

# Geochemical expressions of late- and post-glacial land–sea interactions in the southern Baltic Sea

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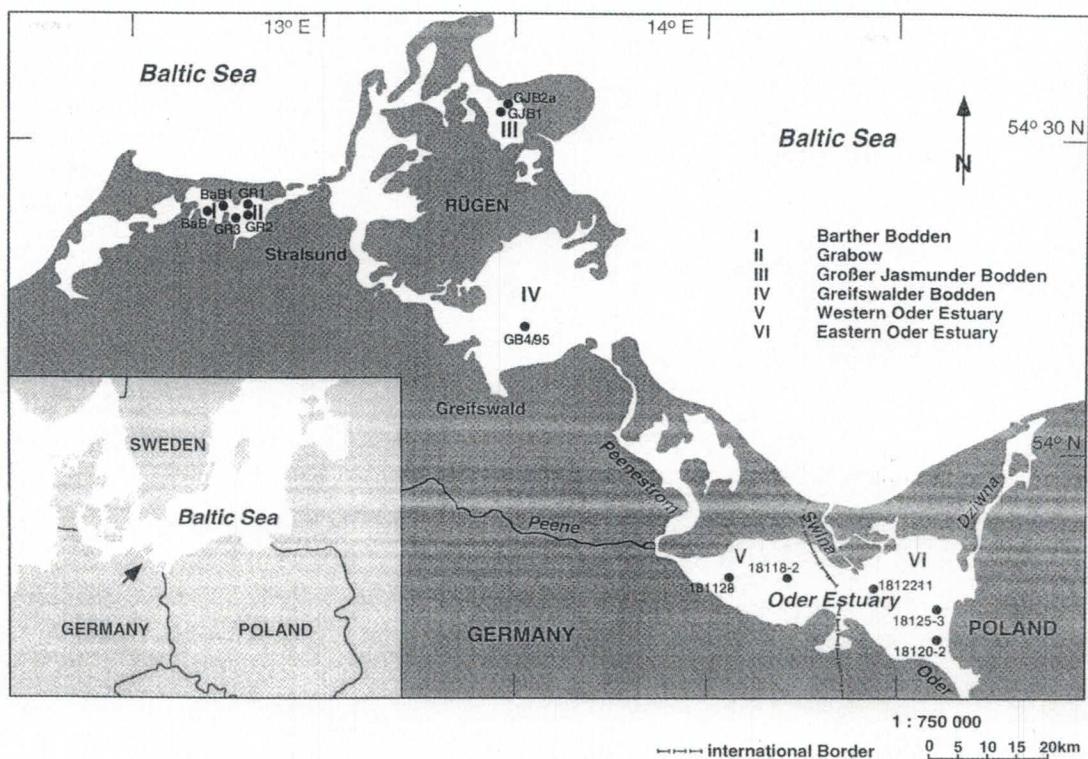
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The coastal region of the southern Baltic Sea has been extremely sensitive to sea-level changes during the Quaternary. The present environment is comprised of coastal lagoons and is characterized by Pleistocene islands connected by Holocene barrier islands. To determine the effects of late- and post-glacial coastal development on the lagoon sediments, 13 sediment cores from 6 lagoons were investigated. Organic carbon to nitrogen ( $C_{org}/N$ ), and organic carbon to sulfur ratios ( $C_{org}/S$ ),  $\delta^{13}C$ ,  $\delta^{15}N$ , organic carbon, biogenic opal and calcium carbonate values were measured and linked to the late- and post-glacial biostratigraphy of the sediments. Although, with the exception of the Oder lagoon, the lagoons show similarities in their paleoenvironments derived from the  $C_{org}/S$  ratios in the sediment, it is possible to derive the influence of the Baltic Sea waters.  $C_{org}/N$  ratios,  $\delta^{13}C$ ,  $\delta^{15}N$ , organic carbon, biogenic opal and calcium carbonate values all reflect changes in productivity over time and influence of river input, transgression and erosion. The results were used to derive the effects of sea-level changes, coastal development and related changes in hydrography and accompanying accumulation processes at the bottom of the lagoons. The results of this study show that, depending on its position to the Baltic Sea, each lagoon responded differently to sea-level changes that occurred during the development of the Baltic Sea and to regional coastal development.

## Introduction

The coastal region of the southern Baltic Sea has been extremely sensitive to sea-level changes over the last 10 000 years, e.g. from the time of the beginning of the final rapid retreat of

the Fennoscandian ice sheet (Zonneveld 1973, Andersen 1981). The present coastal environment with its lagoonal lakes (Fig. 1) is characterized by isolated Pleistocene islands which are connected by barrier islands. These barrier islands, which are sometimes only a few decimeters



**Fig. 1.** Study area and sampling locations. The numbers I to VI indicate the names of the lagoons of this study as shown in the legend.

above sea level, divide the coastal lagoons from the outer Baltic Sea (Janke *et al.* 1993).

The purpose of this biogeochemical investigation of selected sediment cores from several lagoons along the Baltic coast is to explore the development of this environment. So far, very few paleoenvironmental studies of this region have been done (e.g. Kolp 1983, Kliewe and Janke 1978, 1991), with most being focussed on the landward side of the shore (Kliewe and Janke 1978, 1991) rather than on the coastal lakes. This study has a number of objectives. Firstly, to contribute to the understanding of the development of the lagoons during the last 8000 years in response to the pre-existing relief, underlying lithology and oscillations of sea level of the Baltic Sea. Secondly, it investigates how the sediments of the lagoons reflect the response of the coastline to sea-level changes. Furthermore, it describes how the accumulation of sediments changes in response to the transgression

stages of the Baltic Sea and to the closure of the barrier islands. Moreover, the study shows which changes in the trophic state and in salinity levels occurred as a result of the closure of the barrier islands. This study provides new observational data of coastal development and sea-level change for six lagoons in the southern Baltic Sea region.

## Study area

This study focuses on the lagoons along the southern Baltic Sea coast (Fig. 1). The sedimentation history of these coastal lakes (Fig. 1) is closely linked to the different stages which the Baltic Sea and its southern coast have undergone during its development since the late Weichselian maximum ice cover (cf. Ignatius *et al.* 1981). The Holocene stages in the development of the Baltic Sea comprise the Yoldia Sea

with marine influence (10 300–9500 yr BP), the predominantly fresh-water Ancylus Lake (9500–8500 yr BP), the marine Mastagloia and the Litorina Sea, both subjected to marine influence (several stages after 8500–2000 yr BP) and the Mya Sea (2000 yr BP–present) (Björck 1995). These non-marine and marine stages in the development of the Baltic Sea, adjacent to the North Sea and thereby the Atlantic Ocean, are linked to transgression and regression stages. Neotectonic and glacial-isostatic processes lead to a southward shift of the water body and to complex shoreline development controlled by interaction between deglaciation dynamics, differential isostatic rebound of thresholds, erosion of thresholds and global sea-level change (Ignatius *et al.* 1981, Björck 1995).

At the time of maximum glaciation between 20 000 and 18 000 yr B.P. the Fennoscandian ice sheet extended over large areas of the North Sea, as well as the Baltic Sea, and considerable variation can be expected from the time melting began at about 18 000 yr B.P. to the present (Zonneveld 1973, Andersen 1981). The final retreat of the ice was rapid after about 10 000 yr B.P. and the ice sheet vanished by 8000 yr B.P. (Zonneveld 1973, Andersen 1981). Melt-water from all ice sheets continued to be added to the oceans during the late Holocene period raising the equivalent sea-level by 3–4 m over the past 6000 yr (Lambeck *et al.* 1990). The Holocene stages in the development of the Baltic Sea comprise the Yoldia Sea (10 300–9500 yr B.P.), the Ancylus-Lake (9500–8700 yr B.P.), the Litorina Sea (several stages between 8000–2000 yr B.P.) and the Mya Sea (2000 yr B.P.–present).

Although Late Pleistocene and Holocene eustatic and isostatic processes are still not fully understood in the southern Baltic Sea region, a tentative sea-level curve and history of transgression and regression stages for the southern Baltic Sea have been suggested (Kliewe and Janke 1982). According to this curve, the general post-glacial eustatic sea-level rise resulted in an absolute sea-level rise of more than 90 m before 5700 yr B.P. and, with weak oscillations, in a sea-level rise in the magnitude of meters after 5700 yr B.P. This sea-level rise has continued into the present (Kliewe 1995).

Today, the coastal lakes in the southern Baltic

Sea region (Fig. 1) are separated from the Baltic Sea by Holocene sand spits and barrier islands (Janke *et al.* 1993). These barrier islands connect isolated Pleistocene islands (Kliewe and Janke 1991), and water and sediment are mainly exchanged between the lagoons and the Baltic Sea through the lagoon rivers. The present lagoons in the study area all have average salinities less than 9‰ (Brosin 1965, Correns 1972, Schnese 1973, Correns and Jaeger 1979).

Morphologically, the Oder Estuary (Fig. 1) is divided from the open Baltic Sea by glacigen islands which are isolated from each other and which are connected by Holocene barrier islands (Kliewe and Janke 1991). The Oder River enters the lagoonal estuary of approximately 1000 km<sup>2</sup> in the south. The estuary consists of two major basins. Water masses and particulate matter are exchanged between the lagoon and the Baltic Sea via the Swina River and, to a lesser extent, via the Peene and Dziwna outlets. Water depths in the western part of the Oder Estuary are between 4 and 6 m with maximum depths of 7.8 m in the western basin and 13.5 m in the eastern basin (Correns 1972 and references therein, Correns 1976).

The Greifswalder Bodden lagoon (Fig. 1) is a coastal lagoon situated at the western edge of the Oder Estuary. Its surface area is approx. 510.2 km<sup>2</sup>. The water exchange between the Baltic Sea and the Greifswalder Bodden lagoon occurs both in the northwest and over the sill in the east (Correns 1972, Schnese 1973). The average water depth is 5.8 m with a maximum depth of 13.5 m (Correns 1976).

The Grabow and the Barther Bodden lagoons (Fig. 1) belong to a chain of four major successive lagoons. The Grabow lagoon has a surface area of 41.5 km<sup>2</sup> with an extension of 7.4 km from north to south and 6.5 km from east to west respectively. Its average depth is about 2.3 m with a maximum of 4.5 m. The connection to the Barther Bodden lagoon is quite narrow due to submarine sand spits, which has led to high current speeds and related erosion in this "channel" (Brosin 1965, Correns 1976). The Barther Bodden lagoon has a surface area of 19.4 km<sup>2</sup>. Its maximum width is 4.6 km. The average water depth is 1.8 m with a maximum of 6 m. A submarine sand spit in the middle part causes

local water depths as shallow as 0.8 m (Brosin 1965, Correns 1976).

The Großer Jasmunder Bodden lagoon (Fig. 1) belongs to a sequence of coastal lakes. The lagoon is surrounded by moraine hills. Its surface area is approximately 58.6 km<sup>2</sup> with an average depth of 5.3 m. The maximum depth is 10.3 m (Correns 1976).

## Material and methods

Four sediment cores were taken with a vibrocoring at mid-basin sites in both east and west basins of the Oder Estuary, and one core was taken near the entrance of the Oder River (Fig. 1 and Table 1). Water depth was 5.5 to 6.4 m at all sites, and the cores ranged from 1.9 to 4.3 m length. Parts of cores 18112, 18118 and 18120 were lost during handling of the cores. The remaining cores were taken with a vibrocoring in the Greifswalder Bodden, and with a Livingstone corer in the Großer Jasmunder Bodden, Grabow, and Barther Bodden lagoons from water depths ranging from 2.15 to 7.30 m. These cores ranged from 0.7 to 5.4 m in length (Table 1). The cores from all lagoons cover time periods between the late glacial and the present time (Fig. 2).

The cores were divided into 3 to 5 cm samples. Part of each sample was used for diatom and pollen analyses, which are described

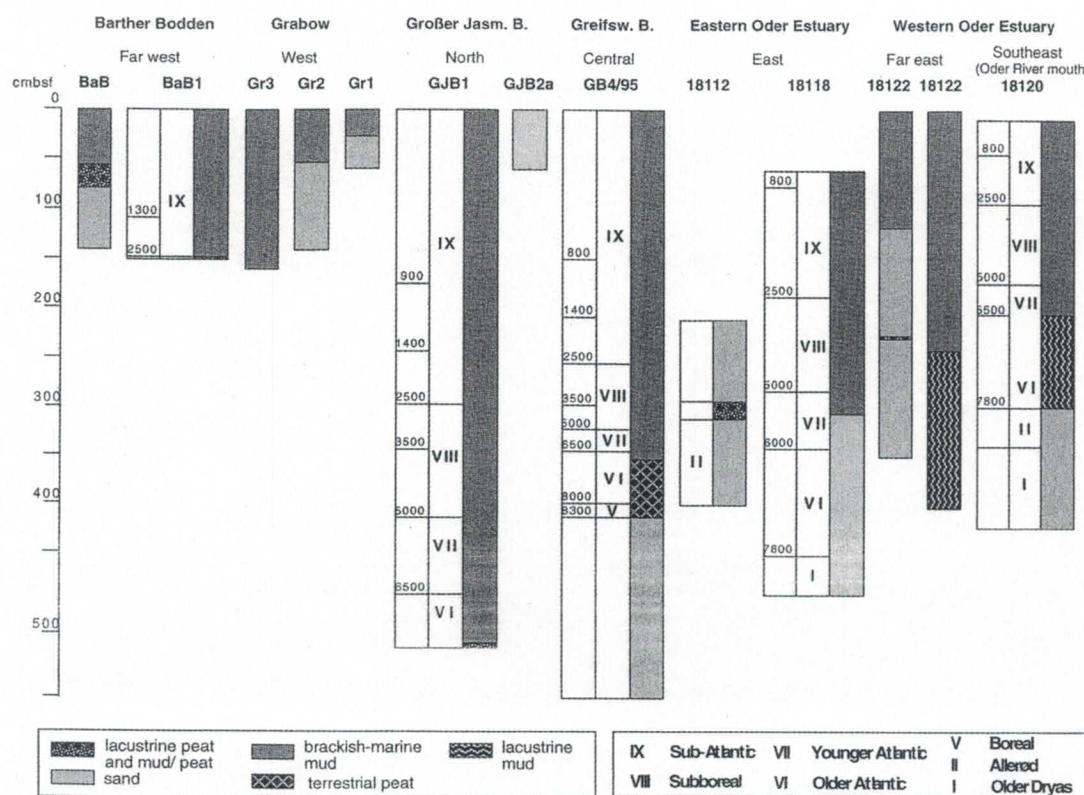
in detail elsewhere (KLIBO 1995, Müller *et al.* 1996) and summarized below. The remainder was sieved to separate the fraction < 63 µm, freeze dried and homogenized with mortar and pestle. The chemical analyses were based on the fraction < 63 µm, except for δ<sup>13</sup>C and δ<sup>15</sup>N analyses for which bulk sediment samples were used. Average reproducibilities ( $\sigma$ ) were calculated based on replicate measurements of internal sediment standards.

Total carbon was measured with a LECO CHN-analyzer (CHN-1000) at 1050 °C ( $\sigma = 0.18\%$ ) using 20–50 mg powdered sediment placed in aluminum capsules. Inorganic carbon was analysed as gas volume produced by adding 50% phosphoric acid using the carbonate module of an ELTRA C-S-analyzer (METALYT CS 100) ( $\sigma = 0.08\%$ ). Calcium carbonate content was calculated from inorganic carbon values by multiplying the inorganic carbon content by a factor of 8.33. Organic carbon content ( $C_{org}$ ) was derived from the difference between total and inorganic carbon content. Total sulfur content was determined with an ELTRA CS-analyzer (METALYT CS 100) at 1400 °C ( $\sigma = 0.17\%$ ) using 20–50 mg powdered sediment placed in aluminum capsules.

Total nitrogen content was measured as described for total carbon ( $\sigma = 0.03\%$ ). Organic carbon to total nitrogen ratios ( $C_{org}/N_{tot}$ ) were used rather than organic carbon to organic nitrogen ratios for the paleoenvironmental recon-

**Table 1.** Sampling locations, water depths, and lengths of sampled sediment cores.

| Core No. | Sampling location | Lat. N   | Long. E  | Water depth (m) | Core length (m) |
|----------|-------------------|----------|----------|-----------------|-----------------|
| 18112-8  | W. Oder Estuary   | 53°49.2' | 14°00.0' | 5.50            | 1.90            |
| 18118-2  | W. Oder Estuary   | 53°49.2' | 14°08.8' | 5.60            | 4.30            |
| 18120-14 | E. Oder Estuary   | 53°42.5' | 14°30.0' | 5.70            | 4.15            |
| 18122-11 | E. Oder Estuary   | 53°46.5' | 14°21.4' | 6.40            | 3.40            |
| 18125-3  | E. Oder Estuary   | 53°45.8' | 14°30.1' | 6.20            | 3.95            |
| Gr1      | Grabow            | 54°24.8' | 12°50.5' | 3.55            | 1.32            |
| Gr2      | Grabow            | 54°23.2' | 12°50.5' | 3.70            | 1.48            |
| Gr3      | Grabow            | 54°23.2' | 12°47.9' | 2.50            | 4.50            |
| BaB      | Barther Bodden    | 54°23.2' | 12°43.8' | 2.15            | 1.32            |
| BaB1     | Barther Bodden    | 54°24.8' | 12°46.7' | 2.75            | 1.52            |
| GJB1     | Gr.Jasm.Bodden    | 54°31.8' | 13°27.6' | 5.75            | 5.42            |
| GJB2a    | Gr.Jasm.Bodden    | 54°32.8' | 13°28.7' | 2.30            | 0.70            |
| GB4/95   | Greifsw.Bodden    | 54°11.6' | 13°30.0' | 7.28            | 5.20            |



**Fig. 2.** Sediment sequences for all cores of this study, shown in centimeters below seafloor (cmbsf). The age models for some cores are shown to the left of the sediment sequences (after Müller 2001a).

structions in this study. This was done because the difference in the ratios was found to be negligible in the study area (Müller and Mathesius 1999).

Molybdate-blue spectroscopy was used to measure biogenic opal in the form of dissolved silicon (Mortlock and Froelich 1989). For the analysis, 100 mg freeze dried and homogenized sediment material was leached in 100 ml 1 N NaOH at 85 °C for 40 minutes. The percentages of Si in opal were transformed into weight%-opal values ( $2.4 \times \% \text{Si-Opal}$ ), accounting for the average water content of diatomaceous silica of about 10% (10% water content =  $\text{SiO}_2 \times 0.4\text{H}_2\text{O}$ , Mortlock and Froelich 1989) with  $\sigma < 0.5\%$ . This method follows largely the procedure described by DeMaster (1981). However, because of the large sample set in this study, the sequence of consecutive leachings used by DeMaster (1981) was replaced by a single measurement taken

40 minutes after leaching had commenced. This was appropriate because it has been shown with core samples from the Oder lagoon that a series of consecutive leachings completely dissolved the biogenic silica after 40 minutes, while the contamination by clay minerals was negligible (T. Leipe, Baltic Sea Research Institute, pers. comm.). Also, NaOH was used as an extraction agent rather than  $\text{Na}_2\text{CO}_3$ . It has been shown that NaOH can be used as an agent when clay mineral interference is negligible and biogenic opal content is high in the sediments (cf. DeMaster 1981). Clay mineral interference was not considered important because the Oder lagoon sediments are characterized by small clay fractions mostly below 10% (Müller and Hoffmann 1998). Furthermore, the sediments show relatively high concentrations of biogenic opal.

Aliquots of the bulk sediment samples were analyzed for organic carbon and nitrogen stable

isotope ratios. Carbonate was removed by adding 2% hydrochloric acid before sample combustion in a Carlo Erba/Fisons 1108 CHN analyzer, and the pure CO<sub>2</sub> and N<sub>2</sub> gases were passed to a Finnigan MAT Delta S mass spectrometer. Measurements were calibrated against carbonate standards (NBS-18, -19 and -20, respectively) and atmospheric nitrogen (Mariotti 1983). Isotope ratios were calculated using the following equation,

$$\delta X (\text{‰}) = (R_{\text{sample}}/R_{\text{reference}} - 1) \times 10^3,$$

where  $X$  and  $R$  are <sup>13</sup>C (or <sup>15</sup>N) and <sup>13</sup>C/<sup>12</sup>C (or <sup>15</sup>N/<sup>14</sup>N), respectively, with  $\sigma = 0.15\text{‰}$  for  $\delta^{13}\text{C}$  and  $\sigma < 0.2\text{‰}$  for  $\delta^{15}\text{N}$ .

Bulk sediment accumulation rates (AR<sub>tot</sub>) and accumulation rates of organic carbon and sulfur (AR<sub>comp</sub>) were calculated according to van Andel *et al.* (1975) and Thiede *et al.* (1982). Values were given in g/(m<sup>2</sup> year) (Müller and Suess 1979, Rea *et al.* 1980):

$$\text{AR}_{\text{tot}} = \text{SR} \times p_{\text{dry}}$$

$$\text{AR}_{\text{comp}} = \text{AR}_{\text{tot}} \times \text{wt\%}_{\text{comp}} / 10$$

where AR<sub>comp</sub> in g/(m<sup>2</sup> year), AR<sub>tot</sub> in g/(cm<sup>2</sup> 1000 years), SR = linear sedimentation rate in cm/1000 years,  $p_{\text{dry}}$  = dry weight per wet volume in g cm<sup>-3</sup> and %<sub>comp</sub> = weight percentage of the component in question.

Dry weight per wet volume of the samples was determined by drying a given sample volume at 60 °C until no further weight changes occurred.

Chronology of the cores in this study is based on the results of pollen and diatom analysis, which were correlated with the standard sequence of chrono-zones for the area (cf. Müller 2001a). One core for each lagoon was dated (Fig. 2). A pollen profile for the Oder lagoon, showing the pollen zones in detail, has been published in Müller *et al.* (1996). In addition, illustrations and discussions of pollen profiles from adjacent coastal lakes and islands can be found in Strahl (1996) and Lange *et al.* (1986). Kliewe and Janke (1982) provide an extended discussion of the development of a regional dating scheme based on pollen analysis and <sup>14</sup>C

dating, including possible errors. From the age models of the cores (Fig. 2), linear sedimentation rates were calculated. These rates were used for the calculation of accumulation rates.

## Results and discussion

### Sediment sequence

Several lakes existed in the area of the present Greifswalder and Oder lagoon during the late last glacial period, with sand being the predominant sediment (Fig. 2). In the Oder lagoon, these late glacial deposits were recognized in four of the five cores (Müller 2001a). Core 18112 from the western basin of the Oder lagoon contains an almost complete section from the Alleröd stade (II) where fine sands alternate with peat. Sediments from this core show an increase in water level at this time due to a change in climate from cool and dry to more humid warm conditions.

A hiatus up to 7800 yr B.P. is found in both the western and eastern basins of the Oder lagoon as reflected in cores 18118 and 18120. This hiatus appears to be due to erosion related to the low sea level during the Ancylus regression period (9200–9000 yr B.P.). This regression has been associated with the drainage of the Ancylus-Lake via the Darss Sill area between the present landmasses of Germany to the south and southern Sweden and Denmark to the north (Björck 1995). The regression period, which was followed by temporary terrestrial stages in large basins of the study area, lasted for almost a millennium, from about 8700 to 7900 yr B.P. (Kliewe 1995). In the Greifswalder Bodden lagoon it is reflected by the growth of peat (Fig. 2).

Between 7800 and 6000 yr B.P., lakes existed in both basins of the Oder lagoon and, possibly less distinct in the Greifswalder Bodden and Großer Jasmunder Bodden lagoons. In the Oder lagoon, cores 18118 and 18120 reflect this lacustrine period, which started in the eastern basin of the lagoon (core 18120) at least in the Older Atlantic stade (VI), and continued far into the Younger Atlantic stade (VII). Although a marine transgression obviously did not occur in the

study area, the lake stages reflect the rising water level at the time. Higher sea level in the area is linked to the onset of the Litorina transgression in the Baltic Sea region about 7900 yr B.P. The sea level rose quickly up to 5700 yr B.P. during the first main stage of the Litorina transgression (Kliewe 1995).

The lacustrine phase in the study area was followed by the Litorina transgression, characterized by three main stages. The first of these affected the area of the southern Baltic Sea around 7000 yr B.P. (Kliewe and Janke 1982). However, the sediments of the Oder lagoon reflect only the second main stage of the Litorina transgression in that mud sediments occur around 5500 yr B.P. in both basins of the lagoon (Fig. 2). The onset of the second main stage is evident in the transgressive sands found on top of the lacustrine/peat sequence in core 18120 from the eastern basin (Müller 2001a). In contrast, in the Greifswalder Bodden lagoon adjacent to the northwest of the Oder lagoon and in the Großer Jasmunder Bodden lagoon in the north of the study area, the influence of the Litorina transgression can be seen around 6500 and 7000 yr B.P. respectively, more than a thousand years earlier than in the Oder lagoon. The findings given above strongly support the suggestion that the onset of the Litorina transgression varies regionally in the southern Baltic Sea area (Kliewe and Janke 1982), with the northernmost lagoons being affected earlier. Such variation must be due to differences in post-glacial isostatic rebound, the position of the lagoon bodies to the Baltic Sea and the pre-existing relief.

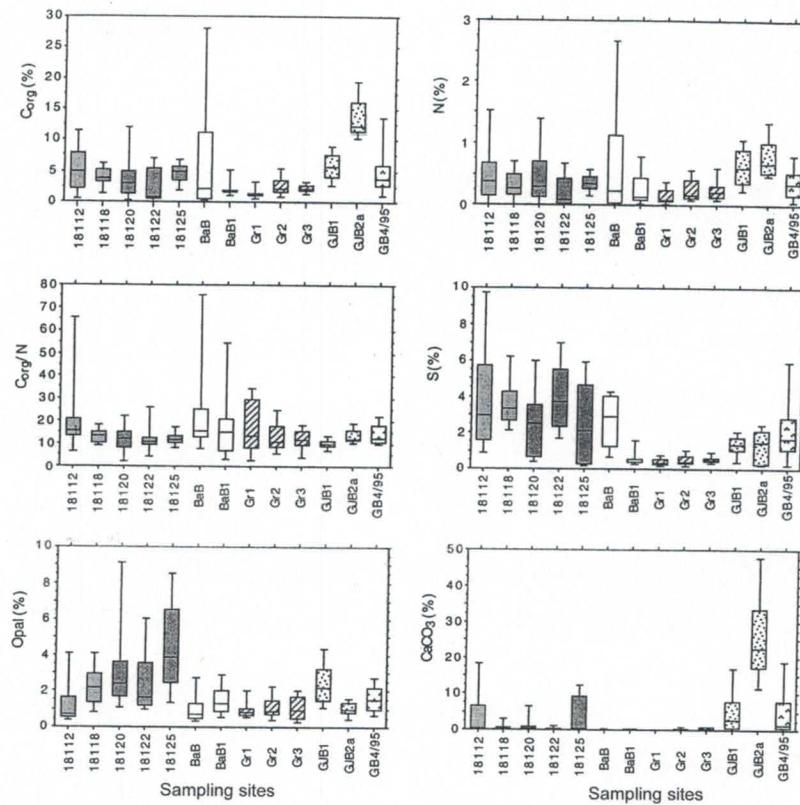
The brackish-marine to brackish muds of this study show a decreasing fraction of sand toward the present. This reflects a rapid increase in quiescence of the inner shores of the Oder lagoon due to the closure of barrier islands (cf. Janke *et al.* 1993). It has been shown that the outer coast sand spits in the southern Baltic Sea region were closed to form barrier islands in the Subboreal regression period from 4000 to 3000 yr B.P. (Fig. 2). Subsequently, contact between sea and coastal lagoons diminished further owing to the growth of sand spits and barrier islands, a process which continues to the present (Kliewe and Janke 1978, 1982, 1991). Locally, i.e. in the Barther Bodden lagoon, the

onset of brackish-marine mud sedimentation can be seen rather late, e.g. 2500 BP in the north-eastern part of the Barther Bodden lagoon (core BaB1) (Fig. 2). This suggests that mud sedimentation was dependent on the build-up of sand spits and barrier islands.

### Chemical characteristics of the sediments

The qualitative data structures for the elemental analyses allow a general comparison of inputs into the different lagoons. The majority of the sediment samples of all lagoons has organic carbon concentrations < 5% (Fig. 3). Organic carbon concentrations can exceed values of 25%, due to the presence of peat layers. High values are found in the Oder Estuary in the eastern part of the study area and close to the Oder River mouth and in the Großer Jasmunder Bodden lagoon in the northern part of the study area. These high values are caused by lacustrine stages with high productivity and, in the case of the Oder Estuary, by terrigenous organic matter input via the Oder River. High organic carbon values are also found in the Greifswalder Bodden lagoon adjacent to the Oder Estuary and in parts of the Barther Bodden lagoon in the far west. These high values in the latter two lagoons are due to layers of peat, which locally underlie the brackish-marine mud sediments.

The data structure for the nitrogen concentrations (Fig. 3) is similar to that of the organic carbon, suggesting similar organic matter sources for all lagoons. Low nitrogen values at high C<sub>org</sub> values (e.g. in parts of the Großer Jasmunder Bodden lagoon) may reflect noticeable terrigenous organic matter contributions. Some lagoons with high C<sub>org</sub> values show also slightly higher N values (e.g. Oder Estuary and parts of Barther Bodden lagoon) suggesting that noticeable contributions from autochthonous organic matter may also have contributed to high organic carbon concentrations. In contrast, relatively high nitrogen values at lower C<sub>org</sub> values suggest significant autochthonous inputs (e.g. Grabow lagoon and parts of the Großer Jasmunder Bodden lagoon). Overall, however, the data structures for organic carbon and nitrogen do not allow



**Fig. 3.** Qualitative data structure of organic carbon ( $C_{org}$ ) and nitrogen (N) contents, organic carbon to nitrogen ratios ( $C_{org}/N$ ), sulfur (S), biogenic opal and calcium carbonate ( $CaCO_3$ ) contents for all sediment cores. The boxes show the percentile range from 10% to 90%, with the median shown by the bold line in each box. The x-axis of each plot shows the sampling sites.

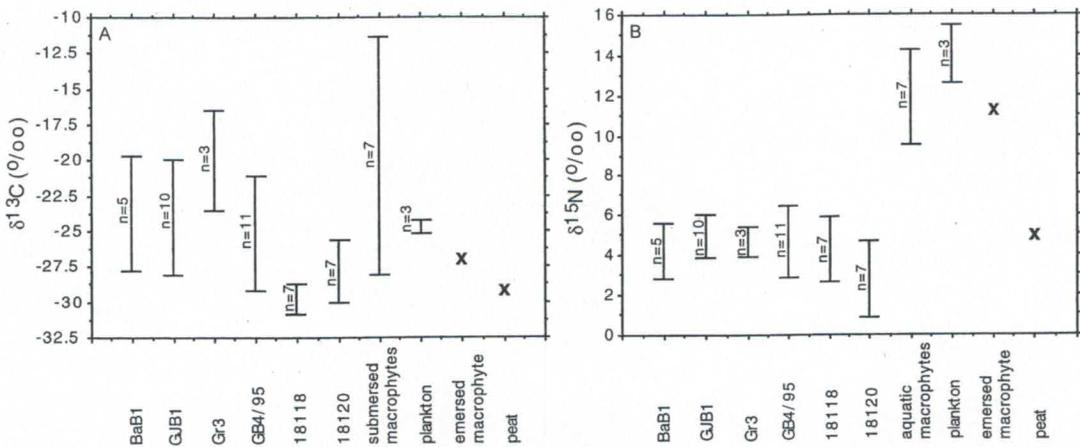
conclusions on organic matter provenance. The  $C_{org}/N$  values (Fig. 3) suggest a contribution from terrigenous organic matter sources in all sediment cores.  $C_{org}/N$  values range from values as low as 2 to values up to 80 suggesting both periods of high autochthonous productivity and contribution from terrigenous organic matter sources.

Sulfur values are clearly highest in the Oder Estuary (Fig. 3). Low values can be found in the Grabow lagoon and parts of the Barther Bodden lagoon. These low values may be caused by low rates of pyrite formation caused by low availability of reactive organic matter. Biogenic opal values are high in the Oder Estuary (Fig. 3). These values reflect periods of high autochthonous productivity. Lacustrine periods with high productivity and high biogenic opal input could be noticed in the Oder Estuary (Müller 2001a). Thereby, the values are slightly higher in the eastern basin of the Oder Estuary than in the western basin, suggesting higher productiv-

ity or more frequent and longer lacustrine stages in the former basin. Calcium carbonate values are high at some sites in the Oder Estuary basins, the Greifswalder Bodden and the Großer Jasmunder Bodden lagoons (Fig. 3). These high values may reflect periods of increased productivity or water exchange with the Baltic Sea, e.g. during transgression stages associated with flooding. It is also possible that these values reflect increased erosion of underlying carbonate rocks during periods of abrupt sea level change.

### Input of organic matter

The  $\delta^{13}C$  and  $\delta^{15}N$  values in the sediments of the lagoons indicate periods of high productivity, lacustrine stages and significant terrigenous inputs in the coastal lagoons. As with previous studies (e.g. Thornton and McManus 1994, Ruttnerberg and Goñi 1997, Müller and Opdyke



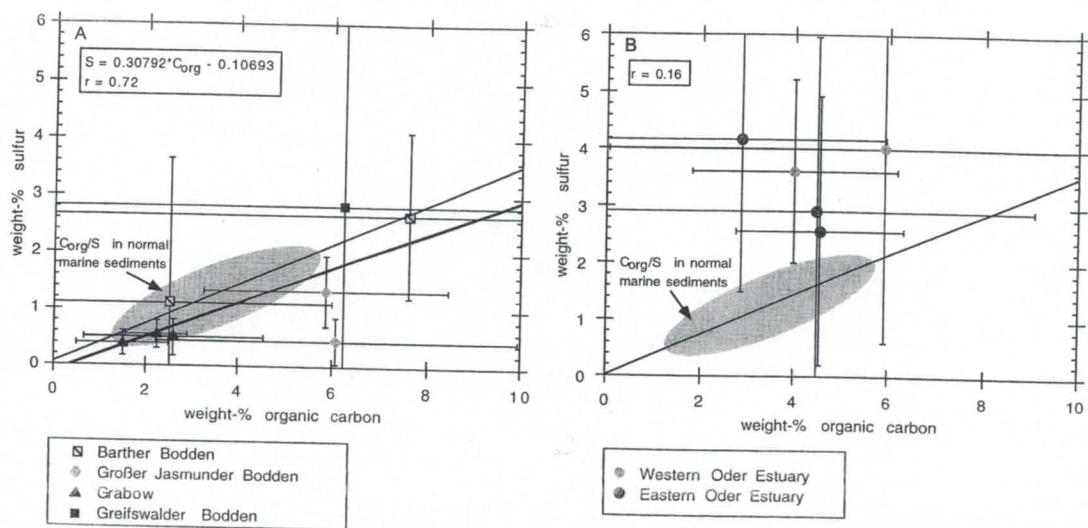
**Fig. 4.** Range of  $\delta^{13}\text{C}$  (A) and  $\delta^{15}\text{N}$  (B) values of organic matter of sources and sediments in the study area. Sample series are from the Western Oder lagoon (core 18118), Eastern Oder lagoon (core 18120), Barther Bodden (core BaB1), Grabow (core Gr3), Großer Jasmunder Bodden (core GJB1) and Greifswalder Bodden (core GB4/95) lagoons. The numbers in the plot ( $n$ ) give the number of measurements for each core or for each organic matter source. Two single measurements are shown for emerged macrophyte and peat material. Isotope values are from Müller and Voss (1999).

2000), several organic tracers (C/N,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ) were applied to test for diagenetic effects so as to improve confidence in the interpretation of the data. Studies of Müller and Voss (1999) and Müller and Mathesius (1999) discussed organic matter sources in the area, and tested the applicability of the C/N and stable isotope data for paleoenvironmental studies in the southern Baltic Sea.

Boundary values representing marine organic matter and terrigenous organic matter such as land plants, shore plants, peat and soils were derived from measurements of organic matter sources in the study area (Müller and Voss 1999). Marine organic matter was considered by these authors to have typical  $\delta^{13}\text{C}$  values around  $-24.3\text{\textperthousand}$  for plankton, and average  $\delta^{15}\text{N}$  values between  $7\text{\textperthousand}$  and  $10\text{\textperthousand}$  (Peters *et al.* 1978) with plankton samples having values of  $15.5\text{\textperthousand}$ . Aquatic macrophytes showed a wide range in  $\delta^{13}\text{C}$  values from  $-28.1\text{\textperthousand}$  to  $-11.4\text{\textperthousand}$  and  $\delta^{15}\text{N}$  values ranging from  $9.5\text{\textperthousand}$  and  $14.2\text{\textperthousand}$ . Terrestrial organic matter (i.e. derived from C3 plants) have typical  $\delta^{13}\text{C}$  values between  $-25\text{\textperthousand}$  and  $-30\text{\textperthousand}$ . Furthermore, terrestrial organic matter has a range in  $\delta^{15}\text{N}$  from  $-6\text{\textperthousand}$  to  $18\text{\textperthousand}$  with average values around  $3\text{\textperthousand}$  or, in the case of nitrogen fixing terrestrial plants, even lower

(Schoeninger and DeNiro 1984, and references therein). C3-macrophytes, growing on the shore, have  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of  $-27\text{\textperthousand}$  and  $11.3\text{\textperthousand}$ , respectively. The corresponding values for peat were  $-29.2\text{\textperthousand}$  ( $\delta^{13}\text{C}$ ) and  $4.9\text{\textperthousand}$  ( $\delta^{15}\text{N}$ ).

The lowest  $\delta^{13}\text{C}$  values can be found in the Oder lagoon (Fig. 4A). The range of the values suggests high fractions of terrigenous organic matter in the sediments of the eastern and the western basins of the Oder lagoon. This is supported by low  $\delta^{15}\text{N}$  in the sediments of both basins (Fig. 4B). Noticeable terrigenous organic matter input is also indicated by low  $\delta^{15}\text{N}$  values in the Greifswalder Bodden and the Barther Bodden lagoons. Overall, terrigenous organic matter input appears to be important in the sediments of all lagoons of this study. Periods of high autochthonous productivity are most evident for the Greifswalder Bodden and the Großer Jasmunder Bodden lagoons but are also noticeable in the other lagoons. The high  $\delta^{13}\text{C}$  values in the Grabow lagoon appear to be caused by terrigenous C4 plant input. They are not due to the burial of aquatic macrophytes as the  $\delta^{15}\text{N}$  values are not higher than in the other lagoons. Had this been so, the values would indicate high burial rates of aquatic macrophytes. Input of C4 plants is also supported by high C/N values in the sediments



**Fig. 5.** Mean  $C_{org}/S$  ratios and standard deviations for the sample series from (A) the Barther Bodden, Grabow, Großer Jasmunder Bodden and Greifswalder Bodden lagoons, and (B) the Eastern and Western Oder lagoon. The normal regression lines in the plots refers to the average C/S ratios and the shaded field marks the empirical field for normal marine sediments according to Berner and Raiswell (1983). In contrast, the bold line in A is the regression line for the sample series shown in the plot. On the upper left, the correlation coefficient is shown.

of these lagoons and by the occurrence of plant remains (Müller and Voss 1999).

#### Paleo-salinities and rock-water interactions

Organic carbon-sulfur systematics in the sediments allow conclusions on paleo-salinities of the water bodies and rock-water interactions in the study area (e.g. Leventhal 1983, Berner and Raiswell 1983, Raiswell and Berner 1985, Boesen and Postma 1988). The data points for the sample series from the Barther Bodden lagoon fall around the regression line of Berner and Raiswell (1983) and also the sample series from the Grabow lagoon fall into the empirically defined area for normal marine sediments according to these authors (Fig. 5A). Normal marine sediments deposited under oxygenated bottom waters with salinities typical of the open ocean, show C/S ratios around 2.8 ( $\pm 0.8$ ) (Berner 1982, Berner and Raiswell 1983). In these sediments, the C/S ratios are determined by the reactivity of organic matter that can be used for metabolism.

The constant C/S ratios in normal marine sediments are a result of the preservation of constant fractions of organic carbon and produced  $H_2S$  in the sediment, under conditions when reactive iron and sulfate are available in excess (Berner 1984). The ratios observed are rather low given the overall low salinities of the coastal lagoons in the study area (Fig. 3). The low ratios in the Grabow and Barther Bodden lagoons appear to reflect the influence of the Baltic Sea water, which has higher salinities than that of the coastal lagoons. This would confirm the suggestion that these lagoons had an active water exchange with the Baltic Sea and were closed off from the Baltic Sea rather late. The slightly lower values in the Greifswalder Bodden lagoon may also be addressed to the influence of the Baltic Sea water. It is possible, however, that the values have also been influenced by the underlying sediment sequences as has been suggested for the Oder lagoon.

The data points for the mean values of organic carbon and sulfur for the sediments from the Oder lagoon show unexpectedly low  $C_{org}/S$  ratios (Fig. 5B), typical of marine sedi-

ments deposited under anoxic bottom waters (Berner and Raiswell 1983). However, the shallow Oder lagoon is polymictic (Correns 1972) and anoxic conditions are unexpected. It has been suggested that the low sedimentary C<sub>org</sub>/S ratios reported in this study are the result of an additional supply of sulfur by groundwater, or from the underlying sequences (Müller 2001a).

In contrast, the samples from the Großer Jasmunder Bodden lagoon fall below the regression line of Berner and Raiswell (1983), thereby resembling sediments of a freshwater environment (Fig. 5A). Dissolved sulfate usually limits pyrite formation in fresh water environments because of its low concentration in the pore waters. This results in high (often > 10) C/S ratios in the underlying sediments (Berner and Raiswell 1983). The high C<sub>org</sub>/S ratios in the sediments in the Großer Jasmunder Bodden lagoon reflect a lagoonal environment with low salinities, which are due to the separation of the lagoon from the Baltic Sea.

Overall, the position of the data points in the plots suggests that pyrite formation is limited by sulfate availability in the coastal lagoons. This is also typical of freshwater environments which are, like the lagoons, characterized of low salinities and low sulfate supply. However, in the Oder lagoon, the organic carbon and sulfur systematics suggest that pyrite formation is not limited by sulfate supply. This is because the high sulfur values suggest additional sulfate supply to the sediments (cf. Müller 2001b). Two other factors can limit pyrite formation besides sulfate availability; the availability of metabolizable matter and that of iron. It is unlikely that pyrite formation in the sediments is iron limited because they are mainly made up of silt (Müller and Hoffmann 1998) characterized by high amounts of iron-bearing minerals. Consequently, the availability of metabolizable organic matter appears to limit pyrite formation in the Oder lagoon sediments.

## Conclusions

Organic carbon to nitrogen, and organic carbon to sulfur ratios, δ<sup>13</sup>C, δ<sup>15</sup>N, organic carbon, biogenic opal and calcium carbonate values in the

sediments of the coastal lagoons of the southern Baltic Sea were linked to the late- and post-glacial biostratigraphy of the sediments. The results were used to derive the effects of sea-level changes, coastal development and related changes in hydrography and accompanying accumulation processes at the bottom of the lagoons.

Overall, clearly identifiable stages in the development of the water bodies were derived from the sediments: post-glacial lake stages with sandy sedimentation, lacustrine phases with high autochthonous productivity, terrestrial stages with peat formation, sedimentation as a result of marine transgression, and brackish sedimentation after the formation of sand spits and barrier islands. These different stages resulted from sea-level changes in the region and may therefore differ from lagoon to lagoon, depending on the position of the lagoon to the Baltic Sea.

The δ<sup>13</sup>C and δ<sup>15</sup>N values in the sediments allow tracing of organic matter provenance and derivation of the effects of river inflow or exposure to the Baltic Sea on the lagoon sediments. For example, the distinct terrestrial input in the sediments of the lagoonal Oder Estuary is evident, which can be attributed to the direct inflow of the Oder River into the lagoon. The δ<sup>13</sup>C values also reflect stages of noticeable autochthonous productivity and help with identification of lacustrine stages, thereby allowing derivation of differences in the paleoenvironments of the lagoons in the study area.

The C<sub>org</sub>/S ratios of the sediments suggest differences in the paleoenvironments between the lagoons. Locally, the chemical composition of the sediments has been influenced by the underlying or nearby lithologies. For example, in the Oder Estuary, the low C<sub>org</sub>/S ratios of the sediments suggest an additional input of dissolved sulfate into the sediments. Although the other lagoons show similarities in their paleoenvironments derived from the C<sub>org</sub>/S ratios in the sediment, it is possible to derive the influence of the Baltic Sea waters. This is because the lagoons that have had longer exposure to the Baltic Sea, show lower mean C<sub>org</sub>/S ratios reflecting the influence of water with higher salinities. In contrast, the lagoons that have been closed off from the influence of the Baltic Sea waters are characterized by sediment with high C<sub>org</sub>/S

ratios similar to the typical values for fresh water conditions.

The new results of this study suggest that each lagoon in the southern Baltic Sea region responded differently to sea-level changes that occurred during the development of the Baltic Sea. These different responses result from the position of the study sites to the barrier islands, river mouths and the different heights of the surrounding land, leading to different degrees in susceptibility of each site to sea-level changes and flooding. This study also highlights the importance of delineating regional from local signals for the lagoons when pursuing paleoclimate studies in the region. Moreover, the study shows that a multi-proxy rather than a single proxy approach helps to exclude uncertainties in the interpretation of the results. It reduces the uncertainties arising from the complexity of the inputs and changes in the study area, thereby improving confidence in the interpretation of the data.

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## References

- Andersen B.G. 1981. Late Weichselian ice sheets in Eurasia and Greenland. In: Denton G.H. & Hughes T.J. (eds.), *The last great ice sheets*, J. Wiley, New York, pp. 1–65.
- Berner R.A. 1982. Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *American Journal of Science* 282: 451–473.
- Berner R.A. 1984. Sedimentary pyrite formation: an update. *Geochimica et Cosmochimica Acta* 48: 605–615.
- Berner R.A. & Raiswell R. 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. *Geochimica et Cosmochimica Acta* 47: 845–862.
- Björck S. 1995. A review of the history of the Baltic Sea 13.0–8.0 ka B.P. *Quaternary International* 27: 19–40.
- Boesen C. & Postma D. 1988. Pyrite formation in anoxic environments of the Baltic. *American Journal of Science* 288: 575–603.
- Brosin H.J. 1965. Hydrographie und Wasserhaushalt der Boddenkette südlich des Darß und des Zingst. *Veröffentl. Geophys. Inst., Univ. Leipzig* 2. Ser. XVII/3: 277–381.
- Correns M. 1972. Beiträge zur Hydrographie des Kleinen Haffs und des Peenestroms. Dissertation Humboldt-Universität Berlin, 239 pp.
- Correns M. 1976. Charakteristische morphometrische Daten der Bodden und Haffgewässer der DDR. *Vermessungstechnik* 24: 459–461.
- Correns M. & Jaeger F. 1979. Beiträge zur Hydrographie der Nordrügenschen Bodden. I. Einführung in das Untersuchungsgebiet, Wasserstandsverhältnisse und Wasserhaushalt. *Acta hydrophys.* 24: 149–177.
- DeMaster J. 1981. The supply and accumulation of silica in the marine environment. *Geochimica et Cosmochimica Acta* 45: 1715–1732.
- Ignatius H., Axberg S., Niemistö L. & Winterhalter B. 1981. Quaternary geology of the Baltic Sea. In: Voipio A. (ed.), *The Baltic Sea*, Kluewer, Amsterdam, pp. 54–104.
- Janke W., Kliewe H. & Sterr H. 1993. Holozäne Genese der Boddenküste Mecklenburg-Vorpommerns und deren künftige klimabedingte Entwicklung. In: Schellnhuber H.J. & Sterr H. (eds.), *Klimaänderung und Küste*, Springer, Berlin-Heidelberg, pp. 137–152.
- KLIBO 1995. Klimawirkung und Boddenlandschaft. *BBWFT Project 01 LK 9405/4*, Greifswald University, 55 pp.
- Kliewe H. 1995. Zeit- und Klimamarken in Sedimenten der südlichen Ostsee und ihrer Vorpommerschen Boddenküste. *Journal of Coastal Research* 17: 181–186.
- Kliewe H. & Janke W. 1978. Zur Stratigraphie und Entwicklung des nordöstlichen Küstenraumes der DDR. *Petermanns Geographische Mitteilungen* 122: 81–91.
- Kliewe H. & Janke W. 1982. Der holozäne Wasserspiegelanstieg der Ostsee im nordöstlichen Küstengebiet der DDR. *Petermanns Geographische Mitteilungen* 135: 1–14.
- Kliewe H. & Janke W. 1991. Holozäner Küstenausgleich im südlichen Ostseegebiet bei besonderer Berücksichtigung der Boddenausgleichsküste Vorpommerns. *Petermanns Geographische Mitteilungen* 1: 1–14.
- Kolp O. 1983. Die schrittweise Verlagerung der Odermündung von der Bornholmulde bis in die Oderbucht infolge holozäner Wasserstandsänderungen im südlichen Ostseeraum. *Petermanns Geographische Mitteilungen* 127: 73–87.
- Lambeck K., Johnston P. & Nakada M. 1990. Holocene glacial rebound and sea-level change in NW Europe. *Geophysical Journal International* 103: 451–468.
- Lange E., Jeschke L. & Knapp H.D. 1986. Ralswiek und Rügen. Landschaftsentwicklung und Siedlungsgeschichte der Ostseeinsel. Teil 1. Die Landschaftsgeschichte der Insel Rügen seit dem Spätglazial. *Schriften zur Ur- und Frühgeschichte* 38, 175 pp.
- Leventhal J.S. 1983. An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition. *Geochimica et Cosmochimica Acta* 47: 133–137.
- Mariotti A. 1983. Atmospheric nitrogen is a reliable

- standard for natural  $^{15}\text{N}$  abundance measurements. *Nature* 303: 680–683.
- Mortlock R.D. & Froelich M.A. 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. *Deep-Sea Research* 36: 1415–1426.
- Müller A. 2001a. Late- and postglacial sea-level change and paleoenvironments in the Oder Estuary, southern Baltic Sea. *Quaternary Research* 55: 86–96.
- Müller A. 2001b: Geochemical expressions of anoxic conditions in a land-locked fjord, western Norway. *Applied Geochemistry* 16: 363–374.
- Müller A., Janke W. & Lampe R. 1996. Zur Sedimentationsgeschichte des Oderhaffs. *Bodden* 3: 167–172.
- Müller A. & Hoffmann K. 1998. Spät- und postglaziale Sedimentationsdynamik und Korngrößenverteilung im Oderhaff, südliche Ostsee. *Leipziger Geowissenschaften* 6: 199–209.
- Müller A. & Mathesius U. 1999. The palaeoenvironments of coastal lagoons in the southern Baltic Sea, I. The application of sedimentary  $\text{C}_{\text{org}}/\text{N}$  ratios as source indicators of organic matter. *Palaeogeography, Palaeoclimatology, Palaeoecology* 145: 1–16.
- Müller A. & Voss M. 1999. The palaeoenvironments of coastal lagoons in the southern Baltic Sea, II.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  ratios of organic matter — sources and sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology* 145: 17–32.
- Müller A. & Opdyke B.N. 2000. Glacial-interglacial changes in nutrient utilization and paleoproduction in the Indonesian Throughflow sensitive Timor Trough, easternmost Indian Ocean. *Paleogeography* 15: 85–94.
- Müller P.J. & Suess E. 1979. Productivity, sedimentation rate, and sedimentary organic matter in the oceans — I. Organic carbon preservation. *Deep-Sea Research* 26A: 1347–1362.
- Peters K.E., Sweeney R.E. & Kaplan I.R. 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnology and Oceanography* 23: 598–604.
- Raiswell R. & Berner R.A. 1985. Pyrite formation in euxinic and semi-euxinic sediments. *American Journal of Science* 285: 710–724.
- Rea D.K., Bourbonniere R.A. & Meyers P.A. 1980. Southern Lake Michigan sediments: Changes in accumulation rate, mineralogy, and organic content. *Journal of Great Lakes Research* 6: 321–330.
- Ruttenberg K.C. & Goñi M.A. 1997. Phosphorus distribution, C-N-P ratios, and  $\delta^{13}\text{C}_{\text{oc}}$  in arctic, temperate, and tropical coastal sediments — tools for characterizing bulk sedimentary organic matter. *Marine Geology* 139: 123–145.
- Schnese W. 1973. Untersuchungen zur Produktionsbiologie des Greifswalder Boddens (südliche Ostsee). I: Die Hydrographie — Salzgehalt, Sauerstoffgehalt, Temperatur und Sestongehalt. *Wiss. Zeitschr. Univ. Greifswald, Mathem.-Naturwissenschaftliche Reihe* 22: 629–639.
- Schoeninger M.J. & DeNiro M.J. 1984. Nitrogen and Carbon isotope composition of bone collagen from marine and terrestrial animals. *Geochimica et Cosmochimica Acta* 48: 625–639.
- Strahl J. 1996. Pollenanalytische Untersuchung eines Vibrokernprofils aus dem NW-Teil des Greifswalder Boddens, südliche Ostsee. *Senckenbergiana maritima* 27: 49–56.
- Thiede J., Suess E. & Müller P.J. 1982. Late Quaternary fluxes of major sediment components to the sea floor at the Northwest African continental slope. In: von Rad U., Hinz K., Sarnthein M. & Seibold E. (eds.), *Geology of the Northwest African Continental Margin*, Springer, Berlin, pp. 605–631.
- Thornton S.F. & McManus J. 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: Evidence from the Tay Estuary, Scotland. *Estuarine, Coastal and Shelf Science* 38: 219–233.
- van Andel Th.H., Heath G.R. & Moore T.C. 1975. Cenozoic history and paleoceanography of the central equatorial Pacific Ocean. *Geol. Soc. Am. Mem.* 143: 134.
- Zonneveld J.I.S. 1973. Some notes on the Last Deglaciation in Northern Europe compared with Canadian conditions. *Arctic Alpine Research* 5: 223–237.

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