Oceanological and Hydrobiological Studies

International Journal of Oceanography and Hydrobiology

Volume 45, Issue 1, March 2016
pages (86-99)

ISSN 1730-413X
eISSN 1897-3191

Precipitation of calcium carbonate in a shallow polymictic coastal lake: assessing the role of primary production, organic matter degradation and sediment mixing

by

Michał Woszczyk*

DOI: **10.1515/ohs-2016-0009**
Category: **Original research paper**
Received: **June 1, 2015**
Accepted: **July 1, 2015**

Department of Quaternary Geology and
Paleogeography, Adam Mickiewicz University,
ul. Dzięgielowa 27, 61-680 Poznań, Poland

Abstract

In this paper, the genesis of carbonates in a shallow, polymictic and eutrophic coastal lake (Lake Sarbsko, Poland) is deciphered. Emphasis is placed upon the relationship between carbonate sedimentation and microbial degradation of organic matter, as well as on vertical mixing of sediments. The cycling of carbonates in the lake was investigated through the analysis of lake water chemistry (pH, Ca^{2+}, Mg^{2+}, alkalinity, SI_{calc}) and the stable carbon isotope composition of dissolved inorganic carbon and sedimentary calcite. It is shown that the calcite is precipitated within a relatively short time owing to the coincidence between the activity of photosynthesizing phytoplankton, the microbial decomposition of organic matter, and the physical mixing of lake deposits. In turn, the precipitated calcite is prone to dissolution within the sediments. The data presented in this paper can be applied to explain the processes affecting the carbonate saturation in freshwater systems and to interpret $\delta^{13}C$ signatures in the sediments of shallow lakes.

Key words: calcite precipitation, coastal lake, stable carbon isotopes, lake sediments

---

* Corresponding author: *woszczyk@amu.edu.pl*

DE GRUYTER

The *Oceanological and Hydrobiological Studies* is online at oandhs.ocean.ug.edu.pl

Introduction

Owing to the fact that carbonates together with silica (terrigenous and biogenic) and organic matter (OM) act as the major constituents of the lake sediments worldwide, knowledge about carbonate sedimentation in freshwater lacustrine systems is fairly extensive. However, carbonate precipitation in shallow coastal lakes, in which this process may be very complex because of the strong influence of bottom sediments on the composition of water, has not yet been thoroughly investigated.

The major control on the formation of carbonates in lakes is maintained by biological processes. $CaCO_3$ is precipitated mainly due to removal of CO_2 during photosynthesis of phytoplankton; however, detrital carbonates, calcareous skeletons, and early diagenesis deliver appreciable amounts of $CaCO_3$ to the sediments (Kelts & Hsu 1978). Recent studies emphasize the role of macrophytes and microbial processes within the extracellular polymeric substances (EPS) in the production of $CaCO_3$-rich deposits in some lakes (Dupraz et al. 2009; Pełechaty et al. 2013; Valero-Garcés et al. 2014). Jędrysek (2005) postulates that the formation of calcite accompanying the bacterial reduction of SO_4^{2-} and methanogenesis can be important in freshwater lakes.

On the other hand, $CaCO_3$ is known to undergo partial dissolution in hypolimnetic waters and within the lake sediments owing to decay of organic matter (Wachniew & Różański 1997; Müller et al. 2006). The balance between the primary production and microbial respiration of organic matter determines the preservation of sedimentary carbonates (Dean 1999; Müller et al. 2006).

The cycling of carbonates within lakes has received much attention during the last decades owing to its geochemical and paleolimnological importance. Indeed, this process contributes to the buffering capacity of lake waters against pH changes (Cole & Praire 2009) and controls the transfer of CO_2 from lakes to the atmosphere. This is due to the fact that part of the CO_2 produced by microbial oxidation of organic matter is used for the dissolution of calcite (Müller et al. 2006), which in turn lowers the pCO_2, increases the pH, and consequently limits the evasion of CO_2 to the atmosphere. Moreover, the cycling of carbonates triggers the cycling of biogenic chemical species, mainly PO_4^{3-}. It has been shown that the precipitation of $CaCO_3$ removes phosphates from water, and the reverse processes – syn- and post-sedimentary dissolution of calcite – contribute to the internal loading of nutrients (de Jonge & Villerius 1989; Dittrich & Koschel 2002). In general, the understanding of carbonate accumulation is indispensable for interpreting the paleorecords of trophic conditions as well as climate on the basis of lacustrine sediments (Dean 1999; Myrbo & Shapley 2006; Ju et al. 2010; Stockhecke et al. 2012).

The best way to study the cycling of carbonates in lakes is to install sediment traps together with a monitoring of lake water chemistry. This shows when the carbonate precipitation occurs and how much $CaCO_3$ is formed and/or dissolved, and it makes possible the calculation of carbonate fluxes (Wachniew & Różański 1997; Ramisch et al. 1999; Tylmann et al. 2012). However, in shallow turbulent water bodies, the deployment of sediment traps is ineffective because of resuspension of bottom deposits. The sedimentary processes in these lakes can be investigated by the analysis of seasonal changes in the chemistry of water. The information on the precipitation and dissolution of $CaCO_3$ is provided by the combination of water pH, concentrations of Ca^{2+}, and alkalinity, as well as stable carbon isotope signatures of dissolved inorganic carbon (DIC) in lake water. However, the best measure of the possibility of carbonate precipitation in lake waters is the saturation index (SI_{calc}) or its alternative, the degree of saturation (Ω) (Wachniew & Różański 1997; Hodell et al. 1998; Müller et al. 2006). It was shown that this index corresponds with sediment trap data (Tylmann et al. 2012) and is strongly negatively correlated with the dissolution rate of calcite (Xu et al. 2012).

The present study attempts to show the cycling of $CaCO_3$ in a shallow polymictic freshwater coastal lake located on the southern Baltic coast in Poland. The specificity of this lake consists in its high productivity, episodic changes in salinity, and intense vertical mixing of the water column and bottom sediments (Woszczyk et al. 2014). Therefore, hydrochemical processes in the lake water column are strongly affected by microbial processes in the sediments.

The purpose of this research was (i) to

explain the genesis of carbonates in the sediments of a shallow coastal lake and show the conditions in which the carbonates precipitate; and (ii) to investigate the effect of degradation of organic matter as well as resuspension of bottom deposits on the carbonate sedimentation.

The analytical approach in this study was to compare the temporal changes in the chemistry of the lake water column with that of the pore waters. On the basis of SI_{calc} and $\delta^{13}C$ in lake water DIC and sedimentary carbonates, the time of carbonate sedimentation and dissolution in the surface sediments were determined.

Study area

Lake Sarbsko (17°27'E, 54°46'N) is a shallow (average depth 1.4 m, maximum 3.5 m) freshwater (salinity <0.1 PSU) coastal lake situated on the southern Baltic coast in Poland (Fig. 1). The lake area is 6.5 km^2. The altitude of the lake surface is ca. 0.5 m a.s.l.; however, the lake water level shows ca. 80 cm fluctuations during the year and varies parallel to the Baltic Sea level. Lake Sarbsko is fed by the Chełst River from the east and a slow-flowing dyke from the south. The outflow (the Chełst outlet) is situated in the western part of the basin, and from here the lake water discharges into the Łeba River and into the Baltic Sea. Lake Sarbsko is occasionally supplied with brackish water, however, the salinity changes are very low.

Owing to the shallowness and orientation along the predominating (SW-W) winds, the lake waters and sediments are prone to intense wind-induced turbulence. Within the study period, the mean daily wind speeds over the lake varied between 1.1 and 15.8 m s^{-1} (8.9 m s^{-1} on average) and the wind fetch was up to 2600 m (Woszczyk et al. 2014). Such conditions are sufficient to cause deep vertical mixing in the lake water column and bottom sediments. The depth of sediment mixing varies throughout the lake, but the maximum values are estimated to be ca. 40 cm (Woszczyk et al. 2014).

Lake Sarbsko reveals high biological productivity. On the basis of the concentrations of chlorophyll-*a* during the enhanced productivity season (up to 147 μg l^{-1} (Woszczyk et al. 2011b)), the lake waters can be classified as hypertrophic. During the study period, two phases of enhanced phytoplankton activity (early spring and late summer) were recognized (Woszczyk et al. 2011b).

Throughout the lake history the intensity of carbonate precipitation varied in relation to salinity. The $CaCO_3$-enriched deposits were accumulated during freshwater phases, while brackish sediments were devoid of carbonates (Bechtel et al. 2007).

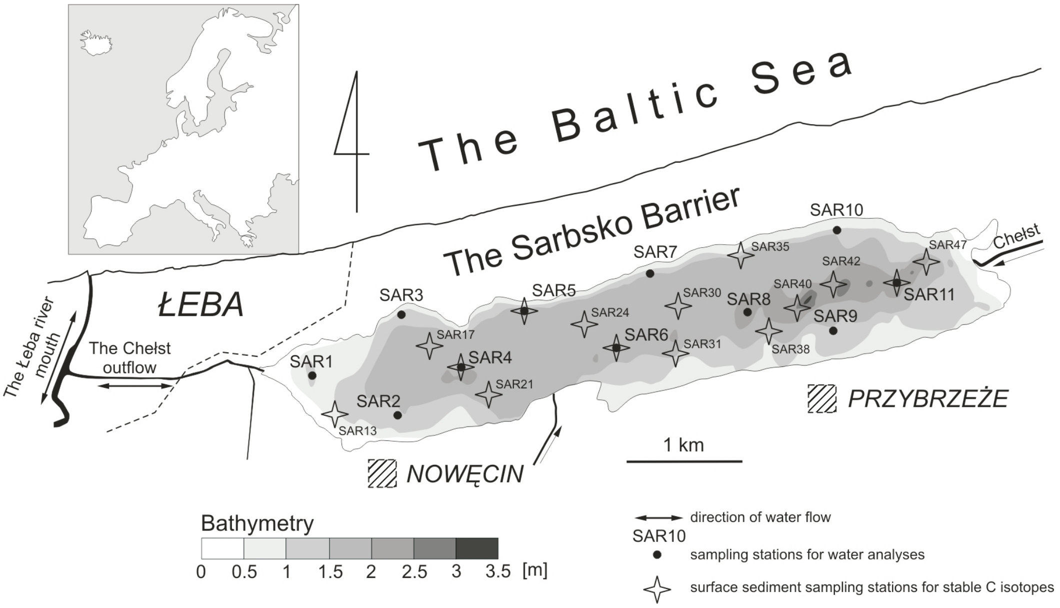

Figure 1

Location and bathymetry of Lake Sarbsko and distribution of the sampling stations

Methods

Water analysis

Eleven sampling sites from different parts of the lake (Fig. 1) were selected for the lake water analyses. This number of sites was necessary because single points could be unrepresentative for such a complex lake. Cieśliński (2013) showed that coastal lakes along the Polish coast are characterized by appreciable short-term hydrochemical variability due to marine inflows. It was believed that sampling of the lake water in different sections of the lake would allow to minimize the effect of these short-term and local fluctuations.

The water was sampled on 13 December 2007, 10 April 2008, 10 July 2008, and 17 September 2008. The samples for C isotope composition in dissolved inorganic carbon (DIC) ($\delta^{13}C_{DIC}$) were poisoned with $HgCl_2$.

The pH and temperature were determined in surface (5-10 cm below the surface), bottom (5-10 cm above the bottom), and pore waters (from the 5 cm surface layer of bottom deposits) with a WTW Multi 350i sensor. The measurements in the surface and bottom waters were made *in situ*, while the pore waters were analyzed immediately after the retrieval.

Pore waters, together with surface sediments, were collected using a gravity corer (Tylmann 2007) and extracted by centrifugation (3000 rpm) in the laboratory within 1-2 days after collection.

The bicarbonates (HCO_3^-) were titrated with 0.1 M HCl using methyl orange as an indicator.

Concentrations of Ca^{2+} were determined with the method of EDTA titration with regard to murexide in pH = 10. The accuracy of the analyses was ±10%.

$\delta^{13}C_{DIC}$ in lake water was analyzed in 2 ml aliquots. CO_2 was released from the samples by adding H_3PO_4. The isotopic measurements were carried out using a Delta ir-MS attached to the MultiFlow system (Micromass Ltd., UK). Results were reported relative to the PDB reference material, using external standards.

Sediment analysis

The sediment samples for the stable carbon isotope composition of $CaCO_3$ were collected from the 5 cm surface layer of sediments obtained with a gravity corer in July 2008 (Tylmann 2007).

The sediment samples were lyophilized and homogenized using an agate mill. The carbonate content was determined by thermal combustion (Heiri et al. 2001) and recalculated to $CaCO_3$ using the formula $CaCO_3[\%] = 2.27\ LOI_{925}$, where LOI_{925} represents the content of CO_2 released during decomposition of calcite at 925°C (Heiri et al. 2001).

The mineralogical form of carbonate in seven samples was determined in powdered untreated sediment by X-ray diffraction using a VRD6 diffractometer. The diffractograms were recorded by the reflection method using CuK_α radiation.

For the purpose of stable C isotope measurements in sedimentary calcite, the organic matter was removed via oxygen plasma ashing (Lebau et al. 2014) using an Emitech K1050X Plasma Asher. OM-free carbonate powders were then reacted with 100% phosphoric acid at 70°C using Gasbench II connected to a ThermoFinnigan Five Plus mass spectrometer. All values are reported in per mil relative to V-PDB by assigning $\delta^{13}C$ values +1.95‰ to international standard NBS19 and -46.6‰ to international standard LSVEC, respectively. Reproducibility and accuracy were monitored by replicate analysis of laboratory standards calibrated to NBS19 and LSVEC and was ±0.04-0.07‰.

Chemical calculations

Carbonate alkalinity (CA) was calculated as follows:

$CA = (HCO_3^-) + 2(CO_3^{2-})$ (Berner 1971)

where: (HCO_3^-) and (CO_3^{2-}) denote activities of HCO_3^- and CO_3^{2-}, respectively.

The saturation index for calcite (SI_{calc}) was calculated as:

$$SI_{calc} = \log \frac{(Ca^{2+})(CO_3^{2-})}{K_c}$$

where:

(Ca^{2+}) – activity of Ca^{2+} in lake waters

K_c – equilibrium constant for the reaction of calcite precipitation.

Partial pressure of CO_2 (pCO_2) was computed according to (Kelts & Hsu 1978)

$$pCO_2 = \frac{(H_2CO_3)}{K_{CO_2}}$$

where

(H_2CO_3) – activity of carbonic acid in lake waters

K_{CO2} – Henry's law constant for CO_2

Activities of H_2CO_3 and CO_3^{2-} were calculated on the basis of temperature-calibrated pH and the concentration of HCO_3^-, using equations adopted from (Kelts & Hsu 1978). Temperature-dependent equilibrium constants in the carbonate system K_1:

$$K_1 = \frac{(H^+)(HCO_3)}{(H_2CO_3)}$$

K_2:

$$K_2 = \frac{(H^+)(CO_3^2)}{(HCO_3)}$$

and K_c (calcite) were calculated according to (Kelts & Hsu 1978).

Ionic strength (I), used for ionic activity calculations, was obtained from the concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- published elsewhere (Woszczyk et al. 2011a).

K_{CO2} was calculated using data provided by Eby (2004).

Results

Chemical composition of lake water

SI_{calc} in Lake Sarbsko waters varied greatly in time and space (Fig. 2). Surface and bottom waters were relatively similar in terms of SI_{calc} and showed increasing saturation from December 2007 to July 2008 and a decrease between July 2008 and September 2008. In December 2007, the SI_{calc} values in the lake water column were mostly negative. In April 2008 and July 2008, the SI_{calc} increased to 0.3-0.8, respectively. In September 2008, it dropped again and at a few sites even negative values were obtained.

With respect to the SI_{calc}, pore waters behaved differently from the lake water column. The highest values were obtained in December 2007 and the minimum occurred in July 2008. In September 2008, the SI_{calc} increased sharply.

The pH of surface and bottom waters increased from December 2007 to the maximum in July 2008, and it dropped in September 2008. In pore waters, the pH was fairly stable from December 2007 to April 2008 and decreased in July 2008. In September 2008, the pH significantly increased.

Ca^{2+} in surface and bottom waters demonstrated a decreasing trend during the whole study period. In pore waters, the maximum concentrations of Ca^{2+} were obtained in December 2008. After that there was a sharp decline in April 2008 and July 2008, followed by a slight enrichment in Ca^{2+} in September 2008.

The highest concentrations of Mg^{2+} in surface and bottom water occurred in December 2007. Then Mg^{2+} was depleted until September 2008. The pore waters were enriched with Mg^{2+} with respect to overlying waters. The highest values of Mg^{2+} in pore waters were observed in December 2007 and the lowest occurred in July 2008.

Mg^{2+} behaves conservatively in relation to salinity (expresses as Cl^- concentrations), whereas Ca^{2+} appears to be a non-conservative constituent of the lake waters (Fig. 2). Thus, the concentrations of Ca^{2+} vary in time and space due to biogeochemical processes rather than simple physical mixing.

In the surface and bottom waters, the CA showed a slight decrease from December 2007 to April 2008. In July, there was a reasonable increase in CA in bottom waters while in the surface waters, the average CA remained similar to April 2008. The lowest values of CA occurred in September 2008. In the pore water, the CA showed an overall decreasing trend from December 2007 to July 2008 and increased in September 2008.

$\delta^{13}C_{DIC}$ in surface, bottom and pore waters changed in a similar manner and showed increasing values from December 2007 to April 2008. In December 2007, the $\delta^{13}C_{DIC}$ in pore waters was mostly positive, however, showed a considerable variability throughout the lake. In July 2008, there was a sharp decline in $\delta^{13}C_{DIC}$ to

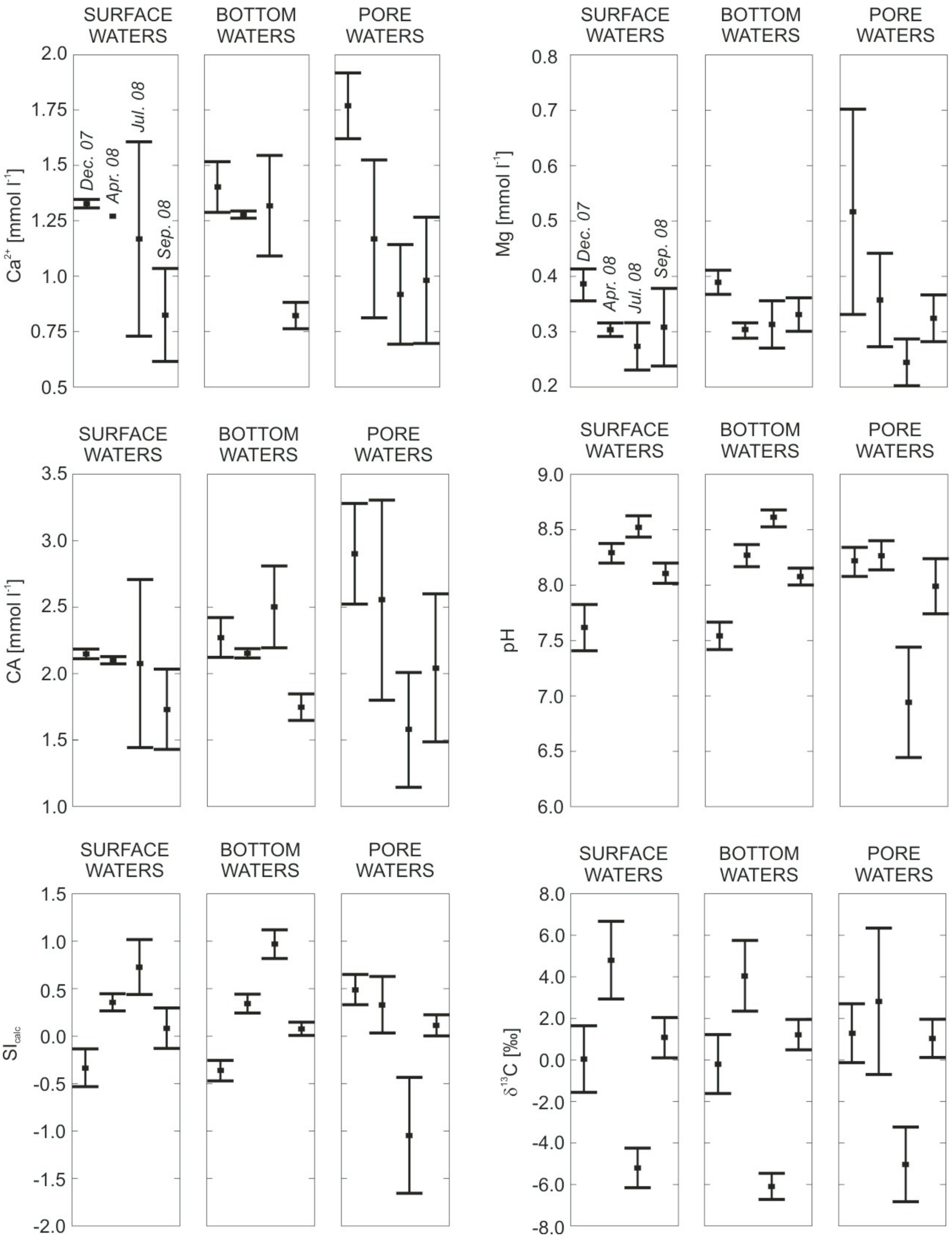

Figure 2

Chemical composition of Lake Sarbsko during the study period. Surface, bottom and pore waters are distinguished. Plots show average values of each parameter ±1 standard deviation in each data set. Dates of collection are given in the upper panels.

highly negative values and in September 2008, the $\delta^{13}C_{DIC}$ increased in the lake water.

$CaCO_3$ content and $\delta^{13}C$ of sedimentary calcite ($\delta^{13}C_{calc}$)

The content of $CaCO_3$ in the surface deposits was between <5 and 28%. Spatial distribution of $CaCO_3$ throughout the lake is shown in Fig. 3. The only carbonate phase is calcite. On the basis of the low Mg/Ca ratio in water (between 0.06 and 0.37), the calcite can be classified as low-Mg calcite (Müller et al. 1972).

The calcite from the surface sediments of Lake Sarbsko had relatively uniform $\delta^{13}C_{calc}$ values of -1.55 to -1.98‰.

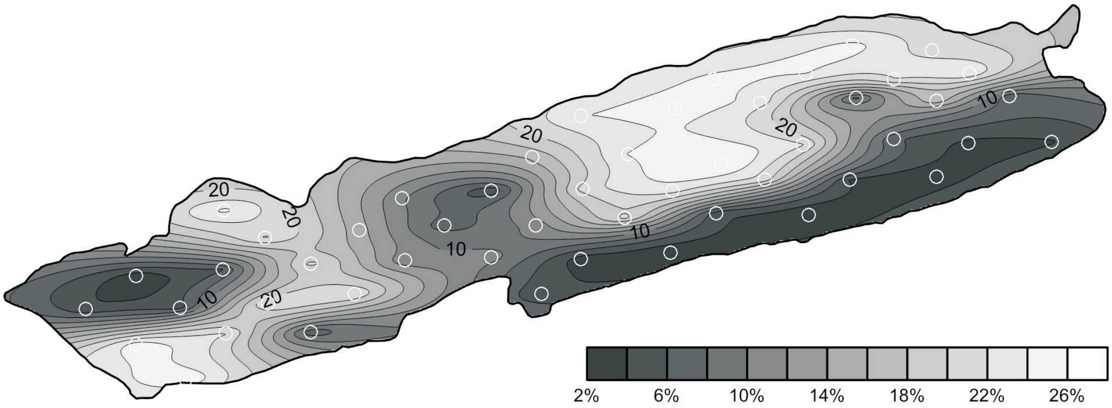

Figure 3

The spatial distribution of $CaCO_3$ within the surface sediments of Lake Sarbsko. White circles indicate sediment sampling sites

Discussion

Interpretation of $\delta^{13}C$ signatures in sedimentary calcite

Hodell et al. (1998) established that $\delta^{13}C_{calc}$ preserves $\delta^{13}C_{DIC}$ from the period of the maximum rate of carbonate accumulation. This is because there is rather low fractionation between DIC and calcite, and the latter tends to be slightly enriched with ^{13}C with respect to DIC (Leng & Marshall 2004). In Polish lakes, the $\delta^{13}C_{calc}$ values in the surface deposits are 1.3-4.1‰ more positive than those of $\delta^{13}C_{DIC}$ (Wachniew & Różański 1997; Piotrowska & Hałas 2009). Similar values were obtained in other geographical regions (Hollander & McKenzie 1991; Hodell et al. 1998; Herczeg et al. 2003; Myrbo & Shapley 2006; Barešić et al. 2011). Consequently, the time of $CaCO_3$ precipitation can be estimated by matching $\delta^{13}C_{calc}$ values to the equilibrium $\delta^{13}C_{DIC}$. However, the interpretation of $\delta^{13}C_{calc}$ values in the sediments of coastal lakes is not that simple because there is no certainty that the sedimentary calcite is in isotopic equilibrium with ambient water. The sediments of coastal lakes are vigorously mixed and consequently calcite crystals, precipitated in different conditions and characterized by different stable C isotope signatures, can be redeposited in the surface layer of the sediments. In addition, the sedimentary calcite might be prone to selective dissolution which decreases the $\delta^{13}C_{calc}$ values in the residual calcite (Herczeg et al. 2003). Thus the measured $\delta^{13}C_{calc}$ values represent the product of mixing of these calcites. Moreover, non-equilibrium conditions of precipitation in the lake can be related to the intense primary production (Barešić et al. 2011).

Despite the above limitations, it seems that on the basis of $\delta^{13}C_{calc}$ and $\delta^{13}C_{DIC}$, it is possible to determine the approximate time of calcite precipitation in Lake Sarbsko. This is because sedimentary calcite is enriched with ^{13}C with respect to DIC, even if the precipitation occurs under non-equilibrium conditions (Barešić et al. 2011). Consequently, slightly negative values of $\delta^{13}C_{calc}$ (-1.55 to -1.98‰) would indicate that the large part of $CaCO_3$ was precipitated from water characterized by more negative mean $\delta^{13}C_{DIC}$, which occurred during the summer 2008. This conclusion seems to be true even if the calcite is affected by partial dissolution in the sediments. Herczeg et al. (2003) estimated that during dissolution, the $\delta^{13}C_{calc}$ signatures in Blue Lake (Australia) became 0.4‰ lower. When this value is added to $\delta^{13}C_{calc}$ measured in Lake Sarbsko sediments, we obtain -1.15 to -1.58‰ which is still too low for $\delta^{13}C_{DIC}$ in December 2007, April 2008 and September 2008.

Some evidence for the close relationship between $\delta^{13}C$ in sedimentary calcite in the lake and the lake water chemistry is provided by the fact the $\delta^{13}C_{calc}$-based reconstruction of salinity well agrees with other geochemical and paleoecological proxies (Bechtel et al. 2007; Woszczyk et al. 2010).

The pore waters

The concentrations of Ca^{2+} and CA as well as the values of SI_{calc} in pore waters in December 2007 were distinctly higher than in surface and bottom waters. Moreover, concentrations of both Ca^{2+} and CA were at their maxima throughout the study period. The high concentrations of these chemical species could have developed owing to microbial decomposition of organic matter (e.g. SO_4^{2-} reduction, methanogenesis) and/or dissolution of $CaCO_3$ in the sediments. The contribution of microbial reactions in delivering DIC to the pore waters is not confirmed unambiguously by $\delta^{13}C_{DIC}$. In the case of sulfate reduction, $\delta^{13}C_{DIC}$ is expected to be negative (Myrbo & Shapley 2006) and methanogenesis leaves DIC with very positive $\delta^{13}C_{DIC}$ (up to ca. +20‰ in pore waters and +13‰ in lake water column) (Gu & Schelske 1996; Gu et al. 2004). On the other hand, the weak correlation of HCO_3^- and Ca^{2+} ($R^2=0.20$) and the average molar ratio of HCO_3^-/Ca^{2+} of only ca. 1.6 argue against enhanced dissolution of $CaCO_3$, because this process releases 2 moles of HCO_3^- per 1 mol of Ca^{2+} (Jahnke & Jahnke 2004). It is thus possible that the chemical composition of pore waters in December 2007 was affected by intrusion of brackish water from the Baltic Sea and/or from the Łeba river. The ingression was shown on the basis of the distribution of chlorides in the lake (Woszczyk et al. 2010), however, the salinity change was appreciably low. The inflow of saltwater could also be responsible for the increased concentrations of Mg^{2+}, lower HCO_3^-/ Ca^{2+} ratio, and higher SI_{calc} (Berner 1971).

Between December 2007 and April 2008, the concentrations of Ca^{2+} and CA decreased, while they remained relatively unchanged in the water column. In addition, the SI_{calc} significantly decreased. Such a change in water chemistry could be due to the removal of Ca^{2+} from the sediments via precipitation.

Despite the relatively high values of SI_{calc} (0.20-0.70), indicating supersaturation of calcite in the pore waters between December 2007 and April 2008, precipitation of $CaCO_3$ is rather unlikely to occur. The precipitation of calcite within this period is unsupported by $\delta^{13}C_{calc}$ values in the lake sediments (Table 1), which seem too low to be in equilibrium with the pore water DIC in December 2007 and April 2008. In addition, the precipitation of $CaCO_3$ is usually accompanied by a decrease in pH (Soetaert et al. 2007), while in December 2007 and April 2008 this parameter was nearly the same. It is believed that precipitation of calcite was hindered by the appreciably high concentrations

Table 1

The content of $CaCO_3$ and the stable C isotope composition of sedimentary carbonates ($\delta^{13}C_{calc}$) from Lake Sarbsko. Locations of sampling sites is shown in Figure 1.

Sample number	Depth b.l.f.* (cm)	$CaCO_3$ (wt.%)	$\delta^{13}C_{calc}$ (‰ V-PDB)
	SURFACE SAMPLES		
SAR 4	0 – 5	24.0	-1.69
SAR 5	0 – 5	10.0	-1.67
SAR 13	0 – 5	28.0	-1.49
SAR 17	0 – 5	25.0	-1.77
SAR 21	0 – 5	25.0	-1.60
SAR 24	0 – 5	28.0	-1.72
SAR 30	0 – 5	25.0	-1.69
SAR 31	0 – 5	25.0	-1.94
SAR 35	0 – 5	25.0	-1.63
SAR 38	0 – 5	24.0	-1.75
SAR 42	0 – 5	28.0	-1.98
SAR 47	0 – 5	27.0	-1.55

*b.l.f. – below lake floor

of dissolved organic carbon (DOC), Mg^{2+} (0.3-0.9 mmol l^{-1}) and/or PO_4^{3-} (0.4-9.1 μmol l^{-1}; (Woszczyk et al. 2011a)) in the lake waters which inhibited nucleation and crystal growth of calcite (Ramisch et al. 1999; Barešić et al. 2011). The inhibitory effect of organic carbon on $CaCO_3$ formation can be observed in the Szczecin Lagoon, where the high contribution of the Oder-derived organic carbon results in low $CaCO_3$ sedimentation throughout the major part of the lagoon (Osadczuk 1999). Müller et al. (2006) report that the presence of 0.3 mmol Mg^{2+} l^{-1} is sufficient to increase the solubility of $CaCO_3$. Therefore, when higher concentrations of Mg^{2+} build up, higher saturation levels would be required to initiate crystallization of $CaCO_3$. Therefore, it seems reasonable that the changes in the concentrations of Ca^{2+} between December and April were caused by diffusion/advection to overlying waters and not by the precipitation of calcite.

During summer, the pore waters became strongly undersaturated with respect to calcite, which created a considerable contrast to surface and bottom waters demonstrating the maximum $CaCO_3$ saturation. The state of undersaturation of pore waters with respect to $CaCO_3$ is usually related to decomposition of organic matter (Wu et al. 1997; Müller et al. 2006), which inevitably leads to a decrease in pH and consequently to a decline in SI_{calc}. Moreover, the enhanced oxidation of sedimentary organic matter has been invoked to explain highly negative shifts in $\delta^{13}C_{DIC}$ due to recycling of ^{12}C-enriched DIC from organic materials (Herczeg & Fairbanks 1987; Wachniew & Różański 1997; Leng & Marshall 2004).

Despite the pore waters being highly undersaturated with respect to calcite in July 2008, there was no evidence of extensive dissolution of $CaCO_3$ resulting in an increase in water pH, in increased concentrations of Ca^{2+} and CA (Müller et al. 2006), or in a positive shift in $\delta^{13}C_{DIC}$ (Herczeg et al. 2003; Myrbo & Shapley 2006). Such changes occurred in September 2008. Moreover, in September 2008, the concentrations of Ca^{2+} and CA revealed a strong positive correlation (R^2=0.99) and the average molar HCO_3^-/ Ca^{2+} ratio was 2.1. This value is very close to the stoichiometric relationship between the products of calcite dissolution according to the reaction $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$.

As mentioned above, the sediments of Lake Sarbsko contain appreciable amounts of $CaCO_3$ (Table 1). A portion of $CaCO_3$ was dissolved in pore waters between July and September 2008, but another part resisted dissolution. It was not possible, in this study, to estimate the fraction of calcite subjected to dissolution; however, it may vary in a very broad range. For example, in Lake Sempach (Switzerland), about 4.5% calcite is dissolved annually (Müller et al. 2006). In Lake Soppensee (Switzerland) and Lake Gościąż (Poland), ca. 80% of precipitated calcite is buried, the rest being re-dissolved (Wachniew & Różański 1997; Gruber et al. 2000). On the other hand, in Lake Lugano (Switzerland/ Italy) and Blue Lake (Australia), only 24% and 12% of epilimnetic calcite, respectively, is preserved (Ramisch et al. 1999; Herczeg et al. 2003). Among many factors conducive to the dissolution of calcite, the intensity of aerobic mineralization of organic matter (Müller et al. 2003), the small crystal size (Teranes et al. 1999) and the presence of chemical impurities within the crystals (Müller et al. 2006) seem to be the most important.

The surface and bottom waters

Ca^{2+}, CA, SI_{calc} and $\delta^{13}C_{DIC}$ in surface and bottom waters of Lake Sarbsko show similar temporal patterns, indicating that the lake waters are constantly well mixed. The SI_{calc} values indicate the increasing saturation with respect to calcite from December 2007 to July 2008 and the declining saturation from July onwards. The state of supersaturation and crystallization of $CaCO_3$, occurring at SI_{calc} >0.2 (Baumgartner et al. 2006), are favored between April and July 2008.

The rapidly decreasing concentrations of Ca^{2+} and CA together with the decreasing SI_{calc} between July and September 2008 indicate the ongoing removal of $CaCO_3$ from the lake water column due to precipitation of calcite. The summer precipitation is very common and can be attributed to photosynthetic activity of phytoplankton (Teranes et al. 1999; Müller et al. 2006). This process seems to produce the major quantity of sedimentary $CaCO_3$ in Lake Sarbsko, which is supported by $\delta^{13}C_{calc}$ ranging from -1.55‰ to -1.98‰ (Table 1). Such values of $\delta^{13}C_{calc}$ seem to be close to the equilibrium with summertime $\delta^{13}C_{DIC}$ of -7.07 to -3.54‰. Keeping in mind the limitations of $\delta^{13}C_{calc}$ signatures in Lake Sarbsko, described in section 5.1, the time of calcite precipitation in the lake can be determined only approximately. It seems reasonable to conclude that formation of calcite in the lake occurred in the water column between late spring and mid-summer. With this respect, Lake Sarbsko is similar to the majority of Polish freshwater lakes (Wachniew & Różański 1997; Tylmann et al. 2012). Additional evidence for the precipitation of $CaCO_3$ from the lake water column during summer is provided by the satellite image of the lake taken in July 2005, showing the widespread whiting (Fig. 4).

Figure 4

Satellite image of Lake Sarbsko from 09 July 2005 showing widespread whiting in the lake. The image comes from Google Earth.

Between April and July 2008, $\delta^{13}C_{DIC}$ in Lake Sarbsko waters dropped by ca. 10‰ (Fig. 2). Such a rapid change might be linked to the removal of ^{13}C by precipitating calcite and also to the enhanced delivery of ^{12}C. There are two processes occurring within the lake in which ^{12}C can be added to the lake waters: degradation of organic matter and chemically enhanced invasion of atmospheric CO_2 in the lake (Wachniew & Różański 1997). Owing to the coincidence between the decline in $\delta^{13}C_{DIC}$ and the decrease in the concentration of dissolved O_2 in bottom waters (Woszczyk et al. 2011a), it seems that the decomposition of organic matter is a more likely cause of the observed changes. The depletion in O_2 indicates the consumption of oxygen in the lake water column and/or diffusion of O_2 to the sediments where OM is respired. During oxic respiration, there is no fractionation of carbon (Shoemaker & Schrag 2010), so this process can account for a highly negative shift in $\delta^{13}C_{DIC}$ (Leng & Marshall 2004).

On the other hand, chemically enhanced invasion of atmospheric CO_2 is observed even in net heterotrophic lakes during periods of intense primary production, when pH is very high (>9) and pCO_2 is much below the atmospheric equilibrium of 360 µatm (3.65×10^{-4} bar) (Herczeg & Fairbanks 1987). In addition, chemical enhancement requires calm meteorological conditions with wind speeds of up to 3-4 m s^{-1} (Wanninkhof & Knox 1996). In Lake Sarbsko in July 2008, pCO_2 was between 1.8×10^{-4} and 3.5×10^{-4} bar at most of the studied sites (3 sites had higher values), especially in the central and eastern part of the lake. Thus, the invasion of atmospheric CO_2 was thermodynamically favored. However, the chemical enhancement of the invasion does not appear to significantly affect the $\delta^{13}C_{DIC}$ under pH values of 8.27-8.62 and in the conditions of high agitation of the water by wind waves. For pH values between 8 and 9 coupled with moderate to high wind stress, the fractionation during CO_2 transfer across the air-lake water interface is estimated to be between -0.1 and -3.8‰ (Herczeg & Fairbanks 1987). On the other hand, if the CO_2 transfer is preferentially due to molecular diffusion, the fractionation is between +6.8 and +9.2‰, which can lead to a slight increase in $\delta^{13}C_{DIC}$ (Herczeg & Fairbanks 1987).

The coincidence of the precipitation of $CaCO_3$ with the oxidation of OM as well as the invasion of atmospheric CO_2 is not easy to explain at this stage of the research, especially that both processes are known to lower pH (Soetaert et al. 2007) and thus create unfavorable conditions for calcite to precipitate. There are many studies showing that degradation of OM in waters is accompanied by dissolution of $CaCO_3$ (Wachniew & Różański 1997; Wu et al. 1997; Müller et al. 2006; Myrbo & Shapley 2006; Tylmann et al. 2012). One can only speculate that the rate of respiration in Lake Sarbsko was too low to stop the precipitation.

The precipitation of calcite in temperate lakes is known to occur until autumn (Teranes et al. 1999; Tylmann et al. 2012) if photosynthesizing phytoplankton is active. In September 2008, however, the SI_{calc} values in most studied sites in Lake Sarbsko were relatively low (<0.1), arguing against precipitation.

The cessation of calcite precipitation in late summer might be linked to the relatively low pH and low CA of lake waters, resulting from the intense decalcification in the preceding period. It is well established that the precipitation of $CaCO_3$ reduces pH and alkalinity (Soetaert et al. 2007) and, consequently, decreases the state of saturation with respect to calcite (Hodell et al. 1998).

Alternatively, the precipitation of $CaCO_3$ from lake waters could be affected by the intense wind-driven mixing of lake waters and sediments which occurred in Lake Sarbsko between July and September 2008 (Woszczyk et al. 2011a). The deep turbulent mixing had a profound effect on the carbonate saturation in the lake via changes in pCO_2 and pH of surface, bottom, and pore waters. In mid-summer there was a steep pCO_2 gradient between the pore and overlying waters, maintaining the large differences in pH. The surface and bottom waters showed pCO_2 of $1.8 \times 10^{-4} – 5.9 \times 10^{-4}$ bar, while pore waters had $12.1 \times 10^{-4} – 275.4 \times 10^{-4}$ bar. Within the two months, owing to intense mixing, pCO_2 in surface and bottom water increased to $4.0 \times 10^{-4} – 12.5 \times 10^{-4}$ bar and became similar to that in pore waters ($5.3 – 13.4 \times 10^{-4}$ bar, with one outlier of 101.4×10^{-4} bar). The decrease in pCO_2 in pore water induced the increase in pH and consequently in $SI_{calc.}$ On the other hand, the increase in pCO_2 in the surface and bottom waters reduced pH and SI_{calc} values in the former. The average value of pCO_2 for the whole lake dropped from 50.4×10^{-4} bar in July to 10.7×10^{-4} bar in September.

There is at least a threefold explanation of such a dramatic decrease in pCO_2. First, some parts of CO_2 could have been used for dissolution of calcite. Second, Balmer & Downing (2011) postulate that vertical mixing fuels the primary production in shallow lakes by transferring the nutrients from the sediments to overlying waters. Elevated concentrations of chlorophyll in Lake Sarbsko in August 2008 (Woszczyk et al. 2011a) indicate that the enhanced bioproductivity in the lake might have contributed to a drop in pCO_2. Third, it seems that the major change in pCO_2, however, was due to evasion of CO_2 to the atmosphere. It is well established that vertical mixing of water stimulates the emission of CO_2 from lakes whenever the CO_2 concentrations in lakes are higher than atmospheric pCO_2 (Eugster et al. 2003; Jonsson et al. 2008; Balmer & Downing 2011).

Despite the fact that it is not possible to quantify the individual contributions of the above three mechanisms to the pCO_2 decrease in the lake, the combination of $CaCO_3$ dissolution, the increased primary production, and the evasion of CO_2 from the lake provides the most plausible explanation of the 5-6‰ increase in $\delta^{13}C_{DIC}$ between July and September 2008 (Wachniew & Różański 1997; Herczeg et al. 2003; Leng & Marshall 2004; Myrbo & Shapley 2006).

Water composition vs distribution of $CaCO_3$ in the sediments

Both the content and spatial distribution of $CaCO_3$ in the sediments of Lake Sarbsko show the overall similarity to the Vistula Lagoon and Curonian Lagoon (Pustelnikovas 1998; Uścinowicz & Zachowicz 1996), i.e. high concentrations of $CaCO_3$ are found within the fine grained (muddy) facies and co-precipitate with the phytoplankton-derived TOC (Woszczyk et al. 2014). At the same time, there is no relationship between the content of $CaCO_3$ within the surface deposits and the composition of water.

It seems, therefore, that hydrodynamic processes play the major role in the distribution of $CaCO_3$ in the lake. The processes involved in the composition and distribution of the surface sediments in Lake Sarbsko have been discussed by Woszczyk et al. (2014).

Conclusions

The precipitation of $CaCO_3$ in Lake Sarbsko occurs in surface and bottom water (and not within the pore waters) owing to intense photosynthesis of phytoplankton.

There is no evidence for the early diagenetic calcite in the lake. $CaCO_3$ is not formed in the pore waters despite the fact that in some periods, the SI_{calc} values are reasonably high. It is hypothesized that the strong oversaturation is caused by higher salinity of pore waters and the inhibiting effect of Mg^{2+} and/or DOC on calcite crystallization.

$\delta^{13}C_{calc}$ in sedimentary calcite argue for a major role of organic matter-derived carbon in precipitated calcite. This is presumably due to the correlation between the maximum phytoplankton activity in the lake water column and the enhanced intensity of microbial decomposition of organic matter in summer. ^{12}C-enriched carbon is released from the decomposing organic matter and incorporated into precipitating $CaCO_3$.

During the precipitation of calcite, Lake Sarbsko water is characterized by undersaturation of CO_2 and the invasion of atmospheric CO_2 to the lake water is favored. Consequently, atmospherically derived carbon can contribute to $\delta^{13}C_{calc}$ signatures.

The conditions for precipitation of calcite in Lake Sarbsko occur during summer. In late summer, it is suppressed by vertical mixing of lake waters and sediments, which leads to an increase in pCO_2 and a decrease in pH in the surface and bottom waters. A similar effect might be caused by the very intense precipitation of calcite in mid-summer. Consequently, both turbulent mixing of the lake and decalcification of lake water can decrease $CaCO_3$ saturation in the lake.

The very negative values of SI_{calc} in pore waters indicate that dissolution of $CaCO_3$ in summer is favored within the sediments.

The results of this study showed the complexity of sedimentary processes in coastal lakes. Further research, based on a higher resolution data set, is needed to shed more light on the relationship between saltwater inflows and carbonate precipitation in coastal lakes as well as on the role of microbial processes in lake water decalcification.

Acknowledgments

The research was financially supported by the Ministry of Science and Higher Education (grant no. NN306 3543 33) and the National Science Center, Poland (grant no. 2012/05/B/ST10/00295). Linguistic improvement was made by R. Hayes (English Edits).

References

Balmer M.B. & Downing J.A. (2011). Carbon dioxide concentrations in eutrophic lakes: undersaturation imples atmospheric uptake. *Inl. Wat.* 1: 125-132. DOI: 10.5268/IW-1.2.366.

Baumgartner, L.K., Reid, R.P., Dupraz, C., Decho, A.W., Buckley, D.H. et al. (2006). Sulfate reducing bacteria in microbial mats: Changing paradigms, new discoveries. *Sed. Geol.* 185(3-4): 131-145. DOI: 10.1016/j.sedgeo.2005.12.008.

Bechtel, A., Woszczyk, M., Reischenbacher, D., Sachsenhofer, R.F., Gratzer, R. et al. (2007). Biomarkers and geochemical indicators of Holocene environmental changes in coastal Lake Sarbsko (Poland). *Org. Geochem.* 38: 1112-1131. DOI: 10.1016/j.orggeochem.2007.02.009.

Berešić, J., Horvatinčić, N., & Roller-Lutz, Z. (2011). Spatial and seasonal variations in the stable C isotope composition of dissolved inorganic carbon and in physico-chemical water parameters in the Plitvice Lake system. *Isot. Envir. Health Stud.* 47(3): 316-329. DOI: 10.1080/10256016.2011.596625.

Berner, R.A. (1971). *Principles of chemical sedimentology*. New York: McGraw-Hill Book Company.

Cieśliński, R. (2013). Short-term changes in specific conductivity in Polish coastal lakes (Baltic Sea basin). *Oceanologia* 55(3): 639-661. DOI: 10.5697/oc.55-3.639.

Cole, J.J. & Praire, Y.T. (2009). Dissolved CO_2. In G.E. Likens (Ed.) *Encyclopedia of inland waters*. Vol. 2 (pp. 30-34). Oxford, Elsevier.

de Jonge, V.N. & Villerius, L.A. (1989). Possible role of carbonate dissolution in estuarine phosphate dynamics. *Limnol. Oceanogr.* 34(2): 332-340. DOI: 10.4319/lo.1989.34.2.0332.

Dean, W. (1999). The carbon cycle and biogeochemical dynamics in lake sediments. *Jour. Paleolim.* 21: 375-393. DOI: 10.1023/A:1008066118210.

Dittrich M. & Koschel, R. (2002). Interactions between calcite precipitation (natural and artificial) and phosphorus cycle in the hardwater lake. *Hydrobiologia* 469: 49-57. DOI: 10.1023/A:1015571410442.

Dupraz, C., Reid, R.P., Braissant, O., Decho, A.W., Norman, R.S. & Visscher, P.T., (2009). Processes of carbonate precipitation in modern microbial mats. *Earth Sci. Rev.* 96(3): 141-162. DOI: 10.1016/j.earscirev.2008.10.005.

Eby, G.N. (2004). *Principles of environmental geochemistry*. Belmont: Brooks/Cole Cenage Learning.

Eugster, W., Kling, G., Jonas, T., McFadden, J.P., Wüest, A. et al. (2003). CO_2 exchange between air and water in an Arctic Alaskan and midlatitude Swiss lake: importance of convective mixing. *Jour. Geophys. Res.* 108(12), ACL7-1 – ACL7-19. DOI: 10.1029/2002JD002653.

Gruber, N., Wehrli, B. & Wüest, A. (2000). The role of biogeochemical cycling for the formation and preservation of varved sediments (Switzerland). *Jour. Paleolim.* 24: 277-291. DOI: 10.1023/A:1008195604287.

Gu, B. & Schelske, C.L. (1996). Temporal and spatial variations in phytoplankton carbon isotopes in a polymictic subtropical lake. *Jour. Plankt. Res.* 18(11): 2081-2092. DOI: 10.1093/

plankt/18.11.2081.

Gu, B., Schelske, C.L. & Hodell D.A. (2004). Extreme 13C enrichments in a shallow hypereutrophic lake: Implications for carbon cycling. *Limnol. Oceanogr.* 49(4): 1152-1159. DOI: 10.4319/lo.2004.49.4.1152.

Heiri, O., Lotter, A.F. & Lemcke, G. (2001). Loss on ignition as a method for estimating organic and carbonate content in sediments, reproducibility and comparability of results. *Jour. Paleolim.* 25: 101-110. DOI: 10.1023/A:1008119611481.

Herczeg, A.L. & Fairbanks, R.G. (1987). Anomalous carbon isotope fractionation between atmospheric CO_2 and dissolved inorganic carbon induced by intense photosynthesis. *Geochim. Cosmochim. Acta* 51: 895-899. DOI: 10.1016/0016-7037(87)90102-5.

Herczeg, A.L., Leaney, F.W., Dighton, J.C., Lamontagne, S., Schiff, S.L. et al. (2003). A modern isotope record of changes in water and carbon budgets ina agroundwater-fed lake: Blue Lake, South Australia. *Limnol. Oceanogr.* 48(6): 2093-2105. DOI: 10.4319/lo.2003.48.6.2093.

Hodell, D.A., Schelske, C.L., Fahnenstiel, G.L. & Robbins, L.L. (1998). Biologically induced calcite and its isotopic composition in Lake Ontario. *Limnol. Oceanogr.* 43(2): 187-199. DOI: 10.4319/lo.1998.43.2.0187.

Hollander, D.J. & McKenzie, J.A. (1991). CO_2 control on carbon-isotope fractionation during aqueous photosynthesis: A paleo-pCO_2 barometer. *Geology* 19: 929-932. DOI: 10.1130/0091-7613(1991)019<0929:CCOCIF>2.3.CO.

Jahnke, R.A. & Jahnke, D.B. (2004). Calcium carbonate dissolution in deep sea sediments: reconciling microelectrode, pore water and benthic flux chamber results. *Geochim. Cosmochim. Acta* 68(1): 47-59. DOI: 10.1016/S0016-7037(03)00260-6.

Jędrysek, M.O. (2005). Sulphate reduction – methane oxidation: a potential role of this process in the origin of C isotope environmental record in freshwater carbonates. Pol. Geol. Inst. Spec. Papers. 16: 18-34.

Jonsson, A., Åberg, J., Lindroth, A. & Jansson, M. (2008). Gas transfer rate and CO_2 flux between un unproductive lake and the atmosphere in northern Sweden. *Jour. Geophys. Res.: Biogeosci.* 113(4): G04006. DOI: 10.1029/2008JG000688.

Ju, J., Zhu, L., Wang, J., Xie, M., Zhen, X. et al. (2010). Water and sediment chemistry of Lake Pumayum Co, South Tibet: implication for interpreting sediment carbonate. *Jour. Paleolim.*, 43: 463-474. DOI: 10.1007/s10933-009-9343-6.

Kelts, K. & Hsu, K.J. (1978). Freshwater carbonate sedimentation. In A. Lerman (Ed.) *Lakes Chemistry Geology Physics* (pp. 295-324). New York, Heidelberg, Berlin: Springer-Verlag.

Lebeau, O., Busigny, V., Chaduteau, C. & Ader, M. (2014). Organic matter removal for the analysis of carbon and oxygen isotope compositions of siderite. *Chem. Geol.* 372: 54-61. http://dx.doi.org/10.1016/j.chemgeo.2014.02.020.

Leng, M.J. & Marshall, J.D. (2004). Palaeoclimate interpretation of stable isotope data from lake sediments. *Quat. Sci. Rev.* 23: 811-831. DOI: 10.1016/j.quascirev.2003.06.012.

Müller, G., Irion, G. & Förstner, U. (1972) Formation and diagenesis of inorganic Ca-Mg carbonates in the lacustrine environment. *Naturwissenschaften*, 59(4): 158-164. DOI: 10.1007/BF00637354.

Müller, B., Wang, Y., Dittrich, M. & Wehrli, B. (2003). Influence of organic carbon decomposition on calcite dissolution in surficial sediments of a freshwater lake. *Wat. Res.*. 37: 4524-4532. DOI: 10.1016/S0043-1354(03)00381-6.

Müller, B., Wang, Y. & Wehrli, B. (2006). Cycling of calcite in hard water lakes of different trophic states. *Limnol. Oceanogr.* 51(4): 1678-1688. DOI: 10.4319/lo.2006.51.4.1678.

Myrbo, A. & Shapley M.D. (2006). Sesasonal water-column dynamics of dissolved inorganic carbon ateble isotopic compositions ($\delta^{13}C_{DIC}$) in small hardwater lakes in Minnesota and Montana. *Geochim. Cosmoch. Acta* 70, 2699-2714. DOI: 10.1016/j.gca.2006.02.010.

Osadczuk, A. (1999). An estuary or a lagoon? *Quat. Sci. Pol.* Sp. Issue 175-186.

Pełechaty, M., Pukacz, A., Apolinarska, K., Pełechata, A. & Siepak, M. (2013). The significance of Chara vegetation in the precipitation of lacustrine calcium carbonate. *Sedimentology* 60: 1017-1035. DOI: 10.1111/sed.12020.

Piotrowska, N. & Hałas, S. (2009). Zmiany składu izotopowego węgla i tlenu w jeziorze Wigry jako źródło informacji paleoklimatycznych. In J. Rutkowski & L. Krzysztofiak (Eds.) *Jezioro Wigry. Historia jeziora w świetle badań geologicznych i paleoekologicznych* (pp. 157-167). Suwałki: Stowarzyszenie „Człowiek i Przyroda".

Pustelnikovas, O. (1998). *Geochemistry of sediments of the Cooronian Lagoon (Baltic Sea).* Vilnius, Institute of Geography.

Ramisch, F., Dittrich, M., Mattenberger, Ch., Wehrli, B. & Wüest, A. (1999). Calcite dissolution in two deep eutrophic lakes. *Geochim. Cosmochim. Acta* 63(19/20): 3349-3356. DOI: 10.1016/S0016-7037(99)00256-2.

Shoemaker, J.K. & Schrag, D.P. (2010). Subsurface characterization of methane production and oxidation from a New Hampshire wetland. *Geobiology* 8: 234-243. DOI: 10.1111/j.1472-4669.2010.00239.x.

Soetaert, K., Hofmann, A.F., Middleburg, J.J., Meysman, F.J.R. & Greenwood, J. (2007). The effect of biogochemical processes on pH. *Mar. Chem.* 105: 30-51. DOI: 10.1016/j.marchem.2006.12.012.

Stockhecke, M., Anselmetti, F.S., Meydan, A.F., Odermatt, D. & Srturm, M. (2012). The annual particle cycle in Lake Van (Turkey). *Palaeogeog., Palaeoclim., Palaeoecol.* 333-334, 148-159. DOI: 10.1016/j.palaeo.2012.03.022.

Teranes, J.L., McKenzie, J.A., Lotter, A. & Sturm, M. (1999). Stable isotope response to lake eutrophication: calibration of a hogh-resolution lacustrine sequence from Baldeggersee, Switzerland. *Limnol. Oceanogr.* 44(2): 320-333. DOI:

10.4319/lo.1999.44.2.0320.

Tylmann, W. (2007). Pobór i opróbowanie powierzchniowych, silnie uwodnionych osadów jeziornych o nienaruszonej strukturze – uwagi metodyczne i stosowany sprzęt. *Przegl. Geol.* 55: 151-156.

Tylmann, W., Szpakowska, K., Ohlendorf, Ch., Woszczyk, M. & Zolitschka, B. (2012). Conditions for deposition of annually laminated sediments in small meromictic lakes: a case study of Lake Suminko (northern Poland). *Jour. Paleolim.* 47(1): 55-70. DOI 10.1007/s10933-011-9548-3.

Uścinowicz, S., & Zachowicz, J. (1996). *Geochemical atlas of the Vistula Lagoon*. Warszawa, Wydawnictwo Kartograficzne PAE.

Valero-Garcés, B., Morellón, M., Moreno, A., Corella, J.P., Martín-Puertas, C., Barreiro, F., Pérez, A., Giralt, S. & Mata-Campo, M.P. (2014). Lacustrine carbonates of Iberian Karst Lakes: Sources, processes and depositional environments. *Sed. Geol.* 299: 1-29. DOI: 10.1016/j.sedgeo.2013.10.007.

Wachniew, P. & Różański, K. (1997). Carbon budget of a mid-lattitude, groundwater-controlled lake: isotopic evidence for the importance of dissolved inorganic carbon cycling. *Geochim. Cosmochim. Acta* 61(12): 2453-2465. DOI: 10.1016/S0016-7037(97)00089-6.

Wanninkhof, R. & Knox, M., 1996. Chemical enhancement of CO_2 exchange in natural waters. *Limnol. Oceanogr.* 41(4): 689-697. DOI: 10.4319/lo.1996.41.4.0689.

Woszczyk, M., Bechtel, A. & Cieśliński, R. (2011). Interactions between microbial degradation of sedimentary organic matter and lake hydrodynamics in shallow water bodies, insights from Lake Sarbsko (northern Poland). *Jour. Limnol.* 70: 293-304. DOI: 10.3274/JL11-70-2-09.

Woszczyk, M., Bechtel, A., Gratzer, R., Kotarba, M., Kokociński, M. et al. (2011). Composition and origin of organic matter in surface sediments of Lake Sarbsko: A highly eutrophic and shallow coastal lake (northern Poland). *Org. Geochem.* 42: 1025-1038. doi:10.1016/j.orggeochem.2011.07.002.

Woszczyk, M., Spychalski, W., Lutyńska, M. & Cieśliński, R. (2010). Temporal trend In intensity of subsurface saltwater ingressions to a coastal Lake Sarbsko (northern Poland) Turing the last few decades. *IOP Conf. Ser. Earth Env. Sci.* 9. DOI: 10.1088/1755-1315/9/1/012013.

Woszczyk, M., Tylmann, W., Jędrasik, J., Szarafin, T., Stach, A. et al. (2014). Recent sedimentation dynamics in a shallow coastal lake (Lake Sarbsko, northern Poland): driving factors, processes and effects. *Marine and Freshwater Research* 65(12): 1102-1115. http://dx.doi.org/10.1071/MF13336.

Wu, F.C., Qing, II.R., Wan, G.J., Tang, D.G., Huang, R.G. et al. (1997). Geochemistry of of HCO3- at the sediment-water interface of lakes from the southwestern Chinese plateau. *Wat. Air Soil Poll.* 99: 381-390. DOI: 10.1023/A:1018331204630.

Xu, J., Fan, Ch. & Teng, H.H. (2012). Calcite dissolution kinetics in view of Gibbs free energy, dislocation density, and pCO_2. *Chem. Geol.* 322-323, 11-18. DOI: 10.1016/j.chemgeo.2012.04.019.