in the Ha Tien Plain, Mekong Delta, Viet Nam

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1 Summary

Actual acid sulfate soils without jarosite in the sulfuric horizon occur widely in the north-western part of the Mekong Delta. They differ morphologically from acid sulfate soils with jarosite in the following aspects: they have peaty clay parent material; have a dark brown subsoil; show low porosity and saturated hydraulic conductivity; pyrite is intensively mixed in the matrix of the subsoil; the sulfuric horizon still contains pyrite; they are potentially acid to great depth.

The absence of jarosite is probably due to the low redox potential in the sulfuric horizon. Redox potential is kept low by the organic matter. Under such conditions, pyrite only oxidizes to ferrous sulfate, not to jarosite.

Résumé

Des sols sulfate-acides sans jarosite, mais présentant toutes les autres caractéristiques de ces sols (pH < 3,5 dans l'horizon oxydé, teneur élevée en sulfures, teneur élevée en Al et Fe dans la solution de sol, saturation élevée en Al), apparaissent sur de grandes superficies dans la partie nord-ouest du Delta du Mekong, dans la Plaine de Ha Tien. Morphologiquement ils diffèrent des sols sulfate-acides à taches de jarosite par:
- un matériau originel tourbeux;
- un sous-sol brun foncé (10 YR 4/3) à brun gris (10 YR 4/1) qui après avoir été exposé à l'air, devient en quelques minutes gris très foncé (N 3/0);
- une porosité et une conductivité hydraulique en milieu saturé, basse;
- un horizon sulfurique contenant encore de la pyrite;
- une teneur en pyrite assez importante, intimement mélangé dans la matrice du sous-sol.

L'analyse de l'acidité totale et potentielle (Méthode Konsten et al. 1986), montre que le sous-sol de ces sols présente une acidité actuelle et potentielle beaucoup plus élevée que les sols sulfate-acides à taches de jarosite.

L'absence du jarosite est probablement due au faible potentiel redox de l'horizon sulfurique, qui est une conséquence de la haute teneur en matière organique. Dans telles conditions, la pyrite est oxydée en sulfate ferreux et non pas en jarosite.
2 Introduction

Field studies of the acid sulfate soil areas of the Mekong delta revealed the occurrence of extensive tracts of acid sulfate soils without the conspicuous straw-yellow jarosite mottles in the oxidized zone, but having all other properties associated with acid sulfate soils: a very low pH $< 3.5$ in the oxidized horizon; high sulfate, aluminum and iron contents in the soil solution; a high Al saturation percentage. Detailed soil profile descriptions of such profiles were made in the field. Samples for thin sections were taken from actual acid sulfate soils without and with jarosite, for micromorphological study.

3 Morphological observations

The morphological studies showed differences in several characteristics between profiles with and profiles without jarosite.

Profiles without jarosite generally have a dark brown (10YR 4/3) to dark grey (10YR 4/1) subsoil. Upon exposure to the air, the colour of the subsoil of these profiles without jarosite changes to very dark grey (N 3/0) within a few minutes. In many cases profiles with jarosite have grey, blueish grey or greenish grey subsoils with a value higher than 4, and in variably a chroma of 1. The colour does not change upon exposure.

The subsoils of profiles without jarosite have a high organic matter content (10-15 mass percent). The organic matter is intensively mixed in the soil matrix, fibrous, and densely packed. The subsoils of profiles with jarosite have a low organic matter content. Organic matter in these soils is usually found as partly decomposed root or leaf remnants.

The subsoils of profiles without jarosite have few very fine pores, and a low saturated hydraulic conductivity. The porosity in the subsoils of profiles with jarosite is high: medium sized or coarse continuous vertical pores are common and there are many fine pores. The saturated hydraulic conductivity is high.

Micromorphological observations confirmed the finely fragmented nature of the organic matter and the intensive mixing with the matrix clay in the subsoils of the profiles without jarosite. A part of the organic matter could be recognized as having cellular structure. Most of these parts were only fragments of leaves or roots. Pyrite, too, was found intensively mixed into the clay matrix. It did not only occur associated with organic matter, but also in the clay, separated from organic matter.

In acid sulfate soils with jarosite, little or no finely fragmented organic matter is found mixed with the matrix clay. Clearly recognizable half decomposed roots and leaves form the majority of the organic matter in these subsoils. The pyrite is concentrated in the root channels and associated with the organic matter.

The lower part of the sulfuric horizon of profiles without jarosite still contains pyrite, seen as isolated pyrite framboids. In sulfuric horizons of acid sulfate soils normally pyrite and jarosite are spatially separated with the exception of cases in which the initial supply of oxygen is abundant and sudden, for example upon artificial drainage (Miedema et al. 1974). The presence of small remnants of pyrite evenly distributed over the lower part of the sulfuric horizon in acid sulfate soils without jarosite may
be an indication of the slowness of the pyrite oxidation in these soils.

In a few places pyrite centres are surrounded by iron (hydr)oxydes but the structure of the framboïds is still visible. This phenomenon may have to be attributed to quick oxidation during preparation of the thin sections. No pyrite was seen in the lower part of the sulfuric horizon of profiles with jarosite.

Thin sections of the sulfuric horizon of profiles without macroscopically visible jarosite do show some small traces of jarosite along the few macropores present. However, these are incorporated in the soil and do not occur as pure jarositans along root channels, as is the case in the acid sulfate soils with jarosite mottles.

Analysis of total and potential acid by the method of Konsten et al. (1986) has shown that the subsols and substrata of soils without jarosite have much higher actual + potential acid contents then soils with jarosite (Brinkman et al. 1986). Pyrite contents up to 4% using the method of Begheyn et al. (1978) have been found in the pyritic subsoil of the profiles without jarosite.

4 Discussion: genesis of acid sulfate soils without jarosite

4.1 Sedimentation of the parent material

The high organic matter content of the sediment can be explained by the age of the sediment: it was formed more than 5500 years ago in a period of rising sealevel and slow sedimentation affecting large areas (Pons 1986; Brinkman et al. 1986). The fragmented and fibrous nature of the organic matter and the intensive mixing of organic matter and pyrite with the matrix clay indicate that originally clayey sediments and peat must have been eroded, reworked, mixed and redeposited by action of the sea. The low macroporosity of the sediment indicates that there was no significant period of mangrove forest vegetation after the redeposition because mangrove roots normally produce common coarse and medium tubular pores.

4.2 Drainage and acidification

When such a dense, highly organic sediment with low porosity is drained, it remains water-saturated due to its spongy structure, and oxidation is very slow. Oxygen diffuses slowly into the water-saturated sediment; microbial decomposition of organic matter keeps the Eh low. Therefore it is likely that upon drainage of the sediment the Eh rises to a level which permits the oxidation of sulfide to sulfate, but not the oxidation of Fe (II):

\[
\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+
\]

Jarosite is formed at low pH (less than 4.0) and at Eh higher than about 400 mV (van Breemen 1976). At lower Eh values, pyrite can still be oxidized, but only to dissolved ferrous sulfate, pH values measured in the sulfuric horizon of acid sulfate soils without jarosite are in the range of 2.4 – 2.6; Eh values are between 300 and 400 mV, measured by pushing a Pt electrode directly into the mud, after standardization by comparison with a ferrous/ferric solution with an Eh of 430 mV.

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The presence of high concentrations of ferrous iron in the Vietnamese acid sulfate soils without jarosite was confirmed by a field test. An aqueous solution of 5% potassium ferric cyanide was added to the soil solution from sulfuric horizons in profiles without jarosite, and showed a strong colour change to dark blue (ferrous ferric cyanide), indicating high concentrations of dissolved ferrous iron. Laboratory analysis showed ferrous iron concentrations in the vicinity of 500 to 1000 ppm Fe, or pFe between 1.5 and 2.

A stability diagram (Figure 1) of jarosite and dissolved ferrous sulphate was calculated for various levels of pFe. Lower values of pFe (meaning high concentrations of ferrous iron) move the boundary between the stability zone of jarosite and dissolved ferrous iron sulfate downwards considerably. However, the above mentioned values of Eh and pH show stability of dissolved ferrous sulfate.

Micromorphological observations confirmed the slow progress of the oxidation process by the presence of partly oxidized pyrite in the lower part of the sulfuric horizon.

Figure 1 Stability diagram of jarosite and dissolved sulfate. Lines indicate solubility isotherms for jarosite at different levels of Fe$^{2+}$. Shaded area indicates pH and Eh measurements in Vietnamese acid sulfate soils without jarosite.
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References

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