

## NOTES ON A PYRITIC ZONE IN UPPER ANCYLUS SEDIMENTS FROM THE BOTHNIAN SEA

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### ABSTRACT

Branchlike aggregates, several millimeters in length, of microscopic pyrite spherules are abundant in a narrow zone in upper *Ancylus* clay deposited approximately 7 500 yrs B.P. in the southeastern part of the Bothnian Sea. The aggregates in general, and often also the individual pyrite spherules, have crusts of marcasite exhibiting a radial growth pattern.

In connection with stratigraphic work on Quaternary clays from the marine area west of the town of Pori, SW-Finland, small pyrite concretions were found to abound in a rather limited zone in gray homogenous clay. Samples containing concretions were taken with a modified Kullenberg piston corer. The cores, taken as far as 25 miles apart, all exhibited exactly the same sedimentary sequences.

The Quaternary clays (Fig. 1) have been deposited on till of the last glaciation. The lowermost sediments are varved clays and silts whose varve thickness decreases upwards exponentially (Ignatius, 1958). They grade into a more or less black sulphidic clay, which in turn changes rather abruptly into the gray homogenous clay containing the pyrite concretions. A few centimeters above the pyrite zone the gray clay as a rule changes sharply into a greenish gyttja-banded clay, which is overlain by a recent, dark, greenish, sulphide bearing, homogenous clay.

The pyrite concretions are mainly concentrated in a layer 1—2 cm thick. No pyrite was detected in the few centimeters of gray clay separating the gyttja-banded clay from the sharp upper

limit of the pyritic zone. Downwards the amount of pyritic concretions decreases gradually to vanish completely only slightly above the sulphidic clay.

According to pollen and diatom analyses on cores from the Bothnian Sea the gyttja-banded clay was deposited during the marine Littorina stage of the Baltic Sea evolution (Ignatius, 1964) and corresponds to pollen zones VI—VIII. The gray clay below the gyttja-banded clay corresponds to the fresh water *Ancylus* stage and the upper part of zone V. Zone boundary V/VI, however, lies somewhat below the boundary between the gyttja-banded clay and the gray homogenous clay thus coinciding rather well with the main pyritic zone. The black sulphidic clay was deposited in the early part of the *Ancylus* stage corresponding to pollen zone IV.

The age of zone-boundary V/VI and thus also the age of the pyritic layer has been estimated to be 7 500 yrs. (Kukkonen, Manuscript under preparation).

The pyrite concretions exhibit variations both in size and shape (Fig. 2). The largest individuals were almost a centimeter in length but at the



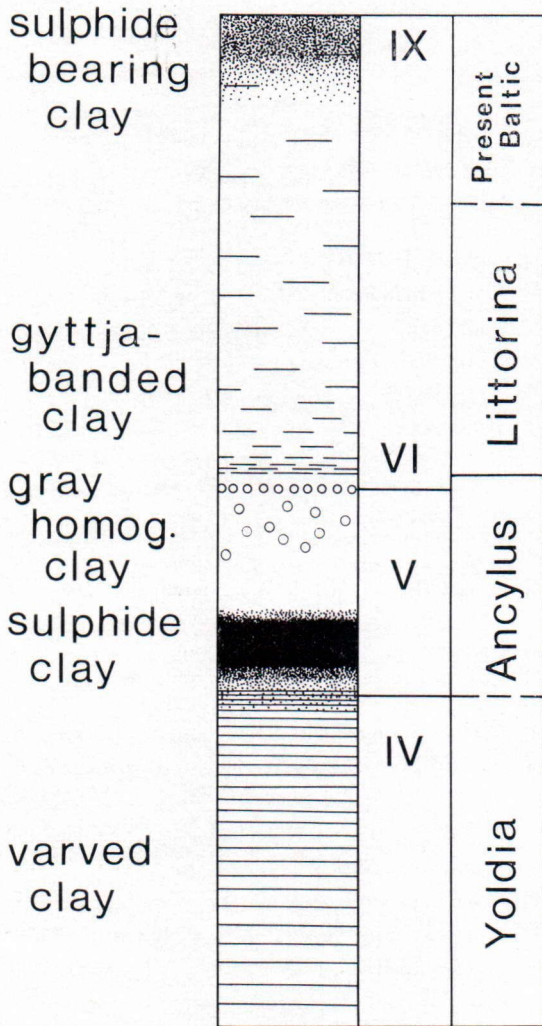


Fig. 1. Diagram indicating the relation between the standard sediment sequence, the pollen zonation and the stages in the Bothnian Sea history. Circles indicate the occurrence of pyrite concretions in cores from the southeastern Bothnian Sea.

most a few millimeters in thickness. Although the size of the concretions varied considerably in a single core sample, quite marked differences in the average sizes were detected between samples from different locations. Also the shapes of the concretions varied from one sample to another. Thus, some of the samples contained rather thick, fingerlike, sometimes even round-

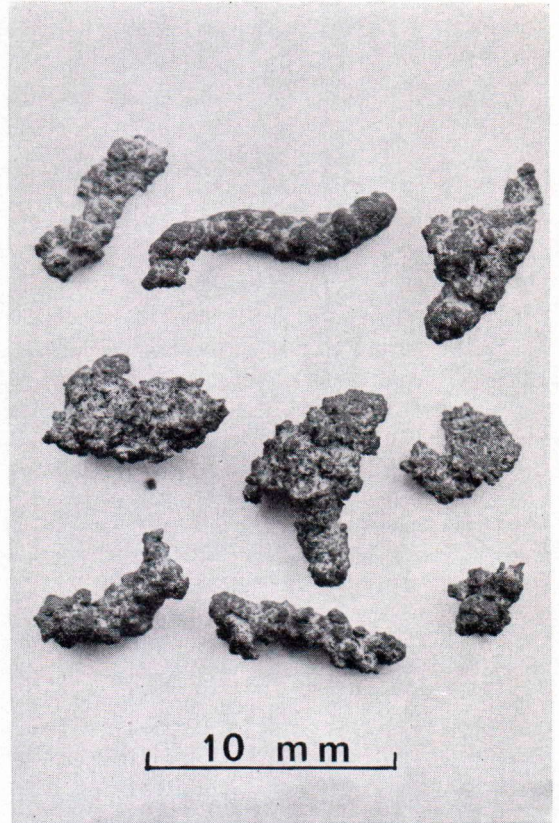


Fig. 2. Aggregates of pyrite spherules separated from homogenous gray Ancyclus clay (sample M10/66).

ish, aggregates while in others the concretions were thin and intricately branched. The latter were also generally smaller in overall size.

A detailed study of the undisturbed core samples indicated that instead of being distributed at random, the pyrite concretions were found to be concentrated into many separate, thin, lenslike layers obviously due to vertical variations in the consistency of the sediment, e.g. grain size and mineral composition.

Thin sections of the clay disclosed that the concretions have caused some distortion in the microstructure of the clay surrounding the pyritic layers and lenses. This seems to indicate a postdepositional formation, since an accretion of pyrite during the deposition of the surround-



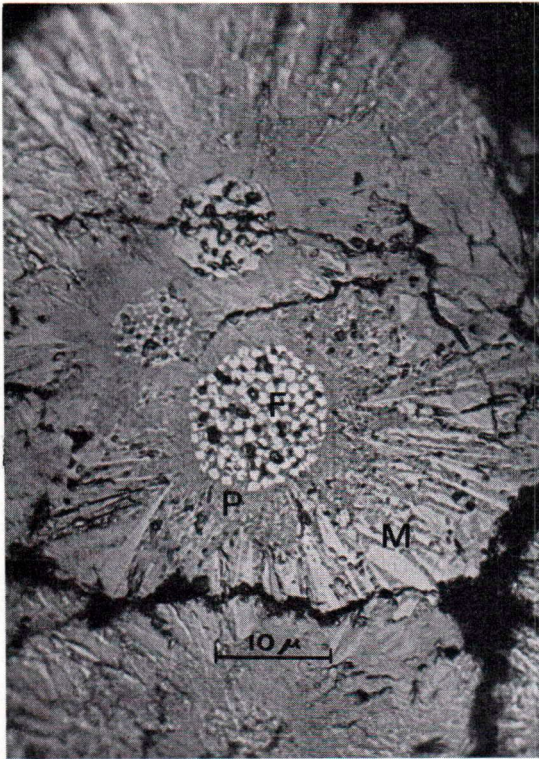


Fig. 3. Micrograph showing the internal structure of a pyrite aggregate (sample M10/66). The core of framboidal pyrite (F) is surrounded by featureless pyrite (P) and pleochroic, radially arranged, laths of marcasite (M).

ing sediment cannot readily account for the noticed deformation.

A microscopic examination of the concretions shows that they are composed of minute, tightly packed spherules, greatly varying in size, but usually less than  $50 \mu$  in diameter. In polished sections the aggregates were found to exhibit marked differences between their internal and marginal parts. The central parts consisted generally of fairly compact pyrite with only faint outlines of the individual spherules visible. In the crustal parts of the aggregates the spherules were clearly discernible. This was particularly due to the fact that the marginal spherules generally had a crust of radially arranged laths of marcasite (Fig. 3). Due to this marcasite crust the individual spherules in the marginal

TABLE 1.  
X-ray powder diffraction data of pyrite concretions

M 10/66		M 3/67		Mineral <sup>1)</sup>
d (Å)	I	d (Å)	I	
3.42	4	3.43	1	M
3.11	2.5	3.13	3	P
2.70	10	2.71	10	P + M
2.68	9			M
2.42	8 (b)	2.42	6	P + M
2.31	3	2.32	1	M
2.205	5	2.205	7	P
1.910	5	1.910	4	P + M
1.753	2.5	1.755	2	M
		1.685	2	M
1.628	8	1.630	7	P
		1.590	1	M
		1.565	1	P
		1.502	2	P + M

<sup>1)</sup> P = pyrite, M = marcasite

parts of an aggregate were larger than those comprising the core of the concretion. Some of the spherules exhibit structures in the central portion of their pyrite cores (Fig. 3) similar to those described as framboidal pyrite by e.g. Love and Amstutz (1966) and Papunen (1968).

The presence of microscopically determined marcasite in the concretions was verified by X-ray diffraction analysis (Table 1). Based on the relative X-ray intensities the marcasite content of the bulk material was estimated to be 20% in sample M10/66. The marcasite concentration in sample M3/67 seemed to be somewhat greater.

Concentrations of some trace elements in two samples of pyrite together with data of the clay surrounding these concretions and of ferro-manganese concretions occurring exposed on the sea floor (Winterhalter, 1966) have been plotted in table 2 for the sake of comparison. Note the similarity in the concentrations of especially the divalent elements Co and Ni in the pyrite and the adjacent clay as compared with the value for the ferro-manganese concretions.

The formation of pyrite versus marcasite in recent or subrecent sediments is generally considered to be a function of pH (e.g. Vallentyne, 1963). Thus, pyrite is formed in neutral or



TABLE 2.

Trace element concentrations (in ppm) in pyrite concretions, in the matrix clay and in recent ferro-manganese concretions.

	Ti	Cu	Co	Ni	Cr	V
Pyrite (M10/66) .....	500	10	60	70	not detected	
Pyrite (M3/67) .....	330	20	40	90		
Clay from the pyrite layer .....	3 900	96	28	78	— <sup>1)</sup>	150
Ferromanganese concretions <sup>2)</sup> .....	— <sup>1)</sup>	110	170	460	30	150

<sup>1)</sup> not analyzed

<sup>2)</sup> from Winterhalter 1966.

alkaline solutions, whereas marcasite requires a more acid environment for its formation. The Ancyclus clay (corresponding to the transition clay with a pH of 6.5—7.5 in Jerbo, 1965) gives a rather neutral reaction, while the gyttja-banded clay is clearly acid with a pH of 5.5—6.5 according to Jerbo (op.cit). However, according to unpublished measurements made by M. Sippola, the numerical pH-values are in general slightly higher than those given by Jerbo; especially the black sulphidic clay (lower Ancyclus) has a definite alkaline reaction.

A change in acidity could be the cause for the formation of the marcasite crust around the pyrite, especially since there are reasons to believe that the upper Ancyclus clay has been higher in pH than present measurements indicate. The few centimeters of gray clay separating the pyrite zone from the gyttja-banded clay represent a time span of 500 yrs or slightly less (cf. Ignatius, 1958). The stratigraphic age of the pyrite was, as previously stated, estimated to 7 500 yrs.

The formation of pyrite is believed to have commenced soon after the deposition of the adjacent clay. Hence, sufficient time has elapsed to permit both the formation of pyrite in the formerly alkaline gray homogenous clay and the later formation of marcasite following the sufficient lowering of pH through ionic diffusion from the acid, younger, gyttja-banded clay. As stated above, the present pyrite concretions contain structures attributed by Love and Amstutz (1966) to sulphur bacteria. Also Papunen (1968) has ascribed framboidal pyrite a biogenic origin. Thus the pyrite concretions could have initiated from colonies of sulphur bacteria, that have provided suitable crystallization centers around which inorganic pyrite and at a later stage, with a lowering of pH, marcasite has precipitated.

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