Baltica

ABOUT THIS YEARBOOK * BALTICA was founded in 1961 at the 6th INQUA Congress in Warsaw by the Lithuanian Academy of Sciences. Seven volumes of the BALTICA Yearbook have already been published during 1963-1982. After a 12 year break the renewed BALTICA, Vol. 8, 1994, was issued in March, 1995.

For more detailed information visit our websites on Lithuania Geosciences:

http://www.geologin.lt/baltica/	Marine geology
http://www.geologin.lt/litosfera/	Lithosphere
http://www.geol.vu.lt/geologija/	Geology
http://www.lgt.lt/	Geological survey
http://www.lgt.lt/geoin/	Geoenvironment, geoindicators

LEIDYKLA SPAUSTUVĖ Indra PUBLISHING & PRINTING HOUSE

ISSN 0067-3064

LIETUVOS MOKSLŲ AKADEMIJA
GEOLOGIJOS INSTITUTAS

Baltica

An International Yearbook on Geology, Geomorphology and Palaeogeography of the Baltic Sea

Volume 14

Special Issue

Paleoenvironment of the Baltic Sea

Vilnius 2001

BALTICA An International Yearbook on Geology, Geomorphology and Palaeogeography of the Baltic Sea

Issued annualy in cooperation with the geologists of the circum-Baltic States

SPONSORED by The Science Council of Lithuania.

EDITOR * Algimantas GRIGELIS, Vilnius, Lithuania.
CO-EDITOR* Boris WINTERHALTER, Espoo, Finland.

SCIENTIFIC PROGRAMME COMMITTEE * Ingemar CATO, Uppsala, Sweden; Emelyan EMELYANOV, Kaliningrad, Russia; Vytautas GUDELIS, Vilnius, Lithuania; Jan HARFF, Rostock-Warnemünde, Germany; Reinhard LAMPE, Greifswald, Germany; Wolfram LEMKE, Rostock-Warnemünde, Germany; Anto RAUKAS, Tallinn, Estonia; Rodney STEVENS, Göteborg, Sweden; Egidijus TRIMONIS, Vilnius, Lithuania; Szymon UŚCINOWICZ, Gdańsk, Poland; Henry VALLIUS, Espoo, Finland; Boris WINTERHALTER, Espoo, Finland.

INDEXING * BALTICA is currently included in the international abstracting and indexing services and databases: Bibliography and Index of Geology, GeoArchive, GeoRef, NISC CD-ROM, GeoSEARCH, Current Geographical Publications, Petroleum Abstracts, and Ulrich's International Periodicals Directory.

EDITORIAL ADDRESS * Prof. Dr.hab. Algimantas Grigelis, Lithuanian Academy of Sciences, 2600 VILNIUS, LITHUANIA * Phone +[370] 2 236504 * Fax +[370] 2 236408 * E-mail grigelis@geologin.lt * Publisher Lithuanian Institute of Geology, Ševčenkos Street 13, 2600 Vilnius, Lithuania.

ELECTRONIC ACCESS * BALTICA is available in electronic form since Volume 13, 2000, and the BALTICA's Announcement, Programme and Contents of Volumes 9-14 can be found on our website www.geologin.lt/baltica

SUBSCRIPTION PRICE * The 2001 subscription rate of volume 14 : USD 10.00; Baltic countries only: Lt 4.00, EEK 16.00, LAT 0.5. Communications regarding subscription should be sent to the Editor's office. Mail postage is not included.

This Yearbook can be ordered from the Lithuanian Institute of Geology, T.Ševčenkos Street 13, 2600 Vilnius, Lithuania.

BALTICA 14 REVIEWERS *

Dr. Elinor Andrén
Dr. Thomas Andrén
Dr. Ingemar Cato
Prof. Kay Christian Emeis
Prof. Emelyan Emelyanov
Prof. Algimantas Grigelis
Prof. Jan Harff
Prof. William W. Hay
Prof. Meilutė Kabailienė
Habil. dr. Grażyna Kowalewska
Dr. Tomas Leipe
Habil. dr. Wolfram Lemke
Prof. Olegas Pustelnikovas
Prof. Anto Raukas
Prof. Rodney Stevens
Prof. Egidijus Trimonis
Dr. Szymon Uścinowicz
Dr. Boris Winterhalter

ISSN 0067-3064

All rights reserved

© Geologijos institutas, 2001

FOREWORD

The idea to publish geological results from the BASYS Project in BALTICA was raised by the Editor of this publication in 1999 at the 3rd BASYS Scientific Conference in Rostock-Warnemünde. The participants of the BASYS subproject-7, "Paleoenvironment", backed the idea, and finally, we have a representative collection of geologically oriented papers emerging from the BASYS project.

The BALTICA Vol. 14 contains 16 papers. The first one - The Introduction - presents the goals of the project, the ways these goals were being addressed, and some of the results obtained. This paper is written by Boris Winterhalter, the Head of the Subproject and Co-editor of the present BALTICA Volume. Other papers are grouped in accordance with tradition: Geology, Stratigraphy, Mineralogy, Geochemistry, and Environment.

In the part on **Geology** B.Winterhalter presents results from acoustic mapping and detailed Holocene core investigations in the North Central Baltic Sea Basin and in the Gotland Deep. M.Repečka discusses the physical properties of bottom sediments in core samples taken from different basins of the Baltic Sea (Bornholm, Gotland, and North Central Baltic) and the stratigraphic correlation between the basins. For more comprehensive descriptions of the sediment cores from the Bornholm, Gotland and North Central Baltic Sea basins collected during cruises undertaken in 1996 and 1997 on board *R/V Petr Kottsov*, the reader is referred to the reports of the BASYS subproject-7 cruises (Harff and Winterhalter (eds.) 1996, 1997).

Stratigraphy issues are discussed in 5 papers. Two articles by W.Brenner and one by W.Hofmann deal with biostratigraphy. They showed the distribution of microfossils in the cores taken from the Gotland Deep, as well as the relationship of microfossil variations to changes in the paleoenvironment. W.Brenner was able to single out microfossil-based ecozones. This is a very interesting and valuable experiment, and conclusions drawn from it should be checked on a wider scale in other Baltic Sea basins. The paper presented by J.Harff, G.C.Bohling, R.Endler, J.C.Davis, H.Kunzendorf, R.A.Olea, W.Schwarzacher and M.Voss deals with physico-chemical stratigraphy of Holocene cores in the Gotland Deep. Sediment cores from within the same basin were compared on the basis of physico-chemical properties and chemical analyses. The computer generated correlation enabled to distinguish six clearly identifiable units in the post-glacial sequence. This study illustrates the advantages in applying this methodology in the differentiation of lithologically identical sections. In a classical approach *sensu stricto* a problem appears that such Holocene zones can also be detected in other Baltic Sea basins. A.Kotilainen, T.Kankainen, A.Ojala and B.Winterhalter acquaint with a highly detailed radiometric and paleomagnetic dating done for the cores taken from Northern Central Baltic Sea; this paper argues the geochronological data and determination of the calendar age of sediments.

Mineralogy issues are tackled by K.Alvi and B.Winterhalter in their paper on mineralization of the Holocene sediments in the Gotland Deep and influence of anoxic conditions on formation of authigenic minerals. M.Mälkki studied recent northern Baltic Sea minerals in suspension (sediment traps) and bottom sediments, their seasonal variations and origin. A detailed investigation using SEM and x-ray methods illustrates recent processes of sediment formation.

The Geochemistry part contains highly detailed results from newest studies. H.P.Nytoft and B.Larsen studied triterpenoids as markers of depositional conditions and determined their distribution in the cores from the Baltic Sea deep basins under oxic and anoxic conditions. H.Vallius and M.Leivuori discuss the chemistry and heavy metal content of surface sediments under conditions of rather undisturbed sedimentation in the North Central Baltic Basin.

Paleoenvironment issues and environmental changes in the Baltic Sea are analyzed in three papers. T.Andrén and E.Andrén raise a question for discussion on how the Second Storegga slide on the western coast of Norway, that occurred ca. 8000 years ago, may have affected the Baltic Sea. H.Kunzendorf, M.Voss, W.Brenner, T.Andrén and H.Vallius determined that variations of molybdenum in the sediments of the Central Baltic Sea could be related to intense algal blooms. M.Voss, G.Kowalewska and W.Brenner used data on tetrapyroles, microfossils and biochemical properties as indicators of environmental changes in the Gotland Deep during the last 10,000 years.

The Index at the end of this issue of BALTICA, Vol. 14 contains a bibliography of publications related to the BASYS subproject-7 "Paleonvironment".

*****

Let the Reader decide about the results of the present publication. The Editor hopes that the reader interested in the Baltic Sea and its history would accept the present publication in a positive manner. This naturally also pertains to those who wish to better understand the present state of the Baltic Sea and its future, in particular.

In conclusion, I would like to express my sincere gratitude to all authors, who presented their papers after a tiring procedure of critical reviewing, to the reviewers and to BALTICA Scientific Committee Members, who applied a highly critical approach to the manuscripts, as well as to Dr. Boris Winterhalter for his numerous consultations as Co-editor and financial support as BASYS subproject-7 leader enabling to issue this Yearbook with color illustrations. I am thankful to my colleagues and personnel of the Baltic Marine Geology Department of the Institute of Geology of Lithuania for all their kind assistance in preparing this issue for publication.

The Lithuanian Science Council supports BALTICA.

BALTICA, in its new form since 1993, has already paved its way to its readers. The Yearbook is already well known and widely quoted; prominent researchers of the Baltic Sea are eagerly presenting their research results. It is especially gratifying that among the contributors the number of young authors is increasing. The BALTICA Scientific Committee would like to co-operate further, improve the scientific contents, quality and appearance, and find better ways for its distribution in order that the Yearbook could reach more and more readers.

Algimantas Grigelis

Vilnius, 1 December 2001.

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 5-8

The BASYS Project and the paleoenvironment of the Baltic Sea

Boris Winterhalter

The present issue of BALTICA, volume 14, is a special issue commemorating the BASYS Project, conceived to promote a better understanding of the Baltic Sea, its past and present environment, as interpreted from the study of sediments.

☐ *Paleoenvironment, Baltic Sea System Study, BASYS, Baltic Sea.*

☐ *Boris Winterhalter [boris.winterhalter@gsf.fi], Geological Survey of Finland, P.O. BOX 96, FIN–02151 Espoo, Finland.*

INTRODUCTION

Under the auspices of HELCOM (Baltic Marine Environment Protection Commission) and ICES (International Council for the Exploration of the Sea) considerable work has been done on the development of monitoring techniques for the Baltic Sea. Various international calibration cruises with multiple ships participating have been conducted. Such projects were targeted towards a better understanding of the present state of the Baltic Sea. Our understanding of the physical, chemical and biological factors influencing the Baltic Sea environment has improved and international co-operation in the implementation of protective measures is already visible in the improved quality of Baltic Sea waters. However, with increasing knowledge, three important aspects crucial to a better understanding of the Baltic Sea environment, have emerged.

Firstly, the widespread and generally accepted assumption that sedimentation in deep basins is a continuous process and laterally uniform (no hiatuses and no re-deposition) is obviously grossly erroneous. Furthermore, the internationally frequented sampling stations have been chosen more-or-less by chance and thus their representability is questionable.

Secondly, the stratigraphic time span covered by the sediment samples used in environmental monitoring programs, seldom provides real background data, i.e. the samples do not stretch sufficiently back in time. This leads easily to hasty and erroneous conclusions as to the state of the sea area and especially as to measures to be taken for further amelioration. It is imperative that parallel with the study of recent and sub-recent sediments included in most monitoring programs, also older sediments should be studied. This is to better understand the effects of climate change and the interrelationship between natural and anthropogenic influence on the marine environment and how these changes are manifested in the sedimentary record.

Thirdly, the study of diagenetic processes in the sediments has often been neglected by scientists concerned with environmental monitoring in the Baltic Sea. A further source for dubious conclusions on the state of the environment can be referred to the recommendations of ICES to conduct bulk chemical analyses on sea bottom sediments. The argument being that comparative studies from different parts of the Baltic Sea can be conducted only on bulk (total) chemical analyses, because the use of weak solvents, typically expressing bio-availability, has been difficult to standardise.

Despite the short comings of present day monitoring practices, as mentioned above, our knowledge of various details of the environmental state of the Baltic Sea is good. However, to better understand how the Baltic Sea functions as a system, it was felt that there is a definite need to collect and analyse new data. These issues were discussed during several workshops in the early 1990'ies. On the basis of a preliminary study, the Gotland Basin Experiment (GOBEX), a multi-disciplinary 3-year project, the Baltic Sea Systems Study (BASYS), was conceived. The multimillion BASYS project was approved by the EU and the project got officially underway on 1st of August1996. It spaned 3 years with over 50 participating institutions and involving hundreds of scientists from various disciplines ranging from atmospheric sciences through oceanography, biology to geology and the paleoenvironment. The open issues mentioned above, constituted the guidelines in outlining the tasks for the BASYS subproject-7, the study of the paleoenvironment of the Baltic Sea.

PROJECT PLANNING

Once the main objectives of BASYS were set, the participants in subproject-7 agreed that the most fruitful input to BASYS would be an improvement in the understanding of the differences between human and natural influence on the Baltic Sea environment. This was considered to be of utmost importance when assessing the anthropogenic influence on the present state of the Baltic Sea and in the evaluation of remedial measures on the future development and state of the marine area. The set goals were addressed by comparing historically recorded recent and sub-recent events with environmentally induced measurable variations in texture and composition registered in the sediments.

Considering the scope of the task, the time constraints, and the limited institutional resources (qualified personnel) available it was decided to tackle three separate sedimentary basins with high accuracy and redundancy in contrast to taking a large number of samples from various parts of the Baltic Sea. The basins, Bornholm Basin (BB), Gotland Basin (GB), and the North Central Baltic Sea Basin (NCB), are known to be temporarily anoxic, thus providing minimum bioturbation of the sediments and good stratigraphic resolution (Fig. 1). Furthermore, these basins were assumed to exhibit a more-or-less continuous deposition throughout the Holocene. To achieve the overall project objective and to acquire information required by other BASYS sub-projects on the background levels through time and burial rates of environmentally detrimental substances, the project was divided into three separate phases:

The first phase *was to establish, in each of the three basins, representative sampling sites, with the best possible continuity and lateral homogeneity of sediment deposition. The decisions on the best sampling sites were based on previously gathered information stored in the archives of the participating institutions and on detailed acoustic maping and coring during the project itself.*

The second phase *consisted of establishing a detailed and accurate time scale for the acquired sediment cores with emphasis on the anthropogenically influenced last few thousand years and in greater detail for the last historically documented 500 years. The cores were sub-sampled at very close intervals, both for dating and for microfossil, chemical and physical analysis, to establish the stratigraphic timescale. The dating was based on radionuclides (Cesium-137, radiocarbon, etc.), on paleomagnetic measurements and stratigraphic markers.*

The third and final phase *involved the determination of physical, chemical and biological parameters that reflect environmental or ecological conditions prevailing at the time of deposition, from 8000 years back in time to the present day. This also included the study of diagenetic processes in the sedimentary column.*

OUTCOME

Detailed site surveys using standard echo-sounding, multibeam sounding, side scan sonar imaging, and ultra-high-resolution deeptow acoustic soundings were made in the three chosen basins during several research cruises both on *R/V Petr Kottsov* (Harff and Winterhalter, 1996 and 1997), time-chartered by the Baltic Sea Research Institute in Warnemünde (IOW), and *R/V Aranda*, operated by the Finnish Institute of Marine Research. Based on the survey data, several long cores (piston, gravity and vibro-hammer) and also a number of short sediment cores were taken for laboratory studies.

Of the three basins chosen for the BASYS paleoenvironment study, the Bornholm and Gotland basins have been, through the years, surveyed by a large number of various expeditions. Despite abundant information additional detailed acoustic surveys (including subbottom profiling, side scan sonar imaging and deeptow high-resolution echo-sounding) were conducted to actually establish the representability of the chosen coring sites. Because no previous information was available for the northernmost basin (NCB), the first major task was to survey a sufficiently large area to get a firm idea of the morphology and bathymetry and the pattern of sediment distribution. This was then followed by a more detailed study using the same methods as for the other two basins. The results of these surveys are presented elsewhere in this volume.

The main sediment coring during the several research cruises on board *R/V Petr Kottsov* and *R/V Aranda* were all oriented towards the acquisition of representative cores and sufficient material to be disseminated to all participating researchers. Therefore, the Kastenlot (giant box corer: 12 m * 30 cm * 30 cm) was chosen as the main sampler providing adequate material for all planned activities. Additional gravity, piston and vibro-hammer cores, taken from the same sites, were used to complement the material subsampled from the Kastenlot cores. Since all of the heavy corers had a tendency to disturb the uppermost decimeters of the sediment, a number of short cores were taken with either the original Niemistö corer (Finnish Institute of Marine Research, Helsinki) or its improvements, the Gemini or Gemax (Geological Survey of Finland, Espoo) twin-barrelled corers, or the Multicorer (Baltic Sea Research Institute, Warnemünde).

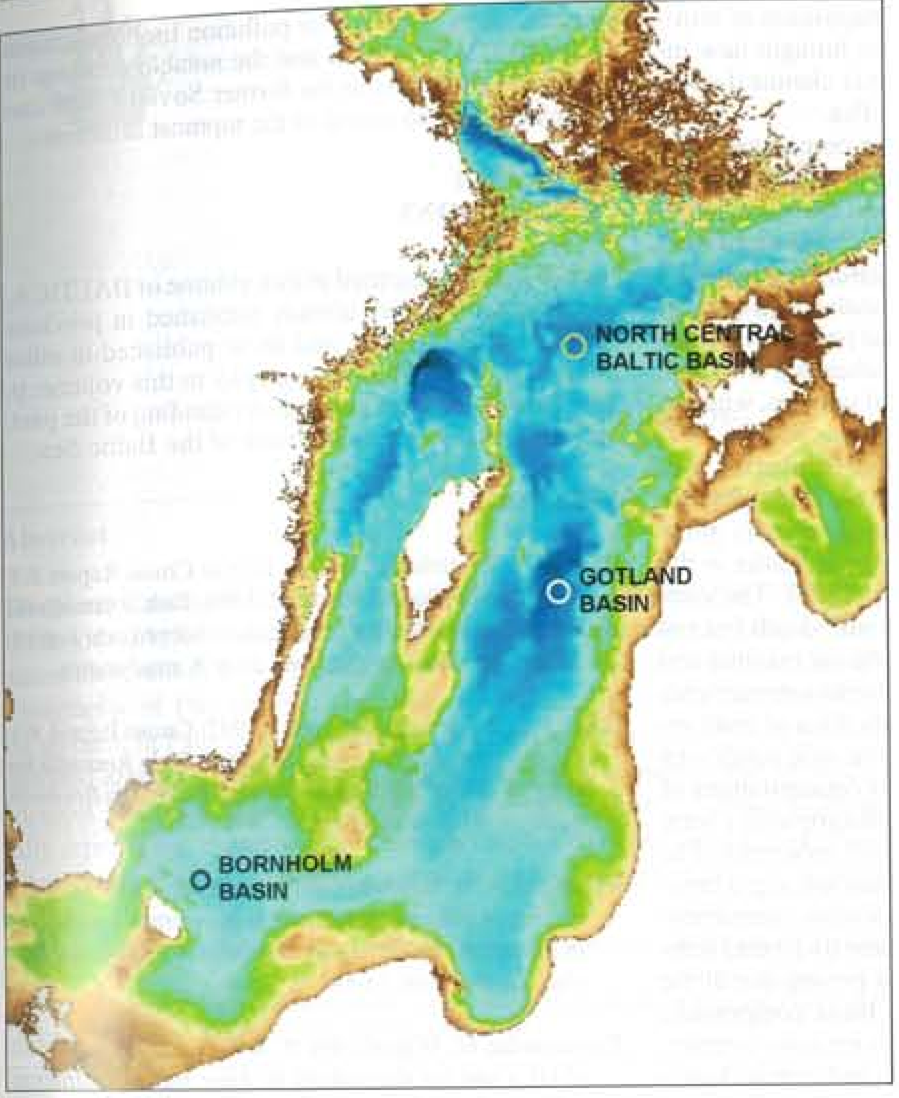

Fig. 1. The location of the three sampling sites used in the BASYS subproject-7, the paleoenvironment of the Baltic Sea. The map is based on bathymetric data from Seifert and Kayser, 1995.

The dating of the sediments was based on radiometric measurements of ^{137}Cs, ^{210}Pb, ^{14}C, and on detailed paleomagnetic analyses. The uppermost 100 years of sediment accumulation were dated from the short cores by direct gamma-ray spectrometry of ^{210}Pb. ^{137}Cs was also determined and especially the Chernobyl accident of 1986 was used for modelling verifications (Kunzendorf, 1999). The dating of the long cores was based on the measurement of oriented subsamples and the comparison of the variations observed in magnetic orientation (declination and inclination) and magnetic intensity and susceptibility with accurately dated "Master Curves" (Kotilainen et al. 2000). The ^{14}C dates of bulk samples and especially of the many macrofossils picked from various levels of the cores and analysed by accelerometer mass-spectrometry (AMS), were used to verify the interpretation of the paleomagnetic data.

Microfossil analyses were used by W.Brenner, E. Andrén and others to correlate the timescale to known and inferred variations in the Baltic Sea environment. Various microfossils are known to be quite abundant in some layers and even "survive" harsh laboratory processing techniques. Especially the laminated sediments were studied for diatoms, cysts, exoskeletons of zooplankton and organic walled microfossils. The aim was to define in the cores from the three basins proxies that could be used to identify and correlate specific sediment characteristics with changes in the environment. Detailed analysis of the distribution of diatoms and cysts were also used to establish the biostratigraphy of the cores. Structural and chemical analysis of bivalve shells, especially from the Bornholm Basin were used for additional information on the variations in salinity and temperature through time.

The study of the sediment cores included visual descriptions, photography, digital image scanning and x-ray imagery of the entire lengths of the cores followed by extensive physical, chemical and mineralogical measurements of sub-samples. The physical measurements included grain-size analysis and measurements of water content, bulk density, porosity. The mineralogical studies were based on x-ray diffraction measurements, mineral microscopy, micro-probe and EDX-coupled SEM analyses of carefully chosen subsamples.

Next, a wide range of various analytical chemical methods were employed in the detailed study of the sediment samples. Analysis of main and trace elements using ICP, AAS and EDX analytical methods on bulk samples provided information on the variations in the chemical composition of the cores with depth. The most striking feature was the excellent correlation of manganese and calcium and their relation to the laminated sediments. The method of subsequent leaching with different solvent mixtures was used to establish the mobility and availability of elements in various diagenetic processes especially for the top few decimeters of sediment. Studies of isotopic composition of nitrogen, oxygen and carbon by M.Voss brought new insight into the provenance of various chemical compounds and on environmental specifics.

Rock-Eval screening of organic compounds was used by H.P.Nytoft to study the provenance and degree of reworking of organic matter. Determination of the origin of organic matter and the evaluation of former redox conditions were based on gas-chromatography (GC) and GC-mass-spectrometry analyses of extractable lipids. The concentrations of the pentacyclic compounds, indicative of bacteria, cyanobacteria and some primitive plants were abundant in all samples, whereas the content of steroid hydrocarbons was low.

The analysis of tetrapyrroles (chlorins i.e. chlorophylls a, b and their derivatives, chlorophylls c and metalloporphyrins) provided supplementary information on the origin and fate of organic matter in the sediments (e.g. Kowalewska et al. 1998). The concentrations of tetrapyrroles varied with depth but not uniformly, there were sharp and irregular maxima and minima in the profile. Poorest in chlorins were samples from the Bornholm Basin being indicative of more intense mixing in this region and more oxic conditions than in the northern regions. Higher concentrations of chlorins and also slight amounts of chlorophylls c were observed in the North Central Basin sediments. The sediments from the Gotland Deep core had, e.g. a thousand years ago, concentrations of chlorins comparable or even higher than those in the recent (0-10 cm) sediments of the Gdańsk Deep, being at present one of the areas of the Baltic Sea richest in these compounds. High concentrations are attributed to intensive primary production, high accumulation rates and anoxia. Variations in relative concentrations of various chlorophyll derivatives are related to variations in phytoplankton species reflecting environmental changes, especially changes in salinity.

The only changes in the chemistry of the sediments, attributable to human impact, occurred at the onset of industrialisation. Increasing amounts of organic and inorganic compounds were discharged into the sea area. E.g. the increase in heavy metals started slowly during the first half of the 20th century, but accelerated very fast after World War II. This led to heavy metal concentrations in the sediments two or several times higher than the natural values. The pollution limiting actions of the 1980's and 1990's and the notable decrease in industrial production in the former Soviet Union can fortunately also be traced in the topmost sediments.

CONCLUSIONS

The papers presented in this volume of BALTICA, together with studies already published in previous volumes of BALTICA, and those published in other journals (see BASYS bibliography in this volume, p. 141-143) all lead to a better understanding of the past, present and future development of the Baltic Sea.

References

Harff, J. & Winterhalter, B. (eds.) 1996: Cruise Report *R/V Petr Kottsov*, Sept. 2 - Sept. 12, 1996, Task: Research for BASYS-Baltic Sea System Studies - Subprojects 7 and 4. *Baltic Sea Research Institute.* 16 p. 6 attachments.

Harff, J. & Winterhalter, B. (eds.). 1997: Cruise Report *R/V Petr Kottsov*, July 22 - Aug. 01, 1997, Task: Research for BASYS-Baltic Sea System Studies. *Baltic Sea Research Institute*. 41 p. 6 attachments.

Kotilainen, A.T., Saarinen, T. & Winterhalter, B., 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166*, 51-64.

Kowalewska, G., Winterhalter, B. & Konat, J. 1998: Chlorophyll a and its derivatives in deep Baltic sediments. *Oceanologia 40 (1)*, 65-69.

Kunzendorf, H. 1999: Dating and assessing the Recent sediments of three deep basins of the Baltic Sea: Indication of natural and anthropogenic changes. *Risø-R-1077(EN), Roskilde*. 97 p.

Seifert, T. and Kayser B. 1995: A high resolution spherical grid topography of the Baltic Sea. *Meereswissenschaftliche Berichte / Marine Science Reports, Institut für Ostseeforschung Warnemünde.*

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 9-17

The BASYS coring site in the North Central Baltic Sea Basin - a geological description

Boris Winterhalter

Abstract

The North Central Baltic Sea Basin (NCB) area was surveyed in 1996 and 1997 with *R/V Petr Kottsov,* and in 1998 with *R/V Aranda*. The BASYS coring site, chosen on the basis of the conducted surveys, is located on a minor elevation (175 m) in a basin with depths in excess of 200 metres. The area is sheltered by an irregular topography of Precambrian crystalline bedrock in the north and bordered along the three other sides by an escarpment in Paleozoic sedimentary rocks rising in places to almost 100 metres below sea surface. The central elevated area was chosen as the main coring site to minimize the influence of lateral sediment transport from adjacent shallower areas. According to acoustic profiles the entire Holocene sediment sequence seems to be fully represented at and around the main site. Anoxic conditions have prevailed for extended periods during the Litorina Sea stage in the deeper parts of the basin, but only for much shorter durations on the elevated part of the basin.

☐ *Central Baltic Sea, NCB coring site, BASYS, Holocene sediments, stratigraphy, anoxia, acoustic profiling.*

☐ *Boris Winterhalter [boris.winterhalter@gsf.fi], Geological Survey of Finland, P.O.Box 96, 02151 Espoo, Finland.*

☐ *Received 1 June 2001; accepted 15 November 2001.*

INTRODUCTION

In the initial stages of the BASYS project planning it was deemed necessary to find, in addition to the rather intensely studied Bornholm and Gotland Basins, a suitable coring site in the northern part of the Baltic Sea. Very little was known beforehand on the sediment distribution north of the submarine Paleozoic Clint (escarpment) running from just north of Hiiumaa, Estonia, southwest towards the shoals north of the island of Gotland, Sweden. Therefore, an extensive acoustic survey was conducted during the first BASYS cruise on board the *R/V Petr Kottsov* (Harff and Winterhalter, 1996). On the basis of this survey and complemented by later acoustic surveys, the final coring site (North Central Baltic - NCB) was located on a minor elevation (depth 175 m), surrounded on three sides by a large and significantly deeper (in excess of 200 m) "embayment" in the clint. The top of the clint lies at a depth of about 100 m. The bottom topography north of the chosen site is characterised by an undulating cover of thick Holocene sediments with somewhat decreasing water depths further north.

The chosen site did not exhibit the thickest late Holocene sediments, but was felt to represent an area where the sedimenting material is primarily derived from authigenic and very fine-grained suspended matter and primary production of organic matter. Mass flow, possibly occurring along the surrounding slopes, would hardly influence the sediments being deposited at the sampling site.

The over ten long sediment cores and an equal number of short cores from the main coring site and along a transect across the deep and partly up the western slope provided the material used by many BASYS partners for analysis on both microfossils, mineralogy, chemistry and physical parameters. Some results have been previously published (see BASYS bibliography in this volume, p. 141-143).

BATHYMETRY AND GEOLOGICAL SETTING

The initial survey by *R/V Petr Kottsov* in 1996 covered an area of approximately 20 by 17 nautical miles. The digitised depth readings, corrected to the average speed of sound derived from CTD casts, were saved to file together with GPS positioning data (WGS-84). The next year multibeam echosoundings were conducted in the central area and the new data were added to the previous data. Further depth data were acquired during the cruise of *R/V Aranda* in 1998. The entire data set was then used with Golden Software, inc. SURFER software to produce the bathymetric map in Fig. 1.

The area around the NCB coring site is controlled by varied bedrock geology (Fig. 2). The crystalline Precambrian basement forming the bedrock of the northern Baltic Sea slopes gently towards the SSE to vanish below the thick Paleozoic and Mesozoic sedimentary rocks of the East-European Platform also forming the bedrock of the south-eastern Baltic Sea (Winterhalter et al. 1981). The crystalline basement is generally characterized by an irregular topography formed by glacial scouring especially along fracture zones (*op. cit.*). The sedimentary rocks on the other hand generally exhibit a rather gentle topography except for the erosional escarpments occurring in places where either fluvial, wave or glacial erosion has been especially active.

The NCB area is located at the northern limit of the sedimentary rocks covering the southern and southeastern Baltic Sea (Fig. 2). Parts of a well defined escarpment (clint), forming the shallower areas and clearly separated from the deeper parts by steep slopes, can be seen in the south and southwest of the NCB site in the map in Fig. 1. A beautiful example of the submarine clint system is the north-south trending shallow area with steep slopes around, in the lower right part of the map. The development of the clint was possible due to the fact that the rather poorly consolidated Cambrian sediments are overlain by more resistant Ordovician limestone (Fig. 2).

The final moulding of the topography of the area into its present form was the result of several separate processes. The multiple glaciations were responsible for the initial sculpturing of the bedrock, which happened mainly along fracture zones in the crystalline bedrock. The overlying Cambrian sandstones and siltstones were readily eroded while the Ordovician limestones were more resistant and formed a partial protection against further erosion. The deep channel between the NCB site and the clint west of it is a typical example of glacial erosion as can be seen in Fig. 3. At least the last major glacial advance came from the north as can be seen in the elongated north to south trending bottom forms.

The irregular topography, left as a result of glacial scouring and deposition of glacial drift, was thereafter covered by fine-grained sediments, ranging from silt and clay to gyttja clay, obliterating some of the glacial forms. The large amounts of sediment being deposited in front of the retreating ice margin after the last major glaciation (Weichselian) initially settled in waters 100-150 metres deeper than today. The bedrock and glacial drift was conformably draped under a rather uniform blanket of silt and clay. With isostatic uplift following deglaciation, the shallower areas were eventually exposed to both wave and current induced erosion. The suspended fine-grained sediment was redeposited in the deeper areas, while the coarser material was left as a lag deposit consisting of silt, sand, gravel or even boulders.

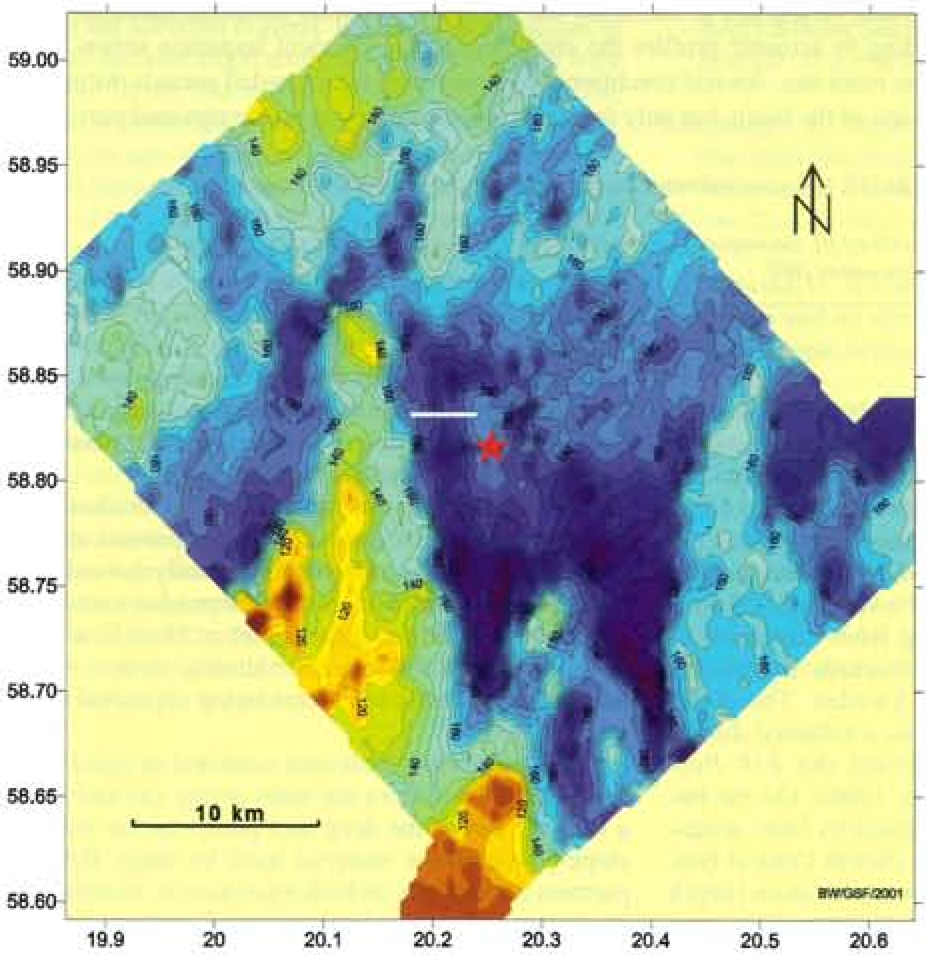

Fig. 1. Bathymetry of the NCB coring site (red star) and the surroundings. The map is based on data collected by *R/V Petr Kottsov* in 1996 and 1997 and by *R/V Aranda* in 1998. The depths have all been corrected using average speed of sound acquired from CTD data. Note that geographic co-ordinates (latitude and longitude) in all figures are given as decimal degree values.

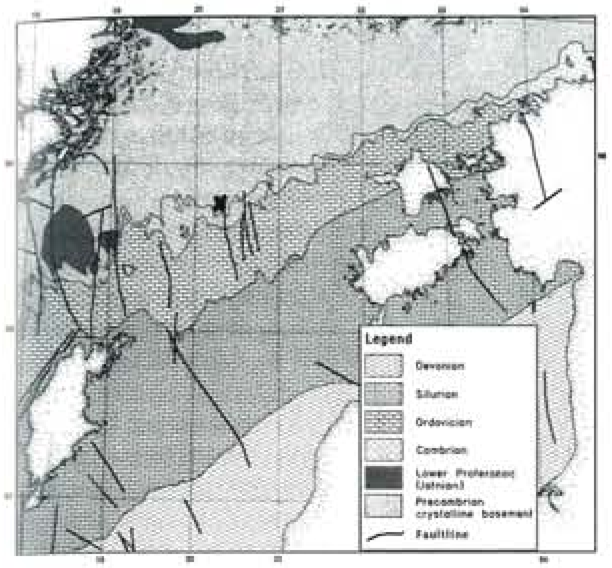

Fig. 2. General bedrock distribution in the central Baltic Sea. The map has been modified from Winterhalter et al. 1981. The fault lines are based on Grigelis 1998. The black "*X*" denotes the location of the NCB coring site.

The onset of the Litorina Sea stage, about 8000 years ago, brought about an increase in the salinity and primary production. This changed the character of the sediment from cohesive, smeary, clay into muddy sediment. High water content and lack of strong cohesion between sediment particles allowed these gyttja clays (muds) to be easily shifted around by even rather weak bottom currents. Thus, the change from a conformable sediment deposition to a type frequently termed "basin fill" prevails in present day depressions in the Baltic Sea (Winterhalter 1992). Due to the activity of bottom currents, differential sedimentation occurs on slopes. Depending on the direction of the prevailing current the Coriolis effect will enhance erosion or deposition. A slope to the right of the current will be eroded while accumulation of sediment will take place to the left of the current and on leeward slopes. The present bathymetry of the study area and surroundings is thus a combined result of differences in bedrock character, differential erosion and sediment deposition.

ACOUSTIC METHODS

To get a better idea of the distribution of the Holocene sediment sequence in and around the NCB coring site an additional survey was conducted in 1998 by the *R/V Aranda*. In addition to the standard DESO 25 echo

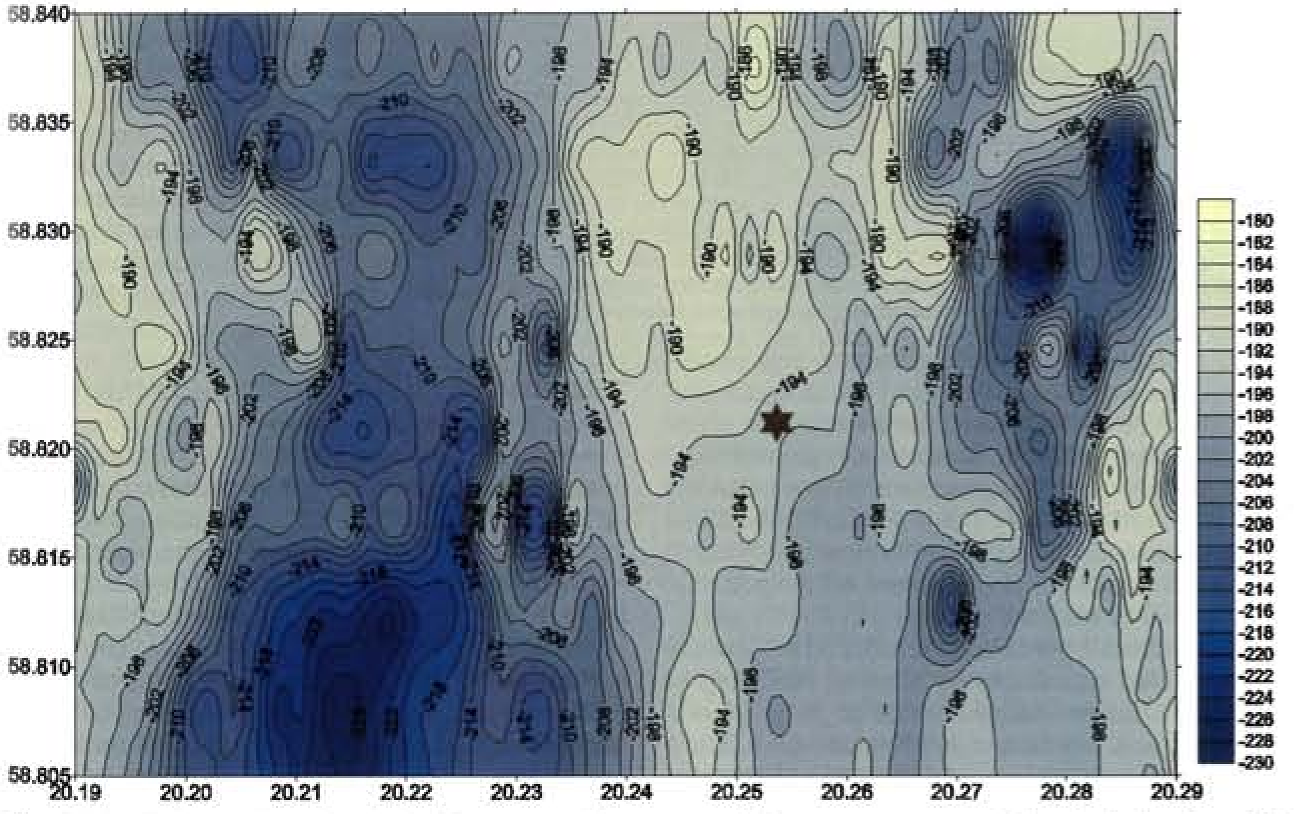

Fig. 3. Detailed map shows the depth below sea surface to acoustic basement represented either by bedrock or drift. (Holocene sediment cover is removed). The elevated area forming the western flank is part of the Ordovician Clint, while the N–S running deep is the result of erosion of the Cambrian sediments. The map covers an area 5.64 * 3.89 km.

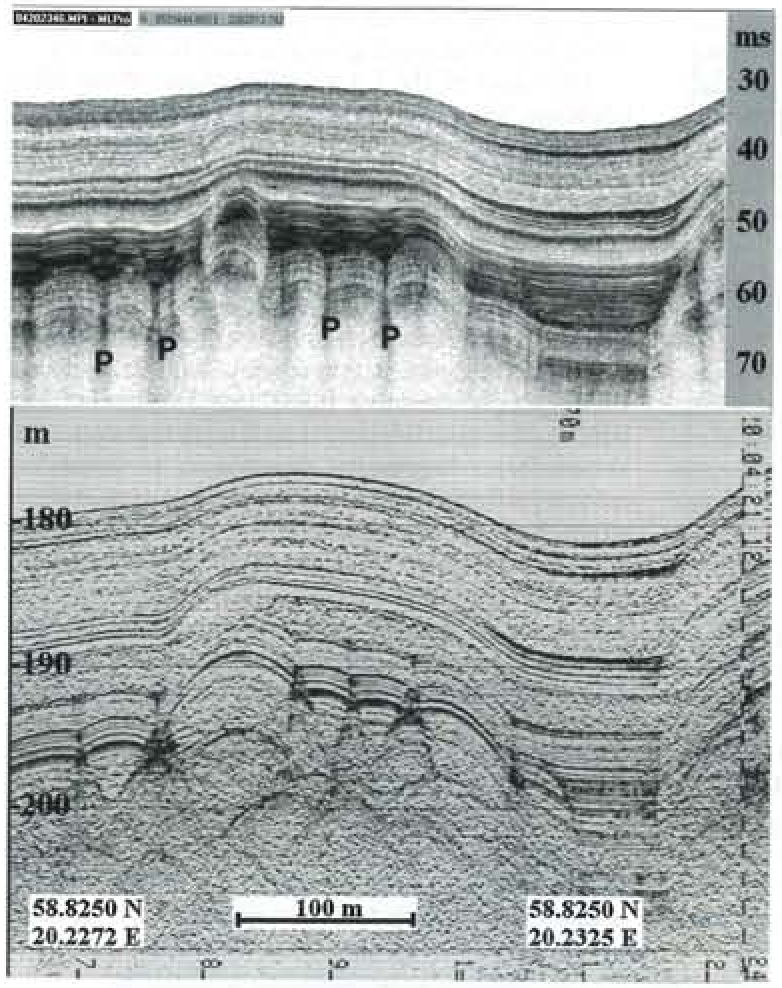

Fig. 4. A comparison between a Meridata UASP deeptow 28 kHz acoustic profile (upper) and a Krupp Atlas DESO 25 12 kHz echogram (lower). The white line in Fig. 6 gives the location of the profiles. Because the ship mounted transducer and the deeptow did not cover exactly the same ground the profiles are similar, but not fully identical. Note also that the hyperbolic reflections from abrupt structure seen in the lower DESO profile are lacking in the upper, deeptow, profile. In addition to the better general resolution of the deeptow data, especially vertical slumps, de-watering and de-gassing structures (P = pockmark) are so much clearer. Note that the vertical scale is in milliseconds (TWT) for the deeptow and in metres for the DESO echogram assuming a sound velocity of 1435 m/s.

sounder working with 12 kHz, a deeptow high-resolution profiler was used in the study. The deeptow unit consisted of a 28 kHz transducer mounted on a tow body, tow depth adjusted via a remotely operated cable winch, and a shipboard data acquisition system (UASP) produced by Meridata Oy, Lohja, Finland. Most of the survey was conducted with the deeptow unit "flown" between 20 and 30 m above seabed off the port side and 200-300 m aft of the ship.

The 12 kHz DESO 25 echo-sounder on *R/V Aranda* has been used extensively for acoustic surveying of Holocene sediment basins because of its very good resolution and penetration in clays and silts (Fig 4 lower), especially when used with a very short pulse length (0.167 ms). However, in deeper water even the rather narrow beam angle of the special 12 kHz transducer is not capable of resolving internal structures in the sediment. To get a better idea of these internal features the deeptow UASP system was used. The digital images (Fig 4 upper) do give distinctly better resolution than the DESO. In addition to the better resolution provide by the deeptow, especially the lack of hyperbolic reflections from abrupt structures makes the deeptow data much more informative than those recorded with the hull mounted transducer. Especially vertical slumps, de-watering and de-gassing structures (P = pockmark) are so much clearer.

The DESO 25 echograms were interpreted and digitised together with differential GPS data. The depths were based on a sound velocity of 1435 m/s. However, considering that a mean sound velocity of 1445 m/s in water was measured during the *R/V Kottsov* cruise in September 1996, it is possible that the actual depths are slightly greater than those used in the map production. The error is anyhow no more than 1-2%. A significantly greater correction is probably necessary in determining the actual thickness of the various sediment units. Endler (1998) had registered in Baltic Sea Holocene sediment cores velocities that were lower than in water (1440-1390 m/s and decreasing downwards). On the other hand sonobuoy data (e.g. Bergman et al. 1982) has generally given a steady increase in velocities from the seabed and down the stratigraphic column. Because of this ambiguity the isopachyte maps and the vertical scale in the profile figures are given either in milliseconds[1] or converted to metres using the sound velocity for water (1435 m/s), because no other validated values have been available.

THE HOLOCENE SEDIMENT COVER

The bedrock in the area is covered, with a few exceptions (bedrock exposures), by unconsolidated sediments up to several tens of metres in thickness. The end of the Late-Weichselian glaciation saw the beginning of a chain of events in the development towards the Baltic Sea we see today. These events are well recorded in the sediments of sheltered deep basins. The conditions prevailing during the various stages have left their mark in the character of the sediment, i.e. in the physical and chemical properties and also in the microflora (see e.g. core descriptions in some of the papers in the present volume, Baltica 14).

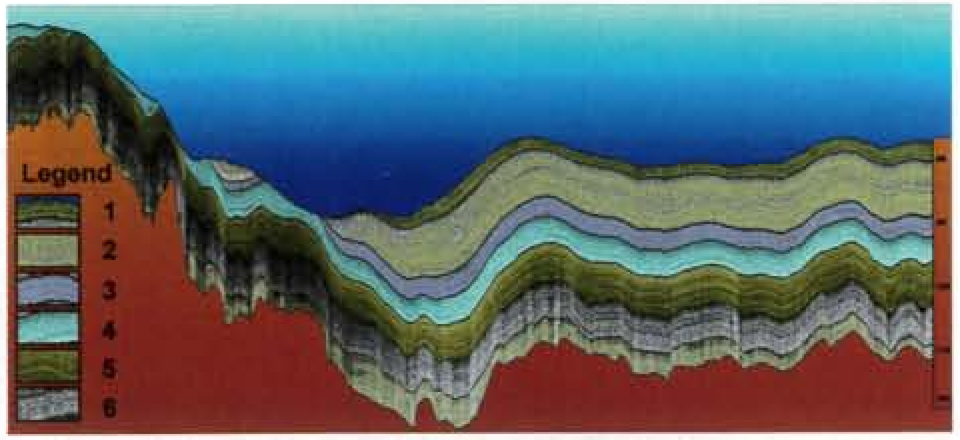

Fig. 5a. A UASP deeptow acoustic profile showing different sedimentary units identified on the basis of their acoustic characteristics. The visible reflectors represent a change in the acoustic impedance (product of sound velocity and density) of the sediment. Especially in the deep basins of the northern Baltic Sea these can often be correlated with stratigraphic data from sediment cores. In the legend: 1. Recent and sub-recent mud; 2. Litorina Sea gyttja clay; 3, Ancylus Lake clay; 4. Yoldia Sea clay; 5. Baltic Ice Lake annually varved glacial clay; 6. Baltic Ice Lake layered or varved glacial silty clay. Vertical scale is in milliseconds. The white line in Fig. 1 shows the location of the profile.

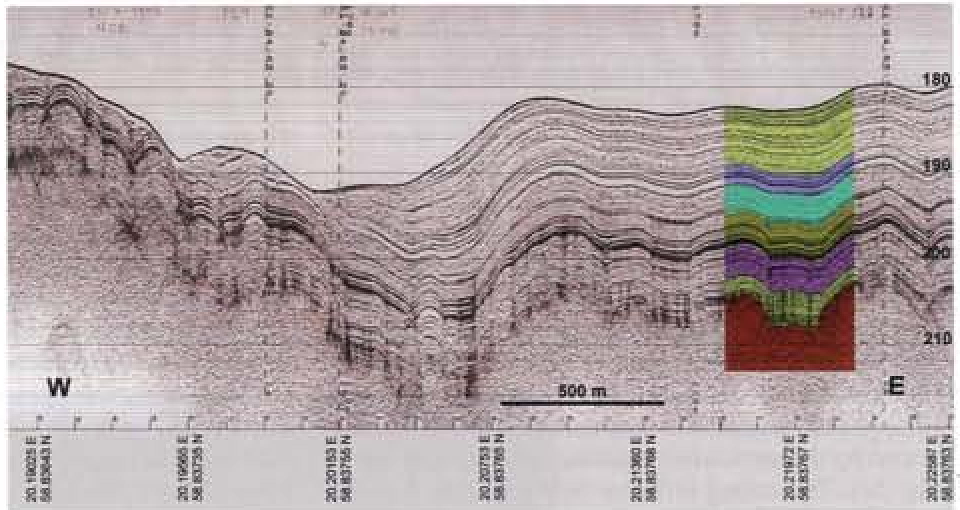

Fig. 5b. A DESO 25 echogram recorded at the same time with the deeptow profile in Fig. 5a. The colour coding is the same as in Fig. 5a. The vertical scale is the depth in metres using the sound velocity of 1435 m/s. The horizontal scale line pertains also to the UASP profile. The co-ordinates (longitude and latitude) are in decimal degrees.

In the course of deglaciation the retreating ice left behind an irregular surface of drift of various composition, including both boulder clay (till), sand and silt. Melt waters from the ice deposited sediment in front of the ice margin. With the retreating ice margin consecutively finer grained sediments were deposited, initially as annually varved glacial silts and clays of the Baltic Ice Lake stage (Ignatius 1958). These were later followed by rather homogeneous clays of both Yoldia Sea and Ancylus Lake stages. The last major stage in the development of the Baltic Sea, the brackish Litorina Sea, produced organic rich sediments that quite often exhibit a basin fill type of a deposition (Winterhalter 1992). The variations in the physical properties of the sediments deposited during the different stages are often sufficient to show up on acoustic profiles. Thus it is often possible to identify various sedimentary units on the basis of their acoustic characteristics (see Fig. 5a and 5b). Especially in the deep basins of the northern Baltic Sea these can often be correlated with stratigraphic data from sediment cores. Because the character of the recorded acoustic echo is related to the physical characteristics of the sediment, the identified boundaries do not necessarily coincide exactly with biostratigraphic boundaries.

Glacial deposits

The lowermost, clearly discernible, sediment unit in the acoustic profiles varies considerably in thickness (greyish bed under unit 6 in Fig. 5a). Based on its acoustic character it probably consists of conformably deposited silt beds displaying a layered or even coarsely varved character. Especially in the deepest parts of the area these semi-conformable bed are often underlain by irregular deposits, up to 15 m thick. These were obviously formed by massive discharges of sediment-laden melt water (mud flow or turbidity current). The gravity flows obviously deposited their sediment load in the deeps while only traces of such material can be seen in elevated areas.

The map in Fig. 6 shows the irregular distribution of the glacial sediments deposited in the immediate vicinity of the retreating ice margin. This becomes quite obvious when comparing the thickness of these early glacial sediments to e.g. the overlying Baltic Ice Lake sediments (units 6 and 5 in Fig. 5a) that exhibit a rather striking uniformity in thickness across the entire area, only excluding those places that have been exposed to erosion during later times.

---

[1] The millisecond values are two-way-travel times (TWT) which means that the actual value in metres comes from multiplying the ms value with the sound velocity for the medium and divided by 2.

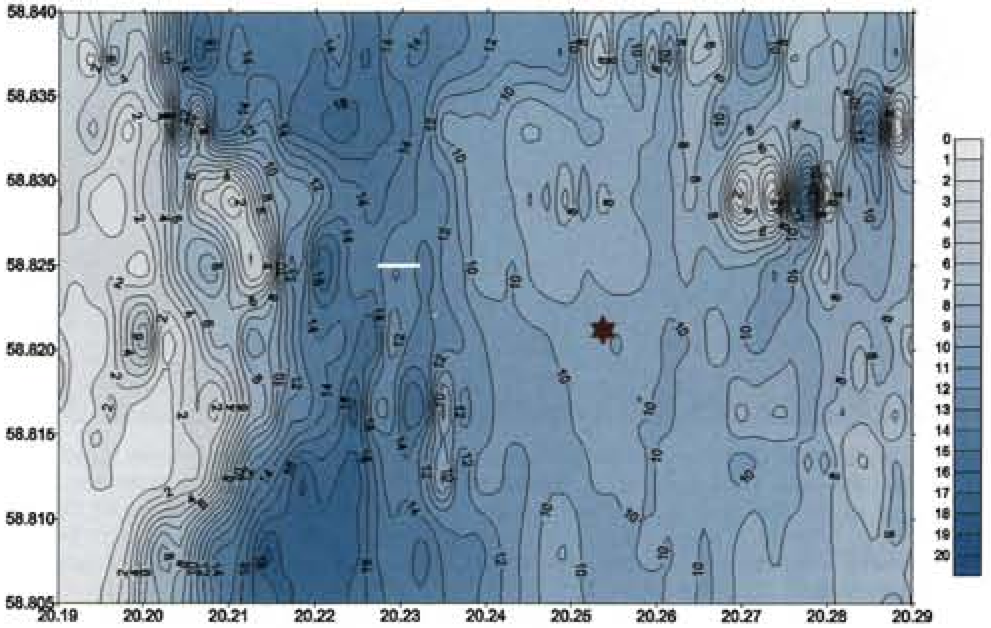

Fig. 6. The thickness in milliseconds (two-way travel time - TWT) of the glacial silt sediments including unit 6 in Fig. 5a, is based on the echo-soundings made by *R/V Aranda* in April 1998 using the shipboard Krupp Atlas DESO 25 echo-sounder utilising a 12 kHz transducer. The default (SURFER) kriging algorithm was used in the gridding of the data based on a grid 50 * 26 nodes. The main NCB coring site is marked with a star. The white line shows the location of the acoustic profiles in Fig. 4. The map covers an area 5.64 * 3.89 km.

Baltic Ice Lake

With the growing distance to the retreating ice margin only clay-sized particles were being deposited. Although isostatic uplift of the crust was in "full swing" the waters were still much deeper than today. The occasional coarse-grained material found in the sediment had probably been ice-rafted. During the early Baltic Ice Lake (BIL) phase variations in sediment deposition are evidenced by the somewhat indistinct reflectors in unit 6 (Fig. 5a). The strong reflector between units 5 and 6 may indicate a re-advance or a surge of the ice margin. Based on the characteristic layering of unit 5 (Fig. 5a), the conditions during deposition were rather calm, i.e. no traces of e.g. scouring by near-bottom currents can be detected in the profiles, except for pockmark type disturbances (see Fig. 4 and paragraph on pockmarks). Whether the lake surface was frozen during a greater part of the year or the climatic conditions were stable enough not to induce strong wind-driven currents, is a question which has not yet been properly addressed.

Taking a closer look at individual reflectors in unit 5, it is obvious that input of sediment has varied both temporally and laterally during the later BIL phase. This can be interpreted to indicate shifting in the time and place of meltwater input, and also in the amount of fine grained sediment suspended in the water. Considering sub-bottom irregularities, minor depressions (negative bottom forms) seem to exhibit slightly higher acoustic reflectivity than positive forms. This can be explained by a differentiation in grain size. Slightly coarser material tends to accumulate in the minor depressions while finer grains settle uniformly. Despite the slight irregularities in sediment accumulation the total thickness of unit 5 is strikingly uniform throughout the study area, averaging 5 to 6 metres (based on assumed average sound velocity of 1500 m/s).

Yoldia Sea

According to Andrén et al. (2000) The Baltic Ice Lake stage ended c. 11,570 cal. yr. BP, when the colour of varved clays changed from brown to grey. This event is associated with a lowering of the water level due to outflow of ice-dammed waters across central Sweden and when a connection with the global ocean was established. The change in sediment character, seen in unit 4 in Fig. 5, is a result of a rapid change in water depth and the later inflow of saline waters (weakly brackish environment).

According to diatom analysis (Andrén et al. *op.cit.*, Heinsalu et al. 2000) the Yoldia Sea stage can be divided into three sub-stages, an initial fresh water stage, followed by a short-lived brackish phase, which ended with the connection across Sweden being cut off due to crust uplift. The beginning of the brackish phase is possibly visible as the weak reflector at one third of the total thickness of unit 4. The end of the brackish phase has not left any clearly discernible reflector. This is easily explained by the fact that the salinity in the deeper water layers decreased slowly, thus no abrupt changes in the sediment character occurred. Because none of the cores so far studied penetrated into unit 4, the actual age of the sediment has not been determined. Thus, it is possible that the upper part of the unit may represent lower Ancylus Lake deposits.

Ancylus Lake

The rapid land uplift, which raised the passages in south-central Sweden above the ocean level at 10,700 yr. BP, and caused the water level to rise in the Baltic basin, is defined as the onset of the Ancylus Lake (Heinsalu et al. 2000). During the first half of this phase, the Ancylus Lake was dammed-up followed by a rapid lowering of the lake when the waters found a new southern outlet. Unit 3 in Fig. 5a is here interpreted to represent Ancylus Lake sediments. Because of the vague transition between Yoldia and Ancylus sediments it is possible, as stated above, that part of lower Ancylus is in the uppermost part of unit 4.

Ancylus sediments are typically divided into two units (Winterhalter et al. 1981). The occurrence of black bands or staining by ferrous sulphide is characteristic for the lower Ancylus Lake clays, while the upper unit consists of homogenous clay with occasional grains of framboidal pyrite (Ignatius et al. 1968). According to Andrén et al. (2000) the uppermost part of the Ancylus Lake sediments in the Gotland Deep are gradational with the lowermost Litorina Sea deposits. Obviously the same is true for the NCB area. Like the Baltic Ice Lake sediments, also the Ancylus clays were deposited conformably and exhibit a rather uniform thickness over large areas.

Litorina Sea and the Present Baltic Sea

Due to the eustatic rise of the ocean level a new connection with the World Ocean was established via the Danish Straits. In the beginning, the inflow of saline water was intermittent. Input of nutrients, amelioration of the climate, lesser input of suspended mineral matter and thus also a decrease in turbidity led to an increase in both terrestrial and lacustrine/marine organic matter in the sediments. The period between 8500–7500 ^{14}C yr. BP is regarded as a transitional phase between the Ancylus Lake and the fully brackish Litorina Sea (Heinsalu et al. 2000).

The lithostratigraphic boundary between the Ancylus Lake and the Litorina Sea sediments is generally marked by an abrupt increase in the content of organic carbon and a sharp change from homogenous clays to, often laminated, gyttja clays (Winterhalter 1992). Contrary to the cohesive nature of the clays, the weak bonds between the individual grains and aggregates of the gyttja clay makes them conducive to easy erosion and transportation even by weak bottom currents. This is the reason why the Litorina sediments (unit 2 in Fig. 5) have a tendency to be deposited either as "basin fill" or asymmetrically in topographically uneven areas.

The lower boundary of the topmost sedimentary unit (unit 1 in Fig. 5a) was during the *R/V Petr Kottsov* cruises, following the suggestion by Th. Andrén (Stockholm University), termed the "Viking Layer", because it coincides with the Medieval Warm Period when Vikings were sailing widely. In addition to a change in lithology also the chemistry of the recent to sub-recent deep basin sediments display a dramatic change due to a substantial increase in primary production. This can also be seen as a rapid rise in chlorophyll derivatives, denoting widespread blooms of cyanobacteria (Kowalewska et al. 1998).

The distribution of unit 1 sediments can be seen in the map in Fig. 7. These very loose sediments, high in organic content, are first deposited as a "fluffy" layer some millimetres or centimetres in thickness. Even after deposition and compaction they are still easily eroded and therefore continuous accumulation can occur only in areas where bottom-near currents are very weak.

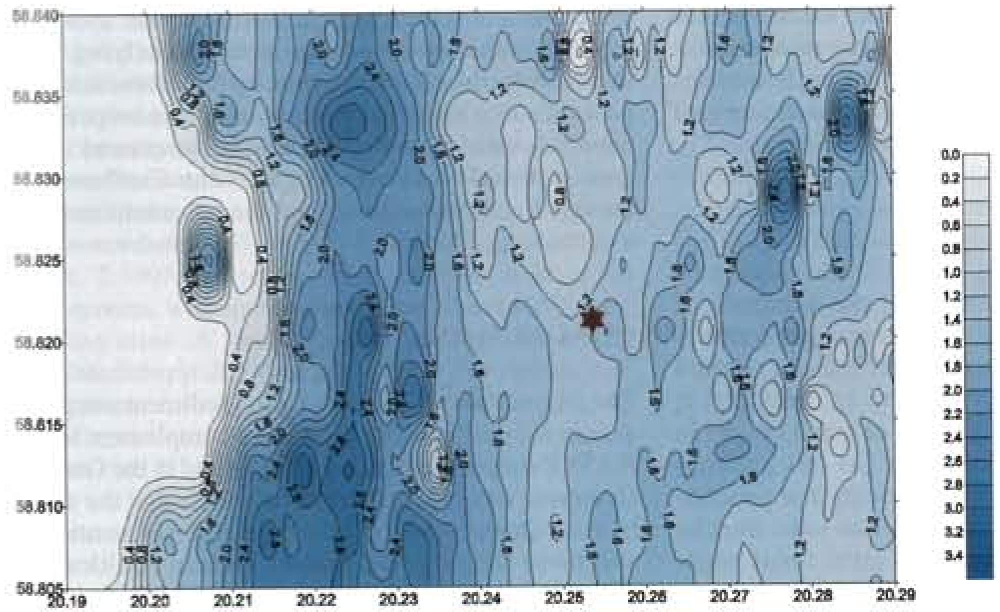

Fig. 7. The thickness in metres (assumed sound velocity 1435 m/s) of the most recent sediments (unit 1 in Fig. 5a) covering the last ca. 1000 years and having a high content of organic matter obviously associated with the Medieval Warm Period. The entire unit is characterised by a very loose structure and high water content. The map covers an area 5.64 * 3.89 km.

Distribution of sediments

The distribution of sediments in the NCB area, as also elsewhere in the deep areas of the Baltic Sea, is mainly governed by water depth and the intensity of near-bottom currents (Kohonen and Winterhalter 1999; Trimonis and Savukynienė 2000). Shallow areas with depths less than 80-100 m (wave base depth) in open sea conditions of the central Baltic Sea are generally void of fine grained recent to subrecent sediments. This is due to storm wave induced water motion that can be very effective as an erosion agent. Also internal waves at the halocline can have an influence on sediment deposition. Water motion in depths below wave base is generally the result of sea level fluctuations induced by variations in air pressure, although gravitational flow either due to salt water inflows or sediment suspended by waves during extreme storms can also be quite effective in eroding formerly deposited fine-grained sediments.

The NCB area is a good example of active erosion of formerly deposited sediments and the differential deposition of Litorina gyttja clay and recent mud. Figures 5a and 5b exhibit a typical distribution of sediments between the main NCB site and the clint forming the western slope of the basin. Although the water depth along the clint slope exceeds the reach of wave induced water motion, it is obvious that sediment has been eroded away. Likewise it is obvious that, due to the cyclonic nature of water currents (anticlockwise) in the Baltic Sea, the prevailing current flows south along the clint slope.

It can further be observed in Fig. 5, that, although partly eroded along the slope, the late glacial (Baltic Ice Lake, Yoldia Sea and Ancylus Lake) sediments exhibit a rather uniform thickness independent of water depth. The postglacial sediments (Litorina and recent) show a completely different picture. The deposition has been rather uniform in the eastern (right) part of the profile, but does dramatically wedge-out towards the west. This is a clear indication that the main current activity is along the western side of the north-south trending deep. A further conclusion that can be drawn from the acoustic profiles is that the main NCB site is suitable for sediment sampling for environmental monitoring and, furthermore, that such samples should not be taken from the deep area to the west of the BASYS site.

Pockmarks

Flodén and Söderberg have noted the existence of gas seeps in the Baltic Sea in several papers (e.g. 1988, 1994). The gas has been identified as a mixture of biogenic and thermogenic origin. In many places the seeps have formed pockmarks or small craters in the bottom. In other instances the gas has accumulated in sub-recent sediments blocking the penetration of high-frequency acoustic pulses used in echo sounding. In the case of the NCB area, fossil pockmarks are quite common (Fig. 4). Flodén (1997) observed recent traces of gas in the sediment by side scan sonar imaging during the *R/V Petr Kottsov* cruises.

According to the side scan images small seabed features with a weak change in acoustic reflectivity were interpreted by Flodén (*op.cit.*) to be indications of very minor gas seeps. On the side scan records they were just visible as round areas, generally about 20 m in diameter. No visible craters or other forms of surface disturbances could be detected neither on the DESO echograms nor in the deeptow records. On the other hand very distinct disturbances (Fig. 4) could be seen in the glacial sediments (units 5 and 6 in Fig. 5), but not in the overlying strata.

The very large disturbances in the early glacial and Baltic Ice Lake sediments (Fig. 4) are difficult to explain unless it is accepted that something has triggered off a "massive" expulsion of gas during a limited time interval. If one assumes that gas hydrates had accumulated under the Weichselian ice sheet, cold and deep water (or high ambient pressure) would maintain the hydrate in solid form until the depth would decrease and/or temperature would increase sufficiently to dissolve the hydrate and liberate the gas, with an "eruption" as the result. The fact that the overlying sediments have not been "visibly" disturbed precludes that if continuing gas escape is occurring, it can happen only at a very slow rate.

The commonly occurring blanking of acoustic signals in the upper part of thick Holocene sediments, often termed "basin effect", were formerly assumed to be signs of biogenic gas formed from the degradation of organic matter in the sediment. However, as a result of the pioneering work conducted by Tom Flodén (Flodén and Söderberg 1988) and the more recent observations by the present author, gas in sediments are at least in part derived from a more deep-seated source. Gas charged sediments are most often associated with fractures in the underlying bedrock. Thus, the gas that could have accumulated as gas hydrate or being visible today as minor seeps could have its source from the bedrock. In the current study area, a plausible source for gas is the Cambrian although fractures in the crystalline basement may be a contributing factor.

CONCLUSIONS

The original task of defining a good sediment sampling area in the northern Baltic Sea as a complement to the BASYS sites in the Bornholm Basin and in the Gotland Deep was successful. The acoustic data and the study of the sediment cores by authors previously mentioned and those found in the present volume (Baltica 14) clearly indicate that the NCB site is suitable for environmental monitoring purposes. Late-glacial and postglacial sediment accumulation seems to have been continuous at the main NCB site for all practical needs.

Higher rates of sedimentation than those observed at the main BASYS site are to be found along the slope west of the site (Fig. 7). However, the closer to the centre of the deep, between the clint slope and the main site, the more the accumulated sediment has been influenced by lateral transportation of material. It is also probable that the concentrations of environmentally sensitive elements and compounds will decrease with increasing accumulation rate because of dilution by "inactive" fine-grained mineral matter eroded from adjacent areas (Kohonen and Winterhalter 1999).

Acknowledgements

The author is indebted to Dr. Wolfram Lemke and Dr. Egidijus Trimonis for their valuable suggestions towards the improvement of the manuscript. I am very grateful for the excellent cooperation with my BASYS colleagues both during the marine cruises and in the later exchange of data and information. I am also deeply indebted to the crews of *R/V Aranda* and *R/V Petr Kottsov* for their input during the survey cruises. This study was partly funded by the EU under the MAST III BASYS project (contract: MAS3-CT96-0058).

References

Andrén E., Andrén T. & Kunzendorf H. 2000: Holocene history of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10, 6,* 687-702.

Bergman, L., Tynni, R. & Winterhalter, B. 1982: Paleozoic sediments in the Rapakivi area of the Åland Islands. *Geological Survey of Finland. Bulletin 317.* 132 p.

Björck, S. 1995: A Review of the History of the Baltic Sea, 13.0-8.0 ka BP. *Quaternary International 27,* 19-40.

Endler, R. 1998: Bathymetry. In K-C. Emeis and U. Struck (Ed.) Gotland Basin Experiment (GOBEX) - Status Report on Investigations Concerning Benthic Processes, Sediment Formation and Accumulation. *Meereswissenschaftliche Berichte — Marine Science Reports, Warnemünde 34,* 21-34.

Flodén, T. 1997: Nature and occurrence of gas in Baltic Sea sediments, with special emphasis on the BASYS sampling sites. A seminar paper. *In* J. Harff and B. Winterhalter (Eds.): *Cruise Report R/V Petr Kottsov, July 22 - August 01, 1997.* Baltic Sea Research Institute, October 1997. 89 p.

Floden, T. & Söderberg, P. 1988: Pockmarks and related seabed structures in some areas of Precambrian bedrock in Sweden. *Geological Survey of Finland, Special Paper 6,* 163-169.

Floden, T. & Söderberg, P. 1994: Shallow gas traps and gas migrating models in crystalline bedrock areas offshore Sweden. *Baltica 8,* 50-56.

Grigelis, A. 1998: Pre-Quaternary geological map of Lithuania in the context of geological map of North Europe, scale 1:2,000,000. Sedimentary Bedrock – Proterozoic III (Vendian) to Neogene. *Lithuanian Institute of Geology and the Geological Survey of Lithuania,* Vilnius.

Harff, J. & Winterhalter, B. 1996: Cruise Report R/V Petr Kottsov, Sept. 2 - Sept. 12, 1996. *Baltic Sea Research Institute, Warnemünde,* October 1996. 41 p.

Harff, J. & Winterhalter, B. 1997: Cruise Report R/V Petr Kottsov, July 22 - August 01, 1997. *Baltic Sea Research Institute,* October 1997. 89 p.

Heinsalu, A., Kohonen, T. & Winterhalter, B. 2000: Early postglacial environmental changes in the western Gulf of Finland, as reflected in the diatom and lithostratigraphy record of the sediment core B–51. *Baltica 13,* 51-60.

Ignatius, H. 1958. On the rate of sedimentation in the Baltic Sea. *Bulletin Commission Géologique de Finlande 180,* 135-145.

Ignatius, H., Kukkonen, E. & Winterhalter, B. 1968: Notes on a pyritic zone in upper Ancylus sediments from the Bothnian Sea. *Bulletin of the Geological Society of Finland 40,* 131-134.

Kohonen, T. & Winterhalter, B. 1999: Sediment erosion and deposition in the western part of the Gulf of Finland. *Baltica 12,* 53-56.

Kowalewska, G., Winterhalter, B. & Konat, J. 1998: Chlorophyll a and its derivatives in deep Baltic sediments. *Oceanologia 40 (1),* 65-69.

Trimonis, E. & Savukynienė, N. 2000: Sedimentation in the Northern Baltic Sea Basin. *Baltica 13,* 77-83.

Winterhalter, B. 1992: Late Quaternary stratigraphy of the Baltic Sea basins - a review. *Bulletin of the Geological Society of Finland,* 64, 189-194.

Winterhalter, B., Flodén, T., Ignatius, H., Axberg, S. & Niemistö, L. 1981: Geology of the Baltic Sea. *In* Voipio. A. (Ed.): *The Baltic Sea,* 1-121. Elsevier Oceanographic Series.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 18-23

On sediment patchiness at the BASYS coring site, Gotland Deep, the Baltic Sea

Boris Winterhalter

Abstract

The recent and subrecent sediments of the Gotland Deep have been the target of extensive studies for decades under various disciplines. Geological, geochemical and biological studies have made use of long and short sediment cores to elucidate the post-glacial development and even the present day state of the Baltic Sea. It has been assumed that sediment deposition has been continuous and uniform. Detailed acoustic profiling and coring in connection with the BASYS project has shown that sediment accumulation, even in the deepest parts of the basin, has, on the contrary, been sporadic and patchy at least during the last millennia. Thus, especially in environmental monitoring the representability of the chosen sediment sampling site should be carefully studied before drawing conclusions on the trends inferred from the acquired data.

☐ *Gotland Basin, Gotland Deep, sediment coring, sediment monitoring, accumulation rate, acoustic profiling.*

☐ *Boris Winterhalter [boris.winterhalter@gsf.fi], Geological Survey of Finland, P.O.Box 96, 02151 Espoo, Finland.*

☐ *Received 13 August 2001; accepted 7 November 2001.*

INTRODUCTION

One of the major depositional areas in the Baltic Sea, the Gotland Basin, and more precisely the Gotland Deep (GD) has been studied extensively for decades. Long sediment cores have been used to study the Holocene development of the Baltic Sea, and short cores to describe the trends in environmental conditions both in the main water body and especially in the near-bottom waters and the bottom itself. The uneven sediment distribution and variations in rate of accumulation in the basin has been mentioned by several authors, e.g. Emelyanov (2001), Gelumbauskaitė (1995), Winterhalter (1992), and also in several of the papers in this volume of Baltica. However, doubts regarding the representability of the sediments from the Gotland Deep for detailed environmental studies have only recently been voiced.

The first concrete indications of irregularities in the accumulation of recent and subrecent sediment in the Gotland Deep were observed during a cruise by the Finnish *R/V Aranda* in the early 1990s when an almost 10 cm thick fluffy surface sediment was observed at monitoring station BY15 (57°19'00"N, 20°02'14"E, 237 m). However, this layer was not observed at the same location the following year. The idea of sediment mobility in the form of lateral displacement as "large drifts" (cf. snow drifts in winter) was conceived.

The deposition of sediment in the Gotland Deep is regulated by the availability of suitable material and the processes involved in its lateral distribution. During the melting and retreat of the continental ice sheet, the source was most obviously the mineral fines transported by meltwater. Later, however, crustal rebound exposed material, formerly deposited in deeper water, to currents powered by barometric pressure differences and wind driven wave action. This suspended material together with authigenic and terrestrial components was transported and deposited into deeper and more tranquil parts of basins. The high-frequency acoustic profile in Figure 1 shows clearly the variations in sediment accumulation along an east/west transect across the Gotland Deep. No recent sedimentation is observed on either flank. This is due to the Coriolis effect directing currents towards a right-hand slope. For northbound currents the eastern flank would be affected and respectively the western slope by southbound currents. In addition to this main counter-clockwise current density flows within the deep parts of the basin tend to redistribute especially fluffy low-density material.

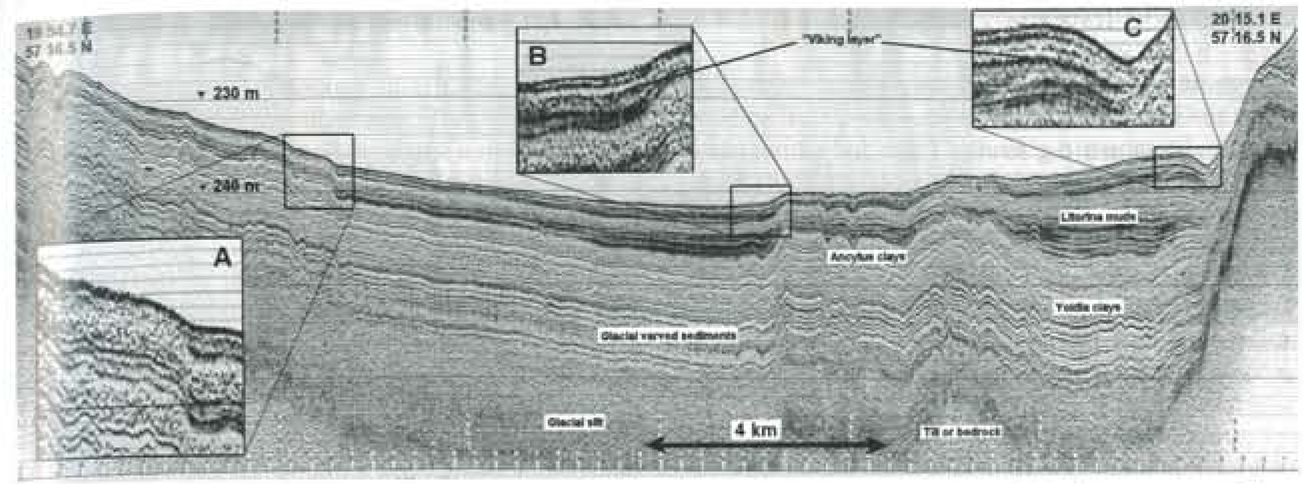

Fig. 1. A 12 kHz echo-sounder profile across the Gotland Deep is showing very strong asymmetrical sediment accumulation. The total thickness of Holocene (Litorina) muds is only slightly over 2 m in the western (left) part of the profile, increasing to almost 10 m near the eastern (right) slope. Inset "A" shows no subrecent mud accumulation in the middle, barely visible mud on the left (up-slope side), but increases up to a metre on the right. Inset "B" shows a similar difference in the thickness of the uppermost unit ("Viking layer"). Inset "C" shows that, although much of the sediment is derived from up-slope, maximum accumulation occurs not at the slope base (deepest) but from several hundred metres to a few kilometres away from the slope, due to slope "hugging" currents. Location of profile is given in Fig. 3.

The patchy nature of sediment deposition in the Gotland Deep was finally and most clearly observed when trying to accurately correlate a number of long sediment cores taken by *R/V Petr Kottsov*, chartered by IOW, in July 1997 as part of the BASYS subproject-7 (Paleoenvironment), from allegedly the identical site.

The location of the BASYS coring site (Fig. 2) had been carefully chosen on the basis of an acoustic survey made by *R/V Aranda* in April 1997 in an area where sedimentation was thought to have been consistent and uniform both temporally and spatially. The final site was located in an area of "continuous" sedimentation but far enough from the eastern slope to minimise the possible influence of slope processes (slumping and creep) that might distort the usefulness of the sediment for monitoring purposes.

The accurate plotting of the co-ordinates (Table 1) for the different cores, showed that the cores were actually collected from within an area less than a hundred metres in diameter (Fig. 3). Although the major sediment units could be precisely compared between the separate cores, many of the details (layers and laminae) visible in one core did not, however, match with features in a nearby core. Because of the detectable differences in the BASYS cores taken from the same site, a specially designed high-resolution deeptow acoustic transducer system was deployed in a survey conducted the following year, to try to detect the reason for the discrepancy.

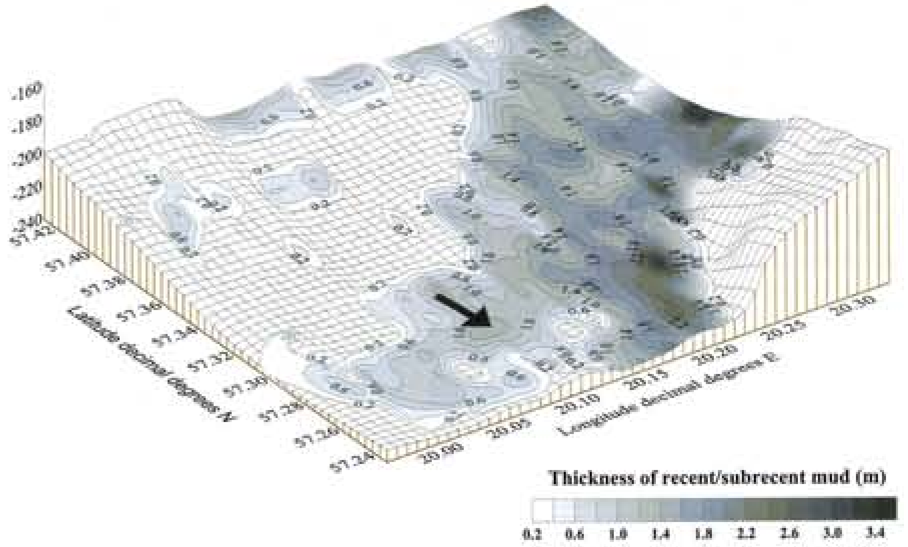

Fig. 2. The distribution and thickness (in metres) of subrecent and recent sediments (of the last millennia) superimposed on a 3D-map of the bathymetry of the Gotland Basin. The black arrow (57.28 N 20.11 E) shows the location of the BASYS coring site. The map is based on interpreted and digitised acoustic profiles (12 kHz) collected during the April 1997 *R/V Aranda* cruise.

MAPPING SURVEY

A large number of chirp and echo-sounding profiles from the Gotland Deep have been presented and discussed in literature (e.g. Endler 1998) indicating variations in spatial and temporal sediment deposition. However, no detailed maps on the actual sediment distribution in the deep area have been available. Therefore in April 1997 *R/V Aranda* conducted an acoustic survey of the Gotland Deep to establish the distribution of Holocene sediments with special emphasis on the most recent deposits (Fig. 2), i.e. from the last millennium attributable to the Medieval Warm Period and termed the "Viking Layer" as suggested by Th. Andrén (personal communication). Further surveys were conducted in 1998 on board the *R/V Aranda*. The bathymetric map in Fig. 3 was based on these surveys. The map also shows the position of the main BASYS coring site (211660) and the location of the deeptow profile through the coring site (white line). The exact locations of the actual cores are shown in the inset of Fig 3.

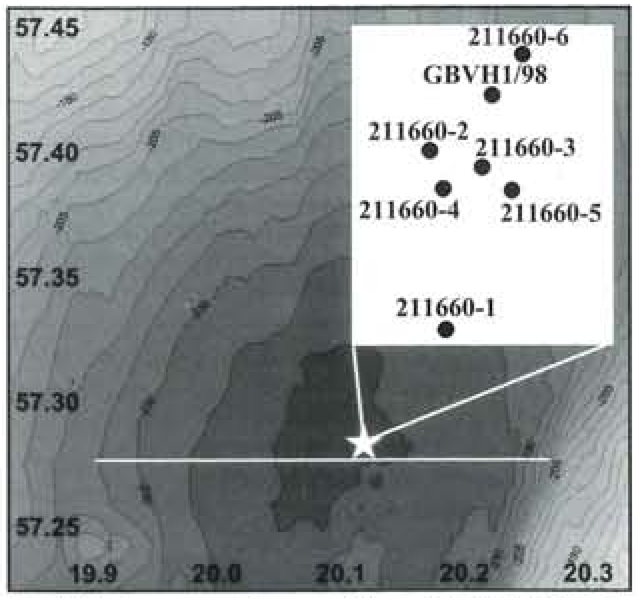

Fig. 3. The location of the cores taken at the BASYS coring site. Height of inset figure is 110 m. The white line (20 km in length) denotes the location of echogram in Fig. 1. Depth contours are in 5-metre intervals.

Sediment sampling

In accordance with the task set up under the BASYS sub-project 7 sufficient sediment material was to be acquired from a single station for use in a whole suite of various analytical procedures. For this reason four long sediment cores and two short ones were taken from the same site during the cruise in 1997 by *R/V Petr Kottsov* (Harff and Winterhalter 1997) and in 1998 an additional long vibro-hammer core by *R/V Aranda*. The site had been chosen as the main sampling station for the BASYS sediment cores representing the Gotland Basin. Although the cores were originally meant to be from the same position, due to position keeping difficulties of *R/V Petr Kottsov* the several planned corings did not take place in exactly the same spot (see Fig. 3). Core GBVH-1 was taken in 1998 by *R/V Aranda*. A verbal and graphic description of cores 211660-2 (short core) and 211660-6 (Kastenlot) are given by B.Larsen (in Harff and Winterhalter 1997).

The cores

The four long cores (211660-1, 211660-4, 211660-5, and 211660-6, Table 1) to be discussed here were all photographed. Core 211660-1 was a piston core photographed with a standard digital camera and the individual picture frames were combined to produce a full-length image of the core at the Stockholm University. Cores 211660-4 and 211660-5, taken with a heavy gravity corer, were hermetically sealed on board and opened and optically scanned at the Institute of Baltic Sea Research (IOW) in Warnemünde. The large box core 211660-6, with a cross section of 30 * 30 cm, was opened on board the *R/V Petr Kottsov* and photographed with a hand held digital camera and consecutively rectified and mounted by the present author to produce the full core image. In the present study, trying to address the patchiness issue, only the uppermost four metres of core, covering the time interval from the onset of the Litorina Sea brackish water phase to the present, are shown in Fig. 4.

When comparing the photographs of the cores, and also the various physical and chemical parameters that had been measured, the striking observation was made that many of the finer details, individual thin layers and laminae, in the cores could not be correlated although the cores were taken practically from the same site. Major units, that is, variations between laminated and homogeneous sections and etc., can be readily correlated, although unit thicknesses do vary. It can be clearly seen in Figure 4, that this is true of all the cores. Part of the observed variability can possibly be explained by changes in sediment compaction as a result of the coring procedure itself, because the cores were taken with different equipment[1]. This does not, however, explain many of the differences observed in the detailed comparison of the different cores.

Table 1. The DGPS co-ordinates (decimal degrees) of the sediment cores taken at the BASYS site in the Gotland Deep. See Fig. 3.

Longitude	Latitude	Station No.	Corer type
20.118536	57.282953	211660-1	Piston corer
20.118448	57.283508	211660-2	Gemini short gravity corer
20.118745	57.283455	211660-3	Gemini short gravity corer
20.118523	57.283388	211660-4	Gravity corer
20.118912	57.283383	211660-5	Gravity corer
20.118976	57.283805	211660-6	Kastenlot
20.118800	57.283680	GBVH1/98	Vibro-hammer corer

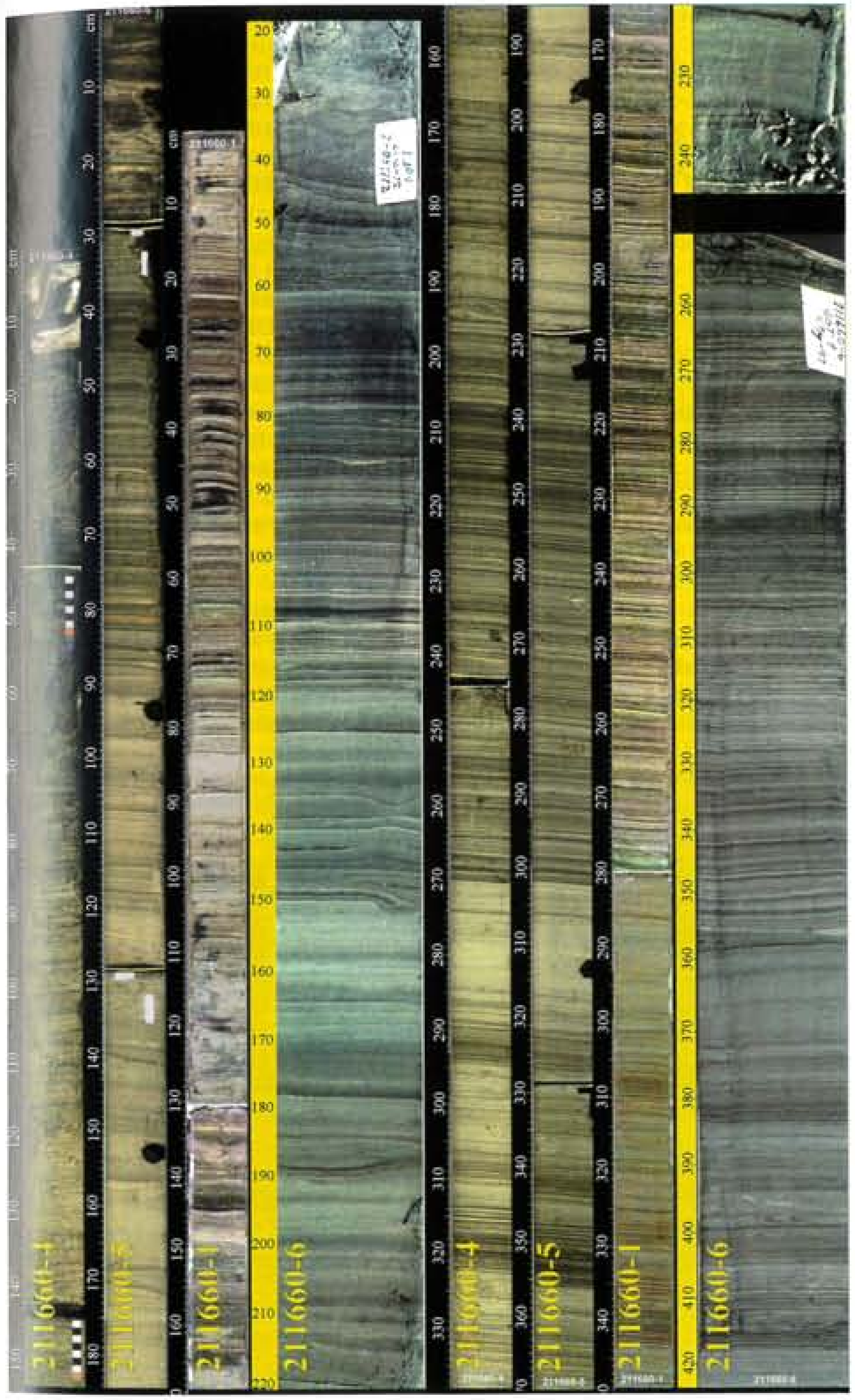

Fig. 4. Comparison of the upper parts of four long cores, covering the time span from the onset of the Litorina Sea brackish water phase to the present. Starting from the left, the cores are 211660-4, 211660-5, 211660-1, and 211660-6, each shown in two sections. The vertical scale is given for each core separately. The greater length of core 211660-6 is due to the fact that it penetrated the bottom at an angle of 20 to 25 degrees. The differences in length between the other cores can be ascribed both to core compaction and differences in sediment accumulation. Although the main features of the cores are similar, clear differences, especially in the fine structures can be observed. These differences in detailed sediment characteristics can be attributed to patchiness in sediment accumulation. For additional discussion, see text.

A similar comparison of various parameters measured from the cores also met with problems when going into greater detail. E.g. Kotilainen et al. (2000) noted difficulties in accurate correlation of the paleomagnetic parameters measured from cores 211660-6 and 211660-1. According to the positioning data cores 211660-4 and 211660-5 were taken just a few tens of metres from each other. The detailed magnetic susceptibility curves in Fig. 5, measured from these two cores at 5-mm intervals with a surface-scanning Bartington-MS2E1 sensor clearly show an agreement in their overall trends. However, a closer study of the measured data, clearly shows variations spanning more than just one measurement. Some of the discrepancy can be explained by the sensitivity

---

[1]) The core 211660-1 was taken with a piston corer provided by the University of Stockholm, 211660-4 and 211660-5 were taken with the IOW gravity corer (Schwerelot) and the 211660-6 was taken with the Kastenlot originally designed by Dr. Friedrich Kögler, Kiel.

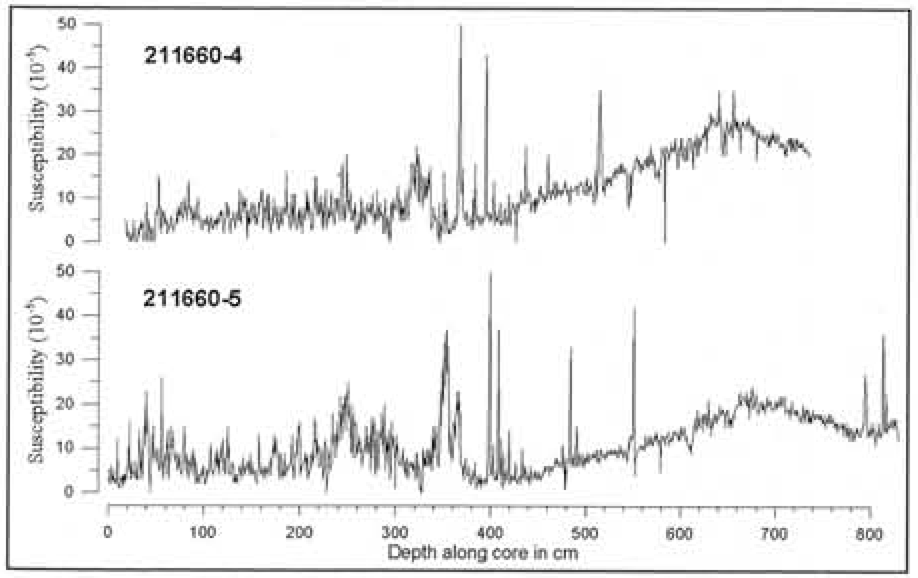

Fig. 5. Magnetic susceptibility measured along two of the cores (211660-4 and 211660-5) with a sampling interval of 5 mm. The cores are clearly not identical although the distance between the cores is only a few tens of metres.

of the method to a sporadic occurrence of e.g. pyrite grains, but there is still room for actual variability due to differences in sediment accumulation[2].

The deeptow record

During the April 1998 cruise of *R/V Aranda* both the standard DESO 25 shipboard echo sounder, with a 12 kHz transducer, and a specially configured deeptow system were utilised. The deeptow utilised a 28 kHz transducer mounted on a tow body with a large Klein K-wing as depressor. The Meridata's MD DSS multi-mode sonar system was used to produce and process the acoustic signals. The system was run both in pinger (for higher resolution) and chirp mode (for better penetration). The deeptow body was kept at some tens of metres above seabed while steaming at slow speed. The acquired profiles show an unprecedented amount of detail, which clearly indicated that detailed correlation of cores taken even within very close proximity to each other would be very difficult, at least on an annual or semi-annual basis. Fig. 6 shows a comparison between the DESO and the deeptow records taken from the BASYS coring site.

It is obvious that the ship-mounted 12 kHz transducer of the DESO echo sounder gives an erroneous impression of the consistency and uniformity of main reflectors. This is due to the fact that the reflected acoustic signal contains energy from a much wider sea floor area than that given by a transducer towed close to the bottom. The deeptow profile shows greater variability in the received signal, thus giving a much more realistic interpretation of the consistency of acoustic reflectors.

A closer study of the acoustic profiles from the coring site (Fig. 6) showed that, indeed, only the more intense reflectors showed lateral uniformity in the accumulation of sediment. It is obvious from the acoustic records that the reason for the difficulty in correlating the cores lies in the uneven sediment deposition at the site. Detectable disturbances or variations in layer characteristics could be observed in the fine features especially in the high-resolution deeptow profiles.

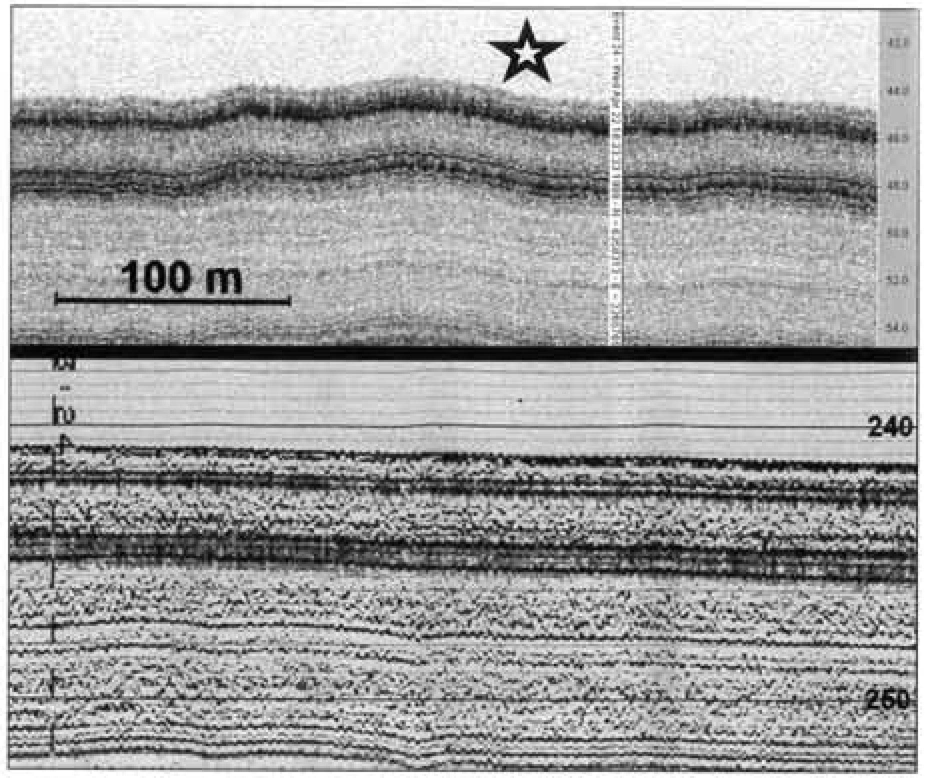

Fig. 6. Sample of deeptow 28 kHz high-resolution echo-profile (top) across the BASYS sampling site and a section of a 12 kHz echogram taken with the hull-mounted DESO 25 echo-sounder on board *R/V Aranda* covering exactly the same stretch of sea floor. The star (*) denotes the approximate location of the BASYS cores. The undulating surface of the deeptow record is due to variations in the altitude of the towed transducer body. In reality the bottom is very flat. Vertical scale in metres. The two sets of reflectors, *i.e.* at approximately 1-1.5 m and 3.5-4 m correspond to the events of high organic productivity (see Fig. 1 in Alvi and Winterhalter, 2001).

---

[2] The magnetic susceptibility of the cores 211660-4 and 5 were measured by Mr Jyrki Hämäläinen at IOW, with a Bartington-MS2E1 and a sampling interval of 5 mm.

DISCUSSION

The patchy nature of recent and sub-recent sediment distribution was known from the acoustic surveys conducted prior to coring. The sampling site was therefore carefully chosen in order to provide uninterrupted sediment accumulation with optimum temporal resolution of the Holocene strata. If coring had been targeted only on the acquisition of the most recent sediment the best temporal resolution (high accumulation rate) would have been provided by coring closer to the eastern slope (Fig. 1). However, this would have introduced an element of error, because at least part of the sediment consists of resuspended material transported down the slope and would thus not mirror the actual conditions in the open sea.

It is obvious that the sediments in the Gotland Basin are much more heterogeneous than previously assumed. It seems that the older, glacial and late-glacial sediments were deposited in a much more stable environment. With the opening of the Danish Straits and the onset of the brackish water phase of the Baltic Sea (Litorina Sea) the situation changed drastically. The inflow of heavy saline waters into the Baltic Sea basin and their propagation as a gravity-propelled current into the deep basins drastically changed the sediment dynamics of the Gotland Basin. The density stratification in the water column together with the formation of internal waves induced water motion reaching the bottom of the deepest basins.

Increased current activity in the deeps together with the change in sediment character from a "sticky" clay to a gyttja clay (mud), rich in organic matter due to the increased productivity (Litorina Sea), was conducive to easier redistribution of accumulating sediments. The conformable deposition typical of the Baltic Ice Lake and Ancylus Lake sediments had thus changed into a "basin fill" (Winterhalter 1992) type of deposition, where even weak bottom currents are capable of redistributing sediment. This resulted in the patchy distribution of recent sediments shown in Figure 2. Thus, sediment cores taken for environmental monitoring purposes should be carefully compared with cores taken during earlier years to ensure that sediment deposition has been a continuous and uniform process.

Acknowledgements

I gratefully acknowledge the input of my BASYS colleagues both in the form of published reports and in providing original data. I would especially like to mention Dr. Thomas Andrén (University of Stockholm) and Michael Meyer (Baltic Sea Research Institute, Warnemünde) for the sediment core images and Jyrki Hämäläinen (Geological Survey of Finland) for the magnetic susceptibility measurements. The author is indebted to Prof. Algimantas Grigelis and Prof. Jan Harff for their valuable suggestions towards the improvement of the manuscript. I am also deeply indebted to the crews of *R/V Aranda* and *R/V Petr Kottsov* for their input during the survey cruises. This study was partly funded by the EU under the MAST III BASYS project (contract: MAS3-CT96-0058).

References

Alvi, K. & Winterhalter, B. 2001: Authigenic mineralisation in the temporally anoxic Gotland Deep, the Baltic Sea. *Baltica 14*, 74-83.

Emelyanov, E. M. 2001: Biogenic components and elements in sediments of the Central Baltic and their redistribution. *Marine Geology 172* (2001), 23-41.

Endler, R. 1998: Acoustic Studies. *In* K-C. Emeis & U. Struck (Ed.) *Gotland Basin Experiment (GOBEX) - Status Report on Investigations Concerning Benthic Processes, Sediment Formation and Accumulation. Meereswiss. Ber., Warnemünde, 34*, 21-34.

Gelumbauskaitė, Ž. 1995: Bottom Relief and Genesis of the Gotland Depression. *Baltica 9*, 65-75.

Harff, J. & Winterhalter, B. 1997: Cruise Report R/V Petr Kottsov, July 22 - August 01, 1997. *Baltic Sea Research Institute, October 1997*. 41 pp.

Kotilainen, A. T., Saarinen, T., Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166 (1-4)*, 51-64.

Perttilä, M. & Niemistö, L. 1993: Selection and characterization of net sedimentation stations for reference use: first results of the 1993 Baltic Sea Sediment Baseline Study. ICES C.M. 1993/E30.

Sviridov, N.I., Sivkov, V.V., Rudenko, M.V. & Trimonis, E.S. 1997: Geological evidence of bottom currents in the Gotland Basin of the Baltic Sea. *Oceanology 37 (6)*, 838-844.

Winterhalter, B. 1992: Late Quaternary stratigraphy of the Baltic Sea basins - a review. *Bull. Geol. Soc. Finland 64*, 189-194.

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 24-33

Physical properties of bottom sediments from three Baltic Sea basins

Marijonas Repečka

Abstract

The Holocene sediments of Bornholm, Gotland and North Central basins in the Baltic Sea consist mainly of pelitic mud. Grain size and physical properties of bottom sediments in core sections show various contents of pelitic particles and may be divided into layers and sub-layers, which can be used for stratigraphic correlation between different basins. Three layers have been distinguished in sediment section from the Bornholm Basin and 4-5 layers in Gotland and North Central basins.

☐ *Bornholm Basin, Gotland Basin, North Central Basin, Baltic Sea, bottom sediments, grain size, physical properties, layers, sub-layers, correlation.*

☐ Marijonas Repečka, Institute of Geology, Department of Baltic Marine Geology. T. Ševčenkos 13, LT 2600 Vilnius, Lithuania.

☐ *Received 19 November 2001, accepted 4 December 2001.*

INTRODUCTION

Sedimentary processes were active during the entire Holocene in the main basins of the Baltic Sea. Pleistocene tills can be seen only on the slopes of basins and separate elevations where Holocene soft sediments are absent or of a small thickness and represented by a coarse type of sediments. The grain-size composition of bottom sediments in the cores is indicative of suitable conditions for sediment accumulation in the basins. Evidently there are neither large hiatus in the cores nor changes in lithology of the sediments. Bottom sediments are pelitic mud (Bezrukov, Lisitzin 1960) containing more than70% of particles less than 0.01 mm.

Changes in grain size and physical properties of bottom sediments in the cores indicate variations in conditions and rates of sedimentation. The main aim of this article is to divide sediments into different units and correlate them between different basins. Changes in thickness of the layers for different basins reflect the rate of sedimentation in these regions. The stratigraphic position of these layers may be determined with the aid of other methods (paleomagnetic measurements, radiocarbon dating, pollen analyses and diatom assemblage zones).

DATA AND METHODS

During BASYS SP-7 marine expeditions on the *R/V Petr Kottsov* cruises in 1996 and 1997 (Harff and Winterhalter 1996, 1997) the samples of bottom sediments from six cores were taken for laboratory investigations (Fig. 1). The grain size of bottom sediments was determined by the pipette method (Petelin 1967). The fractions <0.001 mm, 0.001-0.005, 0.005-0.01, 0.01-0.05, 0.05-0.1, and >0.1 mm have been measured. The sediment of natural moisture is analysed without dispersing and removal of salt or organic matter. Percentages of fractions <0.001, 0.001-0.005, 0.005-0.01 mm were determined. If there is more than 10% (of particles >0.05 mm in the analysed sample, it is additionally sieved.

To determine percentages of moisture in bulk sediment a sample of 3-10 g weight is dried at 105°C. The density of dried terrigenous particles of Baltic Sea bottom sediments is known to be 2.64-2.68 g/cm^3. Knowing the moisture percentage and the density of dry particles of sediment it is possible to find out weight volume dn and volume porosity:

Fig. 1. BASYS coring sites. 211630-9 and 211630-10 cores are taken from site location in the Bornholm Basin, 211660-6 and 211650-4 cores – from Gotland Basin, 211670-7, 00/96/02/1GC-2 and 00/96/02/2GC-4 cores – from North Central Basin. After B.Winterhalter, BASYS-7 final report, CD-ROM 1999.

$dn = (100.dd/(Vm.(dd-1)+100)$, where:

dn - weight volume (bulk density of sediment of natural moisture), g/cm^3;
dd - density of dried particles of sediment, g/cm^3;
Vm - moisture volume, %.

Then: $Vp = (dn)\ Vm$, where Vp - volume porosity;
dn - weight volume, g/cm^3;
Vm - moisture volume, %.

Grain size and physical properties of bottom sediments were determined in cores from the Bornholm, Gotland and North Central basins of the Baltic Sea. Bottom sediment cores from stations 211630-9 (upper part of section) and 211630-10 (lower part of section) represent the Bornholm Basin. Summary length of two cores is 735 cm (0-600 and 440-735 cm). Water depths at the coring site are 93.57 and 93.55 m, respectively. Sediment cores 211660-6 and 211650-4 are from the Gotland Basin. Bottom sediment cores from these stations are 735 and 560 cm long. Water depths at the coring stations are 241.3 and 239.6 m, respectively. The North Central Basin is represented by cores from stations 211670-7 (upper part 0-350 cm interval) and 211670-4 (lower part 100-520 cm interval), 00/96/02/1GC-2 and 00/96/02/2GC-4. Water depths at the coring stations are 175.2, 176.1, 175.8 and 185.4 m, respectively.

RESULTS

Bornholm Basin

Bottom sediments of the Bornholm Basin (BB) at the stations 211630-9 and 10 are represented by pelitic mud (>70% of particles <0.01 mm). The particles >0.05 mm make up only <1% of all bottom sediment particles. The amount of 0.05-0.01 mm particles ranges from 4.8% in the lower part of core to 25% in the 460-465 cm interval (Appendix 1). The cores from Bornholm Basin, may be divided according to grain size and physical properties in the following intervals: 0-80, 80-312, 312-480, 480-580 and >580 cm (Fig. 2). Average amount of pelitic (< 0.01 mm) particles, moisture, density and porosity in different sediment intervals of cores are given in Table 1. In the bottom sediment interval 312-480 cm (station 211630-9) the amount of pelitic particles decreases from upper part downward (91.3-73.9%). In the interval 480-580 cm the amount of pelitic particles increases from 84.6 to 93.6%. The changes in the amount of pelitic particles are most obvious in the lower part of the core. Changes of grain size of bottom sediments in the Bornholm Basin probably depend on different hydrodynamic activity in the sedimentary environment and various sea levels at the different stages of geological development of the Baltic Sea.

The moisture content in the sediment cores decreases downward being 78.3% at the top of the core to 57.4% at the 730-735 cm interval below sea bottom. Moisture decreases more intensively in the upper part of core (0.11% per cm) and less in the lower part (0.006% per cm). Density of bottom sediments increases from 1.15 g/cm^3 at the surface to 1.36 g/cm^3 in the 730-735 cm interval. Porosity of bottom sediments decreases from 90.6% at the top to 78.2% in the lower part of core. The changes in grain size reflect the physical properties of the sediments.

Gotland Basin

Cores from the stations 211660-6 and 211650-4 represent bottom sediments of the Gotland Basin (GB). The recovered core sections consist of pelitic mud. According to grain size and physical properties the bottom sediments may be divided into 6 and 5 separate intervals (layers and sublayers) respectively (Fig. 2, Table 1). Grain size of bottom sediments in the interval 0-60 cm of 211660-6 station does not change and average amount of pelitic particles reaches 84.4%. Upper part of 60-165 cm interval of bottom sediments is enriched

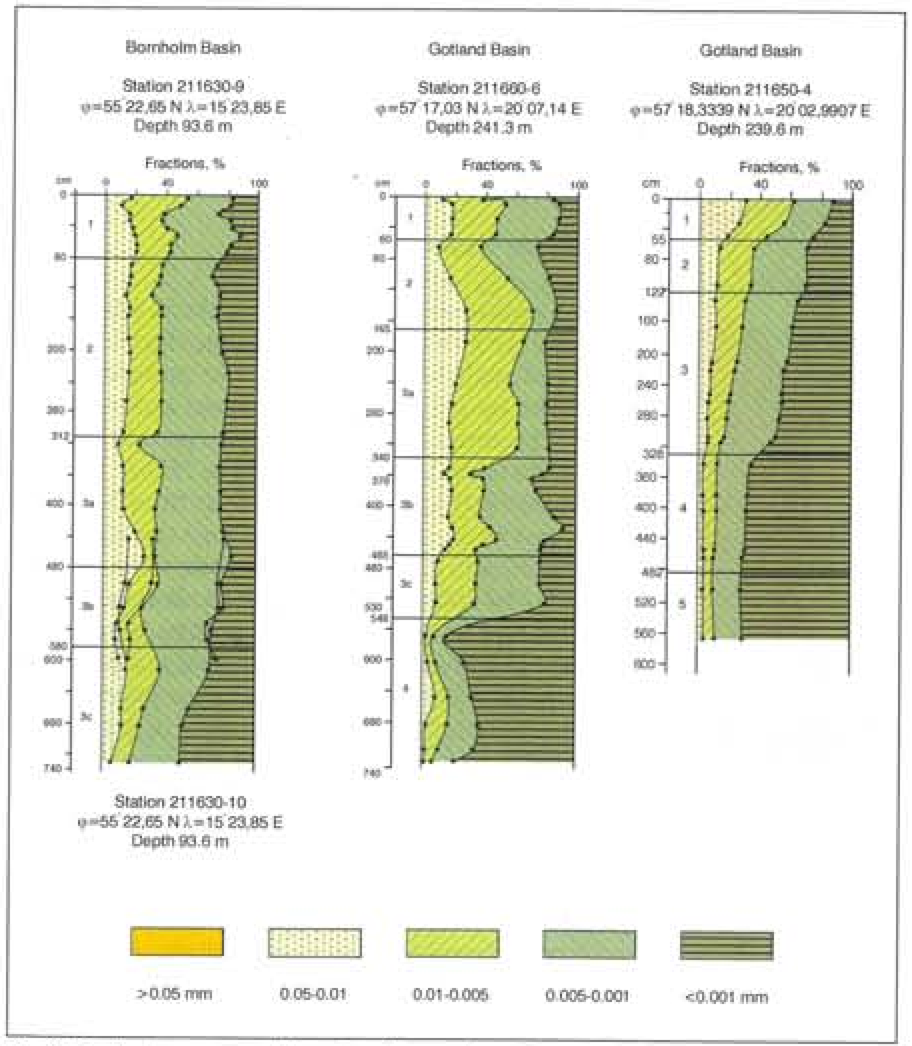

Fig. 2. Grain size composition of sediments from Bornholm and Gotland Basins.

in pelitic particles (91.5%), and the lower part is coarser (72.2% pelitic particles). The amount of 0.05-0.01 mm and 0.01-0.005 mm particles in the interval 165-340 cm reaches 25-15% and 44.5-35% of respectively. The amounts of 0.005-0.001 mm particles in the interval 340-465 and 465-548 cm increase to 50%, whereas those of coarse particles decrease. The amount of <0.001 mm particles sharply increases in the 548-735 cm interval and reaches 85.1%. Changes in amount of different particles downward in the core show more calm hydrodynamic conditions at the moment of sedimentation. These conditions probably differed with different stages of geological development of the Baltic Sea.

Similar changes in grain size of bottom sediments can be observed in the core from station 211650-4. The sediments become finer from the top surface downward. The boundary at the 328-cm depth may be correlated with one at the 548-cm depth in the core 211660-6. The station 211660-6 is located in a deeper, central part of the Gotland Basin, and the rate of sedimentation varies here more sharply. Physical properties of bottom sediments in the Gotland Basin vary downward from the sea floor. Amount of moisture and porosity decrease from 79.8 and 92% to 53.1 and 75.1% in the lower part of the core in the station 211660-6. Density of bottom sediments at this station increases from 1.15 g/cm³ to 1.41 g/cm³. This value in the bottom sediments on the station 211650-4 ranges from 66.3 and 83.9% on the bottom surface to 45.4 and 68.7% in the lower part of core. Density of bottom sediments increases from 1.27 g/cm³ to 1.51 g/cm³.

North Central Basin

Bottom sediments of the North Central Basin (NCB) are represented by cores from stations 211670-7, 4, 00/96/02/2GC-4 and 00/96/02/1GC-2 These cores recovered section of bottom sediments 520, 575 and 550 cm thick. All cores are made up of pelitic mud and only in the 65-69 cm interval in core 00/96/02/1GC-2 the amount of pelitic particles is less than 68 %, thus characterising the sediments as aleuritic-pelitic mud. Sections of bottom sediments in the cores have been divided into 5-7 different layers and sublayers respectively (Fig. 3, Table 1). The grain size and physical properties of bottom sediments in the cores 211670-7,4 and 00/96/2/2GC-4 are very similar and intervals are well correlated. The grain size of bottom sediments in the core 00/96/02/1GC-2 may be divided into 7 different layers and sublayers. The interval 0-19 and 19-65 cm correspond to the intervals 0-41 and 0-42 cm in other cores. The interval 315-413 cm corresponds to 495-550 and 445-520 cm intervals. The interval 413-575 cm in core 00/96/02/1GC-2 is deeper than lower intervals in other cores. The grain size of bottom sediments from the bottom surface downward becomes more dispersed. The amount of >0.05 mm particles decreases and that for <0.01 mm increases. The amount of <0.001 mm particles is substantial in the lower part of cores, especially in the core 00/96/02/1GC-2 downward from interval 413 cm.

Physical properties of the bottom sediments in the North Central Basin vary downward from the bottom surface. Amount of moisture and porosity decreases from 76.9-67.4 and 89.9-84.6% at the top to 56.3-49.8 and 77.6-70.7% in the lower part of the cores respectively. Density of bottom sediments increases from 1.17-1.26 g/cm³ at the top to 1.38-1.45 g/cm³ in the lower part of core section.

Table 1. Average amount of pelitic (<0.01 mm) particles, moisture, density and porosity in the different bottom sediments cores intervals

Interval, cm	n	<0.01 mm, %		Moisture, %		Density, g/cm³		Porosity, %	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
Bornholm Basin									
Station 211630-9									
0-80	8	79.5-90.0	83.4	69.3-78.3	73.5	1.15-1.24	1.20	85.7-90.6	88.0
80-312	11	84.0-89.1	85.4	61.8-70.5	66.8	1.22-1.31	1.26	81.0-86.4	84.2
312-480	6	73.9-91.3	84.4	61.2-63.1	61.8	1.30-1.32	1.31	80.8-82.0	81.1
480-580	8	84.6-93.6	88.9	55.7-61.9	58.0	1.34-1.38	1.36	77.0-81.2	78.6
580-735	5	84.2-95.2	89.2	55.6-57.9	57.1	1.36-1.38	1.37	76.9-78.2	78.0
Gotland Basin									
Station 211660-6									
0-60	4	82.8-88.8	84.4	75.1-79.8	77.0	1.15-1.18	1.17	88.9-92.0	90.1
60-165	3	72.2-91.5	82.6	68.6-78.9	74.7	1.15-1.24	1.19	85.3-90.8	88.6
165-340	5	73.9-83.8	80.2	66.6-67.7	67.3	1.25-1.26	1.25	84.1-84.8	84.5
340-465	8	81.2-86.2	83.8	61.0-68.8	64.4	1.24-1.32	1.29	80.6-85.4	82.7
465-548	3	91.5-91.9	91.6	59.2-60.5	59.9	1.33-1.34	1.33	79.4-80.3	79.9
548-735	6	91.6-99.2	97.2	53.1-56.1	55.2	1.38-1.41	1.39	75.1-77.3	76.6
Station 211650-4									
0-55	3	69.5-82.0	75.2	66.2-66.5	66.3	1.26-1.27	1.27	83.9-84.1	84.0
55-122	2	87.0-88.8	87.9	63.2-65.6	64.4	1.27-1.30	1.28	82.0-83.5	82.8
122-328	9	90.0-96.2	93.6	58.0-61.4	59.3	1.33-1.40	1.35	78.5-80.8	79.4
328-482	5	99.3-99.4	99.3	52.7-54.1	53.5	1.40-1.42	1.41	74.6-75.7	75.2
482-570	2	99.0-99.5	99.2	45.4-48.5	47.0	1.47-1.51	1.49	68.7-71.3	70.0
North Central Basin									
Station 211670-7,4									
0-41	5	84.4-89.6	87.6	66.5-67.4	66.8	1.26-1.26	1.26	84.1-84.6	84.2
41-125	6	82.1-84.5	83.2	59.7-65.6	64.3	1.27-1.34	1.29	79.8-83.5	82.7
125-388	17	90.0-97.2	93.5	53.7-61.5	56.6	1.32-1.41	1.37	75.5-80.9	77.6
388-445	2	90.2-96.4	93.3	53.0-56.6	54.8	1.37-1.42	1.40	75.0-776	76.3
445-520	3	96.0-98.0	96.9	52.6-56.2	54.6	1.38-1.42	1.40	74.7-77.3	76.2
Station 00/96/02/2GC-4									
0-42	3	70.0-94.3	86.0	62.9-76.9	68.8	1.17-1.30	1.24	81.8-89.9	85.3
42-134	3	75.4-86.6	82.4	62.6-69.2	65.8	1.24-1.30	1.27	81.7-85.7	83.6
134-407	7	90.4-96.9	93.7	55.0-61.6	58.2	1.32-1.39	1.36	76.5-81.0	78.7
407-495	4	81.8-89.9	84.8	54.9-58.2	56.2	1.35-1.39	1.38	76.4-78.7	77.4
495-550	3	91.3-98.1	95.8	54.3-56.3	55.5	1.38-1.40	1.39	75.5-77.6	76.7
Station 00/96/02/1GC-2									
0-19	2	76.9-86.2	81.6	64.7-70.5	67.6	1.23-1.28	1.26	83.0-86.8	84.9
19-65	4	76.3-78.9	77.9	64.2-73.9	67.3	1.19-1.29	1.26	82.7-88.3	84.5
65-106	2	68.5-73.2	70.8	64.7-72.3	68.5	1.21-1.28	1.24	83.0-87.4	85.2
106-272	3	89.2-89.7	89.4	58.6-61.2	60.0	1.32-1.35	1.33	79.0-80.8	80.0
272-315	2	78.1-80.8	79.4	60.0-63.7	61.8	1.29-1.33	1.31	80.0-82.4	81.2
315-413	3	93.2-95.5	94.5	55.6-57.0	56.2	1.37-1.38	1.38	76.2-77.8	77.4
413-575	3	95.5-98.1	96.9	49.8-55.2	52.8	1.39-1.45	1.42	70.7-76.6	74.2

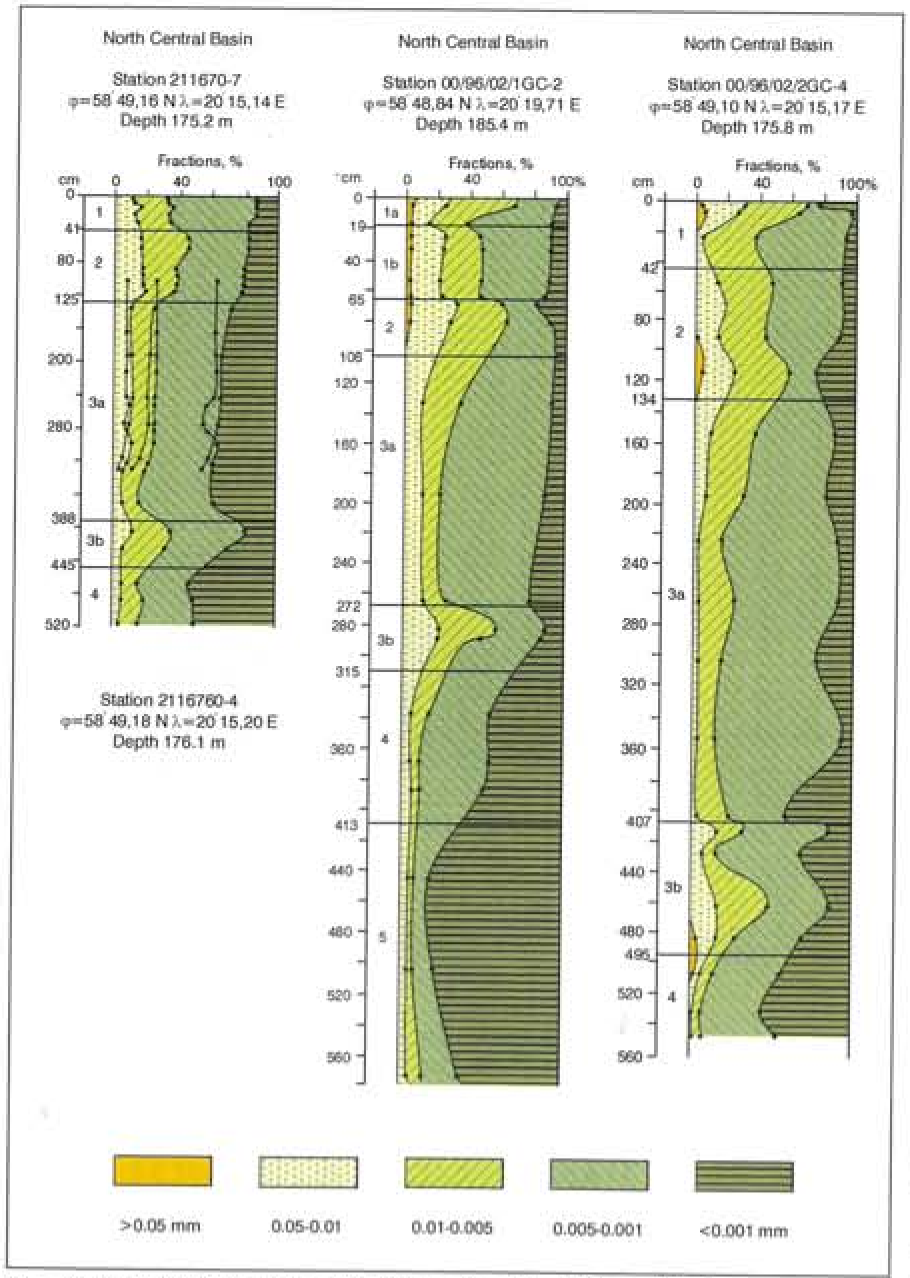

Fig. 3. Grain size composition of sediments from North Central Basin.

DISCUSSION

Sedimentological data for core correlation. Subdivision and tentative correlation of cores from Bornholm, Gotland and North Central basins, according to grain size and physical properties of bottom sediment, is shown in Fig. 4. The layers and sublayers are recognised and may be correlated in different cores. It should be noted that the grain size changes of layer 3 in core 211650-4 (GB) are comparative (?) and this layer hereby could not be divided into sublayers.

Rate of sedimentation in the GB and NCB are similar, but in the BB are 2-3 times higher. The rate of sedimentation in GB is higher in the deeper part of the basin. Lower boundary of the third layer is at 548 cm below sea floor at the station 211660-6 and 328 cm at the station 211650-4. It means, that rate of sedimentation at the station 211660-6 is 67 % higher. The hydrodynamic condition for sediment deposition is calmer at station 21660-6. The rate of sedimentation in the deeper part of NCB (185.4 m, station 00/96/02/1GC-2) is about 60% less, than at the station 00/96/02/2GC-4 (175.8 m). It shows more active hydrodynamic activity in the deeper part of the basin.

A layer of bottom sediments in the cores divided by grain size and physical properties approximately corresponds to that determined by other methods (Andrén, Andrén, Lindeberg 1998, Andrén 1999). There are large intervals between samples for grain size analyses, and changes in lithology approximately show boundaries between divided layers. Samples for grain size analyses were taken from gravity core sections of bottom sediments. Layers of bottom sediments determined from gravity cores didn't correspond to those from piston cores (Andrén 1999). The layers, distinguished by different methods may be correlated in a correct way only if the samples used in the comparative study are taken from the same core.

Sediment layers, characterised by different grain size and physical properties may be correlated to diatom assemblage zones (Andrén 1999). The first layer (Fig. 4) corresponds to the Recent Baltic Sea and the second one to post-Litorina Sea stage. The third layer (a, b sublayers) corresponds to Litorina Sea, the c sublayer - initial Litorina Sea and the upper part of Ancylus Lake stage of the Bornholm Basin. The 3 a, b sublayers in the core from Gotland Basin corresponds to Litorina Sea and upper part of Ancylus Lake stage. Sublayer 3c corresponds to the lower part Ancylus Lake and Yoldia Sea stages. Layers 4 and 5 correspond to different parts of Yoldia Sea stages. It is necessary to note that there is no sharp lithological boundary between Litorina Sea, Ancylus Lake and Yoldia Sea stages. Conditions of sedimentation in the Bornholm Basin in Litorina Sea and in the Ancylus Lake stage in the Gotland Basin were similar. The same sublayers (3c) in Bornholm Basin are related to initial Litorina Sea and upper part of Ancylus Lake stages, when in the Gotland Basin this sublayer is related to the lower part of Ancylus Lake and the upper part of the Yoldia Sea stage.

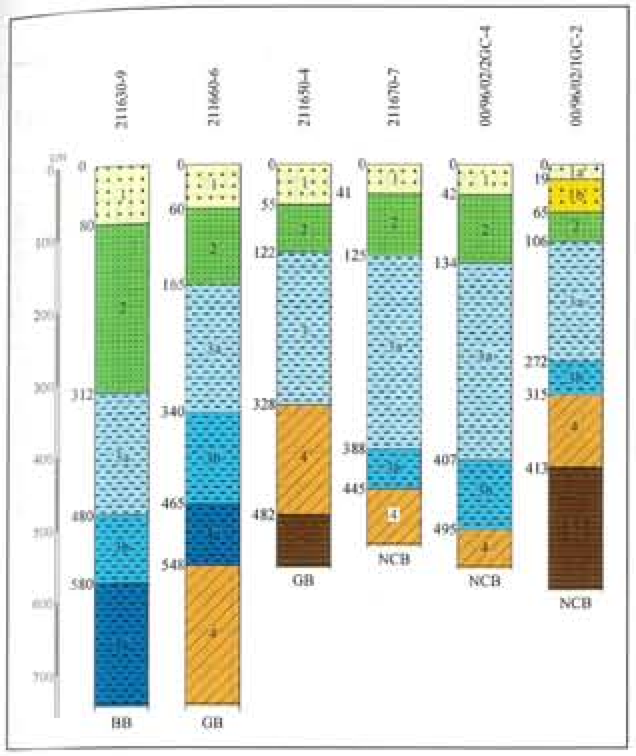

Fig. 4. Correlation of cores from Bornholm, Gotland and North Central Basins, according to grain size composition and physical properties of sediments. Numbers in cores section show layers and letters – sublayers. Graine size composition of sediments is given in figures 2-3.

The grain size and physical properties of bottom sediments show different conditions and rate of sedimentation in the present geological history of the Baltic Sea. The reliable correlation of separate intervals needs proper data for age determination.

CONCLUSIONS

Grain size and physical properties of bottom sediments reflect conditions of sedimentation in the sea. Lithological data make it possible to divide sediment cores into layers and sublayers (units) and correlate them between different basins. It should be noted that the same lithological composition of bottom sediments prevailed during the Litorina stage in the Bornholm Basin and during the Ancylus Lake stage in the Gotland Basin. It means, that the conditions of sedimentation remained unchanged during different stages of geological development of the Baltic Sea.

Acknowledgements

The author thanks Dr. Boris Winterhalter and Dr. Egidijus Trimonis for heplful comments and critical remarks, which helped to improve a manuscript. Also author is indebted to Dr. Rolandas Radzevičius for preparing article for publication and critical reading the manuscript.

References

Andrén, T., Andrén, E. & Lindeberg, S. 1998: Paleoecological development of the Bornholm Basin. *Second BASYS Annual Science Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Andrén, E. 1999: Holocene environmental changes recorded by diatom stratigraphy in the southern Baltic Sea. *Ph.D. thesis, Meddelanden från Stockholms Universitets Institution för Geologi och Geokemi, 302,* 22 p.

Bezrukov, P.L. & Lisitzin, A.P. 1960: Classification of sediments in the recent basins. Proceedings Institute of Oceanology. *USSR Academy of Sciences 32,* 3-14. (In Russian).

Harff, J. & Winterhalter, B. (Eds.). 1996: Cruise Report *R/V Petr Kottsov*, Sept. 2 - Sept. 12, 1996, Task: Research for BASYS-Baltic Sea System Studies - Subprojects 7 and 4. *Baltic Sea Research Institute, Warnemünde, October 1996.* 16 p., 6 attachments.

Harff, J. & Winterhalter, B. (Eds.) 1997: Cruise Report *R/V Petr Kottsov*, July 22 - Aug. 01, 1997, Task: Research for BASYS-Baltic Sea System Studies. *Baltic Sea Research Institute, Warnemünde, October 1997.* 41 p., 6 attachments.

Petelin, V.P. 1967: Grain size analyses of marine bottom sediments. Moscow : Nauka. 125 p. (In Russian).

Appendix 1. Grain size and physical properties of bottom sediments

Interval, cm	Fractions, %							Md, mm	So	Moisture %	Density g/cm^3	Porosity %
	>0.1 mm	0.1-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	<0.01 mm					
Station 211630-9 (Bornholm Basin) φ 55^{0}22.65’ N λ 15^{0}23.58’ E Depth 93.6 m												
0-5		0.4	15.0	37.7	28.9	18.0	84.6	0.0050	2.1	78.3	1.15	90.6
10-15		0.7	9.3	37.8	32.8	19.4	90.0	0.0047	2.2	75.2	1.18	88.9
20-25		0.4	15.5	22.5	34.1	27.9	84.5	0.0036	2.8	74.1	1.19	88.4
30-35		0.7	14.2	20.6	45.8	18.7	85.1	0.0037	2.2	73.9	1.19	88.2
40-45			18.2	21.8	34.6	25.4	81.8	0.0038	2.9	72.7	1.20	87.6
50-55		0.6	17.9	27.8	42.0	11.7	81.5	0.0400	2.0	72.4	1.21	87.5
60-65		0.7	19.8	20.5	40.4	18.6	79.5	0.0040	2.4	71.9	1.21	87.0
70-75		0.7	19.5	21.6	36.1	22.1	79.8	0.0040	2.6	69.3	1.24	85.7
85-90		0.6	15.4	19.9	37.0	27.1	84.0	0.0035	2.8	70.5	1.22	86.4
100-105		0.5	15.5	20.0	37.1	26.9	84.0	0.0030	2.9	70.5	1.22	86.4
110-115		0.6	14.7	20.0	37.6	27.1	84.7	0.0030	2.7	69.8	1.23	86.0
125-130		1.0	12.4	16.7	45.2	24.7	86.6	0.0030	2.5	68.2	1.24	85.1
140-145		0.7	14.9	21.0	35.1	28.3	84.4	0.0030	2.8	68.0	1.24	85.0
150-155		0.6	14.1	22.3	35.8	27.2	85.3	0.0040	2.8	66.3	1.26	84.0
180-185		0.7	14.5	20.3	41.7	22.8	84.8	0.0040	2.5	67.0	1.25	84.4
200-205		0.6	14.9	19.4	41.3	23.8	84.5	0.0040	2.6	66.3	1.27	84.0
230-235		0.6	14.3	21.9	43.0	20.2	85.1	0.0040	2.3	63.3	1.29	82.1
260-265		0.6	12.6	22.5	42.9	21.4	86.8	0.0040	2.4	63.5	1.29	82.2
300-305		0.6	10.3	22.8	42.9	23.4	89.1	0.0030	2.4	61.8	1.31	81.0
320-325		0.6	8.1	13.3	54.3	23.7	91.3	0.0030	2.1	63.1	1.30	82.0
350-355			12.4	24.6	38.4	24.6	87.6	0.0040	2.7	61.6	1.32	81.0
380-385		0.5	14.4	23.3	40.0	24.6	87.9	0.0040	2.8	61.6	1.32	81.0
400-405		0.5	13.4	18.4	43.6	24.1	86.1	0.0030	2.6	61.7	1.31	81.1
430-435		0.5	19.4	11.7	45.9	22.4	80.0	0.0030	2.6	61.5	1.31	80.9
460-465	0.5	0.6	25.0	6.5	48.9	18.5	73.9	0.0040	2.8	61.2	1.32	80.8
495-500		0.6	14.8	19.1	41.7	23.8	84.6	0.0030	2.6	59.3	1.34	79.5
530-535		0.5	10.9	11.5	54.6	22.5	88.6	0.0030	2.0	57.7	1.36	78.4
550-555		0.5	7.4	8.0	51.1	33.0	92.1	0.0023	2.1	56.6	1.37	77.6
570-575		0.5	6.8	10.4	52.1	30.2	92.7	0.0025	2.1	55.7	1.38	77.0
595-600		0.5	9.6	6.4	57.4	26.1	89.9	0.0030	2.1	55.6	1.38	76.9
Station 211630-10 (Bornholm Basin) φ 55^{0}22.65’ N λ 15^{0}23.85’ E Depth 93.6 m												
440-445			14.5	16.5	49.0	20.0	85.5	0.0030	2.2	61.9	1.31	81.2
500-505			12.3	19.7	42.0	26.0	87.7	0.0030	2.6	59.2	1.34	79.4
530-535			10.1	14.2	50.5	25.2	89.9	0.0030	2.2	56.6	1.37	77.6
560-565			10.8	16.2	43.0	30.0	89.2	0.0030	2.4	56.9	1.37	77.8
610-615		0.4	15.4	21.2	31.6	31.4	84.2	0.0030	2.8	57.0	1.37	77.9
660-665		0.5	10.7	14.0	30.9	43.9	88.8	0.0020	2.3	57.8	1.36	78.5
680-685			12.3	12.4	26.3	49.0	87.7	0.0010	2.2	57.9	1.36	78.5
730-735			4.8	12.0	33.2	50.0	95.2	0.0100	2.2	57.4	1.36	78.2
Station 211660-6 (Gotland Basin) φ 57^{0}17.03’ N λ 20^{0}07.14’ E Depth 241.3 m												
0-5		0.3	10.9	25.4	46.9	16.5	88.8	0.0040	2.1	79.8	1.15	92.0
5-10	0.3	0.3	16.1	33.9	36.9	12.5	83.3	0.0050	2.0	78.0	1.16	90.4
25-30	0.3	0.3	16.6	29.8	39.5	13.5	82.8	0.0050	2.0	75.3	1.18	89.0
45-50	1.4	1.7	14.1	28.3	37.4	17.1	82.8	0.0050	2.1	75.1	1.18	88.9
64-68			8.5	28.5	37.0	26.0	91.5	0.0040	2.7	78.9	1.15	90.8
105-110		0.4	15.5	39.1	25.6	19.4	84.1	0.0050	2.1	76.6	1.17	89.7
145-150		0.3	27.5	42.7	16.8	12.7	72.2	0.0070	1.9	68.6	1.24	85.3
185-189	0.3	0.6	25.2	35.0	17.5	21.4	73.9	0.0065	2.5	67.6	1.25	84.7
240-245	0.3	0.3	19.4	34.7	26.1	19.2	80.0	0.0060	2.2	66.6	1.26	84.1
265-270	0.6	0.6	17.0	43.0	18.5	20.3	81.8	0.0060	2.1	67.2	1.25	84.5
290-295	0.6	0.6	15.0	44.5	19.5	19.8	83.8	0.0060	2.1	67.7	1.25	84.8
322-327	0.3	0.3	17.8	39.9	22.4	19.3	81.6	0.0060	2.1	67.2	1.26	84.5
350-354	0.3	0.3	15.0	23.5	42.5	18.4	84.4	0.0040	2.2	68.8	1.24	85.4
354-360		0.4	13.4	15.6	45.2	25.4	86.2	0.0030	2.5	68.6	1.24	85.3
380-384	0.3	0.3	15.5	23.0	30.2	30.7	83.9	0.0030	2.8	68.2	1.25	85.1
413-418		0.2	15.3	21.1	47.9	15.5	84.5	0.0040	2.1	64.6	1.28	82.9
425-430		0.2	18.0	23.7	49.8	8.3	81.8	0.0043	1.9	61.2	1.32	80.7
440-445		0.3	18.5	28.1	32.4	20.7	81.2	0.0046	2.4	61.6	1.32	81.0
445-450			16.7	21.0	38.5	23.8	83.3	0.0037	2.7	61.0	1.32	80.6
455-460		0.3	15.0	20.5	40.5	23.7	84.7	0.0036	2.6	61.2	1.32	80.8
470-475		0.3	8.2	26.6	40.7	24.2	91.5	0.0035	2.5	60.1	1.33	79.9
498-503		0.3	8.2	24.7	43.1	23.7	91.5	0.0034	2.4	60.5	1.33	80.3
525-530		0.2	7.9	24.8	47.1	20.0	91.9	0.0035	2.2	59.2	1.34	79.4
565-570			2.3	4.2	8.4	85.1	97.7	<0.001	>1.1	55.7	1.38	76.8
600-605			3.3	5.2	17.4	74.1	96.7	<0.001	>1.1	55.5	1.38	76.8
645-650			8.4	8.4	15.6	67.6	91.6	<0.001	>1.7	53.1	1.41	75.1
680-685			0.9	15.4	20.4	63.3	99.1	<0.001	>1.8	55.2	1.39	76.6
715-720			0.8	8.8	24.0	66.4	99.2	<0.001	>1.6	56.1	1.38	77.3
730-735			0.8	6.2	14.2	78.8	99.2	<0.001	>1.1	55.7	1.38	77.0
Station 211650-4 (Gotland Basin) φ 57^{0}18.3339’ N λ 20^{0}02.9907’ E Depth 239.6 m												
0-5		1.2	29.3	31.7	25.6	12.2	69.5	0.0070	2.4	66.3	1.27	83.9
30-35		1.0	25.0	28.7	27.0	18.3	74.0	0.0060	2.4	66.5	1.26	84.1
45-50		1.3	16.7	25.6	30.0	26.4	82.0	0.0040	2.9	66.2	1.27	83.9
60-65		1.0	12.0	23.4	33.1	30.5	87.0	0.0030	2.7	65.6	1.27	83.5
110-115		1.0	10.2	22.2	36.5	30.1	88.8	0.0030	2.6	63.2	1.30	82.0
130-135		0.5	9.5	19.0	34.3	36.7	90.0	0.0026	2.4	60.5	1.33	80.3
164-169			9.7	18.5	32.0	39.8	90.3	0.0020	>3.0	60.4	1.33	80.3
211-216			8.2	15.9	32.9	43.0	91.8	0.0020	>2.21	61.4	1.32	80.8
220-225			6.7	14.7	33.2	45.4	93.3	0.0020	>2.14	58.9	1.34	78.9
246-252			6.7	13.3	33.8	46.2	93.3	0.0014	>2.10	58.6	1.35	78.9
260-265			5.0	13.8	35.1	46.1	95.0	0.0014	>2.1	58.0	1.35	78.5
286-290			4.0	12.5	34.5	49.0	96.0	0.0010	>2.0	58.4	1.4	78.7
305-310			3.8	12.5	33.7	50.0	96.2	0.0010	>2.0	58.6	1.35	78.9
310-315			3.8	9.8	32.4	54.0	96.2	<0.001	>1.9	59.0	1.34	79.2
340-345			0.7	11.3	21.3	66.7	99.3	<0.001	>1.6	53.5	1.41	75.2
380-385			0.7	10.6	20.4	68.3	99.3	<0.001	>1.6	53.6	1.41	75.2
400-405			0.7	10.0	20.1	69.2	99.3	<0.001	>1.5	52.7	1.42	74.6
450-455			0.6	10.1	19.0	70.3	99.4	<0.001	>1.4	53.4	1.41	75.2
460-465			0.6	9.3	18.6	71.5	99.4	<0.001	>1.32	54.1	1.40	75.7
500-505			0.5	9.0	18.0	72.5	99.5	<0.001	>1.24	48.5	1.47	71.3
565-570			1.0	9.3	18.1	71.6	99.0	<0.001	>1.32	45.4	1.51	68.7

Interval, cm	Fractions, %							Md, mm	So	Moisture %	Density g/cm^3	Porosity %
	>0.1 mm	0.1-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	<0.01 mm					
Station 211670-7(North Central Basin) φ 58^{0}49.1622’ N λ 20^{0}15.1363’ E Depth 175.2 m												
0-5			10.4	21.7	53.7	14.2	89.6	0.0036	1.9	67.4	1.26	84.6
5-10			15.6	19.3	51.3	13.8	84.4	0.004	2.0	66.9	1.26	84.3
10-15			15.6	22.1	53.5	13.8	84.4	0.0037	2.1	66.9	1.26	84.3
20-25			11.2	22.0	52.5	14.3	88.8	0.0037	1.9	66.5	1.26	84.1
30-35		0.6	12.9	29.2	38.2	19.1	86.5	0.0033	2.2	66.5	1.26	84.1
47-53		0.6	14.8	28.6	37.5	18.4	84.5	0.0040	2.2	65.3	1.28	83.3
60-65			16.0	27.3	32.0	17.7	77.0	0.0040	2.2	65.6	1.27	83.5
86-91		0.6	16.4	18.8	42.6	21.6	83.0	0.0040	2.4	64.4	1.29	82.8
92-97		0.4	16.8	20.7	41.5	20.6	82.8	0.0038	2.4	59.7	1.34	79.8
100-105			16.9	20.4	40.8	21.9	83.1	0.0040	2.5	65.5	1.27	83.5
111-116			17.8	17.8	41.1	23.2	82.1	0.0040	2.6	65.2	1.28	83.3
135-140			9.9	13.8	46.7	29.6	90.1	0.0030	2.2	60.8	1.32	80.5
190-195			9.7	12.3	42.9	35.1	90.3	0.0020	2.2	61.5	1.32	80.9
240-245			6.4	12.1	44.6	36.9	93.6	0.0020	2.1	57.4	1.36	78.2
275-280			7.7	12.4	41.9	38.0	92.3	0.0020	2.3	57.8	1.36	78.5
315-320			4.0	10.2	42.9	42.9	96.0	0.0020	2.0	56.8	1.36	77.8
345-350			2.8	6.8	42.7	47.7	97.2	0.0010	1.9	56.1	1.38	77.3
Station 211670-4 (North Central Basin) φ 58^{0}49.1843 N λ 20^{0}15.2026’ E Depth 176.1 m												
100-105			5.5	19.4	36.9	38.2	94.5	0.0020	2.2	58.3	1.35	78.8
160-165			6.5	18.9	35.2	39.2	93.3	0.0020	2.2	56.1	1.38	77.3
190-195			6.8	18.0	37.2	38.0	93.2	0.0020	2.2	55.3	1.39	76.7
210-215			6.0	17.1	37.8	39.1	94.0	0.0020	2.2	54.7	1.39	76.2
240-245			6.5	15.9	37.7	39.9	95.5	0.0030	2.2	56.6	1.37	77.6
250-255			6.1	17.5	32.7	43.7	93.9	0.0020	2.1	55.8	1.38	77.0
275-280			5.9	16.0	31.9	46.2	94.1	0.0015	2.1	55.7	1.38	77.0
280-285			6.0	15.5	34.4	44.1	94.0	0.0017	2.1	55.1	1.39	76.5
295-300			10.0	18.0	37.6	34.4	90.0	0.0030	2.4	56.6	1.37	77.6
323-328			8.0	12.0	40.1	39.9	92.0	0.0020	2.1	56.5	1.37	77.6
330-335		0.4	3.4	14.0	46.1	36.1	96.2	0.0020	2.1	53.7	1.41	75.5
370-375			3.6	9.4	47.2	39.7	96.3	0.0020	2.0	56.0	1.38	77.2
400-405			9.8	24.2	45.8	20.2	90.2	0.0036	2.2	56.6	1.37	77.6
420-425			3.6	26.2	38.2	32.0	96.4	0.0030	2.4	53.0	1.42	75.0
465-470			4.0	9.6	30.6	56.4	96.6	<0.001	>1.9	55.0	1.39	76.5
485-490			3.4	13.9	30.2	52.5	96.6	<0.001	>2.0	56.2	1.38	77.3
515-520			2.0	10.7	35.0	52.3	98.0	<0.001	>1.6	52.6	1.42	74.7
Station 00/96/2/2GC-4 (North Central Basin) φ58^{0}49.10’ N λ 20^{0}15.17’ E Depth 175.8 m												
0-5	0.4	1.7	26.9	42.0	2.1	26.9	71.0	0.0075	4.0	76.9	1.17	89.9
0-5	1.7	3.5	34.5	21.2	0.5	38.6	60.3	0.0075	>5.2	75.7	1.18	89.2
5-10		0.3	5.4	21.4	71.6	1.3	94.3	0.0037	1.6	66.5	1.26	84.1
25-30		0.3	5.9	32.2	56.0	5.6	93.8	0.0042	1.7	62.9	1.30	81.8
54-59		0.6	14.3	32.3	44.3	8.5	85.1	0.0047	1.8	65.5	1.27	83.5
90-95		1.7	11.7	31.2	45.5	9.9	86.6	0.0040	1.9	62.6	1.30	81.7
112-117		1.7	22.9	33.4	18.1	23.9	75.4	0.0062	2.8	69.2	1.24	85.7
150-155		0.5	9.1	29.9	47.9	12.6	90.4	0.0041	1.9	60.6	1.33	80.4
190-195		0.3	7.8	23.9	50.9	17.1	91.9	0.0030	2.0	59.3	1.34	79.5
220-225		0.3	2.8	14.2	73.4	9.3	96.9	0.0030	1.6	61.6	1.32	81.0
260-265		0.2	4.6	19.6	68.3	7.3	95.2	0.0035	1.6	56.9	1.37	77.8
300-305			4.9	12.5	60.6	22.0	95.1	0.0028	1.9	58.0	1.36	78.6
300-305		1.0	7.4	22.0	59.8	9.8	91.6	0.0037	1.8	57.8	1.36	78.5
350-355		0.7	3.2	10.2	81.6	4.3	96.1	0.0032	1.5	56.9	1.37	77.8
350-355	0.9	0.9	6.1	11.3	56.8	24.0	92.1	0.0028	2.1	56.1	1.38	77.3
400-405			4.8	19.0	35.6	40.6	95.2	0.0021	>2.3	53.7	1.41	75.5
400-405			5.8	16.8	54.2	23.2	94.2	0.0030	2.1	55.0	1.39	76.5
409-415		0.3	16.8	16.0	54.8	12.1	82.9	0.0038	2.0	56.8	1.37	77.8
425-430		0.3	9.8	5.4	56.4	28.1	89.9	0.0026	>2.1	58.2	1.35	78.7
460-465		1.7	13.8	35.3	37.6	11.6	84.5	0.0051	1.9	55.1	1.39	76.5
480-485	0.9	1.8	15.5	11.8	41.2	28.8	81.8	0.0031	>2.7	54.9	1.39	76.4
505-510	1.9	1.9	4.9	7.3	43.8	40.2	91.3	0.0019	>2.0	54.3	1.40	75.5
530-535			2.0	3.5	40.2	54.3	98.0	<0.001	>1.8	56.0	1.38	77.2
530-535			1.9	1.9	36.4	59.8	98.1	<0.001	>1.6	55.9	1.38	77.1
545-550			1.9	6.3	47.5	44.3	98.1	0.0015	>1.8	56.3	1.38	77.6
Station 00/96/02/1GC-2 (North Central Basin) φ 58^{0}48.84’ N λ 20^{0}19.71’ E Depth 185.4 m												
0-5	0.5	2.8	19.9	42.6	27.8	6.5	76.9	0.0070	1.6	70.5	1.23	86.8
15-19	0.4	0.4	13.0	24.6	49.4	12.2	86.2	0.0040	1.9	64.7	1.28	83.0
20-25	0.4	1.2	20.5	23.6	44.3	10.0	77.9	0.0050	2.2	63.6	1.29	82.3
20-25	0.4	2.0	21.5	23.4	43.3	9.6	76.3	0.0050	2.0	64.2	1.29	82.7
20-25		1.6	24.9	26.4	38.4	8.7	73.5	0.0060	2.1	64.8	1.28	83.0
30-35	0.4	1.3	20.0	24.6	42.9	10.8	78.3	0.0050	2.1	65.1	1.28	83.2
50-55	0.4	0.8	19.9	25.9	40.8	12.2	78.9	0.0050	2.1	66.0	1.27	83.8
61-65	1.1	0.8	20.1	25.0	39.4	13.6	78.0	0.0040	2.2	73.9	1.19	88.3
65-69	0.5	0.5	30.5	28.5	21.0	19.0	68.5	0.0060	2.9	72.3	1.21	87.4
77-82	0.4	0.7	25.7	35.9	27.1	10.2	73.2	0.0070	2.1	64.7	1.28	83.0
130-135		0.3	10.0	22.4	58.1	9.2	89.7	0.0040	1.8	61.2	1.32	80.8
190-195		0.3	10.4	10.5	65.7	13.1	89.3	0.0030	1.7	60.2	1.33	80.1
260-265		0.5	10.3	11.6	54.8	22.8	89.2	0.0030	2.1	58.6	1.35	79.0
280-285		0.3	21.6	35.8	30.0	12.3	78.1	0.0060	1.9	63.7	1.29	82.4
291-296		0.6	18.6	18.0	42.7	20.1	80.8	0.0040	2.4	60.0	1.33	80.0
333-338		0.9	5.9	10.4	37.4	45.4	93.2	0.0010	2.0	56.1	1.38	77.3
365-370			4.5	4.7	44.8	46.0	95.5	0.0010	>1.9	57.0	1.37	77.9
380-385		0.2	4.9	5.6	40.2	49.1	94.9	0.0010	>1.9	55.6	1.38	76.9
440-445		0.2	1.7	4.6	9.2	84.3	98.1	<0.001	>1.1	53.3	1.41	75.2
500-505		0.2	2.8	4.7	11.5	80.8	97.0	<0.001	>1.1	55.2	1.39	76.6
570-575		0.2	4.3	8.9	22.5	64.1	95.5	<0.001	>1.7	49.8	1.60	79.8

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 34-39

Distribution of organic walled microfossils within single lamina from the Gotland Basin, and their environmental evidence

Wolfram W. Brenner

Abstract

Initial investigations on laminated sediments from the Gotland Basin show that it is possible to sample sediments in millimetre dimension for quantitative analysis of organic walled microfossils. This first result leads to the assumption, that in the investigated sequence extreme environmental variations within a few years take place. They are reflected in the microfossil content within single laminae. Especially the dinoflagellate cysts *Pyxidiniopsis psilata* and *Ataxiodinium choane* are only abundant in small layers within single lamina. From these results it can be assumed that the assemblage change of organic microfossils in the Litorina Sea phase reflects rather the frequency of specific environmental and/or climatic conditions than general assemblage changes of the microfossils. Additionally, the use of absolute abundance of specific organic-walled microfossils as sedimentation rate indicators is discussed.

☐ *Baltic Sea, Gotland Basin, laminated sediments, organic-walled microfossils, dinoflagellate cysts, environmental change.*

☐ *Wolfram Brenner [wbrenner@geomar.de], GEOMAR, Wischhofstr. 1-3, 24148 Kiel, Germany.*

☐ *Received 15 June 2001; accepted 19 November 2001.*

INTRODUCTION

In the Baltic proper today an area of almost 100 000 km^2 become periodically anoxic, and from this area 70 000 km^2 are covered with laminated sediments (Emelyanov 1988, Jonsson et al. 1990). During the marine-brackish Litorina and Post-Litorina phase of the Baltic Sea the sediments of this area are not continuos laminated, reflecting significant changes in the redox condition at the sediment – water interface even in the deepest parts (e.g. Sohlenius et al. 1996, Jonsson et al. 1990, Andrén et al. 2000, Winterhalter 1992, Sohlenius and Westman 1996, Lepland and Stevens 1998, Huckriede et al. 1996).

Laminated sediments provide the highest available resolution for studies of environmental changes in the fossil record. Due to the difficult preparation of single laminae for micropalaeontological analyses only few investigations have been done hitherto. The most common technique to prepare laminae from unconsolidated sediments is to impregnate the core with resins and to prepare thin sections. It is also possible to put a laminated sediment part without further preparation under a scanning electron microscope or to cut single laminae for micropalaeontological investigations (e.g. Hagadorn et al. 1993, Brodie and Kemp 1994, Grimm et al. 1997, Brenner 1998, Mingram 1998).

In contrast to annually or subannually laminated lake sediments, the lamination of marine sediments is much more complex and controlled by various factors. Even the causes for laminae succession of basins located close to each other can be different as for example the Californian Borderland Basins, Santa Barbara Basin, and Santa Monica Basin. Whereas the lamination in the Santa Barbara Basin is annually in response to the seasonal migration of the North Pacific High Pressure system, in the sheltered geographic position of Santa Monica Basin only strong El Niño Southern Oscillation events allow a deep water overturn, pointing to a laminae succession on 3-6 years time scale (Berelson 1991, Hickey 1991, Hagadorn et al. 1995). Beside the time variation for laminae there are also variations of laminae types within one laminated sequence. Brodie and Kemp (1994) describe three different types of laminae within a laminated sequence from the Peruvian coastal upwelling zone. One type is laminated in the sub-millimetre area and is thought to be annually varved. An other type is a solitary diatom ooze lamina with a thickness of 2-10 mm, which may represent a single diatom bloom as well as a period of several years. The third type is an irregular spaced lamina composed from couplets of diatom layers with a thickness of 1 mm and a terrigeneous influenced part with a thickness of 2-6 mm. The diatom layer represents a single diatom bloom, whereas the terrigeneous influenced part may represent several years. Further inconsistencies of the laminae successions, thought to be annual, are reported by Crusius and Anderson (1992), from the Black Sea.

In the Baltic Sea the composition of single laminae varies. Most common is a combination of light or white layers of rhodochrosite and organic rich grey to black layers composed by clay sediments and organic material. However, Sohlenius and Westman (1998), found layers in the north-western Baltic proper with a thickness up to 2 mm consisting almost entirely of diatoms, and layers up to 0,2 mm of chrysophyte cysts. They interpret these layers as single algae blooms which were deposited in restricted areas of the sea floor within a few days or weeks.

The origin of the rhodochrosite layers is caused by the inflow of oxygen rich Atlantic water into the Baltic Sea. The mechanism for concentration of manganese enriched layers is still controversial (e.g. Huckriede et al. 1996, Huckriede and Meischner 1996, Hartmann 1964, Suess 1979, Emelyanov 1986, Sternbeck and Sohlenius 1997, Lepland and Stevens 1998, Sohlenius and Westman 1998). Börngen et al. (1990) and Stigebrandt (1987) found a periodicity of approximate 15 years for stronger salt influxes into the Baltic Sea. Frequency and intensity of the major inflow of highly saline and oxygenated water into the Baltic Sea show a significant correlation with the North Atlantic atmospheric circulation leading to the assumption that the North Atlantic Oscillation (NAO) is the main influencing factor on the dynamic of the recent Baltic Sea System (Alheit et al. submitted, Koslowsky and Glaser 1999, Matthäus and Schinke 1994, Matthäus 1995, Hänninen et al. 2000).

This clearly shows, that laminated marine sediments can not be simply regarded as the "tree rings of the ocean" but rather as the product of interactive processes which are controlled by sedimentation mechanisms and environmental change. In principle, laminae are a seasonal to annual signal, which can be overwritten by other cyclic processes as NAO, and solar or lunar cycles, which influence the meteorological situation within few years to several decades or centuries.

The subject of this investigation are first improvements of the possibilities for detailed analysis on the origin of single laminae and their variation within a sequence, based on quantitative distribution of organic walled microfossils. These investigations can give a new insight in the dimension of environmental dynamics on annual to decadal scales as well as the velocity of environmental changes.

MATERIAL AND METHODS

The material for the present investigation has been taken from core 211 660-6 (57°17.0283N / 20°07.1386E) of *R/V Petr Kottsov* cruise in July and August at 314-316.5 cm depth below sediment surface. The sampled interval contains three lamina triplets which are composed of dark organic rich, a pale, and a white rhodochrosite layer. This interval is stratigraphically located at the top of the ecostratigraphic interval ESI V after Brenner (2001) of the Litorina Sea phase.

For subsampling the single laminae a quadratic subcore with a side-length of 2 cm were cut from the original core sample and transferred to a glass slide. The sides and the top of the subcore were cleaned with a spatula, so that the lamination could be observed from all sides.

The sample top was cut down to the surface of a lamina, which can be clearly identified by colour change. For the sampling itself, colour changes and sediment structures, which could be identified over the whole surface of the subcore, are used to differentiate the samples. The sediments were cut with a micro spatula.

Prior to the preparation of the organic walled microfossils the samples were freeze-dried. Defined quantities of *Lycopodium* spores have been added to the sample, to get a reference number for the absolute abundance of microfossils in the sediment. In the next step the samples were treated with 10% hydrochloric and 40% hydrofluoric acid to remove the carbonates and silicates. They were extensively washed through a six-micrometer sieve to remove the amorphous organic material. The residue was mounted on microscopic slides with glycerine jelly.

H. Kunzendorf generated the geochemical data with energy-disperse X-ray fluorescence (EDX) at the Gamma Dating Centre at Riso National Laboratory, Roskilde.

Age calculation for the sampled sequence

Voss et al. (2001) calculate a sedimentation rate of 0.16 mm/a for this time interval and Kotilainen et al. (2000) found in the same core deposition rates from 0.17 to 4.28 mm/a varying over very short time intervals with a linear average sedimentation rate of 0.88 mm/a. Huckriede et al. (1996) calculated the sedimentation rate of laminated sequences in the Gotland Basin to be 0.25 to 0.35 mm per year.

The investigated interval is composed of three triplets starting with a dark organic rich layer followed by a pale layer and end with a white rhodochrosite layer. The thickness of the upper two triplets, which are additionally identified by chemical analysis (Fig. 1), is 10 mm and the lower triplet 3 mm. This corresponds to a maximal age of approximately 60, respective 18 years for a triplet after the calculation of Voss et al. (2001) and a minimal age of 11 respective 3.5 years after the average calculation of Kotilainen et al. (2000).

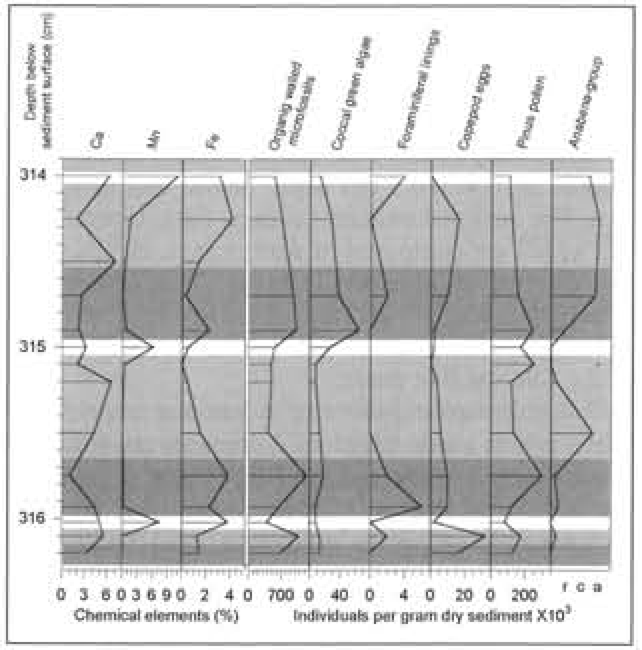

Fig.1. Distribution of Ca, Mn, and Fe in the laminated sequence, absolute abundance of selected organic-walled microfossils. Cyanobacteria of the *Anabena*-group occur in cluster up to several hundred cells make an absolute counting impossible; the abundance is therefore given in: r (rare) – c (common) – a (abundant). The shadowing of the graphic reflect the sediment colour and composition, the white part is the rhodochrosite layer and the grey and dark grey areas reflect the pale and dark sediments.

Cycles of 35 years (Brückner Cycle) and 22 years (Hale Double Sunspot Cycle) which are correlated to the solar activity and the NAO, are well known from Scandinavian tree-rings as well as from varved lake sediments (Hoyt and Schatten 1997, Negendank et al. 1990, Schove 1983, Landscheidt 1990). Taking into account the age calculation of Voss et al. (2001) and Kotilainen et al. (2000) as well as the possibility that the cycles mentioned above are reflected in the laminated sediments as interval between the rhodochrosite layers, it can be assumed, that a 1 cm laminae triplet has a sedimentation rate of 0.28 to 0.5 mm/a. Based on this calculation an age between 1 and 10 years for a single sample used for this investigations can be estimated. However, in this stage of the investigation, these correlations are rather speculative and a detailed analysis of a longer laminated sequence is essential to confirm the reflection of solar cycles in the lamina succession of the Gotland Basin.

Distribution of organic walled microfossil within the laminae

The sampled interval is stratigraphically located at the top of the ecostratigraphic interval ESI V in the Litorina Sea phase after Brenner (2001). The abundance of single species and the composition of the assemblage vary unexpectedly compared to the mean of all samples and to the bulk samples from the Litorina Sea phase of the same core as described by Brenner (2001). Especially *P. psilata* and *A. choane* show extreme changes in abundance within and between the different parts of the laminae (Fig. 2). Even the mean values of the microfossil abundance for the three investigated lamina triplets vary significantly (Fig. 3). Whereas in the upper two triplets the absolute abundance of *O. centrocarpum, L. machaero-phorum* and *Spiniferites* spp. is nearly constant, the abundance in the lower triplet is approximately half (Fig. 3). A similar distribution can be found for pine pollen and for organic walled microfossils in general. Assuming that *O. centrocarpum* is an opportunistic species which is not significantly influenced by environmental changes in the investigated interval, and the distribution of pine pollen do not vary much within a few decades, this finding points to a nearly double sedimentation rate for the lower triplet. Taking this assumption into account, no significant change in the accumulation rate of *O. centrocarpum, L. machaerophorum, Spiniferites* spp. and pine pollen can be found in the three laminae triplets. The absolute abundance of these microfossils may therefore be a good proxy for sedimentation rate.

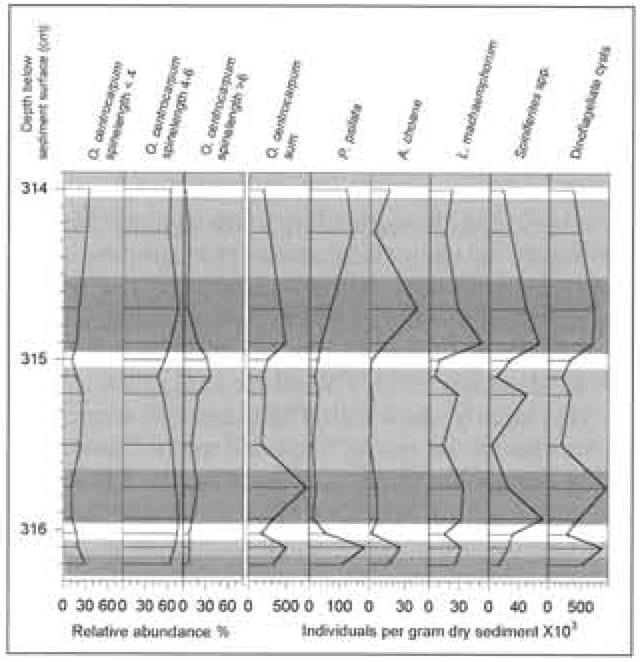

Fig. 2. Relative distribution of *O. centrocarpum* with different processes length, which can be interpreted as salinity signal. Absolute abundance of selected dinoflagellate cysts. The shadowing of the graphic reflect the sediment colour and composition, the white part is the rhodochrosite layer and the grey and dark grey areas reflect the pale and dark sediments.

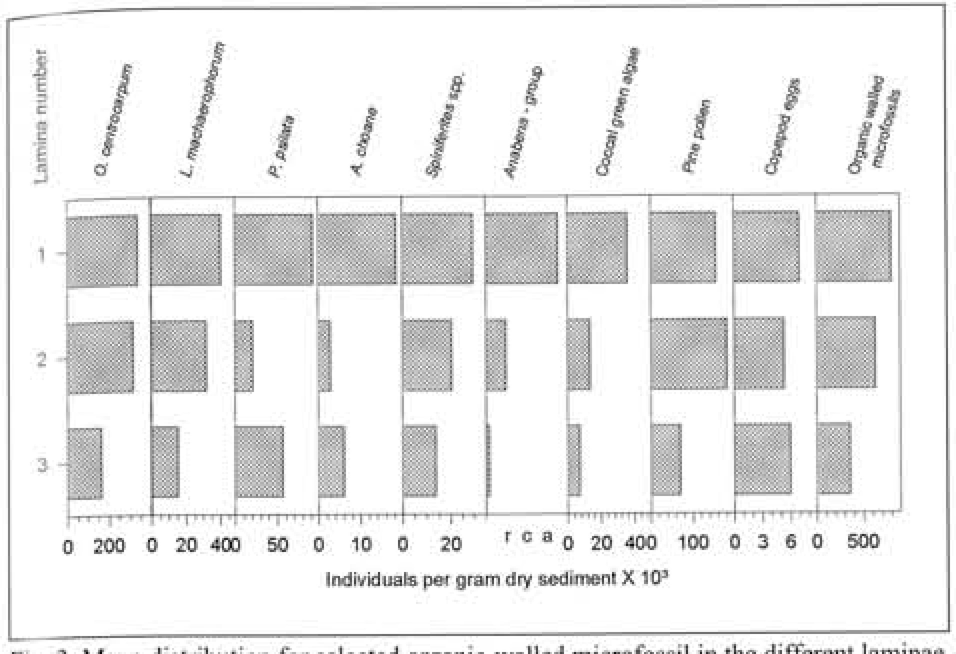

Fig. 3. Mean distribution for selected organic-walled microfossil in the different laminae triplets. Cyanobacteria of the *Anabena*-group occur in cluster up to several hundred cells make an absolute counting impossible; the abundance is therefore given in: r (rare) – c (common) – a (abundant).

P. psilata and *A. choane*, however, are drastically reduced in the middle triplet, coccal green algae are dominant in the uppermost triplet and nearly no cyanobacteria can be found in the lower triplet (Fig. 3). This suggest, that these organisms need specific environmental conditions which occur only in intervals of several years or decades and that those are different to the mechanisms that trigger the laminary sedimentation.

In general, the abundance of organic walled microfossils is higher in the dark parts of the lamina pointing to a higher accumulation of organic material. This can be caused by higher primary productivity as well as by a reduced sedimentation of inorganic material as suggested by Lepland and Stevens (1998) for the Landsort Deep, roughly 180-km north west of the Gotland Basin. No significant abundance change can be found between the pale intervals and the rhodochrosite layer in the upper two triplets, suggesting that there is no difference in sedimentation rate between the pale and the manganese enriched rhodochrosite layer (Figs. 1, 2). In the lower rhodochrosite layer a decrease of organic-walled microfossil abundance suggest a higher sedimentation rate for this layer.

DISCUSSION

Already the distribution of organic-walled microfossils in the investigated lamina triplets shows that there are environmental variations within the single triplets and that there is no correlation between sedimentological processes and the environmental influence on the composition of the organic-walled microfossils assemblage (Fig. 3). Much more differentiation of the organic-walled microfossil assemblage can be seen between the single laminae (Figs. 1, 2). In the dark laminae of the upper two triplets, the dinoflagellate cyst abundance is higher than in the pale part and in the rhodochrosite layer, leading to the assumption that there was a significant higher primary production or the sediment accumulation rate was lower as proposed by Lepland and Stevens (1998). Within the lower triplet, however, the accumulation rate of organic walled microfossils is higher in the pale layer than in the dark layer suggesting that the correlation between sediment colour and productivity should be used carefully.

Assuming that there is no significant change in the forest composition within a few decades up to a century, pine pollen seems to be useful for calculation of the sedimentation rate. The nearly identical abundance variation of the complete organic-walled microfossils assemblage with the pine pollen record seems to confirm the assumption that this value can be used as proxy for sedimentation rates. Identical absolute abundance variation can be found by the dinoflagellate cyst *O. centrocarpum*. Since this cyst is the dominant form in the whole Litorina Sea phase in the central Baltic Sea (Brenner 2001) and it is assumed that the mean productivity within few years do not change significant, this species may be also a useful proxy for sedimentation rates. Based on this assumption, a nearly identical sedimentation rate for the upper two laminae triplets can be proposed, where the sedimentation rate in the pale interval is slightly higher than in the dark one. In the lower triplet however, the distribution of the abundance in the pale and dark interval is vice versa, suggesting that different processes lead to the formation of this lamina.

Furthermore, if the assumption of Huckriede and Meischner (1996) that the sedimentation of the rhodochrosite layer is a rapid process is true, a significant decrease in microfossil abundance should be take place in those layers. Within the investigated sequence the abundance of microfossils in the rhodochrosite layer of the upper two rhodochrosite layers do not change or is continuos compared to the sample above and below, whereas in the lower rhodochrosite layer most organic-walled microfossil show a decrease in abundance (Figs. 1,2). This shows that there is not necessarily an increase in the sediment accumulation rate during sedimentation of rhodochrosite layers and possibly different processes leads to the formation and sedimentation of rhodochrosite.

Relative salinity changes can be identified by the variation of spine length of *O. centrocarpum* (Brenner 2001, Dale 1996), which suggest a slightly higher salinity only in the dark interval at 315.7 to 315.9 cm core depth and in the upper part of the pale interval and the rhodochrosite layer at 315.0 to 315.2 cm (Fig. 2). This finding suggest that there is no correlation between the surface salinity and the sediment succession or lamina formation. The missing of correlation between salinity and dinoflagellate cyst abundance and assemblage is obvious in the investigated sequence, suggesting that this signal might be overwritten by other environmental influences and should be carefully used to interpret the palaeosalinity.

Another very interesting finding is the abundance variability of several dinoflagellate species as *P. psilata* and *A. choane* which are only abundant in the upper and lower triplet and only few specimen are present in the triplet between 315 and 316 cm (Fig. 2). Coccal green algae are only common in the upper triplet with the highest abundance in the lower part of the dark interval, and cyanobacteria of the *Anabena*-group are only present in larger numbers in the upper triplet and in the basal part of the pale interval of the middle triplet (Fig. 1). The fact that some species occur only in specific layers in larger numbers lead to the assumption that they are blooming only under very specific environmental conditions which occur in a frequency of several decades in the case of the investigated sequence. In contrast, no extreme or rapid abundance change of those species can be found, if a sample size of 1 cm is used, as it is the case for the investigation of the whole core 211 660-6 by Brenner (2001). This finding has a significant consequence for the interpretation of relative and absolute abundance change of microfossil assemblages and the environmental interpretation. The increase or decrease of species abundance in a sediment succession must therefore not necessarily be the effect of higher or lower abundance of the species in the primary environment, it could be as well an accumulation or frequency variation of specific environmental conditions which favour the blooming of specific species. Following this hypothesis, natural ecosystems seem to be highly dynamic and extreme changes of the fossil assemblage can take place within several years whereas the system is still stable. Assemblage changes, as for example during the Litorina Sea phase in the Gotland Basin (Brenner 2001), may reflect therefore rather the frequency of specific weather and consequently environmental condition as an environmental change suggested by different assemblage compositions during the different intervals. However, to confirm this hypothesis, which has the potential for a new understanding of the climate driven environmental dynamics and stability, longer laminated sections from different localities must be studied.

Acknowledgements

Thanks are due to Prof. J. Thiede, who facilitates this investigation at GEOMAR, Kiel and Prof. A. Rios-Netto for the possibility to finalise the manuscript at LabMicro, Federal Universidade do Rio de Janeiro. Further thanks are due to Prof. M. Kabailienė and an anonymous reviewer for helpful comments on the manuscript. This work was supported by the European Commission through the BASYS "Baltic Sea System Studies" project (contract number MAS3-CT96-0058.

References

Alheit, J., Lehmann, A. & Winterhalter, B. (submitted): The North Atlantic climate influence on the Baltic Sea environment.

Andrén, E., Andrén, T. & Kunzendorf, H. 2000: Holocene History of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10,* 621-636.

Berelson, W. M. 1991: The flushing of two deep sea basins, southern California Borderland. *Limnology and Oceanography 36,* 1150-1166.

Börngen, M., Hupfer, P. & Olberg, M. 1990: Occurrence and absence of strong salt influxes into the Baltic Sea. *Beiträge zur Meereskunde 61,* 11-19.

Brenner, W. W. 1998: Grundlagen uns Anwendungsmöglichkeiten der Mikro-Absorptionsphotometrie for organisch-wandige Mikrofossilien. *GEOMAR Report 76,* 141.

Brenner, W. W. 2001: Organic walled microfossils from the central Baltic Sea, indicators of environmental change and base for ecostratigraphic correlation. *Baltica 14*, 40-51.

Brodie, I. & Kemp, A. E. 1994: Variation in biogenic and detrital fluxes and formation of laminae in late Quaternary sediments from Peruvian coastel upwelling zone. *Marine Geology 116,* 385-398.

Crusius, J. & Anderson, R. F. 1992: Inconsistencies in accumulation rates of Black Sea sediments inferred from records of laminae and ^{210}Pb. *Paleooceanography 7,* 215-227.

Dale, B. 1996: Dinoflagellate cyst ecology: modeling and geological applications. *In* Jansonius, J. & McGregor, D. C. (Eds.): *Palynology: principles and applications.* American Association of Stratigraphic Palynologists Foundation, 1249-1275.

Emelyanov, E. M. 1986: Basins of the Baltic Sea - Traps for elements. *Finnish Marine Research 253,* 79-96.

Emelyanov, E. M. 1988: Biogenic sedimentation in the Baltic Sea and its consequences. *In* Winterhalter, B. (Ed.): *The Baltic Sea. Geological Survey of Finland, Special Paper,* 127-135.

Grimm, K. A., Lange, C. B. & Gill, A. S. 1997: Self-sedimentation of phytoplankton blooms in the geologic record. *Sedimentary Geology 110,* 151-161.

Hagadorn, J. W., Flocks, J. G., Stott, L. D. & Gorsline, D. S. 1993: A simple method to obtain high-resolution (milimeter-thick) samples from laminated sediments. *Journal of Sedimentary Petrology 63,* 755-758.

Hagadorn, J. W., Stott, L. D., Sinha, A. & Rincon, M. 1995: Geochemical and sedimentological variations in interannually laminated sediments from Santa Monica Basin. *Marine Geology 125,* 111-131.

Hänninen, J., Vuorinen, I., Hänninen, J., Viitasalo, M., Helminen, U., Kuosa, H. & Hjelt, P. 2000: Climatic factors in the Atlantic control the oceanographic and ecological changes in the Baltic Sea. *Limnology & Oceanography 45,* 703-710.

Hartmann, M. 1964: Zur Geochemie von Eisen und Mangan in der Ostsee. *Meyniana 14,* 3-20.

Hickey, B. M. 1991: Variability in two deep coastal basins (Santa Monica and San Pedro) off southern California. *Journal of Geophysical Research 96,* 16689-16708.

Hoyt, D. V. & Schatten, K. H. 1997: The role of the sun in climate change. Oxford University Press, New York - Oxford.

Huckriede, H., Clasen, S. & Meischner, D. 1996: Hydrographic and climatic changes recorded in Holocene sediments of the Central Baltic Sea. *Baltica 9,* 76-91.

Huckriede, H. & Meischner, D. 1996: Origin and environment of manganese-rich sediments within black-shale basins. *Geochimica et Cosmochimica Acta 60,* 1399-1413.

Jonsson, P., Carman, R. & Wulff, F. 1990: Laminated sediments in the Baltic; a tool for evaluating nutrient mass balances. *Ambio 19,* 152-158.

Koslowsky, G. & Glaser, R. 1999: Variations in reconstructed ice winter severity in the western Baltic from 1501 to 1995, and their implications for the North Atlantic Oscillation. *Climatic Change 41,* 175-191.

Kotilainen, A. T., Saarinen, T. & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166,* 51-64.

Landscheidt, T. 1990: Relationship between rainfall in the northern hemisphere and impulses of the torque in the sun's motion. *In* Schatten, K. H. & Arking, A. (Eds.): *Climate impact of solar variability.* Greenbelt, NASA, Washington, D.C., 260 p.

Lepland, A. & Stevens, R. L. 1998: Manganese authigenesis in the Landsort Deep, Baltic Sea. *Marine Geology 151,* 1-25.

Matthäus, W. 1995: Natural variability and human impacts reflected in long-term changes in the Baltic deep water conditions - a brief review. *Deutsche Hydrographische Zeitschrift 47,* 47-63.

Matthäus, W. & Schinke, H. 1994: Mean atmospheric circulation patterns associated with majior Baltic inflows. *Deutsche Hydrographische Zeitschrift 46,* 321-339.

Mingram, J. 1998: Laminated Eocene maar-lake sediments from Eckfeld (Eifel region, Germany) and their short-term periodicities. *Palaeogeography, Palaeoclimatology, Palaeoecology 140,* 289-305.

Negendank, J. F. W., Brauer, A. & Zolitschka, B. 1990: Die Eifelmaare als erdgeschichtliche Fallen und Quellen zur Rekonstruktion des Palaeoenvironment. *Mainzer geowissenschaftliche Mitteilungen 19.*

Schove, J. E. 1983: Sunspot Cycles. Hutchinson Ross Publishing, Stroudsburg, Pennsylvania.

Sohlenius, G., Sternbeck, J., Andrén, E. & Westman, P. 1996: Holocene history of the Baltic Sea as recorded in a sediment core from the Gotland Deep. *Marine Geology 134,* 183-201.

Sohlenius, G. & Westman, P. 1996: Palaeoenvironment in the Ancylus Lake and the Litorina Sea as reflected in sediments from the north-west Baltic proper. *Quaternaria (Stockholm Univ.) 3,* 15.

Sohlenius, G. & Westman, P. 1998: Salinity and redox alteration in the northwestern Baltic proper during the late Holocene. *Boreas 27,* 101-114.

Sternbeck, J. & Sohlenius, G. 1997: Authigenic sulfide and carbonate mineral formation in Holocene sediments of the Baltic Sea. *Chemical Geology 135,* 55-73.

Stigebrandt, A. 1987: A model for the bottom currents of the Baltic deep water. *Journal of Physical Oceanography 17,* 1772-1785.

Suess, E. 1979: Mineral phases formed in anoxic sediments by microbial decomposition of organic matter. *Geochimica et Cosmochimica Acta 43,* 339-352.

Voss, M., Kowalewska, G. & Brenner, W. 2001: Microfossil and biogeochemical indicators of environmental changes in the Central Gotland Basin during the last 10,000. *Baltica 14,* 131-140.

Winterhalter, B. 1992: Late-Quaternary stratigraphy of the Baltic Sea basins - a review. *Bulletin of the Geological Society of Finland 64,* 189-194.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 40-51

Organic-walled microfossils from the central Baltic Sea, indicators of environmental change and base for ecostratigraphic correlation

Wolfram W. Brenner

Abstract

Sediment cores from Bornholm Basin, Gotland Basin and North Central Basin were studied for their organic-walled microfossil assemblages. Absolute abundance and morphometric measurements of these microfossils are used for an ecostratigraphic correlation and interpretation of the environmental changes in the central Baltic Sea basins. Increasing abundance of freshwater phyto- and zooplankton during the final stage of the Ancylus Lake point to a slow eutrophication. Assemblage composition of organic-walled microfossils and changes in processes length of dinoflagellate cyst are used for interpretation of the salinity variation of the Litorina Sea stage. A rapid decrease of absolute dinoflagellate cyst abundance in all three basins occurs at the late Litorina Sea stage. The Post-Litorina Sea stage is marked by a low abundance of dinoflagellate cysts and organic walled microfossils in general. In the uppermost metre of the cores from all three basins a significant increase in the abundance of cladoceran, coccal green algae, and copepod eggs is present, whereas the abundance of dinoflagellate cysts is still low.

☐ Baltic Sea, Bornholm Basin, Gotland Basin, North Central Basin, organic walled microfossils, Holocene, paleosalinity, paleoecology, ecostratigraphic correlation.

☐ *Wolfram Brenner [wbrenner@geomar.de] GEOMAR, Wischhofstr.1-3, 24148 Kiel, Germany.*

☐ *Received 25 June 2001; accepted 9 November 2001.*

INTRODUCTION

In contrast to the inorganic skeletal elements of calcareous or siliceous microfossils organic-walled microfossils consist of extremely stable biopolymeres such as sporopollenin, cutin or chitin. These substances are common in algae, plants and invertebrates remains. Therefore, organic walled microfossils comprise for example spores and pollen (palynomorphs sensu stricto) as well as cyanobacteria, dinoflagellate cysts, leaf cuticle, tintinnid cysts, and even eggs and other remains of annelids, crustacean, and insects. Due to the different environmental preferences of the various organisms, ranging from terrestrial and freshwater to marine forms, organic-walled microfossils are an excellent tool for paleoecological studies.

Up to now, most micropalaeontological investigations in the Baltic Sea deal with siliceous microfossils (e.g.: Abelmann 1985; Andrén and Andrén 1999; Miller and Risberg 1990; Witkowski 1994), or pollen (e.g.: Averdieck 1972; Eriksson 1994; Eronen et al. 1990; Stelle et al. 1994). Only few investigations have been carried out on dinoflagellate cysts in the Baltic Sea and other low salinity environments (Dale 1996; Ellegaard 2000; Matthiessen and Brenner 1995; Matthiessen and Brenner 1996; Matthiessen and Brenner in press; Nehring 1994a; Nehring 1994b; Wall et al. 1973). The present investigation gives a first ecostratigraphic zonation and correlation based on organic walled microfossils in the Central Baltic Sea.

MATERIAL AND METHODS

The sediment cores were sampled during a cruise with *R/V Petr Kottsov* in July and August 1997 by using a box core devise (Table 1). Due to the high water content, the uppermost sediments were mixed and therefore not useful for investigation. Fore this reason two cores from the North Central Basin from the same locality are used (Table 1): one with a longer record (211670-4) and another with undisturbed sediments at the top of the core (211670-7).

Table 1. Core sampling localities

Locality	Core no.	Latitude	Longitude	Depth	Used interval
Bornholm Basin	211630-9	55°22,6500N	15°23,8463E	93,57m	39-540cm
Gotland Basin	211660-6	57°17,0283N	20°07,1386E	241,3m	34-681cm
North Central Basin	211670-4	58°49,1843N	20°15,2026E	176,1m	200-670cm
North Central Basin	211670-7	58°49,1622N	20°15,1363E	175,2m	54-200cm

The sediment cores were sampled continuously with 1 m long U-tubes with a diameter of 2 cm, and cut afterward in 1 cm slices. All samples were freeze-dried. Samples for microfossil investigations were treated with 10% hydrochloric and 40% hydrofluoric acid to remove the carbonates and silicates and extensively washed through a six-micrometer sieve to remove the amorphous organic material. The residues were mounted on microscopical slides with glycerine jelly. Prior to the preparation, a defined quantity of *Lycopodium* spores (10^5 spores per gram dry sediment) was added to the sample, to make the analysis of the absolute abundance of microfossils in the sediment possible.

ENVIRONMENTAL SIGNIFICANCE OF ORGANIC WALLED MICROFOSSILS

Dinoflagellate cysts

Dinoflagellates comprise groups of predominantly unicellular, flagellated organisms that possess both photosynthetic (autotroph) and non-photosynthetic (heterotroph) members. Some species are restricted to the marine realm, others tolerate a wide range of salinity, and others are restricted to freshwater. An important factor for interpreting the fossil record of dinoflagellate cysts is, that only a small part of the living dinoflagellate produce cysts, and the cyst building takes place within a few hours or days and reflect therefore the environmental conditions during a small time interval.

(Dale 1996) summarised the basic elements of the dinoflagellate cyst salinity signal, which is based among others on unpublished core top samples from the Baltic and Black Sea as followed:

- Most of the coastal/neritic cyst species tolerate a broad salinity range from normal marine salinity of about 35 psu to reduced marine salinity of about 20 psu. Below 20 psu the species diversity decrease rapidly.

- Environments with salinity below 3 psu are characterised by cyst assemblages restricted to *Operculodinium centrocarpum (Protoceratium reticulatum)* and small *Spiniferites*. The salinity interval from 3-10 psu in the Black Sea is characterised by the presence of *Pyxidinopsis psilata (Tectatodinium psilatum)*, and above 7 psu there is a general increasing abundance of *Lingulodinium machaerophorum* (*Lingulodinium polyedrum* = *Gonyaulax polyedra*).

- The processes length of *O. centrocarpum*, *L. machaerophorum*, and *Spiniferites spp.* is reduced in water with low salinity.

Recent investigations of dinoflagellate cyst assemblages from surface sediments from the western Baltic, Skagerrak, and North Sea suggest a further signal at about 15 psu where the *O. centrocarpum* dominated low salinity assemblage change to a *L. machaerophorum* dominated assemblage (Matthiessen and Brenner, in press). This signal, however, must be carefully used, because *L. machaerophorum* is in addition an indicator for eutrophication, and assemblage changes can be triggered by nutrients (Dale and Fjellsa 1994; Dale 1996). Furthermore, Reid (1974) and Turon (1984) reported, that *L. machaerophorum* is often found in sediments representing cold winters and warm summers, and Bakken and Dale (1986) reported, that it is not found in areas where summer sea-surface temperature is less than 10°C.

The environmental preference of *Ataxiodinium choane* (*Gonyaulax spinifera*) is not well understood, Dale (1983; 1996) regards it as a cold-temperate species and Wall et al. (1977) as an estuarine form. After Edwards and Andrle (1992) the main distribution of *A. choane* is in areas with a winter surface temperature between 5 and 10°C and a summer surface temperature between 11 and 14°C.

P. psilata is an abundant species in the Black Sea with a main distribution at salinity's between 3 and 7 psu (Dale 1996; Wall and Dale 1973; Wall et al. 1973), therefore it is an indicator of low salinity. Dale (1996) and Mudie et al. (2001) have discussed the problem whether *P. psilata* is the end member in an environmental induced morphological graduation from normally long processes through no processes of *O. operculatum* or a separate species. In the Baltic Sea this species is only present in a small interval with high abundance, whereas in other intervals with similar salinity only few or no *P. psilata* could be found, suggesting that *P. psilata* is a separate species. Furthermore, investigations of single laminae (Brenner 2001) show that *P. psilata* occur only in specific laminae in large numbers, whereas in the laminae between only few specimens are present and that there is no correlation with the abundance of *O. centrocarpum* with short processes. This shows clearly that the occurrence and abundance of *P. psilata* is controlled by additional factors to salinity, which are still unknown.

Green algae

Pediastrum boryanum and *Pediastrum kawraiskyi* dominate the coccale green algae assemblage in the investigated sediments, only few specimens of other *Pediastrum* species, *Botryococcus, Scenedesmus* and *Staurastrum* are present. *Pediastrum* spp. is a common algae in nutrient rich, shallow freshwater, often used as indicator for eutrophication and acidification of lakes (e.g. Cronberg 1982a; Cronberg 1982b; Rosén 1981; Willén 1992). Principally, many coccal green algae are able to survive much higher salinity than 10 psu, but higher NaCl concentrations inhibit the cell division and no further breeding is possible (Brenner and Foster 1994; Latala 1991; Setter and Greenway 1979; Soeder and Stengel 1974).

Two species, *P. boryanum* and *P. kawraiskyi,* are known to be more common in coastal brackish water of the Baltic Sea than in the adjacent rivers (e.g. Bandel 1940; Brandes 1939, Brandt 1896; Kell 1985; Kell 1986; Matthiessen and Brenner 1996; Pankow 1990; Schröder 1897). *Pediastrum duplex* and *Pediastrum simplex* are only known from salinity below 5 psu (Kell 1981; Kell 1985, Pankow 1990). Therefore, autochthonous high abundance of *Pediastrum* in the fossil record of brackish water areas is only possible in shallow coastal areas with a salinity below 10 psu, and the assemblage will be dominated by *P. boryanum* and *P. kawraiskyi*. This leads to the assumption, that he high abundance of the latter specimens in the Gotland Basin may be an indicator for transport by currents from the coastal area into the deeper basins rather than high river runoff.

Cladoceran

Cladoceran are dominant freshwater species. Only few species are present in brackish water or coastal sea area (e.g. Bainbridge 1958; Hofmann 1987; Poggensee and Lenz 1981; Struck et al. 1998). Survival experiments with *Bosmina longispina*, the dominant species in the brackish water of the central Baltic Sea, show best adaptation to a salinity range between 2.5 and 7.5 psu. The animals do not tolerate a salinity of 0.5 psu, and survival rates decrease at higher temperatures with a salinity of 10 psu (Ackefors 1971; Hofmann 1987; Hofmann 2001).

Copepod eggs

Copepod eggs are described from various recent marine sediments, but a large number, particularly the fossil forms, are still not investigated in detail, neither in ecological preferences nor in taxonomy (e.g. Lindley 1986; Lohmann 1904; Marcus 1990; Van Waveren 1993; Van Waveren 1994).

Notable is the significant low abundance of copepod eggs during the salinity maximum in the Baltic Sea and the increased abundance during the Post-Litorina Sea stage. This phenomenon occurs in all three basins and can not be caused by decreasing salinity, because the same species are abundant in the North Sea (Brenner, unpublished data), and similar forms are found in the Banda Sea (Van Waveren 1994) suggesting that they are indicating higher marine conditions. A selective preservation can be excluded since the few eggs in the Litorina Sea stage are well preserved. Possibly food availability or other environmental factors rather than salinity control the abundance of copepod eggs in brackish water sediments. However, to explain the distribution of copepod eggs further investigations are needed.

Blue-green algae (cyanobacteria)

Fossil cyanobacteria are well known in Precambrian and Palaeozoic sediments (e.g. Knoll and Golubic 1992; Nyberg and Schopf 1984; Strother et al. 1983; Wicander et al. 1996). From Mesozoic to Holocene sediments, however, only few palaeontological reports on cyanobacteria are published (e.g. Batten and van Geel 1985; Livingstone and Jaworski 1980; Van Geel et al. 1994).

In the Central Baltic Sea (North Central and Gotland Basin) most of the fossil cyanobacteria and their resting stage (akinets) found in the sediments can be assigned to the genus *Anabena*. In the Bornholm Basin few additional forms are present in the sediment, which can be assigned to the *Rivularia*-group. The lack of "biological characteristics" in fossil cyanobacteria hampers the taxonomic identification of the different species at this stage of the investigation, and the cyanobacterial remains are tentatively assigned to the *Anabena*-group and the *Rivularia*-group. Nevertheless, cyanobacteria are useful indicators of eutrophication (Van Geel et al. 1994; Voss et al. 2001).

Acritarchs

Hensen (1887) described a row of plankton organisms with unknown affinity as Sternhaarstatoblast (now *Radiosperma*), Barbierbeckenstatoblast (now *Halodinium*) and Röhrenstatoblast (now *Hexasterias*) from the Baltic and North Sea. The reported highest

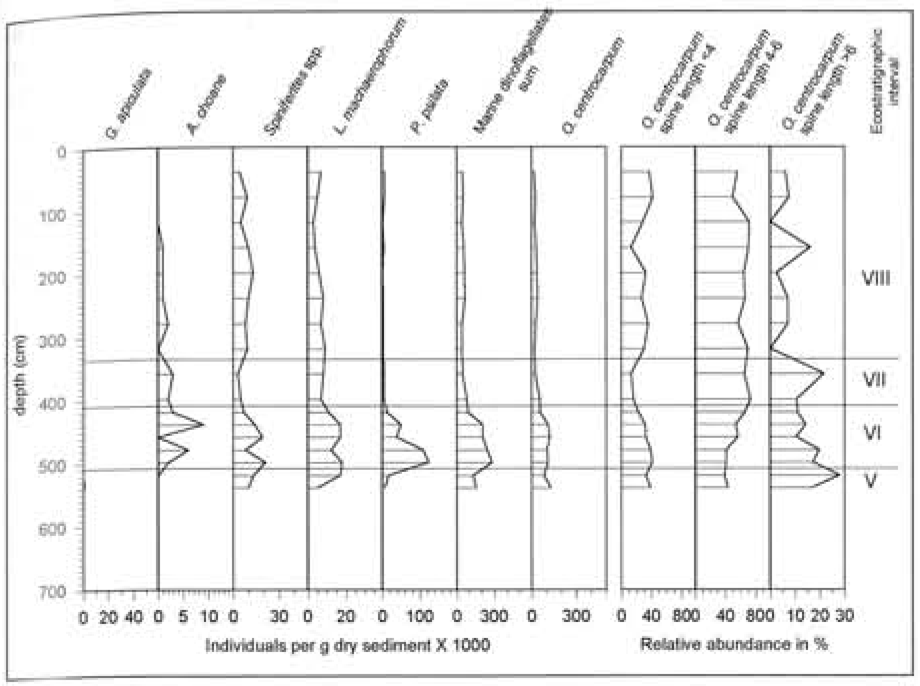

Fig. 2. Distribution of selected dinoflagellate cysts from Bornholm Basin, core 211630-9. Left columns show the absolute abundance of the cysts in the sediment, please note the different scales. The right three columns give the processes length frequency of *O. centrocarpum,* which can be directly used as salinity indicator (see text for details).

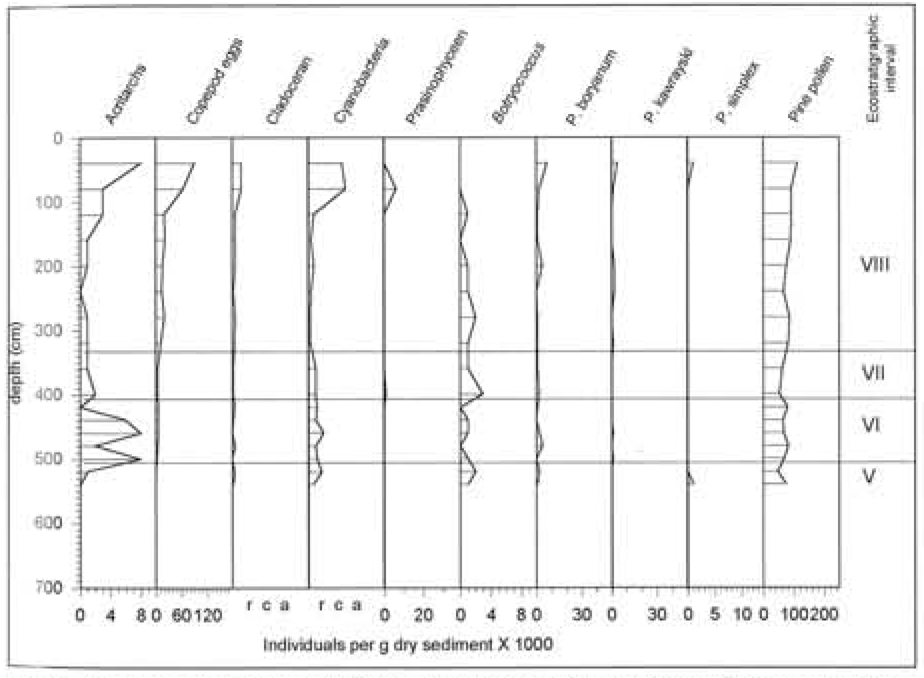

Fig. 1. Absolute abundance of selected organic walled microfossils from Bornholm Basin, core 211630-9, please note the different scales. Cladoceran remains are represented by fragments, and cyanobacteria by colonies of various size. Therefore no absolute values can be given for these two microfossil groups and the abundance is given by r = rare, c = common, and a = abundance.

abundance of *Radiosperma* is in the plankton of central Baltic Sea, leading to the assumption that *Radiosperma* is adapted to lower salinity (e.g. Apstein 1906; Driver 1908; Leegaard 1920; Merkle 1910). However, this organism group is also reported from the seas of Barents and Kara (Meunier 1910), the Laptev Sea (Kunz-Pirrung 1997) and even from upwelling areas off Peru (Biebow 1996) and the Guanabara Bay at Rio de Janeiro (Brenner, unpublished data). Therefore, additional factors to salinity may control the occurrence of this enigmatic organism group, which still is of unknown biological affinity.

Distribution of organic-walled microfossils in the Central Baltic Sea

In general the sediments from the Bornholm Basin (BB, Figs. 1, 2) contain less organic walled microfossils than those from the Gotland Basin (GB; Figs. 3, 4) and North Central Basin (NCB, Figs. 5, 6). The highest absolute abundance of dinoflagellate cyst in the investigated sediments is 283 (BB), 480 (GB) and 474 (NCB) X 10^3 cysts per gram dry sediment, and in all three cores located at the lower part of the ecostratigraphic interval ESI VI (Figs. 2, 4, 6). This difference between BB and the other basins may be caused by higher sedimentation rates rather than by environmental differences (compare Figs. 1, 3, 5), whereas the distribution of species shows clear environmental differences between all three basins. The highest absolute abundance of *O. centrocarpum* shows a clear preference for the Gotland Basin, whereas *P. psilata* have its distribution maximum at the North Central Basin. The portion of *O. centrocarpum* with short processes generally increases from south to north. Other dinoflagellate cysts which are present in lower numbers such as *Spiniferites* spp., *L. machaerophorum,* and *A. choane* do not show a significant preference and can therefore be regarded as opportunistic species.

A significant difference in the distribution of coccal green algae (mainly *Pediastrum* spp.) can be found in all three basins. In all investigated samples of the Bornholm Basin only few specimens could be found (Fig. 1), whereas in the Gotland Basin two significant abundance maximum occur (Fig. 3; ESI IX and ESI VI). In the North Central Basin only one abundance maximum in ESI IX can be found (Fig. 5).

ECOSTRATIGRAPHY AND CORRELATION

During the Holocene no significant evolutionary changes occur, which are useful for biostratigraphic zonation and correlation. For subdivision of stratigraphic useful units, assemblage changes and single abundance maxima of the whole suit of organic walled microfossils as well as changes in spine lengths of *O. centrocarpum*, have been taken into account. In sense of the International Stratigraphic Guide (Salvador 1994) for the subdivision a mixture of assemblage zones, Oppel zones, and acme zones is used and additional elements as morphometric variations of specific dinoflagellate cyst species have been taken into account. Furthermore, the first and last occurrence of the single species do not reflect evolutionary patters, they are only controlled by environmental changes. The main factors influencing the environmental variations of the Baltic Sea are the North Atlantic weather system, the postglacial uplift of Scandinavia and the relative sea level rise (Alheit et al. submitted; Winn et al. 1986; Ekman 1988; Svensson 1991). Such events influence all regions of the Baltic Sea simultaneously, but the effects on the local environment can change significantly. Therefore no zonal definitions in sense of the International Stratigraphic Guide (Salvador 1994) can be given for the Holocene of the Baltic Sea, and the term ecostratigraphic intervals (ESI) is used for stratigraphic subdivision.

As a base for the ecostratigraphic framework core 211 660-6 from Gotland Basin was used. Further correlation of the organic walled microfossils with stable isotope and biochemical indicators are given by Voss et al. (2001). For comparison with diatoms the data of Andrén et al. (2000) are used, which are taken from a piston core at the same position taken some hours before the box core during the same cruise.

ESI I

This zone is only present in the lowermost sample from Gotland Basin at 681 cm and is marked by an extremely low abundance of organic walled microfossils in the sediment. Nevertheless, the preservation of the few fossils is good, suggesting anoxic or nearly anoxic conditions at the seafloor during sedimentation. Therefore it can be assumed, that no selective solution/destruction of the organic-walled microfossils has occurred. Causes for the low abundance of fossils may be nutrient poor or cloudy surface water, which reduces the photic zone, leading to a low primary productivity, and/or a very high sedimentation rate. The presence of *O. centrocarpum* with short spines, few copepod eggs and *Radiosperma* in this sample point to marine influence (Figs. 3 and 4).

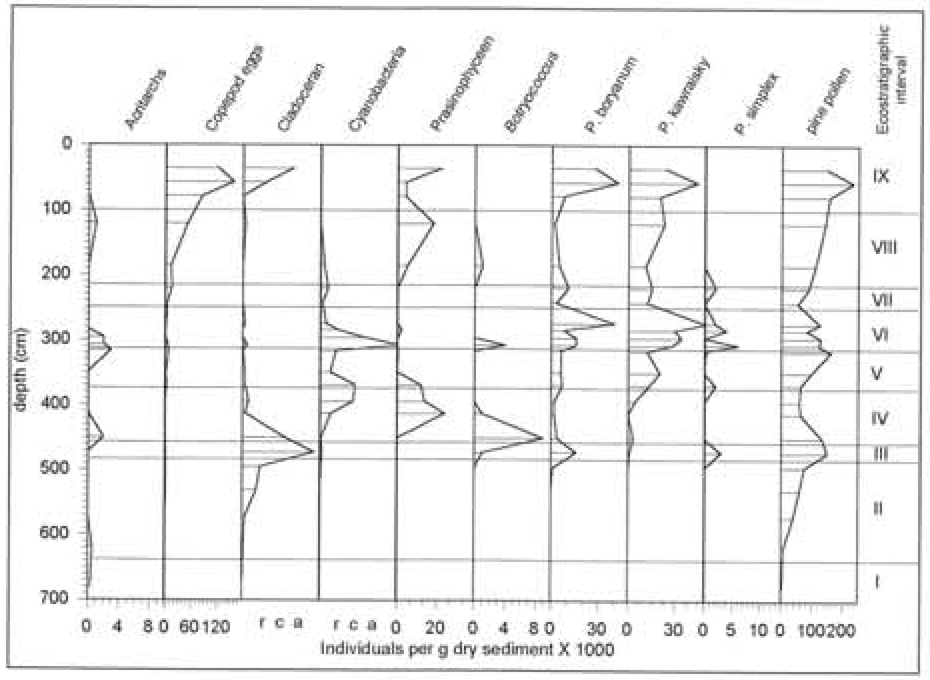

Fig. 3. Absolute abundance of selected organic walled microfossils from Gotland Basin, core 211660-6, please note the different scales. Cladoceran remains are represented by fragments, and cyanobacteria by colonies of various size. Therefore no absolute values can be given for these two microfossil groups and the abundance is given by r = rare, c = common, and a = abundance.

ESI II

This interval is marked by the increase in cysts of the freshwater dinoflagellate *Gonyaulax apiculata* with an abundance maximum at the top of this interval, a slow increase of cladoceran and the absence of *Pediastrum* spp. (Figs. 3-6). This suggests a slow but continuos increase in nutrient or an expansion of the photic zone.

In the North central Basin this interval is represented only in the lowermost sample at 669 cm, and its top and base at Gotland Basin are located at 495 cm and 618 cm, correspondingly.

ESI III

The first occurrence of *Pediastrum* and *Botryococcus* as well as the high abundance of cladoceran and the increase of organic carbon in the sediments points to an eutrophication (Voss et al. 2001). The abundance of *G. apiculata* decrease, and marine dinoflagellate cysts are absent. These patterns can be found in Gotland Basin as well as in North Central Basin. However, in North Central Basin the number of microfossils is smaller than in the Gotland Basin suggesting a lower primary production and/or higher sedimentation rates for the North Central Basin (Figs. 3-6).

Top and base of this interval are located at samples 619 cm and 644 cm from North Central Basin, and at a sample 472 cm from Gotland Basin.

ESI IV

This zone covers the first Litorina transgression. Decreasing abundance of cladoceran remains, compared with increasing abundance of marine dinoflagellate cysts with a first maximum at the top of this interval, as well as increasing processes length of *O. centrocarpum*, suggest a continuos increase of salinity. The patterns of these events are present in Gotland Basin and North Central Basin (Figs. 3-6).

Top and base of this interval are located at samples 579 cm and 604 cm from North Central Basin, and at 394 cm and 450 cm from Gotland Basin.

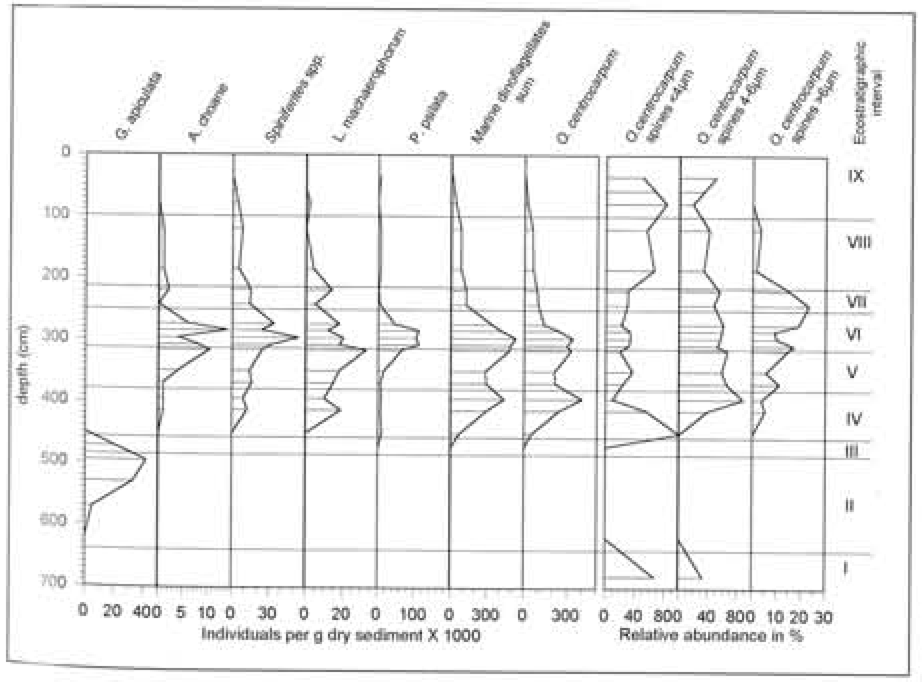

Fig. 4. Distribution of selected dinoflagellate cysts from Gotland Basin, core 211660-6. Left columns show the absolute abundance of the cysts in the sediment, please note the different scales. The right three columns give the processes length frequency of *O. centrocarpum*, which can be directly used as salinity indicator (see text for details).

ESI V

The base of this interval is marked by a slow decrease in abundance of marine dinoflagellate cysts and an absence of *Botryococcus*. Within this interval a general increase of dinoflagellate abundance takes place, especially of *L. machaerophorum* reaching its abundance maximum at the top of this interval at Gotland Basin as well as at North Central Basin. In addition, at this top an abundance minimum of *O. centrocarpum* with short processes, suggesting increasing salinity. At the Bornholm basin the abundance maximum continues to the interval above (ESI VI). This may be caused by slightly higher salinity for this basin as it is suggested by the higher abundance of *O. centrocarpum* with longer processes in this basin compared to Gotland Basin and North Central basin (Figs. 1-6).

Top and base of this interval are located at samples 509 cm and 549 cm from North Central Basin, at 316 cm and 369 cm from Gotland Basin, and the top at Bornholm Basin is located at sample 519 cm

ESI VI

The highest abundance and diversity of dinoflagellate cysts in all three basins mark this interval. Significant for this interval is a high absolute abundance of *P. psilata* (acme zone sensu Salvador 1994). This species is known from the Black Sea where the surface water is warmer than in the Baltic Sea and only from a salinity interval between 3 and 7 psu (Dale 1996; Wall and Dale 1974). Similar conditions regarding salinity are also present in the interval below but with very low abundance of *P. psilata*, suggesting that other factors than salinity control the blooming of *P. psilata*. Investigations of laminae from the Gotland Basin within this interval suggest, that this species blooms only in few years, whereas in other years the abundance is as low as in the interval below (Brenner 2001). This result suggests that the high abundance of *P. psilata* is rather the accumulation effect of specific environmental conditions favouring blooming of this species than a general high abundance.

Top and base of this interval are located at samples 474 cm and 494 cm from North Central Basin, 274 cm and 307.5 cm from Gotland Basin, and at 439 cm and 499 cm from Bornholm Basin.

ESI VII

The base of this interval is marked by a rapid decrease in absolute abundance of dinoflagellate cysts and other organic walled microfossils. The *O. centrocarpum* assemblage however, shows a clear shift to forms with longer processes, suggesting a higher salinity in this interval. The rapid decrease in organic-walled microfossil abundance point to a significant environmental change, which is not caused by salinity variation.

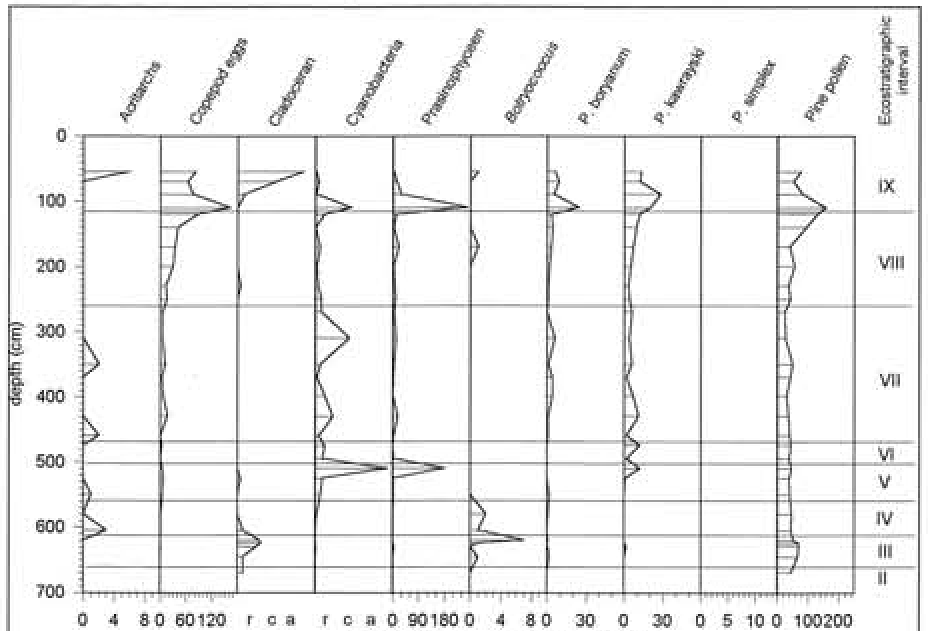

Fig. 5. Absolute abundance of selected organic walled microfossils from North Central Basin, core 211670-4 (depth: 200-670 cm) and core 211670-7 (depth: 54-200 cm), please note the different scales. Cladoceran remains are represented by fragments, and cyanobacteria by colonies of various size. Therefor no absolute values can be given for these two microfossil groups and the abundance is given by r = rare, c = common, and a = abundant.

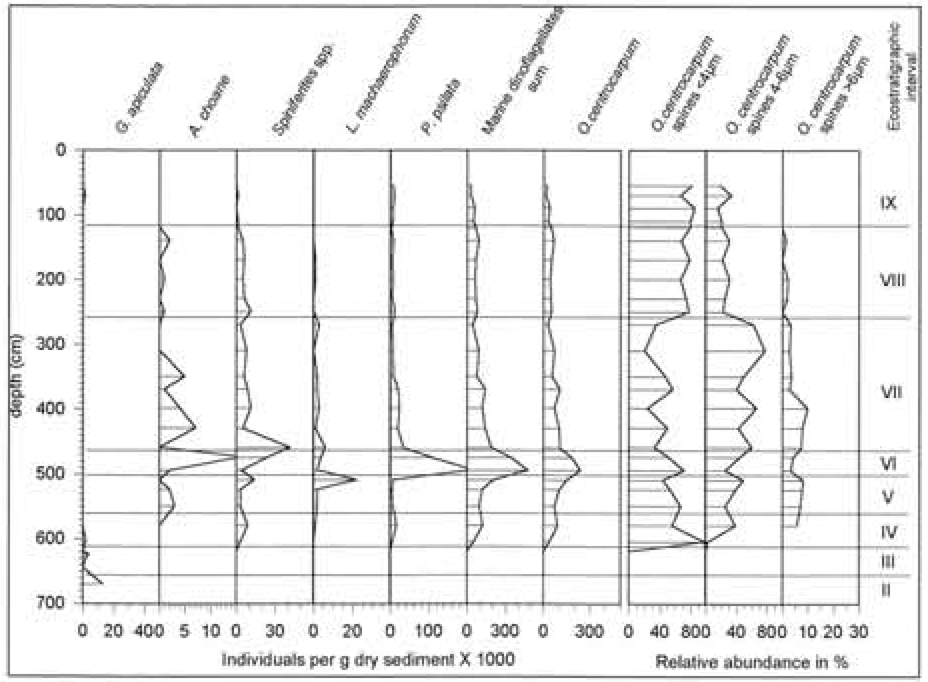

Fig. 6. Distribution of selected dinoflagellate cysts from North Central Basin, core 211670-4 (depth: 200-670 cm) and core 211670-7 (depth: 54-200 cm). Left columns show the absolute abundance of the cysts in the sediment, please note the different scales. The right three columns give the processes length frequency of *O. centrocarpum*, which can be directly used as salinity indicator (see text for details).

Top and base of this interval is located at samples 269 cm and 459 cm from North Central Basin, 219 cm and 242 cm from Gotland Basin, and at 359 cm and 419 cm from Bornholm Basin.

ESI VIII

No significant changes and a low absolute abundance in the organic-walled microfossil assemblages are present in all three basins. Forms with short processes dominate the *O. centrocarpum* assemblage, suggesting a low salinity without significant changes. This interval seems to be without environmental changes so far reflected by organic-walled microfossils.

Top and base of this interval is located in samples 119 cm and 249 cm from North Central Basin, respectively, and in samples 120 cm and 185 cm from Gotland Basin, as well as the base in sample 319 cm from Bornholm Basin.

ESI IX

A significant change in the microfossil assemblage occurs within the uppermost metre of the sediments in all three Basins. This change is marked by a rapid increase of copepod egg, cladoceran remains, pine pollen, and coccal green algae abundances in the North Central Basin and Gotland Basin, whereas the dinoflagellate cysts show no change. Moreover, a similar increase of copepod eggs can be found in equivalent sediments from Kiel Bay (Brenner and Meemken, unpublished data). This abundance change correlates directly for copepod eggs, coccal green algae, cladoceran remains, pine pollen, and a slight shift to longer processes by *O. centrocarpum* (weak salinity increase), pointing to a complex interaction between terrestrial climate, salinity, nutrient and possibly other factors within the ecosystem. This event correlates directly with an abundance maximum of organic carbon and chlorines (Voss et al. 2001; Kowalewska et al. 1999).

The abundance maxima for copepod eggs, coccal green algae and pine pollen (base of ESI IX) are located in "sample 109 cm" in North Central Basin (core 211 670-7) and "sample 57 cm" in Gotland Basin (core 211 660-6). The topmost sample of core 211 630-9 from Bornholm Basin shows an increase of copepod eggs, cladoceran remains and a slight increase of *Pediastrum* and pine pollen. A similar slight increase can be found in the top of ESI VIII at Gotland and North Central Basin. It is therefore assumed that the abundance maximum is above the topmost sample at 39 cm, and ESI IX is not present in this core.

DISCUSSION

Yoldia Sea stage

The marine phase of this stage is possibly represented in the lowermost sample in core 211660-6 (Gotland Basin) and a slightly brackish surface water is suggested by the presence of few specimens of *O. centrocarpum* with short spines (ESI I, Figs. 3, 4). The content of organic-walled microfossils in this sample is low and the interpretation of marine influence should be used carefully. The diatoms of two cores, located close to 2116660-6, record a clear brackish Yoldia phase (Andrén et al. 2000; Sohlenius et al. 1996). The transition between the brackish and freshwater phases of the Yoldia stage is visible in the diatom assemblage in a form of a shift to a freshwater flora dominated assemblage (Andrén et al. 2000; Sohlenius et al. 1996). The low content of diatoms as well as organic-walled microfossils makes it difficult to distinguish the final freshwater phase of the Yoldia Sea from the Ancylus Lake, as there is no salinity or nutrient change influencing the microfossil assemblages (Andrén et al. 2000; Sohlenius et al. 1996).

Ancylus Lake stage

Sediments of the Ancylus stage (ESI II) are present in core 211660-6 (Gotland Basin) and in core 211670-4 (North Central Basin). The lower part of the Ancylus Lake stage is only present in core 211660-6 and is marked by an extremely low abundance of organic-walled microfossils, nearly 1/2000 compared to the Litorina Sea stage. Although the content of organic carbon in the sediments is low according to Voss et al. (2001), the preservation of microfossils is good, even the chitinous cladoceran remains, which are very sensitive to oxidation, are well preserved. This points to a rapid burial and/or anoxic conditions at the sea floor during deposition. The extremely low content of organic-walled microfossils seems to be a primary feature. Very high sedimentation rates could be an explanation, however, this could also have been caused by a very narrow photic zone as a result of turbid water, low temperatures, and/or low nutrient contents in the surface water. Successive increase of diversity and abundance of organic walled microfossils and especially of the cysts of the freshwater dinoflagellate *G. apiculata* to the top of this stage suggest a continuos increase in nutrient and/or an expansion of the photic zone. In contrast to the organic-walled microfossils, the diatom record of the lower Ancylus Sea stage have there an abundance peak, with a similar assemblage as the final freshwater stage of the Yoldia Sea (Andrén et al. 2000; Sohlenius et al. 1996). Due to the high number of fragmented valves within this peak, Andrén et al. (2000) do not exclude that part of this peak is a product of redeposition from the freshwater Yoldia Sea stage. The increase of diatom diversity leads to the same assumption as for the organic walled microfossils.

Ancylus-Litorina transitional stage

During this stage (ESI III) a rapid decrease in abundance of the cysts of the freshwater dinoflagellate *G. apiculata* occurs, whereas cladoceran remains and coccal green algae reach their maximum abundance, possibly indicating a rapid increase in nutrients. This event is more intense in the Gotland Basin than in the North Central Basin, indicated by the higher absolute abundance of organic walled microfossils and the first occurrence of dark, organic carbon rich, laminated sediments. Qualitative screening of laminas from core 211660-6 at 454 cm depth shows that a few single lamina contain *O. centrocarpum* with short processes in low abundance (Brenner, unpublished data). These marine dinoflagellate cysts can be found only by careful sampling of single laminae, because in a 1-cm thick slice of sediment the few marine dinoflagellate cysts are masked by a high abundance of all the other non-marine organic-walled microfossils. Nevertheless, the occurrence of marine dinoflagellate cysts in this interval points to sporadically brackish surface water conditions. Simultaneously to this event there is a drop in the absolute abundance of diatoms, which seems to be characteristic in the whole Baltic Proper (e.g. Abelmann 1985;

Andrén et al. 2000; Sohlenius et al. 1996; Thulin et al. 1992).

Litorina Sea stage

The basal Litorina Sea stage (ESI IV) in the Gotland Basin as well as in the North Central Basin is marked by a continuos increasing abundance of dinoflagellate cysts and increasing processes length of *O. centrocarpum*, indicating a continuous increase in salinity, found as well in the diatom record (Andrén et al. 2000; Sohlenius et al. 1996). After reaching a first saline maximum a slight decrease in salinity is indicated by dinoflagellate cysts followed by an interval with changing, but still high salinity and a further salinity maximum at the top of interval ESI V. The following interval (ESI VI) is marked by a high abundance of *P. psilata,* which is not known from the present Baltic Sea (Dale 1996). A significant environmental change indicated by a rapid and permanent decrease in abundance of dinoflagellate cysts can be found in all three Basins (ESI VII). The processes length of *O. centrocarpum* suggests that the salinity is slightly higher as in the interval below and the rapid decrease of dinoflagellate cyst abundance must be caused by other factors than salinity change, which are till now unknown.

Variation of sedimentation rates at short distances and different sample distribution hamper a detailed correlation of siliceous and organic walled microfossils between cores 211660-1 (Andrén et al. 2000) and 211660-6. However, the assemblage succession of diatom valves at the base of the Litorina Sea stage followed by *Chaetoceros* resting spores and silicoflagellates at the top suggests a general increase of salinity during the Litorina Sea stage as it can be interpreted by the change in processes length of *O. centrocarpum*.

Post-Litorina Sea stage

The whole post-Litorina Sea stage (ESI II and I) is marked by a permanent low abundance of dinoflagellate cysts, and the processes length of *O. centrocarpum* suggests a lower salinity compared to the Litorina Sea stage. Within the lower part (ESI II) only a slight but continuos increase of copepod egg and cladoceran remains can be found in all three Basins. In the Gotland Basin and the North Central Basin an additional slight increase of coccal green algae occurs. The lower interval (ESI II) corresponds to a poor record of siliceous microfossils in the core 211660-1 (Andrén et al. 2000).

In the uppermost part of this stage a rapid increase in copepod eggs, cladoceran remains, coccal green algae and pine pollen indicates a significant change within the environmental conditions in the two northern basins (ESI I). This event is further marked by a rapid increase in diatom abundance (Andrén et al. 2000) and a peak in organic carbon and chlorine (Kowalewska et al. 1999; Voss et al. 2001). The abundance of dinoflagellate cysts does not change significantly within this interval, and the processes length of *O. centrocarpum* suggests a rather constant salinity.

The causes for the observed environmental change may therefore be related to changes in nutrient content and/or temperature of the surface water, which do not influence the dinoflagellate assemblage. The significant increase of copepod egg abundance has no analogue in older sediments of the Baltic Sea. The sparse knowledge on copepod eggs, their taxonomy and ecology does not allow an interpretation of this phenomenon and needs further investigation.

Finally it can be stated that the organic walled microfossils provide an excellent tool for palaeoecological investigations, but much more studies with a higher sample resolution are needed to understand the processes and causes for the environmental variations in the Holocene sediments of the Baltic Sea.

Acknowledgements

This work has been supported by the European Commission through the BASYS Baltic Sea System Studies project (contract number MAS3-CT96-0058). Thanks are due to Prof. J. Thiede, who facilitated this investigation at GEOMAR, Kiel and Prof. A. Rios-Netto for the possibility to finalise the manuscript at LabMicro, Federal Universidade do Rio de Janeiro. Further thanks are due to Prof. M. Kabailienė and an anonymous reviewer for helpful comments on the manuscript.

References

Abelmann, A. 1985: Palökologische und ökostratigraphische Untersuchungen von Diatomeenassoziationen an holozänen Sedimenten der zentralen Ostsee. *Berichte - Reports, Geologisch-Palaeontologisches Institut der Universität Kiel 9*, 200.

Ackefors, J. 1971: *Podon polyphemoides* LEUCKART and *Bosmina coegoni maritima* (P.E. MÜLLER) in relation to temperature and salinity in field studies and laboratory experiments. *Journal of Experimental Marine Biology and Ecology 7,* 51-70.

Alheit, J., Lehmann, A. & Winterhalter, B. (submitted): The North Atlantic climate influence on the Baltic Sea environment.

Andrén, E., Andrén, T. & Kunzendorf, H. 2000: Holocene History of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10,* 621-636.

Andrén, T. & Andrén, E. 1999: Large scale climate forcing on the Holocene history of the Baltic proper. *Abstract in Proceedings of the Third BASYS annual science conference,* 20-22.9.1999, Institute of Baltic Sea Research, Warnemünde, Germany.

Apstein, C. 1906: Plankton in Nord- und Ostsee auf den deutschen Terminfahrten, I. Teil (Volumina 1903). *Wissenschaftliche Meeresuntersuchungen, Neue Folge, Abteilung Kiel 9,* 1-26.

Averdieck, F. R. 1972: Palynologische Untersuchungen an Bohrkernen aus der Flensburger Aussenfoerde (Ostsee). *Meyniana 22,* 1-4.

Bainbridge, V. 1958: Some observations on Evadne normanni LOVÉN. *Journal marine biological Association U.K. 37,* 349-370.

Bakken, K. & Dale, B. 1986: Dinoflagellate cysts in Upper Quaternary sediments from southwestern Norway and potential correlations with the oceanic record. *Boreas 15,* 185-190.

Bandel, W. 1940: Phytoplankton- und Nährstoffgehalt der Ostsee im Gebiet der Darßer Schwelle. *Internationale Revue der gesamten Hydrobiologie 40,* 249-304.

Batten, D. J. & van Geel, B. 1985: *Celyphus rallus*, probable Early Cretaceous rivulariacean blue-green algae. *Review of Palaeobotany and Palynology 44,* 233-241.

Biebow, N. 1996: Dinoflagellatenzysten als Indikatoren der spät- und postglazialen Entwicklung des Auftriebsgeschehens vor Peru. *GEOMAR Report 57,* 100.

Brandes, C.-H. 1939: Über die räumliche und zeitliche Unterschiede in der Zusammensetzung des Ostseeplanktons. *Mitteilungen aus dem Hamburgischen Zoologischen Museum und Institut in Hamburg 48,* 1-47.

Brandt, K. 1896: Über das Stettiner Haff. *Wissenschaftliche Meeresuntersuchungen, Neue Folge, Abteilung Kiel 1,* 105-145.

Brenner, W. & Foster, C. B. 1994: Chlorophycean algae from the Triassic of Australia. *Review of Palaeobotany and Palynology 80,* 209-234.

Brenner, W. W. 2001: Distribution of organic walled microfossils within single laminae from Gotland Basin and their environmental evidence. *Baltica 14,* 34-39.

Cronberg, G. 1982a: *Pediastrum* and *Scenedesmus* (Chlorococcales) in sediments from Lake Växjösjön, Schweden. *Archiv für Hydrobiologie. Supplements 60,* 500-507.

Cronberg, G. 1982b: Phytoplankton change in Lake Trummen induced by restoration. *Folia Limnologica Scandinavica 18,* 1-119.

Dale, B. 1983: Dinoflagellate cysts: "benthic plankton." *In* G. A. Fryxell, (Ed.): *Survival strategies of the algae,* 69-136. Cambridge University Press.

Dale, B. 1996: Dinoflagellate cyst ecology: modeling and geological applications. *In* J. Jansonius & D. C. McGregor (Eds.): *Palynology: principles and applications,* 1249-1275. American Association of Stratigraphic Palynologists Foundation.

Dale, B. & Fjellsa, A. 1994: Dinoflagellate cysts as paleoproductivity indicators: state of the art, potential, and limits. *In* R. Zahn, T. F. Pedersen, M. A. Kaminski & L. Labeyrie (Eds.): *Carbon cycling in the glacial ocean: Constraints on the ocean's role in global change. NATO ASI Ser. I,* 521-537. Springer Berlin, Heidelberg, New York.

Driver, H. 1908: Das Ostseeplankton der 4 deutschen Terminfahrten im Jahre 1905. *Wissenschaftliche Meeresuntersuchungen, Neue Folge, Abteilung Kiel 10,* 127.

Edwards, L. E. & Andrle, V. A. S. 1992: Distribution of selected dinoflagellate cysts in modern marine sediments. *In* M. J. Head & J. H. Wrenn (Eds.): *Neogene and Quaternary dinoflagellate cysts and acritarchs,* 259-288. Association of Stratigraphic Palynologists Foundation, Dallas.

Ekman, M. 1988: The world's longest continued series of sea level observations. *Pure and Applied Geophysics 127,* 73-77.

Ellegaard, M. 2000: Variations in dinoflagellate cyst morphology under conditions of changing salinity during the last 2000 years in the Limfjord, Denmark. *Review of Palaeobotany and Palynology 109,* 65-81.

Eriksson, J. A. 1994: Comparison of modern pollen spectra with fossil pollen data on the Island Stora Karlso, western Baltic Sea, Sweden. *Review of Palaeobotany and Palynology 82,* 192-193.

Eronen, M., Ristaniemi, O. & Lange, D. 1990: Analysis of a sediment core from the Mecklenburg Bay, with a discussion on the early Holocene history of the southern Baltic Sea. *Geologiska Foereningen i Stockholm Foerhandlingar 112, Part 1,* 1-8.

Hensen, V. 1887: Ueber die Bestimmung des Planktons oder des im Meere treibenden Materials an Pflanzen und Thieren. *Berichte der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel 5,* 107.

Hofmann, W. 1987: Stratigraphy of Cladocera (Crustacea) and Chironomidae (Insecta: Diptera) in three sediment cores from the Central Baltic Sea as Related to Paleosalinity. *Internationale Revue der gesamten Hydrobiologie 72,* 97-106.

Hofmann, W. 2001: Distribution of Cladoceran remains in two sediment cores from the Central Baltic Sea. *Baltica 14,* 52-57.

Kell, V. 1981: Das Phytoplankton der Ostsee. *Geodätische und Geophysikalische Veröffentlichungen 4,* 3-26.

Kell, V. 1985: Untersuchungen zur Qualität und Quantität des Phytoplanktons im Greifswalder Bodden (südliche Ostsee) in den Jahren 1977-1984. I. Qualitativer Teil. *Wissenschaftliche Zeitschrift der Wilhelm-Pieck-Universitaet, Rostock. Mathematische-Naturwissenschaftliche Reihe 34,* 32-40.

Kell, V. 1986: Untersuchungen zur Qualität und Quantität des Phytoplanktons im Greifswalder Bodden (südliche Ostsee) in den Jahren 1977-1984. I. Qualitativer Teil. *Wiss. Z. Wilhelm-Pieck Univ. Rostock, naturwiss. R. 35,* 17-21.

Knoll, A. H. & Golubic, S. 1992: Proterozoic and Living Cyanobacteria. *In* M. e. a. E. Schidlowski, (Ed.): *Early Organic Evolution: Implications for Mineral and Energy Resources*. Springer-Verlag Berlin Heidelberg.

Kowalewska, G., Winterhalter, B., Talbot, H. M., Maxwell, J. R. & Konat, J. 1999: Chlorine in sediments of the Gotland Deep (Baltic Sea). *Oceanologia 41,* 81-97.

Kunz-Pirrung, M. 1997: Rekonstruktion der Oberflächenwassermassen der östlichen Laptevsee im Holozän anhand von aquatischen Palynomorphen. *Doctoral thesis, Univ. Kiel 1.* 112 p.

Latala, A. 1991: Effects of salinity, temperature and light on the growth and morphology of green planktonic algae. *Oceanologia 31,* 119-138.

Leegaard, C. 1920: Microplankton from the Finnish waters during the month of May 1912. *Acta Societatis Scientiarum Fennicae 48,* 1-44.

Lindley, J. A. 1986: Dormant eggs of calanoid copepods in sea-bed sediments of the English Channel and southern North Sea. *Journal Plankton Research 8,* 399-400.

Livingstone, D. & Jaworski, G. H. M. 1980: The viability of akinets of blue-green algae recovered from the sediments of Rostherne Mere. *British Phycological Journal 15,* 357-364.

Lohmann, H. 1904: Eier und sogenannte Cysten der Plankton-Expedition. *Ergebnisse der Plankton-Expedition der Humboldt-Stiftung 4,* 1-61.

Marcus, N. H. 1990: Calanoid copepod, cladoceran, and rotifer eggs in sea-bottom sediments of northern Californian coastal waters: identification, occurrence and hatching. *Marine Biology 105,* 413-418.

Matthiessen, J. & Brenner, W. 1995: Organic-walled microfossils in Holocene sediments from Neustadt Bay, western Baltic Sea. *Zentralblatt für Geologie und Paläontologie Teil I, 1994,* 67-81.

Matthiessen, J. & Brenner, W. 1996: Chlorococcalalgen und Dinoflagellaten-Zysten in rezenten Sedimenten des Greifswalder Boddens (südliche Ostsee): *Senckenbergiana Maritima 27,* 33-48.

Matthiessen, J. & Brenner, W. Recent aquatic palynomorphs from the western Baltic Sea, the Skagerrak and the inner German Bight (NW Europe). *Submitted to Journal of Micropaleontology.*

Merkle, H. 1910: Das Plankton der deutschen Ostseefahrt Juli-August 1907. *Wissenschaftliche Meeresuntersuchungen, Neue Folge, Abteilung Kiel 11,* 321-346.

Meunier, A. 1910: Microplankton des Mers de Barents et de Kara. Charles Bulens, Imprimerie Scientifique, Bruxelles.

Miller, U. & Risberg, J. 1990: Environmental changes, mainly eutrophication, as recorded by fossil siliceous microalgae in two cores from the uppermost sediments of the north-western Baltic. *Beiheft Nova Hedwigia 100,* 237-253.

Mudie, P. J., Aksu, A. E. & Yasar, D. 2001: Late Quaternary dinoflagellate cysts from the Black, Marmara and Aegean seas: variations in assemblages, morphology and paleosalinity. *Marine Micropaleontology 43,* 155-178.

Nehring, S. 1994a: Dinoflagellaten-Dauercysten in deutschen Küstengewässern: Vorkommen, Verbreitung und Bedeutung als Rekrutierungspotential. *Berichte des Instituts für Meereskunde, Kiel 259,* 231.

Nehring, S. 1994b: Spatial distribution of dinoflagellate resting cysts in recent sediments of Kiel Bight, Germany (Baltic Sea). *Ophelia 39,* 137-158.

Nyberg, A. V. & Schopf, J. W. 1984: Microfossils in Stromatolic Cherts from the upper Proterozoic Min'Yar Formation, southern Ural Mountains, USSR. *Journal of Paleontology 58,* 738-772.

Pankow, H. 1990: Ostsee-Algenflora.

Poggensee, E. & Lenz, J. 1981: On the population dynamics of two brackish-water cladocera *Podon leuckarti* and *Evadne normanni* in Kiel Fjord. *Kieler Meeresforschungen Sonderheft 5,* 268-273.

Reid, P. C. 1974: Gonyaulacacean dinoflagellate cysts from the British Isles. *Nova Hedwigia 25,* 579-637.

Rosén, G. 1981: Phytoplankton indicators and their relations to certain chemical and physical factors. *Limnologica (Berlin) 13,* 263-290.

Salvador, A. e. 1994: International Stratigraphic Guide - A guide to Stratigraphic Classification, Terminology, and Procedure. The Geological Society of America, Inc., Boulder.

Schröder, B. 1897: Über das Plankton der Oder. *Bericht der Deutschen botanischen Gesellschaft 15,* 482-492.

Setter, T. L. & Greenway, H. 1979: Growth and osmoregulation of *Chlorella emersonii* in NaCl and neutral osmotica. *Australian Journal of Plant Physiology 6,* 47.

Soeder, C. J. & Stengel, E. 1974: Physico-chemical factors affecting metabolism and growth rate. *In* W. D. P. Steward. (Ed.): *Algal Physiology and Biochemistry,* 989. Univ. California Press, Berkley.

Sohlenius, G., Sternbeck, J., Andrén, E. & Westman, P. 1996: Holocene history of the Baltic Sea as recorded in a sediment core from the Gotland Deep. *Marine Geology 134,* 183-201.

Stelle, V., Yakubovska, I. & Savvaitov, A. 1994: Pollen complexes of late- and post-glacial sediments in the Gulf of Riga. *Baltica 8,* 38-42.

Strother, P. K., Knoll, A. H. & Barghoorn, E. S. 1983: Micro-organisms from the late Precambrian Narssärssuk formation, north-western Greenland. *Palaeontology 26,* 1-32.

Struck, U., Voss, M. & von Bodungen, B. 1998: Stable isotopes of nitrogen in fossil cladoceran exoskeletons: Implication for nitrogen sources in the Central Baltic Sea during the past century. *Naturwissenschaften 85,* 597-603.

Svensson, N. O. 1991: Postglacial land uplift patterns of South Sweden and the Baltic Sea region. *Terra Nova 3,* 369-378.

Thulin, B., Possnert, G. & Vuorela, P. 1992: Stratigraphy and age of two postglacial sediment cores from the Baltic Sea. *Geologiska Föreningen i Stockholm Förhandlingar*, 165-179.

Turon, J.-L. 1984: Le palynoplancton dans l'environnement actuel de l'Atlantique nord-oriental; èvolution climatque et hydrologique depuis le dernier maximum glaciaire. *Bulletin de l'Institut de Gèologie du Bassin d'Aquitaine 17,* 1-313.

Van Geel, B., Mur, L. R., Ralska-Jasiewiczowa, M. & Ralska-Jasiewiczowa, G. T. 1994: Fossil akinetes of *Amphanizomenon* and *Anabaena* as indicators for medieval phosphate-eutrophication of Lake Gosciaz (Central Poland). *Review of Palaeobotany and Palynology 83,* 97-105.

Van Waveren, I. M. 1993: Planktonic organic matter in surficial sediments of the Banda Sea (Indonesia) - a palynological approach. *Geolie Ultraiectina 104,* 1-213.

van Waveren, I. M. 1994: Distribution of copepod egg-envelopes in sub-Recent sediments from the Banda Sea (Indonesia). *Scripta Geologica 105,* 53-67.

Voss, M., Kowalewska, G. & Brenner, W. 2001: Microfossil and biogeochemical indicators of environmental changes in the Central Gotland Basin during the last 10,000. *Baltica 14,* 131-140.

Wall, D. & Dale, B. 1973: Paleosalinity relationships of dinoflagellates in the Late Quaternary of the Black Sea. A summary. *Geosci. Man VII,* 95-102.

Wall, D. & Dale, B. 1974: Dinoflagellates in Late Quaternary deep water sediments from Black Sea. *In* (E. T. Degens & D. A. Ross, Eds.): *The Black Sea - its geology and chemistry,* 364-380. American Association of Petroleum Geologists, Memoirs.

Wall, D., Dale, B. & Harada, K. 1973: Descriptions of new fossil dinoflagellates from the Late Quaternary of the Black Sea. *Micropaleontology 19,* 18-31.

Wall, D., Dale, B., Lohmann, G. P. & Smith, W. K. 1977: The environmental and climatic distribution of dinoflagellate cysts in modern sediments from regions in the North and South Atlantic Ocean and adjacent seas. *Marine Micropaleontology 2,* 121-200.

Wicander, R., Foster, C. B. & Foster, R. J. D. 1996: Green and blue-green algae, *Gloeocapsomorpha. In* Jansonius, J. & McGregor, D.C. (Eds.): *Palynology: principles and application. AASP Foundation 3,* 215-225.

Willén, E. 1992: Planktonic green algae in an acidification gradient of nutrient-poor lakes. *Arch. Protistenk. 141,* 47-64.

Winn, K., Averdieck, F. R., Erlenkeuser, H. & Werner, F. 1986: Holocene sea-level rise in the western Baltic and the question of isostatic subsidence. *Meyniana 38,* 61-80.

Witkowski, A. 1994: Recent and fossil diatom flora of the Gulf of Gdansk, Southern Baltic Sea. *Bibliotheka Diatomologia 28,* 312.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 52-57

Distribution of cladoceran remains in two sediment cores from the Central Baltic Sea

Wolfgang Hofmann

Abstract

Cladoceran remains were analysed in two sediment cores from the Gotland Deep and the North Central Basin which cover the period of the last 10,000 years. Cladoceran stratigraphy divided the profiles into three faunal zones: (1) The Ancylus stage was characterised by the co-occurrence of three taxa of freshwater planktonic cladocera, i.e. *Bosmina longispina, Bosmina longirostris,* and *Daphnia* sp. (2) During the Litorina stage foraminifers were present together with very low numbers of *Bosmina longispina*. (3) In the uppermost section of the cores a decrease in the foraminifers and a significant increase in *Bosmina longispina* occurred, possibly due to a drop in salinity (Limnaea stage?). During the Ancylus stage the species *Bosmina longispina* is represented by a freshwater population while the specimens from the uppermost section belong to the brackish water race *Bosmina longispina maritima*. The conspicuous peaks in the frequencies of *Bosmina longispina* and *B. longirostris* observed at the end of the Ancylus stage seem to be a typical phenomenon in the Central Baltic of that time and have been previously reported from the Bornholm Basin and the Gdansk Bay.

☐ *Baltic Sea, Gotland Deep, North Central Basin, sediment, Cladocera, biostratigraphy, Baltic stages.*

☐ *Wolfgang Hofmann [wolfg.hofmann@web.de], Max Planck Institute for Limnology, PO Box 165, 24302 Plön, Germany.*

☐ *Received 4 June 2001; accepted 9 November 2001.*

INTRODUCTION

In the species of the cladoceran families Bosminidae and Chydoridae carapaces and head shields are well preserved in lake sediments. Therefore these subfossil remains have been widely used in paleoecological research. In this connection, Cladocera have been used to demonstrate long-term environmental changes especially with respect to climate, trophic conditions and acidification (Frey 1986, 1988; Hofmann 1987a, 2000; Flößner 1990; Korhola 1992; Brodersen et al. 1998). Core studies in the Bornholm Basin and the Gdansk Bay have shown that before the Litorina stage a planktonic cladoceran fauna typical of oligotrophic freshwater lakes (Hofmann 1987b) inhabited the Baltic Sea. Similar studies in the Western Baltic allowed a detailed analysis of the shift from a freshwater fauna to a brackish/marine assemblage as a result of the Litorina transgression (Hofmann and Winn 2000). The aim of this study is to verify the results from the former core studies in the Central Baltic Sea and to compare the cladoceran data with the results obtained by other methods, such as sedimentology, dating, and analysis of other microfossils.

MATERIAL AND METHODS

The sediment core 211660-6 was taken by a Kastenlot in the Gotland Deep (57° 17.0283 N - 20° 07.1386 E) at 241.3 m water depth. The sediment of the 0-440 cm section consisted of mostly laminated pelitic mud. Below 444 cm, there was homogeneous or weakly laminated pelitic mud (clay). The profile 211670-4/7 combines two cores (211670-4: 58° 049.1843 N - 20° 015.2026 E, water depth 176.1 m and 211670-7: 58° 49.1622 N - 20° 15.1363 E, water depth 175.2 m) from the North Central Basin taken by a Kastenlot (Brenner, 2001b).

Processing of the sediment samples followed a standard procedure for cladoceran analysis of lake sediments (Frey 1986). The fresh sediment was heated in 10% KOH on a stirrer hot plate. After cooling, the sample was screened through a 40-µm sieve. The residue was separated into size fractions > 100 µm and 40-100 µm which were analysed separately. The cladoceran remains and foraminifers were counted in subsamples equivalent to 0.04-2.4 g sediment under a microscope at 100x magnification. The most frequent remains of the cladoceran families' bosminids and chydorids were head shields and carapaces, while in the case of *Daphnia* only the postabdominal claws were present. Fragments were counted according to Frey (1986, Table 32.1). From the counts the concentrations as densities of remains per g dry weight were calculated. The length of the spine at the ventral-caudal angle of the shell (mucro) of *Bosmina longispina* was measured in specimens drawn by using a camera Lucida attachment at 320x. Length and number of segments of the antennules were determined in microscopic slides at 250x. The Median-test and the Nemenyi-test using the software Stateasy (Lozan 1992) tested the significance of the differences between the samples. Chydorid and *Bosmina* taxonomy followed Flößner 1972 and Lieder 1996, respectively. Foraminifers were represented by the inner linings of their shells and corresponded to the *Ammonia / Elphidium* type (Lutze 1965). The species involved were not identified.

RESULTS

The core 211670-4/7 (North Central Basin)

In the core 211670-4/7 48 samples from the 51-673 cm section were analysed. Depth intervals of the samples were 5 cm in the 51-101 cm section, 25 cm in the 101-578 cm section, and 5 cm in the 578-673 cm section. With reference to the cladoceran stratigraphy three faunal zones (CLA1, CLA2, CLA3) were discernible (Fig. 1). In the 598-673 cm section the planktonic Cladocera *Bosmina longispina, Bosmina longirostris*, and *Daphnia* sp. and a few specimens of the benthic chydorid species *Alona quadrangularis* and *Chydorus sphaericus* were present (CLA1). *B. longispina* was by far the most frequent taxon with up to 2800 specimens/g dry weight at 638 cm and a mean concentration of 1750 specimens/g dry weight in the 617-643 cm section. Below and above this section, values ranged from 20 to 300 specimens/g dry weight with an average of 110-specimens/g dry weight. Maximum concentration of *B. longirostris* was 120 specimens/g DW at 629 cm and the mean concentration for the 598-653 cm section was 20 specimens/g DW. In the four samples from below 653 cm no remains of this species were found. Postabdominal claws of *Daphnia* sp. were present in the 629-658 cm section with maximum values at 643 cm (330-specimens/g dry weight) and 638 cm (100-specimens/g dry weight). *Alona quadrangularis* was found in four samples of this section with 1-5 specimens/g DW and one specimen of *Chydorus sphaericus* was found at 658-cm sediment depth. In this zone foraminifers were not present at all.

The faunal zone CLA2, which covered the 126-592 cm section, was characterised by the presence of foraminifers and very low frequencies of *Bosmina longispina*. Concentrations of foraminifers varied irregularly in the range of 20 to 300 specimens/g dry weight with an average of 140-specimens/g dry weight. With the exception of the 592-cm sample *Bosmina longispina* was continuously present. The concentrations were extremely low and ranged from 1 to 7 specimens/g dry weight (average: 3-specimens/g dry weight). There were only three single findings of other cladocerans: one *Bosmina longirostris* at 592 cm, one *Bosmina coregoni* at 428 cm, and one *Disparalona rostrata* at 126 cm sediment depth.

The faunal zone CLA3 (51-101 cm) was distinctly marked by high concentrations of *Bosmina longispina*. Between 126 cm and 101-cm sediment depth the frequency suddenly increased from 7 to 230 specimens/g dry weight. Within this zone there was a further increase towards the top of the core. In the lower section from 76 to 101 cm sediment depth mean concentration of *Bosmina* was 570 specimens/g dry weight, while in the section above 76 cm mean concentration was 5900 specimens/g dry weight (range: 3600-9800 specimens/g dry weight). No other cladocerans were found in this zone. Frequencies of the foraminifers decreased towards the top from an average of 110 specimens/g dry weight (range: 60-150 specimens/g dry weight) in the 76-101 cm section to an average of 40 specimens (range: 20-60 specimens/g dry weight) in the 51-71 cm section.

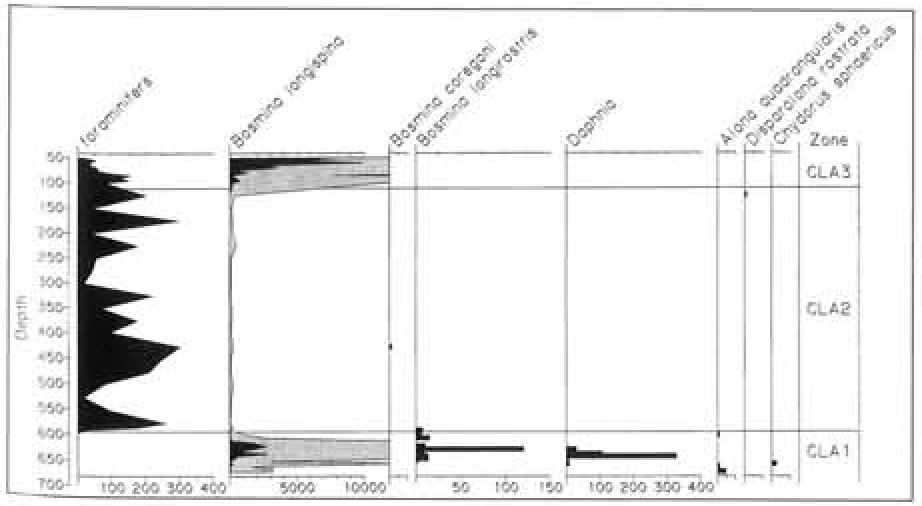

Fig. 1. Core 211670-4/7 - North Central Basin: density of remains (specimens / g dry weight) (Bosmina longispina: exaggeration factor 50) and boundaries of faunal zones CLA1, CLA2, CLA3.

The morphometric data show that the specimens of *Bosmina longispina* from the peaks in zones CLA1 and CLA3 were morphologically different (Fig. 2). The specimens from 51 cm and 101-cm sediment depth had shorter mucrones and shorter antennules with a lower number of segments than the specimens in the samples from 629 cm, 638 cm, and 673-cm sediment depth. The medians of mucro length decreased from 70-95 µm in the 629-673 cm section to 50-55 µm at 101 cm and 51 cm. Likewise, medians of antennules diminished from 183-210 µm to 160-168 µm. These differences were statistically significant (Median-test, Nemenyi-test, number per sample: 25, $p = 0.05$) (Lozan 1992).

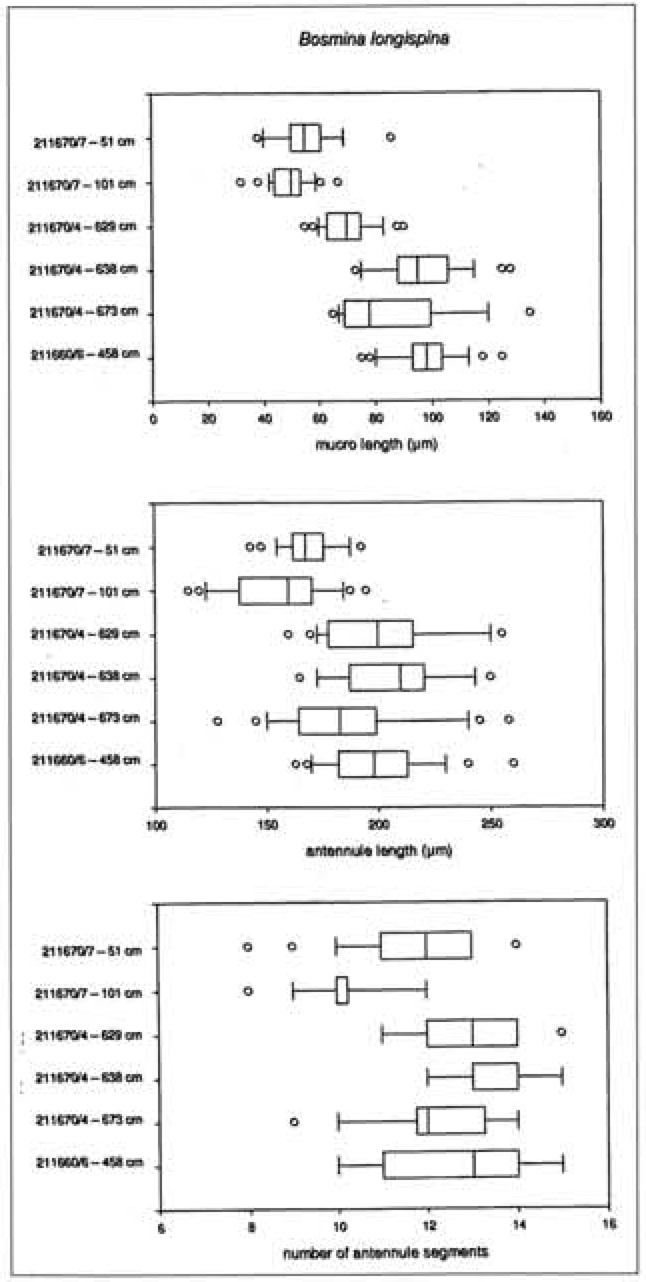

Fig. 2. *Bosmina longispina*: box plots of mucro length, antennule length, and number of antennule segments in five samples from core 211670-4/7 and in one sample from core 211660-6.

The core 211660-6 (Gotland Deep)

In the core 211660-6 45 samples from the 64-691 cm section were analysed. Depth intervals of the samples were 5-10 cm in the 64-117 cm section, 20-30 cm in the 117-434 cm section, and 10 cm in the 434-691 cm section. The distribution pattern of cladocerans and foraminifers divided the profile into three faunal zones (Fig. 3). The zone CLA1 (445-691 cm sediment depth) is characterised by the occurrence of the planktonic cladocerans *Bosmina longispina, Bosmina longirostris*, and *Daphnia* sp. and the absence of foraminifers. The subzones CLA1a and CLA1b differ in the concentration of *B. longispina*. In the zone CLA1a (561-691 cm) concentrations of *B. longispina* ranged from 3 to 140 specimens/g dry weight with an average of 40-specimens/g dry weight. Maximum concentration of *Bosmina longirostris* was 110 specimens/g DW at 628 cm and on an average there were 20-specimens/g dry weight. *Daphnia* claws were only found in two adjacent samples from 581 cm and 593 cm, the concentrations were 30 and 20-specimens/g dry weight, respectively.

In the 454-487 cm section of subzone CLA1b the three planktonic cladocerans exhibited extremely high maximum concentrations. In *Bosmina longispina* 11300 and 18400-specimens/g dry weight were found at 454 cm and 466 cm, respectively. In the remaining samples from this subzone mean concentration (900-specimens/g dry weight) was distinctly higher than in the subzone below. *Bosmina longirostris* showed peak abundance of 1790 and 1000 specimens/g dry weight at 466 cm and 476 cm. The maximum concentration of *Daphnia*, 190-specimens/g dry weight, was found at 487 cm. The horizons of maximum frequencies of the three species were thus arranged in a chronological order, i. e. from *Daphnia* to *B. longirostris* and finally to *B. longispina*. Two chydorid specimens were present in this subzone, one *Alona quadrangularis* at 476 cm and one *Alonella excisa* at 487-cm sediment depth.

The faunal zone CLA2 was separated from the zone CLA1 due to the presence of foraminifers and low frequencies of *Bosmina longispina*. Within this zone, there was an increase in the concentrations of foraminifers. In the 295-435 cm section frequencies ranged from 40 to 90 specimens/g dry weight and mean frequency was 40 specimens/g dry weight, with the exception of a minimum at 349 cm and 379 cm. In the section above 295 cm concentrations were >140 specimens/g dry weight, with the exception of the samples from 80 cm, 90 cm, and 170 cm (range: 60-90 specimens/g dry weight). In total, the concentration of foraminifers in the 80-272 cm section averaged 220-specimens/g dry weight. *Bosmina longispina* was continuously present and was missing only in the 106-cm sample. The concentrations ranged from 4 to 50 specimens/g DW (average: 20-specimens/g dry weight). Only single specimens of the other *Bosmina* species were found: 1-2 specimens of *B. coregoni* at 80 cm, 106 cm, 224 cm, and 295 cm and 1-2 specimens of *B. longirostris* at 295 cm and 349 cm.

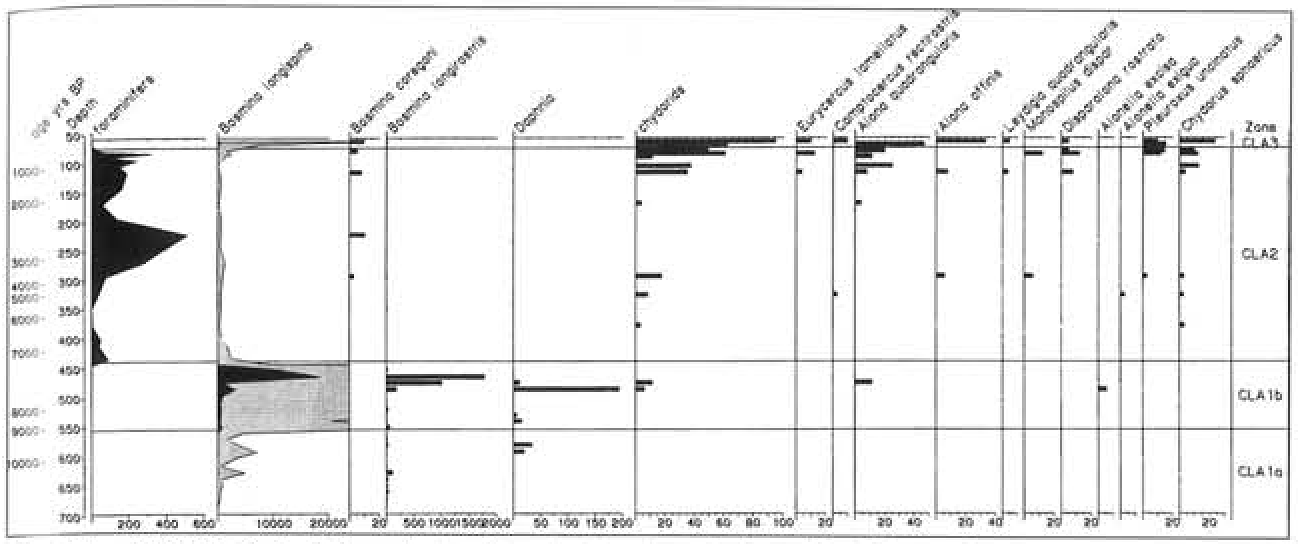

Fig. 3. Core 211660-6 Gotland Deep: density of remains (specimens / g dry weight) (*Bosmina longispina*: exaggeration factor 50), boundaries of faunal zones CLA1, CLA2, CLA3, and ages (years BP) (after Voss et al. 2001).

Chydorid species were very rare in the 144-435 cm section and were present in three of thirteen samples only, i. e. at 170 cm (1 *Alona quadrangularis*), at 295 cm (1 *Alona affinis*, 1 *Monospilus dispar*), and at 327 cm (1 *Camptocercus rectirostris*, 1 *Alonella exigua*, 1 *Chydorus sphaericus*). In the 80-117 cm section chydorids occurred in five of six samples with a mean concentration of 40 specimens/g dry weight. Eight species were present of which *Alona quadrangularis* was most frequent (9 of 27 specimens).

The two uppermost samples from 64 and 69 cm differ from the section below by the absence of foraminifers and by increased concentrations of *Bosmina longispina* (CLA3). Concentrations of the latter were 160 and 600-specimens/g dry weight at 69 cm and 64 cm, respectively. *B. coregoni* and *B. longirostris* were each represented by two specimens from 64 cm. 24 chydorid specimens of eight species were found in these two samples resulting in concentrations of 60 specimens/g dry weight at 69 cm and 90 specimens/g dry weight at 64 cm sediment depth.

The morphology of the specimens of *Bosmina longispina* from 487-cm sediment depth (zone CLA1b) corresponded to the specimens from the zone CLA1 in the core 211670-4/7. The medians of mucro length, antennule length, and number of antennule segments were 98 µm, 198 µm, and 13 segments, respectively.

DISCUSSION

The faunal composition of the CLA1 zones from both cores was almost identical. The presence and relatively high concentrations of the planktonic elements *Bosmina longispina*, *Bosmina longirostris*, and *Daphnia* sp. clearly reflect freshwater conditions, although *B. longispina* tolerates salinities >15‰ and was able to establish a brackish water population in the Baltic Sea, and *B. longirostris* as well as *Daphnia* species have been found in the Baltic Sea at salinities of 6-7‰ (Flößner 1972). However, the co-occurrence of the taxa and their high frequencies which refer to their role as major elements of the zooplankton at that time undoubtedly indicate the existence of a freshwater habitat. Remains of benthic chydorids made up less than 1‰ of the total cladocerans, i. e. the planktonic/littoral ratio was extremely high (Alhonen 1970; Hofmann 1998). This was due to the position of the site far from shore.

Likewise, the faunal zones CLA2 of both cores corresponded with respect to their characteristic features, i. e. the presence of foraminifers combined with very low frequencies of *Bosmina longispina*. *Bosmina longirostris* and *Daphnia* sp. were almost totally absent. The diagrams (see Figs. 1 and 3) show that *Bosmina coregoni* and chydorid species were slightly more frequent in core 211660-6 than in core 211670-4/7 which was particularly true for the upper section of this zone. The appearance of foraminifers is an evident signal of increased salinity, which is also indicated by the elimination of freshwater elements such as *Bosmina longirostris* and *Daphnia* sp. However, especially in the subfossil assemblage of core 211660-6 a slight influence by remains from freshwater cladocerans, i. e. *Bosmina coregoni* and chydorids, is discernible.

Finally, the zones CLA3 of both profiles were separated by the same major changes, i. e. a decrease in the concentration of foraminifers and an increase in *Bosmina longispina*. In the core 211670 the frequency of the latter species was much higher than in the zone CLA1 while in the core 211660 the proportions were exactly the opposite. Besides, chydorids were more frequent in core 211660-6 than in core 211670-4/7.

The CLA1/CLA2 boundary determined by a succession from freshwater cladocerans to marine/brackish foraminifers seems to indicate the shift from the Ancylus stage to the Litorina stage of the Baltic Sea. In core 211660-6 this boundary is situated at about 440-cm sediment depth. According to Voss et al. (2001), this horizon has an age of about 7200 years BP. Actually, this horizon represents a transitional period between the upper boundary of the cladoceran peak at 454 cm and the appearance of foraminifers at 435 cm. Most probably the drastic decline of freshwater cladocerans above 454 cm indicates the begin of increasing salinity. This would be in accordance with Harff et al. (2001) who showed that the 456-cm horizon represents the end of the Ancylus stage. Brenner (2001a) found that freshwater dinoflagellates disappeared at 472 cm and marine dinoflagellates appeared at 450 cm and concluded that the boundary between Ancylus (zone ESI II) and early Litorina stage (zone ESI III) lay within the 450-472 cm section.

Likewise, in the core 211670-4/7 from the North Central Basin the rapid decrease of the planktonic Cladocera, which occurred above 617-cm sediment, depth seems to be the first response to an increase of salinity. According to Brenner (2001a) the end of the Ancylus stage occurred within the 604-619 cm section as indicated by the boundary between the zones ESI III and ESI IV. Also in this case, the CLA1/CLA2 boundary between 592 cm and 598-cm sediment depth, determined by the appearance of foraminifers, is located somewhat above the beginning of the Litorina stage. Thus, in both cores, there was a time lag between the end of freshwater conditions and the first appearance of foraminifers in the sediment. The existence of a transitional zone rather than a sharp boundary is in accordance with the suggestion of a gradual increase of salinity for about 1000 years at the end of the Ancylus period (Huckriede et al. 1996).

The enormous increase in the frequencies of the freshwater cladocerans *Bosmina longispina* and *B. longirostris* at the end of the Ancylus stage observed in the cores from the Gotland Deep and the North Central Basin seems to be a typical phenomenon in the Baltic proper of that time. High frequencies in the same order of magnitude of both *Bosmina* species were also found in sediment cores from the Bornholm Basin and the Gdansk Bay (Hofmann 1987b). Also in these cases, the peak of *Bosmina longirostris* preceded the peak of *B. longispina*. As has been shown by diatom analysis (Abelmann 1985), these peaks were, however, located in the sediment layers of the Mastogloia period rather than in the true Ancylus stage.

The zone CLA2 of both cores represents the Litorina stage of the Baltic proper and corresponds to the zones ESI IV - ESI VIII of Brenner (2001a) while with respect to zone CLA3 the results are ambiguous. The increase of *Bosmina longispina* in both cores and the increase of remains of littoral chydorids in the core from the Gotland Deep coincide with Brenner`s observations, who found increased numbers of copepod eggs, cladoceran remains, *Pinus* pollen and coccal green algae (*Pediastrum*) in the uppermost section of the cores (zone ESI IX). As known from the literature (Lieder 1996) the specimens of *B. longispina* from this zone should represent the endemic brackish water taxon *B. longispina maritima* which at present inhabits the Baltic Sea. The subfossil specimens indeed differed in their morphology from the freshwater animals found during the Ancylus stage (zone CLA1) (see Fig. 2), it is, however, not possible to separate *B. longispina maritima* from freshwater populations by its morphology because this subspecies is in the morphological range of populations from large European oligotrophic lakes, i. e. the so-called lacustris races (Lieder 1996). At present *B. l. maritima* occurs in the eastern and central part of the Baltic Sea. The species avoids the western Baltic Sea because of the higher salinity's (Purasjoki, 1958 (sub *B. coregoni maritima*); Hofmann 1987b; Lieder 1996; Krey 1974 (sub *B. coregoni maritima*). It has been demonstrated by core studies that this species became extinct in the southwestern Baltic (Mecklenburg Bay, Neustadt Bay, Kiel Fjord, Vejsnaes) after the Litorina transgression (Hofmann and Winn 2000). A drop in salinity (Limnaea stage) (Hyvärinen 1988) is a possible explanation for the distinct increase of this species towards the top of the cores. The high frequencies of littoral elements among the microfossils found in the sediment of this zone are attributed by Brenner (2001a) to an increased coastal-basin transport.

References

Abelmann, A. 1985: Palökologische und ökostratigraphische Untersuchungen von Diatomeenassoziationenan holozänen Sedimenten der zentralen Ostsee. *Report Geologisch-Paläontologisches Institut der Universität Kiel 9,* 1-134.

Alhonen, P. 1970: On the significance of the planktonic/littoral ratio in the cladoceran stratigraphy of lake sediments. *Commentationes Biologicae 35,* 1-9.

Brenner, W. 2001a: Organic walled microfossils from the central Baltic Sea, indicators of environmental change and base for ecostratigraphic correlation. *Baltica 14,* 40-51.

Brenner, W. 2001b: Distribution of organic walled microfossils within single lamina from the Gotland Basin, and their environmental evidence. *Baltica 14,* 34-39.

Brodersen, K. P., Whiteside, M. C. & Lindegaard, C. 1998: Reconstruction of trophic state in Danish lakes using subfossil chydorid (Cladocera) assemblages. *Canadian Journal of Fisheries and Aquatic Sciences 55,* 1093-1103.

Flößner, D. 1972: Kiemen- und Blattfüßer, Branchiopoda, Fischläuse, Branchiura. *Tierwelt Deutschlands 60,* 1-499.

Flößner, D. 1990: Die Geschichte der Cladocerenfauna des Kleinen Barsch-Sees, eines sauren, kalkarmen Moorweihers im mitteleuropäischen Flachland. *Limnologica 21,* 125-135.

Frey, D.G. 1986: Cladocera analysis. *In* Berglund, B. E. (Ed.): *Handbook of Holocene Palaeoecology and Palaeohydrology,* 667-692. John Wiley & Sons, Chichester.

Frey, D. G. 1988: Littoral and offshore communities of diatoms, cladocerans and dipterous larvae, and their interpretation in paleolimnology. *J. Paleolimnol. 1,* 179-191.

Harff, J., Bohling G. C., Davis, J. C., Endler R., Kunzendorf, H., Olea, R. A., Schwarzacher, W. & Voss, M. 2001: Physico-chemical zonation of Gotland Basin (Baltic Sea) Holocene sediments. *Baltica 14,* 58-66.

Hofmann, W. 1987a: Cladocera in space and time: analysis of lake sediments. *Hydrobiologia 145,* 315-321.

Hofmann, W. 1987b: Stratigraphy of Cladocera (Crustacea) and Chironomidae (Insecta: Diptera) in three sediment cores from the Central Baltic Sea as related to paleosalinity. *Internationale Revue der gesamten Hydrobiologie 72,* 97-106.

Hofmann, W. 1998: Cladocerans and chironomids as indicators of lake level changes in north temperate lakes. *Journal of Paleolimnology 19,* 55-62.

Hofmann, W. 2000: Response of the chydorid fauns to rapid climatic changes in four alpine lakes at different altitudes. *Palaeogeography, Palaeoclimatology, Palaeoecology 159,* 281-292.

Hofmann, W. & Winn, K. 2000: The Littorina transgression in the Western Baltic Sea as indicated by subfossil Chironomidae (Diptera) and Cladocera (Crustacea). *Internationale Revue der gesamten Hydrobiologie 85,* 267-291.

Huckriede, H., Clasen, S. & Meischner, D. 1996: Hydrographic and climatic changes recorded in Holocene sediments of the Central Baltic Sea. *Baltica 9,* 76-91.

Hyvärinen, H. 1988: Definition of Baltic stages. *Annales Academiae Scientiarum Fennicae A III 148,* 7-11.

Korhola, A. 1992: The Early Holocene hydrosere in a small acid hill-top basin studied using crustacean sedimentary remains. *Journal of Paleolimnology 7,* 1-22.

Krey, J. 1974: Das Plankton. *In* Magaard, L. & Rheinheimer, G. (Eds.): *Meereskunde der Ostsee,* 103-130. Springer, Berlin-Heidelberg-New York.

Lieder, U. 1996: Crustacea Cladocera / Bosminidae. *Süßwasserfauna von Mitteleuropa 8 (2-3),* 1-80.

Lozan, J. S. 1992: Angewandte Statistik für Naturwissenschaftler. Paul Parey, Berlin.

Lutze, G. F. 1965: Zur Foraminiferen-Fauna der Ostsee. *Meyniana 15,* 75-142.

Purasjoki, K. J. 1958: Zur Biologie der Brackwasserkladozere Bosmina coregoni maritima (P. E. Müller). *Annales Zoologici Societatis Zoologicae Botanicae Fennicae Vanamo 19,* 1-117.

Voss, M., Kowalewska, G. & Brenner, W. 2001: Microfossil and biochemical indicators of environmental changes in the Gotland Deep during the last 10,000 years. *Baltica 14,* 131-140.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 58-66

Physico-chemical stratigraphy of Gotland Basin Holocene sediments, the Baltic Sea

Jan Harff, Geoffrey Bohling, John C. Davis, Rudolf Endler, Helmar Kunzendorf, Ricardo A. Olea, Walther Schwarzacher, Maren Voss

Abstract

Late Pleistocene to Holocene sediment cores from the Eastern Gotland Basin, Central Baltic Sea, were investigated by a numerical analysis of MSCL data describing the physical facies and geochemical data. A master core showing an almost complete sediment sequence was subdivided into lithostratigraphic units (zones) using a depth-constrained multivariate classification procedure including the variables p-wave velocity, wet bulk density, and magnetic susceptibility. This zonation coincides with the general stratigraphic frame for Holocene sediments in the Baltic Sea Basins. Using a numerical correlation procedure based on p-wave velocity and wet bulk density, the zonation of Litorina and post-Litorina sediments (units B-1 to B-6) was extended laterally to nearby cores. An acoustic index indicates varying oxygen supply to bottom water during deposition. Principal component scores derived from geochemical data are used as indicators of terrigenous flux into the basin and of bioproduction. Comparisons of grey-scale time series curves within the laminated units with d18O time series curves from Greenland ice cores, tree-ring curves from western Europe, and solar activity suggest a correlation between the Baltic Sea depositional environment and climate change indicators.

☐ *Sediment, physical properties, inorganic geochemistry, nitrogen/carbon isotope signature, grey scale values, physico-chemical zonation, stratigraphic correlation, Holocene, Gotland Basin, Baltic Sea.*

☐ *Jan Harff [jan.harff@io-warnemunde.de], Rudolf Endler, Maren Voss, Baltic Sea Research Institute, Seestr. 15, D-18119 Rostock, Germany; Geoffrey Bohling, John C. Davis, Ricardo A. Olea, Kansas Geological Survey / The University of Kansas, 1930 Constant Ave. Lawrence, KS, USA; Walther Schwarzacher, School of Geosciences, Queen's University, Belfast BT7 1NN, UK; Helmar Kunzendorf, Institute of Geography, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen, Denmark.*

☐ *Received 6 August 2001; accepted 20 November 2001.*

INTRODUCTION

Sediment cores from anoxic basins of the Baltic Sea serve as high-resolution indicators of their depositional environment because of the high sedimentation rate and low degree of bioturbation. Reading these records is particularly important for the reconstruction of climatic changes in the Northern hemisphere and the influence of climate change on the marine environment. Research during the past two decades on Baltic Sea depositional environments began with a general review by Winterhalter et al. (1981), who described the pattern of environmental change during the late Pleistocene and Holocene and the reflection of these changes in the sedimentary facies of Baltic basin sediments. In general, these sediments show a progression from late glacial varved clays (Baltic Ice Lake, fresh water), through transition clays (Yoldia Sea, brackish-marine, and Ancylus Lake, fresh water) to postglacial gyttja clay (Litorina Sea, brackish-marine) and recent muds (recent Baltic Sea, brackish-marine). A summary of the stratigraphic subdivisions of Baltic Late Quaternary sediments developed by Eastern European scientists is given by Emelyanov (1995), who interpreted the vertical changes in facies from a geochemical point of view. A comparable subdivision of Gotland Basin sediments was made by Huckriede et al. (1995), based on geochemical facies that reflected the oxygen supply in the depositional environment. A model by Sohlenius and Westmann (1998) explained not only the sedimentary environment but also the diagenetic formation of sedimentary minerals. Andrén (1999) reconstructed environmental changes during the Holocene based on a complicated lithological and geochemical interpretation of diatom stratigraphy and paleoecology.

New results in investigating of the Baltic Sea Holocene sediments have been achieved by an international research project BASYS (Baltic Sea System Study) Subproject 7, "The paleoenvironment based on the study of deep basin sediments" (Anonymous, 1996) financed by the European Union. The general objectives of this project are described in Winterhalter (2001). This paper reports on statistical data exploration within the frame of BASYS-7 intended to subdivide the late Pleistocene/Holocene sedimentary sequences of the Gotland Basin into facies zones that reflect changes in depositional environments during the late Quaternary. Physical data on sediments are incorporated together with inorganic geochemistry measurements and stable nitrogen and carbon isotope signatures. All data were acquired as part of the BASYS subproject-7. Physical properties, including p-wave velocity, wet bulk density and magnetic susceptibility (Endler 1998), and nitrogen and carbon isotope signatures (Voss et al. 1998) were measured by the Baltic Sea Research Institute (IOW). The Risø National Laboratory (Kunzendorf 1999) made inorganic geochemical analyses.

The age model used in this report is based on paleomagnetic studies by the Geological Survey of Finland (Kotilainen et al. 2000) and radio carbon dating and glacial varve analysis carried out at the University of Stockholm (Andrén et al. 1999, 2000). Multivariate statistical and time series analyses are the result of collaboration between the IOW, the Kansas Geological Survey, and the University of Belfast.

AREA OF INVESTIGATION / SAMPLING

This study concentrates on the Eastern Gotland Basin (Fig. 1), a 249 m deep depression within the central Baltic Sea. The water body is stratified, causing almost permanent anoxic conditions in the bottom water, resulting in a non-bioturbated sediment surface. Based on seismoacoustic surveys, a series of cores were taken in the basin; core 211660-1 was collected using a 9 m piston corer, cores 211660-5, 211640-7, and 211650-5 were collected using a 12 m gravity corer, and core 211660-6 was taken using a 9 m Kastenlot during a cruise of R/V Petr Kottsov in July and August of 1997 (Harff and Winterhalter 1997). Core 211660-6 was lithologically described and sampled for geochemical analysis by the Risø laboratories in Roskilde, Denmark, stable isotope measurement at the Baltic Sea Research Institute Warnemünde, and for paleomagnetic and mineral magnetic studies at the Geological Survey of Finland. Sediment cores 211660-5, 211640-7, and 211650-5 were cut into 1 m long sections of the plastic liner and were taken unopened to the Baltic Sea Research Institute for measurement of the physical properties of the sediment using a multi-sensor core logger. Core 211660-5 was described lithologically by B. Larsen of the Geological Survey of Denmark and Greenland (Harff and Winterhalter 1997) before measuring its physical properties. This core was also sampled at Warnemünde for paleomagnetic and mineral magnetic studies conducted at the Geological Survey of Finland. Core 211660-1 collected by T. Andrén was cut into sections for transport to Stockholm University where it was lithologically described and sampled for geochemical analysis at the Risø laboratories and for paleomagnetic and mineral magnetic studies by the Geological Survey of Finland. In addition, multi-sensor core log data from core 20050-1 (collected during the GOBEX project) was incorporated into this study (Endler 1998).

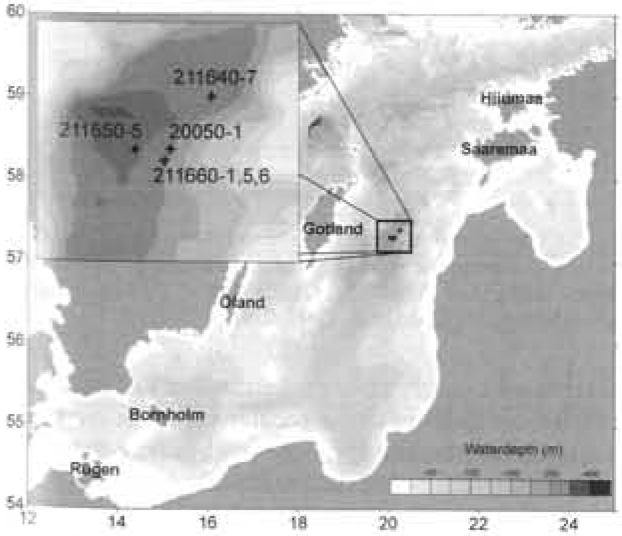

Fig. 1. Area of investigation showing core stations.

DATA

Sediment physics

Non-destructive logging of sediment cores was performed at the Baltic Sea Research Institute Warnemünde, using a Multi-Sensor Core Logger (MSCL) manufactured by GEOTEK Ltd. The scanner processes sections sequentially, producing an unbroken stream of data. Measurements include compression wave velocities and core diameters for calculation of p-wave velocities, gamma ray attenuation for the determination of wet bulk density, magnetic susceptibility, and a colour line scan yielding a digital record of the image of the core.

For this study, cores were cut in longitudinal direction with a special cutting device. The exposed sediment surface was carefully smoothed and prepared for optical scanning during the first pass through the MSCL. Next, a 4-mm thick plastic plate to make a flat, rigid surface required by the p-wave sensor covered the sediment surface. (Without this plate, the spring-loaded transducer would penetrate the sediment and the sensor would measure an incorrect core diameter.) During a second pass, all the other properties (p-wave velocity, wet bulk density, and magnetic susceptibility) were measured.

Calibrations (including corrections for electronic drift and core barrel liner material) were made by logging a special calibration piece before and after each core. Collecting sediment samples and estimating their wet bulk density did additional quality control by a conventional volume/weight method. Sound velocities were corrected to an in situ temperature of 4°C using a velocity gradient of 3.4 m/s per degree.

Grey values produced by the image scanner were made from freshly cut surfaces of cores 211640-7, 211660-5 and 211660-4, which were cut into 1 m sections onboard for scanning. Grey values were classified into 200 categories from black to white, recorded at steps of $81.9 * 10^{-6}$ m. The data are stored in separate digital files, each of which contains over 12,000 grey values for a 1 m section of core. (For more detailed information about multi-sensor core logging, see Boyce 1973; Gunn and Best 1998; Schultheiss and Weaver 1992).

Inorganic geochemistry

An energy-dispersive X-ray fluorescence (EDX) technique using radioisotopes for characteristic X-ray excitation was used for sediment analysis. The analytical system has been described elsewhere (Kunzendorf 1979). Briefly, the detector system consists of a Si (Li) detector coupled to an auto-sampler having a capacity of 48 samples. Sediment is placed into sample containers which have a very thin polyethylene film bottom to reduce self-absorption of the X-rays produced by the sample. Because the procedure is non-destructive, the same samples were also used for other purposes, such as 210Pb dating. Characteristic X-ray spectra from each sample were recorded by a multi-channel analyser and AXIL, a least-squares fitting program, was used to evaluate the complex spectra. The system was calibrated using recommended values for 28 international geological reference materials. Measurements were made for 1 hour using two different radioisotope sources to determine the major elements K, Ca, Ti, Mn and Fe, and the minor and trace elements V, Cr, Ni, Cu, Zn, Ga, As Br, Rb, Sr, Y, Zr, Nb and Mo. Precision of measurement is estimated to be less than 10% of the amount present. Detection limits for most trace elements are no greater than approximately 10 to 20 mg/kg.

Nitrogen- and carbon isotopes

Samples were taken for determination of total carbon and nitrogen and stable isotope composition at 5 cm intervals from surface to 550 cm depth. Cores were kept dark and cool while onboard the ship and were further processed in an onshore laboratory. Samples were dried at 60°C for 24 hours, then homogenized with a mortar and pestle. Roughly 10 mg of sediment were weighed into tin cups for $\delta^{15}N$ analyses. There is a persistent bias of 0.5–1‰ between $\delta^{15}N$ values measured on acidified sediment samples compared to non-acidified samples, so a split of the samples were used for carbon isotope measurements. The splits were weighed into silver cups, acidified with 2n HCl to remove carbonate, and again dried. These were placed into a Thermofinnigan CE 1108 CHN analyser connected to a Finnigan Delta S mass spectrometer via a Conflow II open split interface. Total carbon and nitrogen determinations were calibrated daily using acetanilide. A laboratory internal standard with a known $\delta^{15}N$ value (Pepton, Merck) was analysed after every six determinations. The isotope calibration of a N2 gas bottle was performed with IAEA-N1, N2, and N3 and a gas bottle of CO2 was calibrated for carbon against NBS 21 and 22. Delta values are given in the usual notation: $\delta^{15}N = ((^{15}N/\,^{14}N)_{Sample} \,/\, (^{15}N/\,^{14}N)_{Standard} -1)*1000$. The same procedure is used to calculate $\delta^{13}C$). The standard deviations, as calculated as the Peptone standard, are better than 0.15‰ for $\delta^{15}N$ and $\delta^{13}C$ measurements.

The age model

The age model for core 211660-1 is shown graphically in Fig. 2, which combines results from paleomagnetic studies, ^{14}C dating, and glacial varve analysis. Kotilainen et al. (2000) used magnetic inclination and declination and magnetic susceptibility measurements of sediment core for comparison to the secular variation recorded in varved lake sediments in Finland to date the sedimentary sequence over the past 3000 years. Older sequences are dated by Andrén et al. (2000) by accelerated mass spectrometry carbon analysis. Dating of glacial varves comes from measuring and correlating to the Swedish Time Scale in connection with the Greenland GRIP $\delta^{18}O$ record (Andrén et al. 1999, 2000). Fig. 2 shows the age model for core 211660-1 as a combination of data described before. This age model is extended to the cores 211660-5 and 211660-6 by a lithostratigraphic method explained below.

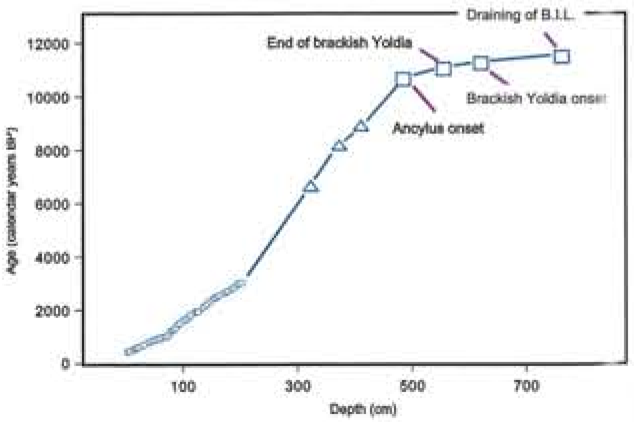

Fig. 2. Combined age model for Gotland Basin core 211660-1. Circles: paleomagnetic dating (after Kotilainen 2000); triangles: calibrated ^{14}C datings (Andrén et al. 2000); squares: varve datings (Andrén et al. 1999, 2000).

RESULTS OF DATA ANALYSIS

Physico-stratigraphic zonation

The initial step in analysis was zonation of master core 211660-5 using a depth-constrained multivariate classification procedure based on the p-wave velocity, wet bulk density, and magnetic susceptibility logs (Harff et al. 1999a, 1999b). Fig. 3 shows the results of zonation. This zonation has been converted to cores 211660-1, and 211660-6 by comparison of paleomagnetic datings (for zones B-4 to B-6 only) and by lithostratigraphic correlation using core desriptions by B. Larsen (Harff and Winterhalter 1997), and MSCL data. The results of the correlation of zone boundaries are shown in Table 1 for the zones B-1 to B-6. Based on this correlation the age model determined for core 211660-1 (Fig. 2) was converted linearly to cores 211660-5, and 211660-6. The age data for the zone boundaries shown in Figure 3 for core 211660-5 were received by using this age transformation. Sedimentary units comprising the Baltic Ice Lake to Ancylus interval are designated A-1 to A-6. Zones B-1 to B-6 are sequences representing deposition in the Litorina Sea to the Recent Baltic Sea. Zones B-1, B-3 and B-5 consist of laminated sediments, and units B-2 and B-4 represent non-laminated sequences. Units A3, A5, and A6 also are non-laminated. This physico-stratigraphic zonation coincides in detail with the lithological core description given by B. Larsen (Harff and Winterhalter 1997). Basin stages (Andrén 1999) are given in Figure 3.

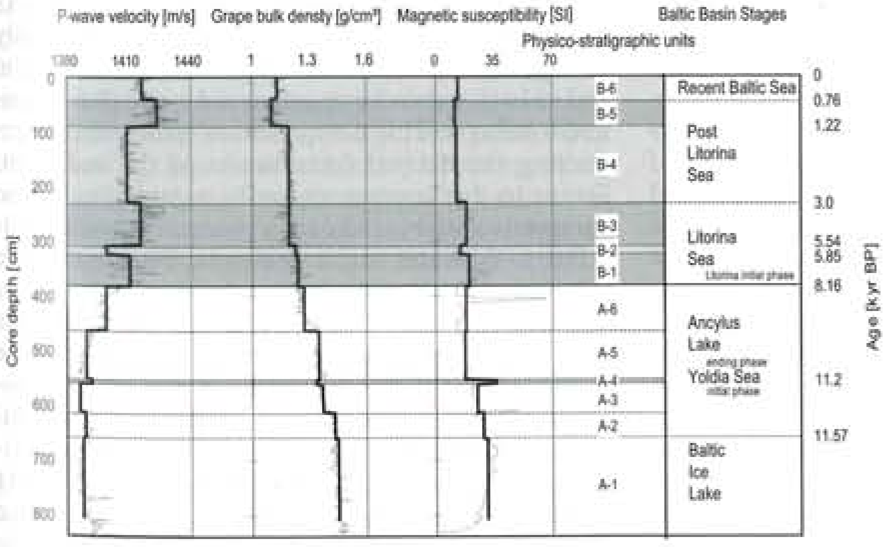

Fig. 3. Physico-stratigraphic zonation of Master Core 211660-5 correlated with Baltic Sea basin stages (Andrén 1999). MSCL data used for the zonation are shown by fine curves. Within the zones data are blocked by averaging and drawn by heavy discrete curves. Ages of zone boundaries given in the Figure are calculated using the age model in Fig. 2 correlated with core 211660-5 by the method described in the text.

Table 1. Lithostratigraphic correlation of Gotland Basin Late Holocene sediment cores based on MSCL data, core descriptions by B. Larsen (Harff and Winterhalter 1997), and paleomagnetic data by A. Kotilainen et al. (2000)

Zone	Core 211660-5 Depth (cm)	Core 211660-1 Depth (cm)	Core 211660-6 Depth (cm)
B-6	0 – 39	0 - 20	0 - 65
B-5	40 – 89	21 - 78	66 - 116
B-4	90 - 228	79 - 203	117 - 267
B-3	229 - 302	204 - 282	268 - 355
B-2	303 - 320	283 - 300	356 - 372
B-1	321 - 378	301 - 368	373 - 442

Physico-stratigraphic correlation

To confirm and extend the zonation of B-intervals defined in core 211660-5, numerical stratigraphic correlation was performed along a loop starting and ending with the master core. The sequence of correlations was from core 211660-5 to core 20050-1 to core 211640-7 and then back to core 211650-5.

The correlations are based on a method developed by Olea (1994) which maximizes a weighted sliding correlation coefficient, constrained by production rules on stratigraphic principles, implemented in the artificial intelligence program CORRELATOR. The program utilizes variation in p-wave velocity and wet bulk density in the two cores being correlated. In order to eliminate any effects of compaction on the acoustic variable, a first-order polynomial trend was subtracted from the measured data. An "acoustic index" was created as the residuals from a linear approximation of the p-wave velocity scaled over the interval (0, 1). By correlating along the closed loop, the zonation of core 211660-5 was extended to other cores and provided a way of defining a sedimentary sequence for the entire central Gotland Basin. The result of numerical correlation is shown in Fig. 4.

It can be shown that laminated sediments within the

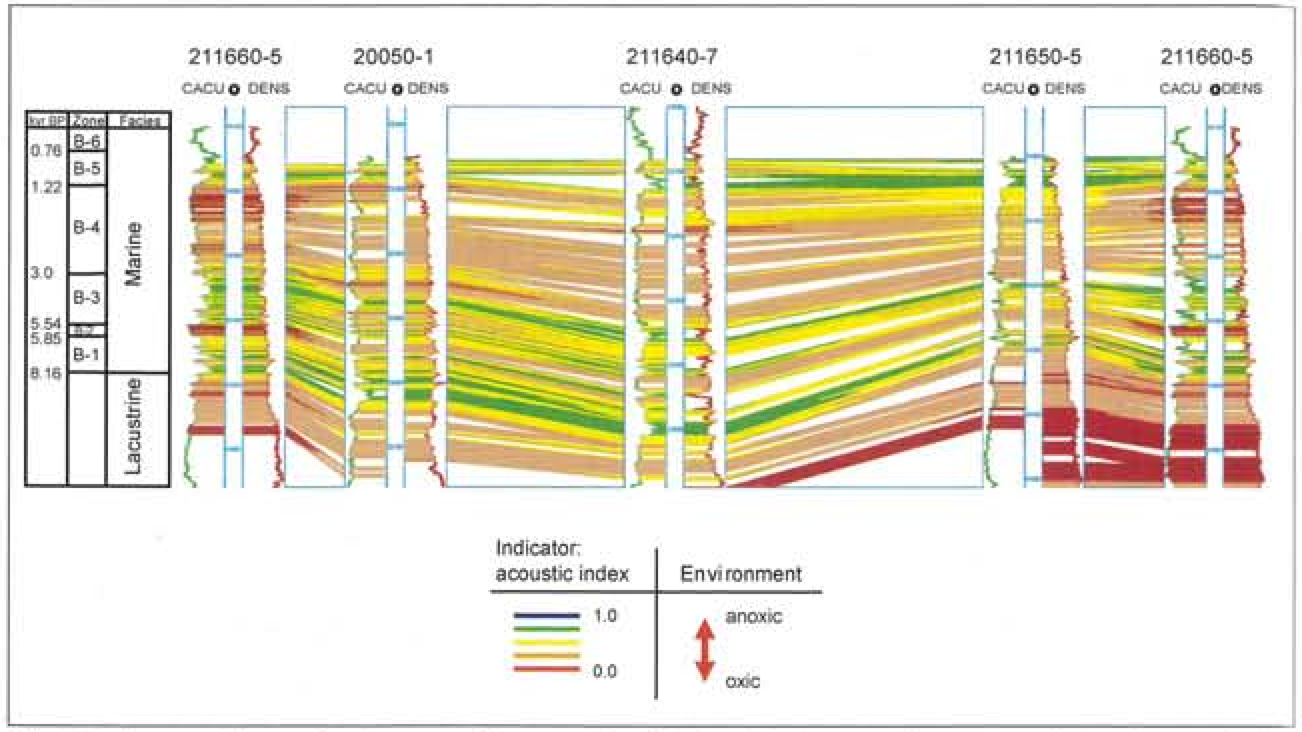

Fig. 4. Facies correlation and environmental interpretation of Gotland Basin cores. The cross section marks a correlation loop of coring sites 211660-5 22250-1 211640-7 211650-5 211660-5. "CACU" stands for the "acoustic index", "DENS" denotes the "wet bulk density". The interpretation of the variable "acoustic index" in terms of ventilation of the depositional environment is given qualitatively by a double arrow in the table below the cross plot. From green to blue the anoxic character of the depositional environment increases. Red stands for oxic depositional conditions.

cores reflecting anoxic environment of deposition show values of the acoustic index close to 1.0, whereas homogenous sediments deposited under oxic conditions of bottom water are represented by an acoustic index near 0. This leads to the assumption that the acoustic index can be used as a qualitative proxy-variable indicating the ventilation of near-bottom water during sediment deposition. Values of the acoustic index are represented by colors in Figure 4. So, the pattern of colors on the cross-section expresses changes in the oxygen supply to the bottom water. Red and orange colors stand predominantly for homogeneous layers of sediment while laminated sediments are expressed by blue and green. The homogeneous, bioturbated sediments of unit A6 are overlain by unit B1, marking the inflow of marine water into the Gotland Basin during the Litorina transgression. The influx of dense, saline water established a stratified water body that prevented oxygen in the surface layers from reaching lower levels, leading to an anoxic environment in the near-bottom water. Anoxic phases of units B1, B3, and B5 are interrupted by periods of stronger ventilation of bottom water, that were probably the result of a less stratified water column, and the consequent movement of oxygen from the surface by vertical mixing. This permitted the re-establishment of benthic life, which caused bioturbated sediments.

Geochemical facies and environment

Sediments from core 211660-1 were sampled and analysed for elements K, Ca, Ti, Mn, Fe, V, Cr, Co, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, and Nb. Principal component analysis with varimax rotation (Davis 1987) was used to summarize the variation in these elements. The first principal component contains 43 % of the total variance of all variables and primarily reflects contributions from –K, –Ti, –Rb, –Zr, +Cu, and +Mo (– stands for negative and + stands for positive loadings). This component is interpreted as reflecting the detrital constituents of the sediment. Scores on this component can be regarded as a new, composite variable indicating changes in terrigenous influx to the basin, and is shown by the curve on the left side of Fig. 5.

The signature of N_{tot}, C_{tot}, C_{org}, and stable isotopes $\delta^{15}N_{tot}$, $\delta^{13}C_{org}$ in sediment core 211660-6 were analysed at the IOW laboratories. A principal component analysis of these data revealed a principle component 1 (PC 1) comprising N_{tot}, C_{tot}, C_{org} with positive loadings (>0.6), and $\delta^{15}N_{tot}$ with negative loading (<-0.6) that account for 70% of the total variation within the set of variables. This component is interpreted as indicator for bioproduction and conservation of organic matter. The relation between production in the surface layer and organic content in the underlying sediment has been shown by Degens and Mopper (1976). The anoxic conditions in the bottom water might even strengthen this effect because microbiological degradation slowed down (Müller 1975).

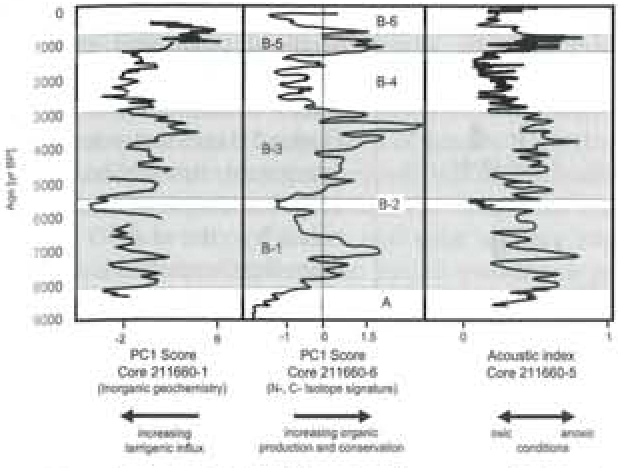

Fig. 5. Indicators of depositional environment during the marine-brackish stages of the Baltic Sea, derived from physical and geochemical data for sediment cores 211660-1, 21160-5 and 211660-6.

Figure 5 is a plot of the two sets of principal component scores and the acoustic index versus age and physico-stratigraphic zonation for cores 211660-1, 211660-5 and 211660-6. The indirect dating of cores 211660-5 and 211660-6 is carried out by the method described above using the correlation of zone boundaries shown in Table 1. The high correlation between the variables is obvious. The graph shows that high organic production and reduced terrigenous influx coincide with laminated sediments deposited under anoxic conditions. This agrees with the interpretation of Sohlenius and Westmann (1998) and Andrén (1999) who asserted that stratification of the Baltic water body resulted from increased water inflow from the North Sea, leading to more marine conditions. Periods of homogeneous sediments, reflecting oxygen-rich bottom conditions, are associated with increases in terrigenous influx and reduced organic conservation. These indicators substantiate the assumption of less saline water conditions. Comparison with the paleotemperature curve for the northern hemisphere given by Schönwiese (1995) confirms that an oxic depositional environment in the Gotland Basin coincided with a colder climate and anoxic environment of sedimentation was correlated with warmer climate.

Grey Scale values and other time series

The sequence of grey values represents a time series description of the core. The large number of observations make some analyses difficult, so the series was reduced by averaging scan values over 1 mm intervals. The averaged series for core 211660-5 is given in Fig. 6 and clearly shows the local stratigraphy defined by the physico-stratigraphic zonation. To study shorter fluctuations in the sequence, it is useful to remove large variations in grey level; for this purpose, a simple harmonic trend using the first eight coefficients of a Fourier series was fitted to the data. The grey level curve roughly coincides with curves of organic carbon, with high carbon values corresponding to high grey levels. There is no apparent evidence of regular annual stratification (varves), suggesting that a single year may be represented by several laminae.

Although there are uncertainties in interpreting the grey level succession, it does provide a very detailed record of environmental changes during Litorina time. Because parts of the grey-level series appear different, spectra were calculated for different intervals of core. Analyses were made using both the maximum entropy method (MEM) and singular spectral analysis (SSA). The well-laminated series in zone B-3 was selected for analysis of periodicity. Using the age model

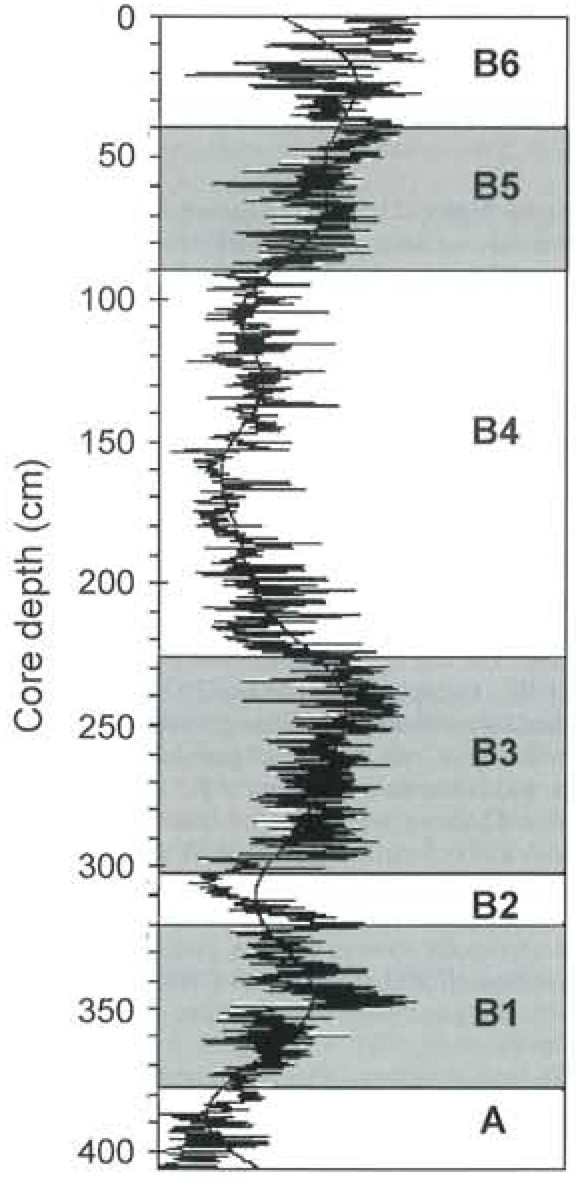

Fig. 6. Grey values and fitted harmonic trend against physico-stratigraphic units and age of core 211660-5.

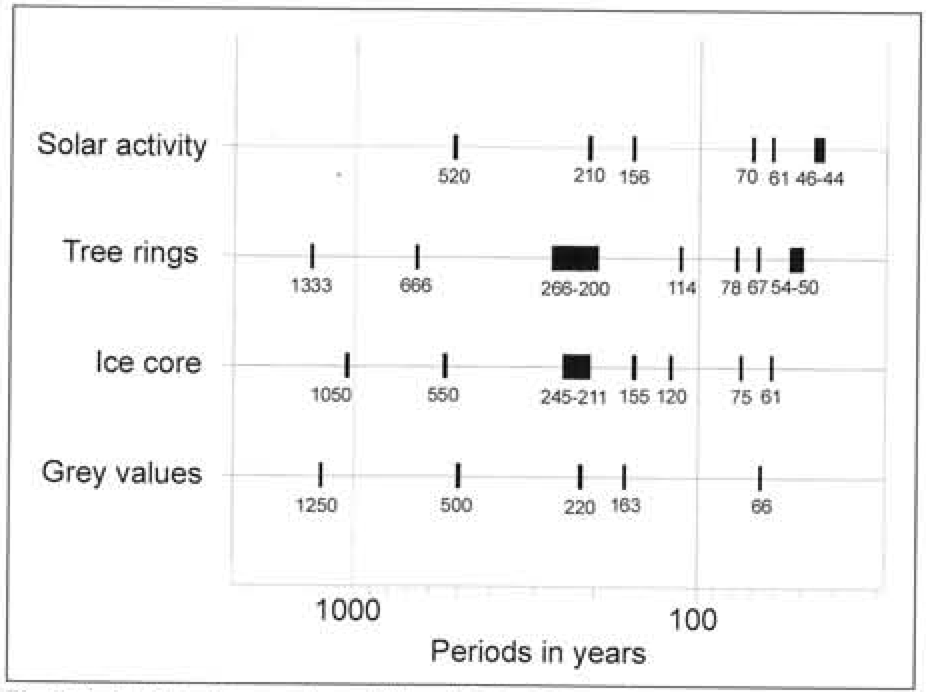

Fig. 7. Periodicity of grey values within unit B-3 of Master Core 211660-5 and tree ring thickness, ice core δ¹⁸O, and solar activity data. Correlation based on the age model in Fig. 2.

given by Figure 2 the data sequence in Figure 6 was converted into time. This conversion allows the comparison of the grey-level time series from Gotland Basin core 211660-5 (zone B-3) to dendrochronological records, to Greenland ice core (GRIP) data, and to solar activity time series (Grootes & Stuiver 1997). The composite record of growth from a large number of trees, in the form of measurements of thicknesses of tree rings, is a complicated record of environmental changes that is very similar to the sedimentary record, which is also mostly determined by changes in the environment. The Belfast 7000 year long chronology based on oak trees from Ireland, North and Central Germany (Pilcher et al. 1984) was used in this comparison. The tree ring series extends from 1983 AD to 5289 BC. Except during the last 200 years which is marked by a sudden increase in growth rate, the mean growth rate of oak trees has been 1.02 mm per annum, with a standard deviation of 8.8 mm.

A $\delta^{18}O$ curve was prepared from data from the NOAA Paleoclimatic Program at World Data Centre A (Anonymus 1997). A spline function was used to obtain five-year intervals, which were further smoothed with a ten-point moving average, giving 50-year average values of $\delta^{18}O$ at intervals of five years. Results of periodicity analysis for the four time series are shown in Fig. 7.

The results of time series analysis show a similarity of the periodic nature of all analysed variables. The periods 66, 163, 220, 520 of the sediment data correspond to periods within the ice core, tree rings and solar activity data. The 1250 frequency of grey values can be compared with ice core and tree ring data. The results suggest that the change of the depositional environment on a time scale from decades to millennia in the Gotland Basin seems to follow comparable rules to the change of paleotemperatures (indicated by the d $\delta^{18}O$ record from the Greenland ice cores) and the environmentally controlled tree ring thicknesses. Up to a centennial scale there is also a correlation with solar activity. Further studies have to explain the cause and effect relation of climate and depositional environment in the Baltic Sea basins.

CONCLUSION

Sediment cores of Late Pleistocene to Holocene age from the Eastern Gotland Basin of the central Baltic Sea were investigated by numerical analyses of physical and geochemical measurements of the sediments. A complete sedimentary sequence of the Late Pleistocene and Holocene of master core 211660-5 was subdivided into lithostratigraphic units by a depth-constrained multivariate classification procedure based on the physical properties p-wave velocity, wet bulk density, and magnetic susceptibility. Units A-1 to A-6 consist of Andrén's (1999) Baltic Ice Lake, Initial Phase of Yoldia Sea, Yoldia Sea, Ending Phase of Yoldia Sea, and Ancylus Lake stages. Units B-1 to B-5 consist of laminated and nonlaminated sequences within the stages Litorina Sea and Post Litorina Sea. Laminated sediments of units B-1, B-3, and B-5 reflect anoxic conditions caused by a stratified water body composed of relative salty bottom water overlain by less saline water. These units are interrupted by nonlaminated sediments of units B-2 and B4, which were deposited under oxygenated conditions. Unit B-6 coincides with Andrén's (1999) phase, Recent Baltic Sea. A combined age model (Andrén et al. 1999, 2000, Kotilainen 2000) was applied to date the sedimentary sequence. Numerical correlation was used to extend the zonation of Litorina and post-Litorina sediments (units B-1 to B-6) from the master core 211660-5 laterally to cores 20050-1, 211640-7 and 211650-5 using the records of p-wave velocity and wet bulk density. An acoustic index indicates changes in oxygen supply to bottom water during deposition. Principal component scores derived from inorganic geochemical data reflect terrigenous flux into the Gotland Basin. Principal component scores for nitrogen, carbon and their stable isotopes indicate the degree of bioproduction and conservation of organic material. Correspondence between principal component scores, acoustic index and paleotemperature curves for the late Quaternary suggests that brackish marine phases were associated with warm periods. Comparison of results from time series analyses of grey scale curves within laminated units to $\delta^{18}O$ data from Greenland ice cores, tree ring curves from western Europe, and solar activity suggests a correlation between the variation of the depositional environment of the Baltic Sea basins and the climate change indicators.

Acknowledgements

The authors express their thanks to Prof. Dr. William W. Hay, GEOMAR Kiel, and Dr. Thomas Andrén, Stockholm University, for their reviews of the manuscript and helpful discussions. Anke Barthel, Dr. Bernd Bobertz, Michael Meyer, and Dr. Raimund Rödel are thanked for their technical assistance during this investigation. Financial support of this study from the European Union is gratefully acknowledged.

References

Andrén, E. 1999: Holocene environmental changes recorded by diatom stratigraphy in the southern Baltic Sea. *Meddelanden från Stockholms Universitets Institution för Geologi och Geokemi No. 302*. 22 p.

Andrén, E., Andrén, T. & Kunzendorf, H. 2000: Holocene history of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10(5)*, 621-636.

Andrén, T., Björck, J., & Johnson, S. 1999: Correlation of Swedish glacial varves with the Greenland (GRIP) oxygen isotope record. *Journal of Quaternary Science 14*, 361-371.

Anonymous, 1996: BASYS Baltic Sea System Study, Technical Annex: European Commission, Directorate General 12 SRD, RTD Action: Environment, MAST 3, Most Relevant Sub-Area A.3.2: Baltic Sea, Contract MAS3-CT96-0058 (DG12-DTEE). 19 p., 10 attachments.

Anonymus, 1997: NSID User Service, The Greenland Summit Ice Cores CD-ROM, GISP-2/GRIP: World Data Center A for Glaciology, CIRES, Univ. Colorado, Boulder, CO.

Boyce, R.E., 1973: Appendix I. Physical property methods. In Edgar, N.T. et al. (Eds.): *Initial Reports, Deep Sea Drilling Project 15*, 1115-1128. US Government Printing Office Washington.

Degens, E. & Mopper, T.K. 1976: Factors controlling the distribution of early diagenesis of organic material in marine sediments. In Riley, J. P. & Chester, R. (Eds.): *Chemical Oceanography 6*, 59112.

Emelyanov, E.M. 1995: Baltic Sea: Geology, Geochemistry, Paleooceanography, Pollution. P.P. Shirshov Institute of Oceanology RAS, Atlantic Branch, Baltic Ecological Institute of Hydrosphere, Academy of Natural Sciences, Kaliningrad. 117 p.

Endler, R. 1998: Multi-sensor core logs of GOBEX gravity cores. *Meereswissenschaftl. Ber. 34*, 38-54.

Grootes, D.M. & Stuiver, X.X. 1997: Oxygen 18/16 variability in Greenland snow and ice 10 Ex3 10 Ex5 year resolution. *Journal Geophysical Research 102*, 12, 20455-26470.

Gunn, D.E. & Best, A.I. 1998: A new automated nondestructive system for high resolution multi-sensor core logging of open sediment cores. *Geo-Marine Letters 18*, 70-77.

Harff, J., Bohling, G.C., Endler, R., Davis, J.C. & Olea, R.A. 1999a: Gliederung holozäner Ostseesedimente nach physikalischen Eigenschaften. *Petermanns Geogr. Mitt. 143, Pilotheft 2000*, 50-55.

Harff, J., Bohling, G.C., Endler, R., Davis, J.C., Olea, R.A. & Schwarzacher, W. 1999b: Holocene sediments from the Baltic Sea Basins as indicators for the paleoenvironment. In Kippard, S.J. et. al.,(Eds.): *Proceedings of the IAMG '99, Trondheim, Norway, 6-11 August, 1999*, 195-200.

Harff, J. & Winterhalter, B. (eds.). 1997: Cruise Report *R/V Petr Kottsov*, July 22 August 01, 1997. Task: Research for BASYS-Baltic Sea System Studies. *Baltic Sea Research Institute, Warnemünde, October 1997*. 41 p., 6 attachments.

Huckriede, H., Clasen, S. & Meischner, D. 1995: Hydrographic and climatic changes recorded in Holocene sediments of the central Baltic Sea. *Baltica 9*, 76-90.

Kotilainen, A.T., Saarinen, T. & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166*, 51-64.

Kunzendorf, H. 1979: Practical experiences with automated radioisotope energy-dispersive X-ray fluorescence analysis of exploration geochemistry samples. Risø-R-407, Roskilde. 24 p.

Kunzendorf, H. 1999: Dating and assessing the Recent sediments of three deep basins of the Baltic Sea: Indication of natural and anthropogenic changes. Risø-R-1077(EN), Roskilde. 97 p.

Müller, P. J. 1975: Diagenese stickstoffhaltiger organischer Substanzen in oxischen und anoxischen Sedimenten. *"Meteor" Forschungsberichte, Reihe C, 22*, 160.

Olea, R.A. 1994: Expert systems for automated correlation and interpretation of wireline logs. *Mathematical Geolog., 26, 8*, 879-897.

Pilcher, J.R., Baillie, M.G.L., Schmidt, B. & Becker, B. 1984: A 7272-year long European tree chronology. *Nature 312*, 150.

Schönwiese, C. 1995: Klimaänderungen. Springer-Verlag, Berlin. 224 p.

Schultheiss, P.J. & Weaver, P.P.E. 1992: Multi-sensor core logging for science and industry. *Oceans 92 Proceedings, Mastering the Oceans through Technology 2*, 608-613.

Sohlenius, G. & Westman, P. 1998: Salinity and redox alternations in the northwestern Baltic proper during the late Holocene. *Boreas 27(29)*, 101-114.

Voss, M., Kowalewska, G. & Brenner, W. 2001: Microfossil and biogeochemical indicators of environmental changes in the Central Gotland Basin during the last 10,000 years. *Baltica 14,* 131-140.

Voss, M., Struck, U. & Bodungen, B. 1998: Paleoenvironmental variability indicated by stable isotope signals in bulk organic matter and exoskeleton remains in core 211660-1 (Central Gotland Sea). BASYS Conference, Stockholm, Sweden, 23-25 Sept. 1998. Abstracts.

Winterhalter, B., Flodén, T., Ignatius, H., Axberg, S. & Niemistö, L. 1981: Geology of the Baltic Sea. *In* Voipio, A. (Ed.): *The Baltic Sea.* Elsevier, 1- 121.

Winterhalter, B. 2001: The BASYS coring site in the North Central Baltic Sea Basin - a geological description. *Baltica, 14,* 8-17.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 67-73

Paleomagnetic dating of a Late Holocene sediment core from the North Central Basin, the Baltic Sea

Aarno Kotilainen, Tuovi Kankainen, Antti Ojala, Boris Winterhalter

Abstract

The scarcity or absence of organic material (organic carbon) in Baltic Sea sediment cores often makes accurate dating of the material difficult. In the present study, changes in the secular variations in the Earth's magnetic field have been used to date sediment core (00/96/02/GC-4) from the North Central Basin (NCB), the Baltic Sea. The results show that the paleomagnetic dating method can be used on these marine sediments, and that it is possible to correlate them with the secular variations observed in annually laminated lake sediments in Finland. According to paleomagnetic data, the sedimentation rate has varied in the study area from 0.2 up to 1.9 mm/a during the past 3000 years. Furthermore, the present results suggest an age of ~ 1200 varve years BP (750 AD) for the onset of a well defined acoustic reflector known as the "Viking Layer".

☐ *Geochronology, Holocene, Litorina Sea, magnetic susceptibility, marine sediments, Baltic Sea, paleomagnetism, secular variations, sedimentation rates,14C, paleoenvironment, Viking Layer.*

☐ *Aarno Kotilainen [aarno.kotilainen@gsf.fi], Geological Survey of Finland, P.O. Box 96, FIN-02151 Espoo, Finland;Tuovi Kankainen [tuovi.kankainen@gsf.fi]; Antti Ojala [antti.ojala@gsf.fi]; Boris Winterhalter [boris.winterhalter@gsf.fi].*

☐ *Received 9 August 2001, accepted 28 September 2001.*

INTRODUCTION

It is well known that accurate radiocarbon dating of Baltic Sea sediments often poses unsurmountable difficulties. This can be due to the scarcity or lack of organic carbon, especially in Late Pleistocene and early Holocene sediments, or due to contamination by resuspended older organic material. The ^{14}C deficiency of water probably also gives ages that are too old thus degrading the accuracy of the ^{14}C method.

The direction and strength of the Earth's geomagnetic field is known to vary through time on timescales from milliseconds to millions of years. Long-term variation with periods ranging from a few years to 104 years is called secular variation of the Earth's geomagnetic field (Merrill et al. 1996). The variations in the geomagnetic field are often stored as measurable parameters in sediments forming a continuous time series (Mackereth 1971). The use of the paleomagnetic method to date sediments is based on the assumption that small magnetic particles, sinking through the water column onto the seafloor, are oriented parallel to the Earth's magnetic field (Barton et al. 1980; Shcherbakov and Shcherbakova 1983; Tucker 1983; Shive 1985). This magnetic orientation remains, in suitable conditions, unchanged even when the particles become buried by continuous sedimentation. Modern, highly sensitive, equipment makes it possible to measure the variations in this orientation from sediment cores.

Since the mid-seventies there have been many paleomagnetic studies on Holocene Fennoscandian lake sediments (Tolonen et al. 1975; Stober and Thompson 1977, 1979; Huttunen and Stober 1980; Saarinen 1994, 1998, 1999), but only a few dealing with Baltic Sea submarine sediments (Rother 1989; Abrahamsen 1995). However, recently Kotilainen et al. (2000) showed the usefulness of this method by accurately dating Late Holocene sediments from the Gotland Deep, Baltic Sea.

In the present study, secular variations in the Earth's magnetic field have been used to date the sediment core 00/96/02/GC-4 (henceforth GC-4) from the NCB (the North Central Basin, Baltic Sea), by correlating results with paleomagnetic data based on annually laminated (i.e. varved) Finnish lake sediments (Saarinen 1998, 1999). In addition ^{14}C dates were determined from this core to construct the gross age model for these sediment deposits.

THE SEDIMENT CORE

The sediment core GC-4 (Lat 58°49.10 N, Lon 20°15.17 E, water depth of 175.8 m) was recovered during the BASYS - Baltic Sea System Studies - cruise on the *R/V Petr Kottsov*, in September 1996, from the North Central Basin (NCB) (Fig. 1). The NCB, like the Gotland Basin (GB), is known to be temporarily anoxic, thus providing minimum bioturbation of the sediments and good stratigraphic resolution, and are assumed to exhibit a more-or-less continuous deposition through the Holocene. The coring station was chosen on the basis of detailed mapping with high-resolution acoustics. A description of the geology of the NCB is given by Winterhalter (2001). The sediment core GC-4 (length of 550 cm) was taken on the top of a flat, wide, moderate elevation (Fig. 2) that was assumed to provide a near continuous high-resolution record of Holocene environmental changes.

METHODS

The NCB station was cored using a gravity corer (GC) with a length of 6 m and a diameter of 130 mm. The core was opened, described and immediately subsampled onboard. The subsamples for paleomagnetic and mineral magnetic studies were taken from a trimmed sediment surface using standard paleomagnetic sampling boxes (internal size approximately 2x2x2 cm) made of polystyrene. Sample boxes (with a small air-bleed hole at the bottom) were pressed perpendicularly into the trimmed surface at an interval of 3 cm, one side parallel to the horizontal bedding surface, and the adjacent side parallel to the long axis of the core. The subsamples were put in cool storage onboard.

Fig. 1. Index map of the study area (white star) showing the general bathymetry of the Baltic Sea in shades of grey based on data from Seifert and Kayser (1995).

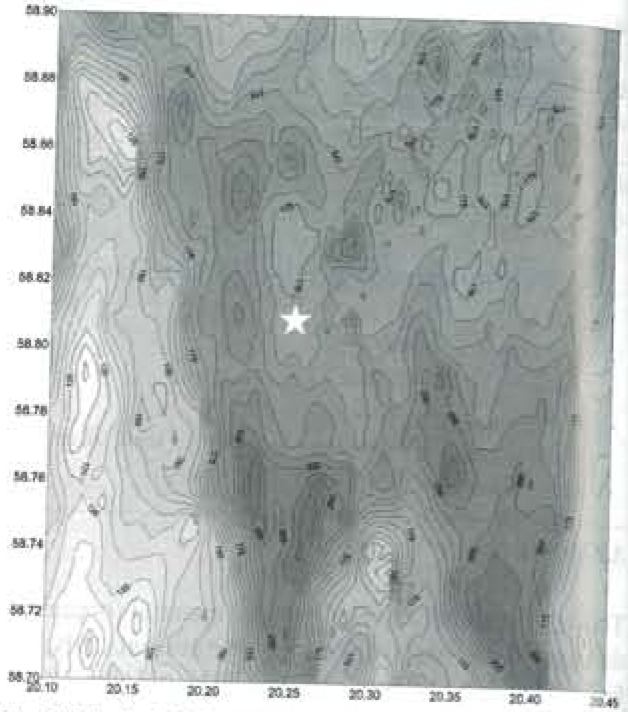

Fig. 2. The detailed bathymetry of the study area (NCB) with 5 m isolines based on the echo-soundings made by R/V Aranda. The white star shows the actual coring site in a water depth of 175.8 m. Note that coordinates are in decimal degrees.

The bulk susceptibility (K) of each sample box was measured after the cruise at the Geological Survey of Finland (GTK), using a Geofyzica Brno KLY-2 Kappabridge Susceptibility meter (Jelinek 1973). These measurements were repeated approximately six months later. Susceptibility values are presented in this work in volume-normalized SI units. The natural remanent magnetization (NRM) is the residual magnetization possessed by rocks and other in situ materials (Thompson and Oldfield 1986). The NRM moment (m) of the samples were measured at the GTK with a triaxial SQUID (Superconducting Quantum Interference Device) magnetometer (model 755R, 2-G Enterprises, see Fuller 1987). The direction of the NRM (declination, D, inclination, I) and the magnitude (M) were calculated using standard techniques (Collinson 1983).

Before using the paleomagnetic data for dating purposes it is important to know its reliability, e.g. during the long storage periods secondary remanence could develop (Lund and Banerjee 1985; Saarinen 1994). Secondary components could be "cleaned" by demagnetizing. In the present study alternating field (AF) demagnetization (Collinson 1983) technique was used. The samples were demagnetized with an automatic demagnetization device attached to the SQUID magnetometer. Selected samples from the different lithological units were sequentially demagnetized in three orthogonal positions starting from AF field value of 0 mT, and increasing it up to 120 mT (0, 5, 10, 15, 20, 30, 40, 50, 60, 70 80, 100, and 120 mT field were used).

Because the NCB station was cored using a gravity corer with no compass device, it was not possible to orient the core with map-north and thus the declination data is relative.

RESULTS

Lithostratigraphy

The simplified lithostratigraphy of core GC-4, shown in Figure 3, is based on the original description by Larsen and Repečka (1996). The surface part (0-5 cm) of this core consisted of black, hemiliquid disturbed, pelitic mud. Similar surface layers were seen in short undisturbed gravity cores taken from the same locality during the *R/V Aranda* cruise in April 1998. In the short gravity cores this unit (0-7 cm) included fluffy, fluid, laminated mud. This supports the assumption that the "real" surface is not missing from the core GC-4.

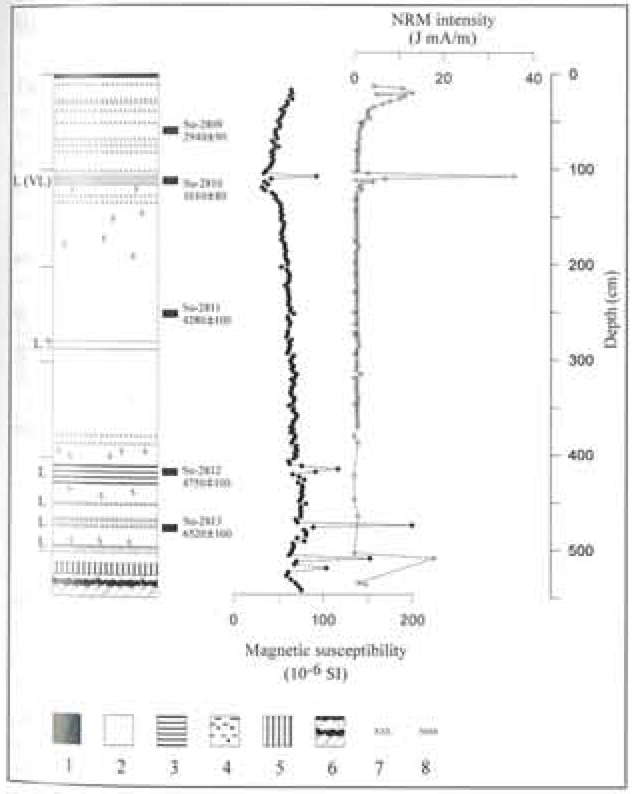

Fig. 3. Lithostratigraphy (modified after Larsen and Repečka 1996), bulk (volume) susceptibility (10^{-6} SI) and the intensity (J mA/m) of NRM in the core GC-4. L and VL indicate lamina and the Viking Layer, respectively. The ages (black squares) given are conventional radiocarbon ages BP (see Table 1). 1 - black, fluffy, disturbed clay gyttja, 2 - homogenous gyttja clay, 3 - finely laminated clay gyttja, 4 - (bluish grey) clay with small black spots and indistinct layering, 5 - (bluish grey) clay with dark grey mottling, colouring by diffuse sulphide, 6 - (bluish grey) clay with bands of sulphide, 7 - fine scale mottling (burrows ?), 8 - sulphide.

Radiocarbon dating

Five radiocarbon dates were determined from the core GC-4, in the dating laboratory of the GTK. The alkali-soluble fraction was used for dating, after an acid-alkali-acid pretreatment. The ages were calibrated to calendar dates using the marine data set (Stuiver et al. 1998) of CALIB 4.0 (Stuiver and Reimer 1993). For calibration it was assumed that the samples had been deposited in 60 to 100 years and that the regional reservoir age is 320 yr. (Mangerud and Gulliksen 1975). Radiocarbon dates are shown in Table 1.

Table 1. Radiocarbon dates from the NCB core GC-4

Laboratory No.	Depth (cm)	^{14}C age (BP)	δ^{13}C (‰)	Calibrated age (cal BP)
Su-2809	59-62	2940± 90	-27.5*)	2890-2710
Su-2810	106-114	1610± 80	-27.4	1310-1160
Su-2811	247-253	4280±100	-27.8	4640-4360
Su-2812	411-415	4750±100	-27.5	5260-4980
Su-2813	469-472	6520±100	-28.6	7230-6990

*) δ^{13}C was estimated

The sample Su-2813 is just above the first laminated sequence observed in the core GC-4 (Fig. 3). If these first laminated sequences in the core indicate the first inflows of saline (or brackish) water from the North Sea to the Baltic Sea, or a change in the sedimentary environment after this inflow event, the uncalibrated ^{14}C age of this sample (Su-2813), 6520±100 (BP), agree with earlier results of the time transgressive beginning of Litorina stage at approximately 7000-7500 (BP) (e.g. Ignatius et al. 1980; Eronen 1983; Hyvärinen 1984; Åker et al. 1988)

Results of magnetic measurements

Bulk susceptibility (K) reflects changes in the lithostratigraphy (Fig. 3). The values of K decrease from the surface down to approximately 104 cm. In the laminated sequence of pelitic mud (98-119 cm) the value of K reaches its minimum (K = 30 x 10^{-6} SI). An exception is a peak at 107 cm. From the depth of 119 cm down to 404 cm the values of K increase slightly. In the laminated mud unit (404-432 cm) the values of K are again just a little lower, an exception is a peak at the depth of 415-417 cm, similar to the one found at the depth of 107 cm. In the lowermost part of the core the bulk susceptibility is more variable and reaches its maximum values (K > 150 x 10^{-6} SI). The second susceptibility run, six months later, indicated that the maxima values found in the first run at the depths of 107, 415-417, 473, and 508 cm, were no longer observed. There were also minor changes in magnetic susceptibility in some other intervals. These observed changes in magnetic properties over the storage period are normally assigned to the oxidation of fine-grained ferrimagnets (Snowball and Thompson 1988; Oldfield et al. 1992). Also post-depositional diagenetic processes may alter the detrital NRM of sediments. These processes could cause the dissolution of magnetite and the authigenesis of ferrimagnetic iron sulphides (greigite or pyrrhotite) and therefore result in unsatisfactory data for paleomagnetic dating and correlation (Snowball and Thompson 1990; Snowball 1997; Sandgren et al. 1997).

The observed changes in the bulk susceptibility record at the depths of ~107, 415-417, 473, and 508 cm might indicate that the paleomagnetic data, at these intervals, has been altered by chemical remanent magnetization (e.g. authigenic greigite). Therefore these depths have not been included in our dataset.

The intensity and directions (D, I) of NRM for core GC-4 are shown in Figures 3 and 4, respectively. The NRM intensity was found to be quite low. Maximum intensities occurred at the depths of 15-26 cm (> 10 mA/m), 107 cm (36 mA/m), and 508 cm (18 mA/m). This intensity curve shows similar patterns with the bulk susceptibility curve (Fig. 3). Maxima in the declination record can be seen at the depths of 21.5, 58.8, 79.1, 95.7, 128, 175.5 and 245.7 cm, and minima at the depths of 37.6, 107.4, 122.1, 165.4 and 222.3 cm (Fig. 4). The declination data is only relative because it was not possible to orient the core. Minima in the inclination record could be found at the depths of 43.6, 61.9, 107.4, 133.8, 148.1, 174.1, 191.2, 208.5, 242.5 and 273.1 cm. The inclination maxima were found at the depths of 21.5, 58.8, 84.5, 111.8, 144, 185.7, 198.4, 222.3, 236.6 and 245.7 cm. The results of alternating field demagnetization indicate that at least the upper part of the core (approximately down to the 430 cm) is generally suitable for paleomagnetic studies.

Paleomagnetic correlation

Five samples from the core GC-4 were dated in the ^{14}C dating laboratory of the GTK. These data were used to construct a coarse age model for the core. Because of several facts, like the observed disturbances in the declination record caused probably by coring, only the upper 250 cm was used for this high-resolution study to guarantee good quality of the paleomagnetic data. The excellent high-resolution record of paleosecular variations in Fennoscandian lake sediment cores by Saarinen (1998, 1999) for the past 3200 years provided a promising setting for this study.

After establishing the coarse age model for the core GC-4, both the declination and the inclination data from this core was visually correlated with the paleomagnetic data from the work of Saarinen (1998, 1999). The correlation (Fig. 4) was mainly relatively straightforward. Inclination maxima at the depths of 111.8 and 185.7 cm were correlated to inclination maxima +I1 and +I3 from the Lake Pohjajärvi core and thus dated to ~1000 and ~2300 varve years BP respectively. The age of inclination maxima +I1 agrees relatively well with the ^{14}C-dating from this level. The only difficulties in the inclination record occurred at the two clear minima found at the depths of 107.4 and 133.8 cm. Comparing our record to the lake data (Saarinen 1998, 1999) both of these minima could represent the inclination minimum -I2 (~1650 varve years BP, Saarinen 1999). Nevertheless, the value from the depth of 107.4 cm was not used, because the disturbance is probably due to postdepositional diagenetic processes (e.g. formation of greigite). Instead of this the minimum from the depth of 133.8 cm was used.

The last declination minimum at the depth of 37.6 cm might correspond with the instrumentally observed western peak in northern Europe at ~1800 AD (Nevanlinna and Sucksdorf 1976), and it has been marked by D1 in the present study. The declination minimum at the depth of 122.1 cm was not very distinct, but it could be correlated with the declination minima D5 (~1220 varve years BP, Saarinen 1999) seen in the Lake Pohjajärvi data.

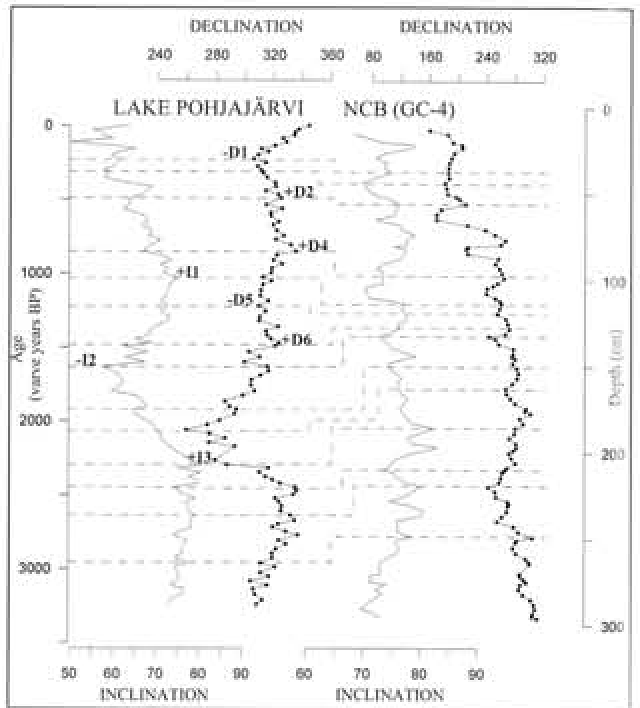

Fig. 4. A comparison of the inclination and declination data (shown in degrees) from the accurately dated sediment core from Lake Pohjajärvi (Saarinen 1998, 1999), Finland, with the measured values for the Northern Central Baltic (NCB) core GC-4. Time scale (varve years BP, in other words years before 1950) shown was established on the basis of the Lake Pohjajärvi core (Saarinen, 1998, 1999). A suggested correlation of the paleosecular variations between the lake core and the NCB core are shown by the dashed lines. -D1, +D2, +D4, -D5, +D6, and +I1, -I2 and +I3 indicate major features in the declination records and inclination records, respectively. The declination and inclination data shown for the NCB core GC-4 is slightly smoothed. The inclination data is shown by the solid lines and the declination data by the black dots.

The declination maxima at the depths of 58.8, 95.7, and 128 cm were matched with the declination maxima +D2, +D4, and +D6 (op.cit.). These declination maxima can be dated at ~500, 850, and 1500 varve years BP. Comparison of other inclination maxima and minima in core GC-4 (Table 2) with the Lake Pohjajärvi data shows good correlation (see Fig. 4). All "tie" points used in the correlation are shown in Table 2.

Because the paleosecular variation curve from the Lake Pohjajärvi core is based on annually laminated lake sediments, where the dating error is estimated to be less than ± 50 years (Saarinen 1999), the accuracy of the paleomagnetic dating shown in the present study should be relatively good (Table 2). It is clear that the accuracy of paleomagnetic dating depends upon the distance between the coring sites to be compared. In this case the latitudinal difference between the Lake Pohjajärvi and the NCB coring sites is ~ 5° and should thus not adversely affect dating, as the westward drifting of the secular variation is ~0.3° /year as stated by Bullard et al. (1950).

Table 2. Paleomagnetic dating of the North Central Basin core GC-4 based on the Lake Pohjajärvi curve (Saarinen 1998, 1999). D and I indicate declination and inclination, respectively. Varve ages to D2, D4, D5, D6, I1, I2 and I3 (rounded to nearest 50 yr.) are from Saarinen (1999)

Symbol	Age (varve years BP)	Depth (cm)	Sedimentation rate (mm/year)
D1	150	37.6	1.9
I	300	43.6	0.4
D2	500	58.8	0.8
I	750	84.5	0.9
D4	850	95.7	1.4
I1	1000	111.8	0.9
D5	1200	122.1	0.5
D6	1500	128.0	0.2
I2	1650	133.8	0.4
I	1900	148.1	0.5
I	2050	159.6	0.8
I3	2300	185.7	1.1
I	2450	208.5	1.5
I	2650	222.3	0.7
I	2950	245.7	0.7

Note that ages shown in the table are varve years (BP), using 1950 AD as a zero year.

Sedimentation rates in the North Central Basin

The results of paleomagnetic dating were used to calculate sedimentation rates for the core GC-4 with the intervals of the matched patterns of declination/inclination (Table 2), during the past 3000 years. Linear sedimentation rates varied from 0.2 to 1.9 mm/year (see Table 2 and Fig. 5). The average rate of sedimentation for this core was 0.83 mm/year for the last 3000 years. Maximum sedimentation rates 1.5, 1.4, and 1.9 mm/year occurred during 2450-2300 varve years BP (208.5-185.7 cm), 850-770 varve years BP (95.7-84.5 cm) and the last 200 years (37.6-0 cm). The lowest calculated sedimentation rates for dated intervals were ≤ 0.5 mm/year during 1900-1000 varve years BP (165.4-168.2 cm).

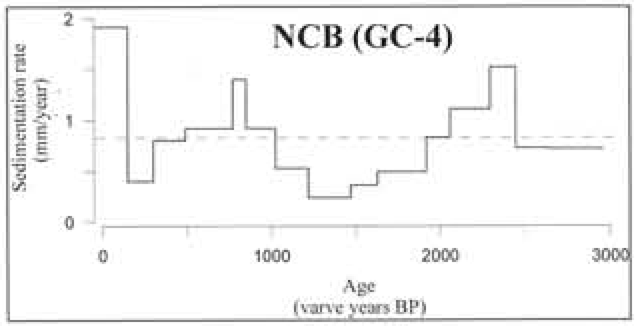

Fig. 5. The sedimentation rates in millimetres per year for the NCB core GC-4 are based on the ages of paleomagnetic features indicated in Figure 4. The dashed line indicates the average sedimentation rate over the last 3000 years.

DISCUSSION

Comparing radiocarbon dates to the results of paleomagnetic dating, the age of the uppermost sample Su-2809 is obviously too old, probably due to the redeposition of older material. It is also possible that the age of the sample Su-2811 is too old for the same reason, but the other ages seem to fit relatively well with the sediment lithostratigraphy. Thus it is reasonable to believe that the variations in the past geomagnetic field, recorded in the NCB sediments, provide a potential high-resolution dating tool to study the Late Holocene sedimentation history of this particular basin. However, some of the bioturbated intervals observed in the core GC-4 may have degraded the paleomagnetic signal. Therefore extra care is required when interpreting the result from these intervals.

Results based on the core GC-4 suggest that sedimentation rates have varied between 0.2 and 1.9 mm/year during the past 3000 years. These rates are relatively similar to those found in sediments from the BASYS coring site in the Gotland Deep (Kotilainen et al. 2000). Sedimentation rate in the topmost part of the core GC-4 (~1.9 mm/year) is very close to recent sedimentation rate of ~2 mm/year in the Gotland Deep, based on ^{210}Pb and ^{137}Cs datings of sediments by Kunzendorf and Christiansen (1997) and Emeis et al. (1998). The average sedimentation rate over the last 3000 years at this NCB site was 0.83 mm/year. The similar average sedimentation rates have been suggested also for the Gotland Deep sediments (Ignatius 1958; Ignatius and Niemistö 1971; Kotilainen et al. 2000).

It has been suggested for the Gotland Deep that the higher sedimentation rates are associated with major saline water inflow events from the North Sea into the Baltic Sea basins and to more homogenous sequences in lithology (Kotilainen et al. 2000). Increased bottom-near turbidity (nephloid layer) and gravity flow activity during these events could enhance sediment accumulation in the deep basins. Clear evidence of fast near-bottom currents (or turbidites) has not been shown in the present study. However, the sporadic pulses of saline water from the North Sea have provided better ventilated bottom water conditions and enhanced benthic activity resulting in bioturbation of the uppermost centimetre of the seafloor.

CONCLUSIONS

The present study supports the earlier assumption that NCB station is better sheltered from the direct influence of bottom-near currents than the Gotland Basin. Sediment surface geochemistry from the NCB (Vallius and Kunzendorf 2001) support also this. However, sediments at NCB site seem to be more bioturbated than in the Gotland Deep, which is probably due to the moderate elevation of this site (see Fig. 2).

The paleomagnetic correlation between Lake Pohjajärvi and NCB data enabled also the dating of the onset of the laminated interval observed in the upper part (100-120 cm) of the core GC-4, which can be dated at 1180 varve years BP. This layer, termed the "Viking Layer" during the 1996 *R/V Petr Kottsov* cruise, could be correlated with the similar layer observed in other NCB cores, and in cores from the Gotland Deep. Paleomagnetic dating of the NCB core 211670-8, and the Gotland Deep core 211660-1 suggest ages of 1200 (Kotilainen, unpublished data) and 1208 varve years BP (Kotilainen et al. 2000), respectively, for the onset of this interval. Very similar age (~1200 varve years BP) of this layer (in core GC-4) suggest that it is possible to use the "Viking Layer" as a marker horizon at least in the Gotland Deep and in the NCB basins.

Acknowledgements

Authors thank the staff and scientists on board the *R/V Petr Kottsov* during the September 1996 cruise for their very valuable help during coring and subsampling. Special thanks to Mr. Matti Leino at Geological Survey of Finland for his help in the paleomagnetic measurements and analyses. Authors also thank Dr. Timo Saarinen for providing his data. The reviewers, Prof. Jan Harff and Prof. Egidijus Trimonis made helpful comments towards the improvement of the manuscript. This study could not have been possible without facilities provided by Prof. Lauri Pesonen. The support received from the Geological Survey of Finland and the financial contribution by the EU, Baltic Sea System Study (BASYS) project MAS3-CT96-0058 are gratefully acknowledged.

References

Abrahamsen, N. 1995: Paleomagnetic investigation. *Aarhus Geoscience 5*, 55-63.

Bullard, E.C., Freedsman, C., Gellman, H. & Nixon, J. 1950: The westward drift of the Earth's magnetic field. *Philosophical Transactions of the Royal Society of London 81*, 103-120.

Barton, C.E., McElhinny, M.W. & Edwards, D.J. 1980: Laboratory studies of depositional DRM. *Geophysical Journal of the Royal Astronomical Society 61*, 355-377.

Collinson, D.W. 1983: Methods in Rock Magnetism and Paleomagnetism. London, Chapman and Hall. 503 p.

Emeis, K. C., Neumann, T., Endler, R., Struck, U., Kunzendorf, H. & Christiansen, C. 1998: Geochemical records of sediments in the Eastern Gotland Basin products of sediment dynamics in a not-so-stagnant anoxic basin? *Applied Geochemistry 13*, 349-358.

Eronen, M. 1983: Late Weichselian and Holocene shore displacement in Finland. In Smith, D.E. & Dawson, A.G. (Eds.): *Shorelines and isostasy. Institute of British Geographers special publication 16*, 183-207.

Fuller, M. 1987: Experimental methods in rock magnetism and paleomagnetism. *In* Celotta, R. & Levine, J. (Eds.): *Methods of Experinmental Physics. Orlando, Academic press, Inc.*, 304-471.

Huttunen, P. & Stober, J. 1980: Dating of paleomagnetic records from Finnish lake sediment cores using pollen analysis. *Boreas 9*, 192-202.

Hyvärinen, H. 1984: The Mastogloia stage in the Baltic Sea history: diatom evidence from southern Finland. *Bulletin of the Geological Society of Finland 56*, 99-115.

Ignatius, H. 1958: On the rate of sedimentation in the Baltic Sea. *Bulletin Commission Géologique Finlande 180*, 135-145.

Ignatius, H. Kukkonen, E. & Winterhalter, B. 1980: Pohjanlahden kvartäärikerrostumat. Summary: The Quaternary deposits of the Gulf of Bothnia. *Geologinen tutkimuslaitos. Tutkimusraportti 45*. 50 p. + 2 app. maps.

Ignatius, H. & Niemistö, L. 1971: Itämeren sedimentit ja sedimentaatio. Summary: Sediments and sedimentation in the Baltic. *Luonnon tutkija 75*, 72-80.

Jelinek, V. 1973: Precision A.C. bridge set for measuring magnetic susceptibility of rocks and its anisotrophy. *Studia geophysica et geodaetica 17*, 36-48.

Kotilainen, A.T. Saarinen, T. & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166*, 51-64.

Kunzendorf, H. & Christiansen, C. 1997: Estimation of recent sedimentation histories in the Gotland Basin using cores from the GOBEX study. *In* Cato, I. & Klinberg, F. (Eds.): *Proceedings of the Fourth Marine Geological Conference the Baltic, Uppsala 1995. Sveriges Undersökning Serie Ca 86*, 111-116.

Larsen, B. & Repečka, M. 1996: Description of cores taken at Cruise 00/96/02 Petr Kottsov, September 2-12, 1996. In Harff, J. & Winterhalter, B. (Eds.): Cruise Report R/V Pettr Kottsov, September 2-12, 1996. *Baltic Sea Research Institute, Warnemünde*, enclosure 4.

Lund, S.P. & Banerjee, S.K. 1985: Late Quaternary paleomagnetic field secular variation from two Minnesota lakes. *Journal Geophysical Research 90*, 803-825.

Mackereth, F.J.H. 1971: On the variation in the direction of the horizontal magnetization in lake sediments. *Earth Planetary Science Letters 12*, 332-338.

Mangerud, J. & Gulliksen, S. 1975: Apparent radiocarbon ages of recent marine shells from Norway, Spitsbergen, and Arctic Canada. *Quaternary Research 5*, 263-273.

Merrill, R.T., McElhinny, M.W. & McFadden, P.L. 1996: The magnetic field of the Earth, paleomagnetism, the core, and the deep mantle. *International Geophysical Series 63*, San Diego.

Nevanlinna, H. & Sucksdorf, C. 1976: Magnetic field in Finland, 1800-1970. *Finnish Meteorological Institute Studies on Earth Magnetism 25*, Helsinki.

Oldfield, F., Darnley, I., Yates, G., France, D.E. & Hilton, J. 1992: Storage diagenesis versus sulphide authigenesis; possible implications in environmental magnetism. *Journal of Paleolimnology 7*, 179-189.

Rother, K. 1989: Petro- und paläomagnetische Untersuchungen an jungquartären Sedimenten der Ostsee. *Veröffentlichungen des Zentralinstituts fur Physik der Erde 109*. 229 pp.

Saarinen, T. 1994: Paleomagnetic study of the Holocene sediments of Lake Päijänne (Central Finland) and Lake Paanajärvi (Northwest Russia). *Geological Survey of Finland, Bulletin 376*. 87 pp.

Saarinen, T. 1998: High-resolution paleosecular variation in northern Europe during the last 3200 years. *Physics of the Earth and Planetary Interiors 106*, 299-309.

Saarinen, T. 1999: Paleomagnetic dating of Late Holocene sediments in Fennoscandia. *In* Zolitschka, B. (Ed.): *High-resolution records from European lakes. Quaternary Science Reviews 18*, 889-897.

Sandgren, P., Hang, T. & Snowball, I.F. 1997: A Late Weichselian geomagnetic record from Lake Tamula, SE Estonia. *Geologiska Föreningens i Stockholm Förhandlingar 119*, 279-284.

Seifert, T. & Kayser, B. 1995: A high resolution spherical grid topography of the Baltic Sea. *Meereswissenschaftliche Berichte / Marine Science Reports, Institut für Ostseeforschung Warnemünde.*

Shcherbakov, V.P. & Shcherbakova, M. 1983: On the theory of depositional remanent magnetization in sedimentary rocks. *Geophysical Surveys 5*, 369-380.

Shive, P.N. 1985: Alignment of magnetic grains in fluids. *Earth Planetary Science Letters 72*, 117-124.

Snowball, I. & Thompson, R. 1988: The occurrence of greigite in sediments from Loch Lomond. *Journal of Quaternary Science 3*, 121-125.

Snowball, I. & Thompson, R. 1990: A stable chemical remanence in Holocene sediments. *Journal of Geophysical Research, B, Solid Earth and Planets 95*, 4471-4479.

Snowball, I.F. 1997: Gyroremanent magnetization and the magnetic properties of greigite-bearing clays in southern Sweden. *Geophysical Journal International 129*, 624-636.

Stober, J.C. & Thompson, R. 1977: Paleomagnetic secular variation studies of Finnish lake sediments and the carries of remanence. *Earth Planetary Science Letters 37*, 139-149.

Stober, J.C. & Thompson, R. 1979: Magnetic remanence acquisition in Finnish lake sediments. *Geophysical Journal of the Royal Astronomical Society 57*, 727-739.

Stuiver, M., Reimer, P.J. & Braziunas, T.F. 1998: High-Precision Radiocarbon Age Calibration for Terrestrial and Marine Samples. *Radiocarbon 40*, 1127-1151.

Stuiver, M. & Reimer, P.J. 1993: Extended 14C data base and revised CALIB 3.0 ^{14}C age calibration program. *Radiocarbon 35*, 215-230.

Thompson, R. & Oldfield, F. 1986: Environmental Magnetism. London: Allen & Unwin. 227 p.

Tolonen, K., Siiriäinen, A. & Thompson, R. 1975: Prehistoric field erosion sediment in Lake Lojärvi, S. Finland and its paleomagnetic dating. *Annales Botanici Fennici 12*, 161-164.

Tucker, P. 1983: Magnetization of unconsolidated sediments and theories of DRM. *In* Creer, K.M., Tucholka, P. & Barton, C.E. (Eds.): *Geomagnetism of Baked Clays and Recent Sediments. Amsterdam: Elsevier*, 9-19.

Vallius, H. & Kunzendorf, H. 2001: Sediment surface geochemistry of three Baltic Sea deep basins. *Ambio 30*, 135-141.

Winterhalter, B. 1996: Description of study area for SP-7. In Harff, J. & Winterhalter, B. (Eds.): Cruise Report R/V Pettr Kottsov, September 2-12, 1996. *Baltic Sea Research Institute, Warnemünde.*

Winterhalter, B. 2001: The BASYS coring site in the North Central Baltic Sea Basin - a geological description. *Baltica 14*, 9-17.

Åker, K., Eriksson, B., Grönlund, T. & Kankainen, T. 1988: Sediment stratigraphy in the northern Gulf of Finland. In Winterhalter, B. (Ed.): The Baltic Sea : papers prepared for a colloquium on Baltic Sea marine geology, Parainen, Finland, 27-29, May 1987. *Geological Survey of Finland. Special Paper 6*, 101-117.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 74-83

Authigenic mineralisation in the temporally anoxic Gotland Deep, the Baltic Sea

Kimmo Alvi and Boris Winterhalter

Abstract

The deep basins of the Baltic Sea and especially the Gotland Deep, east of the island of Gotland, have been temporally anoxic for most of its brackish water history during the past 8000 years. This circumstance has been conducive to the formation of a suite of authigenic minerals both in the water phase, at the water/sediment interface and as a diagenetic process deeper within the sediment itself. In the oxygenated shallow parts of the Baltic Sea, the occurrence of ferro-manganese concretions has been well recorded in literature. However, in the deep basins, oxygen depletion together with bacterial breakdown of detrital organic matter, have led to conditions suitable for the formation of a different suite of authigenic minerals, e.g. Ca-rhodocrosite, Mn-sulphide, pyrite, marcasite, barite, vivianite, and secondary gypsum. Especially the formation of Ca-Mn-carbonate has been found to be an excellent marker of anoxia and salt water inflow events.

☐ *Baltic Sea, saline inflow, anoxia, manganese carbonate, rhodocrosite, pyrite, marcasite, vivianite, barite, gypsum.*

☐ *Kimmo Alvi [kimmo.alvi@gsf.fi], Boris Winterhalter [boris.winterhalter@gsf.fi], Geological Survey of Finland, P.O.Box 96, FIN-02151 Espoo, Finland.*

☐ *Received 13 September 2001; accepted 5 November 2001.*

INTRODUCTION

The occurrence of various authigenic minerals in Baltic Sea sediments has been studied extensively by many researchers (e.g. Manheim 1961; Huckriede 1994; Lepland and Stevens 1998; Mälkki 2000). The influence of oxic versus anoxic conditions in the mineralisation process, including diagenesis, has been discussed in literature. The formation of oxyhydroxides of iron and manganese in oxidising conditions in the Baltic Sea has been reviewed by Winterhalter (1980), Glasby et al. (1997). Many authors (Calvert and Pedersen 1996; Neumann et al. 1997; Lepland and Stevens 1998; Kunzendorf 1999; Heiser 2000; Heiser et al. 2001) have attributed the formation of manganese carbonate to anoxic conditions in a saline marine environment. Except for the work done by Lepland and Stevens (op. cit.) most of the studies are based on analysis of bulk samples. The present study, based on a highly detailed SEM analysis, is an attempt to study specific mineral chemical characteristics of a long sediment core, from the semi-permanently anoxic Gotland Deep (GD), and to try to correlate them and the observed mineral assemblages to known events in the Holocene development of the Baltic Sea.

In the Central Baltic Sea, the Gotland Deep, east of the island of Gotland, is one of the main basins of Holocene sediment deposition in the Baltic Sea proper and a major recipient of saline pulses from the North Sea. It has been an area of active research for many decades and especially the GOBEX-project (Emeis and Struck 1998) provided valuable new data. Since GD is one of the few deep basins in the Baltic Sea with almost constant anoxic bottom conditions, it is especially suitable for studying the effects of intrusion of oxygen-rich saline North Sea waters followed by oxygen depletion and anoxia. Sediments from the Baltic Sea deep basins are traditionally considered to have preserved detailed information of environmental and climatic changes during the Holocene (Westman 1998; Andrén 1999). Increased dating accuracy of sediment cores (Kotilainen et al. 2000) has improved the possibilities of correlation of changes in the sediment record with known and inferred changes in environmental forcing.

The acoustic surveys and the long sediment cores taken during the BASYS project have shown that despite the size and depth (maximum depth of ~249 m) of the GD, sediment deposition has been both sporadic and patchy (Winterhalter 2001). By careful choice of coring locality and through comparison of adjacent sites (Kotilainen et al. 2001), the information we get from deep basin sediments still provides us, for most practical purposes, with a continuous Holocene record. Thus, the analysis of various physico-chemical variables along the sediment core should reflect the prevailing conditions during deposition. This is especially clearly demonstrated by the distribution of many elements, especially those forming such authigenic constituents as Mn-carbonates and ferrous sulphides. Numerous studies have shown that the occurrence of Mn-carbonate is restricted to the deepest parts of the Baltic Sea and that it is a good indicator of anoxic bottom conditions (Mannheim 1961).

In this report both scanning electron microscope and electron microprobe techniques were applied to a long sediment core from the Gotland Deep in order to study peculiarities in Holocene sedimentation processes related to the formation of authigenic and diagenetic minerals. Special emphasis was made on changes in Mn-carbonate- and Fe-sulphide contents.

MATERIAL AND SAMPLE PREPARATION

Core 211660-6 (57°17.0283 N, 20°07.1386 E, depth 241.3 m) was taken with a Giant Box Corer (Kastenlot) during the *R/V Petr Kottsov* BASYS cruise in July-August 1997. Total sediment recovery was 735 cm. The core was opened, photographed, subsampled and described in detail onboard immediately after coring (Harff and Winterhalter 1997). The size of the core (30*30 cm) provided ample material for a large variety of studies. In addition to subsamples taken by other involved laboratories, continuous subsamples for microprobe analysis, magnetic susceptibility and orientation measurements for paleomagnetic studies, and for X-ray radiographs were collected using 50-cm long plastic liners 1.5 cm by 5 cm in cross section.

Sediment description and general stratigraphy

The sediment in core 211660-6 (Fig. 1) extends back in time to ca. 11000-12000 years BP. A verbal description of the core is given in Harff and Winterhalter (1997). The lower part of the core represents glacial varved silts and clays of the Baltic Ice Lake stage. Late glacial clays with a short, weakly marine, interval (Yoldia Sea), follow this with abundant sulphide staining especially increasing in the lower part of the Ancylus Lake sequence. The bluish homogenous clays of the upper Ancylus Lake phase do show a few thin units of weak laminations before the final change from lacustrine to brackish marine conditions. The beginning of the Litorina Sea and the initial deposition of marine muds (increase in organic carbon) are placed at around 8000 years BP. In the deep parts of the Gotland Basin anoxia prevailed with only short spells of oxygenated near-bottom conditions occurring through out most of the last 8000 years. For a good review on the stages of the development of the Baltic Sea, see Björck, 1995.

The core has been dated by a combination of paleomagnetic and conventional radiocarbon methods (Andrén et al. 2000). The most accurately dated last 3015 yrs (Kotilainen et al. 2000) were based on a correlation of paleomagnetic results with those from annually varved Finnish lake sediments (Saarinen 1998). The older part of the core was dated by correlating AMS radiocarbon dates (Th.Andrén, pers. comm.) and magnetic susceptibility data with the British Master Curve (Turner and Thompson 1981, 1982) and preliminary data from some Swedish lakes provided by I.Snowball (pers. comm.). Using these ages and the sediment thickness, the average sedimentation rate for the whole core was calculated to 0.6 mm/a, with maximum values of almost 4 mm/a between 2950-3015 years ago. However, this high deposition rate may at least in part be due to the section break in the core at about 250-cm.

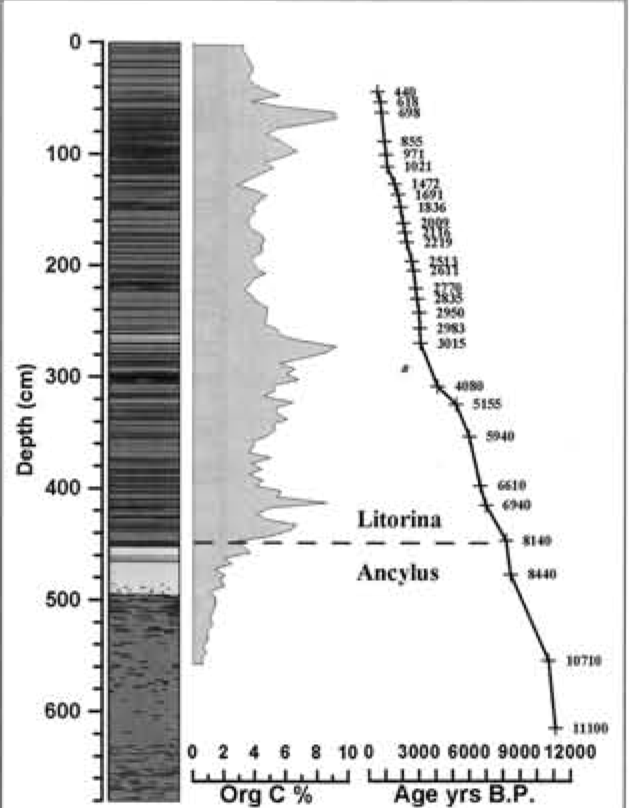

Fig. 1. Schematic sketch of the 680 cm long core, 211660-6, from the Gotland Deep, Baltic Sea (57°17,0283 N, 20°07,1386 E, depth 241,3 m). For details on the age model see the text. The gradual boundary between the fresh water Ancylus Lake clays and the brackish marine Litorina Sea muds is placed at around 443 cm coinciding with the beginning of a rapid increase in organic carbon according to assay data by Maren Voss (pers. comm.).

The boundary between marine muds and the fresh water Ancylus clays is placed at ca. 443 cm (Fig. 1) where the homogenous bluish clays change into the overlying laminated pelitic muds. Although most of these rather organic rich (4-9% C_{org}) muds exhibit a laminated or banded structure, indicative of anoxic conditions, the occurrence of thin layers (on a centimetre or even sub-centimetre scale) of rather homogenous greenish grey sediment has been considered as proof of short intervals with sufficient dissolved oxygen in the bottom-near waters to sustain benthos and bioturbation. It should be noted that benthic activity could occur even though the bottom-near water is anoxic. According to observations by one of the authors (Winterhalter) from a manned submersible drive during the 1995 cruise of the *R/V Logachev*, numerous individuals of the species *Harmotoe* were seen feeding on detrital organic matter while water samples showed the bottom-near water to be anoxic. This clearly indicates that some benthos can temporally survive anoxia.

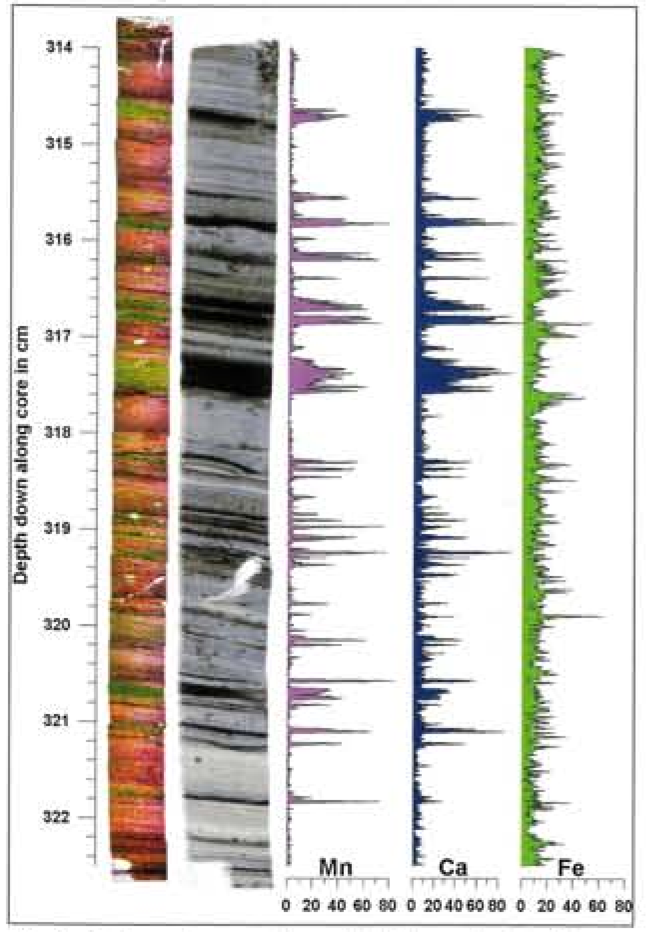

Fig. 2. Colour micrograph mosaic (thin section) and x-ray image (polished section) of a typical core section ca. 8.5 cm in length and the results (relative concentrations as counts) of a WDS (wavelength dispersive spectrometer analysis) scan along the middle of the slide (x-ray image). The colours in the micrograph (thin section) were altered by using a gypsum comparator to enhance the Mn-carbonate layers (green). The x-ray image shows clearly the higher density of the carbonate. The ferrous sulphide occurs as small individual grains or minor aggregates. Therefore they are not clearly discernible on the x-ray image. The minor differences between the thin section and surface slide are due to some loss in material during sawing and polishing of the impregnated sample. Note that the deposition of Mn-carbonate seems to occur after the deposition of FeS.

Below the Ancylus-Litorina boundary, the bluish clay contains millimetre-sized black dots and lenses which grade downwards into black ferrous sulphide (hydrotroilite) layers up to 5 mm thick between 496 to 536 cm. Further down this black sulphide staining becomes again successively rarer and at the depth of 675 cm only few black grains of amorphous hydrotroilite are found.

Sample preparation

Samples for microanalysis were prepared down to a depth of 482 cm, reaching about 40 cm below the Ancylus/Litorina boundary. The core above 50 cm was too watery to be properly sampled for slide preparation. Altogether 50 subsamples, each 8.5 cm long and 1 cm x 0.4 cm by cross section, were taken from the core; slightly overlapping each other in order to obtain full coverage of the sediment column. The samples were dried by a process of replacement of water with acetone and followed by impregnation with epoxy resin (Lamoureux 1994). This was done by immersing the sample in the resin, removal of trapped air in a vacuum desiccator and then replacing the voids with liquid epoxy by slowly opening the desiccator to ambient pressure. Finally the blocks, fully saturated with epoxy resin, were heated at 55°C for 48 hours to allow the epoxy to cure. For preliminary visual inspection, each block was X-rayed using a standard Phillips industrial X-ray source at 40 kV current and 2 min. exposure time on standard X-ray film.

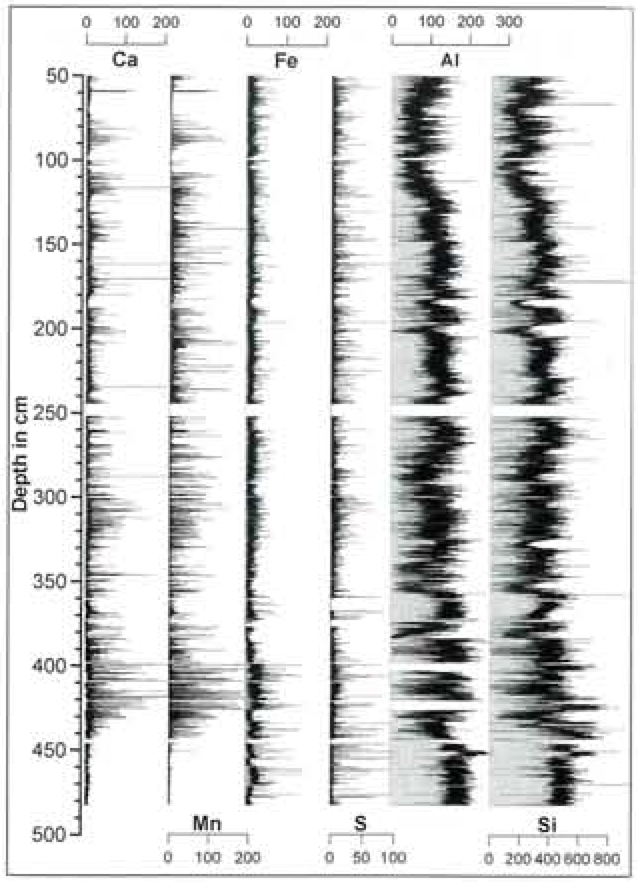

Fig. 3. Linescans from electron microprobe analysis consisting of over 60,000 individual measurement points along the core 211660-6. The horizontal scales denote the number of counts (relative intensity) and are only a crude indication of the abundance of each element. The correlation between Ca and Mn is very clear. The existence of FeS is obvious in the lower part of the core, but higher up the abundance decreases and is also masked by Fe in other minerals. The Al and Si, representing silicates, show a decreasing trend towards the present.

The epoxy impregnated blocks were used to prepare thin sections for mineral microscopy and polished surface sections for microprobe and SEM studies. To prevent build-up of electric surface charges on the polished slides during electron bombardment, which would hamper electron imaging and spectral analysis, the surface was coated with a thin (20-30-nm) film of carbon in a vacuum chamber with a carbon evaporation source.

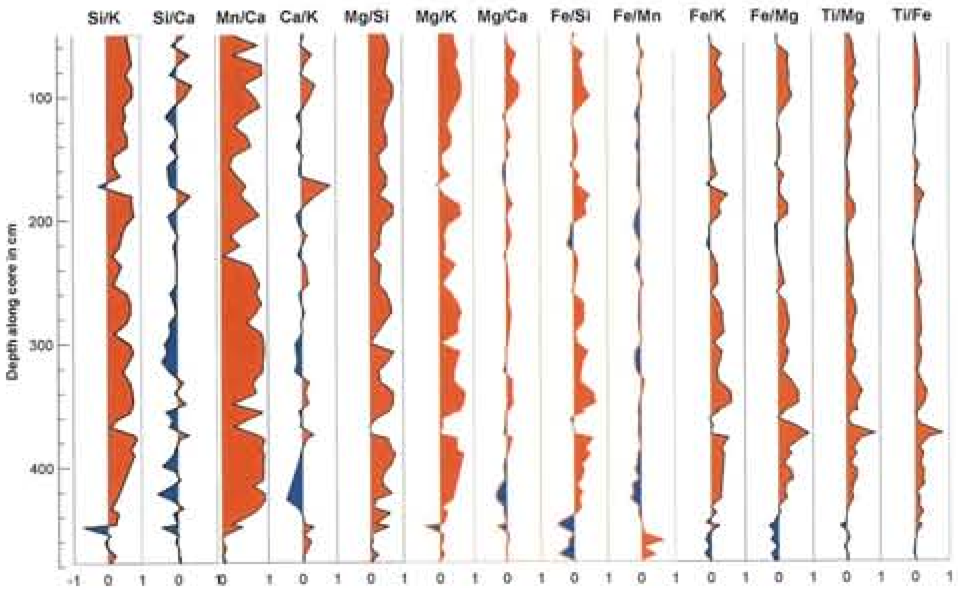

Fig. 4. Correlation between a number of elements based on the linescan data. The scale is from -1 (blue) to +1 (red). The diagram showing the correlation coefficients along the length of the core also gives an indication of the variations in the mineralogy.

MICRO-ANALYTICAL MEASUREMENTS

Electron microprobe (EMP) analysis is a technique for chemically analysing small selected areas of solid samples, in which X- (gamma) rays are excited by a focussed electron beam. The X-ray spectrum contains lines which are characteristic of the elements present. Hence a qualitative analysis is easy to obtain by identifying the lines based on wavelengths *(wavelength dispersive spectrometer analysis, WDS)* or photon energies *(energy dispersive spectrometer analysis, EDS)*. When suitable reference standards are available an accuracy of ±1% (relative) is obtainable and detection limits are typically in the region of 50 ppm. Spatial resolution is limited to around 1 micron due to the spreading of the beam after it enters the sample.

The Cameca SX50 electron probe micro analyser, in operation at the GTK, since 1993, has a 0.2 to 50 kV ion pumped electron gun with a three lens electron optical column and an electron absorber liner tube. The vacuum system is fully automated. The wavelength dispersive spectrometer (WDS) analyser includes four vertical spectrometers, three of them having two diffracting crystals and one with four crystals. With the new multilayer crystals the Cameca SX50 is capable of WDS analysis of light elements starting with Be. A newly acquired JSM-5600LV scanning electron microscope (SEM) was used for more detailed analysis and imaging. The details of the laminated sediment features seen in the thin sections were further studied under an optical microscope especially to get a better understanding of the chemical and mineralogical peculiarities of the laminae.

Electron probe analytical profiling

The electron probe micro-analyser was used to determine the element distribution along a profile across the whole length of each 8.5 cm polished sediment sample by automated profiling with wavelength dispersive spectroscopy (Fig. 2). Each profile consisted of 1024 measuring points bombarded with a circular electron beam of 80-micron diameter. Measuring current was 20 µA at 15 kV with a dwell time of 200 ms per point. The analysis is of a qualitative nature, since the results only show the presence and relative abundance of elements given as counts. No absolute quantities could be measured due to lack of suitable reference material. However, the data gives an excellent idea of element distribution and interrelationship throughout the length of the core.

Following the preliminary test runs showing very good correlation between manganese and calcium and also between iron and sulphur, all surface slides between 50 cm and 482 cm were scanned for Al, Ca, Fe, K, Mg, Mn, S, Si and Ti. Except for a few gaps the results show inter-element-relationships that can be attributed both to provenance of the detrital material and variations in the environment (Fig. 3). Because barium, vanadium, phosphorus and molybdenum, among others, are known to be good environmental indicators, the distribution of such elements was also studied. Unfortunately their concentrations were mostly under the reliability limit and thus scanning was limited to a few slides.

Scanning electron microscope analytical imaging

The electron probe was mainly used for continuous profiling along the entire length of the slide, while the SEM provided element distribution maps of superior quality and semi-quantitative analysis of fixed points. This was especially employed in the detailed study of e.g. manganese rich laminae and the distribution of pyrite.

RESULTS

The almost continuous element distribution profile consisting of over 60,000 point measurements between 50 and 482 cm along core 211660-6 were used in displaying the distribution of calcium, manganese, iron, sulphur, aluminium and silica shown in Fig. 3. The resemblance of the calcium distribution pattern with that of manganese is striking. As will be later shown, this is due to the abundant occurrence of Ca-Mn-carbonate lamina. The minor differences between the two graphs can be easily attri-buted to the sporadic exis-tence of other calcium bearing minerals. For the main marine mud sequence, the similarity between the iron and sulphur graphs is not as obvious as that of the previous pair. The interdependence is mainly limited to the transition between the Litorina muds and Ancylus clay, where ferrous sulphides abound. The upward decreasing trend in aluminium and silica clearly indicate the change of detrital material from predominately terrigeneous silicates to authigenic inorganic and organic detritus.

To get a better idea of the relationships between the different elements, the data from each of the scanned surface slides, averaging 1000 point measurements per slide, were used to calculate the correlation coefficients. The results are presented in Fig. 4. The correlation coefficients can be seen to vary considerably along the length of the core. This clearly indicates that both the provenance of the detrital material and above all the environmental conditions have varied through time.

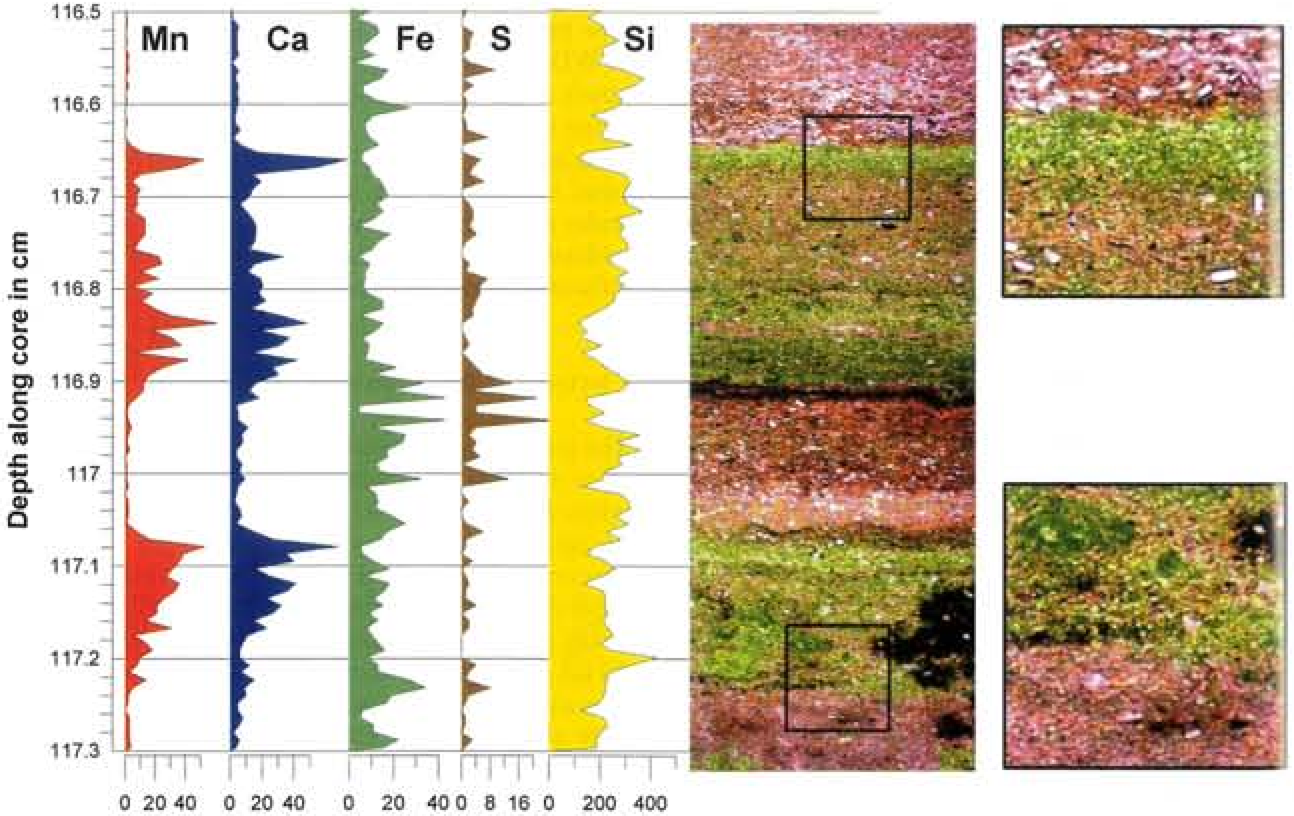

Fig. 5. Short core section showing the sediment matrix and several Mn-carbonate lamina. WDS element linescan showing the relative (WDS) variations in Mn, Ca, Fe, S and Si contents along a core section from the depth of 116.5 to 117.3 cm. The colours in the micrograph (thin section) were altered by using a gypsum comparator to enhance the Mn-carbonate layers (green). The boxed images are 1.2 mm square. The matrix consists of detrital mineral matter and abundant remains of diatoms. Note the intact laminae above 116.9 cm, the underlying black FeS layer, and the disrupted (bioturbated?) laminae below 117.1 cm.

The sediment matrix

The sediment matrix of the marine mud unit consists mainly of clay-sized mineral particles and organic detritus, including skeletal remains of diatoms and chitinous zooplankton. The detrital clay matrix, which makes up by far the bulk of the sediment in core 211660-6, is characterised by notably higher number of counts of Si and Al (see Fig. 3) in the EMP analysis compared to the other analysed elements. In the upper Ancylus sediment Si and Al contents are high with very little variation, reflecting the dominance of inorganic detrital particles. At the Ancylus/Litorina boundary, where the sediment type changes from homogenous into more laminated, variations in Si- and Al contents become more evident. This clearly reflects increasing influx and deposition of organic matter during the early stages of the Litorina Sea (see Fig. 1). In laminated Litorina sediments the silicate content is at its highest in between the lamina and drops significantly within them.

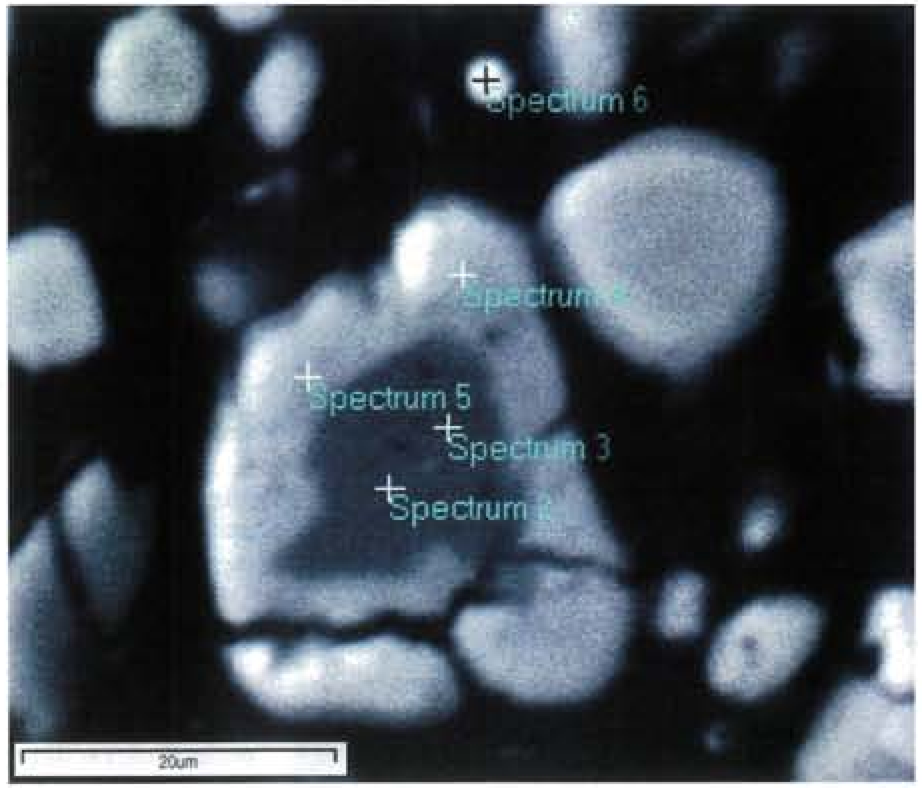

Fig. 6. SEM image of Mn-carbonate grains showing the location of point measurements. Note the dark dolomitic nucleus and the light-coloured Mn-carbonate rim. The results are shown in Table 1.

Table 1. The results of SEM point analysis of Mn-carbonate grain calibrated to standard rock samples. All results in weight percent

Spectrum	C	Na	Mg	Al	Si	S	Cl	K	Ca	Mn	Fe	Br	O	Total
Sum Spectrum	21.63	0.31	0.43	0.87	2.24	0.25	0.00	0.29	2.20	6.35	0.73	0.00	64.70	100
Spectrum 2	0.00	0.00	19.51	0.65	2.20	0.00	0.36	0.00	38.82	4.12	1.35	0.00	33.00	100
Spectrum 3	15.03	0.00	8.97	0.00	0.82	0.17	0.16	0.00	17.34	2.11	0.58	0.00	54.82	100
Spectrum 4	0.00	0.00	1.31	0.00	1.92	0.35	0.00	0.00	19.63	49.43	0.00	1.56	25.80	100
Spectrum 5	0.00	0.00	2.26	0.00	3.31	0.55	0.33	0.46	20.24	45.38	0.00	0.00	27.47	100
Spectrum 6	18.80	0.00	0.00	0.00	0.82	5.77	0.00	0.18	0.35	1.98	8.39	0.74	62.85	100

Sum spectrum is the average composition of the area covered by the image. Spectrums 2 and 3 are from points within the nucleus (dolomitic) and Spectrums 4 and 5 from the Mn-carbonate rim, and spectrum 6 from a small pyrite grain.

Authigenic minerals

Most of the material comprising the sediment is derived from transported and redeposited mineral matter. The source of the material varies from fluvial to aeolian and from coastal to deep-water erosion. This material consists of various mineral fragments although silicates abound and especially quartz, often in the form of diatoms, is an important constituent (Fig. 5). In addition to organic matter of terrestrial and marine/lacustrine origin, minerals formed in the water phase or in the sediment itself from solutions or through recrystallisation make up a small but very important complement to the matrix.

Mn-carbonates

The presence of Mn-carbonate, a common authigenic constituent in laminated Baltic Sea sediments from the deep basins, is indicated by well-correlated peaks of Mn and Ca (e.g. figs. 2 and 5). Precipitation of Mn carbonate is believed to be induced by high alkalinity and availability of dissolved manganese in connection with organic matter deposition and degradation (Lepland and Stevens 1998).

The beginning of the Litorina stage marks the first occurrence of Mn-carbonate and it is present throughout most of the top 450 cm of the sediment column. The roundish Mn-carbonate grains com-

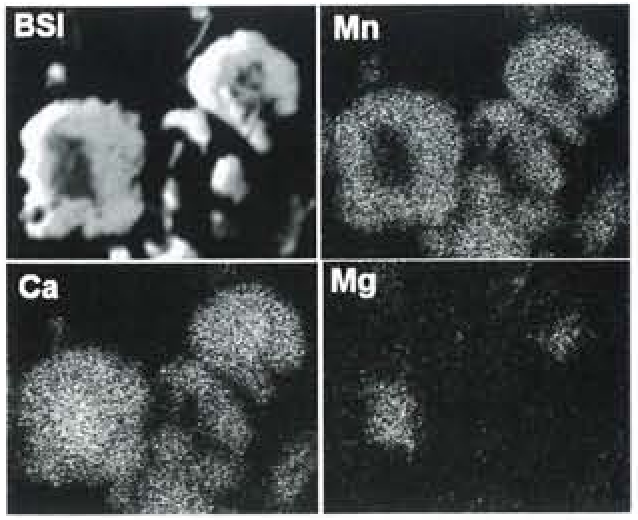

Fig. 7. SEM image of Mn-carbonate grains at the depth of 320 cm. The upper left figure is a close-up (BSI = backscatter image) of carbonate grains with Mg-rich dolomitic (dark) centre, surrounded by Mn-rich carbonate (light). The upper right and two lower figures show the distribution of Mn, Ca and Mg within the grains.

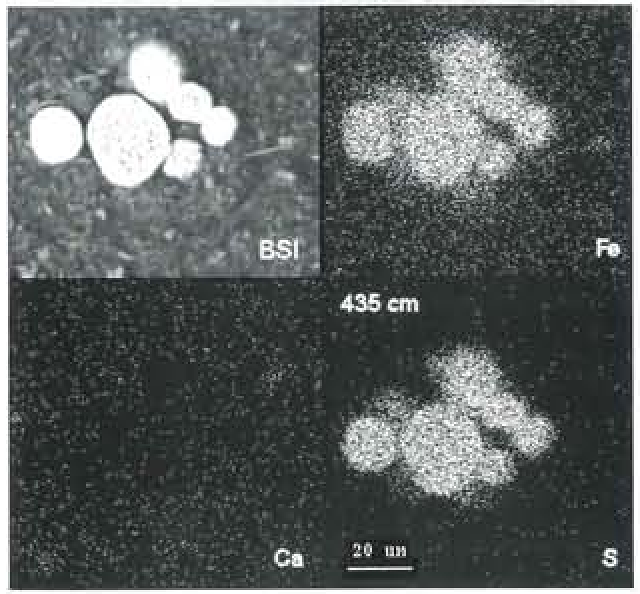

Fig. 8. SEM image of framboidal pyrite grains (high reflectivity in the BSI image) embedded in clay matrix at the depth of 435 cm.

monly occur as conspicuous lamina with thickness between 0.05-5 mm. Particles within the lamina can be individual grains as well as larger aggregates with diameters up to 100-200 µm. The size and the shape of particles as well as the thicknesses of the lamina show no variations with to depth. A closer look at the SEM images of Mn-carbonate grains very often show a distinctive structure; the light coloured Ca-Mn-rich outer shell commonly surrounds a darker centre (nucleus) that has a Mg-rich dolomite composition (Fig. 6 and Table 1). SEM-EDS analysis indicated the composition to vary between $(Mn_{65-80}Ca_{15-30}Mg_{1-5})\ CO_3$ for the outer shell and $(Ca_{50-60}Mg_{30-38}Mn_{5-10})\ CO_3$ for the centre. The small amount of Mn in the nucleus can be an artefact from the preparation of surface slides.

The polished cross-section (Fig. 7) clearly shows the dolomite nuclei, which are probably of detrital origin, rather than a result of diagenesis, although in situ alterations are also a possibility (see Kulik et al. 2000). The alkaline environment, inducing the precipitation of Mn-carbonate, also allows preservation of the detrital dolomite grains, which probably functions as nuclei for Mn-carbonate precipitation. One Mn-carbonate particle, at 320 cm, had an ilmenite ($FeTiO_3$) centre. EMP analysis shows presence of Si and Al also within carbonate lamina (see Fig. 4), although in lesser amounts. This indicates continuous deposition of silicate matter even during the formation of Mn-carbonates.

Fe-sulphides

Fe-sulphides are mainly represented by framboidal pyrite (FeS_2) as illustrated in Fig. 8. In the EMP analysis pyrite is indicated by synchronous peaks of Fe and S. Backscatter intensities of Fe and S are at their highest in upper Ancylus and early Litorina sediments. The size of framboids varies between 5-30 µm. Pyrite framboids commonly occur as distinct aggregates but sometimes they also form thin layers. Typically pyrite-rich layers are often found directly below the Mn-carbonate lamina, so that they can be considered to represent the same anoxic episode. Occasionally framboids are also found embedded within Mn-carbonate lamina.

Below the Ancylus/Litorina boundary Fe-sulphides are present in the form of black dots and lenses (mottling) of amorphous nature, rather than discrete framboids. As a result Fe and S recorded notably higher peaks than in the laminated sediments above.

Other authigenic minerals

A few small grains consisting of Ba and S were observed in some of the samples. The example in Fig. 9 shows that a small grain of pyrite (centre) is surrounded by barite. Considering the way the barite adheres to the pyrite grain it is plausible that the few detected grains of barite are of authigenic origin although a detrital provenance can not be excluded. Due to the insufficient sensitivity of the SEM for barium this issue was not further addressed although there were indications that barium seemed to be related to microfossils.

Böttcher and Huckriede (1997) and Lepland and Stevens (1998) have studied manganous sulphide in Baltic Sea sediments in detail. The probe analyses of the core do indicate the simultaneous occurrence of manganese and sulphur, but also of iron. Since no crystallographic studies were conducted at this stage on the core, to identify specific manganese sulphides, it is possible that sufficient pyrite grains inter-bedded in the manganese carbonate layer distort the results. Lepland and Stevens (*op.cit.*) do point out that if the availability of H_2S exceeds that of Fe, MnS may precipitate as well deve-loped hexagonal crystals.

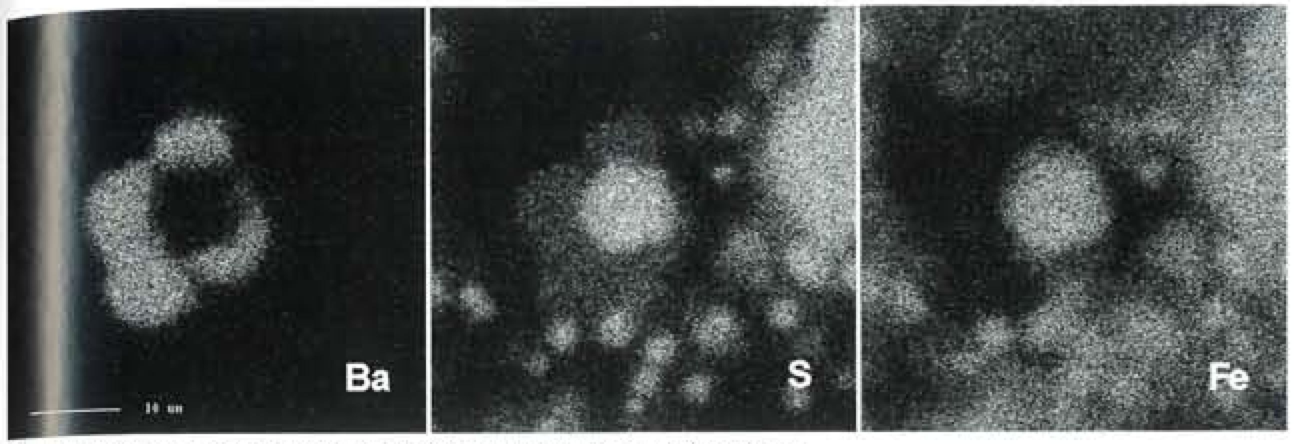

Fig. 9. SEM image of small accretions of barite surrounding a pyrite nucleus.

Vivianite has been observed previously in lower Ancylus sediments in the Baltic Sea (Winterhalter 1992b), but due to the insufficient sensitivity of the applied analytical method for phosphorous the attempt to identify phosphorous was limited to a few tests. It is possible that the observed traces of phosphorous may be part of organic remains. The scarcity of the data did not permit an evaluation of the possible existence of actual grains of vivianite in the studied core.

Beautiful homeomorphic crystals of gypsum (Fig. 10) were observed in several of the slides studied both by SEM and in thin sections by optical microscope. At first glance the way the crystals were embedded in the matrix indicated an authigenic origin. Furthermore, K.St.John (pers. comm.) had observed authigenic gypsum in Canadian offshore sediments precipitated from brine formed during freezing of seawater. This could also have been an explanation for gypsum in Baltic Sea sediments; however, a thorough check of remaining cores in cold storage, showed that the gypsum is an artefact of dehydration of unconsolidated sediment during storage.

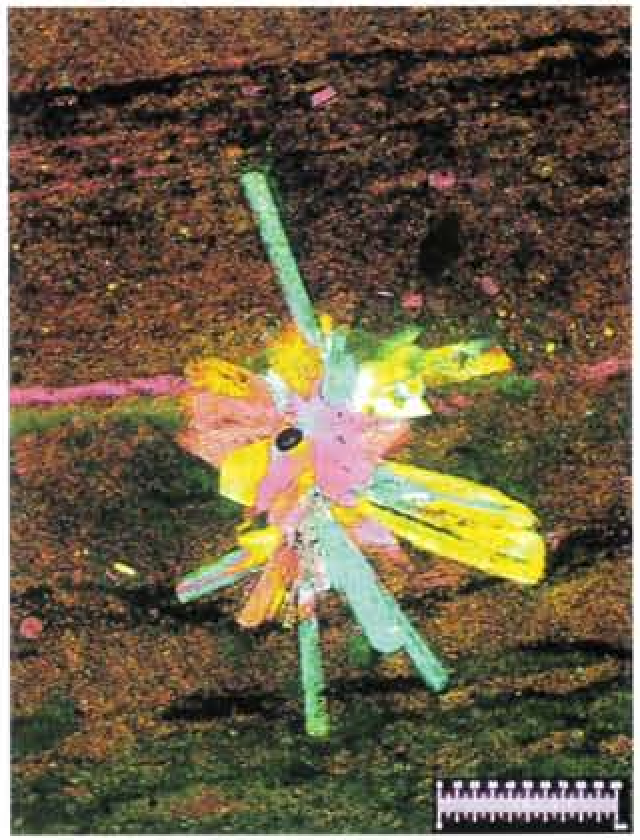

Fig. 10. Optical microscope image showing a rose of gypsum crystals. Although many of the gypsum grains in the core 211660-6 gave the impression that they were syngenetic with the sediment, they had most probably precipitated from the moist sediment during cold storage allowing slow evaporation. The scale line is one millimetre in length.

DISCUSSION

The drastic change in the depositional environment at the Ancylus/Litorina boundary (440 cm core depth in Fig. 1) is well manifested in the distribution of various elements as seen in the microprobe analyses. The inflow of nutrient rich seawater from the North Sea improved light penetration due to flocculation and increasing temperature accelerated primary production (Winterhalter 1992a). The abundant deposition of organic matter, and obviously a density stratification of near-bottom waters eventually resulted in the formation of anoxic conditions in the Gotland Deep. This is reflected by a change from homogenous into laminated sediments at the onset of the Litorina stage. The formation of Mn-carbonate lamina is a direct result of this anoxia.

Precipitation of Mn-carbonate has most likely taken place at the sediment-water interface, rather than within the sediment as sub-surface precipitation (Huckriede

1994; Sternbeck and Sohlenius 1997; Kulik et al. 2000). A direct precipitation in anoxic near-bottom waters is considered unlikely, because this can occur only if the dissolved Mn(II) concentration or the alkalinity is very (unusually) high (Roy 1992; Calvert and Pedersen 1993 1996).

Measurements of Mn-carbonate lamina show no variation with core depth in neither their thickness nor the size of individual grains or particles within the lamina. This obviously indicates that once the laminae has been formed, no further sub-surface precipitation takes place.

The authigenic pyrite occurring abundantly in the Gotland Deep sediments is also related to anoxia. Its formation is controlled by the availability of sulphur derived mainly from saline seawater pulses from the North Sea. Sulphur is brought into the sediment pore-waters by bacterial reduction of sulphate ions. This increases alkalinity, which in turn induces Mn-carbonate precipitation. The ideal model for a sedimentation cycle would therefore begin with deposition of organic matter, which through digestion by scavengers and bacteria, leads to oxygen depletion and high alkalinity. In an increasingly anoxic environment, the amount of reactive sulphur increases, leading to formation of hydrotroilite or pyrite. When the alkalinity in pore-waters is high enough, Mn-carbonate starts to precipitate. Thus, a carbonate laminae can be considered to represent the final product of a single anoxic period. This can be a seen in SEM images from four different depths (see Fig. 5), where a faint layer of pyrite framboids precedes each carbonate laminae. It should be pointed out that some precipitation of amorphous ferrous sulphide might be of diagenetic origin due to sediment compaction and degradation of organic matter.

Presence of Mn-carbonate and pyrite suggests that anoxic conditions of various duration and intensity have prevailed throughout most of the Litorina stage in the Gotland Deep. Since the thickness of Mn-carbonate lamina is usually less than 1 mm, the duration of their formation must have been relatively short. Lepland and Stevens (1998) suggest that seasonal alkalinity variations could be induced by periodic organic matter supply, eventually resulting in annual or semi-annual carbonate laminae. Sternbeck and Sohlenius (1997) give another model. Their model is based on episodic and very rapid (couple of weeks) carbonate precipitation and they argue that the organic matter mineralisation is not fast enough to trigger this. Based on our material, some kind of rhythmic (not cyclic) carbonate precipitation is indeed present (see Fig. 2). SEM image from the depth of 314-322 cm shows many Mn-carbonate lamina, which clearly portray the cyclic changes from detrital clay matrix to authigenic carbonate. Whether the cyclicity is seasonal or related to e.g. the duration of saline pulses is not quite clear.

CONCLUSIONS

EMP analysis reflects well the major changes in sedimentary environment and changes in ratio between detrital- and authigenic matter. A clear change in mineralogy was seen at the Ancylus/Litorina boundary, where the sediment type changed from homogenous detrital matter into more laminated with authigenic Mn-carbonate. Below that level detrital matter was dominant, represented by high Si and Al content and absence of Mn and Ca. The form in which Fe-sulphides were precipitated also changed at the Ancylus/Litorina boundary. In Litorina sediments pyrite occurred mainly as diffusely spread framboids, whereas in Ancylus sediments Fe-sulphides were present also as more extensive lenses and small lumps, portrayed by the decrease in backscatter intensity of Fe and S above ~450 cm. It is obvious that SEM and microprobe analytical techniques should be used when mineralogical information, not achievable by standard bulk analysis, is required.

Acknowledgements

The authors are grateful to the many colleagues who participated in the BASYS cruises and who shared their time and knowledge with their co-workers with special credit to Drs. Maren Voss, Thomas Andrén, Helmar Kunzendorf, and Aarno Kotilainen for allowing us to use their data. Special thanks go to Mr. Bo Johansson, Ms. Marja Lehtonen and Mr. Lassi Pakkanen for the excellent help with the microprobe and SEM analyses. The reviewers, Dr. Szymon Uścinowicz and Dr. Tomas Leipe deserve a warm handshake for their input. We also want to express our gratitude to our superiors at the Geological Survey of Finland for providing the working facilities. The work was supported by EC MAST III project BASYS (Baltic System Study), contract MAS3-CT96-0058.

References

Andrén, E. 1999: Holocene environmental changes recorded by diatom stratigraphy in the southern Baltic Sea. PhD thesis, Meddelanden från Stockholms Universitets Institution för Geologi och Geokemi 302. 22 pp.

Andrén, E., Andrén, T. & Kunzendorf, H. 2000: Holocene history of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10,* 687-702.

Björck, S., 1995: A review of the history of the Baltic Sea, 13.0-8.0 ka BP. *Quaternary International 27,* 19-40.

Böttcher, M.E. & Huckriede, H. 1997: First occurrence and stable isotope composition of authigenic (-MnS in the central Gotland Deep (Baltic Sea). *Marine Geology 137,* 201-205.

Calvert, S.E. & Pedersen, T.F. 1993: Geochemistry of recent oxic and anoxic marine sediments: implications of the geological record. *Marine Geology 113,* 67-88.

Calvert, S.E. & Pedersen, T.F. 1996: Sedimentary geochemistry of manganese: implications for the environment of formation of manganiferous black shales. *Economic Geology 91,* 36-47.

Glasby, G. P., Emelyanov, E. M., Zhamoida, V. A., Baturin, G. N., Leipe, T. Bahlo, R. & Bonacker, P. 1997: Environments of formation of ferromanganese concretions in the Baltic Sea. In K. Nicholson (Ed.): *Manganese mineralization: geochemistry and mineralogy of terrestrial and marine deposits. London: Geological Society of London. Special publication /Geological Society of London 119,* 213-237.

Emeis K-C. & Struck U. (Eds.). 1998: Gotland Basin Experiment (GOBEX), Status report on Investigations Concerning Benthic Processes, Sediment formation and Accumulation. *Mereswissenschaftliche Berichte / Marine Science Reports 34.*

Harff, J. & Winterhalter, B. 1997: Cruise Report R/V Petr Kottsov, July 22 - August 01, 1997. Baltic Sea Research Institute, October 1997. 41 pp.

Heiser, U. 2000: Calcium-rich Rhodocrosite Layers in Sediments from the Gotland Deep, Baltic Sea, as Indicators for Seawater Inflow. *Karlsruher Geochem. 17,* 1-125, Karlsruhe.

Heiser, U., Neumann, T., Scholten, J., Stüben, D. 2001: Recycling of manganese from anoxic sediments in stagnant basins by seawater inflow: a study of surface sediments from the Gotland Basin, Baltic Sea. *Marine Geology 177,* 151-166.

Huckriede, H. 1994: Mangan-Anreicherungen in anoxischen Meeresbecken: Beispiele aus der zentralen Ostsee und dem Unter-Karbon II Mittel- und Westeuropas. Cuviller-Verlag, Göttingen. 123 p.

Kotilainen, A.T., Saarinen, T., & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166 (1-4),* 51-64.

Kotilainen, A. T., Hämäläinen, J. & Winterhalter, B. 2001: Reconstructing a continuous Holocene composite sedimentary record for the eastern Gotland Deep, Baltic Sea. *Submitted to Boreal Research.*

Kulik, D.A., Kersten, M., Heiser, U., & Neumann, T. 2000: Application of Gibbs Energy Minimization to Model Early-Diagenetic Solid-Solution Aqueous-Solution Equilibria Involving Authigenic Rhodochrosites in Anoxic Baltic Sea Sediments. *Aquatic Geochemistry 6 (2),* 147-199.

Lamoureux, S. F. 1994: Embedding unfrozen lake sediments for thin section preparation. *Journal of Paleolimnology 10,* 141-146.

Lepland, A. & Stevens, R. L. 1998: Manganese authigenesis in the Landsort Deep, Baltic Sea. *Marine Geology 151,* 1-25.

Manheim, F.T. 1961: A geochemical profile in the Baltic Sea. *Geochimica et Cosmochimica Acta 25,* 52-71.

Neumann, T., Christiansen, C., Clasen, S., Emeis, K.-C., and Kunzendorf, H. 1997: Geochemical records of salt-water inflows into the deep basins of the Baltic Sea. *Continental Shelf Research 17,* 95-115.

Rothwell, R.G. 1989: Minerals and mineraloids in marine sediments. Elsevier Science Publishers, London. 279 pp.

Roy, S. 1992: Environments and processes of manganese deposition. *Economic Geology 87,* 1218-1236.

Saarinen, T. 1998: High resolution palaeosecular variation in northern Europe during the last 3200 years. *Physics of the Earth and Planetary Interiors 106,* 299-309.

Sternbeck, J. & Sohlenius, G. 1997: Authigenic sulphide and carbonate mineral formation in the Holocene sediments of the Baltic Sea. *Chemical Geology 135,* 55-73.

Turner, G. M. & Thompson, R. 1981: Lake sediment record of the geomagnetic secular variation in Britain during Holocene times. *Geophysical Journal of the Royal Astronomical Society 65,* 703-725.

Turner, G. M. & Thompson, R. 1982: Detransformation of the British geomagnetic secular variation record for Holocene times. *Geophysical Journal of the Royal Astronomical Society 70,* 789-792.

Westman, P. 1998: Salinity and trophic changes in the northwestern Baltic Sea during the last 8500 years as indicated by microfossils and chemical parameters. *Quaternaria, Ser A. Theses and Research Papers 5,* Stockholm 1998.

Winterhalter, B. 1992a: Late Quaternary stratigraphy of the Baltic Sea basins - a review. *Bulletin of the Geological Society of Finland 64,* 189-194.

Winterhalter, Boris 1992b: Authigenic vivianite in lower Ancylus sediments in the western Gulf of Finland. In W. Lemke, D. Lange & R. Endler (Eds). Proceedings of the Second Marine Geological Conference - The Baltic, Rostock, 21-26.10.1991. *Meereswisserschaftliche Berichte 4,* 156-159.

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 84-94

Seasonal behaviour and origin of minerals in suspended matter and underlying sediments in the northern Baltic Sea

Matti Mälkki

Abstract

Several sediment traps were deployed in the Gulf of Finland (GOF) and in the northern Baltic Proper in 1997 in order to clarify the spatial and temporal relationship of the suspended matter to underlying sediments. The sediment cores were collected both in 1997 and 1998. This paper is based on mineralogical and related geochemical studies. According to X-ray diffraction studies, the lithogenic mineral particle composition (illite, chlorite, kaolinite, feldspars, and quartz) is remarkably similar throughout the sediment and suspension samples. The 60% HNO_3-leachable aluminium (Al_{HNO3}) correlates well with that of illite$_{001}$ -peak, thus indicating that even Al_{HNO3} is sufficient for lithogenic mineral evaluation in the northern Baltic Sea. The maximum suspension fluxes for lithogenic particles occur during spring and autumn periods. In contrast, the amorphous ferromanganese oxide concretions (FMC; 5-30 mm) prevail in suspension during summertime. The FMC fraction is virtually absent in underlying surface mud sediment. It is possible that the FMC formation is due to organic matter degradation during sinking, because the Mn_{HNO3}/Al_{HNO3} peak is shifted from an early summer period 9.5-5.6 (Gotland Deep) to a late summer period of 24.7-16.9 (GOF). The existence of FMC in suspension does not appear to be dependent only on the oxygen concentrations in the water column. Manganese carbonates occur in the Gotland Deep (BY15) and in the northern Baltic Proper (LL17) sediments while Mn is almost absent in the GOF sediments. Apparently the "salt-pulse effect" for authigenic Mn-carbonate formation is not so strong as thought in recently published studies. The results show that only the secondary origin of the mineral particles can be demonstrated. It is evident that the processes within a single basin are able to mask basin to basin or coastal to basin processes efficiently.

☐ *Baltic Sea, Gulf of Finland, mineralogy, geochemistry, sediments, suspended matter.*

☐ *Matti Mälkki [matti.malkki@kolumbus.fi], Finnish Institute of Marine Research, P.O.Box 33, FIN-00931, Helsinki, Finland; present address: Trumpettitie 8-10 F 135, 00420 Helsinki, Finland.*

☐ *Received 23 May 2001; accepted 9 November 2001.*

INTRODUCTION

The Baltic Sea area has undergone strong sediment reworking processes due to several glaciation/deglaciation events. The similarity of the silicate particle composition has been observed in most basins of the Baltic Proper (Boström et al. 1978, Emelyanov 1992, Gingele and Leipe 1997). Only the southern coastal areas are known to represent a different clay mineralogical province (Emelyanov 1992, Gingele and Leipe 1997). According to geochemical mass-balance calculations, the main fractions of all post-glacial clays have their source within the Baltic basin, being generated by submarine erosion (Boström et al. 1983). Aluminosilicates alone are not of much help for the characterisation of the geochemistry of Baltic Sea sediments (Belmans et al. 1993). The elemental composition of sediments, however, is only weakly related to the composition of suspended matter in the overlying water body (Brügmann et al. 1992). The geochemical characterisation of suspended matter in the Baltic Sea area is mainly based on non-seasonal, sporadic sampling (Emelyanov and Pustelnikov 1975, Ingri et al. 1991, Brügmann et al. 1992). Bernard et al. (1989) measured the chemical composition of the suspended particles with an electron microprobe, but an XRD-method was not used. Leivuori and Vallius (1998) measured the detailed, seasonal geochemical variation in the suspended matter of the Gulf of Finland (GOF) without any consideration to its mineralogical composition. The purpose of this study is to show a detailed, seasonal mineralogical and related geochemical composition of the suspended sediments in the northern Baltic Sea. These results are compared with the underlying sediments. Finally, the provenance of this material is considered.

STUDY AREA

The sampling stations SL2S, GF2 and JML are situated in the GOF, while LL17, in the Fårö Deep, and BY15 are located in the northern Baltic Proper (Fig. 1). GF2, JML and LL17 are close to the boundary between the crystalline basement and the Paleozoic sedimentary formations of Estonia. SL2S is located in the area of Vendian formations. The GOF sediments are heterogeneous, and sedimentation rates vary both between and within basins (Vallius 1999). Also the morphology of the sea floor around LL17 is variable. This is due to the rugged crystalline basement below a relatively thin sedimentary cover. In contrast, Fårö and Gotland Deeps are situated over Paleozoic bedrock with a rather gentle morphology.

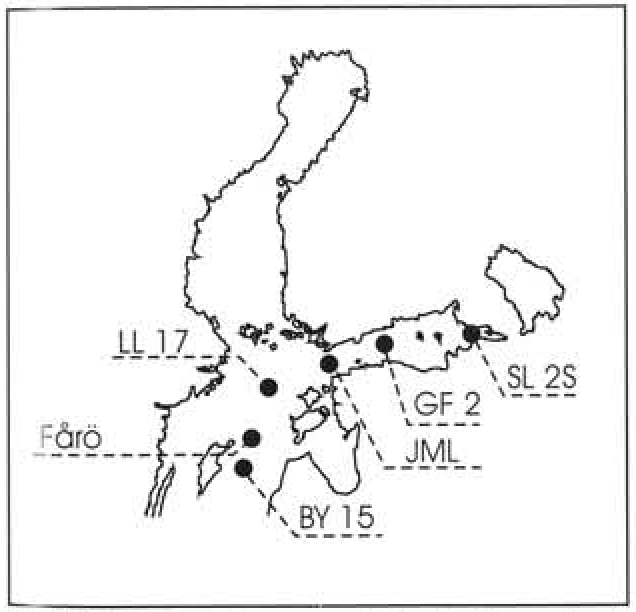

Fig. 1. Sediment trap deployment and underlying sediment sampling sites. Only sediment samples were taken at SL2S.

MATERIALS AND METHODS

The samples were collected from six stations during the Finnish research vessel *R/V Aranda* cruises in 1997 and 1998 (Fig. 1). The co-ordinates of the stations are given in Table 1. The sediment samples were retrieved using a Gemini twin corer (an improved version of the Niemistö-corer, Niemistö 1974). The upper 15 cm of each sediment cores was sliced into 1-2 cm intervals for chemical analyses. Mineralogical determinations were made using only surface and bottom slices. Parallel coring was performed on mineralogical and chemical analyses. All samples were stored immediately in Petri dishes and kept in deep freeze awaiting analyses.

The upper traps were French Technicap models PPS 5/2 (conical with a collection area of 1.0 m^2) and PPS 3/3 (cylindrical, a collection area of 0.125 m^2). The former is equipped with a 24 bottle and the latter with a 12 bottle rotating holder. The lower traps (Eila-trap) consisted of three cylindrical units each with a 0.008-m^2 collection area (Fig. 2).

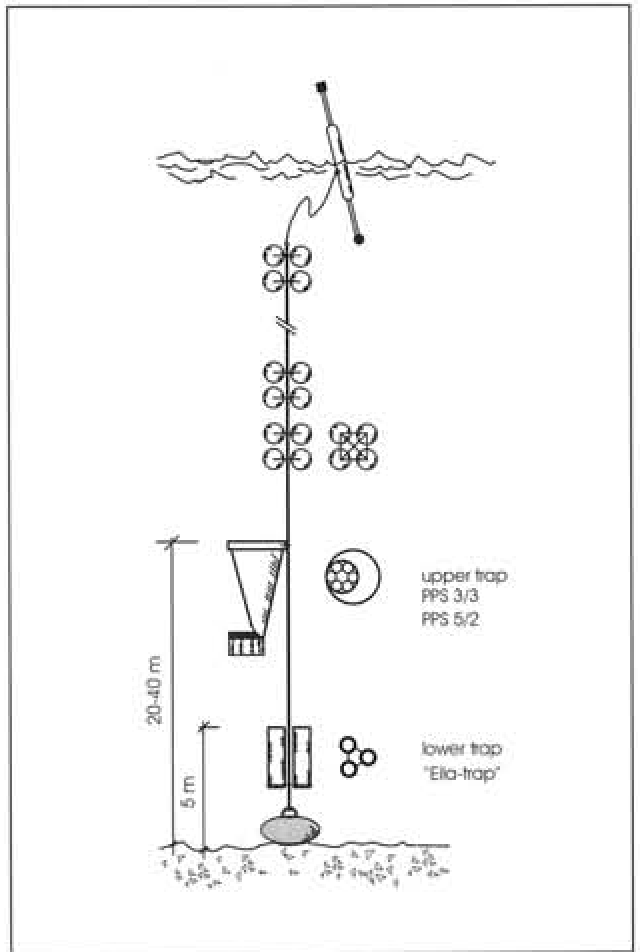

Fig. 2. Setup of sediment traps (GF2, JML, LL17, Fårö Deep, BY15).

Formaldehyde (2% v/v) was used as a preservation liquid to prevent decomposition of the suspended matter. The possibility of contamination (e.g. formation of artefact minerals) was checked by simulating trap conditions in the laboratory. Samples rich and poor in Mn-oxide or Mn-carbonate were subjected to formaldehyde solution for 1-2 months. A Seabird SBE 911 Rosette sampler and a Radiometer titralab III titration equipment were used for dissolved oxygen determination.

In the chemical laboratory at the Finnish Institute of Marine Research, samples were freeze-dried and

Table 1. Sediment cores for mineralogical determination (A). Wdepth = water depth in the study area, surface status is based on the colour of the sediment (oxic,suboxic,anoxic) and the oxygen content (1-2 m above seabed). Oxide and carbonate denote particulate Fe-Mn-oxides and Mn-carbonates determined by microscope (the uppermost 2 cm). - absent, + visible, ++ clearly visible. ND, not determined. Chem YES/NO = also chemical data is present/ chemical data is absent. All stations are situated in muddy accumulation bottoms. Trap coordinates (B). Bias = +n m above seabed; Cperiod = collection period.

(A)

Station	latitude	longitude	Wdepth	date	surface status	chem	oxide	carbonate
SL2S	60.03.49 N	29.11.55 E	29 m	12.12.97	oxic (5.8 ml/l O_2)	NO	-	-
GF2	59.50.56 N	25.51.88 E	82 m	8.4.97	oxic (5.2 ml/l O_2)	YES	-	-
GF2	59.50.30 N	25.51.58 E	84 m	15.4.98	oxic (5.0 ml/l O_2)	NO	(+)	-
JML	59.35.22 N	23.37.33 E	79 m	9.4. 97	oxic (7.2 ml/l O_2)	YES	-	-
JML	59.35.28 N	23.38.92 E	79 m	16.4. 98	suboxic (0.6 ml/l O_2)	NO	-	(+)
LL17	59.01.91 N	21.03.98 E	159 m	20.4. 98	suboxic (0.3 ml/l O_2)	NO	(+)	++
Fårö Deep	57.59.99 N	19.53.81 E	180 m	14.4. 97	suboxic (0.2 ml/l O_2)	YES	-	-
Fårö Deep	58.00.01 N	19.53.99 E	194 m	22.4. 98	suboxic (≈ 0 ml/l O_2)	NO	-	+
BY 15	57.17.00 N	20.13.43 E	240 m	21.4. 97	anoxic (13 µmol/l H_2S)	YES	-	+
BY 15	57.17.00 N	20.07.98 E	241 m	22.4. 98	suboxic (0.2 ml/l O_2)	NO	-	(++)

(B)

Station	latitude	londitude	Wdepth	trap type/bias	Cperiod	oxide	carbonate
GF2	59.50.55 N	25.51.57 E	82 m	Eila /+ 5 m	8.4.-4.7.	(++)	-
				PPS3/3 /+ 20 m	11.4.-9.5.	(+)	-
					9.5.-27.5.	(+)	-
					27.5.-19.6.	-	-
GF2	59.50.54 N	25.51.60 E	84 m	Eila /+ 5 m	4.7.-25.9.	(++)	-
				PPS3/3 /+ 20 m	6.7.-24.7.	ND	ND
					24.7.-16.9.	++	-
GF2	59.50.54 N	25.51.60 E	84 m	Eila /+ 5 m	25.9.-18.12.	+	-
				PPS3/3 /+ 20 m	27.9.-21.10	(++)	-
					21.10.-14.11.	(++)	-
					14.11.-8.12.	(++)	-
JML	59.35.20 N	23.37.88 E	81 m	Eila /+ 5 m	4.6.-3.7. (*)	ND	ND
				PPS3/3 /+ 20 m	ND	ND	ND
JML	59.35.21 N	23.37.77 E	81 m	Eila /+ 5 m	3.7.-25.9.	+	(+)
				PPS3/3 /+ 20 m	6.7.-16.9.	ND	ND
JML	59.35.21 N	23.37.51 E	81 m	Eila /+ 5 m	25.9.-18.12.	+	(+)
				PPS3/3 /+ 20 m	27.9.-21.10.	+	-
					21.10.-14.11.	+	(+)
					14.11.-8.12.	ND	ND
LL17	59.02.16 N	21.05.99 E	215 m	Eila /+ 5 m	11.4.-2.7.	++	(+)
				PPS3/3 /+ 30 m	14.4.-28.4.	(++)	+
					28.4.-15.5.	(++)	(+)
					15.5.-19.6.	++	-
LL17	59.02.14 N	21.06.08 E	223 m	Eila /+ 5 m	2.7.-25.9.	++	(+)
				PPS3/3 /+ 30 m	6.7.-24.7.	++	-
					24.7.-11.8.	++	-
					11.8.-16.9.	++	(+)
Fårö Deep	58.05.53 N	19.50.58 E	182 m	Eila /+ 5 m	14.4.-1.7.	++	(+)
				PPS5/2 /+ 40 m	17.4.-9.5.	+	(+)
					9.5.-26.5.	(+)	(+)
					26.5.-19.6.	++	-
Fårö Deep	58.05.56 N	19.50.61 E	192 m	Eila /+ 5 m	1.7.-24.9.	-	-
				PPS5/2 /+ 40 m	3.7.-15.7.	++	-
					15.7.-24.7.	++	-
					24.7.-11.8.	++	-
					11.8.-26.8.	++	-
					26.8.-7.9. (*)	++	-
					7.9.-13.9.	-	-
BY15	57.17.02 N	20.13.47 E	231 m	Eila /+ 5 m	21.4.-29.6.	++	-
				PPS5/2 /+ 40 m	23.4.-9.5.	+	+
					9.5.-5.6.	(++)	(+)
					5.6.-19.6.	(++)	(+)

(*) XRD is missing

homogenised. Al, Fe and Mn were partially leached with 60% HNO_3 (suprapure) using microwave digestion. Samples (0.4 g) were heated with pressure regulation at 827 kPa for 40 minutes. Then they were cooled, diluted to 50 ml in a volumetric plastic flask, transferred to plastic storage bottles and stored overnight at room temperature until analysis (ICP-AES, TJA-25).

In the mineralogical laboratory at the Department of Geology, Helsinki University, XRD scans 5-35 °2q (step size 0.05 °2q, 1.0 sec. per step) were performed on 15 % H_2O_2 -treated (15 min.) oriented specimens using a voltage of 50 kV and a current of 30 mA. A CuK(a) radiation and a monochromator were used. The clay mineralogy (< 2 mm fraction, oriented specimens, 5-30 °2q) was determined separately using criteria described by Hardy and Tucker (1988) and Moore and Reynolds (1989), see Fig. 3.

The IR-spectroscopy was performed on pressed KBr disks prepared by mixing 2-mg sample with 200 mg KBr. The range 3000 cm^{-1} - 4000 cm^{-1} was measured because the 3620 cm^{-1} and 3700 cm^{-1} peaks are characteristic for kaolin minerals (Russel 1987).

The correlation coefficients are given at 95% confidence level.

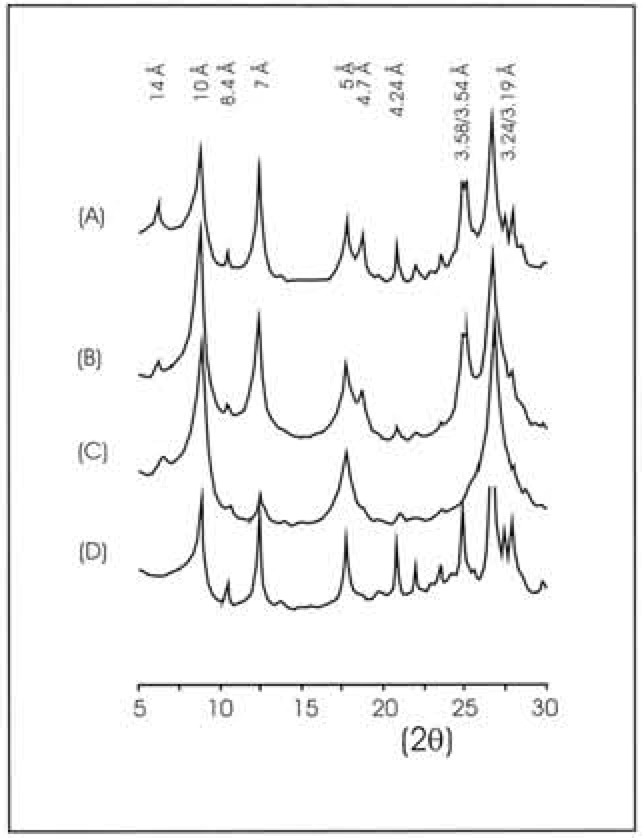

Fig. 3. Typical X-ray diffraction patterns 5-30° (2q) from Baltic Sea sediments. All curves are drawn at the same scale. Untreated (A), K^+ saturated, heated at 350 °C (B), K^+ saturated, heated at 550 °C (C), 1 M HCl leached for 2 hours (D). 14 Å, chlorite (001); 10 Å, illite/biotite (001); 7 Å, chlorite (002)/kaolinite (001); 5 Å, illite/biotite (002); 4.7 Å, chlorite (003); 4.24 Å, quartz (100); 3.58/3.54 Å, kaolinite (002)/chlorite (004) doublet; 3.24Å/3.19 Å, microcline (220)/albite (002) main peaks.

RESULTS AND INTERPRETATIONS

General

No mineral alterations (e.g. authigenic precipitation) are observed during laboratory experiment. It is thus probable that the mineral composition observed in trap samples does not contain undesirable elements due to contamination.

The correlation between Al_{HNO3} (%) and illite$_{001}$ (10Å) reflection height is strong (r = 0.87, n = 38). This indicates that even the HNO_3 -leachable portion of Al is indicative for evaluation of terrigeneous minerals. If the suspended material at site LL17 is excluded, the correlation coefficient between suspended Al_{HNO3} and the total particulate suspended material is very strong (r = 0.98, n = 34; Fig. 4). This probably indicates that the role of primary produced sinking organic substances (compared to resuspension) is minor even 20-40 m above the bottom.

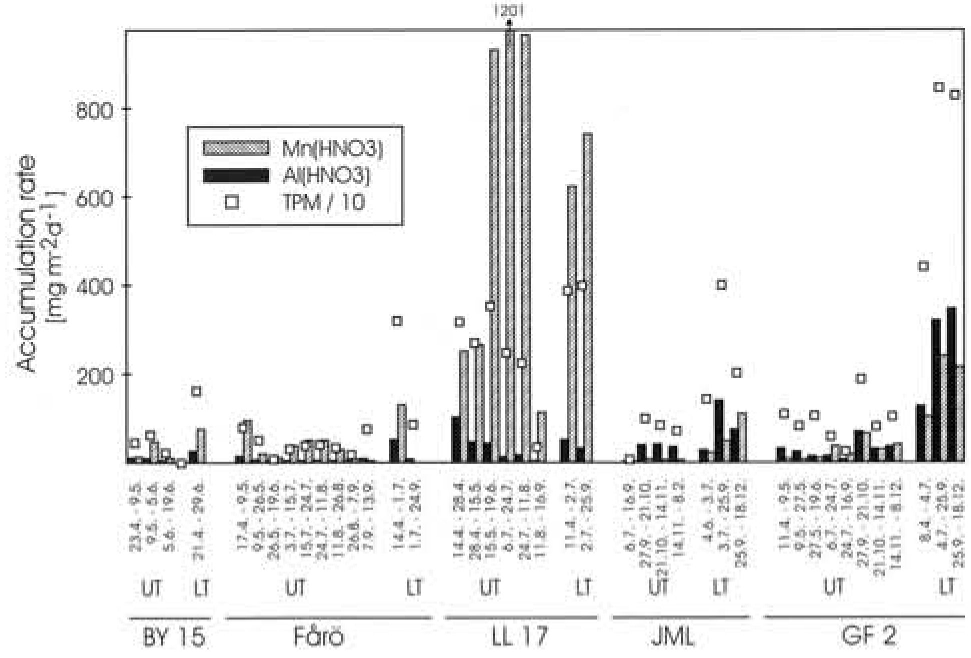

Fig. 4. Accumulation rates of trap material in 1997. UT = upper trap, LT = lower trap. Note that the TPM values are an order of magnitude higher than those shown in vertical axis.

The XRD patterns are almost uniform throughout every sample when the content of the amorphous matter is low (Fig. 5). This probably indicates that the particles are aggregates of several minerals. Organic molecules may adhere to the surfaces and edges of minerals as well as take up interlattice positions in certain clay minerals (Degens and Mopper 1976). Aggregation of individual particles readily occurs if salinity exceeds 1-3 per mil (Krone 1978) which is the case in all the study areas.

In the clay fraction, illite predominates (70%) relative to kaolinite (20%) and chlorite (10%). Only traces of expandable clay minerals (smectite, vermiculite) are present (Fig. 3). IR-peaks for kaolin minerals (3620 cm^{-1}, 3700 cm^{-1}) are clear. Due to a low presence of "true" iron bearing phases it is probable that illite is partly trioctahedral. Räisänen et al. (1992) observed that the trioctahedral micas mostly dissolve in aqua regia leach while the dioctahedral micas do not significantly decompose in aqua regia. Here the 5Å/10Å ratio is ca. 0.3, suggesting the presence of biotite-type clay in Baltic mud sediments.

Sediment cores

Gulf of Finland - The Al_{HNO_3} and Fe_{HNO_3} values are somewhat constant throughout the GF2 and JML cores (Table 2). Microscopically determined pyrite is practically absent. The particle morphology is angular and texture bimodal (Fig. 6). The silicate particle grain size observed by microscope seldom exceeds 100 µm in the central GOF, but in the near shore area (SL2S) the size of quartz and feldspar particles may reach 0.5 mm. Usually the grain size slightly increases downwards relative to the top of the sediment core. The Mn_{HNO_3} values are very close to those of Earth's crust Mn-values (0.1 %). Only very few microscopical carbonate crystals or oxide particles are observed.

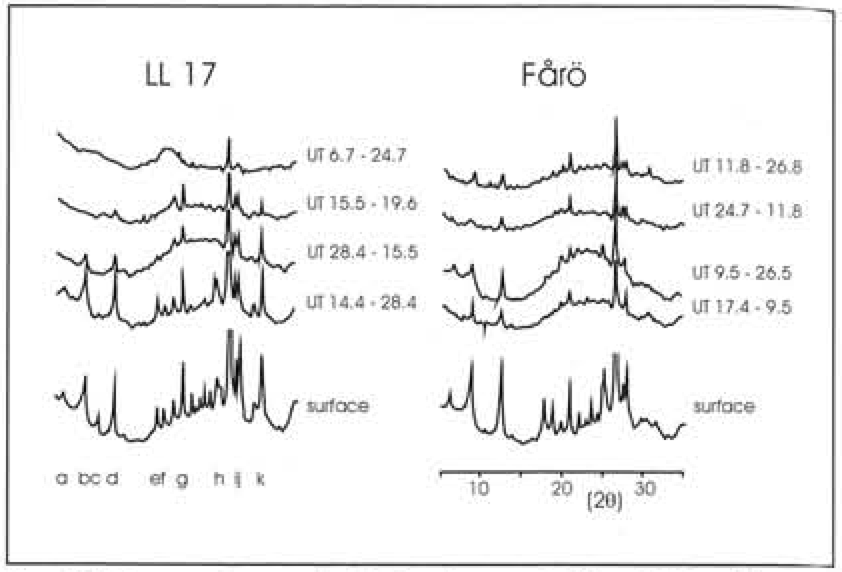

Fig. 5. XRD scans of trap and seabed surface material from LL17 and the Fårö Deep areas. The surface silicate pattern (peaks a-j) is typical for every sample containing lithogenic particles (aluminosilicates+quartz) from sediment and from suspension. Carbonate (k) coexists with silicates both in sediment and suspension at station LL17 while only silicates are present in the Fårö Deep. UT = upper trap, LT = lower trap.

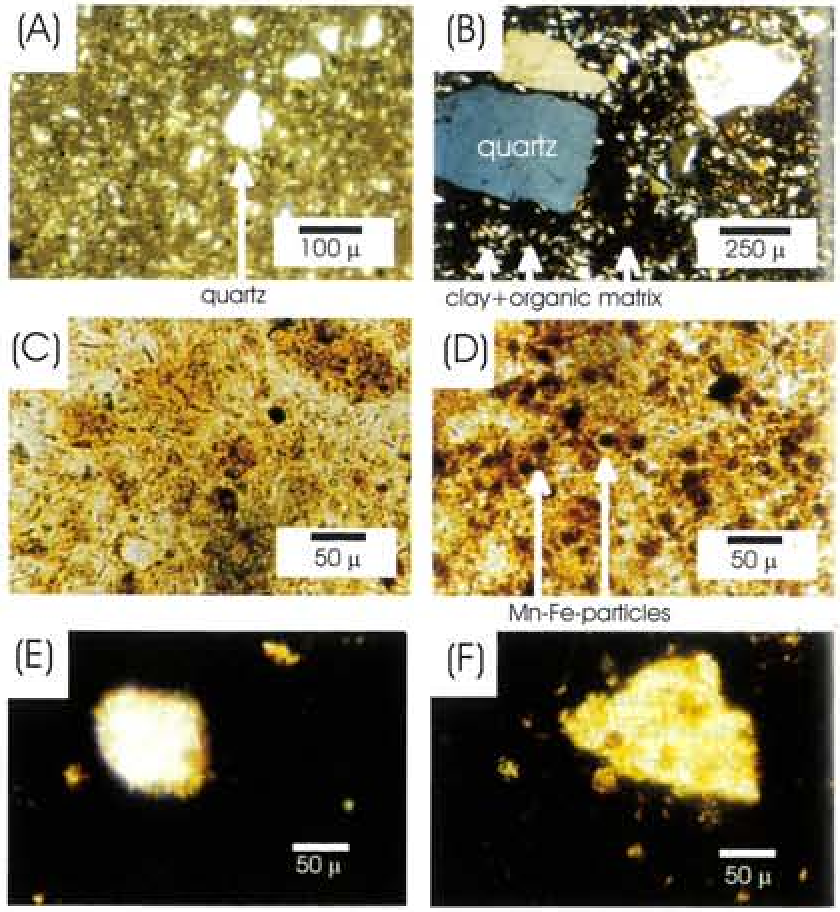

Fig. 6. Figures from sediment and suspension. GF2 sediment, 20-22 cm depth, immersion liquid (IL), crossed nicols (CN), (A); SL2S sediment, 20-22 cm depth, thin section, CN, (B); LL17 sediment, 0-1 cm depth, IL, plane polarised light (PPL), no Mn-oxides are present at surface (C); LL17 suspension, + 5 m, IL, PPL, substantial amounts of Mn-oxides are present, (D); authigenic carbonate crystal at BY15 suspension, + 40 m, IL, CN, (E); detrital carbonate crystal at BY15 suspension, + 40 m, IL, CN, (F);

Baltic Proper - The Al_{HNO_3} and Fe_{HNO_3} values appear to vary slightly more relative to the GOF (Table 2). This is probably because pyrite crystals are observed especially in laminated sequence (11-15 cm) at BY15. Silicate clasts are almost absent. The Mn_{HNO_3} values in the Fårö Deep area are similar in magnitude to the GOF. No oxide particles are found. In contrast, the Mn_{HNO_3} values are remarkably high in laminated sequence at BY15 due to Mn-carbonates. The 2.89 Å peak at LL17 is clear (Fig. 5) indicating the presence either of rhodochrosite or kutnahorite. Considerable amounts of rounded 10 mm biogenic as well as 50-100 mm inorganic (rhombohedral) carbonate particles are observed both at LL17 and BY15. The Mn-poor fluffy layer (2-10 cm) at BY15 is probably the same as fluffy layer presented by Heiser et al. (2001).

Table 2. HNO_3 leachable chemical data (%)

GF2	Al	Fe	Mn	JML	Al	Fe	Mn
upper trap				*upper trap*			
11.4. - 9.5.	2.8	2.9	0.68	6.7. - 16.9.	2.5	2.4	0.75
9.5. - 27.5.	2.9	3.2	0.74	27.9. - 21.10.	4.0	3.9	0.77
27.5. - 19.6.	1.3	1.2	0.72	21.10. - 14.11.	4.9	4.4	0.58
6.7. - 24.7.	2.4	2.6	6.04	14.11. - 8.12.	4.9	4.5	0.68
24.7. - 16.9.	1.8	1.8	6.79	*lower trap*			
27.9. - 21.10.	3.8	4.0	3.47	4.6. - 3.7.	2.4	2.2	1.52
21.10. - 14.11.	3.7	3.8	3.50	3.7. - 25.9.	3.5	4.8	1.17
14.11. - 8.12.	3.4	4.1	3.78	25.9. - 18.12.	3.7	3.8	4.55
lower trap				*sediment (cm)*			
8.4. - 4.7.	2.9	2.8	2.33	0-1	4.2	4.3	0.21
4.7. - 25.9.	3.8	4.2	2.81	1-3	4.2	3.9	0.05
25.9. - 18.12.	4.2	4.2	2.55	3-5	3.8	4.4	0.06
sediment (cm)				5-7	4.3	4.4	0.07
0-1	4.2	4.5	0.26	7-9	4.4	4.1	0.06
1-3	4.1	4.4	0.15	9-10	3.8	4.1	0.06
3-5	4.0	4.6	0.14	11-12	3.6	7.2	0.06
5-7	3.9	4.5	0.14	14-15	4.5	5.0	0.06
7-9	4.1	4.7	0.45	**LL 17 (*)**	**Al**	**Fe**	**Mn**
9-11	3.7	4.5	0.76	*upper trap*			
11-13	3.9	4.2	0.28	14.4. - 28.4.	3.2	3.0	7.88
13-15	3.5	4.9	0.18	28.4. - 15.5.	1.7	1.5	9.74
Fårö	**Al**	**Fe**	**Mn**	15.5. - 19.6.	1.2	1.5	26.3
upper trap				6.7. - 24.7.	0.5	2.1	48.3
17.4. - 9.5.	1.8	1.7	12.0	24.7. - 11.8.	0.7	1.7	42.8
9.5. - 26.5.	1.0	1.0	3.51	11.8. - 16.9.	0.8	2.0	32.9
26.5. - 19.6.	1.4	1.8	12.6	*lower trap*			
3.7. - 15.7.	1.4	2.4	12.2	11.4. - 2.7.	1.3	1.5	16.1
15.7. - 24.7.	1.0	1.8	12.8	2.7. - 25.9.	0.8	2.0	29.5
24.7. - 11.8.	1.1	1.9	12.5	**BY15**	**Al**	**Fe**	**Mn**
11.8. - 26.8.	1.0	2.1	13.4	*upper trap*			
26.8. - 7.9.	0.8	1.6	4.22	23.4. - 9.5.	2.3	3.3	2.6
7.9. - 13.9.	1.1	1.1	0.35	9.5. - 5.6.	1.5	2.8	7.4
lower trap				5.6. - 19.6.	1.8	3.1	4.4
14.4. - 1.7.	1.6	2.3	15.0	*lower trap*			
1.7. - 24.9.	0.8	1.2	0.02	21.4. - 29.6.	1.6	3.9	4.6
sediment (cm)				*sediment (cm)*			
0-1	3.1	4.5	0.06	0-1	3.1	3.7	0.28
1-3	4.9	5.4	0.07	1-2	3.4	3.9	0.12
3-5	5.1	4.8	0.07	2-3	2.7	4.1	0.05
7-8	4.3	4.9	0.07	3-4	2.5	3.8	0.06
9-10	4.6	5.3	0.07	4-5	2.6	2.4	0.06
11-12	4.0	7.0	0.08	7-8	3.3	2.9	0.07
14-15	4.1	7.0	0.09	9-10	3.1	3.1	0.07
				11-12	2.7	3.7	4.26
				14-15	2.2	5.9	3.50

No sediment data at station LL17 (*).

Sediment trap material

Gulf of Finland - The 3-4 % Al_{HNO_3} values are common both at JML and GF2 stations (Table 2). The lowest Al_{HNO_3}-value (1.3 %) occurs in early summer (GF2) evidently due to the settling material derived from the spring bloom periods. Diatoms occur as 30-50 µm diameter; radially developed algae with a crystalline outer shell structure at station GF2. The Al_{HNO_3} values as well as the $illite_{001}$ peaks in the lower traps correspond well with the values measured from underlying surface sediments (Table 2, Fig. 7). The suspended clasts (50-100 mm) are mostly poorly rounded quartz grains.

The Mn_{HNO_3} value was exceptionally high (6-7%) during the collection period of 6.7.-16.9. at station GF2 (Table 2). The observation follows precisely the Mn-behaviour in 1996 described by Leivuori and Vallius (1998). The 5-30 µm reddish, morphologically irregular, Mn-rich concretions occur in sediment trap samples (Fig. 6). Leivuori (2000) observed similar particles of 10 µm or smaller in size during 1996 in GF2 suspension. The mean total accumulation rates between 6.7. and 16.9. (375 mg m^{-2} d^{-1}) are slightly lower than during other measured periods (11.4.-19.6. 1000 mg m^{-2} d^{-1}, 27.9.-8.12., 1245 mg m^{-2} d^{-1}; Fig. 4) at station GF2. Evidently the "dilution" of the lithogenic particles (6.7.-16.9.) is caused by an addition of other substances (e.g. Mn-particles) as well as lower current activity.

Baltic Proper - The maximum Al_{HNO_3} values and the $illite_{001}$ peaks are reached in late spring - early summer (LL17, Fårö Deep, BY15) and autumn (Fårö Deep) (Table 2, Fig. 7). Mn_{HNO_3} reaches the maximum values at LL17 (40-50%) (Table 2) and Fårö (10-15%) stations during summer-early autumn period. According to Ingri et al. (1991) the average suspended particulate Mn/Al ratio in the Baltic Proper is almost three orders of magnitude higher than the ratio in average crust. Manganese and iron may occur as individual oxide particles or manganese is partly replaced by iron, i.e. Mn and Fe may form solid solution series (Fig. 8). Contents up to 88% of suspended Mn-Si-Fe particles have been found in the northern Baltic Proper (Bernard et al. 1989). Silicate clasts are almost absent in both LL17 and Fårö suspension.

Few authigenic (50-100 µm) and detrital, angular (100-200 µm) carbonate crystals are observed in the upper trap material at BY15 (Fig. 6). The d-value (≈ 2.89 Å) indicates the presence of either dolomite or Mn-carbonate. Silicate clasts (<100 µm) are rare in sediment trap material of the Gotland Deep.

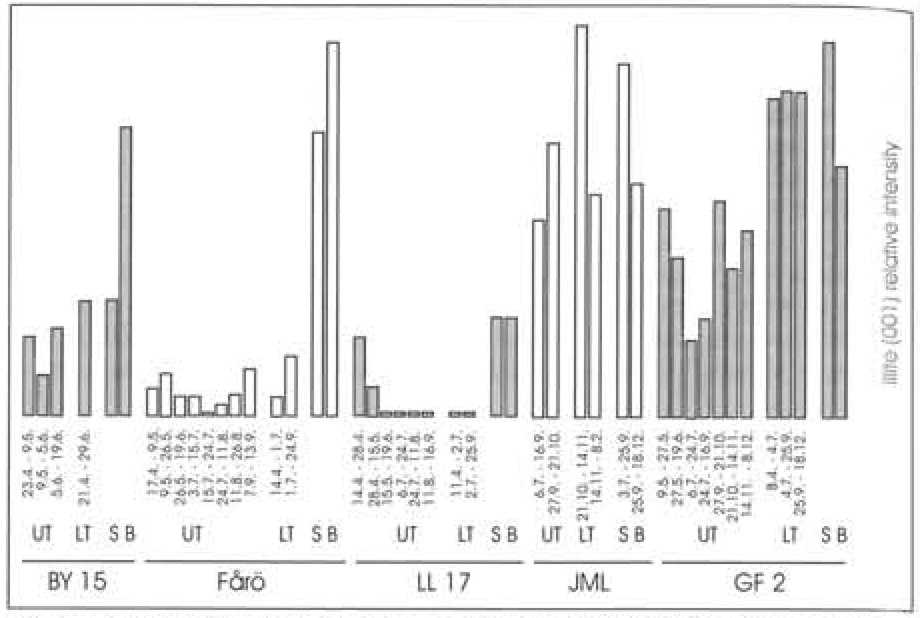

Fig. 7. Illite (001) behaviour in sediment and suspension (1997). S, sediment "surface" (0-2 cm); B, sediment "bottom" (20-22 cm) below surface. UT = upper trap, LT = lower trap.

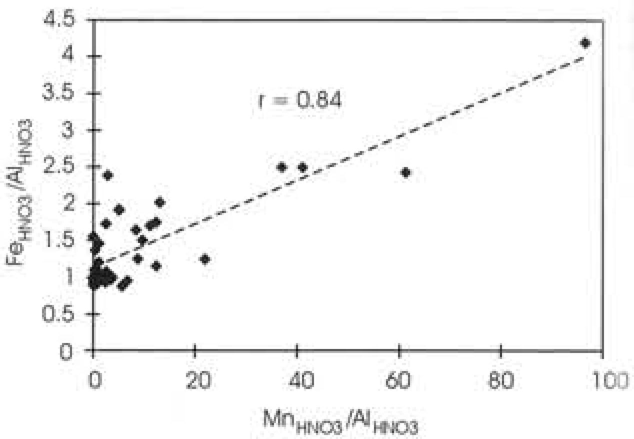

Fig. 8. Fe/Al - Mn/Al correlation (HNO$_3$ leachable fraction) in suspended particles. The Fe/Al = 1 appears to represent the HNO$_3$ leachable "background" fraction of the particles (see Table 2).

DISCUSSION

Silicate and carbonate minerals

Winterhalter (2000) pointed out that the concentration of elements in water and sediment may differ substantially from area to area due to purely natural reasons because of the great variability of the bedrock in the Baltic Sea area. Vallius (1999) noted that the concentrations of most metals in the southern GOF are 80-90% of the concentrations in the northern GOF and this is partly due to the differences in geology between these areas. In addition, Vallius (1999) observed the presence of limestone material in the southern areas of the GOF; the concentrations of Ca and Sr are clearly higher in the southern parts. No differences, however, are found in the relative lithogenic particle composition in the studied sediment and sediment trap samples (Fig. 3). Because trace metals of natural origin appear to be mostly incorporated in the structures of micas and clay minerals in Finnish soil sediments (Räisänen et al. 1992) it is obvious that slight geochemical differences may exist in clay minerals in Baltic Sea sediments. The differences, however, are not possible to observe using only XRD and main lithogenic metals (Al, Fe).

The Quaternary sediments covering the Paleozoic formations are partly composed of material derived from the bedrock (Kadastik 1995, Klagish and Goldfarb 1994), indicating glacial and glaciofluvial mixing processes. Erosion of formerly deposited sediment may have taken place during the latter part of the Litorina Sea stage (Kohonen and Winterhalter 1999) which further mixes old and new sediments. The presence of kaolinite in recent mud sediments in the GOF is an indication of constant mixing of old and new sedimentary materials (Rantataro 1996). Despite difficulties in determining the primary source of the lithogenic particles, indirect conclusions can be made.

The Gulf of Finland - The role of currents and wave erosion is strong which is directly indicated by the clear presence of illite$_{001}$ in suspension throughout the collection period (Fig. 7). The resuspension, however, appears to be rather sporadic than continuous due to the angularity of clasts in suspension. It is probable that the poorly abraded mineral particles collected from trap material are formed during short lifetime currents. This suggests that the capability of basin-basin particle movement toward deeper areas appears to be negligible.

The coherent XRD patterns both in surficial and buried sediments indicate that neither salinity nor diagenesis has had an affect on clay minerals. The stability of clay minerals against alterations may last thousands of years. Gingele and Leipe (1997) observed almost constant distribution of clay minerals at BY15 during a time period of 10 000 yr. It is also likely that the particle transport from land and shallower sea areas toward accumulation bottoms does not affect clay mineral properties. Rantataro (1996) observed that the general mineralogy in harbour basin recent sediments (Helsinki) is very similar compared to the present study (Fig. 3). In addition, Soveri and Hyyppä (1966) and Lintinen (1995) observed almost identical untreated XRD patterns in near-shore areas in mainland till. Emelyanov (2001) stressed that the loose Litorina muds are washed out at velocity of about 50-cm s^{-1}. The residence time for Baltic water masses is 25-40 yr. (Bernard et al. 1989). Apparently the role of currents and sediment reworking processes are superior relative to silicate mineral alterations in the northern Baltic Sea during a moderate time span (e.g. 10,000 yr.). This appears to be contradictory, since anomalies in till fines are known to be of local origin in Finnish soils (Soveri and Hyyppä 1966, Lintinen 1995). Finnish soil material should be expected to be more mixed, because the sea level was substantially higher during the earlier stages of the Baltic Sea.

The Baltic Proper - The maximum illite$_{001}$ and Al$_{HNO3}$ values in suspension never exceed the underlying surface sediment values in the Baltic Proper (Table 2, Fig. 7), thus suggesting suspension from organic-rich bottom sediments. This is supported by the coexistence of the authigenic Mn-carbonate (2.89 Å) and the lithogenic particles in suspension at LL17 and BY15 stations and the lack of carbonate in suspension in the Fårö Deep area (Fig. 5).

The presence of coarse detrital carbonate particles in suspension (40 m above bottom) in the Gotland Deep (Fig. 6) suggests separate lateral current pulses (c.f. GOF), e.g. the salt water pulse through the Danish straits. The Paleozoic sedimentary outcrops in the slope areas (Emelyanov and Kharin 1988, Tuuling et al. 1995) are the possible source of detrital carbonate grains. The geochemical processes in the Gotland Basin appear to be strongly influenced by lateral transport and segregation of material (Emeis et al. 1998). The coastal turbid waters may break through the halocline and thus penetrate into the deeps in the Baltic Proper (Emelyanov 2001). The Gotland Deep is a basin with predominant cyclonic near-bottom water circulation (Sviridov et al. 1997).

Detrital carbonate particles are only observed in the central Baltic Proper. The question arises, have these particles originated from the slope areas around the Gotland Deep? According to the Stokes' Law, a 150 µm particle will sink at a constant velocity of ca. 1cm s^{-1}. According to topography, the 160 m isobath appears to limit the Gotland Deep. The trap depth where detrital carbonate particles are found is ca. 190 m. The estimated lateral trap – slope sediment distance is 20-40 km. A calculation indicates that a 5-15 m s^{-1} horizontal current is needed to establish the origin of detrital carbonate particles from the marginal areas in the Gotland Deep. Emelyanov (2001) argued, however, that only 1m s^{-1} is needed to wash out the coarser marginal sediments. It is, thus, possible that the ultimate origin of detrital carbonate particles observed in this study is farther than the marginal sediments in the Gotland Deep. The angularity of these particles, however, excludes the possibility of vigorous current activity and/or very distant sources. Also the role of ice cover during winter times and stormy weather periods may affect this process.

Manganese

It is suggested that the salt-water inflow affect the behaviour of the ferromanganese concretions (FMC) in the Baltic Sea (Glasby et al. 1996). Boström et al. (1981) reported a mobile Mn-rich particulate matter capable of being transported out from the Baltic Sea area as suspended matter. It is, however, unlikely that the oxide particles observed in this study have a capability of being transported as particles. The studied particles are amorphous (5-55 °2q) while the FMC in shallower areas are known to be weakly

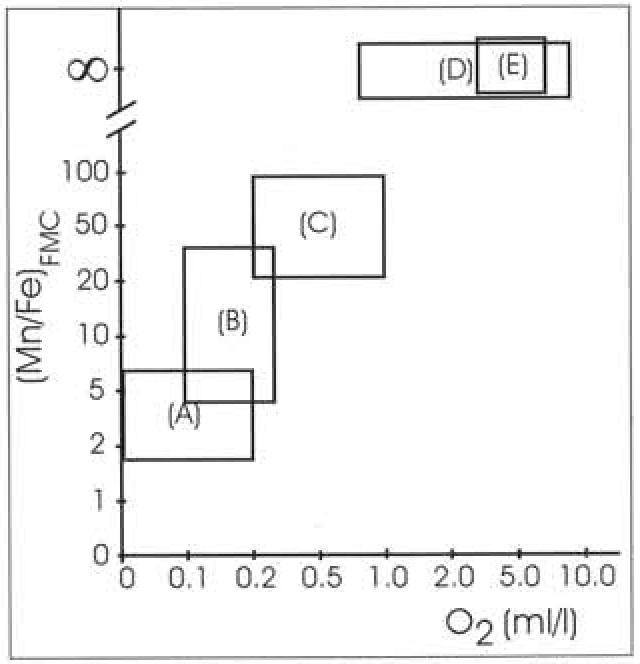

Fig. 9. Suspended particle Mn/Fe dependence with the dissolved oxygen content ("FMC- fraction"). The estimated background phase is eliminated. BY15 (A), Fårö Deep (B), LL17 (C), JML (D), GF2 (E).

cryptocrystalline (Glasby et al. 1996, Zhamoida et al. 1996). The $(Mn/Fe)_{FMC}$ ratio follows the dissolved oxygen content (Fig. 9) indicating formation of the oxide particles *in situ* in the study areas. The suspended particulate Mn/Fe dependence with dissolved oxygen has been established in the southern Baltic Sea (Kremling et al. 1997). The Mn_{HNO3}/Al_{HNO3} peak shifts temporally from BY15 (9.5.-5.6.) via LL17 (6.7.-24.7.) to GF2 (24.7.-16.9.) (Fig. 10) indicating processes by Mn oxidising bacteria after bloom periods and further sinking of matter. Bacteria mediated *in situ* enriched Mn particles in the deep ocean water column have been described by several authors (Cowen and Bruland 1985, Bruland et al. 1994, Kuss and Kremling 1999).

Unlike lithogenic fraction, the suspended oxide fraction appears to disintegrate before reaching bottom or soon after accumulation. The accumulation of the particulate Mn in the deeper basins of the Baltic Proper is related to the fluctuations of the oxygen content (Ingri et al. 1991). The FMC cannot form under anoxic conditions (Glasby et al. 1996). This study, however, indicates that the particulate Mn may persist even at near-zero oxygen level (Fig. 9). Leivuori and Vallius (1998) observed a high Mn enrichment in suspension at GF2 without any significant oxygen level variations. In addition, the surface sediments at GF2 were oxic during the sampling campaign (Table 1). This indicates that the oxygen content is not the only limiting factor for FMC existence. Evidently microbiological processes as well as the oxygen content in the near-bottom waters are both responsible for Mn behaviour there. In contrast, Mn-carbonate prevails in surface sediments in the Baltic Proper. A carbonate laminae formation in the Gotland Deep is closely coupled with the intensity of salt-water inflows (Huckriede and Meichner 1996, Neumann et al. 1997, Sternbeck and Sohlenius 1997). According to these authors, MnO_2 is precipitated in the sediment surface by oxygenated water and MnO_2 will be converted to Mn-carbonates either in surface or soon after burial in a reducing environment. This study, however, suggests that the Mn conversion from oxide to carbonate may occur via dissolved phase in the near-bottom water (< 5 m) without any "true" accumulation. Lepland and Stevens (1998) noted that variations of dissolved Mn(II) concentration in the anoxic bottom waters could contribute to Mn-carbonate formation because the flux of MnO_2 is presumably also seasonal. They conclude, however, that MnO_2 is probably not so pronounced as the seasonality of organic blooms, because Mn(IV) is derived from oxic slope sediments during expansion of anoxic conditions. This study indicates that a substantial part of MnO_2 is formed *in situ* and thus may be of seasonal nature. Finally, Leppänen (1988) observed that during the vernal production stage, the settling matter is most probably decomposed near the sediment surface, after leaving the euphotic layer, rather than during sinking. It is probable that the Mn-oxide disintegration and the Mn-carbonate formation in near-bottom waters are due to this process.

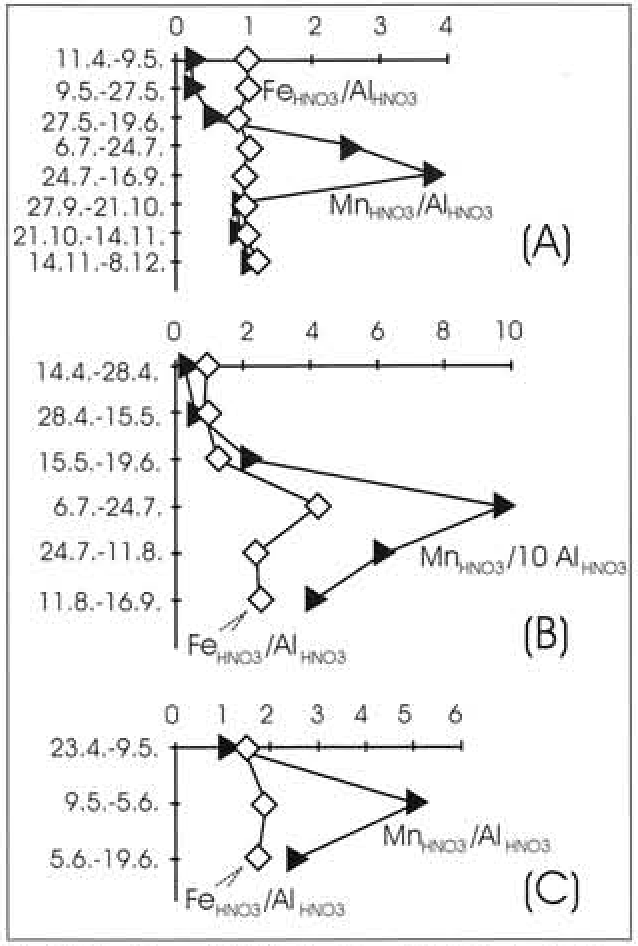

Fig. 10. Fe/Al and Mn/Al behaviour (HNO_3 leachable fraction) in the upper trap material. GF 2 (A), LL 17 (B) and BY 15 (C). Note the different Mn/Al scale at site LL17.

CONCLUSIONS

The study clearly shows that it is almost impossible to establish the ultimate origin of the mineral particles only by XRD and general geochemistry in the deep basin areas of the northern Baltic Sea. The variations in clay mineralogy may indicate a different origin of the matter, which is not observed. The prevailing manganese oxide particles are solely formed *in situ*.

The GOF deep-water environment is sedimentologically more active than that of the Baltic Proper. There is only a weak sediment-suspension interaction for authigenic minerals. Especially for manganese the dissolved intermediate stage exists because Mn occurs mainly as carbonates in sediments while Mn-oxide is the dominant manganese phase in suspension.

Acknowledgements

The author wishes to thank Dr. Mirja Leivuori (Finnish Institute of Marine Research) for providing me the chemical data. Dr. Martti Lehtinen (University of Helsinki, Department of Geology) kindly made all XRD-scans. Dr. Minna Nieminen (Technical University of Helsinki, Department of Chemistry) helped me for IR-measurements. Prof. Rodney Stevens and Dr. Boris Winterhalter improved this ms significantly, my sincere thanks to them. Finally I thank Prof. Matti Perttilä, the contributor of the BASYS 3B ("basin-basin fluxes") group. BASYS is funded by the European Commission Directorate General 12 – Science, Research and Development, Marine Science and Technology Programme MAST III – Contract MAS3-96-0058, International Cooperation Programme INCO – Contract IC20-96-0080.

References

Belmans, F., van Grieken, R. & Brügmann, L. 1993: Geochemical characterization of recent sediments in the Baltic Sea by bulk and electron microprobe analysis. *Marine Chemistry 42*, 223-236.

Bernard, P.C., van Grieken, R. & Brüggmann, L. 1989: Geochemistry of suspended matter from the Baltic Sea. 1. Results of individual particle characterization by automated electron microprobe. *Marine Chemistry 26*, 155-177.

Boström, K., Burman, J.O., Boström, B., Ponter, C., Brandlöf, S. & Alm, B. 1978: Geochemistry, mineralogy and origin of the sediments in the Gulf of Bothnia. *Finnish Marine Research 244*, 8-35.

Boström, K., Burman, J-O., Ponter, C. & Ingri, J. 1981: Selective removal of trace elements from the Baltic by suspended matter. *Marine Chemistry 10*, 335-354.

Boström, K., Burman, J.-O. & Ingri, J. 1983: A geochemical massbalance for the Baltic. *In* Hallberg R. (Ed.): Environmental Biogeochemistry. *Ecological Bulletin* 35, Stockholm, 39-58.

Bruland, K.W., Orians, K.J. & Cowen, J.P. 1994: Reactive trace metals in the stratified central North Pacific. *Geochimica et Cosmochimica Acta 58*, 3171-3182.

Brügmann, L., Bernard, P.C. & van Grieken, R., 1992: Geochemistry of suspended matter from the Baltic Sea 2. Results of bulk trace metal analysis by AAS. *Marine Chemistry 38*, 303-323.

Cowen, J.P. & Bruland, K.W. 1985: Metal deposits associated with bacteria: implications for Fe and Mn marine biogeochemistry. *Deep-Sea Research 32*, 253-272.

Degens, E.T. & Mopper, K. 1976: Factors controlling the distribution and early diagenesis of organic material in marine sediments. *In* Riley, J.P. & Chester, R. (Eds.): *Chemical Oceanography 6.* Academic Press, London, 59-113.

Emeis, K.-C., Neumann, T., Endler, R., Struck, U., Kunzendorf, H. & Christiansen, C. 1998: Geochemical records of sediments in the Eastern Gotland Basin - products of sediment dynamics in a not-so-stagnant anoxic basin? *Applied Geochemistry 13*, 349-358.

Emelyanov, E.M. & Pustelnikov, O.S. 1975: Compositions of river and marine forms of suspended matter in the Baltic. *Geochemistry International 12*, 195-208.

Emelyanov, E. M. & Kharin, G.S. 1988: Geological map of eastern and southeastern Baltic Sea. *In* Winterhalter, B. (Ed.): The Baltic Sea. *Geological Survey of Finland, Special Paper 6*, 59-67.

Emelyanov, E. 1992: The Baltic Proper: Geological structure. *In* Perttilä M. & Brügmann, L. (Eds.), Review of contaminants in Baltic sediments. *ICES cooperative research report 180*, 16-19.

Emelyanov, E.M. 2001: Biogenic components and elements in sediments of the Central Baltic and their redistribution. *Marine Geology 172*, 23-41.

Gingele, F.X. & Leipe, T. 1997: Clay mineral assemblages in the western Baltic Sea: recent distribution and relation to sedimentary units. *Marine Geology 140*, 97-115.

Glasby, G.P., Uścinowicz, Sz. & Sochan, J.A. 1996: Marine ferromanganese concretions from the Polish exclusive economic zone: Influence of major inflows of North Sea water. *Marine Georesources and Geotechnology 14*, 335-352.

Hardy, R.G. & Tucker, M.E. 1988: X-ray powder diffraction of sediments. *In* Tucker M. (Ed.): *Techniques in Sedimentology.* Blackwell Scientific Publications, Oxford, 191-228.

Heiser, U., Neumann, T., Scholten, J. & Stüben, D. 2001: Recycling of manganese from anoxic sediments in stagnant basins by seawater inflow: a study of surface sediments from the Gotland Basin, Baltic Sea. *Marine Geology 177*, 151-166.

Huckriede, H. & Meischner, D. 1996: Origin and environment of manganese-rich sediments within black-shale basins. *Geochimica et Cosmochimica Acta 60 (8)*, 1399-1413.

Ingri, J., Löfvendahl, R. & Boström, K. 1991: Chemistry of suspended particles in the southern Baltic Sea. *Marine Chemistry 32*, 73-87.

Kadastik, E. 1995: Texture and mineralogical characteristics of Weichselian till on Saaremaa island. *Bulletin Geological Survey of Estonia 5 (1)*, 4-11.

Klagish, B. & Goldfarb, Y. 1994: Lithogenic features of the Quaternary Section in the Liepaja Region of the Baltic Sea. *Baltica 8*, 57-63.

Kohonen, T. & Winterhalter, B 1999: Sediment erosion and deposition in the western part of the Gulf of Finland. *Baltica 12*, 53-56.

Kremling, K., Tokos, J.J.S., Brügmann, L. & Hansen, H.-P. 1997: Variability of dissolved and particulate trace metals in the Kiel and Mecklenburg Bights of the Baltic Sea, 1990-1992. *Marine Pollution Bulletin 34 (2)*, 112-122.

Krone, R.B. 1978: Aggregation of suspended particles in estuaries. *In* Kjerfve, B. (Ed.), *Estuarine transport processes.* University of South Carolina Press, 177-190.

Kuss, J. & Kremling, K. 1999: Particulate trace element fluxes in the deep northeast Atlantic Ocean. *Deep-Sea Research 46*, 149-169.

Leivuori, M. & Vallius, H. 1998: A Case study of seasonal variation in the chemical composition of accumulating suspended sediments in the central Gulf of Finland. *Chemosphere 36 (10)*, 2417-2435.

Leivuori, M. 2000: Distribution and accumulation of metals in sediments of the northern Baltic Sea. Ph.D thesis. *Finnish Institute of Marine Research – Contributions, 2,* Helsinki. 43 p.

Lepland, A. & Stevens, R.L. 1998: Manganese authigenesis in the Landsort Deep, Baltic Sea. *Marine Geology 151*, 1-25.

Leppänen, J-M. 1988: Cycling of organic matter during the vernal growth period in the open northern Baltic Proper. VI. Sinking of particulate matter. *Finnish Marine Research 255*, 97-118.

Lintinen, P. 1995: Origin and physical characteristics of till fines in Finland. Ph.D thesis. *Geological Survey of Finland, Espoo.* 95 p.

Moore, D.M. & Reynolds, R.C. Jr. 1989: X-ray diffraction and the identification and analysis of clay minerals. *Oxford University Press, Oxford.* 332 pp.

Neumann, T., Christiansen, C., Clasen, S., Emeis, K.-C. & Kunzendorf, H. 1997: Geochemical records of salt-water inflows into the deep basins of the Baltic Sea. *Continental Shelf Research 17 (1)*, 95-115.

Niemistö, L. 1974: A gravity corer for studies of soft sediments. *Merentutkimuslait.Julk. Havsforskningsinst.Skr. 238*, 33-38.

Rantataro, J. 1996: Anthropogenic impact on recent sediment in Jätkäsaari harbour basin, Helsinki, Finland: A comparison with the geochemistry of unpolluted glacial clay. *Geol. Survey of Finland, Report of Investigation 134*. 47 pp.

Russel, J. 1987: Infrared methods. *In* Wilson, M. (Ed.): *A handbook of determinative methods in clay mineralogy.* Blackie & Son Ltd, Glasgow and London, 133-173.

Räisänen, M-L., Tenhola, M. and Mäkinen, J. 1992: Relationship between mineralogy and the physico-chemical properties of till in central Finland. *Bulletin Geological Society of Finland 64, I,* 35-58.

Soveri, U. & Hyyppä, J.M.I. 1966: On the mineralogy and fine fraction of some Finnish glacial tills. *The State Institute for Technical Research, Helsinki, Finland, Publication 113*. 31 p.

Sternbeck, J. and Sohlenius, G. 1997: Authigenic sulfide and carbonate mineral formation in Holocene sediments of the Baltic Sea. *Chemical Geology 135*, 55-73.

Sviridov, N.I., Sivkov, V.V., Rudenko, M.V. & Trimonis, E.S. 1997: Geological evidence of bottom currents in the Gotland Basin of the Baltic Sea. *Oceanology 37 (6)*, 838-844.

Tuuling, I., Floden, T., Puura, V. & Söderberg, P. 1995: Cambro-Silurian structures of the northern Baltic Proper - preliminary interpretations from high resolution seismic data. *In* Mojski, J.E. (Ed.): *Proceedings of the Third Marine Geological Conference "The Baltic", Warszava*, 26-33.

Vallius, H. 1999: Recent sediments of the Gulf of Finland: An environment affected by the accumulation of heavy metals. Ph.D thesis, *Department of Geology and Mineralogy, Åbo Akademi University,* 45 p.

Winterhalter 2000: The paleoenvironment of the Baltic Sea – a sub-project of BASYS. *Baltica 13*, 88-89.

Zhamoida, V.A., Butylin, W.P., Glasby, G.P. & Popova, I.A. 1996: The nature of ferromanganese concretions from the eastern Gulf of Finland, Baltic Sea. *Marine Georesources & Geotechnology 14*, 161-176.

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 95-107

Triterpenoids and other organic compounds as markers of depositional conditions in the Baltic Sea deep basins during the Holocene

Hans Peter Nytoft, Birger Larsen

Abstract

Sediment cores from three Baltic Sea basins were investigated using methods developed for source rock evaluation and by GC-MS analysis of extractable lipids (Biomarkers). A few samples were also analysed using coal petrography methods. TOC and Hydrogen Index (HI) are generally high in the marine sediments from the Bornholm Basin (4-6%) and the Gotland Basin (4-10%) whereas sediments from the North Central Basin usually have lower TOC (2%) and HI with only a few elevated values in laminated intervals. Sediments from the North Central Basin also had a lower HI suggesting a higher content of terrestrial organic matter. This was also substantiated by the higher content of taraxer-14-ene (a triterpenoid produced by angiosperms) in samples from the North Central Basin. A number of triterpenes including malabaricatriene and fernenes were detected in high concentrations in laminated sediments, suggesting that they are sensitive markers of anoxic depositional conditions.

☐ Baltic Sea, sediments, Rock-Eval, anoxia, triterpenoids, hopanoids, fernenes, malabaricatriene, Yoldia Sea, Ancylus Lake, Litorina Sea.

☐ *Hans Peter Nytoft [hpn@geus.dk], Department of Reservoir Geology, Geological Survey of Denmark and Greenland, Thoravej 8, DK 2400 Copenhagen NV, Denmark; Birger Larsen [bil@geus.dk], Department of Environmental History and Climate Change, Geological Survey of Denmark and Greenland, Thoravej 8, DK 2400 Copenhagen NV.*

☐ Received 27 June 2001; accepted 27 November 2001.

INTRODUCTION

The aim of this study is to use the variation in Hydrogen Index (HI) and in selected organic compounds in the sedimentary columns in three Baltic basins (Fig. 1) to reconstruct the environmental history of the Baltic. Total Organic Carbon (TOC) and often N are the simplest but also very general measures of the organic matter in sediments. The quality of the organic matter is often characterised by the TOC/N ratio (e.g. Andrén et al. 2000 a,b). The organic matter in the three BASYS cores is also characterised by isotope composition of the C and N (Voss et al. 2001) and the contents of chlorins (chlorophyll derivatives) (Kowalewska et al. 1998, Kowalewska et al. 1999). Rock-Eval analysis was originally developed for a quick evaluation of petroleum source rock quality. The method measures the amount of hydrocarbons ($< C_{30}$) released by controlled heating and pyrolysis of the sample, see Espitalié et al. (1985) for details. Since oxygen deficient or anoxic basins such as the Baltic Basins are regarded as prime sites for deposition of source rocks for hydrocarbon

Fig. 1. Map showing sampling sites:

211610 and -20	55° 32 N	15° 21.5 E	75m water depth
211630-9	55° 22.65 N	15° 23.84 E	93m water depth
211660-6	57° 19.98 N	20° 07.14 E	241m water depth
211670-7	58° 49.16 N	20° 15.14 E	175m water depth

genesis, the organic geochemical and sedimentary conditions in such basins (Demaison and Moore 1980) are of general interest.

GC- and GC-MS analysis of lipids gives a more detailed information of the composition and thus origin (provenance) and diagenetic changes of the organic matter. These compounds are derived from biogenic precursor molecules, which sometimes may be inferred. Chain length distribution of *n*-alkanes, *n*-alkanols and *n*-alkanoic acids in sediments provide information on the origin of the organic matter. Long chain compounds originate from land plants, whereas short chain compounds are produced by aquatic organisms (Cranwell 1982, Meyers and Ishiwatari 1993).

In this study, we have particularly focused on tri- and pentacyclic triterpenoids. Only a few papers have described triterpenoids in the Baltic Sea sediments (e.g. Malinski et al. 1988, Pihlaja et al. 1990), and analyses have been restricted to surface sediments. Because of the microbial synthesis of triterpenoids within the sediments, they are important indicators of diagenetic conditions. They contribute substantially to the lipids accumulated in the sediments after decay of living organisms (Ensminger et al. 1974, Ourisson et al. 1979). Ourisson and Albrecht (1992) have estimated that the fossilised hydrocarbon skeletons of the pentacyclic hopanoids biosynthesized by bacteria may represent the most abundant natural organic product on earth. For a general description of these biomarkers see Peters and Moldowan (1993). In most cases, only C_{30} compounds exist, but sometimes, a complete pseudo-homologous series ranging from C_{29} (**a**) to C_{35} (**g**) is possible. The names of those compounds actually identified in the Baltic Sea sediments are shown in Fig. 2. The structure of the compounds discussed herein (numbers in **bold**) is shown in Fig. 3.

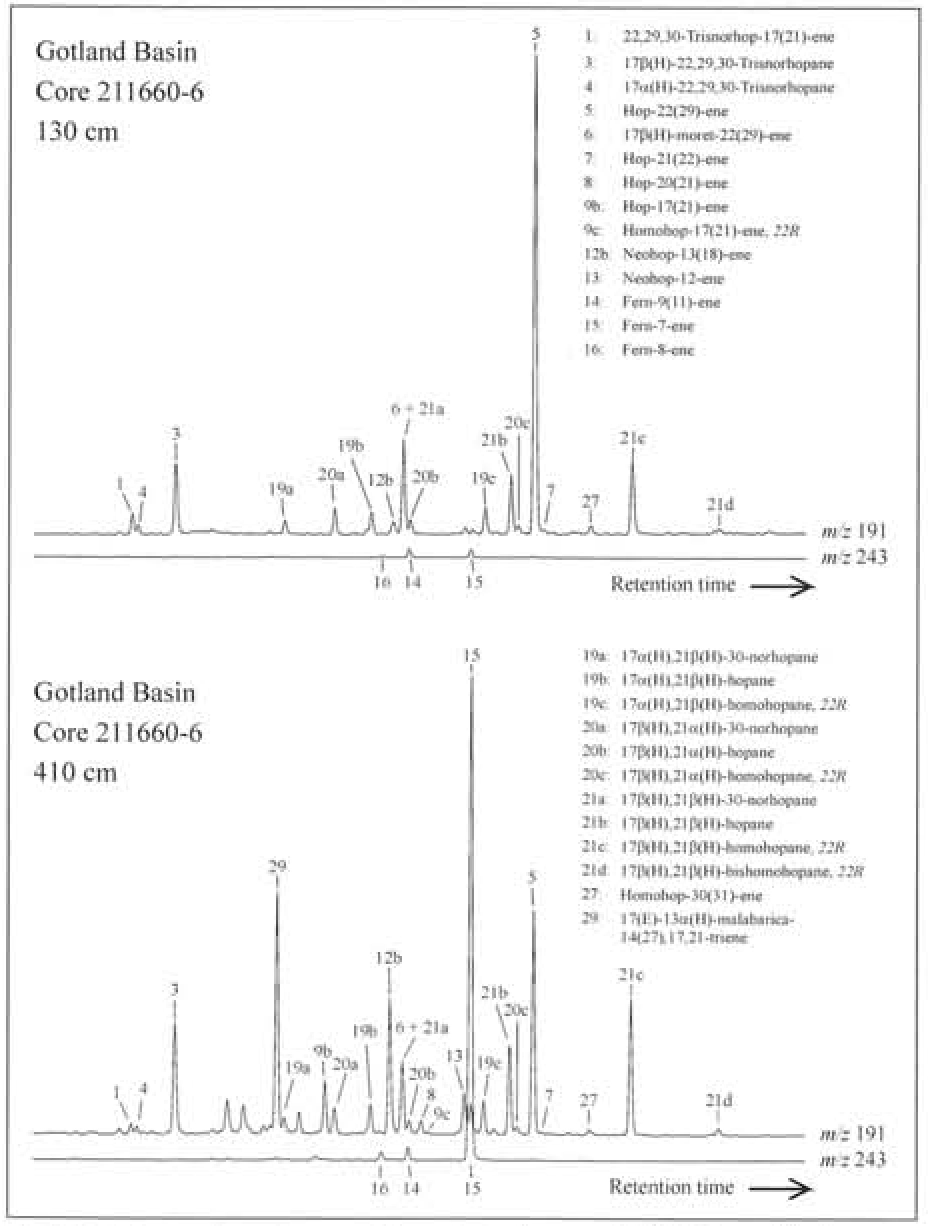

Fig. 2. Partial mass chromatograms of two extracts from core 211660-6 containing hopanes, hopenes and malabaricatriene (*m/z* 191) and fernenes (*m/z* 243) including names of compounds identified.

Hopanoids found in geological samples are the diagenetic products of "biohopanoids", compounds predominantly biosynthesized as membrane constituents of bacteria. They include simple C_{30} compounds as well as extended C_{35} bacteriohopanepolyols and a range of composite hopanoids where the side chain is linked to a complex polar moiety (Rohmer et al. 1992, Innes et al. 1997). The complex, polar hopanoids are not amenable to direct analysis by GC-MS and can only be analysed after degradation and derivatisation (Innes et al. 1997) which means that a lot of information from the original hopanoids is lost. Analysis is usually limited to the simple, apolar, hopanoids such as hopanes and hopenes, as in the present study.

Like hopenes, fernenes are pentacyclic triterpenes, but the positions of some of the methyl groups differ. Fernenes, especially fern-9(11)-ene (**14**), are usually the dominant triterpenes in ferns, and fernenes in sediments were previously believed to be indicators of terrigenous organic matter input, but in addition they reflect bacterial inputs (Brassell and Eglinton 1983). Fern-7-ene (**15**) was found in very high concentrations in sediments from Ace Lake, a saline, meromictic lake in Antarctica with no ferns or higher plants in the vicinity (Volkman et al. 1986). Since fern-7-ene was only abundant in those sediments which contained methanogen markers, it was suggested that fern-7-ene was also associated with anoxic depositional conditions. Fernenes have also been detected in deep-sea sediments (Brassell and Eglinton 1983), sediments from the Alaskan Outer Continental Shelf (Venkatesan and Kaplan 1982), the anoxic Cariaco Trench (Wakeham 1990) and in sediments from the Baltic Sea (Pihlaja et al. 1990).

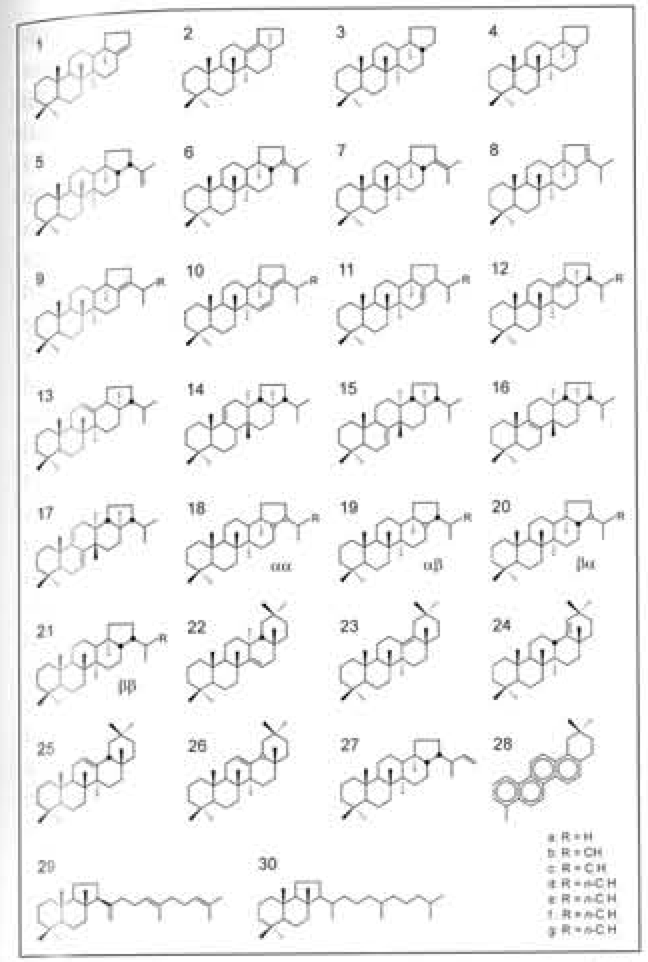

Fig. 3. Structure of compounds identified in Fig. 2 and discussed in text.

17(E)-13a(H)-Malabarica-14(27), 17,21-triene (or just malabaricatriene)(**29**) was identified by Behrens et al. (1999) by NMR studies after isolation from the solvent extract of a recent sediment from the meromictic Lake Cadagno. A high concentration of the still unidentified compound had earlier been found in sediments from the Cariaco Trench, an anoxic marine basin on the continental shelf of Venezuela (Wakeham 1990), in sediments from the Gotland Deep (Pihlaja et al. 1990) and in anoxic surface sediments from the Arabian Sea (Sinninghe Damsté, unpublished results, cited by Behrens et al. (1999). Since malabaricatriene was detected in sulphur-rich ecosystems characterised by the presence of anoxic bottom waters and sediments it was proposed (Behrens et al. 1999) that the hydrocarbon skeleton of malabaricatriene may originate from an unknown, but possibly widespread biological source able to thrive in particular ecosystems (i.e. highly anoxic and rich in reduced sulphur species) and which remains to be discovered.

Various functionalism pentacyclic compounds are produced by higher plants (angiosperms) and their unsaturated degradation products are often found in recent sediments (ten Haven et al. 1992a,b). Most usually have the lupane, oleanane or ursane skeleton, but in some cases other compounds dominate. The mass spectrum of an unknown compound was shown in Venkatesan and Kaplan (1982). This compound was later identified as taraxer-14-ene (**22**) (ten Haven and Rüllkötter 1988). Taraxer-14-ene is the most important terrigenous triterpene in Baltic Sea sediments. Possible precursors of taraxer-14-ene are taraxer-14-en-3-ol and taraxer-14-en-3-one. Taraxer-14-ene is easily converted to olean-12-ene (**25**), which can further isomerise to olean-13(18)-ene (**23**), olean-18-ene (**24**) and 18a(H)-olean-12-ene (**26**) (ten Haven and Rullkötter 1988, ten Haven et al. 1992b, Rullkötter et al. 1994).

MATERIAL AND METHODS

Sampling sites and sample collection

All samples were collected during the July 1997 *R/V Petr Kottsov* cruise. The locations of the sampling stations are given in Fig. 1. The path of the inflow of marine deep bottom water was sampled in a transect of 3 coring sites from the Bornholm Basin (core 211630-9 and –10, Fig. 4) through the Gotland Basin (core 211660-6, Fig. 5) to the North Central Basin (core 211670-7 and 211670-4, Fig. 6). As a supplement, late glacial varved clays in two cores from almost the same position at the margin of the Bornholm Basin (cores 211610 and -20) were studied. In order to sample the whole sequence from the marine Litorina Sea down to the freshwater Ancylus deposits two cores were combined both for the Bornholm and the North Central Basin. Samples covering about 2 cm were taken from the cores every 20 cm. Additional samples (1 - 6 cm) were taken especially from the laminated parts of the cores or from homogeneous bands in otherwise laminated parts. Samples (in most case 100-200 ml) were stored frozen in plastic bags or metal cans until analysis. Half of each sample was dried overnight at 50°C and crushed (< 0.25 mm). The rest was refrozen. In total, 67 sub-samples from the Bornholm Basin, 72 from the Gotland Basin and 61 from the North Central Basin were analysed.

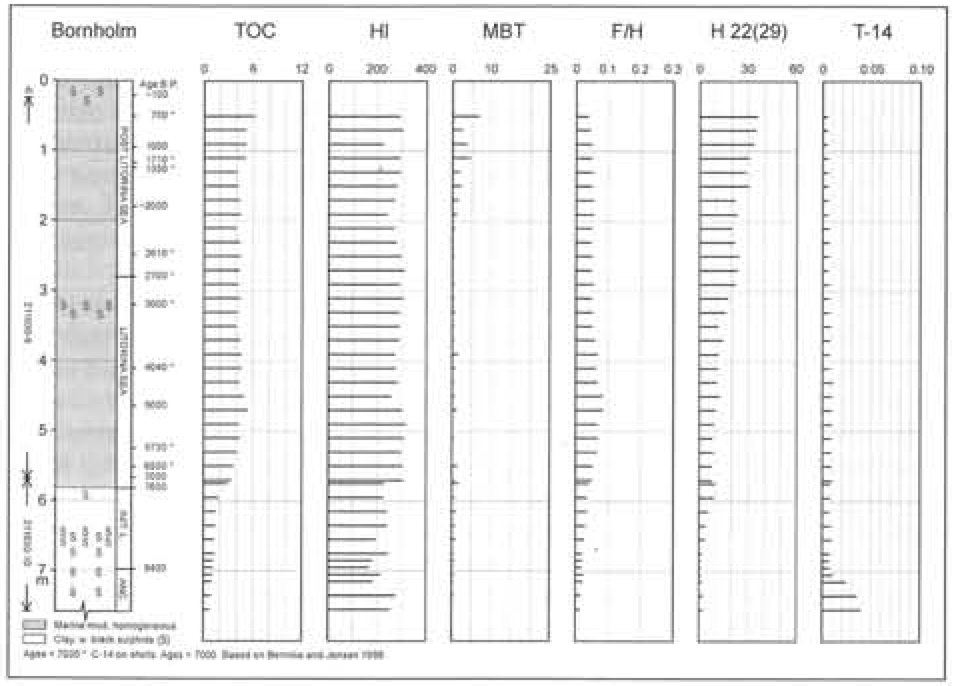

Fig. 4. Data from the Bornholm Basin, core 211630-9 and 211630-10. **TOC**: Total Organic Carbon; **HI**: Hydrogen Index; **MBT**: area of the malabaricatriene peak / total peak area (*m/z* 191). **F/H**; peak area of fernenes (*m/z* 243) / total peak area (*m/z* 191); **H 22(29)**: peak area of hop-22(29)-ene (*m/z* 191) / total peak area (*m/z* 191). **T-14**: peak area of taraxer-14-ene (*m/z* 271) / total peak area (*m/z* 191). Total peak area (*m/z* 191) refers to the sum of peak areas in the partial *m/z* 191 mass chromatogram as shown in Fig. 2.

Description of cores

The sediments in all the cores are silt- and clay rich mud with only limited variation in grainsize (Repeèka and Grigelis 1998). With the high organic content the marine mud can be described as sapropelitic clay or marine clay gyttja. The grey freshwater sediments - the Yoldia- and the Ancylus clays below the marine deposits are in the cores more fine grained and less influenced by organic matter. They are described as pelitic muds or clays (Larsen and Repeèka 1997). A characteristic distribution of black sulphide (FeS) colouring in the clay a few decimetres below the contact to the marine Litorina deposits are observed in clayey sediments all over the Baltic basins. The sulphides are regarded as a diagenetic precipitation caused by H_2S diffusing down into the clay from the marine deposits above (Boesen and Postma 1988). The marked lithostratigraphic boundary between the clays and the marine claygyttja clay has previously been regarded as the boundary between the freshwater Ancylus clay and the marine Litorina clay. However, due to a small content of marine diatoms in the top part of the clay it is now regarded as the Initial Litorina Sea deposits or the Mastogloia Stage. The general stratigraphy is discussed in Sohlenius et al. (1996), Andrén et al. (2000 a,b).

In the Gotland Basin (core 211660-6, Fig. 5) dark intervals with lamination alternate with sequences of lighter grey homogeneous mud. Alternating thin laminated and non-laminated intervals on the thickness scale of 1-10 cm are called A-units. The North Central Basin (211670-7 and 211670-4, Fig. 6) is near the connection to the Bothnian Sea. Here the same types of sequences are found but the laminated intervals are thinner and few in number compared to the Gotland Basin. The Bornholm Basin core (211630-9, Fig. 4) is bioturbated throughout in scale of 1-5 cm and shells mostly *Macoma calcaria* occurs frequently through the marine section. No lamination has been observed in this core, but thin sequences of laminated sediment have occasionally been observed in recent surface samples during anoxic events in the deep Bornholm Basin (Jonsson et al. 1990). Apparently lamination is not preserved in the deposits due to frequent periods with bioturbation and redistribution of the toplayer on the flat and even seafloor.

Dating

The dating on the cores from the Gotland Basin (Fig. 5) and the North Central Basin (Fig. 6) are based on paleomagnetic variations in the inclination and declination compared to the paleosecular variation over the last 3000 years recorded in annually laminated lake sediments in Finland (Kotilainen et al. 2000). They estimate that the accuracy is better than ±50 years in this part of the time scale. The dates older than 3000 years BP (before 1950) are based on ^{14}C dating of shells and organic matter (Andrén et al. 2000a). Data from core 211660-1 are correlated to core 211660-6 by matching the pattern of magnetic susceptibility in the two cores (Kotilainen pers. com. 2000). The ages < 6000 years in the Bornholm Basin (Fig. 4) are based on ^{14}C dating on shells with 300 years reservoir correction (Andrén et al. 2000 b). The older ages are from the age model in the same paper. However the transition from the Ancylus Lake to the Initial Litorina - defined as the first (very small) marine influence on the diatom flora is dated based on terrestrial plants remnants from the first marine influence in the Arkona Basin (Bennike and Jensen 1998).

TC, TOC, TS and Rock-Eval analyses

Sub-samples for TOC-measurements were treated with aqueous SO_2 to remove carbonates. Total carbon (TC) and total sulphur were measured using a Leco CS-200 instrument. Total organic carbon (TOC) was measured using a Leco IR-212 carbon analyser. Rock-Eval analysis was carried out by means of a Rock-Eval 6 apparatus. By Rock-Eval analysis the amount of hydrocarbons that can be thermally distilled from a sediment is measured (S1), followed by hydrocarbons generated by pyrolytic degradation of the organic matter in the sediment (S2). The hydrogen Index (HI) corresponds to the quantity of pyrolyzable organic compounds from S2 relative to TOC in the sample (mg HC/gTOC). It has been found that there is a very good correlation between HI and H/C ratio. For more information on Rock-Eval analysis, see Espitalié et al. (1985).

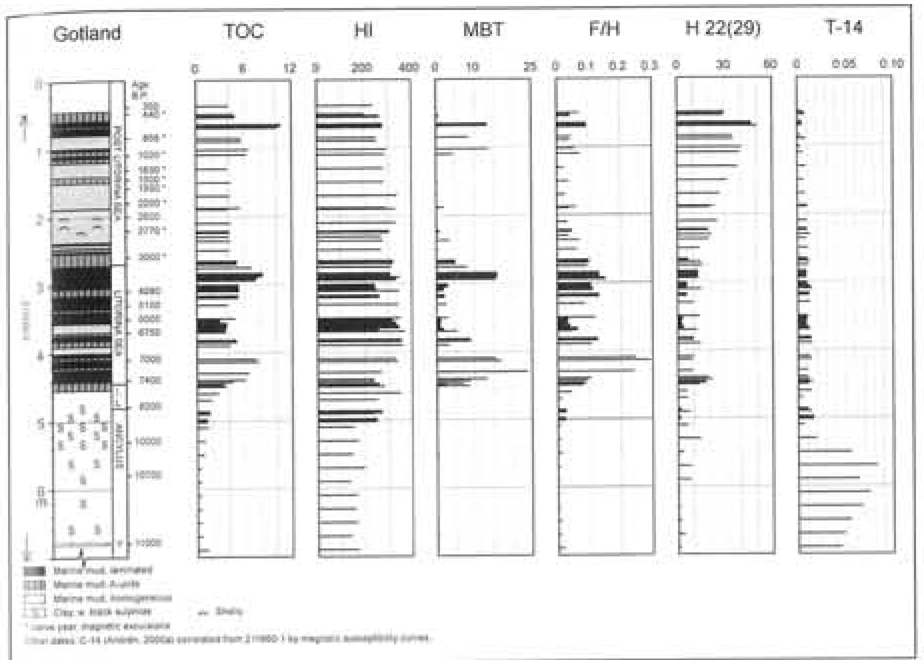

Fig. 5. Data from the Gotland Basin, core 211660-6. **TOC**: Total Organic Carbon; **HI**: Hydrogen Index; **MBT**: area of the malabaricatriene peak / total peak area (*m/z* 191). **F/H**; peak area of fernenes (*m/z* 243) / total peak area (*m/z* 191); **H 22(29)**: peak area of hop-22(29)-ene (*m/z* 191) / total peak area (*m/z* 191). **T-14**: peak area of taraxer-14-ene (*m/z* 271) / total peak area (*m/z* 191). Total peak area (*m/z* 191) refers to the sum of peak areas in the partial *m/z* 191 mass chromatogram as shown in Fig. 2.

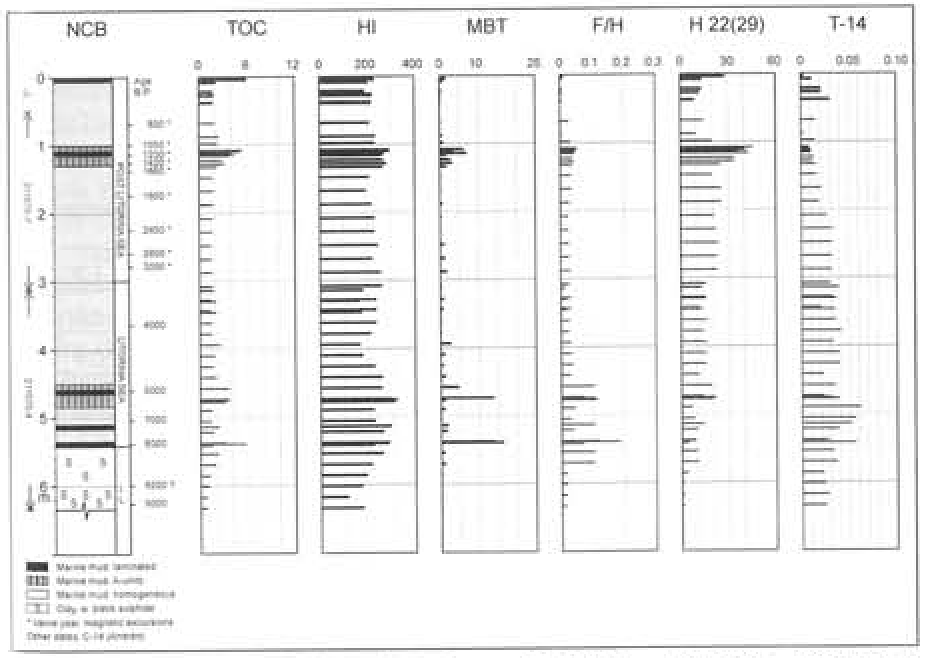

Fig. 6. Data from the North Central Basin, core 211670-7 and 211670-4. **TOC**: Total Organic Carbon; **HI**: Hydrogen Index; **MBT**: area of the malabaricatriene peak / total peak area (*m/z* 191). **F/H**; peak area of fernenes (*m/z* 243) / total peak area (*m/z* 191); **H 22(29)**: peak area of hop-22(29)-ene (*m/z* 191) / total peak area (*m/z* 191). **T-14**: peak area of taraxer-14-ene (*m/z* 271) / total peak area (*m/z* 191). Total peak area (*m/z* 191) refers to the sum of peak areas in the partial *m/z* 191 mass chromatogram as shown in Fig. 2.

Extraction of sediment samples

Solvent extraction was carried out by means of a Soxtec instrument, using dichloromethane/methanol (93:7 vol/vol). Copper powder was used to remove sulphur from the extract. A fraction containing saturated, unsaturated and aromatic compounds was prepared by chromatography on silica gel columns. Such a fraction from a large sample of laminated sapropelitic mud (150 g dry sediment, Gotland Basin 211660-6, 280-290 cm) with a complex distribution of triterpanes was separated into 6 new fractions according to polarity using MPLC (Radke et al. 1980). Each fraction was then analysed using GC-MS in scan mode in order to get clean mass spectra of all compounds investigated.

Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS)

Quantification of lipids in sediments is usually based on GC-analysis with FID-detection. This has the advantage that compounds containing only carbon and hydrogen have almost the same response/weight. However, only major compounds such as n-alkanes and a few hopenes and hopanes can be accurately measured. Minor compounds are best quantified using GC-MS. GC and GC-MS analyses were carried out as described in Nytoft and Bojesen-Koefoed (2001). For GC-MS analysis a HP-5 capillary column (25 m x 0.20-mm i.d., film thickness 0.11 mm) was used. 17(E)-13a(H)-Malabarica-14(27),17,21-triene and taraxer-14-ene coelute using this column and the malabaricatriene peak had to be corrected for coeluting taraxer-14-ene. Conversely, taraxer-14-ene can be quantified using *m/z* 271 without interference from malabaricatriene, because m/z 271 is insignificant in the mass spectrum of malabaricatriene. A few samples were reanalysed using a ZB-5 column (30 m x 0.25-mm i.d., film thickness 0.10 mm) which could separate the two compounds. Compounds were identified using standards that were either obtained from Chiron AS, synthesised in-house, or isolated from other samples using HPLC. A few compounds were identified by comparing their mass spectra with those reported in the literature.

Hopanes and hopenes with the double bond in ring D or E give a very intense *m/z* 191 response. The distribution of these compounds was measured using peak areas from the *m/z* 191 mass chromatogram. All compounds do not give the same molecular response in the *m/z* 191 mass chromatogram and the ratios measured using *m/z* 191 are not necessarily identical to composition in weight %. A few hopenes, fernenes and most triterpenes of terrigenous origin only produce a weak *m/z* 191 fragment and were quantified using other fragments. Internal standard was not used for GC-MS analysis, and only the relative abundance of the various compounds has been measured.

Preparation of reference compounds

Hopanes, hopenes, hopadienes and fern-9(11)-ene were prepared as described in Nytoft and Bojesen-Koefoed (2001). A fraction having a high content of taraxer-14-ene was prepared from Danish lake sediment. Acid catalysed isomerization of lup-20(29)-ene prepared from birch-bark or olean-13(18)-ene isolated from a sediment (Vietnam) gave a mixture of oleanenes and other terrigenous triterpenes (ten Haven and Rullkötter 1988, Rullkötter et al. 1994). Pure fern-9(11)-ene was converted to a mixture of fernene isomers (Ageta et al. 1987). Sterenes and steradienes were obtained from Chiron AS, Trondheim, Norway. No standard of 13a(H)-Malabarica-14(27),17,21-triene was available. In order to confirm the presence of malabaricatriene, an extract with a very high content was hydrogenated (PtO$_2$, isooctane, 10 min.). This removed all the malabaricatriene and two isomeric, saturated compounds **(30)** with almost identical mass spectra were formed as described by Behrens et al. (1999).

Microscopic investigation of organic particles-macerals

The organic particles (500 particles pr sample) of sediments from the BASYS cores were studied in polished sections under the microscope in reflected white and blue light in a few samples (Table 1). All organic particles are defined by their morphology, reflectance and fluorescence colour. The terms below are coal petrography terms for organic constituents (macerals). They are used by organic petrologists to classify and describe organic particulate constituents in coals and organic-rich sediments mostly with focus on their potential as oil- or gas-generative properties. Huminite is derived from decomposition under restricted oxygen availability of cellulose- and lignin-rich tissues of higher land plants. Sporinite, liptodetrinite, A.O.M. (amorphous organic matter) and alginite are derived from specific hydrogen-rich constituents of higher land plants or marine algae. Sporinite is derived from spores and pollen from higher land plants. Alginite is derived from algae. Liptodetrinite includes finely detrital constituents derived from other liptinite macerals. A.O.M. is a groundmass of mostly fluorescing organic matter formed by degradation of probably algal material. Inertinite represents oxidised organic matter generally formed by fire. Acritarchs: Unicellular or apparently unicellular microfossils of unknown affinity. For details see Taylor et al. (1998).

Table 1. Composition of organic matter (mineral matter free, vol. %)

Core	Depth m	Sediment type	TOC %	A.O.M. & Alginite	Acritarchs	Sporinite	Lipto-detrinite	Huminite	Inertinite
211630-9	4.70	M Hom.	5.38	81.5	0.5	7.4	7.4	1.5	1.7
211660-6	0.67	M Lam.	10.6	79.2	1.8	6.8	10.4	1.8	0.0
211660-6	1.50	M Hom.	4.28	85.1	1.8	4.5	6.5	1.2	0.9
211660-6	2.86	M Lam.	8.31	75.9	1.6	12.6	8.5	0.8	0.6
211660-6	4.14	M Lam.	7.74	75.9	3.4	11.1	8.2	1.1	0.3
211670-7	1.00	M Lam.	5.44	85.0	1.6	5.7	6.6	0.8	0.3
211670-7	2.60	M Hom.	1.52	38.3	0	8.8	38.2	0	14.7
211670-4	4.26	M Hom.	1.64	58.4	2.4	12.1	22.3	1.8	3.0
211670-4	4.75	M Lam.	3.67	85.6	1.4	3.5	8.1	0	1.4
211610-1	4.10	F Varv cl.	0.49	25.7	0	5.7	34.3	14.3	20.0
211630-10	7.30	F Ancylus	0.77	23.3	0	6.7	41.7	20	8.3
211660-6	6.30	F Ancylus	0.51	75.7	1.2	1.2	4.9	0	17.0

M=Marine, Hom.= Homogenous mud, Lam.= Laminated mud, F=Freshwater.

RESULTS

TOC

The total organic carbon (TOC) content of the varved, late glacial glacio-lacustrine succession underlying the Yoldia clay is approximately 0.5% (Table 2). From the Yoldia clay through the Ancylus stage deposits, TOC increases gradually from 0.5% to 1%, and through the initial Litorina stage a further increase to approximately 2% is observed. The transition to the Litorina succession is marked by another steep increase in TOC to values close to 4% in the Bornholm and Gotland Basins. Values of TOC are high (usually >4%) in most samples of the indisputably marine Litorina and post-Litorina sediments of the Bornholm (Fig. 4) and Gotland Basins (Fig. 5), whereas samples from the North Central Basin show considerably lower values, generally ~2% (Fig. 6). The marine laminated sediments generally yield 2-3 times higher values of TOC than the marine homogeneous sediments. Intervals consisting of "A-units" show intermediate values of TOC. Similar trends in TOC were recorded by Andrén et al. (2000 a,b) who also report results on S and N, and hence C/N ratios. However, they assumed that the sediments were devoid of mineral Carbon (i.e. TC = TOC). Our results show that this is generally valid for the Ancylus and Initial Litorina deposits, whereas the marine Litorina sediments contain 0.35-0.70% mineral Carbon, rendering the C/N ratios reported by Andrén et al. (2000 a,b) slightly too high.

Table 2. Data for 18 samples of Late Glacial clay from the Bornholm Basin, 211610-1 (15) + 211620-1 (3)

	TOC	HI	MBT	F/H	H 22(29)	T-14
Min.	0.31	35	0	0	0.8	0.007
Max.	1.36	161	2.56	0.01	3.0	0.021
Avg.	0.57	70	0.49	0.01	2.1	0.015

The Hydrogen Index (HI) is a rough indicator of the composition of the organic matter. Values above 150 are considered to indicate increasing amounts of lipoid rich particulate organic matter, and values above 300 to indicate the presence of substantial amounts of such material. Low values suggest refractory terrestrial matter (Tyson 1995). The HI is near 300 (ca. 26% of the TOC) in the sediments from the marine Litorina and Postlitorina intervals in the Bornholm and Gotland Basins and in the laminated intervals (7000-5000 and ca 1400-1200 BP) in the North Central Basin. HI is lower (180-250) in the pre-Litorina intervals below with lower TOC- but details differ from basin to basin. The HI is also about 200-250 in the marine non-laminated intervals in the North Central Basin, indicating that the bulk composition of the organic matter in this low-salinity basin is not very different from that of the pre-Litorina basins and contains a similar proportion of terrestrial organic matter. In the Gotland Deep no clear differences in HI between laminated and homogeneous sediments are recorded. However, in the laminated intervals in the North Central Basin both the TOC and the HI is higher than in the surrounding homogeneous intervals, and the values are close to those of the Gotland Deep. Besides the changes related to change in environment no change with depth/ time is obvious in the cores, so no important modification of the kerogen during the anaerobic diagenesis is indicated.

Alkanes, alkenes, highly branched isoprenoids and steroids

A few samples from the upper part of core 211660-6 (Gotland Basin) contained relatively high concentrations of HBI (see below). All other samples were dominated by higher odd carbon number n-alkanes C_{21}, C_{23} C_{25} C_{27} C_{29} C_{31} and C_{33}, which are of terrestrial origin. In samples from around 150 cm in the same core, *n*-C_{17} (from algae) was also a major component. Minor amounts of *n*-alkenes were detected in most samples. The concentration of highly branched isoprenoids (HBI) was generally very low, but some intervals in core 211660-6 (Gotland Basin) showed high concentrations. Between 5 and 46 % (of resolved compounds from the GC-analysis) were found in samples from the mostly laminated interval 55-110 cm and lower concentrations (< 5 %) in the mostly homogeneous intervals 110-190 and 350-390 cm. A single C_{25} diene, with a mass spectrum identical to that shown in Rowland et al. (1985), accounted for 70-80 % of the total HBI followed by a C_{25} triene (15-20%) and only minor amounts of other C_{25} compounds. Traces of C_{20} HBI were only found in a few samples. The highly branched isoprenoids in sediments are mainly produced by diatoms (Respondek et al. 1997). Rowland and Robson (1990) have reviewed the sedimentary occurrence of these compounds. Sterenes and steradienes were not very abundant compared to hopanes and hopenes in most of the samples, except in samples from the laminated parts of the cores.

Hopanes, hopenes and other triterpenenoids

Hopanes in the Baltic Sea sediments are dominated by 17b(H)-22,29,30-trisnorhopane (**3**), and C_{29}-C_{32} 17b(H),21b(H)-hopanes (**21a-d**), whereas the 17a(H),21b(H)-hopanes (**19**) are relatively minor especially in the youngest sediments. The latter group is dominated by 17a(H),21b(H)-30-norhopane (**19a**), 17a(H),21b(H)-hopane (**19b**) and 17a(H),21b(H)-22R-homohopane (**19c**). C_{29}, C_{30} and C_{31} 17b(H),21a(H)-hopanes (**20a-c**) were detected in most samples. In all three cores, the relative content of saturated compounds (hopanes) increased with depth, indicating an origin from their unsaturated precursors. The late glacial varved clays observed in two cores from the margin of the Bornholm Basin (211610 and -20) contained mainly saturated compounds.

Hop-22(29)-ene (**5**) is the major hopene in most samples. Hop-22(29)-ene is a common constituent of an extremely wide variety of procaryotes (Wakeham 1990). All hop-22(29)-ene is not necessarily of marine origin. Yunker et al. (1993) found a high content of hop-22(29)-ene in Beaufort Sea coastal sediments. Most appeared to originate from the MacKenzie River where bacterial hop-22(29)-ene from eroded peats was the likely source. Hop-22(29)-ene is also found in soil (Ries-Kautt and Albrecht 1989). In the youngest Baltic Sea sediments the relative content is 30-50% decreasing to near zero in the deepest samples (Fig. 4-6). This is probably caused by a combination of isomerization to more stable isomers (Ageta et al. 1987) and hydrogenation of the double bond. An earlier eluting compound with almost the same mass spectrum is present in all samples. This compound was identified as 17b(H)-moret-22(29)-ene (**6**) based on retention time and mass spectral data (Uemura and Ishiwatari, 1995). In Baltic Sea sediments, the relative content of 17b(H)-moret-22(29)-ene increases with depth and roughly corresponds to the decrease in the content of hop-22(29)-ene. In the deepest samples, 17b(H)-moret-22(29)-ene is usually the most abundant triterpene. 17b(H)-moret-22(29)-ene coelutes with 17b(H),21b(H)-30-norhopane (**21a**) (Fig. 2) making quantification difficult. Uemura and Ishiwatari (1995) analysed sediment samples (0-11 cm) from 15 lakes and found the highest 17b(H)-moret-22(29)-ene / hop-22(29)-ene ratio in acidic lakes. Yet another compound with a similar mass spectrum eluting after 17b(H),21a(H)-hopane (**20b**) was found in most samples. The mass spectrum was identical to that of synthetic hop-20(21)-ene (Bisseret and Rohmer, 1993). Hop-20(21)-ene (**8**) has, to our knowledge, not been detected in sediments before. Traces of a hop-16-ene (**11**) (Nytoft and Bojesen-Koefoed 2001) were also detected.

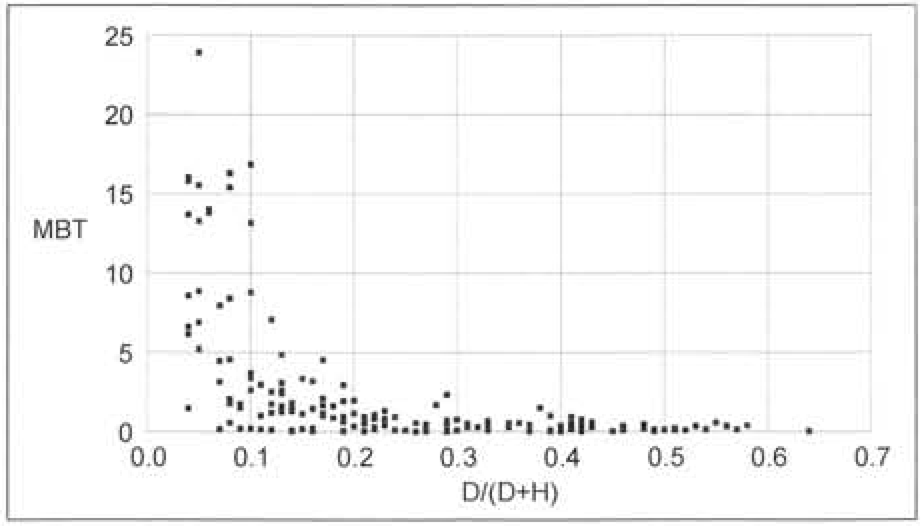

Fig. 7. Oxidation of hop-17(21)-ene to hopa-15,17(21)-diene versus relative content of malabaricatriene in samples from all three basins. **D/(D+H)**: Area of hopa-15,17(21)-diene (*m/z* 393) / ((hop-17(21)-ene (*m/z* 367) + hopa-15,17(21)-diene).

Hop-21(22)-ene (**7**) occurs in low concentrations in all samples whereas hop-17(21)-ene (**9**) is more abundant. Some hop-17(21)-ene could be formed by isomerization of hop-22(29)-ene and hop-21(22)-ene, but the major part is probably of direct bacterial origin (Brassell and Eglinton 1983). The relative content is highest in laminated sediments with high TOC. 22,29,30-Trisnorhop-17(21)-ene (**1**) was found in all samples and *22R*-homohop-17(21)-ene (**9c**) in a few, whereas higher carbon number hop-17(21)-enes were absent.

Neohop-13(18)-ene (**12b**) was the only neohop-13(18)-ene detected in the Baltic Sea sediments. 22,29,30-trisnorneohop-13(18)-ene (**2**) was expected, but could not be identified with certainty in any of the samples. Neohop-13(18)-ene can be formed by rearrangement of hop-17(21)-ene. However, in the Baltic Sea sediments, this is unlikely to have happened in the sediments themselves, since this would have led to the complete disappearance of some of the observed compounds that are much less stable than hop-17(21)-ene, such as hop-22(29)-ene and taraxer-14-ene. A minor part of the neohop-13(18)-ene could be inherited from reworking of older sediments, but the major part is probably produced directly by bacteria in the water column or within the sediment. (Brassell and Eglinton 1983). A related compound, the unstable neohop-12-ene (**13**), was detected in relatively high concentrations, especially in laminated sediments. Neohop-12-ene easily rearranges to neohop-13(18)-ene (Ageta et al. 1987). Neohop-12-ene elutes immediately before fern-7-ene, but because its mass spectrum contains only a relatively small *m/z* 191 fragment, it is difficult to identify unless some of the more abundant ions (*m/z* 175, 203, 218 and 410) are monitored in addition to *m/z* 191.

Hopa-15,17(21)-diene (**10b**) was detected in all samples. Hopa-15,17(21)-dienes have not been identified in sediments until very recently (Nytoft et al. 1999). No biological source has yet been found, and hopadienes are probably formed by oxidation of hop-17(21)-enes. In the laboratory, hopa-15,17(21)-diene is synthesised by epoxidation of hop-17(21)-ene to 17,21-epoxyhopane followed by acid treatment. We have found that hop-17(21)-ene in pentane solution is slowly (months) oxidised by air to 17,21-epoxyhopane and an unstable diene, which can then isomerize to hopa-15,17(21)-diene. The presence of polyunsaturated lipids accelerated the oxidation. Similarly, Tritz et al. (1999) oxidised hop-17(21)-ene by air to 17,21-epoxyhopane in an aqueous phase containing a surfactant. These processes probably also take place in the oxygenated water column and in oxic sediments. The only major ions in the mass spectrum of hopa-15,17(21)-diene are *m/z* = 187 (100 %) and *m/z* 393 (54 %) (Nytoft and Bojesen-Koefoed 2001). The ratio between hopa-15,17(21)-diene (*m/z* 393) and hop-17(21)-ene (*m/z* 367) varied from 0.04 to about 0.65. Low values were found in laminated sediments with a high content of malabaricatriene (see below). Anoxic depositional conditions thus seem to preserve hop-17(21)-ene. Fig. 7 shows the hopa-15,17(21)-diene / hop-17(21)-ene ratio versus relative content of malabaricatriene in samples from the three basins.

Fernenes were detected in all the samples from this study. GC-MS analysis in scan mode revealed the presence of three fernenes (fern-7-ene (**15**), fern-8-ene (**16**) and fern-9(11)-ene (**14**)) and small amounts of ferna-7,9(11)-diene (**17**) (*m/z* 255, *m/z* 408). The fernenes have almost identical mass spectra with *m/z* 243 as base peak and a prominent *m/z* 395 fragment, but since the *m/z* 191 fragment is very minor, fernenes can only be detected in the *m/z* 191 mass chromatogram if their concentrations are very high (Fig. 2). In order to roughly estimate the content of fernenes relative to other triterpenoids we compared the area of the three fernenes in the *m/z* 243 mass chromatogram to the sum of all triterpenoids in the *m/z* 191 mass chromatogram. The relatively fernene content was high in the laminated sediments, but low in bioturbated but with high TOC sediments. A particularly high content was found in the sediments from the Gotland Basin (core 211660-6) around 3 m and from 4.0 to 4.4 m which also show elevated values of TOC (Fig. 5). The content of fernenes in sediments from the Bornholm Basin is very low. These observations suggest that fernenes are useful indicators of anoxic depositional conditions. Fern-7-ene is usually the major isomer (Fig. 2 bottom), but samples with a low total fernene content have higher proportions of fern-8-ene and fern-9(11)-ene (Fig. 2 top). This could reflect minor differences in the bacteria contributing fernenes to the sediments or in diagenesis conditions (Brassell and Eglinton 1983). Fern-7-ene is the least stable of the fernene isomers and can easily rearrange to the more stable isomers catalysed by acids or clay minerals (Ageta et al. 1987).

17(E)-13a(H)-Malabarica-14(27),17,21-triene

Malabaricatriene (**29**) was detected in many of the Baltic Sea sediment samples. In samples from the Gotland Basin (211660-6) the relative content of malabaricatriene in the *m/z* 191 mass chromatogram varied from zero in homogeneous parts covering about half of the core to a maximum value of 24 % in the laminated sediments (Fig. 5). In cores from the North Central Basin (Fig. 6) the content of malabaricatriene was generally low. Only a few elevated values were found in the laminated parts coinciding with a high TOC-content. In the Bornholm Basin (Fig. 4), the content of malabaricatriene was low except for the very recent sediments, which also had higher TOC-values. The very large variations in the content of malabaricatriene thus suggest that it is an even better indicator of anoxia than fernenes.

Terrigenous triterpenoids

Taraxer-14-ene (**22**) was identified in all the Baltic Sea sediment samples. Only traces of olean-12-ene (**25**) were found in some cases, and no other isomerisation products were detected, probably due to the young age of the sediments. An extract with a high content of taraxer-14-ene and smaller amounts of olean-12-ene (Bornholm Basin, 211630, 7.55 m, Ancylus clay) was subjected to a mild acid treatment, which removed all taraxer-14-ene and led to a similar increase in the size of the olean-12-ene peak, thus confirming the presence of the latter. The mass spectrum of taraxer-14-ene having *m/z* = 410 (M^+, 6%); 395 (6%); 286 (42%); 271 (44%); 257 (15%); 218 (40%); 204 (100%); 191 (17%); 189 (24%), is best quantified using *m/z* = 271, since the mass spectrum of the coeluting 17(E)-13a(H)-Malabarica-14(27),17,21-triene does not contain this fragment. The ratio of the area of taraxer-14-ene in *m/z* 271 relative to the sum of areas of all triterpenoids in the *m/z* 191 in the mass chromatogram showed that the relative content was high in the Ancylus lake sediments from the Bornholm Basin and the Gotland Basin (Fig. 4, Fig. 5) and in the varved clay (Table 2). In the marine sediments including the Initial Litorina interval the ratio decreased 5-10 times and remained almost constant. In the marine and fresh water sediments in the North Central Basin the ratio was generally at the same level as the freshwater deposits in the other basins. (Fig. 6), exempt the level in the upper laminated interval.

2,2,9-Trimethyl-1,2,3,4-tetrahydropicene **(28)** (Wakeham et al. 1980) was the major pentacyclic aromatic hydrocarbon in all samples analysed by GC-MS in scan mode. Traces of an isomer with *vic*-dimethyl groups could also be detected. 2,2,9-Trimethyl-1,2,3,4-tetrahydropicene is probably formed by aromatization of taraxer-14-ene or some of its precursors. The content of 2,2,9-trimethyl-1,2,3,4-tetrahydropicene was roughly the same as that of taraxer-14-ene.

Organic particles

The classification of organic particles by microscopy is another method to characterise the organic matter in sediments (Taylor et al. 1998). The results are given in Table 1. This investigation shows that Alginite and particles of amorphous organic matter (A.O.M), which also is degraded algal matter, are the dominant constituent in the marine sediments from the Bornholm, Gotland and the laminated intervals in the North Central Basin. This suggests that more than three fourths of the organic particles in the samples are of marine origin. The land derived Sporinite (pollen and spores), Huminite (cellulose- lignin) and Inertinite (charcoal) make in the order of 10% and if the Liptodetritic particles, with less clear origin is included about 20 % in the marine samples mentioned above. The two samples of homogeneous mud from the North Central Basin have much higher (40-62 %) contents of probable terrestrial input- including soot from fires. The two samples of the freshwater sediments from the early stages of the Baltic from the Bornholm Basin show a strong terrestrial proportion of the small total organic content. The organic matter in the sample of the Ancylus clay from the Gotland Deep is dominated by alginite, suggesting that this site, which was far from the shore in the Ancylus Lake, be dominated by pelagic production.

DISCUSSION

Because of the salinity stratification and the long residence times of the water in the Baltic Sea the bottom water in the deep basins are inherently prone to stagnation and development of suboxic or anoxic conditions. The bottom water layer is exchanged occasionally, when oxygenated saline bottom water enters the basin through the Danish Straits (Matthäus 1995). Variation between oxic and anoxic intervals on the scale of months to hundreds of years is mirrored in the sediments.

Reducing conditions generally prevail a few millimetres below the sediment-water interface in virtually all aquatic sediments (Boesen and Postma 1988), but the presence or absence of oxygen in the bottom waters and at the sediment surface is assessed by inspection of sedimentary structures. Lamination indicates the absence of bottom-dwelling macrofauna, which is usually interpreted as an indication of anoxia at the sediment surface. The lamination is a very fine scale layering (0.2-0.5 mm) of alternating light and darker coloured layers, with occasional yellow laminae consisting of calcium-manganese carbonate. The well-preserved lamination combined with high organic carbon contents (see later) suggests the prevalence of anoxia at the seabed for extended periods of time during deposition. Homogeneous intervals are interpreted to represent periods of oxic or suboxic bottom water conditions, during which benthic and burrowing macrofauna has destroyed the lamination (Eckhéll et al. 2000). However, in the Gotland Deep bivalves have only been found in a short period (2800-2600 BP), so in most of the time anoxic events have been so frequent that a bivalve population has not been able to establish. Couplets of homogeneous and laminated intervals are termed "A-units" and indicate alternating oxic and anoxic bottom water conditions during deposition. Such alternations have occurred over a timescale of 10-100 years, perhaps even less. This is comparable to the present-day conditions in the Gotland Deep (Matthäus 1995). The differentiation between marine and freshwater deposits are based on the diatoms or other organisms (Sohlenius et al. (1996), Andrén et al. (2000 a,b), Voss et al. (2001).

The sulphide colouring of the upper Ancylus clay are regarded as a diagenetic precipitation caused by H_2S diffusing down into the clay from the marine deposits above (Boesen and Postma 1988). The sulphide precipitation is thus due to the change in environment from fresh to marine condition, but is not a sign of special anoxic depositional environment in the pre-Litorina deposits. This process also offers an explanation of the uniform development of the sulphide colouring over most of the Baltic Sea floor. This interpretation of the sedimentary environments is used as a base for the discussion of depositional conditions of the organic compounds.

The correlation between the parameters is most obvious in the North Central Basin cores. Most of the marine section is homogeneous / bioturbated and deposited under oxic conditions but four relatively short intervals laminated and associated intervals with A-units indicate anoxic periods at the seafloor. In these intervals TOC increases by a factor of 2-3 compared to the homogeneous intervals. Also the HI is higher than in the surrounding homogeneous intervals, and the values are close to those of the Gotland Deep. This could suggest, that the marine input from the surface waters is more important, and that other sources to the sediment are less active during the periods of stagnation in the basin bottom water (Table 1).

The relative content of malabaricatriene is low in the oxic intervals but increases by a factor of 3-12 in the laminated intervals. The increase is not observed in the surrounding intervals with A-units, so the presence of malabaricatriene seems to be related to persistent strong anaerobic ecosystems. This pattern is also obvious in the Gotland Basin core. The variation of the relative content of fernenes is less pronounced in the North Central Basin core, but slightly elevated concentrations coincide with a high malabaricatriene content in the short anoxic interval around 1200 BP. High concentrations of fernenes are also observed in the laminated sediments from the early part of the Litorina Sea (8000-5000 BPcal) which is also the case in the Gotland Basin core.

The general picture based on the limited data on organic particles agrees with the distribution of the taraxer-14-ene as shown of figures 4-6. The terrestrial input is a minor but fairly constant component of the preserved organic matter in the marine sections. In the North Central Basin the terrestrial component is relatively higher than in the two other basins. Terrestrial organic components are relatively more important in the freshwater stages during the early stages of the Baltic Sea. A marked decrease in the relative concentrations of taraxer-14-ene seems to correlate with the first intrusion of salt water at the transition from the Ancylus lake to the Initial Litorina, sensu Andrén et al. (2000 a,b) in all three cores even if very minor shifts are observed in the TOC-concentrations and C/N ratios. This transition is not very marked in the North Central Basin, but it is suggested that the change in environment is not so great in the inner brackish part of the Baltic.

CONCLUSIONS

From the glacial varved clay through to the Ancylus stage deposits, TOC increases gradually from 0.5% to 1%, and through the initial Litorina stage a further increase to approximately 2% is observed. The transition to the Litorina succession is marked by another steep increase in TOC to values close to 4% in the Bornholm and Gotland Basins. The clear shift in TOC between the older freshwater stages and the marine Litorina and post-Litorina deposits are not so marked in the proportion of the organic matter measured by the Hydrogen Index. The proportion increases only from about 20% of the TOC in the freshwater deposits to about 33% in the marine deposits. This change is not observed in most of the North Central Basin core. The concentration of TOC and the composition of the organic matter as described by HI are almost constant through time in the marine bioturbated intervals in the cores. It seems not to be influenced by the variations in accumulation rates indicated by the dating. This suggests that the organic matter in each basin is deposited from a well-mixed pool of suspended organic matter and that the concentrations are not controlled by the local depositional conditions during oxic periods. The changes between oxic and anoxic conditions observed in the North Central Basin are discussed above. In periods with anoxic deposition in the Gotland Deep more organic matter is preserved but the composition as described by the HI does not change much. This conclusion does not apply to a number of specific organic compounds. A number of molecular marker ratios have proven to be sensitive markers of anoxic depositional conditions. They include the relative contents of malabaricatriene and fernenes as well as the hop-17(21)-ene/(hop-17(21) + hopa-15,17(21)-diene) ratio. Kowalewska et al. (1998, 1999) and Bianchi et al. (2000) showed that this also applies to chlorophyll.

Taraxer-14-ene is a useful marker of terrestrial marker input. The relative content is generally higher in samples from the North Central Basin, probably related to a higher proportion of river input and recycled sediments due to isostatic uplift in the northern Baltic area and less dilution by marine constituents. The incursion of marine waters into the Baltic basin (Initial Litorina Sea) is marked by a decrease in the relative content of taraxer-14-ene and later (Litorina Sea) by an increase in the content of organic carbon (TOC) and hydrogen index (HI) indicating a decreasing proportion of terrigenous organic matter in the sediments.

Acknowledgements

Kristoffer Jonassen prepared the sediment samples for analysis. TOC, TS and Rock-Eval measurements were done by Lisbeth Løvig Nielsen and solvent extraction, separation and GC-analysis by Ditte Kiel-Dühring. Henrik I. Petersen is thanked for the classification of organic particles by microscopy. Maren Voss, IOW-Warnemünde, supplied seven of the sediment samples from the Gotland Basin (211660-6). We thank Jørgen Bojesen-Koefoed for discussions and many improvements of the manuscript. We also thank reviewer Grazyna Kowalevska and Algimantas Grigelis for numerous helpful comments. This study was a part of Subproject 7, in the EU-funded BASYS - Baltic Sea System Study - project (contract: MAS3-CT96-0058). This paper was published with the permission of the Geological Survey of Denmark and Greenland (GEUS).

References

Ageta, H., Shiojima, K., Arai, Y. 1987: Acid-induced rearrangement of triterpenoid hydrocarbons belonging to the hopane and migrated hopane series. *Chemical and Pharmaceutical Bulletin 35*, 2705-2716.

Andrén, E., Andrén, T., Kunzendorf, H.G. 2000a: The Holocene history of the Baltic Sea as background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10, 6,* 687-702.

Andrén, E., Andrén, T., Sohlenius, G. 2000b: The Holocene history of the southwestern Baltic Sea as reflected in a sediment core from the Bornholm Basin. *Boreas 29,* 233-250.

Behrens, A., Schaeffer, P., Bernasconi, S., Albrecht, P. 1999: 17(*E*)-13a(*H*)-Malabarica-14(27),17,21-triene, an unexpected tricyclic hydrocarbon in sediments. *Organic Geochemistry 30,* 379-383.

Bennike, O., Jensen, J.B. 1998: Late- and postglacial shore level changes in the southwestern Baltic Sea. *Bulletin of the Geological Society of Denmark 45,* 27-38.

Bianchi T.S, Johansson, B., Elmgren, R. 2000: Breakdown of phytoplankton pigments in Baltic sediments: effects of anoxia and loss of deposit-feeding macrofauna. *Journal of Experimental Marine Biology and Ecology 251,* 161-183.

Bisseret, P., Rohmer, M. 1993: Heating of hop-17(21)-ene in molten sulphur: a route to new sedimentary biomarkers of the hopane series? *Tetrahedron Letters 34,* 5295-5298.

Boesen, C., Postma, D. 1988: Pyrite formation in anoxic environments of the Baltic. *American Journal of Science 288,* 575-603.

Brassell, S.C., Eglinton, G. 1983: Steroids and Triterpenoids in Deep Sea Sediments as Environmental and Diagenetic Indicators. *In* Bjorøy et al. (Eds.): *Advances in Organic Geochemistry 1981,* 684-697. John Wiley & Sons Limited.

Cranwell, P.A. 1982: Lipids of aquatic sediments and sedimenting particulates. *Progress in Lipid Research 21,* 271-308.

Demaison, G.J., More, G.T. 1980: Anoxic environments and oil source bed genesis. *American Association of Petroleum Geologists Bulletin 64,* 1179-1209.

Eckhéll, J., Jonsson, P., Meili, M., Carman, R. 2000: Storm Influence on the Accumulation and Lamination of Sediments in Deep Areas of the Northwestern Baltic Proper. *Ambio 29,* 238-245.

Ensminger, A., van Dorsselaer, A., Spyckerelle, Ch., Albrecht, P., Ourisson, G. 1974: Pentacyclic triterpenes of the hopane type as ubiquitous geochemical markers: origin and significance. *In* B. Tissot and F. Bienner (Eds.): *Advances in Organic Geochemistry 1973.* Editions Technip, Paris, 245-260.

Espitalié, J., Deroo, G., Marquis, F. 1985: La pyrolyse Rock-Eval et ses applications. *Revue de l´Institut Français du Pétrole 40,* 563-579.

ten Haven, H.L., Rullkötter, J. 1988: The diagenetic fate of taraxer-14-ene and oleanene isomers. *Geochimica et Cosmochimica Acta 52,* 2543-2548.

ten Haven, H.L., Peakman, T.M., Rullkötter, J. 1992a: D^2-Triterpenes: Early intermediates in the diagenesis of terrigenous triterpenoids. *Geochimica et Cosmochimica Acta 56,* 1993-2000.

ten Haven, H.L., Peakman, T.M., Rullkötter, J. 1992b: Early diagenetic transformation of higher-plant triterpenoids in deep-sea sediments from Baffin Bay. *Geochimica et Cosmochimica Acta 56,* 2001-2024.

Innes, H.E., Bishop, A.N., Head, I.M., Farrimond, P. 1997: Preservation and diagenesis of hopanoids in Recent lacustrine sediments of Priest Pot, England. *Organic Geochemistry 26,* 565-576.

Jonsson, P., Carman, R., Wulff, F. 1990: Laminated sediments in the Baltic - A Tool for Evaluating Nutrient Mass Balances. *Ambio 19,* 152-158.

Kotilainen, A.T., Saarinen, T., Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the Central Baltic Sea during the last 3000 years. *Marine Geology 166,* 51-64.

Kowalewska, G., Winterhalter, B., Konat, J. 1998: Chlorophyll *a* and its derivatives in deep Baltic sediments. *Oceanologia 41,* 65-69.

Kowalewska, G., Winterhalter, B., Talbot, H.M., Maxwell, J.R., Konat, J. 1999: Chlorins in sediments of the Gotland Deep (Baltic Sea). *Oceanologia 41,* 81-97.

Larsen, B., Repeèka, M. 1997: Description of cores taken during the cruise 00/96/02, *R/V Petr Kottsov. In* J.Harf & B.Winterhalter (Eds.): *Cruise Report R/V Petr Kottsov, July 22- August 1, 1997.*

Malinski, E., Witkowski, A., Synak, E., Szafranek, J., Osterroth, Ch., Pihlaja, K. 1988: Hydrocarbon geochemistry of siliciclastic, microbial laminated deposits from Puck Bay, Poland. *Organic Geochemistry 12,* 81-88.

Matthäus, W. 1995: Natural variability and human impact reflected in long-term changes in the Baltic deep water conditions- a brief review. *Deutsche Hydrographische Zeitschrift 47,* 47-65.

Meyers, P.A., Ishiwatari, R. 1993: Lacustrine organic geochemistry - an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry 20,* 867-900.

Nytoft, H.P., Thomsen, J.V., Jørgensen, T.K.C., Bojesen-Koefoed, J.A., Petersen, H.I. 1999: Hopa-15,17(21)-dienes in sediments: Precursors of diahopanes? *19th International Meeting on Organic Geochemistry, 6-10 September 1999, Istanbul, Turkey, Abstracts Part I,* 13-14.

Nytoft, H.P., Bojesen-Koefoed, J.A. 2001: 17a,21a(H)-hopanes: natural and synthetic. *Organic Geochemistry 32,* 841-856.

Ourisson, G., Albrecht, P., Rohmer, M. 1979: The hopanoids: Palaeochemistry and biochemistry of a group of natural products. *Pure & Applied Chemistry 51,* 709-729.

Ourisson, G., Albrecht, P. 1992: Hopanoids. I. Geohopanoids: The most abundant natural products on earth? *Accounts of Chemical Research 25,* 398-402.

Peters, K.E., Moldowan, J.M. 1993: The Biomarker Guide - Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, Englewood Cliffs, New Jersey.

Pihlaja, K., Malinski, E., Poutanen, E.-L. 1990: Saturated and olefinic hydrocarbons in recent sediments from the Baltic Sea. *Organic Geochemistry 15,* 321-333.

Radke, M., Willsch, H., Welte, D.H. 1980: Preparative hydrocarbon group determination by automated Medium Pres-

sure Liquid Chromatography. *Analytical Chemistry 52,* 406-411.

Repečka, M., Grigelis, A. 1998: Grain size and physical properties of bottom sediments. Report for the 2 year period, Lithuanian Institute of Geology. *Report to BASYS: Subproject 7.*

Respondek, M.J., Köster, J., Sinninghe Damsté, J.S. 1997: Novel C_{26} highly branched isoprenoid thiophenes and alkane from the Menilite Formation, Outer Carpathians, SE Poland. *Organic Geochemistry 26,* 295-304.

Ries-Kautt, M., Albrecht, P. 1989: Hopane-derived triterpenoids in soils. *Chemical Geology 76,* 143-151.

Rohmer, M., Bisseret, P. & Neunlist, S. 1992: The hopanoids, procaryotic triterpenoids and precursors of ubiquitous molecular fossils. *In* J. M. Moldowan, P. Albrecht and R. P. Philp (Eds.): *Biological Markers in Sediments and Petroleum.* Prentice Hall, Englewood Cliffs, New Jersey, 1-17.

Rowland, S.J., Yon, D.A., Lewis, C.A., Maxwell, J.R. 1985: Occurrence of 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane and related hydrocarbons in the green alga *Enteromorpha prolifera* and sediments. *Organic Geochemistry 8,* 207-213.

Rowland, S.J., Robson, J.N. 1990: The widespread occurrence of highly branched acyclic C_{20}, C_{25}, and C_{30} hydrocarbons in Recent sediments and biota - a review. *Marine Environmental Research 30,* 191-216.

Rullkötter, J., Peakman, T.M., ten Haven, H.L. 1994: Early diagenesis of terrigenous triterpenoids and its implications for petroleum geochemistry. *Organic Geochemistry 21,* 215-233.

Sohlenius, G., Sternbeck, J., Andrén, E., Westman, P. 1996: Holocene history of the Baltic Sea as recorded in a sediment core from the Gotland Deep. *Marine Geology 134,* 183-201.

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P. 1998: Organic petrology. Gebrüder Bornetraeger Berlin. 704 p.

Tyson, R.V. 1995: Sedimentary organic matter. Chapman & Hall London. 615 p.

Tritz, J.-P., Herrmann, D., Bisseret, P., Connan, J., Rohmer, M. 1999: Abiotic and biological hopanoid transformation: towards the formation of molecular fossils of the hopane series. *Organic Geochemistry 30,* 499-514.

Uemura, H., Ishiwatari, R. 1995: Identification of unusual 17b(H)-moret-22(29)-ene in lake sediments. *Organic Geochemistry 23,* 675-680.

Venkatesan, M.I., Kaplan, I.R. 1982: Distribution and transport of hydrocarbons in surface sediments of the Alaskan Outer Continental Shelf. *Geochimica et Cosmochimica Acta 46,* 2135-2149.

Volkman, J.K., Allen, D.I., Stevenson, P.L., Burton, H.R. 1986: Bacterial and algal hydrocarbons in sediments from a saline Antarctic lake, Ace Lake. *Organic Geochemistry 10,* 671-681.

Voss, M., Kowalewska, G., Brenner, W. 2001: Microfossil and biogeochemical indicators of environmental changes in the Gotland Deep during the last 10,000 years. *Baltica 14,* 131-140.

Wakeham, S.G., Schaffner, C., Giger, W. 1980: Polyaromatic hydrocarbons in Recent lake sediments-II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta 44,* 415-429.

Wakeham, S.G. 1990: Algal and bacterial hydrocarbons in particulate matter and interfacial sediment of the Cariaco Trench. *Geochimica et Cosmochimica Acta 54,* 1325-1336.

Yunker, M.B., MacDonald, R.W., Cretney, W.J., Fowler, B.R., McLaughlin, F.A. 1993: Alkane, terpene, and polycyclic aromatic hydrocarbon geochemistry of the Mackenzie River and Mackenzie shelf: Riverine contributions to Beaufort Sea coastal sediment. *Geochimica et Cosmochimica Acta 57,* 3041-3061.

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 108-114

The chemistry of the surface sediments in the North Central Basin, the Baltic Sea

Henry Vallius, Mirja Leivuori

Abstract

The North Central Basin was investigated thoroughly during the three year BASYS project in 1996 – 1999. The basin was sampled in several locations and the cores were analysed for total concentrations of a multitude of elements. The sediment surface in the studied basin is distinctly laminated and in the central area the thickness of the laminated sequence varies from 6 to 18 centimetres. The data from chemical analyses show that the vertical distribution of elements in the near-surface samples varies in a regular pattern in all cores taken within a range of 2 nautical miles. They all show similar distribution patterns in the laminated sequence, revealing the deposition history of anthropogenically enriched element. These show a rapid increase in the 1950's – 1960's followed by a decrease during the last decade of the 20th century. The basin is an area of homogeneous sedimentation suitable for further environmental studies.

☐ *Baltic Sea, geochemistry, metals, sediment.*

☐ *Henry Vallius [Henry.Vallius@gsf.fi], Geological Survey of Finland, P.O. BOX 96, FIN-02151 Espoo, Finland; Mirja Leivuori [Mirja.Leivuori@fimr.fi], Finnish Institute of Marine Research, P.O. BOX 33, FIN-00931 Helsinki, Finland.*

☐ *Received 31 July 2001; accepted 5 November 2001.*

INTRODUCTION

The Baltic Sea was investigated during the three year, multidisciplinary EU MAST Baltic Sea System Study (BASYS). The Baltic Sea itself and especially the central part of the Gotland Basin has been of scientific interest for a long time and many projects and scientific publications have dealt with different aspects of the basin sediments (Gripenberg 1934, Niemistö and Voipio 1974, Hallberg 1974, Suess and Erlenkeuser 1975, Niemistö and Voipio 1981, Jakobsen and Postma 1989, Tervo and Niemistö 1989, Brügmann and Lange 1990, Hallberg 1991, Emelyanov 1995, Huckriede et al. 1995, Salonen et al. 1995, Huckriede and Meischner 1996, Sohlenius et al. 1996, Sternbeck and Sohlenius 1997, Brügmann et al. 1997, Neumann et al. 1997, Emeis et al. 1998, Heiser 2000, Kotilainen et al. 2000, Mälkki 2000, Vallius and Kunzendorf 2001, Emelyanov 2001). Unfortunately, the Gotland Basin is not stagnant and has a very heterogeneous lateral distribution of sediments (Emeis et al. 1998, Kotilainen et al. 2000, Vallius and Kunzendorf 2001). In this study, however, we are dealing with a smaller basin situated ca. 90 nautical miles to the north of the Gotland Basin, the North Central Basin (NCB, Fig.1). Echo soundings during the study suggest that in this area sedimentation have been less disturbed than in the Gotland Basin throughout the last thousands of years. Thus, this basin should give good data on the history of accumulated matter and harmful elements through the last 100 - 150 years. This paper covers the data from a set of sediment cores, from the centre of the NCB basin (Fig. 2). The geochemical history in the northern Baltic Proper during the pre-industrialised and industrialised era is described. The chemistry of surface sediments in the NCB basin is presented based on total concentrations of cadmium, lead, mercury, copper, zinc, antimony, thallium, uranium, molybdenum, chromium, aluminium, manganese, calcium, magnesium, potassium, cobalt, nickel, arsenic, iron, lithium and carbon. The concentrations at six sites of the basin are compared with each other in order to study the homogeneity of the basin. The data from one central site are presented in greater detail to estimate the vertical variability of deposited elements within the time period represented by this core. Thus historical pollution trends are well visible in the concentration curves of various elements.

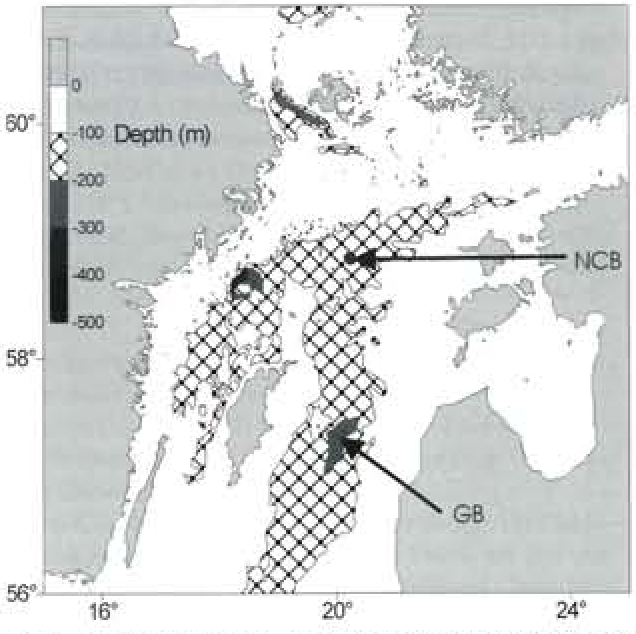

Fig. 1. Central Baltic Sea with the North Central Basin (NCB) and the Gotland Basin (GB) indicated. Bathymetry after Seifert and Kaiser (1995).

STUDY AREA

For this study a basin in the northern Baltic Proper was chosen. It is the North Central Basin (NCB, Fig. 1), from which data has been reported in Vallius and Kunzendorf (2001), Kotilainen et al. (2001) and Winterhalter (2001). Compared to the Gotland Basin the area of the NCB basin is rather small, covering about 5 x 10 nautical miles or some 170 km^2. The middle of the basin forms a hill between deeper channels that are on the southern sides flanked by shallower Paleozoic clint-formations (Fig. 2). The sampling sites are located on the top and flanks of the central hill at depths of 171–197 metres. This is because the central area is interpreted to be an area of calm sedimentation, where the accumulating matter is to a large degree autochthonous and derived from the water mass above, not for instance by mass flows from slopes around the basin.

MATERIALS AND METHODS

The samples for this study were collected during two cruises in 1997 and 1998. The first cruise was the cruise of *R/V Petr Kottsov* on July 22nd – August 1st 1997 (sites A, B, C and D), and the second cruise with *R/V Aranda* during April 14th – April 29th 1998 (sites E and F, Fig. 2). The area was thoroughly echo sounded on a *R/V Petr Kottsov* cruise in 1996 (Endler et al. 1996) and the basin was further echo sounded during both the sampling cruises. *R/V Aranda* is equipped with an Atlas DESO 25, 12 kHz echo sounder with a capability of good penetration through soft sediments. The echo sounding data were recorded both as hardcopies and on the *R/V* Aranda cruise also by a digital recording system, the Meridata MD DSS Multi-mode Sonar System. As a result of technical problems only bathymetric data of the area were recorded on the 1997 *R/V Petr Kottsov* cruise, using an Atlas DESO 25 echo sounder (Winterhalter 1997).

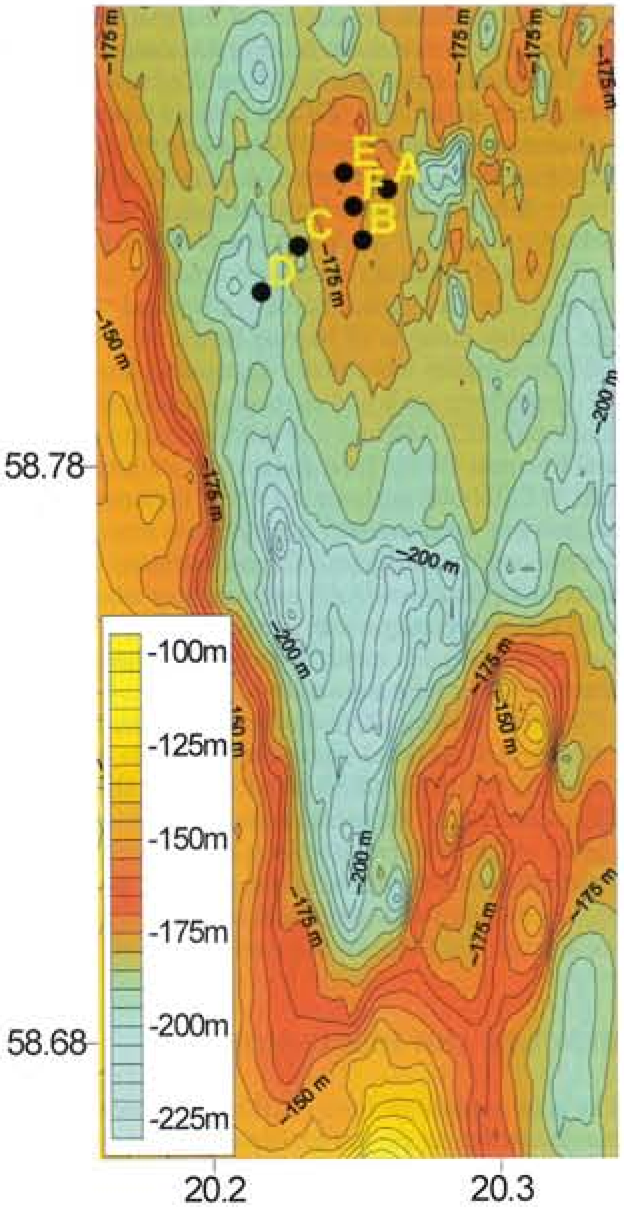

Fig. 2. Bathymetry of the North Central Basin area with sampling sites A – E indicated.

The sampling sites were chosen according to the surveyed echo sounding data. All samples were taken using a second-generation Niemistö double-barrelled corer, the Gemini corer, with an inner diameter of 80 mm. The cores were taken in transparent acrylic core liners and the cores were described immediately on deck. After that the cores were immediately sliced into 1 cm thick sub-samples, put into tightly closed plastic containers and frozen to –20 °C. As our aim was to study the uppermost sediment of the basins the cores were usually sliced down to 15 or 25 centimetres only.

The cores from the *R/V Petr Kottsov* cruise of 1997 were dated for ^{210}Pb and ^{137}Cs at Risø National Laboratory (Kunzendorf 1999). The ^{210}Pb- dating is based on the constant rate of supply (CRS) -model. ^{137}Cs- dating was used for verification of the ^{210}Pb-dating.

Chemical analyses were performed at the laboratories of the Geological Survey of Finland (GSF) and the Finnish Institute of Marine Research (FIMR). At GSF the samples were totally digested with hydrofluoric - perchloric acids and element determinations were made with ICP-MS and ICP-AES techniques (Vallius and Leivuori 1999). Total carbon was analysed using a LECO CHN-600 analyser. At FIMR the samples were microwave oven assisted leached with nitric acid for arsenic and mercury. Arsenic concentration was measured with flameless AAS and mercury measured by cold vapour technique with amalgamation (Vallius and Leivuori 1999). For mercury and arsenic the nitric acid leaching gives total amounts.

For the quality control of analytical performance commercial certified sediment reference materials SRM 2704 (NIST), MESS-2 (NRCC) and GBW07313 (State Bureau of Technical Supervision People's Republic of China) were used. At GSF recoveries for all elements were between 92% (magnesium, manganese) and 113% (lithium). At FIMR recoveries were 92% for arsenic and 99% for mercury.

RESULTS AND DISCUSSION

The echo soundings from NCB basin show that sedimentation during the last few thousand years has been uniform throughout the basin. The bedding is more or less concordant indicating relatively stabile sedimentary conditions in the whole basin area (Winterhalter 2001). There has been some variability in the sedimentation rate, as it is common in the Baltic Sea (Kotilainen et al. 2000), and it seems that these changes are reflected over the whole basin area (Fig. 3). However, in short gravity cores from the surface sediment some differences are to be found (Vallius and Kunzendorf 2001). Altogether six surface cores were sampled and analysed from the central part of the basin (Fig. 2).

It has sometimes been suggested that metal concentrations should be normalised against elements of detrital origin. In the present study normalisation was not done, in part because the mineralogically derived normalisers (aluminium and lithium) are transported from very different source areas, variously affected by glacial erosion and crustal uplift, or, in the case of iron, the normaliser participates in an important way in diagenetic geochemical reactions in the sediments of the Baltic Sea. Brügmann (1992) similarly avoided normalisation. Also sieving of the sediment sample into 20 µm or 63 µm fraction is sometimes recommended. However, according to grain size analyses the mud accumulation basins of the Baltic Sea showed > 95% of total wet weight to be in the < 63 µm fraction (Uścinowicz et al. 1996). Thus sieving was not performed for the samples of this study.

Emelyanov (1988), Jonsson et al. (1990) and Org and Jonsson (1996) report the presence of laminated surface sediments in a large area in the northern Baltic Proper. This is also observed in our study. All cores taken for this study have a very distinctive and usually sharp boundary between a laminated upper part and a quite homogeneous lower part of the core. The laminated part is fluffy mud, usually black or very dark grey, but with ca. 10 grey laminae of about 1mm thickness (Larsen and Repečka 1997). Below the boundary the material is relatively homogeneous pelitic mud, which is rather compact, grey to olive grey in colour and contains some black burrows (0,5 –1 mm ∅) and darker dots (sulphides). The boundary between these parts is located at different depths depending on site. Usually the upper, laminated part of the core is thinner in the shallower parts of the basin. Also the lamination gets clearly more distinct when moving from the deeper sites towards the shallower parts of the basin (e.g. from station D towards F, Fig. 2). This can be explained by the differences in sedimentation rates, lower rates favour more distinct lamination. Also other explanations, such as dissimilar preservation at different sites are possible.

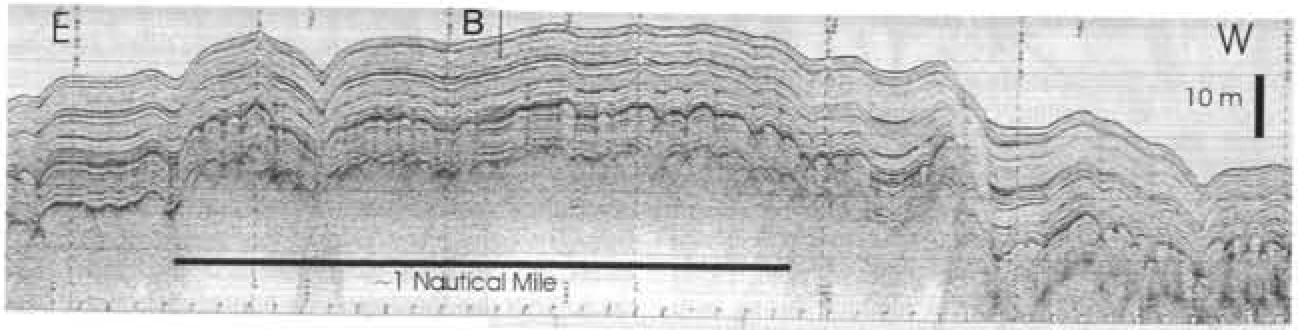

Fig. 3. Example of the sediment strata over the centre of the North Central Basin, as seen from north. Sampling site B is situated 160 m to the south from the site indicated in the figure as B. The echogram is from *R/V Aranda* cruise of April 1998.

Vertical distribution of elements

Site B (depth 175 meters) illustrates the vertical or temporal element distribution (Figs. 4a-c). The vertical distributions of the studied elements are typical for the Baltic Sea. The heavy metals, for instance, show relatively high concentrations near the sediment surface (3-5 cm), although with clearly lower concentrations in the sediment slices nearest to the sediment water interface. Maximum concentrations of mercury, cadmium, antimony, thallium, uranium, copper, lead, zinc, arsenic and nickel are found at depths of 3-5 cm. The molybdenum maximum is located one centimetre higher (2-3 cm). Iron and manganese, elements influenced by diagenesis, have their maximum values at the depth of 5-6 cm. For cobalt strong correlation with iron and manganese is notable (Fig. 4). The vertical distribution of elements of minero-genic origin (magnesium, potassium, aluminium, chromium and lithium) show increased values at depths deeper than 5-6 cm, while both calcium and carbon reveal increasing concentration above that depth. The depth range 5-6 cm represents the boundary between different kind of material. The upper part of the core consists of the laminated, fluffy material, while the lower part consists of more-or-less homogeneous pelitic mud. The difference is well visible in the concentration curves.

The concentrations found in the bottom of the core (15–25cm) are relatively low representing matter deposited before the anthropogenic impact affected the sediments of the Baltic Sea and can be considered to represent background values (Fig. 4). Concentrations of the same order of magnitude have been reported from Gotland Basin sediments from depths of pre-industrial age (Salonen et al. 1995, Emelyanov 1995, Neumann et al. 1997).

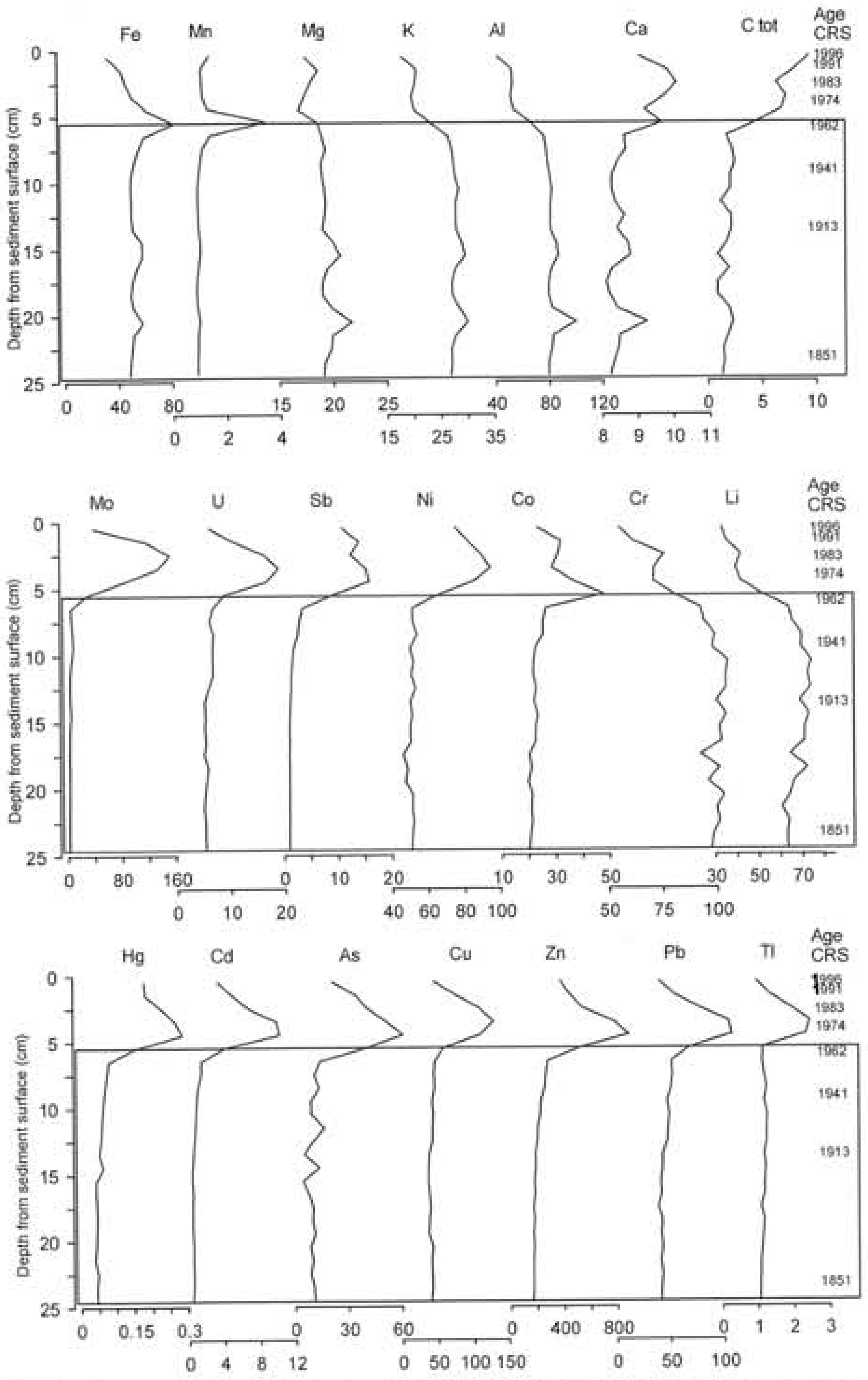

Fig. 4. Sediment chemistry at site B. The lower part of the figures indicate the homogeneous part of the core. Units for Fe, Mn, Mg, K, Al and Ca in g kg^{-1}, carbon as percent, other elements as mg kg^{-1}, dry weight. The presented age is a result of CRS (constant rate of supply) –modelling of ^{210}Pb data (Kunzendorf 1999).

The differences in the sequestering of metals in anoxic sediments are due to several competitive mechanisms i.e. formation of insoluble sulphides or scavenging with iron sulphide, as well as fixation in inorganic and organic complexes (Dyrssen and Kremling 1990). In this case the enrichment of elements of anthropogenic and biogenic origin is clearly enhanced at and above the sharp boundary layer between the upper and lower part of the core. This is to a great extent attributed to the formation of sulphides in the laminated section, and temporally it is connected to the increased pollution of the marine environment in the late 1950's and early 1960's (Fig. 4). As the composition of the cores change so remarkably at the sharp boundary between the two units it can be considered to indicate a hiatus. However, there is no absolute evidence for this based on the present knowledge.

Lateral distribution of elements

At the 6 studied sites almost equal concentrations of elements were found in the surface slices (0-1 cm, Fig. 5). Some dissimilarity is though to be seen when comparing the vertical distribution of elements at studied sites, as seen in examples shown in Fig. 5. Maximum values of lead and copper are to be found in one peak at 6-8 cm at site C and divided into two peaks at site D, that is at 8-9 cm and 11-14 cm, respectively. The distribution of antinomy is more even at both these sites.

Sites A, B, E and F show similar vertical distributions of lead, copper and antimony. These sites are all located in the shallower part of the basin (water depth 171-175 m, Fig. 2). They have a recent sedimentation rate of ca. 2 mm a^{-1}, which is revealed as virtually identical thickness of the laminated sequence (Kunzendorf 1999). Sites C (water depth 186 m) and D (water depth 197 m) are located on the gentle slopes in slightly deeper areas of the basin and here different vertical distributions of elements are to be found. The boundary between the laminated and homogeneous part of the core is situated at the depth of 12 cm at site C and at the depth of 18 cm at site D. Below this boundary the vertical profiles of elements can be considered equal at all sites. At a depth of 10–15 centimetres below the boundary the concentrations reach background values.

The distribution patterns show this basin to be of homogeneous quality throughout the studied area. The laminated sequence shows similar vertical distributions of elements but of different thickness depending on sampling site (Fig. 5). It is thus possible that they are representing the same deposition history. Only at site D, where the thickness of the laminated unit is so extensive and the lamination is weak, this is speculative. There the internal variation is more complicated and the double peaks of copper and lead in the middle of the core might indicate re-deposition of material. Nevertheless, the NCB basin is an area of homogeneous sedimentation, where deposition trends are well recorded in the sedimentary sequence, and it is thus suitable for further environmental studies.

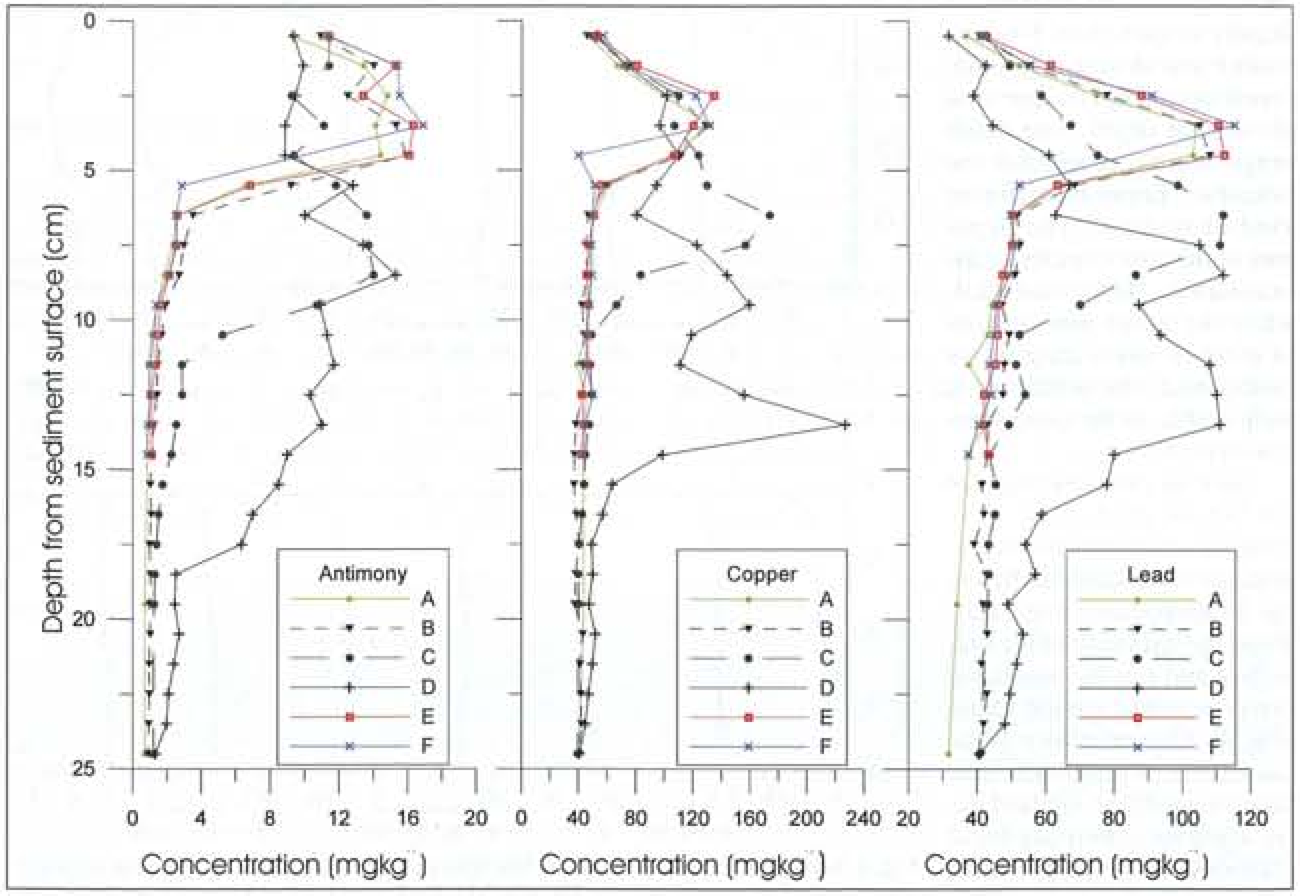

Fig. 5. Concentrations of antimony, copper and lead in the surfaces (0-25 cm) of sites A, B, C, D, E and F. For location on map see Figure 2. Units in mg kg^{-1} dry weight.

CONCLUSIONS

This study revealed an interesting but previously sparingly reported sedimentation basin in the northern Baltic Proper. This basin, the North Central Basin, showed out to be a basin with relatively homogeneous sedimentation throughout the whole basin area, with relatively undisturbed sedimentary records in the uppermost sequence. The whole sampled area of the basin is covered with a laminated sequence of varying depth (6-18 cm). Regardless of the thickness of the laminated sequence the same vertical distribution patterns are to be found in the different cores. Similar to cores from other areas in the Baltic Sea the heavy metals show elevated levels due to pollution from early 1960's to early 1980's, after which the concentrations have decreased considerably. The concentrations of elements are usually within the same order of magnitude as in the surface sediments of the well-known Gotland Basin. The analogous element distributions in the near surface cores ensure that this basin is good for monitoring purposes. The low sedimentation rates, on the other hand, extend the interval between monitoring to a minimum of ten years.

Acknowledgements

The authors wish to thank all the partners in the BASYS project. The European Commission financed the BASYS project MAS3-CT96-0058. We also want to thank the crews of *R/V Aranda* and *R/V Petr Kottsov*, as well as the staffs of the Finnish Institute of Marine Research and the Geological Survey of Finland for assistance during sampling, sample preparation and analysis. The authors gratefully acknowledge Prof. E. Emelyanov and Prof. R. Stevens for their review of this manuscript.

References

Borg, H. & Jonsson, P. 1996: Large-scale metal distribution in Baltic Sea sediments. *Marine Pollution Bulletin 32,* 8-21.

Brügmann, L. 1992: Review of methods for the determination of contaminants in sediments. *In* Perttilä, M. & Brügmann, L. (Eds.): *Review of contaminants in Baltic sediments. ICES Coop. Res. Rep. 180,* 43–68.

Brügmann, L & Lange, D. 1990: Metal distribution in sediments of the Baltic Sea. *Limnologica 20,* 15-28.

Brügmann, L., Hallberg, R., Larsson, C. & Löffler, A. 1997: Changing redox conditions in the Baltic Sea deep basins: Impacts on the concentration and speciation of trace metals. *Ambio 26,* 107-112.

Dyrssen, N. D. & Kremling, K. 1990: Increasing hydrogen sulfide concentration and trace metal behaviour in the anoxic Baltic waters. *Marine Chemistry 30,* 193-204.

Emeis, K.-C., Neumann, T., Endler, R., Struck, U., Kunzendorf, H. & Christiansen, C. 1998: Geochemical records of sediments in the Eastern Gotland Basin—products of sediment dynamics in a not-so-stagnant anoxic basin? *Applied Geochemistry 13,* 349-358.

Emelyanov, E. 1995: Baltic Sea: geology, geochemistry, paleoceanography, pollution. P.P. Shirshov Institute of Oceanology RAS, Atlantic Branch, Kaliningrad Jantarny Skaz. 120 p.

Emelyanov, E. 1988: Biogenic sedimentation in the Baltic Sea and its consequences. *In The Baltic Sea.* Winterhalter, B. (Ed.) *Geological Survey of Finland Special Paper 6,* 127-135.

Emelyanov, E. 2001: Biogenic components and elements in sediments of the Central Baltic and their redistribution. *Marine Geology 172,* 23-41.

Endler, R., Flodén, T. & Winterhalter, B. 1996: Geohydrophysics. *In* Harff, J. and Winterhalter, B. (Eds.): *Cruise report R/V Petr Kottsov, Sept. 2 – Sept. 12, 1996.* Baltic Sea Research Institute, Warnemünde, October 1996. 40 p.

Gripenberg, S. 1934: A study of the sediments of the north Baltic and adjoining sea areas. *Fennia 60,* 1-231.

Hallberg, R. 1974: Paleoredox conditions in the Eastern Gotland Basin during the recent centuries, *Merentutkimuslaitoksen Julkaisuja / Havforsknings-institutets Skrifter 238,* 3-16.

Hallberg, R., O. 1991: Environmental implications of metal distribution in Baltic Sea sediments. *Ambio 20,* 309-316.

Heiser, U. 2000: Calcium-rich rhodocrosite layers in sediments of the Gotland Deep, Baltic Sea, as indicators for seawater inflow. *Karlsruher Geochemische Hefte 17,* 1-125.

Huckriede, H., Clasen, S. & Meischner, D. 1995: Hydrographic and climatic changes recorded in Holocene sediments of the central Baltic Sea. *Baltica 9,* 76-91.

Huckriede, H. & Meischner, D. 1996: Origin and environment of manganese-rich sediments within black-shale basins. *Geochimica Cosmochimica Acta 60,* 1399-1413.

Jakobsen, R. & Postma, D. 1989: Formation and solid solution behavior of Ca-rhodocrosites in marine muds of the Baltic deeps. *Geochimica Cosmochimica Acta 53,* 2639-2648.

Jonsson, P., Carman, R. & Wulff, F. 1990: Laminated sediments in the Baltic – A tool for evaluating nutrient mass balances. *Ambio 19,* 152-158.

Kotilainen, A., Saarinen, T. & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the central Baltic Sea during the last 3000 years. *Marine Geology 166,* 51-64.

Kotilainen, A.T., Kankainen, T., Ojala, A., & Winterhalter, B. 2001: Palaeomagnetic dating of a Late Holocene sediment core from the North Central Basin, Baltic Sea. *Baltica 14,* 67-73.

Kunzendorff, H. 1999: Dating and assessing the Recent sediments of three deep basins of the Baltic Sea: Indication of natural and anthropogenic changes. *Risø Report-R-1077.* 100 pp.

Larsen, B. & Repeèka, M. 1997: Lithological core descriptions. *In* Harff, J. and Winterhalter, B. (Eds.): *Cruise report R/V Petr Kotsov, July 22 – August 01, 1997.* Baltic Sea Research Institute, Warnemünde, October 1997. 41 p.

Mälkki, M. 2000: Sulfide geochemistry and mineralogy from two different Baltic sea environments: Bothnian Sea and Gotland Deep. *Baltica 13*, 24-35.

Neumann, T., Christiansen, C., Clasen, S., Emeis, K.-C. & Kunzendorf, H. 1997: Geochemical record of salt-water inflows into the deep basins of the Baltic Sea. *Continental Shelf Research 17*, 95-115.

Niemistö L. & Voipio A. 1974: Studies of the recent sediments in the Gotland Deep. Merentutkimuslaitoksen *Julkaisuja / Havforskningsinstitutets Skrifter 238*, 17-32.

Niemistö, L & Voipio, A. 1981: Notes on the sediment studies in the Finnish pollution research in the Baltic Sea. *Conseil International pour l'Exploration de la Mer. Raports et Procès-verbaux des Réunions 181*, 87-92.

Salonen V.P., Grönlund T., Itkonen A., Sturm M. & Vuorinen I. 1995: Geochemical record on early diagenesis of recent Baltic Sea sediments. *Marine Geology 129*, 101-109.

Seifert, T. and Kayser, B. 1995: A high resolution spherical grid topography of the Baltic Sea. *Meereswissenschaftliche Berichte /Marine Science Reports*, Institut für Ostseeforschung, Warnemünde.

Sohlenius G., Sternbeck J., Andrén T. & Westman P. 1996: Holocene history of the Baltic Sea as recorded in a sediment core from the Gotland Deep. *Marine Geology 134*, 183-201.

Sternbeck J. & Sohlenius G. 1997: Authigenic sulphide and carbonate mineral formation in the Holocene sediments of the Baltic Sea. *Chemical Geology 135*, 55-73.

Suess, E. & Erlenkueser, H. 1975: History of metal pollution and carbon input in Baltic Sediment. *Meyniana 27*, 63-75.

Tervo, V. & Niemistö, L. 1989: Concentrations of trace metals, carbon, nitrogen and phosphorus in sediments from the northern parts of the Baltic Sea. *ICES* Council Meeting papers /E:7.

Uúcinowicz, S., Narkiewicz, W. & Sokolowski, K. 1996: Mineralogical composition and granulometry of the recent muds of the Baltic Sea. Baseline Study of contaminants in Baltic Sea sediments. – Polish Geological Institute, Sopot-Warszawa. 11 p.

Vallius, H. & Leivuori, M. 1999: The distribution of heavy metals and arsenic in recent sediments of the Gulf of Finland. *Boreal Environment Research 4*, 19–29.

Vallius, H. & Kunzendorf, H. 2001: Sediment surface geochemistry of three Baltic Sea deep basins. *Ambio 30*, 135-141.

Winterhalter, B. 1997: Echo-sounding. *In* Harff, J. and Winterhalter, B. (Eds.): *Cruise report R/V Petr Kotsov, July 22 – August 01, 1997.* Baltic Sea Research Institute, Warnemünde, October 1997. 41 p.

Winterhalter, B. 2001: The BASYS coring site in the North Central Baltic Sea Basin - a geological description. *Baltica 14*, 9-17.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 115-121

Did the Second Storegga slide affect the Baltic Sea?

Thomas Andrén, Elinor Andrén

Abstract

A short event of intense coastal erosion occurring simultaneously with substantial inflow of saline water has been detected in four cores from the deep basins of the Baltic Sea. This is recorded as an increase in freshwater and brackish-freshwater periphytic diatom taxa, C/N-ratio, and $d^{13}C$ values. Radiocarbon dated macrofossil and sediment bulk samples indicate an age of *c.* 8000 calendar years BP.

The Second Storegga slide, either as a direct result of an earthquake triggering the slide and the resulting tsunami wave reaching into the Baltic Sea or as a secondary effect of an earthquake triggered by the slide itself, is the best way to explain the recorded data.

☐ *Baltic Sea, Second Storegga slide, coastal erosion, earthquake.*

☐ *Thomas Andrén [thomas.andren@geo.su.se], Department of Geology and Geochemistry, Stockholm University, S-106 91 Stockholm, Sweden; Elinor Andrén, Department of Earth Sciences, Quaternary Geology, Uppsala University, Villavägen 16, S-752 36 Uppsala, Sweden.*

☐ *Received 31 July 2001; accepted 14 November 2001.*

BACKGROUND

The Baltic Sea is one of the world's largest semi-enclosed seas and water exchange with the ocean takes place through the shallow Öresund and Store Bælt straits (Fig. 1). The first stage in the history of the Baltic basin, following the end of the Late Weichselian glaciation, was the freshwater Baltic Ice Lake (12,500-10,000 ^{14}C yr. BP) (Jensen 1995; T. Andrén et al. 1999). This was followed by the Yoldia Sea stage (10,000-9500 ^{14}C yr. BP), which consisted of two freshwater phases with a short brackish-water phase in between (Svensson 1989). The start of the Ancylus Lake, a dammed-up freshwater lake (Björck 1987) is defined by a synchronous transgression in the southern Baltic basin *c.* 9500 ^{14}C yr. BP (Hyvärinen 1988; Björck 1995). The transitional stage between the Ancylus Lake and the Litorina Sea, with low surface salinity, is referred to here as the Initial Litorina Sea, but in the coastal zone it is known as the Mastogloia Sea stage (Sundelin 1922). The Litorina Sea was the most marine stage in the history of the Baltic. Succeeding this stage was the less marine Limnaea Sea, here called the Post-Litorina Sea (Mölder 1946). The last Baltic Sea stage, represented by conditions similar to the present, was named the Mya Sea (Munthe 1910). However, since the presence of the mollusc *Mya arenaria* was not due to changes in salinity but rather a result of early anthropogenic impact (Hessland 1945), the name Recent Baltic Sea is used in this paper.

The transition from the freshwater Ancylus Lake into the brackish-marine Litorina Sea is supposed to have been a slow process because of a gradual increase in water depth in the inlet areas, as a result of the rising eustatic sea level (*e.g.* Björck 1995; Westman and Sohlenius 1999). Our data indicates that an intense basin-wide coastal erosion and subsequent deposition of eroded material in the deepest basins took place *c.* 8000 calendar years (cal yr.) BP. This event may have been associated with a rise in sea level of the Baltic Sea and here we try to explain the triggering mechanism for the event by evaluating our sedimentological, biostratigraphical and chemical data.

METHODS

Four piston cores from the southern and central Baltic Sea (Fig. 1) have been analysed for their content of C,

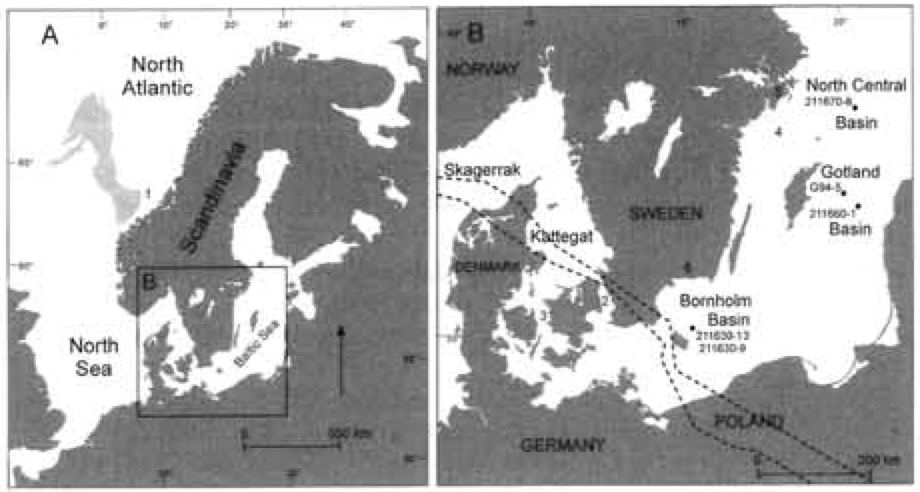

Fig. 1. **A.** Scandinavia, the Baltic Sea and location of the source area and the palaeotsunami deposits related to the Second Storegga slide (1). **B.** Location of the cores investigated, Öresund strait (2), Store Belt strait (3), northwestern Baltic Sea (4), Södertörn (5) and Blekinge (6). The stippled lines indicate the limits of the Tornquist tectonical zone.

N, the stable isotope δ^{13}C, siliceous microfossils and dated by radiocarbon.

The organic carbon and nitrogen content were measured by combusting ground, freeze-dried samples and then the content was inferred from the amount of CO_2 detected by an infrared detector and of N_2 with a heat-conducting detector. Stable $^{13}C/^{12}C$ ratios were measured by continuous flow isotope ratio mass spectrometry (CF-IRMS, Finningan MAT Delta +) after combustion of the sample in a Carlo Erba NC2500.

Sediment samples for siliceous microfossil analyses have been prepared following the methodology described by Battarbee (1986). A random settling technique (Bodén 1991) was used for determination of the concentration of siliceous microfossils in the cores 211630-13, 211660-1 and 211670-8.

Thirty-one bulk sediment samples and eleven macrofossil samples were radiocarbon dated by the tandem Accelerator Mass Spectrometry (AMS) technique (Table 1) at the Ångström Laboratory, Uppsala University, Sweden. For this purpose the NaOH-soluble organic fraction (mainly humus) was used for the bulk sediment samples and the insoluble fraction, consist of the primary organic material, for the fossil samples. A correction against the δ^{13}C value of the PDB standard was applied to the dates.

For the calculation of sediment accumulation rates, the dates were calibrated to calendar years using the terrestrial calibration dataset (intcal98) of the CALIB (Rev 4.0) software (Stuiver et al. 1998). Because of the alternating freshwater and marine stages in the history of the Baltic Sea, it was not possible to use a standard correction for the marine reservoir effect throughout.

One effect of the isostatic rebound that has been going on since the deglaciation is that older deposits reaching the wave base are resuspended and finally deposited at greater water depths. This is a constant process resulting in an excessively old apparent age for the sediment and is not easily quantified.

The high abundance of diatoms in the Ancylus Lake indicates that the major part of the organic carbon originates from production in the lake, and this is confirmed by the δ^{13}C values. Even so, the possibility of the dates being affected by reworked old carbon cannot be excluded. Furthermore, Königsson and Possnert (1988) report possible reservoir ages of as much as 400 years derived from the dating of shell material of Ancylus age from Gotland. Because the Ancylus Lake was a freshwater system, this reservoir age must be the effect of reworked old terrestrial carbon. For this reason our ^{14}C dates throughout were reduced by 400 years to compensate for such an effect.

The level where we also include a correction for the marine reservoir effect is marked by a sharp increase in organic carbon and in the abundance of brackish-marine diatoms. As the δ^{13}C values also shift towards a heavier composition above this level (Fig. 3), it can be assumed that the increase in organic carbon content in the sediment was the result of increased production in the basin and not an increased supply of reworked terrestrial carbon.

The choice of marine reservoir age is based on the relation between the salinity of the Bornholm Basin and that of the Kattegat area. The salinity in the bottom water of the Kattegat, at present, is 30-34‰ (Fält 1982), whereas it is lower in the Bornholm Basin, c. 14-18‰ (Nehring and Matthäus 1991). During the most marine phase of the Litorina Sea stage, the salinity in the Bornholm Basin was higher than at present.

Based on ages obtained from recent marine shells from the coast of Norway and south-west Sweden, Mangerud and Gulliksen (1975) proposed a correction of 440 years for the ocean reservoir effect. Radiocarbon dates for marine and terrestrial samples from the Vedde ash bed indicate a marine reservoir effect of 700-800 years during the Younger Dryas (Bard et al. 1994). It can thus be concluded that the marine reservoir effect in the North Atlantic from the Younger Dryas to the present must have been between about 800 and 400 years.

We chose to use a correction of 300 years for the marine reservoir effect for the sediments deposited when entirely brackish conditions were established during the Litorina Sea stage. According to the diatom record, salinity was lower in the Initial Litorina Sea stage and at the beginning of the Litorina Sea stage,

Table 1. Laboratory reference number, core label, sample depth in core, ^{14}C Age, δ^{13}C, type of material dated, and Calendar years age

Lab. ref.	Core	Depth (cm)	^{14}C age (years BP)	δ^{13}C (‰ PDB)	Type of material	Cal age (years BP)
Ua-13610	211630-9	45	1155±65	-0.12	*Macoma* shells	610±55
Ua-13611	211630-9	120	2075±115	-1.08	*Macoma* shells	1460±130
Ua-13612	211630-9	125	1770±70	0.02	*Macoma* shells	1190±100
Ua-13613	211630-9	255	2805±70	-0.77	*Macoma* shells	2340±85
Ua-13614	211630-9	275	2915±75	-1.20	*Macoma* shells	2390±180
Ua-13615	211630-9	325	3145±70	-1.14	*Macoma* shells	2750±45
Ua-13616	211630-9	415	4010±95	-0.59	*Macoma* shells	3780±130
Ua-13617	211630-9	525	5295±90	-0.79	*Macoma* shells	5540±140
Ua-13618	211630-9	555	6060±90	-0.85	*Macoma* shells	6340±75
Ua-13850	211630-13	20	1380±55 *	-23.36	Bulk sediment	650±55
Ua-13851	211630-13	55	1500±60	-23.43	Bulk sediment	690±45
Ua-13852	211630-13	180	3245±85 *	-23.59	Bulk sediment	2740±140
Ua-13500	211630-13	363	3965±75	-24.70	Bulk sediment	3470±120
Ua-13501	211630-13	433	4710±75	-23.70	Bulk sediment	4480±80
Ua-13502	211630-13	563	6450±80	-27.08	Bulk sediment	6520±125
Ua-15977	211630-13	577	6070±105	-17.60	Fish collagen	6595±80
Ua-13503	211630-13	585	7525±85	-26.81	Bulk sediment	7740±100
Ua-15391	211630-13	586	6465±200	-24.80	Plant remnants	7370±200
Ua-14322	211630-13	636	8860±210	-28.30	Bulk sediment	9490±230
Ua-14323	211630-13	676	8410±150 *	-29.20	Bulk sediment	8990±260
Ua-13504	211630-13	703	9910±115 *	-27.43	Bulk sediment	10740±255
Ua-13157	G94-5	35	1640±55	-27.17	Bulk sediment	850±70
Ua-13158	G94-5	135	3440±55	-26.45	Bulk sediment	2820±70
Ua-10621	G94-5	226	4635±75	-26.80	Bulk sediment	4410±130
Ua-10620	G94-5	271.5	6005±135	-27.30	Bulk sediment	6050±160
Ua-10619	G94-5	272.5	5905±90	-28.27	Bulk sediment	6090±130
Ua-10618	G94-5	317.5	7325±75	-27.44	Bulk sediment	7580±75
Ua-12012	G94-5	331	7370±115	-25.46	Bulk sediment	7680±100
Ua-10617	G94-5	339.5	7640±65	-26.79	Bulk sediment	7960±70
Ua-12013	G94-5	354	7710±110	-28.76	Bulk sediment	8120±60
Ua-10616	G94-5	418.5	7755±110 *	-26.73	Bulk sediment	8170±150
Ua-13505	211660-1	15	1600±100	-25.26	Bulk sediment	790±120
Ua-13506	211660-1	80	2360±70	-25.65	Bulk sediment	1540±90
Ua-13853	211660-1	174	2625±55 *	-23.56	Bulk sediment	1870±50
Ua-14237	211660-1	220	2540±60 *	-21.00	Bulk sediment	1880±60
Ua-14238	211660-1	297.5	6630±95	-26.00	Bulk sediment	6750±110
Ua-13507	211660-1	320	6505±135 *	-27.65	Bulk sediment	6610±130
Ua-14239	211660-1	368.5	7930±235	-24.50	Bulk sediment	8140±250
Ua-13508	211660-1	410	8105±75	-28.54	Bulk sediment	8440±90
Ua-15069	211670-8	80.5	1435±65	-25.30	Bulk sediment	670±45
Ua-15070	211670-8	450.5	4945±70	-24.90	Bulk sediment	4830±200
Ua-15071	211670-8	570.5	8010±90	-25.60	Bulk sediment	8180±280

Note: ^{14}C ages marked with * are regarded as erroneous and not used in the age models. A standard correction corresponding to δ^{13}C= -17.60‰ and -24.80‰ was used by the laboratory for sample Ua-15977 and Ua-15391, respectively.

and a reservoir age of 100 to 200 years was used for these sediments. The shell samples consisted entirely of various *Macoma* species, which require a brackish environment, and all the ^{14}C ages where therefore corrected for a marine reservoir effect of 300 years. The same marine reservoir age was used for the fish skeleton. Neither the *Macoma* species nor the fish are assumed to take up reworked old carbon. The small difference in salinity between the Bornholm and Gotland basins has been ignored and the same marine reservoir correction has been used for both basins.

Finally, it can be noted that Erlenkeuser et al. (1974) report ^{14}C ages of 650 to 850 years for surface sediments from the Kiel Bay, southern Baltic Sea, their range of figures agree well with the total reservoir correction that we use here.

RESULTS

From the deepest part of the Bornholm basin (water depth 94 m), in the southern Baltic Sea, the core 211630-13 (Fig. 1) has recorded a *c.* 12-cm-thick, silty gyttja-clay layer, laying discordant on top of homogenous clay at 594 cm (Fig. 2B). The contact between the homogenous clay and the silty gyttja-clay is erosional and the layer gradually converts upward into a normal gyttja-clay. The lowermost c. 2-cm of this layer displays very small remnants of terrestrial macrofossils. One date of the terrestrial macrofossils from the layer (583-589 cm) has given a calibrated age of 7370±200 and a bulk sediment sample from 585 cm yields an age of 7740±60 cal yr. BP. Finally, one date of a fish skeleton (*Pleuronectes limanda*) found above the silty gyttja-clay layer at 577 cm was of an age of 6595±80 cal yr. BP (Fig. 2B). The time-depth plot resulting from the age of the macrofossil samples indicates an age of *c.* 8000 cal yr. BP for the contact between the clay and the silty gyttja-clay (Fig. 2B).

In the Bornholm Basin, this level marks a drastic change in the environmental conditions. The diatom flora change abruptly from a freshwater to a brackish-marine assemblage (Andrén et al. 2000b) (Fig. 3), the organic carbon content increases from less than 2 to almost 5%, and the C/N ratio indicate a strongest terrestrial influence during Holocene (Fig. 2A). This level marks the transition from Initial Litorina into Litorina Sea in the Bornholm Basin.

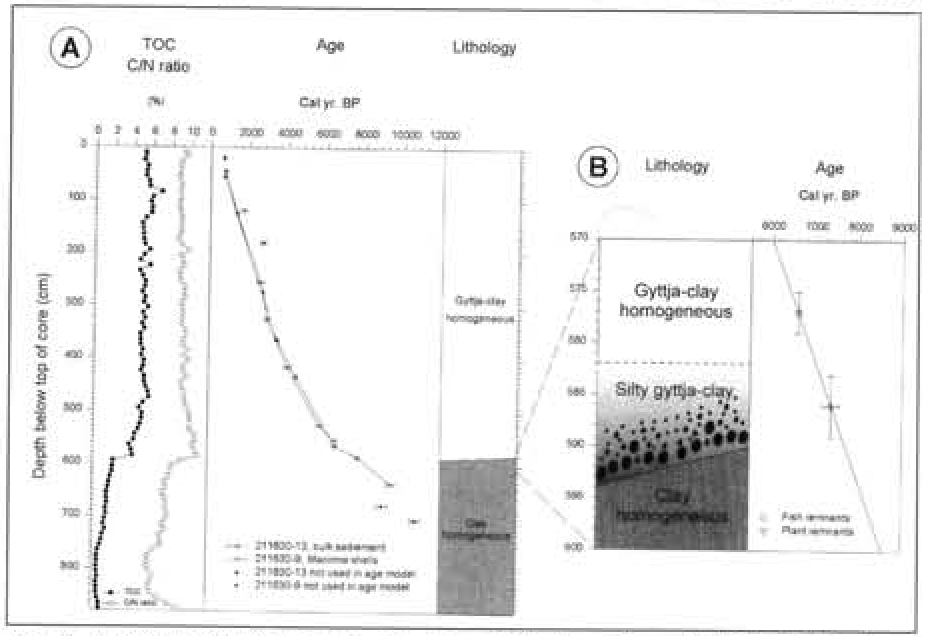

Fig. 2. **A.** TOC, C/N ratio, time-depth plot and lithology of core 211630-13. The time-depth plot of the dated *Macoma* shells from 211630-9, sampled at the same sediment sampling station, is included. **B.** Close up of the lithology and time-depth plot of dated macrofossils in the interval 570-600 cm in core 211630-13.

The sharp contact between the homogenous clay and the gyttja-clay, the abrupt increase in organic carbon and C/N ratio together with the siliceous microfossil record indicates that there are, probably as a result of erosion, sediments missing between the two units.

Two cores from the coast of Blekinge (Fig. 1), one from a water depth of c. 1 m and one from 14 m have recorded a sharp, erosional contact between gyttja-clay and an almost peat-like brownish sediment (Andrén, unpublished data). The organic carbon content increases from c. 8% below this contact to more than 18% above it. A strong terrestrial influence is indicated from the δ^{13}C values, which decrease from *c.* –25% to *c.* –28%, and is further supported by the occurrence of pieces of *Betula* and *Alnus* wood and leaves.

Two cores from the eastern Gotland Basin (Fig. 1), one sampled at a water depth of 240 m (211660-1) and one at 204 m (G94-5), both display an increase in periphytic brackish-freshwater and freshwater diatom taxa at *c.* 8000 cal yr. BP (Andrén et al. 2000a) (Fig. 3). As the δ^{13}C values indicate a marine influence at this time (Fig. 3), a reasonable explanation for the periphytic brackish-freshwater and freshwater diatoms recorded is intense erosion of the coast, lateral transport, and subsequent deposition in the deepest part of the basin. This coastal influence is best recorded in the core from the less deep sediment station (G94-5) where a possible hiatus at the same level is evident from the pollen record. Several of the broad-leaved trees appear at the same level (*e.g. Alnus, Corylus, Ulmus* and *Fraxinus*) without the normal succession (Veski, unpublished data). Such a hiatus is not detectable, however, in the diatom or chemical data. In the Gotland Basin, this level marks the transition from Ancylus Lake into Initial Litorina Sea (Andrén et al. 2000a).

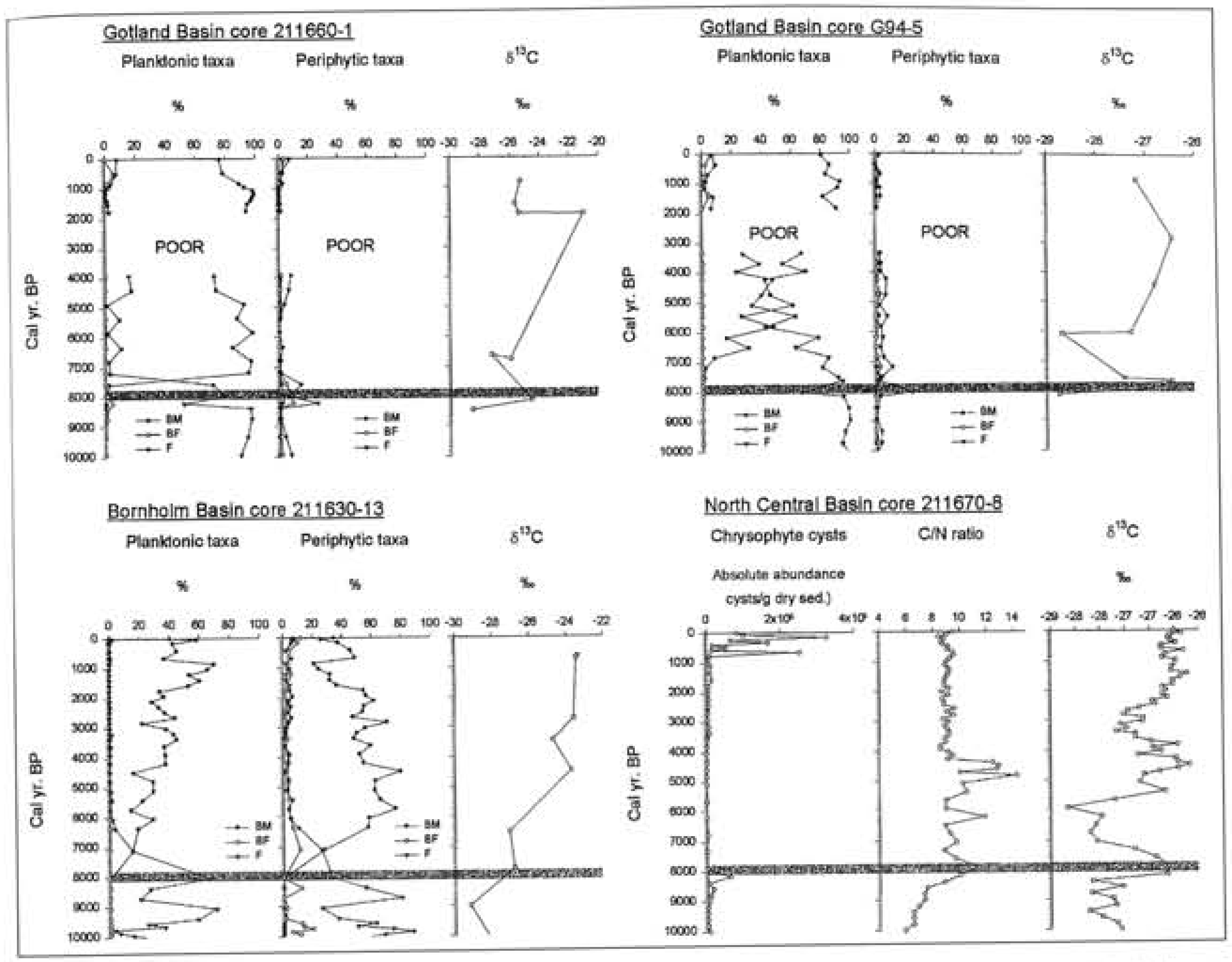

Fig. 3. Percentage of planktonic and periphytic diatom taxa and δ^{13}C values for core 211660-1, G94-5 and 211630-13 plotted versus age. Absolute abundance of Chrysophyte cysts, C/N ratio and δ^{13}C values of core 211670-8 plotted versus age. The shaded line in the plots indicates the age interval for the Storegga tsunami event, 8100 to 7800 cal yr. BP. F = freshwater flora; BF = brackish-freshwater flora; BM = brackish-marine flora.

In the North Central Baltic Basin (Fig. 1), the δ^{13}C record and C/N ratio from core 211670-8, (water depth 178 m), display significant peaks at approximately 8000 cal yr. BP (Fig. 3). This is all the evidence we have from this core, as it is devoid of diatoms in this sequence, possibly due to a very high rate of sediment accumulation. There is, however, an increase in the abundance of chrysophyte cysts associated with this event, which may be a result of the enhanced coastal influence.

DISCUSSION

From several sites in the southern Baltic Sea, there are indications of substantial erosion and a hiatus between the clay and the gyttja-clay, *i.e.* possibly of the same age as the erosional contact and the fossil bearing layer in the deepest part of the Bornholm Basin (*e.g.* Kögler and Larsen 1979; Björck et al. 1990; Borgendahl 2000).

Published data from the north-western Baltic Sea indicates a large increase in periphytic freshwater diatom taxa at a similar stratigraphic level as in the eastern Gotland Basin (Westman and Sohlenius 1999). The dating of this level is not totally conclusive but it seems to have an age of between 7900 to 8100 cal yr. BP.

This, together with the data presented here, indicates that something occurred in the southern and central Baltic Sea *c.* 8000 cal yr. BP that may not be the result of just a slow deepening of the thresholds and a subsequent transgression. The event is best recorded in the Bornholm Basin situated nearest the inlets but it also seems to have had significant effects in the central Baltic Sea. There are different possibilities to explain the recorded data.

The first Litorina transgression (corresponding to the Tapes transgression on the Swedish west coast) was a result of the ongoing eustatic sea level rise due to the warming of the climate in early Holocene. The Litorina transgression is well recorded in lake sediments from south and central Sweden (Berglund 1971; Berglund and Björck 1994; Risberg 1991). It is recorded in the Södertörn area, eastern Sweden (Fig. 1), as a rise in sea level in the order of *c.* 7 m starting c. 8000 ^{14}C yr. BP (corresponding to *c.* 8900 cal yr. BP) and culminating some 1000 ^{14}C years later (Risberg, 1991). In the Blekinge area, southern Sweden (Fig. 1), a rising sea level is recorded during a shorter period of time, c. 400 ^{14}C years, but the amplitude is similar (Berglund 1971; Berglund and Björck 1994). There are no reports of any record in the lake sediments in neither central nor southern Sweden; however, of extensive coastal erosion associated with this transgressional event.

The sub-marine 'so-called' Second Storegga Slide on the western Norwegian continental slope (Fig. 1) (Bugge et al. 1987; Jansen et al. 1987) is suggested to have generated a tsunami wave (Dawson et al. 1993). This event has, based on sedimentological investigations of 25 lakes on the Norwegian west coast, been dated to c. 7200 ^{14}C yr. BP (Bondevik et al. 1997) corresponding to c. 8000 cal yr. BP. Traces of the tsunami impact have been found 10 to 11 m above the contemporary shoreline in the coastal area closest to the slide (Bondevik et al. 1997). The age of the tsunami layer along the eastern coast of Scotland was estimated to be *c.* 7000 ^{14}C yr. BP (Dawson et al. 1993; Shi 1994) and the runup was estimated to be 3 to 6 m. Any record of this event has not been recognised in Baltic Sea sediments and hence the tsunami wave was not previously believed to have affected the Baltic Sea. If the tsunami entered the Baltic Sea it must have passed through the narrow and shallow Öresund strait probably resulting in a rising height of the wave increasing its erosional effect at least in the southern Baltic Sea.

The origin of the Second Storegga slide is not known but both the release of methane gas and the occurrence of an earthquake are possible triggers. The rapid movement (probably in a few hours) of 1700 km^3 of sediments over the continental slope to the abyssal plain, however, must have had huge effects (Jansen et al. 1987, Pedersen et al. 1995). Even if an earthquake did not trigger the slide, the movement of such a huge amount of Quaternary sediments may have triggered an earthquake. If an earthquake associated with the Second Storegga slide activated crustal movements along the Tornquist tectonical zone (Fig. 1), the effects on the southern Baltic Sea must have been considerable. Ground shaking in the southern Baltic Sea as a secondary effect of the Second Storegga slide may have resulted in a very rapid and short-lived fluctuation in the sea level of the Baltic Sea and subsequent coastal erosion.

CONCLUSIONS

In our opinion, the extensive coastal erosional recorded in the Baltic Sea sediments at *c.* 8000 cal yr. BP is not likely the result of a slow gradual rise in sea level, during as much as 1000 years during the first Litorina transgression.

Even if the datings are not fully conclusive, we believe that the best way to explain the sedimentological, biostratigraphical and chemical data presented here is the effect of the Second Storegga slide. Maybe, it was a direct result of an earthquake triggering the slide and the subsequent tsunami wave reached into the Baltic Sea or it was the result of a secondary effect of an earthquake triggered by the slide itself. Either way, the result was heavy erosion of the coasts of the southern and central Baltic Sea and a subsequent deposition of the eroded material in the deepest basins. Both these scenarios are likely to generate the stratigraphies in the southern Baltic Sea presented here.

AcknowledgementS

This investigation was financially supported by the European Union MAST III program (contract no. MAS3-CT96-0058). Additional funding was received from the Crafoord Foundation, Swedish Royal Academy of Sciences, the Swedish Natural Science Research Council (NFR) and Stockholm Marine Research Centre. Gustav Sohlenius and Ivan Romero performed the organic carbon and nitrogen measurements and Magnus Mörth did the analyses of stable isotopes. Siim Veski kindly shared his unpublished pollen data with us and Leif Johansson identified the fish species. Prof. Anto Raukas and an anonymous reviewer provided many comments that improved the final version of the paper. Proper English Ltd. corrected the English.

References

Andrén, E., Andrén, T. & Kunzendorf, H. 2000a: Holocene history of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10(5),* 621-636.

Andrén, E., Andrén, T. & Sohlenius, G. 2000b: The Holocene history of the southwestern Baltic Sea as reflected in a sediment core from the Bornholm Basin. *Boreas 29,* 233-250.

Andrén, T. 1990: Till stratigraphy and ice recession in the Bothnian Bay, University of Stockholm, *Department of Quaternary Research, Report 18.* 59 p.

Andrén, T., Björck, J. & Johnsen, S. 1999: Correlation of Swedish glacial varves with the Greenland (GRIP) oxygen isotope record. *Journal of Quaternary Science 14(4),* 399-410.

Bard, E, Arnold, M., Mangerud, J., Paterne, M., Labeyrie, L., Duprat, J., Mélières, M.-A., Sønstegaard, E. & Duplessy, J.-C. 1994: The North Atlantic atmosphere-sea surface ^{14}C gradient during the Younger Dryas climatic event. *Earth and Planetary Science Letters 126,* 275-287.

Battarbee, R. W. 1986: Diatom analysis. *In* Berglund, B. E. (Ed.): *Handbook of Holocene Palaeoecology and palaeohydrology.* John Wiley, Chichester, 527-570.

Berglund, B. 1971: Littorina transgressions in Blekinge, south Sweden a preliminary survey. *Geologiska Föreningens i Stockholm Förhandlingar 93,* 625-652.

Berglund, B. E. & Björck, S. 1994: Late Weichselian and Holocene shore displacement in Blekinge, SE Sweden. *Acta Universitatis Nicolai Copernici 27,* 75-95.

Björck, S. 1987: An answer to the Ancylus enigma? – Presentation of a working hypothesis. *Geologiska Föreningen i Stockholm Förhandlingar 109,* 171-176.

Björck, S. 1995: A review of the history of the Baltic Sea, 13.0-8.0 ka BP. *Quaternary International 27,* 19-40.

Björck, S., Dennegård, B. & Sandgren, P. 1990: The marine stratigraphy of the Hanö Bay, SE Sweden, based on different sediment stratigraphic methods. *Geologiska Föreningen i Stockholm Förhandlingar 112,* 265-280.

Bodén, P. 1991: Reproducibility in the random settling method for quantitative diatom analysis. *Micropaleontology 37(3),* 313-319.

Bondevik, S., Svendsen, I. J., Jonsen, G., Mangerud, J. & Kaland, P. E. 1997: The Storegga tsunami along the Norwegian coast, its age and runup. *Boreas 26,* 29-53.

Borgendahl, J. 2000: Phosphorus as a possible cause for cyanobacterial blooms – a study of the conditions in the Bornholm Basin during the last 8000 years. Stockholms universitets institution för geologi och geokemi, examensarbete. 34 p.

Bugge, T., Befring, S., Belderson, R. H., Eidvin, T., Jansen, E., Kenyon, N. H., Holtedahl, H. & Sejrup, H. P. 1987: A giant three-stage submarine slide off Norway. *Geo-Marine Letters 7,* 191-198.

Dawson, A. G., Long, D., Smith, D. E., Shi, S. & Foster, I. D. L. 1993: Tsunamis in the Norwegian Sea and North Sea caused by the Storegga submarine landslides. *In* Tinti, S. (Ed.): *Tsunamis in the World.* Kluwer Academic Publishers, The Netherlands, 31-42.

Erlenkeuser, H., Suess, E. and Willkomm, H. 1974: Industrialization affects heavy metal and carbon isotope concentration in recent Baltic Sea sediments. *Geochemica et Cosmochimica Acta 38,* 823-842.

Fält, L.-M. 1982: Late Quaternary sea-floor deposits off the Swedish west coast. Department of Geology, University of Göteborg and Chalmers University of Technology. *Publication A37.* 259 p.

Hessland, I. 1945: On the Quaternary Mya Period in Europe. *Arkiv för Zoologi 37 A.* 51 p.

Hyvärinen, H. 1988: Definition of the Baltic stages. *Annales Academiae Scientiarum Fennicae A. III. 148,* 7-11.

Jansen, E., Befring, S., Bugge, T., Eidvin, T., Holtedahl, H. and Sejrup, H. P. 1987: Large submarine slides on the Norwegian continental margin: Sediments, transport and timing. *Marine Geology 78,* 77-107.

Jensen, J. B. 1995: A Baltic Ice Lake transgression in the southwestern Baltic: evidence from Fakse Bugt, Denmark. *Quaternary International 27,* 59-68.

Königsson, L.-K. & Possnert, G. 1988: Ancylus faunas studied by accelerator ^{14}C dating of single small shells. *In* Winterhalter B. (Ed.): *The Baltic Sea, Geological Survey of Finland, Special Paper 6,* 137-145.

Kögler, F. & Larsen, B. 1979: The West Bornholm basin in the Baltic Sea: geological structure and Quaternary sediments. *Boreas,* 1-22.

Mangerud, J. & Gulliksen, S. 1975: Apparent radiocarbon ages of recent marine shells from Norway, Spitsbergen, and Arctic Canada. *Quaternary Research* 5, 263-275.

Munthe, H., 1910: Studier öfver Gottlands senkvartära historia. *Sveriges Geologiska Undersökning,* Ser. Ca No. 4. 213 pp.

Mölder, K. 1946: Zwei tonprofile aus süd-Pojanmaa., Comptes rendus de la Société géologique de Finlande 19, *Bulletin de la Commission géologique de Finlande 138,* 41-76.

Nehring, D. and Matthäus, W. 1991: Current Trends in Hydrographic and Chemical Parameters and Eutrophication in the Baltic Sea. *Internationale Revue der Gesamten Hydrobiologie 76,* 297-316.

Pedersen, G., Gjevik, B., Harbitz, C. B., Dybesland, E., Johnsgard, H & Langtagen, H. P. 1995: Final report on work undertaken by the University of Oslo. *In* Final report on Contract EV5V-CT92-0175: *Genesis and Impact of Tsunamis on European Coasts.* Commission of the European Communities, Brussels.

Risberg, J. 1991: Palaeoenvironment and sea level changes during the early Holocene on the Södertörn peninsula, Södermanland, eastern Sweden. *Stockholm University, Department of Quaternary Research, Report 20.* 27 p.

Shi, S. 1994: Observational and Theoretical Aspects of Tsunami Sedimentation. *Thesis, Coventry University.* 212 p.

Stuiver, M., Reimer, P. J., Bard, E., Beck, J. W, Burr, G. S., Hughen, K. A., Kromer, B., McCormac, F. G., v. d. Plicht, J. & Spurk, M. 1998: INTCAL98 Radiocarbon age calibration 24,000-0 cal BP. *Radiocarbon 40,* 1041-1083.

Sundelin, U. 1922: Några ord angående förläggningen av L.G. i de av transgression ej drabbade delarna av det baltiska området samt angående tidpunkten för Litorinahavets inträde. *Geologiska Föreningen i Stockholm Förhandlingar 44,* 543-544.

Svensson, N.-O. 1989: Late Weichselian and Early Holocene shore displacement in the central Baltic, based on stratigraphical and morphological records from eastern Småland and Gotland, Sweden. *Lundqua Thesis 25.* 195 p.

Westman, P. & Sohlenius, G. 1999: Diatom stratigraphy in five offshore sediment cores from the northwestern Baltic proper implying large scale circulation changes during the last 8500 years. *Journal of Paleolimnology 22,* 53-69.

Baltica
www.geologin.lt/baltica

Baltica 14 (2001) 123-130

Molybdenum in sediments of the central Baltic Sea as an indicator for algal blooms

Helmar Kunzendorf, Maren Voss, Wolfram Brenner,
Thomas Andrén, Henry Vallius

Abstract

The marine geochemistry of molybdenum is reported to be connected with anoxic sediments and the processes occurring within such settings. Mo occurs in sediments from Baltic Sea deep basins in amounts far exceeding those of other marine deposits. It is however observed enriched only at certain depths in long sediment cores, hence confined to certain times in the Holocene history. The present investigation of long cores from the Baltic Sea deep basins, Bornholm, Gotland and North Central Basins, revealed that Mo correlates with organic carbon and total nitrogen. Geochemical and microfossil studies suggest that the element may be connected with the process of nitrogen fixation by cyanobacteria because Mo is one of the essential micronutrients to facilitate this process. During periods with enhanced algal blooming it is thought that algal remnants with increased Mo contents are transported attached to the particular matter load to the seafloor where, at anoxic conditions Mo is deposited in the form of molybdenite that remains stable after burial.

☐ *Baltic Sea, sediments, dating, molybdenum, blue-green algae, algal blooms, cyanobacteria.*

☐ *Helmar Kunzendorf [hk@geogr.ku.dk], Gamma Dating Centre, Institute of Geography, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark; MarenVoss [maren.voss@io-warnemuende.de], Baltic Sea Research Institute, Seestr. 15, D-18119 Warnemünde, Germany; Wolfram Brenner [wolfram.brenner@geomar.de], GEOMAR Research Centre for Marine Geoscience, Wischhofstr. 1-2, D-24218 Kiel, Germany; Thomas Andrén [thomas.andren@kvgeo.su.se], Department of Quaternary Research, University of Stockholm, S-106 91 Stockholm, Sweden; Henry Vallius [henry.vallius@gsf.fi], Geological Survey of Finland, Espoo, Finland.*

☐ Received 11 June 2001; accepted 14 November 2001.

INTRODUCTION

The marine geochemistry of molybdenum has been connected with anoxic sediments and it has been suggested that its particulate matter transport to anoxic sediments of, e.g., the Black Sea, is negligible, according to the results from sediment trap experiments (Crusius et al. 1996). Therefore the occurrence and accumulation of Mo in some deep basin sediment sequences has been used as an anoxicity indicator (Hallberg 1974).

Mo (and Re) in general can be regarded as geochemical indicators of redox conditions in the water column and in the sediments deposited due to a relatively well-known geochemical behaviour of these elements (Calvert 1976; Calvert and Pedersen 1993). Because the dissolved Mo species Mo_4^{2-} is relatively unreactive in oxic seawater, there is little variation in Mo contents from ocean to ocean, although research has shown significantly decreased Mo in anoxic waters. Mo in the sediments on the other hand is thought to be closely related to the cycling of Mn and Fe in the sediment column. In oxic sediments when Mn/Fe oxyhydroxides are dissolved during burial, Mo is also dissolved. The processes of release and accumulation of Mo have been described in detail (Calvert and Price 1993). In a recent investigation however, Mo has been ascribed to a planktonic source (Dean et al. 1999) and a few other investigations have also stressed that Mo may be connected with organic matter in some marginal marine sediments, but usually, organic carbon accumulations in sediments are thought of being depleted in Mo. As regards the Gotland Basin, Mo data on plankton and sediments were published earlier by especially Russian research groups and can be found elsewhere (Emelyanov 1995).

Recently, however, sediment trap experiments conducted in the Baltic Sea have given evidence for a significant occurrence of this element in trap particulate material. A 1-year trap experiment carried out in the Gulf of Finland showed annual variation of Mo contents in the trap material, with 6.5 mg/kg Mo in April increasing to 57.3 mg/kg Mo in July/August. These values obtained in traps at 64-m water depth (below the halocline) are comparable with those obtained in near-bottom traps showing 31 mg/kg during the period June/August (H. Vallius, pers. comm.).

Considering the relatively high Mo found in the Baltic Sea sediments and especially in the Gotland Basin, there is a need of data on the behaviour of Mo in the marine environment in general and for the Baltic Sea in particular. As already mentioned, relatively few investigations have coupled the Mo in sediments with the biogenic phase, i.e. stemming from the surface waters. Because the central Baltic Sea is constantly exposed to algal blooming in recent years, we have tried to consider cyanobacteria (blue-green and green algae) as being possibly involved in the concentrating of metals like Mo in the sediments. In the present investigation, we discuss the occurrence of molybdenum in the Holocene sediments of the Gotland Basin based on analyses of short and long sediment core sections. Based on these data, the possibility of biological removal of Mo from seawater and its rapid transport to the seafloor via several particulate carriers is suggested. In particular, the importance of the geochemical signals in algal remains for the evaluation of the sediment deposition processes is discussed in the following.

SETTING

The Baltic Sea being one of the world's largest estuaries comprises some four hundred thousand square kilometres. The estuary is characterised by large fluxes of river water inputs and of periodic supply of more salty water from the North Sea migrating at depth to even the central parts of the Baltic Sea. At the same time, there is a water outflow to the North Sea of low-salinity surface waters. There is also a general vertical graduation of water masses in the Baltic; this water fluxes being thought to be greatly influenced by climatic variations. Characteristically, periodic cyclones coming from the west or south-west are observed. Zonal (westerly) winds have recovered too much higher values in recent years and this is coupled with relatively mild winters. Zonal winds were however also strong through the first three decades of the 20th century.

The Gotland Basin belongs to the clearly deeper parts of the Baltic Sea with maximum water depths exceeding 200 m. The hydrographic setting has been discussed elsewhere (Kullenberg 1981; Nehring and Matthäus 1991). Accordingly, a shallow halocline is observed and deep-water inflows from the North Sea, which however are intermittent, do not follow a well-defined pattern. Significant water salinity stratification in the Gotland Basin is visible in that the deep water has salinity's varying between 11-13 PSU while surface waters usually have salinity's at 7.5 PSU. The halocline is estimated at 70-80 m in the Gotland Basin. The uppermost water layer which has a thickness of about 30 m and shows the lowest but also nearly stable salinity's (7-7.7 PSU) is opposed to climatic forcing and drastic seasonal temperature changes from less than 10° C to 17° C (Kostrichkina et al. 1999). A cold, up to 45-m thick intermediate water layer with a salinity of less than 8.5 PSU follows. Inflow of saline water originating in the North Atlantic water masses which proceeds frequently at depth is via the Skagerrak passing the Kattegat, the Danish Sound area and continuing into the central Baltic. Stagnation in major inflows has been observed since 1977 but in 1993 a new major inflow occurred, with the largest salt transport ever registered (17 PSU). The most characteristic feature is however the deep water layer below the halocline which intermittedly is penetrated by the saline inflow water. This deep water is characterised by temperatures of 4-6° C and salinity's varying between 10 and 13 PSU. During periods of stagnation, anoxia is observed in the water column.

Diatoms, green and blue-green algae (cyanobacteria) are the major components of the total biomass at present with a tendency of decreasing diatom fraction on account of increasing cyanobacteria occurrences. In summer and autumn, blue-green algae are the major fraction of the phytoplankton biomass. The recent investigations spanning from 1976 to 1992 (Kostrichkina et al. 1999) have shown that a change in phytoplankton community structure occurred in the mid eighties (decline of diatoms and increase of dinoflagellates and blue-green algae). Along with this, a decline in spring and summer nutrient concentrations at raising water temperatures was observed.

Plankton diversity also changed since 1976-77 in the Baltic Proper and the Gulf of Finland but was also observed in other oceans such as the North Sea and in Californian waters (Vuorinen and Hänninen 1999). All zooplankton species in the Baltic react to salinity changes. River run-off to the Baltic Proper has increased since 1960 from about 95 x10^3 km^3 to about 120x10^3 km^3 in 1995. At the same time, a salinity change from about 12.8 to about 11.2 PSU was observed for the Gotland Deep water below 200-m depth. The run-off was shown to correlate with the North Atlantic Oscillation (NAO) index (Hurrell 1995), with increased rainfalls in years with high NAO.

METHODS

Long piston and box cores were taken from the central part of the Gotland Deep where water depths exceeded 230 m. Because especially in long piston and box cores due to the very fluid conditions of the sediments uppermost parts of the cores very often were lost during coring, only the core material below 40-50 cm from these cores was used for detailed studies. To link the data to the surface, short Niemistö-type gravity cores were also taken. For these and the upper 1-m of a long gravity core, each cm of the core was sampled. Sampling for paleomagnetic measurements of the piston and the long box core was also conducted.

Table 1. Geographical data for the sampling sites

Core	Core length (m)	Coordinates		Water depth (m)
GBT-C	0.516	57.283° N	20.118° E	241.3
211660-1	8.8	57.282° N	20.118° E	241
211660-6	7.35	57.283° N	20.118° E	241.3

Sample material was in this case collected in orientated cubes of 2x2x2 cm dimensions. After finished paleomagnetic measurements, the cube sample material was freeze-dried and used for analytical purposes. Selected geographical data on the cores are given in Table 1 and the position of the three studied cores is shown in Fig. 1.

The geochemical data were generated by automated energy-dispersive X-ray fluorescence (EDX) which was calibrated by use of 28 international geological reference materials. The detailed description of the analytical technique can be found elsewhere (Kunzendorf 1979). The precision for these measurements (evaluated from repeated measurements of the standards) were estimated at about 10% for Mo and the detection limit is about 10 mg/kg. Molybdenum was only one of several other major, minor and trace elements determined in the core samples.

Radiometric dating of sediment cores was conducted by gamma-ray spectrometry of ^{210}Pb and modelling the unsupported ^{210}Pb data with the constant rate of supply model (CRS). ^{137}Cs obtained in the same measurements was used for the verification of the dating results, i.e. comparison with known ^{137}Cs markers (Chernobyl, Sellafield or nuclear bomb testing) was carried out (Kunzendorf et al. 1998). Age models for cores 211660-1 and 211660-6 were constructed using both paleomagnetic measurements calibrated against a "Master Curve" from annually laminated lake sediments from Lake Pohjajärvi, Finland (Kotilainen et al. 2000), and ^{14}C AMS dating. In a first approximation age depth curves were divided into several distinct parts that could be approximated by straight lines.

RESULTS

Molybdenum in the sediment cores

Some of the geochemical data for core GBT-C including Mo are presented in Table 2 while the data for the long cores can be found elsewhere (Kunzen-dorf 1999). From our investigations it appears that there is a strong Mo signal in the sediment cores from the Gotland Basin. Surface core GBT-C and the upper 1-m of box core 211660-6 (Fig. 2) shows significant Mo variations (over 150 mg/kg) in the sediments. Mo concentrations are relatively low (about 50 mg/kg) starting in year

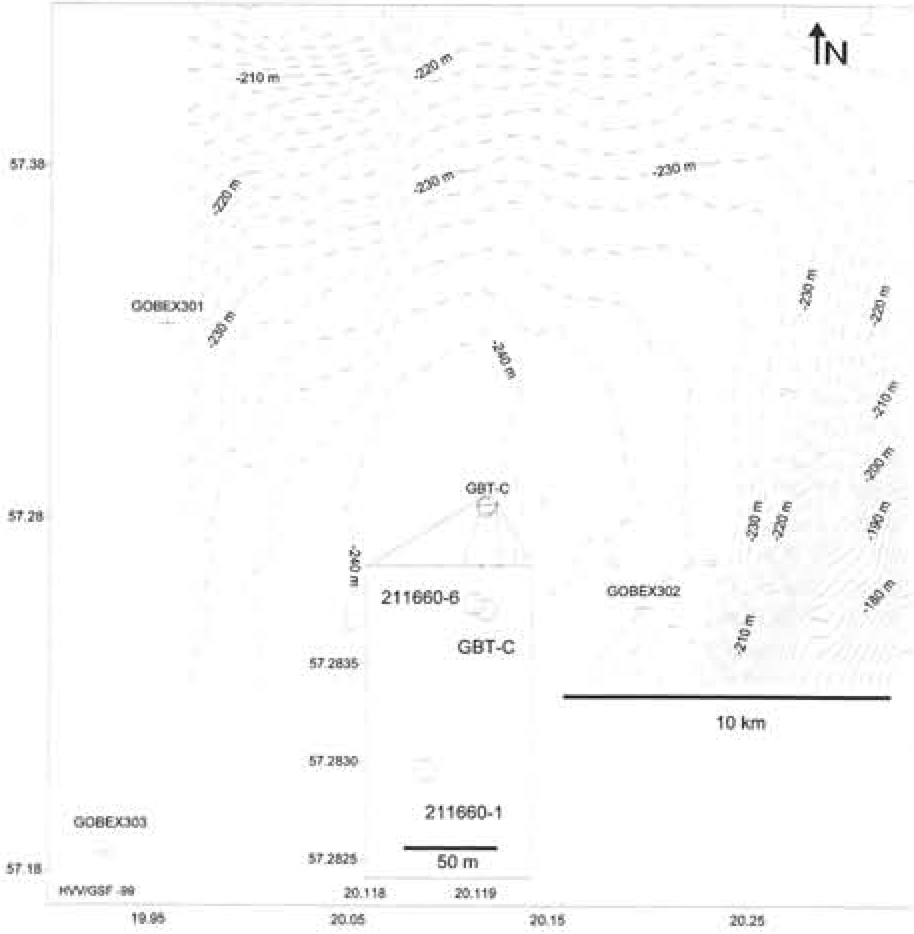

Fig. 1. Detailed bathymetric map of the Gotland Basin with coring sites discussed in this investigation: short (Niemistö-type) core GBT-C, long box core 211660-6 and piston core 211660-1.

Table 2. Selected geochemical data including those of Mo for core GBT-C. All data in mg/kg if not stated otherwise

Depth (cm)	K (%)	Ca (%)	Ti	Mn	Fe (%)	Cu	Zn	Br	Rb	Sr	Zr	Mo
0.5	1.41	0.62	1231	157	3,03	123	290	328	41	88	33	47
1.5	1.59	0.56	1607	279	3,83	138	483	492	83	123	60	101
2.5	1.35	0.47	1229	344	3,16	126	297	459	58	102	42	92
3.5	1.60	0.56	1709	486	2,48	112	339	484	78	115	64	115
4.5	1.67	0.62	2038	613	2,64	123	379	337	76	97	62	118
5.5	1.87	0.66	2358	662	3,13	157	530	358	94	103	78	160
6.5	2.07	0.73	2621	1034	4,63	224	710	426	84	115	88	187
7.5	1.77	0.71	1987	2309	6,86	189	637	288	91	109	66	161
8.5	1.39	3.55	406	138580	5,14	84	367	193	44	189	43	96
9.5	1.49	4.99	66	187687	4,69	60	337	127	46	235	52	105
10.5	1.59	4.00	522	>500000	6,08	53	304	126	63	193	52	109
11.5	1.99	0.97	2323	19240	7,19	122	413	246	108	134	77	172
12.5	2.72	3.64	2203	90181	5,12	41	269	120	102	165	43	23
13.5	3.46	2.19	3538	59475	5,94	49	281	137	110	139	85	28
14.5	3.08	2.64	2534	70859	5,61	34	229	121	124	159	87	45
15.5	3.04	1.50	3062	33935	6,17	76	245	156	132	135	102	108
16.5	3.00	2.78	2351	86318	4,97	28	149	95	113	175	79	25
17.5	3.24	1.74	3140	51505	4,20	43	164	123	142	150	92	34
18.5	3.66	1.11	3782	24015	5,09	39	154	140	151	129	107	25
19.5	3.38	1.46	3408	39375	5,65	38	137	120	135	140	101	25
20.5	3.15	1.21	3287	35890	5,62	44	144	118	140	139	106	26
21.5	3.28	1.74	3285	55051	4,84	38	135	114	129	143	93	20
22.5	2.60	0.80	2862	21216	4,46	37	121	99	149	125	111	33
23.5	3.52	1.34	3580	34248	5,46	42	136	108	148	137	113	31
24.5	3.31	1.00	3665	25061	5,73	40	120	116	148	133	119	33
25.5	3.26	1.12	3267	31839	6,10	44	116	136	141	139	107	31
26.5	3.40	1.40	3415	40130	5,08	43	119	106	151	129	109	40
27.5	3.21	1.49	3197	40855	6,09	30	110	104	143	142	100	44
28.5	3.51	1.28	3665	31861	5,05	47	123	113	141	130	108	39
29.5	3.65	0.86	4206	14149	6,41	54	134	134	157	120	109	48
30.5	3.84	1.20	4284	33847	6,69	48	132	129	144	129	106	57
31.5	3.65	1.71	3634	55789	6,58	49	120	126	134	128	100	50
32.5	3.42	1.73	3352	51298	4,63	47	116	115	139	148	95	65
33.5	3.27	2.14	3206	61065	4,98	41	106	99	133	156	101	47
34.5	3.64	0.72	3938	12419	5,77	48	121	108	167	121	121	55
35.5	3.39	1.07	3552	28471	5,31	40	113	102	154	140	106	48
36.5	3.40	0.83	3771	18959	5,79	43	116	130	152	118	108	40
37.5	3.43	1.05	3681	27688	5,68	51	126	124	132	122	107	39
38.5	3.35	1.08	3593	25296	5,53	53	128	120	140	123	106	50
39.5	3.33	1.64	3138	48280	5,41	60	117	113	119	143	99	65
40.5	3.27	1.68	3199	48586	5,48	49	108	109	126	149	97	48
41.5	3.22	1.17	3468	30612	6,14	60	121	127	129	129	96	63
42.5	3.51	1.19	3612	30586	5,15	56	131	137	138	128	116	52
43.5	3.21	0.92	3551	17602	5,48	56	130	124	140	121	114	53
44.5	3.01	1.22	3196	32727	5,90	65	114	123	122	126	91	61
45.5	3.26	1.79	3100	49970	5,05	37	110	111	134	141	99	37
46.5	2.77	2.34	2626	67108	5,18	43	107	116	112	145	87	58
47.5	2.95	2.07	2588	58771	5,61	50	113	112	111	136	87	61
48.5	2.83	2.68	2312	77895	5,33	54	102	111	100	158	85	100
49.5	3.01	1.08	3291	21954	5,68	87	140	175	121	117	104	93
50.5	2.83	1.76	2788	44523	6,35	93	130	132	112	133	86	140
51	3.43	0.78	3896	13511	5,74	71	139	164	146	126	123	70

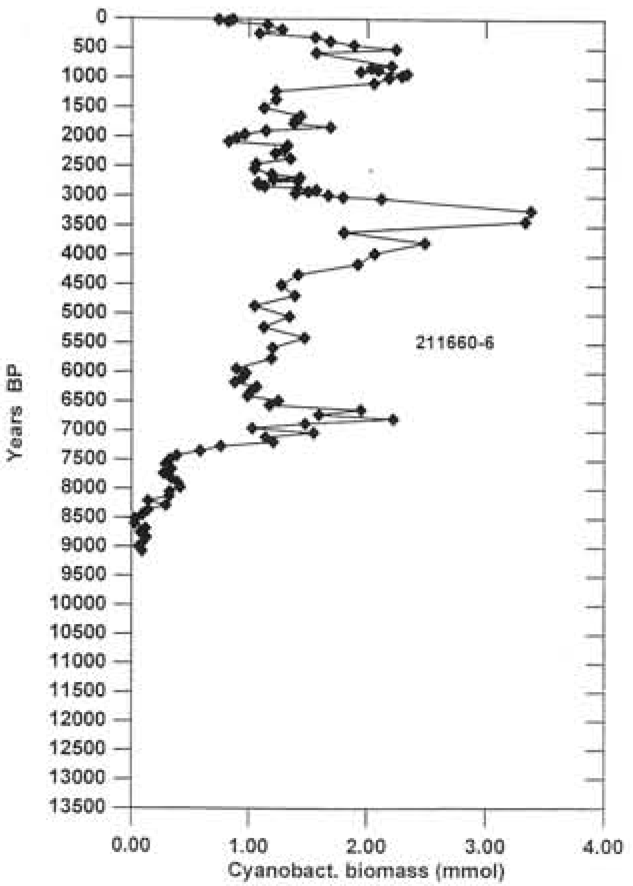

Fig. 2. Mo distribution with depth in cores GBT-C, 211660-6 and 211660-1. The Mo data are plotted against age as estimated from ^{210}Pb (uppermost part of the figure) and ^{14}C AMS dating.

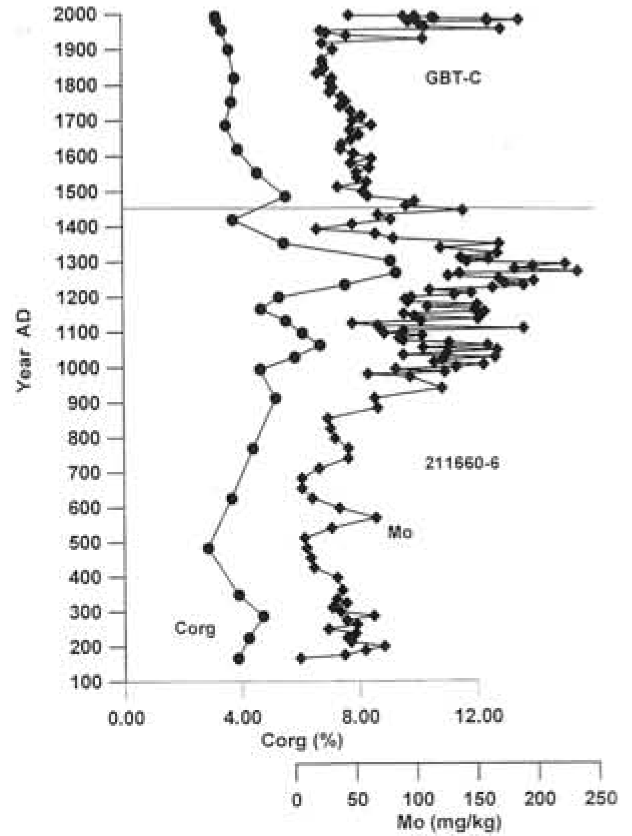

Fig. 3. Plot of Mo vs. organic C in sediment cores GBT-C and core 211660-6 showing good correlation between the two elements.

200 AD until the middle of the 10th century. Mo increases then to about 150 mg/kg and stays relatively high during the next about 400 years, although there is some decrease in the early 13th century. Highest Mo (>200 mg/kg) is observed during the period 1250 to 1400. The Mo distribution shown coincides with occurrences of laminated sediments and Mo correlates with total organic carbon, and total N in the sediments (Fig. 3). It is therefore suggested that Mo be connected with organic C in the sediments, i.e. with the biogenic phase.

Interestingly, Mo accumulations are also observed in piston core 211660-1 at greater depth, i.e. much earlier in time (Fig. 4). Although this piston core most likely lacks the upper about 30 to 40 cm, the Mo distribution with depth shows that the high Mo zone between about 500 and 1200 years BP cm corresponds to the high Mo zone between 1250 and 1400 AD observed in core 211660-6. Two further high-Mo zones in the piston core occur at age intervals 3500-5500 years BP and 6800-7800 years BP. These maxima correspond to a great extent to proposed major inflow periods of salt water into the central Baltic Sea and the Gotland Basin because since the last glaciation, five major saltwater inflow periods into the Baltic have been reported (Andrén et al. 2000).

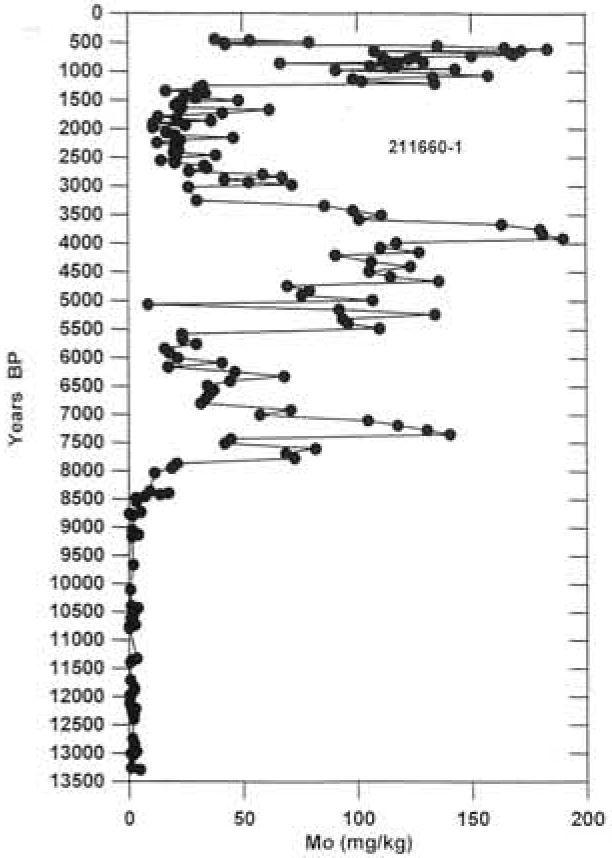

Fig. 4. Mo distribution vs. depth (age) in piston core 211660-1.

Microfossil records

Microfossils preserved in the sediments may be an expression of the biomass available in earlier times and work has shown that an assemblage change takes place in the uppermost part and at depth of the investigated long cores from the Gotland Basin (Brenner, 1998).

Organic-walled microfossils are a heterogeneous group of remains from various organisms, which are preserved in organic substance, phytoplankton (dinoflagellate cysts, coccal green algae, palynomorphs (pollen and spores), and other plant remains. In the investigated cores the preservation of the organic-walled material of the microfossils was good and it can therefore be assumed that fossil assemblages may be used to estimate the original distribution of organisms in the surface sediments at times of deposition. For instance, the high abundance of the coccal green algae *Pediastrum* which lives in freshwater or in shallow, low-salinity water, leads to the interpretation, that an increase of coast-to-basin transport of *Pediastrum* together with nutrients took place in this sediment core interval caused probably by increased river runoff. The synchronous abundance of pine pollen can be interpreted in the same way. It is, however, also possible that there was higher pine pollen productivity. In sediments confined to the Litorina Sea, where salinity and possibly temperature were higher than today, only few copepod eggs could be found, suggesting that the presence of eggs be controlled by factors other than salinity.

In the surface sediment cores (GBT-C and the upper part of 211660-6) this change in coast-to-basin transport is marked by a rapid increase of copepod egg, cladoceran remains and coccal green algae abundances towards the sediment surface. There is also a slight downward decrease of dinoflagellate cysts. Surprisingly there is an abundance change that correlates directly for copepod eggs (marine), coccal green algae (freshwater) and pine pollen (terrestrial) in the cores, with abundance maximum of the three fossil groups at 54 cm depth in the Gotland Basin (core 211 660-6) coinciding also with elevated Mo. A possible explanation of the synchronous abundance of the three different microfossil groups leads to the assumptions that during warmer periods, precipitation increases accompanied by increased erosion. This may explain the higher river runoff with nutrient-rich water, which in turn increases primary productivity by algae and as a consequence, increases the number of consumers such as copepods.

A laminated sediment section of core 211660-6 sampled on a small scale (1 to 3 mm) between core depths 295 to 297 cm shows Mo connected with mainly marine dinoflagellates. Mo is the only of the analysed metals that correlates with the total marine dinoflagellate amount in the sampled laminae (Fig. 5). Three whitish 1-mm thick layers occur at depths 295, 296 and 297 cm which according to the measured Mn and Ca contents are most likely rhodochrosite (Mn(Ca) carbonate) layers. Of the counting of microfossils, usually < 500 counts per g sediment were used. Marine dinoflagellate species were also divided into size groups <4 µm, 4-6 µm and >6 µm. The most abundant microfossils were marine dinoflagellates dominated by *Operculodinium centrocarpum* which when fractional analyses are considered has a dominant size between 4 and 6 mm. At greater depth (about 400 cm), and sampled on a more coarse scale, high amounts of marine dinoflaggelates are also observed and these are again dominated by *Operculodinium c.* Interestingly, the highest Mo (and dinoflaggelate contents) are found in the lower parts of the darkest zones in the layered section.

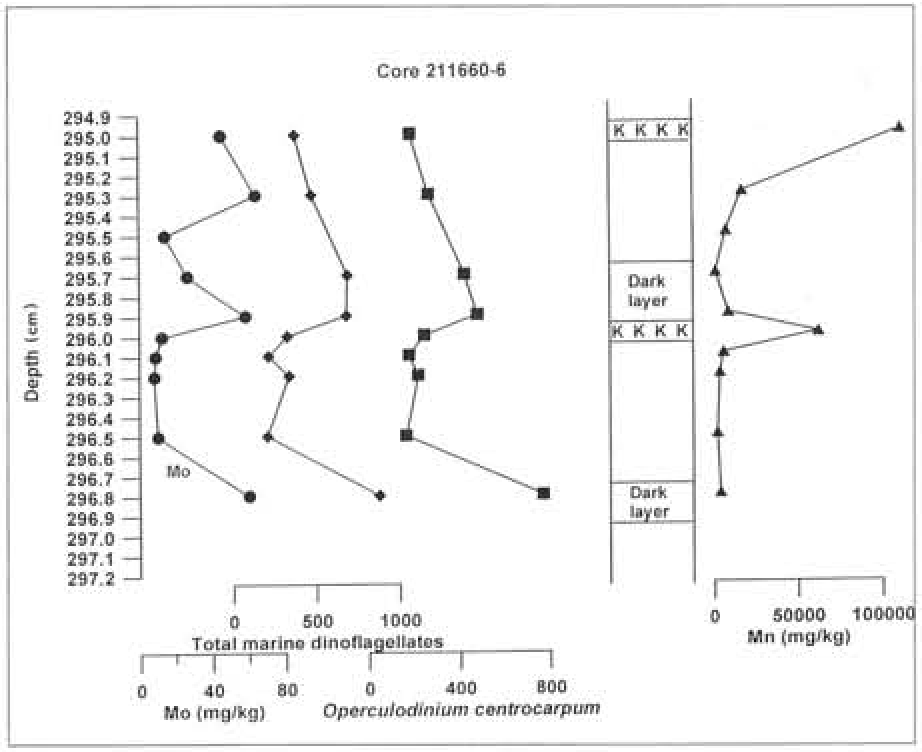

Fig. 5. Mo contents in samples from a finely sampled laminated sediment section of core 211660-6 showing good correlation of Mo with the total amount of marine dinoflagellates and the total amount of the species *Operculodinium centrocarpum* in the same samples. For comparison, Mn is also plotted to indicate that there are also rhodochrosite/kuthnohorite (Mn (Ca) carbonate accumulations in the laminated section.

DISCUSSION

Cyanobacteria characteristics

Because a part of the biomass in the surface waters of several parts of the Baltic and also the Gotland Basin is presently composed of cyanobacterial material it is worthwhile to briefly focus on this biological matter. When considering algae in general, it is worthwhile to mention that not all cyanobacteria are blue-green, they may be bright green; they may also be harmful to animals and sometimes even be lethal. Cyanobacteria may cultivate some bacteria and weed out others by leaking certain compounds, including some that are toxic to animals. These toxin producing bacteria seem to be responding to increases in the amount of N, P and other nutrients washing off the land from fertilisers and animal wastes. Microzones, which are internal microenvironments, are formed by cyanobacterial-bacterial aggregates (Paerl 1985) and such microzones are preferably formed at low turbulence in the surface waters and adequate supplies of dissolved organic matter (DOM). Contrary, such zones are significantly reduced at increased surface water turbulence and decreased DOM availability. Toxic cyanobacterial blooms have been reported in the freshwater realm (Feitz et al. 1999; Rivasseau et al. 1999) and there is more and more concern with these blooms because the toxins they produce - among which are heptapeptides and microcystins - are dangerous for animal and human health.

A few recent experimental studies that concentrate on molybdenum in connection with cyanobacteria growth are of interest here. Attridge and Rowell (1997) in studying cyanobacteria species of *Anabaena* found that their growth was dependent on Mo and V availability. Schrautemeier et al. (1995) reported that in filamentous cyanobacteria two nitrogen fixing systems occur that are based on Mo nitrogenases. Cole et al. (1993) in investigating the uptake of molybdenate in cyanobacteria taxa and natural phytoplankton communities of freshwater lakes found that both tungstate and sulphate were able to inhibit molybdenate uptake. As regards marine and estuarine systems the authors regard that sulphate may reduce molybdenate uptake by up to 20%. The abundance's of planktonic, N-fixing cyanobacteria is effectively indicated by the ratio SO_4^{2-}/Mo (Marino et al. 1990). It has been known that this ratio is rather high in seawater compared to freshwater. Recently, Lin and Stewart (1998) have given a review on nitrate assimilation of bacteria. Accordingly nitrate uptake occurs through a periplasmic binding protein-dependent system. Both molybdenum and iron are involved. However, there are still a number of unsolved problems concerning the mechanism and energetic of the nitrate uptake.

Molybdenum and cyanobacteria occurrences

C and N in the sediment cores of the Gotland Basin in general show a good correlation with Mo suggesting that these elements occur in similar phases. These geochemical and microfossil results are in agreement with recent general discussions on phytoplankton blooms during the geological record (Grimm et al. 1998). Accordingly phytoplankton blooms must be considered a form of self-sedimenting compartment behaving differently to what is known about normal marine sedimentation. These blooms generate flocs with their own aggregating and sinking dynamics producing laminated sediments on anoxic seafloors although the behaviour of especially Mo has not been included into these models. However such flocs are increasingly observed in the Baltic basins.

The zooplankton organism *Bosmina* was investigated earlier. Organic remains contents were higher in laminated sediment sections. At the same time lower $\delta^{15}N$ were found along the entire investigated core section of core 211660-6 suggesting that there is a dominating cyanobacterial biomass preserved in the sediments. Viewing the cyanobacteria biomass distribution (Fig. 6) over the past 8000 years it is clear that there are periods in the Gotland Basin sedimentation history where especially high cyanobacteria biomasses were observed and that these periods also are characterised by unusually high Mo (see Fig. 2 and 4). In a recent publication, the sources for nitrogen in the central Baltic during the past were also estimated by investigating fossil zooplankton exoskeletons from dated sediment cores (Struck et al. 1998). An increase in abundance's of exoskeletons of *Bosmina longispina maritima* is observed since about 1965. There has been an increase in the nutrient load to the Baltic since about 1950 caused by more extensive agricultural activities and waste discharges. It has been agreed on that of the total load of nitrogen to the Baltic Sea, about one third is by airborne input (Emeis et al. 2000) while about 30% of the airborne supply are removed by nitrogen fixing cyanobacteria. There is also an increase in occurrences of cyanobacterial mats in the 1970's and these cyanobacteria occurrences which flag eutrophication, are a major part of food to zooplankton. It is realised that nitrogen fixation by diazotrophic bacteria has been a relatively large source of nitrogen in the Baltic. Because we know that Mo is essential for the N fixation, we may therefore add to this that the cyanobacteria increase observed in the Baltic most likely is accompanied by Mo accumulations in the sediments and that Mo is a marker for such enhanced algal blooming periods.

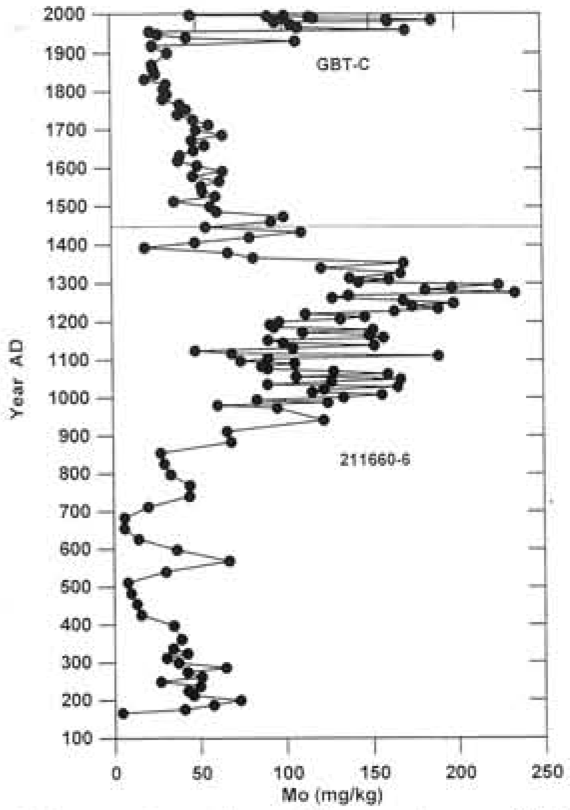

Fig. 6. Amount of cyanobacterial biomass along core 211660-6. The age scale is based on ^{14}C AMS dating results. The amount of cyanobacterial biomass was estimated from the nitrogen production in the sediments assuming that the total nitrogen production is the sum of nitrogen produced by phytoplankton and by cyanobacteria. Using estimated ^{15}N values of both components, a cyanobacterial fraction may be calculated from the total nitrogen in the sediments via a linear mixing equation.

CONCLUSIONS

Based on analytical data of short and long sediment cores from the central Baltic Sea (Gotland Basin) we conclude the following:

Because the analytical evidence suggests that Mo be connected with the biogenic fraction (total carbon, organic C, total nitrogen, microfossils) there is the possibility that this element entirely originates from the primary productivity in the surface waters of the Gotland Basin and adjacent areas.

Because we know of frequently occurring algal blooms in the central Baltic Sea and because cyanobacteria need, among others, the micronutrient Mo for the fixation of nitrogen, Mo is then probably transported to the sea floor mainly by decaying algal remains and to a lesser extent by grazing biota. Mo is then probably released and/or is a residual phase in the reworking and destruction of organic matter by bacteria and incorporated into the sediments probably in the form of MoS_2. If this is the process of Mo accumulation on the seafloor dominating the central Baltic, then high amounts of Mo in anoxic sediments are expected in areas of high surface water productivity periods rather than in connection with variability in redox conditions as outlined by Hallberg (1974) who, as already mentioned, introduced anoxicity ratios based on mainly Mo and Cu and Zn in the sediments.

The significant correlation of organic C and total N to Mo in the Baltic sediments offers therefore the possibility to trace phytoplankton occurrences during time and also to easily outline cyanobacterial blooms in the area by analysing these sediments for Mo.

The above suggested processes, however, need to be confirmed by more detailed studies which were not possible during the presented work.

Acknowledgements

The EU MAST3 Project BASYS (Baltic Sea System Study) partly funded the present work and the coordination during the project period by Prof. Bodo von Bodungen and Dr. Boris Winterhalter is much appreciated. We profited especially from discussions with BASYS colleagues during several BASYS Science Conferences. Skilful analytical work by P. Sørensen, Risø, is also acknowledged here. The thorough reviews of professors Rodney Stevens (Göteborg University) and Emelyan Emelyanov (Kaliningrad) very much improved the text.

References

Attridge, E.M. & Rowell, P. 1997: Growth, heterocyst differentiation and nitrogenase activity in the cyanobacteria in *Anabaena variabilis* and *Anabaena cylindrica* to molybdenum and vanadium. *New Phytologist 135*, 517-526.

Brenner, W. 1998: Organic microfossils - Indicators of environmental change in the Baltic Sea. *Second BASYS Marine Science Conference, Stockholm, Sweden, Sept. 98.* Abstracts.

Calvert, S.E. 1976: The mineralogy and geochemistry of nearshore sediments. *In* J.P. Riley and R. Chester (Ed.): Chemical Oceanography, *Academic Press*, 187-280.

Calvert, S.E. & Pedersen, T.F. 1993: Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological record. *Marine Geology 113*, 67-88.

Cole, J.J., Lane, J.M., Marino, R. & Howarth, R.W. 1993: Molybdenum assimilation by cyanobacteria and phytoplankton in freshwater and salt water. *Limnology and Oceanography 28*, 25-35.

Crusius, J, Calvert, S., Pedersen, T. & Sage D. 1996: Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth and Planetary Science Letters 145*, 65-78.

Dean, W., Piper, D.Z. & Peterson, L.C. 1999: Molybdenum accumulation in Cariaco basin sediments over the past 24 k.y.: A record of water-column anoxia and climate. *Geology 27*, 507-510.

Emeis K.C., Struck U., Kähler P., Kunzendorf H. & Christiansen C. 2000: Changes in the burial rates and C:N:P ratios in Baltic Sea sediments over the last 150 years. *Marine Geology 167*, 43-59.

Emelyanov, E.M. 1995: Baltic Sea: Geology, geochemistry, paleoceanography, pollution. *P.P. Shirshov Institute of Oceanology RAS.* 119 p.

Feitz, A.J., Waite, T.D., Jones, G.J., Boyden, B.H. & Orr, P.T. 1999: Photocatalytic degradation of the blue green alagal toxin microcystin-LR in a natural organic-aqueous matrix.. *Environmental Science & Technology 33,* 243-249.

Grimm, K.A., Lange, C.B. & Gill, A.S. 1998: Self-sedimentation of phytoplankton blooms in the geologic record. *Sedimentary Geology 110,* 151-161.

Hallberg, O. 1974: Paleoredox conditions in the eastern Gotland Basin during the recent centuries. *Havforskningsinsituttets Skrifter (Finland) 238,* 3-16.

Hurrell, J.W. 1995: Decadal trends in the North-Atlantic Oscillation - Regional temperatures and precipitation. *Science 269,* 676-679.

Kotilainen, A.T., Saarinen, T. & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments in the Gotland Deep, Baltic Sea, during the last 3000 years. *Marine Geology 166,* 51-54.

Kostrichkina, E., Kalveka, B. & Ikauniece, A. 1999: The long-term changes of plankton in the eastern Gotland Basin (Baltic Sea) due to its eutrophication in 1976-1990. *BASYS Newsletter 10,* 9-15.

Kullenberg, G. 1981: Physical Oceanography. *In* A. Voipio (Ed.): *The Baltic Sea. Elsevier Oceanography Series 30,* 219-274.

Kunzendorf, H. 1979: Practical experiences with automated radioisotope energy-dispersive X-ray fluorescence analysis of exploration geochemistry samples. *Risø-Report* 407. 24 pp.

Kunzendorf, H., Emeis, K.-C. & Christiansen, C. 1998: Sedimentation in the central Baltic Sea as viewed by non-destructive Pb-210 dating. *Danish Journal of Geography* 98, 1-9.

Kunzendorf, H. 1999: Dating and assessing the Recent sediments of three deep basins of the Baltic Sea: Indication of natural and anthropogenic changes. *Risø Report-R-1077.* 100 p.

Kunzendorf, H., Vallius, H., Voss, M. & Brenner, W. 1999: The recent and sub-recent environment reflected in the chemistry and geology of the topmost sediments. *Proceedings 3. BASYS Annual Science Conference,* IOW-Warnemünde, 20-22/9/99, 9-12.

Lin, J. & Stewart, V. 1998: Nitrate assimilation by bacteria. *Advances in Microbial Physiology 39,* 1-30.

Marino, R., Howarth, R.W., Shamess, J. & Prepas E. 1990: Molybdenum and sulfate as controls of the abundance of nitrogen-fixing cyanobateria in saline lakes in Alberta. *Limnology and Oceanography 35,* 245-259.

Nehring, D. & Matthäus W. 1991: Current trends in hydrographic and chemical parameters and eutrophication in the Baltic Sea. *Das Internationale Revue der Gesamten Hydrobiologie 76,* 297-316.

Paerl, H. 1985: Microzone formation: Its role in the enhancement of aquatic nitrogen fixation. *Limnology and Oceanography 30,* 1246-1252.

Rivasseau, C., Racaud, P., Deguin, A. & Hennion, M.-C. 1999: Evaluation of an ELISA kit for the monitoring of microcystins (cyanobaterial toxins) in water and algae environmental samples. *Environmental Science & Technology 33,* 1520-1527.

Schrautemeier, B., Neveling, U. & Schmitz, S. 1995: Distinct and differently regulated Mo-dependent nitrogen-fixing systems evolved for heterocysts and vegetative cells of Anabaena variabilis ATCC 29413: characterization of the fdxH1/2 gene regions as part of the nif1/2 gene clusters. *Molecular Microbiology 18,* 357-369.

Struck, U., Voss, M. & von Bodungen, B. 1998: Stable isotopes of nitrogen in fossil cladoceran exoskeletons: Implications for nitrogen sources in the central Baltic Sea during the past century. *Naturwissenschaften 85,* 597-603.

Vuorinen, I. & Hänninen, J. 1999: Change of plankton diversity explained by climatic factors – An archipelago sea case study. *BASYS Newsletter 10,* 5-9.

Baltica

www.geologin.lt/baltica

Baltica 14 (2001) 131-140

Microfossil and biogeochemical indicators of environmental changes in the Gotland Deep during the last 10,000 years

Maren Voss, Grazyna Kowalewska, Wolfram Brenner

Abstract

The upper 6.8 metres of a long box core from the Gotland Basin have been analysed for different biogeochemical variables to infer changes in environmental settings during the last 7000 years (Litorina phase) represented by the upper 4.4m. We counted organic walled microfossil remains in 30 samples from the core, analysed pigments, and the concentrations of organic carbon, total nitrogen and $\delta^{15}N$ and, $\delta^{13}C$. Dating of the core and cross correlation with cores from other Baltic Sea basins allowed distinguishing six zones throughout the Litorina phase. Changes in the fossil assemblage and the changes in spine lengths of the dinoflagellate Operculodinium centrocarpum distinguish these ecostratigraphic intervals. From our data set the Litorina phase, is seen as a period with high variability in salinity, temperature, primary production and species composition. However, within this stage environmental conditions were relatively stable for periods of up to 700 years. The differentiation between high sedimentation rates and good preservation and / or little degradation is difficult with the presented data. A short sediment core from the Gotland Deep was used to investigate the recent sedimentation history and showed clear indications of human impacts by increasing $\delta^{15}N$ and $\delta^{13}C$ values in the upper 10-20 cm.

☐ *Baltic Sea, Gotland Basin, paleoenvironment, organic walled microfossils, pigment, $\delta^{15}N$, $\delta^{13}C$, Litorina phase.*

☐ *Maren Voss [maren.voss@io-warnemeunde.de], Baltic Sea Research Institute, Seestr. 15, 18119 Rostock, Germany; Grazyna Kowalewska [gkowal@ocean.iopan.gda.pl], Institute of Oceanology PAS, Sopot, Poland; Wolfram Brenner [wbrenner@geomar.de], Geomar, Wischhofstr.1-3, 24148 Kiel, Germany.*

☐ Received 3 August 2001; accepted 7 November 2001.

INTRODUCTION

The Baltic Sea is characterised by several basins separated by sills that prevent the water exchange with the North Sea and consequently lead to stagnant bottom waters for time periods of varying length. All Baltic Basins show suboxic but only seldom-permanent anoxic sediments. Most pronounced variability in deep water oxygen concentrations during the past 10,000 years is reported from the Gotland deep and well reflected in sediments with little or no lamination (Huckriede et al. 1996, Struck et al. 2000). Non-laminated sediments are considered as indication for benthic life that signals high oxygen concentrations; lamination is taken as indicators of at least part time anoxic conditions with only bacteria being able to survive. Almost one third of the Baltic Sea area today is covered with such laminated sediments, most of them located in the Baltic Proper (Jonsson et al. 1990). The preservation of organism from the euphotic zone is good in such environments and the organic matter content is higher compared to oxic sediments (Müller 1975). Organic microfossil material in the sediments, and the carbon and nitrogen isotopic patterns therein can mirror the physical changes of the overlying waters and reflect different production regimes concurrent with fauna and flora abundance in surface waters (Andrén et al. 1999, Risberg 1990). Pigments are well preserved in the sediments of the central Baltic Sea as may be concluded from previous studies on recent Baltic sediments (Kowalewska 1997, Kowalewska et al. 1998). The content and composition of chlorins and chlorophyll's c in sediments depends first of all on the primary produced organic matter and prevailing phytoplankton species as well as on zooplankton grazing, microbial activity, hydrodynamic conditions, and anoxia.

The dominance of cyanobacteria among the primary producers in the waters of the Gotland deep not only today but also during the last 5000 years has recently been postulated by Bianchi et al. (2000). Pigment and stable isotope data demonstrated their presence throughout the past millennia. Zeaxanthin was taken as typical cyanobacterial pigment and traced in sediment cores from the central Gotland Deep. The studied carotenoids - β,β-carotene were the measure of total plant biomass, zeaxanthin indicated phytoplankton, including some cyanobacterial species, and the stable isotope data demonstrated the occurrence of cyanobacteria in this environment (Bianchi et al. 2000). Stable isotope data of nitrogen can be used to distinguish cyanobacteria from other photoautotrophic organisms (Carpenter et al. 1997) since the nitrogen source for both phytoplankton groups is different. Cyanobacteria assimilate dinitrogen with an isotope value of 0‰ while other phytoplankton takes up nitrate with a mean value of 4-5‰ (Sigman et al. 1997). Low $\delta^{15}N$ values therefore indicate a dominance of cyanobacteria while values around and above 5‰ suggest nitrate-using phytoplankton. The low $\delta^{15}N$ values Bianchi et al. (2000) found therefore demonstrated the occurrence of cyanobacteria. Diatom communities in sediments allowed differentiation between stages of differing salinities during the Baltic Sea development (Paabo 1985, Sohlenius and Westman 1998, Westman and Sohlenius 1999). Therefore, if only one group of species or a small number of variables is considered only a limited conclusion about the paleoenvironmental setting can be drawn.

In this study we analysed a large group of variables:

1. Ten selected palynomorphs/organic-walled microfossils, which indicate many different environmental settings that are shortly described in Table 1.
2. Stable nitrogen and carbon isotope data, and
3. Pigments and some of their degradation products.

The extensive dataset is used to gain insight into the productivity regime, the physical properties of the water, and the past depositional environment at the sea floor of the central Baltic Sea during the past 10,000 years. Additionally, differences between the environmental settings in the Litorina phase and the Ancylus Lake Stage will be discussed. Through the high number of fossil and biochemical variables the study aims to draw a comprehensive picture of the physicochemical settings during the Litorina phase.

MATERIAL AND METHODS

A large set of variables was analysed from the upper 6.8m of a 8m long Box core (211-660-6) taken in the Gotland Deep (57°17.0283N, 20°07.1386E, depth 241.3m) in July 1997 with *R/V Petr Kottsov*. The core was opened and subsampled onboard after a detailed lithological core description. Sediments for total carbon and nitrogen, and stable isotope analysis were sampled continuously in 5-cm intervals from surface to 550-cm depth. Sediments were kept dark and cool onboard and were further processed in the laboratory onshore. There, samples were dried at 60°C for 24 hours, homogenised with mortar and pestle. Roughly 10 mg of sediment were weighed into tin cups for the $\delta^{15}N$ analysis. Since a persistent offset of 0.5–1‰ between $\delta^{15}N$ values of acidified sediment samples, giving heavier values, and not acidified ones was observed a parallel sample was used for the carbon isotope measurements. They were also weighed into silver cups, acidified with 2n HCl to remove carbonate, and again dried. Then the samples were placed into a CHN analyser (Thermofinnigan CE 1108) connected with a mass spectrometer (Finnigan Delta S) via a Conflow II open split interface. Calibration for the total carbon and nitrogen determination was done daily with acetanilide. Every 6th sample was a labinternal standard (peptone, Merck) with known $\delta^{15}N$ value. The isotope calibration of a N_2 gas tank was performed with IAEA-N1, N2, and N3 and for carbon a gas bottle with CO_2 was calibrated against NBS 21 and 22. Delta values are given in the usual notation: $\delta^{15}N =((^{15}N/^{14}N)_{Sample} / (^{15}N/^{14}N)_{Standard} -1).1000$ (same for $\delta^{13}C$, ^{13}C and ^{12}C). Standard deviation as calculated from the peptone standard was better than 0.15‰ for $\delta^{15}N$ and $\delta^{13}C$ measurements.

For microfossil investigation, the sediment core was sampled continuously with 1-m long U-shaped tubes (∅ 2 cm) and cut afterward in 1-cm slices. All samples were freeze dried and stored at the microfossil archive at GEOMAR Institute. Twenty-three samples from 35 cm down to 681-cm depth have been selected for further palynological investigations. Prior to the preparation of the samples, a defined quantity of *Lycopodium* spores was added, to allow the analysis of the absolute number of microfossils in the sediment. The samples were treated with hydrochloric and hydrofluoric acid to remove carbonates and silicates. The residue was washed extensively through a six-micrometer sieve to remove the amorphous organic material. Then each sample was mounted on a microscopical slide and covered with glycerine jelly.

Pigments were measured on 4-cm sections taken each 10-cm from 8 to 512-cm depth by means of an HPLC technique. Detailed procedures of extraction and further analysis are described elsewhere (Kowalewska et al. 1999, Kowalewska 1997, Kowalewska et al. 1996). The following pigments have been determined:

- Chlorins (chlorins = chlorophyl a + chlorophyll b + their derivatives) - chlorophyll a (chl a) occurs in almost all algal species and higher plants, and its derivatives phaeophytin a, pyrophaeophytin are formed during diagenesis and/or zooplankton grazing.

- Chlorophyll b (chl b) occurs in green algae and higher plants and its derivative phaeophytin b (pheo b).

Table 1. Summary of microfossils and their ecological demands

Pine pollen	- are the most common pollen in Holocene sediments of the Baltic. - useful for quantitative calibration of pollen analysis and aquatic microfossil investigation as well as indicator for transport intensity (wind, current and river runoff). - could accumulate during reduced sedimentation rates.
Marine dinoflagellate cysts	- few species present in brackish water - Two signals are useful for salinity interpretation: occurrence limitation of different species on different salinity and morphological changes (variation of spine length) of specific species.
Tectatodinium cf. pelitum = Pyxidinopsis psilata	- dinoflagellate cyst is described as a specific brackish water species (from the Black Sea only) - cyst is only abundant in a specific horizon during the Litorina-phase. - regarded as warm water species (abundance maximum point to the sea surface temperature maximum during the Holocene)
Operculodinium centrocarpum	- cosmopolitan, polyhalob cyst, with reduced spine length under low salinity conditions. Spine length can be directly used as salinity indicator. - In contrast to the Baltic Sea specimens (spine length 1-8 µm) the North Sea forms have spine lengths of 10 to 15µm. (The living dinoflagellate *Gonyaulax grindley*) producing the cyst *Operculodinium centrocarpum* survive salinity conditions down to 2-3PSU.
Lingulodinium machaerophorum	- cyst regarded as salinity and eutrophication indicator. - vegetative stage (living) of *Lingulodinium polyedrum (= Gonyaulax polyedra)* is not found below a salinity of 7-8 PSU.
Freshwater dinoflagellates	- the freshwater dinoflagellate cyst *Gonyaulax apiculata* have been found in the sediments of the Ancylus stage in Gotland Basin and North Central Basin with increasing abundance - suggests a significant nutrient increase for this interval.
Coccal Green algae *(Pediastrum)*	- dominated by *Pediastrum*, a freshwater algae - may be an indicator of river run off. - exists in coastal shallow water with low salinity (below 8-10PSU). The presence in deeper basins may be caused by current transport. - some other planktonic freshwater coccal green algae (*Botryococcus, Scenedesmus* and *Staurastrum*) are summarised as varia
Cladoceran remains	- dominant freshwater species, only few species in brackish water. - abundance controlled by food availability. (-> increasing abundance at the end of the Ancylus stage may be caused by nutrient increase) - decrease at the base of the Litorina phase influenced by increasing salinity.
Copepod eggs	- dominant in the marine realm, described from various marine sediments but not investigated in detail. - significantly low abundance of eggs during the salinity maximum - increase in post-Litorina phase cannot be caused by decreasing salinity.
Blue-green algae (cyanobacteria)	- from brackish environment. most fossil cyanobacteria and akinets found in Baltic Sea Proper can be assigned to the genus *Anabena*. - lack of "biological characteristics" at fossil cyanobacteria hamper the taxonomic identification.
Foraminiferal linings	are rare in the sediments and can be used as indicator for a marine-brackish environment.

- Porphyrins: chlorophyll's c occurs in chromophyte algae, mainly in diatoms and dinoflagellates.

- Carotenoids: b - carotene – the pigment accompanies chlorophyll a, and occurs in the majority of algae species and in higher plants, though more stable than chlorophyll a, (Kowalewska et al. 1998).

Dating of the core was performed by means of paleomagnetic measurements and varve counting which were correlated with an annually laminated sediment core from the Lake Pohjajärvi in Finland (Saarinen 1998). This method gave roughly 120 dated layers. Additionally, ten radiocarbon dates from a parallel piston core were used, which was taken at exactly the same position some hours before the box core (dates published in Andrén et al. 2000). The extrapolation of the ^{14}C dates to the box core was based on magnetic susceptibility measurements, visual description and paleomagnetic measurements of both cores. Between depth tie points the ages were linearly interpolated under the assumption of a constant sedimentation rate between each dated depth horizon (Fig. 1).

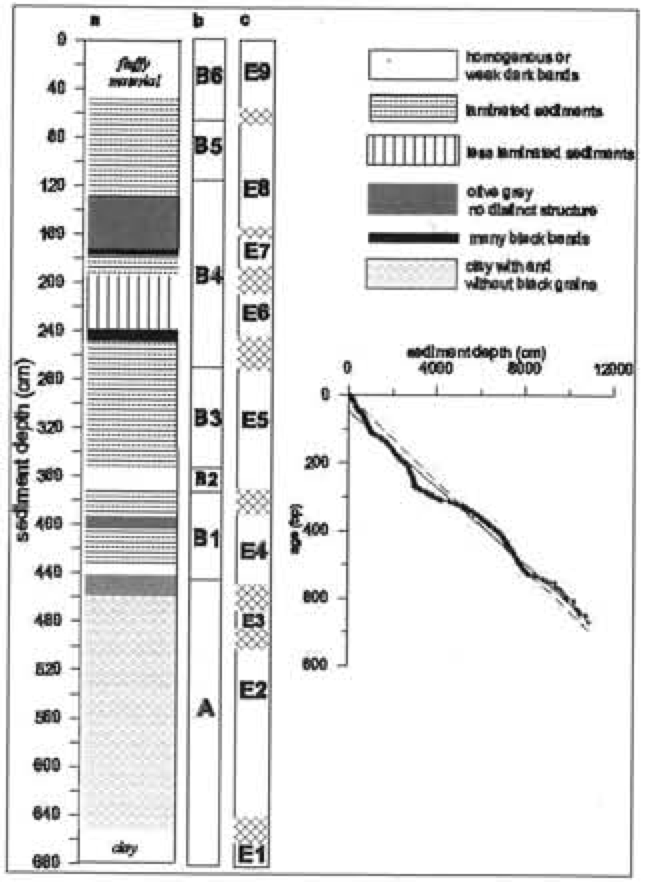

Fig.1. Description of the sediment core (211660-6) from the Eastern Gotland Basin. The left scale shows the sediment depth in cm. A is a rough summary of the detailed core description from B.Larsen (in Harff and Winterhalter 1997). B shows the zonation A and B1-B6 from Harff et al. (2001). Column C shows the ecostratigraphic zonation from Brenner E9-E1 discussed in this paper. The insert gives the correlation of sediment age over depth as interpolated between layers of measured age (for detailed explanation see text). The straight line is a regression with $r^2=0.98$, the dotted line a regression forced through zero with $r^2=0.99$, n for both regressions is 224. Shaded areas between the ecostratigraphic zones indicate unprecise definition of layers due to the sampling resolution of organic walled microfossils.

A short sediment core was taken with a Gemini corer on board of *R/V Aranda* in October 1997. It was cut into 1-cm slides on board and kept cool on board. Samples were sent to the Baltic Sea Research Institute (IOW), where they were further processed for isotopic analysis as described above.

RESULTS AND DISCUSSION

Different criteria may be applied for the identification of layers having common characteristics. Here two approaches have been used: one by means of continuously registered core logging data (sediment colour and acoustical parameters). Those data plus stable isotope values and percentages of carbon and nitrogen were used for a geostatistical analysis and allowed the identification of six distinct layers, B1-B6 in the Litorina phase and A for Ancylus stage in the core from the Gotland Basin (Harff et al. 2001). Similar layers were defined by microfossil assemblages. Nine ecostratigraphic zones (E9-E1) are distinguished, six for the Litorina phase and three for the Ancylus stage. The upper and lower border of each layer could only be defined within a 10-20-cm range due to the sampling resolution. This corresponds to an uncertainty of 70-100 years in the upper two meters of the core and over 600 years in three to four meter depths. Since no significant evolutionary change in the plankton species composition took place during the Holocene, biostratigraphic zonation and correlation can be applied without further sources of error.

The core description by B.Larsen (in Harff and Winterhalter 1997) already revealed two clearly distinguishable parts: the upper almost 4.4 m long layered section, Litorina, and the lower part from 4.4 to over 6.8 m with little or no lamination, comprising Ancylus and Yoldia (Fig.1). Zone E1, the deepest sediment sampled is assumed to represent the Yoldia stage, which will not be discussed here. A layer of 20-40-cm thickness separates Ancylus from Litorina. The Ancylus sediments (A/E3-E2) indicate a distinctive environment 8000 years before present (BP) that differs from all younger layers. Organic carbon and nitrogen contents of 1.6% and 0.8%, respectively, are low compared to Litorina (Fig. 2). However, Ancylus sediments are similar to recent open ocean environments. Stable nitrogen isotope ratios are around 5‰ and $\delta^{13}C$ values –27 to –28‰ (Fig. 2). These nitrogen isotopic values are high for fresh waters. It was expected that the isotopic signature of the organic material represents either terrestrial material around 0‰ $\delta^{15}N$, or the dissolved nitrate values which probably had 1-2‰ such as found in pristine rivers today (Kendall and Caldwell 1998). The source of organic matter in the sediments might therefore only partly be of terrestrial origin. On the other hand degradation of organic matter is assumed to cause increasing $\delta^{15}N$ values (Schäfer and Ittekkot 1993, Voss et al. 1996). The $\delta^{13}C$ values point to a terrestrial origin of organic material (Sweeney et al. 1978) because they are distinctly lower than in most of the upper 4 layers of the core. However, right above Ancylus sediments even lower $\delta^{13}C$ values were found. Therefore a mixture of organic matter sources can be supposed for zone E2 with marine, terrestrial C3 and C4 plant debris. Organic - walled microfossils are rare in the Ancylus sediment (Figs. 3-6, zone E 2) and at the base a factor of 2000 lower than in the maximum in Litorina sediments. However, to the top of this sequence there is a significant of the freshwater dinoflagellate *G. apiculata*, cladoceran remains and pine pollen (factor 100, Figs. 5 and 6). Pigments were hardly detectable. All findings support the assumption of a freshwater or very low salinity water environment with low nutrient concentrations. Presumably deep mixing twice a year aggravated primary production similar to dimictic lakes in temperate regions today. This brought oxygen into the deep water theoretically supporting efficient microbial degradation at the sediment water interface. However, the well-preserved microfossils do not indicate heavy degradation activities.

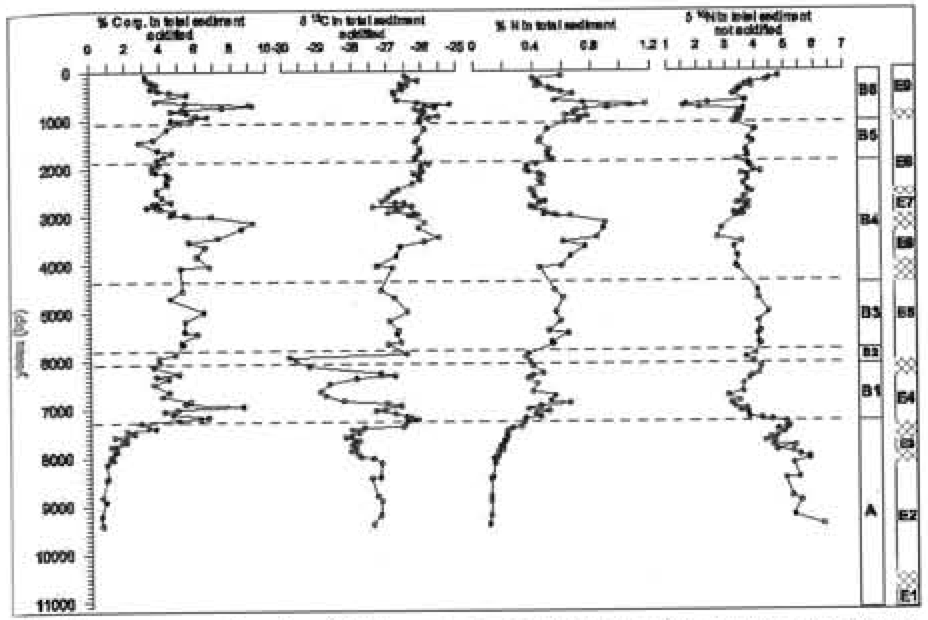

Fig. 2. Percent organic carbon, $\delta^{13}C$ in organic material in the sediment, % total nitrogen, and $\delta^{15}N$ in total sediment against age before present (present = 1950).

The isotope data did not vary significantly between layers B1-B6 by an analysis of variance (ANOVA) and did not reflect the zonation found by the simultaneous use of all variables (Harff et al. 2001). The isotope values are thus briefly discussed for the entire Litorina phase. Nitrogen concentration and isotope values show-opposing trends throughout the core. After autocorrelation calculation of both data sets, the number of dependent variables was reduced from 89 to 28 independent variables. With $r^2 = 0.52$ the significance level is 99.9%. Lower isotope values correspond to higher organic nitrogen contents. In the strongly laminated sections of the core the organic nitrogen content is higher while the $\delta^{15}N$ values are slightly lower. This pattern could be caused by low oxygen concentrations in the water column above the sediment, which favour the growth of sulphur bacteria. These bacteria consume ammonia, the only dissolved inorganic nitrogen species in anoxic waters, and thus produce isotopically light biomass. This has been described for the anoxic layer in the water column of the Gotland Basin today (Eichner 2000, Voss et al. 1997). Sedimenting organic material with attached sulphur bacteria could thus become isotopically light and sink to the sediment. If the degradation is low due to the lack of oxygen (Müller 1975) high organic contents could co-occur with these low $\delta^{15}N$ values. Additional isotope effects of varying oxygen concentrations at the sediment water interface seemed to have little effect on the isotopic signature (Eichner 2000). Since other investigations found increasing $\delta^{15}N$ values during diagenetic processes in the water column and in sediments (Macko et al. 1993, Sweeney and Kaplan 1980), another source of isotopically light material in the sediments is postulated. Cyanobacteria are capable of fixing atmospheric nitrogen with an isotope value of 0‰ and below (Carpenter et al. 1997). All other phytoplankton uses nitrate as their nitrogen source that is isotopically heavier (4-5‰). The low $\delta^{15}N$ values throughout the upper 4.4-m suggest a permanent input of cyanobacterial biomass to the sediments. Usually land derived matter also has such a low $\delta^{15}N$ values. But in this core the $\delta^{15}N$ data in Ancylus sediments suggest higher val-

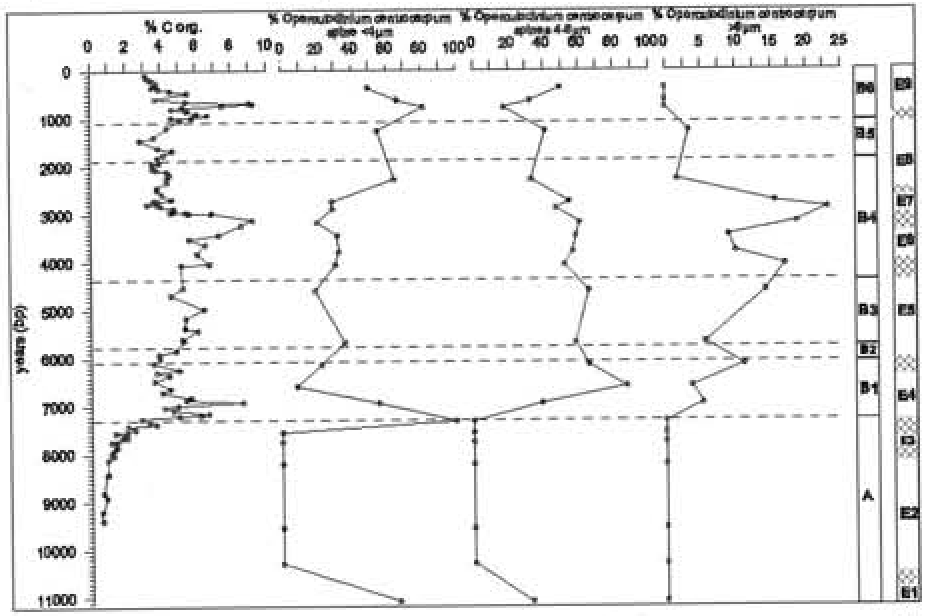

Fig. 3. Percent organic carbon and percent of *Operculodinium centrocarpum* with different spine length of <4µm, 4-6 µm, and >6µm against age before present (present =1950).

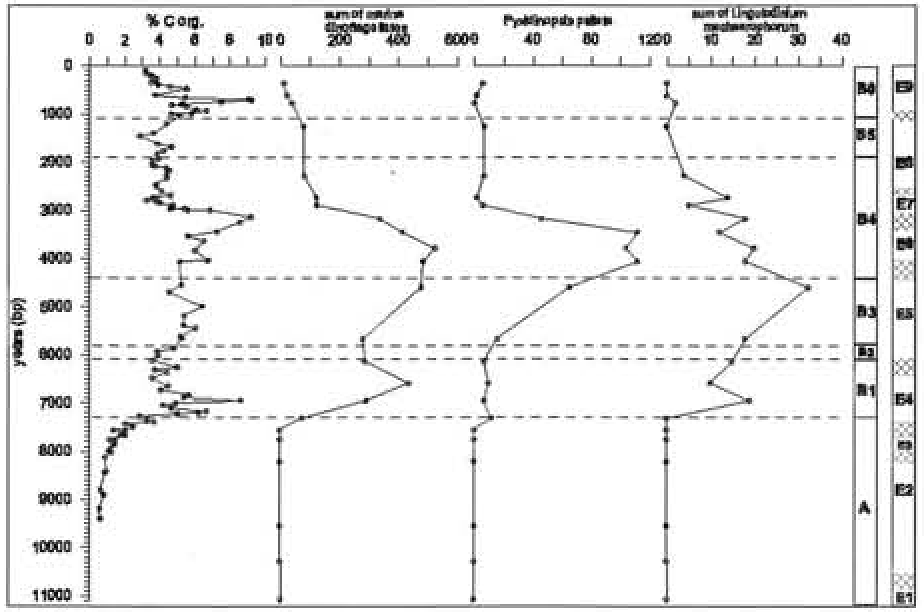

Fig. 4. Percent organic carbon and microfossil assemblages (in number per g of dry sediment) of the sum of marine dinoflagellates, and as representatives of the group the species *Pyxidinopsis psilata,* and *Lingulodinium machaerophorum* are shown against age before present (present = 1950).

ues for terrestrial matter. We assume cyanobacteria to be an important primary producer during formation of Litorina sediments, as already suggested by (Bianchi et al. 2000, Struck et al. 2000). This is somewhat contradicted by the finding of microfossil remains (Fig. 5), because clear peaks of this organism occur only after the transition from Ancylus to Litorina, from B1/E4 to B2/E5. However, cyanobacteria remains are poorly fossilised and therefore occur in high abundance only after extreme bloom events. Their transport to the sediments can either be direct (Grimm et al. 1997) or via fecal pellets of herbivorous organisms. It has been shown that copepods feed on cyanobacteria when blooms are declining (Meyer-Harms et al. 1999). This mechanism is regarded as one possible process of massive sedimentation of cyanobacteria remains. High sedimentation events carry surface blooms with low $\delta^{15}N$ values to depth as shown by sediment trap data (Struck et al., submitted).

The Litorina transgression is marked by the first occurrence of *O. centrocarpum* (Fig. 3). This is the transition zone (E3 to E4 / A) between Ancylus and Litorina which can additionally be identified by a rapid decrease of the dinoflagellate *Gonyaulax apiculata* (Fig. 4) and maximum occurrence of cladoceran remains (Fig. 5), some cyanobacteria and a peak in Chlorococcales and pine pollen numbers (Fig. 6). Pigment concentrations also increase at the end of Ancylus (Fig. 7). $\delta^{15}N$ values decrease and point towards higher occurrence and sedimentation of nitrogen fixing organisms. The environmental change includes presumably an increase of nutrients – especially phosphorous for the cyanobacteria to grow – and a raising salinity. Since the organic walled fossils were in good shape it is assumed that oxidation of organic remains was of minor importance.

The zone E4/B1 is characterised by an increase in cyanobacteria and dinoflagellates. Chlorophyll a and b concentrations are higher than in Ancylus sediments. The $\delta^{13}C$ signal has a high variability and in the middle of the layer a minimum with 3-4‰ lower values (Fig. 2). Generally values of –30‰ are typical for terrestrial C3 plants (Schidlowski et al. 1983). Enhanced transport and sedimentation of organic matter from the land thus is a possible explanation for the low $\delta^{13}C$ values. Microfossils suggest brackish surface waters (*O. centrocarpum,* indicates salinities of 4-6 psu and *L. macheropherum* of 7 psu).

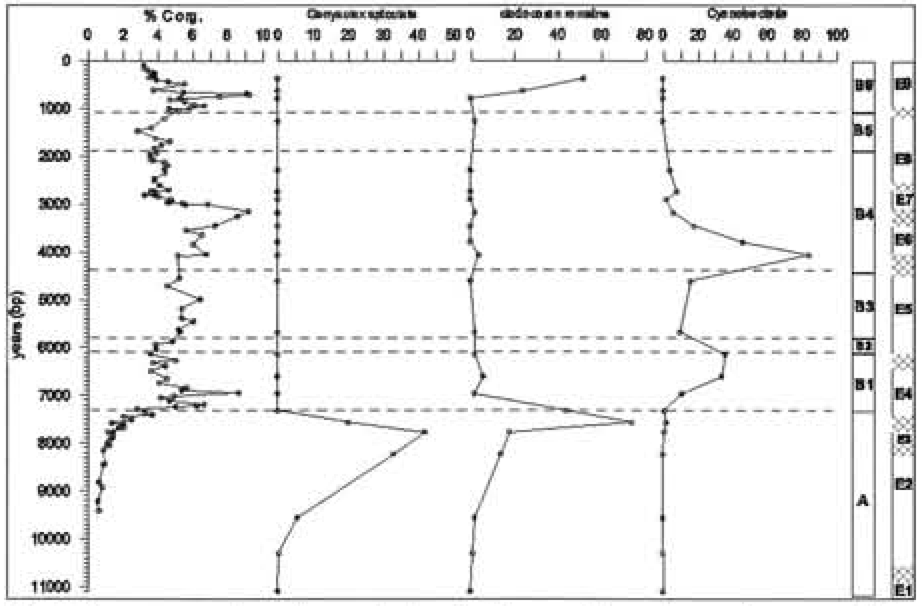

Fig. 5. Percent organic carbon and microfossil assemblages (in number per g of dry sediment), *Gonyaulax apiculata,* cladoceran remains, and cyanobacteria are shown against age before present (present = 1950).

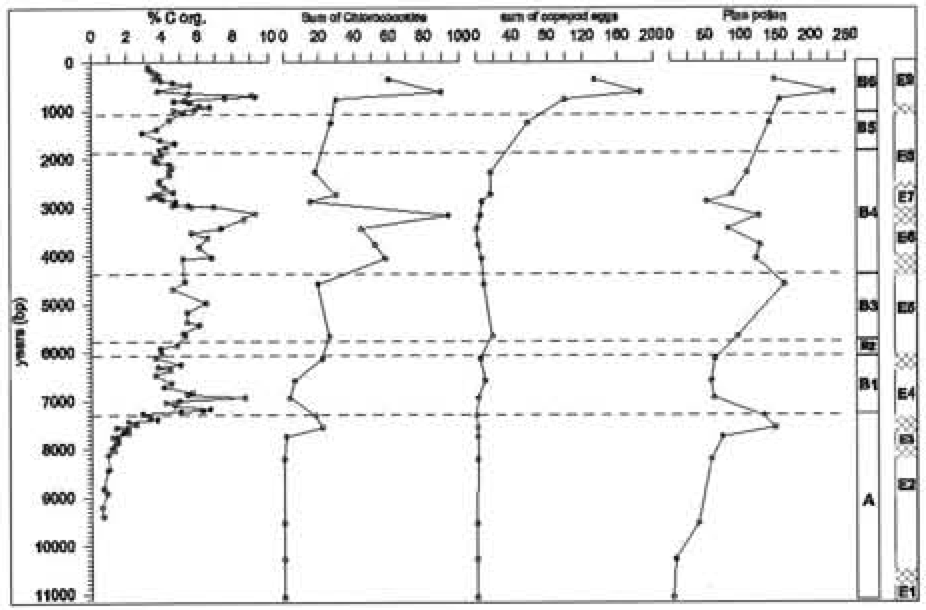

Fig. 6. Percent organic carbon and microfossil assemblages (in number per g of dry sediment) of sum of chlorococcales, copepod eggs and pine pollen are shown against age before present (present = 1950).

The layer B2 comprises the lower part of E5 and is not really pronounced in most of our variables. Only $\delta^{13}C$ show the lowest values throughout the core. The terrestrial input might have been even more pronounced compared to E4. It is hardly possible that any marine particles were produced and sedimented during this period. Together with the low carbon content in the sediment we assume that the primary production was inhibited and land derived input dominated the central Baltic Sea for ca. 200 years.

The zone E5 and B3 is the second Litorina transgression. It is characterised by an increase in the marine dinoflagellate *P. psilata* and *O. centrocarpum* with longer spines (>6µm, Fig. 3) which suggests higher salinities and warmer temperatures than before. The dinoflagellate *L. machaerophorum* increased as well; it usually lives in salinities above 7 psu (Fig. 4). No more obvious changes were recorded. High numbers of pine pollen indicate intensified transport from the coast to the deep basins possibly through higher and more frequent storm events.

The lower part B4 and E 6 is identified by the significant abundance of *P. psilata* and a decrease in *L. machaerophorum.* Since only some dinoflagellates produce cysts in high number this might indicate an even higher production by this group. Stable productivity conditions in terms of temperature, salinity and nutrients must have existed for several hundreds of years. Assuming the zone below as a changing environment, E6 resembles over 700 years of more stable environmental settings.

Layer B4 can be divided into three eco-stratigraphic zones, E6, E7, and the lower part of E8. Zone E6 is characterised by less lamination, higher pigment and organic N and C concentrations than the layer above. This fits to the very high abundance of *P. psilata*, which is known as warm water species and to prefer salinities between 3 and 10psu. Since the spine length of *O. centrocarpum* is low to medium length (<4 to 6µm) where *P. psilata* occurs both fossils indicate brackish waters. Diatoms existed in surface waters in these times, however in low numbers (Andrén 1999). This finding is slightly contradicting to the elevated chlorophyll c concentrations (Fig. 7), because this pigment is the characteristic pigment for diatoms (Parsons et al. 1984). Taking the information together 4400-3500 BP seems to be a productive time with brackish warm-water conditions and presumably good preservation (low oxygen conditions are possible). A pine pollen and Chlorococcales peak mark the transition between E6 to E7. Both are correlated with elevated river run-

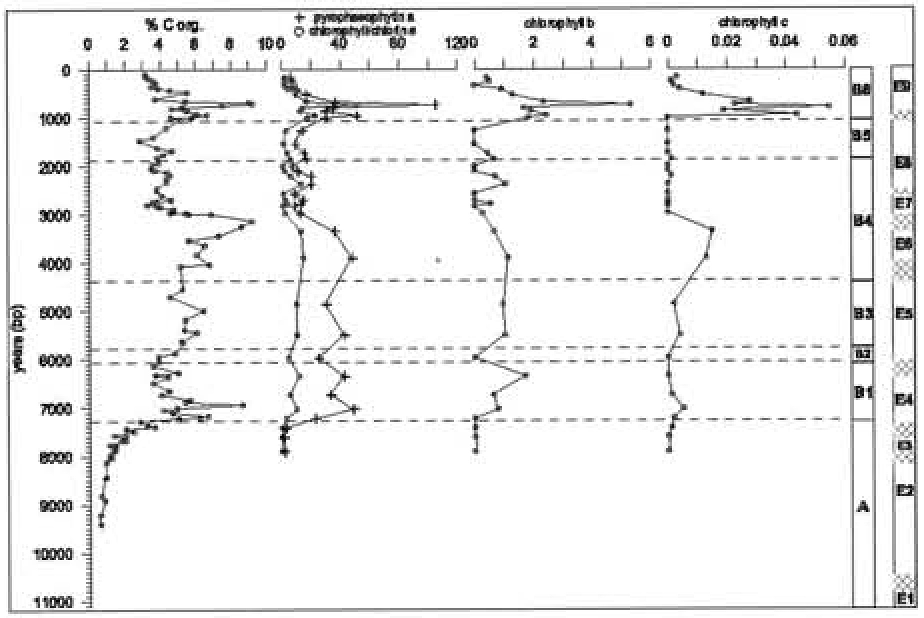

Fig. 7. Percent organic carbon and pigment concentrations in nmol * g^{-1} sediment are shown against age before present (present = 1950).

off and lower salinity, respectively. They might document a short less saline environment. Simultaneously production or conservation must have been very good because the organic carbon rises to almost 10%. Above this layer in E8 salinity decreased further according to *O. centrocarpum* spine length (Fig. 3). Production might have been low, because organic carbon values are around only 4% (Fig. 2).

The sediments above (E8) are poor in any readable signals and the spine length of *O. centrocarpum* is markedly reduced, pointing to a significant decrease in salinity (Fig. 3). The temperature might have been lower as before since the species *P. psilata* decrease (Fig. 4). Fossil concentrations are as low as those of pigments and organic matters are. The layer is clearly different to the uppermost layer E9/B6. Post-Litorina sediments comprising roughly the last 1000 years hide a very dynamic story. Both freshwater and marine organisms increase (Figs. 5 and 6). The spine lengths of *O. centrocarpum* point more towards lower salinities than in E6 and E7. Probably nutrients and temperature changes occurred. Very interesting is the extremely pronounced peak around 70-cm depth reflected in all bulk parameters such as pigments and stable isotope data. It probably represents the Medieval warm period when production must have been enormous compared to the situation today. Pigments show even 2 peaks during this time indicating rapid productivity changes.

The investigation by Andrén et al. (2000) on siliceous fossil stratigraphy differentiates three zones in the Litorina phase in the piston core (211-660-1) which was taken close to the box core discussed here. The borders of these zones do not fit the layers defined in this paper, making a direct comparison difficult. The lower boundary of the Litorina phase in Andrén et al. (2000) has the same age; however, the corresponding sediment depth is roughly 1 metre above. The initial Litorina phase (ca. 7400 and 3500 BP) is described to be brackish marine and might correspond to our layers E4 to E6. The Post Litorina (from 3500 to 700) is poor in species and thus different to the layers E3 and E2 described here with high abundance's of cyanobacteria and dinoflagellates. However, the observation of the medieval warm period fits the picture. Andrén□s uppermost layer is characterised as brackish marine with increasing nutrient concentrations and supposed to correspond to E8 partly and E9. Since we found indicators for lower salinities, the species indications from siliceous fossils on the one hand and other organic walled microfossils on the other hand do not fit together. One reason might be the limited description of the organic walled species demands in the literature. These data often do not consider natural variability e.g. in spine length or specimen specific adaptation abilities to changing salinities. However, this reason can only explain part of the discrepancies found. Uncertainties in the dating might be an additional problem to correlate both cores.

The uppermost 10 to 20-cm from the short core constitute the most recent sediments that where not properly sampled by the long core discussed above. Overlap of both cores is seen in 20-45-cm depth, where sediments of the short core are similar in their isotopic and organic signature to the uppermost centimetres of the long core. Therefore we assume that the long core misses the upper 20-cm.

The organic material in the surface sediments from the short core is less degraded and therefore has higher organic matter contents (Fig. 8). The increase in $\delta^{13}C$ values towards the surface is roughly 1‰ when the mean value for the upper 20-cm is compared to the mean value for the layer B6/E9 (-26.4‰) from the box core, or the 20-45-cm part of the short core (-26.3‰). The increase can be interpreted as signal of high nutrient concentrations when inorganic carbon becomes depleted during primary production and therefore enriched in ^{13}C in the biomass (Struck et al. 2000). The increase in the $\delta^{15}N$ of the surface sediments is only visible in the upper few centimetres (Fig. 8). It is assumed that an increasing input of anthropogenically produced nitrogen reaching the central Baltic Sea from riverine input. Dissolved and particulate nitrogen in eutrophied rivers has been shown to carry a high $\delta^{15}N$ signal (Voss et al. 2000, and Struck 1997). Below that signal the $\delta^{15}N$ values vary heavily and the mean is even lower than the uppermost layer of the box core. This has been interpreted as signal from cyanobacterial biomass (Struck et al. 2000). The changes are pronounced and happen in relatively short time compared the duration of the other ecostratigraphic zones. Human impact during the last decades therefore seems to induce rapid environmental responses that are visible in the sediments. This has also been described by (Andrén 1999) who assume input of fertilisers as a significant new nutrient source changing also the diatom assemblages in sediments of the central Gotland Deep.

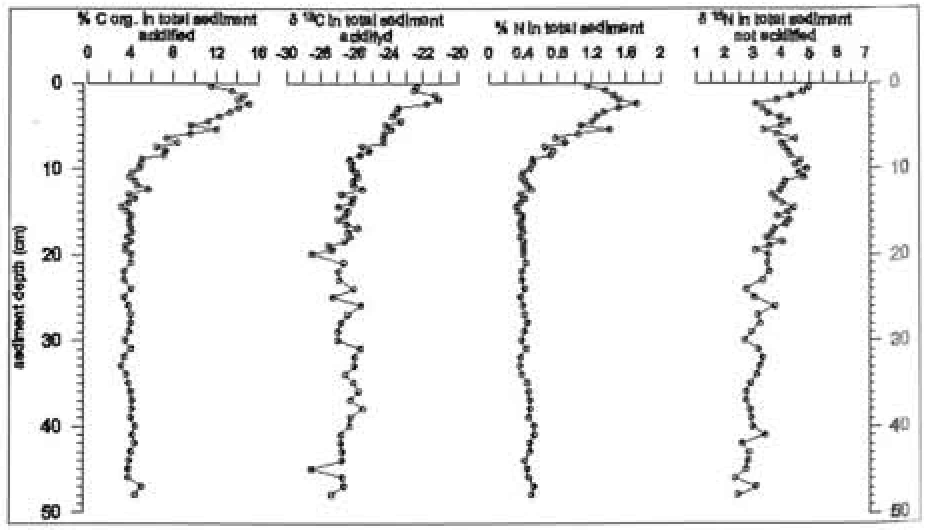

Fig. 8. Isotope data from a short core covering the true sediment surface, taken by the Geological Survey of Finland in 1998. Note that the scales are different to Fig. 2.

CONCLUSIONS

The complex environmental settings such as temperature, salinity, mixing depth, and productivity can only be reconstructed if many proxies are analysed simultaneously. Here a large group of variables (microfossils, pigments, stable isotopes etc.) was investigated in the same sediment core to identify the paleoenvironmental conditions in the Baltic Sea in the past. The Litorina phase was a very dynamic environment with marine-brackish waters and varying temperature and nutrient concentration. We could show that every few hundred year's changes in the physical environment and accompanying in the productivity of the surface waters occurred throughout the last 7000 years. However, it was almost impossible to distinguish good preservation conditions from high productivity events. Here additional markers might be a helpful tool.

Acknowledgements

This work was supported by the European Commission (Research Directorate General-Environment Programme-Marine Ecosystems) through the BASYS Baltic Sea System Studies project, contract number MAS3-CT96-0058; and by INCO, contract number IC20-CT96-0080. The short core was kindly taken during a cruise with *R/V Aranda* by the Geological Survey in Finland. The comments from the two reviewers Prof. K.-C. Emeis and Prof. O. Pustelnikovas are greatly acknowledged.

References

Andrén, E. 1999: Holocene environmental changes recorded by diatom stratigraphy in the southern Baltic Sea. *Geology and Geochemistry 302* (5 papers), Stockholm University, Stockholm.

Andrén, E., Andrén, T., & Kunzendorf, H. 2000: Holocene History of the Baltic Sea as a background for assessing records of human impact in the sediments of the Gotland Basin. *The Holocene 10,* 621-636.

Andrén, E., Shimmield, G., & Brand, T. 1999: Environmental changes of the last three centuries indicated by siliceous microfossil records from the southwestern Baltic Sea. *The Holocene 9,* 25-38.

Bianchi, T. S., Engelhaupt, E., Westman, P., Andren, T., Rolff, C., & Elmgren, R. 2000: Cyanobacterial blooms in the Baltic Sea: Natural or human-induced? *Limnology and Oceanography 45,* 716-726.

Carpenter, E. J., Harvey, H. R., Fry, B., & Capone, D. G. 1997: Biogeochemical tracers of the marine cyanobacterium Trichodesmium. *Deep-Sea Research I 44,* 27-38.

Eichner, C. 2000: Mikrobielle Modifikation der Isotopensignatur des Stickstoffs im marinen partikulären Material. *PhD Thesis, Universität Rostock.* 99 p.

Grimm, K. A., Lange, C. B., & Gill, A. S. 1997: Self-sedimentation of phytoplankton blooms in the geologic record. *Sedimentary Geology 110,* 151-161.

Harff, J., Bohling, C. G., Endler, R., Davis, J. C., Kunzendorf, H., Olea, R. A., Schwarzacher, W., & Voss, M. 2001: Physico-chemical stratigraphy of Gotland Basin (the Baltic Sea) Holocene Sediments. *Baltica 14,* 58-66.

Harff, J., & Winterhalter, B. 1997: Cruise Report, R/V *Petr Kottsov* July 22-Aug 01 1997, 100 p. Baltic Sea Research Institute, Warnemünde.

Huckriede, H., Clasen, S., & Meischner, D. 1996: Hydrographic and climatic changes recorded in Holocene sediments of the Central Baltic Sea. *Baltica 9,* 76-91.

Jonsson, P., Carman, R., & Wulff, F. 1990: Laminated sediments in the Baltic - A tool for evaluating nutrient mass balances. *Ambio 19,* 152-158.

Kendall, C., & Caldwell, E. A. 1998: Fundamentals of Isotope Geochemistry. *In* Kendall, C., & McDonell, J. J. (Eds.): *Isotope Tracers in Catchment Hydrology.* 839 p. Elsevier, Amsterdam.

Kowalewska, G. 1997: Chlorophyll a and its derivatives in recent sediments of the southern Baltic Sea collected in the years 1992-1996. *Oceanologia 39,* 413-432.

Kowalewska, G., Winterhalter, B., & Konat, J. 1998: Chlorophyll and its derivatives in deep Baltic sediments. *Oceanologia 40,* 65-69.

Kowalewska, G., Winterhalter, B., Talbot, H. M., Maxwell, J. R., & Konat, J. 1999: Chlorins in sediments of the Gotland Deep (Baltic Sea). *Oceanologia 41,* 81-97.

Kowalewska, G., Witkowski, A., & Toma, B. 1996: Chlorophylls c in bottom sediments as markers of diatom biomass in the southern Baltic Sea. *Oceanologia 38,* 227-249.

Macko, S. A., Engel, M. H., & Parker, P. l. 1993: Early diagenesis of organic matter in sediments: Assessment of mechanisms and preservation by use of isotopic molecular approaches. *In* Engel, M. H., & Macko, S. H. (Eds.): *Organic Geochemistry,* 211-224. Plenum Press, New York.

Meyer-Harms, B., Reckermann, M., Voss, M., Siegmund, H., & Bodungen, B. 1999: Food selection by calanoid copepods during a bloom of N_2 fixing cyanobacteria in the Gotland Sea (Baltic Proper). *Marine Ecology Progress Series 191,* 243-250.

Müller, P. J. 1975: Diagenese stickstoffhaltiger organischer Substanzen in oxischen und anoxischen marinen Sedimenten. *"Meteor" Forschungsergebnisse:* Reihe C. 1-60.

Kotilainen, A. 1999: A status report on the BASYS - subproject 7 - Baltic Sea paleoenvironment. *The 6th International Conference on Paleo-oceanography.*

Kotilainen, A., Hämäläinen, J. & Winterhalter, B. Reconstructing a continuous Holocene composite sedimentary record for the eastern Gotland Deep, Baltic Sea. *Submitted to Holocene.*

Kotilainen, A., Saarinen, T. & Winterhalter, B. 1998: Paleomagnetic dating of the Gotland Deep late Holocene sediments. *Second BASYS Annual Science Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Kotilainen, A., Salonen, T. & Winterhalter, B. 2000: High-resolution paleomagnetic dating of sediments deposited in the Gotland Deep, Baltic Sea, during the last 3000 years. *Marine Geology 166 (1-4)*, 51-64.

Kotilainen, A. & Winterhalter, B. 1999: 3000 years of the North Atlantic climate variability recorded in the sediments from the Gotland Deep, Baltic Sea. *Submitted to Paleo-Oceanography.*

Kowalewska, G. 2001: Algal pigments in Baltic sediments as markers of ecosystem and climate changes. *Climate Research 18*, 89-96.

Kowalewska, G., Winterhalter, B. & Konat, J. 1998: Chlorophyll a and its derivatives in deep Baltic sediments - communication. *Oceanologia* 40 (1), 65-69.

Kowalewska, G., Winterhalter, B., Konat, J., Dobrowolska, S. 1998: Chlorins in deep Baltic sediments. *Second BASYS Annual Science Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Kowalewska, G., Winterhalter, B., Talbot, H., Maxwell, J.R., Konat, J. 1999:. Chlorins in sediments of the Gotland Deep (Baltic Sea). *Oceanologia 41(1)*, 81-97.

Kunzendorf H. 1997: Variability of recent sedimentation rates in the North Central Basin of the Baltic Sea (BASYS-7). *The Fifth Marine Geological Conference - The Baltic, 6-11 October 1997, Vilnius, Lithuania.* Abstracts.

Kunzendorf H. 1999: Recent sedimentation history of three deep basins of the Baltic Sea as viewed by Pb-210 dating and geochemical records. *Third BASYS Annual Science Conference, 20-22 September 1999, Warnemünde, Germany.* Abstracts.

Kunzendorf H. 1999: Variability of recent sedimentation rates in the North Central Basin of the Baltic Sea. *Baltica 12*, 62-65.

Kunzendorf, H., Emeis, K.-C. & Christiansen, C. 1998: Sedimentation in the central Baltic Sea as viewed by non-destructive Pb-210 dating. *Danish Journal of Geography 98*, 1-9.

Kunzendorf, H. & Larsen, B. 1998: High-resolution geochemical record of the 0.5-to-1.5 m section of a long box core from the Gotland Basin. *Second BASYS Annual Science Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Kunzendorf H. & Larsen B. 2000: A 300 years cyclicity in sediment deposition in the Gotland Basin? *6th Marine Geological Conference – The Baltic, 7-9 March, Hirtshals, Denmark.* Abstracts.

Kunzendorf H. & Larsen B. 2002: A 200-300 years cyclicity in sediment deposition in the Gotland Basin, Baltic Sea, as deduced from geochemical evidence. *Applied Geochemistry 17*, 29-38.

Kunzendorf, H., Larsen, B., Kotilainen, A., Andrén, T. 1999: High-resolution geochemical record of a 1.5 m long core from the Gotland Basin: indication of changing salt water inflow patterns and surface productivity. *EUG 10, Journal of Conference, 28 March–1 April 1999, Strasbourg, France.* Abstracts Vol. 4, No.1, 207.

Kunzendorf, H., Larsen, B., Kotilainen, A., Winterhalter, B. 1999: On the salt-water inflow cyclicity in the Gotland Basin as displayed by a 1.5 m sediment geochemical profile. *Second Nordic Marine Sciences Meeting, 2-4 March 1999, Hirtshals, Denmark.* Abstracts.

Kunzendorf H. & Vallius H. 2000: Geochemistry of a long core from the North Central Basin (Baltic Sea): comparison with the Gotland Basin. *6th Marine Geological Conference The Baltic, 7-9 March, Hirtshals, Denmark.* Abstracts.

Kunzendorf, H., Vallius, H., Voss, M., Brenner, W. 1999: The recent and sub-recent environment reflected in the chemistry and geology of the topmost sediments. *Third BASYS Annual Science Conference, 20-22 September 1999, Warnemünde, Germany.* Abstracts.

Leivuori, M., Riikonen, J., Pantero, P., Vallius, H. 1999: Chemical characteristics of the accumulating suspended sediments in the northern Baltic Sea. *Third BASYS Annual Science Conference, 20-22 September 1999, Warnemünde, Germany.* Abstracts.

Leivuori, M., Riikonen, J. & Vallius, H. 1998: Heavy metals in the accumulating suspended sediments in the northern Baltic Sea. *Second BASYS Annual Science Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Repečka, M., Grigelis, A. 1998: BASYS-7 grain size and sedimentological data for cores correlation. *Second BASYS Annual Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Repečka, M., Cato, I. (Editors) et al. 1998: Bottom Sediment Map of the Central Baltic Sea. Scale 1:500000. *LGT Series of Marine Geological Maps / SGU Series Ba no.54. Vilnius-Uppsala.* 2 sheets. [Authors: Repečka, M., Cato, I., Kjellin, B., Stiebriņš, O., Kovalenko, F., Lutt, J., Tammik, P., Uścinowicz, Sz.].

Sohlenius, G., Emeis, K.-C., Andrén, E., Andrén, T. & Kohly, A. 2001: Development of anoxia during the fresh – brackish water transition in the Baltic Sea. *Marine Geology 177*, 221-242

Struck, U., Voss, M., Mumm, N., v. Bodungen, B. 1998: Stable Isotopes of Nitrogen in fossil Cladoceran Exoskeletons: Implications for nitrogen sources in the Baltic Sea during the last century. *Naturwissenschaften 12*, 597-603.

Vallius, H. & Kunzendorf, H. 2001: Sediment surface geochemistry of three Baltic Sea deep basins. *Ambio 30*, 135-141.

Vallius, H., Kunzendorf, H. & Leivuori, M. 2001: Biochemical enrichment of metals into Baltic Sea sediments. *Baltic Sea Science Congress 2001, 25-29 November 2001, Stockholm, Sweden.* Abstracts.

Vallius, H., Räisänen, M.L., Leivuori, M., Kovanen, T., Hamström, S., Hämäläinen, L., Lehto, O. 1998: Chemistry of the recent surface sediments – total dissolution and sequential leach. *Second BASYS Annual Science Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Voss, M., Struck, U. & v. Bodungen, B. 1998: Paleoenvironmental variability indicated by stable isotope signals in bulk organic matter and exoskeleton remains in core 211-660-6 (Central Gotland Sea). *Second BASYS Annual Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Voss, M. & Struck, U. 1998: On the chitin delta 15N vs bulk 15N in sediments. *Second BASYS Annual Conference, 23-25 September 1998, Stockholm, Sweden.* Abstracts.

Winterhalter, B. 2000: The paleoenvironment of the Baltic Sea a sub-project of BASYS. *Baltica 13*, 88-89.

Winterhalter, B. 2001: Climate change and the Baltic Sea. *Baltic Sea Science Congress 2001, 25-29 November 2001, Stockholm, Sweden.* Abstracts.

Baltica Vol. 14, 2001
An International Yearbook on Geology, Geomorphology
and Palaeogeography of the Baltic Sea

Scientific Editor: A.Grigelis
Scientific Co-editor: B.Winterhalter
Cover design: R.Tumasonis
Layout: S.Tūzas

SL 1490. 2001 12 20. Circ. 400. Ord. No. 3561
Published by Algimantas Grigelis, Geologijos institutas
Address: Ševčenkos Str. 13, 2600 Vilnius, Lithuania
http://www.geologin.lt/baltica
Printed by: UAB "Utenos Indra", Maironio Str. 12, LT-4910 Utena, Lithuania

---

BALTICA An International Yearbook on Geology, Geomorphology and Palaeogeography of the Baltic Sea

MANUSCRIPT ADDRESS * Editor Prof.Dr.hab.Algimantas GRIGELIS,
Lithuanian Academy of Sciences, 2600 VILNIUS, LITHUANIA *
Fax +[370 2] 236408; E-mail: grigelis@geologin.lt

INSTRUCTIONS TO AUTHORS

BALTICA publishes ARTICLES (up to 20 type pages, including illustrations and references) and BRIEF REPORTS: i.e. REVIEWS (400 words), INFORMATION (200 words), and BIBLIOGRAPHY. The manuscripts for BALTICA should satisfy these instructions.

[A] MANUSCRIPTS must be submitted in triplicate: one original and two copies; do not send diskettes until they contain the final version only. Submitted papers are subject to an external review, usually by two referees. The reviewed manuscript is sent back to the author for corrections.

[B] Authors of accepted manuscripts should submit the final *(revised)* version including tables and illustrations both in form of printed text and on a 3.5" diskette, preferred as the Microsoft Word files. Please don't prepare the page set-up by yourself, use only flush left alignment and the same font of characters; the words published in italic type should be underlined. All illustrations should be stored as separate files in TIFF, EPS or CDR format.

[C] The accepted articles are not returned to the author. Only the page-proofs are sent to the author. Additions and changes in the proofs are not allowed. The author(s) will receive one copy of journal free of charge. Offprints should be ordered by the authors along with the proof return.

The manuscript should be typed on one side of a standard size sheet [A4–21x28 cm, type area 18x24 cm], double-spaced with a blank space [3 cm wide] on the left margin. The manuscript should be arranged as follows:

[1] Title (short but informative).

[2] First name in full and Name of the author in capital letters.

[3] Abstract (not exceeding 10 lines), starting from [2] and [1], and a set of keywords (not exceeding 12 words).

[4] Current address of the author(s), affiliation, e-mail address and telefax number of each author, and dating of the manuscript.

[5] Main text; no more than three grade headings should be used, their printing started from the left margin but do not use capital letters. SI units should be used constantly with their standard symbols. On the left blank space, marginal notes (Fig. Figs. Table) are given; literature citations in the text are given as follows: (Johnsson 1990), (Johansson & Petersson 1990), (Petersson *et al.* 1990 – for three or more authors).

[6] References are given alphabetically under the author's or editor's surname; titles of magazines and publications should be given unabbreviated; if references are in Russian (Cyrillic) or other non-Latin alphabets they should be translated into English. Only published papers are to be included in the reference list. The publisher should be mentioned for books.

[7] The figure captions should be listed on a separate sheet; the original drawings should not include captions.

[8] Table captions should be given above the tables. Keep the number of tables to a minimum and make them as simple as possible. The tables should be numbered in Arabic numerals.

ILLUSTRATIONS should have two columns width of 18x24 cm, an intermediate width of 11x14 cm, or only one column width of up to 8 cm. Line drawings should have lines of even thickness and blackening. Lettering of items in composite figures should always use capital letters. The legend of figures should be textual. Maps and schemes should be presented with a linear scale given. The illustrations should be of quadrangular shape with a frame or without it. It is recommended to produce illustrations a bit larger, but not exceeding 180x240 mm, and to indicate the proposed reducing. The author's name and the figure number should be written very lightly on the back side. The photos should be clear, sharply contrasted, printed on a white, smooth paper. Avoid designing figures and tables to be turned 90° on the page.

The copies of the original should be of equal quality as the originals. BALTICA will not publish plates. Tonal illustrations should be placed in the text. Color illustrations can be accepted after consultations with the Editor.

ELECTRONIC MANUSCRIPTS. BALTICA is electronic available since Volume 13, 2000. The only final version of the manuscripts has to be submitted on the diskettes to the editor. There is the author's responsibility to make the text, tables and figures identical to the printout.

As a rule THE ARTICLES will be published in a first-in-first-out order.

4

Baltica

Volume 14 • Pages 1-144 • Vilnius • December 2001
http://www.geologin.lt/baltica

Contents

Geology

Stratigraphy

Mineralogy

Geochemistry

Environment

Baltica Library

ISSN 0067-3064