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# Age and evolution of the Littorina Sea in the light of geochemical analysis and radiocarbon dating sediment of cores from the Arkona Basin and Mecklenburg Bay (SW Baltic Sea)

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Abstract: Two sediment cores from the Mecklenburg Bay and Arkona Basin were analysed in terms of their geochemical composition and stratigraphy. The main stages of the Baltic Sea evolution – Baltic Ice Lake, Ancylus Lake, and Littorina Sea – were identified in both analysed cores. The most pronounced period was the transition between the Ancylus Lake and the Littorina Sea. The character of the initial stage of the Littorina Sea was clearly defined in the Mecklenburg Bay sediments and is marked by a stepwise increase in loss on ignition and contents of biogenic silica, calcium, magnesium, iron, and strontium. The record of the onset of the Littorina Sea in the Arkona Basin sediments is marked by an abrupt change of the geochemical parameters. The age of the initial Littorina Sea in the Mecklenburg Bay was estimated at about 8200 cal years BP and was probably older than the transgression within the Arkona Basin.

Key words: geochemistry, radiocarbon dating, Ancylus Lake, Littorina Sea, southwestern Baltic Sea

# Introduction

The Baltic Sea was formed as a result of sea level and salinity fluctuations in post-glacial history controlled by isostatic uplift of the Fennoscandia and eustatic changes of the Atlantic Ocean level. During the Holocene, the connection to the Atlantic opened and closed a few times, which caused marine and lacustrine Baltic phases. The last such change took place in the early Atlantic period, when the Ancylus Lake freshwater was inundated by saline waters from the North Atlantic and consequently the Littorina Sea was created. The age of the first appearance, the character of the changes, and the possible marine flooding pathway remain unresolved. Most of the previous studies were conducted on sediments from coastal regions and did not bring comprehensive answers. The transitional period between the first inflow of saline waters into Ancylus Lake and the establishment of the proper brackish-water Littorina Sea was recognized and named the Mastogloia Sea after the diatom genus Mastogloia (Witkowski et al. 2005) or as the initial Littorina Sea (Andrén et al. 2000, Berglund et al. 2005, Emelyanov and Vaikutienė 2013).

The age of the first inflows of Littorina transgression differ between studies from different areas. The follow-

ing are the datings of the first signs of the marine environment: 8650 cal BP in Wismar Bay (Schmolcke et al. 2006), 8640 cal BP in Rega River Valley (Witkowski et al. 2009), 8550 cal BP on the Gardno-Leba Plain (Rotnicki 2009), 7360 cal BP in the Szczecin Lagoon (Borówka et al. 2005, Borówka, Cedro 2011) on the Polish coast, 8500 cal BP in southern Sweden in Blekinge (Berglund et al. 2005), and 7200 cal BP in the Arkona Basin (Rößler et al. 2011).

The most interesting unresolved problem of the evolution of the Littorina Sea is the marine transgression pathway. Some studies indicate a possible route of marine transgression via the Great Belt (Rößler et al. 2011). However, other results from investigations in the southern Baltic area favour an initial Littorina transgression pathway via the Øresund Strait (Björck 1995, Berglund et al. 2005). The marine transgression pathway was explained by differences between radiocarbon dates from the Arkona Basin and Mecklenburg Bay.

The presented geochemical studies on data from two selected sediment cores taken from different southwestern Baltic Sea basins, the Arkona Basin and Mecklenburg Bay, are an attempt to discuss the problems presented above.

# Study area

The investigated cores were taken from two basins of the southwestern Baltic Sea: Arkona Basin and Mecklenburg Bay (Fig. 1). Mecklenburg Bay is a basin situated in the western Baltic with a depth of up to 25 m b.s.l. between the shores of Germany to the south and the Danish islands to the north. The Arkona Basin is situated to the east of Mecklenburg Bay, with a depth of up to 48 m b.s.l., between Rügen and the Pomeranian Bay to the south and the southern coast of Sweden to the north. The Arkona Basin is limited to the east by Bornholm Island and to the west by the Danish islands. Arkona Basin is separated from Mecklenburg Bay by the shallow threshold called Darss Sill.

# Materials and methods

## Sample collection

The cores were taken by the Institute for Baltic Sea Research (Warnemünde, Germany) using a gravity corer aboard the research vessels FS *A. v. Humboldt* and FS *Elisabeth Mann Borgese* during the period 2001–2012. For the purpose of this paper, two cores were selected (Fig. 1). Core 233220 was taken from the southwestern part of the Arkona Basin, 12 km to northwest of Rugia Island. Core EMB1218-3-3 was taken from the northern part of the Arkona Basin, 10 km to the east of Fehmarn Island. The cores were cut into 1-m sections for storage and samples of 1-cm thickness were collected from the cores. Samples were selected at 5-cm intervals for the purpose of geochemical analysis.

## Geochemical analysis

Geochemical analyses of the cores were conducted to determine the loss on ignition and contents of terrigenous silica, biogenic silica, and the metals magnesium (Mg), calcium (Ca) iron (Fe), and strontium (Sr). The loss on ignition was determined by the combustion of dried sediment samples at 550°C. The total silica content was determined by digestion of combusted sample with aqua regia in a water bath by standing for 16 h at room temperature followed by boiling for 2 h. Terrigenous silica content was determined as the residuals after dissolution of biogenic silica in a solution of sodium hydroxide (Bechtel et al. 2007). The metal content was measured in digested liquid samples using the technique of flame atomic absorption spectrometry (ISO 11466) (Boyle 2001).

Sediment samples and shells were dated at the Poznań Radiocarbon Laboratory using <sup>14</sup>C accelerator mass spectrometry (AMS). The radiocarbon dates from lacustrine deposits were calibrated using the Intcal09 table (Reimer et al. 2009), while dates from marine sediments were calibrated using Marine09 data sets (Reimer et al. 2009) with a reservoir age of 375 years based on the Chrono Marine Reservoir Database (Lougheed et al. 2013). The radiocarbon dates were calibrated with Calib6.11 software (Stuiver and Reimer 1993).

#### Statistical analysis

The cores were subdivided into geochemical units based on the constrained hierarchical clustering algorithm by the method of incremental sum of squares (Grimm 1987)



Fig. 1. Map of the southwestern Baltic Sea area with the positions of the discussed cores

implemented in the R Rioja package (Juggins 2013). The number of significant units was determined by the broken-stick algorithm (Bennett 1996), also implemented in the Rioja package (Juggins 2013).

## Results

#### **Core 233220**

Core 233220 was taken at a depth of 40.4 m b.s.l. from the Arkona Basin and had a length of 570 cm (Fig. 1). The bottom section of the core at the depth of 480-570 cm was built of olive grey silt and silty clay. The overlaid section at the depth of 441-480 cm was built of olive black humus clay with plant remains in the upper part. The humus clay was covered by a thin 1-cm layer of olive grey fine sand. The upper section of the core at a depth of 0–440 cm contained olive grey mud, laminated underneath and with a sharp lower boundary.

The core was divided into seven geochemical units (Fig. 2). Unit AB-220-1 (480-570 cm) included silt and silty clay and was characterized by low contents of loss on ignition (1.5-2%), biogenic silica (0.2-2%), and iron (0.9-1.5%) and a high content of terrigenous silica (85-92%). The content of calcium ranged from 1.2 to 3%; similarly magnesium in the same samples ranged from 0.4 to 0.9% and strontium ranged from 15 to 36  $\mu$ g g<sup>-1</sup>.

The sediment sample taken from unit AB-220-2 at a depth of 450 cm was dated at  $8910 \pm 50$  BP (9481–

Table 1. Resu	lts of 1	radiocarbon d	ating						
Sample code		N Lat.	E Long.	Type of materi	Dept	h below bed	Radiocarbon	Calibrated age 1	σ Laboratory
		IN Lat.	E Long.	Type of materi	sur	face (cm)	age <sup>14</sup> C (BP)	range; cal year B	P code
EMB1218-3-	-3/392	2 54°23.690′	11°27.542′	Mytilus sp.		392	$6980\pm40$	7464-7654	Poz-55719
EMB1218-3-	-3/445	5 54°23.690′	11°27.542′	Cerastoderma	sp.	445	$7390\pm50$	7829-8070	Poz-55720
EMB1218-3-	-3/470	54°23.690′	11°27.542′	Cerastoderma	sp.	470	$7490\pm50$	7939-8165	Poz-55723
EMB1218-3-	-3/517	54°23.690′	11°27.542′	peat		517	$9450\pm50$	10,589–10,744	Poz-55725
233220/4	30	54°38.076′	13°43.360′	mud		430	$8170\pm50$	8537-8770	Poz-48478
233220/4	-50	54°38.076′	13°43.360′	humus silt		450	$8910\pm50$	9481-9793	Poz-48479
lithology	AMS dates	LOI %	Si ter %	Si biog %	Ca% 0 <u>2.0</u>	Mg %	Fe %	Sr µg/g 4.0 0 20 40	units coniss 누
200 - 200 - 300 - 300 -		and the second for				A States of the	And horses	AI AI	B-220-7

fine sand

plant remains

0 ... а.

mud 9793 cal BP; Table 1). The sediments of unit AB-220-2 (441-480 cm) were characterized by high loss on ignition (9-11%) and terrigenous silica content (76-87%) and low biogenic silica (0.3-2.3%). The contents of the rest of parameters decreased upward: calcium from 0.7 to 0.3%, magnesium from 1 to 0.4%, iron from 3.1 to 1.7 %, and strontium from 32 to 26  $\mu$ g g<sup>-1</sup>. The fine sand sample layer of unit AB-220-3 (440-441 cm) contained mainly terrigenous silica (96%), while the rest of the parameter values were trace amounts. The mud sediments of units AB-220-4 and AB-220-5 were similar to those of unit AB-220-2 in respect of loss on ignition (5-8%) and contents of iron (1.5–3.4%) and strontium (22–41  $\mu$ g g<sup>-1</sup>) but differed in respect of the contents of biogenic silica (2.8-7.6%), calcium (0.9-2.6%), and magnesium (0.7-1.4%). The content of terrigenous silica increased upward from 69 to 85%. The lithology of the sediments of these units was rather similar to that of the sediments of unit AB-220-6. The humus detritus sample taken from the bottom part of unit AB-220-4 at a depth of 430 cm was dated at  $8170 \pm$ 50 BP (8537-8770 cal BP; Table 1).

Unit AB-220-6 (240-300 cm) was characterized by upward decreases in most of the geochemical parameters: biogenic silica from 3.8 to 2.4%, calcium and magnesium from 0.5 to 0.2%, iron from 1.2 to 0.9%, and strontium from 14 to 9  $\mu$ g g<sup>-1</sup>. The loss on ignition was 3–4%. The content of terrigenous silica continued to increase upward from unit AB-220-5 from 87 to 91%. The uppermost unit, AB-220-7 (0-240 cm), included sediments with rather stable and low contents of most geochemical parameters:

Fig. 2. Geochemical composition of the core 233220 from the Arkona Basin

silt and silty clay

humus clay

0.5 1.0

AB-220-4 AB-220-3 AB-220-2 AB-220loss on ignition (1-2%), calcium (0.15-0.2%), magnesium (0.1-0.15%), iron (0.3-0.7%), and strontium  $(3-9 \ \mu g \ g^{-1})$ . Only the biogenic silica (1-7%) and terrigenous silica (87-96%) contents showed significant fluctuations.

## Core EMB1218-3-3

Core EMB1218-3-3 was taken at a depth of 23.3 m b.s.l. from the Mecklenburg Bay (Fig. 1). The sediment samples representing transition periods between the Baltic Ice lake, Ancylus Lake, and Littorina Sea periods were selected from the core section of 361 to 539 cm,

The bottom section of the core at the depth of 533–539 cm was built of olive grey silty clay (Fig. 3). The layer of silty clay was covered by brownish black peat gyttja at a depth of 512-533 cm. The overlaid section at a depth of 491-512 cm was built of light olive grey sandy silt. The upper section of 0–491 cm was olive grey mud with layers of abundant malacofauna shells. The sediments of the core were divided into five geochemical units (Fig. 3). The unit MB-3-1 was built from light grey clay and the most interesting feature was the high content of calcium (22%), magnesium (1.2%), and strontium (390  $\mu$ g g<sup>-1</sup>) and low content of biogenic (7%) and terrigenous silica (33%). The overlaid unit MB-3-2 represented a peat gyttja layer with characteristic geochemical features: a high content of loss on ignition (38%) and iron (3.5%) and a low content of terrigenous silica (32%). The content of the rest of the parameters decreased upward: calcium from 4 to 0.8%, strontium from 130 to 60  $\mu$ g g<sup>-1</sup>, magnesium from 1.7 to 1%, and biogenic silica from 12 to 7%. The upper layer of peat taken at a depth of 517 cm was dated at 9450  $\pm$  50 BP (10589–10744 cal BP). This date could be estimated as the time range for the beginning of the Ancylus Lake period in this area. The unit MB-3-2 of peat gyttja was covered by a geochemically different unit, MB-3-3, of sandy silt. Unit MB-3-3 was characterized by a high content of terrigenous silica (70-80%) and low content of the rest of the parameters: loss on ignition (6%), biogenic

silica (3–6%), magnesium (0.3–0.4%), calcium (0.3%), iron (2%), and strontium (22–27  $\mu$ g g<sup>-1</sup>).

The most pronounced feature of unit MB-3-4 (461-491cm) was the upward increases of the loss on ignition from 9 to 12%, biogenic silica from 13 to 14%, magnesium from 1 to 1.8%, calcium from 0.5 to 3.4%, and strontium from 29 to 66 µg g<sup>-1</sup>. A shell of Cerastoderma sp. taken at a depth of 470 cm from the upper part of unit MB-3-4 was dated at  $7490 \pm 50$  BP (7939–8165 cal BP). The uppermost unit, MB-3-5 (361-462cm), was characterized by a more stable geochemical composition: the loss on ignition was 12.5%, biogenic silica was 12-15%, terrigenous silica was 55%, magnesium was 1-1.7%, calcium was 3.5%, and iron was 4-5%. Upward increases in the content were visible in the case of strontium from 50 to 75 µg g<sup>-1</sup> and calcium from 2 to 3%. The Cerastoderma sp. shell taken from a depth of 445 cm was dated at  $7390 \pm 50$  BP (7829–8070 cal BP). A *Mytilus* sp. shell sample from a depth of 392 cm was dated at  $6980 \pm 40$  BP (7464-7654 cal BP).

## Discussion

The analysed cores from the Mecklenburg Bay and Arkona Bas were divided into units that were related to the main stages of the Baltic Sea evolution in the Holocene – the Baltic Ice Lake, Ancylus Lake, and Littorina Sea – according to the radiocarbon age and geochemical composition. The Yoldia Sea stage was not recognized in the analysed sediment cores.

#### **Baltic Ice Lake stage**

The lithology, geochemistry, and age of sediments from units AB-220-1 in core 233220 from the Arkona Basin and MB-3-1 from the Mecklenburg Bay suggest that they were deposited during the Baltic Ice Lake stage (Bennike and Jensen 2013, Jensen et al. 1997). Thus the high con-



Fig. 3. Geochemical composition of the core EMB1218-3-3 from the Mecklenburg Bay

tents of calcium, magnesium, and strontium were related to the clay minerals fluxes (Higgins and Schrag 2010). The unit MB-3-2 of peat gyttja with a high content of organic matter reflected the local lacustrine environment that developed after the final regression of the Baltic Ice Lake (Jensen et al. 1997). A similar peat gyttja layer was not found in the core taken from the deeper part of the Arkona Basin. The age of the final stage of the Baltic Ice Lake was well established according to the bottom layer of peat gyttja dated at 9450  $\pm$  50 BP (10589–10744 cal BP). This date is related to the period of regression of the Baltic Ice Lake in the Mecklenburg Bay area at 10 300 cal BP (Jensen et al. 1999).

## Ancylus Lake stage

The sediments from units AB-220-3 and AB-220-4 from core 233220 and MB-3-3 from core EMB1218-3-3 were deposited during the Ancylus Lake stage. The common features of these sediments were a high content of terrigenous silica and upward decreases of loss on ignition, magnesium, calcium, iron, and strontium. The above description confirmed the weak primary production and increase of mineral material supply during the Ancylus Lake stage (Andrén et al. 2000). The date of  $8910 \pm 50$ BP (9481-9793 cal BP) of the humus sample from core 233220 placed the deposition of unit AB-220-2 during the period of maximum extension of the Ancylus Lake (Jensen et al. 1999). The thin 1-cm sand layer (unit AB-220-3) that covered the humus clay (unit AB-220-2) was deposited during the Ancylus Lake regression (Moros et al. 2002).

#### Littorina Sea stage

The first signs of a marine environment were recorded in mud of units AB-220-4 in core 233220 from the Arkona Basin and MB-3-4 in core EMB1218-3-3 from the Mecklenburg Bay. The appearance of marine environment was reflected by increases in the content of biogenic silica, loss on ignition, and the metals magnesium, calcium, iron, and strontium. The changes in geochemical composition suggest a transformation of the environment with increasing primary production and salinity. A high content of magnesium and iron in the Littorina sediments that covered the lacustrine deposit was also reported from the Gdańsk Basin (Emelyanov and Vaikutienė 2013) and has been explained as oxygenation of dissolved magnesium and iron in lacustrine water caused by marine inflows. The high content of iron in marine sediments was a result of the process of iron bonding in sulfide minerals (Sohlenius et al. 2001). The increasing content of loss on ignition and biogenic silica is related to the increase in primary production during the Ancylus Lake and Littorina Sea transition period. Similar phenomena were noted in the Bornholm Basin and Gotland Deep (Andrén et al. 2000, Sohlenius et al. 2001). The high primary production in the Littorina Sea sediments was also recorded by blooms of cyanobacteria (Sohlenius et al. 2001, Rößler et al. 2011). The calcareous organisms such as molluscs and foraminifera removed strontium and magnesium from the sea water (Turekian 1964), and thus the high content of these elements clearly reflects the development of the marine environment. The distinct increases of primary production and salinity confirmed by changes in diatom composition were also reported in other cores from the Arkona Basin and Pomeranian Bay (Kostecki and Janczak-Kostecka 2011, 2012).

The course of those changes was more stepwise in the Mecklenburg Bay (units MB-3-4 and MB -3-5) than in the Arkona Basin (units AB-220-4 and AB-220-5), where the geochemical parameters reached high values in just a thin layer of mud. The initial Littorina Sea stage called Mastogloia Sea (Witkowski et al. 2005) was clearly recorded in the sediments of Mecklenburg Bay but was often not found in the Arkona Basin sediments (Rößler et al. 2011). The abrupt change of the environment in the analysed sediments of Arkona Basin could be explained by the rapid appearance of the marine environment or the possibility of a hiatus between units AB-220-3 and AB-220-4.

The dating of  $7490 \pm 50$  BP (7939–8165 cal BP) from the Cerastoderma sp. shell taken from a depth of 470 cm from core EMB1218-3-3, 21 cm above the Ancylus-Littorina (A/L) transition layer suggested that the initial Littorina Sea appeared in Mecklenburg Bay earlier than 8200 cal BP. Similar ages of 8400 and 8300 cal BP were also reported in previous studies in Mecklenburg Bay (Borówka et al. 2005) according to the diatom composition, where the initial stage of the Littorina was called the Mastogloia stage. The bulk sample of mud from core 233220 taken at a depth of 430 cm, 10 cm above the A/L transition layer, was dated at  $8170 \pm 50$  BP (8537-8770 cal BP). In respect of the bulk sample of dated material, the possibility that the date may be too old cannot be excluded. The age error arises from the fact that the dated sediment was reworked with older material and bulk dates should be regarded as a few hundred years older (Kortekaas et al. 2007, Rößler et al. 2011, Sohlenius et al. 2001). The problems described above suggest that the age of the initial Littorina Sea stage in the Arkona Basin should be estimated at a few hundred years younger than 8600 cal BP and thus the first marine inflows could have appeared later than in Mecklenburg Bay. Some studies reported the age of Littorina transgression as 7200 cal BP in Arkona Basin (Rößler et al. 2011) and 7850 cal BP in the adjacent Bornholm Basin (Andrén et al. 2000). Based on the results described above, the possibility of Littorina transgression via the Great Belt into Mecklenburg Bay and then to the Arkona Basin could not be excluded.

The upper part analysed only in core 233220 (AB-220-6 and AB-220-7) relates to the Post-Littorina Sea stage. The predominant feature of these units was an upward stepwise increase of the terrigenous silica content and decreases of the rest of the geochemical parameters. This could be interpreted as the stepwise decline of primary production and water salinity in the Post-Littorina

stage, which was also reported in Gdańsk Basin (Emelyanov and Vaikutienė 2013) and Bornholm Basin (Andrén et al. 2000).

# Conclusion

On comparing the sediment cores from the Mecklenburg Bay and Arkona Basin, it could be concluded that the boundary between the Ancylus Lake and Littorina Sea environmental conditions was distinctly recorded in the geochemistry of the deposits. The initial stage of the Littorina transgression in Mecklenburg Bay was dated at before 8200 cal BP and marked by stepwise increases in the content of loss on ignition, biogenic silica, magnesium, iron, calcium, and strontium. In the core from the Arkona Basin, the Littorina transgression appeared slightly later than in Mecklenburg Bay, and was recorded as an abrupt change of the environment without a stepwise initial phase. Differences in the age and geochemical composition of the units examined represent the initial Littorina stage and suggest the possibility that the first inflows of Littorina transgression occurred via the Great Belt into the Mecklenburg Bay and then into the Arkona Basin.

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