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PYRITE FORMATION IN ANOXIC ENVIRONMENTS OF THE BALTIC

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ABSTRACT. Two types of anoxic environments are found in the Baltic: the Bornholm deep with low O_2, but H_2S free, bottom waters, and the Gotland deep with H_2S-containing bottom waters. Recent sediments in both environments are rich in organic matter and pyrite. However, the two types behave differently with respect to the process of iron sulfide formation. The Bornholm deep is characterized by high rates of sedimentation and sulfate reduction. In its central part, large amounts of metastable iron sulfides (FeS) accumulate, which are converted to pyrite only over a period of more than 500 yrs. The reactive iron content of the sediments limits the amount of iron sulfidized, while the supply of sulfate determines whether FeS or FeS_2 is dominant. The low salinity of Baltic seawater causes sulfate starvation and results in the accumulation of FeS in the center of the Bornholm deep.

In the Gotland deep, rates of sedimentation and sulfate reduction are lower. Only very little FeS accumulates in the sediment, and here it appears that to some extent pyrite precipitation occurs directly without an intermediate FeS stage. Available reactive iron is apparently, in both environments, the limiting factor for iron sulfide formation.

In the Bornholm deep, C/S ratios range from normal marine to slightly higher values. In the Gotland deep, the H_2S-containing bottom waters cause a decoupling of the processes of organic matter accumulation and iron sulfide formation. This results in a large scatter of C/S ratios which probably is typical for euxinic environments.

In the Gotland deep, freshwater clay below the marine muds is presently being sulfidized by downward diffusion of H_2S. This process of sulfidization can be described quantitatively by a diffusion model developed by Berner (1969).

INTRODUCTION

Pyrite is one of the most widespread authigenic minerals in marine sediments, and, therefore, considerable attention has been paid toward understanding the process of pyrite formation through both experimental studies (Berner, 1964, 1967, 1970; Roberts, Walker, and Buchanan, 1969; Rickard, 1974, 1975; Pyzik and Sommer, 1981) and studies of natural sediments (Berner, 1970, 1984; Goldhaber and Kaplan, 1974, Rozanov, Volkov, and Yagodinskaya, 1974; Jørgensen, 1977; Filipek and Owen, 1980; Howarth and Jørgensen, 1984).

Basically pyrite is formed in sediments of two environmental settings. The normal case is where oxic bottom waters are superimposed on sediments that become anoxic at shallow depth. Recent studies

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(Jørgensen, 1977; Troelsen and Jørgensen, 1982; Howarth and Jørgensen, 1984; Berner and Westrich, 1985) have shown that this situation is very dynamic, and most organic matter and produced H_2S are reoxidized at the sediment-water interface.

Pyritic sediments may also form where anoxic bottom waters, with or without H_2S, overlie anoxic sediments. Quantitatively, the most important examples of such environments are anoxic silled basins, like the Black Sea and the Baltic (Grasshoff, 1975; Demaison and Moore, 1980). An important difference is that here reoxidation at the sediment-water interface is not possible. This may result in accumulation of large amounts of organic matter, typical for euxinic sediments (Raiswell and Berner, 1985). Furthermore it may affect the process of iron sulfide formation, both because conditions at the sediment-water interface are different, but also because iron sulfide formation may already have started in the water column. Generally, anoxic environments are much less studied than normal marine ones, and for a large part, such studies are confined to the Black Sea (Rozanov, Volkov, and Yagodinskaya, 1974; Hirst, 1974; Leventhal, 1983).

It is the purpose of this paper to elucidate the process of pyrite formation in the anoxic basins of the Baltic. The Baltic is an ideal site for the student of authigenic mineral formation in anoxic sediments. Previous studies have identified iron sulfides (Hartman, 1964; Suess, 1976; Bloomquist, ms), manganese carbonates (Manheim, 1961, 1982; Hartmann, 1964; Suess, 1976, 1979; Bloomquist, ms; Emelyanov and others, 1982), and the only known occurrence of MnS in recent sediments (Debyser, 1961; Suess, 1979).

At the present time, the Baltic is the largest brackish water body at the Earth surface. A permanent halocline at 50 to 80 m depth (Grasshoff, 1975) causes stagnant bottom water conditions in the deep basins. Only during infrequent heavy storms is fresh seawater pressed from the North Sea through the Danish Straits into the central part of the Baltic. Salinity decreases east and northward from the Bornholm Deep to the Landsort Deep (fig. 1) (Kullenberg, 1981). Salinities in the deep waters of the Bornholm and Gotland deeps have been measured since 1900 and show variations from 14 to 21 permil and 11 to 14 permil, respectively (Fonselius, 1986); at present the salinity values are 16 and 12.5 permil. Generally the salinity in the Baltic has decreased since the start of the present marine stage at 7700 yr BP. Bloomquist (ms) reports for surface waters of the southern Baltic a decrease from 13 permil during the early marine stage to the present day value of 8 permil.

The sediments in the deep Baltic basins consist of organic rich marine muds. The thickness of the mud deposits is highly variable and may amount to 20 m, which were deposited since 7700 yrs BP (Larsen, 1979). Below the marine mud we encounter the Ancylus clay which represents the freshwater stage of the Baltic from 9200 to 7700 yrs BP (Kögler and Larsen, 1979). A number of our piston cores did penetrate

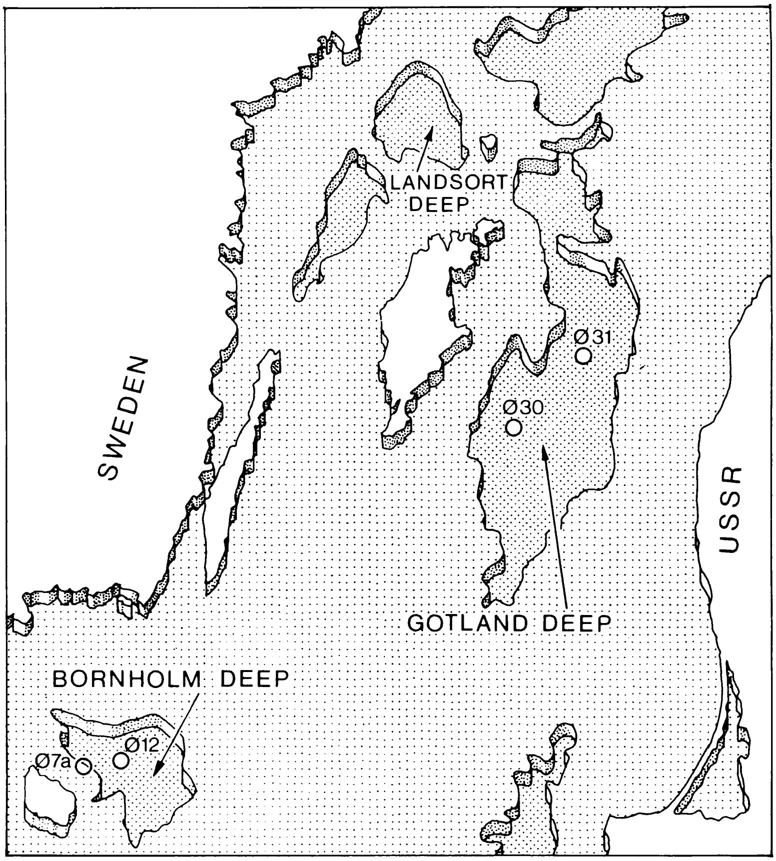

Fig. 1. Anoxic basins and core locations in the Baltic. In the Bornholm deep, core data are; Ø 7a at 70 m depth and 55° 18′N, 15°01′50″E; Ø 12 at 90 m depth and 55°21′N, 15° 17′E. In the Gotland deep core data are; Ø 30 at 165 m depth and 57°00′N, 19°20′E; Ø 31 at 230 m depth and 57°20′N, 20°03′E.

through the marine mud into the Ancylus clay, which displays an entirely different chemistry.

Our studies of pyrite formation in the Baltic have been aimed at two purposes: (A) the formation of pyrite in the marine mud and limiting factors for pyrite formation, (B) the present day sulfidization of the freshwater Ancylus clay by downward diffusion of hydrogen sulfide from the marine mud into the Ancylus clay.

This is the first of a two-part contribution on authigenic mineral formation in the deep basins of the Baltic. A subsequent paper (Jakobsen and Postma, in preparation) will deal with the formation of Ca-rhodochrosite in the same sediments.

METHODS

Sediment cores were taken with a piston-corer capable of recovering cores of up to 4 m length and 8 cm in diameter. Cores were stored upright at *in situ* temperature (5°C) until analysis, which was done aboard the ship as soon as possible, but always within 48 hrs.

Cores within coreliners were sectioned and placed into a N_2-filled glove box. In the glove box, pore water extraction and analysis of oxidation-sensitive components were carried out via the methods of Postma (1981). Pore waters were extracted with a Reeburgh-type sediment squeezer through 0.45 μm membrane filters with up to 4 atm N_2-pressure. Also in the glove box, pH was measured, alkalinity titrated, and reagents added for spectrophotometric analysis of Fe^{2+} and H_2S. Remaining sediments and filter cakes were frozen and stored for later analysis.

pH was measured with a Radiometer PHM-80 and a GK2401G-combination electrode using appropriate buffers at the same temperature as the samples. Fe^{2+} was determined with the Ferrozine method modified after Stookey (1976). For H_2S analysis, each sample was drained directly from the sediment squeezer into a Zn-acetate solution, in order to avoid loss of H_2S. The H_2S concentration was then measured on the ZnS suspension with the methylene blue method (Cline, 1969). Chloride was titrated with $AgNO_3$, using a chromate-dichromate indicator (Grasshoff, 1976). Sulfate was determined with Howarth's (1978) titrimetric method. Both chloride and sulfate analyses were calibrated with standard seawater.

Acid volatile sulfide was determined by H_2S-distillation with 10 percent HCl under a stream of nitrogen. Frozen chunks of sediment were entered in the reaction vessel, and at the end of the distillation, the sediment suspension was gently boiled. Evolving H_2S was trapped in a Zn-acetate solution and analyzed by the methylene blue method (Cline, 1969).

After distillation, the sediment was filtered and washed repeatedly with H_2O. Dissolved Fe in the filtrate was determined by AAS. The remaining sediment was digested overnight with aqua regia, and the released sulfate determined gravimetrically. SO_4-S measured in this way is attributed to pyrite-S, even though it includes organic-S (Kaplan, Emery, and Rittenberg, 1963; Goldhaber and others, 1977). However, at the organic matter and pyrite contents of the marine sediments in the Baltic, the contribution of organic-S will be small (Postma, 1982). For sediments low in organic-S, the aqua regia procedure yields similar results as the Cr(II) reduction method (Zhabina and Volkov, 1978; Howarth, 1984).

Total organic carbon was measured by combustion in a LECO IR-212 after removal of carbonates with HCl. All chemical sediment data are presented on a dry weight basis.

RESULTS

Anoxia occur in the deep basins of the Baltic with variable frequency and intensity, depending on sill depths and distance to the source of freshwater supply (Grasshoff, 1975; Fonselius, 1986). In some basins anoxia occur only sporadically, whereas others are close to perennial anoxicity with H_2S in bottom waters. This enables us to examine the process of pyrite formation in different types of anoxic environments.

The Bornholm deep (fig. 1) is an example of an environment where anoxia are of short duration, whereas H_2S is normally absent in the bottom waters. In contrast, the Gotland deep (fig. 1) is more or less permanently anoxic with H_2S contained in bottom waters.

Bornholm deep.—Anoxic bottom waters occur here for periods of up to a few years but are normally of much shorter duration (Kögler and Larsen, 1979; Fonselius, 1986). At the time of sampling (September 1983) the 1 ml/l O_2 level was found at a depth of 75 m, while minimum values were at 0.15 to 0.25 ml/l O_2 close to the sediment surface. Hydrogen sulfide is seldom present in the bottom water (Fonselius, 1986). According to the classification of Rhoads and Morse (1971) the environment in the Bornholm deep can be described as dysaerobic (0.1-1.0 ml/l O_2).

The halocline was found at 50 to 70 m depth which is close to the bottom, since maximum water depth is 105 m, and in most of the Bornholm deep it is much less. This explains the unstable stagnant conditions in the basin while its proximal position to the source of water exchange through the Danish Straits is also of importance (Kullenberg, 1981).

The uppermost sediment layer in the Bornholm deep consists of marine mud, and it was not totally penetrated by our cores. The sediments reflect the periodic changes between oxic and anoxic bottom water conditions, as a whole range from non-bioturbated to bioturbated sediments is found (Kögler and Larsen, 1979). This is in agreement with the dysaerobic character of the environment (Rhoads and Morse, 1971). The marine muds are rich in organic matter whose concentration is very constant with depth (core Ø12; 4.2 ± 0.6 mole/kg org-C). The maximum thickness of the marine mud sequence in the central part of the Bornholm deep has been estimated to 20 m, which corresponds to a sedimentation rate of 0.26 cm/yr (Larsen, 1979). For site Ø12, the accumulation rate was determined by ^{210}Pb dating to be 1115 g/m^2yr dry matter (Pheiffer Madsen, 1985). At a porosity of 0.85 this yields a sedimentation rate of 0.29 cm/yr, which is close to the average. In the marginal part of the Bornholm deep (core Ø7a) the sedimentation rate is somewhat less (Kögler and Larsen, 1979).

The distribution of iron sulfides in the sediments of the Bornholm deep is shown in figure 2. Core Ø7a is situated in the marginal part of the basin at a water depth of 70 m, which is near the lower boundary of the halocline where bottom waters at the time of sampling contained about 1 ml/l O_2. Core Ø12 was taken at 90 m depth near the depocenter of the Bornholm deep where bottom waters presently are dysaerobic.

Since our main interest concerns the role of iron in the process of pyrite formation, measured concentrations of pyrite-S and FeS-S were recalculated to the amount of sulfide-bound iron. FeS and FeS + FeS_2 distributions are both shown in figure 2. The difference between the two curves reflects the amount of pyrite present. Most conspicuous for both cores is that the amount of iron bound as sulfide is very constant from close to the sediment surface and downward. With few exceptions

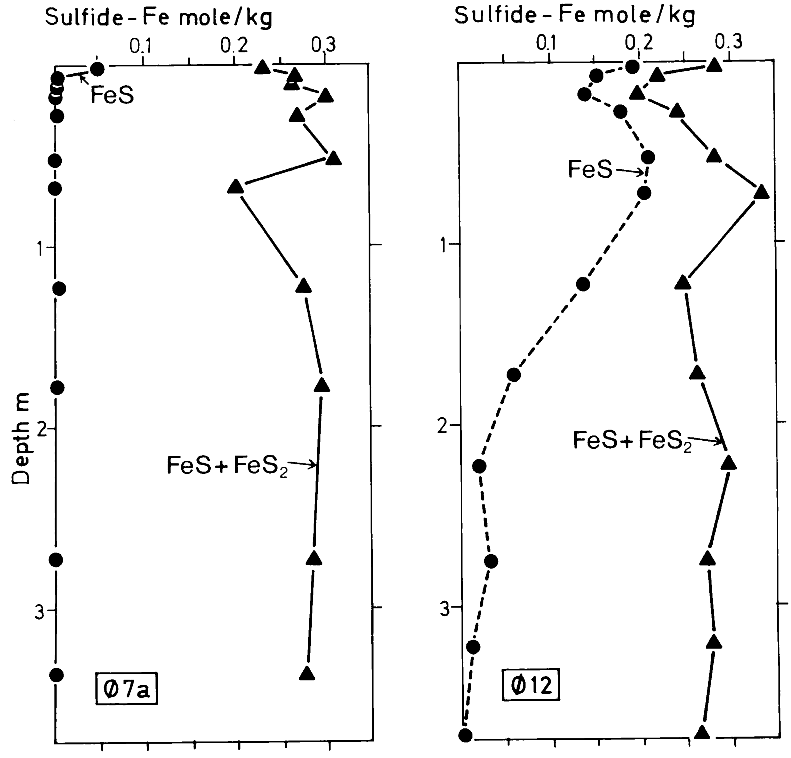

Fig. 2. Iron sulfide distribution in sediments of the Bornholm deep. The Fes + FeS_2 curve indicates total sulfide-bound iron. The difference between the curves reflects the presence of pyrite. Core Ø7a is from the marginal part of the basin at 70 m depth while Ø12 is from the central part at 90 m depth (fig. 1). Concentrations are expressed as mole/kg (dry wt).

the sulfide-bound Fe is for both cores within the range 0.25 to 0.30 mole/kg Fe. Thus, below the top layer, very little additional iron is sulfidized during diagenesis.

A way to evaluate the extent of sulfidization of available iron in a sediment is the degree of pyritization. The degree of pyritization (P or DOP) is defined (Berner, 1970; Raiswell and Berner, 1985) as the ratio between pyrite-Fe and total reactive Fe. Total reactive Fe consists of pyrite-Fe plus Fe extractable by hot HCl. According to Berner (1970) the iron extractable by hot HCl is also reactive toward sulfidization by H_2S. One problem with the DOP parameter is that if significant amounts of FeS are present, such as in core Ø12 (fig. 2), then the amount of sulfidized iron is strongly underestimated. Therefore we modify the DOP to the degree of sulfidization, DOS, which is defined as

$$\mathrm{DOS} = \frac{\mathrm{Fe}_{\mathrm{sulfide}}}{\mathrm{Fe}_{\mathrm{total}}}$$

Here $\mathrm{Fe}_{\mathrm{sulfide}}$ is $\mathrm{Fe}_{\mathrm{pyr.}}$ plus $\mathrm{Fe}_{\mathrm{FeS}}$, whereas $\mathrm{Fe}_{\mathrm{total}}$ is $\mathrm{Fe}_{\mathrm{pyr.}}$ plus Fe extractable by hot HCl. In most sediments $\mathrm{Fe}_{\mathrm{FeS}}$ is very small, so that DOP equals DOS; however, this is not true in the Bornholm deep.

Values for DOS in both cores of the Bornholm deep are shown in figure 3. Generally DOS ranges between 0.2 and 0.55 which is in good agreement with values for normal marine sediments (Berner, 1970; Jørgensen, 1978). However DOS values for Ø7a from the marginal part of the basin are distinctly higher than in Ø12 in the central part of the basin. This is surprising since the amount of sulfide-bound iron is the same in both cores (fig. 2). Apparently more HCl-soluble Fe is present in the sediment of Ø12 which is not easily sulfidized.

Pyrite formation proceeds in marine sediments mainly through an intermediate iron monosulfide (FeS) phase which with time is transformed to pyrite (Berner, 1970, 1984; Jørgensen, 1977; Howarth and Jørgensen, 1984). In aerobic bottom water environments, the amount of FeS is normally very small compared with FeS_2 (Berner, 1970; Jørgensen, 1978), and this is also found in the marginal part of the Bornholm deep (core Ø7a, fig. 2). However, in the central part of the Bornholm deep (core Ø12, fig. 2) very high contents of iron monosulfides amounting up to 75 percent of the sulfide-bound iron are found.

With depth, the iron monosulfide is transformed to pyrite, and since the amount of sulfide bound to iron remains roughly constant (fig. 2), the process must essentially be addition of sulfur. This is in good agreement with conclusions derived by others (Berner, 1970; Sweeney and Kaplan, 1973). Note also that traditional plotting of FeS_2-S for core Ø12 would show a strong increase with depth, while the amount of sulfide-bound iron remains constant.

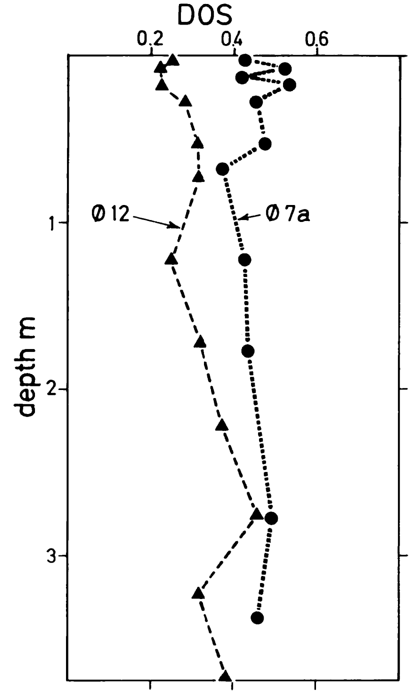

Fig. 3. Degree of sulfidization in marine sediments of the Bornholm deep, DOS = $Fe_{sulfide}/Fe_{total}$. For location, see figure 1.

The rapid depletion of sulfate in pore waters (fig. 4) indicates high rates of sulfate reduction. Boesen (ms) obtained sulfate reduction rates for core Ø12 by mathematical modelling following the procedures of Berner (1980). Core Ø12 was also the only one of our piston cores complete enough in the top layers to enable modelling. Calculated peak rates of sulfate reduction for core Ø12 were in the range 72 to 126 nmole/cm^3day, while depth integrated rates yield 5.0 to 6.9 mmole/m^2day. These values are well within the range for fjords and bays in Jørgensen's (1982) compilation.

In the Gdansk deep, another of the Baltic deeps which is comparable to the Bornholm deep, Lein (1983) measured $^{35}SO_4$ peak reduction rates of up to 83 nmole/cm^3day, in good agreement with our values.

Our estimates of sulfate reduction rates in the Bornholm deep indicate that 25 to 30 percent of the reduced sulfate is accumulated as iron sulfide in the sediment while the remainder is reoxidized or escapes from the sediment surface. For comparison, Jørgensen (1977) found for Limfjorden that 90 percent was reoxidized, while Berner and Westrich

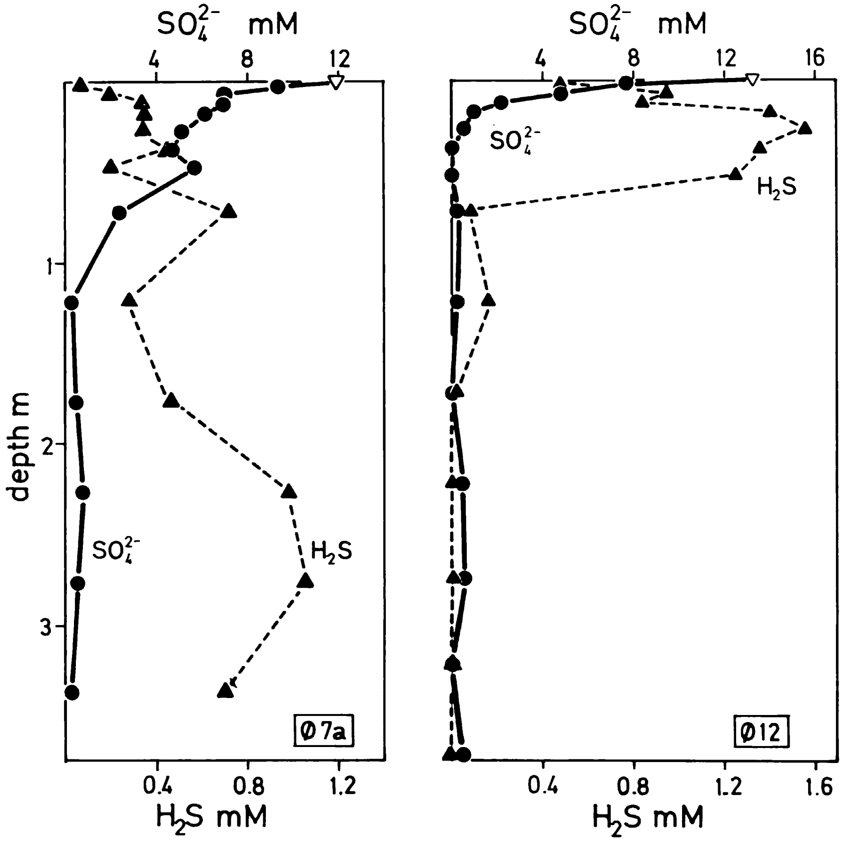

Fig. 4. Pore water chemistry in marine sediments of the Bornholm deep. For location, see figure 1.

(1985) estimated a sulfur loss from 72 to 94 percent, excluding one core with a sulfur loss of only 25 percent.

Gotland deep.—Anoxic bottom water conditions lasting for periods of at least 10 yrs have been common in the history of the Gotland deep (Ignatius and others, 1981; Hallberg, 1974; Fonselius, 1986). The halocline is here normally situated between 60 and 70 m depth (Kullenberg, 1981). Since the maximum water depth is 250 m, the system is much more stable than the Bornholm deep. At the time of sampling the 1 ml/l O_2 level was between 100 and 150 m depth, while below this depth no oxygen is present. Since the last major water renewal in 1952, the bottom waters have mostly been H_2S-containing, and the present H_2S period has lasted for 8 yrs (Fonselius, 1986). Thus, according to Rhoads and Morse's (1971) classification, the present environment is anaerobic or azoic. Still during the past, the Gotland deep has occasionally also known aerobic bottom water conditions (Ignatius and others, 1981).

The surface sediments of the Gotland deep consist of marine muds which in several intervals display a fine lamination corresponding to anoxic bottom water periods. A further characteristic of these sediments is the occurrence of authigenic manganese-carbonate (Manheim 1961, 1982; Hartmann, 1964; Suess 1976, 1979), for which new results will be discussed elsewhere. Below the marine muds, freshwater clay sediments of the Ancylus period (9200–7700 yr BP) are found. Both our cores penetrated down into these Ancylus clays.

Sedimentation rates in the Gotland deep are lower than in the Bornholm deep. While the maximum thickness of marine muds in the Bornholm deep is about 20 m (Larsen, 1979), they amount to only 5 to 7 m in the Gotland deep (Niemistö and Voipio, 1974; Ignatius and others, 1981). Sedimentation rates do, however, vary greatly even in the deepest part of the Gotland deep (Niemistö and Voipio, 1974).

In our core Ø31 (fig. 1) at 230 m depth, in the deepest part of the Gotland deep, we found only 1.77 m marine mud which, assuming continuous sedimentation, corresponds to a rate of only 0.023 cm/yr. The marginal core (Ø30) contained 1.29 m marine mud, which corresponds to an average sedimentation rate of 0.017 cm/yr. Thus it appears that sedimentation rates in the Gotland deep are 3 to 10 times lower than in the Bornholm deep.

The content of organic matter in the marine mud of the Gotland deep is high and quite variable, ranging from 2.3 to 9.4 mole/kg org.-C (figs. 8 and 10). Still the general level is, however, about the same as in the Bornholm deep (fig. 10). This is surprising, considering the much lower sedimentation rates in the Gotland deep. Zsolnay (1971) made a comparative study of organic matter in sediments of the Gotland and Bornholm deeps and estimated, based on pristane contents, that the primary production is 1.5 times higher over the Bornholm deep. Zsolnay furthermore concluded that organic matter in sediments of the Gotland deep is of a less degraded type, containing a larger percentage of less condensed and unsaturated compounds. Thus, the same level of organic matter contents in both basins appears to be the result of a high primary production and high sedimentation rate (dilution by clastics) in the Bornholm deep versus lower sedimentation rate and less degradation of organic matter in the Gotland deep. Note that this is different from environments with oxygenated bottom waters where higher sedimentation rates normally are associated with higher organic contents (Goldhaber and Kaplan, 1975).

The distribution of iron sulfides in the central Gotland deep is shown cumulatively in figure 5. Similar data for a station more marginal to the deep is shown in table 1. The boundary between marine muds and freshwater Ancylus clay is indicated by M/F. Most conspicuous is that the marine muds are high in iron sulfides, while the Ancylus clay only contains iron sulfide near the interface with the marine muds. The

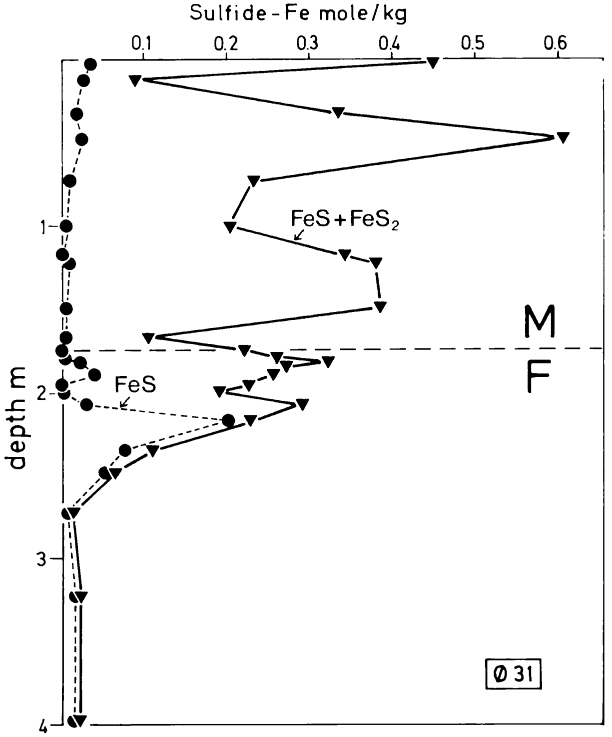

Fig. 5. Iron sulfide distribution in marine and freshwater sediments in the Gotland deep. The marine/freshwater interface is indicated by the dotted line marked M/F. The difference between the FeS and FeS + FeS_2 curves represents pyrite. For location, see figure 1.

variability of the iron sulfide content in the marine muds of the Gotland deep (fig. 5, table 1) is much larger than in the Bornholm deep (fig. 2). However the general level appears to be the same in both environments or only slightly higher in the Gotland deep. A comparison of DOS between the Bornholm deep (fig. 3) and the marine muds of the Gotland deep (fig. 6) shows the latter has DOS values slightly higher (0.3–0.6) than the central part of the Bornholm basin (0.2–0.45, core Ø12) but quite comparable to the marginal core (Ø7a). Note that below the marine mud/freshwater clay interface the uppermost DOS values are the same as in the marine mud, which indicate a similar reactivity of iron toward H_2S in both types of sediment. Farther down, DOS-values decrease with iron sulfide concentrations, showing that the availability of H_2S here limits iron sulfide formation.

Hydrogen sulfide is present in the marine muds at all depths (fig. 7 and table 2). However the concentrations in the Gotland deep are low and do not exceed 0.25 mM, while in the Bornholm deep, values of up to

TABLE 1

Sediment composition of core Ø30 in the Gotland deep. The top layers (0–129 cm) consist of marine mud, below that freshwater clay is found. Fe-total is FeS_2-Fe plus HCl extractable iron. DOS is the degree of sulfidization

Depth cm	C-org mole/kg	FeS_2-S mole/kg	FeS-S mmole/kg	Fe-total mole/kg	DOS
0–5	4.10	0.79	2.37	0.82	0.48
25–30	3.13	0.48	0.86	0.65	0.37
45–50	3.58	0.51	1.13	0.72	0.36
70–75	4.48	0.53	5.59	0.79	0.34
99–100	5.68	1.01	10.3	0.73	0.70
120–125	9.40	0.91	10.0	0.96	0.48
127–128	6.26	0.61	5.40	0.63	0.49
145–146	1.53	0.41	0.03	0.58	0.35
159–160	0.89	0.67	0.02	0.78	0.43
167–168	—	0.22	0.	0.50	0.22
170–175	—	0.06	142.	0.80	0.22
180–181	1.41	0.04	40.8	0.70	0.09
220–225	0.63	0	4.16	0.78	0.01
272–277	—	0	2.42	0.62	0
320–325	0.34	0	0.01	0.51	0
409–414	0.41	0	0.02	0.77	0

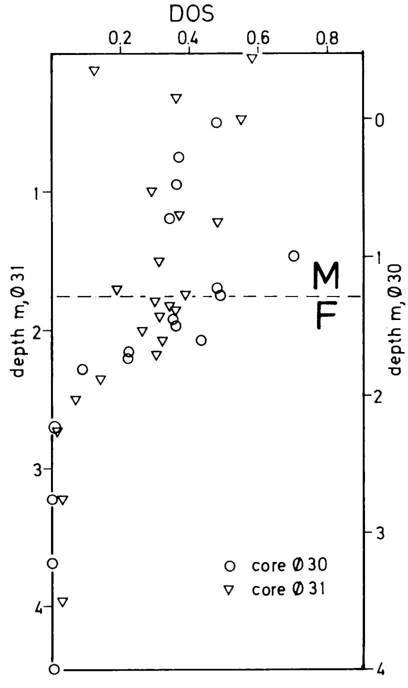

Fig. 6. Degree of sulfidization in marine and freshwater sediments in the Gotland deep. The marine/freshwater interface is indicated by the dotted line marked M/F. DOS = $Fe_{sulfide}/Fe_{total}$. Depths in both cores are normalized to the marine/freshwater interface.

1.5 mM were measured. In good agreement, sulfate depletion is moderate (fig. 7, table 2) in the marine mud, and the concentration remains constant in the freshwater Ancylus clay. Since the sedimentation rate in the Gotland deep is much lower than in the Bornholm deep, this suggests that sulfate reduction rates also are considerably lower. In agreement, Lein (1983) reported from the Gotland deep $^{35}SO_4$-reduction rates which are about one third lower than in the Bornholm deep. An interesting result of Lein (1983) is that the major part of the radioactive ^{35}S label is found in the pyrite fraction. Howarth and Jørgensen (1984) report that in normal marine sediments only 14 to 32 percent of the ^{35}S label is recovered in the pyrite fraction while the remainder is found in the FeS fraction. This supports Berner's (1970) contention that pyrite formation mainly proceeds through an intermediate FeS stage. Lein's (1983) results suggest that pyrite formation under euxinic conditions in some cases, as in the Gotland deep, may

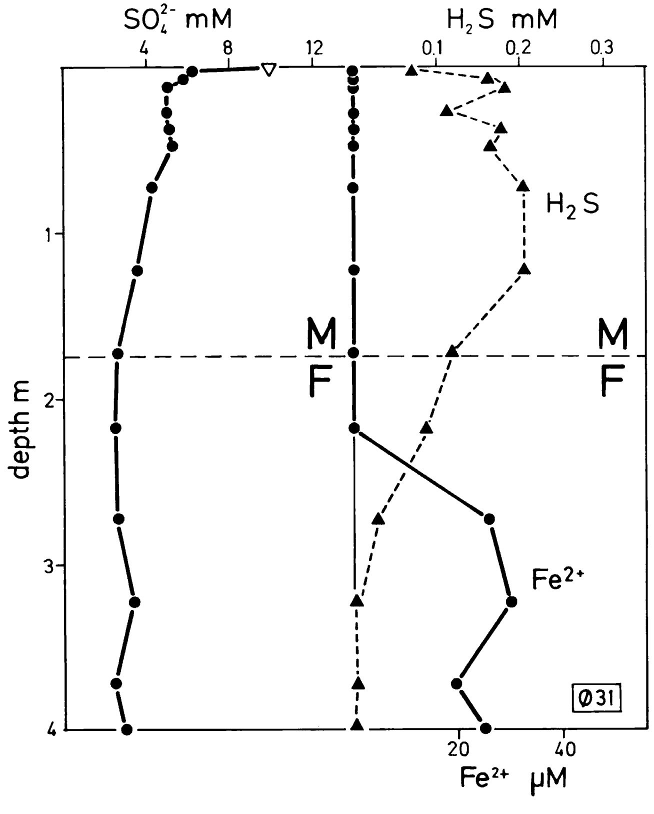

Fig. 7. Pore water chemistry in marine and freshwater sediments in the Gotland deep. The marine/freshwater interface is indicated by the dotted line marked M/F.

TABLE 2

Pore water composition of core Ø30 in the Gotland deep. BW = bottom water. The top layers (0–129 cm) consist of marine mud, below that freshwater clay is found

Depth cm	Cl^- mM	SO_4^{2-} mM	H_2S μM	Fe^{2+} μM
BW	—	10.0	—	—
0–5	184	6.7	59	0
5–10	190	6.0	134	0
10–15	193	6.9	200	0
15–20	196	6.9	188	0
25–30	193	6.3	154	0
35–40	198	6.4	147	0
45–50	193	5.6	205	0
70–75	193	5.4	(27)	0
120–125	193	5.7	247	0
170–175	196	5.3	37	0
220–225	198	5.0	5	11
272–277	206	4.9	2	39
320–325	189	6.5	3	15
370–375	179	5.7	0.2	66
409–414	198	4.5	0.6	75

proceed directly without an intermediate FeS phase. In good agreement the concentration of FeS in the marine muds of the Gotland deep (fig. 5 and table 1) is very low. In salt marshes (Howarth, 1979; Howarth and Giblin, 1983; Howarth and Merkel, 1984), pyrite formation without intermediate FeS also appears to be the dominant process. Howarth (1979) argued that the reason for this is that pore waters are undersaturated for FeS. At the H_2S level of the Gotland deep (fig. 7), we calculated with Wateqf (Plummer, Jones, and Truesdell, 1976) that Fe^{2+}-concentrations in that case should be less than 0.05 μM which is well below our detection limit.

The organic-rich marine muds are superimposed on freshwater clay from the Ancylus period which is poor in organic matter (fig. 8). At the interface between the two deposits, sulfidization of the freshwater clay apparently takes place. Porewater data (fig. 7 and table 2) show that no further sulfate depletion (nor alkalinity production) occurs in the freshwater clay while hydrogen sulfide appears to diffuse downward. Dissolved Fe^{2+} (fig. 7 and table 2) shows a reverse gradient with higher values in the lower part which decrease upward. In the zone where both H_2S and Fe^{2+} are present, iron sulfide precipitation must take place. Sediment data are in good agreement with this general picture. Iron sulfide is only present in the upper part of the freshwater clay (fig. 5 and table 1) and shows a downward decrease coinciding with the hydrogen sulfide profile. At the same time DOS values decrease (fig. 6). Near the iron sulfide front, FeS is found almost exclusively. The presence of FeS is also easily observed on fresh cores since it results in pronounced black banding. Such black sulfide bands in the upper part of the freshwater

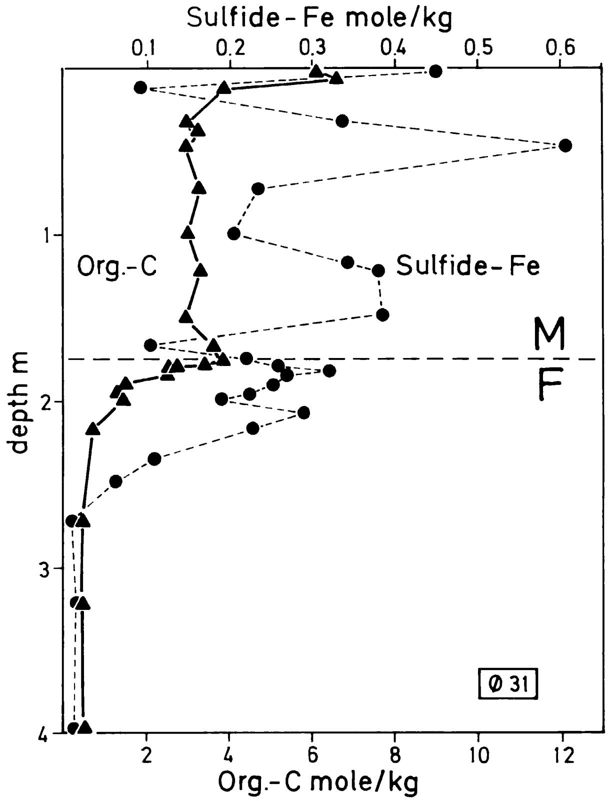

Fig. 8. Distribution of organic carbon and iron sulfide between marine and freshwater sediments in the Gotland deep. The marine/freshwater interface is indicated by the dotted line marked M/F.

Ancylus clay have been observed at many places in the Baltic (Papunen, 1968; Bloomquist, ms; Kögler and Larsen, 1979). The overall process seems to be: The freshwater clay is low in organic carbon and originally contains little iron sulfide. The superimposed marine mud is rich in organic matter, sulfate reduction takes place, and the resulting H_2S diffuses downward and sulfidizes the freshwater clay. However, this picture is slightly idealized, since the top of the Ancylus clay also contains organic carbon (fig. 8). Still pore water data clearly show that downward H_2S diffusion takes place. A diffusion model for this process of sulfidization will be discussed in a later section.

The conversion of FeS to FeS_2 within the iron sulfide front (fig. 5, table 1) confronts us with a stoichiometric problem. For FeS formation we may write:

$$2FeOOH + 3HS^- \rightarrow 2FeS + S^\circ + H_2O + 3OH^-$$

Then FeS can be oxidized to pyrite, stoichiometrically by:

$$FeS + S^{0} \rightarrow FeS_2$$

The total reaction between H_2S and FeOOH as oxidant now becomes:

$$2FeOOH + 3HS^{-} \rightarrow FeS + FeS_2 + H_2O + 3OH^{-}$$

Thus if no oxidant other than iron oxide is present, equal amounts of pyrite and FeS should be the final result while we observe that nearly all FeS is converted to FeS_2. The conversion of FeS to FeS_2 at the surface of normal marine sediments is no problem, since here additional S^{0} can be supplied by H_2S oxidation (Jørgensen, 1977). However, in the Ancylus clay no other oxidant appears to be present. Both oxygen and nitrate must be absent in Fe^{2+} containing pore water, and the Mn-oxide content is far too low. The only alternative electron acceptor present is sulfate. However, sulfide/sulfate reactions have been strongly rejected by Berner (1970). Unless a hithero unknown oxidant exists, the only explanations seem to be either downward diffusion of polysulfides or that the FeS/FeS_2 distribution reflects an historical change. The latter possibility seems, however, unlikely to us.

DISCUSSION

Limiting factors for pyrite formation.—Principally, two factors may limit the amount of pyrite formed in a sediment: these are reactive iron and dissolved sulfide. The latter is controlled again by organic matter and sulfate. Based on observed C/S relationships and low degrees of pyritization, Berner (1970, 1984) argued that available organic matter, and thereby H_2S, is the limiting factor in normal marine sediments. On the other hand, Jørgensen (1978) maintains that since only 10 percent of the produced H_2S is conserved in the sediment as iron sulfide, reactive iron must be the limiting factor.

With respect to euxinic environments, it is generally considered (Leventhal, 1983; Berner, 1984; Raiswell and Berner, 1985) that reactive iron is the limiting factor for the amount of iron sulfide formed. Several lines of evidence support that this is the case in both the Bornholm and Gotland deep.

First, in the Gotland deep about 100 m of H_2S bearing water overlies the sediment and H_2S is also present in the pore water (fig. 7). Also because sedimentation rates are low here, any reactive iron should have ample opportunity to react with H_2S.

In the Bornholm deep, bottom waters are depleted in oxygen but free of H_2S. Therefore all iron sulfide formation must occur within the sediment. The most striking feature here is the constant amount of sulfide-bound-iron from close to the sediment surface down to 3 to 4 m depth (fig. 2). At the measured sedimentation rate of 0.29 cm/yr, this sediment sequence represents a period of more than 1000 yrs. Particularly core Ø7a (fig. 4) has very high H_2S concentrations in the pore water down to 3.5 m. Thus both time and H_2S are here available for further diagenetic iron sulfide formation. However, since sulfide-bound-iron does not increase with depth (fig. 2) one must conclude that all iron available for iron sulfide formation reacts in the top layer of the sediment. Thus, reactive iron constrains the amount of iron sulfidized.

While the content of sulfide-bound-iron is the same in cores Ø7a and Ø12 (fig. 2), the sulfur concentration in the sediments is very different. This is due to the presence of large amounts of FeS in core Ø12 (fig. 2). The pore water of Ø12 contains only appreciable amounts of H_2S in the upper 75 cm (fig. 4), and the limited conversion of FeS to FeS_2 seems therefore due to sulfur starvation (Berner, 1974; Berner, Baldwin, and Holdren, 1979). In contrast, the pore water of core Ø7a contains abundant H_2S at all depths (fig. 4), and here almost all iron sulfide is present as pyrite (fig. 2). Therefore, while the reactive iron content limits the amount of sulfide–bound–iron, available H_2S controls the FeS/FeS_2 ratio.

The low salinity of the Baltic seawater confines the amount of sulfate available for reduction. This is the main reason for the exhaustion of sulfate in the porewater of the Bornholm deep at less than 1 m (fig. 4). Therefore salinity may control the FeS/FeS_2 ratio (see also Berner, Baldwin, and Holdren, 1979.

Kinetic studies (Rickard, 1974; Pyzik and Sommer, 1981) have shown that the rate of iron sulfide formation increases with the dissolved sulfide concentration. Therefore it is expected that more iron sulfide forms in high H_2S environments within a given period of time. The H_2S concentration level varies a great deal in different parts of the Baltic. Figure 9 shows for the different cores the amount of sulfide-bound iron versus maximum H_2S concentrations in the pore water. Assuming diagenetic conditions that approach steady state, a given sediment layer must pass through the zone of maximum H_2S and pyritize accordingly. However, figure 9 shows that the amount of sulfide-bound iron is independent of the maximum H_2S concentration in the pore water. This is not an artifact of different sedimentation rates, since a similar plot of DOS against maximum H_2S concentration gives the same trend. Apparently any iron that may sulfidize does so regardless of the H_2S concentration, within the range 0.2 to 1.5 mM. Therefore, our general conclusion is that reactive iron controls the amount of sulfide-bound iron formed in both dysaerobic and euxinic environments of the Baltic.

Generally one expects that the degree of sulfidization (DOS or DOP) should be greater in euxinic than in normal marine environments. This is particularly true if one accepts that organic matter is the limiting factor for pyrite formation in normal marine sediments. Also, DOS values should be higher in the Gotland deep than in the Bornholm deep, since the former contains H_2S-rich bottom waters and has a lower sedimentation rate.

The Gotland deep marine sediments yield DOS values in the range of 0.30 to 0.60 (fig. 6) which is slightly higher than for the central

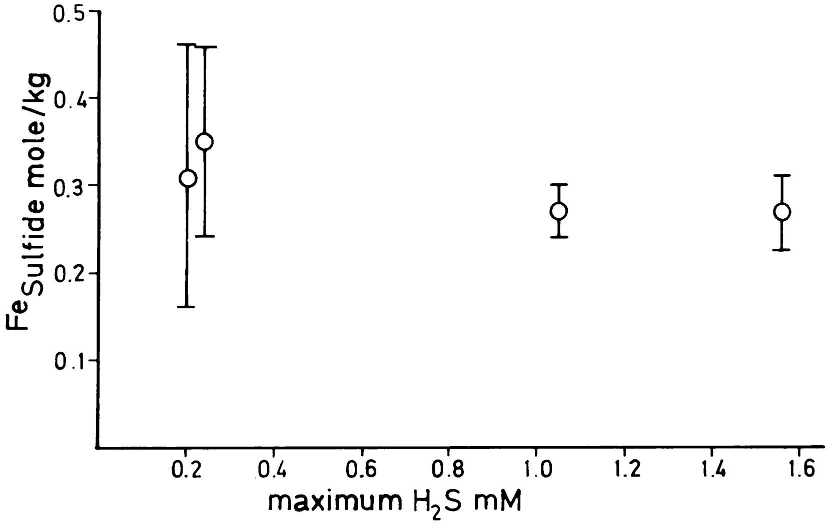

Fig. 9. The relation between the amount of sulfidized iron in the sediments and maximum H_2S concentration in the pore waters for anoxic basins of the Baltic. The two data points at the right side are from the Bornholm deep, and the two data points at the left side are from the Gotland deep. Error bars reflect standard deviation.

Bornholm deep (DOS = 0.20–0.45, core Ø12, fig. 3) but in the same range as the marginal core Ø7a (fig. 3). Apparently there is no significant difference in DOS between these two environments. For comparison the Black Sea sediments yield DOP values in the range 0.1 to 0.5 (Raiswell and Berner, 1985) which is comparable to the Baltic but also quite similar to what is found in normal marine environments (Berner, 1970; Jørgensen, 1978. This makes us speculate on the significance of DOS/DOP values and more specifically on HCl-extractable iron as a measure for reactive iron. It appears that, in recent sediments, DOS/DOP values higher than about 0.6 are only reported from swamp sediments, where values up to 0.95 are found (Postma, 1982). Typical for this environment is the near absence of clays and other fine-grained terrigeneous material. Berner (1970) reported that iron released by hot HCl treatment reflects maximum possible reactivity toward H_2S. However, HCl-treatment releases large amounts of iron from silicates (Petersen, 1976) while H_2S, at least in short term experiments, extracts very little iron from silicates (Drosdoff and Troug, 1935). Although silicate-iron may be released during later diagenesis (Curtis, 1967; Drever, 1971), this process appears to be of minor importance in recent sediments. Different DOS/DOP values in recent sediments may therefore reflect more the content of fine-grained non-reacting Fe-bearing silicate than the amount of iron available for iron sulfide formation, probably mainly iron oxides. This would explain why present-day euxinic environments do not yield higher DOS/DOP values than normal marine environments.

In ancient sediments, euxinic environments display much higher DOP values than normal marine sediments (Raiswell and Berner, 1985; Raiswell, Buckley, and Berner, 1987). A possible explanation for the difference in DOP behavior between ancient and recent sediments could be that slowly released silicate-iron is the main iron source for later diagenetic pyrite formation, while the high organic content of such sediments ensures continuing reducing conditions.

C/S ratios and sedimentary environment.—Recently, interest has arisen for distinguishing euxinic from normal marine environments in the fossil sedimentary record by means of C/S ratios (Levanthal, 1983; Berner and Raiswell, 1983; Berner, 1984; Raiswell and Berner, 1985). Normal marine environments are recognized by correlating organic carbon and sulfur contents with a molar ratio of 7.5 ± 4.0 (Berner and Raiswell, 1983). In contrast euxinic environments, using the Black Sea as a recent example, show much higher C/S ratios.

The C/S correlation in normal marine sediments has a dynamic origin. H_2S is produced by bacterial sulfate reduction and may precipitate as iron sulfide, However, the amount of sulfide that ends up as iron sulfide is only a fraction, 5 to 30 percent (Jørgensen, 1977; Berner and Westrich, 1985) of the total production of H_2S. Organic carbon will be consumed by sulfate reduction and also by aerobic degradation. Jørgensen (1977) found for Limfjorden that only 12 percent of the organic carbon produced in the overlying water did accumulate in the sediment. Thus a C/S plot represents the relation between the small remainders of the original pools of sulfide and organic carbon. According to Berner (1984) the origin of the constant C/S ratio in normal marine sediments is that constant fractions of organic carbon and produced H_2S are preserved in the sediment. An implicit assumption here is that abundant reactive iron and sulfate are available so that the amount of iron sulfide is controlled by the input of reactive organic matter.

In euxinic environments such as the Black Sea and Gotland deep, bottom waters contain H_2S. This means that iron sulfide formation may already start in the water column. Furthermore, advection of H_2S-containing waters may result in high pyrite/low organic carbon sediments. These factors are the reason why C/S values from euxinic environments deviate from the normal marine C/S ratio and can be used to identify fossil euxinic environments (Levanthal, 1983; Berner, 1984; Raiswell and Berner, 1985).

Figure 10 shows C/S distributions in the sediments of the Bornholm and Gotland deeps. Also outlined in figure 10 are the ranges of C/S ratios in normal marine and Black Sea sediments. Note that the Bornholm and the Gotland deeps behave differently with respect to their C/S ratios. Compared to the Black Sea both C and S values are high in the Gotland deep while low C/S ratios are not obvious (fig. 10).

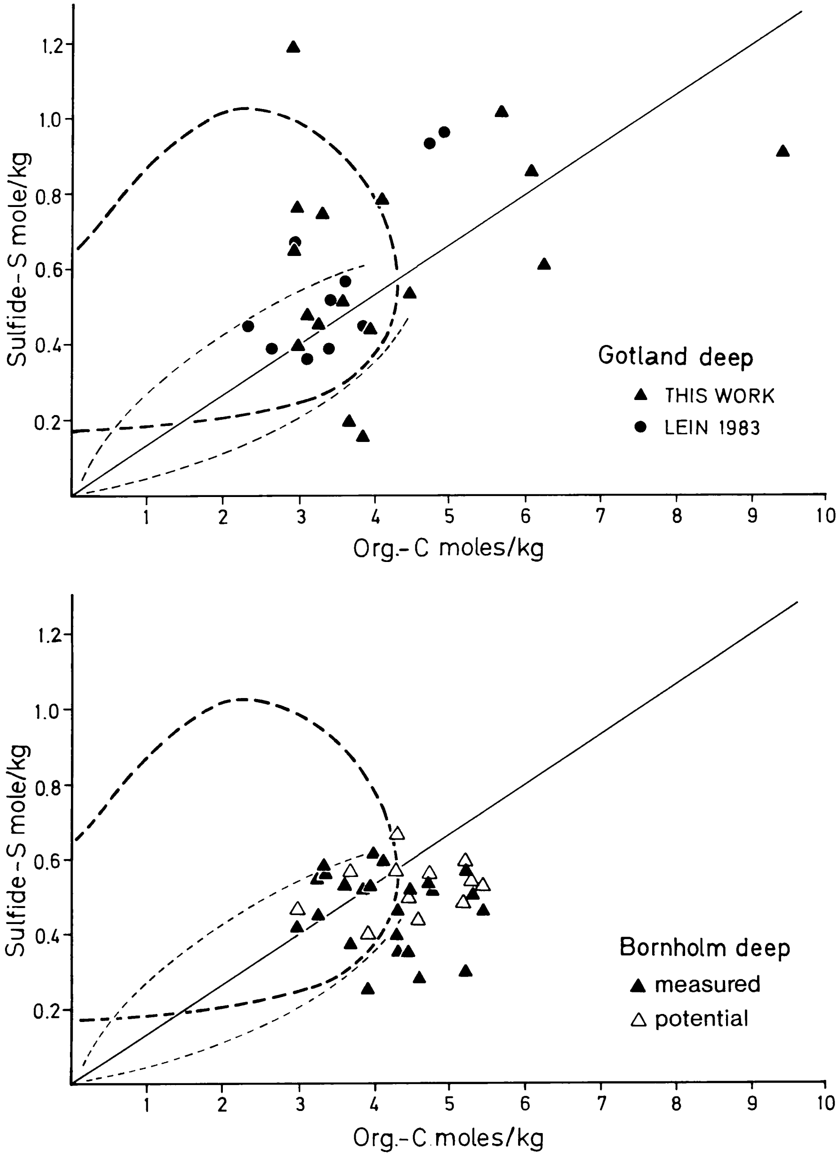

Fig. 10. Relation between sulfide-S and organic carbon in sediments of the Gotland deep (upper part) and Bornholm deep (lower part). Also indicated is the range of normal marine C/S ratios, straight line and light dotted, and the Black Sea C/S range, heavy dotted (after Berner and Raiswell, 1983). Only data from marine muds are included. The potential C/S values in the Bornholm deep reflect the values obtained when all FeS present is recalculated to FeS_2.

The considerable scatter of C/S data in the Gotland deep sediments is in good agreement with the decoupling of organic carbon accumulation and iron sulfide formation in euxinic environments. A separation into syngenetic and diagenetic iron sulfide, such as proposed by Raiswell and Berner (1985), is not obvious for the Gotland deep data (fig. 10). Perhaps data that scatter away from the normal marine C/S ratio could be a more typical aspect of euxinic environments. In any case it would be quite difficult to recognize a fossil equivalent of the Gotland deep sediment from C/S data alone. Supportive evidence from sedimentary structures such as lamination and lack of burrowing activity would be advisable. In the Bornholm deep (fig. 10), C/S ratios are less variable, showing values ranging from normal marine toward higher C/S ratios. Some of these sediments (fig. 2) contain large amounts of FeS, due to sulfate exhaustion in the pore water, which results in high C/S ratios. If the FeS-S content is recalculated to FeS_2-S, the potential C/S ratio which should be attained during further diagenesis can be plotted. These potential C/S values are also shown in figure 10 and fit nicely at the upper end of the normal marine egg as expected for an organic carbon control on the sulfur content. However, this potential sulfur content is equivalent to the sulfide-bound iron content. Since reactive iron controls the content of sulfide-bound iron, the agreement with the normal marine C/S ratio is not due to organic carbon control on iron sulfide formation but rather to a coupling of organic carbon and iron sedimentation (Berner, 1984). Raiswell and Berner (1985) suggest that the latter case should result in DOP/DOS values independent of the organic carbon content. However, our DOS/organic carbon data do not carry this out, probably due to larger variations of DOS compared to variations in organic carbon. Generally the Bornholm deep example illustrates that the origin of C/S ratios is complex and requires a very careful interpretation.

Sulfidization at the marine-freshwater interface.—Both the Baltic and the Black Sea have changed between freshwater and marine conditions in recent geological history (Ignatius and others, 1981; Ross, Stoffers, and Trimonis, 1978). This appears to be a logical consequence of their restricted character, necessary to maintain stratification in brackish/marine stages, but which, due to eustatic fluctuations, may result easily in occasional freshwater periods.

In the context of iron sulfide formation, the change from marine to freshwater conditions has as its most important consequence the shift from a high to a low sulfate environment. In the Baltic there was an additional change from organic-poor freshwater sedimentation to organic-rich marine/brackish sedimentation (fig. 8). As described in an earlier section, both the distribution of iron sulfide in the sediment (fig. 5) as well as the pore water chemistry (fig. 7) suggest that downward diffusion of dissolved sulfide causes progressive sulfidization of the underlying freshwater clays.

This type of situation, where organic-rich sediments are superimposed on organic-poor sediments, has been treated both theoretically and experimentally by Berner (1969). Depending on the amount of reactive iron available in the organic-rich layer, three cases were identified (fig. 11): In the low iron situation, H_2S production rapidly exceeds available iron, resulting in downward H_2S diffusion and iron sulfide precipitation in the top of the organic-poor layer. In the high iron case (fig. 11), available iron exceeds H_2S production, so that only dissolved organic matter diffuses downward. This causes the reduction of iron oxides in the organic-poor layer, and the upward flux of Fe^{2+} will give rise to an iron-sulfide enriched layer near the interface. The third case is the intermediate one, where distinct iron sulfide bands are precipitated, which resembles Liesegang banding.

Comparison of these ideal cases with the data from the Gotland deep gives some problems. Berner (1969) arbitrarily defined the high iron case as where the original iron concentration, which is able to react with H_2S, is greater than ten times the initial molar concentration of sulfate and organic-S available for sulfide formation. In the marine muds of the Gotland deep, this ratio was estimated to be 13, using actually sulfidized iron as measure for the reactive iron content. Accordingly it belongs to the high iron case. However, no accumulation of iron sulfide at the marine/freshwater interface is observed (fig. 5). Actually both the content of iron sulfide in the upper freshwater clay (fig. 5) and the downward diffusion of H_2S (fig. 7) are in better agreement with the low iron case. Thus the criteria for identification of the low and high iron cases need to be revised.

Furthermore, pore water profiles (fig. 7) seem at first hand to be in better agreement with the intermediate case (fig. 11). However, in order to produce a distinct iron sulfide band, the upward Fe^{2+}-flux ($J_{s[Fe^{2+}]}$)

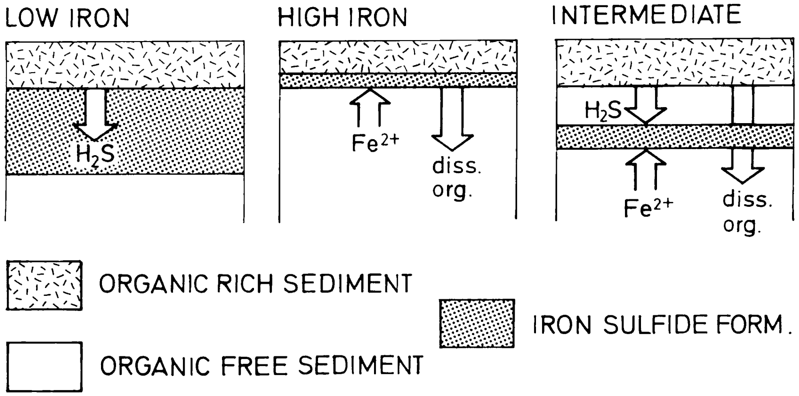

Fig. 11. Models for iron sulfide formation at the interface between high organic matter sediments and low organic matter sediments (after Berner, 1969).

should more or less balance the downward H_2S-flux ($J_{s[HS^-]}$; HS^- is the dominant diffusing species at seawater pH) that is;

$$J_{s[Fe^{2+}]} \simeq -J_{s[HS^-]}$$

Application of Fick's first law of diffusion yields

$$-D_{s[HS^-]}\,\Phi\,\frac{d[HS^-]}{dx} \simeq D_{s[Fe^{2+}]}\,\Phi\,\frac{d[Fe^{2+}]}{dx}$$

Where Φ is porosity and $D_{s[HS^-]}$ and $D_{s[Fe^{2+}]}$ are whole sediment diffusion coefficients. For tracer diffusion coefficients, Li and Gregory (1974) report that $D_{o[HS^-]} \simeq 3D_{o[Fe^{2+}]}$. Assuming the same ratio for whole sediment diffusion coefficients and from the concentration gradients for HS^- and Fe^{2+} (fig. 7), it was calculated that the diffusive flux of HS^- is about 30 times that of Fe^{2+}. Thus the Fe^{2+} flux is by far subordinate to the downward HS^- flux, and since the iron sulfide front is sharp (fig. 5), it means that virtually all iron is sulfidized *in situ* by reactions between dissolved sulfide and iron oxides in the sediment. Our conclusion is therefore that the situation at the interface between freshwater and marine sediments is best described by Berner's (1969) low-iron model.

Here, the downward migration of the iron-sulfide front can be described by the mass balance expression;

$$\frac{dX}{dt} = \frac{-\Phi D_{s[HS^-]}(\partial[HS^-]/\partial x)_{x-X}}{fL} \qquad (1)$$

where

X = position of the iron sulfide front (cm) below the marine/freshwater interface
t = time (sec)
Φ = porosity
$D_{s[HS^-]}$ = whole sediment diffusion coefficient (cm^2/sec)
f = concentration of solid reactive iron in the sediment ($\mu mole/cm^3$)
L = number of moles sulfide that react with one mole iron to form iron sulfide

Substitution of Fick's 2nd law and solving yields (Berner, 1969):

$$X = \left[\frac{4\Phi[HS^-]_o D_{s[HS^-]}t}{\sqrt{\pi}fL + \Phi[Hs^-]_o}\right]^{1/2} \qquad (2)$$

Where $[HS^-]_o$ is the concentration at the marine/freshwater interface. This solution is valid if the term $X/2\sqrt{D_{s[HS]}t}$ is constant and less than 0.5. In the Baltic this term equals ~0.02. Schematically, the model is illustrated in figure 12.

Several input parameters are required. First time (t) reflects the start of marine sedimentation 7700 yrs ago (Bloomquist, ms). Measured

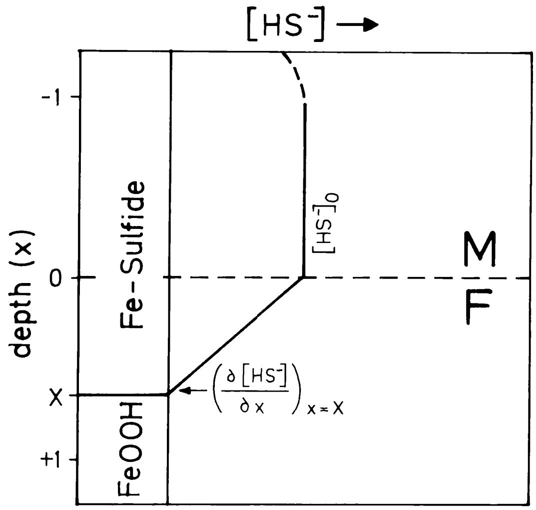

Fig. 12. Schematic outline of the low iron model for diffusion of HS^- and iron sulfide formation at the interface between high organic marine sediments (M) and low organic freshwater sediments (F).

porosities (Φ) range from 0.69 to 0.76. Since porosity must have been larger in the past, a constant value of 0.8 is used in the calculations. The value of $[HS^-]_o$ was estimated as the average of the three highest values in the marine mud and is assumed constant through time. Goldhaber and Kaplan (1975) have shown that maximum concentrations of dissolved sulfide can be correlated with the sedimentation rate. Since the maximum dissolved sulfide concentrations in the Gotland deep are found in the lower part of the marine mud (fig. 7 and table 2), the reasonable assumption of a constant sedimentation rate should result in more or less constant values for $[HS^-]_o$ through time.

$D_{s[HS^-]}$ at 5°C and $\Phi = 0.8$ can be calculated from $D_{o[HS^-]}$ values of Li and Gregory (1974) using the empirical relations of Lerman (1979) and Berner (1980) and yield a value of $6.9 \pm 0.3 \cdot 10^{-6}$ cm^2/sec. An alternative estimate of $7.2 \cdot 10^{-6}$ cm^2/sec was obtained from the assumption that $D_{o[HS^-]}/D_{o[Cl^-]} \simeq D_{s[HS^-]}/D_{s[Cl^-]}$ using data of Li and Gregory (1974). An average of $D_{s[HS^-]} = 7.05 \cdot 10^{-6}$ cm^2/sec was used in the model. Effects of ion-pairing on D_s (Lasaga, 1979) can be neglected.

The concentration of reactive iron (f) was obtained from the mean concentration of sulfide-iron in the upper layers of the freshwater clay (fig. 5 and table 1). Finally, L indicates the number of moles of dissolved sulfide that react with one mole iron to form iron sulfide. Here, the final product is pyrite, albeit through an intermediate FeS phase. For the reaction between H_2S and FeOOH to form pyrite, one obtains a value of L equal to 2.

Since the model describes the amount of dissolved sulfide that diffuses downward, the presence of FeS (fig. 5) introduces a problem in estimating a measured value for the depth of the iron sulfide front (X) below the interface. This was solved by adjusting the total depth of the iron sulfide front to the level where the amount of FeS-S below equals the amount of sulfur necessary to convert FeS above this level to FeS_2.

The results are shown in table 3 and show very good agreement between measured and calculated values for the iron sulfide front. The results are not affected significantly by small variations in values of Φ, t, $D_{s[HS^-]}$, f, and L, although different $[HS^-]_o$ estimates could introduce larger errors. Generally, our conclusion is therefore that Berner's (1969) low-iron model quantitatively describes the ongoing sulfidization of the freshwater clay below the marine mud. Berner (1969) tested his model in short term (~0.5 yr) experiments where the migration of the iron sulfide front was followed visually. The fact that the model can be applied both to short time experiments as well as to our 7700 yr old situation in the Gotland deep is particularly encouraging. Note also that the application of the low iron model is in agreement with our earlier conclusion, that reactive iron is the limiting factor for pyrite formation in the marine mud.

Running the model forward in time, we may predict (eq 2) decreasing migration rates for the iron sulfide front. Therefore, although the first half meter was pyritized within 10,000 yrs, pyritization of the whole sequence of up to 4 m freshwater clay (Kögler and Larsen, 1979) would take more than 1 my. Actually, decreasing values of $[HS^-]_o$ and Φ would slow the migration of the iron sulfide front even more.

Finally, if the Baltic in the future changes back to freshwater conditions, sulfate would become rapidly depleted, and sulfide production would cease. In that case, it is likely that the black FeS-band at the iron sulfide front (fig. 5) would become preserved in the sediment. Such preserved black bands have been found in a similar setting in the Black Sea by Berner (1974).

TABLE 3

Measured and calculated values for the iron sulfide front advancement in the freshwater clay of the Gotland deep. For explanation, see text

Core	$[HS^-]_o$ $\mu mol/cm^3$	$f \pm \sigma$ $\mu mol/cm^3$	X calc. cm	X meas. cm
Ø30	0.217	182 ± 78	42	44 ± 3
Ø31	0.196	166 ± 33	43	43 ± 5

CONCLUSION

The results of this study demonstrate that pyrite formation in anoxic environments of the Baltic may vary considerably, depending on factors such as sedimentation rate, the presence or absence of H_2S in the bottom waters, and salinity.

In the Bornholm deep, high sedimentation rates combined with low O_2, but H_2S free bottom waters, result in the accumulation of high contents of iron monosulfides and near normal marine C/S ratios. Reactive iron limits the amount of sulfide-bound iron, while sulfate availability controls the FeS/FeS_2 ratio.

In the Gotland deep, with lower sedimentation rates and H_2S-containing bottom waters, little iron monosulfide accumulates. Reactive iron limits here iron sulfide formation. Due to decoupling of organic matter accumulation and iron sulfide formation, large variations in C/S ratios are displayed. The freshwater muds underlying the marine muds are presently sulfidized by downward H_2S diffusion.

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REFERENCES

Berner, R. A., 1964, Iron sulfides formed from aqueous solution at low temperatures and atmospheric pressure: Jour. Geology, v. 72, p. 293–306.

——— 1967, Thermodynamic stability of sedimentary iron sulfides: Am Jour. Sci., v. 265, p. 773–785.

——— 1969, Migration of iron and sulfur within anaerobic sediments during early diagenesis: Am. Jour. Sci., v. 267, p. 19–42.

——— 1970, Sedimentary pyrite formation: Am. Jour. Sci., v. 268, p. 1–23.

——— 1974, Iron sulfides in pleistocene deep Black Sea sediments and their paleooceanographic significance, *in* Degens, E. T., and Ross, D. A., eds., The Black Sea-geology, chemistry, and biology: Am. Assoc. Petroleum Geologists Mem. 20, p. 524–531.

——— 1980, Early diagenesis; a theoretical approach: Princeton, N.J., Princeton Univ. Press, 241 p.

——— 1984, Sedimentary pyrite formation; an update: Geochim. et Cosmochim. Acta, v. 48, p. 605–615.

Berner, R. A., Baldwin, T., and Holdren, G. R., Jr., 1979, Authigenic iron sulfides as paleosalinity indicators: Jour. Sed. Pet., v. 49, p. 1345-1350.

Berner, R. A., and Raiswell, R., 1983, Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: A new theory: Geochim. et Cosmochim. Acta, v. 47, p. 855–862.

Berner, R. A., and Westrich, J. T., 1985, Bioturbation and the early diagenesis of carbon and sulfur: Am. Jour. Sci., v. 285, p. 193–206.

Bloomquist, R. G., ms, 1977, Chemical characteristics of interstitial water from the Southern Baltic Sea: Ph.D. thesis, Univ. Stockholm, 111 p.

Boesen, C., ms, 1985, Tidlig diagenese af svovl og jern i Østersøens muddersedimenter: M.S. thesis, Univ. Copenhagen, 136 p.

Cline, J. D., 1969, Spectrophotometric determination of hydrogen sulfide in natural waters: Limnology Oceanography, v. 14, p. 454–458.

Curtis, D. D., 1967, Diagenetic iron minerals in some British Carboniferous sediments: Geochim. et Cosmochim. Acta, v. 31, p. 2109–2123.

Debyser, J., 1961, Contribution a l'etude geochimique des vases marines: Inst. Francais du Petrole, 249 p.

Demaison, G. J., and Moore, G. T., 1980, Anoxic environments and oil source bed genesis: Am. Assoc. Petroleum Geologists Bull., v. 64, p. 1179–1209.

Drever, J. I., 1971, Magnesium-iron replacement in clay minerals in anoxic marine sediments: Science, v. 172, p. 1334–1336.

Drosdoff, M., and Troug, E., 1935, A method for removing and determining the free iron oxide in soil colloids: Am. Soc. Agronomy Jour., v. 27, p. 312–317.

Emelyanov, E. M., Pilipchuk, M. F., Volostnykh, B. V., Khandros, G. S., and Shaidurov, Y. O., 1982, Fe and Mn forms in sediments in the geochemical profile of the Baltic Sea: Baltica, v. 7, p. 153–171.

Filipek, L. H., and Owen, R. M., 1980, Early diagenesis of organic carbon and sulfur in outer shelf sediments from the Gulf of Mexico: Am. Jour. Sci., v. 280, p. 1097–1112.

Fonselius, S. H., 1986, On long-term variations of dissolved oxygen in the deep water of the Baltic Sea: Baltic Monitoring Symposium, Tallin, 1986, Proc.

Goldhaber, M. B., and Kaplan, I. R., 1974, The sulfur cycle, *in* Goldberg, E. D., ed., The sea, v. 5, Marine Chemistry: New York, John Wiley & Sons, p. 569–655.

——— 1975, Controls and consequences of sulfate reduction rates in recent marine sediments: Soil Sci., v. 119, p. 42–55.

Goldhaber, M. B., Aller, R. C., Cochran, J. K., Rosenfeld, J. K., Martens, C. S., and Berner, R. A., 1977, Sulfate reduction, diffusion, and bioturbation in Long Island Sound sediments: report of the FOAM group: Am. Jour Sci., v. 277, p. 193–237.

Grasshoff, K., 1975, The hydrochemistry of landlocked basins and fjords, *in* Riley, J. P., and Skirrow, G., eds., Chemical Oceanography: London, Academic Press, p. 455–597.

——— 1976, Methods of Seawater Analysis: Weinberg, Verlag Chemie, 317 p.

Hallberg, R. O., 1974, Paleoredox conditions in the eastern Gotland Basin during the recent centuries: Merentutkimuslait. Julk., v. 238, p. 3–16.

Hartmann, M., 1964, Zür Geochemie von Mangan und Eisen in der Ostsee: Meyniana, v. 14, p. 3–20.

Hirst, D. M., 1974, Geochemistry of sediments from eleven Black Sea cores, *in* Degens, E. T., and Ross, D. A., eds., The Black Sea-geology, chemistry, and biology: Am. Assoc. Petroleum Geologists Mem. 20, p. 430–455.

Howarth, R. W., 1978, A rapid and precise method for determining sulfate in seawater, estuarine waters, and sediment pore waters: Limnology Oceanography, v. 23, p. 1066–1069.

——— 1979, Pyrite: its rapid formation in a salt marsh and its importance in ecosystem metabolism: Science, v. 203, p. 49–51.

——— 1984, The ecological significance of sulfur in the energy dynamics of salt marsh and coastal marine sediments: Biogeochemistry, v. 1, p. 5–27.

Howarth, R. W., and Giblin, A., 1983, Sulfate reduction in the salt marshes of Sapelo Island, Georgia: Limnology Oceanography, v. 28, p. 70–82.

Howarth, R. W., and Jørgensen, B. B., 1984, Formation of ^{35}S-labelled elemental sulfur and pyrite in coastal marine sediments (Limfjorden and Kysing Fjord, Denmark) during short-term $^{35}SO_4^{2-}$ reduction measurements: Geochim. et Cosmochim. Acta, v. 48, p. 1807–1818.

Howarth, R. W., and Merkel, S., 1984, Pyrite formation and measurement of sulfate reduction in salt marsh sediments: Limnology Oceanography, v. 29, p. 598–608.

Ignatius, H., Axberg, S., Niemistö, L., and Winterhalter, B., 1981, Quaternary geology of the Baltic Sea, *in* Voipio, A., ed., The Baltic Sea: Amsterdam, Elsevier, p. 54–121.

Jørgensen, B. B., 1977, The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark): Limnology Oceanography, v. 22, p. 814–832.

——— 1978, A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. III. Estimation from chemical and bacteriological field data: Geomicrobiology Jour., v. 1, p. 49–64.

——— 1982, The microbial sulphur cycle, *in* Krumbein, W. E., ed., Microbial Geochemistry: Oxford, Blackwell, p. 91–124.

Kaplan, I. R., Emery, K. O., and Rittenberg, S. C., 1963, The distribution and isotopic abundance of sulphur in recent marine sediments off Southern California: Geochim. et Cosmochim. Acta, v. 27, p. 297–331.

Kögler, F. C., and Larsen, B., 1979, The West Bornholm basin in the Baltic Sea: geological structure and quaternary sediments: Boreas, v. 8, p. 1–22.

Kullenberg, G., 1981, Physical Oceanography, *in* Voipio, A., ed., The Baltic Sea: Amsterdam, Elsevier, p. 135–181.

Larsen, B., 1979, Forsøg på bestemmelse af akkumulations-raten af spormetaller og næringssalte i marine sedimentationsområder: Nordiska Symposium om Vattenforskning, 5th, Proc., p. 285–295.

Lasaga, A. C., 1979, The treatment of multi-component diffusion and ion pairs in diagenetic fluxes: Am. Jour. Sci., v. 279, p. 324–346.

Lein, A. Y., 1983, Biogeochemistry of the anaerobic diagenesis of recent Baltic Sea sediments, *in* Hallberg, R., ed., Environmental Biogeochemistry: Stockholm, Ecolog. Bull., v. 35, p. 441–461.

Lerman, A., 1979, Geochemical Processes: Water and Sediment Environments: New York, John Wiley & Sons, 481 p.

Leventhal, J. S., 1983, An interpretation of carbon and sulphur relationships in Black Sea sediments as indicators of environments of deposition: Geochim. et Cosmochim. Acta, v. 47, p. 133–138.

Li, Y. H., and Gregory, S., 1974, Diffusion of ions in sea water and in deep-sea sediments: Geochim. et Cosmochim. Acta, v. 28, p. 703–714.

Manheim, F. T., 1961, A geochemical profile in the Baltic Sea: Geochim. et Cosmochim. Acta, v. 25, p. 52–70.

——————1982, Geochemistry of manganese carbonates in the Baltic Sea: Stockholm Contr. Geology, v. 37, p. 145–159.

Niemistö, L., and Voipio, A., 1974, Studies on the recent sediments in the Gotland deep: Merentutkimuslait. Julk, v. 238, p. 17–32.

Papunen, H., 1968, On the sulfides in the sediments of the Bothnian Sea: Geol. Soc. Finland Bull, v. 40, p. 51–57.

Petersen, L., ms, 1976, Podzols and Podzolization: Doctoral thesis, Kgl. Vet. Landbohøjsk., Copenhagen, 293 p.

Pheiffer Madsen, P., 1985, Sediment accumulation rates in the Baltic Sea: Danish Isotope Centre, rept., 41 p.

Plummer, L. N., Jones, B. F., and Truesdell, A. H., 1976, WATEQF-A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters: U. S. Geol. Survey Water Resources Inv., Rept. 76-13, 71 p.

Postma, D., 1981, Formation of siderite and vivianite and the pore-water composition of a recent bog sediment in Denmark: Chem. Geology, v. 31, p. 225–244.

—————— 1982, Pyrite and siderite formation in brackish and freshwater swamp sediments: Am. Jour. Sci., v. 282, p. 1151–1183.

Pyzik, A. J., and Sommer, S. E., 1981, Sedimentary iron monosulfides: kinetics and mechanism of formation: Geochim. et Cosmochim. Acta, v. 45, p. 687–698.

Raiswell, R., and Berner, R. A., 1985, Pyrite formation in euxinic and semi-euxinic sediments: Am. Jour. Sci., v. 285, p. 710–724.

Raiswell, R., Buckley, F., and Berner, R. A., 1987, Degree of pyritisation of iron as a paleoenvironmental indicator of bottom water oxygenation: submitted to Jour. Sed. Pet.

Rhoads, D. C., and Morse, J.W., 1971, Evolutionary and ecological significance of oxygen deficient marine basins: Lethaia, v. 4, p. 413–428.

Rickard, D. T., 1974, Kinetics and mechanism of the sulfidation of geothite: Am. Jour. Sci., v. 274, p. 941–952.

—————— 1975, Kinetics and mechanism of pyrite formation at low temperatures: Am. Jour. Sci., v. 275, p. 636–652.

Roberts, W. M. B., Walker, A. L., and Buchanan, A. S., 1969, The chemistry of pyrite formation in aqueous solution and its relation to the depositional environment: Mineralog. Deposita, v. 4, p. 18–29.

Ross, D. A., Stoffers, P., and Trimonis, E. S., 1978, Black Sea sedimentary framework: Deep Sea Drilling Proj. Initial Rept., v. 42, p. 359–372.

Rozanov, A. G., Volkov, I. I., and Yagodinskaya, T. A., 1974, Forms of iron in surface layer of Black Sea sediments, *in* Degens, E. T., and Ross, D. A., eds., The Black Sea-geology, chemistry, and biology: Am Assoc. Petroleum Geologists Mem. 20, p. 532–541.

Stookey, L. L., 1976, Ferrozine a new spectrophotometric reagent for iron: Anal. Chemistry, v. 42, p. 779–781.

Suess, E., ms, 1976, Porenlösungen mariner Sedimente-ihre chemische Zusammensetzung als Ausdrück frühdiagenetischer vorgänge: Doctoral thesis, Kiel Univ., 193 p.

———— 1979, Mineral phases formed in anoxic sediments by microbial decomposition of organic matter: Geochim. et Cosmochim. Acta, v. 43, p. 339–352.

Sweeney, R. E., and Kaplan, I. R., 1973, Pyrite framboid formation: laboratory synthesis and marine sediments: Econ. Geology, v. 68, p. 618–634.

Troelsen, H., and Jørgensen, B. B., 1982, Seasonal dynamics of elemental sulfur in two coastal sediments: Estuarine Coastal Shelf Sci., v. 15, p. 255–266.

Zhabina, N. N., and Volkov, I. I., 1978, A method of determination of various sulfur compounds in sea sediments and rocks, *in* Krumbein, W., ed., Environmental Biogeochemistry and Geomicrobiology, v. 3, Methods, Metals and Assessment: Ann Arbor, Ann Arbor Science Pub., p. 735–746.

Zsolnay, A., 1971, Diagenesis as a function of redox conditions in nature: a comparative survey of certain organic and inorganic compounds in an oxic and anoxic Baltic basin: Kieler Meeresforschungen, v. 27, p. 135–165.