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Eprints ID : 11496

**To link to this article** : DOI : 10.1177/0959683609104027  
URL : <http://dx.doi.org/10.1177/0959683609104027>

**To cite this version** : De Vleeschouwer, François and Piotrowska, Natalia and Sikorski, Jaroslaw and Pawlyta, Jacek and Cheburkin, Andriy and Le Roux, Gaël and Lamentowicz, Mariusz and Fagel, Nathalie and Mauquoy, Dmitri *Multiproxy evidence of 'Little Ice Age' palaeoenvironmental changes in a peat bog from northern Poland*. (2009) *Holocene*, vol. 19 (n° 4). pp. 625-637. ISSN [0959-6836](http://dx.doi.org/10.1177/0959683609104027)

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# Multiproxy evidence of ‘Little Ice Age’ palaeoenvironmental changes in a peat bog from northern Poland

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**Abstract:** ‘Little Ice Age’ (LIA) climatic deteriorations have been abundantly documented in various archives such as ice, lake sediments and peat bog deposits. Palaeoecological analyses of peat samples have identified these climatic deteriorations using a range of techniques, for example palynology, plant macrofossils, testate amoebae or carbon isotopic analyses. The use of inorganic geochemistry and the reconstruction of dust fluxes has remained a challenge in tracing the nature of LIA climatic changes. Although the idea of enhanced erosion conditions and storminess is commonly discussed, the conditions for dust deposition in peatlands over Europe during the LIA are rarely favourable, because the natural forest cover over Europe was much more important than nowadays, preventing dust deposition. This intense forest canopy masks the deposition of dust in peatlands. In northern Poland, near the Baltic shore, the Słowińskie Błota area was deforested around AD 1100, ie, just before the LIA, and therefore constitutes a key area for the reconstruction of LIA climatic change. With the support of a well-constrained chronology, climatic fluctuations are recorded in an ombrotrophic bog using inorganic geochemistry, plant macrofossils and carbon isotopic analyses. The reconstruction of LIA climatic changes is in good agreement with other records from Poland and NE Europe. However, a c. 50-year discrepancy can be observed between various records. This discrepancy is possibly due to progressive time-dependent cooling gradient from north to south Europe.

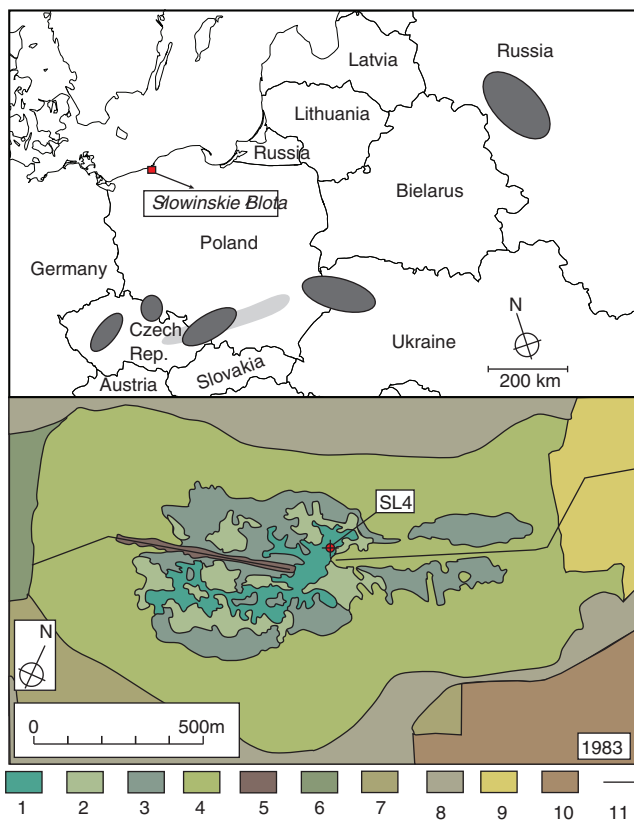
**Key words:** Peat, multiproxy, ‘Little Ice Age’, geochemistry, stable isotopes, radiocarbon, lead 210, last millennium, Poland.

## Introduction

Recent studies have demonstrated the potential of ombrotrophic bogs to record past pre-industrial fluctuations of elements during the Holocene (eg, Kylander *et al.*, 2005, 2007). Other studies have assessed the potential of peat bogs to record past climatic fluctuations during the last c. 3000 years using botanical (eg, Mauquoy

*et al.*, 2002a; Barber *et al.*, 2003) and palynological (eg, Anshari *et al.*, 2001; Davis *et al.*, 2003; Finsinger *et al.*, 2006) proxies. However, climatic fluctuations during the last millennium have been rarely characterized using inorganic geochemistry (eg, Shotyk *et al.*, 1998; Kylander *et al.*, 2007). In addition, multiproxy analyses of northeastern European peat deposits, which include inorganic geochemistry, are scarce (eg, Lukashev *et al.*, 1974; Twardowska *et al.*, 1999; Vile *et al.*, 2000; Novak *et al.*, 2003; Mihaljevic *et al.*, 2006; Syrovetsnik *et al.*, 2007).

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**Figure 1** Top. Site location and surrounding eastern European Pb-Zn ore (light grey) and coal (dark grey) basins (after Bibler *et al.*, 1998; Mukai *et al.*, 2001). Bottom. Peatland preservation indices based on stereoscopic aerial photographs (after Herbichowa, 1998). 1, open peatland complex of *Sphagno-tenelli-Rhynchosporium albae*, *Sphagnetum magellanici typicum* and <5% single dwarf pines of c. 2 m high; 2, open *Sphagnetum magellanici pinetosum* peatland with more densely (max.10%) distributed pines of 2 to 5 m high; 3, small patches of open *Sphagnetum magellanici pinetosum* peatland with initial state of *Vaccinio uliginosi-Pinetum*, small patches of *Sphagnetum magellanici typicum* and sparse pine of 4 to 8 m high; 4 (4+5), 8 m to 20 m high pine and birch-pine cover (50% to 80%) tree (*Vaccinio uliginosi-Pinetum* and *Betuletum pubescentis*); 5, community with *Calluna vulgaris* on dried peat; 6, degenerated form of alder and young pine forest; 7, meadow and pasture communities (class *Molinio-Arrhenatheretea*) on humified peat; 8 (9+10), deciduous forest meadow communities from *Molinio-Arrhenatheretea* class on mineral soils; 9, initial stage of development of peatland vegetation and young forest planted in remnants of peat exploitation; 10, anthropogenic vegetation (ie, recent); 11, active ditches

The climate of the last millennium is characterized by a warm period known as the ‘Medieval Warm Period’ (MWP) between c. AD 1000 and 1300. It is followed by a series of climatic deteriorations between c. AD 1300 and 1800, the so-called ‘Little Ice Age’ (LIA). The causes of these climatic deteriorations may be due to changes in solar activity (van Geel *et al.*, 1999; Mauquoy *et al.*, 2004). Cold periods coincide with solar activity minima, as recorded by low sunspot numbers (Stuiver and Braziunas, 1993). During periods of reduced solar activity there is an increased production of  $^{14}\text{C}$ , as there is less solar magnetic shielding against cosmic rays (van Geel *et al.*, 1999). The  $\Delta^{14}\text{C}$  is thus anti-correlated with the number of sunspots. The highest  $\Delta^{14}\text{C}$  values are observed during cold periods. Climatic deteriorations during the LIA have been investigated using various archives, for example, ice cores (eg, O’Brien *et al.*, 1995; Dahl-Jensen *et al.*, 1998), lake sediments (eg, Blass *et al.*, 2007; Haltia-Hovi *et al.*, 2007) and

peat deposits (eg, Mauquoy *et al.*, 2002a). These climate reconstructions record several periods of climatic deteriorations, namely the Wolf (AD 1300–1380), Spörer (AD 1420–1470) Maunder (AD 1645–1715) and Dalton (AD 1790–1820) minima. However, it remains challenging to attempt tracking these rapid climatic changes using peat inorganic geochemistry, a tool that has been abundantly used to reconstruct past human activities.

Pomeranian Baltic bogs are located on the Southern edge of the cupola-like raised bog area of Europe (Osvald, 1923, 1925; Kulczyński, 1949). Palaeoenvironmental high-resolution multiproxy studies on these mires are very rare in NE Europe. Most of the previous research has focused on past vegetation changes (Wodziczko and Thomaschewski, 1932; Ołtuszewski, 1948; Ołtuszewski and Borówko, 1954; Szafranski, 1961; Latałowa and Pędziszewska, 2003). The investigation of Herbichowa (1998) provided a Holocene record of local vegetation and basic geochemistry of Słowińskie Błota bog and Staniszewskie bog. In addition, recent investigations using a multiproxy approach are currently in progress (Lamentowicz *et al.*, 2009).

This paper attempts to use the atmospheric soil dust flux (ASD) derived from titanium concentration of a peat record to reconstruct the possible climatic events during the last millennium in northern Poland. Other proxies (carbon stable isotopes and macrofossils) and accurate age dating are also used in order to tentatively picture the various phases characterizing this cold period. Special attention is given to the environmental conditions inferred by the various proxies during the LIA. A comparison with other records from this peat bog and with records over Europe allows us to draw a sketch of the LIA synchronicity over northeast Europe.

## Site description

Słowińskie Błota bog is located 8 km to the southeast of Darłowo city, and 10 km away from the Baltic Sea (Figure 1 top). Up to the end of eighteenth century, Słowińskie Błota bog had been an open bog (ie, not covered by trees). It has been drained twice: (1) in 1880 when surrounding ditches were dug and (2) in 1970 when two ditches were dug through the central part of the bog. The latter were renewed in 1985 (Herbichowa, 1998). The actual vegetation is composed of several species of *Sphagnum*. In the outer parts, *Vaccinium uliginosum*, *Calluna vulgaris* and *Betula pubescens* are present (Figure 1 bottom).

## Methods

### Coring and subsampling

A 1 m core (SL4) was retrieved from the central part of the bog (Figure 1 bottom), but away from the 1970 drainage ditches, using a stainless steel 10 cm × 10 cm Wardenaar corer (Wardenaar, 1986). The core was then wrapped in plastic bags and stored in a fridge. The edges of the core were removed to avoid any metal contamination by the corer. The remaining core was then sliced into 1 cm thick samples using a titanium knife. Each sample was stored in a plastic bag. In this study, we present various proxies obtained on SL4: macrofossils, inorganic geochemistry,  $\delta^{13}\text{C}$ , radiocarbon and lead dating. They are compared with selected water-table change indicators from a second core (SL2) retrieved in the same bog, 10 m away from SL4. SL2 has also been dated and analysed for biological proxies such as pollen, macrofossils and testate amoebae by Lamentowicz *et al.* (2009).

### Chronological control

#### $^{210}\text{Pb}$ analyses

Polonium was extracted from 2 g of dry peat powder using a sequential  $\text{H}_2\text{O}_2$ - $\text{HNO}_3$ - $\text{HCl}$  digestion. To control efficiency of

**Table 1** Results of  $^{210}\text{Pb}$  analysis

Lab nr.	Mean depth (cm)	$^{210}\text{Pb}$ corrected date (AD)	Uncertainty (yr)	Lab nr.	Mean depth (cm)	$^{210}\text{Pb}$ corrected date (AD)	Uncertainty (yr)
0–1	0.5	2006	1	18–19	18.5	1978	2
1–2	1.5	2005	2	19–20	19.5	1975	2
2–3	2.5	2004	2	20–21	20.5	1973	3
3–4	3.5	2003	2	21–22	21.5	1970	3
4–5	4.5	2002	2	22–23	22.5	1966	3
5–6	5.5	2001	2	23–24	23.5	1962	3
6–7	6.5	2000	2	24–25	24.5	1958	3
7–8	7.5	1999	2	25–26	25.5	1953	3
8–9	8.5	1998	2	26–27	26.5	1946	3
9–10	9.5	1997	2	27–28	27.5	1936	3
10–11	10.5	1996	2	28–29	28.5	1928	3
11–12	11.5	1995	2	29–30	29.5	1919	3
12–13	12.5	1993	2	30–31	30.5	1911	3
13–14	13.5	1991	2	31–32	31.5	1902	4
14–15	14.5	1988	2	32–33	32.5	1890	4
15–16	15.5	1985	2	33–34	33.5	1870	6
16–17	16.5	1983	2	34–35	34.5	1824	8
17–18	17.5	1980	2				

deposition and alpha detection, a portion of HCl containing a known amount of artificial  $^{208}\text{Po}$  was added before evaporation and deposition on a silver disc. Efficiency of deposition up to 80% was commonly achieved.

Alpha activity was measured with a spectrometer Canberra model 7401, with a surface-barrier Si semiconductor detector. The sensitive area of the detector is  $300\text{ mm}^2$  and its energy resolution is 20 keV. This enables a good separation of  $^{210}\text{Po}$  ( $E = 5.308\text{ MeV}$ ) and  $^{208}\text{Po}$  ( $E = 5.105\text{ MeV}$ ) peaks. As absolute activities of both isotopes are rather low, each measurement lasted two days in order to obtain sufficient accuracy. The results of the calculation were corrected for radioactive decay of  $^{208}\text{Po}$  since the moment of its calibration, and decay of  $^{210}\text{Pb}$  since the moment of polonium extraction from sediments.

The Constant Rate of Supply (CRS) model (Appleby, 2001) was applied in order to build the  $^{210}\text{Pb}$  age model. The activity of autigenic  $^{210}\text{Pb}$  is assumed to be constant along the sediment column. It is determined by measurements on sediments old enough

to contain no allochthonous  $^{210}\text{Pb}$ . The activity of allochthonous lead is then calculated by subtracting the activity of autigenic lead from the total lead activity. Uncertainties were calculated using the propagation of errors technique according to ISO, *Guide to the expression of uncertainty in measurement*. Results are summarized in Table 1.

#### $^{14}\text{C}$ dating

Macrofossils were carefully selected from eight peat samples of SL4, after soaking in mQ water and transfer in a Petri dish, following the protocol developed by Kilian *et al.* (1995) and Mauquoy *et al.* (2004). In this way only the parts of aboveground plants were selected for  $^{14}\text{C}$  dating. Young carbon contamination by downward growing rootlets was therefore prevented. In the samples from Słowińskie Błota, the main macrofossils collected were *Sphagnum* spp. stems and opercula, *Calluna vulgaris* stems, *Erica tetralix* stems and inflorescences and *Andromeda polifolia* leaves (Table 2). Charcoal fragments and some seeds were also

**Table 2** Description of samples chosen for  $^{14}\text{C}$  AMS dating and results of measurements and calibration

Lab no.	Sample depth (cm)	$^{14}\text{C}$ age (BP)	95.4% age interval	Sample composition
GdA-1097	$34.5 \pm 0.5$	$200 \pm 30$	1741–1857*	<i>Sphagnum</i> spp. branches and opercula, <i>Erica tetralix</i> inflorescence
GdA-1088	$36.5 \pm 0.5$	$95 \pm 25$	1683–1738	<i>Sphagnum</i> spp. branches and opercula, <i>Calluna vulgaris</i> branches, <i>Erica tetralix</i> inflorescence, seeds
GdA-1098	$43.5 \pm 0.5$	$455 \pm 30$	1416–1480	<i>Sphagnum</i> spp. branches and opercula, <i>Calluna vulgaris</i> branches and leaves, <i>Erica tetralix</i> inflorescence, <i>Andromeda polifolia</i> leaves, charcoal, seeds
GdA-1099	$52.5 \pm 0.5$	$875 \pm 40$	1165–1261	<i>Sphagnum</i> spp. branches and opercula, <i>Calluna vulgaris</i> branches and leaves, <i>Erica tetralix</i> inflorescence, charcoal
GdA-1100	$57.5 \pm 0.5$	$935 \pm 30$	1084–1176	<i>Sphagnum</i> spp. branches and opercula, <i>Calluna vulgaris</i> branches and leaves, charcoal
GdA-1089	$68.5 \pm 0.5$	$1055 \pm 30$	974–1026	<i>Sphagnum</i> spp. stems
GdA-1090	$79.5 \pm 0.5$	$1130 \pm 30$	862–956	<i>Sphagnum</i> spp. stems
GdA-1091	$97.5 \pm 0.5$	$1230 \pm 30$	675–797	<i>Sphagnum</i> spp. stems

\* Calibrated age range obtained as a result of summarizing distribution of probability of calibrated age and  $^{210}\text{Pb}$ -derived age, assuming Gaussian distribution for the latter.

**Table 3** Elemental geochemistry on dry bulk samples

Mean depth (cm)	Mean density (g/cm <sup>3</sup> )	Mean acc. rate (cm/yr)	Age cal.	Unc. cal.	Cl (ppm)	K (ppm)	Ca (ppm)	Ti (ppm)	Fe (ppm)	Br (ppm)	Rb <sup>a</sup> (ppm)	Sr (ppm)	Zr <sup>a</sup> (ppm)
4.5	0.023	0.830	2002	3	611	2836	4316	36	851	12.8	5.44	8.77	D.L.
5.5	0.024	0.826	2001	2	408	1820	2628	32.36	490	13.1	4.22	6.47	D.L.
6.5	0.024	0.973	2000	2	390	1850	2539	27.3	622	13.7	3.78	6.51	D.L.
7.5	0.024	1.120	1999	2	452	1493	1657	34.9	574	12.1	3.37	5.34	D.L.
8.5	0.027	1.024	1998	2	380	1330	1472	35.1	677	16.1	3.06	5.51	D.L.
9.5	0.03	0.883	1997	2	421	1237	1065	38.7	718	17.3	3.71	5.89	D.L.
10.5	0.032	0.590	1996	2	487	1411	1113	69	1024	14.8	2.52	4.94	D.L.
13.5	0.057	0.369	1991	2	455	1084	802	31.6	1521	21.3	3.22	8.16	D.L.
16.5	0.056	0.429	1983	3	380	923	1209	62.8	6635	29.3	3.8	16	4.11
18.5	0.05	0.358	1978	3	301	766	1134	57.7	6949	27.9	3.73	15.4	D.L.
21.5	0.044	0.275	1970	3	328	659	1310	81	5382	28.92	2.71	17.5	3.58
23.5	0.047	0.176	1962	3	278	621	1207	95.3	5181	31.3	3.39	17.7	4.13
26.5	0.065	0.117	1945	3	262	770	1250	244	3901	33.5	4.46	21.4	13.7
29.5	0.066	0.095	1920	3	307	1148	1024	272	2840	59.3	5.41	18.1	21.4
32.5	0.065	0.029	1888	5	330	748	895	138	1996	42	1.88	12.3	9.32
34.5	0.058	0.020	1820	41	205	615	772	155	2021	23.1	2.86	11.7	12.9
36.5	0.071	0.022	1719	31	309	1171	943	376	2248	35.2	6.56	19.1	35.5
38.5	0.116	0.026	1627	29	405	980	807	353	1634	45.1	5.59	17	35.6
41.5	0.101	0.031	1512	31	645	511	696	206	1152	56.8	2.95	11.7	19.7
43.5	0.141	0.033	1447	32	802	423	656	180	1139	67.3	2.38	10.8	16.1
45.5	0.149	0.036	1387	35	881	258	708	148	1231	59	1.34	11.4	14.2
47.5	0.126	0.036	1331	39	884	223	795	138	1057	60.1	1.55	13.1	16.4
51.0	0.05	0.073	1234	46	625	130	853	56	1306	54.6	D.L.	11.2	D.L.
52.5	0.048	0.054	1214	47	477	96.4	901	34.3	1183	37.5	D.L.	11.1	D.L.
54.5	0.045	0.063	1177	47	362	92	855	42.5	1229	36.6	D.L.	12	D.L.
57.5	0.03	0.071	1129	45	294	84.1	801	23.6	1319	32	D.L.	11.5	D.L.
59.5	0.033	0.077	1101	42	413	109	1137	60.1	1318	38.9	D.L.	14.47	2.6
61.5	0.031	0.089	1075	39	439	97.6	1260	38.5	1635	39.2	D.L.	15.3	D.L.
66.5	0.035	0.103	1019	30	348	94.1	1007	23.3	1505	28.1	D.L.	12.6	D.L.
68.5	0.031	0.114	1000	27	285	92	885	18.9	1271	24.3	D.L.	10.8	D.L.
71.5	0.032	0.122	974	32	374	102	1087	20.2	1332	25.8	D.L.	12.1	D.L.
73.5	0.035	0.126	957	36	433	95.2	923	32.5	880	30.8	D.L.	11.1	D.L.
77.5	0.028	0.122	925	43	406	93.5	907	22.4	1336	34	D.L.	11.4	D.L.
79.5	0.028	0.116	909	46	406	98.9	772	25.5	1026	33.7	D.L.	8.51	D.L.
82.5	0.037	0.110	883	49	366	101	837	28.3	842	33.7	D.L.	8.02	D.L.
84.5	0.04	0.106	865	51	354	103	663	32.5	735	35.5	D.L.	8.08	D.L.
86.5	0.04	0.104	846	52	441	113	721	37.1	749	44.9	D.L.	8.52	D.L.
88.5	0.028	0.101	827	54	438	104	689	30.4	679	42.3	D.L.	7.87	D.L.
91.5	0.024	0.099	797	56	462	103	684	34.5	505	37.3	D.L.	8.08	D.L.
95.5	0.031	0.098	757	59	419	112	746	34.9	688	37.6	D.L.	8.32	D.L.
97.5	0.025	0.098	736	60	413	101	720	22.5	651	33.4	D.L.	6.97	D.L.
Uncertainty (%)					10	10	3	7	7	5	5	5	10
LLD					30	2.5	1.5	0.9	0.9	0.6	0.8	1	2.5

<sup>a</sup> D.L., measurements below detection limit.

collected when other plants were not present in sufficient quantities for <sup>14</sup>C AMS. Before measurement, samples were pre-treated using an acid-alkali-acid washing sequence in order to remove any carbonate, bacterial CO<sub>2</sub> and humic/fulvic acids. The graphite targets were produced according to a protocol used in the Gliwice Radiocarbon Laboratory (Goslar and Czernik, 2000). <sup>14</sup>C measurements were performed at Poznan Radiocarbon Laboratory (Poland) following the protocol described by Goslar *et al.* (2004).

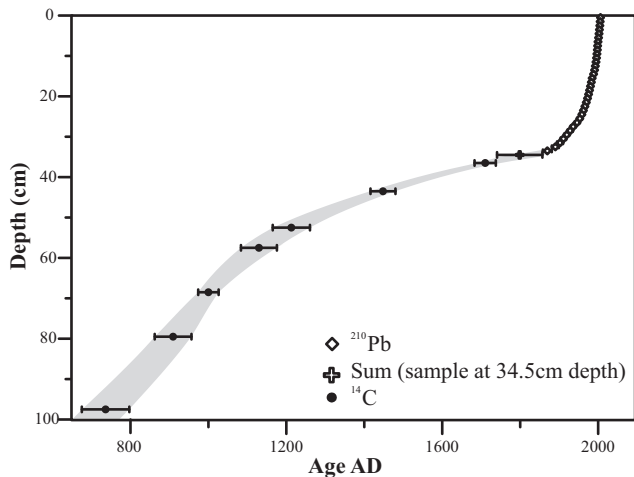
### X-ray fluorescence

Forty-one samples were selected along SL4 core for XRF analysis. Samples were freeze-dried and then powdered in an automatic agate mortar (400 rpm, 1 h). One gram of the resulting powder was analysed for selected elements at the Institute of Environmental Geochemistry (Heidelberg, Germany). Energy-dispersive Miniprobe Multielement Analyzer EMMA (Cheburkin and Shotyk, 1996)

was used to analyse Br, Rb, Sr and Zr while energy dispersive XRF spectrometer TITAN (Cheburkin and Shotyk, 2005) was used to analyse minor elements Cl, K, Ca and Ti. The two analysers are calibrated with various organic international standards: coals (NIST1632b, NIST1635, SARM19 and SARM 20) and plant material (NIST 1515, NIST 1547, NIST 1575, BCR60 and BCR 62). The results, detection limits and uncertainties are given in Table 3.

### Plant macrofossils

Plant macrofossil samples from SL4 were boiled with 5% KOH and sieved (mesh diameter 125 µm). Macrofossils were scanned using a binocular microscope (×10–50), and identified using an extensive reference collection of type material (Mauquoy and van Geel, 2007). Volume percentages were estimated for all components with the exception of seeds, *Eriophorum vaginatum* spindles,



**Figure 2** Age–depth model constructed on the basis of  $^{210}\text{Pb}$  and  $^{14}\text{C}$  dating (see text for details). Diamonds represent results of  $^{210}\text{Pb}$  dating; cross represents midpoint of 95.4% age interval obtained as a result of summarizing  $^{210}\text{Pb}$  and  $^{14}\text{C}$  calibrated age; circles represent midpoints of 95.4% calibrated  $^{14}\text{C}$  age range (see Table 2). Error bars and the grey-shaded area show 95.4% confidence interval of age for dated horizons and the model respectively

*Sphagnum* spore capsules, *Meliola ellisii* (Type 14) fruit-bodies and charcoal particles, which were counted and expressed as the number ( $n$ ) present in each subsample. Zonation of the macrofossil diagrams was made using psimpoll 4.25 (optimal splitting by information content).

### Stable isotopes

Samples for isotopic investigations were taken at each centimetre of the SL4 peat monolith. Each sample was washed in distilled water. Then one *Sphagnum* stem was selected from each sample using low-power microscopy. Loader *et al.* (2007) reported statistically significant differences between the carbon isotopic composition of bulk organic material in pendant leaves, branch leaves and stems of growing *Sphagnum*. Therefore all the leaves, if present, were carefully removed. Then, stems were dried in an oven at 50°C. Because isotopic composition of carbon in bulk organic material closely follows the isotopic pattern measured in  $\alpha$ -cellulose and nitrocellulose (Ménot-Combes *et al.*, 2004; Skrzypek *et al.*, 2007), all the measurements were performed on bulk organic material of *Sphagnum* stems. Fragments of stems weighing about 50  $\mu\text{g}$  were used for each measurement. The samples were packed in tin capsules and combusted in the EuroVector EuroEA3000 elemental analyser at 1020°C. The resulting gases were separated by the gas chromatography method and  $\text{CO}_2$  was transferred to a GV Instruments IsoPrime isotope ratio mass spectrometer. The  $\delta^{13}\text{C}$  values are expressed in ‰ VPDB with an uncertainty equal or better than 0.22‰.

## Results

### Ombrotrophy

Low strontium values have already been used to indicate the ombrotrophy of peat deposits (eg, Shotyk *et al.*, 2002; De Vleeschouwer *et al.*, 2007), ie, bogs that are exclusively fed by atmospheric inputs (eg, rain, snow, fog, dust). In Słowińskie Błota, Sr values below 20 ppm (Table 3) indicate the ombrotrophic nature of the entire 1 m peat profile. The plant macrofossils (see Figure 4) also consistently indicate the presence of acidic, nutrient-poor conditions characteristic of ombrotrophic peat bogs.

### Age–depth relationship

Calibration of radiocarbon dates was undertaken using the IntCal04 calibration curve (Reimer *et al.*, 2004) and OxCal 4.0 software (Bronk Ramsey, 1995, 2001). *A priori* information from the  $^{210}\text{Pb}$ -derived ages was used in a *P-sequence* model (Bronk Ramsey, 2008). The results of calibration are summarized in Table 2.

From the base of the core to 34.5 cm depth,  $^{14}\text{C}$  was used to build an age–depth model. For the sample from depth 34.5 cm the probability distribution of calendar ages obtained with both  $^{210}\text{Pb}$  and  $^{14}\text{C}$  methods were combined, resulting in the interval AD 1741–1857. Above 34.5 cm the results of  $^{210}\text{Pb}$  dating were used.

For building the age–depth model a non-linear approach (generalized additive model, GAM) was used, as described by Heegaard *et al.* (2005). The calculations were performed within each period on the middle-point of the 95.4% range of calibrated age, while an uncertainty equal to the half of this range was assumed. The results of  $^{210}\text{Pb}$  dating are described by Gaussian distribution and in their case the 1-sigma range was used. On the depth scale, the resulting age–depth relationship provides a mean age and an age range for each slice of peat (Figure 2).

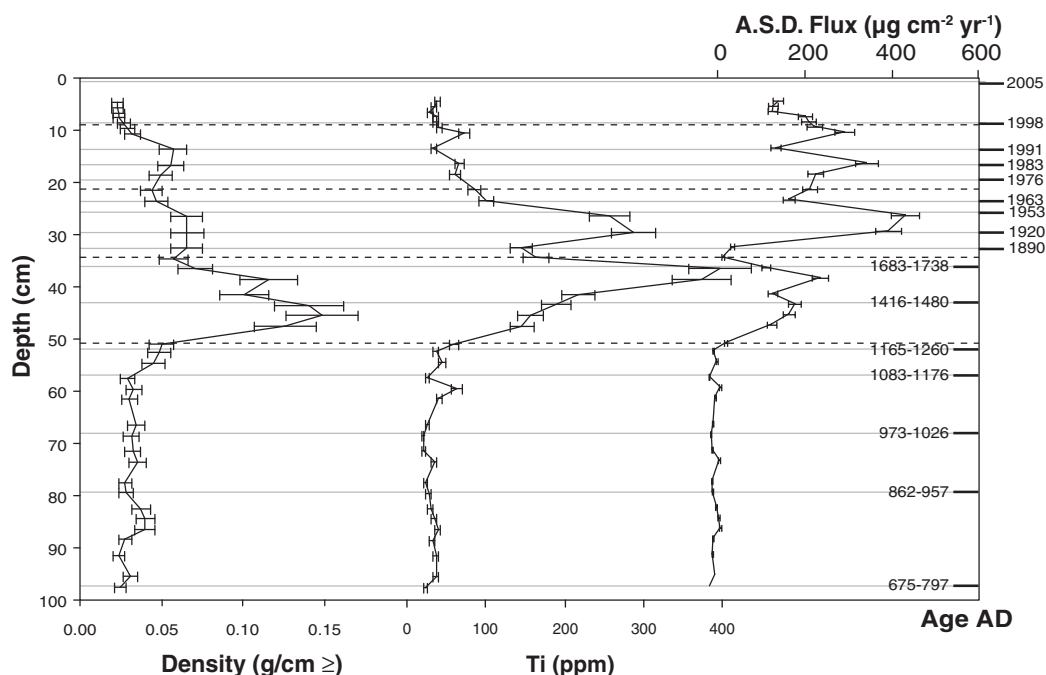
From the base (c. AD 675–800) of the core to 52.5 cm depth (c. AD 1065–1260), the mean peat accumulation rate is rather high (mean = 1 mm/yr). Then, the mean accumulation rate decreases towards 0.3 mm/yr from 52.5 cm depth (c. AD 1065–1260) to 34.5 cm depth (AD 1740–1860). For the samples between 34.5 and 0 cm depth, the mean accumulation rate is higher, and reflects the fresh, uncompacted nature of the acrotelm peat deposits.

### Bulk density, Ti concentration and atmospheric soil dust flux

The bulk density and Ti profiles record small variations from the base of the core to 50 cm depth (Figure 3). Then a sharp peak in bulk density occurs between 50 and 35.5 cm depth. Peak values in the Ti profile also occur in the same depth interval. From 30 to 20 cm depth, the bulk density stabilises between 0.05 g/cm<sup>3</sup> and 0.06 g/cm<sup>3</sup>. However, at this depth, the Ti profile displays a second peak. Values of bulk density then decrease gradually towards the surface of the profile. Titanium concentration fluctuations have been used to indicate fluctuations in soil dust inputs to bogs (Görres, 1993; Holynska *et al.*, 1998; Shotyk *et al.*, 1998). These changes in soil dust inputs can be due to various causes, such as agricultural activities (Hölzer and Hölzer, 1998) or variation in natural atmospheric soil dust fluxes (Shotyk *et al.*, 1998).

Atmospherically derived Soil Dust (ASD) can be calculated using geochemical elements such as Ti (Shotyk *et al.*, 2002) or Sc (Shotyk *et al.*, 2001). Since these elements are conservative, it can be assumed that their amount in ‘soil dust’ is similar to their amount in the upper continental crust. Using the Ti concentration in upper continental crust (0.40%, McLennan, 2001), the concentration of ‘soil dust’ in a peat sample can be deduced (Shotyk *et al.*, 2001). Taking into account the bulk density and the mean accumulation rate derived from  $^{14}\text{C}$  and  $^{210}\text{Pb}$  dates, ASD in a sample can be calculated (Shotyk *et al.*, 2002).

The ASD flux for the Słowińskie Błota profile can be divided into five zones (Figure 3). From the base of the core to 50 cm depth, ASD values are very low, with a mean averaging 22  $\mu\text{g}/\text{cm}^2$  per yr. Given the  $^{14}\text{C}$  dates, this part of the core was deposited during the early Middle Ages. This period is followed by a period of increased ASD (mean = 156  $\mu\text{g}/\text{cm}^2$  per yr) between 50 cm and 35 cm depth, spanning the eleventh to the beginning of the eighteenth centuries (late Middle Ages and early Modern Era). Then ASD reaches very high values (mean = 446  $\mu\text{g}/\text{cm}^2$  per yr) between 30 and 25 cm depth, ie, during the first half of the twentieth century. From 24 to 13 cm depth, ie, during from c. AD 1960 to 1990, values



**Figure 3** Density (Ti), and atmospheric soil dust flux versus depth.  $^{14}\text{C}$  age intervals and some  $^{210}\text{Pb}$  reference points are also reported

average  $249 \mu\text{g}/\text{cm}^2$  per yr. Then the ASD decreases drastically towards lower values (mean =  $204 \mu\text{g}/\text{cm}^2$  per yr) at the surface.

### Detecting sources using enrichment factors

Ti was used to calculate enrichment factors (EF) relative to the upper continental crust (UCC). Ti has been used in other studies as a conservative element to calculate EF (eg, Kempter, 1996; Shotyk *et al.*, 2002).

Given the location of Słowińskie Błota, the main particle sources to the bog are rainwater, sea-salt sprays, ASD and anthropogenic particles from various origins (coal burning, mining and smelting). Table 4 summarizes the EF for each element in the five main intervals encountered in the 1 m core.

K, Rb and Zr show very low enrichment factors. Most of these elements are therefore fed by ASD. Conversely, the higher K EF in the surface layers could be linked to plant recycling. Ca and Sr also record low enrichment factors, the lowest one being observed between 50 cm and 25 cm depth. In the basal (100–50 cm) and uppermost (25–0 cm) part of the core, these elements record a moderate increase in enrichment factor (Ca EF and Sr EF (100–50 cm) = 4; Ca EF and Sr EF (10–0 cm) = 9 and 2,

respectively). These values may be explained by sea-salt sprays from the nearby Baltic Sea.

By contrast, Cl and Br display high enrichment factors ( $7 < \text{Cl EF} < 84$  and  $445 < \text{Br EF} < 2906$ ). These elements are strongly enriched in seawater relative to the upper continental crust, making sea-salt sprays the most likely source for Cl and Br. However, Cl, Br, Ca and Sr cannot be used as quantitative indicators of marine aerosols inputs, although partly fed by sea-salt sprays. Indeed Shotyk (1997) showed that more than 90% of the elements supplied to the bog by marine-influenced rainwater are not retained by the peat.

### Plant macrofossils

The results presented in Figure 4 and Table 5 record the main features of the four macrofossils zones. Relationships between the plant macrofossil components were explored using principal components analysis (PCA) (Figure 5). The SL4 macrofossil stratigraphy registers relatively low local water-table depths in zone SL4-1, given the abundance of *Sphagnum* section *Acutifolia* leaves, whilst charcoal fragments are sporadic and not present in significant numbers. Towards the top of the zone the samples from

**Table 4** Enrichment factors calculated in the five depth intervals of the core using values from the upper continental crust (McLennan, 2001) and Ti as a conservative element

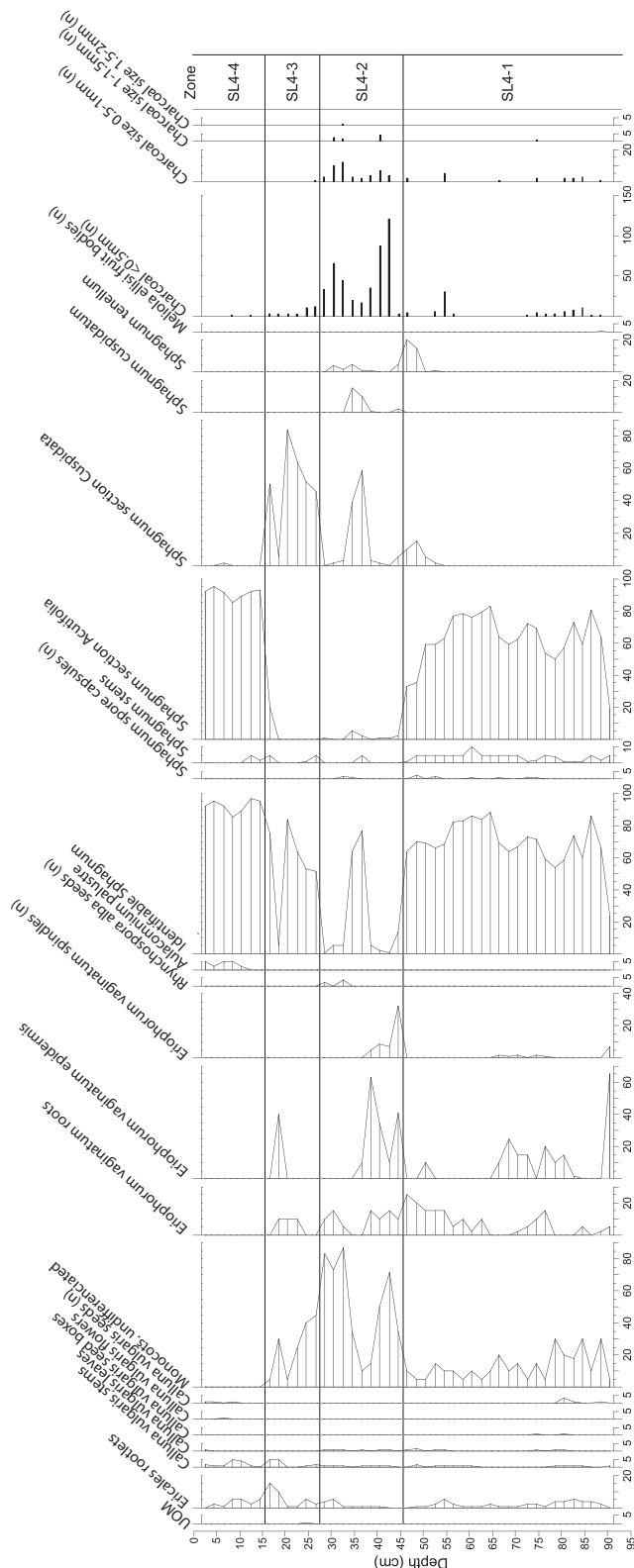
	Concentrations in UCC ( $\mu\text{g}/\text{g}$ )	Values/Ti UCC	100 cm–50 cm E.F. (Ti)	50 cm–35 cm E.F. (Ti)	35 cm–25 cm E.F. (Ti)	20 cm–10 cm E.F. (Ti)	10 cm–0 cm E.F. (Ti)
Cl	640	0.16	84	20	7	41	82
K	28650	7.15	0	0	1	2	7
Ca	29450	7.34	4	1	1	2	9
Br	1.6	0.0004	2906	676	445	1054	1050
Rb	110	0.03	— <sup>a</sup>	1	1	2	4
Sr	316	0.08	4	1	1	3	2
Zr	237	0.06	0	2	1	0	— <sup>a</sup>

<sup>a</sup> Value missing as concentrations in these intervals are below detection limits.

**Table 5** SL4 macrofossil zonation

Macrofossil zone	Depth (cm)	Main features
SL4-4	15.5–2	Very low presence of charcoal fragments with abundant <i>Sphagnum</i> section <i>Acutifolia</i> leaves. Leaves of <i>Aulacomnium palustre</i> occur between 10.5 and 2.5 cm and form up to 5% of the peat matrices
SL4-3	27.5–15.5	Strong reduction in the number of charcoal fragments, with a large increase in <i>Sphagnum</i> section <i>Cuspidata</i> leaves, which record peak values at 20.5 cm. <i>Ericales</i> rootlets and <i>Calluna vulgaris</i> stems increase between 18.5 and 16.5 cm
SL4-2	45.5–27.5	Abundant charcoal fragments are present throughout the zone, with the highest number recorded between 42.5 and 40.5 cm. The major components of the peat matrices are Monocots undifferentiated and <i>Eriophorum vaginatum</i> epidermis and roots. High values of <i>Sphagnum</i> section <i>Cuspidata</i> leaves (up to 59%) were recorded between 36.5 and 34.5 cm. Seeds of <i>Rhynchospora alba</i> occur at 32.5 and 28.5 cm
SL4-1	91–45.5	Abundant <i>Sphagnum</i> section <i>Acutifolia</i> leaves with some <i>Eriophorum vaginatum</i> epidermis and roots. Charcoal fragments are infrequent, and where present do not record high values. Towards the top of the zone (52.5–46.5 cm) leaves of <i>Sphagnum</i> section <i>Cuspidata</i> and <i>Sphagnum tenellum</i> appear and increase in abundance (maximum abundance values of 15 and 20%, respectively)

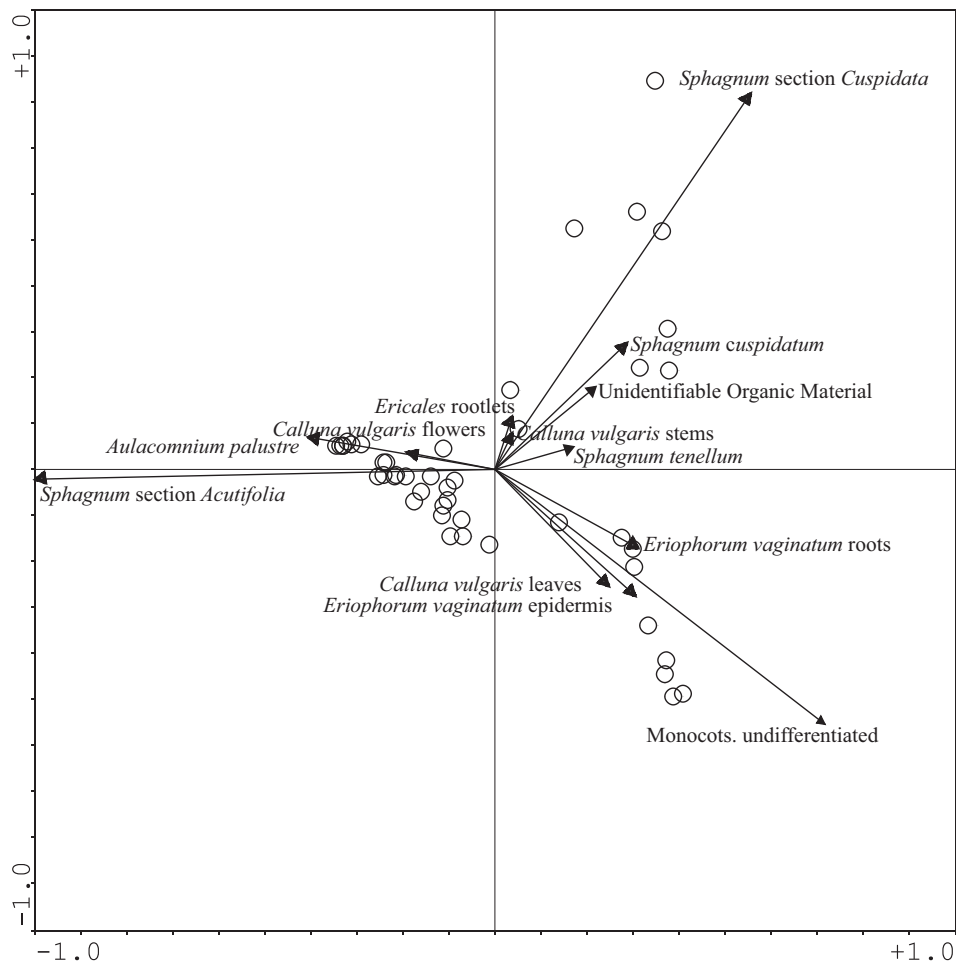
mid-point depths 52.5–46.5 cm (c. AD 1210 to AD 1360), record increased mire surface wetness, given the presence of *Sphagnum* section *Cuspidata* and *Sphagnum tenellum* leaves. In zone SL4-2 high percentage values of *Sphagnum* section *Cuspidata* and peak percentage values of *Sphagnum cuspidatum* (mid-point depths between 36.5 and 34.5 cm, AD 1720 to AD 1820) alternate with high values of Monocots undifferentiated, *Eriophorum vaginatum* epidermis/spindles and the highest recorded values of charcoal fragments. This zone therefore records the highest mire surface wetness in the peat profile and additionally the greatest disturbance, given the abundant presence of macroscopic charcoal indicating the occurrence of surface peat fires (charred leaves and stems of *Calluna vulgaris* are present in the peat matrices in this zone). Charcoal fragments decrease markedly in zone SL4-3, whilst the disappearance of aquatic *Sphagnum cuspidatum* and the increased representation of *Calluna vulgaris* stems indicate lower local water-table depths. Local water-table depths appear to have decreased further in zone SL4-4, as *Sphagnum* section *Acutifolia* leaves return as the dominant component of the peat matrices. Fires appear to have been very infrequent in the final zone, since charcoal fragments are rare. The Eigen values of axis 1 (0.598) and axis 2 (0.209) represent 80.7% of the cumulative percentage variance of the species data (Figure 5). Axis 1 seems to be determined by a moisture/burning gradient, with hummock microform taxa on the



**Figure 4** Percentage of plant macrofossil in SL4. Zonations made using information content in psimpoll 4.25

left (*Sphagnum* section *Acutifolia* leaves, *Aulacomnium palustre* and *Calluna vulgaris* flowers/seeds). Two groups on the right of the PCA ordination indicate hollow microform taxa (*Sphagnum cuspidatum*/section *Cuspidata* and *Sphagnum tenellum*) and plants (*Eriophorum vaginatum* and *Rhynchospora alba*) associated with the burning of the bog surface (Sillasoo *et al.*, 2007).





**Figure 5** Principal component analysis biplot of the SL4 plant macrofossil data. The ordination was performed using CANOCO for Windows version 4.02, using the following options: focus scaling on interspecies correlations, species scores divided by standard deviation, centering/standardization by species

### Stable isotopes

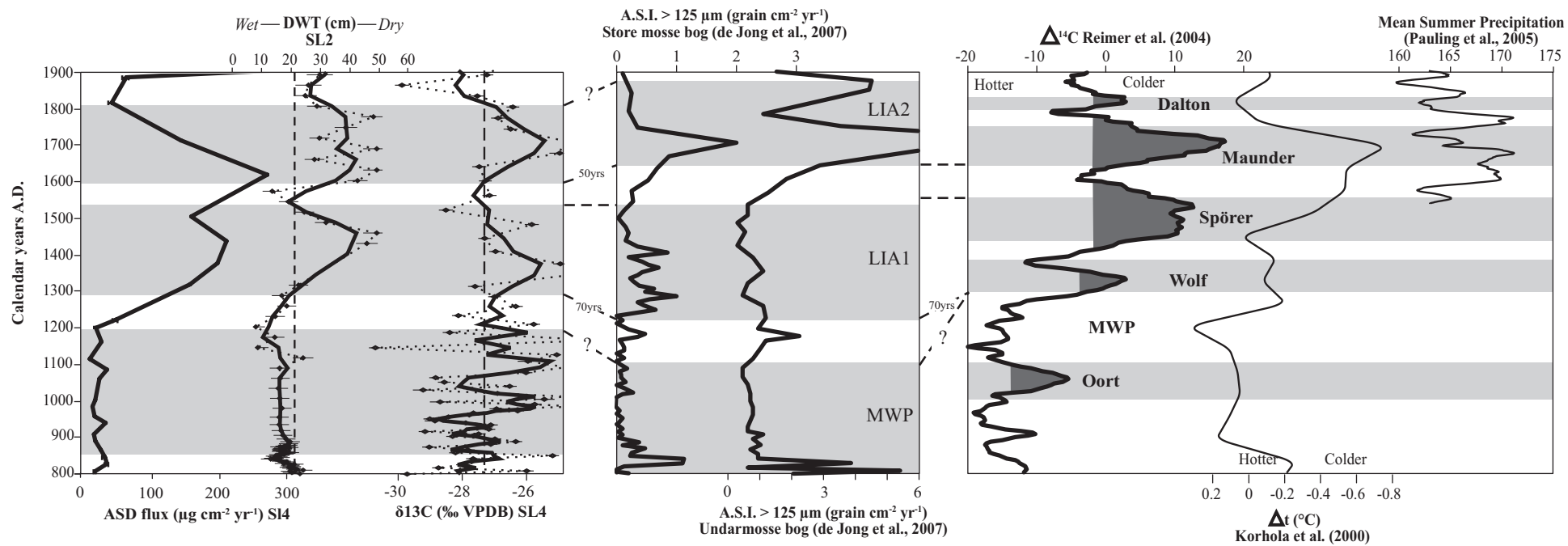
The raw  $\delta^{13}\text{C}$  data are presented in Figure 6 and record a large spread of individual points. This scatter is due to the differences of carbon isotopic composition in different *Sphagnum* species (Hornibrook *et al.*, 2000). The raw data points were therefore smoothed using a three-point running average filter. Mean values for the raw  $\delta^{13}\text{C}$  data up to AD 1900 are equal to  $-27.39\text{‰}$  VPDB. The smoothed curve was zoned into four periods. The first period (AD 800–1200) is characterized by rather large fluctuations of  $\delta^{13}\text{C}$  oscillating below (AD 800–1000) and above (AD 1000–1200) the mean value for the whole core. During the second period from *c.* AD 1200 to *c.* AD 1580, the  $\delta^{13}\text{C}$  values first increase up to  $-25.6\text{‰}$  VPDB at *c.* AD 1370, and then decrease down to the mean value for the whole core. A similar pattern was observed for the third period from *c.* AD 1580 to *c.* AD 1850 with the maximum of  $-25.5\text{‰}$  VPDB at *c.* AD 1700. During the fourth period (from *c.* AD 1850) human disturbance (exploitation of the peat) probably caused large decreases of the  $\delta^{13}\text{C}$  signal. Indeed, the  $\delta^{13}\text{C}$  value in *Sphagnum* organic matter depends on several factors, the most important being the amount of water stored in the hyaline cells. Models showed that a decreasing amount of water stored in the hyaline cells will increase isotopic fractionation resulting in a decrease of the  $\delta^{13}\text{C}$  value (Ménot-Combes *et al.*, 2004). The successive drainage of Słowińskie Błota caused a drop of local water-table and lead to the decrease of water content in leaves, explaining the drop in the  $\delta^{13}\text{C}$  during this period.

### Discussion

#### Causes of LIA deterioration in Słowińskie Błota

The ASD flux profile versus depth (Figure 3) displays five peaks around 46 cm (*c.* AD 1370), 38 cm (*c.* AD 1650), 28 cm (*c.* AD 1930), 16.5 cm (*c.* AD 1984) and 10.5 cm depth (*c.* AD 1996). Above 30 cm depth, ASD can be explained by increasing industrial activities, especially coal mining and burning, and lead smelting in Poland (eg, Strzyszczyk and Magiera, 2001). However, the lower part of the ASD flux profile (100–30 cm) may be explained by natural changes in ‘soil dust’ inputs, possibly related to climatic fluctuations. When the ASD flux is plotted against time (Figure 6), the interval between *c.* AD 1200 and AD 1800 records two ASD peaks. These occur at 46 cm (around *c.* AD 1370) and 38 cm (*c.* AD 1650) and may register LIA climatic deteriorations.

In peat bogs, LIA climatic deteriorations have been detected by Barber *et al.* (2000) and Mauquoy *et al.* (2002b). In another peat bog from North Poland, Lamentowicz *et al.* (2008) recorded two periods of reduced peat accumulation between AD 1100–1500 and AD 1650–1900, respectively. These authors linked the oldest period to the LIA, whereas they explained that in their case, the youngest period is due to both LIA and human activity (ie, peat exploitation). In their work, van der Linden and van Geel (2006) also detected Wolf and Spörer minima in a *Sphagnum*-bog from southernmost Sweden using combined plant macrofossil, pollen and C/N analyses. Periods of reduced



**Figure 6** Atmospheric soil dust flux, mire surface wetness derived from testate amoebae and  $\delta^{13}\text{C}$  versus time in Słowińskie Błota. Raw data (dotted line), three-point average (solid line) and mean value (dashed vertical line) are given for both mire surface wetness and  $\delta^{13}\text{C}$ . Comparison with aeolian sediment influx (ASI) found in two peat bog sequences (Store Mosse and Undarmosse) from south Sweden (de Jong *et al.*, 2007),  $\Delta^{14}\text{C}$  curve (Reimer *et al.*, 2004), temperature anomalies curve (Korhola *et al.*, 2002) and 50-year running precipitation data presented over Northern Europe (Pauling *et al.*, 2005)

peat accumulation during the LIA may have been due to lower spring-summer temperatures slowing down the primary productivity of peat-forming vegetation, and cold winters causing freezing of the bog surface (Mauquoy *et al.*, 2004). Reductions in the rate of peat accumulation have the immediate effect of increasing the relative amount of 'soil dust' found in the peat profile during the LIA. During this time span, evidence for enhanced storminess and particle transport has also been demonstrated by de Jong *et al.* (2007) in a raised bog from South Sweden and by Meurisse *et al.* (2005) in peat-dune complexes from Northern France. More specifically, Maasch *et al.* (2005) also suggested that the LIA could be divided into two periods: a first wet oceanic period from AD 1230 to AD 1620 followed by a dry period from AD 1700 to AD 1950. During other cold events such as the Younger Dryas stadial, it has also been demonstrated that erosion rates were enhanced, causing more resistant minerals to be weathered and transported to a peat bog, drastically increasing the ASD flux (Shotyk *et al.*, 2002). However, during the LIA, such changes are recorded when specific conditions are encountered. For instance, de Jong *et al.* (2007) demonstrated clearly that changes in storm regimes in Southern Sweden and short-term changes in climatic conditions that occurred during the LIA could be recorded thanks to nearby sand dune complexes providing easily erodible material that can be transported by wind up to the peat bogs. The same specific conditions can be applied to Słowińskie Błota, which is also very near the seashore and dune complexes. Moreover, the PCA ordination of the plant macrofossil data shows a burning/disturbance gradient superimposed on to the mire surface wetness gradient. Surface fires on peat bogs can cause increased mire surface wetness (Väliranta *et al.*, 2007), since hummock microforms can be destroyed, causing a reduction of the local microrelief and therefore promoting increased mire surface wetness (Sillasoo *et al.*, 2007). Given this, it is possible that the increases in mire surface wetness detected with the plant macrofossil analysis are due to disturbance by fires. Pollen data from the other high-resolution study of Słowińskie Błota bog (SL2) showed the beginning of deforestation at *c.* AD 1100 (Lamentowicz *et al.*, 2009). Consequently, increased landscape openness, surface fires and proximity to the seashore will allow soil material to be available for erosion and subsequent deposition as ASD in the mire. In other words, *c.* 150 years before the onset of the LIA soil was made available for future erosion, providing an ideal source of particles to be transported by wind to the peat bog.

In Słowińskie Błota, the increase of ASD is also correlated with a shift in DWT (Figure 6), reflecting that the onset of LIA is characterized by increased storminess and dryness of the area. Moreover, the lower Cl EF and Br EF values between 50 and 30 cm depth (Table 4) may indicate a more continental climate over North Poland during this period. These results do not correspond with the initial wet shift observed by de Jong *et al.* (2007) at the beginning of the LIA. However, de Jong *et al.* (2007) also pointed out that the climatic anomalies associated with the LIA and MWP they have evidenced in their record are reflected as periods with predominantly dry *or* wet conditions. They noticed that these aeolian activity peaks started during the recorded hydrological transitions, regardless of the direction of these shifts. In North Poland, Lamentowicz *et al.* (2008) explained that the development of peat bogs in this area could be driven by westerlies during wet periods, and by more continental influence during dry periods. No more precise explanation has been found so far to explain why LIA is recorded by dry shifts in Baltic bog whereas it is recorded by wet shifts in other areas such as in Southwest Sweden. Therefore, we can conclude that in our record, the ASD peaks are found during LIA, but that in some locations, they can be accompanied by wet shifts whereas in other areas, they can be accompanied by dry shifts.

## Timing of the LIA in NE Europe

The first dry shift recorded by the ASD flux in Słowińskie Błota corresponds to the dry shift found by Lamentowicz *et al.* (2008) in another Baltic bog between AD 1100 and AD 1500. These authors also record a second zone of climatic disturbance between AD 1650 and AD 1700–1900. They explain that this second shift starts with a transition to wetter conditions, followed by a dry period, reflecting climatic instability. They claim a possible human influence superimposed to climatic dry shifts. However, the lack of evidence for human impact until AD 1800–1850 together with the strong correlation between Słowińskie Błota bog and the peat bog studied by Lamentowicz *et al.* (2008) support a climate-driven environmental change in both sites between AD 1650 and AD 1800. The LIA timing found in our record fits also well with the period of decreased temperature (*c.* AD 1400–1800) found by Jędrysek *et al.* (2003) in a peat core from SW Poland, although this study is lower in resolution than our work. Our results described here are also in good agreement with the timescale found for this event in tree rings from various locations in Poland (Pazdur *et al.*, 2007), and with results found by van der Linden and van Geel (2006), who detected climatic deteriorations during the Wolf and Spörer minima between AD 1300 and AD 1550 in a peat bog profile from Southern Sweden. Moreover, as in the present study, they also found a synchronous increase in bulk density during this time interval. Their bulk density values vary between 0.05 and 0.15 g/cm<sup>3</sup> during the LIA, whilst values lower than 0.05 g/cm<sup>3</sup> in other time intervals were recorded outside the LIA time interval.

In Słowińskie Błota, the ages of the high ASD peaks are highly consistent with LIA intervals recorded in both southern Swedish peat deposits (Figure 6) and lake sediments from Finland (Weckström *et al.*, 2006; Haltia-Hovi *et al.*, 2007), which suggests that LIA climatic deteriorations may have occurred synchronously in NE Europe. No dust peak is recorded before AD 1300 because the early 'Medieval Warm Period' is characterized by relatively stable conditions and low wind activity (de Jong *et al.*, 2007). When comparing our data with results from de Jong *et al.* (2007) and other data (Figure 6), slight age discrepancies occur between the various phases of climatic fluctuations and are linked to the various sampling resolutions and constraints associated with age–depth models (Figure 6). The uppermost ASD peak found in Słowińskie Błota may correspond to the Maunder minimum. However, because of our sampling resolution, it is also possible that this ASD encompasses the Dalton minimum. The lowermost ASD peak may record both the Wolf and Spörer minima, indifferently. Nevertheless accepting a 70-year discrepancy for the base of this zone (AD 1300 in SL4 and AD 1230 found by de Jong *et al.*, 2007), the time span for this earlier stage of the LIA is in good agreement with results from de Jong *et al.* (2007). It can therefore be concluded that the transition between the various LIA minima will be approximately synchronous in NE Europe regardless of the area.

## Response to precipitation and temperature changes

A three-point running average smoothing procedure was performed on testate amoebae water-table reconstruction data (DWT<sub>TA</sub> in Figure 6) from Lamentowicz *et al.* (2009) and these were then compared with the isotopic data of SL4.  $\delta^{13}\text{C}$  in living plant organic material is controlled by photosynthesis (Farquhar *et al.*, 1982). Carbon isotopic fractionation between atmospheric CO<sub>2</sub> and non-vascular plant cellulose was proposed by Figge and White (1995). Climatic factors that should be considered when analysing variations of carbon isotopic composition in non-vascular plants are: temperature, humidity and the partial pressure of CO<sub>2</sub> (Ménnot-Combes *et al.*, 2004). However, decomposition of peat organic material may disturb the 'original' carbon isotopic composition in peat (Kracht and Gleixner, 2000). To check if it

was possible to derive more than local climatic changes from the  $\delta^{13}\text{C}$  signal, our  $\delta^{13}\text{C}$  results were compared with the reconstructed European summer precipitation curve for the last 500 years (Pauling *et al.*, 2005) and reconstructed temperature anomalies for Fennoscandia (Korhola *et al.*, 2002). It seems that the isotopic data are not synchronized to reconstructed mean summer precipitation for Europe. In the present study, the factors driving the  $\delta^{13}\text{C}$  remain difficult to identify. The  $\delta^{13}\text{C}$  curve is in good agreement with the reconstructed temperature data for Fennoscandia, although time-dependent discrepancies occur. Wolf and Maunder minima are clearly recorded in the  $\delta^{13}\text{C}$  curve although the Spörer minimum remains unclear as for both ASD and  $\text{DWT}_{\text{TA}}$  records. This slight delay between climatic events recorded by ASD,  $\text{DWT}_{\text{TA}}$  and  $\delta^{13}\text{C}$  in Słowińskie Błota and Fennoscandia suggests that during last two millennia, the temperature over the southern Baltic shore decreased a few decades later than in Northern Europe during the LIA minima. Conversely, the shift towards higher temperature during optima occurred a few decades earlier than in Northern Europe.

## Conclusions

The main natural sources of major elements recorded in the 1 m Słowińskie Błota peat profile are 'soil dust' and sea-salt sprays, which account for the main part of K, Ca, Zr, Ti, Fe, and Cl and Br data variability.

'Little Ice Age' climatic deteriorations have rarely been identified using ASD fluxes in European peat bogs. LIA climatic deteriorations have only been detected in specific areas where peat bogs are surrounded by easily eroded material (eg, de Jong *et al.*, 2007). In Słowińskie Błota, the particular fact that the surrounding areas were deforested by human activities 150 years before the LIA provides a unique opportunity for soils to be extensively eroded and transported. As a result, LIA climatic changes can therefore be successfully tracked using ASD in this bog. LIA climatic deteriorations are recorded in the Słowińskie Błota bog profile between *c.* AD 1200 and *c.* AD 1800 using the ASD, plant macrofossils and  $\delta^{13}\text{C}$ . The results are in very good agreement with other records, claiming synchronicity of the LIA over NE Europe, regardless the causes and/or consequences of the LIA. In our record, these cooler and drier periods are characterized by increased soil dust fluxes possibly related to an increase in erosion processes and an increased continentality of climate. Multiproxy data (macrofossils, testate amoebae and  $\delta^{13}\text{C}$ ) strongly support the ASD flux record by showing changing humidity and temperature conditions during this period.

## Acknowledgements

We are grateful to Helen Kurzel (IEG, Heidelberg) for her help in with the XRF analyses of the samples, Konrad Tudyka and Agnieszka Wiszniowska for their help with the  $^{14}\text{C}$  sample preparation, and Arkadiusz Bulak for his help with the  $^{210}\text{Pb}$  preparation and measurements. We also warmly thank Maarten Blaauw (Queens University, Belfast) for constructive comments on the age modelling. This work is part of a larger project 'Climatic changes in Pomerania (N Poland) during the last millennium based on multiproxy high-resolution studies' (coord. M. Lamentowicz) granted by the Polish Ministry of Science and Higher Education (Contract No.: 2P04G03228). Geochemical analyses and  $^{14}\text{C}$  dating were granted by an individual support from the University of Liège ('classic credit' to N. Fagel) and EU-funded ATIS project ('Absolute Time Scales and Isotope Studies for Investigating Events in Earth and Human History',

MTKD-CT-2005-029642). At the time of this research, F.D. was supported by FRIA (FNRS) fellowship.

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