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Comprehensive lithostratigraphic, geochemical and petrophysical investigations on the indicator core sample of Late Quaternary deposits from the Gdańsk Basin

The core comprises deposits of the Baltic Ice Lake and four Early Holocene lake basins (Yoldia I, Yoldia II, Older Ancylus and Younger Ancylus, including the Mastogloia Phase) as well as marine deposits of Litorina and Postlitorina Sea. Observed changes of lithologic, geochemical and petrophysical parameters reflect main paleogeographic conditions and evolution of Baltic basins, from the Baltic Ice Lake period till the contemporary sea basin. Changes of grain size composition and lithostratigraphic data indicate that in the region described marine sedimentation continued during last 11 thousand years without interrupting. The deposits have been subdivided according to their physical and chemical properties; the composition of the sorption complex depends on physical and chemical properties of the environment and informs about conditions of sedimentation. Accumulations of autigenic iron sulphides and phosphates as well as barium sulphates are related to geochemical barriers which depend on pH and Eh values.

A 6.22 m long indicator core sample was taken from the board of scientific-research ship *Akademik Kurczatow* during her 44th mission in the deep (100 m) northern section of Gdańsk Basin (Fig. 1). Due to obtained lithostratigraphic palynologic data the sampled deposits have been subdivided into Late Pleistocene and Holocene suites (Fig. 2).

A Late Pleistocene section (lithostratigraphic complex of the Baltic Ice Lake — LSK IV by A. I. Blazhchishin, 1985; A. I. Blazhchishin et al., 1987) comprises red coloured, striped (including microbeddings) and homogenous clays in places with admixture of glacier material. The lower section of LSK IV (622—586 cm) contains inclusions of colloidal iron sulphide-hydrotroilite and is reffered to Alleröd interval according to pollen data. The upper section of LSK IV (586—518 cm) contains a stadial-type pollen assemblage (Upper Dryas).

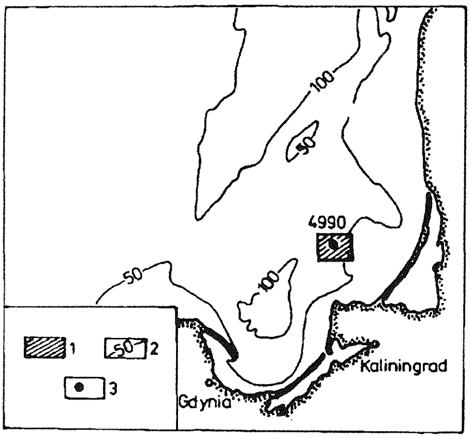


Fig. 1. Operation area

1 — location of investigated area; 2 — isobath (in meters); 3 — location of investigated core sample and number of research station

Schemat rejonu prac

1 — lokalizacja obszaru badawczego; 2 — izobaty (m); 3 — lokalizacja badanego rdzenia i numer stacji

A specific intercalation of bedded dark clay containing hydrotroilite (which is an indicator mineral of the central Baltic Sea; see A. I. Blazhchishin, 1985) was found in the layer described. The Pleistocene-Holocene boundary is found in the middle of the column, close to the intercalation with microconcretions of barite. They were formed due to processes of exchange during diffusion of SO_4^{2-} ions from the Holocene layer. It is worthy of notice that the microconcretions occur at the geochemical barrier which is recognizable due to change of Eh value.

The Holocene layer consists of lacustrine (LSK V) and marine (LSK VI) complexes. The Lower Holocene lacustrine complex is mostly complicated and there are three clay sequences in it.

Red coloured deposits of Lower Preboreal (Yoldia I) are built of homogenous clays (bottom) and bedded clays at the top (518—414 cm). Above there is a sequence of spotted gray clays with colloidal iron sulphides (414—318 cm) containing two horizons of hydrotroilite at the bottom. This layer represents the upper interval of Preboreal (Yoldia II) and the lower part of Boreal (Ancylus). Beneath the upper hydrotroilite horizon there is a layer with black, soot-like microconcretions of greigite type sulphides. Similarly to barite occurrence their appearance is connected with abrupt Eh change. Within deposits cored in the vicinity of the research station ST 4978 there are phosphate microconcretions in the same depth interval.

The third section of LSK V (318—205 cm) is represented by pyritized gray clays with admixture of colloidal matter of diagenetic origin. The clays are of typical flazer structure caused by diagenesis. The layer is referred to the Upper Boreal (Late Ancylus and Mastogloia Phase).

The Holocene marine complex (LSK VI) is composed of homogenous sapropelic clays with two horizons of microbedded sapropels (205 — 0 cm). According to palynologic data the layer has been subdivided into Atlantic and Early Subboreal periods (Litorina Sea). The upper interval (Postlitorina Sea) consists of homogenous bioturbated clays and is referred to Late Subboreal — Subatlantic Period basing on the results of pollen analysis.

Microbedded sapropels contain up to 7% of organic coal and are typical of Late Atlantic and Early Subboreal.

All changes of lithologic, petrophysic and geochemical properties of cored deposits reflect geological processes and evolution of Late Quaternary Baltic basins.

As inferred from grain size distribution and lithostratigraphic data the sedimentation in marine basin was uninterrupted during late- and postglacial period. Deposits are entirely clayey and the rate of sedimentation was rather low in comparison with the southern Gdańsk Deep.

High dispersion of deposits (about 90% of pelite including 50—55% of subcolloidal matter) is typical of Baltic Ice Lake, Yoldia Sea as well as early phase of Ancylus Lake.

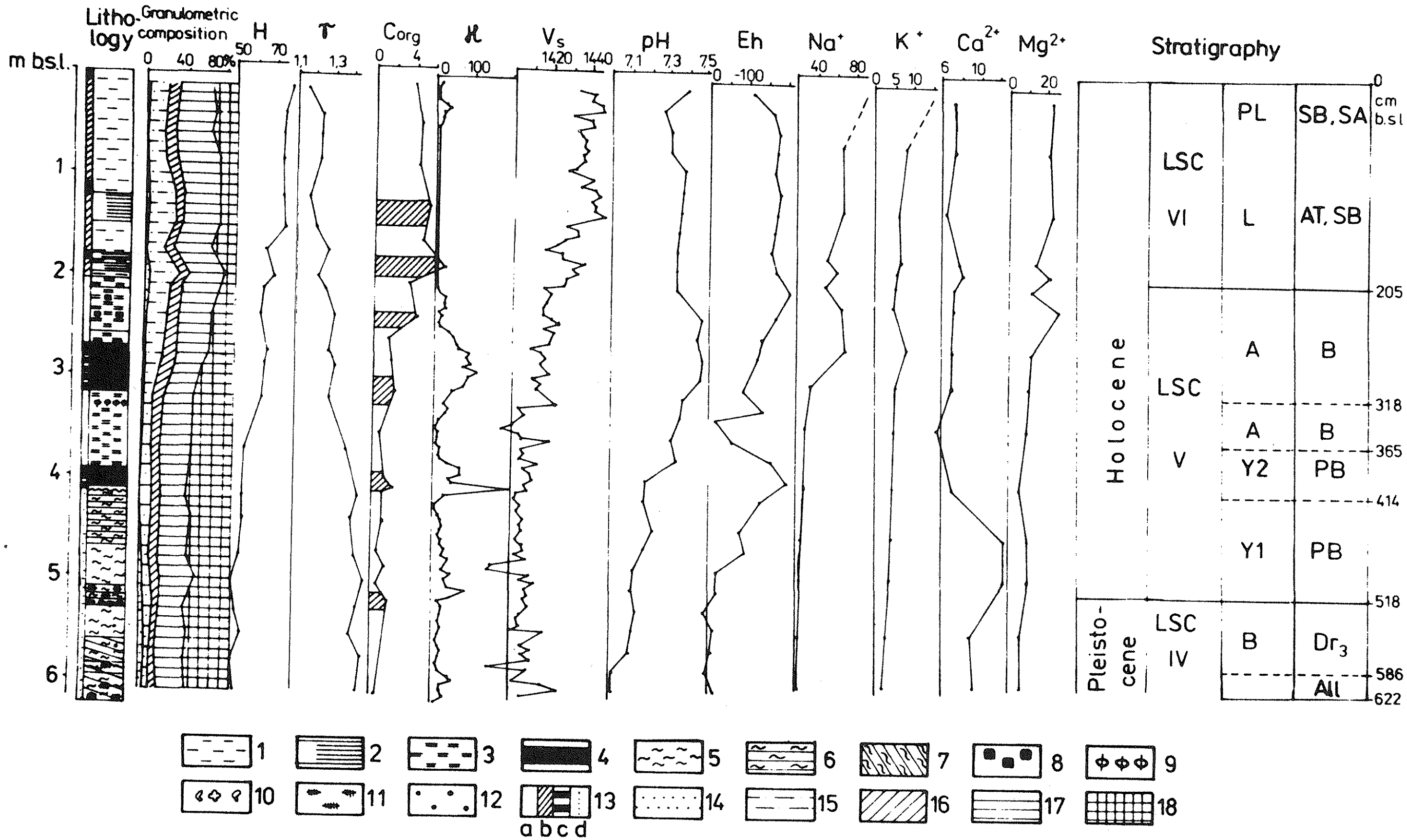
Unlike Holocene deposits, late glacial sediments contain remarkable amount of coarse grains and sandy material of glacier or eolian origin. At the bottom of the Early Holocene layer grain size becomes slightly bigger (regression of Baltic Ice Lake), and at the boundary of Yoldia I and Yoldia II there is a sedimentary gap represented by a folded horizon.

Beginning with the declining of Anylus Lake phase remarkably coarser material was subjected to deposition (especially within marine Holocene deposits). Subcolloids attain merely 30—35% and fine aleurites (silt) content increases to 20—30%. According to granulometric data the transgression of Litorina Sea is distinctly recorded.

Core deposits become naturally more dense with depth and their composition changes. Sapropelic clays of marine Holocene are of minimum density (1.16—1.22 g/cm^3) and of maximum humidity and porosity (65.5—80 and 75—91% respectively). At the bottom of sampled deposits density increases to 1.40—1.46 g/cm^3 but humidity and porosity decrease to 51—55 and 73.5—74% respectively.

Considerable changes of mention petrophysical properties were found in Middle Holocene sequence (Litorina), at the horizon of Ancylus Lake regression and at the boundary between Lower and Upper Preboreal (Early and Late Yoldia). These horizons appear even more distinctly in sound speed records which range from 1430—1447 km/s in Late Holocene clays to 1390—1410 km/s in the lower part of the sequence. Moreover the boundary between Lower and Middle Holocene as well as at the sequence of striped (microbedded) clays of Baltic Ice Lake which occurs below the Holocene bottom limit are clearly recognizable on the same sound speed curve. The latter one does not appear in acoustic records.

Magnetic susceptibility recording is also useful in subdividing Quaternary deposits. Minimum κ values ($1\cdot10^{-5}$—$5\cdot10^{-5}$ units) are characteristic of marine Holocene clays of low density which are enriched in organic matter while small peak of κ (14.36 units) is caused by occurrence of sulphides found in other cores from sapropelic deposits, A. I. Blazhchishin (1985). The highest values of magnetic susceptibility (10—30 units) have been recorded in Early Holocene and late glacial clays. There are few peaks of κ ($100\cdot10^{-5}$—$200\cdot10^{-5}$ units) which are caused by the occurrence of manganese sulphide. They are mainly related to both upper and lower horizon of hydrotroilite as well as to intercalations of dark clay at the boundary of the Upper Dryas and Preboreal.


m b.s.l.
Litho-logy
Granulometric composition
0 40 80%
H
50 70
ϒ
1,1 1,3
Corg
0 4
ℵ
0 100
Vs
1420 1440
pH
7,1 7,3 7,5
Eh
0 -100
Na+
40 80
K+
0 5 10
Ca2+
6 10
Mg2+
0 20
Stratigraphy
1
2
3
4
5
6
0
cm b.s.l
205
318
365
414
518
586
622
Holocene
Pleisto-cene
LSC VI
LSC V
LSC IV
PL
L
A
A
Y2
Y1
B
SB, SA
AT, SB
B
B
PB
PB
Dr3
All
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Microconcretions of sulphides separated from the Upper Holocene deposits are of high magnetic susceptibility which varies from 49 to 90 thousand units.

According to the results of Mössbauer spectrometry the sulphides contain mainly Fe_3O_4 (29—81%), and FeS_2 (19—66%) with small admixture of $FeSO_4 \cdot H_2O$ (up to 5%). Due to X-ray structure analysis it appeared that microconcretions were composed of greigite and pyrite-marcasite and their chemical was as follows: sulphur 17.3—32.6%, iron 22.7—39.2%, phosphorus 0.13—0.70%, titanium up to 0.3%, chromium up to 0.2%, copper up to 0.2% and nickel up to 0.5%. Microconcretions were formed during diagenesis under highly reductive conditions at the last half of crystallization of amorphic monosulphide-hydrotroilite.

Acummulations of autigenic sulphides are connected with the lowest Eh values (-200 mV) in the second layer of hydrotroilite. Similar negative peaks are typical of Boreal deposits (Upper Ancylus) and transition to marine Holocene deposits (Mastogloia Phase). However between two highly reductive layers of hydrotroilite there is a Eh horizon which merely attains -20 mV. Possibly originally non reductive conditions are recorded there while striped, brown clays of Lower Preboreal are of secondary negative Eh values (as low as -120 mV). The low Eh values are found down to 4.8 m.

pH changes recorded in the entire investigated column allow to infer that water of Baltic Ice Lake and Early Yoldia Sea was oxygenated and the environment was of nearly neutral reaction. This phenomenon is consequently followed by increase of exchangeable Ca^{2+} content and occurrence of carbonates in deposits. During Late Yoldia and Ancylus

Fig. 2. Lithology and geochemical parameters of core Late Quaternary deposits from Gdańsk Basin

Lithology: 1 — sapropelic clay; 2 — microbedded clay; 3 — homogenous, spotted clay of low density; 4 — hydrotroilite layer; 5 — homogenous clay of high density; 6 — striped clay; 7 — cross stratified clay; 8 — microconcretions of pyrite; 9 — microconcretions of iron phosphates; 10 — microconcretions of barite; 11 — microconcretions of iron monosulphides; 12 — glacial material; 13 — colour of deposits: a — gray, b — greenish-gray, c — black and blackish-gray, d — brown; granulometric composition, grain size in milimeters: 14 — > 0.05; 15 — 0.05—0.01; 16 — 0.01—0.005; 17 — 0.005—0.001; 18 — < 0.001; physical and chemical parameters: H — humidity (%); γ — density (g/cm^3); $C_{org.}$ — organic coal content (%); κ — magnetic susceptibility (SJ units); V_s — sound speed (km/s); pH — chemical reaction; Eh — red-ox potential (mV); stratigraphy: IV—VI — lithostratigraphical complexes; B — Baltic Ice Lake, Y1 — Yoldia Sea 1, Y2 — Yoldia Sea 2, A — Ancylus Lake, L — Litorina Sea, P — Postlitorina Sea; All — Alleröd, Dr3 — Upper Dryas, PB — Preboreal Period, B — Boreal Period, A — Atlantic Period, SB — Subboreal Period, SA — Subatlantic Period

Litologia i parametry geochemiczne w rdzeniu późnoczwartorzędowych osadów Basenu Gdańskiego

Litologia: 1 — ił sapropelowy; 2 — sapropel mikrowarstwowany; 3 — ił o mniejszym stopniu gęstości, homogeniczny i plamisty; 4 — warstewki hydrotroilitu; 5 — ił o dużej gęstości, homogeniczny; 6 — ił prążkowany; 7 — ił skośnie warstwowany; 8 — mikrokonkrecje pirytu; 9 — mikrokonkrecje fosforanów żelaza; 10 — mikrokonkrecje barytowe; 11 — mikrokonkrecje monosiarczków żelaza; 12 — materiał pochodzenia lodowcowego; 13 — barwa osadów: a — szara, b — zielonkawo-szara, c — czarna i czarno-szara, d — brunatna; skład granulometryczny, średnice ziarn (mm): 14 — > 0,05; 15 — 0,05—0,01; 16 — 0,01—0,005; 17 — 0,005—0,001; 18 — < 0,001; parametry fizykochemiczne: H — wilgotność (%); γ — gęstość (g/cm^3); $C_{org.}$ — zawartość węgla organicznego (%); κ — podatność magnetyczna (jednostki SJ); V_s — szybkość dźwięku (km/s); pH — odczyn chemiczny; Eh — potencjał utleniająco-redukcyjny (mV); stratygrafia: IV—VI — kompleksy litostratygraficzne; B — bałtyckie jezioro lodowe; Y1 — morze yoldiowe 1, Y2 — morze yoldiowe 2, A — jezioro ancylusowe, L — morze litorynowe, P — morze postlitorynowe; All — alleröd, Dr3 — górny dryas, PB — okres preborealny, B — okres borealny, A — okres atlantycki, SB — okres subborealny, SA — okres subatlantycki the environment was of slightly alcalic reaction, Eh value considerably varied and no carbonates were recorded in sediment. Finally, in the upper sequence of marine deposits pH values corresponds to moderately alcalic reaction, and Eh values are typical of reductive environment. Above results are consistent with former ones by G.Bublitz, T. Szczepańska (1987).

Variability of sorption complex composition considerably depends on physical and chemical properties of the environment and corresponds with sedimentary conditions (T. Szczepańska, B.Walna, 1983; A. I. Blazhchishin, 1985; A. I. Blazhchishin et al.,1986). In marine Holocene deposits, in comparison with the top of the core, there is a considerable decrease of sodium ion content (a main ion of the sorption complex) and to minor degree of potassium ion content. These changes are recorded in the Upper Boreal section of deposits and are correlated with pH value curve. Abrupt decrease of Na^+ ion sorption and to minor degree of K^+ and Mg^{2+} are found in the upper hydrotroilite layer and solely Na^+ sorption comes down in the lower hydrotroilite layer. The lowest sorption values of mentioned ions are recorded in late glacial deposits. Discussed exchangeable ions are indicators of paleobasins salinity.

As it was reported before according to hydrochemical data, at the decline of Alleröd there was a slight increase of salinity (A. I.Blazhchishin, 1982). Due to recorded increase of exchangeable magnesium it is possible to infer that salinity was higher during Yoldia Stage. However it coincides with exchangeable Ca^{2+} peak which content is twice as high in the Lower Preboreal deposits as in the overlying layer. According to above data which correspond with type of diatoms (A.Gajgalas et al., 1988) it is inferred that Gdańsk Basin was a fresh water basin during Preboreal Period.

Basing on lithologic and geochemical data a considerable difference in character of basins has been found between Lower and Upper Preboreal as well as between Early and Late Ancylus.

Most specific is a proportion of exchangeable cations and alkali metals content. Some other geochemical anomalies are also very characteristic. A transitional Upper Boreal section which precede a marine lithostratigraphic complex LSK VI, most probably was formed under slightly saline conditions. It is a support of the hypothesis of four different basins instead of classic opinion on two ones (i.e. Yoldia Sea and Ancylus Lake).

Analyses of arrangement of main deposit-forming chemical components and several microelements lead to similar conclusions. For instance organic carbon distribution (Fig. 2) may reflect the productivity of the basins which seems to be the highest in Middle and Upper Holocene. However after reducing organic matter to absolute mass (i.e. with regard to rate of sedimentation) it became clear that a slightly saline basin of the second half of the Boreal Period (8500—8000 years BP) had been mostly productive.

Figure 2 illustrates few peaks of organic carbon within Holocene deposits which are correlable with concentrations of autigenic minerals.

The comprehensive lithostratigraphic and geochemical investigations upon the indicator core sample from Gdańsk Basin resulted in paleogeographic description and allowed to follow geochemical evolution of the Baltic Sea beginning with the Ice Lake Period till nowadays. The main indices of this evolution are as follows: tendency of climatic changes and adequate migration of chemical components, their increasing mobility as well as decreasing of rate of sedimentation and progressing diagenesis. Especially the latter processes are typical of acoustically anomalous zones where streams of gaseous hydrocarbons dislocate intensively (A. I.Blazhchishin et al., 1987).

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BADANIA LITOSTRATYGRAFICZNE, GEOCHEMICZNE I PETROFIZYCZNE RDZENIA WSKAŹNIKOWEGO PÓŹNOCZWARTORZĘDOWYCH OSADÓW BASENU GDAŃSKIEGO

Streszczenie

W ramach współpracy nad problemem *Mirowoj okiean* opracowano rdzeń reperowy o długości 6,22 m pobrany z dna północnej, głębokowodnej części Basenu Gdańskiego podczas 44 rejsu s/b *Akademik Kurczatow* w 1986 r. Badania osadów przeprowadzono na pokładzie statku, a następnie w laboratorium na lądzie. Na

podstawie danych petrograficznych i fizykochemicznych: uziarnienia, wilgotności i gęstości osadów, szybkości dźwięku, podatności magnetycznej, zmienności pH i Eh, składu kompleksu sorbcyjnego oraz diagramu pyłkowego rozpoziomowano osady na odpowiadające głównym fazom rozwojowym Bałtyku.

Dane palinologiczne pozwoliły na wyodrębnienie w badanym rdzeniu warstw: allerödu (622 — 586 cm), górnego dryasu (586 — 518 cm), wczesnego preborealu (518 — 414 cm), późnego preborealu (414 — 365 cm), wczesnego borealu (365 — 318 cm), późnego borealu (318 — 205 cm), atlantyku, subborealu i subatlantyku (205 — 0 cm).

Osady allerödu i górnego dryasu, reprezentowane przez iły czerwone, mikrowarstwowe, homogeniczne (bałtyckie jezioro lodowe) stanowią kompleks litostratygraficzny IV (LSK IV). Dolnoholoceńskie iły morza yoldiowego, o niskiej zawartości węglanu wapnia, oraz iły w części górnej wzbogacone siarczkami żelaza, z dwoma hydrotroilitowymi poziomami, mikrokonkrecjami greigitu i pirytu (jezioro ancylusowe) stanowią kompleks litostratygraficzny V (LSK V). Środkowo-górnoholoceńska warstwa morska (LSK VI) składa się z zielonkawo-szarych iłów ze śladami bioturbacji i dwoma poziomami warstwowanych sapropeli. W osadach morskiego holocenu wydzielono stadium morza litorynowego i politorynowego.

Z danymi litostratygraficznymi korelują parametry litologiczne, petrofizyczne i geochemiczne. Zmienność ich odzwierciedla ewolucję basenów czwartorzędowych występujących w niecce Bałtyku. Sedymentacja przebiegała tu w strefie halistatycznej odpowiednio głębokiego basenu. Praktycznie była to sedymentacja ciągła, z wyjątkiem okresu "nieciągłości" w środkowym preboreale. Szybkość sedymentacji w poszczególnych stadiach wynosiła: bałtyckie jezioro lodowe — 0,85 mm/a, morze yoldiowe — 1,39 mm/a, pierwsza faza morza ancylusowego — 1,14 mm/a, druga faza morza ancylusowego — 0,90 mm/a, morze litorynowe i politorynowe tylko 0,27 mm/a.

Na podstawie zmienności parametrów fizycznych w osadzie wyodrębniono następujące poziomy: granicę górną mikrowarstwowanych iłów, strefę nieciągłości w środkowym preboreale, regresję jeziora ancylusowego, granicę między dolnym i środkowym holocenem oraz regresję morza litorynowego.

Na podstawie wyników podatności magnetycznej wydzielono trzy warstwy ze skupieniami mikrokonkrecji siarczków, wśród których — według danych spektroskopii mössbauerowskiej — dominują Fe_3S_4 i FeS_2 z niewielką domieszką $FeSO_4 \cdot H_2O$. Nagromadzeniom tych siarczków odpowiadają najniższe wartości Eh (do —200 mV). Między dwiema silnie zredukowanymi hydrotroilitowymi warstwami stwierdzono ślady dawnych warunków tlenowych. W stadium bałtyckiego jeziora lodowego i wczesnej fazy morza yoldiowego warunkom tlenowym odpowiadało środowisko bardzo słabo kwaśne i obojętne oraz obecność chemogennych węglanów. Dla stadiów: późnoyoldiowego i ancylusowego charakterystyczne jest środowisko słabo alkaliczne i znaczne wahania potencjału utleniająco-redukcyjnego. Silnie redukcyjnym własnościom morskich iłów holoceńskich odpowiada środowisko alkaliczne oraz zauważalne zmiany potencjału redoks.

Występowanie kationów wymiennych Na^+, K^+, Ca^{2+} i Mg^{2+} zależy od fizykochemicznych warunków sedymentacji, a ich udział ilościowy stanowi ważną informację paleogeograficzną. Wskaźniki paleohydrograficzne świadczą o obecności w dolnym holocenie nie dwóch tradycyjnych (morze yoldiowe i jezioro ancylusowe), lecz czterech różnych basenów. W okresie preborealnym Basen Gdański był słodkowodny, tzn. morze yoldiowe w tym rejonie nie rozprzestrzeniało się; był tu basen bałtyckiego jeziora lodowego. Produktywność biologiczną można ocenić na podstawie zawartości $C_{org.}$ oraz szybkości sedymentacji. Najbardziej produktywnymi biologicznie były: morze litorynowe i szczególnie słonawowodny basen późnoborealny.

W rezultacie przeprowadzonych badań określono sytuację paleogeograficzną i cechy geochemicznej ewolucji Basenu Gdańskiego od stadium bałtyckiego jeziora lodowego do morza współczesnego.