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Environmental changes in the Bornholm Basin as deduced from the geochemistry of short and long sediment cores

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Abstract Several short sediment cores were taken in the Bornholm Basin, Baltic Sea, mainly during a large marine geological European Union research project (MAST, BASYS). A long box core exceeding 5 m length was also recovered during the project. Pb/Cs dating was conducted on all the short cores. Because of irregular radioactivity curves observed in some of the short cores, they were regarded as disturbed by mainly anthropogenic activity. All the short core sediment samples were analysed for selected major, minor and trace elements by energy–dispersive X–ray fluorescence (EDX). A dated short sediment core showed increasing Cu and Zn since the 1920s but declining metal contents since the 1980s. Because there are no laminated sediments observed in the short cores, mainly oxic depositional conditions are suggested. Therefore, there was also no Mo mineralisation and/or rodochrosite deposition observed in the sediments. The chemical data for the long core showed a significant upwards decreasing trend for K, and this may most likely be explained by the gradual dilution of the sediments with finer, mainly carbon–containing particles. A most interesting curve is obtained for the trace element Br in the long core, suggesting several salinity optima during the Litorina Sea and present time sedimentation stages.

Keywords *Bornholm Basin, Holocene sediments, sediment cores, ^{210}Pb/^{137}Cs dating, geochemistry, major, minor and trace elements.*

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INTRODUCTION

The Bornholm Basin occupies about 40x10^3 km^2 to the northeast of the island Bornholm. Its maximum water depth is over 90 m. On the way to the central Baltic Sea oxygen–enriched deep water steming from the North Sea enters the Bornholm Basin via the Arkona Basin and the Bornholm Gat (a large scale submarine channel; e.g. Christoffersen *et al.* 2007). A joint Russian–Danish effort on the geology of the Bornholm Basin has recently been published (Emelyanov *et al.* 1995). Water from major rivers and drainage channels supply surface water such that the Baltic Sea is regarded as large brackish water mass. However, North Sea water is not supplied continuously but during certain weather situations. In this respect the Bornholm Basin is fairly important for the oxygen budget of the central and deep parts of the Baltic Sea.

The Bornholm Basin has a well–defined halocline at about 60 m water depth which is caused mainly by the permanent stratification of brackish Baltic Sea water and saline waters originating in the North Sea. Characteristically, major salt water inflows occur but there is no clear pattern for them although it can be said that they usually occur on a one per every second year rather than every year basis. As regards sediment accumulation rates there is a strong variation (e.g. Emelyanov *et al.* 1995b).

Intensive Russian work in the Baltic Sea west and east of the island Bornholm was conducted in the eighties and nineties (Emelyanov *et al.* 1995a). The latter work was mentioned above (Emelyanov *et al.* 1995). More recently, Christoffersen *et al.* (2007) investigated the depositional conditions in the Bornholm Basin. The Holocene history of the central Bornholm Basin was also studied by measurements on several long cores by Andrén *et al.* (2000). Danish work comprised also the early study of the West Bornholm Basin by Kögler & Larsen (1979).

In the present paper we focus on work conducted within the large European Marine Science Research (MAST) project BASYS conducted during the years 1998–2001 with participation of most of the countries bordering the Baltic Sea (Winterhalter 2001). Of three deep basins studied, the Bornholm Basin was sampled with additional work confined to long sediment cores. We report here geochemical work conducted on seven short and one long sediment core. A thorough ^{210}Pb dating study on the short cores was used to judge the validity of the geochemical data. Both selected major, minor and trace elements were studied in the cores to outline possible environmental changes during time in the Bornholm Basin.

STUDY AREA AND SEDIMENT SAMPLING

Over the years, major inflows of saline water originating from the North Sea have been observed, and in general there is oxygenated water on the Bornholm Basin bottom. Sedimentary supply to the basin is by shore erosion, suspended material, atmospheric dust and biogenic material (Stryuk *et al.* 1995). The geology of the Bornholm Basin based on extensive geophysical work has been presented by Sviridov *et al.* (1995). As regards the uppermost 30 cm of Bornholm Basin sediments they may be described as greenish–grey terrigeneous pelitic sediments (Emelyanov & Lukashina 1995).

The positions of the short sediment cores (about 20–30 cm length) investigated are shown in Fig.1. Altogether seven short cores were taken, most of them not more than 200 m apart. Coring position and water depths for the cores investigated can be found elsewhere. A long piston core (211630-9) was also collected nearby these localities. Furthermore, a long piston core (St18023) collected during a separate and earlier study was also available (Christoffersen *et al.* 2007) but is not considered in the present study. For core 211630-9, 1x1x1 cm cubes were taken at varying core depths, often between 5 and 10 cm apart. These cubes were part of a palaeomagnetic age study (e.g. Kotilainen *et al.* 2000) and then used directly for chemical analysis.

Because the Bornholm Basin is situated close to the island Bornholm where at times intensive fishery was conducted and after World War II dumping activities were carried out, sediment corers very likely may have penetrated disturbed sediment areas. Therefore, before a clear sedimentation pattern can be established using other data, core geochemistry may be invalidated and of limited value. A most sensitive indirect method to check whether the cores have disturbed sediments is the study of the depth distribution of naturally occurring radioisotope ^{210}Pb and of anthropogenic radioactive isotopes such as ^{137}Cs.

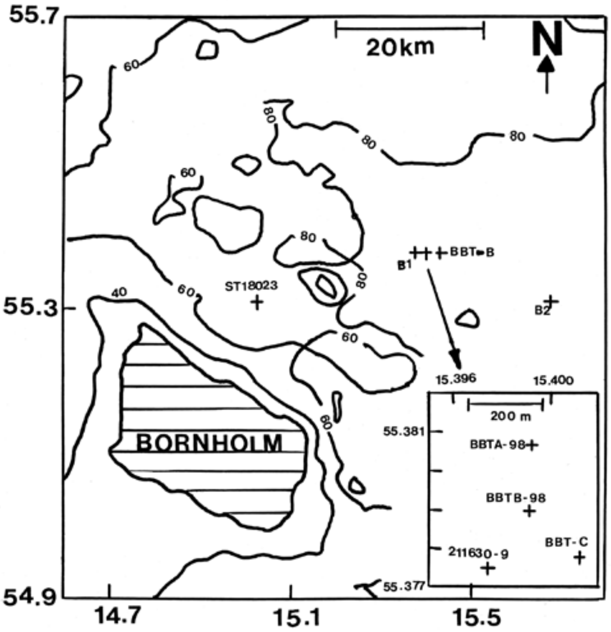

Fig. 1. Sampling sites for cores used in the investigation.

Side scan sonar investigations around the central sampling location showed extensive trawling marks suggesting that trawling boards reached at least one meter into the sediment. The systematic side scan sonar survey suggests also that the sampling area may have been used as a dumping site from stationary ships. The sediments from the Bornholm Basin are often bioturbated and shells and open burrows are observed. It is therefore crucial that the state of the sediment deposition with depth should be studied with great care.

ANALYTICAL PROCEDURES

Dating

^{210}Pb/^{137}Cs dating (Pb/Cs) was used on the short sediment cores. The technique applies direct gamma–ray spectrometry of the isotopes ^{210}Pb and ^{137}Cs. A description of the technique can be found in the literature (e.g. Kunzendorf *et al.* 1998). Briefly, the ^{210}Pb dating instrumentation consists of ultra–low background Ge (p and n–type) detectors and with remote construction of detector and detector preamplifier system. A lead shielding of the systems of 10 cm old (Boliden quality) lead with an overall activity of less than 50 Bq/kg was used together with a 5 mm thick Cu encapsulation. The dating systems were calibrated against samples with known ^{210}Pb and ^{137}Cs activities.

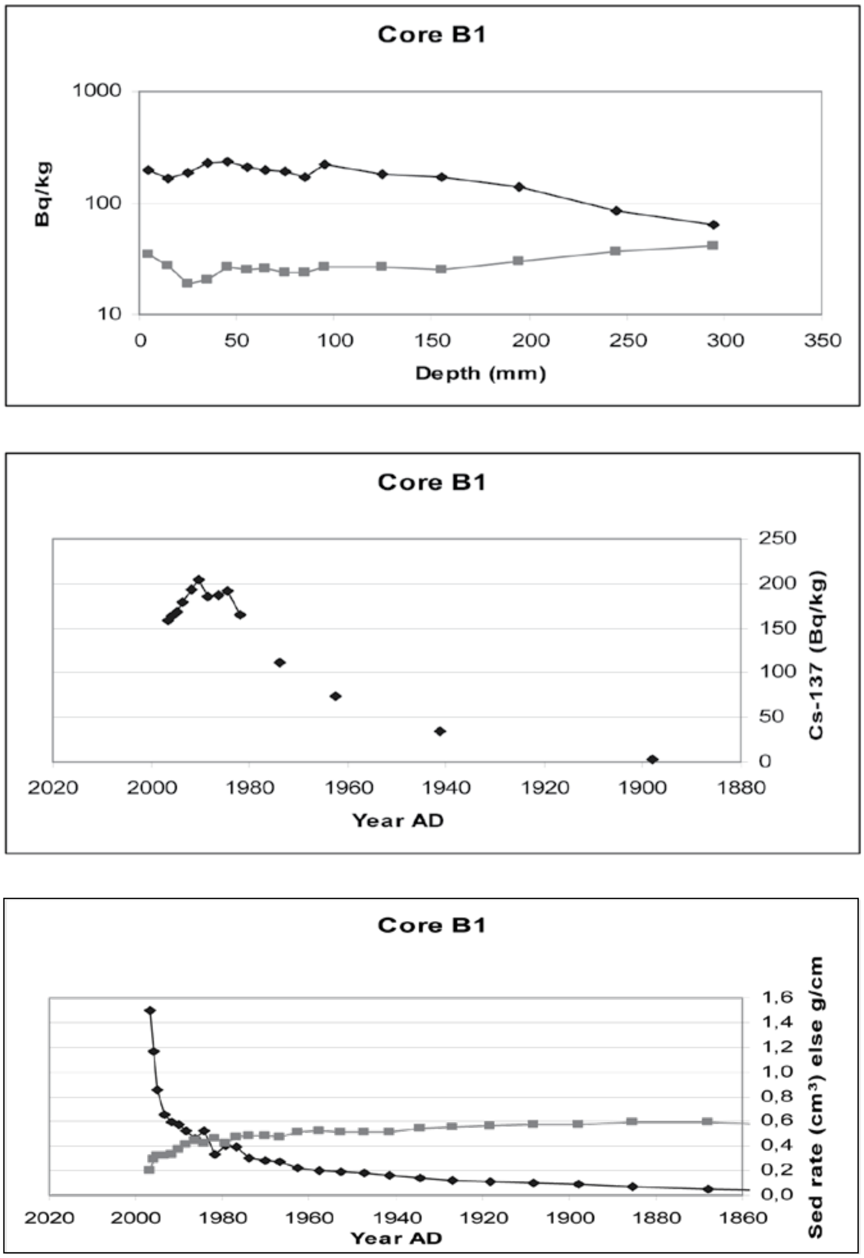

Fig. 2. Upper part of the figure is ^{210}Pb total (diamonds) and supported activity (quadrates), second part is ^{137}Cs over time, and lower part is sedimentation rate in cm/year (diamond symbol) and bulk density (quadratic symbols) along core B1.

Freeze–dried slices from short sediment cores were homogenised and dry sediment material was filled into polyethylene sample containers before counting low–energy gamma radiation. Usually, at least 5 g of sample material was used for gamma–ray spectrometry but because uppermost slices have reduced bulk densities due to increased fine fractions, less sediment material had to be used for the counting. Tightly closed sample containers were then stored for about 3 weeks to allow for eventual re–establishment of radioactive equilibrium after possible radon escape from the sample material. Rn escape was only observed in very few cases stemming probably from chemical or physical attack on Rn containing mineral grains. The most important factor with ^{210}Pb detection is however to reduce self–absorption of the 46.5 keV ^{210}Pb gamma–rays within the sample or on its way to the detector as much as possible. An important feature here is the use of nearly equal filling heights of the sediment samples. Because samples had to be counted at least one day, turn–around figures for the dating facility are low and this makes the dating expensive. Therefore, of a 30 cm long sediment core only about 10 one-cm sections were counted.

Using bulk dry sediment densities (dry weight divided by wet volume of the sediment slice) and unsupported ^{210}Pb activities (supported ^{210}Pb subtracted from the total ^{210}Pb activity), a modified constant rate of supply (CRS) model was applied (e.g. Appleby, Oldfield 1992). Sea salt corrections were not introduced because of their difficult quantification. However, sea salt was monitored indirectly by Br concentrations also determined in the sediment samples.

^{137}Cs was determined in the same measurements and dating results could therefore be compared and/or adjusted according to the occurrences of known ^{137}Cs markers (Chernobyl accident with a maximum in 1986; Sellafield outlets peaking in 1975; and nuclear bomb testing at maximum in 1963). Fig. 2 shows both unsupported ^{210}Pb and ^{137}Cs activities along sediment core B1.

An age model for the long core 211630-9 was constructed using both the ^{210}Pb modelling results, palaeomagnetic measurements calibrated against a 'master curve' from annually laminated lake sediments from Lake Pohjajärvi, Finland, and ^{14}C AMS dating results (e.g. Andrén *et al.* 2000; Kotilainen *et al.* 2000).

CHEMICAL ANALYSIS

A modified energy–dispersive X–ray fluorescence (EDX) technique using radioisotopes for characteristic X–ray excitation was applied. A Si(Li) detector system was used coupled to a sample changer with a capacity of 48 samples. Samples were, if possible, analysed in the same sample containers that were also used for the palaeomagnetic measurements, i.e. the bottom of the sample containers comprised a very thin polyethylene film to reduce self–absorption of characteristic X–rays produced in the sample. The system has been described elsewhere (Kunzendorf 1979) but an available conventional least–squares fitting unit, AXIL, was used to evaluate the complex characteristic X–ray spectra. The system was then calibrated against recommended values of 28 international geological reference materials. Measuring times of one hour per sample and two different radioisotope sources were applied. In this way, major elements K, Ca, Ti, Mn and Fe and minor and trace elements V, Cr, Ni, Cu, Zn, Ga, As Br, Rb, Sr, Y, Zr, Nb and Mo were determined on a routine basis.

RESULTS AND DISCUSSIONS

The short cores

Only the dating results for core B1 are given in Table 1 and they are plotted in Fig. 2. Characteristically, all short cores showed slowly declining ^{210}Pb activity curves generally expressing high sedimentation rates but such curves may however also occur in disturbed sediments. Some of the short cores showed irregular declining total ^{210}Pb curves. Especially, ^{137}Cs curves of cores B2, BBT-A98 and BBT-C (all not plotted) show continuously with depth decreasing activities with no indication of a Chernobyl peak and they must therefore be regarded as disturbed sediments. Contrary, cores BBT-B98 and BBT-B show ^{137}Cs peaks at about 10 cm depth and then increasing activities towards the sediment surface. Such graphs suggest that the surface 5 cm probably were removed at some time and other, older surface material was deposited afterwards. In conclusion, because the sampling sites are relatively close, core B1 data only were used in the following discussions.

Table 1. Selected data for the cores taken in the Bornholm Basin.

Core name	Cruise	Longitude (degree E)	Latitude (degree N)	Water depth (m)
B1	Aranda 4/97	15,37483	55,37833	92,5
B2	Aranda 4/97	15,675	55,31217	92
BBT-B	Kottsov-97	15,43074	55,3776	93,2
BBT-C	Kottsov-97	15,40121	55,3777	93,6
BBTA-98	Aranda	15,39923	55,38065	92
BBTB-98	Aranda	15,39912	55,37898	93
211630-9	Kottsov-97	15,39785	55,3773	93,5

Modelling the data (Table 2, Fig. 2) for core B1 shows that the ^{137}Cs peak is situated chronologically in the mid–1980s and that ^{137}Cs activity has been declining ever since (Fig. 2). The high sedimentation rates observed in the upper 4 cm of the core (Fig. 2, lowest part of the figure) are the result of low surface sediment particle density at relatively constant total ^{210}Pb activities. More advanced modelling may give better estimates for the surface but because of the generally disturbed sediment surfaces in the Bornholm Basin due to often occurring anthropogenic activity there is little reason to refine the modelling. In general, however, sedimentation rates have increased during the last century.

Table 2. Total ^{210}Pb, supported ^{210}Pb, unsupported ^{210}Pb and ^{137}Cs along core B1. The modelled age for each section is also given.

Depth (cm)	^{210}Pbtotal (Bq/kg)	^{210}Pbsupp. (Bq/kg)	^{210}Pbuns. (Bq/kg)	^{137}Cs (Bq/kg)	Modelled age
0,5	199,7	34,9	164,8	159,4	1996,7
1,5	165,5	27,7	137,8	163,6	1995,9
2,5	185,7	18,8	166,9	168,0	1994,9
3,5	228,7	20,5	208,2	179,1	1993,5
4,5	235,9	26,6	209,3	193,5	1991,9
5,5	209,6	25,0	184,6	204,0	1990,2
6,5	198,7	25,7	173,0	184,8	1988,4
7,5	193,4	23,6	169,9	186,5	1986,3
8,5	173,1	24,0	149,1	192,3	1984,3
9,5	220,8	27,1	193,7	164,9	1981,8
12,5	183,6	26,9	156,7	111,1	1973,7
15,5	172,3	25,4	146,9	74,2	1962,5
19,5	138,8	30,4	108,4	34,5	1941,3
24,5	84,1	36,8	47,3	2,4	1897,9
29,5	63,8	41,1	22,7	0	

This compares with the data for more than 20 core samples taken in the Bornholm Basin and presented by Christoffersen *et al.* (2007). According to these authors bottom water runs along the northern rim of the Christiansø Saddle and produces a wedge when progressing towards the central basin. In the form of a contour current water eroded on its path the southern flanks of the basin and sediment accumulation was mainly in the northernmost areas of the Bornholm Basin. Wedge sediment accumulation has been going on during the marine Holocene. The bulk surface sediments of most short cores have between 5 and 6 % total organic carbon (TOC). From grain size studies it may be concluded that sand–size particles are preferably deposited from water transported along the rim but finer sediments travel longer to the central basin.

The results of Cu and Zn analysis along the dated core B1 are shown in Fig. 3 and those for K and Mo

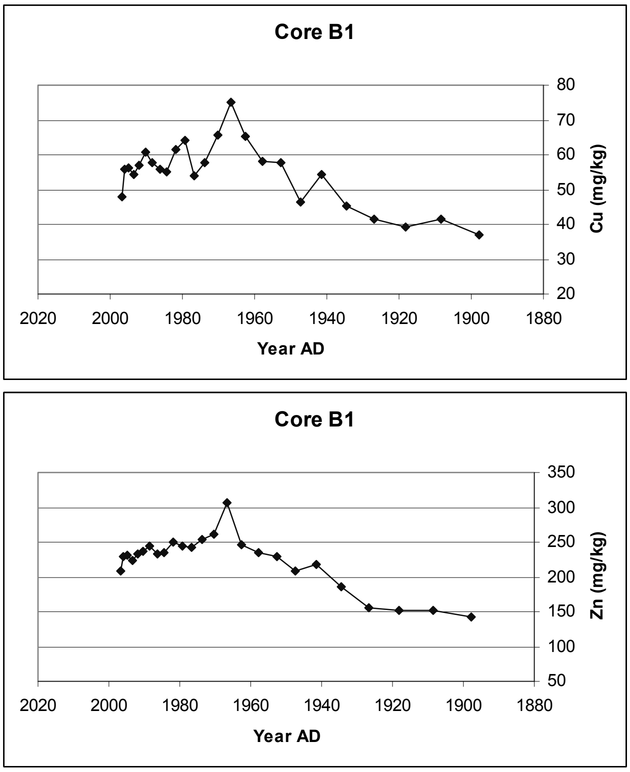

Fig. 3. Cu (upper graph) and Zn distribution during the past 100 years.

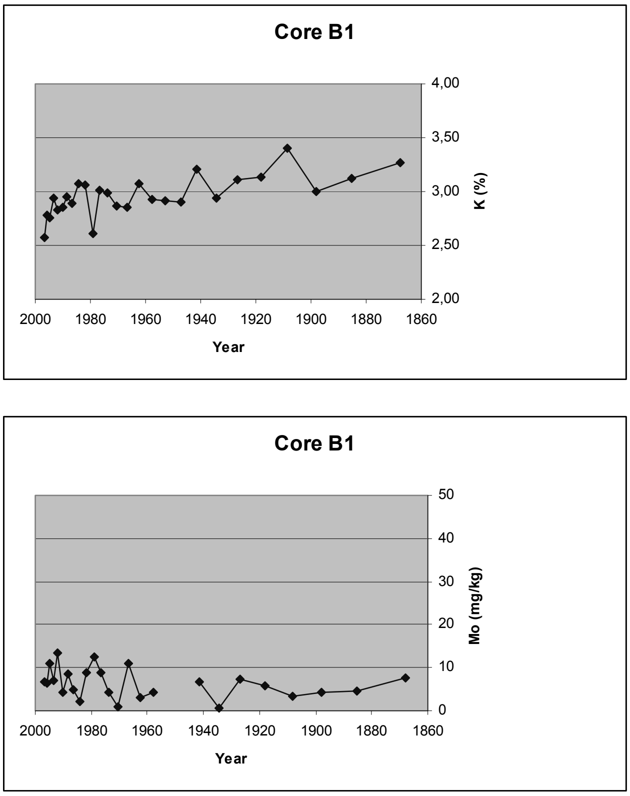

Fig. 4. K (upper curve) and Mo against time in core B1.

in Fig. 4. For both trace elements (Cu and Zn) a clear trend is observed. It appears that since about 1920 Cu values increased by a factor of about 2 and so did the Zn values. There is a maximum of Cu and Zn around the end–1960s which may suggest an ongoing decrease of industrial activities and the reduction of the heavy metal load to the Bornholm Basin. A decreasing trend is observed in the uppermost sediments, i.e. a slight decline. However, the decline may be temporary because data from after 1997 were not available and in our time Cu and Zn values may have increased again.

Our results may be compared with data given in the literature. Struck *et al.* (2000) discussed the increased input of nutrients in the Baltic Sea area stemming from the much increasing agricultural and industrial activity after especially the 1950s. For this purpose, nitrogen and carbon isotopes were studied in Pb/Cs dated short sediment cores from the Odra estuary, the Arkona Basin, the Bornholm Basin and the Gotland Basin. While there is an increase of $\delta^{15}N$ in the sediments in the first three areas over the past 80 years, the significantly lower values in the upper sediment part from the Gotland Basin shows significantly lower values. The authors suggest nitrogen–fixing cyanobacterial blooms being responsible for a lower $\delta^{15}N$ value. Plankton blooms were also found responsible for heavier $\delta^{13}C$ in three of the four areas with the Arkona Basin being an exception.

Action of waves and currents transports organic matter to the open sea where it finally settles on the ocean floor. According to Christoffersen *et al.* (2007) the organic matter accumulation rate in Baltic Sea sediments is mainly by biodegradation followed by wave erosion and density currents and final particle settling in depositional centres. The Bornholm Basin with water depths exceeding 90 m is such a deposition centre with sediments rich in organic matter (e.g. Christoffersen *et al.* 2007). The authors argue that previous studies have focused on too few samples, i.e. too few sediment cores, to describe the complicated sedimentation processes that include strong and varying bottom currents. However, the most important problem is very likely the occurrences of disturbed sediment surfaces to allow meaningful geochemical conclusions.

The long core

The dominating feature for the Baltic Sea is, as already mentioned, the existence of a permanent halocline, for the Bornholm Basin occurring at 40–50 m water depth (e.g. Sohlenius *et al.* 2001). After the last glaciation of the Baltic Sea two brackish and two freshwater periods have occurred, and at present the brackish Litorina Sea stage continues.

As regards the Bornholm Basin, the above authors focus on the same coring station, 211630, as in the present study. They have divided the cores into four general lithological units where the uppermost unit (IV) for the Bornholm Basin down to about 5.9 m is characterised by homogeneous mud. They report the occurrence of Mn and Mo in the Litorina mud samples where Mn is usually bound in the mineral rhodochrosite. Palaeoredox conditions determine the distribution of traces in the sediments. They also used shallow–seismic data from a detailed methane mapping of the basin. Interestingly, some cores have only Pleistocene lag deposits and are interpreted as sediments with no Holocene deposition. The detailed seismic study suggests that bottom water inflow into the Bornholm Basin has been an ongoing feature over the marine Holocene and has also generated a wedge–formed sediment layer with high sedimentation rates. Contrary to the formation of laminated sediments in the Gotland Basin (Vallius, Kunzendorf 2001) there are no long oxygen depletion periods observed and hence bioturbation is not depressed. An important geochemical study mainly of long sediment cores from the Gotland Basin has also been published (Huckriede *et al*. 1995).

Salinity and Bromine

As already mentioned, to obtain a reliable age model based on ^{14}C for the sampling station 211630, bulk sediments of core 211630-13 and *Macoma* shells from core 211630-9 were used. These data have been published by Andrén *et al.* (2000). Interpolation between these data down to 560 cm was carried out (Fig. 5). According to Andrén *et al.* (2000), diatom preservation in sediments from the Bornholm Basin is generally good. The ^{14}C dates may however be influenced by reworked old carbon and therefore all the dates were corrected by 400 years. The chemical data for core 211630-9 (Table 3) were then plotted against the calibrated ^{14}C ages (Figs 6, 7).

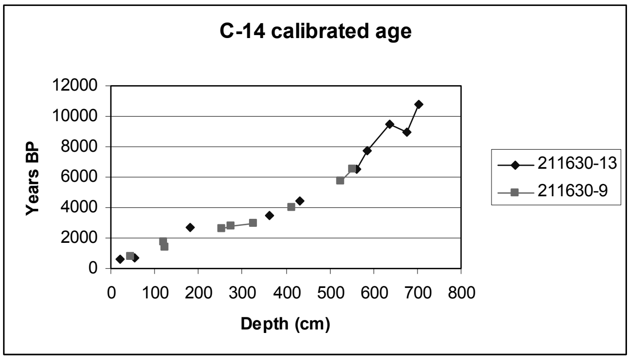

Fig. 5. ^{14}C age data for the central Bornholm Basin exemplified by cores 211630 according to Andrén et al. 2000.

First influence of saline water was reported to have occurred 8900 years BP for the Bornholm Basin (Sohlenius *et al.* 2001; core 211630-13). In core 211630-13 there is a change to a brackish–marine flora at about 7500 BP. According to the age model used by the authors, this is equivalent to a core depth of > 650 cm and is therefore not recorded in the sediments of the core 211630-9 which terminates at about 560 cm.

In general, the transition from the Ancylus Lake to the Litorina Sea stage was not abrupt when the Baltic Sea became brackish. Clay sediments were replaced by organic C–rich mud. Hence the transition of Ancylus Lake to Litorina Sea sediments was marked by a significant increase of TOC, and the transition being then relatively abrupt. Salinity stratification prevents seasonal mixing of the water mass. TOC enrichment is due to a higher productivity and better TOC preservation in the Litorina sediments.

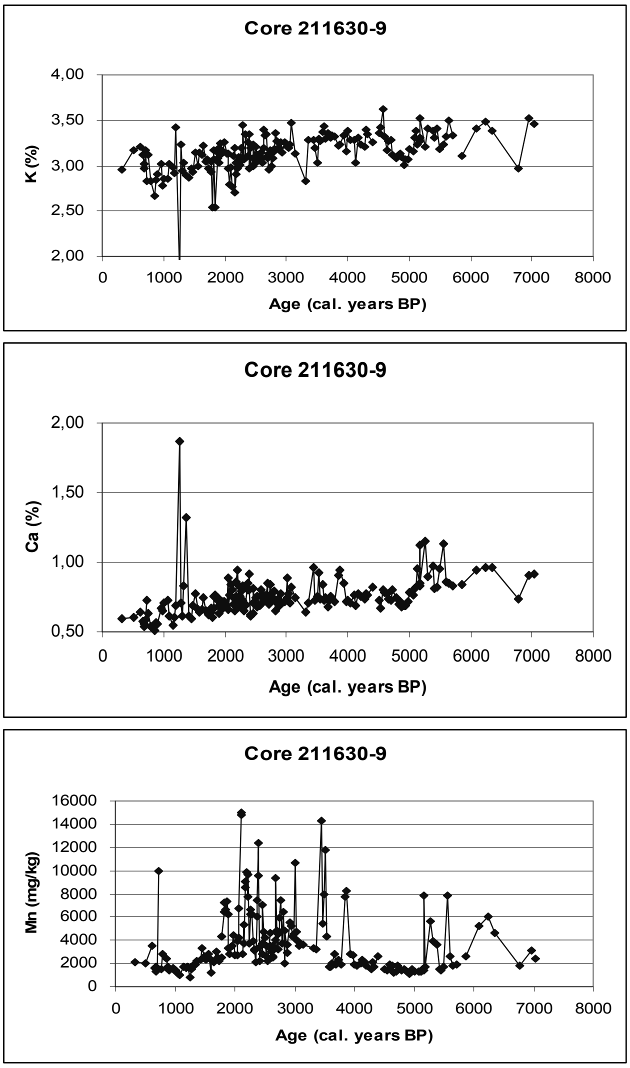

Fig. 6. K, Ca and Mn along core 211630-9

During the main Litorina Sea stage which proposedly occurred between 7850 and 2750 cal. years BP, several salinity changes (transgressions) were reported. Interestingly, it was also reported that the main Litorina Sea Stage in general was characterised by higher salinities than found in the present Baltic Sea. Using the ^{14}C dating results of long cores from the sampling site 211630 (e.g. Andrén *et al.* 2000) the transition of the Litorina Sea stage to present sediments may be viewed by the trace element Br which may flag the salinity of the waters persistent at sedimentation times. It has been reported that near–bottom water salinity over the years is comparable to the deep layer salinity (Stryuk *et al.* 1995). The mechanism of salinity transport from the North Sea area is facilitated during remaining north–westerly storms pressing saline water at depth to the Bornholm Basin and pushing older less saline bottom water via the Stolpe Channel farther to the north.

Table 3. Selected chemical elements along core B1 from the Bornholm Basin.

Depth	K	Ca	Ti	Mn	Fe	Cu	Zn	Br	Rb	Sr	Zr	Mo
cm	(%)	(%)	mg/kg	mg/kg	(%)	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
0,5	2,57	0,58	3119	5590	4,34	48	209	431	138	135	110	7
1,5	2,78	0,55	3534	2102	4,57	56	230	392	147	124	134	6
2,5	2,76	0,55	3441	2513	4,55	56	232	389	160	127	133	11
3,5	2,94	0,57	3603	4433	4,70	54	224	390	149	126	127	7
4,5	2,83	0,60	3471	5855	4,92	57	233	415	145	129	126	13
5,5	2,85	0,53	3539	1790	4,55	61	238	376	132	123	125	4
6,5	2,96	0,55	3778	1079	4,53	58	245	352	133	107	127	8
7,5	2,90	0,56	3807	2173	4,67	56	233	337	134	113	139	5
8,5	3,07	0,58	3762	2100	5,29	55	235	340	126	115	124	2
9,5	3,06	0,55	3771	2095	5,25	62	250	320	128	106	125	9
10,5	2,61	0,53	3480	1622	4,78	64	245	337	142	131	127	13
11,5	3,01	0,53	3829	1155	4,90	54	243	315	134	104	137	9
12,5	2,99	0,56	3714	1323	5,57	58	253	307	143	119	136	4
13,5	2,87	0,57	3602	1402	5,21	66	262	305	141	120	141	1
14,5	2,86	0,57	3396	1415	5,40	75	306	314	129	106	126	11
15,5	3,08	0,53	3688	1311	5,02	65	245	297	134	111	135	3
16,5	2,93	0,54	3727	1233	4,62	58	236	293	154	125	145	4
17,5	2,91	0,55	3609	1741	4,85	58	229	291	152	118	142	
18,5	2,91	0,53	3589	2588	5,16	46	209	279	142	117	144	
19,5	3,21	0,63	3976	2764	5,62	55	219	287	149	119	134	7
20,5	2,94	0,60	3718	3257	5,52	45	185	265	148	129	136	1
21,5	3,11	0,58	3893	2829	5,44	41	156	262	126	108	136	7
22,5	3,14	0,61	3787	3977	5,27	39	152	267	142	120	137	6
23,5	3,40	0,64	4169	4560	5,77	41	151	272	135	111	140	3
24,5	3,00	0,66	3887	6245	5,50	37	142	258	140	117	132	4
29,5	3,12	0,60	4067	1813	4,92	46	133	295	141	110	135	5
34,5	3,27	0,59	4148	2376	5,69	48	127	277	144	120	131	8
39,5	3,08	0,75	3507	12327	5,60	38	113	251	127	121	126	2

We have therefore chosen the trace element Br as a marker element for salinity because this element, first of all may be determined easily by the analytical method (EDX). Also, the element is usually occurring together with chlorine in saline waters. Our plot of the trace element bromine (Fig. 7) is backing the observation of higher salinities in Litorina Sea sediments because Br is measured to be more than 25% higher at times with increased salinities. As seen in the figure, the Br curve may display not more than four transgressions, i.e. intervals with increasing Br, but not about six transgression as mentioned by Andrén *et al.* (2000). The maximum salinity being reported to have occurred between 6000 and 4000 cal. years BP is also found in the Br plot which shows the highest values between 5100 and 4300 cal. years BP. The curve for Br shows also that the sediments from the initial Litorina Sea (low Br) turn into brackish water influence between about 6200 and 5000 years BP. Apparently, during the time span between 5000 and 4000 years BP salinities are declining somewhat again. Thereafter, salinity increases again between 4000 and 3000 years BP, followed by relatively constant salinity values up to present times. This compares with the diatom assemblage zones (DAZ) given by Andrén *et al.* (2000). A gradual decrease is observed between 420 and 360 cm sediment depth after which Br increases again towards the transition to the Post–Litorina stage (280 cm).

According to Andrén *et al.* (2001) the succession of sediments in core 211630-9 contains the 5th–7th diatom assemblage zones, i.e. sediments of the Litorina Sea stage (about 7850–2750 cal. yr BP), of the Post–Litorina Sea stage (2750–800 cal. yr BP) and sediments of the recent Baltic Sea stage (about 800 cal. years to present). Although the chronological estimates are the results of interpolation between measured ages, the sediment geochemical data may be discussed on this basis. Accordingly, the change from the Post–Litorina Sea stage to the present sediments starts with a decline of the warm water species in the diatom assemblage, i.e. at about 65 cm core depth. Geochronologically, this corresponds to the begin of the Little Ice Age. The Litorina Sea stage lasted from 2750 to 800 years BP according to the authors.

Terrestrial input

Because the sediment core was taken from the central Bornholm Basin, the relatively short distance to the Scandinavian hinterland is supposed to be a significant source of sediment particles. There are however no major rivers from the Swedish mainland and sediment transport must therefore be regarded normal surface sediment drainage with superimposed airborne particle transport and secondary transport of already deposited sediment particles.

Characteristically, potassium contents of the sediments along core 211630-9 (see Fig. 6) show an upwards decreasing trend. A first explanation for this behaviour would be with sediment depth increasing density, for instance caused by normal sediment compaction. However, sediment cores from the Baltic Sea were usually found to show an up to 10 cm thick very fine particle layer on top followed by a largely increasing density over the next few cm which at depth then is only increasing very little. Such a curve is however not displayed by the K data. One could also argue that the K curve is closely displaying the terrestrial material input to the sediments which also was gradually decreasing since about 6000 cal. years BP, i.e. the time span covered by the sediment core. It may also be that more and more fine particles were added to the sediments and in that way diluting the terrestrial part of the sediment. This is somewhat backed by the slightly upwards increasing TOC values in the core investigated by Andrén *et al.* (2000). Why there is this increase of TOC since 6000 years BP is however not clear.

Because the deposition of element K is through K feldspar containing particles mainly it would mean that the decline of K during the past about 6000 years would be caused by less and less terrestrial material being transported to the Bornholm Basin. It could perhaps also be interpreted as the visible consequence of uplift of the Scandinavian mainland favouring deposition of more and more fine material. In this respect, the observed curves in Fig. 4 and 6 may be the result of post–glacial uplift. However, the explanation for K decline over time must await further studies.

Other major elements

As regards the major element Ca (see Fig. 6), there is a significant decrease of the element from the lowermost Litorina Sea Stage to the present. The curve for Ca is more complicated and shows a decrease of the element during Post–Litorina time. It is usually found that Ca which is more concentrated in saline than in fresh water may also be a salinity indicator.

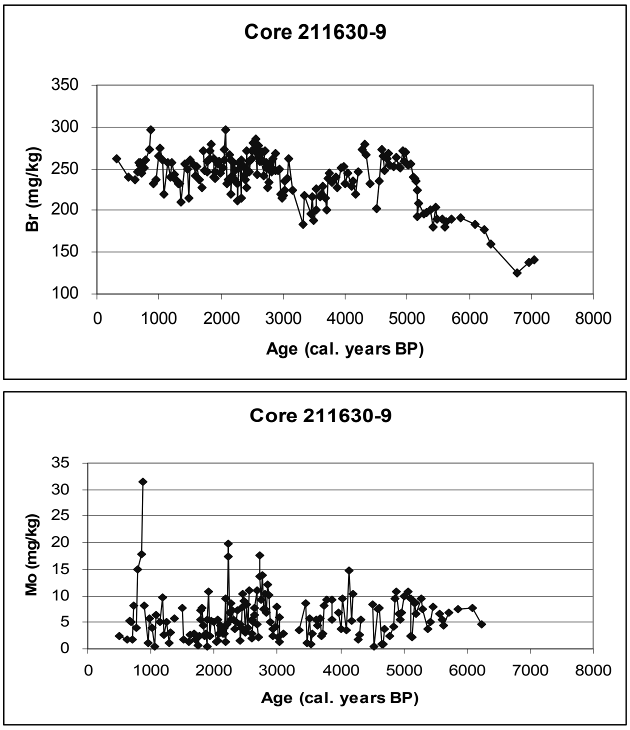

Fig. 7. Br and Mo along core 211630-9.

Manganese and Ca have been found to be concentrating in Baltic Sea sediments, especially in the Gotland Basin (e.g. Huckriede *et al.* 1995; Kunzendorf *et al.* 2001). The mechanism of accumulation there is co–precipitation with the mineral rhodochrosite [$(Ca,Mn)CO_3$] in connection with oxic deep water inflow to the deep basins. This process requires anoxic conditions prevailing before the deep water inflow. Such conditions have not been reported in greater detail for the Bornholm Basin which mostly is oxic over longer periods of time. Therefore, the curves for Ca and Mn (see Fig. 6) show little co–variation, although there is perhaps as shown in the figure rhodochrosite growth in the earliest Litorina Sea stage, especially during periods 3500–3900 and 5200–5600 cal. years BP.

Mn elevations in Bormholm Basin sediments may be in the form of hauerite (MnS_2) and not as rhodochrosite, and in such cases no Ca–Mn covariance in the curve is observed. Fig. 6 presents a high Mn content section between 2000 and 3000 cal. years BP.

Molybdenum

Contrary to the data obtained for long cores from the Gotland Basin (e.g. Kunzendorf *et al.* 2001) there is little evidence that Mo plays a role in sediments of the Bornholm Basin (see Fig. 7). Over the time span considered there is very little Mo, usually less than 10–20 mg/kg, i.e. close to the detection limit of the analytical method. This has also been expected because there are no laminated sediments and shifting oxic/anoxic periods are rare. This is in contrast to the observations made in the Gotland Basin where extremely high Mo contens are observed (e.g. Kunzendorf *et al.* 2001).

General observations

Some general remarks may be important which are based on the previous work regarding the Baltic Sea. According to Andrén *et al.* (2001) the Litorina Sea stage transits gradually into the Post–Litorina Sea stage and this is most reliably marked by a decrease of siliceous microfossils. High productivity was deduced from peaks of *Chaetoceros* resting spores and marine plankton organisms (ebridians). The observed peaks for these species shown in Andrén *et al.* (2001) corresponds time wise to a known warmer period between AD 900–1300 (1050–650 cal. yrs BP). The decline of siliceous microfossils may be expressed by increased Ca in the sediment at about 1200 cal. yrs. BP.

The recent Baltic Sea stage starts at the known Little Ice Age (14th to 17th century) corresponding to about 800 cal. yrs BP (Andrén *et al.* 2001). In general, the Little Ice Age in Scandinavia is by dendrochronology most probably ascribed to the 16th and mid–18th centuries. Because of the increased occurrence of marine plankton organisms a colder climate is suggested. The geochemical data for the Bornholm Basin core 211630-9 show no clear features at corresponding sediment depths.

Development of a brackish–marine flora was developed in combination with an increase in bottom water salinity (Andrén *et al.* 2001). These authors point to the occurrence of significant cyanobacterial blooms probably caused by a high primary productivity during these times which however are not backed by high Mo in the long sediment core, although there is elevated Mo in the uppermost part of the long core (see Fig. 6).

According to Andrén *et al.* (2000), the total carbon and nitrogen increase observed at about 600 cm core depth corresponds to about 8000 cal. yrs BP. The increase is about a factor of 3 for total carbon. This means that during the Initial Litorina Sea stage primary production increased significantly. As regards the first transgression of marine water into the Ancylus Lake this has been proposed to have also occurred at about 8000 cal. years BP. As already mentioned the investigated core was too short to generate geochemical data. The first inflow of marine water into the Ancylus Lake was not by one single pulse or event but probably by several different pulses. During the main Litorina Sea stage several transgressions were reported but the maximum salinity was observed between 6000 and 4000 cal. years BP and this has been discussed above in this paper. In general, little change in the sedimentation environment over the entire time was found.

The Bornholm and Arkona Basins were frequently oxygenated during the Holocene and also bioturbation is frequently observed. In general, in the deepest parts of the Baltic Sea (>250 m water depth) hypoxia conditions have been present during the past ca. 8500 years (Zillén *et al.* 2008). In the shallower areas (water depths < 250 m) three hypoxia periods have been observed: 7000–6000 cal. yr BP, 4000–2000 cal. yr. BP, and AD 1200–1900. The time interval of 7000–6000 cal. yr BP is characterised by, e.g. salinity decline, lower TOC coinciding with glacier advance in northern Sweden. Homogeneous sediment formation is also observed between 4000 and 2000 cal. yr BP, characterised by lower salinity values. Between 2000 and 800 cal. yr BP laminated sediments occur again.

CONCLUSIONS

Six short and one long sediment core have been studied from the Bornholm Basin. Short sediment cores are often disturbed by natural and/or anthropogenic reworking of sediments. Visual inspection of the short cores is not enough to select the right cores for further sediment studies. A good method to outline undisturbed sediment cores is the combination of visual inspection and radioactivity measurements, e.g. radiometric dating.

Cu and Zn data from a short core show increasing values stemming from industrial outlets starting in the 1920s and peaking in the 1980s but show at present a decline as a result of probably more controlled marine outlets. The potassium decline in the long sediment core since about 6000 cal. years BP suggests that the terrestrial supply to the sediments is being diluted by an input of fine particles, most probably airborne supply from the European continent.

Salinity changes during Litorina Sea, Post–Litorina Sea and the present are viewed by the salinity indicator Br. Chemical data suggest that salinities did not change abruptly but transitionally over several hundreds of years.

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