Pergamon

PII S0016-7037(99)00049-6

A study of oxygen isotopic fractionation during bio-induced calcite precipitation in eutrophic Baldeggersee, Switzerland

Jane L. Teranes,[1,*] Judith A. McKenzie,[1] Stefano M. Bernasconi,[1] Andre F. Lotter,[2] and Mike Sturm[3]

[1]Geological Institute, Swiss Federal Institute of Technolgy (ETH), Zürich, Switzerland
[2]Geobotanisches Institut, Universitaet, Bern, Switzerland
[3]Department of Environmental Physics/Sedimentology Section, EAWAG, Duebendorf, Switzerland

Abstract—In order to better understand environmental factors controlling oxygen isotope shifts in autochthonous lacustrine carbonate sequences, we undertook an extensive one-year study (March, 1995 to February, 1996) of water-column chemistry and daily sediment trap material from a small lake in Central Switzerland. Comparisons between calculated equilibrium isotope values, using the fractionation equation of Friedman and O'Neil (1977) and measured oxygen isotope ratios of calcite in the sediment-traps reveal that oxygen isotopic values of autochthonous calcite ($\delta^{18}O$) are in isotopic equilibrium with ambient water during most of the spring and summer, when the majority of the calcite precipitates. In contrast, small amounts of calcite precipitated in early-spring and again in late-autumn are isotopically depleted in ^{18}O relative to the calculated equilibrium values, by as much as 0.8‰. This seasonally occurring apparent isotopic nonequilibrium is associated with times of high phosphorous concentrations, elevated pH (~8.6) and increased $[CO_3^{2-}]$ (~50 μmol/l) in the surface waters. The resulting weighted average $\delta^{18}O$ value for the studied period is −9.6‰, compared with a calculated equilibrium $\delta^{18}O$ value of −9.4‰. These data convincingly demonstrate that $\delta^{18}O$ of calcite are, for the most part, a very reliable proxy for temperature and $\delta^{18}O$ of the water. *Copyright © 1999 Elsevier Science Ltd*

1. INTRODUCTION

Stable oxygen isotope measurements on biologically induced carbonates, most commonly calcite, in lacustrine sedimentary sequences have become a valued tool for reconstructing high-resolution paleoenvironmental changes in continental areas, due to the rapid response of lake ecosystems to environmental perturbations. Annually laminated (varved) lake sediments, in particular, provide the highest possible time resolution (seasons to years) in long (centuries to millennia) proxy-data time series, and are essential for determining rates and magnitudes of environmental and climate change.

Assuming that the bulk of the calcite precipitates at approximately the same time during the annual cycle each year, when the range of the surface-water temperatures is about the same, variations in $\delta^{18}O$ values of sedimented calcite primarily represent past changes in the isotopic composition of the water. Water $\delta^{18}O$ values in small lakes with limited catchment areas, in turn, can change rapidly in response to variations of $\delta^{18}O$ values in atmospheric precipitation. Thus, oxygen isotope ratios in lacustrine sequences are paleo-precipitation archives that can be used to reconstruct mean average annual air temperatures (Stuiver, 1970; Siegenthaler and Eicher, 1986; von Grafenstien et al, 1996), and/or dominant synoptic atmospheric circulation patterns in the region (McKenzie and Hollander, 1993; Fischer, 1996).

Interpretations of isotopic variations in lacustrine sequences are necessarily based on the assumption that oxygen isotopes fractionate between water and calcite according to empirically derived equilibrium fractionation equations (Epstein and

Mayeda, 1953; Friedman and O'Neil, 1977). Recent isotopic studies of $CaCO_3$ precipitated in highly eutrophic lacustrine systems, however, have reported isotopically depleted oxygen isotope values relative to predicted equilibrium values, thereby challenging the premise that isotopic variations in lacustrine sequences can be accurately interpreted exclusively in terms of climatological and/or environmental changes (Fronval et al, 1995; Gat and Lister, 1995; Teranes, 1998).

A number of complications to standard equilibrium equations have been reported in other materials, ranging from biological to synthetic $CaCO_3$, used for isotopic analyses. McConnaughey (1989) noted covarying isotopic depletions in $\delta^{18}O$ and $\delta^{13}C$ data from biologically precipitated carbonates. Occurrences of isotopically depleted carbonates were related to elevated pH and higher CO_3^{2-} concentrations in the ambient water. McConnaughey (1989) proposed that "kinetic" isotopic effects were responsible, reasoning that CO_3^{2-} molecules favor the lighter isotopes during the exchange of oxygen and carbon atoms between CO_2 and CO_3^{2-}. Similarly, a recent re-examination of the oxygen isotope data of McCrea on inorganic calcite precipitation also linked oxygen isotopic fractionation to carbonate species equilibrium (Usdowski and Hoefs, 1993). Based on laboratory measurements of oxygen isotope exchange between dissolved carbonate and water at different pH values, Usdowski et al. (1991) demonstrated that oxygen fractionation factors vary as a function of the major carbonate component equilibrium. A study of synthetic carbonates by Kim and O'Neil (1997), in which carbonates were precipitated reproducibly in isotopic equilibrium and nonequilibrium with the solution by varying the concentrations of bicarbonate and cation, lends further data supporting the hypothesis that isotopic equilibrium is dependent on carbonate equilibrium. Finally, a series of recent experimental studies on cultured foraminifera

*Address reprint requests to Jane L. Teranes, Department of Geological Sciences, University of Michigan, 2534 C.C. Little Bldg., Ann Arbor, MI 48109-1063, USA.
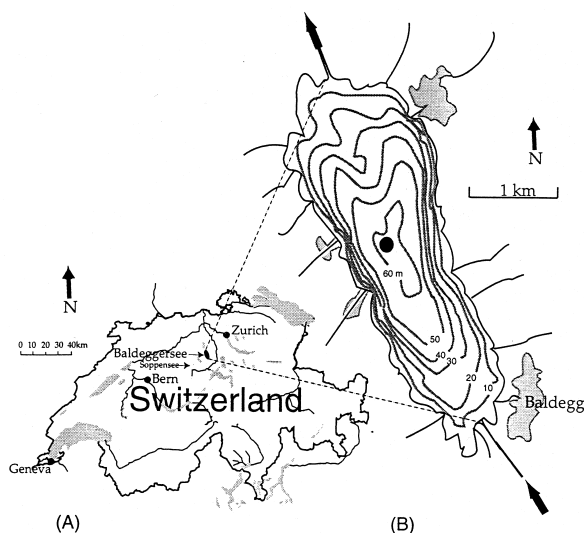
Fig. 1. Map of the Baldeggersee study area presenting (**A**) the geographical locations of Baldggersee (47° 12′N, 8°16′E), Soppensee, and the city of Bern. (**B**) Baldeggersee bathymetric map with water depths in 10s of meters, stream inflow and outflow, and location of the sediment trapping device (●).

clearly demonstrate that the $\delta^{18}O$ and $\delta^{13}C$ values of foraminifera shells decrease reproducibly with increasing $[CO_3^{2-}]$ (Spero et al., 1997). Although an apparent cause for isotopic nonequilibrium is often not clear, the similarity between these varied studies on biological and inorganic $CaCO_3$ precipitation implicate a common mechanism involving carbonate equilibrium, as measured by varying concentration of dissolved CO_3^{2-} ions.

The above discussion demonstrates the need for a detailed investigation of the various factors influencing isotopic fractionation in lake systems before interpreting high resolution oxygen isotopic stratigraphies in terms of continental environmental change. Towards this goal, we carried out an extensive water chemistry and sediment trap study in Baldeggersee, a small eutrophic lake located in Central Switzerland. Baldeggersee provided an ideal "natural beaker" to study isotopic fractionation processes. Sediment trap material, collected daily between March, 1995 and February, 1996, together with chemical and isotopic monitoring of the water column, provide an unparalleled data set with which to analyse the various controls on seasonal calcite accumulation and its isotopic composition in a lake environment. Ultimately, this study provides criteria for recognizing isotopic nonequilibrium that can be applied to other lacustrine sediment records, facilitating accurate environmental interpretations of lacustrine archives.

2. STUDY SITE

Baldeggersee is a monomictic lake situated at 463 m a.s.l on the Swiss Plateau approximately 16 km north of Lucerne in Central Switzerland (47°10′N, 8°17′E; Fig. 1). The lake's surface area is 5.2 km^2, maximum depth is 67 m, and the total lake volume amounts to 0.173 km^3. The lake's catchment area, totalling 67.8 km^2, is drained by approximately 13 small streams. There is one outflow located at the northern end of the

lake (Fig. 1). The hydrologic residence time is approximately 4.3 years (Wehrli et al., 1997).

The local seasonal air temperature cycle largely determines the water temperature and seasonal cycle in Baldeggersee (Livingstone and Lotter, 1997). Long-term (1901–1993) averages of precipitation and temperature in the region, as monitored by the Swiss Meteorological Association (SMA) at the nearby station in Bern (Fig. 1), are 1008 mm and 8.4°C, respectively. The warmest month on average is July, with an average temperature of 18°C; the coldest month is January with an average temperature of −1°C.

During the last 100 years, Baldeggersee has undergone major changes in productivity and eutrophication in response to nutrient loading from agriculture and industrialization in the lake's watershed. Total phosphorous concentration in the lake started increasing at the beginning of the century and rose exponentially between 1956 and 1974 (Wehrli et al., 1997; Lotter, 1998). Strict governmental restrictions on phosphorous and nitrogen fluxes into natural waters imposed in 1974 resulted in an improvement of Baldeggersee water quality. A lake restoration program, in effect since 1982, pumps oxygen into the hypolimnion in late summer to early autumn in an attempt to re-oxygenate the lake bottom waters. Despite these efforts, severe annual anoxia continues in the deepest parts of the lake (Wehrli et al., 1997).

Progressive eutrophication of the lake has altered oxygen concentrations in the hypolimnion, thereby significantly influencing the sediment record in Baldeggersee. Since the onset of anoxia in the bottom waters at the turn of the century, seasonal sediment production has been preserved as distinct "light" (spring/summer) and "dark" (late summer/autumn) laminations (varves) in the Baldeggersee sedimentary record from the period of 1885 to present (Lotter et al., 1997). Light layers are composed mainly of calcite (60% to 80%) that precipitates in the lake surface waters as a result of biologically induced disequilibrium during spring and summer photosynthetic blooms (Kelts and Hsü, 1978; Lotter et al., 1997; Hodell et al., 1998). The light layers are thick and occasionally, banded (multiple, conspicuous calcite layer). Dark layers are composed of lesser amounts of authigenic calcite (30% to 50%) precipitated during lake summer–autumn productivity blooms, winter detrital material and strongly decomposed organic fine-detritus (Lotter et al., 1997). Figure 2 presents an idealized sketch of seasonal sediment production in Baldeggersee.

3. EXPERIMENTAL METHODS

Baldeggersee water column samples were taken at 0 m, 2.5 m, 7.5 m, 10 m, 30 m, and 60 m water depths at monthly intervals from February, 1995 to October, 1996. pH and temperature were measured with a SEACAT probe (Sea-Bird Electronics Inc. USA). Alkalinity was determined by titration with a Metrohm Autotitrator (Metrohm, Herisau). pH and alkalinity measurements were used to calculate the concentrations of the dissolved carbonate species, $H_2CO_3^*$, HCO_3^- and CO_3^{2-} (Stumm and Morgan, 1981). All concentrations are reported as in molarity, M, defined as moles of solute per liter.

The sediment trap device, TECHNICAP (Markasub© Basel, Switzerland) was deployed for a three year period (March, 1994 to October, 1996) at 60 m water depth, approximately 6 m above the lake bottom (Fig. 1). The sediment trap consists of a 190 cm tall funnel, which collects sediments over a 5000 cm^2 surface area into one of 24 individual collection containers. The collection containers electronically rotate every 24 h and the total sample containers were changed ap-

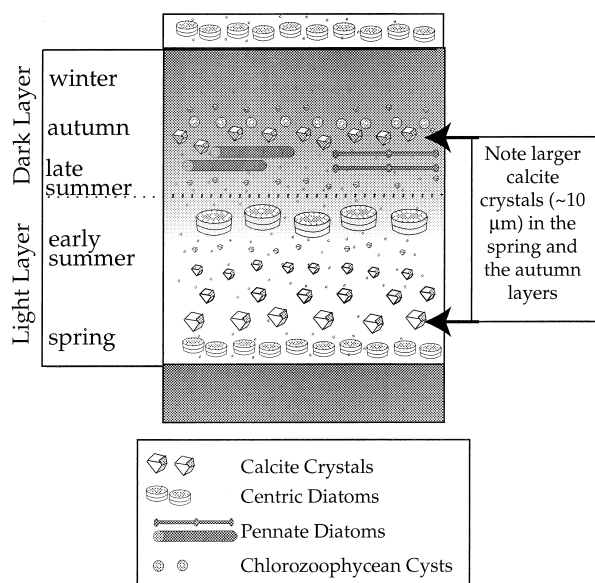## Idealized Baldeggersee Sediment Production

Fig. 2. Schematic drawing of the seasonal sediment production and the varve formation at various stages during the eutrophic evolution of Baldeggersee. Note the relative calcite grain sizes during different seasons.

Fig. 3. 1995–1996 seasonal cycle of epilimnetic water chemistry. Data represent surface water (0–7.5m) averages.

proximately every 3 weeks. All sediment samples were weighed, freeze-dried, and then weighed again to obtain dry weights and porosity for accumulation rate estimation. The material from each sample was thoroughly homogenized with an agate mortar and pestle for chemical analysis. Isotopic analyses were performed on samples from all three years of sediment trap collection; this paper concentrates on results from the 1995 to 1996 productivity cycle when corresponding water column data were also measured.

The carbonate content of the sediment trap material was measured with a Coulometric Inc. 5011 CO2 Coulometer® using approximately 20 mg of homogenized bulk sample. A molar weight conversion factor of 8.33 was used to calculate the calcite percentage in the bulk sample. External error, resulting from weighing errors or incomplete reaction times, was calculated to be ±0.1% to 0.5%, based on routine measurements of a known standard of Na_2CO_3. Theoretical machine precision is ±0.1%. All $CaCO_3$ results are plotted as accumulation rates.

Water samples were analyzed for oxygen isotope composition at the ETH Stable Isotope Laboratory in accordance with IAEA guidelines. Water samples were prepared for oxygen isotopic analysis by the CO_2 equilibration method, as described by Epstein and Mayeda (1953). Two mL aliquots of water samples were loaded on a VG-automated shaker preparation system. The isotope ratios of the resulting equilibrated CO_2 gas were measured on a VG Optima mass spectrometer and are expressed in terms of δ-values as per mil deviations from the international V-SMOW (Standard Mean Ocean Water) standard. The $\delta^{18}O$ measurements are accurate within ±0.15‰.

Carbon and oxygen isotope compositions of carbonates from sediment trap material were measured at the ETH Stable Isotope Laboratory. The sediment trap material was roasted at 375°C for 1 h under vacuum to combust organic matter prior to isotopic analysis. All carbonate samples for isotopic analysis were reacted in orthophosphoric acid at 90°C on a VG Isogas autocarbonate preparation system. Isotopic ratios of the CO_2 gas were then measured on-line by a triple-collector VG Isogas precision isotope ratio mass spectrometer (PRISM). Isotope compositions are expressed in the δ notation as per mil deviations from the international PDB (Pee Dee Belemnite) standard. Analytical precision based on routine analysis of an internal reference standard (Carrara Marble) was ±0.10‰ for $\delta^{18}O$ and ±0.05‰ for $\delta^{13}C$.
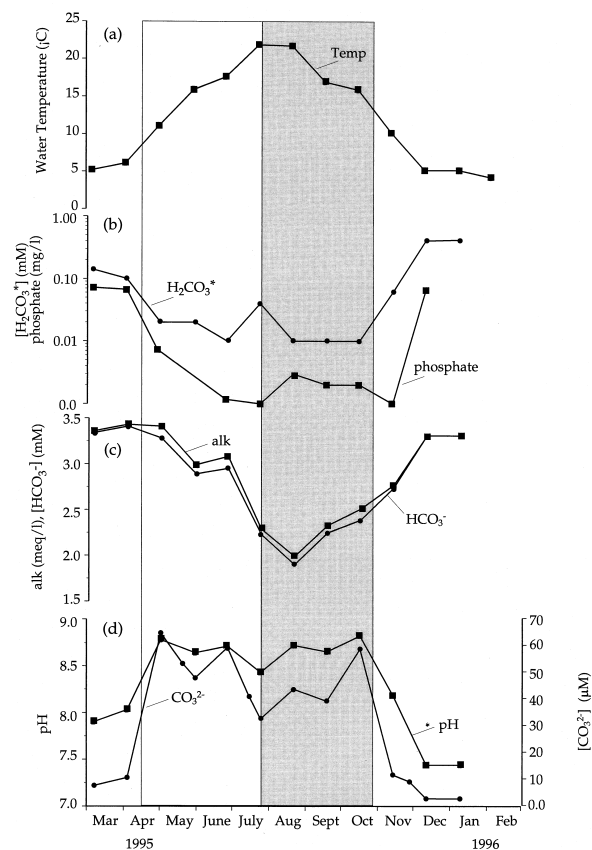
4. RESULTS

4.1. Water Column Temperature and Isotopic Results

Figure 3 presents significant changes in surface water parameters (average 0 to 7.5 m) in Baldeggersee that occur throughout an annual productivity cycle (March, 1995 through February, 1996). The outlined regions on the graph define the seasonal periods of sediment production during the spring/summer (unshaded box), and the late summer/autumn (shaded box). Surface-water temperature varied significantly throughout the productivity period, from 5°C in early spring to 22°C by late summer (Fig. 3a). Warming surface waters in the early spring and increasing light intensity triggered major algal blooms in late April/early May, 1995, dominated by centric diatoms. This photosynthetic activity removed significant amounts of phosphate and inorganic carbon from the surface waters (Figs. 3b and 3c). Utilization of aqueous CO_2 raised the pH and the carbonate ion concentration in the epilimnion (Fig. 3d) until the middle of May, when carbonate ion supersaturation favored calcite precipitation. The onset of calcite precipitation is marked by a significant drop in total alkalinity and ΣCO_2, which then continued to decrease throughout the spring/summer cycle (Fig. 3c).

Primary productivity slowed considerably in the middle of summer, 1995, then increased again with the onset of pennate diatom blooms from August through October, 1995. Primary
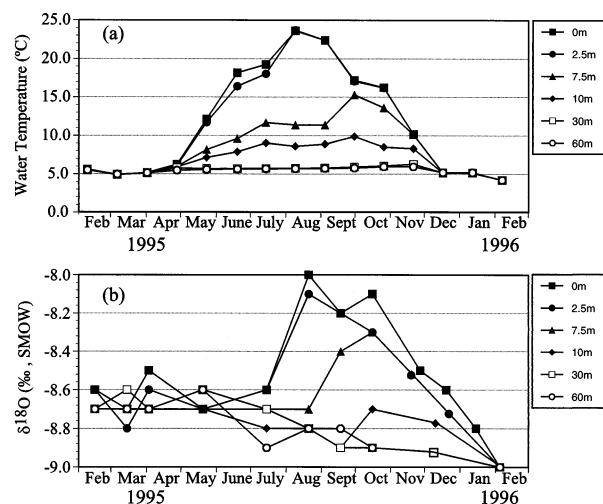
Fig. 4. Baldeggersee water column profiles of (A) monthly temperature measurements and (B) monthly oxygen isotopic values (± 0.15‰) between February, 1995 and February, 1996.
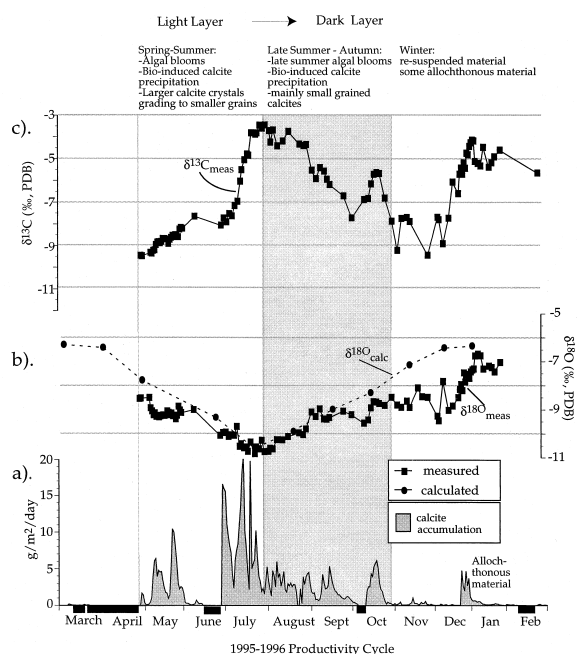

Fig. 5. Sediment trap calcite accumulation and isotopic data from March, 1995–February, 1996. (A) Daily calcite accumulation, black bars represent periods when no sediment was collected due to technical problems with the sediment traps. (B) Measured $\delta^{18}O$ values ($\delta^{18}O_{meas}$) versus calculated $\delta^{18}O$ values ($\delta^{18}O_{calc}$) for precipitating calcite. See text for discussion. (C) Measured $\delta^{13}C$ values of precipitating calcite.

productivity again utilized dissolved inorganic carbon (Fig. 3b) slightly shifting the pH and carbonate equilibrium to favor calcite precipitation (Fig. 3d). However, epilimnic conditions in late summer/autumn are chemically very different than during the spring/summer calcite precipitation events. Note especially that alkalinity, bicarbonate concentrations (Fig 3c) and [CO_3^{2-}] (Fig. 3d) are relatively reduced in late summer/autumn.

Figure 4 presents monthly profiles of temperature and oxygen isotope ratios in the water column for the study period. Surface waters warm significantly throughout the seasonal productivity cycle, from temperatures of 5°C in the spring to 22°C by late summer (Fig. 4a). The profiles clearly show the temperature and oxygen isotope stratification in the lake. Progressive evaporation of the warmer surface waters isotopically increases the $\delta^{18}O$ value of epilimnetic waters by up to 0.8‰ by early autumn (Fig. 4b). Thermal stratification collapsed in November, mixing the water column, bringing nutrients back to the surface water and restoring the pH, alkalinity, and phosphate concentrations to levels observed in the previous winter (Figs. 3 and 4b). Within just one year of monitoring, the average $\delta^{18}O$ value of the well-mixed water column has decreased by 0.3‰ [compare March, 1995 ($\delta^{18}O = -8.7‰$) with February, 1996 ($\delta^{18}O = -9.0‰$); Fig. 4b], showing that significant changes in $\delta^{18}O$ values of the lake water can occur within just 1 year.

Calculated equilibrium oxygen isotopic compositions for the inorganic precipitates in Baldeggersee can be obtained using the isotopic composition of the Baldeggersee surface water, ambient water temperature, and the well-established, temperature-dependent oxygen isotope equilibrium fractionation equation between calcite and water, adapted from Friedman and O'Neil (1977).

$$t°C = 16.0 - 4.14(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2 \qquad (1)$$

where δ_c and δ_w refer to the oxygen isotopic composition of the calcite and lake water, respectively.

4.2. Sediment Trap Results

Figure 5 displays the accumulation rate and isotopic composition of the calcite collected in sediment traps for a complete annual productivity cycle (March, 1995 to February, 1996). As in Fig. 3, the unshaded boxed region on the graph represents the period for spring and early summer sediment production that would eventually constitute the light layer of the varved sediments in the core. The grey-shaded boxed region represents the period of sedimentation production that would eventually constitute the dark layer. Calcite precipitation originates within the uppermost 5 m of the water column. Settling velocities of calcite are estimated to be >55 m per day based on appearance of calcite in the sediment trap within one day in association with times of calcite plumes.

Due to technical difficulties with the sediment trap device, no sediment was recovered between March 22 and April 28, 1995. Another gap in sediment recovery occurred from June 15 to 28, 1995, when the spring/summer calcite flux was presumably quite high. Black bars along the x-axis in Fig. 5 indicate these hiatuses. Biologically induced calcite precipitation most likely began in May, 1995 and continued as relatively short-lived isolated peaks (of up to 10 g/m²/day) until the end of June, 1995 (Fig. 5a). During July, 1995, calcite production was high; individual events produced as much as 20 g/m²/day. Summer calcite precipitation slowed to about 5 g/m²/day in August, and continued sporadically until the end of October, 1995.

Figure 5b presents measured calcite oxygen isotope data ($\delta^{18}O_{meas}$) and theoretical $\delta^{18}O$ values, as calculated using

equation 1 ($\delta^{18}O_{calc}$) and temperature and $\delta^{18}O$ values of the surface water (see Fig. 4). It is important to note that because the sediment trap material was collected daily, the isotopic composition of the trap calcite can be compared directly with calculated isotopic equilibrium values for the exact day that monthly water measurements were taken. Thus, this study avoids some of the problems commonly associated with monthly sediment trap studies that try to resolve monthly sediment accumulation with single-day water chemistry measurements.

Measured and calculated $\delta^{18}O$ values agree from July through September, when the majority of the calcite precipitates, indicating that calcite precipitated in isotopic equilibrium. In contrast, measured $\delta^{18}O$ values from the early calcite precipitated in May, 1995, constituting a major part of the spring to summer sediment layer, are significantly more negative ($\delta^{18}O = -9.1‰$) than calculated isotopic equilibrium calcite ($\delta^{18}O = -8.3‰$). The early spring calcite is composed of significantly larger calcite grains (see Fig. 2). Again in late autumn (i.e., October, 1995), measured calcite $\delta^{18}O$ values are more negative ($\delta^{18}O = -8.7‰$) than the calculated isotopic equilibrium values ($\delta^{18}O = -8.3‰$), and calcite grain sizes are again noticeably larger.

No calcite precipitates in the cold winter waters. Thus, $\delta^{18}O$ values (average $= -7.7‰$) of the insignificant amount of calcite collected in the sediment traps from late autumn and into the winter (less than 1 g/m^2/day; Fig. 4) reflect a mixture of resuspended calcite (i.e., isotopically more depleted calcite originally precipitated in the warm spring surface waters) and allochthonous material (i.e., isotopically more enriched with respect to calculated values for calcite precipitate). The small daily accumulations of calcite from the late autumn to the winter do not contribute much to the isotopic composition of the individual sedimented dark layers. Although small amounts of resuspended and allochthonous material may also be present in the sediment traps during other parts of the year, they will not contribute significantly to the isotopic composition of the daily material.

Figure 5c presents the measured calcite $\delta^{13}C$ values from the sediment trap material. $\delta^{13}C$ values vary throughout the seasonal cycle; there is a large increase from very negative $\delta^{13}C$ values through May and June, 1995 (average $\delta^{13}C = -8.8‰$) to $\delta^{13}C$ values of $-5.0‰$ in July, 1995. Although detailed measurements of the carbon isotopic composition of the dissolved inorganic carbon (DIC) would be necessary to investigate isotopic equilibrium fractionation in the carbon system, it is interesting to note that very negative spring calcite $\delta^{13}C$ values correspond to times of depleted oxygen isotope values. However, given the high degree of primary productivity in the Baldeggersee surface waters, it is also reasonable to assume that epilimnion $\delta^{13}C$ values of DIC increased dramatically over the spring/summer productivity cycle due to preferential removal of ^{12}C from the surface waters by primary producers (McKenzie, 1982; McKenzie, 1985; Hollander and McKenzie 1991; Schelske and Hodell, 1991). Thus, changes in the DIC $\delta^{13}C$ values, and not varying carbon isotope fractionation in the DIC-calcite system, could also account for the changes in calcite $\delta^{13}C$ values.

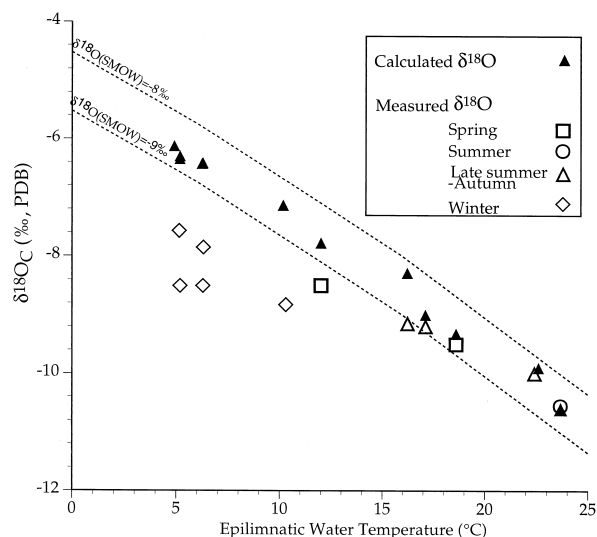Fig. 6. Measured and calculated $\delta^{18}O$ values of precipitating calcite versus measured epilimnion water temperatures. Dashed lines define the boundaries for isotopic equilibrium based on possible minimum ($-9‰$) and maximum (-8‰) seasonal boundaries of the $\delta^{18}O$ values of the lake water and the oxygen isotope equilibrium according to eq. 1.

5. DISCUSSION

5.1. Sediment Trap Accumulations

Comparison of Figures 3 and 5 shows that calcite production in Baldeggersee follows the characteristic model of bio-induced calcite precipitation in response to primary productivity (Kelts and Hsü, 1978). Distinct peaks of calcite production occur from May through July, 1995 following the pattern of diatom blooms. During late July and August, 1995, when primary productivity is significantly reduced, calcite precipitation occurs at a lower, albeit steady rate. During September and October, 1996, calcite precipitation again occurs as distinct, but smaller peaks in response to pennate diatom blooms.

Calcite accumulation in Baldeggersee sediment traps, between 5 to 20 g/m^2/day, is relatively high for a lake system. Sediment trap studies are known to be subject to inherent "overtrapping" processes that are likely to overestimate actual sediment accumulation rates measured in the sediment cores (Pennington, 1974; Evans, 1994). However, the calcite accumulation rates in the sediment traps are only about 20% higher than the calculated average calcite accumulation rates from the Baldeggersee core and, therefore, are acceptable as being within reasonable error.

5.2. Interpretation of Sediment Trap Isotopic Results

This sediment trap study illustrates the seasonal variation in oxygen isotopic fractionation between calcite and water. Figure 6 plots a summary of the calculated and measured $\delta^{18}O$ values vs. surface water temperature measurements for several individual days during the 1995 through 1996 productivity cycle. Note that measured calcite isotope ratios are only compared directly to calculated isotope ratios for the individual days when water temperature and isotopic composition measurements were taken (see section 4.2).

During the summer, when the majority of the calcite precipitates, precipitation occurs in isotopic equilibrium with the ambient water. However, the first measured calcite precipitated in the spring is depleted in ^{18}O by as much as 0.8‰, relative to calculated $\delta^{18}O$ values (Fig. 5), and thus plot outside the boundaries for isotopic equilibrium (Fig. 6). During autumn, calcite grains can be slightly depleted in ^{18}O, by 0.4‰, as compared to calculated values (Fig. 5). These values plot on the boundary of calculated isotopic equilibrium (Fig. 6). As expected, resuspended winter calcite values plot outside the range of calculated equilibrium values (Fig. 6).

In order to assess the influence of isotopic depletion on the isotopic signal in the varved Baldeggersee core sediments, and on bulk analyses of lacustrine sediments in general, it is necessary to consider the relative contribution of each calcite precipitation event to the final isotopic composition the sediment. We employed mass balance equations, incorporating the amount of calcite precipitate and its isotope composition, to determine the measured and calculated isotopic values by season, for the light and dark layers in the sediment core, and for a hypothetical bulk carbonate analysis of the core material.

Figure 7 and Table 1 presents the seasonal and varve oxygen isotope compositions based on mass balance equations for both measured and calculated calcite $\delta^{18}O$ values. In the modern Baldeggersee system, oxygen isotope depletion in the spring calcite results in a light layer that is depleted in ^{18}O by 0.4‰, with respect to calculated equilibrium values. The measured dark layer $\delta^{18}O$ value is equivalent to the calculated value; a slight influx of isotopically heavier calcite in the winter is enough to compensate for the isotopically depleted calcite values that occur in autumn.

In addition, Table 1 lists the results of a mass balance calculation for the theoretical isotopic composition of Baldeggersee bulk carbonate isotopic analysis. These results show that measured isotopic composition of bulk sediment would only be 0.2‰ more negative than calculated values (calculated $\delta^{18}O =$ −9.4‰; measured $\delta^{18}O =$ −9.6‰). This result indicates that, for most purposes, bulk carbonate isotopic measurements can be assumed to represent oxygen isotopic equilibrium conditions and that shifts in the isotopic composition can be accurately interpreted in terms of their paleoenvironmental and/or climatological significance.

Any discussion of isotopic equilibrium is, obviously, relative to the chosen oxygen isotope fractionation equation between calcite and water at low temperatures. We chose to use equation 1 (Friedman and O'Neil, 1977) because it remains the expression most widely accepted for the compilation of oxygen isotope paleo-temperature scales. Similar, yet distinct, temperature fractionation equations equations have previously been published by McCrea (1950) and by Epstein and Mayeda (1953). More recently, equilibration experiments and a re-determination of the acid fractionation factor have revealed a new expression for the oxygen isotope fractionation between calcite and water at low temperatures (Kim and O'Neil, 1997). Applying this new equation produces lower calculated equilibrium values for the Baldeggersee sediment trap calcite (i.e., using the Kim and O'Neil, 1997 isotope fractionation expression would reduce, although not totally eliminate, the amount of isotopic depletions noted in the measured sediment trap material rela-
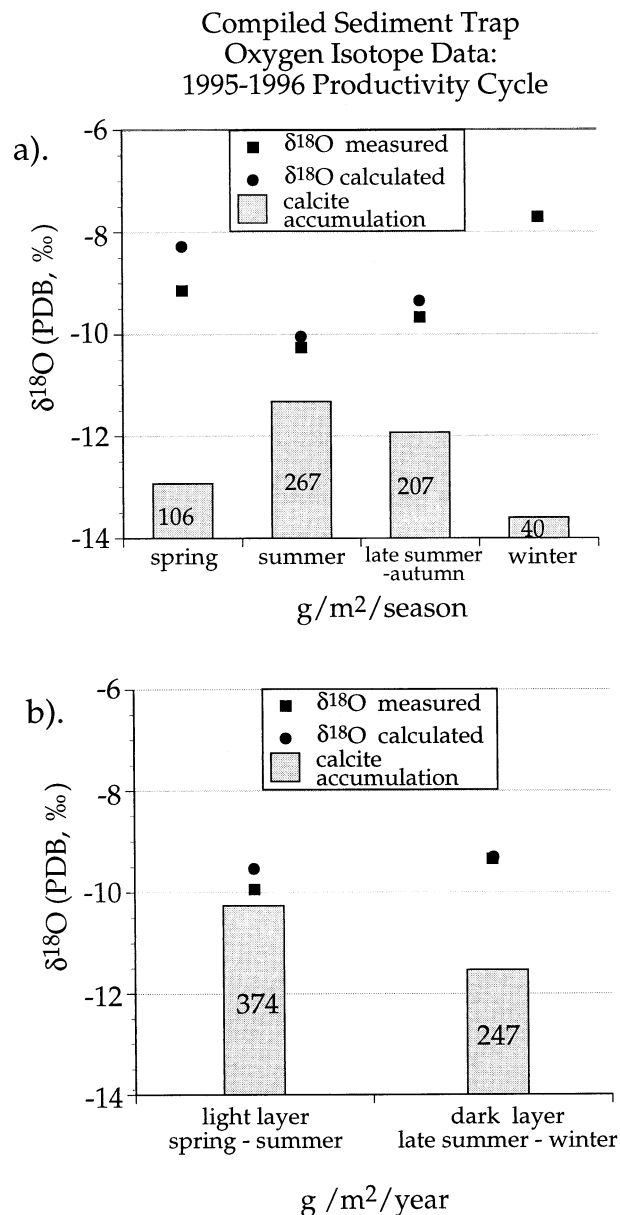

Fig. 7. Compiled oxygen isotopic values for individual seasons and the light and dark layer based on isotope mass balance equations using calcite accumulation data and $\delta^{18}O_{meas}$ values from daily sediment trap material trap material for the 1995–1996 productivity season.

tive to calculated equilibrium values). Regardless of the oxygen isotope equilibrium expression, however, oxygen isotopic fractionation still varies seasonally in the Baldeggersee system and isotopically depleted values are always noted in calcite precipitated in early spring.

5.3. Isotope Depletion and Carbonate Ion Concentration

Figure 8 presents the relationship between the observed isotopic depletion, $\Delta^{18}O = \delta^{18}O_{meas} - \delta^{18}O_{cal}$, during the 1995 through 1996 productivity cycle and measured epilimnion $[CO_3^{2-}]$ in Baldeggersee. The graph clearly shows that elevated

Table 1. Compiled Sediment Trap Isotope Data:

Season	Calcite g/m^2	$\delta^{18}O$(‰) Measured	$\delta^{18}O$ (‰) Calculated
Spring	107	−9.1	−8.3
Summer	267	−10.3	−10.0
Late summer-autumn	207	−9.7	−9.3
Winter	40	−7.7	*

Varve	Calcite g/m^2	$\delta^{18}O$(‰) Measured	$\delta^{18}O$(‰) Calculated
Light layer	374	−9.9	−9.5
Dark layer	247	−9.3	−9.3

Bulk Carbonate	Calcite g/m^2	$\delta^{18}O$ (‰) Measured	$\delta^{18}O$ (‰) Calculated
Bulk carbonate	621	−9.6	−9.4

* No calcite precipitate.

carbonate ion concentrations in the surface waters (i.e., > 50 μM) correspond to an ^{18}O depletion in the calcite with respect to predicted equilibrium values. The oxygen isotope depletion/$[CO_3^{2-}]$ slope is determined to be -0.022‰/μM ($R^2 = 0.80$).

A comparable negative relationship between epilimnion $[CO_3^{2-}]$ and calcite isotopic composition was found in Soppensee, a small, meromictic, hard-water, eutrophic lake also located in central Switzerland (Fig. 1). Fischer (1996) demonstrated that the majority of the calcite precipitated in isotopic equilibrium. However, in agreement with our model, the Soppensee isotopic values varied with surface water $[CO_3^{2-}]$. When $[CO_3^{2-}]$ is highest; that is, in the spring when concentrations are >25 μM, precipitated calcite $\delta^{18}O$ values are 1.1‰ less than calculated equilibrium values.

Experimental work by Spero et al. (1997), using cultured foraminifera, also demonstrated an isotopic depletion with increasing $[CO_3^{2-}]$. Using elevated $[CO_3^{2-}]$ values (100 to 700

Fig. 8. Effect of surface water $[CO_3^{2-}]$ on the $\delta^{18}O$ values measured in daily sediment trap calcite from Baldeggersee. Higher surface water $[CO_3^{2-}]$ are associated with relatively negative $\delta^{18}O$ values with respect to equilibrium calculated values (i.e., large $\Delta\delta^{18}O$ values). Note that the grap only plots $\delta^{18}O_{meas}$ values during times of calcite precipitation when corresponding $\delta^{18}O_{calc}$ values could be calculated from surface water temperature and $\delta^{18}O$ measurements. $[CO_3^{2-}]$ concentrations vary seasonally: higher concentrations occur in the spring leading to depleted oxygen isotopic values.

$\mu mol/kg$), an order of magnitude higher than the average surface water concentrations in the Swiss hard water lakes, Spero et al. (1997) determined a $\delta^{18}O/[CO_3^{2-}]$ slope of -0.002‰/($\mu mol/kg$). Their slope is approximately an order of magnitude less than $\delta^{18}O/[CO_3^{2-}]$ slopes we determined in freshwater systems.

In summary, sediment trap $\delta^{18}O$ values from authigenic calcite in both Baldeggersee and Soppensee decrease in response to elevated $[CO_3^{2-}]$ concentrations in the surface water. Elevated $[CO_3^{2-}]$ values are observed in the spring in both lakes and elevated $[CO_3^{2-}]$ values occur again in the late autumn in Baldeggersee (See Fig. 3). In Baldeggersee, isotopically depleted calcite in the early spring and late autumn are also associated with larger calcite grain sizes (>10 μm).

5.4. Mechanism for Isotopic Depletion

We propose that the observed relationship between isotopic depletion and increased $[CO_3^{2-}]$, as well as elevated pH, is most likely a result of varying oxygen fractionation factors as a function of the dissolved carbonate equilibrium in the surface waters. Usdowski et al. (1991) have previously demonstrated that oxygen isotope fractionation factors between aqueous CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}, with respect to H_2O, vary with pH. Fractionation experiments by Usdowski et al. (1986, 1991) indicate that the hydration of CO_2 ($CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$) yield significantly different values for the equilibrium fractionation of the oxygen isotopes than reactions involving the hydroxylation of CO_2 ($CO_2 + OH^- \leftrightarrow HCO_3^-$). As pH increases, hydration of the CO_2 is overruled by hydroxylation, resulting in isotopically more depleted $CaCO_3$ values.

Isotopic depletions in biogenic carbonates have additionally been attributed to rate-dependent fractionations explained by a redistribution of isotopes between the dissolved carbon species, that is, faster precipitation rates are related to smaller isotopic fractionations between calcite and water. McConnaughey (1989) has studied some of the same processes in biologically precipitated calcite, invoking "kinetic" effects, resulting from discrimination against the heavy isotopes ^{18}O and ^{13}C during CO_2 hydration and hydroxylation, to explain much of the observed strong $\delta^{13}C/\delta^{18}O$ covariance in the coral *Tubastrea*.

The mechanism by which kinetic effects occur, as outlined by McConnaughey (1989), involves carbonate solubility reactions. Slow reactions between dissolved CO_2 and H_2O, occurring via CO_2 hydration or hydroxylation, preferentially concentrate the lighter ^{16}O and ^{12}C isotopes. The rate of exchange of oxygen isotopes is slow enough to allow HCO_3^- to remain out of isotopic equilibrium with H_2O for several hours at normal lake water pH values (McConnaughey, 1989). Isotopic equilibration between HCO_3^- and CO_3^{2-} is effectively instantaneous because the protonation of CO_3^{2-} and the deprotonation of HCO_3^- are extremely fast reactions. At high enough rates of calcification, this results in isotopically depleted CO_3^{2-} ions being incorporated in the calcite crystal. McConnaughey (1989) further argues that CO_2 hydration and hydroxylation reactions exhibit variable kinetic isotope effects with changes in pH; the kinetics of isotope exchange decrease strongly with increasing pH. Therefore, at high pH and $[CO_3^{2-}]$, CO_3^{2-} favors
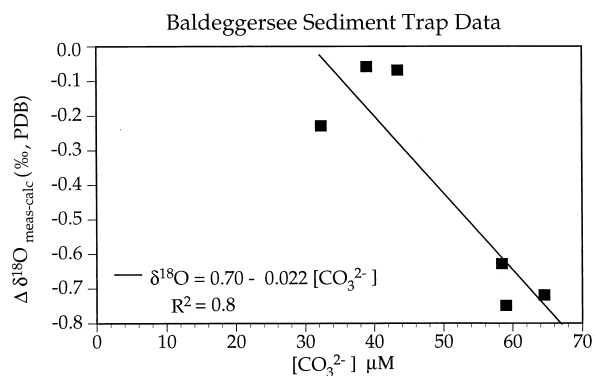
the lighter isotope in the exchange of atoms between CO_2 and CO_3^{2-}. A kinetic explanation was also supported by Spero et al. (1997) to explain experimentally determined $\delta^{13}C$ and $\delta^{18}O$ decreases with increasing $[CO_3^{2-}]$ in the ambient water.

Although this kinetic isotopic effect has been observed exclusively in biologically precipitated carbonates, kinetic fractionation could also partially explain isotopic depletion in inorganically precipitated calcite in eutrophic lake systems. Initial higher concentrations of PO_4^{2-} in spring and in the late autumn surface waters in Baldeggersee (see Fig. 3) lead to greater carbonate supersaturation. Carbonate supersaturation either occurs through phosphate inhibition of calcite precipitation (Kunz and Stumm, 1984; Niessen and Sturm, 1987) or, alternatively, because bio-induced calcite precipitation is not necessary for organisms to generate protons for nutrient assimilation when phosphorus is abundant (McConnaughey and Whelan, 1997). Then, when either spring or autumn primary productivity ensues and sufficient phosphate is removed from the surface waters, calcite precipitates rapidly from the supersaturated system. The resulting relatively large calcite grains are depleted in ^{18}O and ^{13}C due to apparent isotopic nonequilibrium between the dissolved and solid phases at the time of calcite precipitation.

The process of calcite precipitation in Baldeggersee is considered as biologically induced; that is, precipitation occurs as a chemical equilibrium response to biological activity in the surface waters. Recent studies on mechanisms for calcite precipitation in North American lakes (e.g., Thompson et al., 1997), however, have suggested that phototrophic picoplankton, such as the cyanobacteria Synechococcus, contribute actively to the epicellular biomineralization of calcite. We do not have any data to address the possibility for calcite precipitation occurring in microenvironments surrounding cell walls in the Baldeggersee surface water. It is conceivable, however, that if this is indeed the case, the observed fractionation of oxygen (and possibly carbon) isotopes might be due to this biological component.

The phenomenon of isotopic depletion is clearly observed in $\delta^{18}O$ values from spring calcite in both Baldeggersee and Soppensee and, to a lesser degree, in the autumn calcite in the modern Baldeggersee system. ^{13}C depletion in the precipitated calcite is more difficult to ascertain because carbon isotopic compositions in calcite are additionally affected by photosynthesis and respiration activities in the lake, which significantly alter the $\delta^{13}C$ values of DIC. As a result, changes in $\delta^{13}C$ values can deviate significantly from $\delta^{18}O$ changes in the calcite. Future detailed studies to monitor the seasonal $\delta^{13}C_{DIC}$ changes would allow a more quantitative analysis to determine if spring calcite are also isotopically depleted in ^{13}C relative to predicted equilibrium values in Baldeggersee.

Kim and O'Neil (1997) recently addressed the subject of "reproducible" isotopic nonequilibrium in synthetic $CaCO_3$ from laboratory experiments and demonstrated that the degree of isotopic nonequilibrium increased with increasing HCO_3^- concentrations. They also reported a clear positive relationship between nonequilibrium and carbonate grain size. Nonequilibrium was not related to rate of carbonate precipitation (Kim and O'Neil, 1997).

6. CONCLUSIONS

Results presented here show that there are distinct seasonal responses of carbon and oxygen isotopes in lacustrine calcite, which can be isolated and investigated through examination of daily sediment trap collections and surface water chemistry. These results provide the following three new insights about isotopic responses in lacustrine systems, which, in turn are important for climate and environmental reconstruction from lacustrine sequences. (1) During most of the year, calcite does precipitate in expected isotopic equilibrium, thereby reassuring that, in most cases, the oxygen isotopic composition of lacustrine sediment sequences can be used as a reliable proxy for temperature and $\delta^{18}O$ value of the water. (2) Some cases of isotopically depleted calcite values have been noted in the early spring and again in late autumn in Baldeggersee in association with higher surface-water phosphorous concentrations (>0.01 mg/L), increased carbonate ion concentrations (>50 μM), and increased calcite precipitation rates. (3) Rapidly precipitated, isotopically depleted calcite is characterized by relatively large, calcite crystals (>10 μm).

These findings build on other studies indicating that isotopic depletion can overprint useful climatic and/or environmental signals (Fronval et al., 1995; Gat and Lister, 1995; Spero et al., 1997). Furthermore, we can extrapolate that isotopic depletions will become more significant with increasing eutrophic state of the lake system, thereby decreasing the reliability and usefulness of the isotopic studies of lacustrine sediments from eutrophic and hypertrophic systems, or in cases where there is evidence for major changes in the lake's trophic level throughout the core. The noted positive association between the degree of isotopic depletion and the calcite crystal grain size implies that large, calcite grains can be used to recognize potential isotopically depleted calcite in sediment sequences from all geologic time-scales, thereby avoiding erroneous climatological or environmental interpretations.

REFERENCES

Epstein S. and Mayeda T. (1953) Variation of ^{18}O content of waters form natural sources. *Geochim. Cosmochim. Acta* **4,** 213.

Evans R. D. (1994) Empirical evidence of the importance of sediment resuspension in lakes. *Hydrobiologia* **284,** 5–12.

Fischer A. (1996) Isotopengeochemische Untersuchungen ($\delta^{18}O$ und $\delta^{13}C$) im Wasser und in den Sedimenten des Soppensees Klimaveränderungen und Entwicklungsgeschicht des Sees seit dem Spätglazial. Ph.D. dissertation, ETH-Zürich.

Friedman I. and O'Neil J. R. (1997) Compilation of Stable Isotope Fractionation Factors of Geochemical Interest: Data of Geochemistry. *Geo. Surv. Prof. Paper* **440-KK,** U.S. Gov. Printing Office.

Fronval T., Jensen N. B., and Buchardt B. (1995) Oxygen isotope disequilibrium precipitation of calcite in Lake Arreso, Denmark. *Geology* **23,** 463–466.

Gat J. R. and Lister G. S. (1995) The "catchment effect" on the isotopic composition of lake waters; its importance in palaeolimnological interpretations. In *Problems of stable isotopes in tree-rings,*

lake sediments and peat-bogs as climatic evidence for the Holocene (ed. B. Frenzel). Vol. 15. Chap. 1, pp 1–16. Akademie der Wissenschaften und der Literatur.

Hodell D. A., Schelske C. L., Fahnenstiel G. L., and Robbins L. L. (1998) Biologically induced calcite precipitation and its isotopic composition in Lake Ontario. Limnol. Oceanogr. **43,** 187–199.

Hollander D. J. and McKenzie J. A. (1991) CO_2 control on carbon isotope fractionation during aquatic photosynthesis: A paleo-pCO_2 barometer. *Geology* **19,** 929–932.

Kelts K. and Hsü K. J. (1978) Freshwater carbonate sedimentation. In *Lakes: Chemistry, Geology, Physics* (ed. A. Lerman) Chap. 9, pp. 297–323. Springer-Verlag.

Kim S. T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta* **61,** 3461–3475.

Kunz B. and Stumm W. (1984) Kinetik der Bildung und des Wachstums von Calciumcarbonat. *Vom Wasser,* **62,** 279–293.

Livingstone D. M. and Lotter A. F. (1997) The relationship between air and water temperatures in lakes of the Swiss Plateau: a case study with palaeolimnological implications. *Jour. of Paleolimnol.* **19,** 181–198.

Lotter A. F., Sturm M., Teranes J. L. and Wehrli B. (1997) Varve formation since 1885 and high-resolution varve analyses in hypereutrophic Baldeggersee (Switzerland). *Aqu. Scien.* **59,** 304–325.

McConnaughey T. (1989) ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochim. Cosmochim. Acta* **53,** 151–162.

McConnaughey T. A. and Whelan J. F. (1997) Calcification generates protons for nutrient and bicarbonate uptake. *Earth-Science Reviews* **42,** 95–117.

McCrea J. M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18,** 849–857.

McKenzie J. A. (1982) Carbon-13 cycle in Lake Greifen: A model for restricted ocean basins. In *Nature and Origins of Cretaceous Carbon-rich Facies* (eds. S. O. Schlanger and M. Cita). pp. 197–208. Academic Press.

McKenzie J. A. (1985) Carbon Isotopes and Productivity in the Lacustrine and Marine Environment. In *Chemical Processes in Lakes* (ed. W. Stumm). Chap. 5, pp. 99–118. John wiley & Sons.

McKenzie, J. A. and D. J. Hollander. 1993. Oxygen isotope record in recent carbonate sediments from Lake Greifen, Switzerland (1750–1986): application of continental isotopic indicator for evaluation of changes in climate and atmospheric circulation patterns. In *Climate Change in Continental Isotopic Records* (eds. Swart, P. K., K. C. Lohmann, J. A. McKenzie, and S. Savin). Vol. 78 pp. 101–112. AGU Geophysical Monography.

Niessen F., and Sturm M. (1987) Die Sedimente des Baldeggersees (Schweiz)-Ablagerungsraum und Eutrophierungsentwicklung Wärend der letzten 100 Jahre: *Arch Hydrobiol.* **108,** 365–383.

Pennington W. (1974) Seston and sediment in five Lake District lakes. *J. Ecol.* **62,** 215–251.

Schelske C. L. and Hodell, D. A. (1991) Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. *Limnol. Oceanogr.* **36,** 961–975.

Siegenthaler, U., and Eicher, U, 1986. Stable oxygen and carbon isotopic analyses. In *Handbook of Holocene palaeoecology and palaeohydrology.* (ed. B. E. Berglund). pp. 407–422. John Wiley & Sons.

Spero H. J., Bijma J., Lea D. W., and Bemis B. E. (1997) Effect of seawater carbonate chemistry on foraminiferal carbon and oxygen isotopes. *Nature,* **390,** 497–500.

Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry.* John Wiley & Sons.

Stuiver, M. 1970. Oxygen and carbon isotope ratios of fresh-water carbonates as climate indicators. *J. of Geophys. Research* **75,** 5247–5257.

Teranes, J. L. (1998) Climatic significance and biogeochemical controls of stable isotopes in a lacustrine sequence from Baldeggersee, Switzerland. Ph.D. Dissertation, ETH-Zürich.

Thompson, J. B., Schultze-Lam, S. M. Beveridge, T. J. and Des Marais, D. J. (1997) Whiting events: Biogenic origin due to the photosynthetic activity of cyanobacterial picoplankton. *Limnol. Oceanogr.,* **42,** 133–141.

von Grafenstein U., Erlenkeuser H., Müller J., Trimborn P., and Alefs j. (1996) A 200 year mid-European air temperature record preserved in lake sediments: An extension of the $\delta^{18}O_{p\text{-}air}$ temperature relation into the past: Geochim. Cosmochim. Acta, **60,** 4025–4036.

Usdowski E. and Hoefs J. (1986) $^{13}C/^{12}C$ partitioning and kinetics of CO_2 absorption by hydroxide buffer solutions. *Earth Planet. Sci. Lett.* **80,** 130–134.

Usdowski E. and Hoefs J. (1993) Oxygen isotope exhange between carbonic acid, bicarbonate, carbonate, and water: A re-examination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotopes between the carbonate species and water. *Geochim. Cosmochim. Acta,* **57,** 3815–3818.

Usdowski E., Michaelis J., Böttcher M. E., and Hoefs J. (1991) Factors for the oxygen isotopic equilibrium fractionation between aqueous and gaseous CO_2, carbonic acid, bicarbonate, carbonate, and water (19°C). *Zeitschrift Physikal. Chem.* **170,** 237–249.

Wehrli B., Lotter A. F., Schaller T., and Sturm M. (1997) The high-resolution varve project in Baldeggersee (Switzerland); project overview and limnological background data. *Aqu. Scien.* **59,** 285–294.