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IRON IN THE BALTIC SEA CLAY SEDIMENTS

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Abstract. This paper presents the results of investigations of two samples derived from the recent Baltic sediments. The methods used were: Mössbauer spectroscopy, IR absorption spectroscopy, EPR spectroscopy, X-ray deffractometry, chemical analysis and sedimentation analysis of grain-size distribution. Conclusions were drawn regarding iron minerals occurring in the sediments of the brackish basin as related to the assemblage of clay minerals. The processes of sedimentation and early diagenesis in the sediments were discussed.

INTRODUCTION

Clay sediments of the Vistula estuary and the Gdańsk Basin were the object of mineralogical and sedimentological studies carried out by the present authors.

The investigated area comprised the Gdańsk Bay and Gdańsk Deep, which constitute a morphologically distinctive part of the South Baltic. The maximum depth of the sea in the centre of the Gdańsk Deep is 117 m below sea lovel. The Gdańsk Bay and Deep, bearing a common name of the Gdańsk Basin, have been a depositional site for mud and clay sediments since the Pleistocene. The source of the sediment is the suspension supplied by the Vistula and the abrasion processes active along the seashores and in some parts of the basin bottom.

Sedimentation in the Gdańsk Basin is controlled by thermohalic conditions in the sea water — first of all, by the fact that the water mass consists of two layers. The lower layer of a salinity about 11‰ is separated by a transition mixing layer from the upper layer of a salinity about 7‰. This arrangement, together with the system of surface (drift and gradient)

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currents determines the distribution of the Vistula waters, and therefore also of the suspension, in the area of the Gdańsk Basin.

During the investigations of the mineralogy of these young deposits, several questions emerged, connected with the occurrence of iron in the sediment. It was particularly important to:

— analyse the process by which iron introduced to the Baltic by the Vistula in the form of suspension (0.21—1.10 mg Fe/dm³) and ionic solution (0.014—0.049 mg Fe/dm³) was sized by the sediment when only 0.015—0.141 mg Fe/dm³ of total iron was found in the sea water at the mouth of the Vistula (acc. to Zimna 1974);

— state whether this process was cyclic and controlled by the rhythm of the North Sea water advection and the resulting periods of stagnation;

— determine the forms of iron occurrences in the deposits with particular emphasis on their position in the structure of clay minerals;

— study the behaviour of iron in the early diagenetic processes and determine the equilibrium phases for the given physico-chemical conditions with special emphasis on sulphides, hydroxides and carbonates.

Any attempts to determine the Fe^{3+}/Fe^{2+} ratio and define the structural position of iron in the constituents of polymineral estuary deposits by conventional methods either presented considerable experimental difficulties or were a failure. Therefore, to solve these problems, it was imperative to use both the classical methods and new spectroscopic techniques (Mössbauer and EPR spectroscopy).

EXPERIMENTAL AND RESULTS

Characteristics of the material studied

Samples were derived from a 10 m core taken with a gravity probe at a depth of 100 m below sea level in the western part of the Gdańsk Deep. Two samples were subjected to analysis: *sample A* from the level —2.5 m

Table 1

Grain-size distribution for sample A determined by sedimentation method

$D(\mu m)$	Weight %	$D(\mu m)$	Weight %
<60	96.3	<10	80.1
<45	95.0	< 6	71.8
<25	90.3	< 3	62.0
<15	85.1	< 2	57.3

and *sample B* from —5.0 m below the sediment surface, corresponding to the Postlitorina and Litorina periods in the cycle of Baltic sedimentation. The samples were selected so as to represent the stratigraphically distinctive beds of the deposits formed in the continuous cycle of marine sedimentation. These beds arose in environments differing in their physico-chemical parameters such as salinity, temperature, Eh, pH, etc.

The sediment studied is an unconsolidated clay of the gyttja type. It is strongly saturated with water (about 70%) and contains up to 5% of organic matter. The grain-size distribution of sample A is given in Table 1. Viewed in the scanning microscope, the sediment appears to consist of concentrations of quartz grains and aggregates of clay minerals. The latter rarely occur in the form of face-to-face aggregates, usually forming unoriented face-to-edge associations. The plates of clay minerals exhibit an irregular habit, and their grains average 1—2 µm in size. They are not cemented with amorphous material.

Mineralogical composition

Under the polarizing microscope, in transmitted light, both samples were found to contain quartz grains embedded in the groundmass consisting of clay minerals with predominant illite. Also visible are larger flakes of detrital muscovite, glauconite and feldspar grains, as well as gypsum needles which crystallized during the preparation of sample. To determine the assemblage of clay minerals, fractions < 2 µm were subjected to X-ray diffraction analysis in a DRON-1.5 diffractometer, using filtered Cu-K_α radiation. X-ray diffraction patterns revealed the presence of illite, chlorite and minor amounts of kaolinite, swelling minerals of the smectite group, vermiculite and random mixed-layer structures (Figs. 1, 2).
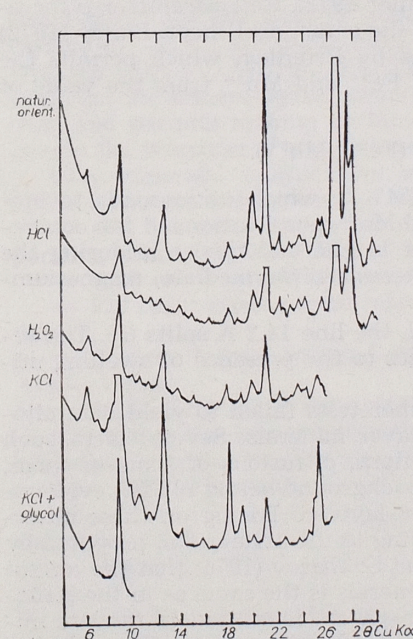

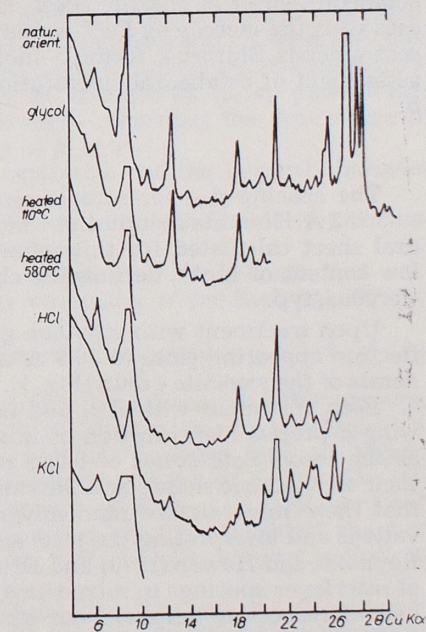Fig. 1. X-ray diffraction patterns of sample A

Fig. 2. X-ray diffraction patterns of sample B

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The diffractograms were also analysed from the point of view of iron substitution in the crystal lattice of clay minerals.

The illite reflection 9.9 Å is slightly displaced towards lower angles due to the presence of mixed-layer illite/smectites. The position of the 060 line of illite (1.503 Å) suggests that its parameter $b = 9.02$ Å. According to Maxwell and Hower (1967), such position of the 060 reflection should correspond to a content of Fe^{2+} and Mg^{2+} cations of 0.2—0.25 per half the unit cell.

Besides the line 1.503 Å, a less pronounced line 1.528—1.530 Å ($b = 9.18$ Å) appears in X-ray diffraction patterns. It corresponds presumably to the 060 reflection of glauconite, for which the b parameter is 9.13—9.19 Å (Weaver, Wampler, Pecuil 1967).

Chlorite yields sharp diffraction lines 14.2, 7.1, 4.72 Å. The reflection 14.2 Å remains sharp after 3 h heating at 580°C while the reflection 7.1 Å decreases in intensity upon such treatment. These three lines disappear upon hot treatment of the sample with 1 : 1 HCl for 4 h (Figs. 1, 2). This evidences that the structure of chlorite is fine-grained and defective, and that there is extensive substitution of Fe^{2+} for Mg^{2+}. In the sample heated at about 120°C the reflection 14.2 Å is not perceptibly displaced towards lower d_{hkl} values. However, upon treatment with potassium, it is partly shifted to 10.0 Å. Appropriate tests (Figs. 1, 2) have shown that the sediment in question contains not only chlorite but small amounts of kaolinite and vermiculite as well.

It is possible to investigate by X-ray methods Fe^{2+} substitution in the octahedral sheet of chlorite (Post, Plummer 1972). Cell parameter b increases with the increasing Fe^{2+} content in the octahedral sheet. Bailey (1972) recommends Shirozu's formula modified by Brindley, which permits the assessment of octahedral substitution of Fe^{2+} and Mn^{2+} from the value of b:

$$b = 9.21 \text{ Å} + 0.037 \ (Fe^{2+}, Mn^{2+}).$$

The spacing d_{060} for sample A is 1.547 Å, which corresponds to $b = 9.282$ Å. The total content of Fe^{2+} and Mn^{2+} per 6 cations of the octahedral sheet calculated for this parameter is 1.95 and this, considering the low content of Mn^{2+}, defines the chlorite as an intermediate, magnesium-ferrous, type.

Upon treatment with ethylene glycol, the line 14.2 Å splits up. The reflection appearing close to 16.9 Å testifies to the presence of swelling minerals of the smectite group (Fig. 1).

Both treatment with KCl and the other tests failed to yield data allowing a precise identification of mixed-layer minerals. Several facts, such as the incomplete series of basal reflections, diffusions of some of them, their asymmetric shapes and the raised background below 10° 2Θ, evidence that these minerals are randomly mixed-layered. Basing on these observations and interpreting the tests according to the assumption proposed by Reynolds and Hower (1970) and Drits and Sakharov (1976) that the nature of interlayer spacings in mixed-layer minerals is the same as in the structure of respective minerals, our structures were identified as random mixed-layer illite/montmorillonite, vermiculite/chlorite and possibly chlorite/swelling chlorite.

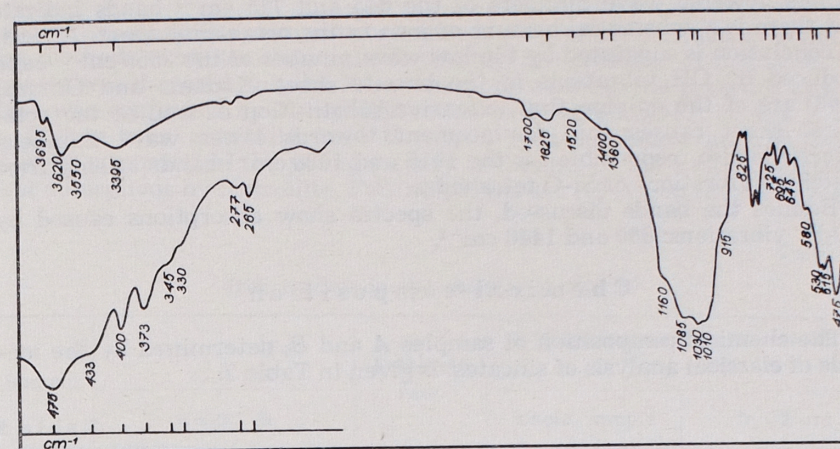X-ray diffractometry has also revealed the presence of quartz, potas-

Fig. 3. Infra-red absorption spectrum of sample A

sium and sodium-calcium feldspars, and carbonates (calcite, dolomite and siderite). Siderite concentrates in the $< 2\mu m$ fraction, in which it prevails over the other carbonates. Its content is higher in sample A. It is presumably authigenic siderite, being in equilibrium with the environment.

Infrared absorption spectra were obtained with UR-10 (middle infrared) and Digilab (middle and far infrared) spectrometers. Investigations were carried out on $<2 \ \mu m$ fractions of untreated samples and on sample A hot-treated with 1 : 1 HCl for 4 h. The spectrum of untreated sample (Fig. 3) confirms the mineralogical composition determined by X-ray powder method and permits making certain inferences regarding the occurrence of iron in the structure of clay minerals.

Clay minerals, mainly illite, are responsible for the general character of the spectrum. Illite gives the following bands:

— 470, 530 cm^{-1} (the latter coincides with that from chlorite), corresponding to bending vibrations of Si-O-Si bonds;

— 1020 cm^{-1} caused by stretching vibrations of these bonds;

— 920 cm^{-1} arising from interlayer vibrations of the Si-O-(Al, Fe) type;

— 825 cm^{-1} from internal vibrations of the octahedral sheet, of the Al-O-Al type;

— 3420, 3620 cm^{-1} owing to stretching vibrations of (OH)$^-$ groups.

The absorption bands attributed to illite fail to define its polytypic modification because the diagnostic band 1080 cm^{-1}, which does not appear in $1M$ modification, coincides with the absorption band of quartz. The absorption from OH stretching vibrations occurring near to 3620 cm^{-1} can suggest a greater amount of Fe^{3+} substitution in the octahedral sheet of illite (Dominik 1977). In illites lower in Fe^{3+} this band appears close to 3630 cm^{-1}.

Besides the bands coinciding with those of illite, chlorite displays absorptions due to tetrahedral and octahedral sheet vibrations that, according to Hayashi and Oinuma (1965), permit inferences as to the amount of Fe substitution in the octahedral sheet of this mineral. According to the cited

authors, lowered wave numbers of the 645 and 725 cm^{-1} bands indicate that there is a substantial amount of iron in the octahedral sheet. A similar conclusion is suggested by the low wave number of the 3550 cm^{-1} band produced by OH vibrations in the brucite sheet. Kodama and Oinuma (1963) are of the opinion that extensive substitution of iron in the octahedral sheet causes this displacement towards lower wave numbers. Chlorite is also responsible for the 1015 and 1030 cm^{-1} bands arising from stretching vibrations of Si-O tetrahedra.

Besides the bands discussed, the spectra show absorptions caused by $(CO_3)^{2-}$ vibrations: 880 and 1440 cm^{-1}.

Chemical composition

The chemical composition of samples A and B, determined by the methods of classical analysis of silicates, is given in Table 2.

Table 2

Chemical composition of the samples A and B*

Sample	SiO$_2$	TiO$_2$	Al$_2$O$_3$	MnO	CaO	MgO	Na$_2$O	K$_2$O	CO$_2$	P$_2$O$_5$	S$_c$	SO$_3^{2-}$	S$_s$
							%						
A	52.7	0.59	12.4	0.07	1.3	2.7	1.9	3.2	0.6	0.19	1.46	3.01	0.26
B	59.1	0.59	12.3	0.13	0.9	2.2	1.8	3.2	1.0	0.16	1.24	2.67	0.17

* Analysed in the Geological Institute, Warsaw.

One of the major chemical components is magnesium. It occurs partly in the coarse fraction of the sediments, being mainly fixed in dolomite. In the clay fraction, on the other hand, it is primarily a constituent of chlorites. It is difficult to determine the form of occurrence of sodium, which is mainly confined to the clay fraction (3.8% in <2 μm fraction of sample B as compared with 1.8% in the whole sample). It can enter into the composition of swelling minerals, but it is also possible that it acts as the exchange cation in zeolites. The latter have been detected by X-rays (reflections 8.39, 6.35, 3.83 Å), but their presence failed to be confirmed by other methods. It is worth noting at this point that the formation of zeolites in brackish basins is still an open question (Füchtbauer, Müller 1977). The statement that sodium assumes the role of the exchange cation in the sediments studied is borne out by the results of chemical analysis made along the profile: the Vistula estuary-centre of the Gdańsk Deep, according to which the sodium content in the sediments increases seawards.

Iron is present in the sediments of the Gdańsk Deep in an amount of 7—10 wt.%, expressed in terms of Fe$_2$O$_3$. It is introduced to the sediments together with the mineral material but, as mentioned in the introduction, it is also supplied by precipitation from ionic solution. The content of iron, along with the division into oxidation states, is given in Table 3.

The bulk of iron is fixed in the clay fraction. It occurs in the crystal lattice of layer silicates — illite, chlorite and glauconite. Iron appears also

as siderite, sulphides, vivianite, goethite and possibly haematite. None of the methods used has shown unmistakably the presence of hematite. Vivianite was detected only by X-ray methods whereas the presence of goethite was confirmed by X-ray diffraction patterns and DTA curves.

It has been generally held that iron monosulphides, amorphous to X-rays, occurring in the young estuary sediments of the Baltic Sea represent amorphous hydrotroilite, FeS·nH$_2$O. Berner (1971), on the other hand,

Table 3

Iron content in the samples A and B*

Sample	Fe^{3+}	Fe^{2+}	Fe^{3+}/Fe^{2+} ratio	Total iron content expressed as Fe$_2$O$_3$ weight %	
	weight %			whole sample	fr.<2 μm
A	2.3	1.73	1.33	5.76	
B	3.1	1.19	2.57	6.08	7.0

* Analysed in the Geological Institute, Warsaw and Academy of Mining and Metallurgy, Cracow.

states that they are mackinavite (Fe$_{1+x}$S) and greigite (Fe$_3$S$_4$). The two sulphides form under the conditions of anaerobic estuary sediment due to a reaction between H$_2$S, HS$^-$, S° and fine-grained goethite or dissolved Fe^{2+} of Fe^{3+} ions (Berner 1964). Roberts et al. (1969) defined the conditions that promote the formation of a monosulphide mixture with the features similar to those noted in the sediment under study. In their opinion, such process is possible in a sediment in which reducing conditions prevail, provided that a certain amount of oxygen is available in the bottom water layer. In that case, the source of Fe^{2+} ions is FeOOH, in which the ferric iron is also used to oxidize H$_2$S to S°. The presence of an oxidizer (periodic availability of oxygen in the bottom water), an excess of Fe^{3+} and, consequently, an excess of elementary sulphur lead, in the sediments of the Gdańsk Deep, to the formation of HCl-soluble mono- and polysulphides of the greigite type rather than to the rise of disulphides of the pyrite type. The extremely small size of monosulphide crystallites is a result of rapid nucleation due to oversaturation during sedimentation because iron sulphides are very sparingly soluble (Berner 1971). The content of HCl-soluble sulphides, determined by Neglia-Favretto method, is 0.3 wt.% for sample B, which means that only 4.7% of total iron is fixed in the form of monosulphide.

It is feasible that apart from clay minerals, the bulk of Fe^{3+} is fixed in hydroxides and oxyhydroxides, mainly in fine-crystalline α-FeOOH or Fe$_2$O$_3$·H$_2$O, amorphous to X-rays, being in fact FeOOH oxyhydroxide. When aging in the alkaline sea water solution, the latter can convert into crystalline goethite (Chaley 1972). Goethite has a layered structure in which Fe^{3+} is in octahedral coordination.

Iron that precipitates from the Vistula water flowing into the Gdańsk Bay seems to be fixed primarily in the form of ferric iron oxyhydroxides

and subsequently, by way of the reactions discussed, passes into sulphides or carbonates.

EPR spectra

The use of EPR spectroscopy to the studies of polymineral samples presents considerable difficulties for various reasons such as sensitivity of this method, especially regarding structural defects, absence of characteristic signals from individual ions, and insensitiveness to Fe^{2+} at room temperature. Therefore, our samples were subjected to chemical treatment prior to the investigations in order to remove some mineral components and oxidize the iron.

EPR spectra were obtained at room temperature with the X-28 spectrometer designed at the Wrocław Polytechnic. Analyses were carried out on the $< 2\,\mu m$ fraction from sample A prepared in different ways, i.e. untreated, hot-treated with 1:1 HCl for 4 h, and oxidized, when heated, with perhydrol. The spectra are shown in Figure 4, along with informa-
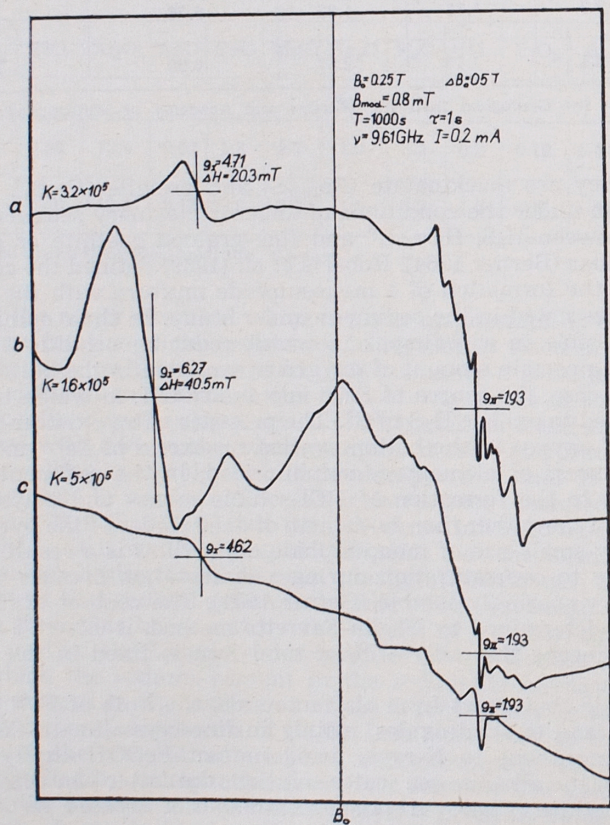

Fig. 4. EPR spectra of sample A

a — untreated sample, b — perhydrol treated, c — HCl treated

tion regarding the experimental conditions. It will be noticed that in view of marked differences in the EPR signal intensity for respective preparations, the spectra were taken at varying amplification, defined by the constant K. The following conclusions emerge from the experimental data:

— the resonance signal at $g=4.6$ testifies to the presence of ferric iron in the crystal lattice of layer silicates, mainly illite. This line does not disappear upon treatment with HCl,

— treatment with HCl results in the weakening of the signal $g = 4.6$, which shows that its source is also the Fe^{3+} ion in the structure of other minerals sensitive to HCl (iron hydroxides, chlorite),

— a broad line at $g=2.0$, which disappears upon treatment with HCl and becomes considerably more pronounced in the sample oxidized with perhydrol, is to be attributed to free oxides, mainly iron oxyhydroxides adsorbed on the surface of other minerals,

— the line $g=1.93$, exhibiting a hyperfine structure due to magnetic interaction of the nucleus of a spin of 5/2 (e.g. of aluminium), testifies to the presence of permanent defects in the structure of clay minerals in the form of extensive isomorphic substitution. Chlorite seams to be the main source of the signal since this signal is the strongest in the untreated sample,

— displacement and considerable intensification of the signal $g=6.3$ are certainly due to violent oxidation by perhydrol. This process not only enriches the sample in Fe^{3+} by oxidizing also a part of structural Fe^{2+} from layer silicates but also induces changes in the crystal lattice of the minerals, affecting mainly electron distribution. It can be inferred, therefore, that the content of structural Fe^{2+} in the sample is high.

Mössbauer spectra

Mössbauer spectra were taken at room temperature with an Elron spectrometer using a 400-channel analyzer at the Institute of Physics of the Jagiellonian University. The Lorentzian lines were least squares fitted to the measured spectra by computer.

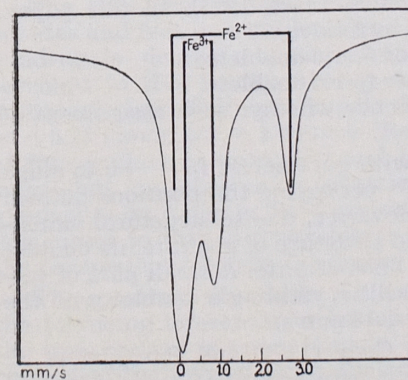The spectra give an image which is a superposition of at least two

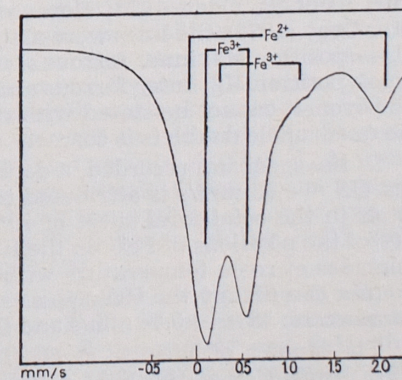Fig. 5. Mössbauer spectrum of untreated sample A ($T = 300$ K)

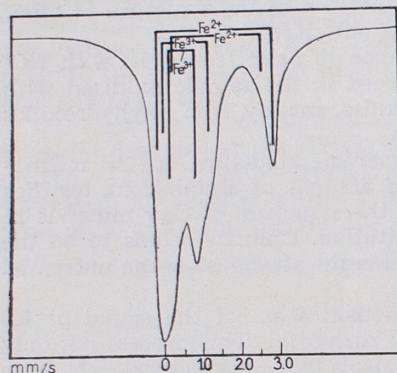Fig. 6. Mössbauer spectrum of sample A treated with HCl ($T = 300$ K)

quadrupole doublets (Figs. 5—7). Zeeman splitting due to superparamagnetism of iron oxyhydroxides and sulphides has not been noted at room temperature, which fact provides further evidence that these substances are fine-dispersive.

For untreated sample A (Fig. 5) the spectrum was resolved into two quadrupole doublets, and fitting of a great number of lines did not lower the chi-square value. For sample A hot-treated with 1:1 HCl three doublets were fitted (Fig. 6) while four quadrupole doublets were fitted for sample B, two for each of the unequivalent positions of Fe^{2+} and Fe^{3+} (Fig. 7).

Fig. 7. Mössbauer spectrum of untreated sample B (T = 300 K)

The calculated Mössbauer parameters are listed in Table 4. Isomer shifts are given relative to iron metal.

The absorption line area is proportional to the number of iron ions in the given structural position and to the Mössbauer fraction. Only at low temperatures, at which the Debye-Waller factors for Fe^{3+} and Fe^{2+} are nearly equal, the relative areas for thin absorbents are a good measure of the Fe^{3+}/Fe^{2+} ratio. Therefore, the values of this ratio calculated in this paper are only approximate, being 1.30 for untreated sample A and 1.73 for sample B (the data from chemical analysis are resp. 1.33 and 2.57).

From the spectra obtained it appears that both Fe^{2+} and Fe^{3+} ions are only in octahedral coordination in the lattice of clay minerals. The octahedral sheet comprises at least two unequivalent positions: M1 (hydroxyl groups in the trans arrangement) and M2 (hydroxyl groups in the cis arrangement). The assignment of a spectral line to particular positions in the octahedral sheet is a matter of dispute (Weaver, Wampler, Pecuil 1967; Rolf, Kimball, Odan 1977; Rozenson, Heller-Kallai 1977). In this paper, after Coey (1975), the lines were assigned as follows:
— position M1: inner ferrous and outer ferric doublets;
— position M2: outer ferrous and inner ferric doublets.
However, it cannot be stated with confidence whether such assignment of the quadrupole doublets is correct.

In the spectrum recorded, a doublet with parameters $IS = +0.45$ mm/s and $QS = 0.65$ mm/s is attributed to Fe^{3+} occupying the positions defined as cis in the octahedral sheet of illite. However, due to structural similarity of the positions of Fe^{3+} in the layered structure of goethite, its doublet coincides at room temperature with the lines of illite. A small part of ferric iron can occupy the trans positions in illite, yielding a doublet with the parameters: $IS = +0.54$ mm/s and $QS = 1.13$ mm/s.

The studies of Weaver et al. (1967), Coey (1975) and Punakivi et al. (1975) suggest that the Fe^{2+} doublet with parameters: $IS = +1.33$ mm/s, $QS = 2.16$ mm/s corresponds partly to ferrous iron occupying the trans-position in illite. Analysis of the spectrum of HCl-treated sample A free

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Table 4

Iron lines parameters in Mössbauer spectra of the samples A and B

Sample	Parameter	Fe^{3+}_I	Fe^{3+}_{II}	Fe^{2+}_I	Fe^{2+}_{II}	Fe^{3+}/Fe^{2+} ratio
A (untreated)	IS QS	$+0.50\pm0.006$ 0.65$\pm$0.003 0.57$\pm$0.002		$+1.26\pm0.006$ 2.63$\pm$0.011 0.44$\pm$0.002		1,30
A (treated with HCl)	IS QS	$+0.33\pm0.02$ 0.58$\pm$0.01 0.46$\pm$0.01	$+0.65\pm0.05$ 1.36$\pm$0,2 1.04$\pm$0,2	$+1.11\pm0.02$ 2.81$\pm$0.04 0.55$\pm$0.03		3,03
B (untreated)	IS QS	$+0.45$ 0.66 0.55	$+0.54$ 1.13 0.35	$+1.23$ 2.76 0.36	$+1.33$ 2.16 0.48	1,73

Note: Isomer shifts are given relative to iron metal. Values in mm/s.

from iron hydroxides and chlorites is, however, inconsistent with this interpretation. The remaining doublet of octahedral Fe^{2+}, which is to be attributed to undissolved illite, has different parameters: $IS = +1.11$ mm/s, $QS = 2.81$ mm/s.

Chlorites contain almost exclusively Fe^{2+} (alongside of other bivalent ions) which occupies presumably the cis positions in the octahedral sheet of the 2:1 layer. It participates in lines: $IS = +1.26$ mm/s, $QS = 2.63$ mm/s for sample A and $IS = +1.23$ mm/s, $QS = 2.76$ mm/s for sample B, strongly affected by HCl treatment. In the authors' opinion, a part of Fe^{2+} occupies the trans position with the corresponding doublet: $IS = +1.33$ mm/s, $QS = 2.16$ mm/s. It also seems feasible that the two Fe^{2+} doublets can be assigned not to the trans and cis positions but to differences in the symmetry of the 2:1 layer and brucite sheet, the latter giving greater quadrupole splitting.

The HCl-treated sample is free from chlorite, as well as from carbonates and free iron oxides (Fig. 1), displaying in the Mössbauer spectrum quadrupole doublets arising from iron in the structure of minerals resistant to HCl treatment, e.g. in glauconite. Typical glauconite yields a characteristic Fe^{3+} quadrupole doublet with average parameters: $IS = +0.15$ mm/s, $QS = 1.0$ mm/s (Rolf et al. 1977 and others). The absence of this doublet in untreated and HCl-treated sample A (Figs. 5, 6) indicates that the glauconite occurring in this sample differs from typical glauconite by a higher Fe^{2+} content and that the position of ferric iron in it is closer to that in ferric-ferrous illites (Füchtbauer, Müller 1977) with the parameters given by Raclavsky et al. (1975).

The spectrum of sample A treated with 1:1 HCl for 4 h (Fig. 6) allows the following inferences to be made. First of all, the general decrease in the iron content is nonuniformly distributed between Fe^{2+} and Fe^{3+}, the content of the former being diminished more appreciably. Treatment with HCl affects the position of absorption lines attributed to illite, making interpretation difficult. Simultaneously, there appears an exceptionally

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broad doublet ($\Gamma = 1.044$ mm/s) with parameters: $IS = +0.65$ mm/s, $QS = 1.36$ mm/s. It seems certain that these lines are produced by octahedral ferric and ferrous iron, both ions occupying extremely distorted positions. This situations is probably due to certain impairment of the lattice of clay minerals caused by acid treatment.

The linewidth is generally greater than theoretical. This is essentially due to the diversity of the surroundings of iron occupying structurally similar positions in various minerals (illite, chlorite, goethite) of the poly-mineral sample.

Owing to structural similarity, goethite yields lines coinciding with the illite Fe^{3+} doublet. From the data obtained by other authors it appears, however, that IS and QS values for goethite should deviate slightly from those for illite, but such lines failed to be recorded in the spectra of untreated samples. It seems that a spectrum taken at helium temperature of 4.2 K could yield more complete data on goethite because magnetic splittings can then be studied and this not only provides interesting information on the magnetic sublattices present in this mineral but also allows for its precise identification (Hrynkiewicz, Kulgawczuk, Tomala 1965).

More detailed analysis of the octahedral positions of the Fe^{2+} ion in the crystal lattice of monosulphides is hindered by the coincidence within the doublet with parameters: $IS = +1.23$ mm/s, $QS = 2.76$ mm/s (for sample B).

Slight inflexions of the spectra of untreated samples suggest the presence of iron coordinated in the lattice of siderite. Mössbauer parameters for this iron are somewhat lower than those for octahedral Fe^{2+} in clay minerals.

DISCUSSION AND CONCLUSIONS

In the process of seizing of iron from the Vistula water by the Gdańsk Deep sediment the following phenomena have been noted:

1. Precipitation of ferric iron hydroxides. It has been found that the alkaline marine environment promotes oxidation of ferrous iron present in the Vistula water by lowering the normal potential of this reaction. In a pH range from 5 to 8, a slight increase in pH results in substantial lowering of the normal potential, so that iron is oxidized even though the Eh of the environment has not been raised. Since at pH values higher than 3 ferric iron undergoes hydrolysis, the increase of pH alone is responsible for the precipitation of iron in the form of ferric hydroxides.

2. The formation of HCl-soluble ferrous mono- and polysulphides in the anaerobic environment of the Gdańsk Deep deposits. The reactions proceed between H_2S, HS^- or $S°$ and ferric hydroxide, fine-dispersive goethite or Fe^{2+} ion. The sulphides presumably form by stages, passing through the phase of ferric hydroxide, with Fe^{3+} serving as oxidizer of H_2S (mainly in the anaerobic periods of stagnation). That the reaction preceeds in this way is also evidenced by a change in the Fe^{3+}/Fe^{2+} ratio in the top part of the core studied. As appears from classical analysis, Fe^{3+} prevails in the near-surface layer (the ratio is 3.5—3.7) while the Fe^{2+} content increases markedly below a level of -1.5 m (for sample A this ratio is 1.33 at a level of -2.5 m) (Fig. 8). However, the lack of correlation between

these changes and the observed increase in the content of sulphide sulphur in the near-surface deposits shows that the reduction of ferric iron from hydroxides also gives rise to siderite and, subsequently, leads to the reversible reaction $FeCO_3 - FeS$, which attains equilibrium at Eh $= -355$ mV and is sensitive to variations in Eh. It is interesting to note that below -2.5 m the Fe^{3+}/Fe^{2+} ratio increases again to about 2.5, as illustrated by sample B. This change, however, concerns the processes of transformation of clay minerals, e.g. chloritization and illitization, operating in the lower parts of the sediments (Fig. 8).

3. The formation of authigenic siderite which, under these circumstances, is the best indicator of alkalinity and the reducing conditions prevailing in the sediment (Fig. 9).

4. The transformation of clay minerals towards Fe^{3+} and, in the first place, Fe^{2+} substitution in the octahedral sheet. The scale of this process is difficult to assess because little is known about the mineralogical composition of the suspension carried by the Vistula. Nevertheless, the increased content of iron in illites and chlorites is unquestionable.
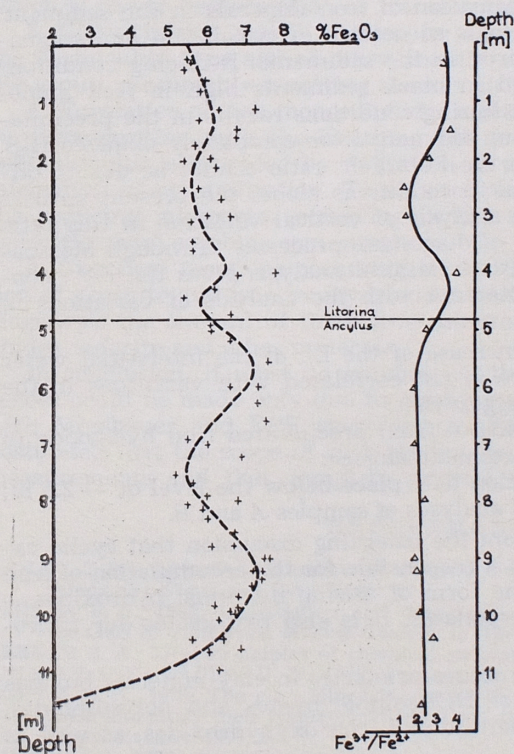

Fig. 8. Iron content and Fe^{3+}/Fe^{2+} ratio in the vertical profile of the core
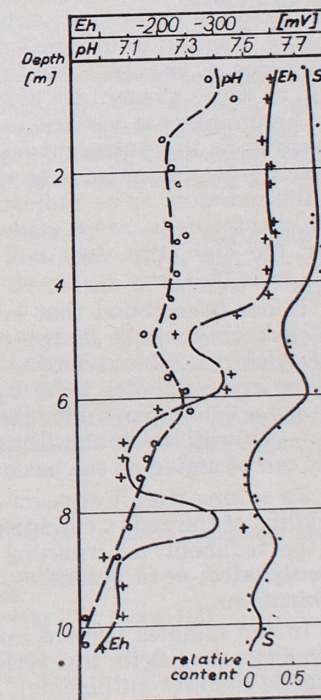Analysed in: Geological Institute in Warsaw, Gdańsk Medical Academy, Academy of Mining and Metallurgy in Kraków

Fig. 9. Siderite (S) content in $< 2\,\mu m$ fraction of the sediment and variations in Eh and pH in interstitial water

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Owing to the peculiar character of water circulation in the Baltic Sea and the rhythmicity of advections from the North Sea, the process of seizing of iron by the sediment is periodic. Both the severely limited contact of the Baltic waters with the world ocean and the positive water balance due to intensive river runoff lead to the characteristic stratification of the water masses in the Baltic. Moreover, the stability of water masses is so high that the saline bottom layer hardly participates in vertical circulation. Oxygen is supplied to the bottom layers almost exclusively by advection — inflow of ocean water (Łomniewski 1976). Advecations occur at irregular intervals, and each inflow is followed by a period of stagnation which is the more persistent the stronger the advection, because it increases the stability of water masses. The advections and periods of stagnation determine the availability of oxygen and the redox conditions both in the bottom water layer and in the sediment. In the sediment they cause the redox potential to vary from — 200 mV to — 50 mV (data for the Gothland Deep — Łomniewski 1976). In the Gdańsk Deep the Eh values are generally lower, ranging between — 400 mV and — 100 mV.

Hallberg et al. (1977) relate this periodicity, characteristic of the Baltic, to bacterial activity and the formation of iron minerals in the sediment. They maintain that the continuous succession of circulation and stagnation leads to accumulation of iron in the sediments. Reducing conditions during stagnation are reflected in black sediments high in iron monosulphides. A change towards oxidizing conditions results in the precipitation of white elementary sulphur sediment from completely oxidized H_2S.

Assuming that variations in the Fe^{3+}/Fe^{2+} ratio cannot be due to differences in the palaeogeographical conditions alone, the present authors attach great importance to the analysis of vertical variation in this ratio in the sediment as an indicator of diagenetic processes. Although Mössbauer spectroscopy has revealed that classical analysis gives the Fe^{3+} content too high, this does not interfere with the analysis of variations in this ratio (Fig. 8).

It has been found that an increase of the Eh of the interstitial water towards the bottom of the core is not correlated with variations in the Fe^{3+}/Fe^{2+} ratio. This seems to suggest that:

— iron sulphides form by stages from precipitated iron hydroxide in the layer 0.0—2.5 m under the sediment surface;

— chloritization and illitization take place below the level of — 2.5 m; this can be stated on the basis of analyses of samples A and B.

To summarize, it appears from the foregoing discussion that cyclic variability of the redox conditions is responsible for the accumulation of iron in the sediment, determining the form of arising minerals: hydroxides — —sulphates — sulphides — carbonates. It is also responsible for microlaminations.

In the samples studied iron occurs primarily in clay minerals but has also been found in the form of HCl-soluble mono- and polysulphides, siderite (mainly authigenic), goethite and iron oxyhydrides, as well as vivianite.

In layer silicates and aluminosilicates substantial amounts of iron are present in illite, chlorite and glauconite, the latter being in fact ferric-ferrous illite appearing in the form of glauconite grains. In these minerals iron occupies only octahedral sites of different symmetry, from those of the highest symmetry, defined in this paper as M1 (trans), through the M2 (cis) positions of lower symmetry, to markedly distorted sites whose occurrence may be a secondary phenomenon caused by treatment with HCl.

Samples A and B differ in the relative content of Fe^{3+}/Fe^{2+}. In the more oxidized sample B, Fe^{2+} showing a splitting QS = 2.16 mm/s seems to be more resistant. If the present author's view were accepted that this Mössbauer parameter corresponds to Fe^{2+} from chlorite rather than illite, a higher content of chloritic iron would be implied in the deeper sample. This would evidence that chloritization occurred in the sediment, with ferrous iron participating in this process. A higher Fe^{3+} content in illite, on the other hand, would testify to the presence of illitization proceeding by ferric iron substitution.

The foregoing discussion leads to the conclusions regarding the early diagenetic processes operating in the deposits. These processes comprise:

1. A decrease in the content of organic matter and of iron fixed in it.

2. Fixing of free silica. Its content in interstitial water diminishes systematically downwards (from about 700 meq/dm³ to about 200 meq/dm³), which is due to neoformation or transformation of layer minerals.

3. Chloritization and illitization by aggradation of open structures of the vermiculite type and of other, mainly swelling minerals of the smectite group, presumably involving the mixed-layer stage.

4. Formation of iron monosulphides and siderite and their consolidation or decomposition with the changing pH and Eh. The rise of mono- and polysulphides is attended by migration of the components to the sites of nucleation of crystallization. These sites are presumably associated with the reducing microareas occurring in the deposits, as evidenced by the dendritic, point sulphide concentrations.

5. Chemical reactions occurring in the deposits, involving decomposition of goethite and iron oxyhydrides. It follows, therefore, that during diagenesis the amount of these iron minerals decreases in favour of sulphides, siderite and other minerals.

In conclusion, it must be emphasized that several of the above inferences could be made only due to combining of the conventional methods with Mössbauer and EPR spectroscopy. For further investigations it is postulated that the scope of such studies be extended by low-temperature measurements and that complete profiles of sediments be investigated.

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ŻELAZO W OSADACH ILASTYCH BAŁTYKU

Streszczenie

Przedstawiono rezultaty badań dwóch próbek współczesnych osadów
bałtyckich obejmujących: sedymentacyjną analizę składu ziarnowego, che-
miczną analizę klasyczną i aktywacyjną, termiczną analizę różnicową, dy-
fraktometrię rentgenowską, spektroskopię absorpcyjną w podczerwieni,
spektroskopię EPR i spektroskopię össbauerowską. Wyciągnięto wnioski
odnośnie form mineralnych występowania żelaza w osadzie basenu brakicz-
nego na tle zespołu występujących tam minerałów ilastych. W badanych
próbkach żelazo znajduje się w strukturze minerałów ilastych w war-
stwie oktaedrycznej illitu, chlorytu i glaukonitu. Poza minerałami ilastymi
żelazo występuje w mono- i polisiarczkach, syderycie, wodorotlenkach
i wiwianicie. Poczyniono uwagi na temat procesu sedymentacji i wczes-
nej diagenezy w badanym osadzie.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy próbki A

Fig. 2. Dyfraktogramy próbki B

Fig. 3. Widmo w podczerwieni próbki A

Fig. 4. Widma EPR próbki A
  a — próbka surowa, b — traktowana perhydrolem, c — traktowana HCl

Fig. 5. Widmo mössbauerowskie próbki A w stanie naturalnym ($T = 300$ K)

Fig. 6. Widmo mössbauerowskie próbki A traktowanej HCl ($T = 300$ K)

Fig. 7. Widmo mössbauerowskie próbki B w stanie naturalnym ($T = 300$ K)

Fig. 8. Zawartość żelaza i stosunek Fe^{3+}/Fe^{2+} w profilu pionowym rdzenia
  (Analizy wykonano w: Instytucie Geologicznym Warszawa, Akademii Medycznej
  Gdańsk, Akademii Górniczo-Hutniczej)

Fig. 9. Zawartość syderytu (S) we frakcji poniżej 2 μm osadu oraz zmiany Eh i pH
  w wodzie interstycjalnej

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ЖЕЛЕЗО В ГЛИНИСТЫХ ОТЛОЖЕНИЯХ БАЛТИЙСКОГО МОРЯ

Резюме

Представлены результаты исследований двух образцов современных
отложений Балтийского моря. Во время исследований были сделаны:
седиментационный анализ зернового состава, классический и актива-
ционный химический анализ, термический дифференциальный анализ,
рентгеновские дифрактограммы, анализы методом ИК-спектроскопия,
спектроскопии EPR и спектроскопии Мессбауэра. Были сделаны выводы
относительно минеральных форм присутствия железа в отложениях бра-
кического бассейна на фоне комплекса присутствующих в них глинистых
минералов. В изучаемых образцах железо находится в структуре гли-
нистых минералов в октаэдрическом слое иллита, хлорита и глауконита.
Кроме глинистых минералов железо находится в моно- и полисульфи-
дах, сидерите, гидратах и в вивианите. Были сделаны замечания по по-
воду процесса седиментации и раннего диагенезиса в изучаемых отло-
жениях.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Дифрактограммы образца A

Фиг. 2. Дифрактограммы образца B

Фиг. 3. ИК-спектр образца A

Фиг. 4. Спектры EPR образца A
  a — сырой образец, b — образец обработанный пергидролем, c — образец обработан-
  ный HCl

Фиг. 5. Спектр Мессбауэра образца A в натуральном виде ($т = 300$ К)

Фиг. 6. Спектр Мессбауэра образца A обработанного HCl ($т = 300$ К)

Фиг. 7. Спектр Мессбауэра образца B в натуральном виде ($т = 300$ К)

Фиг. 8. Содержание железа и соотношение Fe^{3+}/Fe^{2+} в вертикальном профиле керна
  Анализы были проведены в: Геологическом Институте в Варшаве, Медицинской Академии
  в Гданске, Институте Ядерной Техники Горно-Металлургической Академии

Фиг. 9. Содержание сидерита (S) во фракции меньше 2 μm наноса и изменения Eh
  и pH в интерстиционной воде