

Reconstructions of the early and middle Holocene climate and environment based on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records in biogenic carbonates; Lake Niepruszewskie, western Poland

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ABSTRACT:

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The present study investigates environmental conditions during sediment accumulation in Lake Niepruszewskie, western Poland. Palaeolimnological reconstructions are based on stable isotope composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of a wide range of biogenic carbonates occurring in the sediments, including shells of several gastropod species and the bivalve genus *Pisidium*, carapaces of ostracods belonging to the subfamily Candoninae and encrustations and oogonia of the aquatic macrophyte genus *Chara*. According to the radiocarbon dates obtained, accumulation of the sediment sequence began in the early Atlantic and terminated in the early Subboreal.

Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records reveal significant and frequent fluctuations that are attributed to repeated changes in the Lake Niepruszewskie water balance. However, conditions of prevailing long water residence time, accompanied by high productivity within the lake, are reflected in a ^{13}C -enriched carbon-isotope record. Minimum $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were recorded for the earliest Atlantic and maximum values characterize the interglacial optimum during the middle and late Atlantic.

Discrepancies observed between isotope records of particular taxa reflect the specific season and subhabitat of each carbonate secretion. ^{13}C -enriched *Chara* encrustations and oogonia are consistent with their precipitation within the photic zone, which is commonly ^{13}C -enriched due to the photosynthetic activity of macrophytes and phytoplankton. The carbon isotope composition of *Lymnaea auricularia* shells indicates that breathing behaviour leaves its imprint on $\delta^{13}\text{C}$ in snail shells. In aquatic air-breathing pulmonate gastropods this results in ^{13}C -depletion in shells. Isotope records of individual shells of two snail species, *Valvata piscinalis* and *Gyraulus laevis*, indicate that in order to obtain mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values that are representative of a 5 cm thick sampling interval, stable isotope signatures of more than five shells must be obtained.

Key words: Biogenic carbonates; Stable carbon and oxygen isotopes; Lacustrine sediments palaeoclimate; Palaeoenvironment; Holocene; Western Poland.

INTRODUCTION

The use of carbon and oxygen stable isotope composition of biogenic carbonates precipitated in a

lake as a climatic and environmental tracer is not straightforward since knowledge of the growth period, habitat, etc. of the organism sampled is essential for a full interpretation. However, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

records in lacustrine carbonates of biogenic origin have been successfully applied in numerous investigations of past climate and environment (e.g. Fritz *et al.* 1987; Gasse *et al.* 1987; Abell and Williams 1989; Abell and Hoelzmann 2000; Leng *et al.* 1999; Apolinarska 2009; Apolinarska and Hammarlund 2009). Most investigations focused on 2–4 different types of biogenic carbonates: ostracod carapaces belonging to the subfamily Candoninae in particular (e.g. Hammarlund *et al.* 1997, 1999; Holmes *et al.* 1997; Schwalb and Dean 1998; von Grafenstein *et al.* 2000; Ricketts *et al.* 2001), shells of the bivalve genus *Pisidium* (e.g. Hammarlund and Buchardt 1996; Hammarlund *et al.* 1997, 1999, 2002; Böttger *et al.* 1998; von Grafenstein *et al.* 2000) and encrustations on stems of the aquatic macrophyte genus *Chara* (e.g. Hammarlund *et al.* 1999, 2000, 2003; von Grafenstein *et al.* 2000). Isotope investigations of gastropods, whose shells remain rarely used in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ studies, among many other species included: *Lymnaea auricularia* (Aucour *et al.* 2003), *Bithynia tentaculata* opercula (Hammarlund *et al.* 1999, 2003) and *Gyraulus laevis* (e.g. Böttger *et al.* 1998; Hammarlund and Buchardt 1996).

The main aim of the investigation is reconstruction of climatic and environmental conditions during the early and middle Holocene based on isotopic analyses of carbonates derived from sediments deposited in Lake Niepruszewskie in the Poznań Lake District, western Poland. The results obtained are used to verify and supplement the earlier interpretations based on mollusc assemblages occurring in the sediments (Apolinarska and Ciszewska 2006). Combined carbon and oxygen stable isotope records obtained from gastropod and bivalve shells, ostracod carapaces and *Chara* encrustations and oogonia are used to establish whether the stable isotope records of the taxa are good indicators of palaeoclimate and palaeoenvironment.

There have been only a few investigations of the geology of the Lake Niepruszewskie basin, the infilling sediments and the lake's surroundings. The genesis of the tunnel valley occupied by the lake and the infilling sediments were described by Bartkowski (1957), Rotnicki (1960) and Gogołek (1993). The climatic and environmental significance of mollusc assemblages occurring in the Lake Niepruszewskie sediments was presented by Apolinarska and Ciszewska (2006). In contrast to the small number of geological investigations, extensive studies have been carried out on the ecological and chemical conditions in the modern lake and its catchment. Those include: floristic diversity of littoral zone communities (Ławniczak 2002, 2006), chemical composition of the

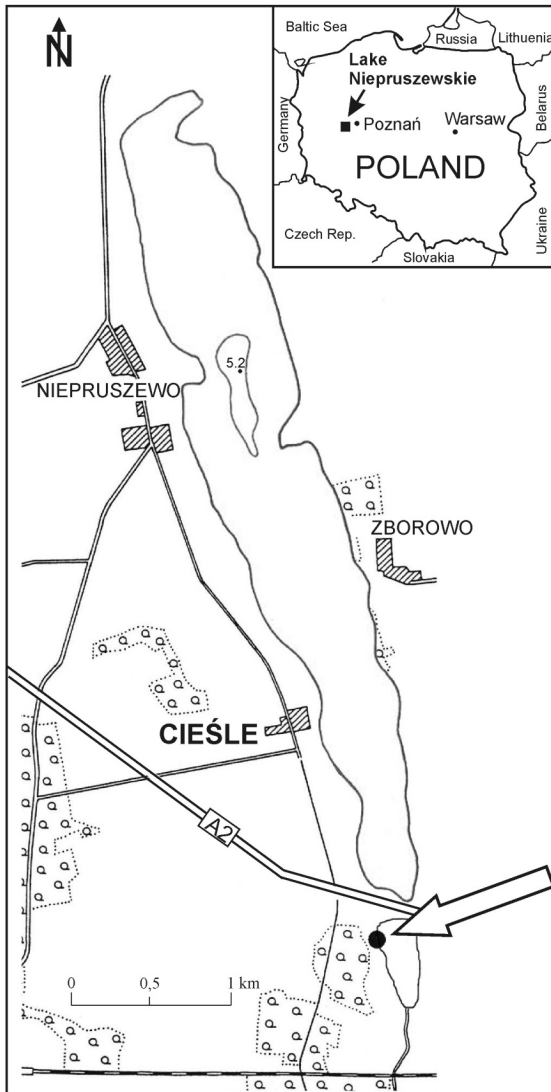
lake waters (e.g. Ławniczak and Zbierska 2006) and water pollution in the lake catchment (Zbierska and Ławniczak 2003a,b).

SITE DESCRIPTION

Lake Niepruszewskie is situated in the eastern part of the Poznań Lake District (Kondracki 2000), about 25 km west of the city of Poznań in western Poland (Text-fig. 1). A flat moraine upland at 83–93 m a.s.l., with the Lusowski sandur in its northern part, occurs east of the lake. The land west of the lake is geomorphologically more differentiated. Undulating and flat moraine upland at 85–90 m a.s.l. is diversified with kames and eskers with heights up to 107 m a.s.l. (Gogołek 1993). The area is characterized by numerous postglacial tunnel valleys orientated N-S and WNW-ESE, where rivers and lakes occur at present. Lake Niepruszewskie is an elongated lake filling the northern part of the Niepruszewo-Strykowo tunnel valley formed as a result of subglacial erosion during the Early Leszno Phase (the maximum extent of the last Pleistocene glaciation in the area of Poland) and subsequently filled with fluvioglacial sands and gravels of the same age (Gogołek 1993). The Lake Niepruszewskie tunnel valley is terminated by a kame at Kalwy in the north and Bukowsko-Mosińskie eskers in the south. The lake has a surface area of ca 2.4 km² within a ca 53 km² catchment. It receives discharge from several small streams. The River Samica, the only surface outflow of Lake Niepruszewskie, rises from the southern part of the lake. Due to its insignificant depth, with a maximum of 5.2 m, the lake has a polymictic character. Hence, water stratification with respect to physical and chemical parameters is absent or poorly marked (Ławniczak, personal communication).

The Niepruszewo-Cieśle sediment record was cored 200 m south of the southern shore of Lake Niepruszewskie, about 1.5 km south of the village of Cieśle, in a lacustrine chalk mine. At present, a small reservoir separated from Lake Niepruszewskie by motorway A2 occurs in the area of the former mine (Text-fig. 1).

The study area is influenced by both Atlantic and continental air masses, the influence of the former being more pronounced. The present climate is characterized by a mean annual precipitation of ca. 500 mm and a mean annual temperature of 8.0°C (July mean 17.9°C; January mean –2.1°C). A seasonal precipitation minimum causes a water deficit during the summer months (Kondracki 2000).



Text-fig. 1. Topographic map of the study area with an outline map of Poland showing the location of Lake Niepruszewskie in the inset. The site investigated is indicated by an arrow

MATERIALS AND METHODS

Fieldwork and subsampling

The stable isotope analyses were performed on biogenic carbonates derived from a 2.63 m sediment sequence cored in the early 1990s. Sediment samples were collected in an open trench down to a vertical depth of 0.95 m and with a 0.5 m long Instorf peat borer from the deeper part of the deposit down to 2.63 m. In the upper unit (0–0.95 m) of the sequence 5 cm thick sediments were sampled continuously, whereas in the lower part (0.95–2.63 m) 5 cm thick samples

were taken at ca 0.25 m intervals. The coarse resolution in the lower unit of the sequence and the thick samples used for isotope analysis are a consequence of the fact that the sediment succession was originally sampled for analysis of mollusc assemblages that requires greater sample volume (Apolinarska and Ciszewska 2006).

Sample preparation and isotope analyses

Sediment samples were soaked and boiled in water in order to break down the sediments and were subsequently gently passed through 2.0, 0.5 and 0.125 mm sieves under running water. Shells, carapaces, encrustations and oogonia were handpicked after drying and then sorted and counted under a low-power binocular microscope. The most continuous presence in the sequence and abundance of shells and carapaces were the main criteria for choosing taxa for the analysis. Absence of particular taxa in some samples resulted in discontinuity of the isotope record (Text-figs 2, 3). Isotope data were obtained from shells of the gastropod species *Valvata pulchella* Studer, *Valvata piscinalis* (Müller), *Lymnaea auricularia* (Draparnaud), *Gyraulus laevis* Alder and *Bithynia tentaculata* (Linnaeus) opercula, the bivalve genus *Pisidium* as well as carapaces of adult individuals belonging to the ostracod subfamily Candoninae, encrustations and oogonia of the submerged macrophyte genus *Chara*.

Shells for stable isotope analysis were carefully examined in order to eliminate all the specimens that might have undergone dissolution. Special attention was given to mollusc shells as they are usually composed of aragonite, the mineral prone to diagenetic alteration. The shell microstructure of a few specimens was examined in polished sections using a scanning microscope (SEM) and compared to the microstructure observed by Faliński (1989a,b, 1990) in shells of recent individuals of the same species. Recrystallization of shell carbonate was not observed. The preservation of original molluscan shell aragonite of selected individuals was confirmed by X-ray diffraction analysis in the Institute of Geology, University of Poznań. The above results indicate that the gastropod and bivalve shells were exposed to minimal diagenetic alteration and thus are likely to preserve their primary isotopic signatures.

The isotope analysis was preceded by careful cleaning of the carbonates in order to eliminate contamination that could affect the isotope data. Preparation techniques included gentle removal of sediment with a soft brush followed by treatment with 30% hydrogen peroxide (H_2O_2) for 24 hours to remove organic remains, mainly periostracum. Subsequently specimens

were washed several times in distilled water, dried at room temperature and powdered. In order to obtain mean isotope values for a sediment layer biogenic carbonate samples comprised 5–6 specimens of a particular taxon (i.e. mollusc shells and ostracod carapaces). However, analyses of individual mollusc shells enabled investigation of the range of isotope values in a sediment sample. Isotopic analyses were performed in the stable isotope laboratory at the University of Erlangen, Germany. Carbonate powders were reacted with 100% phosphoric acid at 75°C using a Kiel III online carbonate preparation line connected to a ThermoFinnigan 252 mass-spectrometer. All isotopic data are reported in per mil (‰) relative to V-PDB by assigning a $\delta^{13}\text{C}$ value of +1.95‰ and a $\delta^{18}\text{O}$ value of -2.20‰ to NBS19. Based on repeated analysis of laboratory standard the analytical precision was within $\pm 0.07\%$.

Radiocarbon dating

Radiocarbon dating was carried out in Poznań Radiocarbon Laboratory, where ^{14}C activities are measured using the technique of accelerator mass spectrometry (AMS). ^{14}C activities were measured both in mollusc shells and terrestrial plant remnants in order to estimate the hard water effect on the ^{14}C record in gastropod and bivalve shells.

RESULTS AND INTERPRETATION

Sequence chronology and inferred sedimentation rate

Analysis of ^{14}C activities in mollusc shells (6 580 \pm 40 BP, Poz-13831) and *Pinus* periderm (6 340 \pm 70 BP, Poz-22311) derived from a sediment sample collected at a depth of 0.95–1.0 m enabled the hard water effect for ca 240 \pm 80 years to be assessed. The molluscan radiocarbon dates: 7 770 \pm 40 BP (depth 1.90–1.95 m, Poz-13830), 4 845 \pm 35 BP (depth 0.05–0.10 m, Poz-13829) were corrected according to the ageing effect measured and amount to 7 530 \pm 90 BP and 4 605 \pm 90 BP respectively (standard error of the corrected dates was calculated) (Text-fig. 2). According to the radiocarbon dates obtained accumulation of the Niepruszewo–Cieśle sediment sequence was restricted to the early and middle Holocene; it began in the early Atlantic and terminated in the early Subboreal. The inferred average sedimentation rate in the lower unit of the sequence, the 1.90–0.95 m depth interval, was 0.84 mm·y⁻¹, while, in the upper unit, the 0.95–0.05 m depth interval, sediments accumulated at a mean rate of 0.52 mm·y⁻¹.

Carbon and oxygen stable isotope phases

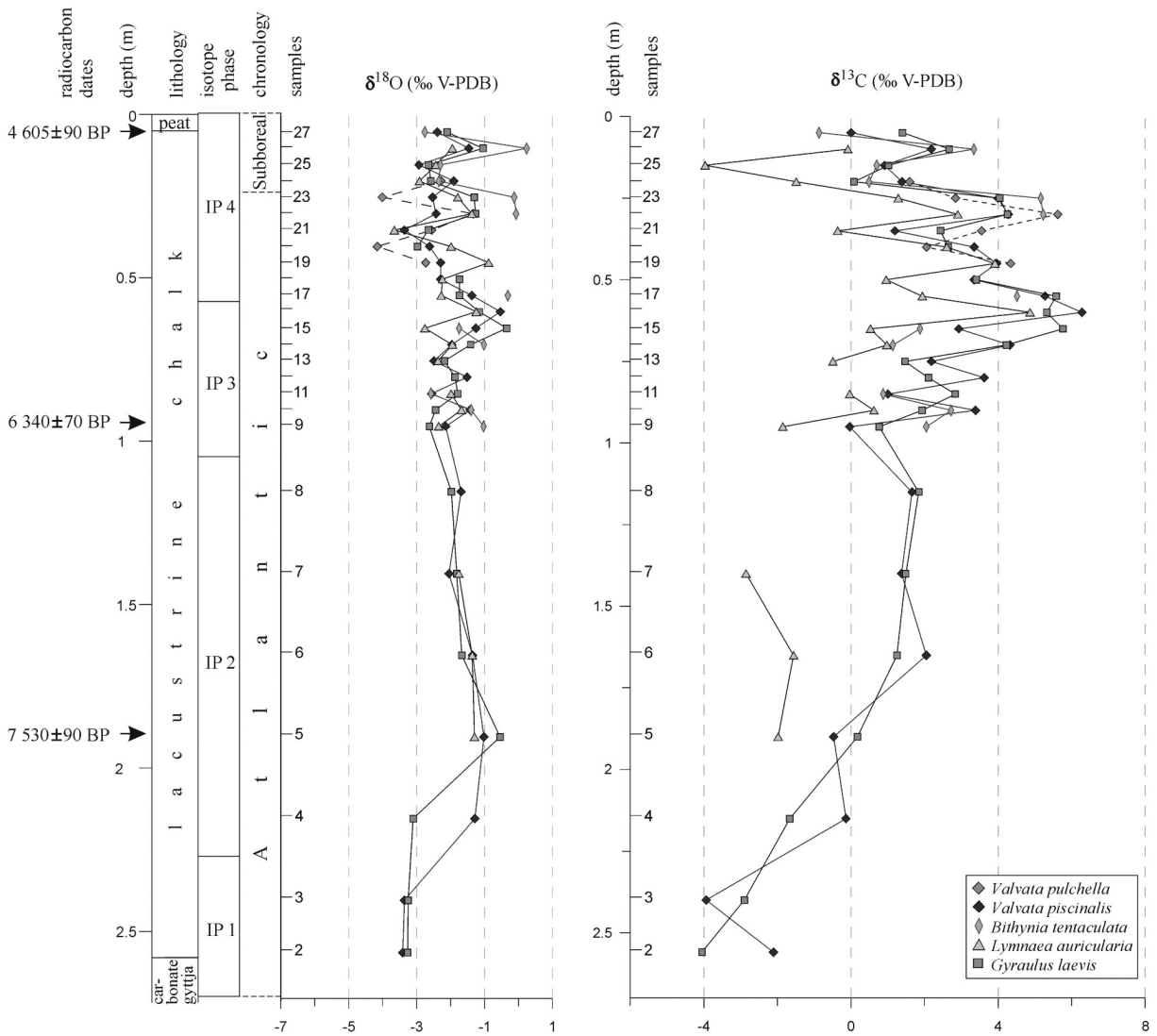
Isotope phase 1

The early Atlantic time (isotope phase 1) is characterized by ^{18}O -depleted gastropod shells compared to the shells in younger samples (Text-fig. 2). The isotopic record obtained may be a consequence of high water stands reconstructed for lakes in northern and central Poland (e.g. Lake Gopło, Ralska-Jasiewiczowa and Starkel 1988) during the early Atlantic (8 500–8 200 BP). The minimum $\delta^{13}\text{C}$ values in the shells of *Valvata piscinalis* and *Gyraulus laevis* in the sequence described (Text-fig. 2) indicate a significantly lower productivity level in the lake during the initial time of lacustrine chalk deposition, resulting in less intensive removal of ^{12}C from the DIC (dissolved inorganic carbon) of the lake waters by macrophytes and phytoplankton. Additionally, ^{13}C -enrichment of the DIC was prevented by a short water residence time in the lake as a consequence of increased precipitation with the Atlantic onset. Increased humidity hindered isotopic equilibrium between HCO_3^- in the lake and atmospheric CO_2 , a process that results in ^{13}C -enriched DIC (Uzdowski and Hoefs 1990).

Distinction in climatic and/or environmental conditions during sediment deposition between the lowermost unit of the sequence and younger sediments is confirmed by sparse and poorly diversified mollusc assemblages inhabiting the lake restricted exclusively to the initial stage of its development (Apolinarska and Ciszewska 2006).

Isotope phase 2

Isotope phase 2 begins with strong ^{13}C and ^{18}O enrichments in carbonates (Text-figs 2, 3). Assuming that the ca 2‰ increase in $\delta^{18}\text{O}$ value originates exclusively from a difference in temperature, this would equal ca 5°C warming (in the area of Poland a 1°C rise in air temperature results in a ca +0.4‰ alteration in $\delta^{18}\text{O}$ calcite precipitated from lake water, Ralska-Jasiewiczowa *et al.* 2003). However, the increase in temperature during the early Atlantic was not that pronounced. Enhanced evaporation induced by warmer conditions during the Atlantic and successive lowering of the lake level and/or prolonged water residence time in the lake are suggested here as major factors responsible for ^{18}O -enrichment of the lake waters. This suggestion is supported by the data on the evaporation/precipitation ratio for central Poland during the early Atlantic (Rotnicki 1991). ^{18}O -enrichment in carbonates, during the time period described, was noted



Text-fig. 2. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures derived from shells of snail species occurring in the Lake Niepruszewskie sediments plotted against depth, lithology and chronology of the sediments and radiocarbon dates obtained (samples 5, 9, 27). Note the high degree of consistency between the isotope records of all the species. For the sake of clarity the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of biogenic carbonates other than snail shells are presented in Text-fig. 3

also at other European sites. Increase in the $\delta^{18}\text{O}$ of bulk carbonates from Lake Steisslingen in south-western Germany by 2‰ was explained as resulting from combined temperature rise and intensification of evaporation (Mayer and Schwark 1999).

The warm climate during the Atlantic favoured macrophytes and phytoplankton development in the lake, leading to a ^{13}C -enrichment of the DIC (Text-figs 2, 3). Under conditions of a full water exchange in the lake similar to those obtaining today (1.7 years; Jańczak 1991) and relatively shallow water (maximum of 5.2 m at present), intensive productivity could have greatly increased $\delta^{13}\text{C}_{\text{dic}}$. Palynological data for the area of Poland point to the establishment of a

dense woodland cover, resulting in enhanced evapotranspiration during the time period described (Ralska-Jasiewiczowa and Starkel 1988). This in turn resulted in decreased water discharge to lakes from their catchments. Additionally, the climate of the Atlantic, although humid, favoured intensified evaporation leading to lake level lowering. Such hydrologic conditions favoured the establishment of isotopic equilibrium between atmospheric CO_2 and HCO_3^- , the process leading to ^{13}C -enrichment of the DIC.

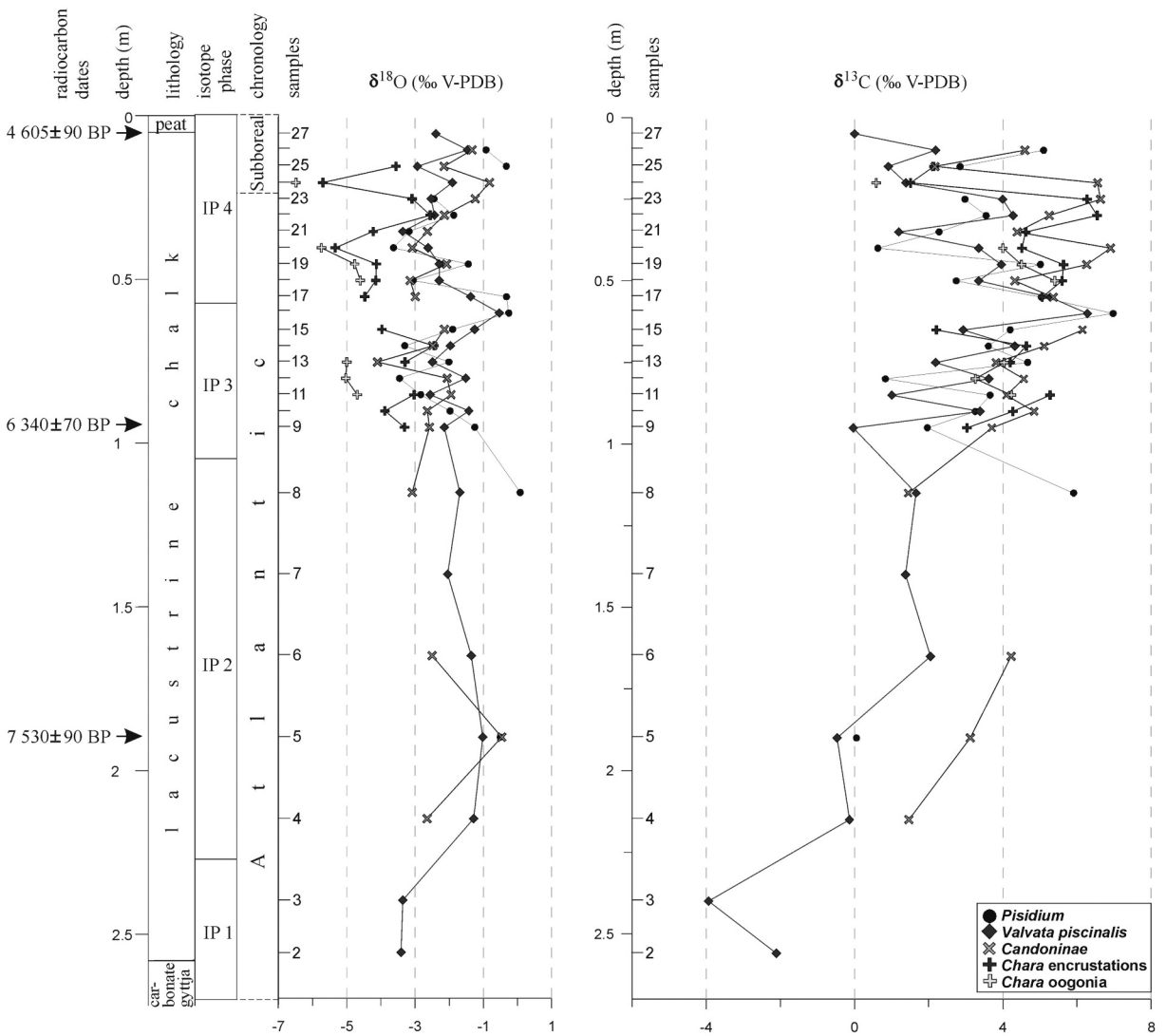
In the upper unit of isotope zone 2 the $\delta^{13}\text{C}$ increase is accompanied by decreased $\delta^{18}\text{O}$ values (Text-figs 2, 3). According to Rotnicki (1991), air temperature rose by ca 1°C during the later part of the early

Atlantic ($7\,560 \pm 70$ to $6\,620 \pm 100$ BP) in central Poland, the time unit coeval with the period of accumulation of samples 5–9 ($7\,530 \pm 90$ BP to $6\,340 \pm 70$ BP). Hence, the decrease in the $\delta^{18}\text{O}$ values contradicts the climate changes. A decrease in the evaporation/precipitation ratio suggested by Rotnicki (1991) for the time period in question in central Poland could provide an explanation of the situation observed. A change towards conditions of an intensified water exchange in the lake could have been responsible for the opposite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ trends (Text-figs 2, 3). Decrease in the water residence time in the lake counteracted the influence of evaporation on $\delta^{18}\text{O}_{\text{water}}$ and resulted in a slight, gradual negative shift in $\delta^{18}\text{O}$ val-

ues (Text-fig. 2). The change in the lake's hydrological balance was not strong enough to entirely overprint the ^{13}C -enrichment of the DIC by the photosynthetic activity of macrophytes and phytoplankton.

Isotope phase 3

Strong, gradual ^{13}C -enrichment of the DIC, observed in the middle Atlantic (isotope phase 3) indicates a high level of productivity in the lake, confirmed by mollusc assemblages consisting mostly of taxa characteristic of shallow lakes with well developed vegetation (Apolinarska and Ciszewska



Text-fig. 3. Carbon and oxygen stable isotope records obtained from carbonates of biogenic origin at the Niepruszewo-Cieście site plotted against depth, lithology and chronology of the sediments and radiocarbon dates obtained (samples 5, 9, 27). Isotope phases (IP) distinguished on the basis of general changes and prevailing trends of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves. Stable isotope values of *Valvata piscinalis* represent isotope records in snail shells

2006). An intensive photosynthetic activity of primary producers must have been accompanied by a long water residence time in the lake, resulting in further ^{13}C -enrichment of the DIC (see Isotope phase 2).

The $\delta^{18}\text{O}$ record in isotope phase 3 is twofold. In the lower unit the range of $\delta^{18}\text{O}$ values is generally insignificant (Text-figs 2, 3; 1.0–0.75 m depth interval), and remains in accordance with the relatively stable climate of the Atlantic. The upper unit is characterized by a +2‰ shift in $\delta^{18}\text{O}$ values (Text-figs 2, 3; depth of 0.75–0.6 m) which could be tantamount to a 5°C rise in temperature. According to Rotnicki (1991), the stage of the Atlantic under discussion was characterized by high, relatively stable temperatures in central Poland and hence such a change in temperature is improbable. The shift in the oxygen stable isotope record may be due to evaporative enrichment of the lake waters in ^{18}O . The data for central Poland (Rotnicki 1991) suggest an increase in the evaporation/precipitation ratio during the time unit in question. The warm and humid climate of the middle Atlantic resulted in expansion of terrestrial vegetation. This in turn caused enhanced evapotranspiration, decreased supply of waters from the catchment and consequent decline in the water level and/or a rate of water exchange in the lake. A prolonged water residence time is reflected in increased $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The $\delta^{18}\text{O}$ record in isotope phase 3 (Text-figs 2, 3) indicates that the major shift in $\delta^{13}\text{C}$ (see above) was in fact a two-stage process. In the lower unit the ^{13}C -enrichment resulted mainly from the intensive productivity in the lake, while in the upper one it was strengthened by the longer water residence time in the lake.

The interpretation presented is consistent with the data by Hammarlund *et al.* (2003) for Lake Igelsjön, southern Sweden, where the mid-Holocene is described as an interval of relatively low net precipitation, partly due to high summer temperatures. The intensive aquatic productivity during conditions of prolonged water residence time, i.e. a relatively high evaporation/inflow ratio, is consistent with the above interpretation.

Isotope phase 4

Sediments included in isotope phase 4, which accumulated during the late Atlantic and the early Subboreal, are characterized by significant fluctuations in the carbon and oxygen isotope records of all the carbonates analysed (Text-figs 2, 3). Repeated shifts in the oxygen stable isotope composition by 2–2.5‰ would be tantamount to 5°C oscillations in temperature, which did not occur during the late Atlantic. The temperature variations could have had greater influence on $\delta^{18}\text{O}$ during

deposition of the youngest samples of early Subboreal age (Text-fig. 2), when mean annual temperature decreased by 0.5–1°C in relation to the climatic optimum during the Atlantic. However, this would result in a 0.2–0.4‰ drop in $\delta^{18}\text{O}$ values, substantially less pronounced than the changes observed (Text-figs 2, 3). An overall trend of decreasing $\delta^{13}\text{C}$ signatures is characterized by strong fluctuations of up to 4‰ (Text-figs 2, 3) indicative of frequent and significant variations in $\delta^{13}\text{C}_{\text{dic}}$. If the fluctuations observed were attributed exclusively to changes in productivity, they would indicate cyclic significant withdrawal and successive establishment of aquatic plants. This, however, was improbable in the relatively stable climatic conditions during the Atlantic (e.g. Ralska-Jasiewiczowa and Starkel 1991) which were favourable for the development of aquatic vegetation. The most probable explanation for the fluctuations noted in both carbon and oxygen isotope composition are transformations in the hydrological balance of the lake. ^{13}C - and ^{18}O -enriched isotope values represent time intervals when the water residence time in the lake was prolonged and the lake evolved into a more closed basin. ^{13}C - and ^{18}O -depleted isotope signals constitute a record of the periods when water supply increased, leading to a decrease in $\delta^{13}\text{C}_{\text{dic}}$ and $\delta^{18}\text{O}_{\text{water}}$. Following the above interpretation it can be concluded that, during the late Atlantic and early Subboreal, Lake Niepruszewskie showed an overall trend to shorten the water residence time. This was interrupted by shifts to more stagnant conditions in the lake.

Isotope composition of the taxa

A general positive covariance between the first-order shapes of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records of the taxa analysed (Text-figs 2, 3) indicates that the changes in the carbon- and oxygen-isotope composition of the carbonates reflect fluctuations in $\delta^{13}\text{C}_{\text{dic}}$ and $\delta^{18}\text{O}_{\text{water}}$. Thus, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of the carbonates may serve as a reliable source of information on past climate and environment. Most of the discrepancies in the isotope records observed between the taxa are a consequence of different times and places of carbonate precipitation.

^{12}C -enrichment in the shells of *Lymnaea auricularia* (Text-fig. 2), is a consequence of the snail's autecology. The saturation level of dissolved oxygen in lake waters during summer is often insufficient for the snail. Such environmental conditions force *Lymnaea auricularia* to approach the water surface in order to take in oxygen. ^{12}C -enrichment in the shell originates from the snail inhaling atmospheric CO_2 , commonly ^{13}C -depleted in comparison with carbon dioxide dis-

solved in water (usually HCO_3^-). The results obtained are consistent with the data presented by Aucour *et al.* (2003), who found *L. auricularia* shells ^{13}C -depleted in comparison with other riverine snail species investigated. The above interpretation is additionally supported by the findings of McConnaughey *et al.* (1997), who noted that breathing atmospheric air may significantly influence the $\delta^{13}\text{C}$ of snail shells, leading to ^{12}C -enrichment.

Isotopically heavy $\delta^{13}\text{C}$ records of encrustations and the carbonate layer surrounding the oogonia of the submerged macrophyte *Chara* are a consequence of the *Chara* subhabitat restricted to the photic zone, which is enriched in ^{13}C due to photosynthetic removal of ^{12}C by macrophytes and phytoplankton. Also, due to higher proportion of $^{12}\text{CO}_2$ incorporated preferentially into *Chara* stems the remaining DIC becomes ^{13}C -enriched, what results in isotopically heavier calcite precipitated as incrustation (cf. Pentecost and Spiro 1990, Andrews *et al.* 1997). ^{18}O -depletion in encrustations and oogonia (Text-fig. 3), in comparison with $\delta^{18}\text{O}$ in mollusc shells, is in accordance with the main precipitation season of the former carbonates during the warmest season of the year (von Grafenstein *et al.* 2000; Hammarlund *et al.* 2003). The $\delta^{18}\text{O}$ of carbonates decreases by 0.24‰ per 1°C rise in water temperature (Craig 1965; Kim and O'Neil 1997). The second factor that results in a ^{18}O -depleted record is the shallow depth of *Chara* growth, where waters are commonly warmer, and thus lead to decreased $\delta^{18}\text{O}$ of encrustations and oogonia. Slightly ^{13}C -depleted $\delta^{13}\text{C}_{\text{oogonia}}$ compared to $\delta^{13}\text{C}_{\text{encrustations}}$ (Text-fig. 3) indicate that the layer surrounding the oospore was encrusted with calcite during the spring time when the DIC had not yet been ^{13}C -enriched due to photosynthesis, as during the most intensive formation of encrustations in the summer. However, the above conclusions are contradicted by the $\delta^{18}\text{O}$ signal (Text-fig. 3), indicating higher mean temperature during oogonia calcification than during the period of formation of encrustations. This may be explained by evaporative ^{18}O -enrichment of the Lake Niepruszewskie waters during the summer, leading to increased $\delta^{18}\text{O}_{\text{encrustations}}$ overprinting the temperature effect. This is probable since due to the shallow depth of the lake, evaporation could have had a strong influence on the isotope composition of the lake waters. An alternative explanation of the ^{13}C -depleted $\delta^{13}\text{C}_{\text{oogonia}}$ compared to $\delta^{13}\text{C}_{\text{encrustations}}$ is the kinetic isotope effect, that results in discrimination against heavy isotopes assimilation during fast calcification (McConnaughey 1989) suggested for *Chara* oospores (Jones *et al.* 1996; Andrews *et al.* 2004).

When interpreting the isotope record of biogenically secreted carbonates the so called vital effects must be considered. Vital effects shift the isotope composition of the carbonate out of equilibrium with $\delta^{13}\text{C}_{\text{dic}}$ and $\delta^{18}\text{O}_{\text{water}}$ as a result of physiological factors controlled by an animal. The isotope record of snail shells is thought not to be influenced by vital effects (Fritz and Poplawski 1974). However, the aragonite composition of shells results in a 0.6‰ shift in $\delta^{18}\text{O}$ relative to $\delta^{18}\text{O}$ of calcite precipitated in the same ambient conditions (Tarutani *et al.* 1969). Thus, snail shells are ^{18}O -enriched compared to ostracod carapaces and *Chara* carbonates. Vital effects have been measured for the $\delta^{13}\text{C}$ record in *Pisidium* shells and Candoninae carapaces, -0.2‰ and $+0.8\text{‰}$ respectively. Also, $\delta^{18}\text{O}_{\text{Candoninae}}$ is shifted out of isotope equilibrium with ambient water by $+2.2\text{‰}$ (von Grafenstein *et al.* 1999).

Range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records in a sediment layer

Stable isotope analysis of individual shells of two snail species *Valvata piscinalis* and *Gyraulus laevis*, revealed a significant range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values recorded in shells derived from a single sediment layer (Text-fig. 4). The $\delta^{18}\text{O}$ range reaches 3.8‰ in one sample, 2.5‰ on average. In the case of the $\delta^{13}\text{C}$ record, the range is much greater and accounts for 9.5‰, 3.4‰ on average. The significant spread of the carbon and oxygen isotope values measured is possible, since a 5 cm thick sediment layer represents ca 60 years of accumulation (see section – Sequence chronology and inferred sedimentation rate). A period of six decades may be characterized by significant changes in climate and environment, reflected in strong $\delta^{13}\text{C}_{\text{dic}}$ and $\delta^{18}\text{O}_{\text{water}}$ fluctuations. The data presented indicate that the isotope signal derived from an individual shell is unlikely to provide $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values representative for a sediment layer a few cm thick. In order to obtain reliable $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records several shells must be analyzed. For a 5 cm thick sediment layer the mean isotope record derived from five homogenized shells does not necessarily reflect the mean $\delta^{13}\text{C}_{\text{dic}}$ and $\delta^{18}\text{O}_{\text{water}}$ for the period when the sediments were accumulated (Text-fig. 4). The accuracy of the results may be improved either by decreasing the thickness of sediment sampled or by increasing the number of shells analyzed. In the study by Jones *et al.* (2002), five to six shells of *Gyraulus piscinaris* or *Valvata cristata* derived from a 1 cm thick sampling interval were required for analysis before the maximum range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in shells of each snail species was reached.

SUMMARY AND CONCLUSIONS

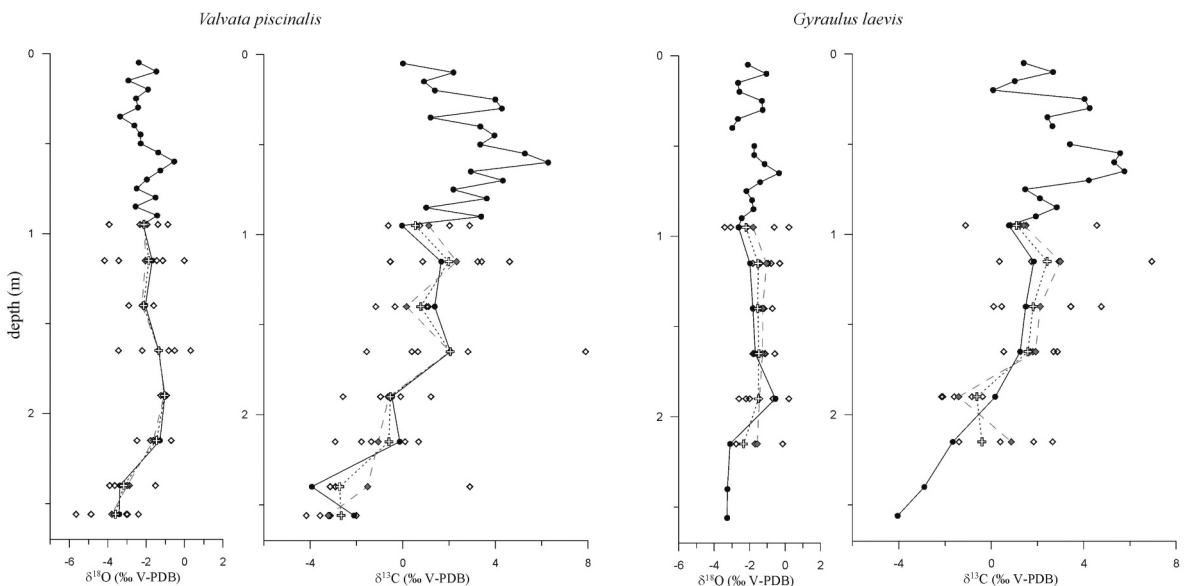
The sediment sequence collected adjacent to the southern shore of Lake Niepruszewskie, western Poland, comprises deposits accumulated between the early Atlantic and early Subboreal. The radiocarbon dates obtained point to a significant decrease in the sedimentation rate up the sequence. This is attributed to the development of a dense vegetation cover in the lake catchment during the Atlantic, resulting in diminished run-off carrying terrigenous material to the lake.

Shifts in stable carbon and oxygen isotope composition of the carbonates analysed are a consequence of both climate changes and fluctuations in the hydrological balance of the lake. The sequence studied starts with ^{13}C - and ^{18}O -depleted records in biogenic carbonates which are considered to be due to the increased precipitation with the Atlantic onset resulting in a short water residence time in the lake. A subsequent increase in $\delta^{18}\text{O}$ values resulted from a rise in the mean annual temperature, accompanied by enhanced evaporation and/or lake level lowering (isotope phase 2). The warm climate favoured the development of macrophytes and phytoplankton, which is reflected in ^{13}C -enriched values. A slight decrease in the $\delta^{18}\text{O}$ record indicates that the lake became more open in the later part of the early Atlantic (isotope phase 2). The middle Atlantic (isotope phase 3) is characterized by the most significant $\delta^{13}\text{C}$ in-

crease in the sequence, during conditions of high productivity and long water residence time in the lake. The latter is confirmed by the $\delta^{18}\text{O}$ signal. Significant fluctuations in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ record in isotope phase 4 are interpreted as resulting from repeated changes in the water residence time in the lake. During the late Atlantic and early Subboreal the lake became more open and/or water level in the lake increased, as indicated by gradually decreasing $\delta^{13}\text{C}$ values. The climatic and environmental reconstructions based on the carbon and oxygen isotope record are consistent with the conclusions based on the mollusc fauna assemblages occurring in the sediments.

The positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records of different biogenic carbonates proves that changes in their isotope composition reflect fluctuations in $\delta^{13}\text{C}_{\text{dic}}$ and $\delta^{18}\text{O}_{\text{water}}$ and thus may serve as a reliable source of information on past environmental conditions. The discrepancies in the isotope values between the taxa analysed are spatial (i.e. habitat) and/or temporal (i.e. time of calcification) effects. This is seen best in the carbon-isotope record. The ^{13}C -enriched carbon-isotope composition of *Chara* encrustations and oogonia compared to those of mollusc shells results from the sub-habitat of their precipitation, which is restricted to the photic zone, with ^{13}C -enriched DIC due to the photosynthetic activity of macrophytes and phytoplankton.

One of the factors controlling the stable isotope composition of snail shells is mollusc breathing be-



Text-fig. 4. Range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values recorded in shells of two snail species, *Valvata piscinalis* and *Gyraulus laevis*. Circles (●) – $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of 5–6 homogenized shells, presented also in Text-fig. 2; open diamonds (◇) – $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signal of individual shells; filled diamonds (◆) – arithmetic mean of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of individual shells; crosses (✚) – arithmetic mean value of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of 5–6 homogenized shells (circles) and arithmetic mean of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of individual shells (filled diamonds)

haviour. The $\delta^{13}\text{C}$ record in *Lymnaea auricularia* shells indicates that aquatic pulmonate snails, using a pneumostome to inhale atmospheric air, have ^{12}C -enriched skeletons. This results from the $\delta^{13}\text{C}$ of atmospheric CO_2 being isotopically lighter than HCO_3^- dissolved in water.

The results summarized above indicate that if the conditions in which carbonates precipitate are well known then the differences in the carbonate isotope record may allow conclusions to be made about seasonal and intra-reservoir $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ diversity in the lake.

Mean carbon and oxygen isotope records derived from five homogenized snail shells may not represent the true $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signal for a 5 cm thick sampling interval. There are two possible solutions to the problem. The first requires increasing the number of shells analysed per sample. The second possibility is to decrease the sediment sample thickness.

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