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# Post-glacial history of sea-level and environmental change in the southern Baltic Sea



***Marloes Kortekaas***

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# LUNDQUA Thesis 57

## Post-glacial history of sea-level and environmental change in the southern Baltic Sea

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**Marloes Kortekaas**

### Avhandling

Att med tillstånd från Naturvetenskapliga Fakulteten vid Lunds Universitet för avläggande av filosofie doktorsexamen, offentligen försvaras i Geologiska Institutionens föreläsningssal Pangea, Sölvegatan 12, Lund, fredagen den 30 mars 2007 kl. 14:15

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Title and subtitle Post-glacial history of sea-level and environmental change in the southern Baltic Sea		
<p><b>Abstract</b></p> <p>A new palaeoenvironmental record of the post-glacial history of the southern Baltic Sea (~14 ka to present) is presented. During this period, large water level and salinity changes occurred in the Baltic Basin due to opening and closing of connections to the North Atlantic. Previous attempts to establish a detailed chronology for these palaeoenvironmental changes have been conducted mainly in coastal settings, where organic material for <sup>14</sup>C dating is abundant. Many of these records are, however, discontinuous due to large water level fluctuations. In the relatively deep water of the Arkona Basin (45 m deep) in the southern Baltic Sea the sediment record is expected to be more or less continuous, but lack of organic material for <sup>14</sup>C dating has impeded previous studies.</p> <p>Here, palaeoenvironmental change in the Arkona Basin is reconstructed on the basis of geochemical, sedimentological, mineral magnetic and palaeontological investigations. Additionally, independent physically based chronological control is, for the first time, obtained using Optically Stimulated Luminescence (OSL) dating on fine quartz sand from a ~10.86 m long sediment core. Tests of luminescence characteristics confirmed the suitability of the material for OSL dating and the ages agree well with the available AMS <sup>14</sup>C ages on shells; in contrast, bulk sediment <sup>14</sup>C ages are generally ~1000 years too old. Stratigraphic marker horizons in this deep basin are now absolutely dated, allowing comparison and testing of existing models of post-glacial Baltic Sea regional development.</p> <p>Glacial varved clay was deposited during the Baltic Ice Lake stage and a sand layer representing the Baltic Ice Lake drainage to the North Atlantic is dated to ~11.6 ka. This event is followed by a period of low water level and enhanced influence from the Oder River. A period of very rapid sedimentation occurs between ~10.9 and ~10.4 ka and is attributed to the Ancylus Lake transgression. A first anomalous slightly brackish water inflow is recorded at ~9.8 ka, but there is no clear evidence for fully brackish conditions until ~6.5 ka. At that time, the lithologic change to clay gyttja represents a distinct shift in the circulation mode, with the onset of a high-productivity, brackish circulation system in the southern Baltic. Post-depositional diffusion of sulphur from the clay gyttja most likely explains the presence of greigite (Fe<sub>3</sub>S<sub>4</sub>) concretions in the underlying silty clay unit.</p> <p>With this new chronology an anomaly appears between the classical model of the Littorina transgressions with brackish conditions starting ~8.5 ka, supported by studies in coastal lagoons, and our first clear brackish/marine influence occurring as late as ~6.5 ka based on studies performed in the deeper basins. This implies that the circulation system of the present Baltic Sea, with fully brackish conditions and the Danish-German Straits as the dominant inflow areas, only started from ~6.5 ka onwards.</p>		
Key words: Baltic Sea, Holocene, Littorina transgression, Optically Stimulated Luminescence (OSL), sea-level changes, mineral magnetics, greigite		
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# Post-glacial history of sea-level and environmental change in the southern Baltic Sea

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This thesis is based on four papers listed below as Appendices I-IV. All papers are submitted to peer-reviewed international journals. Paper I is reprinted with the permission of Elsevier Science Ltd. Paper IV is reprinted with the permission of Ancient TL. Paper II and III have been submitted to the journals indicated and are under consideration. Additional data is presented in Appendix V.

Appendix I: Kortekaas, M., Murray, A.S., Björck, S. and Sandgren, P., in press. OSL chronology for a sediment core from the southern Baltic Sea; a complete sedimentation record since deglaciation. *Quaternary Geochronology*.

Appendix II: Kortekaas, M., Björck, S., Bennike, O., Murray, A.S., Röbller, D. and Snowball, I.F. Late Weichselian and Holocene palaeoenvironmental changes in the southern Baltic Sea constrained by a high-resolution OSL chronology. Manuscript submitted to *Marine Geology*.

Appendix III: Kortekaas, M., Snowball, I.F. and Sandgren, P. The occurrence of ferrimagnetic greigite in Baltic Sea sediment and its implication for palaeoenvironmental interpretation. Manuscript submitted to *Geophysical Journal International*.

Appendix IV: Kortekaas, M. and Murray, A.S., 2005. A method for the removal of mica from quartz separates. *Ancient TL*, 23 (2), 43-46.

Appendix V: M. Kortekaas and A.S. Murray. Using luminescence to determine the timing of palaeoenvironmental change in the Bornholm Basin; some preliminary data.



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# 1. Introduction

## 1.1 Background

The periodic exchange of water between ice sheets and oceans has been the main contribution to sea level change during the Quaternary, resulting in sea level lowstands during ice ages and relative highstands during interglacials. Superimposed on these global regression-transgression cycles are the more local and regional fluctuations caused by changes in uplift and subsidence, and climate (Lambeck and Chappell, 2001). The rapid decay of continental ice sheets since the last glacial maximum (LGM) after  $\sim 19$  ka led to a global sea level rise of  $\sim 130$  m (Yokoyama et al., 2000), submerging many of the continental shelf areas until global sea level rise slowed down and ceased around 6 ka (e.g. Bard et al., 1996).

Some marine basins or seas are partially isolated from the world's oceans by a sill that restricts water exchange between the enclosed basin and the ocean. As a consequence, these basins have a distinctive hydrography, chemistry and biology (Anderson and Devol, 1987; Middelburg et al., 1991). When situated in arid zones, evaporation often exceeds the total input of fresh water in the basins, which may result in oxygenated and nutrient depleted bottom waters (Passier et al., 1998; Coulibaly et al., 2006). In humid zones, on the other hand, the nutrient supply via fresh-water input is relatively high and the basins may act as nutrient traps, often resulting in higher primary productivity (Anderson and Devol, 1987; Middelburg et al., 1991). When renewal of deep-water is slow, anoxic conditions may develop in the bottom waters (Middelburg et al., 1991).

The shallow spillways that connect these intra-shelf seas to the ocean imply that small changes in relative sea level can cause major changes in the circulation system of these basins. This sensitivity makes such basins suitable for high-resolution studies of global sea level as well as regional tec-

tonic and climatic changes. The effect of sea level rise after the LGM caused major water level and salinity changes in different semi-enclosed seas over the world (e.g. Middelburg and de Lange, 1989; Arz et al., 2003). These areas had been previously isolated from the oceans by a lower eustatic sea level, and basins with a positive water balance had become fresh. Global sea level rise inundated these freshwater basins again. Examples of intra-shelf basins that experienced isolation and inundation phases include the Black Sea (Ryan et al., 1997), Kau Bay (Middelburg and de Lange, 1989), the Yellow Sea (Kim and Kennett, 1998) and the Baltic Sea (e.g. Björck, 1995).

The Baltic Sea (Fig. 1) differs from other semi-enclosed seas in that the interaction between glacio-isostatic uplift, eustatic sea-level rise and deglaciation of thresholds has caused a complex four-phased development since the last deglaciation, with two alternating fresh and brackish water stages and different connection pathways to the ocean. In addition, the elongated Baltic Sea is made up of a series of progressively deeper and larger basins to the north, each separated by sills that control the inflows (Emeis et al., 2003). Transitions between the different phases are thus not abrupt or equally strong in the different sub-basins, but show a time-transgressive pattern along a north-south traverse; the trend in this pattern depends on the location of the Baltic/Atlantic passage (Sohlenius et al., 2001).

The post-glacial history of the Baltic Sea has been studied for more than a century (Gudelis and Königsson, 1979), but inconsistencies and conflicting datasets remain. The different nature of the various palaeoenvironmental records and uncertainties in their absolute and relative chronologies have resulted in different viewpoints. Most studies have been conducted in the deep central and northern basins (e.g. Andrén et al., 1999; Brenner, 2005; Sohlenius, 1996), while studies in the southern Baltic were mainly conducted in coastal settings with abundant remains

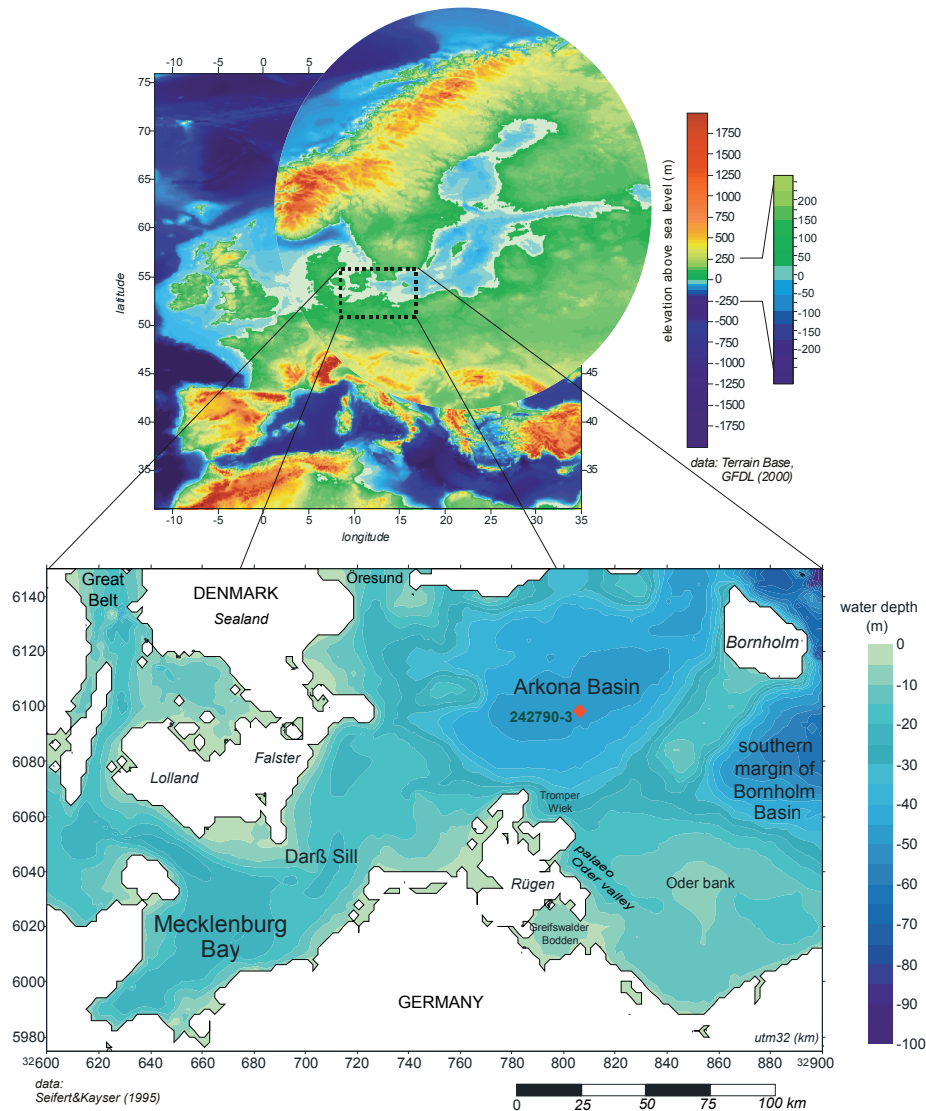


Fig. 1 Location of the study area in the southwestern Baltic Sea (adjusted from Bobertz, 2000 in Rößler, 2006).

of terrestrial plants for  $^{14}\text{C}$  dating (e.g. Berglund, 2004; Yu et al., 2005). Due to the large water level changes (up to 25 m) in the southern Baltic (e.g. Björck, 1995), these coastal records often contain discontinuities. Uncertainties in chronologies have arisen because earlier studies were based on  $^{14}\text{C}$  ages on bulk sediment samples, and varying amounts of reworked 'old' carbon reduce the accuracy of the age determinations (e.g. Kortekaas et al., in press; Björck et al., in press). In addition, the reservoir effect in the Baltic Sea is poorly known and is likely to have varied over time with

the changing salinities (Wastegård and Schoning, 1997; Hedenström and Possnert, 2001).

Although the southern Baltic Sea is surrounded by densely populated areas, and any future change in the Baltic will have their highest social impact there, high-resolution studies of palaeoenvironmental changes in this area are scarce. Reconstruction of the past frequency and magnitudes of sea level and salinity changes is important for predicting changes in the Baltic Sea in response to future climate change and human impact (Curry, 2006). The unusual physical and geochemical character-

istics of transitional facies in the Baltic Sea may be used as paradigm for other silled basins and transitional facies preserved in the geologic record.

## 1.2 Project Objectives

This project aims to reconstruct the Late Weichselian and Holocene environmental changes in the southern Baltic Sea (Fig. 1). The study focuses on a sediment core from the Arkona Basin (45 m water depth); supporting evidence is obtained from a similar sediment core from the Bornholm Basin. Both basins are deep enough to have remained water-filled even at the lowest sea-level stand, and thus one can expect continuous sedimentation since the last deglaciation. Furthermore, their position close to the shallow inlet area of the Danish and Swedish straits makes them particularly suitable for studying time-transgressive circulation changes.

Physical, sedimentological, geochemical and palaeontological methods are used to reconstruct palaeoenvironmental change. Independent physically based chronological control is based on Optically Stimulated Luminescence (OSL) dating, supported by a set of  $^{14}\text{C}$  dates and varve counting. This novel chronologic approach allows the comparison and testing of the validity of existing models of post-glacial Baltic Sea development.

The purposes of this study are two-fold, with both palaeoenvironmental as well as geochronological aims. More specifically the project aims are:

- To identify and target sediment records from the southern Baltic Sea that register continuous sedimentation since deglaciation.
- To obtain a detailed record of palaeoenvironmental change in the southern Baltic Sea.
- To investigate the suitability of the Baltic sediments for OSL dating.
- To establish an accurate, high-resolution age-depth relationship based on OSL dating, radiocarbon dating, varve counting and palaeomagnetism, and to compare and evaluate these different geochronological methods.
- To compare the palaeoenvironmental records with regional and global climate and sea-level records to infer causal relationships and processes.

## 2. Setting of the study area

### 2.1 The modern Baltic Sea

The Baltic Sea is a semi-enclosed estuarine marginal sea of the North Atlantic and its water exchange with the ocean is restricted by the shallow sill areas of the Danish and Swedish Straits (Fig. 1). It is positioned between approximately  $54^{\circ}\text{N}$  -  $66^{\circ}\text{N}$  latitude and  $10^{\circ}\text{E}$  -  $30^{\circ}\text{E}$  longitude with a surface area of  $412,560 \text{ km}^2$  and is considered to be the largest brackish water body in the world. The bathymetry is irregular with a succession of deeper basins to the north, each separated by a sill. The average depth is rather shallow (52 m), but the deepest basin (Landsort Deep) reaches a depth of 459 m (<http://www.io-warnemuende.de/>).

At present, salinity is primarily a function of the supply of fresh water from precipitation and from rivers draining the large catchment area ( $\sim 1,700,000 \text{ km}^2$ ) and the inflow of salt water from the Kattegat (Stigebrandt and Gustafsson, 2003). The annual freshwater input (including precipitation) is  $\sim 665 \text{ km}^3$  and the annual evaporation amounts to  $185 \text{ km}^3$ . Salt water from the Skagerrak-Kattegat flows into the Baltic Basin ( $470 \text{ km}^3/\text{year}$ ) through the Belt Sea with a sill at Darss (sill depth 18 m) and through the Öresund (sill depth 8 m), and spreads out at depth, successively intruding into the different sub-basins (Samuelsson, 1996; <http://www.io->

warnemuende.de/). As a result, the northernmost parts have the lowest surface water salinity and resemble freshwater environments (salinities of 1‰). Surface water salinity increases towards the south to 8-12‰. Within the basin, the water circulation is driven by the density differences of water masses and by wind (Emeis et al., 2003). Both the horizontal and vertical salinity gradients between the Skagerrak and Baltic Basin are steep and the mid-water halocline has a depth of <20 m in the Kattegat, ~30 m in the Arkona Basin, ~60 m in the Bornholm Basin and around 80 m in the Gotland Basins. Below this halocline the salinity increases to ~19-21‰ in the southern Baltic Sea (Piechura and Beszczyńska-Möller, 2004). The position and slope of the halocline is determined by freshwater runoff and wind. Any shift in the predominance of runoff versus deep-water inflow will shift the salinity gradient vertically and horizontally and will result in shifts of gradients in productivity and species composition (Emeis et al., 2003).

Occasionally, large inflows of salty oxygen-rich bottom-water occur. These inflow events are related to specific meteorological conditions and occur every few years, usually during the autumn or winter. Extended periods of easterly winds (usually associated with dry conditions in the catchment) drive the surface water out of the Baltic Sea and cause a pres-

sure deficit in the Baltic Basin. When such a period is followed by a low pressure system over the western North Atlantic and a high-pressure system over north-west Europe (with strong westerly winds), a wave of salty water flushes the deep basins (Börngen et al., 1990 in Andrén, 1999; Lass and Matthäus, 1996). Between these inflow events, the bottom waters quickly stagnate (Matthäus and Lass, 1995) and extensive areas of hypoxia and anoxia develop (e.g. Conley et al., 2002).

## 2.2 The pre-Quaternary bedrock

In contrast with the land areas of Sweden and Finland, the sea floor of the Baltic Sea consists mainly of sedimentary rocks. Only the basement of the northern and central western parts is dominated by crystalline Precambrian bedrock that gently slopes towards the SSE and disappears below Palaeozoic and Mesozoic sedimentary rocks of the East-European Platform (Winterhalter et al., 1981). The crystalline basement is generally characterized by an irregular topography formed by glacial scouring especially along fracture zones, while the sedimentary rocks in the south generally exhibit a smooth topography except for some erosional escarpments (Martinsson, 1979). The western part of the Baltic Sea is

*Table 1. Summary of the different stages of the Baltic Sea development with ages from the classical model (Björck, 1995; Yu et al., 2003; Berglund et al., 2005; all based on calibrated <sup>14</sup>C dating). Note that a possible opening of the lowland north of Mt. Billingen at ~13 ka is not included.*

Baltic stages	salinity	pathway	cal ka BP classical model
Littorina Sea	brackish	Öresund/Danish straits	8.5-present
Early Littorina Sea	fresh-brackish	Great Belt	10.1-8.5
Ancylus Lake	fresh	Närke Strait-Otteid/Göta Älv	10.7-10.1
Yoldia Sea	brackish	Billingen/Närke Strait-Otteid/Göta Älv	11.6-10.7
Baltic Ice Lake	fresh	Öresund	15-11.6

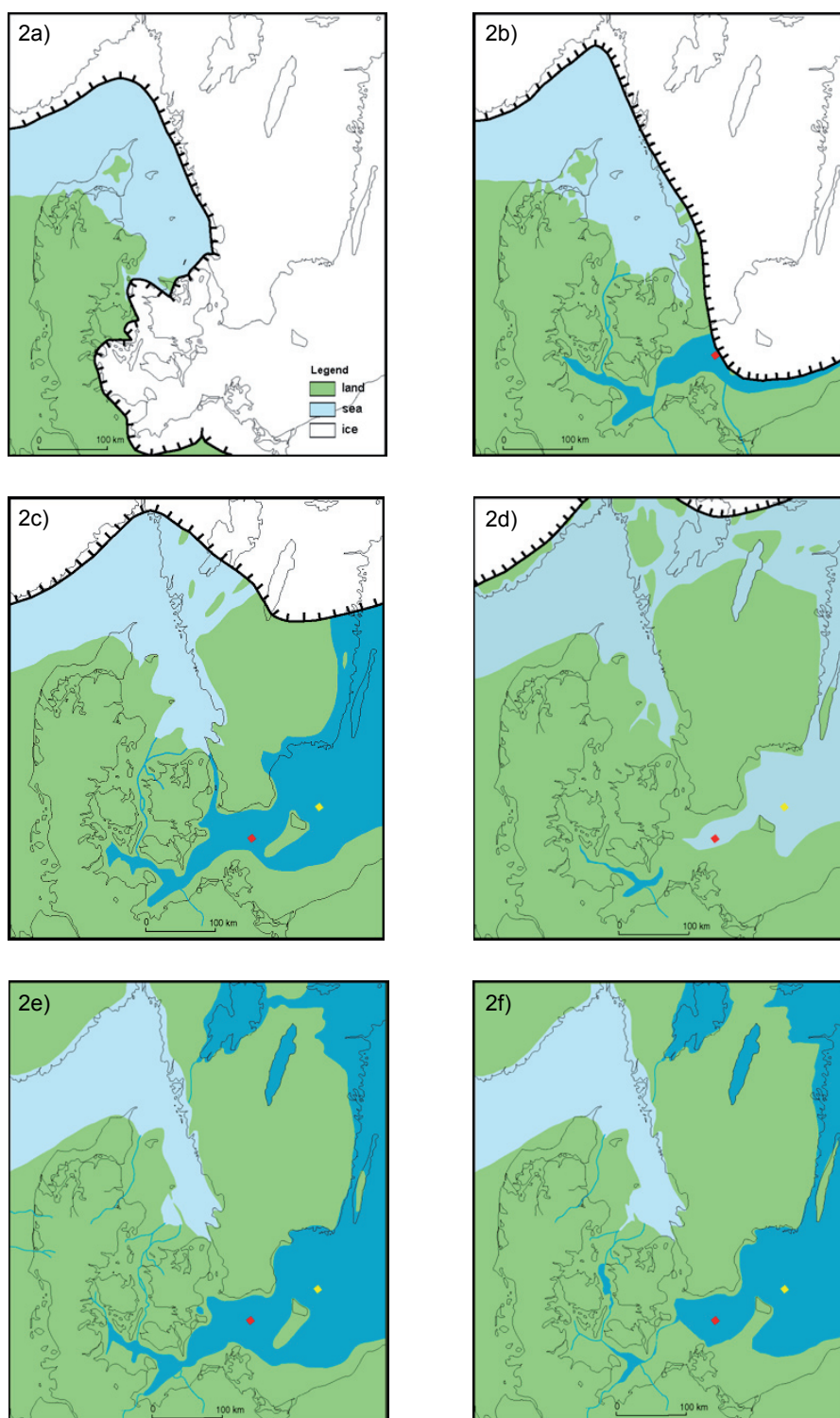


Fig. 2 Palaeogeographical maps with a) Late Weichselian glaciation, b) Baltic Ice Lake formation, c) Baltic Ice Lake, d) Final drainage of the Baltic Ice Lake and beginning of the Yoldia Sea, e) Ancylus Lake transgression, f) Ancylus Lake regression (adjusted from Jensen *et al.*, 2002). The core locations are shown by a red point (Arkona Basin: 242790-3) and a yellow point (Bornholm Basin: 243010-3).



affected by the Tornquist zone, a NW-SE trending deep-seated fault zone that separates the East European Platform from the Central European Platform (Puura et al., 2003).

### 2.3 Late Quaternary development

The interaction between glacial rebound and the simultaneous eustatic sea-level rise in the adjacent North Atlantic has governed the Late Weichselian and Holocene development of the Baltic Basin and caused major water level and salinity changes (e.g. Lambeck, 1999). Generally, the Baltic Basin history is separated into four stages representing intervals of either (i) water exchange with the North Atlantic or (ii) fresh-water conditions, without inflow from the Atlantic (Munthe, 1910). An overview of the classical model of the different stages of Baltic Sea development with relative water levels and connections to the North Atlantic is shown in Table 1. The closing and opening of the Baltic/Atlantic passages would provide natural and definite stage boundaries – if they could be reliably determined and dated. In the following section, the different stages will be briefly described.

#### *Baltic Ice Lake stage*

When the ice retreated in the southern Baltic at ~16 ka, melt-water filled the Baltic Basin and formed the freshwater Baltic Ice Lake (Fig. 2a-c) (e.g. Björck, 1995, Houmark-Nielsen and Kjær, 2003). Varved glacio-lacustrine clay was deposited along the margin of the receding ice sheet (Andrén et al., 1999). An outlet of the Baltic Ice Lake through the Öresund area was suggested by Björck and Digerfeldt (1991) on the basis of extrapolated shore-level curves. Isostatic rebound most likely caused a gradually decreasing water depth at the Öresund, resulting in erosion of this strait to its bedrock threshold at -8 m, and at ~14.0 ka the level

of the Baltic Ice Lake started to rise above the sea level in the North Atlantic (Björck and Digerfeldt, 1991; Björck, 2006). An outlet of the Baltic Ice Lake via the Öresund was also proposed by Bergsten and Nordberg (1992) who documented high sedimentation rates in the southeastern Kattegat due to erosion of the Öresund.

At ~13.0 ka the Baltic Ice Lake level seems to have been lowered by ca. 5-10 m (e.g. Björck, 1979; Svensson 1991) and ice retreat across the isostatically depressed south-central Swedish lowlands north of Mt. Billingen is suggested to have opened up a new drainage route to the North Atlantic (Björck 1979). During this lake level lowering, the first land bridge between the continent and Sweden was established. During the Younger Dryas cold phase, the ice margin re-advanced and blocked the route over the south-central Swedish lowlands, causing a new damming of the Baltic, as suggested by a transgression in Blekinge and Fakse Bay around 12.7 ka (Björck, 1981; Bennike and Jensen, 1995, respectively).

After the complete ice retreat from the south-central Swedish lowlands the ice-dammed Baltic Ice Lake drained suddenly, causing a water level drop of ~25 m in the Baltic Basin. Observations that point towards a sudden drainage are the similarities in age of lake isolations separated by height differences of ~25 m on Gotland (Svensson, 1989). The absence of beach ridges on the island of Gotland in this 25 m interval is additional evidence for this rapid lake level lowering as are the drainage deposits west of Mt. Billingen (Björck, 1995). A coarse sand layer within the lacustrine clays in the Baltic has also been related to this event and is suggested to have been produced by density currents (Svensson, 1991; Moros et al., 2002). A high-resolution record of  $\delta^{18}\text{O}$  in benthic foraminifers (*Elphidium excavatum*) from the Skagerrak area shows two  $\delta^{18}\text{O}$  anomalies at the same time period, indicating short-lasting but strong fresh-water influences (Erlenkeuser, 1985; Bodén et al., 1997). The final drainage of the Baltic Ice Lake seems to have occurred slightly before the



end of the Younger Dryas stadial (e.g. Björck, 1995; Andrén et al., 1999) and is supposed to have delivered 0.12 to 0.25 Sverdrup (Sv) fresh water into the North Sea over a period of 1-2 years, corresponding to a total fresh-water volume of  $\sim 7840 \text{ km}^3$  (Björck et al., 1996; Jakobsson et al., in press). The rapid release of such an amount of fresh water into the North Atlantic could have triggered a minor short-lived disturbance of the North Atlantic circulation as described by e.g. Björck et al. (1996), Andrén et al. (2002) and Nesje et al. (2004). Through correlations between tree-rings, ice core proxies, lake sediments and clay varves the drainage has been dated to ca. 11.6 ka (Björck et al., 1996, 1997; Andrén et al., 1999).

#### *Yoldia Sea stage*

With the opening of the passage to the North Atlantic at 11.6 ka, the 900-1000 year long Yoldia Sea stage commenced (Fig. 2d). Although the water level had dropped to sea level, salt water could only penetrate into the Baltic for  $\sim 150$  years during the middle of the stage, presumably because of the narrow outlet and the large freshwater discharge from the Baltic (Björck, 1995; Wastegård et al., 1995). Svensson (1989, 1991) has divided the Yoldia Sea stage into three phases, with brackish conditions only during the middle phase. The stage was named after the marine mollusc *Portlandia* (*Yoldia*) *Arctica* (Munthe, 1900). During the initial freshwater phase, meltwater was still flowing out from the Baltic Basin. After ca. 300 (varve) years, the first brackish-water influence is seen in the Baltic and may have been triggered by a climatic deterioration, the Preboreal Oscillation (PBO) (Björck et al., 1996, 1997). This short cooling may have decreased the influence of meltwater from the receding ice sheet and allowed a temporary inflow of saline bottom waters at the same time as the Närke Strait opened up. Apart from marine bivalves, evidence for brackish waters is also based on the presence of foraminifera and on

salinity peaks in the diatom flora (Wastegård et al., 1995; Lepland et al., 1999). The duration of this brackish phase in the northwestern Baltic has been estimated as  $\sim 150$  years based on the presence of foraminifera in varved clay sequences (Wastegård and Schoning, 1997). There is no evidence for a marine influence in the southwestern Baltic (Arkona Basin) (Bennike and Lemke, 2001), although Björck et al. (1990) and Andrén (1999) proposed the presence of brackish conditions in the Hanö Bay and Bornholm Basin, respectively. The final freshwater phase lasted for another 400-500 years and show a fresh water diatom flora (Andrén et al., 2000).

Due to the low water level during the Yoldia Sea stage, the southern Baltic was much smaller than today (Fig. 2d). The island of Bornholm may have been connected to the German mainland (Björck, 1995) and a large land bridge existed between Sweden, Denmark and the European mainland. A pine forest down to a depth of at least -35 m occupied large parts of the former lake bottoms, as is indicated by the findings of buried pine stumps and peat surfaces on the sea floor in Hanö Bay. Trunks from this forest have been dated to  $\sim 10.8 \text{ cal ka BP}$  ( $9.5\text{-}9.6 \text{ }^{14}\text{C ka BP}$ ) (Björck and Dennegård, 1988).

#### *Ancylus Lake stage*

Early Holocene warming resulted in rapid deglaciation and pronounced isostatic uplift in the south-central Swedish threshold area, closing the connection between the Baltic and North Atlantic. This caused tilting and renewed damming of the Baltic and the beginning of the *Ancylus* Lake stage at  $\sim 10.7 \text{ ka}$  (Björck and Dennegård, 1988), named after the findings of the freshwater mollusc *Ancylus fluviatilis* (Munthe, 1910). As isostatic uplift in the southern Baltic had almost ceased, the transgression during this isolated stage was  $\sim 20 \text{ m}$  (Svensson, 1989) and seemed to have rapidly drowned the pine forests from the Yoldia Sea stage in Hanö Bay (Fig. 2e) (Björck and Dennegård, 1988).

A regression of ~10 m has been described by several authors at ~10.3 ka (e.g. Svensson, 1991; Björck, 1995; Jensen et al., 1999) and implies drainage of the Ancylus Lake and a pathway to the ocean (Fig. 2f). As the Öresund threshold was uplifted to a higher elevation than the more southerly-located Darss Sill area, an outlet 'Dana River' was proposed in this southern area (e.g. Björck, 1995). Jensen et al. (1999) show that a calm lacustrine-fluvial environment dominated the threshold area indicating that it was not a sudden but rather a slow drainage, possibly combined with outflow through the Göta Älv in south-central Sweden during the initial stage (Björck et al., in press).

### *Littorina Sea stage*

When eustatic sea level reached the level of the shallow thresholds in the Danish/German straits (Great Belt and Fehmarn Belt) and in the Öresund, marine waters were able to re-enter the Baltic. The hydrography of the Baltic Basin then changed from the fresh-water environment of the Ancylus Lake to the brackish circulation system of the Littorina Sea, named after the findings of the gastropod *Littorina littorea* (Lindström, 1886).

The start of the Littorina transgression is much debated and it is presumed that a transitional phase existed with episodic marine influxes (Witkowski, 2005; Berglund et al., 2005), often called the Mastogloia Sea (e.g. Hyvärinen, 1988). Both shoreline displacement (e.g. Björck and Digerfeldt, 1991) and modelling studies (Lambeck, 1999), show that the water level in the Baltic was at the same elevation as the ocean from ~10.1 ka onwards. A first brackish water influence based on diatom data is described in coastal lagoons in Blekinge at ~9.8 ka and brack-

ish conditions are described in these coastal lagoons from ~8.5 ka onwards (Yu et al., 2003; Berglund et al., 2005). Similar results were found in the Bornholm Basin by Andrén et al. (2000) based on <sup>14</sup>C ages on bulk sediment. On the other hand, Bennike et al. (2004) describe <sup>14</sup>C ages of the first marine shell in the Great Belt at ~8.1 cal ka BP and in the Mecklenburg Bay at ~7.6 cal ka BP. Based on <sup>14</sup>C ages on foraminifera and shells, brackish conditions are not observed in the Arkona Basin before ~7 cal ka BP (Moros et al., 2002; Rößler, 2006).

The Littorina Sea stage shows a multiple transgression pattern in areas where the Littorina isobase is lower than 10 m asl. The actual number of Littorina transgressions is much debated. In Blekinge (SE Sweden), six minor transgression/regression phases have been identified, based on analyses of sediment cores (Berglund, 1964; Yu, 2003). In Denmark several (4-5) minor transgressions have been identified, based on geoarchaeological data (Christensen, 1995). Although the main Littorina transgression is regarded as a response to eustatic sea level rise, the minor water level changes are assumed to be related to variations in regional climate (Berglund et al., 2005) and could, therefore, have been caused by changes in North Atlantic Ocean circulation. It has also been suggested that final occasional deglaciation pulses in North America and Antarctica caused more rapid sea level rises, followed by dominance of uplift/regression (Yu, 2003; Björck, 2006). Hyvärinen et al. (1988) suggest that most of the oscillations are probably caused by local factors and cannot be considered as transgressions involving the whole basin.

Development of anoxic conditions in the deep depositional basins is often related to the start of the Littorina transgression when increased nutrient influxes produced higher productivity and the

Table 2. Core locations

Core ID	Basin	Datum	Latitude	Longitude	Water depth (m)
242790-3	Arkona	07.01.2002	54.951 N	13.780 E	45
243010-3	Bornholm	15.01.2002	55.528 N	15.584 E	75

inflows of brackish water created a stratified water mass which prevented the seasonal mixing of the water column (e.g. Sohlenius et al., 2001; Emeis et al., 2003).

### 3. Methods, materials and rationale

In this project a sediment core from the Arkona Basin in the southern Baltic Sea was examined and analysed using a range of physical, sedimentological, geochemical and palaeontological methods to obtain a high-resolution age-depth relationship and a detailed reconstruction of palaeoenvironmental change. A less extensive study was performed on a sediment core from the Bornholm Basin. More detailed descriptions of the methodologies can be found in the different appendices. Author contributions to the following analyses are described in Table 3.

#### 3.1 Sediment cores and sampling

Core locations were chosen in the central part of the Arkona and Bornholm Basins where continuous sedimentation records were expected and shallow seismic surveys showed that no major unconformities occur in the subsurface (Moros, pers. comm.). A 10.86 m long gravity core (242790-3) from the Arkona Basin and a 10.67 m long gravity core (243010-3) from the Bornholm Basin were recovered by the German research vessel R/v Poseidon in 2002 (Table 2). After retrieval the gravity cores were cut into 1 m sections and stored in a cold room at 4°C. The cores were split length-wise in March 2003. One half of each core was used for taking samples for Optically Stimulated Luminescence (OSL) dating under subdued amber light conditions (Paper I, IV and V), while the other half was used for different palaeoenvironmental analyses.

Lithological descriptions were made directly after splitting, and digital images of the split core sections (Arkona Basin) were made using a line-scan camera of a Multi-Sensor Core Logger (MSCL) at the Bremen ODP Core Repository (BCR). These images were stored in 20-cm increments which were spliced together to create a composite image. Two dimensional micro-radiographic images were obtained for sections of the core that visibly contained many iron sulphide stains and concretions (2.86-3.36 m and 3.86-4.86 m; Arkona Basin) (Paper III) using an Itrax core scanner at Cox Analytical, Gothenburg, Sweden.

#### 3.2 Chronological approach

In order to obtain a reliable chronology for palaeoenvironmental change and to relate this change to regional and global climate and sea-level reconstructions, a combination of OSL and  $^{14}\text{C}$  dating and varve counting was applied to core 242790-3 from the Arkona Basin (Paper I and II). The chronology of the sediment record from the Bornholm Basin is based on OSL ages only (Appendix V). An attempt was made to determine inclination and declination to obtain information on the past changes in directions of the geomagnetic field above 3 m and below 6 m in core 242790-3 (Arkona Basin), but the PSV signals were not reliable and could not be compared to master curves from Sweden (e.g. Zilén, 2003) and Finland (Ojala and Saarinen, 2002) as a means of relative dating.

##### 3.2.1 Optically Stimulated Luminescence (OSL) dating

The relatively new technique of Optically Stimulated Luminescence (OSL) dating opens up the possibility of dating sediments that could not be dated before; this technique uses mineral grains to obtain an age of deposition and is not dependent

Table 3. Author contributions to analyses and data interpretation in Appendices I-IV.

	Appendix I	Appendix II	Appendix III	Appendix IV
Funding application analyses	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i> <i>Per Sandgren</i>	<i>Marloes Kortekaas</i>
Core description	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>
Grain size	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	-	<i>Marloes Kortekaas</i>
Mineral Magnetics	-	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i> <i>Ian Snowball</i>	-
XRF	-	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	-
CNS	-	<i>Marloes Kortekaas</i> <i>Mrs. Benisch (IOW)</i>	<i>Marloes Kortekaas</i> <i>Mrs. Benisch (IOW)</i>	-
Diatom analyses	-	<i>Jan Risberg (SU)</i>	-	-
Macrofossil analyses	-	<i>Ole Bennike (GEUS)</i>	-	-
Gammaspectrometry	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	-	-
Varve counting	<i>Marloes Kortekaas</i> <i>Per Sandgren</i>	<i>Marloes Kortekaas</i> <i>Per Sandgren</i>	-	-
OSL dating	<i>Marloes Kortekaas</i>	<i>Marloes Kortekaas</i>	-	<i>Marloes Kortekaas</i>
<sup>14</sup> C dating	<i>Poznan Lab., Poland</i> <i>Lund University Lab.</i>	<i>Poznan Lab., Poland</i> <i>Lund University Lab.</i>	-	-
Age-depth relationship	-	<i>Marloes Kortekaas</i> <i>Svante Björck</i> <i>Andrew Murray</i>	-	-
Data interpretation	<i>Marloes Kortekaas</i> <i>Andrew Murray</i>	<i>Marloes Kortekaas</i> <i>Svante Björck</i> <i>Ole Bennike</i> <i>Andrew Murray</i> <i>Doreen Rößler</i> <i>Ian Snowball</i>	<i>Marloes Kortekaas</i> <i>Ian Snowball</i>	<i>Marloes Kortekaas</i> <i>Andrew Murray</i>

on the preservation of organic material. Although OSL dating has been applied mainly to terrestrial deposits, recent studies demonstrate that marine sediments can also be dated accurately (Stokes et al., 2003; Olley et al., 2004). The OSL dating was performed by the author at the Nordic Laboratory for Luminescence Dating at Risø, Denmark.

OSL dating makes use of the ability of quartz or feldspar to trap and accumulate charge in crystal defects. This charge is derived from the environmental ionizing-radiation flux produced by tho-

rium, uranium, potassium-40, and at a lower level by cosmic rays and rubidium-87. The fundamental concept of OSL dating of sediments is that exposure to daylight reduces the trapped charge population in quartz and feldspar crystals to a low level. Exposure to daylight can occur during erosion, transport and deposition of the sediment, and is known as the bleaching event. It empties the electrons in the light-sensitive traps and thus sets the latent signal to near-zero. Subsequently, when additional sediment covers the deposit, the light is blocked and the sedi-

ment starts again to absorb a dose from the environmental ionizing-radiation field. The 'memory' of the accumulated exposure to nuclear radiation is carried by trapped electrons. The more prolonged the exposure to radiation, the greater the number of trapped electrons (e.g. Aitken, 1998).

When trapped charge is emptied, some fraction of the energy is released as light (luminescence) and the dating procedure involves the measurement of this luminescence to determine the absorbed radiation dose (the palaeodose or rather its equivalent in the laboratory - the equivalent dose;  $D_e$ ). This palaeodose, divided by the dose rate from the environmental ionizing radiation, provides the burial age of the deposit.

Depending on the sand content, sample slices of between 2 and 10 cm were taken from the split cores under amber light conditions (Paper I, IV and App. V). The outer 1.5 cm from the face of the split core and the contact with the core liner were discarded to avoid contamination from light exposed and/or disturbed material. The samples were wet-sieved to obtain the 63-106  $\mu\text{m}$  sand fraction (Arkona Basin) and/or 32-63  $\mu\text{m}$  silt fraction (Bornholm Basin) and chemically treated to obtain pure quartz. Mica contamination was minimized using a detergent solution in an ultrasonic bath (Kortekaas and Murray, 2005). In total 32 samples were taken from the sediment sequence from the Arkona Basin and 6 samples from the Bornholm Basin sequence. Sand content was very low in the latter core and the 32-63  $\mu\text{m}$  silt fraction was used at some levels. At three levels, measurements were performed on both sand and silt fractions to check the comparability.

The Single Aliquot Regenerative dose (SAR) protocol (Murray and Wintle, 2000) was applied to 2 mm diameter aliquots. All measurements were performed on a Risø TL/OSL reader with blue (470 nm) light stimulation and U-340 luminescence detection filters (Bøtter-Jensen et al., 2000). At the end of each run the aliquots were optically stimulated at 280°C for 40 s to minimise recupera-

tion (Murray and Wintle, 2003). Each aliquot was checked for feldspar contamination at the end of the measurement sequence by giving a regenerative dose equal to the 2<sup>nd</sup> regeneration dose, followed by a 100 s IR stimulation at room temperature and a 40 s blue LED stimulation. Aliquots with a ratio IR/blue of >5% were rejected.

To determine the dose rate, sediment surrounding the OSL samples was used. The samples were dried, homogenised by grinding, cast in wax to retain radon and stored for 1 month to establish equilibrium between  $^{222}\text{Rn}$  and  $^{226}\text{Ra}$ . The radionuclide concentrations were measured using high-resolution gamma spectrometry (Murray et al., 1987). Counting time was ~24 hours and the typical sample mass was ~100 g mineral weight. The measured water content of the samples was assumed to be the (saturated) water content over its entire burial period.

The possibility of partially bleached sediment was examined by checking the dose distributions of the small (2 mm) aliquots (Wallinga, 2002). The  $D_e$  distributions were plotted for all samples and samples showing a skewed distribution (indicating partially bleached sediment - 5 out of 32 samples examined) were rejected from the final age-depth relationship (Paper I and II).

### 3.2.2 Radiocarbon dating

Bivalves in living position and bulk samples were selected from core 242790-3 (Arkona Basin) for accelerator mass spectrometry (AMS) radiocarbon dating, which was performed at the Poznan Laboratory in Poland and Radiocarbon Laboratory of Lund University in Sweden. All  $^{14}\text{C}$  ages in this study have been calibrated to calendar years before present (cal. yrs, where present means 2000 AD) using OxCal v. 3.10 ( $2\sigma$ ) (Bronk Ramsey, 2001) in order to enable comparison with the OSL ages. A marine (brackish) reservoir correction of 400 years was used for the samples in the upper 3 m.



### 3.2.3 Varve counting

Varve counting was performed by two persons on the glacial varved clay in the lower 3.75 m of the Arkona Basin core to estimate the length of time represented and to compare this value with the OSL ages obtained in this varved clay unit.

## 3.3 Palaeoenvironmental methods

The multi-proxy approach of mineral magnetic, sedimentological, geochemical and palaeontological analyses is intended to provide information on hydrographical changes such as salinity, biological productivity, terrestrial input and redox-conditions in the basin.

### 3.3.1 Mineral magnetic analyses

Various mineral magnetic analyses were performed to provide information on the type and concentration of different magnetic minerals (Paper III). The split-core surfaces from both cores were initially scanned for their magnetic susceptibility ( $\kappa$ ) using a Bartington MS2E1 high-resolution surface scanning sensor coupled to a TAMISCAN automatic logging conveyor. These scans give a relative estimation of magnetic mineral concentration. More detailed mineral magnetic analyses were performed on contiguous samples at 2.2 cm intervals using standard palaeomagnetic plastic sample cubes (internal volume 7 cm<sup>3</sup>) on core 242790-3 (Arkona Basin). The samples were stored at 4°C prior to analysis in the Palaeomagnetic and Mineral Magnetic Laboratory (PPML) at the GeoBiosphere Science Centre, University of Lund, Sweden. After measurement of the different mineral magnetic properties in a fresh (wet) state, the samples were freeze-dried in order to normalize all magnetic parameters by dry mass.

The mass specific, initial (low field) magnetic

susceptibility ( $\chi$ ) was measured using a Geofyzica Brno KLY-2 Kappabridge. Anhyseretic Remanent Magnetisation (ARM) was induced using a Molspin AF demagnetiser in a peak alternating field of 100 milliTesla (mT) imposed on a direct bias field of 0.1 mT. The ARM provides a measure of the content of fine-grained ferrimagnetic minerals (King et al, 1982). Subsequently, the samples were exposed to a forward saturating magnetic field of 1 Tesla (T) in a Redcliff 700 BSM magnetiser after which the saturation isothermal remanent magnetisation (SIRM) was determined with a Molspin Minispin magnetometer. The SIRM estimates the concentration of mineral grains capable of carrying a magnetic remanence, but is also influenced by the magnetic grain size differences (Thompson and Oldfield, 1986).

After the SIRM measurements the samples were placed in a successively increasing reversed magnetic field at steps of 10 mT while the isothermal remanent magnetisation (IRM) was measured each time on the Molspin Minispin magnetometer. The coercivity of remanence ( $B_{0cr}$ ) is the reverse direct field that generates zero magnetisation of the sample after saturation and the value can be diagnostic for magnetic mineralogy and grain size. Thereafter, the samples were magnetised in a low negative magnetic field of 0.1 T and the  $IRM_{-100mT}$  was measured on the Molspin Minispin magnetometer. A similar measurement in a negative magnetic field was performed at 0.3 T.

Various ratios of these different mineral magnetic properties are characteristic for different magnetic mineralogy and magnetic grain sizes. The  $SIRM/\chi$  ratio was calculated to investigate possible changes in both magnetic grain size and mineralogical composition. S-ratios are computed as  $S_{100} = IRM_{-100}/SIRM$  and  $S_{300} = IRM_{-300}/SIRM$  and give an indication on the relative proportion of magnetically soft or hard mineral species within each sample (Walden et al., 1999). The  $\chi_{ARM}/SIRM$  ratio is used to estimate the proportion of fine-grained ferrimagnetic particles with respect to the



total amount of magnetic particles.

Extracts of ferrimagnetic iron sulphide concretions were taken from different depths of core 242790-3 (Arkona Basin) to perform additional magnetic measurements. Room temperature magnetic hysteresis loops and the coercivity of remanence were measured with a Princeton Measurements Corporation AGM2900-2 at a maximum field of 1 T while thermomagnetic analyses were carried out on a Geofyzica Brno KLY2 Kappabridge coupled to a CS2 furnace. These measurements are performed in order to confirm the interpretation of magnetic mineralogy based on the bulk samples as described above and provide more detailed information about the magnetic properties.

### 3.3.2 Grain size analyses

Contiguous samples taken at 2.2 cm intervals were wet-sieved to obtain the grain size fraction > 63  $\mu\text{m}$  (as dry weight %) between 2.70 m and 7.86 m from core 242790-3 (Arkona Basin). The sand fraction has been used as a parameter for enhanced hydrodynamic energy at water-level low stands (Moros et al., 2002), as discussed, for example, in Paper II.

### 3.3.2 Geochemical analyses

Non-destructive geochemical analyses were performed at 1 or 4 cm resolution on split-core surfaces from core 242790-3 (Arkona Basin) using a Cortex X-ray fluorescence (XRF) core scanner (AAVATECH) (Jansen et al., 1998; Röhl and Abrams, 2000) at the Bremen ODP Core Repository. The molybdenum X-ray source (3-50 kV) of the scanner allows elemental analyses of K, Ca, Fe, Mn, Cu, Ti and Sr. The XRF data were collected over a 1  $\text{cm}^2$  area using 30-s count time and relative element intensities were finally expressed in counts per second (Paper II). Micro XRF-scanning was performed between

2.86-3.36 m and 3.86-4.86 m of core 242790-3 (Arkona Basin) using an Itrax core scanner at Cox Analytical, Gothenburg, Sweden (Paper III).

Geochemical analyses of C, N and S were carried out at the Institute for Baltic Sea Research (IOW) (Arkona Basin) and Lund University (Bornholm Basin) on 1 cm samples at 16, 8, 4 or 2 cm intervals. The samples were first freeze dried and homogenised prior to the measurements. Total carbon (TC) and nitrogen (N) concentrations were measured on 10 mg subsamples placed in tin capsules, using a LECO CHN-900 micro multi-elemental determinator. Samples from core 242790-3 (Arkona Basin) were also measured on a multi EA 2000 CS to obtain total carbon (TC), total inorganic carbon (TIC) and sulphur (S) concentrations. The TIC content was determined by placing a 50 mg subsample in a closed system with 6 ml  $\text{H}_3\text{PO}_4$  (50%) at 80°C. TC and S concentrations were measured on a 50 mg subsample by combustion. Total carbon (TC) was thus measured by two different methods and the average of the two methods is used as the final TC value. The content of organic carbon (TOC) was then calculated as  $\text{TC} - \text{TIC}$  and the carbonate content calculated from  $\text{CaCO}_3$  wt % =  $\text{TIC} * 8.33$ . The C/N ratio was calculated as the ratio between TOC and N. Samples from core 243010-3 (Bornholm Basin) were only measured for TC, N and S-content.

### 3.3.3 Palaeontological analyses

Samples for palaeontological analyses were selected from different stratigraphic-lithologic levels of core 242790-3 (Arkona Basin) to try to reconstruct salinity and general eutrophic-oligotrophic conditions at the time of deposition (Paper II).

Sixteen sub-samples of ~100 ml bulk sediment were disintegrated by wet-sieving through a 0.1 mm sieve. Identification of the macrofossils was done using a low power stereo-microscope. Eleven sub-samples of ~5 ml bulk sediment were picked for ba-

sic diatom analyses. Samples were prepared according to the method described by Battarbee (1986).

## 4. Summary of Papers

### 4.1 Paper I

*Kortekaas, M., Murray, A.S., Sandgren, P. and Björck, S., 2007. OSL chronology for a sediment core from the southern Baltic Sea: a continuous sedimentation record since deglaciation. Quaternary Geochronology (in print).*

Most studies on the post-glacial environmental history in the southern Baltic Sea are based on sediment sequences from coastal areas where abundant organic material is available for  $^{14}\text{C}$  dating. As large water level changes occurred during this period, many of these records are discontinuous. In the deeper basins of the southern Baltic Sea the sediment record is expected to be continuous, but lack of organic material for  $^{14}\text{C}$  dating impeded previous studies. The aim of this study is to investigate the applicability of Optically Stimulated Luminescence (OSL) dating on a sediment core (242790-3) from the centre of the Arkona Basin (45 m water depth). The sediment core is 10.86 m long and does not show any visible erosional disconformities; it appears to consist of a continuous sediment sequence from the Baltic Ice Lake stage (~15 ka) up to the present. Furthermore, its position close to the shallow inlet area of the Danish and Swedish straits makes it an excellent location for studying post-glacial circulation changes in the southern Baltic Sea.

The single aliquot regenerative dose (SAR) procedure (Murray and Wintle, 2000) was used to date 32 samples, using fine sand (63-106  $\mu\text{m}$ ) quartz extracts. High-resolution gamma spectrometry was used to analyze sediment surrounding the OSL samples to determine the dose rates. The measured water content was assumed to be the saturated water

content throughout the burial period. Additional age-control was obtained through AMS  $^{14}\text{C}$  dating on both shells and bulk sediment samples, and by varve-counting of the glacial varved clay in the lower part of the core.

Tests of luminescence characteristics confirmed the suitability of the material for OSL dating and the use of small aliquots enabled us to use dose ( $D_e$ ) distributions to check for partial bleaching (Wallinga, 2002).  $D_e$  distributions in the units above the glacial varved clay were indistinguishable from normal, suggesting that partial bleaching is not a problem, and the mean  $D_e$  can be used to calculate the age. However, some of the samples from the glacial varved clay (bottom of the core) may not have been sufficiently bleached as the  $D_e$  distributions show a slight positive skewness. In addition, the number of varves suggests that deposition of this unit took place within ~1 ka, whereas the corresponding OSL ages suggest a longer period of deposition.

In all the units above the glacial varved clay, the agreement between the OSL ages and the  $^{14}\text{C}$  ages on bivalves is good. However, most of the bulk sediment  $^{14}\text{C}$  ages appear ~1000 years too old in the Littorina Sea deposits (top 2.9 m of the core) and >3000 years too old in the underlying fresh water deposits. The age discrepancy between the OSL (and shell  $^{14}\text{C}$  ages) and bulk  $^{14}\text{C}$  ages is most likely caused by incorporation of old reworked carbon in the bulk  $^{14}\text{C}$  samples. The sandy horizon at 7 m depth has previously been described as a stratigraphic horizon for the Baltic Ice Lake drainage when water level dropped with ~25 m (Moros et al., 2002). This horizon is OSL dated to ~11.6 ka, an age which is in agreement with other published evidence (e.g. Björck et al., 1996). The transition to clay gyttja is generally ascribed to the main Littorina transgression, and this layer is OSL dated to ~6.5 ka. This young age is confirmed by other studies in the Arkona Basin based on macrofossil  $^{14}\text{C}$  ages (e.g. Moros et al., 2002) but disagrees with studies performed in coastal lagoons where brackish conditions appear at ~8.5 ka (e.g. Yu et al., 2003; Ber-

glund et al., 2005).

Both the agreement between OSL and  $^{14}\text{C}$  ages on bivalves in the top of the core and the OSL age of the stratigraphic horizon of the Baltic Ice Lake drainage in the lower part of the core give us confidence that the OSL signal was fully reset before burial in these units above the glacial varved clay. Based on the smooth succession of these 32 OSL ages, our sediment core appears to be a record of continuous sedimentation without any major erosional hiatuses and enables us to develop an age-depth relationship for the entire sediment sequence, spanning the Baltic Ice Lake stage till present. We show that OSL dating of marine sediment cores in the Baltic Sea has great potential and that sediment sequences from the deeper basins can now be accurately dated despite the lack of organic material.

#### 4.2 Paper II

*Kortekaas, M., Björck, S., Bennike, O., Murray, A.S., Röföler, D. and Snowball, I.F., submitted. Late Weichselian and Holocene palaeoenvironmental changes in the southern Baltic Sea constrained by a high-resolution OSL chronology. Marine Geology.*

The post-glacial history of the Baltic Sea is characterised by large water level and salinity changes as a result of the opening and closing of the connections between the Baltic Basin and the North Atlantic. The general picture of the circulation changes in the Baltic Sea is fairly well known, but problems and conflicting data-sets still exist. The latter arise primarily from the different nature of the palaeoenvironmental records studied and the uncertainties in their individual chronologies. The purpose of this study is to compare and test the validity of existing models of the post-glacial Baltic Sea development by performing a high-resolution study, dated with independent physically based tools, on a sediment record from a deep basin in the southern Baltic Sea. We present biological and high-resolution

geochemical and mineral magnetic data for a 10.86 m long sediment core (242790-3) from the centre of the Arkona Basin (45 m water depth). For the first time, independent physically based chronological control is obtained by Optically Stimulated Luminescence (OSL) dating; a lack of macrofossils for  $^{14}\text{C}$  dating impeded previous studies in the deeper basins.

This new palaeoenvironmental record covers the post-glacial history of the southern Baltic Sea and previously described stratigraphic horizons (e.g. Moros et al., 2002) are now absolutely dated with this new OSL chronology. Glacial varved clay was deposited for a period of <1 ka during the Baltic Ice Lake stage and the general disappearance of the varved character from ~13 ka represents a period of ice retreat and decreased sedimentation rate in the Arkona Basin. A sand layer represents the final Baltic Ice Lake drainage to the North Atlantic (Moros et al., 2002) and is dated to ~11.6 ka, which is in agreement with other published evidence (e.g. Björck et al., 1996). As carbonates are expected to mainly originate from in-basin sources like submerged tills, boulder clays and dolomite outcrops, the sudden decrease in total inorganic carbon (TIC) between ~11.6 and ~10.9 ka implies a water level lowstand and a major change in the main sediment source. The proposed water-level lowstand would imply that this part of the record represents the Yoldia Sea stage. Although marine influence during this stage has been recorded in the Gotland Basin (e.g. Andrén et al., 2002) and Bornholm Basin (Andrén et al., 2000), no evidence is found for brackish conditions in the Arkona Basin, in agreement with previous studies (Lemke, 1998; Moros; 1998). The environment in the Arkona Basin was probably dominated by the fresh-water influence of the Oder River as the river mouth was situated at Kap Arkona during this period (Kolp, 1983).

We propose that the increased sedimentation rate, high TIC content and abundant phytoliths until ~10.4 ka are associated with the Ancylus Lake transgression. The dominance of fresh water mac-

rofofossils in the overlying clayey sediments with iron monosulphide precipitates suggest a fresh-water environment between ~10.4 and ~6.5 ka. Albeit, brackish water ostracode shells (*Cytheromorpha fuscata*) were found at ~9.8 ka and imply a short period of brackish water conditions in the Arkona Basin. A similar event has been described in the Bornholm Basin (Andrén et al., 2000) and in coastal lagoons in southern Sweden (Yu et al., 2005). At ~10 ka water level in the Baltic Basin was at the same level as in the Kattegat Sea, hence occasional marine influxes could be possible after this time (e.g. Lambeck, 1999). An increase in TOC, S and N starts at ~8.6 ka, while a peak in TOC, sand and terrestrial macrofossils is dated to ~8.2 ka. As the macrofossil and diatom data suggest a fresh-water environment until the lithologic change to clay gyttja at ~6.5 ka, the occurrence of sulphur in these sediments is most likely explained by post-depositional sulphidic precipitation, where the dissolved sulphide diffused downwards from the overlying clay gyttja deposits (e.g. Sohlenius, 1996). The increase in sand and terrestrial macrofossils between ~8.6 and ~7.9 ka implies increased sediment transport from the shores to the centre of the basin. Shoreline displacement studies show a water level rise after ~8.5 ka (e.g. Yu et al., 2003) but the decrease in TIC seems to indicate a water level lowering in the Arkona Basin. The change in geochemistry and lithology may possibly be explained by an increase in ice cover during the colder winters around this time (the so-called 8.2 ka cold event recently reviewed by e.g. Rohling and Pälike, 2005). Wind erosion and the entrainment of particles in ice along the shores, followed by the break-up of ice-cover during spring are known to transport coastal material to the deeper parts of a basin (e.g. Dethleff et al., 2000). A relatively rapid change in the circulation system of the Arkona Basin appears at ~6.5 ka, with the start of a high-productivity, marine circulation system. The increase in organic carbon (TOC), sulphur and nitrogen coincides with the first occurrence of marine diatoms, foraminifera and shells. Both bottom water and surface water proxies indicate a brackish circulation system after ~6.5 ka in the Arkona Basin.

With the age-depth relationship derived from OSL ages (and supported by AMS <sup>14</sup>C macrofossil ages) we can date stratigraphic marker horizons, allowing us to compare and test the validity of existing models of post-glacial Baltic Sea development. Some of the stratigraphic horizons are in agreement with the existing model of post-glacial events while other stratigraphic units have to be placed in different palaeoenvironmental settings due to large differences between the new OSL chronology and the earlier bulk <sup>14</sup>C ages. The new chronology appears to give rise to a discrepancy between the classical model of the Littorina transgression (brackish conditions starting ~8.5 ka, largely based on studies in coastal lagoons) and a later first marine influence at ~6.5 ka based on studies performed in the Arkona Basin. The new chronology shows that the palaeoenvironmental record is continuous and that it is unlikely that part of the early Littorina transgression sequence is missing in sediment records from the Arkona Basin (as suggested by Witkowski et al., 2005). It may be that small coastal lagoons are much more sensitive to palaeoenvironmental changes than the large deep water basins within the Baltic Sea. Small changes in salinity could thus show up as major palaeoenvironmental changes in the coastal sites, while the circulation system in the deeper basins is hardly affected. Increased humidity between 9.0 and 7.0 ka might have caused an increased fresh-water input from the Oder River into the Arkona Basin. We suggest that the major circulation change seen at ~6.5 ka in the Arkona Basin corresponds to the time when the Danish Belts became the dominant inflow path for North Atlantic waters.

#### 4.3 Paper III

*Kortekaas, M., Snowball, I.F., Sandgren, P., submitted. The occurrence of ferrimagnetic greigite in Baltic Sea sediments and its implication for palaeoenvironmental interpretation. Geophysical Journal International.*

The occurrence of iron sulphides is ubiquitous in anoxic marine, brackish and lacustrine sediments due to a plentiful supply of sulphate and readily

available iron in pore waters (Berner, 1984; Roberts and Weaver, 2005). Pyrite ( $\text{FeS}_2$ ) is often considered to be the most commonly occurring iron sulphide, but the application of mineral magnetic methods has shown that some of its precursors, the metastable iron sulphides greigite ( $\text{Fe}_3\text{S}_4$ ) and monoclinic pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) are also preserved in the geologic record (e.g. Snowball and Thompson, 1990; Roberts and Turner, 1993). As both syn-depositional and post-depositional formations of iron sulphides occur, palaeoenvironmental interpretation of iron sulphide-bearing sediment sequences is often problematic. The presence of black sulphide staining and greigite concretions in post-glacial Baltic Sea sediments has been described by many authors (e.g. Sohlenius, 1996; Winterhalter, 1982; Huckriede et al., 1996; Lepland et al., 1999) but the origin has been debated. Huckriede et al. (1996) considered the concretions to be a syn-depositional (authigenic) mineral phase, indicating anoxic bottom water conditions during deposition. On the other hand, Sohlenius (1996) suggested that greigite forms as a post-depositional (diagenetic) mineral through downwards diffusion of sulphide rich porewaters from overlying marine sediments. The aim of this study was to investigate the distribution and origin of magnetic minerals in a sediment sequence from the centre of the Arkona Basin in the southern Baltic Sea (core 242790-3). Micro-radiographic images and XRF-scanning were performed to study the appearance of iron sulphide concretions in the core. Different magnetic properties were measured on both bulk sediment samples and on extracts of ferrimagnetic iron sulphide concretions from different depths to confirm the interpretation of magnetic mineralogy.

The variations in susceptibility, SIRM, coercivity of remanence ( $B_{0\text{cr}}$ ),  $\chi_{\text{ARM}}/\text{SIRM}$  and S-ratios give indications of the dominance of particular magnetic minerals during the different sedimentary environments covered by this sediment sequence. As can be expected in natural sediment, a mixture of different magnetic minerals and grain sizes appears

to be present in the sediment core, generally with haematite and magnetite as the main contributors to the magnetic signals. During the Baltic Ice Lake stage (~14 to ~11.6 ka), the dominant contributor to the magnetic signal seems to be fine-grained haematite (suggested by the elevated  $S_{100\text{mT}}$  ratios and ( $B_{0\text{cr}}$ ) values). At the drainage of the Baltic Ice Lake (~11.6 ka), the sediment grain size increased as water level dropped by 25 m. Greater sorting in this unit is most likely responsible for the increase in magnetic grain size, and the low ( $B_{0\text{cr}}$ ) values imply an increase in the proportion of magnetite.

The presence of iron sulphides in the Ancylus Lake deposits is implied from the radiographic images and geochemical data; this implication is strengthened by the mineral magnetic data, which indicate that greigite dominates the magnetic signal. Elevated  $\chi$  and SIRM/ $\chi$  in combination with low  $\chi_{\text{ARM}}/\text{SIRM}$  values have been described as diagnostic for the presence of natural sedimentary greigite (Roberts, 1995; Snowball, 1991 and 1997b). A distinct difference in greigite appearance can be observed from the radiographic images, with clear nodules occurring mainly between 3.0 and 3.2 m. These greigite nodules between 3.0 and 3.2 m depth are composed of larger magnetic grains than the ones deeper down (4.0 - 5.6 m), indicating that the minerals in the upper part formed more slowly than those at greater depth.

The overlying marine clay gyttja unit shows low susceptibility and SIRM values indicating a low concentration of ferrimagnetic minerals. The coercivity of remanence ( $B_{0\text{cr}}$ ) and S-ratios indicate that this unit has a magnetic mineral assemblage dominated by a combination of magnetite and haematite.

We propose that the greigite concretions observed in the sediment sequence of the Arkona Basin are diagenetic, and formed only after the establishment of a fully brackish system represented by the clay gyttja unit. As iron was most likely the limiting factor for iron sulphide formation within the clay gyttja, sulphides were able to diffuse downwards through the silty clay deposits of the Ancylus



lus Lake stage. The occurrence of iron sulphides in fresh water deposits underlying transgression horizons has been described from many transgression sequences (e.g. Middelburg et al., 1991; Snowball and Thompson, 1988; Sohlenius, 1996). The small magnetic grain size of the iron sulphide concretions between 4.0 and 5.6 m implies that the minerals were formed rather quickly, possibly related to an excess of available iron and low availability of sulphur. Any sulphur species that diffused down to this level precipitated immediately. The decrease in greigite concentration as shown by the decrease in e.g. SIRM/ $\chi$  down-core also suggests a post-depositional formation of greigite. The larger grain size of the greigite nodules directly underlying the clay gytja unit could possibly be due to the slightly larger and continuing sulphur supply.

#### 4.4 Paper IV

*Kortekaas, M. and Murray, A.S., 2005. A method for the removal of mica from quartz separates. Ancient TL, 23 (2), 43-46.*

Sediment samples often contain appreciable amounts of mica, a complex group of alumino-silicate minerals with a typical strong cleavage, resulting in their platy structure. Standard laboratory techniques to obtain pure quartz or feldspar for luminescence dating (Aitken, 1985) do not seem to reject mica minerals, and it is not known whether mica contamination actually influences the luminescence measurements from quartz or feldspar. In this paper we describe a simple and effective procedure to remove mica from etched quartz samples using a detergent solution in an ultrasonic bath. To investigate the possible influence of mica on quartz luminescence measurements, three aliquots of pure sedimentary mica grains were measured using a single aliquot regenerative dose (SAR) protocol. OSL and TL measurements were performed on museum specimens of mica to compare these signals to sedimentary mica and quartz samples.

The sediment in this study was obtained from core 242790-3 from the southern Baltic Sea. After standard chemical treatment, some of the samples contained up to 60% mica by volume. The low sand content of our samples precluded the use of statically charged surfaces to remove mica, as too large a fraction of the quartz was lost in this process. Instead, the samples were put in a detergent solution (sodium pyrophosphate,  $\text{Na}_4\text{P}_2\text{O}_7$  (22.3 g/l) or dishwashing detergent solution) in an ultrasonic bath for ~30 minutes. The visible mica contamination, relative to quartz, decreased by ~90%, when the overlying soap solution was decanted; we presume that the mica simply floated off at this stage.

It appears that the mica luminescence signal is small compared to the quartz signal, and so contamination with quartz cannot be completely ruled out. The TL glow curves from both a mica contaminated samples and purified quartz samples are also similar. OSL decay curves from both sedimentary mica and museum muscovite show that they seem to have an initial fast decaying component similar to that of quartz, but that the signal also contains a significant slow component. It appears, however, that saturation for sedimentary mica and museum muscovite occurs at much higher doses than for quartz. Although we cannot completely rule out that the sedimentary mica aliquots were not contaminated, it seems prudent to minimise mica content when this forms a large part of a quartz sample after etching, especially in older samples. Future research is necessary to determine whether these observations are generally applicable and whether mica itself has any potential as a luminescence dosimeter.



## 5. Synthesis

### 5.1 A new chronological approach, and its implications

Obtaining reliable chronologies is a vital part of understanding palaeoenvironmental changes documented in geological sequences and of relating these changes to regional and global records. Apart from the many age-equivalent stratigraphic approaches, absolute dating of Late Quaternary marine and limnic sediment sequences is mainly based on  $^{14}\text{C}$  dating of available organic material. As atmospheric  $^{14}\text{C}$  production has varied in the past,  $^{14}\text{C}$  ages have to be calibrated to ‘calendar years’ and so relatively large absolute uncertainties are inevitable during so-called ‘radiocarbon plateaus’ (e.g. Ammann and Lotter, 1989; Björck et al., 1996). Additional uncertainty is caused by the often poorly-known reservoir effects and by possible contamination of the organic material dated.

Despite the common application of Optically Stimulated Luminescence (OSL) dating to terrestrial chronologies, this technique remains largely untested in the marine environment. A first attempt to date marine sediments using thermolumines-

cence (TL) dating was presented in the late 1970s (Wintle and Huntley, 1979, 1980) but a variety of uncertainties discouraged the widespread use of the technique in marine environments; the main concern was whether the exposure of the sediments to daylight immediately prior to deposition was sufficient to completely remove any existing residual latent TL signal. As sediment source areas are usually at considerable distances, and bottom water currents are often the major sediment transportation mode, incomplete re-setting of the luminescence signal in mineral grains prior to burial in the sedimentary record seemed likely, and overestimation of the TL ages was expected. More practical complications involved the limited amount of material available as marine sediment records are generally obtained through coring. With the development of OSL which exploits the most light-sensitive signals from minerals, its application for dating marine sediments was re-investigated (Stokes et al., 2003; Olley et al., 2004). Both studies show the potential of the technique for dating deep-sea sediments from locations where considerable amounts of aeolian sedimentation can be expected (Stokes et al., 2003; Olley et al., 2004).

The application of OSL dating in this project

*Table 4. Uncorrected  $^{14}\text{C}$  ages on foraminifera, molluscs and bulk sediment (humic acid residues and base residues) from the transition to clay gyttja. Samples were taken from sediment cores from the centre of the Mecklenburg Bay (MB) and Arkona Basin (AB) (reproduced from Rößler, 2006).*

core location and depth	sample	uncal. $^{14}\text{C}$ yrs BP (BP=1950)
MB-242770-1: 586-588cm	benthic foraminifers	7265 ± 35
MB-242770-1: 586-588cm	mollusc shells	7575 ± 35
MB-242770-1: 586-588cm	bulk sample, humic acid residues	7975 ± 60
MB-242770-1: 586-588cm	bulk sample, base residues	8205 ± 40
AB-242800-1: 355cm	benthic foraminifers	6225 ± 30
AB-242800-1: 359-360cm	<i>Arctica islandica</i> shell	6495 ± 35
AB-242800-1: 355cm	bulk sample, humic acid residues	6680 ± 50
AB-242800-1: 355cm	bulk sample, base residues	7370 ± 45

This dataset is taken from Rößler (2006).

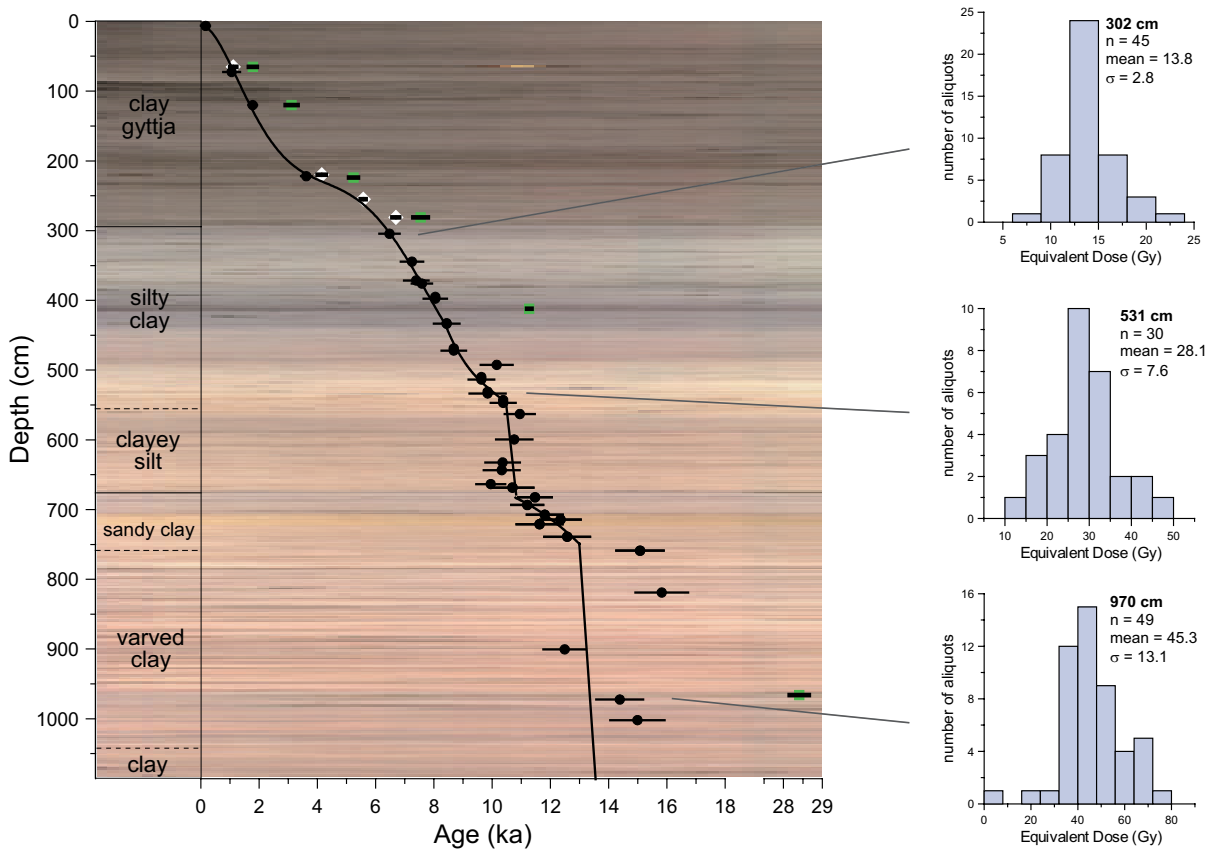


Fig. 3 Age-depth relationship based on OSL ages, varved clay and  $^{14}\text{C}$  ages on marine shells (plotted next to the stratigraphy on a stretched photograph of the core (black dots: OSL ages, green squares: bulk  $^{14}\text{C}$  ages, and white diamonds:  $^{14}\text{C}$  ages on shells). Equivalent dose distributions are shown from samples of the top, middle and bottom of the core. The distribution in the glacial varved clay (bottom of the core (970 cm)) shows a positive skewness, indicating that partial bleaching might be the cause of age overestimation.

shows the great potential of the method for dating sediment sequences in marginal seas and continental shelf areas where fluvial systems, coastal currents and possibly aeolian sedimentation bring 'well-bleached' mineral grains relatively quickly into the sedimentary record (Paper I, II, V). The main concern of incomplete bleaching can be addressed by analysis of the distribution of populations of equivalent dose ( $D_e$ ) estimates from small aliquots (Paper I) and, of course, by comparison with independent age control. Each OSL age is calculated as the mean of at least 30  $D_e$  measurements and well-bleached samples show typical normal or Gaussian distributions (Murray et al., 1995). Skewed dose distributions are an indication that the sample contains a small percentage of poorly bleached grains (Murray et al., 1995; Wallinga, 2002). Most  $D_e$  distributions from

the sediment core from the Arkona Basin (Paper I) approach normal distributions and as the ages correlate well with  $^{14}\text{C}$  ages on shells it is concluded that the sediment was well-bleached prior to deposition at the core location (Fig. 3). Some of the samples from the glacial varved clay in the bottom of the core may not have been completely bleached; the  $D_e$  distributions show a slight positive skewness. The final age-depth relationship for the lower 3 m of the sediment sequence is hence based on the varve counts (~600 years) (Paper II).

The application of OSL dating in the southern Baltic Sea shows that it is possible to obtain a high-resolution age-depth relationship for sediment cores from the deeper basins despite the lack of organic material and/or macrofossils for  $^{14}\text{C}$  dating. Based on the succession of OSL ages, the sediment core

from the Arkona Basin appears to be a record of continuous sedimentation without any major erosional hiatuses from ~14 ka till the present. Comparisons between the OSL ages and the calibrated  $^{14}\text{C}$  ages on macrofossils show good agreement, but the bulk  $^{14}\text{C}$  ages are generally at least ~1000 years too old (Paper I). The discrepancy between bulk  $^{14}\text{C}$  ages and  $^{14}\text{C}$  ages on macrofossils in sediments from the southern Baltic Sea has been confirmed recently by Rößler (2006). She showed that in the Mecklenburg Bay as well as in the Arkona Basin, bulk samples on base residue appear 1000  $^{14}\text{C}$  years older than ages on benthic foraminifera (see Table 4). As most palaeoenvironmental records in the deeper basins of the Baltic Sea are based on  $^{14}\text{C}$  dating of bulk sediments, large errors on the actual timing of the inferred development should be expected.

The reservoir effect in the Baltic Sea is poorly known and is likely to have varied over time with the changing salinities (Wastegård and Schoning, 1997; Hedenström and Possnert, 2001). In this study, a marine reservoir effect of 400  $^{14}\text{C}$  years was assumed. Based on  $^{14}\text{C}$  ages on terrestrial macrofossils and bulk sediment samples in coastal lagoons, Hedenström and Possnert (2001) suggested a reservoir effect of 750 years during the most saline phase of the Littorina Sea stage. In order to be able to determine any statistically significant difference between OSL ages and  $^{14}\text{C}$  ages on macrofossils, many more paired OSL and macrofossil  $^{14}\text{C}$  ages are required. However, the present dataset does suggest that the reservoir effect during the most saline phase (approximately between 2.9 and 2.5 m in core 242790-3) was ~700 instead of 400  $^{14}\text{C}$  years.

OSL dating performed on the Bornholm Basin core (243010-3) shows that in this deeper basin, OSL seems again to be an applicable dating technique providing good age control (Appendix V). Generally, it seems that both sand and silt are bleached to similar degrees, and thus give similar ages; this allows the use of OSL dating even when the sand fraction is extremely low.

## 5.2 Palaeoenvironmental change in the Arkona Basin

With the novel approach of producing the age-depth relationship using OSL dating, it is now possible to date directly stratigraphic marker horizons in the Arkona Basin; these could not be dated before due to the lack of organic material for  $^{14}\text{C}$  dating. The sandy horizon that has been described as a stratigraphic marker horizon for the drainage of the Baltic Ice Lake (Moros et al., 2002) is dated here to ~11.6 ka, corresponding well with the age assigned to this event in other studies (e.g. Björck et al., 1996).

This drainage event is followed by a period of low water levels as indicated by the geochemical data. The sudden change in geochemistry implies a change in sediment source. As inorganic carbon (TIC) originates mainly from in-basin sources such as submerged tills, boulder clays and dolomite outcrops, low TIC and Ca/Ti ratios imply a substantial water level lowering until ~10.9 ka. A brackish water influx is recorded in the northern basins of the Baltic Sea during this time (Yoldia Sea) and it has been suggested that this also reached the Bornholm Basin (Andrén et al., 2000). Although the Arkona Basin was connected to the Bornholm Basin during this period, the environment within the Arkona Basin seems dominated by the fresh water influence from the Oder River, whose mouth was situated at Kap Arkona during the Late Glacial (Kolp, 1983). No clear evidence for brackish conditions in the Arkona Basin has been found in this study (Paper II), in agreement with earlier studies (Lemke, 1998; Moros et al., 2002).

A period of very rapid sedimentation occurs between ~10.9 and ~10.4 ka (indicated by the near-vertical age-depth relationship). The increase in concentrations of sand and phytoliths in this unit implies a large terrestrial input and possibly a water level rise that flooded the vegetated surfaces of the former Yoldia Sea shores. The increase in TIC would also agree with such a hypothesis. As the

macrofossil data indicate fresh-water conditions, it is likely that this unit corresponds to the Ancylus Lake level rise as described in the literature (e.g. Björck, 1995); in contrast to the preliminary interpretation of the stratigraphy in Kortekaas et al. (in press).

The sedimentation rate decreases after  $\sim 10.4$  ka and the increased clay content implies a transition to a low energy environment. Macrofossil and diatom data indicate that a fresh-water environment dominates between  $\sim 10.4$  and  $\sim 6.5$  ka, apart from one anomalous brackish water inflow at  $\sim 9.8$  ka. Brackish water conditions at this early time have been reported from the Bornholm Basin (Andr n et al., 2000) and from coastal lagoons in Blekinge (Yu et al., 2005; Berglund et al., 2005). Sea level in the North Atlantic is considered to be at the same level as water level in the Baltic Basin from  $\sim 10.1$  ka onwards, and occasional brackish water influxes could be expected after this time (e.g. Lambeck, 1999; Bj rck et al. in press).

Elevated magnetic parameters between  $\sim 10.4$  and  $\sim 6.5$  ka indicate the presence of greigite ( $\text{Fe}_3\text{S}_4$ ),

a meta-stable ferrimagnetic iron sulphide that is formed under anoxic conditions with low sulphur availability (Roberts and Weaver, 2005). The origin of greigite in Baltic sediments has been debated and Huckriede et al (1996) considered it to be a syn-depositional mineral phase, indicating anoxic bottom water conditions during deposition. On the other hand, Sohlenius (1996) suggested that the greigite formed as a post-depositional mineral through the slow downwards diffusion of sulphide-rich pore waters from overlying marine sediments. Paper III shows that the magnetic grain size appears to be small in the lower part of the record, where the greigite appearance is slightly laminated and seems to be associated with organic matter content. Magnetic grain size is larger in the upper unit, where greigite appears as nodular concretions. As the diatom and macrofossil data suggest a fresh-water environment until the lithologic change to clay gyttja at  $\sim 6.5$  ka, the occurrence of sulphur in these sediments most likely represents downwards diffusion of sulphur species from the overlying clay gyttja

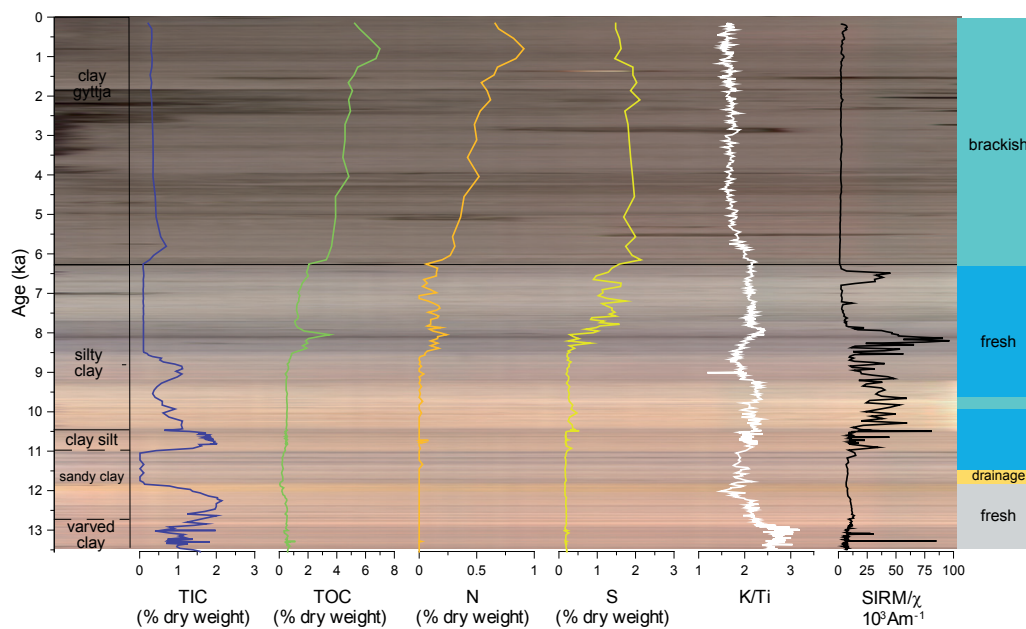


Fig. 4 Sediment description of the Arkona Basin sequence (242790-3) showing TIC, TOC, N, S, K/Ti and SIRM/ $\chi$  plotted against time. The photograph of the core is rescaled according to the age-depth relationship from Fig. 3 and the stretched image is shown as background. A palaeoenvironmental model is shown right.

deposits. Hence, the appearance of greigite in the sediment sequence is most likely post-depositional.

At ~8.6 ka, TOC, S and N concentrations increase, while a peak in TOC and sand is dated to ~8.2 ka (Paper II). The decrease in TIC and Ca/Ti implies a water level lowering again but shoreline displacement studies show a water-level rise after ~8.5 ka in the southern Baltic Sea (e.g. Yu et al., 2003) as an effect of global sea level rise. Such a marine transgression event could explain the increase in sand and terrestrial macrofossils were it not that macrofossil and diatom data suggest that a fresh-water environment prevailed. It is also possible that we see a globally forced transgression, but without any clear sign of increased salinity. Alternatively, the increase in sand and terrestrial macrofossils between ~8.6 and ~7.9 ka could be explained by an increase in ice cover during the colder winters around this time; the so-called 8.2 ka cold event as recently reviewed by e.g. Rohling and Pälike (2005). Wind erosion and the entrainment of particles in ice along the shores, followed by the break-up of ice-cover during spring are known to transport coastal material to the deeper parts of the basin (e.g. Dethleff et al., 2000). Titanium is a conservative proxy for the siliciclastic component of sediment, while potassium is more abundant in the feldspar component. The K/Ti ratio can be used as an indicator for sediment source as freshly eroded sediment from igneous and metamorphic rocks in Scandinavia are enriched in feldspars and should show a high ratio. On the other hand, more weathered sediment from the drainage basins of the European mainland are likely to be depleted in feldspar content, and should show a lower K/Ti ratio. High K/Ti ratios indeed occur during the Baltic Ice Lake stage and around ~8.2 ka, supporting the idea of a more northern sediment source during these colder times (Fig. 4). As northern winds tend to dominate during cold periods, increased aeolian sediment transport from northern source areas is expected to accumulate sediment on the sea-ice in the Baltic Sea. Hence, such a mechanism could explain the increased K/Ti ratios during

the early deglaciation and 8.2 ka cold event.

A sharp change in the circulation mode is observed at ~6.5 ka when an increase in TOC, N and S contents and the presence of marine macrofossils and diatoms suggest the start of a high-productivity, brackish circulation system in the Arkona Basin. The increase in TIC at this time is related to the occurrence of benthic foraminifera (*Ammonia beccarii*) indicating brackish conditions in the bottom waters. Circulation change in the surface water is indicated by the low C/N ratio implying that planktonic sources start to dominate the TOC supply (Bordovskiy, 1965). The growth of nitrogen-fixing cyanobacterial blooms as a result of the inflow of phosphorous-rich sea water was suggested by Bianchi et al. (2000); this hypothesis is consistent with the data in this study. The elevated levels of TOC and N around 1.1 ka could indicate an increase in primary productivity related to the Medieval Warm Period, as has been suggested previously by Andr en et al. (2000).

The start of a brackish circulation system in the Arkona Basin at ~6.5 ka has been confirmed by other studies in this basin (Moros et al., 2002; R  b ler, 2006) and the associated lithological change to clay gyttja has been described as the stratigraphic horizon of the Littorina transgression. The age, however, disagrees with studies performed in coastal lagoons (e.g. Yu et al., 2003; Berglund et al., 2005) and studies in German coastal areas where a marine transgression is recorded ~7.8 ka (e.g. Hoffmann and Barnasch, 2005; Lampe, 2005). The new OSL chronology contradicts the arguments that sediment records from the Arkona Basin include erosional hiatuses between 8.5 and 6.5 ka (e.g. Witkowski et al., 2005) and alternative explanations for this discrepancy must be sought.

Small coastal lagoons are likely to be more sensitive to palaeoenvironmental changes than the deep basins within the Baltic Sea. Small changes in salinity could thus show up as major palaeoenvironmental changes in the coastal sites, while the circulation system in the deeper basins is hardly affected. As the



salinity in the Baltic Sea is a function of the input of fresh-water supply as well as the sea-level variations in the Kattegat Sea (Stigebrandt and Gustafsson, 2003), a relatively enhanced fresh-water input from the rivers from the European continent could have minimized the possible impact of a marine influx via the Danish-Swedish straits. Possibly, the low TIC content between 8.6 and 6.5 ka is related to a relative enhanced influence of the Oder River in the Arkona Basin during this period. Increased humidity was described between 9.0 and 7.0 ka based on elevated lake levels in northern Europe (Digerfeldt, 1988), and this may be consistent with a possible enhanced fresh water supply. It is also possible that a more detailed diatom analysis would be a more sensitive tool for small-scale salinity changes; the latter are difficult to distinguish using geochemistry and macrofossil analyses.

The first evidence for marine/brackish water in the Mecklenburg Bay was detected after  $\sim 7.6$  ka based on calibrated  $^{14}\text{C}$  ages on molluscs and foraminifera (Bennike et al., 2004; Witkowski et al., 2005; Rößler, 2006) and the threshold of the

Darß sill is considered to have delayed the ingression into the Arkona Basin by another 500-1000 years (Lemke, 1998; Rößler, 2006). These data sets imply that fully marine through-flow via the Danish Belts only occurred after  $\sim 6.5$  ka and paper II proposes the possibility that the change in circulation mode seen at  $\sim 6.5$  ka in the Arkona Basin is related to the timing when the Danish Belts became the dominant inflow path for North Atlantic waters. Hence, the circulation system of the present Baltic Sea, with the Danish Belts as the dominant inflow areas (Westman et al., 1999), started to exist from  $\sim 6.5$  ka onwards.

### 5.3 Basin-wide changes

The geochemical analyses of core 243010-3 from the Bornholm Basin (75 m water depth) show a slight increase in TC, S and N starting at  $\sim 8.3$  ka (Fig. 5). Although the chronology of the Bornholm Basin is only based on six OSL ages, the timing of this change in both the Bornholm and Arkona Basin

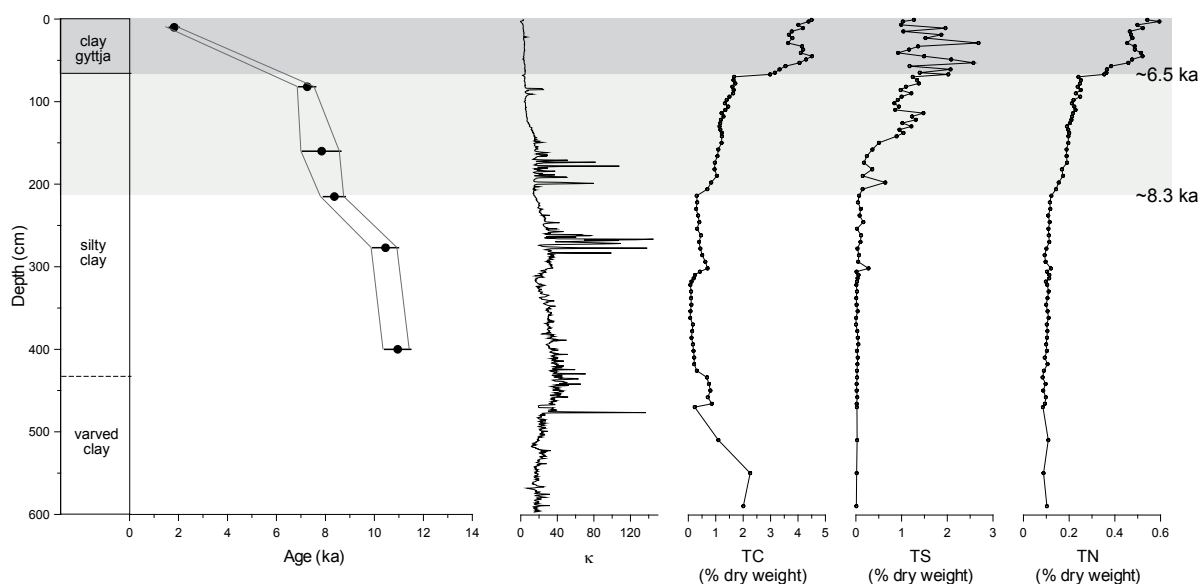


Fig. 5 Sediment description and OSL ages of core 243010-3 from the Bornholm Basin. Magnetic susceptibility, TC, S and N contents are plotted against depth. The lithologic change to clay gyttja displays very similar geochemical characteristics to the lithologic change in the Arkona Basin (Paper II) and has an age of  $\sim 6.5$  ka according to this relatively low-resolution age-depth relationship. (More details on the OSL data can be found in Appendix V).



seems to be similar (Appendix V). The increase of *Bosmina* species after this time in the Arkona Basin (Paper II) is also reported from sediment cores from the Bornholm Basin, although only described in a stratigraphic context there (Hoffmann and Winn, 2000). *Bosmina* species are planktonic and indicate oligotrophic-mesotrophic surface waters. Whether the increase in nutrients from about 8.6 - 8.3 ka is related to increased fluvial input or to a slight brackish water influence or a combination of the two, is debatable, but it is likely that surface waters in the southern Baltic Sea mix quickly and therefore the change is most likely synchronous in the two basins.

The sharp increase in TC, S and N around ~6.5 ka is consistent with the lithologic change to clay gyttja, and indicates a similar change in circulation mode as seen in the Arkona Basin. This lithologic change is related to the start of a fully brackish circulation system in the Arkona Basin (Paper II). Andrén et al. (2000) found a similar transition in their study, and if only their  $^{14}\text{C}$  ages on macrofossils are considered, the transition occurs approximately at the same time. The same transition is also found in the Gotland Basin in the central Baltic Sea but the majority of studies performed in this basin are based only on  $^{14}\text{C}$  ages on bulk sediment (e.g. Sohlenius et al., 1996; Lepland et al., 1999; Bianchi et al., 2000). As the circulation mode change at ~6.5 ka as seen in the Arkona and Bornholm Basins is most likely related to an increase in productivity (Bianchi et al., 2000), and the time-lag in the surface gradient of nutrients is likely to be within the error of dating measurements, it is anticipated that this change occurred simultaneously across the entire Baltic Basin.

#### 5.4 Future research

The obvious discrepancy between records from the deeper basins and studies performed in coastal lagoons requires further research. High-resolution detailed diatom analyses might provide a more detailed record of low salinity changes in the deeper basins prior to ~6.5 ka. Investigations of sediment records south of the Öresund Strait could also provide information on the first occurrence of salinity in this area. Better chronological control is needed for sediment cores from the deeper basins, as most studies are based on bulk  $^{14}\text{C}$  dating. OSL dating of the quartz sand or silt in the core and/or radiocarbon dating on selected foraminifera or molluscs from the transition to clay gyttja (marine mud) would help determine whether this is indeed a lithostratigraphic boundary that represents a synchronous basin-wide change. This study supports that of Rößler (2006) and suggests that dating of bulk sediment in the Baltic Basin should be avoided; bulk  $^{14}\text{C}$  ages generally tend to be of the order of 100s to 1000s of years too old.

Proper geochemical investigations undertaken directly on board a research vessel, where samples are taken in an argon or nitrogen atmosphere to avoid oxidation, would provide valuable information on pore-water chemistry and iron-sulphide geochemistry, and hence allows the build up of a more detailed picture of the geochemical processes recorded in the sediments. Furthermore, X-ray diffraction (XRD) analyses of the greigite nodules would help in determining whether the outer shell of the nodules is composed of a different type of iron sulphide and could thus assist in understanding of the formation process.

## 6. Conclusions

The objectives of this project involved testing the suitability of Optically Stimulated Luminescence (OSL) dating on sediment records from the deeper basins in the southern Baltic Sea. Together with multi-proxy studies of physical, sedimentological, chemical and palaeontological parameters, it is concluded that one can obtain a detailed record of palaeoenvironmental change in the southern Baltic Sea using these methods. In this novel approach of producing an age-depth relationship using OSL dating, it was possible to date stratigraphic marker horizons in the southern Baltic Sea; these were previously undatable because of the lack of organic material for  $^{14}\text{C}$  dating. Some of the horizons are in agreement with the existing model of post-glacial events while other stratigraphic units have to be placed in different palaeoenvironmental settings. This shows that it is necessary to revise parts of the post-glacial stratigraphy of the southern Baltic Sea. Based on the appendices in this study, the following conclusions can be drawn:

- OSL dating of marine sediments in the southern Baltic Sea has great potential for application to sediment records from marginal seas and continental shelf areas; sediment sequences from deeper basins can now be accurately dated despite the lack of organic material. Based on the succession of OSL ages, the sediment core from the Arkona Basin (242790-3) appears to be a record of continuous sedimentation without any major erosional hiatuses.
- Comparison of OSL ages with  $^{14}\text{C}$  ages shows good agreement, provided that the  $^{14}\text{C}$  ages are based on macrofossils.  $^{14}\text{C}$  ages performed on bulk sediment samples are generally at least ~1000 years too old. The OSL signals are well-bleached in most of the stages of the Baltic Sea history; i.e. the signal is reset to zero before deposition. However, partial bleaching probably contributes to an overestimation in the OSL ages in the glacial varved clay (Baltic Ice Lake stage), and as a result the number of varves in this unit was used for this part of the age-depth relationship. Measurement of palaeosecular variations of the earth magnetic field appears impossible as a dating tool in the Arkona Basin, possibly because of the diagenetic formation of ferrimagnetic iron sulphides.
- The sandy horizon previously described as the stratigraphic marker horizon of the main Baltic Ice Lake drainage is dated to ~11.6 ka. This event was followed by a period of low water level and enhanced influence from the Oder River in the Arkona Basin. A period of very rapid sedimentation occurs between ~10.9 and ~10.4 ka and is attributed to the Ancylus Lake transgression.
- A first anomalous slightly brackish water inflow is recorded at ~9.8 ka, but there is no clear evidence for fully brackish conditions until ~6.5 ka in the Arkona Basin. Sharp changes in the proxies are seen at this time, which is interpreted as a distinct shift in the circulation mode; increased TOC, N and S contents together with the presence of marine macrofossils imply the onset of a high-productivity, brackish circulation system in the Arkona Basin. The classical model for the Littorina transgression, with brackish conditions starting ~8.5 ka, is not supported by the results of this study; here it is suggested that a late first clearly brackish influence occurred at ~6.5 ka.
- Magnetic mineralogy shows that greigite ( $\text{Fe}_3\text{S}_4$ ) concretions occur in the fresh-water silty clay unit underlying the brackish clay gyttja deposited after ~6.5 ka. The larger magnetic grain size of the nodules in the upper silty clay unit indicates a slow formation process relative to the lower unit with smaller magnetic grain sizes, possibly due to a continuous sulphur supply from the brack-

ish clay gyttja. We propose that the greigite concretions observed in the sediment sequence of the Arkona Basin are diagenetic, and formed only after the establishment of a fully brackish system represented by the clay gyttja unit. As iron availability probably limited iron sulphide formation within the clay gyttja, sulphides were able to diffuse downwards through the silty clay deposits.

- The study performed in the Bornholm Basin (core 243010-3) shows a similar transition to a high-productivity, brackish water system at ~6.5 ka. This suggests that the circulation system of the present Baltic Sea, with fully brackish conditions and the Danish-German Straits as the dominant inflow areas, only started from ~6.5 ka onwards. This transition is likely to be synchronous in the entire Baltic Basin.

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## 8. Svensk sammanfattning

### *Postglaciala havsnivå- och miljöförändringar i södra Östersjön.*

Havsnivåförändringar har under den senaste 2.6 miljoner åren, under kvartärperioden, styrts av tillväxande och avsmältande inlandsisar. Under istider, då mycket vatten är bundet i inlandsisarna, är havsnivån låg medan den är hög under mellanliggande varmetider. Förutom denna globala regressions-transgressionscykel förekommer lokala och regionala nivåförändringar av varierande storlek. I områden som varit täckta av inlandsisar höjer sig landet som ett resultat av att isens tyngd försvinner, den s.k. glacialisostatiska komponenten. Denna landhöjning fortsätter långt efter att inlandsisen försvunnit på grund av jordskorpan tröghet. I andra områden sjunker landet som ett resultat av andra geologiska processer. Även lokala klimatförändringar påverkar havsytans nivå. Under den kallaste fasen för ca 20 000 år sedan var världshavet yta 130 m lägre än i dag till följd av det vatten som var bundet i inlandsisarna. Då isarna något senare började smälta började också havsnivån att stiga och områden som varit torrlagda översvämmades. Den globala havsyttehöjningen, eller eustatiska stigningen, var fullbordad för ungefär 6000 år sedan.

I gränsområdet mellan haven och kontinenterna finns bassänger som är avskilda från världshavet genom ett grundare område, ett tröskelområde, vilket försvårar vattenutbytet med världshavet. Som ett resultat av att vattenytan var mycket lägre under istiden var flera kustnära bassänger helt avskilda från världshavet: de hade ofta blivit sjöar. Då vattenytan steg under isavsmältningen etablerades på nytt kontakt mellan dessa bassänger och världshavet. Små förändringar i havsytans nivå kan vara tillräckliga för att radikalt förändra cirkulationen i dessa bassänger. Den här typen av bassänger är särskilt lämpliga för studier av globala havsytteförändringar och exempel på sådana bassänger är Svarta Havet, Gula Havet och

Östersjön.

I Östersjöbassängen kan man allt sedan isavsmältningen urskilja fyra stadier som ett resultat av det komplicerade samspelet mellan de glacialisostatiska och eustatiska komponenterna. Två av dessa är sötvattensstadier, de två andra brackvattensstadier. Östersjöns kontakt med världshavet skedde inom olika geografiska områden under de två brackvattensstadierna. Bilden av denna allmänna utveckling är tämligen väl accepterad men i vissa avseenden pekar data åt olika håll. Kronologiska osäkerheter har uppstått eftersom de tidigare undersökningarna ofta baserades på kol-14 datering av sediment. Varierande mängd gammalt kol i denna typ av prover leder till osäkerheter om sedimentens verkliga ålder, dvs när de verkligen avsattes. Vidare är många undersökningar baserade på undersökningar av kustnära lagerföljder. Eftersom de postglaciala vattenståndsförändringarna har varit stora kännetecknas denna typ av lokaler ofta av diskontinuerlig sedimentation. Trots att de södra delarna av Östersjön omges av tätbefolkade områden och varje framtida förändring i Östersjöns nivå kommer att ha sin största sociala betydelse här är högupplösande paleomiljöundersökningar få i detta område.

Syftet med den här avhandlingen är att presentera en detaljerad beskrivning av de postglaciala förändringarna i södra Östersjön, baserat på studier av sedimenten i två djupa bassänger, Arkonabassängen och Bornholmsbassängen, varifrån två 11 meter långa borrhärlor har analyserats. Fysikaliska, geokemiska och paleoekologiska undersökningar på kärnan från Arkonabassängen visar en detaljerad bild av miljöförändringarna. För första gången baseras kronologin på Optisk Stimulerad Luminescens (OSL) datering; en metod som använder mineraler för att bestämma åldern och är till skillnad från kol-14 metoden inte beroende av att organiskt material har bevarats och påträffas i sedimenten. En mindre omfattande studie är utförd på kärnan från Bornholmsbassängen. Resultaten från de båda borrhärlorna visar mycket god överensstämmelse och

pekar på en likartad utvecklingshistoria.

OSL metoden visar att det nu har blivit möjligt att datera sediment från Östersjöns djupare delar trots avsaknaden av organiskt material för kol-14 datering. Jämförelser mellan OSL åldrar och kol-14 åldrar visar god överensstämmelse under förutsättning att kol-14 dateringarna baseras på skal. Kol-14 dateringar baserade på sedimentprover är i storleksordningen mer än 1000 år ”för gamla”. Med utgångspunkt från de OSL daterade nivåerna i Arkonabassängen synes sedimentationen ha varit kontinuerlig utan några signifikanta sedimentationsavbrott. Stratigrafiska lednivåer har nu kunnat dateras, vilket möjliggör jämförelser och tester av existerande modeller av Östersjön postglaciala utvecklingshistoria.

Glacial varvig lera avsattes under det Baltiska issjöstadiet och ett sandlager som tolkas som Baltiska issjöns tappning ner till havsnivån har kunnat dateras till ~11 600 år i Arkonabassängen. Denna händelse följdes av en period med lågt vattenstånd då sedimenten påverkades av utströmmande vatten från floden Oder, vilken mynnar strax söder om Arkonabassängen. En period med mycket snabb sedimentation inträffade mellan 10 800 och 10 400 år före nutid, vilket tillskrivs den s.k. Ancylostansgressionen. Ett första inflöde av svagt bräckt vatten har daterats till 9800 år före nutid, men det finns inga klara bevis på fullt utvecklade brackvattensförhållanden förrän 6500 år före nutid. Den distinkta litologiska förändringen från siltig lera till leryttja vid denna tidpunkt representerar en dramatisk förändring i cirkulationsmönstret: ett högproduktivt, bräckt cirkulationssystem i södra Östersjön inleddes. Förekomst av greigite( $\text{Fe}_3\text{S}_4$ ) i den underliggande siltiga leran kan förklaras av (post-depositionell) diffusion av sulfid från den leriga gyttjan, dvs först efter dess avsättning.

Med denna nya kronologi uppstår en anomali med den klassiska modellen för den s.k. Littorinansgressionen där brackvattensförhållanden börjar 2000 år tidigare, dvs 8500 år före nutid; en modell som stöds av undersökningar i kustnära bassänger och laguner. Resultaten av den här undersökningen

tyder på att ett cirkulationssystem som påminner om dagens, med ett fullt utvecklat brackvattenssystem och de danska bälten som de dominerande inströmningsområdena, inte inleddes förrän för 6500 år sedan.

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