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Krzysztof GÖRLICH\*, Edward A. GÖRLICH\*\*, Pham Quoc HUNG\*\*\*

## IRON-BEARING MINERALS IN THE BALTIC SEA SURFACE SEDIMENTS: A MÖSSBAUER EFFECT STUDY

**Abstract.** Six samples of bottom sediments from Gdańsk Basin were studied with Mössbauer spectroscopy to find the distribution of ferrous and ferric ions between different crystal chemical sites of iron-bearing minerals. The samples were collected at depths from 25 to 90 m b.s.l., and at distances from 5 to 55 km from the Vistula River mouth. The Mössbauer spectra were obtained at room temperature (300K) for the clay fraction of the sediments ( $< 2 \mu\text{m}$ ). Present study, along with previous chemical and mineralogical analyses allowed us to state that  $\text{Fe}^{3+}$  ions occupy M (1) and M (2) sites in the octahedral sheets of illite and smectite. There is ferric iron in non-clay superparamagnetic phases.  $\text{Fe}^{2+}$  is present in the octahedral sheet of chlorite. Ferrous iron is also present in the unidentified hydroxide phases which are stable, and thus more abundant in the reducing environment of the fine sediments below 50 m water depth.

### INTRODUCTION

Mössbauer spectroscopy was applied to investigate changes in iron ions distribution between different crystal chemical sites of fine crystalline minerals in the surface sediments of Gdańsk Basin. Deposition of fine sediments in this area is dominated by precipitation and settling of the dissolved and suspended load carried into the Gdańsk Basin by the Vistula River (Fig. 1).

In the present paper an attempt is made to trace the estuarine processes taking place in the water mass by studying fine fraction of the resulting surface sediments in the different points of the Gdańsk Basin. The work is focussed on the iron bearing phases, as iron is commonly regarded to be the most reactive inorganic component of the estuarine sedimentary system. As the environment of the sediment changes from oxic (down to 50 m water depth) to anoxic (below 50 m) it is interesting to observe sensibility of the valency states of iron to the change in oxidation state of the sediment.

\* Institute of Geological Sciences, Polish Academy of Sciences, Cracow (31—002 Kraków, ul. Senacka 3).

\*\* Jagiellonian University, Institute of Physics, Cracow (30-059 Kraków ul. Reymonta 4).

\*\*\* University of Hanoi, Department of Nuclear Physics, Vietnam.

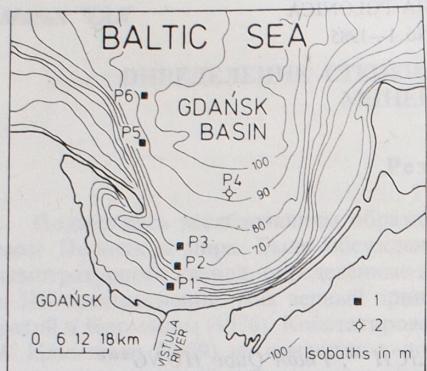


Fig. 1. Geographic setting and sampling sites in the Gdańsk Basin. Isobaths are at 10 m intervals  
1 — grab samples, 2 — 85 cm long sediment core

Mineralogy of the sediments in the study area was described in detail by Stoch et al. (1980), and early diagenetic transformations of iron-bearing phases in these sediments were discussed by Görlich et al. (1978, 1984).

#### MATERIAL

In this paper the clay fraction (< 2 µm) of the sediments is discussed. The sediments studied contain variable amounts of clay fraction: from 5% in sample P1 to 30% in sample P6. According to previous works (Görlich et al. 1978, Stoch et al. 1980) the clay fraction consists of clay minerals (up to ca. 90% of clay fraction), particulate organic matter and fine-crystalline non-clay phases. The latter are mostly X-ray amorphous, and thus their quantitative determination is ambiguous.

Different methods were used to evaluate the form and quantity of X-ray amorphous components of sediments. Organic matter was determined as loss by heating at 720 K of previously dried samples. The content of low-aluminium allophanes by dissolution in 0.8 n NaOH (Görlich 1978). The results are gathered in Table 1.

Table 1

Natural humidity, concentration of allophanes and concentration of organic matter in natural samples P3, P5 and P6

Sample N°	Natural <sup>1</sup> humidity wt. %	Allophanes wt. %	Organic matter wt. %
P3	62	8	4.2
P5	43	— <sup>2</sup>	3.2
P6	74	5	6.9

<sup>1</sup> By drying at 380 K.

<sup>2</sup> Not determined.

Table 2  
Clay fraction content, natural humidity and chemical composition of core P4 at different levels below sediment surface (natural samples)

Level m	Natural humidity wt. %	Clay fraction wt. %	SiO <sub>2</sub> wt. %	Al <sub>2</sub> O <sub>3</sub> wt. %	Fe <sub>2</sub> O <sub>3</sub> wt. %
0.08	75	13	52.1	13.4	6.7
0.25	74	15	50.3	11.9	5.5
0.35	76	12	52.9	13.6	6.7

The content of iron hydroxides and oxyhydroxides was determined by Mössbauer method at 4.5 K in the sediment core close to P6 position (Görlich et al. 1984) and is ca. 3% (calculated as FeOOH). The concentration of iron monosulphides determined by Neglia-Favretto method is ca. 0.3% in the same locality.

Homogeneity of the surface layer of sediment (about 30 cm thick) which is collected in distorted state in grab samples under study, was checked on the single sediment core P4. The results gathered in Table 2 confirm assumption that for the purpose of this study the surface layer of sediments may be regarded as homogeneous.

The clay-mineral assemblage consists of illite (40% to 55% of clay fraction), chlorite (20% to 35% of clay fraction) and smectites (35% to 10% of clay fraction). The range of values given in brackets corresponds with the weight per cent content of given mineral near the mouth of the Vistula River and at the 55 km distance, respectively. These values represent the trend of changes of clay composition in surface sediments. In the vicinity of the river mouth there is a distinct contribution to the XRD patterns from swelling chlorites and mixed-layer illite/smectite (Stoch et al. 1980).

Illite is dioctahedral ( $d_{000} = 0.1503$  nm), and the IR absorption band of OH

Table 3  
Concentration of iron in the clay fraction and Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio

Sample N°	Depth m	Distance from Vistula mouth km	Iron content wt. % Fe <sub>2</sub> O <sub>3</sub> <sup>1</sup>	Fe <sup>3+</sup> /Fe <sup>2+</sup> ratio <sup>2</sup>
P1	25	5	9.9	7.4
P2	60	12	3.7	2.7
P3	65	17	5.3	2.8
P4	90	35	7.2	2.8
P5	85	45	3.2	2.8
P6	90	57	5.5	2.8

<sup>1</sup> Determined by PIXE method.

<sup>2</sup> Determined by Mössbauer spectroscopy.

stretching vibrations near  $3620\text{ cm}^{-1}$  may suggest considerable  $\text{Fe}^{3+}$  substitution in octahedral sheet.

Chlorite is poorly crystalline, magnesium-ferrous type as indicated by the distribution of intensities of XRD basal reflections and low wave numbers of IR absorption bands:  $645$ ,  $725$  and  $3550\text{ cm}^{-1}$  (Görlich et al. 1978). Considerable ferrous substitution is confirmed by the reduction of  $0.701\text{ nm}$  XRD reflection of chlorite after heating at  $850\text{ K}$  (Stoch 1974).

Concentrations of iron in the clay fraction of the samples P1 to P6 are given in Table 3. The iron content was measured by PIXE method on the samples submitted to Mössbauer measurements.

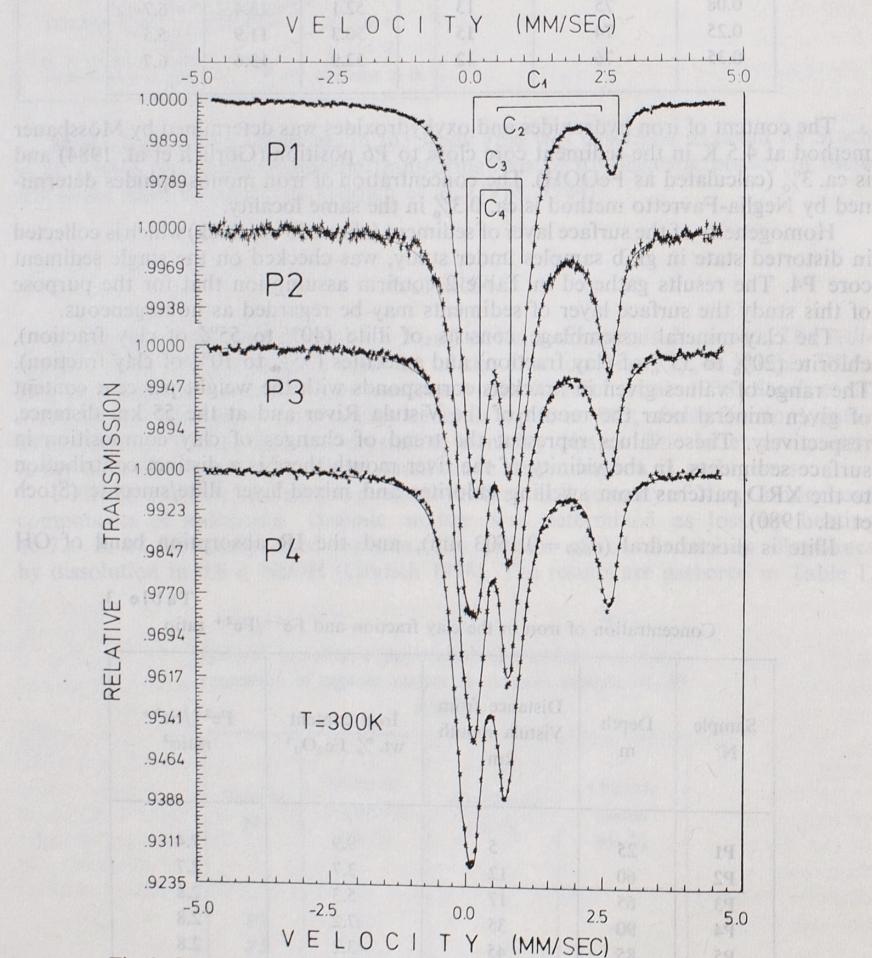


Fig. 2. Gamma resonance absorption spectra of samples P1 to P4 at room temperature. Solid lines are the resulting best fitted theoretical curves. Bar diagrams show the line positions of the component spectra. If it is assumed that the recoil-free fraction is the same for all sites and valencies of iron, the intensities represent relative abundances illustrated in Figure 4

## EXPERIMENTAL AND RESULTS

Gamma resonance absorption measurements were performed using a standard constant acceleration Mössbauer spectrometer and a  $^{57}\text{Co}(\text{Cr})$  source. The velocity scale was calibrated with Fe-metal absorber. The spectra were measured at room temperature. All absorbers had the same thickness of about  $100\text{ mg/cm}^2$ .

Six samples of clay fraction ( $< 2\text{ }\mu\text{m}$ ) of surface sediments were submitted to Mössbauer measurements (Fig. 1). The samples were quasi-natural (washed and air-dried) to avoid impact of chemical DCB cleaning procedure (Ericsson et al. 1984). Spectra obtained are illustrated in Figures 2 and 3.

The spectra were fitted using the least squares minimization routine with two doublets corresponding to the divalent iron ( $C_1$  and  $C_2$  in Figures 2 and 3) and two

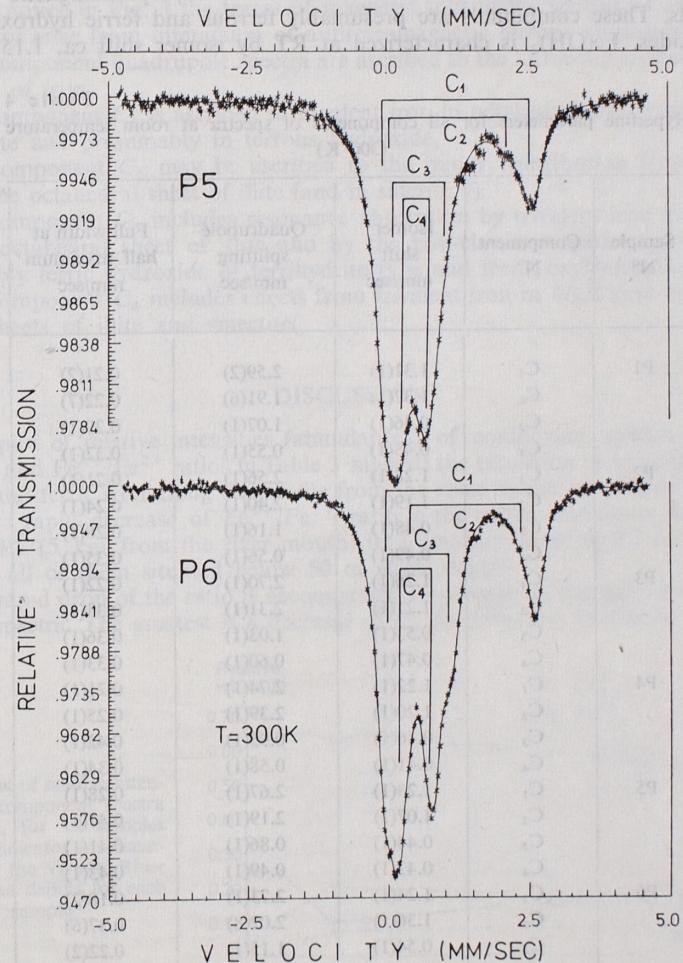


Fig. 3. Gamma resonance absorption spectra for samples P5 and P6 at room temperature  
Details as in Figure 2

doublets for trivalent iron ( $C_3$  and  $C_4$ ). Each doublet is a set of two Lorentzian lines. The hyperfine parameters obtained for satisfactory fits are listed in Table 4.

There is a considerable range of variability of parameters along the profile from P1 to P6. On one hand, it is due to the correlation between parameters in the fitting procedure and results from the change in amplitudes of the component spectra. On the other hand, it reflects the complex nature of the fitted quadrupole-split doublets.

Some doublets are superpositions of resonance absorption by iron species in the different crystal chemical positions. As found in the other study of Gdańsk Basin sediments (Görlich et al. 1984)  $C_1$  and  $C_3$  quadrupole components contribute at helium temperature (4.5 K) to Zeeman split components. Thus,  $C_1$  and  $C_3$  components at RT most probably include effects from iron in the superparamagnetic non-clay compounds. These compounds are presumably ferrous and ferric hydroxides and oxyhydroxides.  $\text{Fe(OH)}_2$  is characterized at RT by isomer shift ca. 1.15 mm/sec

Table 4  
Hyperfine parameters for all components of spectra at room temperature  
(300 K)

Sample N°	Component N°	Isomer <sup>1</sup> shift mm/sec	Quadrupole splitting mm/sec	Full width at half maximum mm/sec
P1	$C_1$	1.31(1)	2.59(2)	0.21(2)
	$C_2$	1.37(1)	1.91(6)	0.22(7)
	$C_3$	0.46(1)	1.07(1)	0.29(1)
	$C_4$	0.48(1)	0.55(1)	0.32(1)
P2	$C_1$	1.28(1)	2.56(1)	0.21(1)
	$C_2$	1.19(1)	2.40(1)	0.24(1)
	$C_3$	0.48(1)	1.16(1)	0.28(1)
	$C_4$	0.49(1)	0.56(1)	0.35(1)
P3	$C_1$	1.26(1)	2.70(1)	0.22(1)
	$C_2$	1.21(1)	2.31(1)	0.33(1)
	$C_3$	0.53(1)	1.03(1)	0.36(1)
	$C_4$	0.47(1)	0.60(1)	0.33(1)
P4	$C_1$	1.22(1)	2.74(1)	0.21(1)
	$C_2$	1.20(1)	2.39(1)	0.25(1)
	$C_3$	0.46(1)	0.95(1)	0.42(1)
	$C_4$	0.41(1)	0.58(1)	0.34(1)
P5	$C_1$	1.23(1)	2.67(1)	0.28(1)
	$C_2$	1.07(1)	2.19(1)	0.47(1)
	$C_3$	0.44(1)	0.86(1)	0.41(1)
	$C_4$	0.43(1)	0.49(1)	0.43(1)
P6	$C_1$	1.24(1)	2.73(1)	0.18(2)
	$C_2$	1.36(1)	2.02(8)	0.37(6)
	$C_3$	0.54(1)	1.15(1)	0.22(2)
	$C_4$	0.46(1)	0.59(1)	0.29(1)

<sup>1</sup> Relative Fe-metal.

and quadrupole splitting ca. 2.9 mm/sec, which are close to  $C_1$  parameters.  $\text{FeOOH}$   $\gamma$  and  $\alpha$  polymorphs reveal at room temperature isomer shifts between 0.30 and 0.65 mm/sec and fit in  $C_3$  component. The presence of superparamagnetic  $\gamma\text{-FeOOH}$  in the sediments at the locality close to P6 was confirmed by measurements at 4.5 K in the above cited study by Görlich et al. (1984).

Siderite may contribute to  $C_2$  component with its parameters:  $IS = 1.24$  mm/sec and  $EQ = 1.80$  mm/sec.  $C_4$  component at RT includes interaction of ferric iron in the octahedral sheets of two different clay minerals: illite and smectite.

The question of presence of ferrous monosulphides is unresolved here. In spite of the dark to black colour of the anoxic sediments (samples P2 to P6) there is only about 5% of iron bound in monosulphides. It is probably below detection limit of the Mössbauer method as found by Rozenson and Heller-Kallai (1978). However, one may notice in Fig. 3 the traces of magnetic split in the spectra of P5 and P6, which may arise from interaction of antiferromagnetic ferrous monosulphide.

The component quadrupole spectra are ascribed to the following crystal chemical positions of iron:

(1) Component  $C_1$  is ascribed to divalent iron in octahedral and brucitic sheets of chlorite and presumably in ferrous hydroxide.

(2) Component  $C_2$  may be ascribed to the minor contribution from divalent iron in the octahedral sheet of illite (and in siderite?).

(3) Component  $C_3$  includes resonance absorption by trivalent iron in the M(1) sites of octahedral sheet of illite and by the non-clay superparamagnetic phase, presumably ferric hydroxide of ferrihydrite type and ferric oxyhydroxides.

(4) Component  $C_4$  includes effects from trivalent iron in M(2) sites of the octahedral sheets of illite and smectite.

## DISCUSSION

The plot of relative intensities (abundances) of component spectra  $C_1$  to  $C_4$  in Fig. 4 and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios in Table 3 suggests the transition in site preference of ferrous and ferric iron along the profile from the river mouth in seaward direction. There is a rapid decrease of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio in the surface sediments, from 7.4 in sample P1 (5 km from the river mouth) to a constant value of 2.8 for the other samples, all of them situated below 50 m water depth.

The rapid drop of the ratio is accompanied by changes in the intensities of component spectra. The greatest is a decrease of  $C_3$  contribution. It may be related to

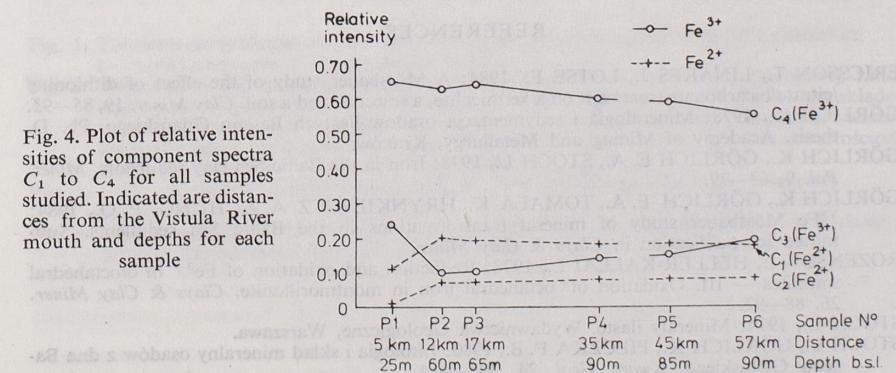


Fig. 4. Plot of relative intensities of component spectra  $C_1$  to  $C_4$  for all samples studied. Indicated are distances from the Vistula River mouth and depths for each sample

the decrease in content of ferric hydroxides of ferrihydrite type. The maximum content of this phase would be thus situated immediately at the mouth of the Vistula River, reflecting the rapid precipitation and flocculation of  $\text{Fe}^{3+}$  by destabilization upon the first contact of fresh and brackish waters. Further slow increase in the intensity of  $C_3$  component is due to the increasing concentration of illite in the sediment and to the settling of ferric oxyhydroxide phase from the suspension which has avoided deposition at the barrier of primary destabilization.

Monotonous decrease of  $C_4$  component intensity from P1 to P6 is explained by the decreasing content of smectites which contribute to this component.

The general increase of the intensities of  $C_1$  and  $C_2$  components is explained by the correlated decrease in the relative intensities of trivalent components and by growing concentration of ferrous hydroxide and iron-bearing illite. Greater increase of  $C_2$  when compared with  $C_1$  indicates growing contribution of ferrous ions in illite.

## CONCLUSIONS

The distinction between the two valency states of iron by Mössbauer spectroscopy is in the present study explicit. On the contrary, the assignment of quadrupole components to the specific crystal chemical sites is ambiguous. There is much room left for interpretation. Therefore, it was necessary to use as extensively as possible supplementary data from XRD, IR absorption and chemical analysis.

There are two distinct zones of estuarine deposition of fine sediments in the Gdańsk Basin. The first, down to ca. 10 km from the Vistula River mouth includes rapid flocculation of swelling clay minerals of smectite group, accompanied by precipitation and flocculation of ferric hydroxides. Smectites are nearly completely removed from the suspension in this first zone. In the second zone, further in seaward direction, there dominates sedimentation of iron-bearing illites and chlorites. A considerable part of ferrous phases in this zone is built up of non-clay minerals (ferrous hydroxides) which are stable and thus in greater abundance in the reducing environment of the sediments below 50 m water depth (samples P2 to P6). The amount of ferric oxyhydroxides ( $\gamma\text{-FeOOH}$ ) is increasing with depth.

Flocculation of dissolved and particulate matter by mixing of fresh and brackish waters controls sedimentation in the immediate vicinity of the river mouth. Settling of the modified residual suspension which passed through the barrier of destabilization, controls formation of fine sediments further than 10 km from the Vistula River mouth.

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Krzysztof GÖRLICH, Edward A. GÖRLICH, Pham Quoc HUNG

## MINERAŁY ŻELAZA W POWIERZCHNIOWYCH OSADACH MORZA BAŁTYCKIEGO: STUDIUM METODĄ MÖSSBAUERA

### Streszczenie

Sześć próbek osadów dennych z Basenu Gdańskiego zbadano spektroskopią móssbauerowską w celu znalezienia regularności w rozmieszczeniu jonów żelazowych i żelazowych w różnych pozycjach krystalochemicznych. Próbki osadu po-brano czerpakiem Petersena z głębokości 25–90 m p.p.m., w odległości 5–55 km od ujścia Wisły (fig. 1). Fizyczne i chemiczne cechy osadu przedstawiono w tabelach 1–3. Widma móssbauerowskie zarejestrowano w temperaturze pokojowej (300 K) dla próbek z frakcji ilastej osadów ( $< 2 \mu\text{m}$ ) — fig. 2 i 3. Pomierzone parametry nadsubtelne zebrane w tabeli 4. Stwierdzono, że jony  $\text{Fe}^{3+}$  zajmują pozycje  $M(1)$  i  $M(2)$  w warstwie oktaedrycznej illitu i smektytu. Żelazo trójwartościowe znajduje się również w nieilastycznych fazach superparamagnetycznych.  $\text{Fe}^{2+}$  znajduje się w warstwie oktaedrycznej chlorytu. Żelazo dwuwartościowe znajduje się również w niezidentyfikowanej żelazowej fazie wodorotlenkowej, która jest trwała, a stąd obfitała w redukcyjnym środowisku drobnych osadów zalegających poniżej głębokości 50 m p.p.m. Obliczone względne intensywności widm składowych (fig. 4) pozwalały ustalić zmienność stosunku  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (tab. 3) oraz zmiany preferencji w osadzie pozycji krystalochemicznych, a także zmiany form mineralnych w jakich występuje żelazo.

Stwierdzono dwie strefy sedymentacji estuarnej materiału drobnoziarnistego. Pierwsza, sięgająca do 10 km w głąb morza od ujścia Wisły, zdominowana jest przez flokulację, a w efekcie depozycję minerałów pęczniących grupy smektytu oraz wy-trącanie się i flokulację wodorotlenków żelazowych. Smektyty są usuwane z zawie-siny głównie w tej pierwszej strefie. Druga strefa jest zdominowana przez sedymenta-cję illitu i chlorytu. W tej strefie osiąda zmieniona zawiesina, która pokonała barierę destabilizacji w strefie pierwszej. Oprócz minerałów ilastych deponowane są tutaj oksywodorotlenki żelazowe, których ilość w osadzie rośnie z głębokością basenu.

### OBJAŚNIENIA FIGUR

- Fig. 1. Położenie geograficzne obszaru badań i miejsca pobrania próbek w Basenie Gdańskim  
1 — próbki czerpakowe, 2 — rdzeń długości 85 cm
- Fig. 2. Widma absorpcji rezonansowej gamma próbek P1 do P4 w temperaturze pokojowej. Linia ciągła jest najlepiej dopasowaną krzywą teoretyczną. Pokazano położenie linii widm składowych. Jeżeli założyć, że frakcja bezodrzutowa jest taka sama dla wszystkich pozycji i wartości żelaza, intensywności widm składowych odpowiadają względnym zawartościom żelaza w poszczególnych pozycjach, przedstawionym na fig. 4
- Fig. 3. Widma absorpcji rezonansowej gamma próbek P5 i P6 w temperaturze pokojowej  
Szczegóły jak na fig. 2
- Fig. 4. Wykres względnych intensywności widm składowych  $C_1$  do  $C_4$  dla wszystkich badanych próbek. Zaznaczono odległość od ujścia Wisły i głębokość poboru próbek

МИНЕРАЛЫ ЖЕЛЕЗА В ДОННЫХ ОТЛОЖЕНИЯХ  
БАЛТИЙСКОГО МОРЯ — ИЗУЧЕНИЕ  
МЁССБАУЭРОВСКИМ МЕТОДОМ

Резюме

Шесть образцов донных отложений из Гданьского бассейна были изучены методом мёссбауэровской спектроскопии с целью найти закономерность размещения ферри- и ферроионов в различных кристаллохимических положениях. Образцы осадка были отобраны черпаком Петерсена с глубины 25—90 м ниже уровня моря, на расстоянии 5—55 км от устья р. Вислы (фиг. 1). Физические и химические свойства осадка представлены на таблицах 1—3. Мёссбауэровские спектры зарегистрированы в комнатной температуре (300 К) для образцов глинистой фракции отложений ( $< 2 \text{ мкм}$ ) (фиг. 2 и 3). Измеренные сверхтонкие параметры собраны на таблице 4. Обнаружено, что ионы  $\text{Fe}^{3+}$  занимают положение M(1) и M(2) в октаэдрическом слое иллита и смеクтита. Трехвалентное железо присутствует также в неглинистых суперпарамагнитных фазах.  $\text{Fe}^{2+}$  находится в октаэдрическом слое хлорита. Двухвалентное железо присутствует также в неидентифицированной гидроокисной феррофазе, которая устойчива, и отсюда более обильная в восстановительной среде мелкозернистых осадков, залегающих ниже глубины 50 м н.у.м. Рассчитанные относительные интенсивности составных спектров (фиг. 4) позволяют установить непостоянство соотношения  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (табл. 3), а также изменения предпочтений в занятии кристаллохимического положения, а также изменения минеральных форм, в каких присутствует железо.

Обнаружены две зоны эстуарного осадконакопления мелкозернистого материала. В первой, достигающей 10 м вглубь моря от устья Вислы, господствует флокуляция и в итоге осаждение набухающих минералов группы смеクтита, а также осаждение и флокуляция ферригидроокислов. Смеクтиты удаляются из взвеси преимущественно в этой первой зоне. Во второй зоне господствует седиментация иллита и хлорита. В этой зоне осаждается измененная взвесь, которая одолела барьер дестабилизации в первой зоне. Кроме глинистых минералов, осаждаются здесь оксигидроокислы трехвалентного железа, которых количество в осадке растет с глубиной бассейна.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Географическое положение района исследований и места отбора образцов в Гданьском бассейне  
1 — ковшовые образцы, 2 — кери длиной 85 см
- Фиг. 2. Спектры резонансного поглощения гамма образцов P1 до P4 в комнатной температуре. Сплошная линия наиболее подходит к теоретической кривой. Показано положение составных спектров. Если предположить, что фракция без отброса такая же для всех положений и валентностей железа, то интенсивности составных спектров соответствуют относительным содержаниям железа в отдельных положениях, представленных на фиг. 4
- Фиг. 3. Спектр резонансного поглощения гамма образцов P5 и P6 в комнатной температуре. Подробности как на фиг. 2
- Фиг. 4. График относительных интенсивностей составных спектров C<sub>1</sub> до C<sub>4</sub> для всех изучаемых образцов. Указаны расстояния от устья р. Вислы и глубина отбора образцов