

MINERALOGY AND PETROLOGY OF HOLOCENE SEDIMENTS FROM THE WESTERN BALTIC SEA

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Summary. A total of 115 late-Holocene sediment samples obtained from two cores taken in the Eckernförder (EB) and Geltinger (GB) Bays were subjected to detailed grain size, chemical, and mineralogical analyses. The sediments are composed of muddy, low calcareous and terrigenous materials deposited under reducing conditions. Post-depositional processes included the formation of pyrite and glauconite, as well as, an upward-depletion of manganese concentration in the sediment column. The grain size composition of the sediments reflects different conditions of deposition in the topography and hydrography of the two bays. The sediments from core EB are more clayey than those of core GB. Upward changes in the mean grain size values in both cores are attributed to increased coastal erosion. Quartz, clay minerals (illite, smectite, chlorite, kaolinite, mixed-layers), feldspars (K-feldspar, plagioclase), carbonates (calcite, aragonite, dolomite), and to a lesser degree, micas and heavy minerals constitute the main sedimentary components. No significant down-core trend of change in the mineralogical composition of the sediments could be detected. This suggests rather uniform depositional conditions during the time period represented by the cores. The concentrations of SiO_2 , Al_2O_3 , Fe, CaO, MgO, TiO_2 , Na_2O , K_2O , P_2O_5 , Mn, Ba, and Sr were found comparable with those of average sedimentary rocks.

Riassunto. Sono state effettuate analisi granulometriche, chimiche e mineralogiche di dettaglio su 115 campioni di sedimenti, tardo olocenici, provenienti da due carote prelevate rispettivamente nelle Baie di Eckernförder (EB) e di Geltinger (GB). I sedimenti sono costituiti da materiali fangosi e terrigeni a basso contenuto di carbonati depositatisi in condizioni riducenti. La presenza di pirite e glauconite è imputabile a processi post-deposizionali così come la diminuzione della concentrazione del manganese nei sedimenti più recenti. La variazione della granulometria nei sedimenti è indice delle diverse condizioni deposizionali dettate dalla topografia e dall'idrografia delle due baie. I sedimenti provenienti dalla carota EB sono più argillosi di quelli della carota GB. Ulteriori variazioni della granulometria nei sedimenti in entrambe le carote è da imputare ad un incremento dell'erosione costiera. I principali componenti sedimentari sono costituiti da: quarzo; minerali argillosi (illite, smectite, clorite, caolinite); feldspati (K-feldspato, plagioclas); carbonati (calcite, aragonite, dolomite) e, in minor misura, miche e minerali leggeri. Non è stata individuata alcuna variazione significativa nella composizione mineralogica dei sedimenti più antichi. Questo fatto suggerisce la permanenza di condizioni deposizionali piuttosto uniformi durante il periodo rappresentato dalle carote. È stato riscontrato che i valori delle concentrazioni di SiO_2 , Al_2O_3 , Fe, CaO, MgO, TiO_2 , K_2O , P_2O_5 , Mn, Ba e Sr sono comparabili con i tenori medi delle rocce sedimentarie.

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1. Introduction

The Baltic Sea is an epi-continental brackish sea located in a humid climate. Its western part (the Mecklenburg, Lübeck, and the Kiel Bays) forms the so-called Belt Sea or western Baltic Sea (Fig. 1). The greater Kiel Bay area can further be divided into Flensburger Fjord (including Geltinger Bay), the Schlei, Eckernförder Bay, and Kieler Förde (Fig. 1).

The geological evolution of the western Baltic Sea and its coastal zones has been investigated by several authors (e.g. Köster 1961; Gripp, 1964, 1971; Horn, 1965; Edgerton et al., 1966; Seibold et al., 1971; Glückert, 1973; Prange, 1978). These studies clearly show that the present coastal morphology of the Kiel Bay was largely shaped du-

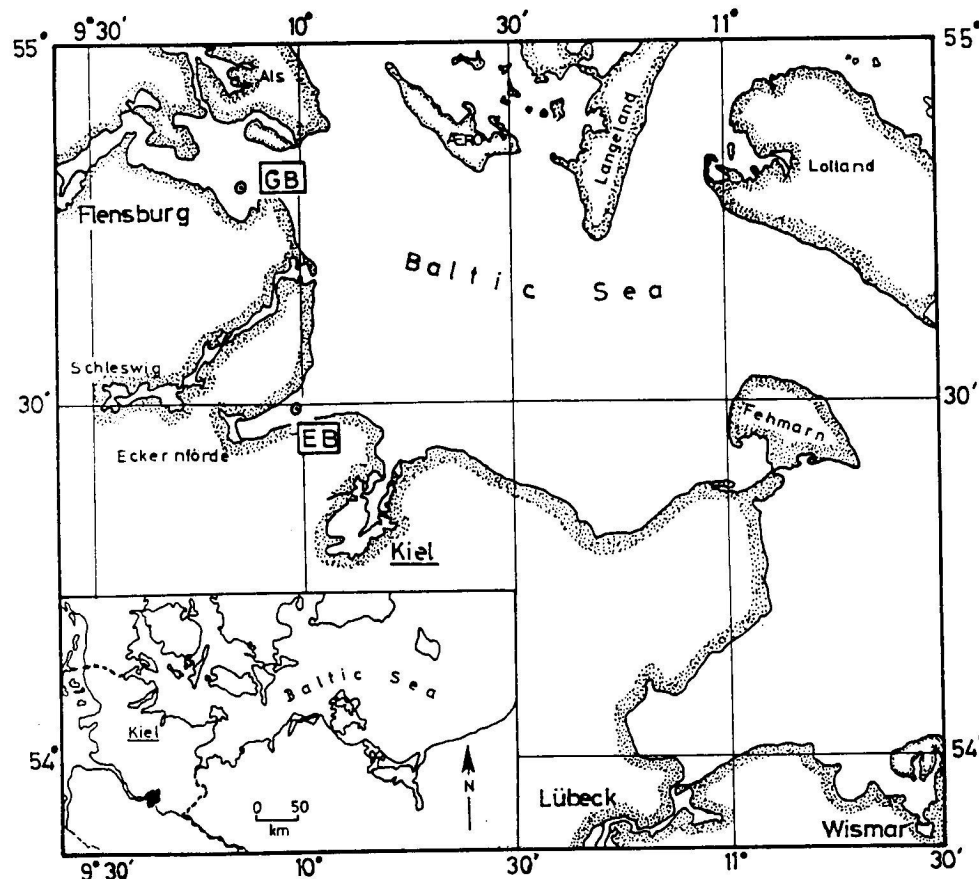


Fig. 1 — Map of study area showing the two coring stations in the western Baltic Sea. EB=Eckernförder Bay (EB), and GB=Geltinger Bay.

ring the last glacial period. The moraines (Pleistocene till), which cover the sea-floor and its surrounding coastal cliffs over a Tertiary basement, are considered the main source of sediment supply to the western Baltic Sea including the Kiel Bay. The bottom sediments of the Kiel Bay with respect to various hydrographic conditions are described by several authors (Groschopf, 1938; Pratje, 1948; Jarke, 1951; Brand, 1955; Seifert, 1955; Schlichting, 1960; Barner, 1965; Walger, 1966; Lüneburg, 1971; Seibold et al., 1971; Exon, 1972; Healy and Wefer, 1980).

Biogenic and organic components of the Kiel Bay sediments are discussed by Köhlmorgen-Hille (1963), Schwenke (1964), Lutze (1965, 1974), Zeitzschel (1965), Arntz (1971), Seibold et al. (1971), Exon (1972), Horstman (1972), Bansemir and Rheinheimer (1974), Arntz et al. (1976).

Some geochemical data from the western Baltic Sea sediments, particularly, those associated with iron and manganese concretions were presented by Hartman (1964) and Djafari (1977). More recent studies have been concerned with the impact of environmental stress and the extent of pollution in the Baltic Sea (Erlenkeusser et al., 1974; Kuijpers, 1974; Suess and Erlenkeusser, 1975; Brüggman et al., 1980; Müller et al., 1980).

In this paper, a detailed description of the types and modes of distribution of the late Holocene sediments from the western Baltic Sea is presented, and the relationships

5° between sediment composition, and various topographical and hydrographic conditions are discussed.

2. Methods and materials

During the cruises of the R/V "Senckenberg" in the western Baltic Sea in July 1978, two vibrohammer cores of Holocene sediment, 202 and 258 cm in thickness, were taken in the Eckernförder (21 m water depth) and the Geltinger (20 m water depth) Bays (Fig. 1). After visual examination the cores were then subdivided at 2 cm intervals and stored frozen in plastic bags.

A total of 115 samples were used for the following determinations: grain size; x-ray bulk and clay mineralogy; major elements (Si, Al, Ti, Fe, Mn, Ca, Mg, Na, K), and Sr and Ba; and heavy and light minerals.

For grain-size determination, bulk samples were divided into three fractions: clay (<0.002 mm ϕ); silt (0.002 - 0.063 mm ϕ), and sand (>0.063 mm ϕ) (according to Müller, 1964).

Heavy and light mineral grains were separated by standard petrographic techniques described elsewhere (Ergin, 1982).

For the bulk mineralogy, untreated and homogenized samples were dried at 50 - 60°C , powdered, and analyses done with a Phillips x-ray diffractometer under the following conditions: $\text{CuK}\alpha$ -radiation, nickel filter, 36 kV/ 24 mA, and 1° beam slit. Goniometer speed was $0.5^\circ = 2^\circ/\text{min}$. All samples were X-rayed from 2 to $65^\circ = 2^\circ$. The paper speed, scale, and time factor were chosen to produce optimum results. The semiquantitative estimates of mineralogy by XRD were obtained using the method of Rex and Murray (1970). This method is based on multiplying of factors by the measured peak heights for each individual mineral and summing these to 100 percent.

For the clay mineralogy, finer fractions less than 0.002 mm in size were separated from the bulk sample and smeared onto glass slides, and then x-rayed under the following conditions: untreated (air-dried) (2 - $30^\circ/2^\circ$); glycolated (2 - $15^\circ/2^\circ$); heated 250°C (2 - $15^\circ/2^\circ$); and heated 550°C (2 - $15^\circ/2^\circ$). Semiquantitative determinations were made by multiplying the peak area (determined planimetrically) with the factors of Biscaye (1965) and the sum of these was 100 percent.

To determine the concentrations of Si, Al, Fe, Mn, Ca, Mg, Na, K, Ti, Ba, and Sr, a fraction of the bulk sample was fused with $\text{Li}_2\text{B}_4\text{O}_7$ at 950°C , and the melt dissolved by 10% HNO_3 -solution and analyzed by a Beckmann 1288 Atomic Absorption Spectrometer following the procedures of Ingamels (1970), and Bock (1972). P was analyzed with a spectrophotometer after digestion of the bulk sample with molybdivanadophosphoric acid complex, according to Shapiro and Brannock (1962).

3. Results and discussion

The results of textural, mineralogical and chemical analyses are summarized in Figs. 2 to 10, and Tables 1 to 6.

3.1. Grain size distribution

The average grain size distribution is 32% clay, 66% silt, and 1% sand in core EB; and 21% clay, 61% silt, and 17% sand in core GB (Table 1).

A plot of the relative percentages of sand, silt, and clay fractions of sediments in the cores EB and GB (Fig. 2) reveals that the Geltinger Bay sediments contained more sand portion than the sediments of the Eckernförder Bay. This can largely be attributed to the different hydraulic regime in the two bays (Ergin, 1982). As has been reported by numerous authors (e.g., Seibold et al., 1971; Exon, 1972), the wind-generated wa-

Table 1 — Grain size parameters of late-Holocene core sediments from the Eckernförder (EB) and Geltinger (GB) Bays. Results are given in percent except for median grain size in μm (10^{-3} mm). S.D. = Standard deviation.

Grain size	Core	Mean	Range	S.D.
CLAY	EB	32	24-42	3,8
	GB	21	9-33	5,3
SILT	EB	66	56-75	4,0
	GB	61	45-69	—
fine	EB	26	17-29	—
	GB	19	13-25	—
medium	EB	27	20-47	—
	GB	20	12-27	—
coarse	EB	13	9-19	—
	GB	22	14-26	—
SAND	EB	1	<1-3	0,7
	GB	17	8-44	5,7
MEDIAN	EB	4	3-7	0,8
	GB	12	5-48	6,0

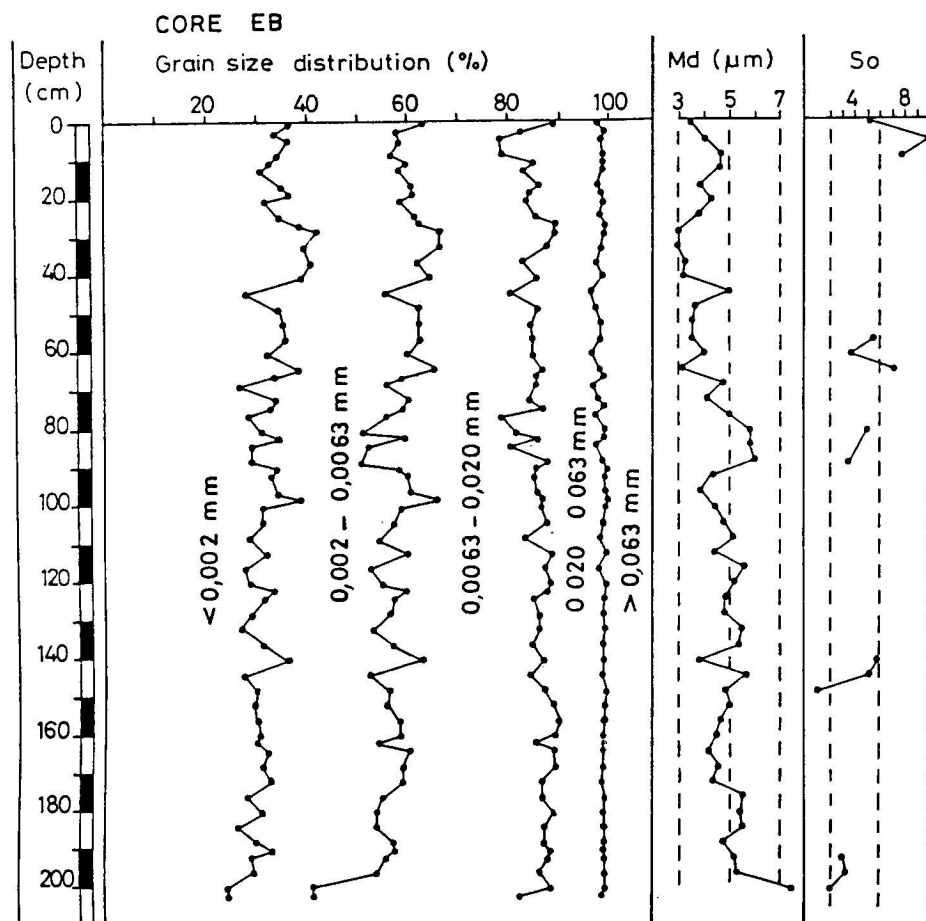


Fig. 3 — Grain size distribution in core EB. Note the upward-decreasing median grain size (Md) values (fining-upward) and the worsening of sorting.

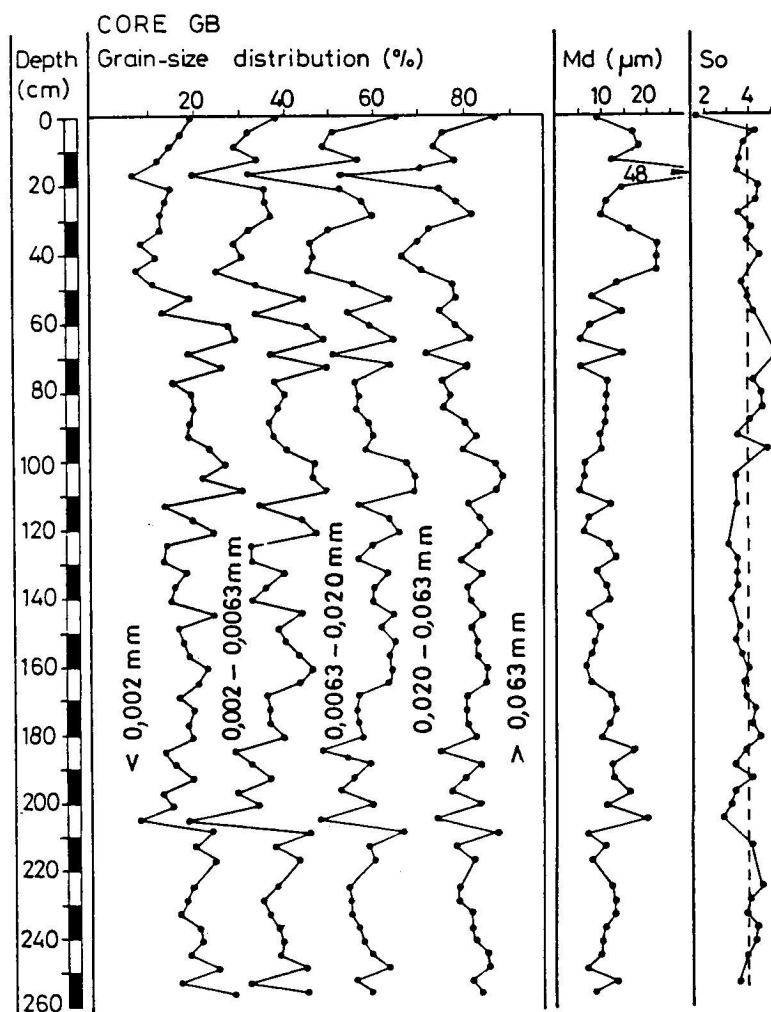


Fig. 4 — Grain size distribution in core GB. Note the overall poor sorting and the upward-increasing median (Md) values (coarsening-upward).

which corroborates the comparably high-energy regime prevailing in the Geltinger Bay waters. Moreover, in core EB, as the sediments become finer grained, their sorting deteriorates.

Although sediment colour varies, when moist, clay-rich sediments of the core EB are typically dark greenish gray. Slightly lighter colours are common in more sandy sediments of core GB, ranging from gray to greenish gray. In general, the sediment colours reflect more or less the state of reduction.

3.2. Bulk and clay mineralogy

Quartz, clay minerals, feldspars, micas, and carbonates constitute up to 90% of the mineral assemblages in both cores (Figs. 6 and 7, Table 2). The quartz content averages 50% in core EB and 57% in core GB. The feldspar (mostly microcline, orthoclase and albite) contents are on the average 17% in core EB and 19% in core GB, whereas the K-feldspar/plagioclase ratio is around 0,9 in both cores (Fig. 8). The quartz/feldspar ra-

Table 2 — X-ray bulk mineralogy of late-Holocene core sediments from the Eckernförder (EB) and Geltinger (GB) Bays. Results are given in percent. Note the clay mineralogy = 100%. *) Illite-Smectite Mixed Layered clay minerals. **) Quartz/Feldspar, and K-Feldspar/Plagioclase ratios. S.D. = Standard deviation.

Minerals	Core	Mean	Range	S.D.
QUARTZ	EB	50	39-59	3,7
	GB	57	42-75	6,4
CLAY	EB	32	24-42	3,8
	GB	21	9-33	5,3
Illite	EB	57	49-66	3,9
	GB	55	44-61	4,4
Smectite	EB	20	11-29	4,9
	GB	21	17-35	4,0
Il-Sm Mx Ly*	EB	2	<1-8	2,6
	GB	7	<1-12	4,7
Chlorite	EB	9	7-11	1,2
	GB	7	6-9	0,9
kaolinite	EB	11	8-14	1,7
	GB	8	7-12	1,3
FELDSPARS	EB	17	10-26	3,4
	GB	19	10-29	4,1
K-feldspar	EB	8	4-15	2,2
	GB	9	3-15	2,3
Plagioclase	EB	9	5-13	1,7
	GB	9	4-17	2,6
Qtz/Fsp**	EB	3	2-5	0,7
	GB	3	1-5	0,9
Kfs/Plag**	EB	<1	<1-2	0,2
	GB	1	<1-2	0,2
CALCITE	EB	<1	<1-8	1,6
	GB	<1	<1-16	2,0
DOLOMITE	EB	<1	<1-3	0,7
	GB	<1	<1-3	0,4
ARAGONITE	EB	<1	<1-9	n.d
	EB	n.d	n.d	n.d

tio is approximately 3 in both cores (Fig. 8).

In general, both quartz and feldspar as well as quartz/feldspar and K-feldspar/plagioclase ratios show nearly constant values throughout the cores. This is an indication that the feldspars were not significantly altered by weathering or diagenesis, although feldspar grains are usually less stable than quartz in terms of abrasion and dissolution in many marine sediments (e.g. Passaretti and Eslinger, 1987).

In spite of their primary origin from the Scandinavian Shield (where various kinds of rocks of different geologic ages occur), the sediments in the studied cores indicate no major compositional changes in the adjacent land areas (glacial till). Of course, mineralogical modal analysis from the greater Baltic Sea area may possibly reflect several sedimentary provenances, as proposed for other regions (Saccani, 1987).

Dolomite is the most frequently occurring carbonate mineral having an average of about 1%, but calcite and aragonite reach quantities of up to 10% in certain intervals (Figs. 6 and 7). Calcite and aragonite are mainly derived from the remains of benthonic organisms (e.g. pelecypods and foraminifers). In contrast, dolomite grains are generally detrital. Total carbonate contents of the sediment usually reflect the relative abundance of the carbonate minerals (Figs. 6 and 7).

Clay minerals make up an average of about 28% and 19% (on quartz free basis) of the bulk mineral suite in cores EB, and GB, respectively. The average relative abundances of the main clay mineral groups are 57%, and 55% illite; 20%, and 21% smectite (expandable); 11%, and 9% kaolinite; 9%, and 7% chlorite; and 2%, and 7%

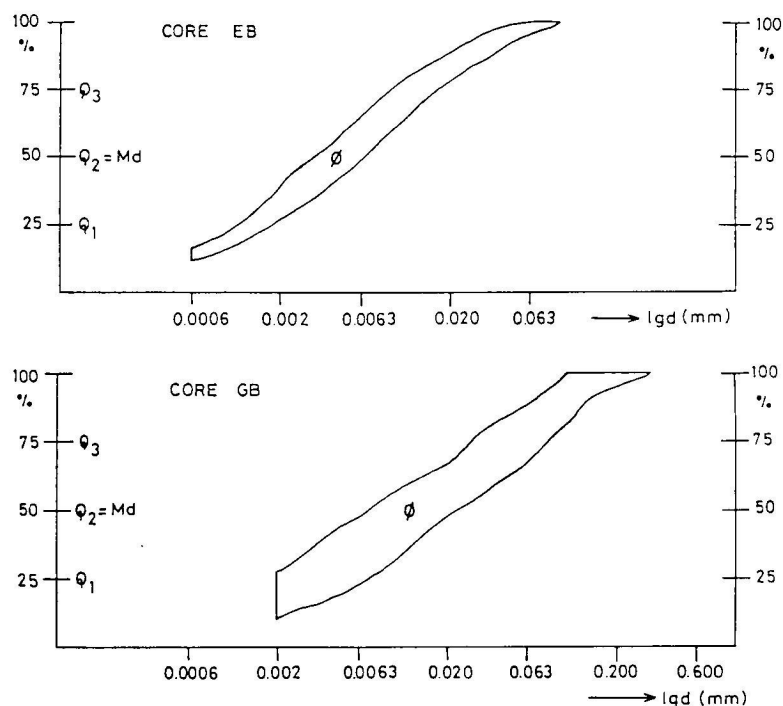


Fig. 5 — Diagram showing upper and lower boundaries of cumulative percentage curves (plotted on an arithmetic scale) of sediments from cores EB (above) and GB (below). Note that the sediments are composed of grains of various different sizes and according to the degree of admixture of these grades, they may be termed as poorly sorted deposits.

illite-smectite-mixed layer (expandable) clay minerals in cores EB, and GB, respectively (Table 2).

Downcore distributions of the contents of individual clay minerals as well as the ratios of illite/smectite and chlorite/kaolinite show no major trend with depth in the cores (Fig. 8). This suggests limited diagenetic changes of the clay mineral assemblages. Some fluctuations in the illite/smectite ratio particularly in core GB can be explained in terms of variations in the grain size distribution. Furthermore, the crystallinity index for smectite (v/p ratio) was almost constant throughout both cores (Fig. 8).

As shown in Table 3, the mineral constituents of the sediments vary in harmony with the average mineral compositions of Pleistocene tills from the surrounding land areas, which are considered to act as the major terrigenous source of sediment supply in the Kiel Bay.

From this data, it can be concluded that no significant changes in the sources of sediment supply have occurred in recent times. The slight fluctuations throughout the cores can be satisfactorily explained in terms of variations of terrigenous-biogenic admixtures.

3.3. Other constituents

The low sand content of the sediments made it difficult to investigate the heavy mineral compositions of the cores. Amphiboles (hornblende), garnet (spessartine, almandine), pyroxene (augite), epidote, rutile, apatite, magnetite, and ilmenite were the common heavy minerals which could be recognized in the coarse fractions (> 0.063 mm ϕ). The concentrations of heavy minerals reached a maximum relative abundance level of 5%,

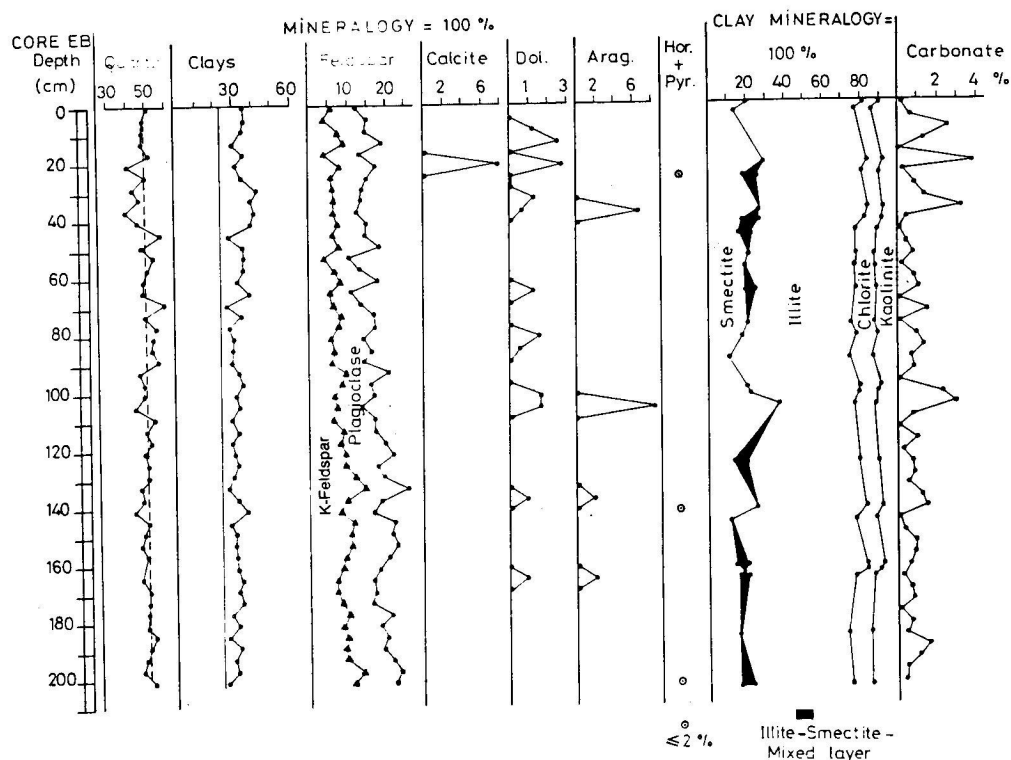


Fig. 6 — X-ray bulk and clay mineralogy of sediments in core EB. Carbonate content was determined wet-chemically and expressed as %CaCO₃.

being lower (<2%) in core EB.

Micas (biotite, muscovite, and chlorite) were also determined in silt and sand fractions of sediments, but their concentrations were usually less than 2-3% of the bulk samples.

In most samples, pyrite was present throughout the cores in the form of irregular grains, as casts and replacements of burrows and often as framboids. However, it constitutes less than 1% of the bulk of the sediments. Occurrences of iron sulphides indicate reducing deposition conditions. This is also evident from H₂S development in the bottom waters of the studied areas in summer. The relatively high organic carbon contents of the sediments (avg. 6% C_{org}; Ergin, 1982) suggests that the iron sulphides are the product of the oxidation of organic matter by microbially mediated sulphate reduction (Stumm and Morgan, 1981).

Minor occurrences of green and earthy appearing glauconite pellets were observed

Table 3 — Comparison of principal mineral composition of the two studied cores (EB and GB) with that of Pleistocene till from the western Baltic Sea surroundings (Seibold et al., 1971; Heyde-man and Müller-Karch, 1980).

Mineral	Core EB	Core GB	Pleistocene till
Quartz	50	54	40-90
Feldspars	17	17	5-20 (plus micas)
Clay minerals	32	27	0-7
Carbonates	1	1	0-50

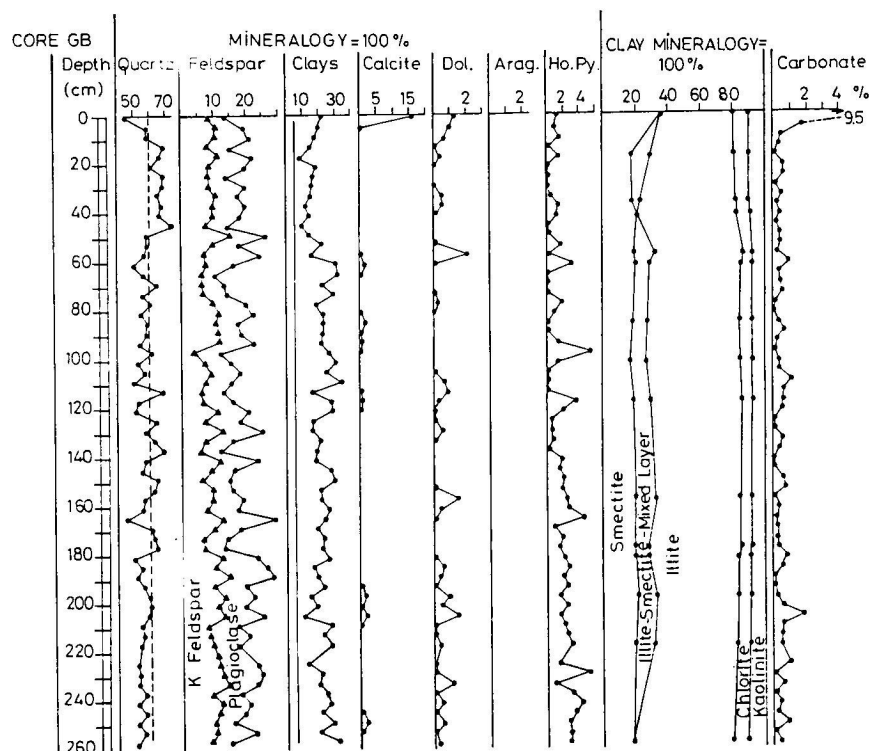


Fig. 7 — X-ray bulk and clay mineralogy of sediments in core GB. Carbonate content was determined wet-chemically and expressed as %CaCO₃.

throughout the cores, particularly in the coarse-grained fractions. In addition, glauconite was present as infill of foraminifer chambers, as well as coating on pre-existing quartz grains. Glauconite comprises less than 1% of the sediment bulk. Authigenic glauconite, like that of iron sulphides, can be used as an index mineral to provide information regarding the deposition environment. For example, glauconitization in shallow marine sediments may be favoured by slightly reducing conditions in a microenvironment (Odin and Letolle, 1980), where organic participation and anaerobic bacteria are also involved (Fairbridge, 1983).

Opaline silica from the remains of diatoms, radiolaria and sponges is another form of silicate present in the sediments (less than 1%).

Rock fragments from different types of source (transported as moraines from Scandinavia) can be identified in the coarse-grained sand fractions. They are basically flintstones, slates, mica and chlorite schists. They constitute up to 2% of the sediments.

Table 4 — Major sedimentary constituents of the two late-Holocene cores (EB and GB).

Allochthonous

Terrigenous constituents:

Quartz, feldspars, clay minerals, micas, dolomite, heavy minerals, rock fragments

Anthropogenic constituents:

Coal and slag particles

Autochthonous

Calcite, aragonite, opal, pyrite, glauconite

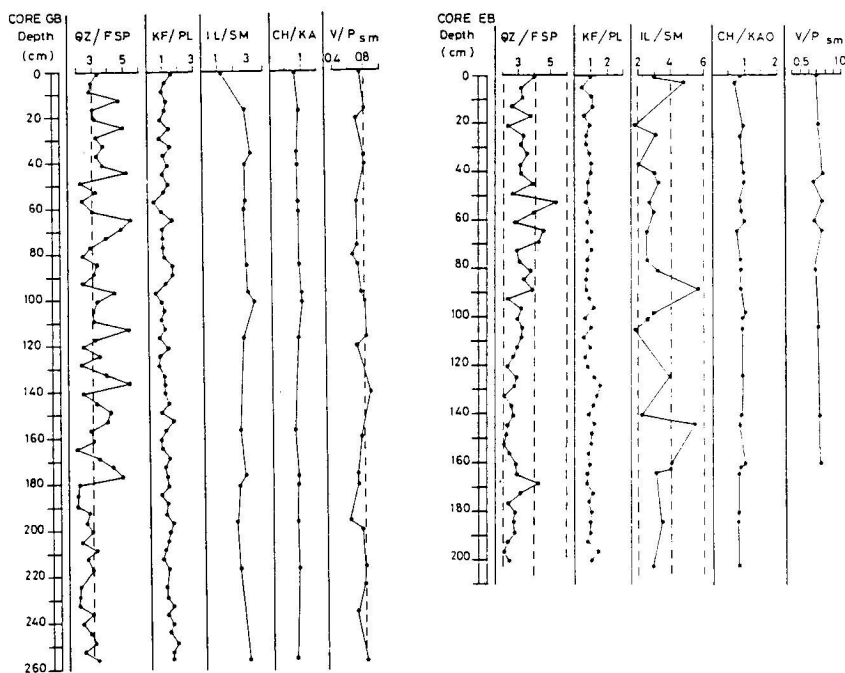


Fig. 8 — Quartz/feldspar-, K-feldspar/plagioclase-, illite/smectite-, and chlorite/kaolinite-ratios, as well as crystallinity index of smectite (v/p ratio; after Biscaye, 1965) of sediments in the cores EB and GB.

Table 5 — Chemical compositions of late-Holocene sediments from the cores EB and GB. Results are given in percent except for Mn, Ba, and Sr in ppm; S.D. = Standard deviation.

Element	Core	Mean	Range	S.D.
SiO ₂	EB	55,80	43,80-64,10	4,4
	GB	63,20	54,50-77,50	4,5
Al ₂ O ₃	EB	10,80	9,91-12,37	0,65
	GB	8,65	7,78-10,86	0,49
TiO ₂	EB	0,63	0,53-0,73	0,04
	GB	0,49	0,36-0,67	0,07
Fe (total)	EB	3,89	3,55-4,12	0,13
	GB	2,52	2,05-3,25	0,24
Mn	EB	790	468-1562	198
	GB	299	180-500	65
MgO	EB	1,79	1,65-1,99	0,07
	GB	1,06	0,68-1,59	0,17
CaO	EB	1,55	1,04-3,11	0,46
	GB	1,07	0,52-4,95	0,58
Na ₂ O	EB	0,88	0,76-0,96	0,03
	GB	0,87	0,73-1,03	0,07
K ₂ O	EB	2,54	2,34-2,68	0,09
	GB	2,11	1,86-2,34	0,09
P ₂ O ₅	EB	0,26	0,22-0,35	0,02
	GB	0,23	0,15-0,30	0,03
Ba	EB	246	202-298	21
	GB	212	174-366	25
Sr	EB	58	30-78	9
	GB	42	28-105	11

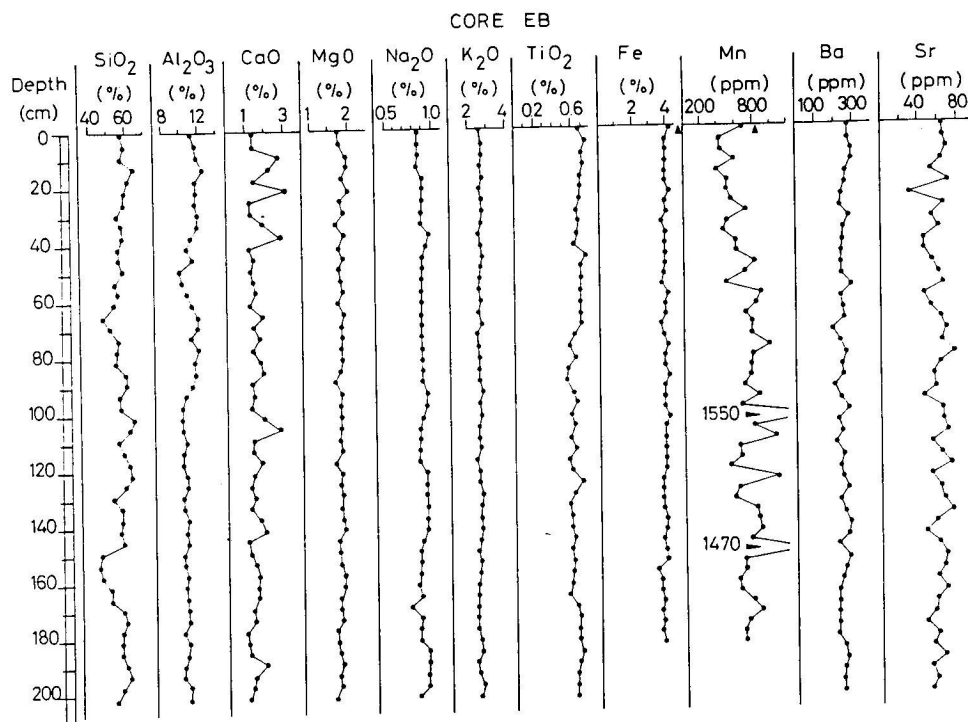


Fig. 9 — Chemical composition of sediments in core EB.

Coal and slag particles, usually of anthropogenic origin, are also found in the upper 20 cm sections of the cores. Their contents are less than 1%, but locally they may represent as much as 3% in the bulk samples.

In summary, the mineralogy of the sediments in the western Baltic Sea is determined largely by the detrital origin of the inorganic materials (allochthonous, including anthropogenic substances) with a lower amount of biogenic and authigenic materials (autochthonous) (Table 4).

Table 6 — Comparison of chemical data from the two late-Holocene sediment cores of this study (EB and GB) with that of average shale, limestone and sandstone (Turekian and Wedepohl, 1961). Results are given in percent except for Mn, Ba, and Sr in ppm.

	Shales	Limestones	Sandstones	Core EB	Core GB
SiO ₂	58,9	5,13	70,0	55,8	63,2
Al ₂ O ₃	16,7	0,8	8,3	10,8	8,65
TiO ₂	0,76	0,06	0,58	0,63	0,49
Fe (tot.)	4,7	0,38	0,98	3,89	2,52
Mn	850	1100	50	790	299
MgO	2,6	7,79	1,9	1,79	1,06
CaO	2,2	42,29	4,3	1,55	1,07
Na ₂ O	1,6	0,05	0,58	0,88	0,87
K ₂ O	3,6	0,32	2,1	2,54	2,11
P ₂ O ₅	0,2	0,09	0,1	0,26	0,23
Ba	580	10	170	246	212
Sr	300	610	20	58	42

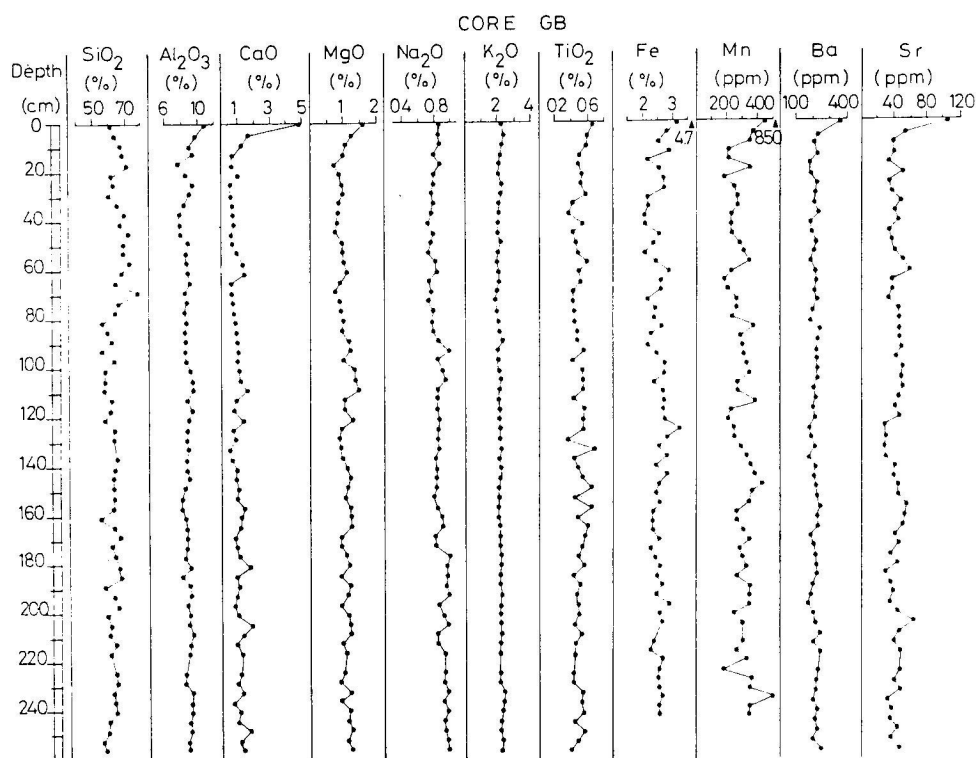


Fig. 10 — Chemical composition of sediments in core GB.

3.4. Sediment bulk chemistry

Mean and range values of the major elements or their oxides, respectively are listed in Table 5.

As shown in Figs. 9 and 10, there is very little change in the abundances of elements throughout the entire sedimentary section. Elevated SiO_2 -contents imply the presence of relatively high quartz percentages in the sediments. Al_2O_3 concentrations suggest the clay minerals to be the most important Al-associations controlling the distribution of Al along the cores. CaO , Sr and to some extent, MgO profiles usually follow the carbonate profiles (calcite, aragonite and dolomite). Na_2O contents are probably due to the presence of feldspars, whereas the K_2O concentrations should reflect close associations with the clay and mica minerals as well as with the feldspars.

The upward decreasing Mn contents in the upper core intervals of EB (Fig. 9) indicate diagenetic alterations (e.g. changes in the redox conditions) of the sediments. This is in good agreement with the fact that the deep waters of the Eckernförder Bay contain high concentrations of Mn (Djafari, 1977).

It can be concluded that the majority of the element concentrations presented here reflect the primarily terrigenous-detrital origin of the sediments. Biogenous input is predominately represented by opaline silica, and carbonates (calcite, aragonite). The variations in the elemental compositions of sediments are attributed to the variations in the relative abundances of their mineralogic compositions. This conclusion is also supported by a comparison of the chemical data of this study with those from average sedimentary rocks, such as shales, limestones and sandstone (Table 6). These lithologies are believed

to be the counterparts of muddy, calcareous, and sandy sediments with respect to their mineralogical compositions.

4. Conclusions

Carbonate poor, terrigenous muddy sediments at the two coring sites were mainly deposited under reducing conditions. Diagenetic minerals throughout both cores include pyrite and glauconite.

Differences in the hydrodynamic conditions of the two coring sites are related to the variations in sediment composition, being more clayey in EB and more sandy in GB. The increasing and decreasing mean grain sizes in the cores are the effects of the extent of coastal erosion.

The bulk mineralogical compositions of the sediments can be explained in terms of the admixture of terrigenous and biogenous materials represented by quartz, clay minerals (illite, smectite, chlorite, kaolinite, and illite-smectite-mixed layers), feldspars (both K-feldspar and plagioclase), carbonates (calcite, aragonite, dolomite), and minor amounts of micas and heavy minerals. The uniform distribution of the terrigenous minerals down the cores suggest no major changes in the source of materials transported into the bays.

The bulk chemical composition of the sediments varies in sympathy with the minerals identified, and shows similarity to those from average sedimentary rocks. Slightly upward-decreasing Mn contents of the sediments in core EB is probably due to diagenetic manganese remobilization as a result of the different redox conditions within the sediment column.

In addition to the allochthonous materials derived from the surrounding land, various kinds of anthropogenic substances (e.g., coal and slag fragments) were found to be particularly concentrated in the upper parts of the cores.

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