

## Cycling of calcite in hard water lakes of different trophic states

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### Abstract

Based on oxygen ( $O_2$ ), pH, calcium ( $Ca^{2+}$ ), and carbonate ( $CO_3^{2-}$ ) sediment pore-water concentration profiles, we compare the benthic dissolution of autochthonous calcite in oligotrophic Lake Lucerne and eutrophic Lake Sempach. Despite their difference in trophic state, the two lakes have similar benthic  $O_2$  regimes because L. Sempach is artificially oxygenated. This peculiarity enabled the study of the direct effect of trophic state on benthic calcite dissolution. Although areal benthic  $O_2$  fluxes did not differ,  $O_2$  penetrated deeper into the sediment of the oligotrophic L. Lucerne, where most organic matter (OM, 96%) was degraded aerobically, whereas in L. Sempach, aerobic and anaerobic decomposition contributed about equal amounts to the biogenic carbon dioxide production. Release rates of bicarbonate from L. Sempach sediments exceeded those of L. Lucerne nearly two-fold. The  $HCO_3^- : Ca^{2+}$  ratio of benthic fluxes was 3.7 in L. Lucerne compared to 10.3 in L. Sempach, suggesting that in L. Sempach most of the released  $HCO_3^-$  did not originate from calcite dissolution. Furthermore, benthic calcite dissolution in L. Lucerne exceeded that in L. Sempach by two-fold, despite lower pH values in the pore water of L. Sempach. Differences in benthic microbial decomposition of OM and redissolution of calcite crystals are explained by the longer residence time of OM and calcite in the oxic sediment layer of the oligotrophic lake and the larger weight-specific surface area of its smaller autochthonous calcite crystals. We suggest that trophic state and  $O_2$  supply to the sediment are key parameters controlling the cycling of calcite and organic carbon in lakes.

The cycling of calcium ( $Ca^{2+}$ ) and carbonate species ( $HCO_3^-/CO_3^{2-}$ ) is a prominent seasonal process in hard-water lakes. It is driven by biogenic calcite precipitation and its redissolution related to aerobic decomposition of organic matter. Although the processes controlling calcite precipitation are relatively well understood, the factors controlling redissolution of calcite are not. The goal of this study was to help elucidate those factors and thus better understand the cycling of two biogeochemically important elements (calcium [Ca] and carbon [C]) in freshwater systems.

Most calcite formed in hard-water lakes precipitates during the early algal bloom in spring and mid-summer, when nutrient-enriched surface waters stimulate intense carbon dioxide ( $CO_2$ ) assimilation. The consequent increase in pH shifts the  $HCO_3^-/CO_3^{2-}$  equilibrium, causing calcite supersaturation (Brunskill 1969; Stabel 1986; Gruber et al. 2000). Müller et al. (1998a) reported increasing calcite supersaturation as increasing total phosphorus (P) concentrations in lakes increased, presumably because  $HPO_4^{2-}$  inhibits the formation of crystals

from calcite nuclei (Stumm 1992; Dove and Hochella 1993; Hartley et al. 1995). Increasing supersaturation combined with retarded crystallization eventually leads to precipitation around fewer nuclei, producing larger calcite crystals. Therefore, the size of benthic calcite crystals has been calibrated as a proxy indicator of former trophic states in paleolimnology (Lotter et al. 1997, 1998; Teranes et al. 1999).

Calcite dissolution depends on the surface area of the crystals and the production of protons due to aerobic decomposition of organic matter, either in the water column or the oxic sediment layer. Contrary to deep oceans, only a small fraction of the particulate organic matter is decomposed during the settling process in shallower lakes. For example, in oxic lakes most diagenetic decomposition of organic matter occurs in the uppermost sediment layer (Jørgensen and Revsbech 1983; Sweerts et al. 1991; Müller et al. 2002; Lorke et al. 2003). Therefore, we inferred that this is also the major site of calcite dissolution, and we focused attention on this narrow zone of intense biogeochemical activity.

In this study, we used  $Ca^{2+}$ , pH, and  $CO_3^{2-}$ -sensitive liquid membrane electrodes complemented by oxygen ( $O_2$ ) microelectrode measurements to quantify calcite dissolution in undisturbed sediment cores and to document the effect of artificial oxygenation of lakes on the alkalinity of Lakes Baldegg, Sempach, and Hallwil in Switzerland. Based on these data, we conclude that trophic state, lake depth, and  $O_2$  supply to the sediment are key parameters defining the burial rate of organic matter and calcite in sediments of hard-water lakes.

### Sites and methods

Lake Lucerne is an oligotrophic pre-alpine lake in central Switzerland. At the sediment sampling site Kreuz-

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trichter, at a depth of 112 m, the sediment surface is oxic throughout the year (Bühner and Ambühl 2001).

The eutrophic, oligomictic Lake Sempach situated on the Swiss Plateau (maximum depth 87 m) has been aerated since 1984 with up to 3 t O<sub>2</sub> d<sup>-1</sup> in summer and compressed air during the mixing period (Gächter and Wehrli 1998). The nearby eutrophic Lakes Baldegg (maximum depth 66 m) and Hallwil (maximum depth 47 m) have been similarly oxygenated and aerated since 1982 and 1986, respectively (Mengis et al. 1997; Moosmann et al. 2006). Before these remediation activities, the water columns of the latter two, nearly meromictic lakes were anoxic at depths >10 m during most of the year. Lakes Hallwil and Baldegg are hydraulically connected; i.e., the outflow of L. Baldegg is the major tributary of L. Hallwil.

Liquid membrane ion-selective electrodes for pH, Ca<sup>2+</sup>, and CO<sub>3</sub><sup>2-</sup> were prepared as described by Müller et al. (1998b). Calibration of the sensors was performed with standard solutions (pH: 7, 8, 9; Ca<sup>2+</sup>: 10<sup>-5</sup> mol L<sup>-1</sup> to 10<sup>-2</sup> mol L<sup>-1</sup>) at about 5°C. Carbonate solutions were prepared from sodium bicarbonate (10<sup>-3</sup>, 2 × 10<sup>-3</sup> mol L<sup>-1</sup> and 5 × 10<sup>-3</sup> mol L<sup>-1</sup>) in 0.01 mol L<sup>-1</sup> Tris-buffer of pH 8.30. HCO<sub>3</sub><sup>-</sup> activity was calculated from measured CO<sub>3</sub><sup>2-</sup> activity and pH using the dissociation constants from Plummer and Busenberg (1982), corrected for the ionic strength applying the Güntelberg approximation (Stumm and Morgan 1996).

Clark-type O<sub>2</sub> microelectrodes with guard cathode and tip diameters of 10–100 µm were obtained from MasCom. The O<sub>2</sub> electrode was calibrated as follows: The current measured in the sediment-overlying water was set to the O<sub>2</sub> concentration determined by Winkler titration, and the constant current recorded in deeper sediment strata was set to zero O<sub>2</sub>. Intermediate values were linearly interpolated. Signals for all the electrodes were recorded through a low-impedance filter and the MacLab 8e A/D interface and software (WissTech GmbH).

To investigate the effect of season and depth on the benthic cycling of organic matter and calcite, we collected sediment cores at the end of summer stagnation and during winter overturn with a gravity corer (Kelts et al. 1986) at various depths in both lakes. Based on visual inspection, the coring did not disturb the sediment surface. Additionally, because no macrobenthos were observed in the cores, we infer that bioturbation and bioventilation did not contribute significantly to the transport of solutes into or out of the sediment cores.

The pH of the sediment-overlying water was measured with a field pH meter with temperature compensation (Metrohm) immediately after the core was collected. Additionally, we determined O<sub>2</sub> by Winkler titration, alkalinity by titration with 0.01 mol L<sup>-1</sup> hydrochloric acid (HCl) to pH 4.3, and Ca<sup>2+</sup> concentration with ion chromatography (Metrohm IC 690 equipped with a Super-Sep column).

Within 30 min after sampling, pore-water profiles were measured in the intact sediment cores placed in a bucket with ice. Core temperatures after measurements were between 4°C and 7°C. As the ambient core temperature was up to 16°C in October, respiration rates may have been

lowered by a factor of two and, thus, may have affected concentration profiles from cores sampled at depths <12 m. A rack containing one O<sub>2</sub> microelectrode, duplicate sensors for Ca<sup>2+</sup> and pH, and triplicate sensors for CO<sub>3</sub><sup>2-</sup> was mounted on a computer-controlled micromanipulator (Newport Instruments), allowing vertical movement in discrete steps. Before measurement, sensors were equilibrated in the sediment-overlying water to constant readings. Electrodes drifting >0.1 mV min<sup>-1</sup> were replaced or discarded. Measurements were performed in vertical steps of 0.5–0.2 mm, allowing about 20 s for sensor equilibration after each step. The sediment–water interface was located either visually or by the sudden change in the concentration profiles. Ion activities determined in the sediment-overlying water by chemical analysis were used to adjust the electrode profiles (Maerki et al. 2006). The simultaneous records of replicate electrodes were averaged. Standard analytical errors were discussed in Müller et al. (2002, 2003). Briefly, standard deviations for pH, CO<sub>3</sub><sup>2-</sup>, and Ca<sup>2+</sup> concentrations were <0.1 pH unit, 0.5–1.0 µmol CO<sub>3</sub><sup>2-</sup> L<sup>-1</sup>, and 10–50 µmol Ca<sup>2+</sup> L<sup>-1</sup>. The saturation index  $\Omega$  for calcite was calculated from Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> activity measurements ({Ca<sup>2+</sup>} and {CO<sub>3</sub><sup>2-</sup>}) and solubility constants (K<sub>so</sub>) given by Plummer and Busenberg (1982). Concentration measurements were converted to activities by correcting for ionic strength. The ionic strength in the pore water was estimated from Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations. Considering a relative error ( $\frac{1S.D.}{\text{average}}$ ) of replicate measurements of 6% and 12% for {Ca<sup>2+</sup>} and {CO<sub>3</sub><sup>2-</sup>}, respectively, we arrive at a relative error of >18% for the product {Ca<sup>2+</sup>} {CO<sub>3</sub><sup>2-</sup>}. No interfering ions were present in the pore water at concentrations high enough to affect membrane potentials. HCO<sub>3</sub><sup>-</sup> concentrations were calculated from measurements of pH and CO<sub>3</sub><sup>2-</sup> applying an acidity constant pK<sub>a2</sub> of 10.56 at 5°C (Stumm and Morgan, 1996).

The two-layer diffusion-reaction model described by Müller et al. (2003) was fitted to the measured pore-water concentrations to calculate in-sediment reaction rates and the associated rates of diffusion of solutes across the sediment–water interface. Diffusion coefficients (D<sub>0</sub>) were used from Li and Gregory (1974). Values for porosity ( $\phi$  = 0.92) and the formation factor (F = 1.33) were based on measurements of the water content of core samples (Maerki et al. 2004). Reaction rates reported in Tables 1, 2 apply only to the oxic sediment layer. Areal fluxes across the sediment–water boundary may deviate from average dissolution or consumption within the oxic layer caused by additional processes occurring in deeper anoxic sediment layers.

## Results

Tables 1, 2 list estimated fluxes of O<sub>2</sub>, Ca<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> across the sediment–water interface observed at the end of the stratification period and during overturn in Lakes Lucerne and Sempach. They also report O<sub>2</sub> consumption and Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> production rates determined for the

Table 1.  $O_2$  penetration depth and diffusive fluxes and reaction rates for  $O_2$ ,  $Ca^{2+}$ , and  $HCO_3^-$  in Lake Lucerne determined in the upper (oxic) zone for sediments collected at indicated water depths in October 1998 and January 1999 by a two-layer diffusion-reaction model. The pH was measured in the sediment-overlying water. Positive and negative fluxes indicate diffusion from the water into the sediment (uptake) and vice versa (release); positive and negative reaction rates indicate production and consumption.

Depth (m)	pH	$z_{\text{max}}^{\text{O}_2}$ (mm)	Fluxes (mmol m <sup>-2</sup> d <sup>-1</sup> )			Rates (mol m <sup>-3</sup> d <sup>-1</sup> )		
			O <sub>2</sub>	Ca <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	O <sub>2</sub>	Ca <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>
October 1998								
5	8.50	3.9	13.5	-2.0	-8.5	-3.5	0.64	3.2
22	8.05	3.0	10.9	-2.7	-7.5	-3.7	0.28	6.6
43	7.97	2.7	8.7	-2.1	-7.8	-3.2	0.83	2.8
56	8.00	1.4	12.8	-3.2	-14.0	-9.2	1.2	4.6
77	7.95	1.5	8.5	-4.1	-8.9	-5.5	1.5	3.2
90	7.85	2.3	8.5	-1.4	—	-3.7	0.28	5.5
Average:			10.5	-2.6	-9.3	-4.8	0.79	4.3
January 1999								
5	8.15	4.6	8.5	-1.8	-8.2	-1.8	0.23	0.4
22	8.15	7.4	6.5	-1.5	-12.7	-0.9	0.09	4.0
42	8.15	5.1	9.3	-4.1	-8.4	-1.8	0.69	1.4
51	8.15	5.1	7.0	-1.5	-8.6	-1.4	0.14	3.7
71	8.15	3.4	9.3	-6.7	-13.3	-2.8	2.0	3.2
91	8.15	5.2	8.6	-2.7	-14.4	-1.7	0.55	3.5
Average:			8.2	-3.1	-10.9	-1.7	0.62	2.7

oxic sediment layer. Figures 1–5 present  $O_2$ , pH,  $Ca^{2+}$ ,  $HCO_3^-$ , and  $\Omega$  profiles observed in the sediment-overlying water and the uppermost 10 mm of sediment.

In L. Lucerne,  $O_2$  fluxes were highest at a depth of 5 m ( $13.5\ mmol\ m^{-2}\ d^{-1}$ ) in October (Table 1, Fig. 1).  $O_2$  penetrated 3.9 mm below the sediment surface compared to  $\leq 3$  mm at all other sites. In January,  $O_2$  penetrated significantly deeper into the sediment than in autumn. In L. Sempach,  $O_2$  penetrated only 1.3 mm to 2.7 mm below the sediment surface during stagnation (Table 2, Fig. 1). In oligotrophic L. Lucerne, the average volumetric benthic  $O_2$

consumption rate was lower and  $O_2$  generally penetrated deeper into the sediment than in eutrophic L. Sempach. Despite the higher  $O_2$  concentration in the sediment-overlying water during overturn, areal consumption rates and volumetric reaction rates were higher during the stratification period; therefore,  $O_2$  penetrated deeper into the sediment during winter in both lakes. L. Lucerne sediments released more  $Ca^{2+}$  although they consumed less  $O_2$  than L. Sempach.

Values of pH decreased sharply in the oxic sediment of both lakes (Fig. 2). Below the oxic layer (i.e., 1–7 mm

Table 2.  $O_2$  penetration depth and diffusive fluxes and reaction rates for  $O_2$ ,  $Ca^{2+}$ , and  $HCO_3^-$  in Lake Sempach determined in the upper (oxic) zone for sediments collected at indicated water depths in October 1998 and March 1999 by a two-layer diffusion-reaction model. The pH was measured in the sediment-overlying water. Positive and negative fluxes indicate diffusion from the water into the sediment (uptake) and vice versa (release); positive and negative reaction rates indicate production and consumption.

Depth (m)	pH	z <sub>max</sub> <sup>O<sub>2</sub></sup> (mm)	Fluxes (mmol m <sup>-2</sup> d <sup>-1</sup> )			Rates (mol m <sup>-3</sup> d <sup>-1</sup> )		
			O <sub>2</sub>	Ca <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	O <sub>2</sub>	Ca <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>
October 1998								
8	8.30	1.3	24.4	-1.5	-33.6	-18.4	0.37	6.4
14.5	7.40	1.6	6.6	-1.9	-6.3	-4.1	1.4	0.7
30	7.73	1.9	12.1	-1.0	-11.7	-6.4	0.18	12.0
45	7.85	2.6	11.9	-1.0	-31.7	-4.6	0.14	5.1
63	7.66	2.7	12.2	-1.2	-6.7	-4.6	0.32	0.8
85	7.11	1.2	8.5	-1.0	-25.5	-7.4	0.37	7.4
Average:			12.6	-1.3	-19.3	-7.6	0.46	5.4
March 1999								
9.5	8.00	4.9	8.6	-2.9	-11.3	-1.7	0.37	2.0
18	8.00	4.6	10.6	-0.8	-7.6	-2.3	0.14	0.6
30	8.00	5.0	8.2	-2.5	-9.8	-1.7	0.60	1.4
46	8.00	4.9	9.9	-2.1	-24.7	-2.0	0.28	3.7
60	8.00	2.9	8.5	-2.0	-18.3	-2.9	0.55	1.1
85	7.95	3.1	9.6	-1.7	-16.5	-3.1	0.64	2.3
Average:			9.2	-2.0	-14.7	-2.3	0.43	1.8

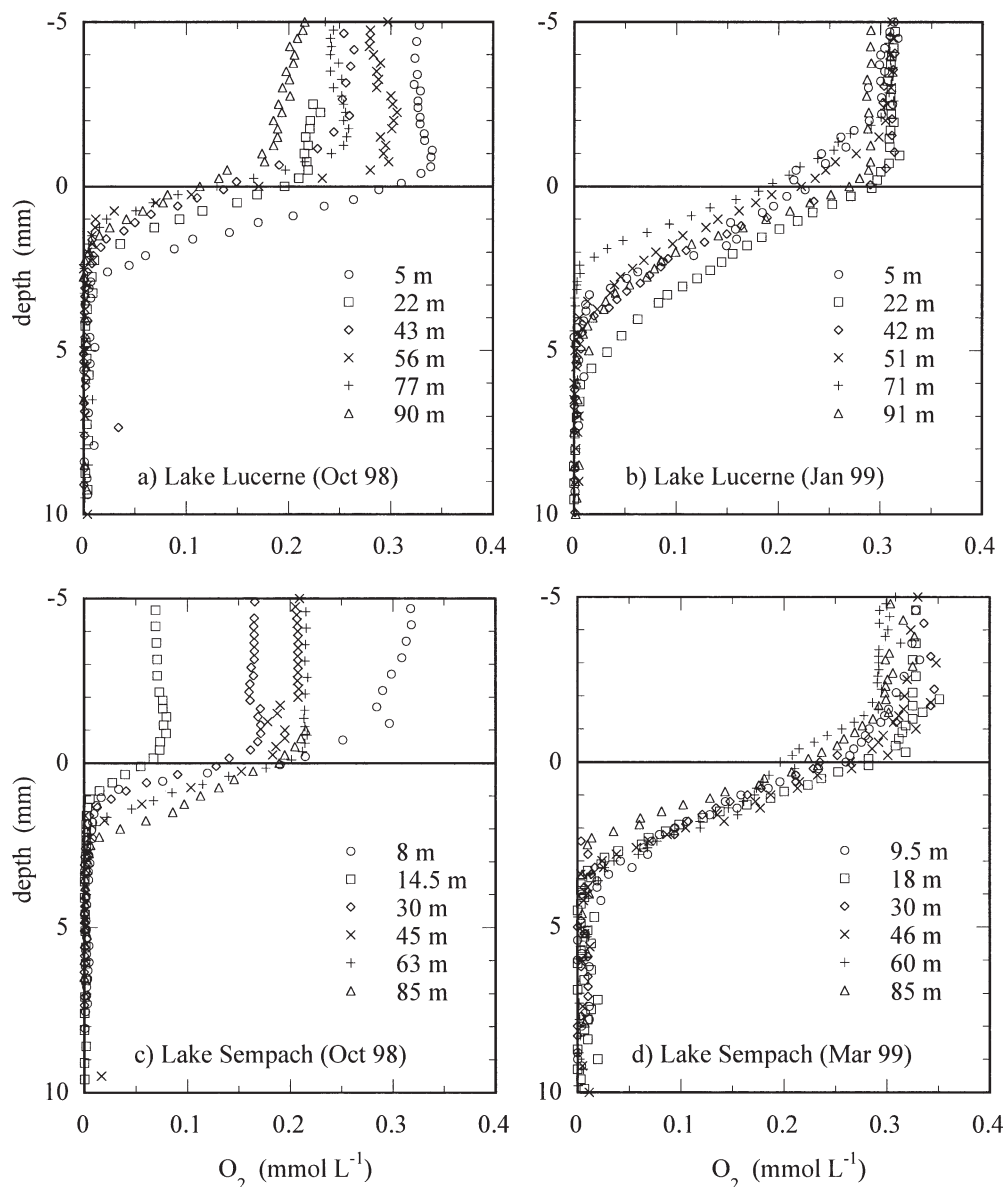


Fig. 1. Sediment pore-water profiles of  $O_2$  at various lake depths from Lake Lucerne in (a) October 1998 and (b) January 1999 and Lake Sempach in (c) October 1998 and (d) March 1999.

below the sediment surface) pH remained constant or even increased slightly. At all sampling depths in L. Sempach, sediment pH values were markedly lower in October than during overturn. This tendency was less pronounced in the sediments of L. Lucerne.

In both lakes,  $Ca^{2+}$  concentrations increased with increasing sediment depth to approximately constant values below 3–5 mm (Fig. 3). Subsurface  $Ca^{2+}$  gradients were generally steeper in winter, resulting in generally higher  $Ca^{2+}$  fluxes than during autumn (Tables 1, 2).

At the range of pH values observed in the sediment cores and overlying waters (pH 6.8–8.4),  $HCO_3^-$  is the dominant inorganic carbon species. Its flux across the sediment–water interface is thus characteristic for the benthic carbon cycling. In the sediment-overlying water of L. Lucerne, alkalinity was 1.8–2.2 mEq  $L^{-1}$  all year (Fig. 4). Below the sediment–water interface, bicarbonate

concentrations increased by about 25% to 50% and reached maximum values about 2 mm to 4 mm below the interface.  $HCO_3^-$  fluxes out of the sediment were similar in October (7.5–14.0 mmol  $m^{-2} d^{-1}$ ) and in January (8.2–14.4 mmol  $m^{-2} d^{-1}$ ) (Table 1). In L. Sempach, alkalinity values were higher than in L. Lucerne and ranged from 2.0 mEq  $L^{-1}$  to 3.0 mEq  $L^{-1}$ . Contrary to the  $Ca^{2+}$  gradient below the sediment surface, the  $HCO_3^-$  gradient was significantly steeper in L. Sempach, suggesting higher  $HCO_3^-$  fluxes and higher reaction rates in L. Sempach than in L. Lucerne (Table 2).

The sediment-overlying water of both lakes was close to saturation with respect to calcite toward the end of the stratification period and during overturn (Fig. 5). The saturation index  $\Omega$  decreased from the sediment-overlying water to the pore water and was clearly lower in the

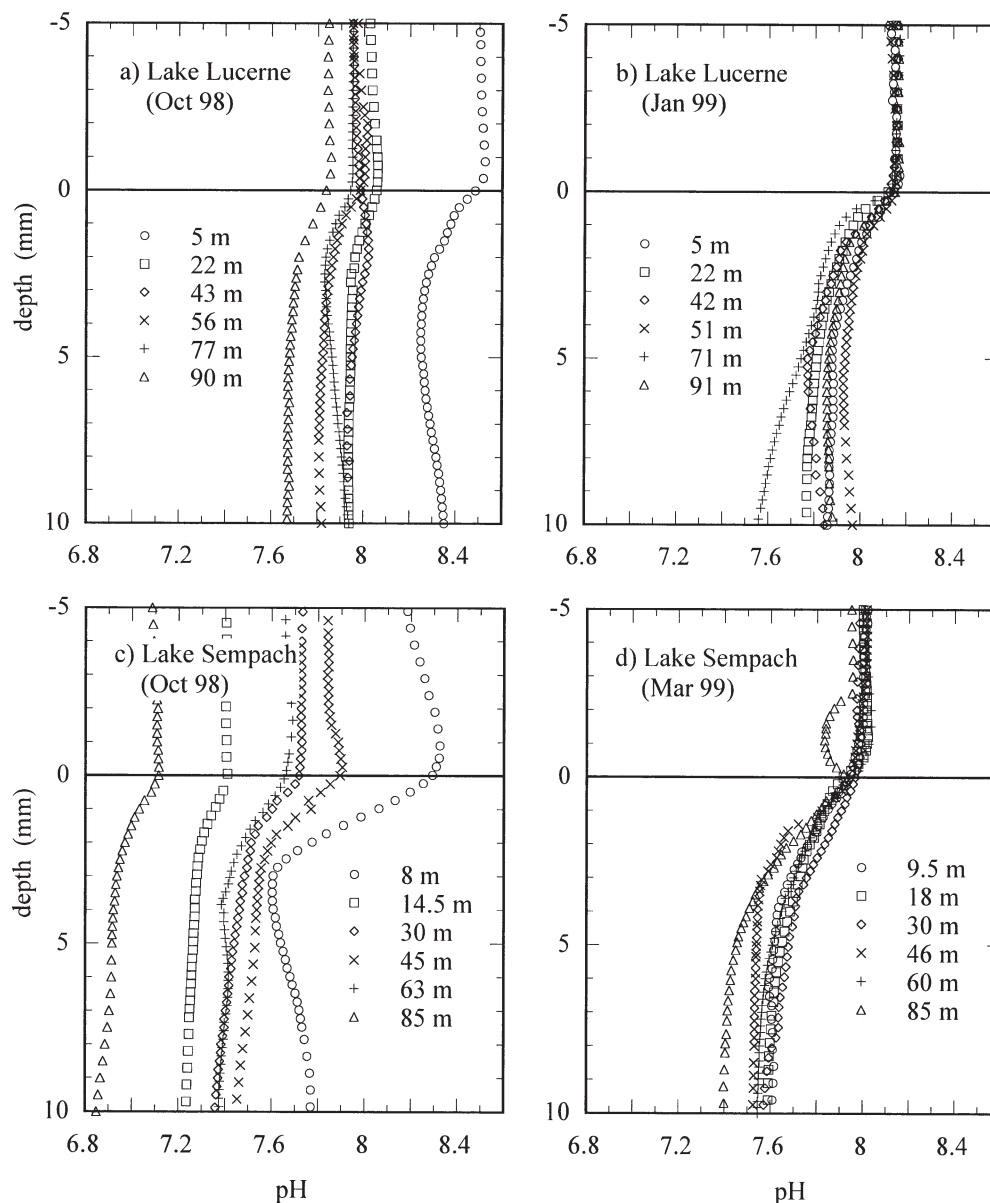


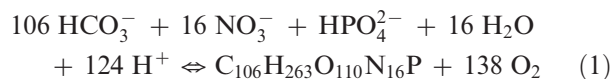
Fig. 2. Sediment pore-water profiles of pH at various lake depths from Lake Lucerne in (a) October 1998 and (b) January 1999 and Lake Sempach in (c) October 1998 and (d) March 1999.

sediments of L. Sempach. In both lakes,  $\Omega$  clearly exceeded one in the sediment cores from shallow water depths (5 m in Fig. 5a, and 8 m in Fig. 5c) in October. This supersaturation was probably caused by photosynthetic activity at the sediment surface. Pore-water samples collected with diffusion plates ("peepers") (Müller et al. 2003) as well as results from the monthly L. Sempach monitoring program confirmed that the sediment-overlying water was supersaturated with respect to calcite at shallow water depths, but that the solubility product of calcite was not attained at greater lake depths.

## Discussion

Assuming the Redfield ratio for C : nitrogen (N) : P in organic matter (OM) in aquatic systems, production or

aerobic decomposition of 1 mol of OM consumes or generates an average of 106 mol  $\text{HCO}_3^-$  and 124 mol  $\text{H}^+$  (Stumm and Morgan 1996).



Accordingly, if production exceeds decomposition plus invasion of atmospheric  $\text{CO}_2$ , pH and consequently the chemical activity of  $\text{CO}_3^{2-}$  can increase to the point that the solubility of calcium carbonate ( $\text{CaCO}_3$ ) is exceeded. In fact, calcite precipitation induced by primary production is a common, well known feature in alkaline hard-water lakes (Stabel 1986; Dittrich et al. 2003).

During summer, when the maximum epilimnic pH values and, hence, the  $\text{CO}_3^{2-}$  activities increase with



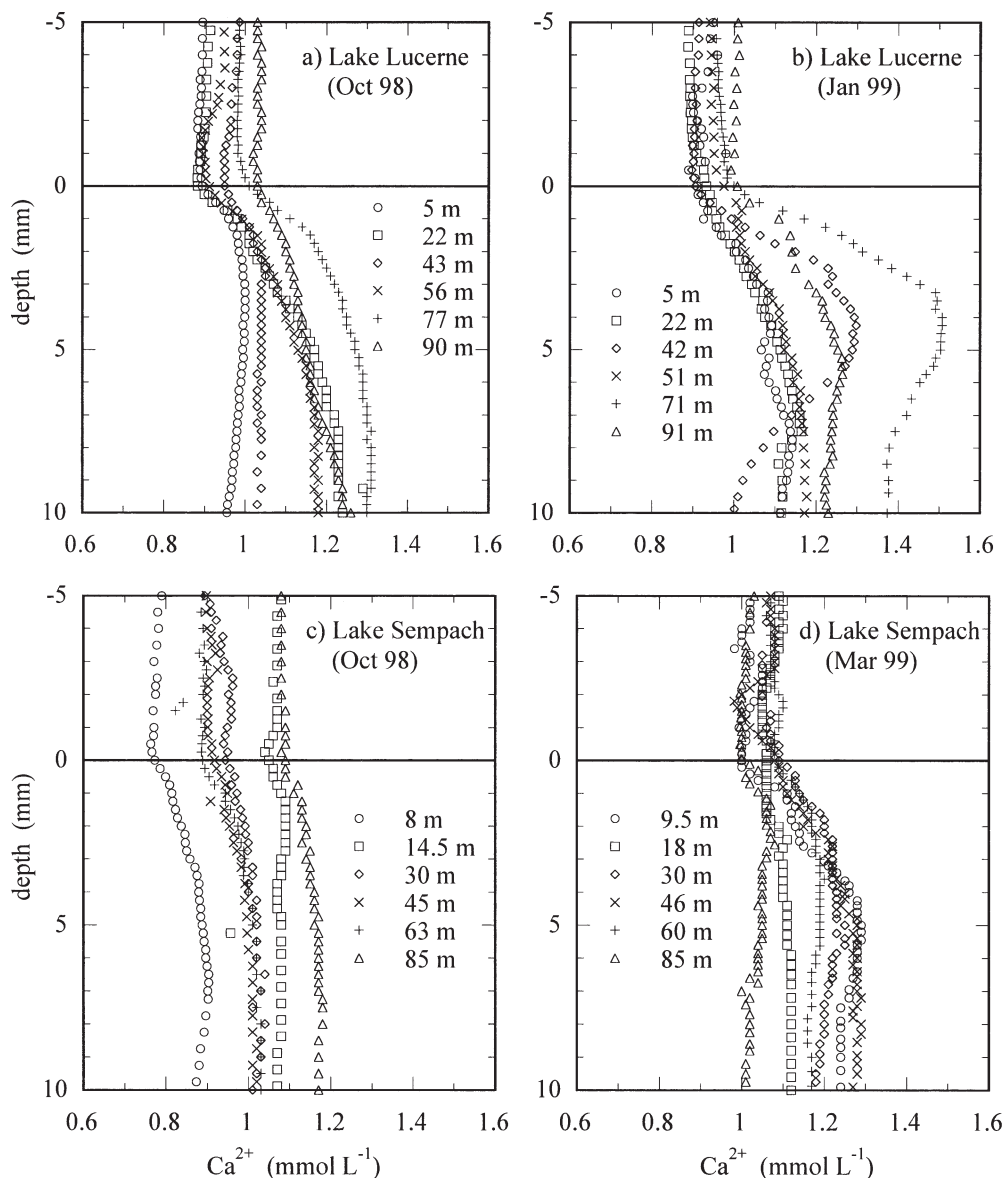
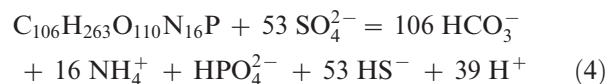
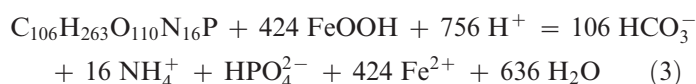
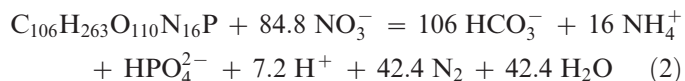


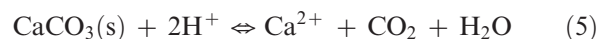
Fig. 3. Sediment pore-water profiles of  $\text{Ca}^{2+}$  at various lake depths from Lake Lucerne in (a) October 1998 and (b) January 1999 and Lake Sempach in (c) October 1998 and (d) March 1999.

increasing productivity of a lake, more  $\text{CaCO}_3$  is expected to precipitate from eutrophic than from oligotrophic lakes. This has been empirically confirmed by Vollenweider (1971).

Compared to oxic respiration (Eq. 1 read from right to left), anaerobic decomposition of OM produces fewer protons per mole of OM mineralized (Eq. 2–4); and some even consume protons (Eq. 3).



For thermodynamic reasons, the productivity of microbial communities decreases with the following sequence of oxidants:  $\text{O}_2 > \text{NO}_3^- \geq \text{Fe}^{3+} > \text{SO}_4^{2-}$  (Stumm and Morgan 1996). Because calcite reacts with protons according to Eq. 5



and with  $\text{CO}_2$  (in its hydrated form as carbonic acid  $\text{H}_2\text{CO}_3$  according to Eq. 6,



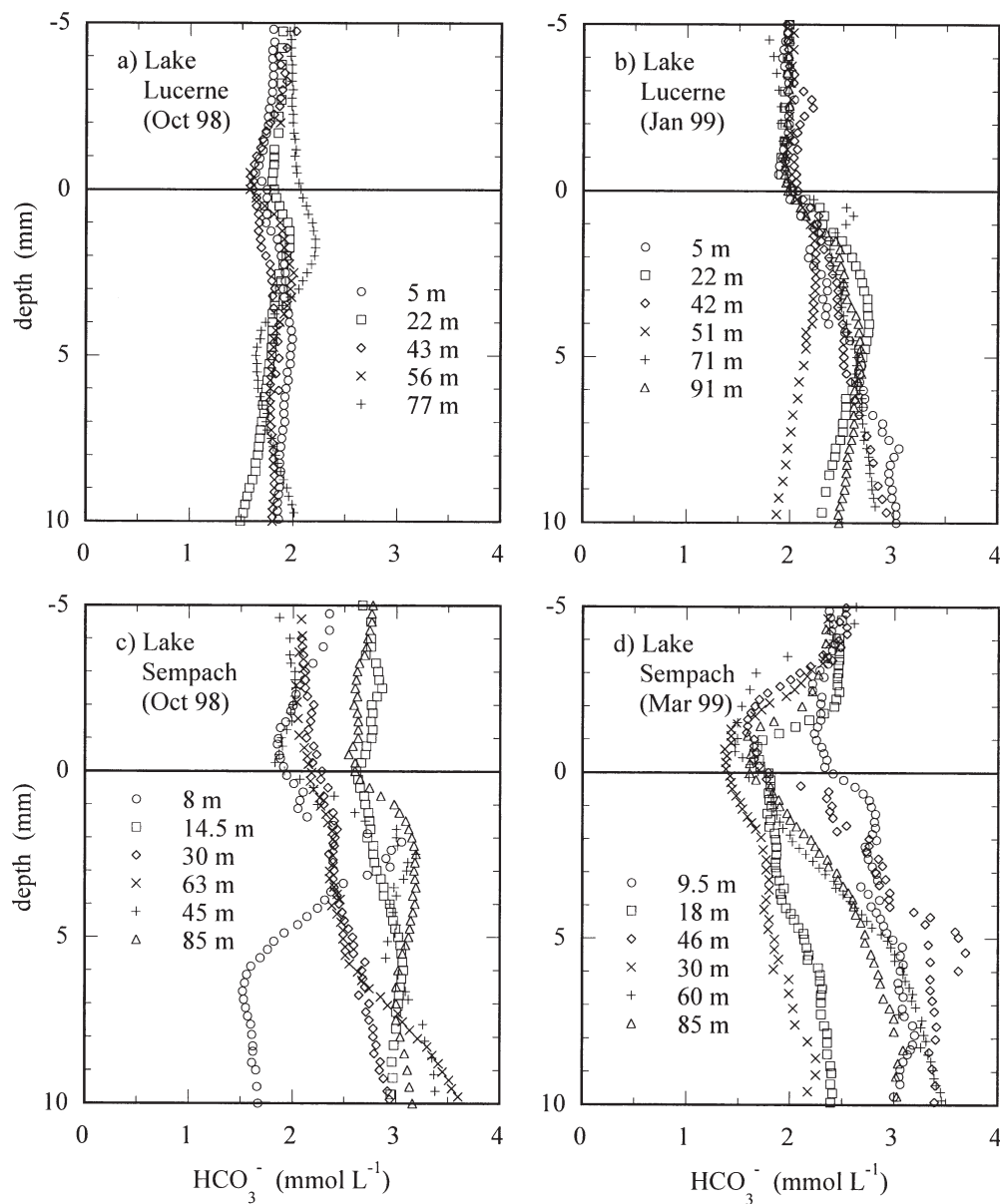


Fig. 4. Sediment pore-water profiles of  $\text{HCO}_3^-$  (calculated from measurements of pH and  $\text{CO}_3^{2-}$ ) at various lake depths from Lake Lucerne in (a) October 1998 and (b) January 1999, and Lake Sempach in (c) October 1998 and (d) March 1999.

oxidation of OM with  $\text{O}_2$  (Eq. 1) dissolves more calcite than oxidation with  $\text{NO}_3^-$ ,  $\text{Fe}^{3+}$ , or  $\text{SO}_4^{2-}$  (Eq. 2–4).

Fluxes of  $\text{O}_2$  from the overlying water into the sediments replenish the  $\text{O}_2$  consumed by bacteria decomposing OM and oxidizing  $\text{NH}_4^+$ ,  $\text{CH}_4$ ,  $\text{HS}^-$ ,  $\text{Fe}^{2+}$ , and  $\text{Mn}^{2+}$  migrating from deeper sediment strata into the oxic sediment surface. All the  $\text{O}_2$  supplied to the sediment is consumed in the top few millimeters (Fig. 1). According to Eq. 1, oxidation of OM produces 0.9 equivalents of  $\text{H}^+$  per equivalent of  $\text{O}_2$  consumed, explaining the steep decrease of pH at the top of the sediment (Fig. 2). The seasonally variable supply of  $\text{O}_2$  to the sediment surface resulted in steeper pH gradients and lower pore-water pH values during the productive season than during winter. Interestingly, this

did not result in an increased dissolution of calcite. Alkalinity is produced (Eq. 2–4) below the maximum penetration depth of  $\text{O}_2$  in the sediment ( $z_{\text{max}}^{\text{O}_2}$ ), causing the pH to increase in deeper sediment strata (not shown) and thus suggesting preservation of the residual calcite.

Despite the higher release rate of  $\text{HCO}_3^-$  in the eutrophic L. Sempach ( $14.7 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $19.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; Table 2) than in L. Lucerne ( $9.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $10.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; Table 1), calcite dissolved more readily in the sediments of the oligotrophic L. Lucerne ( $2.6 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $3.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; Table 1) than in the sediment of L. Sempach ( $1.3 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $2.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ ; Table 2). The  $\text{Ca}^{2+}$  profiles in Fig. 3 suggest that  $\text{CaCO}_3$  dissolution was restricted to the top

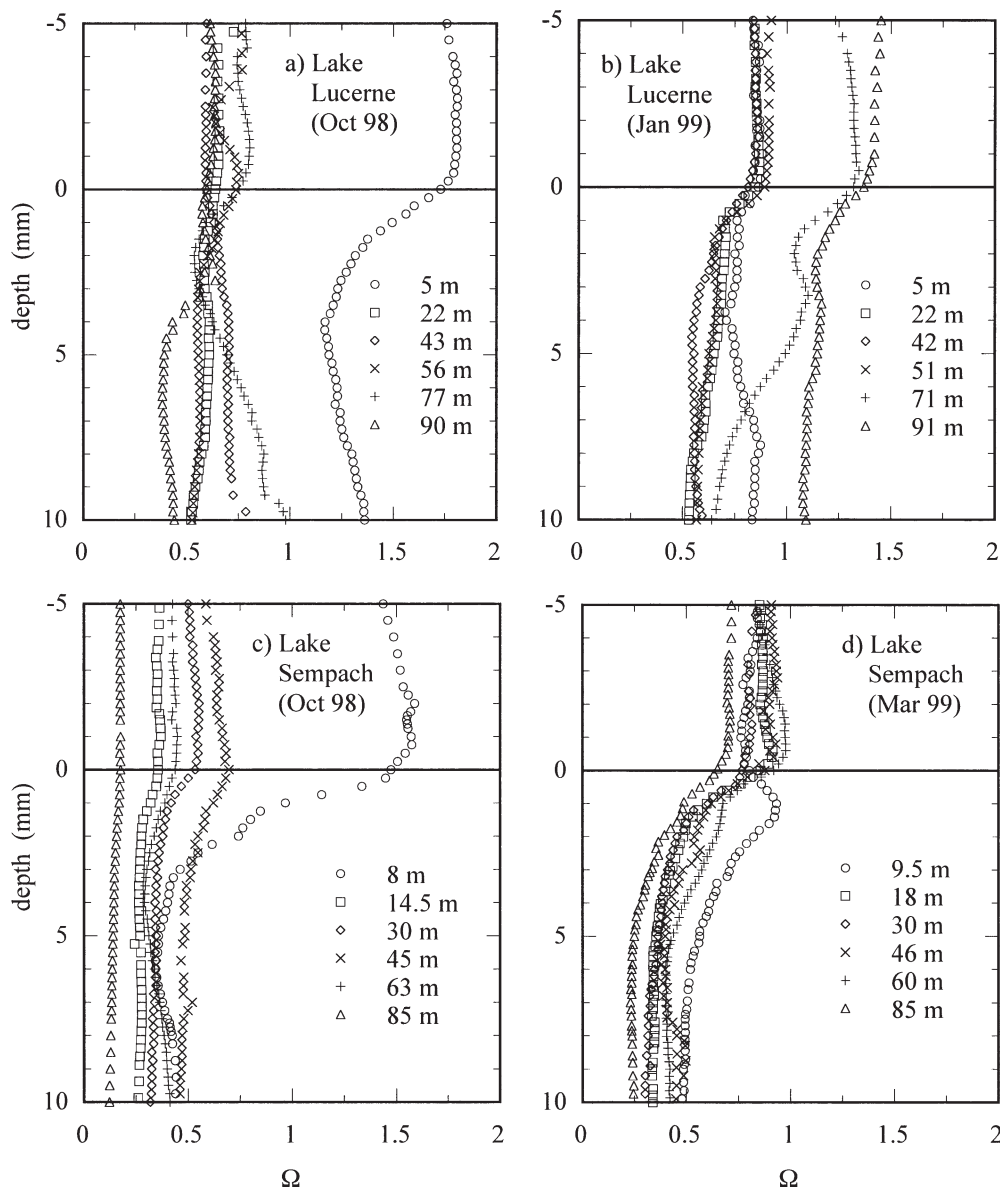


Fig. 5. Sediment pore-water profiles of the saturation index  $\Omega$  for calcite, calculated from measurements of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  as  $\Omega = \{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\}/K_{s0}$  at various lake depths from Lake Lucerne in (a) October 1998 and (b) January 1999 and Lake Sempach in (c) October 1998 and (d) March 1999.

5 mm of the sediments in both lakes, although sediment strata deeper than 5 mm also contributed to the benthic  $\text{HCO}_3^-$  release in L. Sempach (Fig. 6) because of anoxic decomposition of OM. This latter observation implies that in L. Lucerne, most OM was decomposed aerobically, whereas in the aerated L. Sempach, aerobic and anaerobic decomposition contributed about equal amounts of  $\text{CO}_2$ .

The saturation index for calcite in the sediment-overlying water generally was between 0.75 and 1 with the exception of L. Sempach in October, where the bottom waters were clearly undersaturated ( $\Omega$  ranged from 0.15 to 0.6) (Fig. 5). Interestingly, the saturation index decreased with increasing sediment depth, i.e., the sediment pore waters were less saturated with respect to calcite with

increasing depth. The undersaturation was more pronounced in the sediments of the more eutrophic L. Sempach, where pH values were also lower. In October, the shallowest sediments of both lakes (Fig. 5a at 5 m and Fig. 5c at 8 m) show oversaturation, which may be a result of the increased pore-water pH due to photosynthesis during daytime. Apparently, calcium carbonate can even dissolve in water that is oversaturated with respect to pure calcite (Figs. 3, 5) suggesting that tabulated solubility products for calcite may not be appropriate for the biogenically precipitated calcites in lake sediments. Calcite crystals in sediments are not pure, but contain high proportions of contaminants such as magnesium (Mg), manganese (Mn), or iron (Fe). Friedl et al. (1997) observed



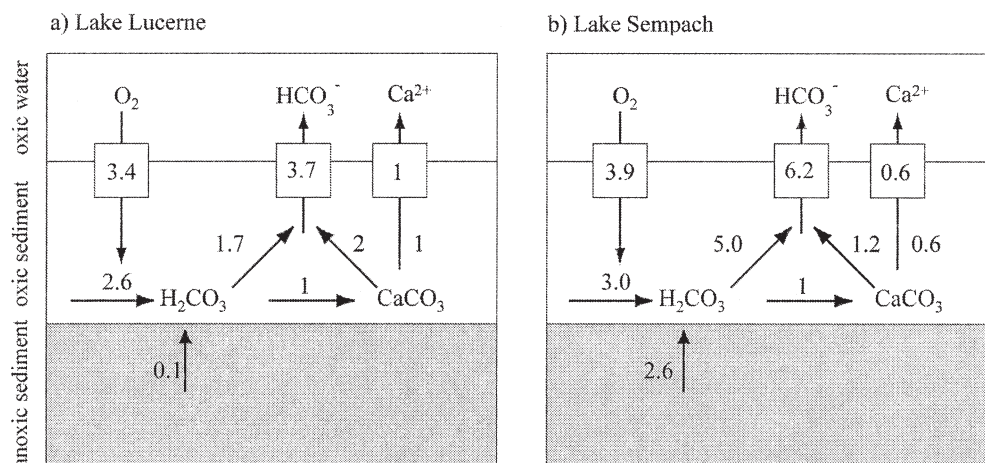


Fig. 6. Synoptic presentation and interrelation of annual fluxes of  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{O}_2$  of (a) Lake Lucerne and (b) Lake Sempach calculated from pore-water concentration profiles (numbers in squares). Estimated differences (see text) complete the calcite cycle across the sediment–water interface and in the oxic and anoxic sediment layers. Numbers are in  $\text{mol m}^{-2} \text{yr}^{-1}$ .

calcites containing large amounts of Mn ( $\text{Mn}_x\text{Ca}_{1-x}\text{CO}_3$ , with  $x = 0.2\text{--}0.3$ ) in surface sediments of Lake Sempach. The addition of Mn decreases the solubility product, whereas other substituting cations (e.g., Mg) increase the solubility. Hence, the presence of about  $0.3 \text{ mmol L}^{-1}$   $\text{Mg}^{2+}$  in the bottom water may increase the solubility of the resulting calcite precipitates, whereas dissolved  $\text{Mn}^{2+}$  from the anaerobic mineralization of organic carbon may decrease the solubility in the pore water causing lower free concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . Nevertheless, in both lakes the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  profiles (Figs. 3, 4) suggest calcite dissolution in the oxic layer, resulting in  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  effluxes into the sediment-overlying water.

Hedges et al. (1999) and Hartnett et al. (1998) showed for marine pelagic sediments that the mineralization of OM and, hence, production of  $\text{H}^+$  and  $\text{CO}_2$  are proportional to the exposure time of OM to  $\text{O}_2$  in the sediment pore water. Thus, according to Eq. 5 and 6, increasing amounts of  $\text{CaCO}_3$  are expected to dissolve with increasing residence time of OM and  $\text{CaCO}_3$  in the oxic sediment layer. In October,  $\text{O}_2$  penetration depths were on average 2.5 mm in L. Lucerne and 1.9 mm in L. Sempach. Mass accumulation rates reported for Lakes Lucerne and Sempach were  $0.041 \text{ g cm}^{-2} \text{yr}^{-1}$  (Spadini et al. 2003) and  $0.073 \text{ g cm}^{-2} \text{yr}^{-1}$  (Wieland et al. 1993), respectively. Assuming the same water content (90%), porosity (0.95), and density ( $2.35 \text{ g cm}^{-3}$ ) for the top sediment layers in both lakes, we estimated an  $\text{O}_2$  exposure time of 8.6 months in L. Lucerne but only 3.7 months in L. Sempach. In agreement with our expectations, the  $\text{Ca}^{2+}$  fluxes across the sediment water interface were higher in the oligotrophic L. Lucerne than in the eutrophic L. Sempach (Tables 1, 2). Furthermore, at sediment depths exceeding 5 mm,  $\text{Ca}^{2+}$  pore-water concentrations were approximately constant (i.e., independent of sediment depth; Fig. 3), inferring those calcites are protected from dissolution in anaerobic sediments. Thus, most of the released  $\text{Ca}^{2+}$  must have been generated within the oxic sediment layer.

Figure 6 interrelates the  $\text{O}_2$ ,  $\text{Ca}^{2+}$ , and  $\text{HCO}_3^-$  fluxes across the sediment–water interface of Lakes Sempach and Lucerne. Observed average fluxes of  $\text{O}_2$  to the sediment were  $3.4 \text{ mol m}^{-2} \text{yr}^{-1}$  in the oligotrophic L. Lucerne and  $4.0 \text{ mol m}^{-2} \text{yr}^{-1}$  in the eutrophic, aerated L. Sempach, respectively. Assuming all  $\text{O}_2$  was consumed to decompose OM, the corresponding aerobic  $\text{H}_2\text{CO}_3$  production rates were  $2.6 \text{ mol m}^{-2} \text{yr}^{-1}$  and  $3.1 \text{ mol m}^{-2} \text{yr}^{-1}$ , respectively (Eq. 1).

Because calcite dissolves after reaction with  $\text{H}_2\text{CO}_3$  (Eq. 6), the observed benthic  $\text{Ca}^{2+}$  fluxes suggest equimolar consumption of biogenic  $\text{H}_2\text{CO}_3$ , i.e.,  $1 \text{ mol m}^{-2} \text{yr}^{-1}$  in L. Lucerne and  $0.6 \text{ mol m}^{-2} \text{yr}^{-1}$  in L. Sempach. Consequently, calcite dissolution contributed  $2 \text{ mol m}^{-2} \text{yr}^{-1}$  and  $1.2 \text{ mol m}^{-2} \text{yr}^{-1}$  of  $\text{HCO}_3^-$  to the benthic fluxes in Lakes Lucerne and Sempach, respectively. Hence, 54% of the total benthic release of  $\text{HCO}_3^-$  originated from  $\text{CaCO}_3$  dissolution in L. Lucerne. Despite the lower pH values in the pore water of L. Sempach, calcite dissolution contributed only 19% of the total benthic  $\text{HCO}_3^-$  in L. Sempach. This might be attributable to (1) the longer concurrent residence time of calcites and OM in the oxic layer of L. Lucerne and (2) the smaller calcite crystals to be expected in the sediment of the oligotrophic L. Lucerne sediment. Lotter et al. (1997, 1998) and Teranes et al. (1999) have shown that  $\text{CaCO}_3$  crystal size and epilimnic  $\text{HPO}_4^-$  concentrations are positively related. Smaller crystals are characterized by larger weight-specific surface area ( $\text{cm}^2 \text{g}^{-1}$ ). The longer exposure of calcites and OM to  $\text{O}_2$  (resulting in higher  $\text{H}^+$  and  $\text{CO}_2$  production) and the larger total surface area of the smaller calcite crystals can explain why the benthic calcite dissolution in oligotrophic L. Lucerne exceeded that of L. Sempach. According to Fig. 6,  $\text{H}_2\text{CO}_3$  production from anoxic mineralization ( $J_{\text{anoxic}}^{\text{H}_2\text{CO}_3}$ ) can be calculated as

$$J_{\text{anoxic}}^{\text{H}_2\text{CO}_3} = J^{\text{HCO}_3^-} - J^{\text{Ca}^{2+}} - J_{\text{oxic}}^{\text{H}_2\text{CO}_3} \quad (7)$$

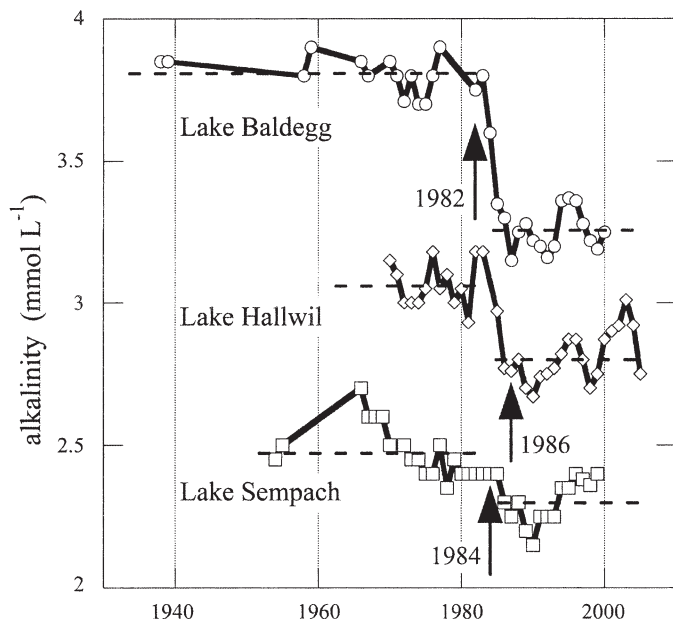


Fig. 7. Alkalinity at spring overturn in Lakes Baldegg, Hallwil, and Sempach. The arrows mark the start of artificial aeration (1982, 1986, and 1984, respectively). The dashed horizontal lines are the mean values of alkalinity before and after aeration (Lake Baldegg: before,  $3.80 \pm 0.07$ , after,  $3.26 \pm 0.07$ ; Lake Hallwil: before,  $3.06 \pm 0.08$ , after,  $2.81 \pm 0.09$ ; Lake Sempach: before,  $2.47 \pm 0.09$ , after,  $2.31 \pm 0.08$ ).

where  $J^{\text{HCO}_3^-}$  and  $J^{\text{Ca}^{2+}}$  are the fluxes of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  across the sediment–water interface, and  $J^{\text{H}_2\text{CO}_3}_{\text{oxic}}$  is the  $\text{H}_2\text{CO}_3$  produced by the oxic mineralization of organic carbon. Accordingly, anoxic mineralization contributed  $0.1 \text{ mol m}^{-2} \text{ yr}^{-1}$  (4%) to the total benthic  $\text{H}_2\text{CO}_3$  production in L. Lucerne, and  $2.5 \text{ mol m}^{-2} \text{ yr}^{-1}$  (45%) in L. Sempach. Thus, in L. Lucerne 96% of the biogenic  $\text{CO}_2$  originated from oxic decomposition of OM. In L. Sempach, oxic and anoxic decomposition contributed about equal amounts.

Figure 7 compares alkalinity of Lakes Baldegg, Sempach, and Hallwil at overturn before and after artificial aeration. All three lakes are eutrophic, of comparable size and depth, and have similar mineralogical catchments. Artificial mixing during overturn and hypolimnetic oxygenation during summer stagnation led to a decrease in alkalinity in L. Baldegg and Sempach right after the start of the remediation measures (arrows in Fig. 7). In Lake Hallwil alkalinity decreased before oxygenation was started likely because the outflow of Lake Baldegg (aerated since 1982) is the major tributary of L. Hallwil. This indicates that in addition to the theory of classical limnology (Vollenweider 1971) assuming that the alkalinity of lake water depends on (1) the alkalinity of the inflowing waters, (2) the productivity of the lake and thus the intensity of the biogenic calcite precipitation, (3) the flushing rate of the lake, (4) the lake depth, and (5) the ratio of the epilimnion volume to the total lake volume, the alkalinity is also

affected by the capacity of the lake to permanently eliminate  $\text{CaCO}_3$  in its sediment and thus by the  $\text{O}_2$  supply to the lake sediment.

Benthic production of alkalinity is defined as

$$\text{Alk} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- + \text{HS}^- - \text{H}^+ \quad (8)$$

As Eq. 8 indicates, the only way that oxygenation can affect the benthic production of alkalinity is by changing the concentrations of the species occurring in the equation. As discussed above (Eq. 1–4), oxic decomposition of OM generates more protons than anoxic decomposition. Accordingly, it seems likely that the anoxic sediment surfaces in Lakes Baldegg, Sempach, and Hallwil released fewer protons before oxygenation than today. Hence, the pH of the sediment-overlying water should have decreased in the summers after the artificial oxygenation started. This could not be observed, however, possibly because of the enhanced mixing of the hypolimnetic water by the artificial aeration.

In summary, by comparing benthic profiles and fluxes of  $\text{O}_2$ ,  $\text{Ca}^{2+}$ , and  $\text{HCO}_3^-$  in an oligotrophic and an aerated, eutrophic lake, it appears that benthic calcite dissolution is restricted to the oxic uppermost few millimeters of the sediment. Interestingly, benthic calcite dissolution was higher in oligotrophic L. Lucerne despite its lower benthic  $\text{CO}_2$  production rate and its higher pore-water pH values. Instead, (1) the longer contact time of  $\text{CaCO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{H}^+$  in the thicker oxic zone and (2) the higher weight-specific surface area of calcite crystals in the oligotrophic L. Lucerne appear to be major factors explaining why less calcite dissolved in the sediment of the eutrophic L. Sempach than in the sediment of L. Lucerne. Therefore, Vollenweider's model (1971) of the controls on lake-water alkalinity should be modified to include the benthic biogeochemical processes we have demonstrated.

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