

An Interpretation of the Occurrence of Pyrite at two Localities in Western Jutland, Denmark

Bjarne Holm Jakobsen

Jakobsen, Bjarne Holm: An Interpretation of the Occurrence of Pyrite at two Localities in Western Jutland, Denmark. *Geografisk Tidsskrift* 85: 9-14, Copenhagen, June 1985.

The pronounced occurrence of pyrite in two geomorphologically different wetland areas in Western Jutland, Denmark is described. Two models for pyrite formation are outlined and discussed.

Bjarne Holm Jakobsen, Ph.D., Geographical Institute, University of Copenhagen, Østervoldgade 10, DK - 1350 Copenhagen K.

Key words: *Pyrite formation, marsh area, lowland moor area.*

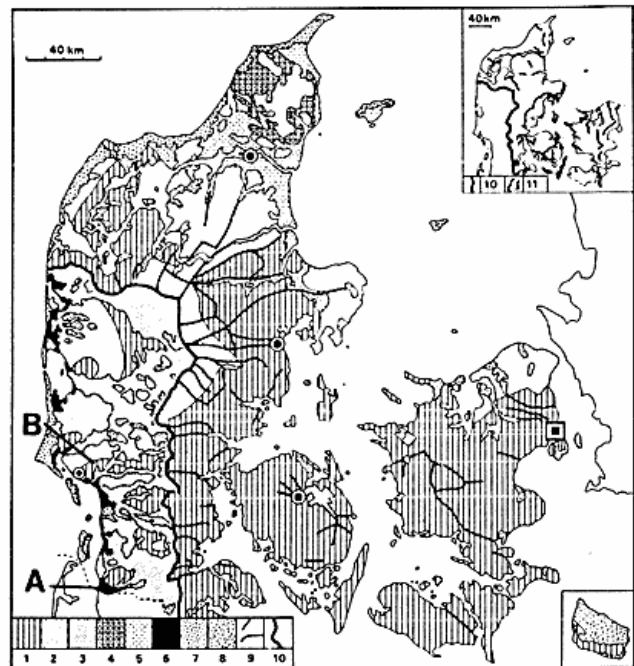
The western part of Jutland, Denmark south and west of the maximal extension of the Weichsel ice sheet, is characterized by a pre - Weichselian glacial landscape and outwash plains from the Weichselian period. Due to the relative high age and the precipitation surplus the uppermost layers are strongly weathered. This weathering has generally leached out an often high content of CaCO_3 , in Denmark characteristic for glacial till, due to the high lime content of the pre - Quaternary deposits. Great amounts of manganese and iron are hereby mobilized.

This mobilized iron, transported by ground water and watercourses is precipitated in other places in the landscape in ferric form as e.g. various oxyhydroxides and in ferrous form as e.g. pyrite, siderite and vivianite.

Much work has been done on the formation of pyrite (e.g. Berner, 1970; Curtis, 1967; Howarth, 1979; Rickard, 1975; Postma, 1982). This paper presents some results from a study of five localities in western Jutland, Denmark, each representing different characteristic positions in the landscape. Results from two localities are shown. The other localities will be dealt with elsewhere.

THE LOCALITIES OF STUDY

The two localities Udbjerg (A) and Roust (B) are shown in figure 1. Locality A representing a marsh area, where the postglacial relative rising of the sea level has caused a sedimentation of peat, gytja and marine clay on a former well drained outwash plain. About 400 years ago the area was diked. At present the area is used for agricultural



Geomorphological map of Denmark

1. Moraine landscape, mainly clayey soil
2. Moraine landscape, mainly sandy soil
3. Outwash plain
4. Late glacial raised sea-floor
5. Raised sea-floor, Litorina
6. Salt marsh
7. Dune landscapes
8. Granite landscapes
9. Tunnel valley
10. Main stationary line of the ice (Würm glaciation)
11. Recession stage of the ice (Würm glaciation)

Fig. 1. The sites of study. Udbjerg (A) and Roust (B).

Fig. 1. De undersøgte lokaliteters placering. Udbjerg (A) og Roust (B).

pose (grassland) with the ground water seasonally varying from the surface to about 0,8 m in depth. Locality B representing a bog area situated near a watershed in the pre - Weichselian glacial landscape, where mainly gytja and peat of varying decomposition have accumulated. Due to minor ditching the ground water level varies seasonally from the surface to about 0,5 m in depth.

METHODS

In order to point out localities representative for the areas, the sediments and their distribution were described accomplishing an extensive boring program. By sampling and measuring the Eh and pH, the redoxcline was determined. Dried samples used for chemical analyses gave information on the distribution of pyrite and the content of iron soluble in 20% hydrochloric acid. Pyrite was deter-

mined by successive extractions of the soil with hydrochloric acid and nitric acid. The pyrite content is calculated from the iron content in the nitric acid extract (Petersen, 1969). Based on this information a typical locality was chosen for each area.

At these two localities the sediments were described in detail, the redoxcline determined by Eh/pH measurements inserting the electrode directly into the sediment, and the following analyses carried out on dried samples: Determination of pyrite, total S, total C, carbonate, sulphate and aqua regia soluble Fe, Mn and Ca. Furthermore the samples were analysed by X - ray diffraction. Pyrite was determined as described above. Total S was determined by a modified Eschkas metode. After heating at 850° C for two hours in a mixture of Na₂CO₃ and MgO, oxidation using H₂O₂, dissolution in hydrochloric acid and evaporation to precipitate SiO₂, the sample is soaked with hydrochloric acid and sulphate dissolved in distilled water and determined gravimetrically using BaCl₂ (Dansk Standardiseringsråd, 1977). Total C was determined by combustion in a LECO induction furnace. The evolved CO₂ was measured by absorption of light in the infrared area. The carbonate is dissolved in 4 N hydrochloric acid measuring the evolved CO₂. Sulphate is determined gravimetrically using BaCl₂ after boiling with 20% hydrochloric acid (Rasmussen, 1961). Aqua regia soluble Fe, Mn and Ca was analysed with AAS. X - ray diffraction analyses were carried out using Co - K α radiation.

At locality B a number of pipes were placed vertically in the ground just outside the bog area in the higherlying pre - Weichselian glacial landscape. From these pipes water samples were collected to describe some chemical characteristics of the upper ground water flowing into the bog area. At locality A no such sampling was made, as no specific present ground water flow from the higherlying surrounding landscape was expected to influence the locality in the middle of the polder area.

Immediately after sampling temperature, pH, total alkalinity and conductivity was measured. Part of the water sample was added a zinkacetate solution and 1 M NaOH to precipitate dissolved sulphide. Another part of the sample was filtered through a 0,00045 mm membrane filter using nitrogen as pressure gas. Within a few hours from sampling total iron, sulphate, sulphide and chloride was determined.

Total alkalinity was determined by titration to pH 4,5 with hydrochloric acid. Conductivity measurements were adjusted to 20° C with 2% / degree centigrade (Ferskvandsbiologisk laboratorium, K.U., 1977). Sulphide was determined spectrophotometrically with the N,N-dimethyl-P-phenylen-diaminsulphate method (Cline, 1969). Sulphate was determined by titration with bariumperchlorate at pH 2,5-4 using a special micro sulphate titration indicator Thorin (Merck). Chloride was measured using a specific chloride electrode. Iron was

analysed with the phenantroline method (American Public Health Association, 1971).

RESULTS

The description of the sediments at the two localities is based on borings and shown below. The descriptive terms used are from the Soil Survey Manual (USDA, 1951).

Locality A Udbjerg: Ground level about 0 m DNN (Danish Normal Zero), ground water level +0,3 m, landuse grass land.

- 0- 20 cm Loam, grey brown (10 YR 5/2), red mottles.
- 20- 60 cm Loam containing about 10% coprogenous gyttja, dark grey brown (10 YR 4/2), black and yellow mottles (jarosite), pH=3,3, Eh=182 mV, 8,5 °C.
- 60- 80 cm Loam containing about 10% hemic material, grey (5 GY 5/1), black mottles, pH=3,9, Eh= +102 mV, 8,3 °C.
- 80-125 cm Coprogenous gyttja containing about 10% hemic material and about 75% loam, dark olive grey (5 Y 3/2), smell of H₂S, pH=6,5, Eh= +171 mV, 8,1 °C.
- 125-170 cm Hemic material containing about 10% coprogenous gyttja and about 50% loam, dark grey brown (2,5 Y 3/2), smell of H₂S, pH=6,7, Eh= +175 mV, 8,0 °C.
- 170-200 cm Sapric material containing about 50% loam, dark brown (7,5 YR 3/4), strong smell of H₂S, pH=6,8, Eh= +162 mV, 8,0 °C.
- 200-250 cm Fine sand, olive grey (5 Y 5/2), smell of H₂S, pH=6,9, Eh= +171 mV, 8,2 °C.

The relative rising of the sea level has caused the sedimentation of peat on the outwash plain. This peat is then covered by gyttja and marine loam, until diking stopped further sedimentation. Over a long period sedimentation took place in a brackish environment, where iron brought into the area by the Vidå river could precipitate as iron sulphides in organic rich delta sediments. In the upper 60 cm of the profile, reclamation has caused oxidation of pyrite and formation of jarosite along ped surfaces followed by very low pH values. X - ray diffraction showed the occurrence of kalium jarosite, normally the dominating form of jarosite in acid sulphate soils (van Breemen, 1982).

Locality B Roust: Ground level about 20,5 m DNN, ground water level +0,10 m, vegetation boggy meadow with shrubs.

- 0- 10 cm Sapric material containing about 30% loam, very dark brown (7,5 YR 2/2), pH=3,8, Eh= 462 mV, 10,0 °C.
- 10- 55 cm Hemic material containing about 20% loam,

Depth cm	Pyrite FeS ₂ %	Total Fe%	Total SZ	Total CZ	CO ₃ - C%	SO ₄ - S%
A 20- 40	0,24	4,97	1,40	5,36	0,01	1,10
40- 60	4,98	5,60	3,90	5,20	<0,01	1,18
60- 80	5,30	5,54	4,30	4,76	<0,01	1,06
80-100	6,12	5,64	5,30	9,00	0,02	0,94
100-125	6,80	5,63	6,20	14,99	0,02	1,21
125-150	5,94	5,08	5,50	19,14	0,03	1,08
150-170	6,96	5,55	6,10	31,64	0,01	1,49
170-200	4,87	3,86	5,00	30,84	<0,01	0,88
200-250	0,27	0,51	0,43	0,51	<0,01	0,06
B 0- 10	0,88	3,98	0,73	40,71	<0,01	0,13
20- 30	0,97	1,85	0,87	45,08	<0,01	0,12
40- 50	1,42	1,76	1,40	45,50	<0,01	0,20
60- 70	9,90	7,27	6,80	39,43	<0,01	0,85
70- 80	10,44	7,63	7,20	40,00	<0,01	0,99
80- 90	10,25	8,35	7,80	39,69	<0,01	1,19
90-100	8,80	6,25	6,30	41,71	<0,01	1,00
100-115	7,65	5,85	5,20	41,62	<0,01	0,83
120-130	0,61	1,34	0,83	2,02	<0,01	0,11
150-160	0,16	1,69	0,52	0,33	0,07	0,05

Table 1. Chemical analyses of sediments from locality A and B.
Tabel 1. Kemiske analyser af sedimentet fra lokalitet A og B.

dark reddish brown (5 Yr 3/4), strong smell of H₂S, pH=4,0, Eh= 321 mV, 9,1 °C.

55- 70 cm Coprogenous gytija containing about 40% sapric material and 30% loam, very dark grey brown (2,5 y 3/2), smell of H₂S, pieces of wood, pH= 4,5, Eh= 20 mV, 7,0 °C.

70-115 cm Sapric material containing about 10% coprogenous gytija and 30% loam, very dark grey brown (10 YR 3/2), smell of H₂S, pieces of wood, pH=5,5, Eh= +98 mV, 8,0 °C.

115-140 cm Loam, grey brown (2,5 Y 5/2), black mottles, pieces of wood, pH=5,8, Eh= +136 mV, 8,2 °C.

140-160 cm Fine sand, grey (5 G 5/1), black mottles, pH=6,0, Eh= +108 mV, 8,0 °C.

The sediment chemistry shows a high content of pyrite at both localities (table 1). At locality A, the marsh area, the pyrite content ranges from 4,9 to 7,0 percent dry weight in the organic rich sediment below the redoxcline. At locality B, the lowland moor area, the comparable pyrite content ranges from 7,7 to 10,4 percent dry weight.

At locality A the degree of pyritization P (P= %Fe-pyrite/%Fe-pyrite + %Fe-HCl), as defined by Berner (1970), ranges from 0,51-0,59 below the redoxcline in the organic rich sediment (table 2). Looking at the remaining iron content the black mottling of the sediment show, that some acid volatile iron sulphide (here termed monosulphide) probably is present. No direct analysis has been made to determine the content of monosulphide. But subtracting sulphur combined in pyrite, sulphate and organic matter (1%×organic matter) from the total % S (table 1), shows that a great part of the remaining iron probably could be found as acid volatile monosulphide. By this indirect method, which must be subject to some uncertainty, it can be seen, that from 70% to nearly 100% of the

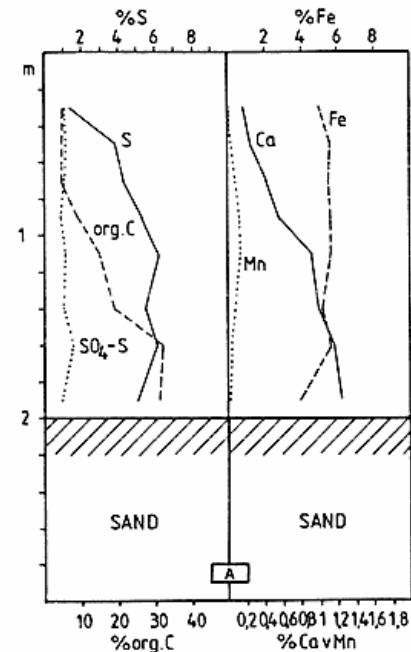


Fig. 2. Total sulphur, sulphate sulphur, organic carbon and aqua regia soluble iron, manganese and calcium, expressed in percent dry weight.

Fig. 2. Total svovl, sulfat svovl, organisk kulstof og aqua regia oploseligt jern, mangan og calcium, angivet i procent tør vægt.

total iron content probably is present in the sediment as Fe²⁺ combined in sulphide.

Below the redoxcline a little carbonate was found and identified as CaCO₃ by X - ray diffraction.

All horizons show a relative high content of sulphate. By X - ray diffraction K-jarosite was identified above the redoxcline as before mentioned. Below the redoxcline gypsum was identified. Looking at the total Ca content (fig. 2) not all sulphate can be present as gypsum. It is assumed, that some iron and aluminium sulphate of uncertain composition could be present (van Breemen, 1982).

While the total iron content is rather constant down the profil the Ca, Mn and S content especially gets low above the redoxcline (fig. 2).

At locality B the degree of pyritization P ranges from 0,57-0,66 in the organic rich sediment below the redoxcline (table 3). Looking at the total S content and subtracting sulphur from pyrite, sulphate and organic matter it seems, that probably very little iron is present as monosulphide.

In the sandy sediment below the organic deposits a small content of carbonate was found (table 1). The only carbonate identified by X - ray diffraction was a mixed carbonate with small reflections between siderite, rhodochrosite and calcite. Mixed carbonates are known from several river bogs in Denmark (e.g. Postma, 1977; Jakobsen, 1984).

Depth cm	Org.C %	T-Fe %	P-Fe %	P
A 20- 40	5,4	5,0	0,1	0,02
40- 60	5,2	5,6	2,3	0,41
60- 80	4,8	5,5	2,5	0,45
80-100	9,0	5,6	2,9	0,51
100-125	15,0	5,6	3,2	0,56
125-150	19,1	5,1	2,8	0,54
150-170	31,6	5,6	3,2	0,58
170-200	30,8	3,9	2,3	0,59
200-250	0,5	0,5	0,1	0,25

Table 2. Organic carbon, forms of iron and degree of pyritization of the sediment at locality A.

Tabel 2. Organisk kulstof, jern-former og pyritiseringsgrad i sedimentet ved lokalitet A.

The pronounced sulphate content below the redoxcline showed to contain gypsum, which was the only sulphate indentified by X - ray diffraction. Due to the relative low content of total Ca, some of the sulphate, as at locality A, probably is present combined in not well defined iron and aluminium sulphate.

Depth cm	Org.C %	T-Fe %	P-Fe %	P
B 0- 10	40,7	4,0	0,4	0,10
20- 30	45,1	1,9	0,5	0,24
40- 50	45,5	1,8	0,7	0,38
60- 70	39,4	7,3	4,6	0,63
70- 80	40,0	7,6	4,9	0,64
80- 90	39,7	8,4	4,8	0,57
90-100	41,7	6,3	4,1	0,66
100-115	41,6	5,9	3,6	0,61
120-130	2,0	1,3	0,3	0,21
150-160	0,3	1,7	0,1	0,04

Table 3. Organic carbon, forms of iron and degree of pyritization of the sediment at locality B.

Tabel 3. Organisk kulstof, jern-former og pyritiseringsgrad i sedimentet ved lokalitet B.

Unlike locality A the content of total iron decreases from the redoxcline upwards, with a slight increase in the uppermost horizon (fig. 2).

Results of ground water analyses from near locality B are shown in table 4. The ground water laterally flowing into the moor area from the higherlying glacial landscape shows to be low in alkalinity and enriched by both

Month	°C	pH	Alk.	Fe45	SO ₄	Cl	S	L
11	9,0	5,45	0,36	22,40	79	25	-	-
1	8,6	5,34	0,27	19,60	79	37	1,75	338
3	8,7	5,51	0,26	21,60	69	32	0,98	288
5	11,1	5,65	0,15	17,80	73	33	0,40	345
7	12,2	5,51	0,23	18,30	61	32	0,52	329
9	13,5	5,48	0,28	19,80	74	36	0,53	330
11	9,0	5,37	0,28	22,20	83	40	0,84	426

Table 4. Characteristics of ground water flowing into the moor area at locality B, november 1982 - november 1983.

Tabel 4. Egenskaber ved grundvandet der strømmer til mosen ved lokalitet B, november 1982 - november 1983.

dissolved sulphate and sulphide, compared to fresh water, normally occurring in the glacial landscape. Also the content of iron, which is assumed to be in a ferrous state, supported by the totally clear appearance of the ground water, reaches values as high as 22,4 mg/l. Throughout the year the iron content is rather constant about 20 mg/l.

DISCUSSION

Formation of pyrite in delta areas is well known throughout the world, and also described in detail for the Skjern Å delta sediments, at the Ringkøbing Fjord, Denmark (Halaburt, Larsen and Postma, 1978). Sea water sulphate brought into the area is bacterially reduced, and the produced H₂S reacts with river transported reactive iron compounds. Probably an intermediate formation of monosulphide normally takes place (Berner, 1964; Rickard, 1974, 1975).

This rather simple model satisfactorily explains the formation of pyrite at locality A, while data from locality B reveal deviations from the model.

At locality A a total iron content of about 4-6% dry weight to a very high degree is combined in sulphides (70-100%). The limiting factor for the accumulation of pyrite in the sediment has apparently been the supply of river transported reactive iron, while before reclamation the supply of sulphate from sea water has probably been abundant. At present, several hundred years after reclamation the external sources of both reactive iron and sulphate are very small, while internal a little reactive iron and sulphur could be generated by weathering and mineralization. The total amount of ironsulphides at locality A, apart from losses due to oxidation, is therefore expected to stay rather constant. Some redistribution in the profile could probably take place, where sulphate and reactive iron generated in the top horizons by present day pyrite oxidation could precipitate below the redoxcline, where reduction of sulphate will take place. Looking at fig. 2, table 1 and the results from X - ray diffraction analyses mentioned before, sulphate generated by pyrite oxidation partly is precipitated as jarosite and gypsum, respectively mainly above and below the redoxcline. some of the sulphate probably also left the sediment by run-off. Only a minor part of the iron from pyrite oxidation seems to have left the sediment by run-off, most of it is probably precipitated as jarosite and oxyhydroxides.

At locality B the total iron content reaches values as high as 8,4% dry weight. Up to about 70% of this iron is combined in iron sulphides. As very reactive iron and both sulphate and sulphide is currently being brought into the moor area by a lateral ground water flow, it seems most likely, that the limiting factor for present day pyrite formation is the supply of dissolved H₂S. This situation, where the sources of both iron and sulphur are found in the ground water flow, seems to be a rather common cha-

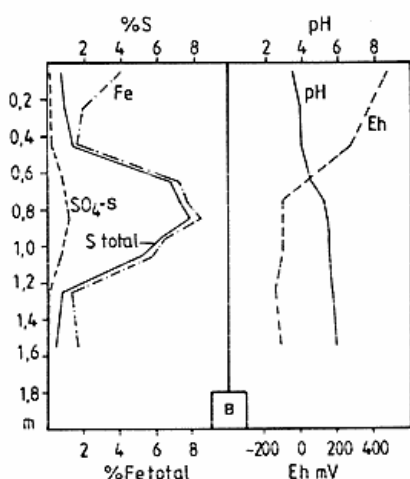


Fig. 3. Total sulphur, sulphate sulphur and aqua regia soluble iron, expressed as percent dry weight. pH and Eh profile.

Fig. 3. Total svovl, sulfat svovl og aqua regia opløseligt jern, angivet i procent tør vægt. pH og Eh profil.

racteristic of the upper ground water in part of the glacial landscape. Data from the other localities in this study (in preparation) supports this assumption.

In this specific area the geological stratification, among others described by Jessen (1922) reveals, that deposits from the Tertiary period, known to contain pyrite, probably formed in a brackish swamp sediment, are found in several places near the surface, often in a dislocated form. Contact between this pyrite containing deposits and the flowing groundwater or even the unsaturated zone, explains the high iron and sulphur content locally occurring in the upper ground water flowing into lowland moor areas.

Pyrite formation at locality B from external sources of iron and sulphur will currently increase the total iron and sulphur content of the organic rich deposits. Unpublished data from other comparable localities in Western Jutland reveals pyrite contents as high as 30-35% dry weight.

As a result of some ditching pyrite oxidation takes place in the upper horizons (fig. 3). As confirmed by X-ray diffraction part of the generated sulphate is precipitated as gypsum in the deeper horizons. The leached sulphate from the upper horizons probably after reduction also contributes to the total amount of dissolved H_2S forming pyrite in the deeper horizons. Most of the iron from pyrite oxidation probably also leaches from the very organic rich upper horizons. The slight increase in iron content in the uppermost horizon is caused by oxidation of the organic deposit (table 1 and fig. 3).

Comparing the pronounced recent pyrite formation at locality A and B makes it possible to distinguish between two typical models for pyrite formation in Western Jutland. Model A where sulphur from sea water meets river transported reactive iron compounds forming pyrite in reduced brackish swamp sediments. Model B where both

sulphur and reactive iron is supplied to a lowland moor area from the groundwater, which locally appears to be enriched by these components.

In a model A situation the accumulation of iron is closely related to the sedimentation, and reclamation stops any further significant supply of iron and sulphur. In a model B situation a more permanent accumulation of pyrite will take place in the organic rich sediments.

As both types of pyrite formation are widespread in western Jutland (Madsen et al., 1984), it seems important to distinguish between the two models. A better understanding of the dynamic state in different potential wetland areas regarding iron mineral formation is achieved. The different function various types of wetland areas have as to protect watercourses against an increasing iron content is better understood. In both a model A and a model B situation a possible lowering of the ground water table will cause a destabilization of the pyrite content due to oxidation. Special for the model B situation however is, that the present accumulation of iron in pyrite will decrease and a more directly run-off of iron rich ground water into the open drainage system will take place.

Resumé

To pyritholdige lokaliteter i Vestjylland er undersøgte. A-Udbjerg beliggende i Tøndermarsken og B-Roust beliggende i en mose nær Alslev Å's vandskel på Varde Bakke. De sedimentkemiske data ved lokalitet A peger på en afsluttet jernakkumulation i sedimentet, hvor en meget stor andel (70-100%) forekommer bundet i jernsulfider. Ophobningen af jernsulfider er sket ved mødet mellem sulfatholdigt havvand og jernholdigt åvand i de organiske, reducerede deltasedimenter. Ved lokalitet B afslører undersøgelsen af det til området strømmende grundvand, at en permanent strøm af svovl og jern, sandsynligvis hidrørende fra tertiære aflejringer, bidrager til en stadig akkumulation af bl.a. pyrit i mosen. Op mod 70% af jernet forekommer bundet i jernsulfider. Disse to modeller for pyritdannelse menes at være fremtrædende og karakteristiske for det vestjyske område. Det forekommer at være nødvendigt at skelne klart mellem de to modelsituationer, ikke mindst i forbindelse med en vurdering af følgerne ved en eventuel sænkning af grundvandstanden (dræning).

References

- American Public Health Association (1971): Standard Methods for the Examination of Water and Wastewater.
- Berner, R. A. (1964): Iron sulphides formed from aqueous solution at low temperatures and pressures. *J. Geol.*, v. 72, p. 293-306.
- Berner, R. A. (1970): Sedimentary Pyrite Formation. *Am. Jour. Sci.*, v. 268, p. 1-23.
- Cline, J. D. (1969): Spectrophotometric Determination of Hydrogen Sulfide in Natural Waters. *Limnol. Oceanogr.*, v. 14, p. 454-458.
- Curtis, C. D. (1967): Diagenetic iron minerals in some British Carboniferous Sediments. *Geochim. et Cosmochim. Acta.*, v. 31, p. 2109-2123.
- Dansk Standardiseringsråd. (1977): Limnologisk Metodik. Akademisk Forlag.

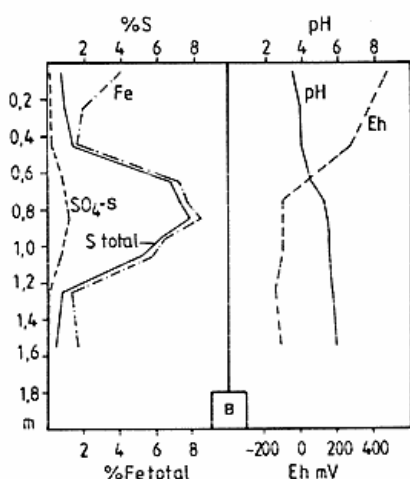


Fig. 3. Total sulphur, sulphate sulphur and aqua regia soluble iron, expressed as percent dry weight. pH and Eh profile.

Fig. 3. Total svovl, sulfat svovl og aqua regia opløseligt jern, angivet i procent tør vægt. pH og Eh profil.

racteristic of the upper ground water in part of the glacial landscape. Data from the other localities in this study (in preparation) supports this assumption.

In this specific area the geological stratification, among others described by Jessen (1922) reveals, that deposits from the Tertiary period, known to contain pyrite, probably formed in a brackish swamp sediment, are found in several places near the surface, often in a dislocated form. Contact between this pyrite containing deposits and the flowing groundwater or even the unsaturated zone, explains the high iron and sulphur content locally occurring in the upper ground water flowing into lowland moor areas.

Pyrite formation at locality B from external sources of iron and sulphur will currently increase the total iron and sulphur content of the organic rich deposits. Unpublished data from other comparable localities in Western Jutland reveals pyrite contents as high as 30-35% dry weight.

As a result of some ditching pyrite oxidation takes place in the upper horizons (fig. 3). As confirmed by X-ray diffraction part of the generated sulphate is precipitated as gypsum in the deeper horizons. The leached sulphate from the upper horizons probably after reduction also contributes to the total amount of dissolved H_2S forming pyrite in the deeper horizons. Most of the iron from pyrite oxidation probably also leaches from the very organic rich upper horizons. The slight increase in iron content in the uppermost horizon is caused by oxidation of the organic deposit (table 1 and fig. 3).

Comparing the pronounced recent pyrite formation at locality A and B makes it possible to distinguish between two typical models for pyrite formation in Western Jutland. Model A where sulphur from sea water meets river transported reactive iron compounds forming pyrite in reduced brackish swamp sediments. Model B where both

sulphur and reactive iron is supplied to a lowland moor area from the groundwater, which locally appears to be enriched by these components.

In a model A situation the accumulation of iron is closely related to the sedimentation, and reclamation stops any further significant supply of iron and sulphur. In a model B situation a more permanent accumulation of pyrite will take place in the organic rich sediments.

As both types of pyrite formation are widespread in western Jutland (Madsen et al., 1984), it seems important to distinguish between the two models. A better understanding of the dynamic state in different potential wetland areas regarding iron mineral formation is achieved. The different function various types of wetland areas have as to protect watercourses against an increasing iron content is better understood. In both a model A and a model B situation a possible lowering of the ground water table will cause a destabilization of the pyrite content due to oxidation. Special for the model B situation however is, that the present accumulation of iron in pyrite will decrease and a more directly run-off of iron rich ground water into the open drainage system will take place.

Resumé

To pyritholdige lokaliteter i Vestjylland er undersøgte. A-Udbjerg beliggende i Tøndermarsken og B-Roust beliggende i en mose nær Alslev Å's vandskel på Varde Bakke. De sedimentkemiske data ved lokalitet A peger på en afsluttet jernakkumulation i sedimentet, hvor en meget stor andel (70-100%) forekommer bundet i jernsulfider. Ophobningen af jernsulfider er sket ved mødet mellem sulfatholdigt havvand og jernholdigt åvand i de organiske, reducerede deltasedimenter. Ved lokalitet B afslører undersøgelsen af det til området strømmende grundvand, at en permanent strøm af svovl og jern, sandsynligvis hidrørende fra tertiære aflejringer, bidrager til en stadig akkumulation af bl.a. pyrit i mosen. Op mod 70% af jernet forekommer bundet i jernsulfider. Disse to modeller for pyritdannelse menes at være fremtrædende og karakteristiske for det vestjyske område. Det forekommer at være nødvendigt at skelne klart mellem de to modelsituationer, ikke mindst i forbindelse med en vurdering af følgerne ved en eventuel sænkning af grundvandstanden (dræning).

References

- American Public Health Association (1971): Standard Methods for the Examination of Water and Wastewater.
- Berner, R. A. (1964): Iron sulphides formed from aqueous solution at low temperatures and pressures. *J. Geol.*, v. 72, p. 293-306.
- Berner, R. A. (1970): Sedimentary Pyrite Formation. *Am. Jour. Sci.*, v. 268, p. 1-23.
- Cline, J. D. (1969): Spectrophotometric Determination of Hydrogen Sulfide in Natural Waters. *Limnol. Oceanogr.*, v. 14, p. 454-458.
- Curtis, C. D. (1967): Diagenetic iron minerals in some British Carboniferous Sediments. *Geochim. et Cosmochim. Acta.*, v. 31, p. 2109-2123.
- Dansk Standardiseringsråd. (1977): Limnologisk Metodik. Akademisk Forlag.

- Halaburt, J., Larsen, V. and Postma, D. (1978): Skjernå deltaets forvittringssituation. Ringkøbing Amtsråd.
- Howarth, R. W. (1979): Pyrite: its rapid formation in a salt marsh and its importance in ecosystem metabolism. *Science*, v. 203, p. 49-51.
- Jakobsen, B. H. (1984): En beskrivelse og tolkning af nogle sedimentkemiske forhold i en række lavbundsområder vest for hovedstilsandslinien. Ph. D. Thesis, University of Copenhagen.
- Jessen, A. (1922): Geologisk Kort over Danmark, Kortbladet Varde. Danmarks Geologiske Undersøgelse I Række Nr. 14.
- Madsen, H. B., Jensen, N. H., Jakobsen, B. H. and Platou, S. W. (1984): Okkerkortlægning, potentielt svovlsure jorder i Nordjyllands, Viborg, Ringkøbing, Ribe og Sønderjyllands amtskommuner. Landbrugsministeriet – Arealdatakontoret 1984.
- Merck, E., A. G.: Thorin Merck, Indikator für die Mikrosulfattiteration.
- Petersen, L. (1969): Chemical determination of pyrite in soils. *Acta. Agri. Scand.*, v. 19, p. 40-44.
- Postma, D. (1977): The occurrence and chemical composition of recent Fe-rich mixed carbonates in a river bog. *Jour. Sed. Petrology*, v. 47, p. 1089-1098.
- Postma, D. (1982): Pyrite and siderite formation in brackish and freshwater swamp sediments. *Am. Jour. Sci.*, v. 282, p. 1151-1183.
- Rasmussen, K. (1961): Uorganiske svovlforbindelsers omsætning i jordbunden. Thesis. De Studerendes Råd ved Den Kgl. Veterinær- og Landbohøjskole, København.
- Rickard, D. T. (1974): Kinetics and mechanism of the sulfidation of goethite. *Am. Jour. Sci.*, v. 274, p. 941-952.
- Rickard, D. T. (1975): Kinetics and mechanism of pyrite formation at low temperatures. *Am. Jour. Sci.*, v. 275, p. 636-652.
- U.S.D.A. (1951): Soil Survey Manual by the Soil Survey Staff. U.S. Soil Conservation Service. Agricultural Handbook No. 18.
- van Breemen, N. (1982): Genesis, Morphology and Classification of Acid Sulphate Soils in Coastal Plains. Soil Science Society of America. Madison.

Notes on the use of extractable iron and clay minerals for determination of soil age

William C. Mahaney and K. Sanmugadas

Mahaney, William C. and Sanmugadas, K.: Notes on the use of extractable iron and clay minerals for determination of soil age. *Geografisk Tidsskrift* 85: 14-19, January 1985.

Changes in soil morphologic properties assist in dating and correlating Quaternary deposits in the Rocky Mountain glacial sequence. Determinations of the ratio of acid oxalate to citrate-dithionite extractable Fe (Fe ratio) gives a trend with age that promises to add another relative dating (RD) method to the field of soil stratigraphy.

William C. Mahaney and K. Sanmugadas, Assoc. prof. and lab. technician at the Atkinson College, York University, Dept. of Geography, 4700 Keele Street, Downsview, Ontario, M3J 2R7 Canada.

Keywords: Soil Stratigraphy, Relative age determinations.

Soil morphology has been used to differentiate deposits in the Rocky Mountain Quaternary glacial sequence as described by Mahaney and Fahey (1976), Mahaney (1978), and Mahaney *et al.* (1984). A number of soil chemical parameters are useful in age differentiation, but most lose their time-dependent character after a few millenia (Mahaney, 1974, 1978). Our research reveals that the ratio of oxalate extractable to dithionite extractable Fe may be used for age differentiation over fairly long periods of time (e.g. several hundred thousand years).

A sequence of Pleistocene glacial deposits along the east flank of Fremont Lake, Wyoming (Figure 1) was chosen for detailed measurements of the Fe ratio (Fe_o/Fe_d) in a well drained sequence, from youngest to oldest, of an Inceptisol, and two Alfisols. The Inceptisol, tentatively classified as a Dystric Cryochrept, (post-Pinedale soil), is 15,000 yrs. BP; the youngest Alfisol, tentatively classified as a Typic Cryoboralf (post-Bull Lake soil), is older than 100,000 yrs. BP; and the oldest Alfisol, tentatively classified as a Typic Eutroboralf (pre-Bull Lake soil), is probably 0.5 million yrs. BP or older (Mahaney *et al.*, 1982). Climatic details are unknown, but all sites are located in the montane forest of Douglas fir (*Pseudotsuga menziesii*) and aspen *Populus tremuloides*). Deposits have been mapped by Richmond (1974) and Mahaney *et al.* (1984), and samples were collected at sites shown on Figure 2. Sample