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Distribution and Enrichment of Redox-Sensitive Metals in Baltic Sea Sediments

Franz Xaver Gingele and Thomas Leipe

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The distribution and enrichment of the redox-sensitive metals Mn, Fe, Co, Ni, Cu, Zn and Pb were investigated in 3 cores from the Arkona and Bornholm Basins in the western Baltic Sea. No substantial enrichment of Mn can be observed in the marine Holocene muds. The lack of a surficial Mn accumulation indicates that oxic conditions near the sediment surface - recently associated with periodical saltwater inflows from the North Sea - do not persist long enough to form a significant Mn peak. However, layers rich in Mn and Cu are found in sediments of the Yoldia Sea stage and Mastogloia Sea stage below the anoxic muds. These accumulations are believed to record an oxic-suboxic sequence during the times of deposition. Strong fluctuations in the input of organic matter and bottom water oxygen fostering a rapid deepening and shallowing of the redox boundary and local, rapid sedimentation events may be responsible for the preservation of this sequence. Enrichments of Zn and Pb are encountered near the suboxic top of the cores. The lack of similar enrichments in the preserved suboxic sequences confirms the anthropogenic source of near surface heavy metal accumulations.

Keywords: Baltic Sea, Bornholm Basin, Arkona Basin, geochemistry, redox-sensitive metals, heavy metals, paleoenvironment.

INTRODUCTION AND APPROACH

The distribution of the reactive part of many transition metals in marine deposits is partly controlled by the redox status of the sediment. The reactive fraction of manganese, iron, copper, zinc, lead, nickel, cobalt, molybdenum, uranium and others responds to changes in the early diagenetic environment and gives limited evidence on the redox control on the post-depositional redistribution of these elements (Lynn & Bonatti 1964; Jarvis & Higgs 1987; Shaw et al. 1990; Thomson et al. 1993). The driving process is the decomposition of organic matter resulting in a characteristic succession in the consumption of oxidants, starting with oxygen, the electron acceptor, which yields the greatest amount of free energy per mole. After oxygen is depleted, nitrate and manganese oxihydroxides are utilized (Froelich et al. 1979). Redox-sensitive metals may be released from organic matter in the oxic zone (Cu, Zn, Pb) (Whitfield & Turner 1987; Gerringa 1990; Lapp 1991) or from minerals, which become unstable during burial into the suboxic and anoxic zone (Mn, Fe, Co; Wallace et al. 1988; Heggie & Lewis 1984). Their mobilization, diffusion along gradients in the pore water and reprecipitation leads to the formation of metal-rich layers and zones where the sediment is depleted of these metals (Klinkhammer et al. 1982). Under ideal conditions solid phase enrichments are theoretically arranged in a clear succession of concentration peaks along the redox gradient (Thomson et al. 1993). However, this succession is rarely found due to a high sorptive capacity of Mn- and Fe-hydroxides for many trace elements, low solubility of sulphides and organic complexes or a wide sample spacing. Manganese, being most susceptible to early diagenetic redistribution is widely used to study redox conditions. Under "steady state" conditions a conspicuous manganese spike develops near the oxic-suboxic boundary and migrates upward with continuing sedimentation. The manganese peaks occurring at deeper sedimentary levels are related to depositional or paleoenvironmental changes (Thomson et al. 1984; Finney et al. 1988; Dean et al. 1989; Pruysers et al. 1993). Changes in organic carbon flux, bottom water oxygen and sedimentation rates can result in changes of the redox boundary and interfere with "steady-state" conditions.

The manganese cycle was a well studied topic in the Baltic Sea basins during the last few years (Hartmann 1964; Huckriede 1994; Neumann et al. 1996). In the anoxic basins dissolved manganese diffuses from the sediment into the stagnant bottom water (Kremling 1983). In the course of periodical salt-water inflows from the North Sea bottom waters get oxygenated and manganese precipitates on the sea-floor after oxidation to MnO_2. The following stratification of the water column and rain of organic matter re-establishes anoxic conditions and manganese is reduced again. However, in the deep basins a certain share of MnO_2 is transformed to Ca-rich rhodochrosite during burial in the suboxic zone and remains stable under anoxic conditions (Jakobsen & Postma 1989), thus resulting in manganese-enriched layers. These layers of rhodochrosite, detected in laminated sediments of the Gotland Basin and central parts of the Bornholm Basin were used to reconstruct the history of saltwater inflows into the Baltic Sea (Huckriede 1994; Neumann et al. 1996). In the Arkona and most of the Bornholm Basin bioturbation destroys laminated sequences. So far, most studies concentrated on the Holocene muds in the deep basins. Metal enrichments in sediments of the Baltic Ice Lake, Ancylus Lake and Yoldia Sea are rarely recorded.

Accumulations of Cu, Zn and Pb in carbonate phases in the suboxic zone were observed in the Arkona (Damm 1992), Bornholm (Leipe et al. 199 and Gotland Basins (Salonen et al. 1995). Accordi to the authors, anthropogenic sources (Leipe et 1995) or early diagenetic redistribution (Damm 199 are regarded as the responsible processes.

The purpose of this study was to compare th distribution of redox-sensitive metals in cores fro the Arkona and Bornholm Basins, which contain sedimentary sequence typical of the western Balti Sea. The drastic changes in the sedimentary env ronment from the Late Glacial to present is be lieved to leave a characteristic imprint on met distribution. The development of metal enrichmen is expected and can be used to reconstruct pale environmental conditions. The results may also co tribute to the discussion of authigenic or anthropo genic origin of heavy metal enrichments in th suboxic zone of Baltic Sea sediments.

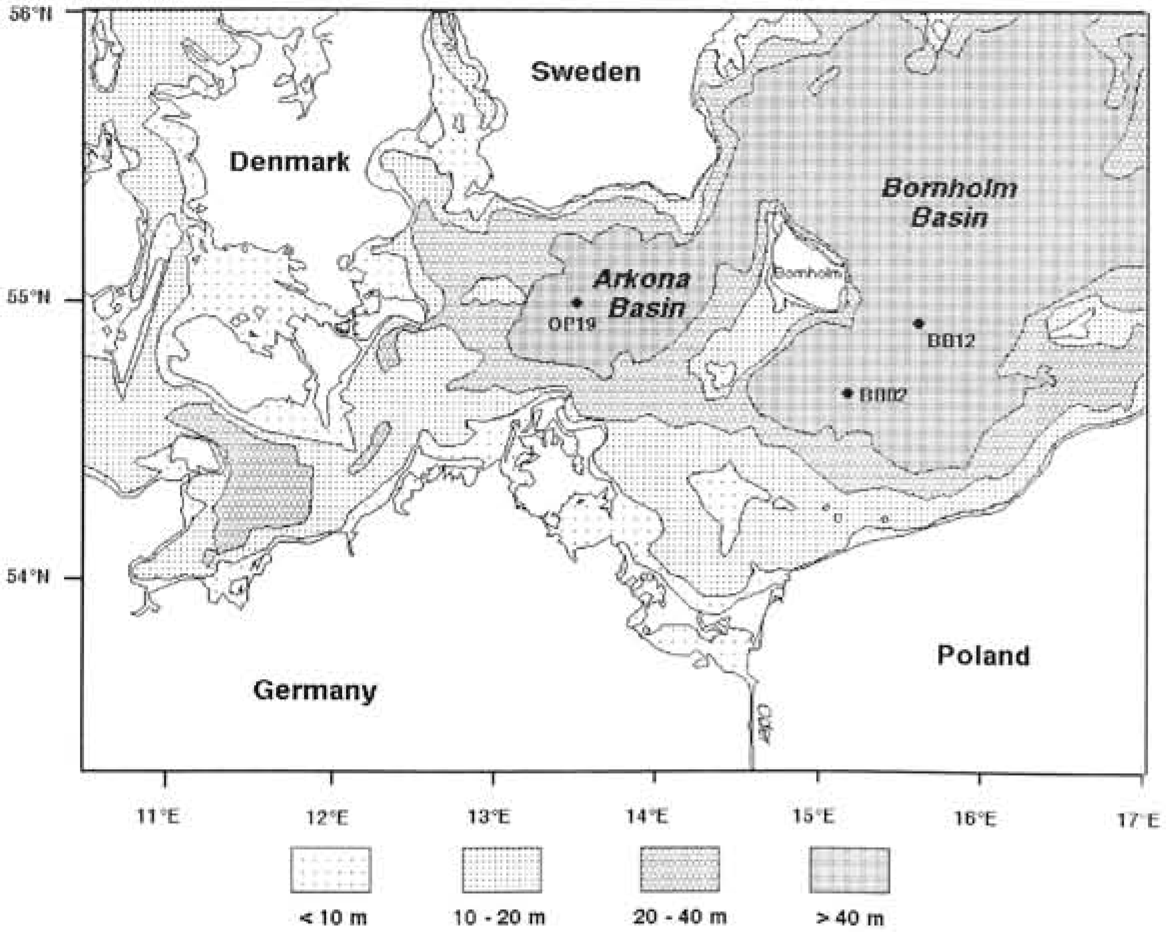

Fig. 1. Investigation area and location of sediment cores

Table 1. **Location of sediment cores**

Core	Latitude	Longitude	Water depth (m)	No. of samples
OP19	55°59.5´N	13°30.1´E	46	147
BB02	54°40.0´N	15°09.9´E	60	60
BB12	54°55.0´N	15°35.1´E	77	90

MATERIAL, METHODS AND STRATIGRAPHY

Three sediment cores from the Arkona- and Born holm Basins were recovered with a gravity core during R.V. *A. v. Humboldt* cruises AvH92/44/25 an AvH93/44/30 in 1992 and 1993 (Fig. 1, Table 1). Niemistö-corer was used to retrieve undisturbed samples from the uppermost 1-2 cm of the sediment surface. Cores were split in half, described for lithology and colour and sampled in 2 cm, 5 cm and 10 cm intervals, depending on lithological variations encountered. After freeze-drying, subsamples were analysed for organic carbon, carbonate and sulphur with a CS infrared analyzer (ELTRA Metalyt 1000CS). Nitrogen was determined with a CHN-analyzer (FOSS-HERAEUS). Pyrite concentrations were assessed with quantitative XRD-measurements on a Philips PW 1830 device, using CoKα radiation (40 kV, 40 mA). Details of the procedure and the compilation of the pyrite calibration curve are given in Gingele (1992). Geochemical data were obtained from total digestions with various acids (HNO_3, HF, $HClO_4$, HCl) and measured with an ICP-AES. Precision was better than 10% for Co, Cu, Ni and Pb and better than 3% for Al, Mn, Fe and Zn (Neumann et al. 1996). Absolute concentrations were normalized to Al to compensate for dilution by nonterrigenous components (Table 2). A lithostratigraphic framework was established following a classification introduced by Larsen (1974) and Kögler & Larsen (1979) in the West Bornholm Basin, and Björck (1995) in the Baltic Sea in general. They distinguish three main units (I-III), which rest on the glacially deposited boulder clay. The features used for classification are colour, lithology and grain size, supported by average values of organic compounds (organic carbon, carbonate, nitrogen, phosphorus, sulphur). Recently, evidence from diatoms and palynological investigations on cores from the Bornholm Basin (Emelyanov & Lukashina 1995; Emelyanov et al. 1995) confirms this lithostratigraphical approach. Since our cores did not penetrate into the basal boulder clay three main lithostratigraphical units ("Unit I-III") could be distinguished (Fig. 2). A detailed stratigraphical classification of cores BB02 and BB12 relating lithostratigraphical units to Baltic stages was published by Huckriede et al. (1995). It is based on carbon cycles calibrated on cores from the Gotland Deep and supported by diatom assemblages.

Unit I (> 10 300 years B.P.) comprises sediments of the late glacial Baltic Ice Lake, mainly brown or multicoloured varved clays. Pale brown, indistinctly varved clays are encountered in cores BB02 from 472-536 cm core depth and core BB12 from 395-436 cm (Fig. 2). They were related to the youngest deposits of the Baltic Ice Lake (Huckriede et al. 1995). In core OP19 greyish-pink clays with sandy layers from 190-480 cm core depth were classified as the Baltic Ice Lake sediments.

Unit II (10 300 - 7800 years B.P.) represents clays of the postglacial Ancylus Lake (Boreal stage) and Yoldia Sea stage (Early Preboreal). It is found in both cores from the Bornholm Basin and in core OP19 from the Arkona Basin (Fig. 2). The rather homogenous grey clays have been divided into three subunits (A-C) by carbonate and organic carbon content (Kögler & Larsen 1979). Subunit A can be clearly attributed to the freshwater Ancylus Lake. However, no clear temporal correlation is

Table 2. **Mean values and standard deviation for Al-normalized redox-sensitive metals for each core and stratigraphic unit.** Values were multiplied by 10^3 for convenient handling. Lithogenic background for Baltic Sea sediments after Damm (1992)

	Mn/Al	**Fe/Al**	**Co/Al**	**Ni/Al**	**Cu/Al**	**Zn/Al**	**Pb/Al**
Unit III (Marine Mud)							
BB02	7.18 ± 1.81	707 ± 77	0.297 ± 0.036	0.706 ± 0.029	0.785 ± 0.091	1.59 ± 0.25	0.421 ± 0.273
BB12	14.02 ± 3.30	820 ± 99	0.424 ± 0.050	0.824 ± 0.086	0.352 ± 0.092	2.01 ± 0.57	0.446 ± 0.256
OP19	7.69 ± 1.05	723 ± 99	0.338 ± 0.042	0.722 ± 0.079	0.619 ± 0.141	1.95 ± 0.62	0.653 ± 0.430
Unit II (AY Clay)							
BB02	10.94 ± 1.81	594 ± 66	0.315 ± 0.029	0.638 ± 0.108	0.632 ± 0.143	1.44 ± 0.23	0.325 ± 0.046
BB12	16.96 ± 22.60	712 ± 98	0.367 ± 0.038	0.786 ± 0.132	0.433 ± 0.162	1.77 ± 0.19	0.334 ± 0.052
OP19	6.74 ± 1.22	660 ± 124	0.324 ± 0.055	0.656 ± 0.120	0.504 ± 0.202	1.44 ± 0.17	0.272 ± 0.040
Unit I (Varved Clay)							
BB02	6.86 ± 0.92	646 ± 45	0.344 ± 0.060	0.618 ± 0.079	0.593 ± 0.053	1.52 ± 0.13	0.333 ± 0.047
BB12	7.49 ± 0.30	655 ± 21	0.373 ± 0.037	0.665 ± 0.040	0.322 ± 0.022	1.71 ± 0.07	0.331 ± 0.039
OP19	6.94 ± 0.87	537 ± 20	0.279 ± 0.012	0.595 ± 0.018	0.355 ± 0.031	1.31 ± 0.05	0.256 ± 0.039
Terrigenous background:							
Baltic Sea sediments (Damm 1992)	3.3	366	0.16	0.66	0.63	1.58	0.33
Slates (Turekian & Wedepohl 1961)	10.6	590	0.24	0.85	0.56	1.19	0.25

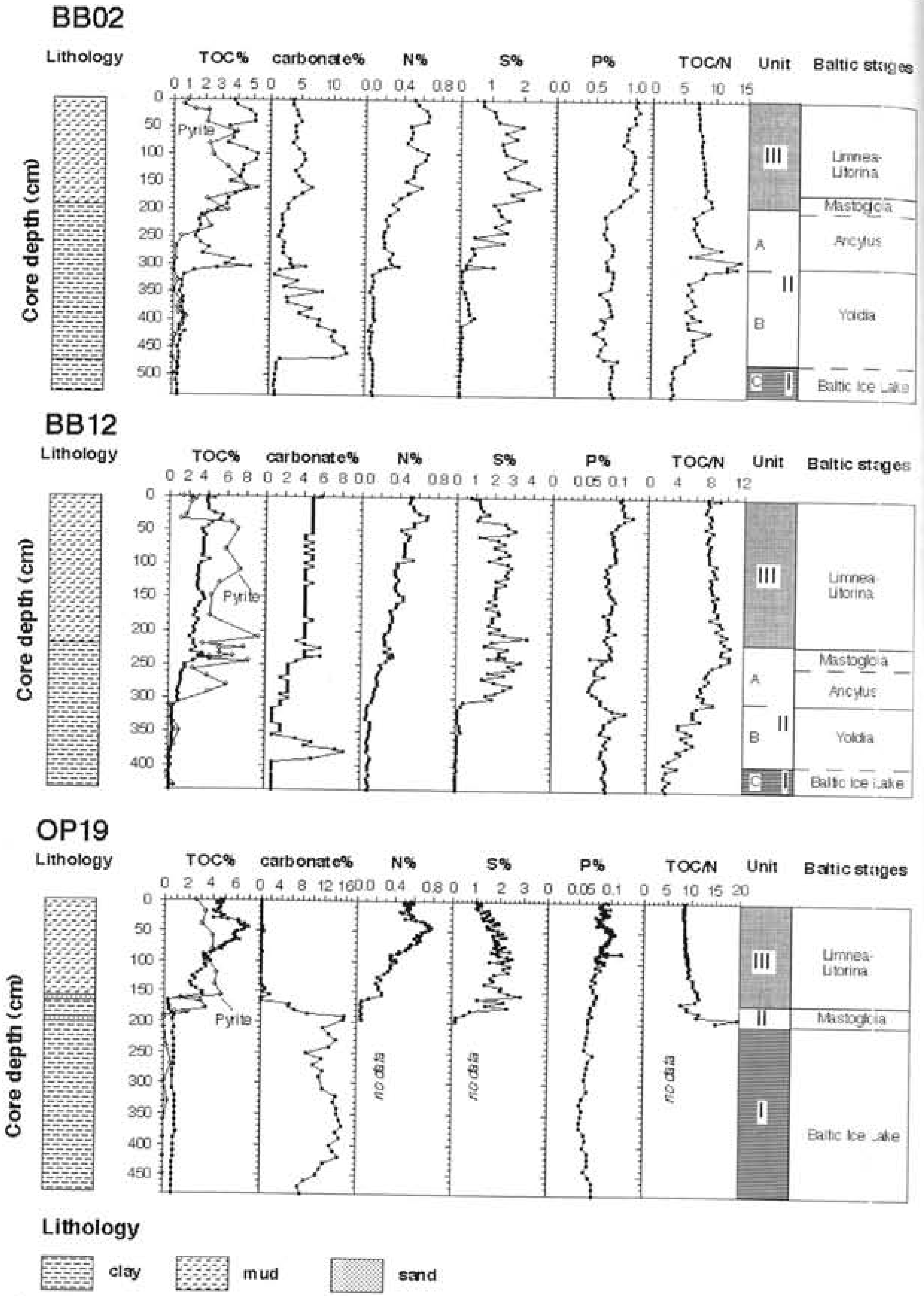

Fig. 2. Lithology and downcore distribution of biogenic components TOC (total organic carbon), carbonate, total nitrogen, TOC/N-ratio, sulphur- and phosphorus content. Pyrite percentages are depicted near the TOC-distribution. Lithological and stratigraphical units I - III are indicated in the shaded column. Baltic stages according to Huckriede et al. (1995)

given by Kögler and Larsen (1979) for the subunits B and C. They may be contemporaneous to later stages of the Baltic Ice Lake, the Yoldia Sea or early stages of the Ancylus Lake. Based on comparison with sediments of the Gotland Basin Huckriede et al. (1995) attributed subunits A and B to the Ancylus and Yoldia stages, whereas subunit C is interpreted as deposits of the Baltic Ice Lake. Thus unit I in cores BB02 and BB12 may be correlated with subunit C of Kögler and Larsen (1979). A better resolution of Yoldia stage sediments is proposed by Wastegård et al. (1995) and Sohlenius (1996). They distinguish an early freshwater phase, a short brackish phase and a late freshwater phase, which leads to Ancylus stage sediments. The brackish phase is characterized by high carbonate contents and corresponds to subunit B.

Subunits A and B are observed in the cores from the Bornholm Basin. In core BB12 subunit A from 215-304 cm core depth consists of grey clays with sulphidic black spots. Grey clays persist to the end of the core. A drop in TOC-contents and increasing amounts of carbonate characterize subunit B from 304-395 cm core depth. The onset of subunit C (unit I) is indicated by a sharp drop in carbonate. In core BB02 subunit A from 192-304 cm core depth consists of bluish-grey clays in the upper 60 cm, which turn into brownish-grey clays below. Subunit B from 304-472 cm core depth comprises grey to brownish-grey clays with increasing amounts of carbonate. A conspicuous TOC-peak from 280-320 cm core depth is of terrigenous origin as evidenced by TOC/N-ratios, possibly redeposited peat (Huckriede et al. 1995). We summarize subunits A-B with the term AY-clays introduced by Kögler & Larsen (1979). The transition from the upper Ancylus clay (IIA, Ignatius et al. 1968) to the Holocene marine mud was extensively studied by Sohlenius et al. (1996) in the Gotland Basin. They suggest a transitional Mastogloia Sea stage (Hyvärinen 1988) in the basin sediments. Near the transition TOC-records of core BB12 closely match that of the core from Sohlenius et al. (1996), suggesting that the upper part of subunit IIA corresponds to the transitional stage of Sohlenius et al. (1996). This was confirmed by Huckriede et al. (1995). They found diatom evidence for a transitional Mastogloia Sea stage in cores BB02 and BB12 (Fig. 2). However, this is not reflected by lithology or colour.

Only 0.3 m of greyish clays framed by thin sandy layers are recorded between greyish pink Late Glacial clays and olive green Holocene muds in core OP19. This may be due to erosion or nondeposition of Ancylus Lake deposits in the early Holocene (Duphorn et al. 1995). Thus unit II in core OP19 may represent deposits of the Mastogloia Sea.

Unit III is equivalent to "marine" muds, which were deposited in the basins of the Baltic Sea, following the Litorina transgression from 7800 years B.P. to present. Olive grey sandy muds and muds, rich in organic matter accumulated in varying thickness in the depressions of the western Baltic. Marine mud with a thickness of 2 m in the Bornholm and 1.6 m in the Arkona Basin cores is recognized mainly by colour, lithology and high content of organic carbon (Fig. 2). Though bioturbation is intense Huckriede et al. (1995) propose a subdivision of the marine mud into lithozones. This subdivision was based on carbon cycles calibrated on cores from the Gotland Deep.

RESULTS

Sedimentary and Early Diagenetic Environment

As discussed above burial rate and availability of the reductant organic matter and oxygenation of bottom waters are the main factors for the early diagenetic environment, which control the mobilization and enrichment of redox-sensitive elements. It can be inferred from TOC-contents, sulphur and phosphorus concentrations and abundance of biogenic constituents.

Sediments of the late glacial Baltic Ice Lake are characterized by low contents of TOC and sulphur. Pyrite was mostly below detection limits in bulk mineralogical analyses (Fig. 2). The lack of sulphides and low TOC-contents may be interpreted as evidence for a low input of reactive organic matter and/or a well-oxygenated environment in which organic matter was remineralized efficiently. This is confirmed by positive redox potentials (Eh) measured in Baltic Ice Lake sediments in the Bornholm Basin (Emelyanov et al. 1995). There was no salinity stratification of the water body established. Though local sedimentation conditions might have varied considerably, the general source for the terrigenous matter was glacially eroded material supplied by meltwater suspensions. The average sedimentation rate was 1 mm/a (Emelyanov et al. 1995).

Sediments of the lower Holocene are summarized with the term AY-clays and comprise deposits of the Yoldia Sea stage as well as the Ancylus Lake stage. Correlation between cores BB12 and BB02 is achieved by carbonate and TOC-contents. Similarly low in TOC- and sulphur content to the sediments of the Baltic Ice Lake, but containing bioturbation structures, subunit B was most likely formed under oxic bottom water conditions. Pyrite and sulphur increase slightly only in the middle of subunit B. This points to some marine influence here, because the formation of sulphides is favoured by sulphate in the water and by anoxic conditions as a consequence of salinity stratification. Supported by carbonate contents of up to 10%, which are diagnostic for saline phases of the Yoldia stage (Wastegård et al. 1995; Sohlenius 1996), subunit B is related to the brackish Yoldia Sea stage (Fig. 2).

The most striking feature in the record of biogenic compounds (Fig. 2) is the transition from subunit B to A. Organic carbon and sulphur contents rise considerably and negative Eh-values are encountered (Emelyanov et al. 1995). In core BB12 the transition from IIB to IIA is mainly marked by a sharp increase in sulphur contents. A TOC-rich layer in core BB02 from 280-320 cm results from locally redeposited peat (Huckriede et al. 1995). Subunit A is believed to have formed in the freshwater environment of the Ancylus Lake (Kögler & Larsen 1979). This is supported for our cores by freshwater diatom assemblages described by Huckriede et al. (1995). Pyrite spherules were reported in subunit A from the Bornholm Basin (Kögler & Larsen 1979; Huckriede et al. 1995). Abundant pyrite was detected in subunit A of cores BB02 and BB12, supporting the assumption of Borg (1985) that anoxic conditions were established during this time (Fig. 2). Stressing the positive correlation between TOC- and sulphur contents Huckriede et al. (1995) concluded with material from the Gotland Deep that oxygen deficient bottom waters due to salinity stratification were established in the upper part of subunit A. However, Boesen & Postma (1988) and Sohlenius et al. (1996) have shown that pyrites of late Ancylus Lake clays are of late diagenetic origin, formed by downward diffusion of sulphide from anoxic Litorina stage sediments. In cores BB02 and BB12 pyrites occur throughout subunit A. TOC records show a poor correlation to pyrite and sulphur contents. Therefore we agree with Boesen & Postma (1988) and Sohlenius et al. (1996) that the pyrites of the Ancylus Lake clays are most probably of late diagenetic origin.

AY-clays reach an average thickness of 2.8 m and 2.0 m in cores BB02 and BB12, which is consistent with records found by Emelyanov et al. (1995), resulting in an average sedimentation rate of 1 mm/a.

In the Arkona Basin only 0.3 m of lower Holocene sediment was encountered, which may be related to the Mastogloia Sea 8000 - 7500 B.P. (Hyvärinen 1988; Duphorn et al. 1995). A transitional Mastogloia Sea stage was also described in cores BB02 and BB12 by Huckriede et al. (1995). It is characterized by a first maximum in TOC contents.

Low oxic bottom water conditions and salinity stratification were established with the onset of marine-brackish ingressions initiated by the Litorina transgression 7800 B.P. The inflow of higher saline dense bottom waters pushed the halocline to shallower depths and supplied nutrient rich water to the photic zone. A rise in primary production followed. The rain of organic carbon to the bottom increased, resulting in higher oxygen consumption and low oxic bottom water conditions (Sohlenius et al. 1996). The latter fostered the formation of pyrites in the sediment, which reached up to 5% in the marine Holocene muds (Fig. 2). Average sedimentation rates computed for the 2 m of Holocene mud in the Bornholm Basin and 1.6 m in the Arkona Basin reach 0.25 mm/a and 0.2 mm/a respectively. Recent datings with ^{210}Pb (Leipe et al. 1995) on sediment surfaces suggest sedimentation rates of 3.2 mm/a for the Bornholm and 1 mm/a for the Arkona Basin, which is one magnitude higher than average values. This rather indicates regional differences in sedimentation conditions than drastic changes in sedimentation rates during the Holocene.

Since no pore water analyses have been performed on the cores for this work, pore water profiles near the sediment-water interface are inferred from investigations in the immediate vicinity of our cores (Damm 1992; Emelyanov et al. 1995).

Generally, the basins of the western Baltic Sea are characterized by a salinity stratification and low oxic bottom water conditions. The enclosure by shallow sills allows only limited and periodic water exchange with the North Sea. Substantial manganese enrichments near the sediment surface, diagnostic for a truly oxic layer were not detected in cores from the Bornholm and Arkona Basins (this paper; Damm 1992; Emelyanov et al. 1995). The flux of dissolved manganese from pore waters to anoxic bottom waters was shown for the Arkona Basin (Damm 1992). It can be concluded that the uppermost centimetres of cores OP19 and BB02 are presently free of oxic conditions. A doubling of manganese concentrations is observed in the upper 10 cm of core BB12 indicating at least temporary persistence of oxic conditions at this site. Suboxic conditions are characterized by the mobilisation of manganese and iron, formation of Fe-carbonates and enrichment of Cu, Zn and Pb (Damm 1992). The downcore extension of the suboxic zone was estimated at 16-23 cm for the Arkona Basin (Damm 1992). A reduction of manganese in the uppermost 20 cm and an enrichment of Cu, Zn and Pb in the uppermost 30 cm may outline the extension of the suboxic zone in core OP19. In the cores BB02 and BB12 from the Bornholm Basin it is estimated at 20 and 10 cm respectively. Below 30 cm anoxic conditions within the Holocene mud are assumed for all cores.

Distribution of Redox-Sensitive Metals

Concentrations of redox-sensitive metals were normalized to aluminium to account for variations in the terrigenous background concentrations. It can

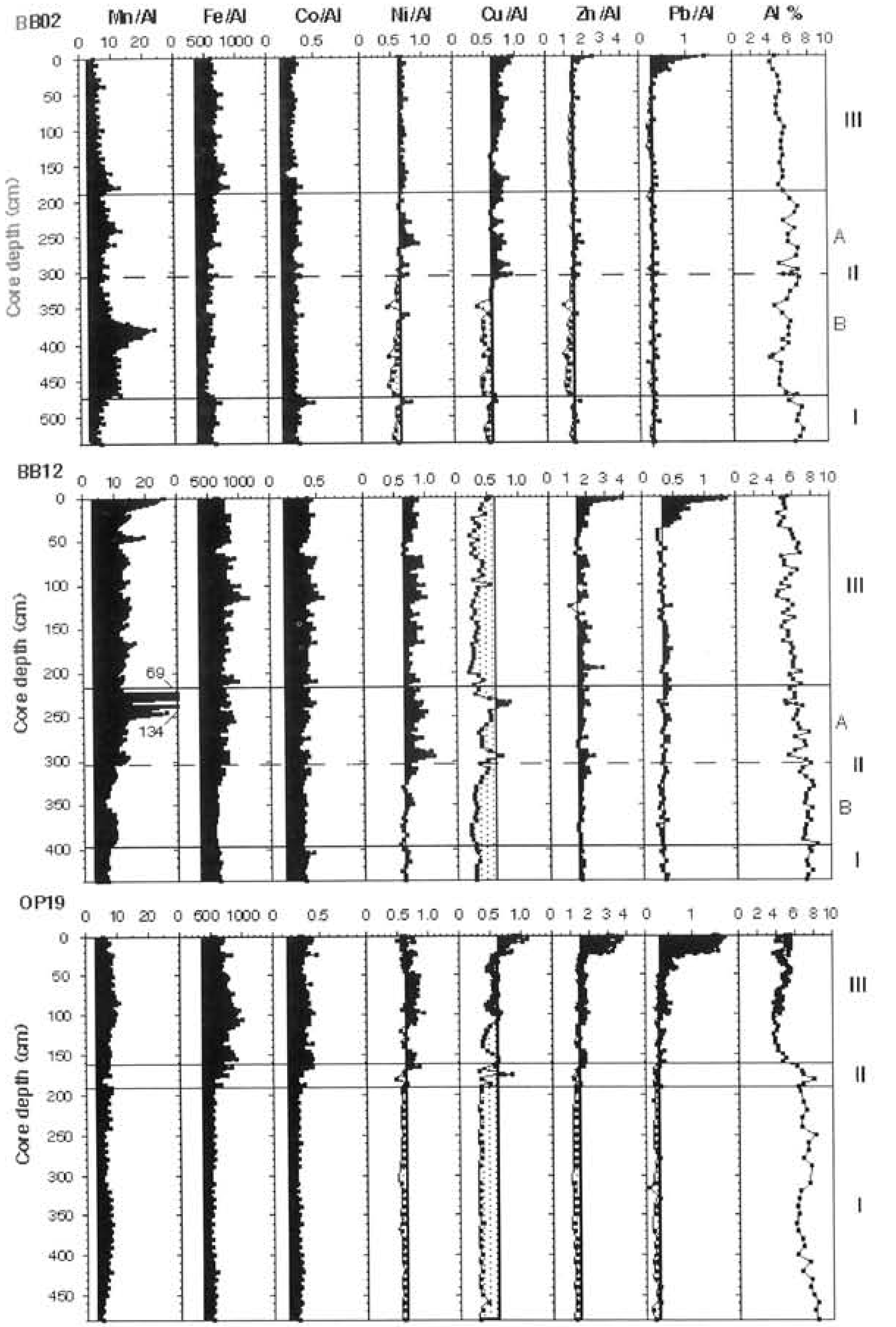

Fig. 3. Downcore distribution of Al-normalized concentrations of redox-sensitive metals. Reference line between dark and light shading is the background metal/aluminium-ratio representative of terrigenous muds in the Baltic Sea (Damm 1992)

be ruled out that metal-rich layers in our cores are due to variations in the terrigenous background (Fig. 3).

Manganese

Mn/Al ratios in the core from the Arkona Basin show little variation throughout all lithological units (Fig. 3). In the uppermost 20 cm a manganese minimum indicates the suboxic zone. Manganese concentrations range in 280-530 ppm, which is well within the range of 330-740 ppm given for sediments of the Arkona Basin (Brügmann et al. 1980). In the Bornholm Basin values vary widely from 280 to 10500 ppm (Hartmann 1964). Core BB02 from the southwestern margin ranges in 220-1400 ppm, whereas 500-7400 ppm are recorded for BB12 in the deeper part of the basin. Mn/Al ratios depict a manganese depleted suboxic layer in the uppermost 20 cm of core BB02 and a manganese-enriched oxic surface layer (0-5 cm) in core BB12. However, a more substantial enrichment is recorded in subunit IIB (BB02) from 370-470 cm core depth and in 3 sharp spikes in subunit IIA of BB12, (Fig. 3).

Iron, Cobalt and Nickel

Generally, sediments in basins of the Baltic Sea are relatively rich in Fe and Co. This is confirmed by Fe/Al and Co/Al ratios (Fig. 3), which exceed background values calculated by Damm (1992) as well as those from Turekian & Wedepohl (1961) for terrigenous slates (Fig. 4). Fe/Al ratios are highest in the anoxic core sections of unit III and subunit IIA and decrease below. Increased Fe/Al ratios in unit I of core BB02 may be due to the presence of iron-rich chlorites in these late glacial sediments (Gingele & Leipe 1997). With the exception of site BB02 Co/Al ratios show a pattern similar to Fe/Al ratios with maxima in the anoxic core sections. The same behaviour can be observed for Ni/Al ratios. Fe as well as Co and Ni show highest values in the deepest core BB12.

Copper

Cu/Al ratios do not show a common pattern in the analysed cores. In the Arkona Basin they are below or near the natural background throughout most of the core. A surficial enrichment in the suboxic zone 0-20 cm coincides with Pb and Zn maxima. At the BB02 site Cu/Al ratios are remarkably consistent with Ni/Al ratios, showing higher values in the anoxic sediments of unit II and subunit IIA. Cu contents are low in core BB12, which results in Cu/Al ratios of 50% below the expected terrigenous background (Fig. 3, 4). Two conspicuous Cu maxima appear in subunit IIA and can be correlated to Mn and Ni peaks.

Zinc and Lead

Zn and Pb are the only elements, which display a similar pattern in all three cores. They are enriched near the sediment surface in the suboxic zone and fluctuate tightly around background values throughout the rest of the core. Enrichment factors are 2-2.5 for Zn and 5 for Pb. A surface layer enriched in heavy metals was found in many cores from the Baltic Sea basins. Some authors favour anthropogenic input as a major source (Leipe et al. 1995) others stress the early diagenetic mobility as the main process (Damm 1992).

DISCUSSION

Enrichments of redox sensitive metals are found in all our cores. Unfortunately, they rarely occur in similar stratigraphical positions, which makes it difficult to relate them to common changes in paleoredox conditions. Enrichments are not directly related to TOC peaks. Manganese being the element most susceptible to redox changes shows significant enrichments only in the cores from the Bornholm Basin cores. In core BB02 the lower part (350-470 cm core depth) of subunit IIB is characterized by increased Mn values (factor 2-5). As subunit IIB is related to the Yoldia Sea stage these enrichments may record rapid and multiple fluctuations of inflow of saline waters and periods of stagnation, thus providing the first record of a Mn-enrichment scenario typical for present-day basins of the Baltic. Subunit IIB is likewise depleted of Ni, Cu and Zn (Fig. 3). Enrichment of Mn and depletion of Ni, Cu and Zn are typical features of present day oxic layers (Gobeil et al. 1987). Subunit IIB is poor in organic carbon, which may explain the development of a broad oxic layer. The preservation of this "oxic" element distribution requires rapid burial to seal reactive manganese phases in subunit IIB from the reductant reactive organic matter present in anoxic Holocene muds above. This could have been achieved by the local but rapid sedimentation of terrigenous matter, which marks the onset of subunit IIA in core BB02. The high input of organic carbon is related to refractory organic matter (peat, Huckriede et al. 1995) as evidenced by a maximum in TOC/N-ratios (Fig. 2). The local sedimentation event could have caused atemporarily increased sedimentation rate in general. This scenario would result in a rapid shallowing of the redox boundary thus burying most of the "oxic" layer of subunit IIB below the zone of manganese mobilization.

In core BB12 no manganese enrichments are found in subunit IIB. Thickness of the subunit is half of that in core BB02. Near the transition to

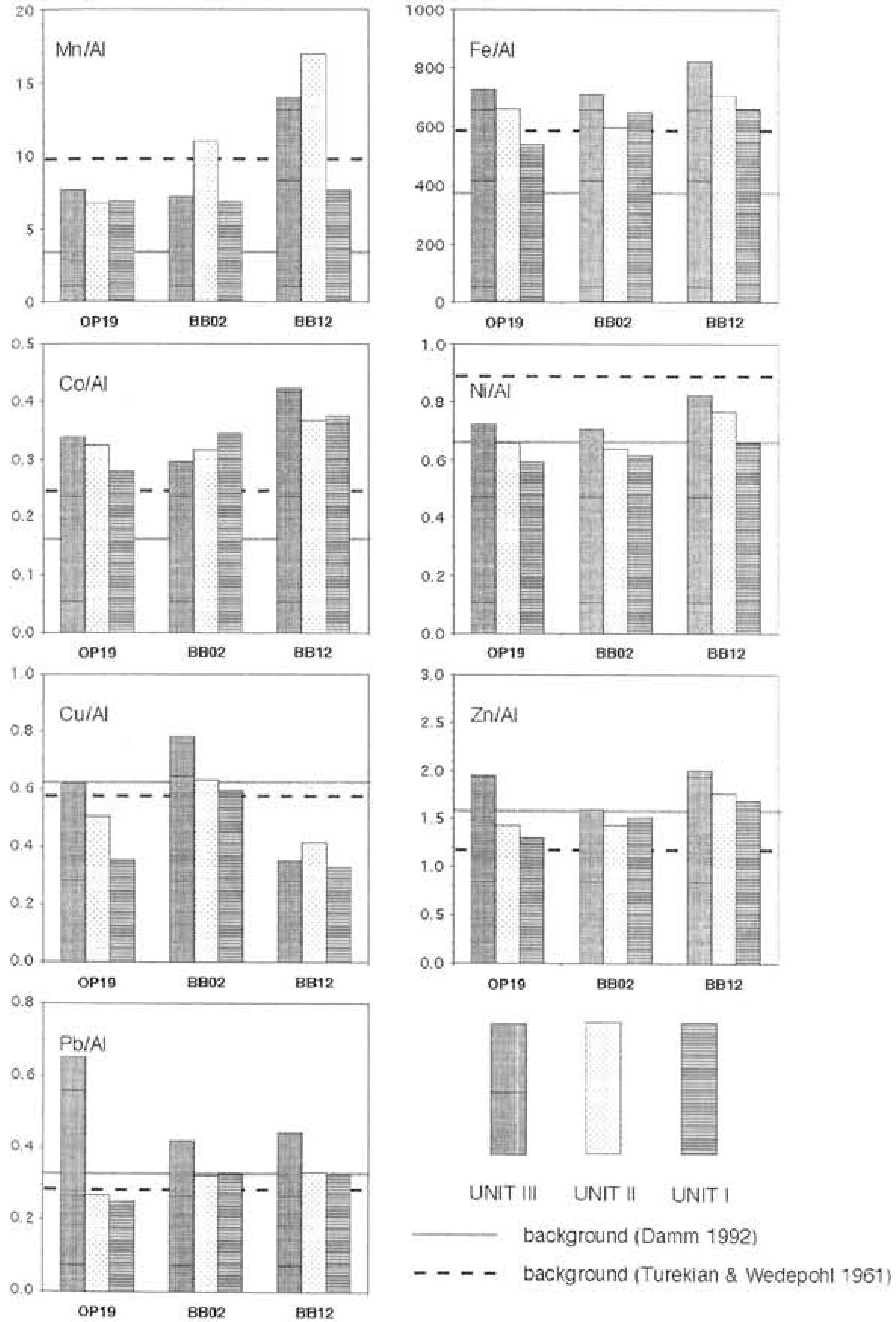

Fig. 4. Mean values of Al-normalized (Me/Al $\times 10^3$) concentrations of redox-sensitive metals for each stratigraphic unit of the analysed cores. Lines represent the background metal/aluminium-ratio of terrigenous muds in the Baltic Sea (Damm 1992) and terrigenous shales (Turekian & Wedepohl 1961)

subunit IIA only a slight and steady increase in organic carbon content and TOC/N-ratios is recorded. Obviously redox conditions in this core were not favourable for the preservation of reducible manganese phases. However, substantial manganese enrichments (factor 5-10) are found in 3 sharp spikes below the transition from subunit IIA to unit I (Mastogloia Sea stage). In combination with a peak in copper concentrations a few centimeters below they may represent a fossilized oxic-suboxic sequence. The coprecipitation of manganese and copper phases was suggested by several authors (Hem et al. 1989; Jarvis and Higgs 1987; Thomson et al. 1993). A second and smaller peak in copper concentrations occurs near the base of subunit IIA. A related manganese peak may have been eroded by early diagenetic mobilisation. Since manganese is more susceptible to redox changes (Thomson et al., 1993) copper phases may survive longer. Mn enrichments in Mastogloia Sea sediments may record rapid fluctuations between oxic and anoxic bottom water conditions triggered by increased inflow of brackish-saline water from the North Sea (Neumann et al. 1996). They are also observed in Mastogloia Sea sediments of the Gotland Deep (Huckriede et al. 1995). However, a scenario for the preservation of the manganese peaks at this stratigraphic position is difficult to conceive. They correspond directly to a first prominent maximum in organic carbon content (Fig. 2), which can also be observed in sediments of the Gotland Deep. A drop in organic carbon flux (Wilson et al. 1985), oxygenation of bottom waters (Finney et al. 1988) and reduced sedimentation rates can deepen the oxic layer and preserve manganese peaks. A drop in organic carbon flux in the initial phase of the Litorina transgression (unit I), could be the main preservation factor. In later stages, when anoxic Holocene mud has been deposited a rapid shallowing of the oxic-postoxic redox boundary is required to save these manganese peaks from remobilization. At the transition between the Ancylus and Litorina stages there was a number of environmental parameters, which changed more or less simultaneously: salinity, primary production, climate and water circulation (Sohlenius et al. 1996), thus making it difficult to assign changes in redox conditions to a single paleoenvironmental factor. Unfortunately no manganese enrichments are found in Mastogloia Sea sediments in core OP19 and only a minor peak is detected at this level in BB02. This may be due to different sedimentation conditions in the Arkona Basin and/or insufficient water depths at site BB02 and OP19. Therefore the suggested scenarios for the preservation of Mn enrichments cannot be confirmed with our material alone. The study of additional cores and acquisition of pore water data are required. The occurrence of metal rich layers at similar stratigraphic levels - as observed in the Gotland Deep - could substantially support paleoceanographic interpretations. Finally, we have to consider a late diagenetic origin for the Mn enrichments. Late diagenetic formation of pyrites was shown in Ancylus Lake sediments by Boesen & Postma (1988) and Sohlenius et al. (1996). Theoretically these pyrites could carry substantial amounts of other trace metals. However, in our cores from the Bornholm Basin the most prominent Mn and Cu enrichments are correlated to minima in the pyrite record (Fig. 2,3). Thus it seems unlikely that the enrichments are related to pyrite genesis.

Surficial enrichments of Zn, Pb and to a lesser extent Cu can be observed in our cores as well as on many other sites in the western Baltic Sea (Brügmann & Lange 1983, 1990; Damm 1992; Leipe et al. 1995; Szefer & Skwarzec 1988). An anthropogenic source (Leipe et al. 1995) or mainly early diagenetic origin (Damm 1992) is suggested. Zn and Pb distribution is similar in cores BB02 and BB12. No significant enrichment is recorded below the subsurface maximum (Fig. 3). In the subunits IIA and IIB, where buried oxic and suboxic layers are indicated by manganese maxima no increase in Zn and Pb concentrations can be detected. Therefore we conclude that the surficial Zn and Pb enrichments represent mainly anthropogenic pollution accumulated in the course of industrialization. Pb, which is mainly introduced by airborne pollution (Pheiffer-Madsen & Larsen 1986) reaches highest values in the Arkona Basin (Fig. 4). This may be due to the proximity of industrial centres or the additional input of aquatic Pb from river suspensions (Leipe et al. 1995). Zn has its major source in aquatic input with North Sea water (Damm 1992). Dilution by different sedimentation rates may be responsible for the fluctuations in Zn-values within basins (Fig. 4).

Maximum concentrations for Cu, which exceed those in the subsurface layer occur in a fossilized metal rich layer in core BB12 from the Bornholm Basin. Thus it cannot be ruled out that early diagenetic redistribution is responsible for a large fraction of Cu enriched in the subsurface peaks.

CONCLUSIONS

Enrichments of the redox sensitive metals Mn and Cu are found in sediments of the Yoldia Sea stage and transitional Mastogloia Sea stage in the Bornholm Basin. Occurring below the anoxic Holocene muds they are considered as buried oxic-postoxic metal distributions of early diagenetic origin. They are believed to record a Mn enrichment mechanism, which is active in present-day anoxic basins of the Baltic Sea, triggered by fluctuations in bottom water oxygenation. Their preservation is related to changes in organic carbon supply, sedimentation rate, local sedimentation events and rapid fluctuations of the oxic-suboxic redox boundary. No Mn enrichments are found in the shallow Arkona Basin. The Mn record from the deep Bornholm Basin site can be correlated to records from the Gotland Deep.

The lack of substantial enrichments of Zn and Pb in "preserved" oxic-suboxic layers of AY-clays points to an anthropogenic source for surficial enrichments of these metals.

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On the Luminescence Dating of Eolian Deposits in Estonia

Anto Raukas and Galina Hütt

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The dating of the eolian deposits needs new precise physical methods. In the paper the reliability of results of thermo- and optically stimulated luminescence dating method are discussed. Most of the dates of eolian deposits from the coastal and inland dunes of Estonia fit well with predicted geological ages.

Keywords: thermoluminescent (TL) and infrared optically stimulated (IR OSL) dating, coastal and inland dunes, Baltic Sea, Lake Peipsi.

INTRODUCTION

It is extremely complicated to determine the age of eolian deposits due to multiple redeposition of sediments and lack of suitable dating methods.

The deficit of organic matter in eolian deposits makes it difficult to obtain material for conventional radiocarbon dating. Besides, seeds and other organics may be reworked in eolian deposits and, therefore, predate the deposits in which they occur. *In situ* organics such as soil horizons typically indicate periods of dune stability, and hence can only be used to broadly bracket periods of dune activity. Thermo- and optically stimulated luminescence (TL and OSL) dating, on the other hand, is ideally suited for dune deposits as it provides a date corresponding to the last time the sediments were exposed to sunlight, and thus can be used to determine a period of eolian activity (Prescott 1983; Rendell et al. 1994; Clarke 1994; Wintle et al. 1994).

The OSL dating method, using quartz, was proposed by Huntley et al (1985). Currently, the infrared optically stimulated luminescence (IR OSL) dating technique, based on alkali feldspars, is of wider use due to the simple technical solution. The method, the first results of dating and physical bases were proposed by Hütt et al. (1988), Hütt & Jack (1996a, b).

Compared to the TL method, an advantage of OSL dating is the new readout technique which permits to choose more light sensitive grains. It is just this phenomenon that leads to more successful realization of zero-point: minimum nonbleached, residual signal to the time of sedimentation. In case of dunes, which have been exposed to sun during a very long period, this residual can be reconstructed in the laboratory.

LUMINESCENCE DATING PROCEDURE

The samples under study were taken from different age sections all over Estonia. Alkali feldspars (100-160 μm) were extracted from these sediments following the techniques described earlier (Mejdahl 1983; Hütt & Smirnov 1983).

The light source used for stimulation was a semiconductor laser with emission in the wavelength region 810±1 nm. The light beam intensity on the sample was 6 mW/cm^2, thus corresponding to ordinary sunny day conditions. The laser was operated in the pulse mode with a pulse length of 3 seconds. An exposure of this duration and intensity did not cause bleaching of the sample, which could be seen from the fact that repeated light pulses produced emission signals of the same intensity. The use of a very weak stimulation light pulse gives two advantages. Firstly, the most light sensitive grains i.e. those best bleached in nature, will mainly be touched upon. Secondly, a week stimulation pulse will not change the dosimetrical properties caused by changes of electron population in the traps. For detection of the emitted light an OSL/TL reader constructed in Tallinn jointly by the researchers of the Institute of Geology and the Ingrid company was used.

The optical response for the samples studied was determined and the wavelength region used for stimulation was chosen in order to reach electrons in stable traps. The emitted light was detected in the UV-band around 380 nm.

After gamma irradiation from a ^{60}Co source (dose rate 1 Gy/min) the samples were stored at room temperature for three weeks before measurement.

The accumulated dose was reconstructed using the additive dose method. The dose-rate was calculated from the U, thermoluminescence and K concentrations, determined by gamma-spectroscopy from the bulk sample with natural water content, and the internal potassium content in the feldspar grains was measured by flame-photometry.

The error of the determined accumulated dose has been calculated using the jack-knifing method, following Grün & MacDonald (1989); but everyone must keep in mind that it is only an analytical error.

Residual signal was reconstructed in the laboratory after natural sun bleaching during 20 hours, which corresponded to the age less then 300 years in the case of IR OSL, and about 1000 years for TL. In age calculations, residual signals were taken into account.

DISTRIBUTION OF EOLIAN SEDIMENTS IN ESTONIA AND THEIR PREDICTED GEOLOGICAL AGE

In Estonia both inland and coastal dunes are encountered. The eolian redistribution of fine aqueoglacial and beach material is highly controlled by land uplift, palaeoclimatic parameters (wind direction and activity, soil moisture) and the grain size of initial sediments (Raukas 1968). Due to the deficiency of sand, concentration of heavy storms to autumn and winter time and high precipitation rate, dunes are relatively low (mainly 5-15 m) and rendered stationary by vegetation (Photo 1).

The Estonian continental dunes, located in the Iisaku-Illuka area (Rähni 1959), are of parabolic and transversal (Photo 2) type and indicate a western-northwestern palaeowind direction (Zeeberg 1993). Both mark the transport pathways for sediment through older dune systems or glaciolacustrine kames. They are 0.2-2.7 km long and up to 15-20 m high. Their west and north-west windward slopes are slanting (3-18°), while the opposite leeward slopes are much steeper (18-24°). On the top and slopes of dunes there are small cover-sand hillocks.

Most probably, these cover-sands, dunes and drift sands originate from the Younger Dryas and the beginning of the Pre-Boreal, when in the Alutaguse Lowland a significant regression of Lake Peipsi took place and the so-called Small Peipsi was formed (Raukas & Rähni 1969). Sand and silt material has been derived here from local source material, e.g. from glaciofluvial and glaciolacustrine deposits (Fig. 1) reworked by ancient Lake Peipsi. Dunes were commenced here immediately after source deposits became available and the process stopped when they became overgrown with vegetation.

Nowadays the inland dune areas in north-eastern Estonia are surrounded by peat bogs and covered by pine forests. Their maximum ages may be

Photo 1. Dunes in Estonia are relatively low and rendered stationary by vegetation. Rannametsa. Photo by A. Aal

Photo 2. Transversal ridge-like dunes occur usually parallel to one another in echelon-like series. Continental dunes near Iisaku. Photo by A. Raukas

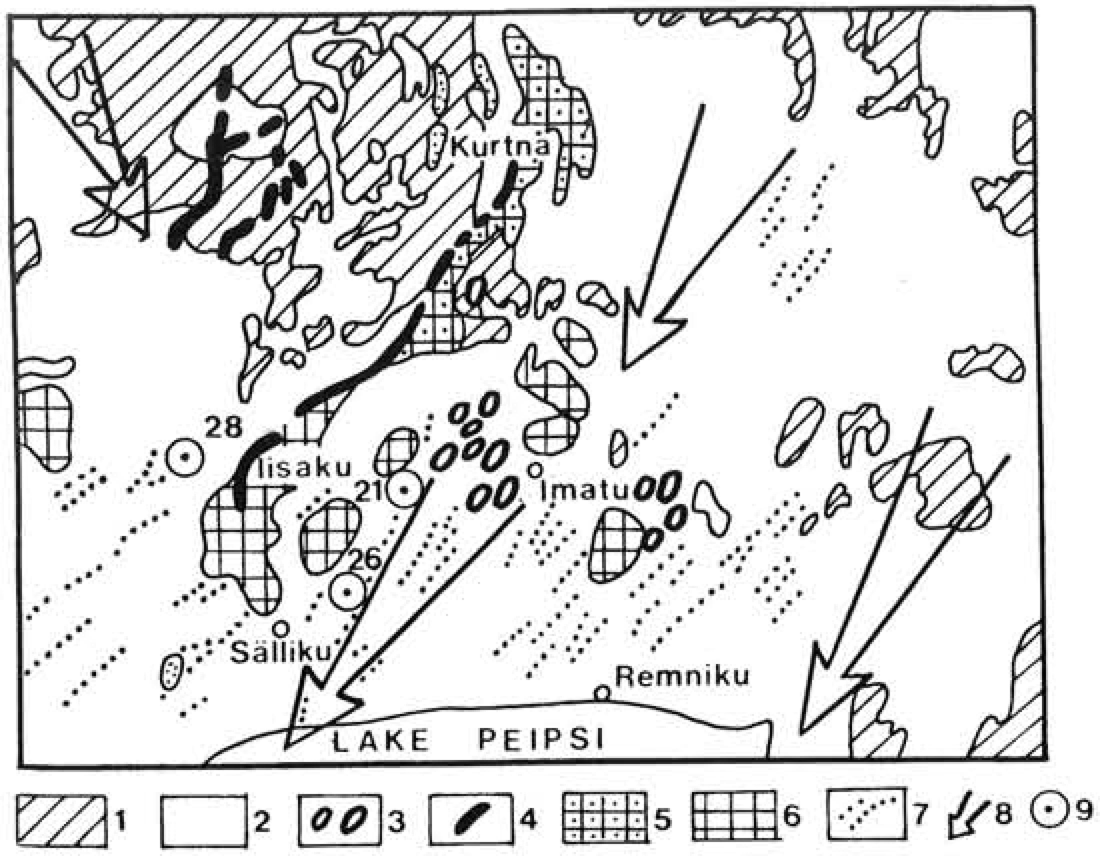

Fig. 1. Glacial topography and inland dunes in the Iisaku-Illuka area: 1 - till plain; 2 - glaciolacustrine plain; 3 - drumlin; 4 - esker; 5 - kame; 6 - limnoglacial kames; 7 - dunes; 8 - ice movement; 9 - boreholes. After Raukas et al. 1988

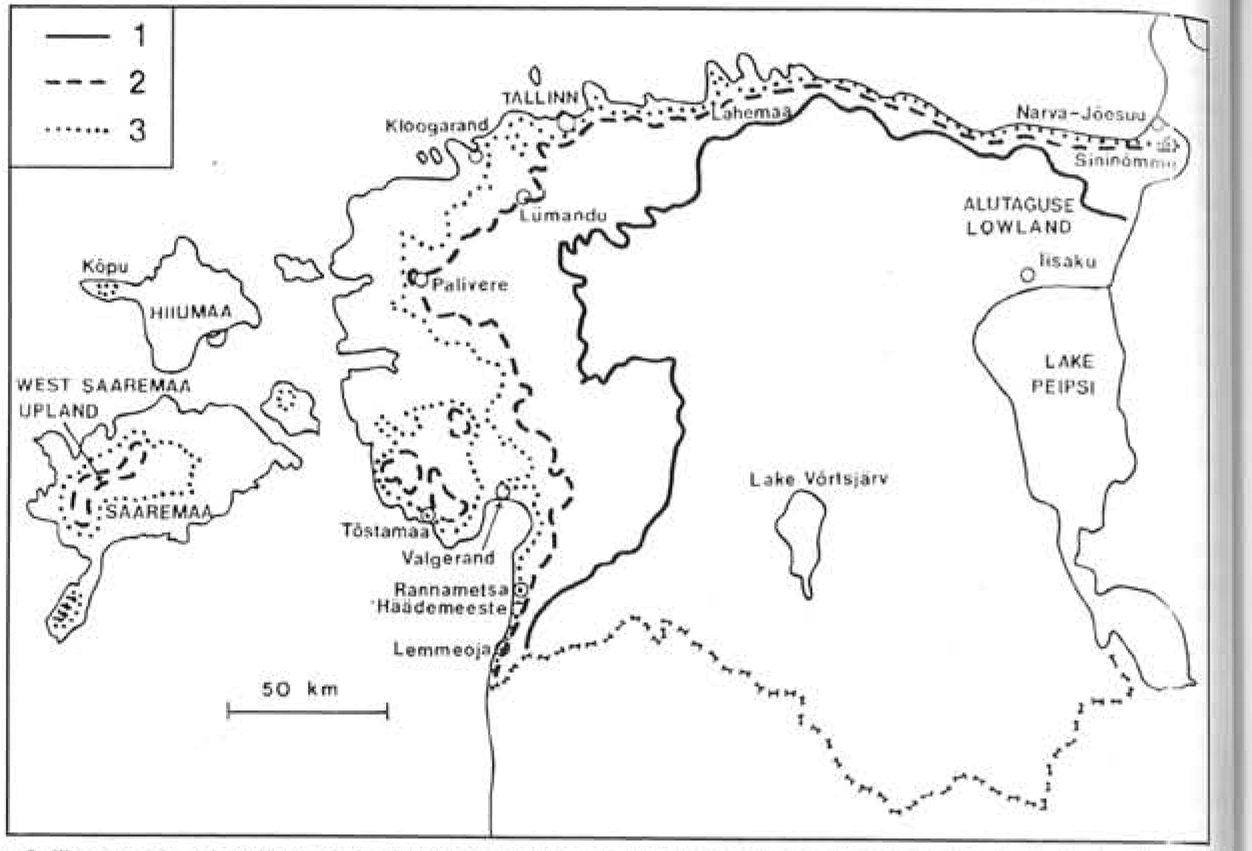

Fig. 2. Transgressive shorelines of the Baltic Sea in Estonia and main localities, mentioned in the text: 1 - The Balti Ice Lake shoreline B_{III}; 2 - Ancylus Lake shoreline A_1; 3 - maximum transgression of the Litorina Sea

inferred from the sediments or soils of which the dunes started to develop. These, mostly glaciolacustrine plains and kame fields, were formed some 12,200 years BP (Raukas et al. 1971). However, the sand became available for redeposition only after it had drained and dried, possibly after the retreat of the glacier of the Palivere Stadial some 11,000 years BP (Raukas 1992). Unfortunately, this cannot be checked by palynological sampling of dune sands or dating of organic remains.

The Estonian coastal dunes are scattered all over Lower Estonia where sandy-silty sediments urgent for their formation have been available (Fig. 2). The largest dunes, up to 20-25 m in height, formed during the transgressive phases of the Baltic Ice Lake, Ancylus Lake and Litorina Sea (Eltermann & Raukas 1966). Rising sea levels lead to shoreline erosion, destruction of fore-dune and beach ridge vegetation, and initiation of transgressive dunes (Cooper 1958). The most prominent dunes in the vicinity of the Baltic Ice Lake transgressive shoreline are located in the Lahemaa National Park and on the Kõpu Peninsula. The dunes originating from the Ancylus stage occur on the West Saaremaa Upland, on the Tõstamaa and Kõpu peninsulas and near Häädemeeste. Those related to the Litorina Sea transgressive shoreline are found at Sininõmme (Photo 3), Rannametsa (Photo 4) and Tõstamaa (Photo 5). The greatest number of dunes occur on west-facing shores, where westerly and south-westerly winds predominate.

Photo 3. Litorina dune at Sininõmme, displaying the typi cal eolian lamination. Photo by A. Raukas

Photo 4. Ridge-like dune at Rannametsa. Photo by A. Raukas

Photo 5. Dated section of eolian sands at Tõstamaa. Photo by A. Raukas

As a result of the neotectonic uplift of the Earth's crust, coastal dunes are nowadays situated at some distance from the contemporary shore and at different absolute heights (Eltermann & Raukas 1966; Martin 1988). At the present seashore only low fore-dune ridges, some metres in height, occur, e.g. at Kloogarand, Narva-Jõesuu and Valgerand. The biggest contemporary dunes with specific morphology, termed the "basket trap" dunes by Orviku (1933), are situated on the northern coast of Lake Peipsi. Some small dunes occur also around Lake Võrtsjärv (Tavast et. al. 1983).

The eolian sands of Estonia are mostly fine-grained (0.1-0.25 mm) and bimineral, consisting mainly of quartz and feldspars (Raukas 1968). In the northern part of the country and on the western islands, where the initial deposits are rich in carbonates, in some places the dune sands contain, next to quartz and feldspars, also great amounts of carbonates (at Palivere 11.2-26.2%, in the St. Andreas dune field on the Kõpu Peninsula 2.2-13.1%).

Depending on their closeness to the ancient shorelines the Estonian coastal dunes are traditionally called the Ancylus transgressive shoreline dunes, Litorina dunes etc., however, they have been most likely repeatedly re-blown in the upper part and may be rather young in age. Forest cuttings and fires, military actions and other human activities may trigger the movement of surficial sand (Photo 6), but mostly sand transported by wave currents to the shore was re-blown from beach ridges into close-lying dunes which soon became isolated by relative water level lowering. The soil profile, occasionally several metres thick (e.g. Lemmeoja), shows that after the deposition at least some dunes became overgrown with vegetation and never moved again. Wet environmental conditions, sparse population and rapid spreading of vegetation prevented extensive redistribution of loose sandy sediments by wind in Estonia.

RESULTS AND DISCUSSION

In order to check the reliability of the results obtained on eolian sediments by the conventional TL and OSL methods, we undertook a detailed research of the sediments of coastal and inland dunes in different areas of Estonia.

It is a well-known fact that the beaches of transgressive phases of the Baltic Sea are much better developed in Estonia than those of regressive

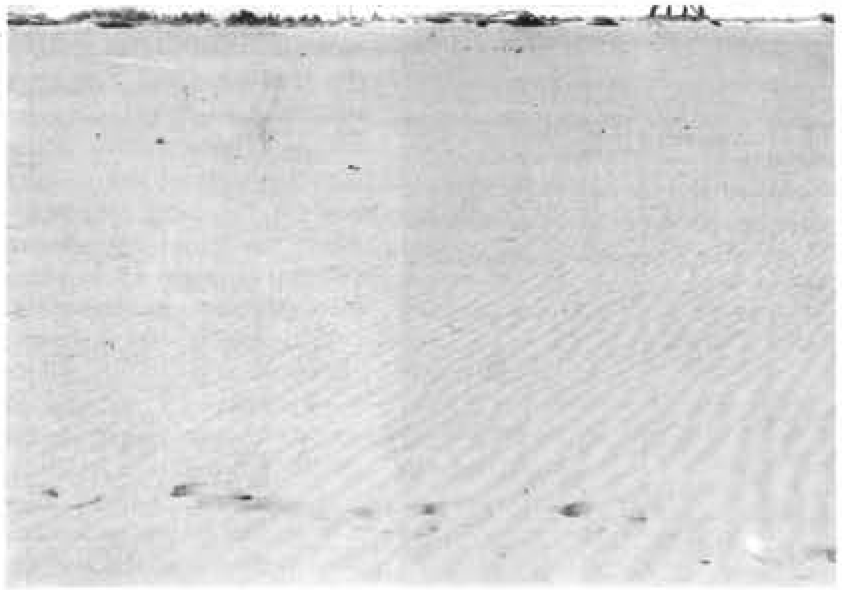

Photo 6. Eolian sands at Kroodi near Tallinn exposed after human activities. Photo by A. Raukas

phases (Raukas 1966). In the course of the sea invasion, against the background of the moderate crustal uplift, the shorelines were rather stable during long intervals of time, causing the accumulation of deposits of great thickness.

During the regressions on gently sloping shores under the general conditions of deficiency of sedimental matter there were no geological preconditions for the formation of huge coastal relief forms.

In the area under consideration, three main transgressions in the history of the Baltic Sea took place:

(1) Transgression of the Baltic Ice Lake B_{III} about 10,500 years ago;

(2) Transgression of the Ancylus Lake A_1 about 9,200-9,000 years ago and

(3) Transgression of the Litorina Sea between 7,000-6,000 years ago, depending on the intensity of the land uplift (Raukas 1991).

All the above-mentioned transgressive shorelines are bounded by extensive perched sand dunes, located along the top of beach ridges of different genesis, interspersed with low-elevated re-blown dunes with no direct connections to beach ridges. We have dated the eolian deposits from all these transgressive shorelines, trying to sample the bottom-most parts of the dunes.

The eolian sediments from the top of the transgressive Baltic Ice Lake beach ridge in the Lahemaa National Park near the Võsu-Rakvere road were sampled and dated. The OSL date of 10,250±1500 years obtained on a sample from a depth of 3.2 m agrees pretty well with the predicted geological age. At the same time, the date 13,600±1300 from the Kurgja section at a depth of 2.7 m in SW Estonia is about 3,000 years older than the predicted geological age.

Eolian sediments from the top of Ancylus beach ridges were taken for dating in the Tõstamaa Peninsula from a depth of 3.1 m (9,600±960 years) and in the Lahemaa National Park near Koljaku from a depth of 2.1 m (6,100±700 years). The obtained dates are reliable if to consider the possible redeposition of eolian sediments in Koljaku before they became finally fixed by a stationary vegetation.

On the Litorina Sea shoreline, deposits from Tõstamaa (Photo 5) at a depth of 3.4 m (6300±600 years) and Rannametsa (Photo 1) were dated. The bottom-most part of the Rannametsa dunes at a depth of 8.4 m yielded an age of 10,400±1100 and the uppermost part at a depth of 2.4 m an age of 4,300±500 years. The first date has a full agreement with the predicted geological age, the second one seems to be wrong and the third one reliable if to take into account possible secondary redeposition of the material.

In the area of inland dunes in North East Estonia, the samples for TL dating were taken from 3 profiles (Fig. 1, 3). The results obtained confirm Holocene age of eolian deposits and probably the multiple redeposition of initial Younger Dryas glaciolacustrine and eolian sediments (Raukas et al. 1988). Dune sands, 2 km north of Lake Imatu (Fig. 3A), gave two consistent dates: 4,000±500 years at a depth of 0.4 m and 5,900±600 years at a depth of 2.5 m. Dune sands west of Iisaku settlement yielded three dates (Fig. 3B): 5,200±550 years at a depth of 0.6 m, 6,900±600 years at a depth of 3.5 m and 3,000±500 years at a depth of 11 m. The latter date is not reliable but the reason for that is not clear. In the third profile near Valgesoo (Fig. 3C), the date of 13,600±1500 years from a depth of 0.4 m is not reliable, all the other: 2.4 m (4,700±500 years), 3.7 m (5,400±500 years) and 4.8 m (7,100±700 years) below the surface are consistent with each other. The dates sum to be rather reliable and indicate different phases of eolian activity.

To compare the results obtained, two samples were taken from the upper part of recently re-blown dunes from the northern coast of Lake Peipsi at a depth of 1.5 m (Remniku W) and 2.5 m (Remniku O), and from an ancient dune of Lake Peipsi near Sälliku at a depth of 3 m (Fig. 1). The results obtained were rather realistic: for the Remniku W 1,000±200 years, for the Remniku E 500±500 years and for the Sälliku 8000±3000 years. The predicted geological age for the Sälliku sample was about 10,000 years.

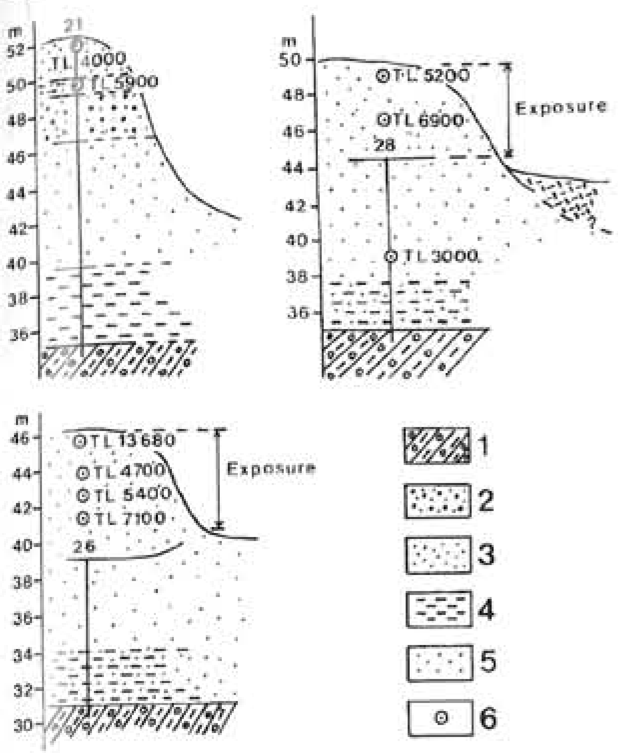

Fig. 3. Sections dated with TL method. For location of sections and boreholes see Fig. 1: 1 - till; 2 - glaciofluvial deposits; 3 - glaciolacustrine sand; 4 - glacio-lacustrine silt; 5 - eolian sand; 6 - location of dated samples

CONCLUSIONS

The aim of the present work is to point out that the luminescence dating method can be used for correlating eolian deposits on the basis of both relative and luminescence age. Most of the dates obtained are in agreement with the stratigraphy and the predicted geological ages. In spite of the rather poor resolution of luminescence dating results for the Holocene time range, this tool of study is quite fruitful and enables to solve some important geological problems. In case of eolian sediments, disagreement between luminescence dating and geological predicted ages can stimulate geologists to revise their point of view about genesis of studied sediments. In the coming years, it is important not only to date more samples from eolian sediments of different age but also to carry out further study of the mechanism of formation of wind-blown deposits, because without considering the peculiarities of their formation, the most accurate measurements of their luminescence properties will be meaningless.

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Recent Muds of the Gulf of Gdańsk

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Mud is deposited in the Gulf of Gdańsk in four subenvironments related to different hydrological conditions and sedimentary processes. The first area of mud deposition is located in front of Vistula River outlet, where intensive flocculation of suspended matter is taking place in the mixing zone of the river and marine waters. The second area – in Puck Bay (western part of the Gulf of Gdańsk) is semi-enclosed by the Hel Peninsula and deposition of mud could takes place above the pycnocline. The third and fourth mud depositional areas are located in more open parts of the Gulf of Gdańsk. The third one is related to the zone where the pycnocline makes contact with the sea bottom, at a depth of 50-85 m, and the fourth area covers the zone below the pycnocline, with anoxic conditions. Mud depositional areas were examined using side scan sonar, sub-bottom profiler and box corer for X-ray radiographs to study the sedimentary structures and concentrations of selected trace elements were analysed.

Keywords: Baltic Sea, Gulf of Gdańsk, mud deposition, environment of sedimentation, sedimentary structures, contents of Al, Cd, Cr, Ni, P, Pb, Zn, enrichment factors.

INTRODUCTION

The Gulf of Gdańsk is the southernmost part of the Gdańsk Basin. The external sea boundary of the Gulf of Gdańsk is conventionally taken to be a straight line connecting the promontories of Rozewie on Polish coast and Taran on Sambia Peninsula. In the extreme western part of the Gulf of Gdańsk there lies the Puck Bay protected from the more open waters by the Hel Peninsula about 32 km long. The south-eastern part of the Gulf of Gdańsk is fringed by about 55 km long Vistula Spit, which forms the Vistula Lagoon. The area of the Gulf of Gdańsk is c. 5,000 km^2. The maximum water depth is 108 m, and occurs in the northern part of the Gulf, in the Gdańsk Deep.

The drainage area of the Gulf of Gdańsk is about 221,310 km^2. Most important is the Vistula River which drains an area of 193,911 km^2. The catchment area of the Pregola and other rivers flowing into the Gulf of Gdańsk via Vistula Lagoon and Pilava Strait is about 23,439 km^2, and of other rivers of the western coast about 3,960 km^2. The total average river discharge into the Gulf of Gdańsk is about 1,300 m^3/s, in particular Vistula discharges 1,027 m^3/s. (Majewski, 1990). The Vistula supplies the bulk of contaminants entering the Gulf of Gdańsk. Important are also numerous sources of pollution scattered along the Gulf: the harbours of Gdańsk and Gdynia, municipal and industrial waste of the Gdańsk and Gdynia agglomeration, outlets of storm water channels, sewage from ships lying in the roadsteads of the ports. Pollutants of unknown amounts and composition come to the Gulf from the Kaliningrad area and from the biggest military base of the Baltic Sea located in Baltiysk (Pilava Strait).

The aim of this paper is to gain insight into the recent sea bed sediments and chemical components, especially to evaluate the chemical pollution of muddy sediments accumulated in the Gulf of Gdańsk under very strong anthropogenic pressure.

SEDIMENTS AND SEDIMENTARY PROCESSES

The sedimentary material comes into the Gulf of Gdańsk as a result of cliff erosion by storm waves and currents, transport by rivers and as a result of human activity. Only a very rough estimation of the amount of supplied material is possible.

Eroded cliffs along the Gulf of Gdańsk supply annually about 0.25-0.35 mln. tonnes of gravel, sand and finer fractions from the coast of Sambian Peninsula (Gudelis, Emelyanow, 1982; Blazhchishin, 1984), and about 0.05 mln tonnes from the western coast (Subotowicz, 1982). Considering the length and height of eroded cliffs and the rate of erosion, the amount of sedimentary material eroded from the Sambian coast seems to be overestimated.

The Vistula River discharges into the sea c. 1.8 mln. tonnes of sediment per year, in that c. 0.75 mln tonnes as bedload and c. 1.05 mln. tonnes in suspension (Cyberski, 1982). Transport by other rivers is much smaller, and can be neglected in the balance of sedimentary material.

Anthropogenic sources of sediments are important in the Gulf of Gdańsk. About 1.25-4.25 mln. tonnes of sediment per year comes to the sea from amber mines of the Sambian Peninsula (Emelyanov, Wypych, 1987; Blazhchishin 1984, Gudelis, Emelyanov, 1982). About 1.25-3.15 mln. tonnes of dredged spoils from Gdańsk, Gdynia, Baltiysk and Kaliningrad ports and waterways are dumped annually in the Gulf of Gdańsk (Andrulewicz, Dubrawski, 1995, Łazarienko, Majewski, 1975).

The distribution of sediments on the seabed of the Gulf of Gdańsk is dependent mainly on local hydrodynamic conditions caused by coast and seabed topography, as well as on the palaeogeography of the area. North-east of the Hel Peninsula sand occurs down to 70-80 m depths. In the Puck Bay the limit of sandy sediments is close to the 20 m depth contour. South-eastwards from the Puck Bay, in the southern part of the Gulf of Gdańsk, sands have reached the 60 m isobath. In the south-eastern and eastern parts of the Gulf, on the slopes of the Vistula Spit and Sambian Peninsula the boundary between sands and sandy-muddy sediments occurs at a depth of 30-40 m. The muds cover the depressions of Puck Bay and the central part of the Gulf of Gdańsk. The rate of mud deposition in the Gulf of Gdańsk varies from 1.43 to 1.86 mm/year in the southern part and up to 2.07 mm/year in the northern part of the Gulf (central part of the Gdańsk Deep) (Pempkowiak 1991, Walkusz et al. 1992, Szczepańska, Uścinowicz 1994). Muddy sediments occur also locally in front of the Vistula outlet cone (Uścinowicz, Zachowicz, 1993).

SCOPE AND METHODS OF INVESTIGATIONS

In 1994, the Geological Survey of the Netherlands and the Polish Geological Institute have carried out geological and geochemical investigations in the Gulf of Gdańsk (Laban et al. 1994). Among others the four main mud deposition areas were studied. The distribution of selected trace elements (Cd, Cr, Ni, P, Pb, Zn) in muds deposited in different subenvironments of sedimentation in the Gulf is presented.

Seismic survey was carried out using an ORE-140 high resolution acoustic system with 4 RX transducers in a polyester fish in which a TSS-320 heave compensator was mounted. Frequency filtering was done with a Krohn-Hite type 3323 system. The position was recorded with a TSS-312 alphanumeric annotator. Also the EG&G type 259 side-scan sonar, a 100kc Model 272 tow fish, and an EPC 8700 thermal recorder were used. Range used was 2×250 m. Shallow seismic and sonar profiling performed made up 180 km.

Sampling was done using a box corer with a round coring tube with a 0.3 m diameter and maximum penetration of 0.5 m. The muddy sediments were sampled at 11 sites (Fig. 1). With special boxes, subsamples were taken from the box corer for X-ray radiographs to study sedimentological structures. Also subsamples from the uppermost layer (0-2 cm) and from the lower part of the core, most often at a depth of 22-24 cm were taken for chemical analysis. Only in front of the Vistula outlet cone background subsamples were taken from the layers 34-36 cm and 38-40 cm.

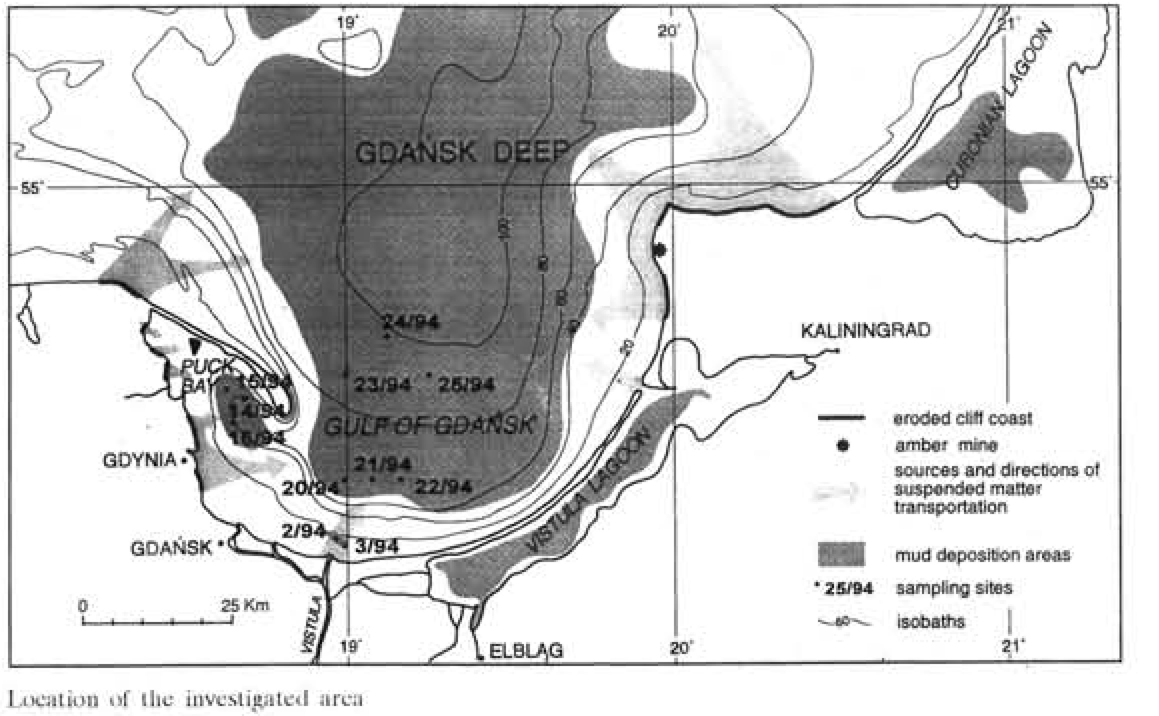

Fig. 1. Location of the investigated area

Positioning during the seismic surveys and sampling was done with Differential GPS, Trimble type.

X-ray radiographs were made by using a Hewlett Packard Faxitron X-ray system: 10-110 kV output voltage, 3 mA continuous current, with a beryllium window (0.63 mm) X-ray tube; the tube voltage was 90-110 kVp, film type Agfa Structurix D7(Pb), exposure time 1-2.5 min, and a Pb-masking was applied to enhance contrast.

Chemical analyses were done in the laboratory of the Geological Survey of the Netherlands. Total sediment samples were dried overnight at 105°C. Pressed powder tablets were automatically prepared of 10 g samples with 7 wax pills (1.2 g, containing EMU-Pulver 120 FD and wax). The sample material was ground together with the wax pills for 60 seconds in a Herzog Swing Mill with Tungsten-Carbide vessel. The elements, except for Cd, were analysed on pressed powder tablets by XRF using an ARL 8410. For calibration, pressed powder tablets of international rock standards were used. The following detection limits were established: Al 0.1%, P 0.01%, Cr 5, Ni 1, Pb 5, Zn 5 ppm. For analysis of the extractable (total) Cd the following method was used: 2.5 g of a dry sample was soaked in 20 ml of 10% HCl on boiling water bath for 3 hours. After dilution to 50 ml with water, the tube was centrifuged at 20,000 rpm for 3 minutes, leaving a clear solution above the residue. After dilution (50 times) with 0.05 N HCl the Cd content was determined using a Scintrex AAZ-2 Atomic Absorption Spectrometer with Zeeman background correction. International standards were taken into account. The lower detection limit of the analysis is 0.2 ppm Cd. Results of chemical analysis are presented in Table 1. Both absolute concentrations and to aluminium (Al) normalized data are given.

RESULTS OF INVESTIGATIONS

In the Gulf of Gdańsk mud is deposited in four subenvironments with different hydrologic features: 1 - area in front of the Vistula mouth, 2 - Puck Bay, 3 - southern part of the Gulf of Gdańsk, 4 - northern (deepest) part of the Gulf of Gdańsk.

The present outlet of the Vistula River was artificially constructed and opened in 1895. Since

Table 1. **Results of chemical analyses**

Core no.	Layer (cm)	Cd (ppm)	Cr (ppm)	Ni (ppm)	P (%)	Pb (ppm)	Zn (ppm)	Al (%)	Cd/Al	Cr/Al	Ni/Al	P/Al	Pb/Al	Zn/Al
2/94	0-2	4.80	54	6	0.10	16	37	2.05	2.34	26.3	2.9	0.05	7.8	18.0
	34-36	3.87	167	49	0.12	96	511	5.92	0.65	28.2	8.3	0.02	16.2	86.3
3/94	0-2	2.89	72	8	0.10	16	44	2.26	1.28	31.8	3.5	0.05	7.1	19.4
	38-40	1.27	102	20	0.07	44	187	3.92	0.32	26.0	5.1	0.02	11.2	47.8
14/94	0-4	2.05	110	34	0.18	68	186	4.95	0.41	22.2	6.9	0.04	13.7	37.6
	22-24	0.40	105	43	0.08	47	125	6.49	0.06	16.2	6.6	0.01	7.2	19.3
15/94	0-2	1.87	133	39	0.28	80	216	5.33	0.35	25.0	7.3	0.05	15.0	40.5
	22-24	0.42	107	48	0.07	40	119	6.90	0.06	15.5	7.0	0.01	5.8	17.3
16/94	0-2	0.96	99	31	0.16	58	140	5.42	0.18	18.3	5.7	0.03	10.7	25.8
	22-24	0.31	95	41	0.07	28	89	6.45	0.05	14.7	6.4	0.01	4.3	13.8
20/94	0-2	1.34	75	24	0.22	48	118	4.22	0.32	17.8	5.7	0.05	11.4	27.9
	22-24	0.24	75	26	0.08	35	70	5.18	0.05	14.5	5.0	0.02	6.8	13.5
21/94	0-2	1.93	86	33	0.17	72	167	4.82	0.40	17.8	6.8	0.04	14.9	34.6
	20-22	0.13	84	32	0.09	43	96	5.86	0.02	14.3	5.5	0.02	7.3	16.4
22/94	0-2	1.38	86	31	0.23	65	154	4.68	0.29	18.4	6.6	0.05	13.9	32.9
	22-24	0.15	88	34	0.10	36	82	6.15	0.02	14.3	5.5	0.02	5.9	13.3
23/94	0-2	–	86	40	0.18	102	209	4.64	–	18.6	8.6	0.04	22.0	45.1
	22-24	–	83	32	0.10	66	100	5.77	–	14.4	5.5	0.02	11.4	17.3
24/94	0-2	–	95	44	0.18	106	228	5.41	–	17.6	8.1	0.03	19.6	42.2
	22-24	–	99	44	0.10	83	151	6.93	–	14.3	6.4	0.02	12.0	21.8
25/94	0-2	2.16	95	40	0.16	104	218	5.06	0.43	18.8	7.9	0.03	20.6	43.1
	22-24	0.28	102	44	0.10	75	127	6.79	0.04	15.0	6.5	0.01	11.0	18.7

that time the outlet cone of bed load material is being accumulated. Intensive flocculation of suspended matter is taking place in the mixing zone of the river and marine waters. The mud deposition in front of the outlet cone of the Vistula River occurs at a water depth of c. 14-18 m. Side scan sonar records show in this area a flat sea floor with a pattern of vague sand ribbon-like features in the direction of the current which are overlain by ripples. Four box cores were taken at the foot of the outlet cone slope, and in two of them muddy sediments were found (box cores 2/94 and 3/94). The sediments are strongly bioturbated by *Nereis diversicolor* Muller and *Mya arenaria* (Linnaeus).

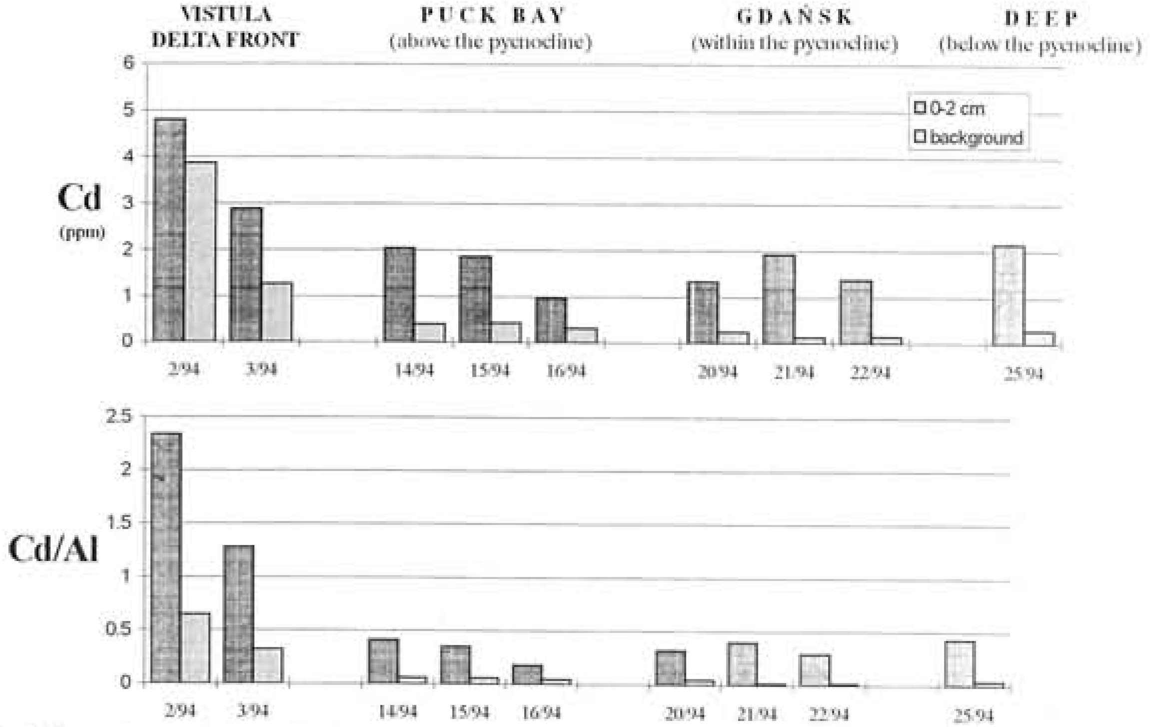

Fig. 2. Cd in muds of the Gulf of Gdańsk

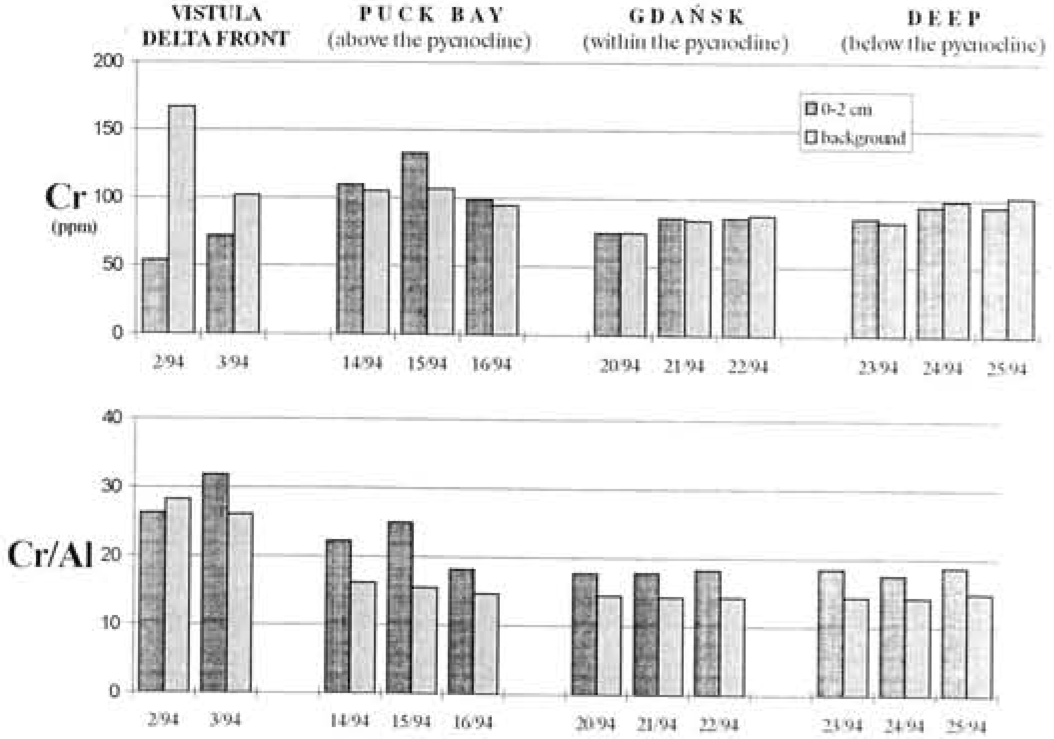

Fig. 3. Cr in muds of the Gulf of Gdańsk

Anthropogenic influence on the chemical composition of muds is evident, but the ratios between concentrations of the elements in the uppermost samples (0-2 cm) and reference samples (34-36 cm) are not similar for different elements. For cadmium anthropogenic influences from land run-off seems to be reflected by the highest concentrations in cores from the delta front area, both in uppermost and reference samples (Fig. 2). Absolute contents of chromium are higher in the samples from the lower parts of the cores, but after normalization to Al they are only slightly higher than in the samples from the surface (core 2/94) or a little bit lower (core 3/94) (Fig. 3). A trend is more distinct in the case of

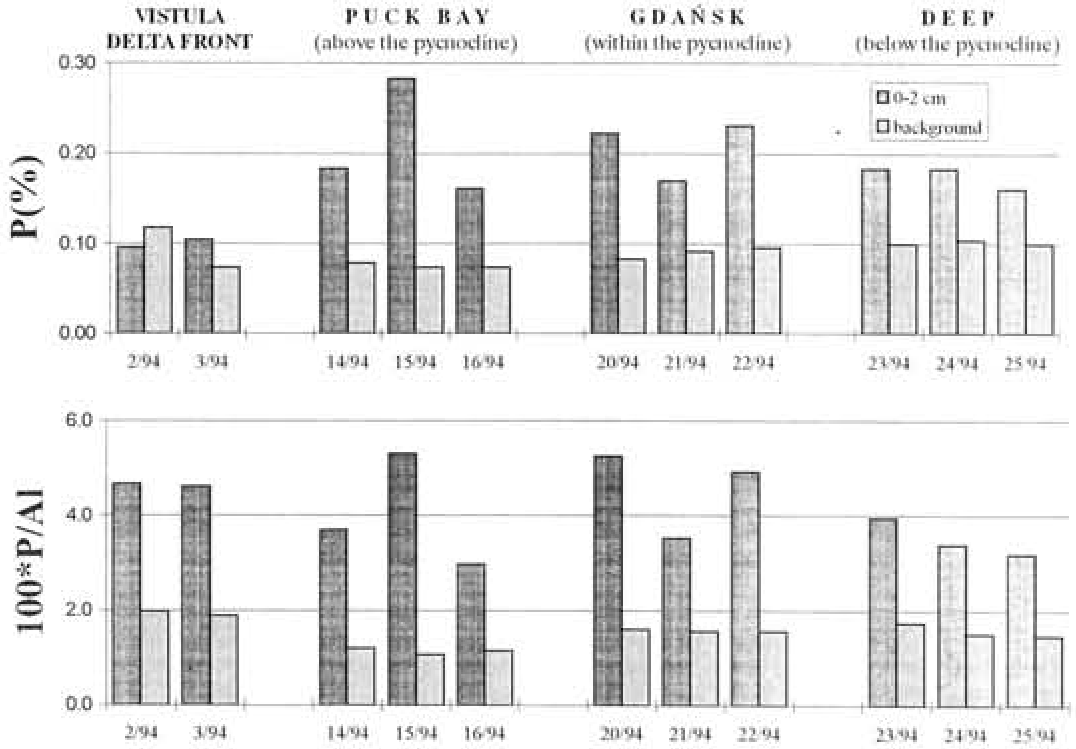

Fig. 4. P in muds of the Gulf of Gdańsk

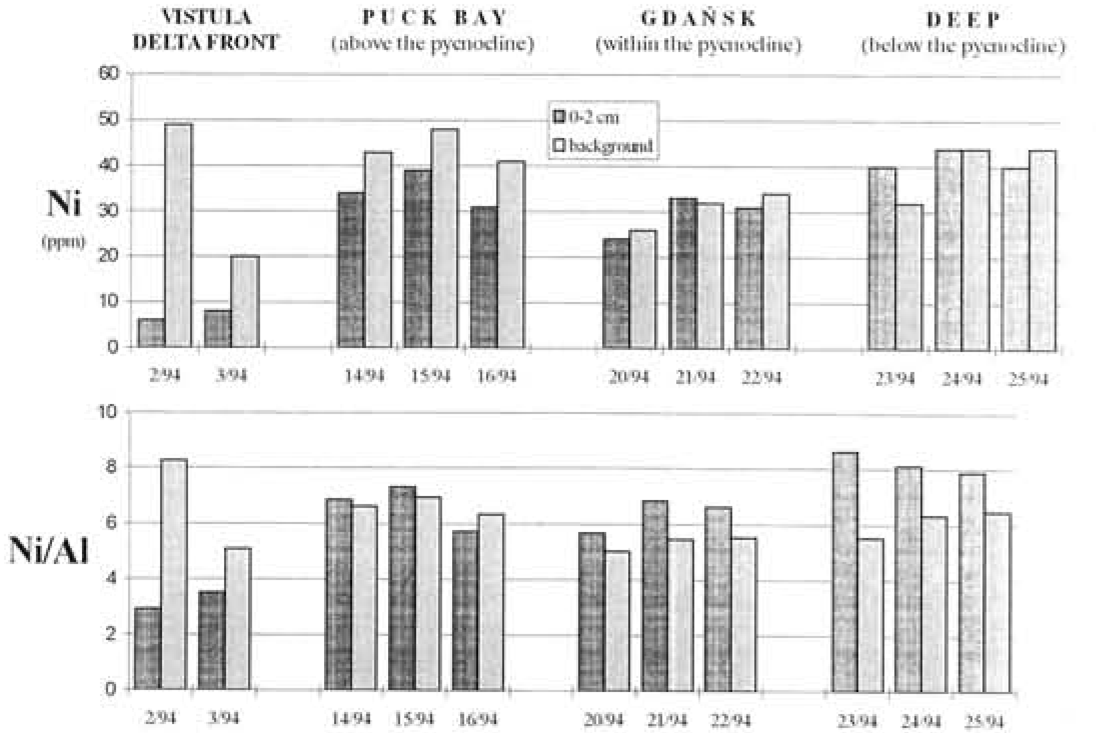

Fig. 5. Ni in muds of the Gulf of Gdańsk

phosphorus; normalized contents are distinctly higher in the samples from the sea bed surface, whereas absolute values are similar in both layers (Fig. 4). Contents of nickel, lead and zinc are higher in the lower parts of the cores (Fig. 5, 6, 7). Also normalized data show higher Zn, Pb and Ni concentrations in the reference samples. Such a vertical distribution of different elements in the very dynamic environment of the delta front, with a high rate of sediment accumulation could reflect changes in the chemical composition of the Vistula River waters during the last decade (Cyberska et. al 1996).

Deposition of recent muds in the Puck Bay takes place above the pycnocline, at a water depth of 25-30 m. Side-scan sonar records revealed a smooth, flat sea bed with locally vague reflections, probably caused by sea bed trawling. In the shallower part, bioturbation is more common than in the deeper part, where also erosion surfaces occur in the sedimentary column, clearly visible on X-ray radiographs.

In the Gulf of Gdańsk within the pycnocline, at a water depth of c. 55-85 m, muds are deposited under oxic conditions. Side-scan sonar records show a smooth, flat sea floor. The mud is only slightly bioturbated, up to 5 cm, by *Macoma baltica* (Linnaeus). Erosion surfaces, most probably caused by nearbottom currents connected with internal waves, are more common and typical for this area.

In the northern part of the Gulf of Gdańsk, below the pycnocline at a water depth of more than c. 85 m, mud deposition takes place under anoxic conditions. The upper part of the sediments, up to 6-14 cm, shows well developed horizontal lamination, without bioturbation. Deeper, the sediments are homogeneous, also without erosion surfaces.

The contents and regularities in the vertical distribution of trace elements are generally similar for the three above described areas. Cadmium, phosphorus, lead and zinc occur always in distinctly higher amounts in the uppermost parts of the sediments (samples from horizon 0-2 cm), than in their lower parts (samples from horizon 22-24 cm), both for absolute and normalized to Al values (Fig. 2, 4, 6 and 7). Chromium and nickel concentrations are at a similar level of absolute values in both investigated horizons, but after normalization, they display a slight enrichment in the uppermost horizon (Figs. 3 and 5).

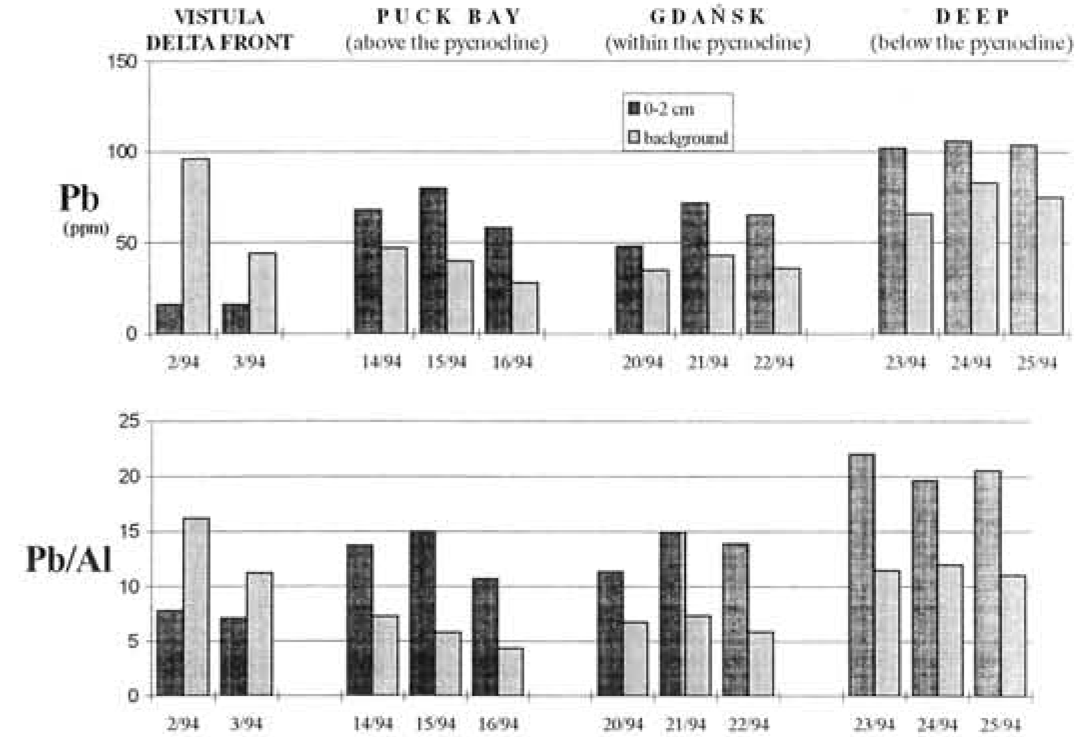

Fig. 6. Pb in muds of the Gulf of Gdańsk

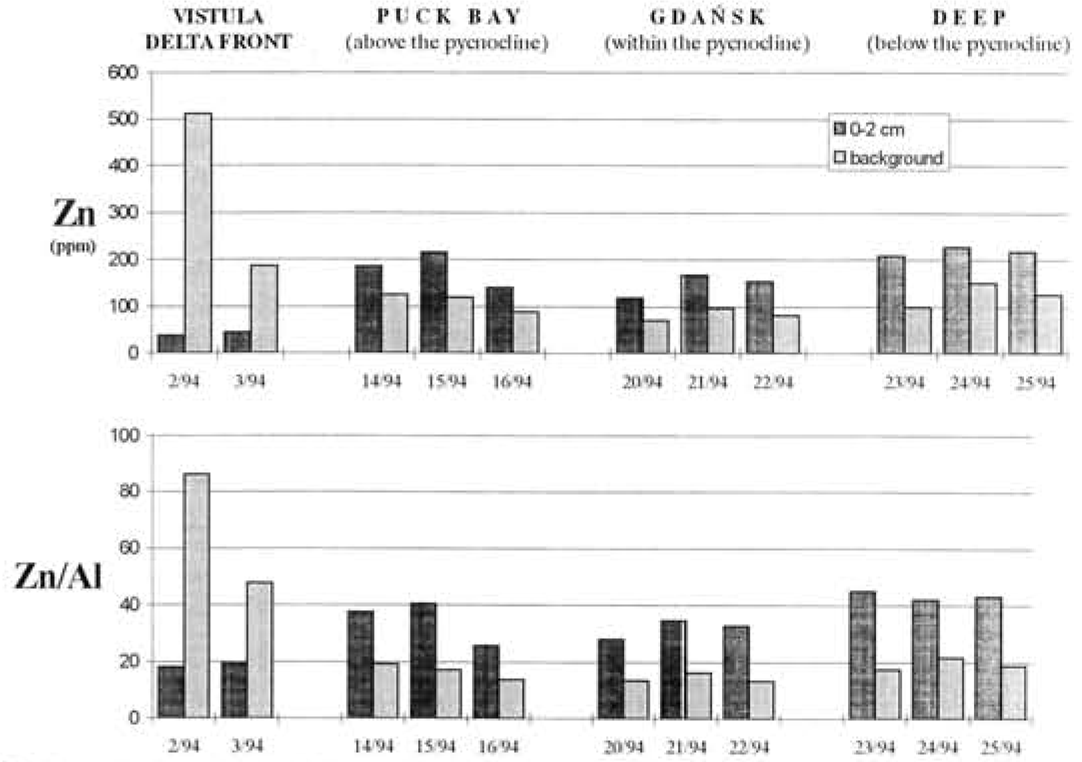

Fig. 7. Zn in muds of the Gulf of Gdańsk

DISCUSSION AND CONCLUSIONS

Enrichment of the surface sediments by some elements may be a result of sediment natural geochemical properties or anthropogenic influences. Evaluation of the degree of contamination of the surface layer can be done by comparing it with that of a reference layer, the so-called geochemical background. In order to determine the position of the geochemical background layer, which should not be distorted by anthropogenic influences, many natural factors should be taken into account, such as follows: rate of sedimentation, depth of mixing of sediments caused by bioturbation and near-bottom currents, and rate and range of pore water diffusion. Also it should be borne in mind that natural processes of sediment accumulation may be disturbed by human activity e.g. fishing, shipping, military activities etc. In the Gulf of Gdańsk, with a sedimentation rate of 1 to 2 mm/year, a 20 cm thick layer of mud has been formed during the last 100-200 years. Macroscopic observations and X-ray radiographs of cores have shown that contemporary bioturbation processes, as a rule, do not penetrate deeper than c. 10 cm (except the area in front of the Vistula River mouth and Puck Bay). Despite of bioturbation of the muds from the Puck Bay, the vertical distribution of elements in this area (Table 1) shows that sediments from the horizons of 22-24 cm were deposited also before the beginning of the intense industrial development in the Baltic Sea drainage area. Only muds deposited in the shallow water area in front of the Vistula River mouth have been fully formed during industrial times and contain in the whole sedimentary column anthropogenic contaminants. The following background values of elements (in ppm, only for P in %) were found (Table 2).

Table 2

	Cd	Cr	Ni	P	Pb	Zn
Puck Bay	0.31-0.42	95-105	41-48	0.07-0.08	28-47	89-125
Gulf of Gdańsk (within the pycnocline)	0.13-0.24	75-88	26-34	0.08-0.10	35-43	70-96
Gulf of Gdańsk (below the pycnocline)	0.28	83-102	32-44	0.10	66-83	100-151

The above values are similar to typical total background concentrations of metals in the Baltic muds given by Perttila & Brugman (1992). Only concentrations of trace elements in the Puck Bay are a slightly higher. It is possible that contaminants migrate down because of bioturbation, and that background contents of elements in the Puck Bay area are located deeper than 22-24 cm. Nevertheless the enrichment factors (EF) normalized to Al – a measure of deposit contamination – are higher than 1 for all investigated elements and even higher than 3 for some elements.

Grain size is an important factor controlling the distribution of both natural and anthropogenic components in the sediments. The other factor is organic matter (Cato 1977, 1989). Contaminants are mainly associated with the clay minerals and to the organic residues of the sediments. To compensate this problem sediment data can be normalized by dividing the raw concentration data by the weight of the fine-grained fraction, by the content of aluminium – a major constituent of clay minerals or by the content of organic carbon. Normalization of sea bed geochemical data with Al is the normalization tool used in this environmental impact study. The aluminium normalization is based on the fact that there are natural ratios between trace metals and Al that exist in the absence of any human influence. The concentration of aluminium is always assumed to be a natural (e.g. Windom et al., 1989). The advantage of using this method is clearly demonstrated in Figs. 2-7, especially for Cr and Ni (Figs. 3 and 5), where the absolute background and surface data are similar.

The Gulf of Gdańsk, including the Puck Bay, is one of the most endangered areas, where exceptionally large changes have occurred. In the surface layer of sediments in the gulf the content of many elements - especially cadmium, lead and zinc - has markedly increased. In the Gulf of Gdańsk, visible symptoms of eutrophication are present in form of enrichment of sea bed surface sediments with phosphorus.

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The Glacial Erosional Valley System of the Hanö Bay, Southern Baltic Sea

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Seismic reflection profiling in the Hanö Bay, southern Baltic Sea, has revealed a system of buried erosional valleys cut into the loosely consolidated Cretaceous and Paleogene sedimentary bedrock. Together with similar valley systems in the south-eastern and south-western Baltic Sea and on land in the southern Baltic coastal region, it is part of a distinct belt of periglacial erosional valleys.

The Hanö Bay valleys are of different ages, and also of different morphological forms. The older valleys are v-shaped in form and have steep, smooth walls. Comparisons with similar valley systems and their infillings on land, where age determinations are based on drillings, suggest that this older valley system was formed during the Elsterian and Saalean glaciations. The younger valleys are generally larger, with u-shaped forms and steep, smooth walls. These large valleys are suggested to have been formed during the latest glaciation, the Weichselian. Some small valleys, attributed to the Saalean and Weichselian glaciations, have been found cutting into the infillings of the proposed Elsterian valleys.

The deposits infilling the valleys are subdivided due to their seismic appearances. Three depositional and erosional cycles have been recognised. Each cycle contains a till-like unit at the bottom followed by a sandy deposit. The upper surface of each cycle marks an erosional event.

The valley system is interpreted to have been formed by fluvial agents closely inside ice fronts and it has the appearance of repeated periglacial drainage systems.

Keywords: Baltic Sea, Hanö Bay, Quaternary glaciations, erosional valleys, glacial erosion.

INTRODUCTION

From 1975 to 1980 seismic reflection profiling was performed in the Hanö Bay (Fig. 1) as part of sedimentary bedrock studies (Kumpas 1980a, 1980b). The reflection data includes information on the bedrock morphology and on the glacial and postglacial deposits. Renewed inspection of the seismic data has revealed a system of buried erosional valleys cut into the rather loosely consolidated Cretaceous and Paleogene sedimentary bedrock. All valleys are restricted to the deep southern and south-eastern parts of the Hanö Bay where they sometimes are associated with tectonic lineaments (Fig. 2). The present paper is focused on the formation and infilling of these very prominent features that are deeply imprinted in the sedimentary bedrock.

Our knowledge about the early glaciations in the southern Baltic area is still fragmentary. It is, however, known that the Hanö Bay area was covered by ice during several Quaternary glaciations - and their maximum situated several hundred kilometres from the rim. The Weichselian glaciation and the postglacial records are better understood. Duphorn et al. (1979) investigated the late-glacial varved clays of the Bornholm Basin and the Hanö Bay. They divided the deposits into four lithostratigraphic units. The units consist of mud belonging to the Litorina stage; clay belonging to the Ancylus and Yoldia stages; varved clays from the Baltic Ice Lake and Weichselian glacial deposits, mainly tills.

The Late Weichselian to Holocene development of the area is described by Björck & Dennegård (1988). Their investigation included datings of pine stumps and peat found in the shallower parts of the Bay. The pine stumps suggest that the northern Bay above about 50 m depth was covered by a forest at about 9700-9300 BP. Later the sea inundated the area and at depths between 7 and 14 m peat was accumulated. Björck et al. (1990) dis-

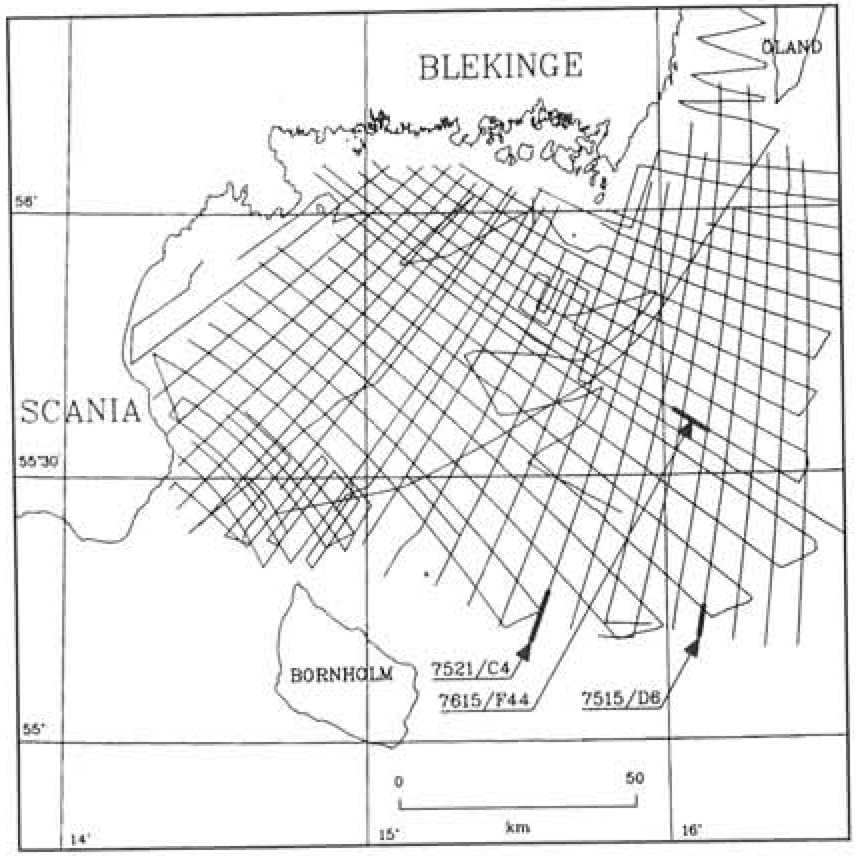

Fig. 1. Location of seismic lines in the Hanö Bay

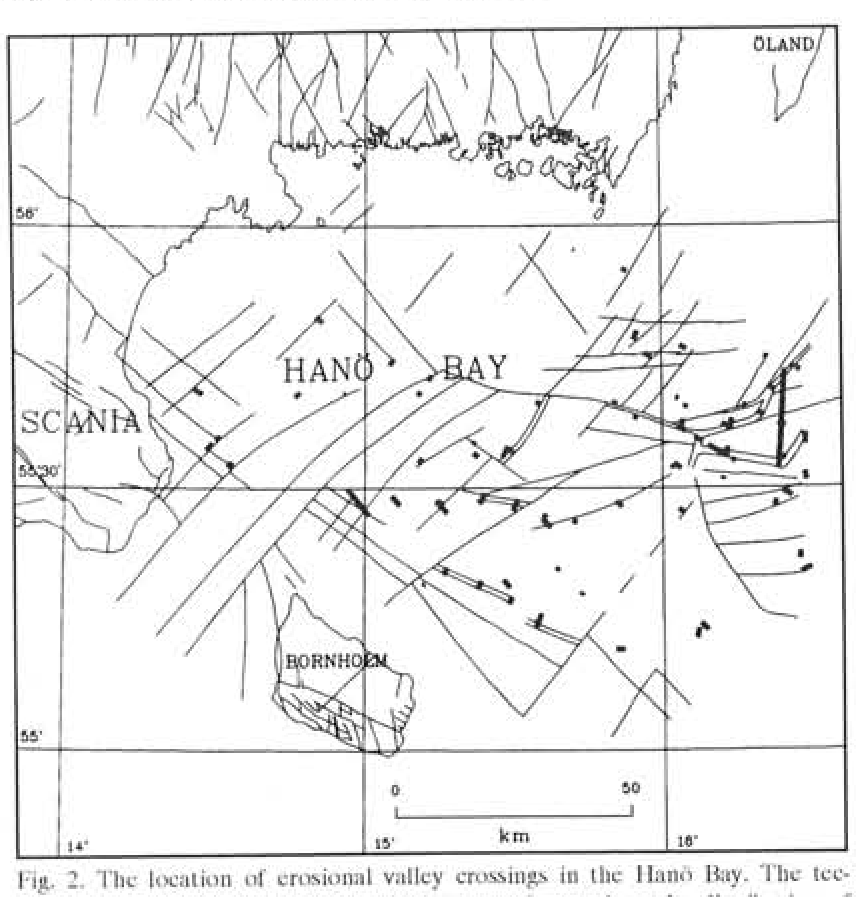

Fig. 2. The location of erosional valley crossings in the Hanö Bay. The tectonic pattern (Wannäs & Flodén 1994) is superimposed on the distribution of valleys. The figure shows that the valleys frequently follow these tectonic lineaments. Thick lines mark the location of erosional valley structures

cussed the general marine stratigraphy of the Hanö Bay. They tentatively divided the deposits into four seismic units ranging from the Late Weichselian to the Holocene.

Based on marine seismic profiling, Bjerkéus et al. (1994a) reported the presence of assumed periglacial erosional valleys in the south-eastern part of the Baltic Sea. The valleys are deeply cut into the soft terrigenous deposits of the Lower and Middle Devonian and they are completely infilled by Quaternary deposits. A regional outline of the periglacial valley systems in the southern Baltic by Flodén et al. (1997) initiated the present study of the Hanö Bay valley system. The valley systems in the southern Baltic Sea are interpreted to have been formed by fluvial agents closely inside ice fronts. Abandoned river valleys of different generations are also described from the Baltic Sea (Gelumbauskaitė 1996), but no such features have been identified in the present area.

MATERIALS AND METHODS

The seismic reflection data used in the present investigation was collected in 1975-80 using a single channel profiling system based on a PAR-600 air gun. The reflected signals were received by a hydrophone cel containing 100 hydrophone elements equally distributed within a 20 m hose. The signals were filtered onboard and 100-200 Hz records were displayed on a precision graphic recorder. The graphically displayed time interval was 0.5 s. As the material was primarily intended for investigations of the sedimentary bedrock the resolution of about 2.5 m was not sufficient for any detailed subdivision of the Quaternary deposits. To get a better view of the Quaternary deposits a small area was reinvestigated in detail and a frequency interval of 250-500 Hz was displayed. This resulted in records with a resolution of about 1-1.5 m. Despite the rather limited resolution, it was possible to outline the valley system and also to obtain a general impression of their infillings. It should be noted that in the present paper the interpretation of the valley infillings is solely based on their seismic appearances.

For the seismic investigations the Decca Navigator chain OA/MP was used for positioning. The accuracy received was no better than +/- 100 m. The water depth and bottom topography were recorded by an Elac LAZ 17 echosounder.

GEOLOGICAL SETTING

The Hanö Bay is located in the southern Baltic Sea along the southern boundary of the Fennoscandian Shield. The area has been subjected to repeated tectonic disturbances ever since the Palaeozoic. However, the present day Hanö Bay basin, and the horst structures along its southern edge, was mainly developed in the Mesozoic and Tertiary. The Mesozoic sedimentary bedrock was deposited in a southwards sloping basin fringing the Fennoscandian land mass in the north. Apart from the horst areas around Bornholm no early Mesozoic bedrock is exposed in the Bay (Kumpas 1980b). Apart from some possible Paleogene outcrops of local extensions, the sedimentary bedrock surface is everywhere sculptured in supposed Upper Cretaceous rocks (Kumpas 1980b). The Cretaceous bedrock probably consists of limestones, sandstones and clays whereas the Paleogene system is represented by soft calcareous sediments (Kumpas 1978). Nearshore along the Blekinge coast in the north, the seafloor consists of Precambrian crystalline bedrock, irregularly overlain by till and clay. This gives the seafloor a more rugged appearance along the coast as compared to the deeper part of the Bay that has a rather flat seafloor. Apart from the coastal area, Precambrian crystalline bedrock is exposed on the Christiansö Horst in the south as well as on the island of Bornholm.

CONCEPTS OF VALLEY FORMING PROCESSES

Over the years, a great number of authors have advocated different opinions about the formation of erosional valleys in periglacial environments (Björnsson 1979; Ehlers & Wingfield 1991; Liedke 1981; Woodland 1970). Ussing (1907, 1913) was the first to describe the 'tunnel valleys' of Jutland in Denmark. He stated that they were formed by ice excavation together with subglacial meltwater erosion. Although some authors (Andersen 1973; Berthelsen 1972; Hansen 1971) may disagree with the interpretations put forward by Ussing, the formation of valleys by high-velocity water discharge near the ice margin has been widely accepted.

Wright (1973) described the hydrodynamics of subglacial waters below the Weichselian Superior ice lobe in Minnesota. He found that the geothermal flux and friction heat are sufficient agents to melt a glacier at its basal part without melting the foot of the glacier which remains frozen. In the Baltic Sea area, which formed an enclosed basinal structure already during the first part of the glacial period (Puura & Flodén 1997), it is reasonable to assume that water accumulated under the ice during long periods of time. Occasionally, the water would force its way through the frozen foot of the ice, and debris brought by the water would greatly increase the erosive power. As the water pressure was gradually reduced, the water changed from an erosional agent to a depositional agent and the newly formed valleys were rapidly filled. Thus, the erosional valleys in the Hanö Bay are most likely formed by meltwater erosion at, or closely inside, the ice front.

Another possible valley forming process is put forward by Hay et al. (1993). Due to the great load of the ice on the underlying bedrock a wedge or a bulge forms at the rim of the ice. Water may break through this bulge along streams or rivers. As the ice load is eventually removed the bulge will drop and the valleys created by sub-aerial streams will also drop. This process may, however, be valid only in larger context as the bulge would greatly exceed the lengths of the valleys found in Hanö Bay. The infill of valleys formed by this process would be clastic sediments and no till would be found. However, it is not possible to exclude the possibility of different valley forming processes along the ice margin.

THE EROSIONAL VALLEY SYSTEM

The erosional valley system discussed in this paper is limited to the south-eastern part of the Hanö Bay. The vertical succession of the units infilling the valleys indicates that these are of at least three different generations. The older of the valleys are more or less v-shaped in their form (Fig. 3). Their walls are generally steep and smooth and they look almost vertical in the seismic records. The bedrock surface at the flanks of the valleys generally dips gently towards the centre of the valley itself and then suddenly drops several tens of metres. The deepest valley of this generation is incised some 80 m into the sedimentary bedrock. These older valleys are mainly infilled by Quaternary till and glaciofluvial material and overlain entirely by Weichselian till and younger clay sequences.

The younger valleys are commonly wider structures with rather flat bottoms and steep, almost vertical walls in the seismic records (Fig. 4). The infilling of these large structures consists mainly of Quaternary clays and silt. Very little till is deposited in these younger valleys. It seems as if the Weichselian ice sheet only levelled the bedrock surface and then deposited a rather uniform till layer on top. This till was later, in some places, cut through by erosion and the large u-shaped valleys were formed. The seismic signature of the infilling of these valleys is rather transparent in appearance.

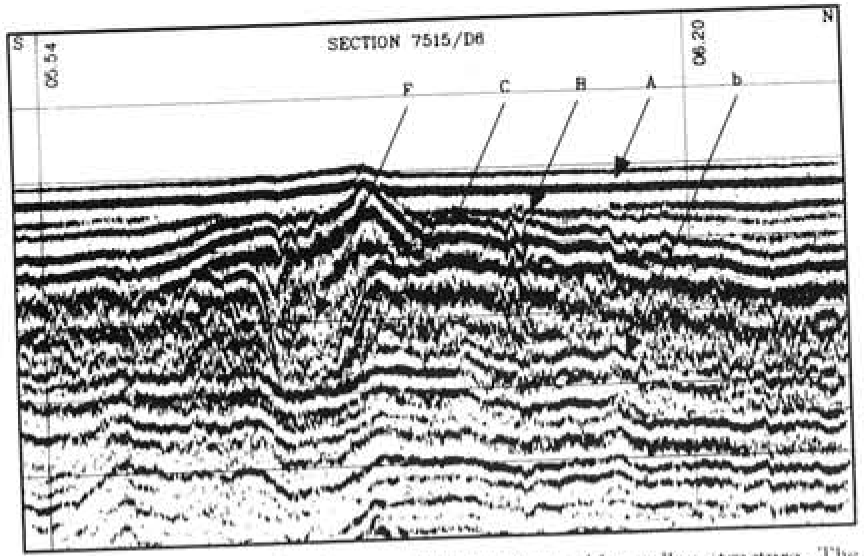

Fig. 3. Seismic profile showing an example of an older valley structure. The vertical scale is 25 ms TWT between the lines corresponding to approx. 18.5 m in the water column and the horizontal scale about 4.5 km between position marks. A - Postglacial clay unit; B - Weichselian meltwater clay unit; C - Weichselian upper till unit; F - pre-till sand and gravel unit; b - sedimentary bedrock surface. For location see Fig. 1. Note that the subdivision in postglacial and glacial varved clays is based on echosounding records and therefore very diffuse in this figure

The Infilling of the Valleys

The glacial and postglacial sedimentary units that appear in the valley area have been subdivided according to their seismic appearance (Figs. 3 & 4). The subdivision of the postglacial and glacial varved clays is, however, based on echosounding records. The postglacial clays have a very transparent appearance in the echosounding records whereas the glacial varved clays have very faint but persistent internal reflectors and sharp bounding reflectors. In the single channel seismic records tills show very irregular internal reflectors, the signal scatters when reflected by the stones or boulders in the till. Sand and gravel have very short regular internal reflectors and sharper bounding reflectors.

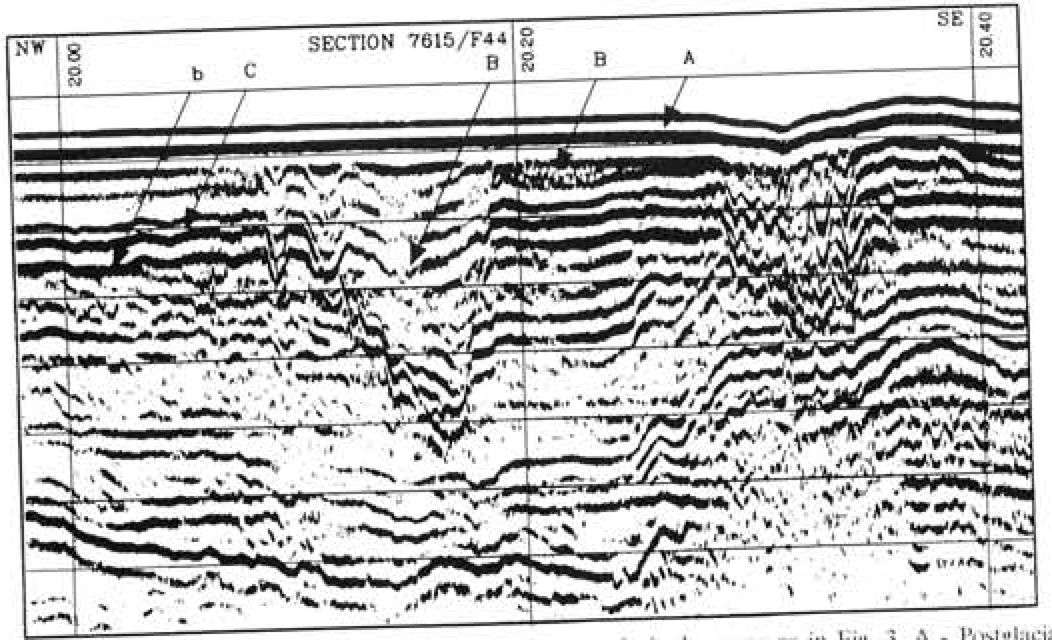

Fig. 4. Seismic section with an example of a younger valley. The scale is the same as in Fig. 3. A - Postglacial clay unit; B - Weichselian meltwater clay unit; C - Weichselian upper till unit; b - sedimentary bedrock surface. Note that the subdivision in postglacial and glacial varved clays is based on echosounding records and therefore very diffuse in this figure. For location see Fig. 1

Unit A - a postglacial clay unit: A postglacial clay unit is present across the deep southern and south-eastern part of the Hanö Bay. Till is exposed at the seafloor surface in the shallow northern part of the Bay and postglacial clays are present only within small depressions in the till surface.

Unit B - a late glacial glacilimnic varved clay unit: Glacilacustrine clays are present below the postglacial clays in the Bay. Unlike the postglacial clays of unit A, the glacial varved clays are found as infillings of the large, valleys, which suggests that the valleys were formed when the last glacier melted away. The total thickness of the postglacial and glacial varved clays, Units A and B together, is about 40 m in the south-eastern part of the Bay.

Unit C - a Weichselian upper till unit: The upper till unit is more or less evenly distributed across the incised area, resting on a very flat erosional surface. In the shallower parts of the Bay, towards the north and north-west, this till unit is exposed at the seabed. In the deeper parts it is overlain by Units A and B. The thickness of unit C ranges from about 5 m in the shallower parts of the Bay to about 30 m.

Unit D - a lower sediment unit: This unit is mostly found interlayering with Unit F. Some very shallow valleys of the second and third generations are sometimes infilled with this unit. The thickness of the unit is generally only a few metres.

Unit E - a middle till unit: The middle till unit is found infilling shallow valleys that are defined as second generation valleys. As in the case of unit C, the upper surface of this till unit is erosional. The thickness of the unit ranges from about 10 to 30 m.

Unit F - a sand and gravel unit: This unit which is partly older than the tills in unit E is found interlayering with unit G and unit E. Sometimes Unit F constitutes the entire infill of a valley. The thickness ranges from approx. 5 m on the flanks of the valleys to about 40 m where it completely infills a valley structure.

Unit G, a basal till unit: This deposit is very randomly distributed, not all valleys contain this basal till deposit. The upper surface of the unit is erosional on which the succeeding units have been deposited. The thickness of the sequence is about 10 m as an average.

DISCUSSION

In the Hanö Bay the erosional valleys were formed during at least three different events of erosion and infilling. The deposits infilling the valleys form distinct sedimentary cycles consisting of a basal till, followed upwards by fluvial deposits, and terminated by an erosional surface. These erosional surfaces are of regional extension and may separate between deposits laid down during different glaciations.

The upper erosional surface of the first sedimentary cycle found in the first generation valleys, is interpreted as a pre-Weichselian surface, possibly separating the Elsterian and Saalean glaciations. Cut into this surface are the valleys of the second event (Fig. 5). These second generation valleys are sometimes cut into the soft sedimentary bedrock or into the infillings of older valleys, which shows that they truly belong to different generations. Like the first generation valleys these younger valleys are infilled by till followed by a fluvial sequence. The development of the third, youngest generation of valleys is similar to the previous two except for the infilling. The third generation valleys are entirely infilled by late glacial varved clays and overlain by post-glacial clays (Fig. 4).

In the seismic records three generations of till have been distinguished, from the base and upwards Unit G, Unit E and Unit C. As mentioned above, these till units are clearly separated from each other by erosional surfaces. In the valleys of the first

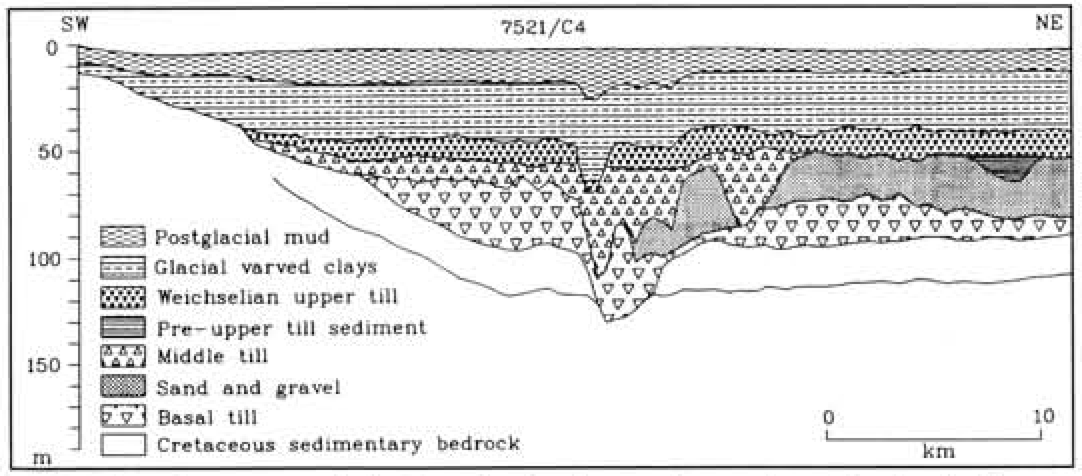

Fig. 5 Sketch drawing of an interpreted seismic section showing several generations of erosional valley structures and their infill. Note that the depths are metres below sea floor. For location see Fig. 1

and second generation, several sandy deposits overlying the till units have been distinguished (Fig. 3). These sandy deposits also show an erosional upper surface on which successive deposits have been laid down.

Some of the large u-shaped valleys of the third generation cuts through the upper till unit, Unit C (Fig. 4), and practically no till is found at the bottom of these structures. The till that occasionally is present in these large valleys has a very patchy distribution pattern which may suggest that they have been transported by slumping. Thus, the large young valleys appear to be completely infilled by the basal parts of the overlying late glacial varved clay unit, unit B (Fig. 4). The valleys that are located in the deeper parts of the Bay are all covered by a rather thick sequence of the late glacial varved, unit B and postglacial clays, unit A. The valleys found in the shallower areas are covered by a fairly thin sequence of the upper till unit, Unit C. Unit C has been deposited on a very flat surface and has the appearance of a bottom moraine deposited during the last glaciation.

Seismic reflection profiling shows that erosional valleys are widely distributed in the deeper parts of the Hanö Bay. There are a few valleys present in the shallower parts too, but they are very small and shallow. The older valleys are found within an area extending from the north-eastern to the south-western parts of the Bay (Fig. 6), whereas the younger valleys are mainly found in the northern parts of the south-eastern Hanö Bay (Fig. 7).

Taking the tectonic pattern into account, evidently the tectonic faults may have had a strong influence on the positions of valley formation. Thus, some of the valleys found in the deeper parts of the Bay are partly located along tectonic faults (Fig. 2). Some of the younger valleys are also found to proceed along the trends of older valleys, i.e. the older structures have been re-used in younger times.

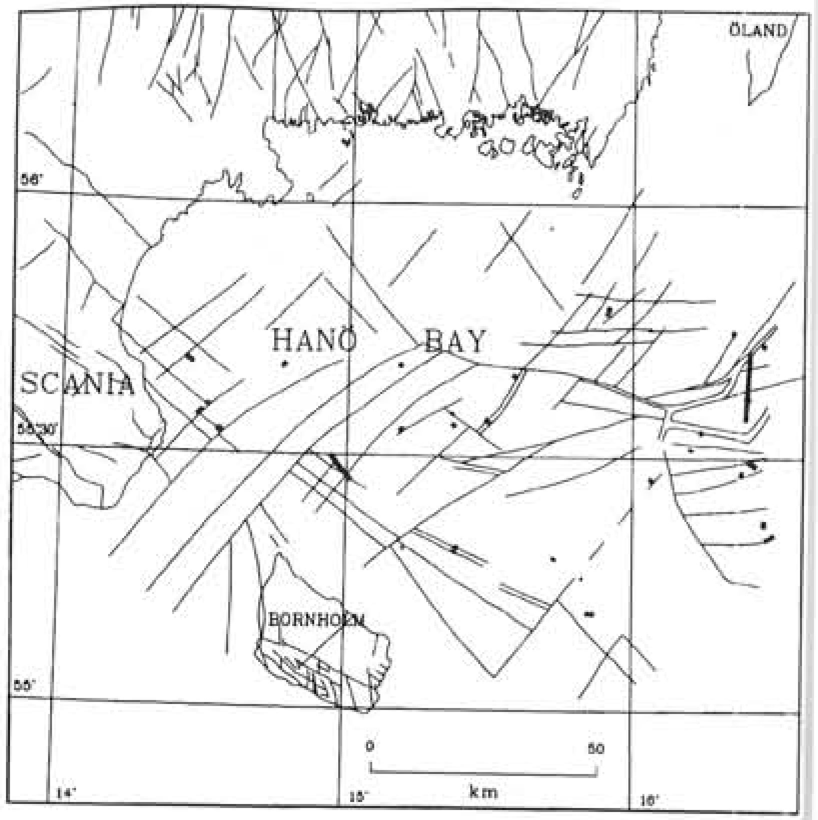

Fig. 6. The distribution of older valley structures in the Hanö Bay. The older valleys are more scattered in their distribution than the younger ones

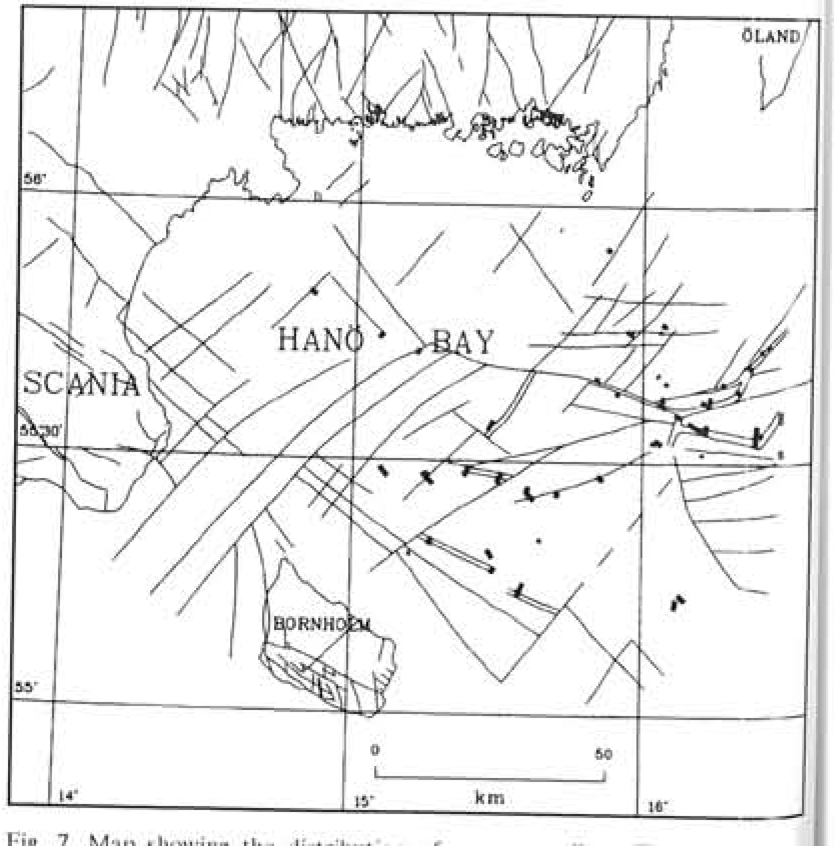

Fig. 7. Map showing the distribution of younger valleys. They are almost entirely concentrated to the eastern, deeper part of the Bay

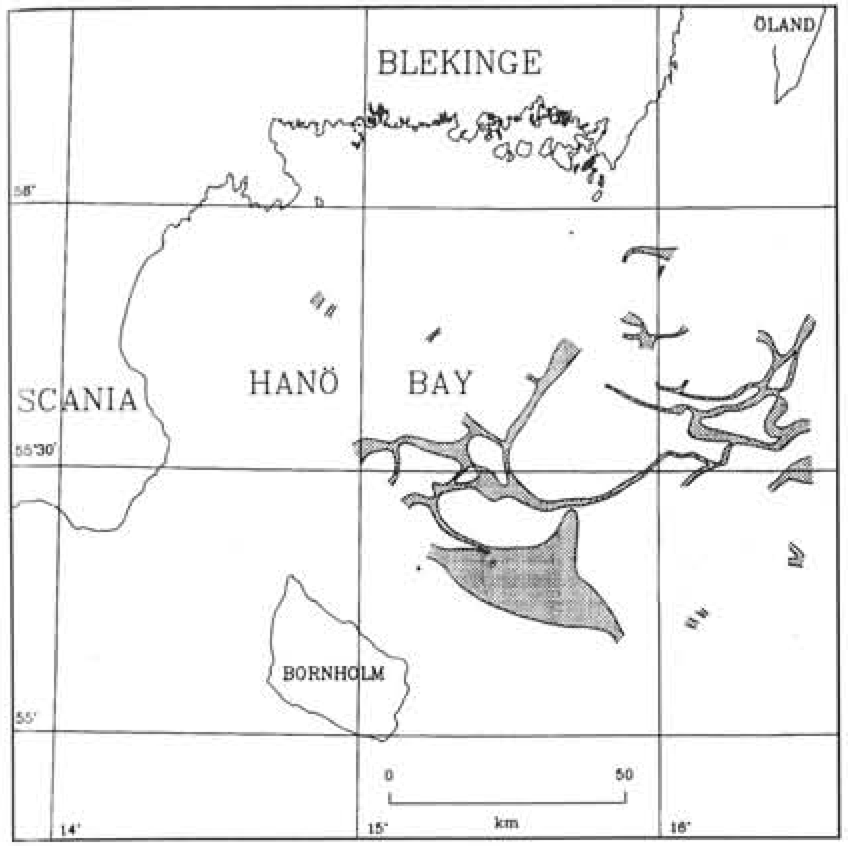

Fig. 8. The periglacial drainage pattern of Hanö Bay

The depths of the valleys vary considerably. Structures located close to each other may have differences in depth of several tens of metres. When connecting adjacent valleys with each other, a deep valley is generally found at the centre and shallow valleys to the sides.

The valley system of the Hanö Bay has the general appearance of a periglacial drainage area where the forces of the water have been variable from place to place. Prominent valley systems were only formed in those parts where high water velocities were combined with low erosional resistance of the bedrock.

The distribution pattern of the Hanö Bay valleys (Fig. 8) is similar to that of other nearby periglacial drainage areas as for example the Arkona Basin (Flodén et al. 1997) and the south-eastern part of the Baltic Sea (Bjerkéus et al. 1994a,b).

Comparison with Other Areas

At least three different generations of channels have been found in the Hanö Bay area. In north-western Germany a similar system of valleys attributed to the Elsterian has been described by Ehlers et al. (1984). The infilling consist mostly of fluvial sequences such as sandy and clayey deposits. However, the valleys found in most mainland areas seems to be cut down into thick Quaternary deposits. More seldom the erosion has cut deep valleys in the sedimentary bedrock. However, in the North Sea valleys cut into the sedimentary bedrock have been found (Ehlers & Wingfield 1991). These structures are of rather short duration and infilled by several layers of Quaternary deposits. As in Hanö Bay, the valleys in the North Sea are of several generations where the younger valleys sometimes cut into the infilling of older alleys. Contrary to the Hanö Bay valleys, the infillings of the North Sea valleys do not contain any till deposits (Ehlers & Wingfield, 1991).

In the south-eastern part of the Baltic Sea, offshore Latvia, deep erosional valleys have been found. In this area the erosion has cut deep into the loosely consolidated Lower and Middle Devonian terrigenous sandstones (Bjerkéus et al. 1994a,b). These valleys are considerably deeper than the ones found in the Hanö Bay, the bottom of the deepest valley is located about 330 m below sea level, and the actual valley structure is about 230 m deep. The infillings of the valleys resemble those found in the valleys of the Hanö Bay, namely till units interlayered with sandy and stratified units.

Valleys found in Germany also reveal several erosional and depositional events. Contrary to valleys in the North Sea and in the Baltic Sea, the valleys in Germany are found within the thick Quaternary deposits. The valleys direct radially away from what was the centre of the glaciation and towards the ice margin (Ehlers et al. 1984). Till is rarely found at the bottom of the deeper structures on the German mainland where it is found it is believed to be slumped from the base of the glacier (Ehlers et al. 1984). However the shallow valleys are sometimes filled with morainic material which suggests that these shallow valleys are formed mainly by glacial erosion and that the deeper ones by meltwater erosion (Grube 1979).

Deep valley structures are also present offshore Britain. The valleys belong to three different glaciations and are, thus, attributed to the Elsterian, Saalean and Weichselian. (Wingfield 1989). The valleys are mainly cut into unlithified Pleistocene and Tertiary deposits (Wingfield 1989) and are, like the valleys in Hanö Bay, of rather short horizontal extensions.

CONCLUSIONS

- The valleys cut deeply into the soft Cretaceous bedrock, partly lined up with the tectonic lineaments.
- The valleys are mainly found in the deep southeastern part of the Hanö Bay, although a few shallow ones are found in the northern shallow part. They are thus found where the ice moved from bedrock into softer sediments.
- The structures are, as far known, of rather short horizontal extension and exhibits an elongated u-shape lengthways when connected with adjacent valleys.
- The valleys are of three generations, the older ones are rather narrow and V-shaped whereas the younger ones are wide and U-shaped.
- Comparisons with valleys described from other areas along the north European glacial margin, suggest that the Hanö Bay valleys were formed during three different glaciations, namely the Elsterian, Saalean and Weichselian. Future drillings will decide this.
- The valleys of the youngest generation, which are clearly of a Weichselian age, are wider and larger than those of the inferred Elsterian and Saalean glaciations.
- The Weichselian ice seems to have been slightly more erosive in the Hanö Bay than in the southeastern Baltic Sea area. This is evident from the rather large U-shaped valleys that cut through the upper till sequence.
- The valleys are considered to have been formed by meltwater erosion at, or closely inside, the ice front.

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Classification of Sea Floor Geology by Complex Acoustic Methods, at Chłapowo, Poland

Stanisław Rudowski
and Leonard Gajewski

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Results of detailed shallow water studies of the sea bottom using complex acoustic methods are presented. On the nearshore bottom at the village of Chłapowo near Cape Rozewie four acoustic facies were recognised and geologically interpreted as different kinds of bottom. The aim of the study was to test and adapt the methods in methodological and regional aspect so they might become standard methods for detailed classification and mapping of surface sediments and bottom structures, especially for shallow-water works in the nearshore zone, related to investigations of sediment balance, predictions of coastline development and for the needs of coastal protection.

Keywords: bottom types, nearshore, acoustic methods, Baltic.

INTRODUCTION

Progress in acoustic methods and techniques makes it now possible to obtain a very good recognition and determination of the sea bottom surface and of its structure. However, these methods are designed mainly for investigations in relatively deep water (water depths larger than 10-20 m). Acoustic investigations in shallower water are up till now rather rare (*cf.* Berne et al 1994), nevertheless they are very important to studies of nearshore processes and to engineering investigations. These studies require specific equipment and methods adapted to the shallow water conditions of the nearshore zone, where bottom is very

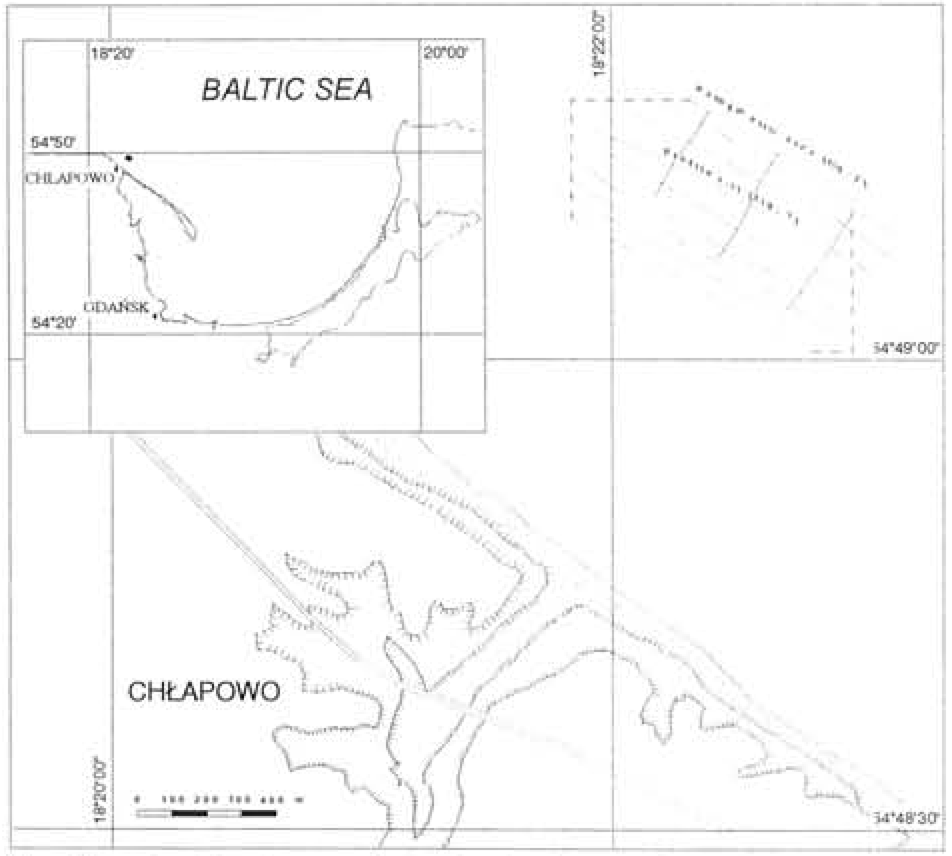

Fig. 1. Location of study area and situation of seismoacoustic and side scan sonar profiles; the profile I-II records are given in Fig. 3

often uneven and changes quickly in space and time. Very detailed preparatory studies are needed to develop principles for future standard investigations along a given stretch of coastline. This standardisation is necessary for the determination of the actual dynamic state of the coast, for the prediction of its development and for planning and design of coastal protection systems, and also for other different tasks, e.g. hydroengineering, hydrodynamics, sedimentological, lithological etc studies.

A part of the nearshore bottom (Fig. 1) at the village of Chłapowo near Cape Rozewie was selected as one of the basic study areas on the Polish Baltic Coast. The study area of about 1 – 1 km is located about 1 km off the beach in water depths of 8-15 m. (Fig. 2). The selected area is situated within that part of the coastal zone which plays a significant role in the sediment budget, both with respect to along- and cross-shore sediment transport, and due to the intense erosion of the shore it is well determined geologically (*cf.* Rudowski 1965, 1986; Subotowicz 1995). The marine field investigations were carried out in December 1996 from the research vessel „Dr Lubecki". The onshore studies were carried out in summer 1997.

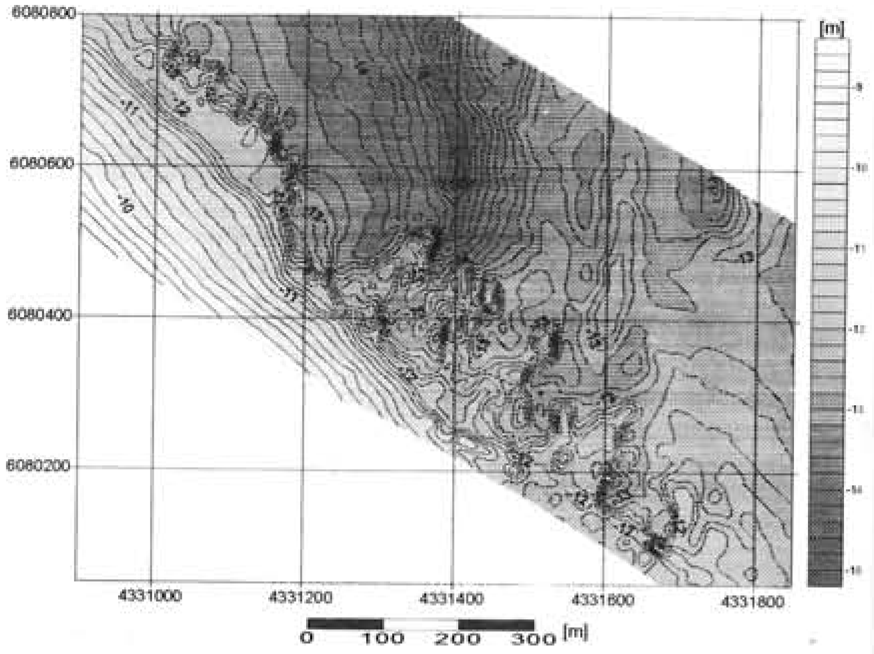

Fig. 2. Detailed bathymetric map of the study area compiled on the basis of multibeam echosounder registration

MATERIALS AND METHODS

Measurements in the nearshore zone require first of all good resolution and penetration up to 10 m in order to ensure proper recognition of the surface and subsurface bottom structures and the determination of kinds of bottom. It is also necessary that the survey should proceed quickly so that recordings can be made over a relatively large bottom in uniform and favourable weather conditions. This can be achieved by using an integrated hydroacoustic system, adjusted to fit shallow water conditions.

The multi-beam Sea Bat 9001 (455 Hz) echosounder and Wesmar HDSS 700 (307 kHz) high resolution side scan sonar were used for determination of the bottom surface, and the Seabed -Oretech 3010B (3,5-14 kHz) high resolution sub-bottom profiler was used for the recognition of sub-bottom structures. The sub-bottom profiles were measured along the same lines as the side scan profiling. Numerous grab samples and 13 vibrocores were taken. The DGPS positioning system (accuracy better than 1 m.) was used for location along all profiles at 1 s intervals and for locating samples of sediments. Simultaneously with sub-bottom and side scan profiling, water depth was measured with a DESO 15 (210 kHz) echosounder to provide calibration data.

All seismic and positioning data were stored digitally on board and processed by using the CODA DA system. The CODA DA-200 system is a comprehensive tool for digital acquisition and postprocessing of analogue signals from a variety of sensors, including sidescan sonars, sub-bottom profilers, single-beam and multi-beam echosounders, etc. The analogue data are acquired at the 200 kHz sampling rate with resolution of 12 (optionally 16) bits. The digitised data are continuously stored on a DDS DAT tape. The DA-200 system allows for one-line display, processing and interpretation. The on-line display options include filtering of the digitised signal, image enhancement, slant range correction for side-scan sonar images, etc. The Geo-Kit option used during the measurements enhances the standard tagging option by the measurement of seabed features (height over the seabed, length, width); point, line and polygon features tagging with possibility of annotation and classification both in on-line and post-processed mode. The system is provided with a unique High Speed Tape Operating System with random access, GoTo, Stop, Play, Fast Forward, Rewind built-in features providing high performance tape reviewing and processing.

The co-ordinate system used is WGS-84, ellipsoid WGS-84. The presented data were transformed to TM projection with scale 1, central meridian

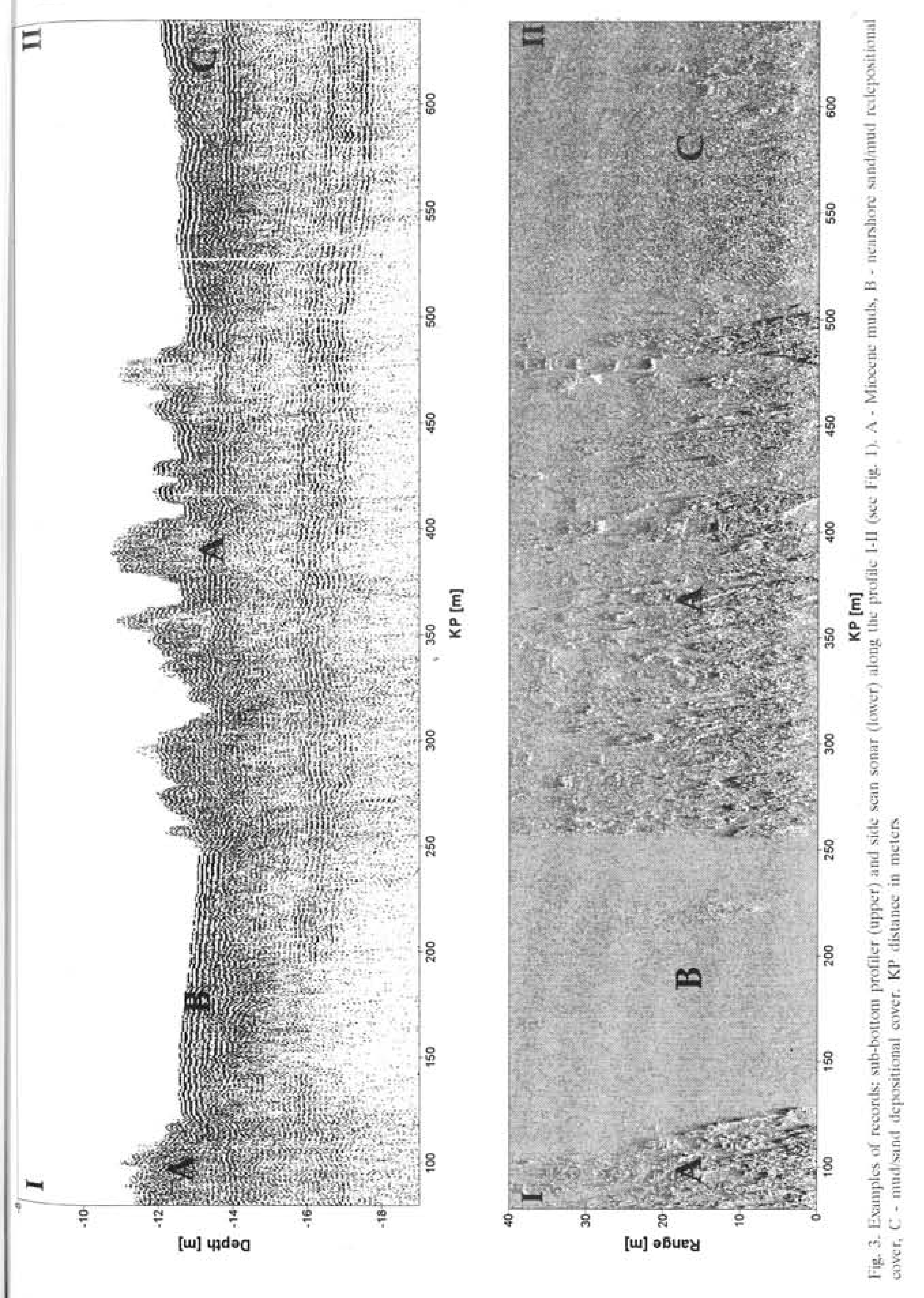

Fig. 3. Examples of records: sub-bottom profiler (upper) and side scan sonar (lower) along the profile I-II (see Fig. 1). A - Miocene muds, B - nearshore sand/mud redepositional cover, C - mud/sand depositional cover. KP distance in meters

210°E, false easting 4,500,000 m. The maps were prepared with Golden Software's SURFER 6.0.

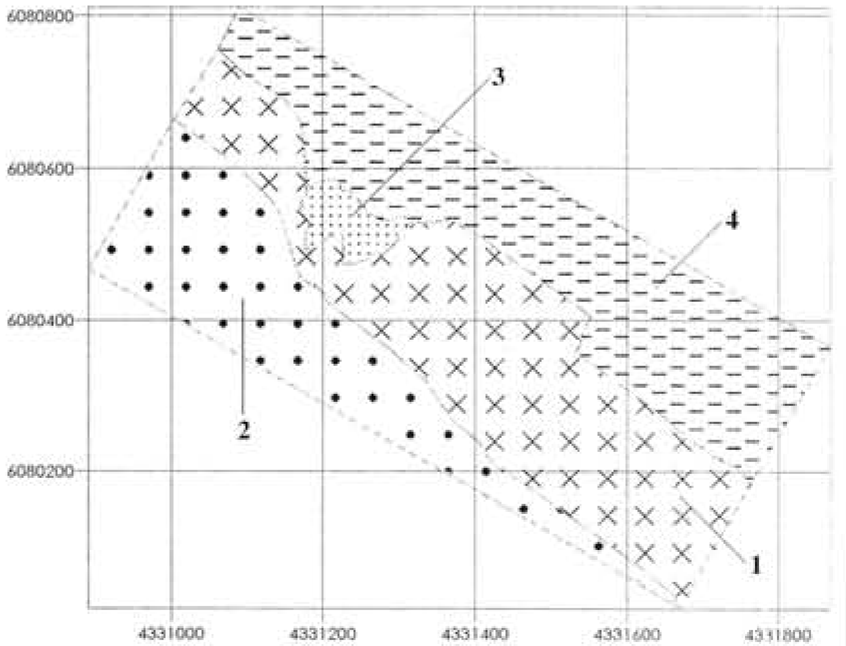

Fig. 4. Bottom types: 1 - uneven surface of an erosional area of Miocene muds with isolated hummocky relief, 2 - flat, erosional surface of redeposition of fine sand (transition zone), 3 - flat erosional surface of redeposition of mud/sand sediments (transition zone), 4 - surface of sand/mud deposition

RESULTS

By means of detailed analysis of all acoustic data and of results of sediment sampling, and using the knowledge on regional onshore and offshore geomorphology and geology, four main acoustic facies (*cf* Payton 1977) were distinguished, and next interpreted as bottom kinds (Fig. 4).

Bottom Kind 1. Very uneven, erosion surface of the outcrops of Miocene muds. Numerous, randomly placed cuts and hummocks up to 3 m. high. The pattern of channels, situated perpendicularly to the coastline, is well visible in the bathymetric map (Fig. 2) and in sonar images (Fig. 3). Horizontally stratified muds were determined up to 10 m beneath the bottom surface. Very often they are disturbed stream channels of Miocene age, forming cut-and-fill sedimentary structures.

Bottom Kind 2. Flat erosional surface of redeposition, with strongly packed fine sands. It is a transition zone where sand is transported from the surf zone seawards. The sand cover is 0.5-1.5 m thick and lies on an erosional, uneven surface of Miocene muds.

Bottom Kind 3. Flat, erosional surface of redeposition of sand/muddy sediments. Muds and very fine sands form a thin - up to 0.5 m thick - cover of the erosional depression in the surface of Miocene muds.

Bottom Kind 4. Surface of deposition of muddy/sandy deposits. Muddy sand and sandy mud transported and eroded from bottom kinds 1-3 is deposited here, forming a deposition cover of over 1.5 m thickness. There are some channels, up to 2-3 m wide and about 0.5 m deep, on the bottom surface. These channels tend to transport some sediments towards deeper parts of the bottom.

CONCLUSIONS

Determination of bottom kinds and of their distribution using the tested methods is very accurate and fitted to detailed mapping.

Obtained information on the nearshore bottom at Chlapowo indicates an increasing erosional trend in this coastal area and an increasing tendency of moving material washed out of the shore and bottom seawards rather than along the shore.

Continuation of these regional and methodological studies is necessary in order to develop recommendations for detailed standard investigations, needed for the classification of bottom types, determination of sediment budget, prediction of coastline development, coastal protection and for investigations of bottom geomorphology, geology and coastal hydrodynamics.

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Suspended Matter Erosion and Sedimentation Experiments in the Oder Estuary

Kirsten Burkhardt, Herbert Kühl and Gerhard Witte

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In co-operation with the Institute of Geography at the University of Greifswald and the Institute of Hydrophysics at the GKSS Research Centre, measurements of SPM settling velocity, critical bottom shear stress and erosion rate were carried out using samples from the Oder estuary. The critical erosion shear stress of sediments in the Greifswalder Bodden is higher than in the Achterwasser or in the Kleines Haff. The erosion rates of all the locations considered are significantly different. A correlation was found between the settling velocity and the contents of organic matter in the deposited particles. The fastest and slowest settling fraction show the highest contents of organic material.

Keywords: Oder estuary, critical shear stress, settling velocity, erosion, sediment, particles.

INTRODUCTION

Suspended particulate matter (SPM) in rivers and coastal waters is of significant importance to the transport of nutrients and both organic and inorganic toxic agents. These pollutants are predominantly bound to SPM and accumulate at the bottom due to sedimentation processes. Calm regions are therefore sinks for SPM and form a considerable reservoir for heavy metals and organic pollutants. The remobilisation of pollutants from SPM produces an additional impairment to the water quality.

The behaviour of SPM under current conditions can be described by four processes:

- sedimentation, whereby the settling velocity mainly depends on the water turbulence and particle size and density,
- resuspension as re-entry of freshly deposited suspended matter into the water column or erosion, if consolidated sediment is whirled up,
- vertical mixing due to turbulence,
- advective transport due to currents.

A decisive criterion for the exchange of matter is the relation between water volume and surface area (Lampe 1996, in: Lozan et.al. 1996). In the Oder estuary this relation is generally small and sediments are mixed up by waves due to relatively small forces. Accordingly, the sediments are weakly consolidated and storm events or high discharges of the river Oder produce a considerable additional input of suspended matter into the Baltic Sea.

A knowledge of SPM settling velocity, critical shear stress and erosion/resuspension rate forms the basis for estimating the seasonally fluctuating transport of suspended matter and pollutants.

In a co-operation with the Institute of Geography at the University of Greifswald and the Institute of Hydrophysics at the GKSS Research Centre, measurements of SPM settling velocity, critical bottom shear stress and erosion/resuspension rate were carried out using samples from the Oder estuary. In particular, the seasonal change of these parameters was the subject of the investigations. Fig. 1 gives an overview of the sampling locations.

METHODS

Erosion Experiments

For the erosion/resuspension experiments a modified EROMES apparatus was employed. This is a patented development of the GKSS Research Centre for erosion measurements on naturally formed

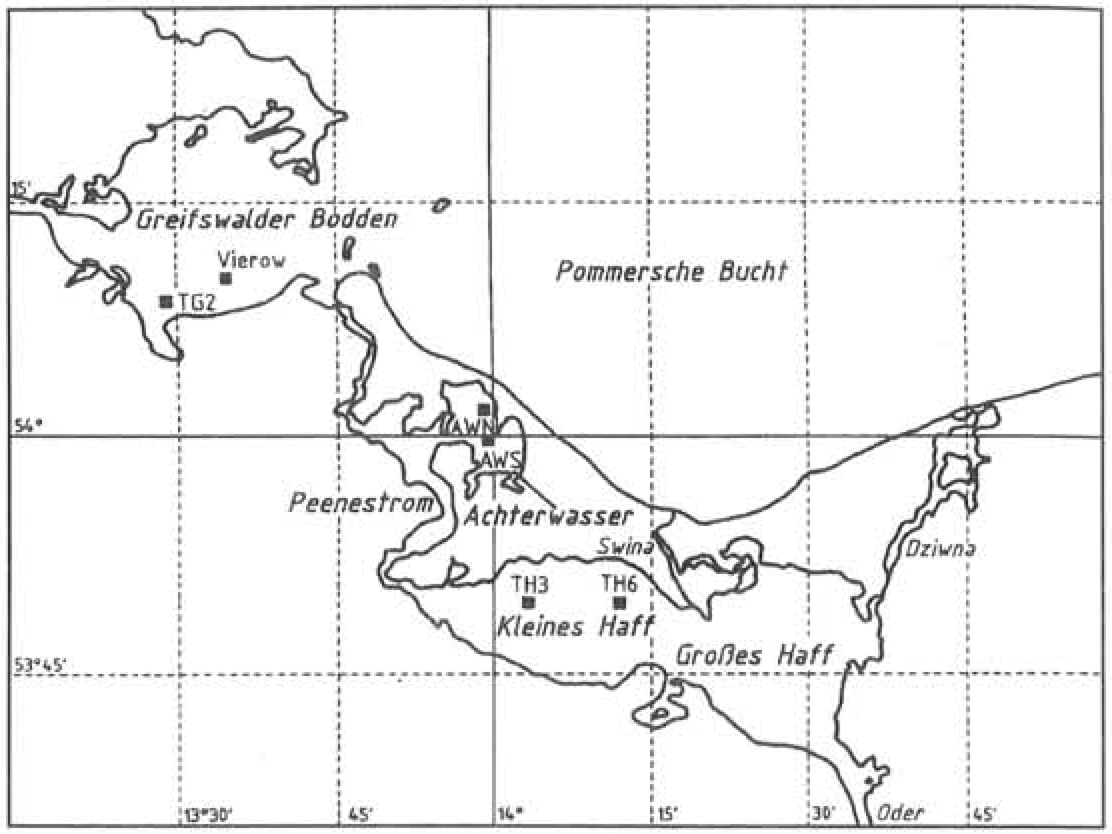

Fig. 1. Sampling locations in the Oder estuary (Greifswalder Bodden, Peenestrom, Achterwasser, Kleines Haff)

muddy sediments (Schünemann & Kühl 1991). The sampled sediment core remains confined in a perspex tube of 10 cm in diameter with a water column above the sample. The bottom shear stress is induced by a rotating propeller above the sediment surface. Special mounting baffles in the tube prevent rotation of the water column and vertical balancing currents. The applied shear stress is a function of the propeller speed and is calibrated using quartz sands of specified grain size and known critical shear stress (Shields 1936; Unsöld 1984). Fig. 2 shows the modified EROMES system.

During the experiment, the propeller speed is continuously increased by 0.1 N/m² every 5 minutes. This increase was tested in many experiments and ensures a quasi-static erosion process marked by a nearly constant erosion rate at the end of each interval.

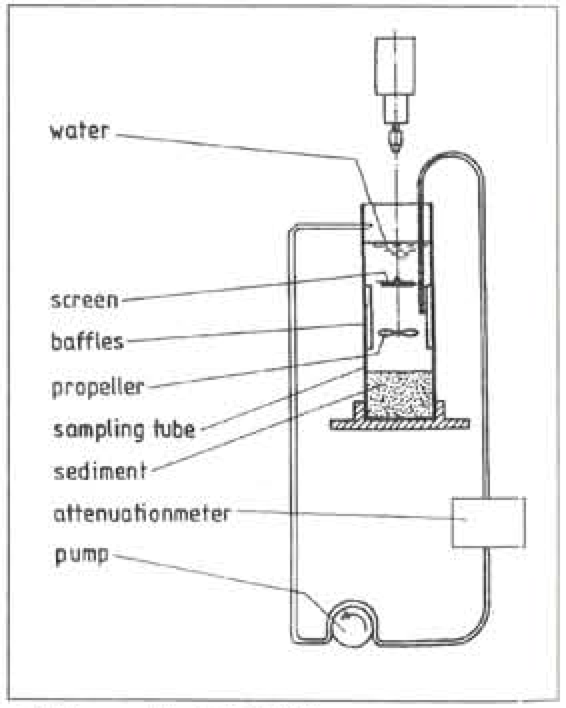

Fig. 2. The modified EROMES system

The critical bottom shear stress is characterised by a significant increase in SPM concentration in the water column which is measured by an optical silt meter. Three water samples are taken during each experiment to calibrate this attenuation meter: one at the beginning to quantify the background concentration, one in the middle and one at the end. After having reached a given maximum concentration of eroded sediment of about 100 mg/l the erosion test is terminated. The attenuation and its calibration versus propeller speed time are input data for the evaluation of the EROMES experiment. The erosion rate as a function of the applied shear stress is the time derivative of the measured SPM concentration. The critical shear stress is calculated by fitting the curve of the erosion rate.

Settling Velocity Measurements of Artificially Resuspended Matter

To characterise the settling properties of the particles eroded by the EROMES apparatus, the suspension was filled in a bottom withdrawal tube. Subsequently, water samples were taken at given logarithmic time steps to determine the SPM content for the calculation of the frequency distribution of the settling velocities (Owen & Eng 1976). This freshly eroded SPM certainly differs in size and composition of the particles from that of natural SPM. For this reason, a second sample of the eroded particles is filled in a gently rotating horizontal tube to build up flocks before the start of a second settling velocity experiment.

This so-called EROSINK method (Witte & Kühl 1996) ensures that the complete range of possible settling velocities is considered: the lower values for the freshly eroded particles and the higher values for the flocculated matter.

Settling Velocity Measurements of Natural Suspended Matter

A modified MAKDAN tube (KC Maskiner, Silkeborg, Denmark) was used for the settling velocity determination of natural suspended matter. This innovative device is a combination of a SPM sampler for slack water and a settling tube using a withdrawal pipette. It is made of perspex. The sampled water column is 446 cm high, the inner diameter is 123 mm and has a volume of 5 litres. The inlet of the pipette tube is positioned 94 mm above the bottom of the settling tube.

Fig. 3 shows schematically the settling tube in two operational situations. Suspended from a wire, the tube is open at both the upper and the lower end and lowered into the required water depth (left). A gap of 0.5 m remains between the bottom and the suspended tube. A messenger is sent down and the tube moves downwards to the bottom seal, thus trapping a cylindrical water volume. With a time delay of some seconds, the sealing cap follows the tube and closes the cylinder on top. After raising the device and placing it into an operating rack, the suspension samples are withdrawn at given time steps for the settling experiment.

RESULTS

Sediment Properties

The sediments of the Oder estuary are characterised by a high degree of sedimentation (especially of organic material) and remobilisation due to hydroturbation and bioturbation (Leipe 1986). The muddy sediments investigated from the different sampling locations are very similar. They are soft, have a grey or black colour and a high content of organic matter. They are homogeneous and weakly consolidated because of the permanent processes of erosion and deposition. Fig. 4 shows the particle size distributions of the sediments from different locations in the Oder estuary. Due to the high contents of silt <63 μm, all sediments are muddy and stabilised by cohesive forces between the clay particles (Spork et al. 1995).

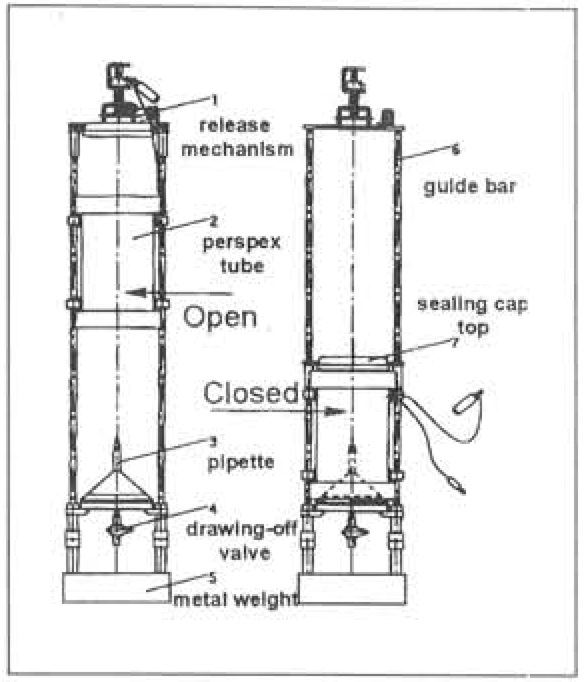

Fig. 3. Modified MARKDAN SPM sampler and settling tube for pipette withdrawal

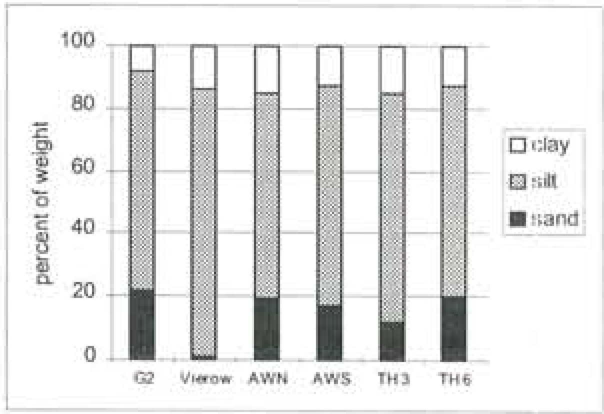

Fig. 4. Particle size distribution of muddy sediments from Oder estuary

Erosion/Resuspension

Critical Shear Stresses

Fig. 5 shows a Box & Whisker plot of the critical shear stresses for the different locations in the Oder estuary. The erosion of sediments from the

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Distribution and Enrichment of Redox-Sensitive Metals in Baltic Sea Sediments

Franz Xaver Gingele and Thomas Leipe

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The distribution and enrichment of the redox-sensitive metals Mn, Fe, Co, Ni, Cu, Zn and Pb were investigated in 3 cores from the Arkona and Bornholm Basins in the western Baltic Sea. No substantial enrichment of Mn can be observed in the marine Holocene muds. The lack of a surficial Mn accumulation indicates that oxic conditions near the sediment surface - recently associated with periodical saltwater inflows from the North Sea - do not persist long enough to form a significant Mn peak. However, layers rich in Mn and Cu are found in sediments of the Yoldia Sea stage and Mastogloia Sea stage below the anoxic muds. These accumulations are believed to record an oxic-suboxic sequence during the times of deposition. Strong fluctuations in the input of organic matter and bottom water oxygen fostering a rapid deepening and shallowing of the redox boundary and local, rapid sedimentation events may be responsible for the preservation of this sequence. Enrichments of Zn and Pb are encountered near the suboxic top of the cores. The lack of similar enrichments in the preserved suboxic sequences confirms the anthropogenic source of near surface heavy metal accumulations.

Keywords: Baltic Sea, Bornholm Basin, Arkona Basin, geochemistry, redox-sensitive metals, heavy metals, paleoenvironment.

INTRODUCTION AND APPROACH

The distribution of the reactive part of many transition metals in marine deposits is partly controlled by the redox status of the sediment. The reactive fraction of manganese, iron, copper, zinc, lead, nickel, cobalt, molybdenum, uranium and others responds to changes in the early diagenetic environment and gives limited evidence on the redox control on the post-depositional redistribution of these elements (Lynn & Bonatti 1964; Jarvis & Higgs 1987; Shaw et al. 1990; Thomson et al. 1993). The driving process is the decomposition of organic matter resulting in a characteristic succession in the consumption of oxidants, starting with oxygen, the electron acceptor, which yields the greatest amount of free energy per mole. After oxygen is depleted, nitrate and manganese oxihydroxides are utilized (Froelich et al. 1979). Redox-sensitive metals may be released from organic matter in the oxic zone (Cu, Zn, Pb) (Whitfield & Turner 1987; Gerringa 1990; Lapp 1991) or from minerals, which become unstable during burial into the suboxic and anoxic zone (Mn, Fe, Co; Wallace et al. 1988; Heggie & Lewis 1984). Their mobilization, diffusion along gradients in the pore water and reprecipitation leads to the formation of metal-rich layers and zones where the sediment is depleted of these metals (Klinkhammer et al. 1982). Under ideal conditions solid phase enrichments are theoretically arranged in a clear succession of concentration peaks along the redox gradient (Thomson et al. 1993). However, this succession is rarely found due to a high sorptive capacity of Mn- and Fe-hydroxides for many trace elements, low solubility of sulphides and organic complexes or a wide sample spacing. Manganese, being most susceptible to early diagenetic redistribution is widely used to study redox conditions. Under "steady state" conditions a conspicuous manganese spike develops near the oxic-suboxic boundary and migrates upward with continuing sedimentation. The manganese peaks occurring at deeper sedimentary levels are related to depositional or paleoenvironmental changes (Thomson et al. 1984; Finney et al. 1988; Dean et al. 1989; Pruysers et al. 1993). Changes in organic carbon flux, bottom water oxygen and sedimentation rates can result in changes of the redox boundary and interfere with "steady-state" conditions.

The manganese cycle was a well studied topic in the Baltic Sea basins during the last few years (Hartmann 1964; Huckriede 1994; Neumann et al. 1996). In the anoxic basins dissolved manganese diffuses from the sediment into the stagnant bottom water (Kremling 1983). In the course of periodical salt-water inflows from the North Sea bottom waters get oxygenated and manganese precipitates on the sea-floor after oxidation to MnO$_2$. The following stratification of the water column and rain of organic matter re-establishes anoxic conditions and manganese is reduced again. However, in the deep basins a certain share of MnO$_2$ is transformed to Ca-rich rhodochrosite during burial in the suboxic zone and remains stable under anoxic conditions (Jakobsen & Postma 1989), thus resulting in manganese-enriched layers. These layers of rhodochrosite, detected in laminated sediments of the Gotland Basin and central parts of the Bornholm Basin were used to reconstruct the history of saltwater inflows into the Baltic Sea (Huckriede 1994; Neumann et al. 1996). In the Arkona and most of the Bornholm Basin bioturbation destroys laminated sequences. So far, most studies concentrated on the Holocene muds in the deep basins. Metal enrichments in sediments of the Baltic Ice Lake, Ancylus Lake and Yoldia Sea are rarely recorded.

Accumulations of Cu, Zn and Pb in carbonate phases in the suboxic zone were observed in the Arkona (Damm 1992), Bornholm (Leipe et al. 199 and Gotland Basins (Salonen et al. 1995). Accordi to the authors, anthropogenic sources (Leipe et a 1995) or early diagenetic redistribution (Damm 199 are regarded as the responsible processes.

The purpose of this study was to compare th distribution of redox-sensitive metals in cores fro the Arkona and Bornholm Basins, which contain sedimentary sequence typical of the western Balti Sea. The drastic changes in the sedimentary env ronment from the Late Glacial to present is be lieved to leave a characteristic imprint on meta distribution. The development of metal enrichmen is expected and can be used to reconstruct paleo environmental conditions. The results may also con tribute to the discussion of authigenic or anthrop genic origin of heavy metal enrichments in th suboxic zone of Baltic Sea sediments.

MATERIAL, METHODS AND STRATIGRAPHY

Three sediment cores from the Arkona- and Born holm Basins were recovered with a gravity core during R.V. *A. v. Humboldt* cruises AvH92/44/25 an AvH93/44/30 in 1992 and 1993 (Fig. 1, Table 1). A

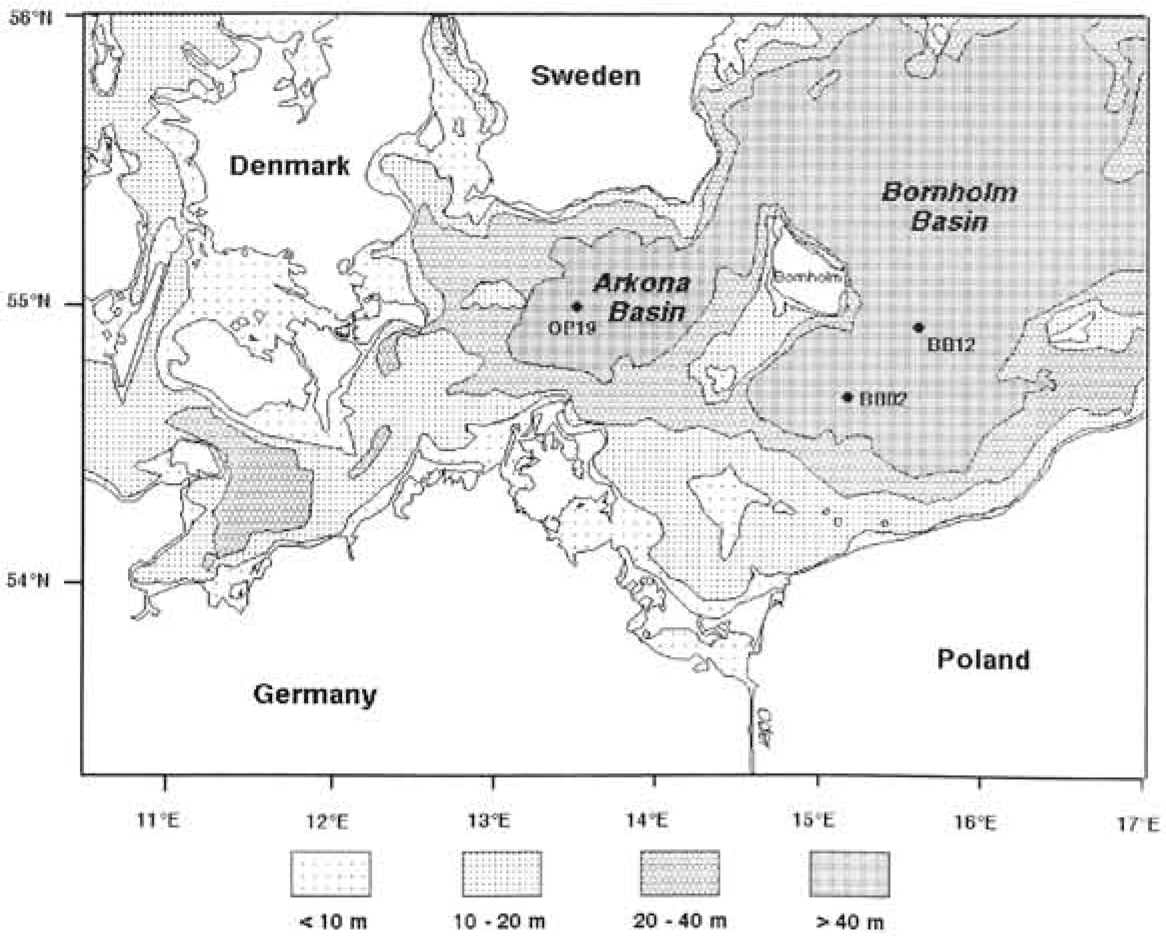

Fig. 1. Investigation area and location of sediment cores

Table 1. **Location of sediment cores**

Core	Latitude	Longitude	Water depth (m)	No. of samples
OP19	55°59.5´N	13°30.1´E	46	147
BB02	54°40.0´N	15°09.9´E	60	60
BB12	54°55.0´N	15°35.1´E	77	90

Niemistö-corer was used to retrieve undisturbed samples from the uppermost 1-2 cm of the sediment surface. Cores were split in half, described for lithology and colour and sampled in 2 cm, 5 cm and 10 cm intervals, depending on lithological variations encountered. After freeze-drying, subsamples were analysed for organic carbon, carbonate and sulphur with a CS infrared analyzer (ELTRA Metalyt 1000CS). Nitrogen was determined with a CHN-analyzer (FOSS-HERAEUS). Pyrite concentrations were assessed with quantitative XRD-measurements on a Philips PW 1830 device, using CoKα radiation (40 kV, 40 mA). Details of the procedure and the compilation of the pyrite calibration curve are given in Gingele (1992). Geochemical data were obtained from total digestions with various acids (HNO$_3$, HF, HClO$_4$, HCl) and measured with an ICP-AES. Precision was better than 10% for Co, Cu, Ni and Pb and better than 3% for Al, Mn, Fe and Zn (Neumann et al. 1996). Absolute concentrations were normalized to Al to compensate for dilution by nonterrigenous components (Table 2). A lithostratigraphic framework was established following a classification introduced by Larsen (1974) and Kögler & Larsen (1979) in the West Bornholm Basin, and Björck (1995) in the Baltic Sea in general. They distinguish three main units (I-III), which rest on the glacially deposited boulder clay. The features used for classification are colour, lithology and grain size, supported by average values of organic compounds (organic carbon, carbonate, nitrogen, phosphorus, sulphur). Recently, evidence from diatoms and palynological investigations on cores from the Bornholm Basin (Emelyanov & Lukashina 1995; Emelyanov et al. 1995) confirms this lithostratigraphical approach. Since our cores did not penetrate into the basal boulder clay three main lithostratigraphical units ("Unit I-III") could be distinguished (Fig. 2). A detailed stratigraphical classification of cores BB02 and BB12 relating lithostratigraphical units to Baltic stages was published by Huckriede et al. (1995). It is based on carbon cycles calibrated on cores from the Gotland Deep and supported by diatom assemblages.

Unit I (> 10 300 years B.P.) comprises sediments of the late glacial Baltic Ice Lake, mainly brown or multicoloured varved clays. Pale brown, indistinctly varved clays are encountered in cores BB02 from 472-536 cm core depth and core BB12 from 395-436 cm (Fig. 2). They were related to the youngest deposits of the Baltic Ice Lake (Huckriede et al. 1995). In core OP19 greyish-pink clays with sandy layers from 190-480 cm core depth were classified as the Baltic Ice Lake sediments.

Unit II (10 300 - 7800 years B.P.) represents clays of the postglacial Ancylus Lake (Boreal stage) and Yoldia Sea stage (Early Preboreal). It is found in both cores from the Bornholm Basin and in core OP19 from the Arkona Basin (Fig. 2). The rather homogenous grey clays have been divided into three subunits (A-C) by carbonate and organic carbon content (Kögler & Larsen 1979). Subunit A can be clearly attributed to the freshwater Ancylus Lake. However, no clear temporal correlation is

Table 2. **Mean values and standard deviation for Al-normalized redox-sensitive metals for each core and stratigraphic unit.** Values were multiplied by 10^3 for convenient handling. Lithogenic background for Baltic Sea sediments after Damm (1992)

	Mn/Al	Fe/Al	Co/Al	Ni/Al	Cu/Al	Zn/Al	Pb/Al
Unit III (Marine Mud)							
BB02	7.18 ± 1.81	707 ± 77	0.297 ± 0.036	0.706 ± 0.029	0.785 ± 0.091	1.59 ± 0.25	0.421 ± 0.273
BB12	14.02 ± 3.30	820 ± 99	0.424 ± 0.050	0.824 ± 0.086	0.352 ± 0.092	2.01 ± 0.57	0.446 ± 0.256
OP19	7.69 ± 1.05	723 ± 99	0.338 ± 0.042	0.722 ± 0.079	0.619 ± 0.141	1.95 ± 0.62	0.653 ± 0.430
Unit II (AY Clay)							
BB02	10.94 ± 1.81	594 ± 66	0.315 ± 0.029	0.638 ± 0.108	0.632 ± 0.143	1.44 ± 0.23	0.325 ± 0.046
BB12	16.96 ± 22.60	712 ± 98	0.367 ± 0.038	0.786 ± 0.132	0.433 ± 0.162	1.77 ± 0.19	0.334 ± 0.052
OP19	6.74 ± 1.22	660 ± 124	0.324 ± 0.055	0.656 ± 0.120	0.504 ± 0.202	1.44 ± 0.17	0.272 ± 0.040
Unit I (Varved Clay)							
BB02	6.86 ± 0.92	646 ± 45	0.344 ± 0.060	0.618 ± 0.079	0.593 ± 0.053	1.52 ± 0.13	0.333 ± 0.047
BB12	7.49 ± 0.30	655 ± 21	0.373 ± 0.037	0.665 ± 0.040	0.322 ± 0.022	1.71 ± 0.07	0.331 ± 0.039
OP19	6.94 ± 0.87	537 ± 20	0.279 ± 0.012	0.595 ± 0.018	0.355 ± 0.031	1.31 ± 0.05	0.256 ± 0.039
Terrigenous background:							
Baltic Sea sediments (Damm 1992)	3.3	366	0.16	0.66	0.63	1.58	0.33
Slates (Turekian & Wedepohl 1961)	10.6	590	0.24	0.85	0.56	1.19	0.25

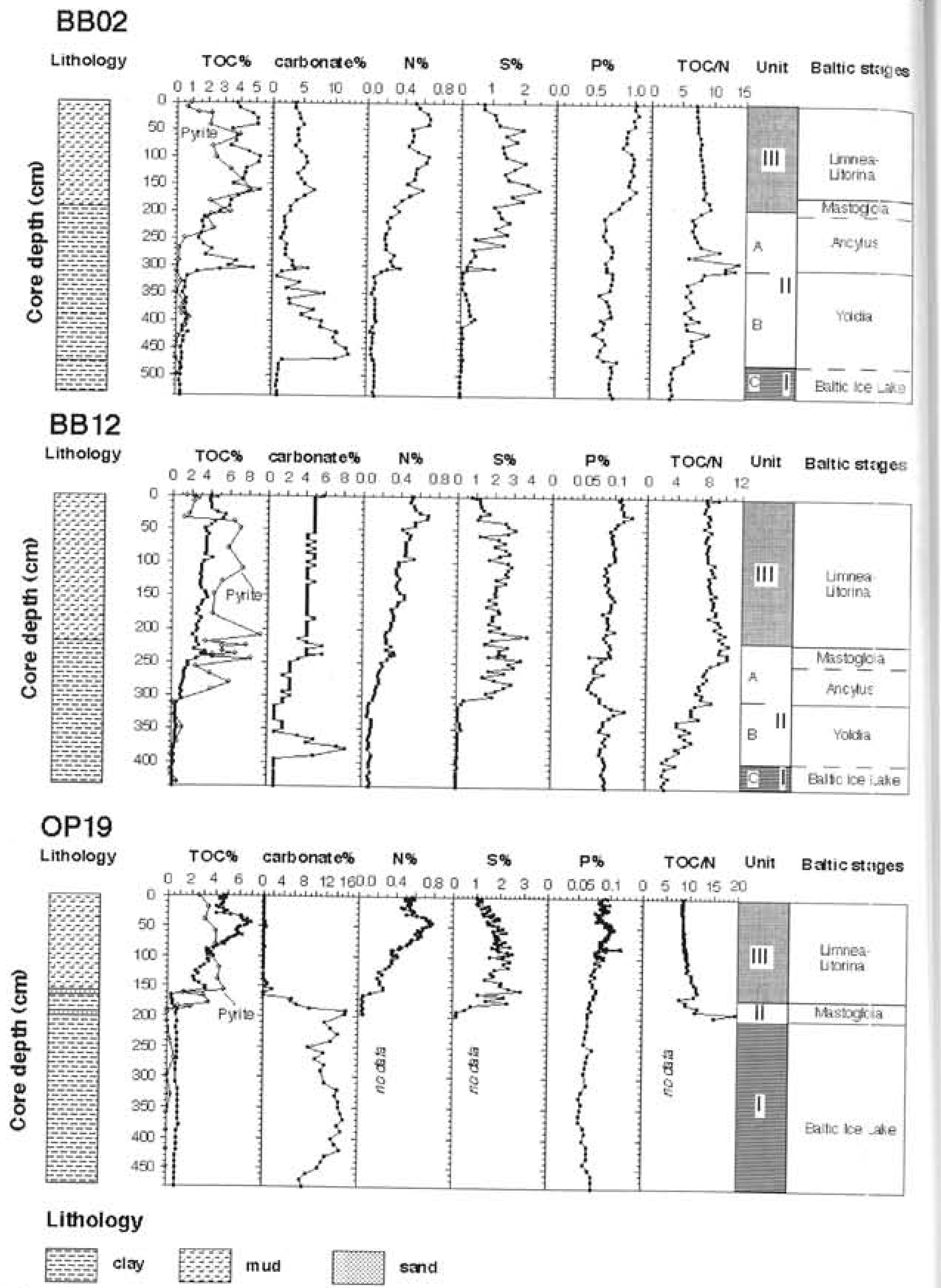

Fig. 2. Lithology and downcore distribution of biogenic components TOC (total organic carbon), carbonate, total nitrogen, TOC/N-ratio, sulphur- and phosphorus content. Pyrite percentages are depicted near the TOC-distribution. Lithological and stratigraphical units I - III are indicated in the shaded column. Baltic stages according to Huckriede et al. (1995)

given by Kögler and Larsen (1979) for the subunits B and C. They may be contemporaneous to later stages of the Baltic Ice Lake, the Yoldia Sea or early stages of the Ancylus Lake. Based on comparison with sediments of the Gotland Basin Huckriede et al. (1995) attributed subunits A and B to the Ancylus and Yoldia stages, whereas subunit C is interpreted as deposits of the Baltic Ice Lake. Thus unit I in cores BB02 and BB12 may be correlated with subunit C of Kögler and Larsen (1979). A better resolution of Yoldia stage sediments is proposed by Wastegård et al. (1995) and Sohlenius (1996). They distinguish an early freshwater phase, a short brackish phase and a late freshwater phase, which leads to Ancylus stage sediments. The brackish phase is characterized by high carbonate contents and corresponds to subunit B.

Subunits A and B are observed in the cores from the Bornholm Basin. In core BB12 subunit A from 215-304 cm core depth consists of grey clays with sulphidic black spots. Grey clays persist to the end of the core. A drop in TOC-contents and increasing amounts of carbonate characterize subunit B from 304-395 cm core depth. The onset of subunit C (unit I) is indicated by a sharp drop in carbonate. In core BB02 subunit A from 192-304 cm core depth consists of bluish-grey clays in the upper 60 cm, which turn into brownish-grey clays below. Subunit B from 304-472 cm core depth comprises grey to brownish-grey clays with increasing amounts of carbonate. A conspicuous TOC-peak from 280-320 cm core depth is of terrigenous origin as evidenced by TOC/N-ratios, possibly redeposited peat (Huckriede et al. 1995). We summarize subunits A-B with the term AY-clays introduced by Kögler & Larsen (1979). The transition from the upper Ancylus clay (IIA, Ignatius et al. 1968) to the Holocene marine mud was extensively studied by Sohlenius et al. (1996) in the Gotland Basin. They suggest a transitional Mastogloia Sea stage (Hyvärinen 1988) in the basin sediments. Near the transition TOC-records of core BB12 closely match that of the core from Sohlenius et al. (1996), suggesting that the upper part of subunit IIA corresponds to the transitional stage of Sohlenius et al. (1996). This was confirmed by Huckriede et al. (1995). They found diatom evidence for a transitional Mastogloia Sea stage in cores BB02 and BB12 (Fig. 2). However, this is not reflected by lithology or colour.

Only 0.3 m of greyish clays framed by thin sandy layers are recorded between greyish pink Late Glacial clays and olive green Holocene muds in core OP19. This may be due to erosion or nondeposition of Ancylus Lake deposits in the early Holocene (Duphorn et al. 1995). Thus unit II in core OP19 may represent deposits of the Mastogloia Sea.

Unit III is equivalent to "marine" muds, which were deposited in the basins of the Baltic Sea, following the Litorina transgression from 7800 years B.P. to present. Olive grey sandy muds and muds, rich in organic matter accumulated in varying thickness in the depressions of the western Baltic. Marine mud with a thickness of 2 m in the Bornholm and 1.6 m in the Arkona Basin cores is recognized mainly by colour, lithology and high content of organic carbon (Fig. 2). Though bioturbation is intense Huckriede et al. (1995) propose a subdivision of the marine mud into lithozones. This subdivision was based on carbon cycles calibrated on cores from the Gotland Deep.

RESULTS

Sedimentary and Early Diagenetic Environment

As discussed above burial rate and availability of the reductant organic matter and oxygenation of bottom waters are the main factors for the early diagenetic environment, which control the mobilization and enrichment of redox-sensitive elements. It can be inferred from TOC-contents, sulphur and phosphorus concentrations and abundance of biogenic constituents.

Sediments of the late glacial Baltic Ice Lake are characterized by low contents of TOC and sulphur. Pyrite was mostly below detection limits in bulk mineralogical analyses (Fig. 2). The lack of sulphides and low TOC-contents may be interpreted as evidence for a low input of reactive organic matter and/or a well-oxygenated environment in which organic matter was remineralized efficiently. This is confirmed by positive redox potentials (Eh) measured in Baltic Ice Lake sediments in the Bornholm Basin (Emelyanov et al. 1995). There was no salinity stratification of the water body established. Though local sedimentation conditions might have varied considerably, the general source for the terrigenous matter was glacially eroded material supplied by meltwater suspensions. The average sedimentation rate was 1 mm/a (Emelyanov et al. 1995).

Sediments of the lower Holocene are summarized with the term AY-clays and comprise deposits of the Yoldia Sea stage as well as the Ancylus Lake stage. Correlation between cores BB12 and BB02 is achieved by carbonate and TOC-contents. Similarly low in TOC- and sulphur content to the sediments of the Baltic Ice Lake, but containing bioturbation structures, subunit B was most likely formed under oxic bottom water conditions. Pyrite and sulphur increase slightly only in the middle of subunit B. This points to some marine influence here, because the formation of sulphides is favoured by sulphate in the water and by anoxic conditions as a consequence of salinity stratification. Supported by carbonate contents of up to 10%, which are diagnostic for saline phases of the Yoldia stage (Wastegård et al. 1995; Sohlenius 1996), subunit B is related to the brackish Yoldia Sea stage (Fig. 2).

The most striking feature in the record of biogenic compounds (Fig. 2) is the transition from subunit B to A. Organic carbon and sulphur contents rise considerably and negative Eh-values are encountered (Emelyanov et al. 1995). In core BB12 the transition from IIB to IIA is mainly marked by a sharp increase in sulphur contents. A TOC-rich layer in core BB02 from 280-320 cm results from locally redeposited peat (Huckriede et al. 1995). Subunit A is believed to have formed in the freshwater environment of the Ancylus Lake (Kögler & Larsen 1979). This is supported for our cores by freshwater diatom assemblages described by Huckriede et al. (1995). Pyrite spherules were reported in subunit A from the Bornholm Basin (Kögler & Larsen 1979; Huckriede et al. 1995). Abundant pyrite was detected in subunit A of cores BB02 and BB12, supporting the assumption of Borg (1985) that anoxic conditions were established during this time (Fig. 2). Stressing the positive correlation between TOC- and sulphur contents Huckriede et al. (1995) concluded with material from the Gotland Deep that oxygen deficient bottom waters due to salinity stratification were established in the upper part of subunit A. However, Boesen & Postma (1988) and Sohlenius et al. (1996) have shown that pyrites of late Ancylus Lake clays are of late diagenetic origin, formed by downward diffusion of sulphide from anoxic Litorina stage sediments. In cores BB02 and BB12 pyrites occur throughout subunit A. TOC records show a poor correlation to pyrite and sulphur contents. Therefore we agree with Boesen & Postma (1988) and Sohlenius et al. (1996) that the pyrites of the Ancylus Lake clays are most probably of late diagenetic origin.

AY-clays reach an average thickness of 2.8 m and 2.0 m in cores BB02 and BB12, which is consistent with records found by Emelyanov et al. (1995), resulting in an average sedimentation rate of 1 mm/a.

In the Arkona Basin only 0.3 m of lower Holocene sediment was encountered, which may be related to the Mastogloia Sea 8000 - 7500 B.P. (Hyvärinen 1988; Duphorn et al. 1995). A transitional Mastogloia Sea stage was also described in cores BB02 and BB12 by Huckriede et al. (1995). It is characterized by a first maximum in TOC contents.

Low oxic bottom water conditions and salinity stratification were established with the onset of marine-brackish ingressions initiated by the Litorina transgression 7800 B.P. The inflow of higher saline dense bottom waters pushed the halocline to shallower depths and supplied nutrient rich water to the photic zone. A rise in primary production followed. The rain of organic carbon to the bottom increased, resulting in higher oxygen consumption and low oxic bottom water conditions (Sohlenius et al. 1996). The latter fostered the formation of pyrites in the sediment, which reached up to 5% in the marine Holocene muds (Fig. 2). Average sedimentation rates computed for the 2 m of Holocene mud in the Bornholm Basin and 1.6 m in the Arkona Basin reach 0.25 mm/a and 0.2 mm/a respectively. Recent datings with ^{210}Pb (Leipe et al. 1995) on sediment surfaces suggest sedimentation rates of 3.2 mm/a for the Bornholm and 1 mm/a for the Arkona Basin, which is one magnitude higher than average values. This rather indicates regional differences in sedimentation conditions than drastic changes in sedimentation rates during the Holocene.

Since no pore water analyses have been performed on the cores for this work, pore water profiles near the sediment-water interface are inferred from investigations in the immediate vicinity of our cores (Damm 1992; Emelyanov et al. 1995).

Generally, the basins of the western Baltic Sea are characterized by a salinity stratification and low oxic bottom water conditions. The enclosure by shallow sills allows only limited and periodic water exchange with the North Sea. Substantial manganese enrichments near the sediment surface, diagnostic for a truly oxic layer were not detected in cores from the Bornholm and Arkona Basins (this paper; Damm 1992; Emelyanov et al. 1995). The flux of dissolved manganese from pore waters to anoxic bottom waters was shown for the Arkona Basin (Damm 1992). It can be concluded that the uppermost centimetres of cores OP19 and BB02 are presently free of oxic conditions. A doubling of manganese concentrations is observed in the upper 10 cm of core BB12 indicating at least temporary persistence of oxic conditions at this site. Suboxic conditions are characterized by the mobilisation of manganese and iron, formation of Fe-carbonates and enrichment of Cu, Zn and Pb (Damm 1992). The downcore extension of the suboxic zone was estimated at 16-23 cm for the Arkona Basin (Damm 1992). A reduction of manganese in the uppermost 20 cm and an enrichment of Cu, Zn and Pb in the uppermost 30 cm may outline the extension of the suboxic zone in core OP19. In the cores BB02 and BB12 from the Bornholm Basin it is estimated at 20 and 10 cm respectively. Below 30 cm anoxic conditions within the Holocene mud are assumed for all cores.

Distribution of Redox-Sensitive Metals

Concentrations of redox-sensitive metals were normalized to aluminium to account for variations in the terrigenous background concentrations. It can

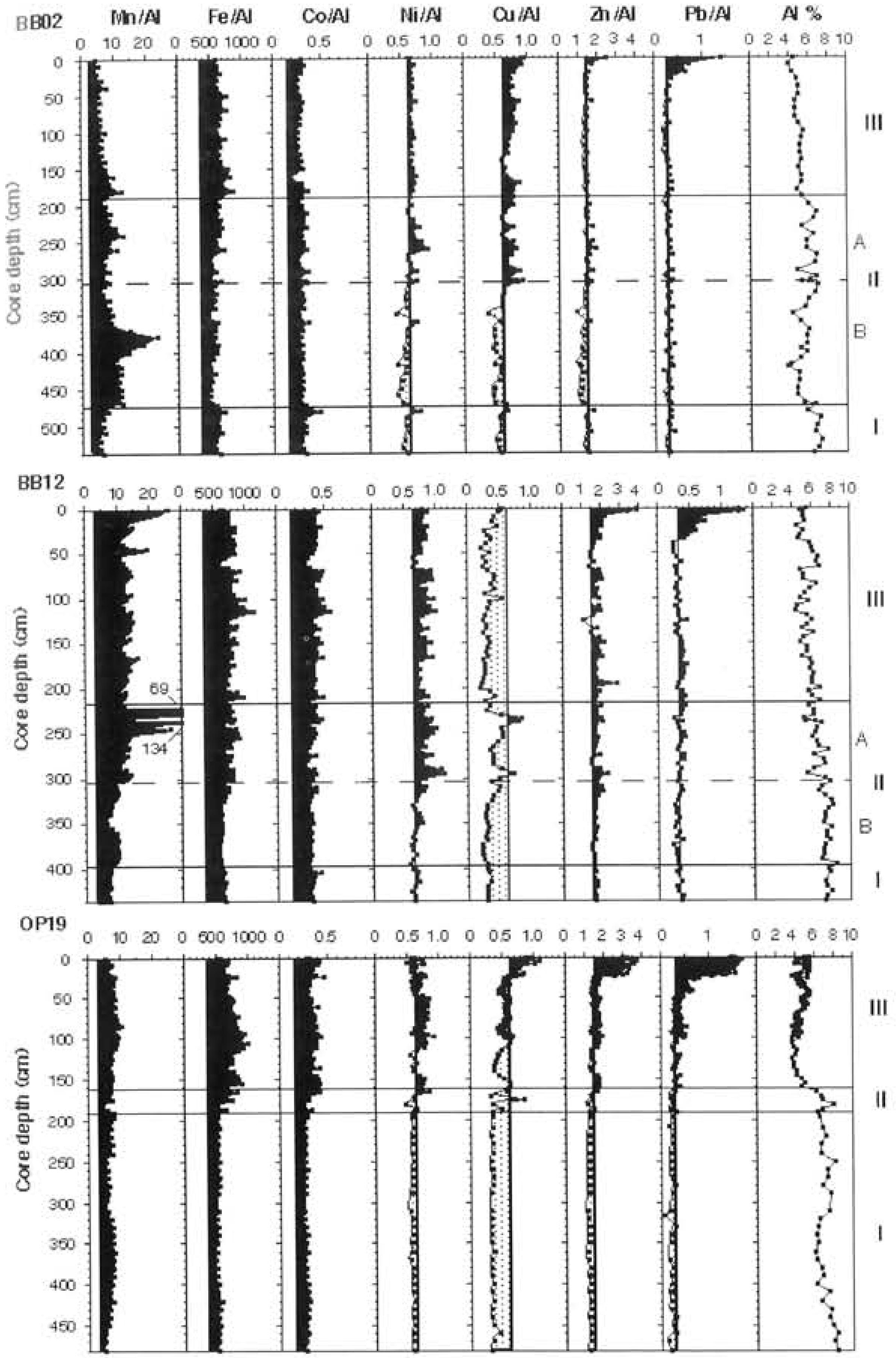

Fig. 3. Downcore distribution of Al-normalized concentrations of redox-sensitive metals. Reference line between dark and light shading is the background metal/aluminium-ratio representative of terrigenous muds in the Baltic Sea (Damm 1992)

be ruled out that metal-rich layers in our cores are due to variations in the terrigenous background (Fig. 3).

Manganese

Mn/Al ratios in the core from the Arkona Basin show little variation throughout all lithological units (Fig. 3). In the uppermost 20 cm a manganese minimum indicates the suboxic zone. Manganese concentrations range in 280-530 ppm, which is well within the range of 330-740 ppm given for sediments of the Arkona Basin (Brügmann et al. 1980). In the Bornholm Basin values vary widely from 280 to 10500 ppm (Hartmann 1964). Core BB02 from the southwestern margin ranges in 220-1400 ppm, whereas 500-7400 ppm are recorded for BB12 in the deeper part of the basin. Mn/Al ratios depict a manganese depleted suboxic layer in the uppermost 20 cm of core BB02 and a manganese-enriched oxic surface layer (0-5 cm) in core BB12. However, a more substantial enrichment is recorded in subunit IIB (BB02) from 370-470 cm core depth and in 3 sharp spikes in subunit IIA of BB12, (Fig. 3).

Iron, Cobalt and Nickel

Generally, sediments in basins of the Baltic Sea are relatively rich in Fe and Co. This is confirmed by Fe/Al and Co/Al ratios (Fig. 3), which exceed background values calculated by Damm (1992) as well as those from Turekian & Wedepohl (1961) for terrigenous slates (Fig. 4). Fe/Al ratios are highest in the anoxic core sections of unit III and subunit IIA and decrease below. Increased Fe/Al ratios in unit I of core BB02 may be due to the presence of iron-rich chlorites in these late glacial sediments (Gingele & Leipe 1997). With the exception of site BB02 Co/Al ratios show a pattern similar to Fe/Al ratios with maxima in the anoxic core sections. The same behaviour can be observed for Ni/Al ratios. Fe as well as Co and Ni show highest values in the deepest core BB12.

Copper

Cu/Al ratios do not show a common pattern in the analysed cores. In the Arkona Basin they are below or near the natural background throughout most of the core. A surficial enrichment in the suboxic zone 0-20 cm coincides with Pb and Zn maxima. At the BB02 site Cu/Al ratios are remarkably consistent with Ni/Al ratios, showing higher values in the anoxic sediments of unit II and subunit IIA. Cu contents are low in core BB12, which results in Cu/Al ratios of 50% below the expected terrigenous background (Fig. 3, 4). Two conspicuous Cu maxima appear in subunit IIA and can be correlated to Mn and Ni peaks.

Zinc and Lead

Zn and Pb are the only elements, which display a similar pattern in all three cores. They are enriched near the sediment surface in the suboxic zone and fluctuate tightly around background values throughout the rest of the core. Enrichment factors are 2-2.5 for Zn and 5 for Pb. A surface layer enriched in heavy metals was found in many cores from the Baltic Sea basins. Some authors favour anthropogenic input as a major source (Leipe et al. 1995) others stress the early diagenetic mobility as the main process (Damm 1992).

DISCUSSION

Enrichments of redox sensitive metals are found in all our cores. Unfortunately, they rarely occur in similar stratigraphical positions, which makes it difficult to relate them to common changes in paleoredox conditions. Enrichments are not directly related to TOC peaks. Manganese being the element most susceptible to redox changes shows significant enrichments only in the cores from the Bornholm Basin cores. In core BB02 the lower part (350-470 cm core depth) of subunit IIB is characterized by increased Mn values (factor 2-5). As subunit IIB is related to the Yoldia Sea stage these enrichments may record rapid and multiple fluctuations of inflow of saline waters and periods of stagnation, thus providing the first record of a Mn-enrichment scenario typical for present-day basins of the Baltic. Subunit IIB is likewise depleted of Ni, Cu and Zn (Fig. 3). Enrichment of Mn and depletion of Ni, Cu and Zn are typical features of present day oxic layers (Gobeil et al. 1987). Subunit IIB is poor in organic carbon, which may explain the development of a broad oxic layer. The preservation of this "oxic" element distribution requires rapid burial to seal reactive manganese phases in subunit IIB from the reductant reactive organic matter present in anoxic Holocene muds above. This could have been achieved by the local but rapid sedimentation of terrigenous matter, which marks the onset of subunit IIA in core BB02. The high input of organic carbon is related to refractory organic matter (peat, Huckriede et al. 1995) as evidenced by a maximum in TOC/N-ratios (Fig. 2). The local sedimentation event could have caused atemporarily increased sedimentation rate in general. This scenario would result in a rapid shallowing of the redox boundary thus burying most of the "oxic" layer of subunit IIB below the zone of manganese mobilization.

In core BB12 no manganese enrichments are found in subunit IIB. Thickness of the subunit is half of that in core BB02. Near the transition to

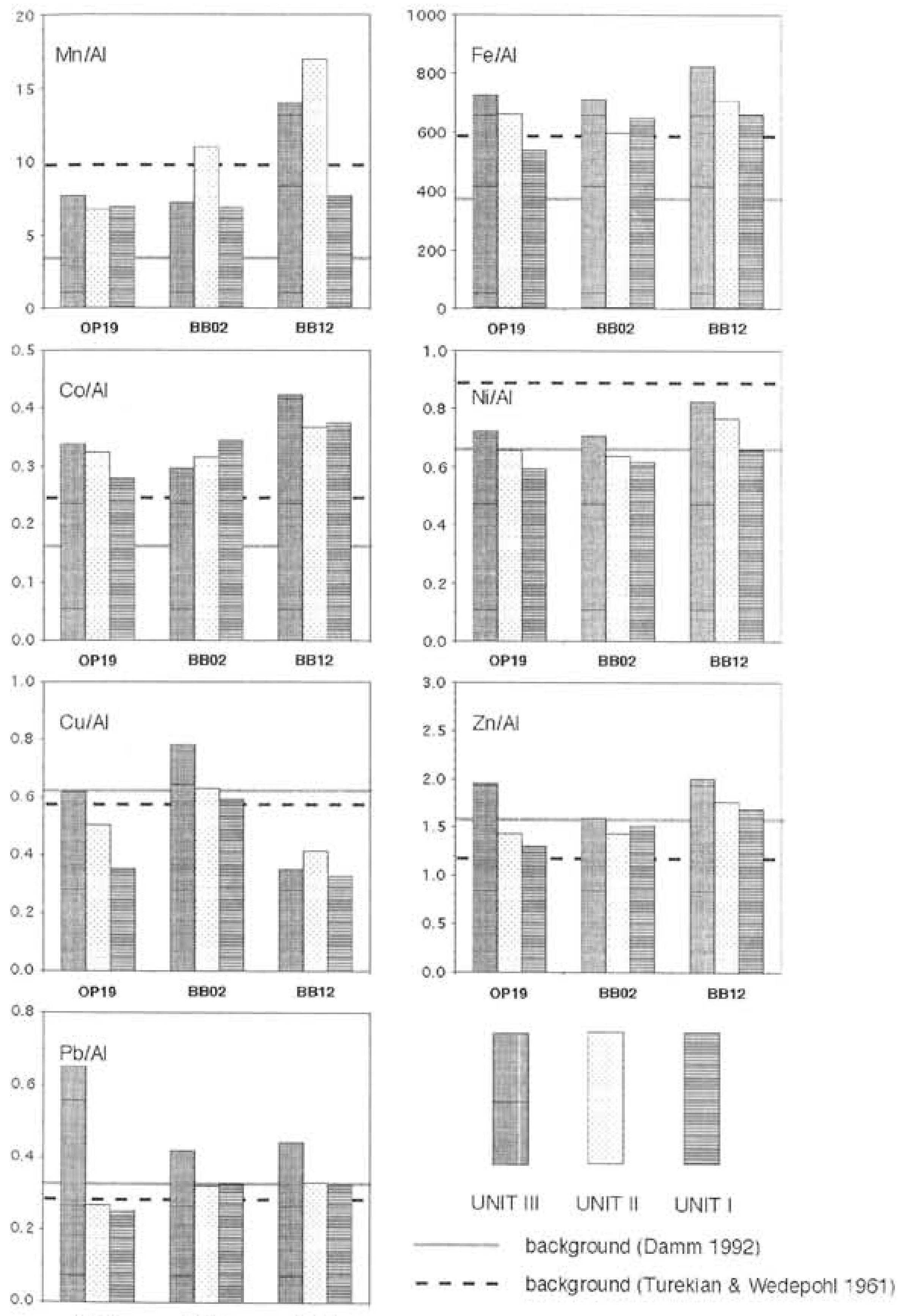

Fig. 4. Mean values of Al-normalized (Me/Al × 10^3) concentrations of redox-sensitive metals for each stratigraphic unit of the analysed cores. Lines represent the background metal/aluminium-ratio of terrigenous muds in the Baltic Sea (Damm 1992) and terrigenous shales (Turekian & Wedepohl 1961)

subunit IIA only a slight and steady increase in organic carbon content and TOC/N-ratios is recorded. Obviously redox conditions in this core were not favourable for the preservation of reducible manganese phases. However, substantial manganese enrichments (factor 5-10) are found in 3 sharp spikes below the transition from subunit IIA to unit I (Mastogloia Sea stage). In combination with a peak in copper concentrations a few centimeters below they may represent a fossilized oxic-suboxic sequence. The coprecipitation of manganese and copper phases was suggested by several authors (Hem et al. 1989; Jarvis and Higgs 1987; Thomson et al. 1993). A second and smaller peak in copper concentrations occurs near the base of subunit IIA. A related manganese peak may have been eroded by early diagenetic mobilisation. Since manganese is more susceptible to redox changes (Thomson et al., 1993) copper phases may survive longer. Mn enrichments in Mastogloia Sea sediments may record rapid fluctuations between oxic and anoxic bottom water conditions triggered by increased inflow of brackish-saline water from the North Sea (Neumann et al. 1996). They are also observed in Mastogloia Sea sediments of the Gotland Deep (Huckriede et al. 1995). However, a scenario for the preservation of the manganese peaks at this stratigraphic position is difficult to conceive. They correspond directly to a first prominent maximum in organic carbon content (Fig. 2), which can also be observed in sediments of the Gotland Deep. A drop in organic carbon flux (Wilson et al. 1985), oxygenation of bottom waters (Finney et al. 1988) and reduced sedimentation rates can deepen the oxic layer and preserve manganese peaks. A drop in organic carbon flux in the initial phase of the Litorina transgression (unit I), could be the main preservation factor. In later stages, when anoxic Holocene mud has been deposited a rapid shallowing of the oxic-postoxic redox boundary is required to save these manganese peaks from remobilization. At the transition between the Ancylus and Litorina stages there was a number of environmental parameters, which changed more or less simultaneously: salinity, primary production, climate and water circulation (Sohlenius et al. 1996), thus making it difficult to assign changes in redox conditions to a single paleoenvironmental factor. Unfortunately no manganese enrichments are found in Mastogloia Sea sediments in core OP19 and only a minor peak is detected at this level in BB02. This may be due to different sedimentation conditions in the Arkona Basin and/or insufficient water depths at site BB02 and OP19. Therefore the suggested scenarios for the preservation of Mn enrichments cannot be confirmed with our material alone. The study of additional cores and acquisition of pore water data are required. The occurrence of metal rich layers at similar stratigraphic levels - as observed in the Gotland Deep - could substantially support paleoceanographic interpretations. Finally, we have to consider a late diagenetic origin for the Mn enrichments. Late diagenetic formation of pyrites was shown in Ancylus Lake sediments by Boesen & Postma (1988) and Sohlenius et al. (1996). Theoretically these pyrites could carry substantial amounts of other trace metals. However, in our cores from the Bornholm Basin the most prominent Mn and Cu enrichments are correlated to minima in the pyrite record (Fig. 2,3). Thus it seems unlikely that the enrichments are related to pyrite genesis.

Surficial enrichments of Zn, Pb and to a lesser extent Cu can be observed in our cores as well as on many other sites in the western Baltic Sea (Brügmann & Lange 1983, 1990; Damm 1992; Leipe et al. 1995; Szefer & Skwarzec 1988). An anthropogenic source (Leipe et al. 1995) or mainly early diagenetic origin (Damm 1992) is suggested. Zn and Pb distribution is similar in cores BB02 and BB12. No significant enrichment is recorded below the subsurface maximum (Fig. 3). In the subunits IIA and IIB, where buried oxic and suboxic layers are indicated by manganese maxima no increase in Zn and Pb concentrations can be detected. Therefore we conclude that the surficial Zn and Pb enrichments represent mainly anthropogenic pollution accumulated in the course of industrialization. Pb, which is mainly introduced by airborne pollution (Pheiffer-Madsen & Larsen 1986) reaches highest values in the Arkona Basin (Fig. 4). This may be due to the proximity of industrial centres or the additional input of aquatic Pb from river suspensions (Leipe et al. 1995). Zn has its major source in aquatic input with North Sea water (Damm 1992). Dilution by different sedimentation rates may be responsible for the fluctuations in Zn-values within basins (Fig. 4).

Maximum concentrations for Cu, which exceed those in the subsurface layer occur in a fossilized metal rich layer in core BB12 from the Bornholm Basin. Thus it cannot be ruled out that early diagenetic redistribution is responsible for a large fraction of Cu enriched in the subsurface peaks.

CONCLUSIONS

Enrichments of the redox sensitive metals Mn and Cu are found in sediments of the Yoldia Sea stage and transitional Mastogloia Sea stage in the Bornholm Basin. Occurring below the anoxic Holocene muds they are considered as buried oxic-postoxic metal distributions of early diagenetic origin. They are believed to record a Mn enrichment mechanism, which is active in present-day anoxic basins of the Baltic Sea, triggered by fluctuations in bottom water oxygenation. Their preservation is related to changes in organic carbon supply, sedimentation rate, local sedimentation events and rapid fluctuations of the oxic-suboxic redox boundary. No Mn enrichments are found in the shallow Arkona Basin. The Mn record from the deep Bornholm Basin site can be correlated to records from the Gotland Deep.

The lack of substantial enrichments of Zn and Pb in "preserved" oxic-suboxic layers of AY-clays points to an anthropogenic source for surficial enrichments of these metals.

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On the Luminescence Dating of Eolian Deposits in Estonia

Anto Raukas and Galina Hütt

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The dating of the eolian deposits needs new precise physical methods. In the paper the reliability of results of thermo- and optically stimulated luminescence dating method are discussed. Most of the dates of eolian deposits from the coastal and inland dunes of Estonia fit well with predicted geological ages.

Keywords: thermoluminescent (TL) and infrared optically stimulated (IR OSL) dating, coastal and inland dunes, Baltic Sea, Lake Peipsi.

INTRODUCTION

It is extremely complicated to determine the age of eolian deposits due to multiple redeposition of sediments and lack of suitable dating methods.

The deficit of organic matter in eolian deposits makes it difficult to obtain material for conventional radiocarbon dating. Besides, seeds and other organics may be reworked in eolian deposits and, therefore, predate the deposits in which they occur. *In situ* organics such as soil horizons typically indicate periods of dune stability, and hence can only be used to broadly bracket periods of dune activity. Thermo- and optically stimulated luminescence (TL and OSL) dating, on the other hand, is ideally suited for dune deposits as it provides a date corresponding to the last time the sediments were exposed to sunlight, and thus can be used to determine a period of eolian activity (Prescott 1983; Rendell et al. 1994; Clarke 1994; Wintle et al. 1994).

The OSL dating method, using quartz, was proposed by Huntley et al (1985). Currently, the infrared optically stimulated luminescence (IR OSL) dating technique, based on alkali feldspars, is of wider use due to the simple technical solution. The method, the first results of dating and physical bases were proposed by Hütt et al. (1988), Hütt & Jaek (1996a, b).

Compared to the TL method, an advantage of OSL dating is the new readout technique which permits to choose more light sensitive grains. It is just this phenomenon that leads to more successful realization of zero-point: minimum nonbleached, residual signal to the time of sedimentation. In case of dunes, which have been exposed to sun during a very long period, this residual can be reconstructed in the laboratory.

LUMINESCENCE DATING PROCEDURE

The samples under study were taken from different age sections all over Estonia. Alkali feldspars (100-160 μm) were extracted from these sediments following the techniques described earlier (Mejdahl 1983; Hütt & Smirnov 1983).

The light source used for stimulation was a semiconductor laser with emission in the wavelength region 810±1 nm. The light beam intensity on the sample was 6 mW/cm^2, thus corresponding to ordinary sunny day conditions. The laser was operated in the pulse mode with a pulse length of 3 seconds. An exposure of this duration and intensity did not cause bleaching of the sample, which could be seen from the fact that repeated light pulses produced emission signals of the same intensity. The use of a very weak stimulation light pulse gives two advantages. Firstly, the most light sensitive grains i.e. those best bleached in nature, will mainly be touched upon. Secondly, a week stimulation pulse will not change the dosimetrical properties caused by changes of electron population in the traps. For detection of the emitted light an OSL/TL reader constructed in Tallinn jointly by the researchers of the Institute of Geology and the Ingrid company was used.

The optical response for the samples studied was determined and the wavelength region used for stimulation was chosen in order to reach electrons in stable traps. The emitted light was detected in the UV-band around 380 nm.

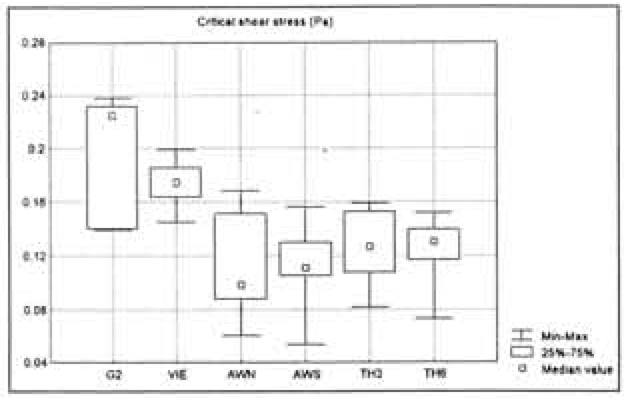

Fig. 5. Critical shear stresses of sediments in the Oder estuary (Box and Whisker plot)

Greifswalder Bodden (G2 and Vie) starts at higher shear stresses than that in the other locations. The Greifswalder Bodden is deeper and consequently the sediments are not eroded and re-deposited as frequently as at the other locations. Therefore, the sediments are more strongly consolidated, have a higher density and a higher erosion stability. The sediments of the Achterwasser show the smallest resistance to erosion. Here the organic content of sediments is very high and organic material on the sediment surface is easily eroded.

Critical Shear Stress and Organic Matter

The organic matter contents of the particles which were eroded during the erosion experiments, were characterised by measuring their particulate organic carbon (POC). The measured values are shown in the following table.

The erosion shear stress is lower with higher contents of POC and the matter eroded at first is mainly organic. A biological stabilisation of the sediment surface as found by Witte et al. (1995) could not be established.

Due to cohesion, the erosion of the mineral particles starts at higher stress levels.

Eroded Mass

To characterise the complete erosion behaviour of the sediment samples, determination of the erosion rate (eroded mass as a function of time) is required. The eroded mass in sum was calculated up to a shear stress level that is double the critical shear stress, as characteristic parameter.

Table 1. **Annual mean of content of POC in the sediment and in the resuspended matter in the different locations of the Oder estuary**

Location	POC (%) of resuspension	POC (%) of sediment
G2	10.88	2.31
Vierow	8.54	2.93
AWN	16.71	11.67
AWS	16.73	11.67
TH3	12.65	9.03
TH6	11.98	7.94

While the critical shear stress is low in Achterwasser due to loose sediments on the surface, the eroded mass is considerably small there. The Achterwasser is of a high ratio of water depth to cross sectional area, so that the effect of waves appears only on the surface. That is why the sediment is not so often resuspended and consequently more consolidated.

A maximum of eroded mass was detected in Kleines Haff. After overcoming the critical shear stress, this sediment can be eroded rapidly. The Kleines Haff is of a small ratio of water depth to cross sectional area. The sediment is often resuspended by waves and not so consolidated. Small wind forces can erode large amounts.

Settling

Witte et al. (1995) define three classes of settling velocities for the SPM transport of tidal inlets in the German Bight (Table 2).

Although this classification is a result of the tidal rhythm and the prevailing water depth (only SPM with high settling velocities has a chance to settle during slack water), it is also used for the Oder estuary.

Settling Velocities of Artificially Resuspended Fresh Particulate Matter

The main fraction of the suspended matter (50-70%) has a median settling velocity of <0.01 cm/s. This fraction is of significant importance for suspended matter transport, because of its long-time stay in the water column.

The suspended matter fraction with the lowest median settling velocity was found in the Greifswalder Bodden. At this location the eroded material was mainly organic with a low density. The reason for this is the high erosion resistance of these sediments which causes selective resuspension of primary organic matter.

Fig. 6 shows the dependence of the fraction of suspended matter with the higher median settling velocity of 0.01-0.1 cm/s on the concentration of resuspended matter. The fraction of suspended matter with a settling velocity of 0.01-0.1 cm/s increases with the overall concentration of resuspended particulate matter. The reason for this is the increasing bottom shear stress during the experiment combined with an increasing SPM concentration.

Table 2. **Classes of settling velocities for the SPM transport**

Class 1	$v_s < 0.01$ cm/s	Transport over long distances
Class 2	$0.01 \le v_s \ge 0.1$ cm/s	
Class 3	$v_s > 0.1$ cm/s	Transport over short distances fast accumulation

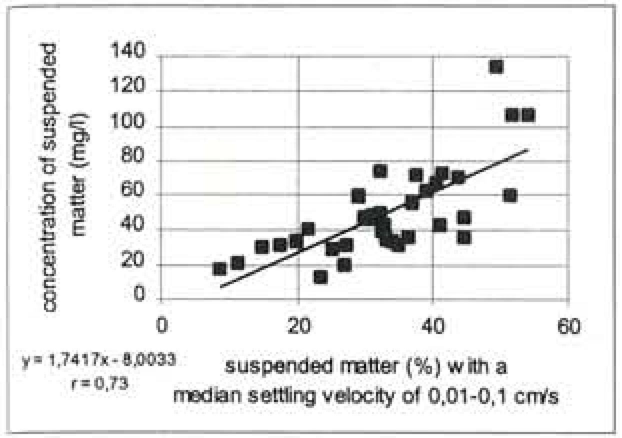

Fig. 6. Concentration of resuspended matter as a function of the suspended matter fraction with a median settling velocity of 0.01-0.1 cm/s

Settling Velocities of Artificially Resuspended Flocculated Particulate Matter

A series of sediment samples from two north/south cross-sections in the Kleines Haff was analysed to examine the flocculation potential of the artificially eroded SPM.

Fig. 7 shows the measured median settling velocities for both freshly eroded and artificially flocculated SPM as a function of concentration at the end of the EROMES experiment. No significant correlation was found for concentrations up to about 100 mg/l. At higher concentration levels (more than 300 mg/l), there is a remarkable difference; the settling velocities of the flocculated matter are about a factor of ten higher than those of the freshly eroded, unflocculated SPM. Therefore, it is to be expected that flocculation processes will only occur in the near bottom area of the water column.

Settling Velocities of Natural Suspended Particulate Matter

Following a storm event, settling velocity experiments were carried out using natural suspended matter from the water column. These experiments with the modified MARKDAN sampler took place on board a fishing-boat in the southern and the northern region of the Kleines Haff. The water depth was between 3 and 5 m and the samples were taken 1 m above the sea bottom.

Fig. 8 shows the measured median settling velocity as a function of SPM concentration. Again, a distinct correlation could not be found at the lower concentrations. The settling velocities are very low (class 1). Higher settling velocities were measured near the northern shore which are only caused by a higher contents of sandy material in the SPM. The organic matter in the SPM amounted to between 20 and 45%.

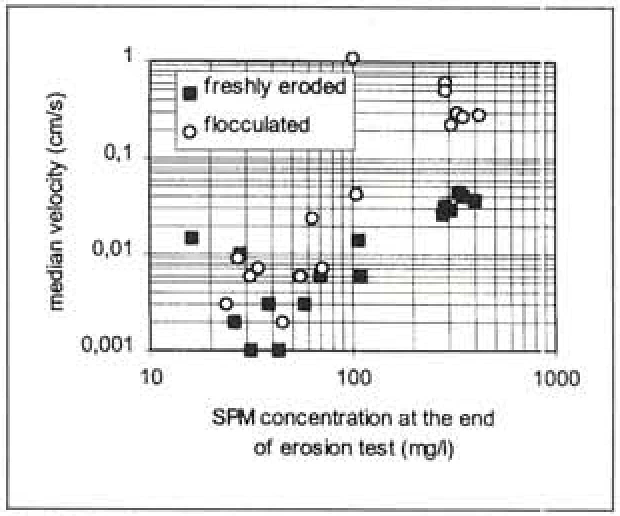

Fig. 7. Median settling velocity of both freshly eroded suspended matter and after artificial flocculation as a function of SPM concentration at the end of the erosion test (Kleines Haff)

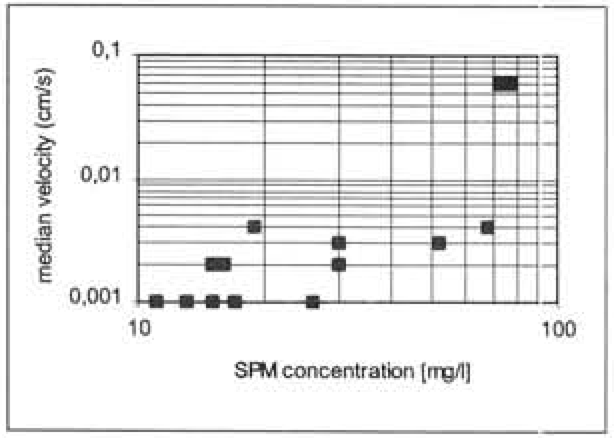

Fig. 8. Median settling velocity of natural SPM samples from the Kleines Haff as a function of concentration

Settling Velocity and Organic Matter

The organic carbon contents of the water samples (withdrawn during the settling test) were measured. Fig. 9 shows a correlation between the settling behaviour and the organic matter contents. This is almost the same at all locations. The particles settling at the beginning with high POC contents are flocs consisting of mineral grains in an organic matrix. The POC contents of the samples decrease during the settling test and increase at the end of the experiment. Low settling velocities are linked to high contents of organic matter. This fraction remains in the water column and is scarcely deposited. The contents of organic material in the suspended matter are considerable higher in the Achterwasser than at the other locations. This was also found by Fietz (1996). The organic matter is essential to the settling velocities of the fast as well as of the slow settling fraction.

Settling Velocities in the Oder Estuary Compared to Other Regions

Fig. 10 compares the settling velocities in the Oder estuary with those in other German estuaries (Elbe, Weser, Ems) measured by the GKSS Research Centre (Müller & Puls 1996). The diagram shows the ranges of measured median settling velocities plotted against SPM concentration. The data for the Oder estuary result from the settling tests with artificially resuspended fresh particulate matter and bear a resemblance to the measured data for the Elbe and Weser estuary. However, in the Elbe estuary the settling velocities seem to be somewhat higher because of intensive flocculation as a consequence of biological activities (Michaelis & Fanger 1994).

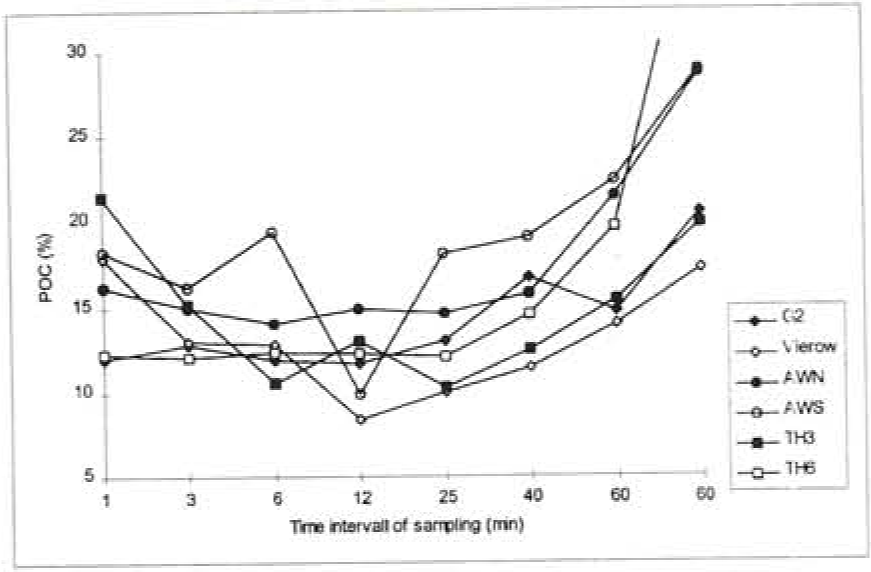

Fig. 9. Particulate organic carbon contents in the settling test samples

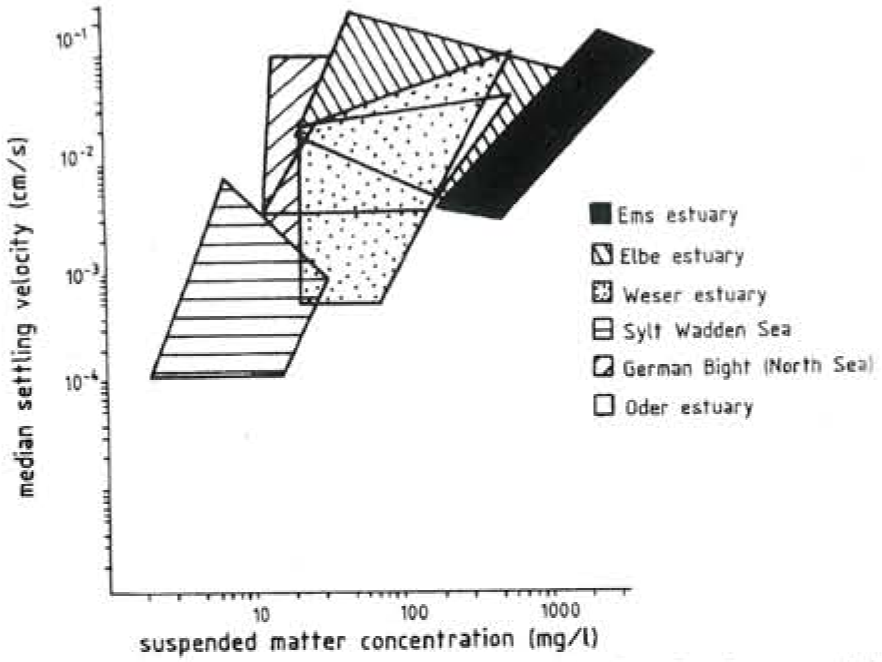

Fig. 10. Median settling velocities in German estuaries plotted against suspended matter concentration (modified after Müller & Puls 1996)

CONCLUSIONS

The critical bottom shear stresses, the erosion rates and the settling velocities of artificially resuspended and natural SPM have been measured using samples from the Oder estuary (Greifswalder Bodden, Achterwasser, Kleines Haff). Furthermore, the grain size distribution of the sediments and the contents of organic matter were analysed.

In this investigation only muddy sediments with a maximum sand fraction of about 20 % and a clay fraction of about 15 % were examined.

The compositions of the sediments from the different locations in the Oder estuary are fairly similar.

A seasonal change in the dynamic parameters characterising SPM was not found during the six month period of the experiments.

The critical erosion shear stress of sediments in the Greifswalder Bodden (especially at the location G2) is higher than in the Achterwasser or in the Kleines Haff. The erosion rates of all the locations considered are significantly different.

Organic material can be eroded more easily than the clay or silt particles. Consequently, the critical shear stress is low if there is a considerable quantity of organic material on the sediment surface.

The sediments in the Achterwasser show a low critical shear stress level but they are well consolidated and therefore have low erosion rates. A maximum erosion rate is visible in the Kleines Haff but without a significantly different critical shear stress.

A dependence of the grain size of the muddy sediments examined on the erosion behaviour was not found.

A correlation between SPM concentration and settling velocity was measured only at concentrations higher than 100 mg/l. This is caused by flocculation processes.

The in situ measured settling velocities are very low (<0.005 cm/s).

A correlation was found between the settling velocity and the contents of organic matter in the deposited particles. The fastest and slowest settling fraction show the highest contents of organic material. While the latter is normal for purely organic particles, the former is a consequence of flocculation with mineral particles in an organic matrix.

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New Data About Mineral Composition of Latvian Beach Placers

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The chrome-pyropes (pyropes) are found among the garnets distributed in Latvian beach placers, which spread both on the Kurzeme Coast of the Baltic Sea and on the Vidzeme Coast of the Gulf of Riga. All garnets observed by authors have been studied in detail. The chrome-pyropes contain high amount of pyrope molecule - 64.8-71.7 mol. %, and the content of uvarovite molecule is 6.7-9.7 mol. %. In all cases this mineral is highly magnesian and poor in iron. The pyrope-almandines (pyrope molecule 25.7-29.8 mol. %) are present among garnets also. The garnets occurring in the placers are mainly represented by almandines of different types. According to chemical composition chrome-pyropes from beach placers of Latvia are obviously similar to those known from kimberlites of Canadian Arctic and other districts, as well as to the pyropes from terrigenous Devonian deposits of Northern Timan.

Keywords: chrome-pyrope (pyrope), pyrope-almandine, almandine, garnets, chemical composition, beach placers, Baltic Sea, Gulf of Riga, Latvia.

INTRODUCTION

The beach placers are formed due to repetitive washing of a large amount of initial clastic materials. Therefore they are unique nature objects reflecting general mineral features of source areas more exactly than host beach sands, as well as other Quaternary deposits.

The mineral composition of beach placers is investigated in Latvia since 1956-1957. Investigations were connected with prospecting works as a rule. The basic areas of the placers distribution have been revealed on the beach of Latvia both on the Kurzeme Coast of the Baltic Sea and on the Vidzeme Coast of the Gulf of Rīga. Placers are represented by accumulations of heavy minerals, which generally are located along the inner border of a beach. These accumulations are small in size and thickness, as well as interrupted character of their distribution. Thickness of placers changes from some centimetres to several tens of centimetres, but sometimes reaches up to 1,0 m. Thin-bedded layers with visible and invisible occurrence of heavy minerals are quite often observed in the structure of placers. The placers clearly differ from the light sandy deposits by their violet, violet-reddish or violet-black colours. These accumulations overlay both the Devonian deposits and Quaternary tills and clays.

Dominant minerals in the placers are garnets, ilmenite, magnetite. In less amount there occur also leucoxene, rutile, zircon, amphiboles, pyroxenes, tourmaline, epidote, disthen, staurolite, sphene and some other minerals. The mineralogical analyses compiled by J.Churilova, N.Zuments, J.Majore, V.Timofejeva are known from the papers and reports (Lunts et al. 1960, Ulst & Majore 1960, Majore et al. 1961, Stinkule 1961, Lunts 1962, Kogan & Churilova 1963, Ulst 1963). Numerous results of mineralogical analyses are stated in reports of Chetirbotskaya (1960) and Chetirbotskaya et al. (1960) also.

METHOD AND RESULTS

The detailed mineralogical studies were compiled by authors of present paper for well-known placers of the beach on the Kurzeme Coast of the Baltic Sea and on the Vidzeme Coast of the Gulf of Rīga. These new mineralogical studies was begun after preparation of some general publications about mineral deposits of Latvia (Kuršs 1995) and about the placers of the Latvian Coast (Veinbergs and Savvaitovs 1996). The locations of sampled sites are shown in Fig. 1. The aim of studies was to determine the new minerals unknown earlier, as well as to point out the typomorphic signatures of the minerals allowing to indicate the source areas. For the mentioned purposes the large samples with a mass of 0,5-20 kg were taken from the placer deposits. The sand and coarse silt material of specimens was investigated by mineralogical method after the treatment with gravity separation. The separate grains of some different minerals and their varieties were analysed by electron microprobe in order to determine the chemical composition of minerals.

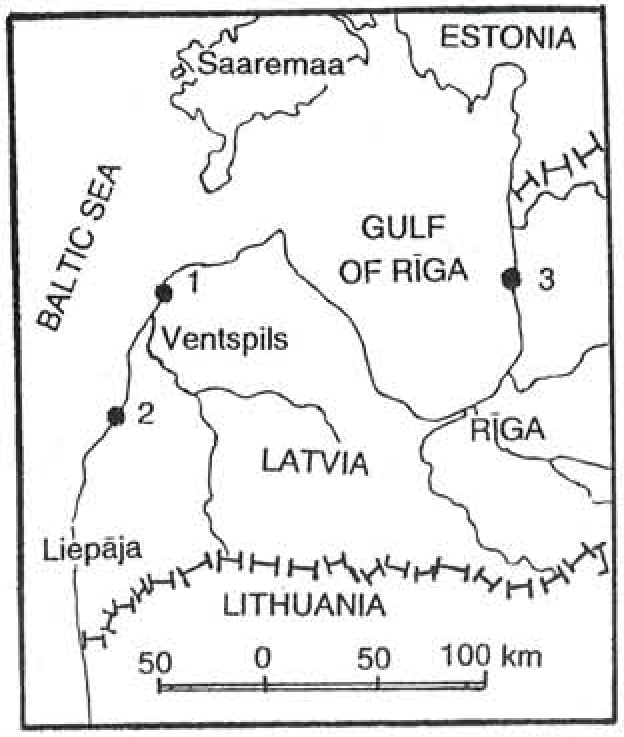

Fig. 1. Location of investigated beach placers: 1 - Liepene, 2 - Labrags, 3 - Ķurmrags

Table 1 **The garnets in grain size spectrum of placers**

Locations of sampled specimens and their mass (g)	Grain size of fractions (mm)	Content of garnets (%)	Content of chrome-pyrope grains
Kurzeme Coast of the Baltic Sea:			
Liepene, 2380	0.5-1.0	16.3	
	0.25-0.5	67.1	34
	0.1-0.25	46.2	16
	0.05-0.1	3.8	
Labrags, 751.4	0.25-0.5	49.6	22
	0.1-0.25	57.0	12
	0.05-0.1	5.9	
Vidzeme Coast of the Gulf of Riga:			
Ķurmrags, 677.4	0.25-0.5	47.8	4
	0.1-0.25	36.7	3
	0.05-0.1	8.6	
According to data of Lunts (1962)	>1.0	40.0	
	0.5-1.0	49.9	
	0.25-0.5	76.5	
	<0.25	65.7	

The chrome-pyropes (pyropes) have been discovered among the garnets occurring in the beach placers. Considering these results, all other varieties of the garnets were investigated in detail too.

Chemical composition and molecular percentage of end-member molecules of the garnets from the placers of the Vidzeme Coast were studied previously by Lunts (1962). According to investigations of Lunts, the garnets distributed in placers are subdivided into some typomorphic varieties, all of them corresponding to almandine characterized by a high content of pyrope molecule (16-20 mol. %). However, the garnets corresponding directly to pyropes were not established in this study.

Garnets are dominant minerals in the composition of the Latvian placers. Their maximum contents are determined in grain size fractions of 0.5-0.25 and 0.25-0.1 mm. Distribution of garnets in grain size spectrum are illustrated in Table 1. It is necessary to note that similar distribution has also been observed earlier (Ulst & Majore 1960, Lunts, 1962).

The chrome-pyropes (pyropes) were found in the placers both on the Kurzeme Coast and on the Vidzeme Coast, however their higher content was observed on the Kurzeme Coast. The chrome-pyrope garnets in all sampled sites are identical - violet clastic grains with glass luster and index of refraction 1.743-1.746. The grain size of this mineral ranges from 0.1 to 0.7 mm, and the form usually is irregular and acute-angled. Rather smoothed, sometimes possibly rounded, forms are observed for the larger grains only. Surface of the smoothed grains is dull and rough; crystallographic facets on the surfaces of grains have not been observed. Chemical composition for some of the chrome-pyrope grains found are demonstrated in Table 2. In all cases they are highly magnesian and poor in iron. The chrome-pyropes with the colour and chemical composition different from above-mentioned grains are not found in the sampled sites.

All other varieties of the garnets in beach placer deposits of Latvia are mainly represented by almandines. According to colour, two general types are clearly distinguished among them: light-coloured (I) and dark-coloured (II) ones. The proportion of the light coloured garnets is about 75-80%, but content of the dark coloured garnets ranges in 20-25%. Such a ratio is common for sandy beach deposits of Latvian Coast generally, and it is the same also for the placers.

Studies in details reveal occurrence of still more varieties of almandine according to colour - light rose and light rose-violet, red-brownish and orange-brownish. These varieties of the almandine are distinguishable clearly.

The almandines of the placers usually are characterised by irregular and acute-angled grain forms. Crystallographic facets are sometimes observed on the surface of the grains. The grains with characteristic rhombododecahedron shape occur too; such shapes, as a rule, are observed in the large grain size fractions. The almandines with rounded form are relatively rare. The index of refraction is more than 1,781, and mineral has a glass luster.

Chemical compositions for the colour-varieties of almandine grains are demonstrated in Table 3. All varieties contain high amount of iron and are poor in magnesium in contrast to the chrome-pyrope (pyrope). The content of chrome is small. The proportion of almandine molecule in orange-brownish, rose and rose-violet varieties of these garnets ranges from 66.6 to 84.6 mol. % as a rule. The red-brownish almandines in contrast to other colour-varieties usually are characterized by higher contents (up to 18.43 %) of manganese, but content of a spessartine molecule reaches up to 41.5 mol. %.

Table 2. **Chemical composition of chrome-pyropes** (wt. and mol. %)

Chemical composition	Kurzeme Coast of the Baltic Sea		Vidzeme Coast of the Gulf of Riga			
	Liepene		Ķurmrags			
SiO_2	41.75	41.46	41.78	42.78	41.85	41.79
Al_2O_3	21.39	20.30	21.21	22.02	22.08	21.70
FeO	8.34	9.02	8.74	7.33	8.27	8.84
MgO	18.66	17.79	18.48	19.41	19.32	19.11
CaO	5.93	6.51	5.93	5.30	5.57	5.29
MnO	0.51	0.52	0.49	0.35	0.38	0.40
TiO_2	0.04	0.06	0.12	0.01	0.11	0.18
Cr_2O_3	3.35	4.36	3.25	2.80	2.35	2.70
	99.97	100.2	100.0	100.0	99.93	100.1
Garnet end member molecules:						
Uvarovite	9.7	8.9	9.4	8.2	6.7	7.7
Andradite	2.5	2.7	3.0	2.1	2.8	3.4
Pyrope	67.9	64.8	67.4	71.7	69.7	69.3
Spessartine	1.1	1.1	1.0	0.7	0.8	0.8
Grossular	3.3	5.9	3.1	3.7	4.9	2.6
Almandine	15.5	16.6	16.1	13.6	15.1	16.2

Table 3. **Chemical composition of almandines** (wt. and mol. %)

Chemical composition	Kurzeme Coast of the Baltic Sea													
	Liepene													
	orange-brownish					rose								
SiO_2	36.74	35.80	36.58	35.94	35.68	36.54	37.53	36.64	36.73	37.16	37.77	37.16	37.17	36.26
Al_2O_3	20.76	20.14	20.77	20.05	20.44	20.99	21.55	21.19	21.16	21.24	21.62	21.38	21.28	20.51
FeO	34.35	36.25	33.85	26.65	38.01	36.79	31.42	34.25	34.80	33.39	32.64	34.59	35.02	37.26
MgO	3.31	1.99	1.32	0.52	0.89	3.54	7.45	3.88	4.24	4.36	6.40	4.42	4.38	3.78
CaO	2.91	3.07	4.55	3.24	0.88	0.80	1.07	1.54	0.92	1.06	0.96	1.03	1.20	0.85
MnO	1.77	2.76	2.85	13.43	4.02	1.28	0.78	2.51	2.06	2.77	0.60	1.35	0.92	1.07
TiO_2	0.01	0.00	0.01	0.14	0.00	0.04	0.01	0.00	0.00	0.01	0.00	0.08	0.00	0.00
Cr_2O_3	0.00	0.00	0.00	0.03	0.06	0.03	0.02	0.00	0.03	0.02	0.03	0.00	0.02	0.01
	99.85	100.0	99.93	100.0	99.98	100.01	99.83	100.01	99.94	100.01	100.02	100.01	99.99	99.74
Garnet end member molecules:														
Uvarovite				0.1	0.2	0.1			0.1	0.1	0.1		0.1	0.3
Andradite	5.4	5.7	5.5	4.9	2.2	1.3	1.8	4.1	1.0	1.8	1.0	2.6	3.2	2.2
Pyrope	13.4	7.9	5.5	2.1	3.6	14.0	28.8	15.6	16.7	17.3	25.1	7.7	17.7	14.8
Spessartine	4.1	6.3	6.7	30.9	9.2	2.9	1.7	5.7	4.6	6.3	1.3	3.1	2.1	2.4
Grossular	3.1	3.1	8.0	4.5	0.2	0.8	1.1	0.3	1.5	1.2	1.6	0.4	0.3	
Almandine	74.0	77.0	74.3	57.5	84.6	80.9	66.6	74.3	76.1	73.3	70.9	76.2	76.6	80.3

Table 3. (continued). **Chemical composition of almandines** (wt. and mol %)

Chemical composition	Vidzeme Coast of the Gulf of Riga											
	Ķurmrags											
	red-brownish					rose-violet						
SiO_2	37.38	36.23	35.29	35.50	37.20	36.75	35.69	36.69	36.83	37.50	35.65	37.62
Al_2O_3	19.93	20.28	20.03	20.38	21.07	20.91	20.39	21.21	21.14	21.62	20.58	21.52
FeO	15.52	35.31	24.90	30.25	26.73	34.17	33.60	35.71	33.71	32.45	34.95	33.83
MgO	2.13	0.79	0.52	0.00	1.09	2.24	1.38	2.81	2.06	7.04	1.49	5.18
CaO	6.99	1.37	0.78	1.23	2.69	0.94	0.48	0.60	1.28	1.02	0.31	0.98
MnO	17.92	5.99	18.43	12.47	11.15	4.91	8.44	2.87	4.97	0.29	7.00	0.81
TiO_2	0.09	0.03	0.05	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Cr_2O_3	0.00	0.01	0.00	0.00	0.03	0.08	0.04	0.00	0.01	0.04	0.00	0.07
	99.96	100.0	100.0	99.83	99.98	100.0	100.0	99.99	100.0	99.97	99.99	100.01
Garnet end member molecules:												
Uvarovite		0.1			0.1	0.2	0.1		0.1	0.1		0.2
Andradite	4.9	2.3	1.7	1.8	4.2	1.0	0.9	1.1	3.0	1.8	0.8	2.4
Pyrope	8.5	3.3	2.1		4.6	9.0	5.5	11.3	8.4	27.4	5.9	20.8
Spessartine	40.5	13.8	41.5	28.8	26.8	11.4	19.0	6.6	11.6	0.6	15.9	1.8
Grossular	14.9	1.6	0.5	1.7	3.8	1.5	0.3	0.6	0.6	0.9		0.2
Almandine	31.2	78.9	54.2	67.7	60.5	76.9	74.2	80.4	73.3	69.2	77.4	74.6

Sometimes high concentrations of manganese and spessartine molecule are observed also in some separate grains of orange-brownish colour. The grains characterized by the higher content of manganese have a less proportion of almandine molecule - 31.2-60.5 mol. %. The content of pyrope molecule varies in a wide range - from 2.1 to 28.8 mol. % of the total molecule composition of almandine. The largest content of pyrope molecule have been determined in rose-violet grains (up to 27.4 mol. %) and rose grains (up to 28.8 mol. %).

According to chemical composition data the almandines are subdivided into three groups. The first group is characterized by highest contents of MgO (5.18-7.48 wt. %), and is richest in pyrope molecule (20.8-28.8 mol. %). This group is rare, being represented only by some rose and rose-violet grains of almandine. The second group comprises almandines containing highest amounts of MnO (11.15-18.43 wt. %) and is the richest in spessartine molecule (26.8-40.5 mol. %). This group is mainly represented by red-brownish grains, however some orange-brownish grains also correspond to it. The content of almandine molecule ranges from 31.2 to 67.7 mol. % and is the lowest among all almandines. The third group of almandines is characterized by higher content in FeO (33.39-38.01 wt. %) and richer in almandine molecule (74.3-80.9 mol. %). Usually this group is represented by the orange-brownish, rose and rose-violet grains with the content of pyrope molecule from 2.1 to 17.7 mol. %.

Colourless and grey varieties are found among the garnets too. Similar grains of the garnets are noted by Ozols (1991) in tills of Kurzeme.

DISCUSSION AND SUMMARY

According to principal indices of chemical composition, the chrome-pyrope (pyrope) garnets found in Latvian beach placers are obviously similar to those known from kimberlite of Canadian Arctic (Mitchell & Fritz 1973) and from terrigenous Devonian deposits of Northern Timan (Ilupin et al. 1979). The chemical composition of Latvian chrome-pyropes is close also to pyropes from the other regions known by published literature (Ilupin et al. 1990).

The composition of chrome-pyropes and other garnets from Latvia (Table 2 and 3) recalculated in the end member garnet molecules is shown in Fig. 2. Included are also the data after Mitchell and Fritz (1973). Fig. 2 demonstrates that the Latvian chrome-pyropes are similar by composition to the pyropes found in kimberlites. It is also seen that some grains of Latvian garnets are somewhat similar to pyrope-almandines occurring in kimberlites. They are characterised by content of pyrope molecule 25.7-29.8 mol. %, and thus differ rather well from the typical pyrope-almandines of kimberlites. If compared to typical pyrope-almandines, they are somewhat poorer in pyrope and grossular molecules.

The composition of pyropes in Northern Timan according to data of Ilupin et al. (1979) are shown in Table 4, which together with data of Table 2 give evidence about the similarity of the pyropes of Northern Timan to the chrome-pyropes of the Latvian beach placers. Lower TiO_2 content in chrome-pyropes of Latvian beach placers seems to

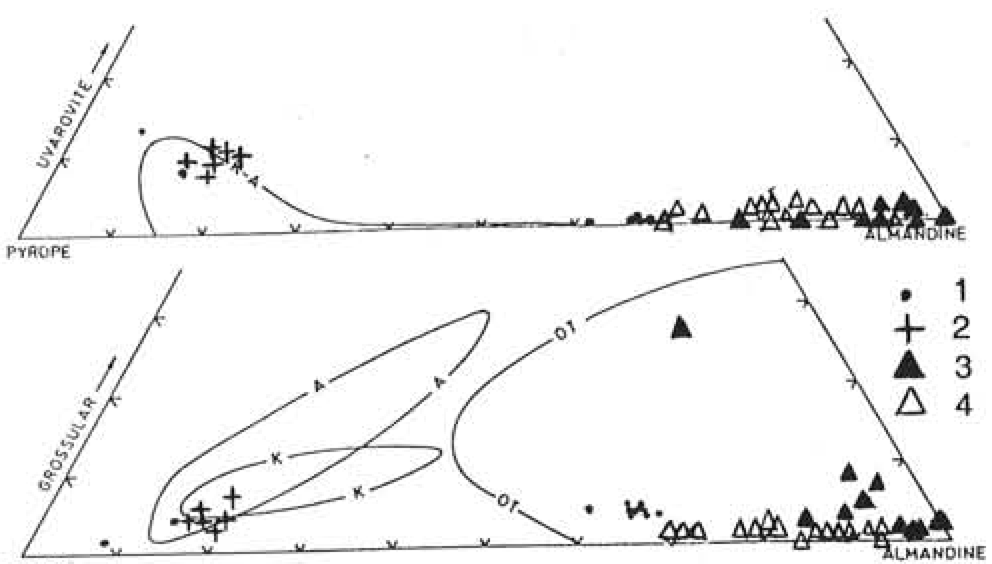

Fig. 2. The composition of garnets in Latvian beach placers recalculated into the end member garnet molecules and compared with composition of garnets from the Somerset Island kimberlite, Kimberly (K), Arizona (A) and Ontario tills (OT). (data by Mitchell & Fritz 1973): 1 - chrome-pyropes and pyrope-almandines from the Somerset Island kimberlite, 2 - chrome-pyropes or pyropes from the Latvian beach placers, 3 - dark-coloured almandines from the Latvian beach placers, 4 - light-coloured almandines from the Latvian beach placers

Table 4. **Chemical composition (wt.%) of the pyropes from the Devonian deposits of Northern Timan after Ilupin et al.** (1979)

	Orange-reddish		Red		Violet-reddish				
SiO_2	42.92	42.86	42.65	42.84	42.86	42.68	42.65	42.21	42.33
TiO_2	0.72	0.64	0.28	0.47	0.03	0.03	0.17	0.13	0.01
Al_2O_3	21.40	19.81	20.86	20.18	21.64	19.78	18.88	18.47	17.73
Cr_2O_3	1.35	2.70	2.30	3.02	2.38	3.92	4.40	5.12	5.89
FeO	8.06	7.54	7.86	7.17	8.51	7.66	7.33	6.93	6.41
MnO	0.29	0.38	0.44	0.26	0.64	0.42	0.32	0.40	0.37
MgO	21.32	21.04	20.23	20.61	19.14	19.51	19.39	20.11	20.68
CaO	4.60	5.11	5.10	5.19	5.61	6.04	5.89	6.00	5.87
	100.66	100.08	99.72	99.74	100.81	100.04	99.03	99.37	99.29

be the only difference. The above-mentioned pyropes from Latvia are represented only by violet grains, but the orange-reddish and red coloured grains of pyrope are not found in Latvia for the present.

The composition of garnets found in beach placers of Latvia is plotted on FeO-MgO-CaO diagram in Fig. 3. Added are also the data about garnets from kimberlites of the Kimberly district of Southern Africa (Ilupin et al. 1990) and Northern Timan Devonian deposits (Ilupin et al. 1979). The compositional fields for pyropes of Northern Timan and of Latvian beach almost coincide, and the field of garnets from kimberlites of the Kimberly district are close to them too. The different types of almandines have compositional field separated from the fields of pyropes.

The discussion shows that the chrome-pyropes of Latvian beach are similar by composition to the pyropes from kimberlites. Consequently, the chrome-pyrope garnets found in Latvian beach placers can be related to kimberlites located among another rocks on the source areas. Probably the almandine-garnets with relatively high contents of pyrope-molecule (25.7-29.8 mol. %) resembling pyrope-almandines have a connection with kimberlites too.

The pyropes are found in the Latvian beach placers for the first time. Previously they were known in the Devonian deposits. The finds of pyropes in the Quaternary sediments were reported also by Sorokin et al. (1992) and Segliņš /ed./ (1996). Basing on the finds of pyropes in the Devonian deposits and tectonical factors, the attempts have been made to forecast the diamond pipes in Latvia (Sorokin 1997, Segliņš /ed./ 1996). The finds of pyropes in beach placers, being the object of present paper, show that the method to forecast of diamond in Latvia must be broadened and supplemented. It cannot be excluded that the pyropes both from the Devonian deposits and Quaternary sediments also including the beach placers were transported from far away. According to Kuršs (1992) the main provenances of clastic material during Devonian were located in the Fennoscandian Shield area. It is well-known that the drift of clastic material from Fennoscandia (erratic material by Gaigalas & Melešytė, 1993) took place several times also during Quaternary. The possibility of a long distance transport for such minerals as pyropes has been discussed earlier (Savvaitovs 1995). Possibly the kimberlite fields found in Finland (Mining Magazine, 1994), as well as some rocks of ultrabasite composition, which also spread on the Fennoscandia, served as the real sources of pyropes. However, the possibility of a short distance transport for some part of Latvian pyropes could not be excluded.

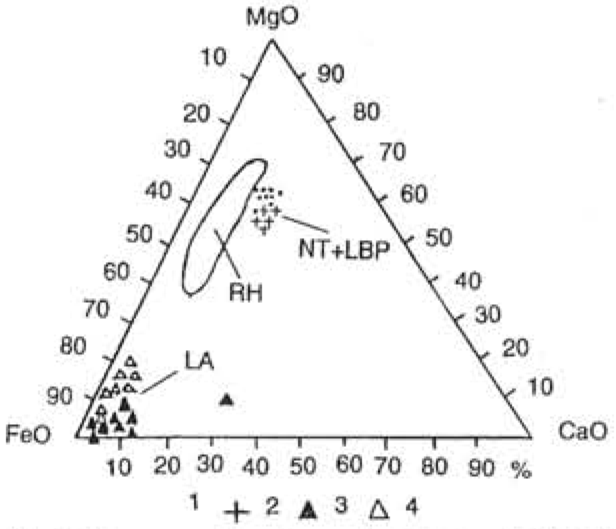

Fig. 3. The composition of garnets plotted on FeO-MgO-CaO diagram: 1 - pyropes from the Devonian deposits of Northern Timan (Ilupin et al. 1979), 2 - chrome-pyropes or pyropes from the Latvian beach placers (Liepene, Ķurmrags), 3 - dark-coloured (orange-brownish, red-violet) almandines, 4 - light-coloured (light-rose, rose-violet) almandines. Fields of pyropes and garnets: RH - from kimberlites of Kimberly district in Southern Africa (Ilupin et al. 1990), NT+LBP - from the Devonian deposits of the Northern Timan and the Latvian beach placers, LA - field of almandines from the Latvian beach placers

The different types of almandines can be useful for identification of separate source areas. Some positive results in this aspect were reached by Ozols (1991) for the tills of Kurzeme.

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BALTICA INFORMATION

NEW IGCP PROJECT: IMPACT AND EXTRATERRESTRIAL SPHERULES

In 1995, by Dr. Alex Bevan (Australia), Dr. Csaba H. Detre (Hungary), Dr. Billy B. Glass (USA), Dr. Katarina Jakabska (Slovakia), Prof. Ziyan Ouyang (China), Mrs. Eva Papp (Australia), Prof. Anto Raukas (Estonia) and Prof. Gheorghe Udubasa (Romania) proposed a new International Geological Correlation Programme (IGCP) project "Impact and Extraterrestrial Spherules: New Tools for Global Correlation" (short title: "Impact and Extraterrestrial Spherules"). The Scientific Board of the IGCP 24th Session (Paris, 29 January - 1 February 1996) accepted it for 5 years (1996-2000) as Project 384. The Inaugural Meeting of the project was held in Beijing, in the framework of the 30th International Geological Congress (4-14 August, 1996), convened by Prof. Z. Ouyang. Dr. Csaba H. Detre was appointed Chairman of the project and Prof. A. Raukas was elected head of the working group "Impact Craters and Spherules".

Fig. Distribution of impact craters and meteorite falls in the Baltic States. I - Craters: E1 - Kaali; E2 - Kärdla; E3 - Ilumetsa; E4 - Tsõõrikmäe; E5 - Neugrund; La1 - Dobele; L1 - Mizarai; L2 - Vepriai. II - Meteorite falls: 1 - Kaande (Oesel); 2 - Tännasilma; 3 - Pilistvere; - Kaiavere; 5 - Iigaste; 6 - Nerft; 7 - Buschoff; 8 - Lixna; 9 - Padavarninkai; 10 - Jodzie; 11 - Žemaitkiemis

The mentioned project will be extremely important for the Baltic Sea area, rich in impact craters of different age and size. Several tens of impact craters, ranging from Neoproterozoic to Holocene in age and from less than 100 m to more than 50 km in diameter are located both in the crystalline basement and in the sedimentary cover of the old East European Craton in the Fennoscandian–Baltic region. In the Baltic States alone at least 18 impact craters and a lot of meteorite falls have been registered (see Fig.). The biggest impact crater in the Baltic States is the Vepriai crater in Central Lithuania, which is 8 km in diameter and is situated in Palaeozoic rocks. The crater is filled with up-to-160 m thick Middle Jurassic Lower Callovian sediments, which indicate the age of the impact event. The crater is covered by 70-to-100 m thick Cretaceous rocks and Quaternary sediments.

The oldest palaeometeoritic matter known in the Baltic States so far has been recovered in the Viru-Roela borehole in the central part of Estonia where it is enclosed in the Lower Cambrian sandstone at depth of 320 metres. According to H. Viiding, every square metre in the area of meteor fall has received more than 5 kg of meteoritic matter, which encourages us to use this layer for correlation purposes. Around the Kaali craters on Saaremaa Island, West Estonia, the soil contains a lot of fragments of meteorite and pulverized meteoritic matter, established in small amounts in an area of several hundred square kilometres. Cosmic and impactite matter in lakes and bogs around the Kaali crater field allows to date the impact event very precisely and to find chronostratigraphical markers for geomorphological and stratigraphical studies.

During the history of the Earth the global occurrence of spherules seems to have altogether five abundance peaks: in the Late Devonian, on the Permian–Triassic boundary, most well known K/T boundary, in the Late Eocene and in the Quaternary.

It is obvious that the investigation of the spherules has to be carried out on a global scale, but it will give excellent results also in the regional correlations.

Anto Raukas

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