Stable isotope response to lake eutrophication: Calibration of a high-resolution lacustrine sequence from Baldeggersee, Switzerland

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Abstract

Stable isotope analyses of discrete seasonal layers from a 108-yr annually laminated freeze-core from Baldeggersee, a small, eutrophic lake in central Switzerland, provide information on the climatological and environmental factors, including lake eutrophication, that control oxygen and carbon isotopic composition of epilimnic biologically induced calcite precipitate.

During the last 100 yr, Baldeggersee has undergone major increases in productivity and eutrophication in response to nutrient loading from agriculture and industrialization in the lake's watershed. Calibration of the isotopic signal in Baldeggersee to historical limnological data quantitatively links evidence of isotopic depletion in the sedimented calcite to trophic state of the lake. $\delta^{18}O$ values from the spring/summer ''light'' sediment layers steadily diverged to more depleted values in response to historical eutrophication: measured $\delta^{18}O$ values were up to $-1.5‰$ more negative than calculated equilibrium $\delta^{18}O$ values. Evidence for ^{13}C depletion in the calcite, relative to equilibrium values, is more difficult to ascertain because of an overall dominance of isotopic enrichment in the dissolved inorganic pool as productivity in Baldeggersee increases. A positive association exists between the degree of oxygen-18 depletion and the calcite crystal size. Thus, large amorphous calcite grains can be used as a proxy for recognizing apparent isotopic nonequilibrium in sediment sequences from highly productive lacustrine environments from all geologic time scales.

In contrast to the light layers, the oxygen isotopic composition of the calcite in the late summer/fall ''dark'' sediment layers is unaffected by the apparent isotope nonequilibrium. Oxygen and carbon isotope values from the dark laminae in the Baldeggersee sediment therefore provide environmental and climatological proxies that can be calibrated with known environmental and regional climate data for the last century.

Stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope measurements from lacustrine, biologically induced, authigenic calcite precipitate have been used to reconstruct a variety of paleoenvironmental and paleoclimatic changes. Oxygen isotope records in lake sediments have been shown to be accurate paleoprecipitation archives, providing information on rapid continental climate change (Stuiver 1970; Siegenthaler and Eicher 1986; McKenzie and Hollander 1993). Variations in $\delta^{13}C$ values have been successfully used to detect significant changes in the rate or amount of surface-water pro-

ductivity and anoxia in the bottom waters (McKenzie 1982, 1985; Hollander and McKenzie 1991; Schelske and Hodell 1991; Hollander et al. 1992). Yet our understanding of the exact environmental causes of isotopic variations in lake systems remains inadequate, particularly in comparison with the high-resolution nature of emerging lacustrine isotopic records from a range of geologic time scales (*see* McKenzie and Hollander 1993; Goslar et al. 1995; Fischer 1996).

Interpretations of climatological causes of isotopic variations in lake systems are typically based on the assumption that calcite precipitates in known isotopic equilibrium with the lake water, in accordance with the equilibrium equations of Epstein et al. (1953) and Friedman and O'Neil (1977). This basic assumption has recently been challenged by data from Lake Arresø, Denmark, where it was proposed that oxygen isotope disequilibrium could occur in calcite precipitate from highly eutrophic lakes during high-productivity events (Fronval et al. 1995). In addition, a sediment trap study from eutrophic Baldeggersee incorporating water chemistry data and oxygen isotopic analysis from daily sediment trap material revealed apparent oxygen isotopic nonequilibrium. Relatively large calcite grains, apparently precipitated out of isotopic equilibrium (by as much as $-0.8‰$) were found in the early spring when surface-water phosphate

Table 1. Lithological descriptions and varve units. Adapted from Lotter et al. (1997b).

| Unit	Time	Lithological description	Varve characteristics	Lake eutrophication history
A	1993–1988	Unconsolidated dark-brown sediment	Very thick varves consisting of several inconspicuous light layers; accurate separation of light and dark layers is difficult.	Lake restoration program in effect. Bottom waters periodically oxidated; sediment–water interface anoxic
B	1987–1983	Weakly consolidated rust-brown to sienna-brown sediment	Thick varves with several conspicuous light layers; easily separable light and dark layers	Lake restoration program initiated in 1982; oxygen and air pumped into the bottom waters
C	1982–1970	Consolidated brown sediment	Two or three conspicuous lighter layers per varve	Peak of phosphate concentration in 1974–1975
D	1969–1963	Consolidated brown sediment with thicker varves	Varves sometimes include two conspicuous light layers	Exponentially increasing total phosphate concentrations in the water column
E	1962–1906	Consolidated brown sediment	"Normal" varves; easily separable light and dark layers	Steadily increasing trophic level with notable steps in 1909 (hypertrophic > 0.10 mg phosphate/liter) and again in the mid-1950s
F	1905–1895	Sienna-brown sediment with thin light and smaller dark layers	Varves are thin and undulating. Exact separation of each seasonal layer is difficult.	Eutrophic conditions in the lake
G	1894–1885	Brown sediment with undulated couplets of light and dark layers	Initiation of recognizable and countable varves. Exact separation of seasonal layer is difficult.	Perennial anoxia in the lake bottom waters established
H	pre-1885	Light sediment with weak, inconspicuous large couplets of light and dark layers and intermixed homogenous marl beds	Weakly laminated sediment	Bottom waters periodically anoxic
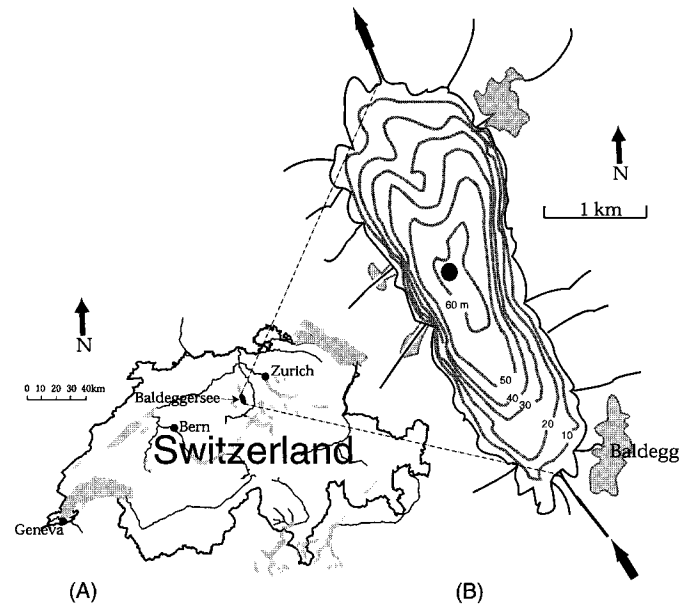
Fig. 1. Map of the Baldeggersee study area presenting (A) location of Baldeggersee (47°10′N, 8°17′E) and the city of Bern, and (B) the Baldeggersee bathymetric map with water depth, stream inflow and outflow, and core recovery location (●).

and carbonate ion concentrations are highest (Teranes et al. in press).

The aim of this paper was to interpret 108 yr of calcite accumulation, organic C and N accumulation, and $\delta^{18}O$ and $\delta^{13}C$ data from a seasonally sampled Baldeggersee sediment freeze-core. High-resolution sampling, the long-standing water-quality monitoring program on the lake, and Baldeggersee's varying eutrophic history (*see* Table 1) renders it an ideal location to evaluate the biogeochemical controls on stable isotopic values in lacustrine carbonates and, in particular, to test the geochemical and isotopic response to eutrophication.

Regional setting

Baldeggersee is a monomictic lake situated at 463 m a.s.l. on the Swiss Plateau approximately 60 km NE of Bern in central Switzerland (47°10′N, 8°17′E; Fig. 1). The lake basin was formed during the last glaciation. The lake has a maximum depth of 66 m, a volume of 0.173 km³, and a surface area of 5.2 km² (Wehrli et al. 1997). The lake is fed by 13 small streams that drain 67.8 km² of catchment area; there is no significant groundwater input into the lake (Kunze 1992). There is one outflow located at the northern end of the lake (Fig. 1). The mean hydraulic residence time is 4.3 yr (Wehrli et al. 1997).

During the last 100 yr, Baldeggersee has undergone major changes in productivity and eutrophication in response to nutrient loading from agriculture and industrialization in the lake's watershed (Wehrli et al. 1997; Lotter 1998). Total phosphate concentration in the lake began increasing at the beginning of this century and rose exponentially between 1956 and 1974. Strict restrictions on phosphorous and nitro-

gen fluxes into natural waters, imposed by the Swiss government in 1974, have resulted in steady improvement in Baldeggersee water quality. In addition, a lake restoration program, in effect since 1982, pumps oxygen into the hypolimnion in the late summer/early autumn in an attempt to oxygenate the lake bottom waters (Wehrli et al. 1997). Despite these efforts, severe annual anoxia has continued in the deepest parts of the lake.

Long-term (1901–1993) averages of precipitation and temperature in the region, as monitored by the Swiss Meteorological Association at the meteorological station in Bern, Switzerland (Fig. 1), are 1,008 mm and 8.4°C, respectively. The warmest month on average is July, with average temperatures reaching 18°C; the coldest month is January, with an average temperature of -1°C. Livingstone and Lotter (1997) demonstrated that temperatures on the Swiss Plateau are rather homogenous, i.e., the weather station in Bern certainly accurately represents the temperature conditions at Baldeggersee. Precipitation is a more regional phenomenon; precipitation amount at Baldeggersee could differ from the Bern station.

Varve formation

Chemical and physical characteristics of the epilimnion, primary productivity, and sediment production are all intricately linked to nutrient availability and the lake's seasonal cycle (Kelts and Hsü 1978; McKenzie 1982, 1985). The seasonal productivity cycle in Baldeggersee, in turn, is largely determined by the local seasonal air temperature cycle (Livingstone and Lotter 1997). Figure 2 presents generalized changes in surface-water parameters in Baldeggersee throughout the seasonal cycle. Figure 3 presents an idealized sketch of the varve components (Sturm and Lotter 1995).

Strong thermal stratification of the water column begins in late April/early May (Fig. 2A) when warming surface waters and increasing light intensity trigger major algal blooms, consisting mainly of centric diatoms. Photosynthetic activity adds O_2 to the surface waters while removing volumes of CO_2 (Fig. 2B,D). Utilization of aqueous CO_2 significantly raises the pH and the carbonate ion concentration in the epilimnion (Fig. 2C) until the beginning of June, when carbonate ion supersaturation favors calcite precipitation (Kelts and Hsü 1978). The onset of calcite precipitation is marked by a significant drop in total alkalinity (Fig. 2D). The sequences of relevant carbonate solubility reactions associated with calcite precipitation are presented in Stumm and Morgan (1981). The boxed, unshaded region on the graph defines the season zone of spring to midsummer calcite precipitation (Fig. 2). Spring and summer sediment production results in a thick, light, occasionally banded (multiple, conspicuous light layers) calcite-rich (60–80% calcite) sediment layer, referred to as the spring/summer or light layer.

Algal blooms commonly occur again between September and November in Baldeggersee and consist mainly of pennate diatoms. For a second time in the annual cycle, primary productivity takes up dissolved CO_2, slightly shifting the pH and carbonate equilibrium to favor calcite precipitation (Fig. 2C). The boxed, shaded region on the graph defines the sea-

sonal zone of late summer to autumn calcite precipitation. Note that epilimnic conditions in autumn are chemically very different from those in spring: phosphate concentrations (Fig. 2B) and total alkalinity (Fig. 2D) are greatly reduced, and pH and [CO_3^{2-}] only reach values of 8.5 and 0.020 mM, respectively (compared with values of 8.7 and 0.050 mM, respectively, during the spring productivity blooms; Fig. 2C).

Starting in late autumn, thermal stratification breaks down, mixing the water column, bringing nutrients back to the surface water, and restoring the pH and alkalinity to previous levels (*see* data for December–February, Fig. 2). Sedimentation during these winter months consists predominantly of clays and strongly decomposed fine-grained organic detritus (Lotter et al. 1997b). The late summer/autumn calcite and winter sedimentation together eventually constitute the late summer/winter, or dark layer, in the Baldeggersee sediment.

Figure 3A–C illustrates how calcite grain size has fluctuated in response to the lake's trophic level. During the period when phosphate concentrations in the lake's surface waters were the highest (1963–1982; *see* Table 1), precipitated calcite crystals grew to >30 μm in diameter (Fig. 3B). Figure 4 displays a scanning electron microscopy (SEM) photomicrograph illustrating the size and anhedral characteristics of a typical calcite grain from the 1965 light sediment layer. Calcite grain size decreased again following initiation of the lake restoration program and the subsequent decrease of phosphate concentration in the lake water (Fig. 3C).

Materials and methods

In October 1993, three freeze-cores (BA93-A, B, and C) were recovered from the deepest part of Baldeggersee at a water depth of 66 m (Fig. 5; Lotter et al. 1997a). Varves were identified and counted using petrographic thin sections of the core. The established varve chronology was confirmed with independent ^{137}Cs and ^{210}Pb dating of annual layers (Lotter et al. 1997b). The determined date for the onset of laminations, 1885, corresponds exactly to the results of Nipkow (1927), who counted 40 layers down to the onset of laminations in a core recovered from Baldeggersee in 1925.

Core BA93-B was sampled between the 1993 surface layer and the lower limit of the prominent 1956 turbidite, and Core BA93-A was sampled for the period covering 1955–1885. Sampling was carried out in a cold room at temperatures between -20 and -15°C. Seasonal samples were obtained by scratching off each alternating, undulatory light or dark layer with a thin, sharp blade. Prominent, conspicuous turbidite layers were easily identified and also sampled separately. With this procedure, the collected material represents a 108-yr seasonally sampled lacustrine sediment record.

All samples were weighed, freeze dried, and then weighed again to obtain dry weight and porosity for accumulation rate estimations. The material from each sample was then divided in two equal parts; one half was thoroughly homogenized for further analytical work.

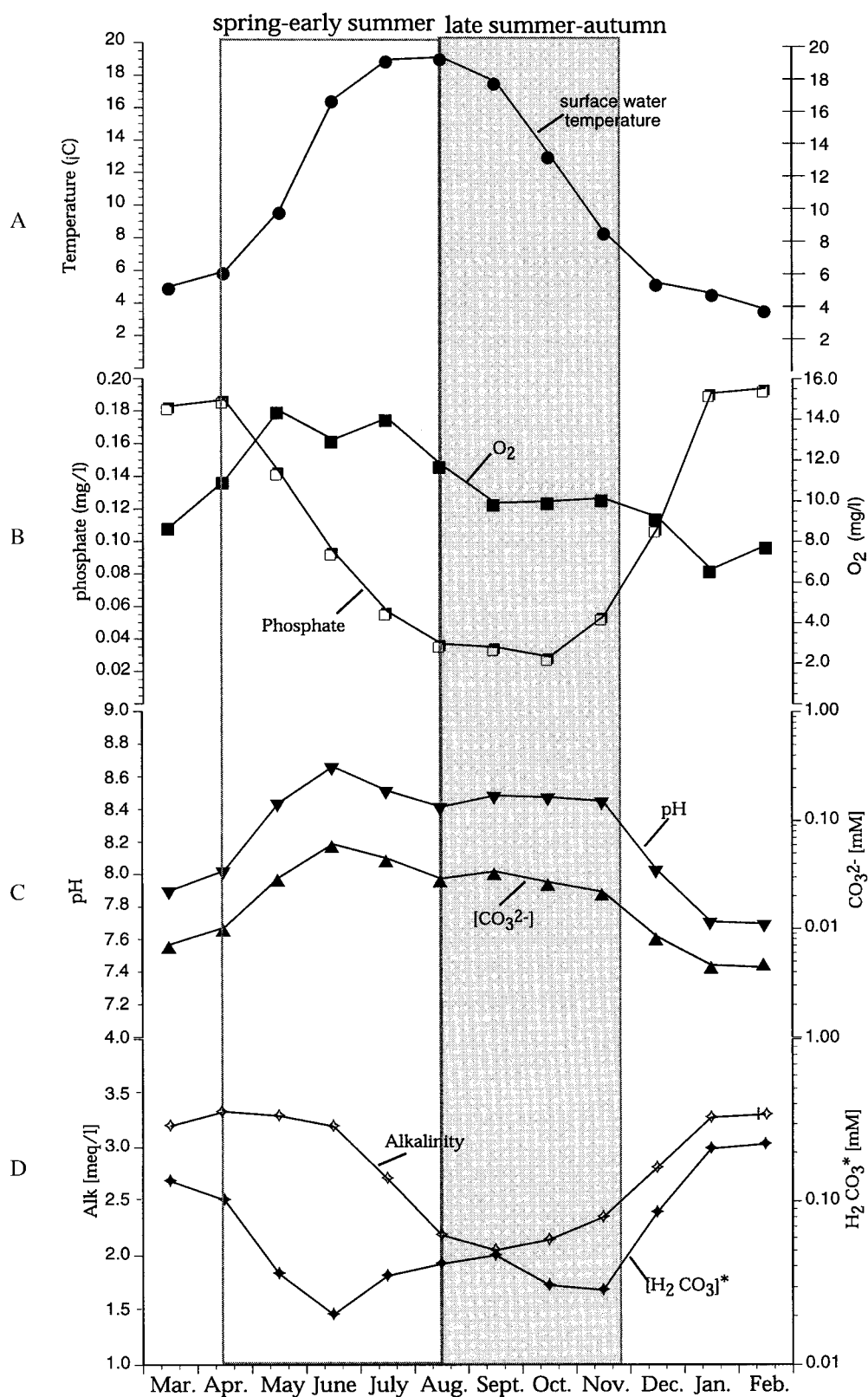The carbonate content of the samples was measured by Coulometric 5011 CO_2 Coulometer® using approximately 20

Fig. 2. Generalized seasonal cycle of epilimnetic water chemistry. Data represent long-term surface-water (0–7.5 m) averages from the years 1981–1993. Data collected by EAWAG Limnological Research Center-Kastanienbaum.

A. Eutrophic-early stages of Hypertrophic conditions 1885-1945   B. Hypertrophic Conditions 1946-1982   C. Lake Restoration Program 1982-present
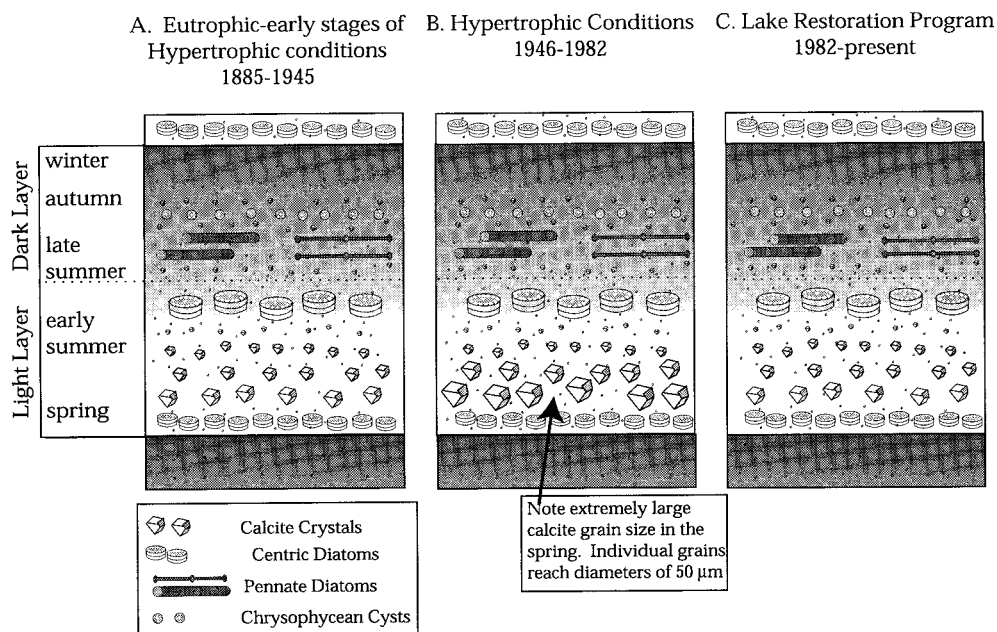

Fig. 3.   Schematic drawings of biochemical varves at various stages during the trophic evolution of Baldeggersee. Note especially the relative calcite grain sizes. Drawing modified from Sturm and Lotter (1995).

mg of homogenized bulk sample. External error, resulting from weighing errors or incomplete reaction times, was calculated to be ±0.1–0.5% based on routine measurements of a known standard of Na_2CO_3. Theoretical machine precision is ±0.1%.
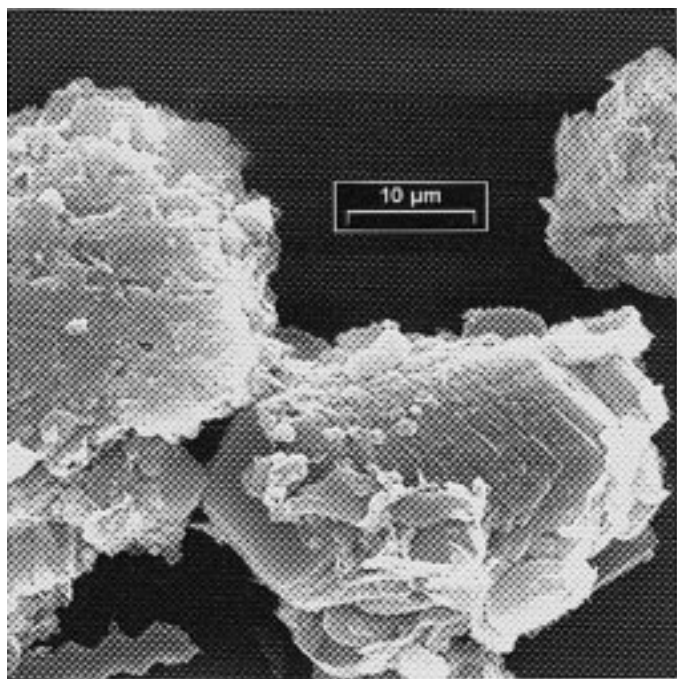

Fig. 4.   SEM photomicrograph of a large, anhedral calcite crystal typically found in the lake sediment deposited during the eutrophic to hypertrophic period of the lake's evolution. This sediment sample is from the 1965 light layer.

Total carbon and nitrogen for the BA-93 core samples were measured using a Carlo-Erba CNHS® analyzer with autosampler. Percent organic carbon was calculated by subtraction of carbonate carbon from total carbon.

Bulk sediment accumulation was calculated for each seasonal layer on the basis of surface area and dry weight (Lotter et al. 1997b). Component sediment accumulation was calculated to determine total accumulation rate of organic carbon and nitrogen and $CaCO_3$ by multiplying weight percent of each component, relative to the total dry weight, by the bulk sediment accumulation. Measured organic carbon and nitrogen accumulations from sediment samples were used to calculate the C/N atomic ratios.

Carbon and oxygen isotope compositions of carbonates from discrete laminae were measured at the ETH Stable Isotope Laboratory. 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 online by a triple-collector VG Isogas precision isotope ratio mass spectrometer. Isotope compositions are expressed in the δ notation as per mil deviations from the international Pee Dee Belemnite carbonate standard. Analytical precision based on routine analysis of the internal reference standard (Carrara Marble) was ±0.10‰ for $\delta^{18}O$ and ±0.05‰ for $\delta^{13}C$.

Results

Figures 6, 7 present the geochemical results from the 108-yr Baldeggersee laminated sequence. The annual nature of the laminations allowed for an exact dating of the core; thus, sampling and analysis of each layer provided geochemical information on a seasonal basis. Light and dark laminae
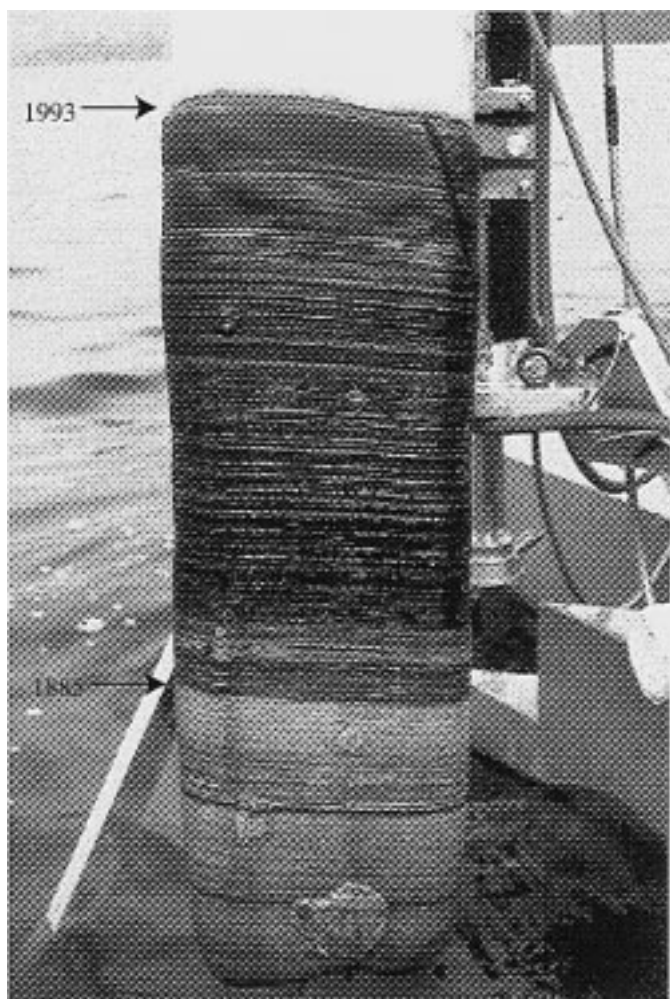
Fig. 5. Photo of the frozen core from Baldeggersee, 67 cm in length, recovered in autumn 1993, as indicated by the top arrow. The onset of annual laminations, indicated by the bottom arrow, was determined in 1885 by varve counting (*see text for details*).

from identical years are plotted separately to emphasize the seasonal offsets. The geochemical signals are best interpreted in conjunction with the productivity history of the lake and changes in varve characteristics (*see* Table 1). The lithologic units plotted in Figs. 6, 7 are defined in Table 1.

Varve characteristics—For the majority of the freeze-core (Units B, C, D, and E), the varves are relatively thick, and the distinct light and dark layers were easy to sample accurately (*see* Table 1). Lithologic Units F and G (1885–1906) are characterized by very thin varves, and the seasonal layers were difficult to completely separate. Thick varves at the onset of Unit A (1993–1988) contained several individual, inconspicuous lighter layers, and the seasonal boundary between spring and late summer sediment production was often difficult to identify. In these three units (Units A, F, and G), where seasonal layers are difficult to separate completely, geochemical signals may overlap in the various geochemical indicators measured, most notably in the $CaCO_3$ accumulation curve (Fig. 6).

$CaCO_3$ accumulation—$CaCO_3$ in the core was determined to be predominately calcite (Lotter et al. 1997*b*). Calcite accumulation rates averaged 133 g m^{-2} yr^{-1} in the dark laminae and 634 g m^{-2} yr^{-1} in the light laminae (Fig. 6). Interannual variability in the dark layer is minimal, except throughout Unit B and the first part of Unit A, where an increase in $CaCO_3$ is observed. In contrast, noteworthy stratigraphic trends occur in $CaCO_3$ accumulation in the light sediment layers, and interannual variations are significant. Calcite accumulation in the light laminae increased until the 1930s, reaching 750 g m^{-2} yr^{-1}, and then gradually decreased to average rates of 550 g m^{-2} yr^{-1} by the 1960s. Varve thickness paralleled these trends (*see* Table 1). $CaCO_3$ accumulation rates reached a maximum of 1,000 g m^{-2} yr^{-1} in Unit D, corresponding to the time of heavy phosphorous loading and eutrophic conditions in the lake (*see* Fig. 6; Table 1), but then decreased again in Unit C. $CaCO_3$ accumulation rates in the light layer gradually decreased again throughout Units B and A, to average values of 500 g m^{-2} yr^{-1}.

Calcite $\delta^{13}C$ and $\delta^{18}O$ values—Figure 6 presents the carbon and oxygen isotopic values of the calcite. As the $\delta^{13}C$ values varied considerably from year to year, a 5-yr running average serves to help recognize stratigraphic trends. During the first half of Unit E, $\delta^{13}C$ values were relatively stable at −6.5‰ for the light layers and −5.5‰ for the dark layers. In the 1940s, contemporaneous with decreases in varve thickness and $CaCO_3$ accumulation, $\delta^{13}C$ values in both the light and dark layers increased abruptly by approximately 1.0‰. Throughout the upper part of the core, calcite $\delta^{13}C$ values fluctuated around average values of −5.5 and −4.8‰ for light and dark layers, respectively. Throughout the core, there was a pronounced enrichment of dark laminae $\delta^{13}C$ values with respect to light-layer $\delta^{13}C$ values of between 0.5 and 1.0‰.

Calcite oxygen isotope values in the light and dark layers were similar throughout Units G and F and the first half of Unit E, varying only slightly around an average value of −9.0‰. During the latter half of Unit E, the light and dark layers started to diverge; $\delta^{18}O$ values in the dark layers trended briefly toward slightly enriched values (−8.5 to −8.0‰), whereas $\delta^{18}O$ values from the light sediment layer became progressively depleted. At the end of the 1950s, $\delta^{18}O$ values in both light and dark layers showed a depletion trend, reaching values of −11.0 and −10.0‰, respectively, by the end of Unit C. Throughout Units B and A, $\delta^{18}O$ values of both the light and dark layers increased to more enriched values; light-layer $\delta^{18}O$ values showed a proportionally greater increase, thereby decreasing the absolute difference between light- and dark-layer $\delta^{18}O$ values (Fig. 6).

Organic carbon and nitrogen accumulation—Figure 7 plots the organic C and N accumulations and the C/N atomic ratio. Organic C accumulation was fairly stable at the beginning of the record (lithologic units G, F, and E); average values were relatively low (12–15 g m^{-2} yr^{-1}). The transition to Unit D, in 1963, was marked by a sharp increase in organic C accumulation to values around 30 g m^{-2} yr^{-1}. These changes in organic C accumulation roughly paralleled calcite

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CaCO₃ Accumulation
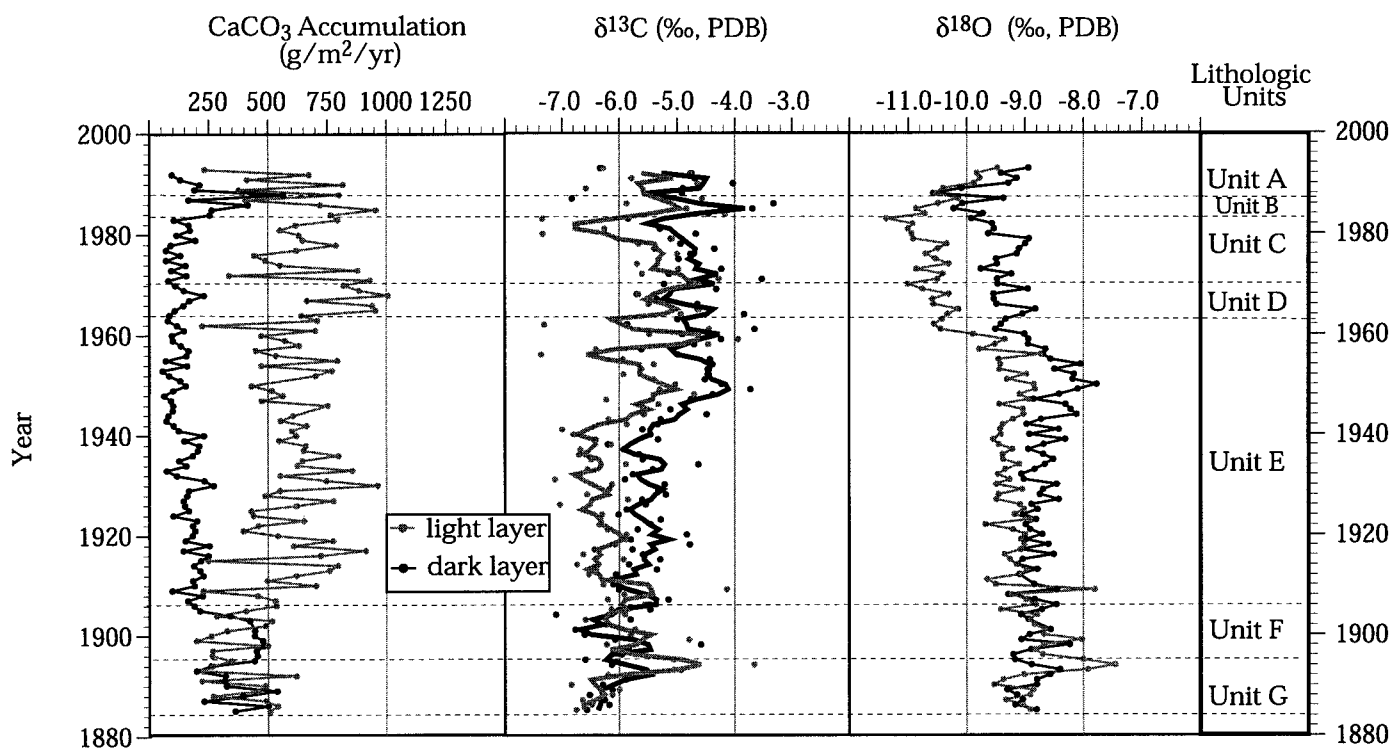(g/m²/yr)

δ¹³C (‰, PDB)

δ¹⁸O (‰, PDB)

Lithologic
Units

Fig. 6.   Stratigraphic plots of CaCO₃ accumulation and stable isotope analyses of autochthonous calcite from the Baldeggersee laminated sequence divided into lithologic units. Results from the light and dark laminae are plotted separately to emphasize the distinct seasonal signals. In Units A, F, and G, difficulties in separating seasonal layers resulted in a mixing of the seasonal geochemical signals, most noticeably in the CaCO₃ accumulation.

Organic C Accumulation
(g/m²/yr)

Organic N Accumulation
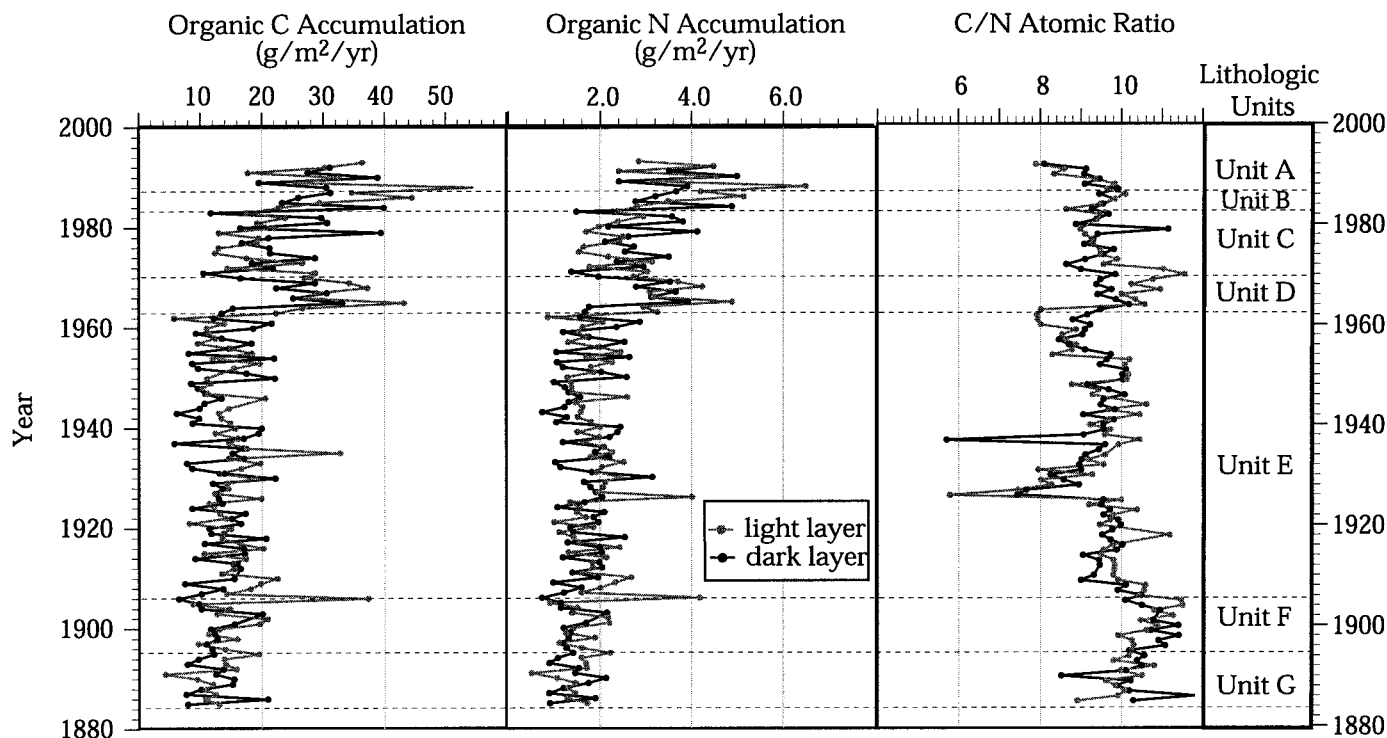(g/m²/yr)

C/N Atomic Ratio

Lithologic
Units

Fig. 7.   Stratigraphic plots of organic C and N accumulation and C/N atomic ratios from the Baldeggersee laminated sequence divided into lithologic units. Results from the light and dark laminae are plotted separately to emphasize the distinct seasonal signals.
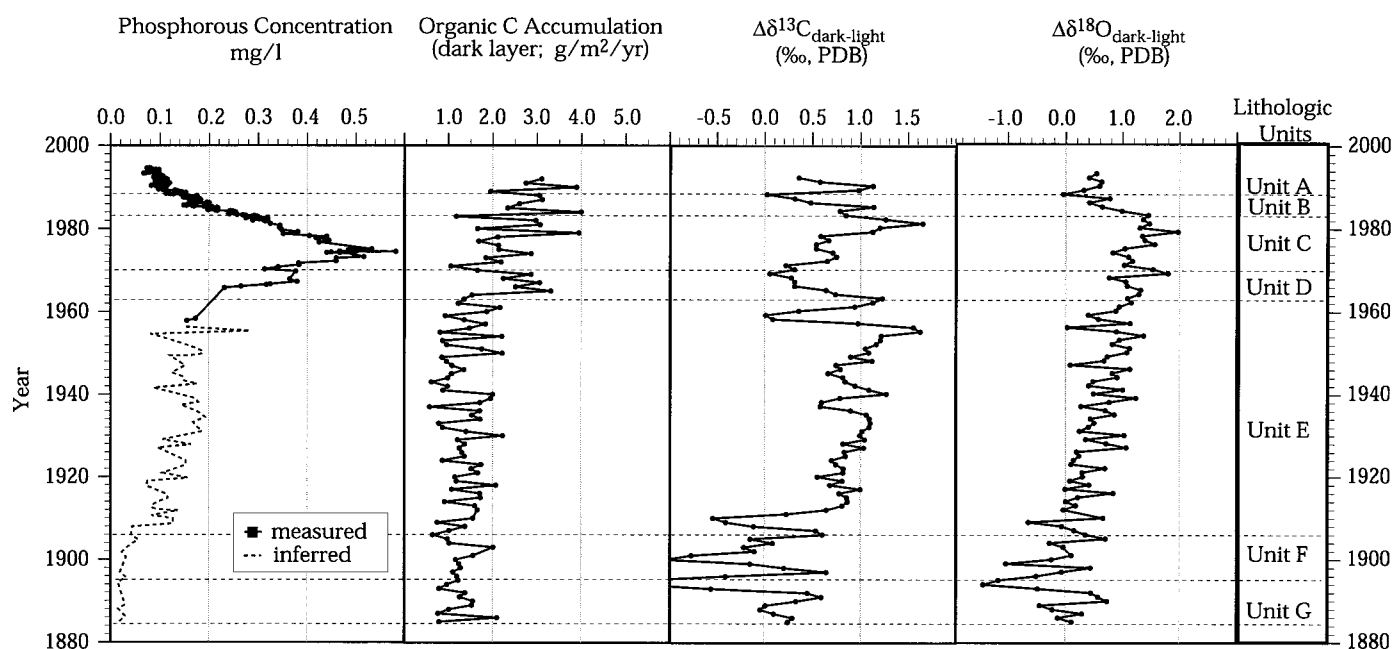
Fig. 8. Stratigraphic plots of measured and inferred average phosphorous concentration in the Baldeggersee water column and selected geochemical proxies for lake eutrophication in the laminated sedimentary sequence including: organic carbon accumulation in the dark layer, the calculated difference between dark- and light-layer $\delta^{13}C$ values ($\Delta\delta^{13}C_{dark-light}$), and the calculated difference between dark- and light-layer $\delta^{18}O$ values ($\Delta\delta^{18}O_{dark-light}$). Inferred phosphorous concentration data are from Lotter (1998).

accumulation in the light laminae; organic C and calcite accumulation rates both reached a maximum in Unit D, corresponding to the time of heavy phosphorous loading and hypertrophic conditions in the lake (*see* Figs. 6, 7; Table 1). Organic C accumulation decreased again in Unit C to rates around 20 g m^{-2} yr^{-1}. Despite the lake restoration program initiated in 1982, aimed at reducing primary productivity and oxygenating the bottom waters, organic C accumulation in the sediments increased again in Units B and A, returning to accumulation rates of 30 g m^{-2} yr^{-1}. This noted increase occurred because the organic carbon in the more recent sediment had experienced less respiration and because primary productivity in the lake has not significantly waned in the last decades despite the exponential drop in phosphate concentrations.

The flux of organic nitrogen to the sediments paralleled the general stratigraphic trends of the organic C flux. The seasonal difference both in organic C and N accumulations remains minimal (i.e., light- and dark-layer accumulation rates were essentially the same), despite the longer term trends in accumulation rates. Notable peaks occasionally occurred in the organic C and N accumulations, particularly in the light layers (1906, 1935, 1964, 1967, and 1988; Fig. 7). These peaks most likely record the combination of unusually high primary productivity and rapid settling of the organic matter. Although we do not have any petrographic data to determine if the peaks might reflect a terrestrial organic matter source, we tried to avoid samples with large terrestrial input by sampling out all visible turbidite samples. The occurrences of these "notable peaks" could possibly reflect the presence of very fine-grained turbidites that were overlooked. These do not, however, bias our data set or our in-

terpretations. A distinct $\delta^{18}O$ minimum, recorded in the 1986 light layer, corresponds to maximum peaks in organic C accumulation, dark-layer $\delta^{13}C$ value, and calcite accumulation in the light layer (Figs. 6, 7).

C/N atomic ratio values average 9.6, with no major difference between the light and dark layers (Fig. 7). There is a slight down-core trend toward increasing C/N ratios, most likely due to early diagenetic processes that result in selective nitrogen loss on the organic matter. C/N ratios are highest in Units F and G, with values = >10, and then decrease throughout Unit E. Unit D is characterized by another excursion to higher C/N ratios (average C/N = 10). C/N values are lower again throughout Units C and B and decrease steadily throughout Unit A, dropping to values of approximately 8.0.

Discussion

Geochemical responses to lake eutrophication—We interpret the first-order fluctuations in calcite accumulation rates, calcite $\delta^{13}C$ values (Fig. 6), and organic C and N accumulation (Fig. 7) to be a direct result of the eutrophication history and primary productivity in Baldeggersee, following processes that have been outlined and discussed in other studies of lacustrine sediments (McKenzie 1982, 1985; Lee et al. 1987; Hollander and McKenzie 1991; Schelske and Hodell 1991; Hollander et al. 1992; Hodell et al. 1998).

Figure 8 plots the measured and inferred average phosphorous concentration in the Baldeggersee water column (Lotter 1998). The first major increase in inferred total phosphorous concentrations (TP) occurred in 1909, when the TP

values shifted from below 0.05 mg liter^{-1} to over 0.10 mg liter^{-1}. According to the classification of OECD (1982), this would signify a change from eutrophic to hypertrophic conditions. The inferred TP values generally increased until the mid-1950s. In 1956, another step in TP concentrations occurred, increasing to levels of 0.2–0.3 mg liter^{-1}. Measured TP reached a maximum in 1977 and then subsequently decreased. Here, we roughly equate phosphate loading with primary production in lakes, as phosphate is generally considered to be the limiting nutrient in many lake systems, including Baldeggersee. Up-core increases in the flux of organic C and N (*see* Fig. 7) are the result of increasing organic matter production and preservation, which, in turn, is related to nutrient influx (P loading) and expansion of the oxygen-depleted water mass.

The biologically induced calcite production is a function of epilimnetic CO_2 removal, and therefore, accumulation of calcite in the sediments is also directly proportional to amount of primary production. Other studies of lake sediments have documented a similar increase in calcite accumulation in response to eutrophication (phosphate loading; Schelske and Hodell 1991; Hodell et al. 1998; Mullins 1998). This process is depicted by the close correlation of organic C and N and $CaCO_3$ accumulation rates in the Baldeggersee core (Figs. 6, 7).

The degree of photosynthetic activity, on both seasonal and interannual time scales, determines calcite $\delta^{13}C$ values. Progressive enrichment of ^{13}C in the epilimnion dissolved inorganic carbon (DIC) pool results in increasing $\delta^{13}C_{DIC}$ values over the seasonal productivity cycle by approximately 2.5‰ (Teranes 1998) and is manifested in the sedimentary record as a pronounced ^{13}C enrichment (between 0.5 and 1.0‰) in the dark layers relative to the light layers (Fig. 6). Long-term enrichment in ^{13}C in the water-column DIC pool is a combined result of photosynthetic activity and preservation of ^{12}C-rich organic matter in anoxic lake bottom waters, i.e., with the transfer of ^{12}C from the surface waters to the sediments. This process is manifested in the Baldeggersee sediment record as a progressive $\delta^{13}C$ enrichment in calcite in both the light and dark layers with increasing eutrophication.

Although variations in the geochemical signals in Baldeggersee sediments primarily reflect the lake eutrophication history, a detailed examination of the high-resolution seasonal record reveals that certain geochemical tracers, specifically calcite accumulation and $\delta^{13}C$ values, do not respond linearly to the recorded eutrophic history, nor is the timing of changes in all indicators simultaneous. Rather, the exact response is an interaction of many factors superimposed on the general productivity trend. For example, seasonal $\delta^{13}C$ values, plotted in Fig. 6, show significant annual variation in response to interannual variability in photosynthetic activity, which is superimposed on the long-term increasing productivity trend.

Another example is organic C accumulation, which is influenced by preservation potential in the water column, as well as primary productivity. This is especially well illustrated in Unit E, where organic C and N accumulation to the sediments does not increase (1906–1962; Fig. 7), despite measured and inferred increases in phosphorous concentra-

tions (Fig. 8) and the coincident large shift in $\delta^{13}C$ values in the dark laminae (Fig. 6). This is most likely explained by lower organic matter preservation potential up until the 1960s, i.e., less persistent bottom water anoxia.

During deposition of Unit D (1963–1970), known lake hypertrophic conditions (total phosphate = >0.1 mg liter^{-1}) produced the predicted geochemical response. Conditions were ideal for both production and preservation of carbonates and organic matter. Thus, accumulation of organic C and N and calcite in the sediments was very high. Calcite $\delta^{13}C$ values increased, reaching values of −4.8‰ in the light layer and −4.2‰ in the dark layer.

Measured nutrient levels were highest in the lake throughout Unit C (Fig. 8); however, geochemical signals did not respond completely as expected. Organic C and N, calcite accumulation, and $\delta^{13}C$ values all decreased. Lithologic units B and A, which were deposited after initiation of the lake restoration program, did not recover as expected to the dramatic lowering of nutrient input during the last 20 yr. Primary productivity has not significantly waned nor have organic C and N accumulations substantially decreased, despite the exponential drop in P loading, thus illustrating a substantial release of phosphate from the sediments (Gächter 1987).

The only geochemical parameter that responded linearly and directly to the known trophic history of Baldeggersee was the oxygen isotope composition of calcite in the light layer. Light laminae $\delta^{18}O$ values decreased (~−2‰ shift) with increased nutrient loading in the lake and then trended back to less depleted values in direct response to phosphate abatement (Fig. 6). In addition, the offset between dark- and light-layer $\delta^{18}O$ values, $\Delta\delta^{18}O_{dark–light}$ (plotted in Fig. 8), was not constant, as would be expected from temperature-dependent oxygen isotope equilibrium fractionation equations, but rather, increased in response to nutrient loading.

Using temperature-dependent oxygen isotope equilibrium fractionations between calcite and water (0.24‰ °C^{-1}; Epstein et al. 1953), measured ambient water temperature during spring/summer and late summer/autumn calcite precipitation events (T = 13 and 15°C, respectively; *see* Fig. 2A), and the average seasonal evaporative enrichment of the surface-water ($\Delta \delta^{18}O_L$ = +0.8‰), equilibrium calcite $\delta^{18}O$ values can be derived for average light- and dark-layer calcite $\delta^{18}O$ values. Results from these calculations show that theoretical $\delta^{18}O$ values for late summer/autumn calcites (dark layer) should be slightly enriched relative to spring/early summer calcites, but the difference should not be >0.3‰. However, as Figs. 6, 8 show, only before 1930 and again after 1987 are the actual light- and dark-layer calcite $\delta^{18}O$ values ($\Delta\delta^{18}O_{dark–light}$) similar; the intervening years are marked by a steady separation of the light and dark layers, up to as much as 2‰, with the light-layer calcite $\delta^{18}O$ values being lower.

Assuming that the bulk of the calcite precipitates at approximately the same time during the annual cycle when the relative range of the surface-water temperatures is about the same each year (McKenzie and Hollander 1993) and that any change in oxygen isotopic values of the lake water ($\delta^{18}O_L$), beyond a small seasonal enrichment, would equally induce variations in the $\delta^{18}O$ values of the sedimented pre-

cipitate in both the light and dark layers, it follows that an increase in the offset of $\delta^{18}O$ values between the layers must be due to an additional isotope fractionation effect. Furthermore, the magnitude of this isotope fractionation effect must vary with the trophic state of the lake, as the offset between the layers parallels eutrophic evolution of the lake. We suggest that, in the highly eutrophic Baldeggersee system, isotopic composition of the calcite in the light and dark layers actually record very distinct processes. $\delta^{18}O$ values in the dark layer are mainly a function of changing isotopic composition of the Baldeggersee water with time, whereas $\delta^{18}O$ values in light-layer calcites are additionally subject to apparent isotope nonequilibrium fractionation, which creates the observed isotopic depletion.

Figure 8 displays the clear positive relationship between phosphorous concentrations and the calculated offset between the dark and light laminae $\delta^{18}O$ values. Excluding Units F and G, when seasonal samples could not be accurately separated, the light and dark layers steadily diverge in accordance with increased TP in the lake and then converge again during the last 20 yr with the lake restoration program. Note that during Unit C (1970–1982), phosphorous concentrations and $\Delta\delta^{18}O_{dark–light}$ both reached maximum values (Fig. 8).

Oxygen isotopic analyses of sediment trap calcite (Teranes et al. in press) indicate the same relationship between phosphorous concentration and apparent oxygen isotope nonequilibrium, i.e., isotopically depleted $\delta^{18}O$ values relative to calculated equilibrium values, albeit on a seasonal scale. Analysis of a complete annual cycle of water chemistry data and daily sediment trap material collected from Baldeggersee has shown that, whereas during most of the year calcites precipitate in predicted isotopic equilibrium, isotopically depleted large calcite grains are associated with high phosphate concentrations and elevated carbonate ion concentrations in the spring surface waters. Here, we suggest that the same mechanism responsible for isotopically depleted spring calcites also results in a negative $\delta^{18}O$ shift in the light layers of the Baldeggersee sediment record. Furthermore, the clear relationship between phosphorous concentrations and noted oxygen isotopic depletions, as illustrated in Fig. 8, indicates that increasing P loading is very likely a process that decreases the paleoclimatological usefulness of oxygen isotope values in authigenic lake carbonate.

Isotopic depletions have been recognized in other small eutrophic lake systems. Data from a >100-yr isotopic record from eutrophic Lake Arresø, Denmark (Fronval et al. 1995), for example, display a negative shift in oxygen isotope values of 2.0–2.5‰ between calcite from the preindustrial phase and modern calcite. Applying the paleotemperature equation of Epstein et al. (1953), Fronval et al. (1995) concluded that the modern calcite did not precipitate in isotopic equilibrium with the water. This noted ^{18}O depletion is further evidence that high phosphate concentrations, enhanced primary production, and elevated pH and $[CO_3^{2-}]$ values are all linked to isotopic depletions in lacustrine calcite.

Large $\delta^{13}C$ variations observed in the Baldeggersee carbon isotope stratigraphy (Fig. 6) reflect the complex interaction of both seasonal isotopic processes and stratigraphic trends in $\delta^{13}C$ that occur in both the light and dark laminae due to progressive burial of ^{12}C-rich organic matter. Figure 8 plots the difference between the dark-layer $\delta^{13}C$ values and the light-layer $\delta^{13}C$ values ($\Delta\delta^{13}C_{dark–light}$). The $\delta^{13}C$ record starts to respond to progressive eutrophication throughout Unit E, similar to the $\delta^{18}O$ record (i.e., decreasing $\delta^{13}C$ values in the light layer). However, larger variations in the upper part of the section indicate progressive ^{13}C enrichment in the water-column DIC, which is superimposed on any possible $\delta^{13}C$ nonequilibrium depletion trend in the light layers.

Mechanism for oxygen-18 isotopic depletion—Niessen and Sturm (1987) demonstrated that calcite grain size in the Baldeggersee sedimentary record increases synchronously with the progressive eutrophication of the lake. Subsequent high-resolution sampling of the Baldeggersee freeze-core has established that average calcite grain size in the Baldeggersee sediment can be used as a proxy indicator of former trophic state, i.e., P loading in the lake (Lotter et al. 1997b). Oxygen-18 isotopic depletion of the Baldeggersee calcite also correlates with larger than average calcite crystal size, as noted in calcite from the light layer and, thus, to trophic evolution of the lake.

Figure 9 plots the grain size distribution in the annually laminated Baldeggersee sediments (Lotter et al. 1997b), together with the degree of oxygen isotopic offset between the dark and light laminae. The isotopic offset, $\Delta\delta^{18}O$, can be considered a proxy for the degree of relative ^{18}O depletion in calcites from the light layer in excess of any $\delta^{18}O$ variation affecting both the light and dark layers. Both trophic state proxies steadily increased throughout the first part of the century, reaching maximum values in the 1970s (coincident with maximum phosphorus loading in the lake), and then sharply decreased in response to diminished nutrient loading in the lake after 1980. These data demonstrate that the degree of isotopic depletion in the spring calcites is positively correlated with calcite crystal size.

Although certainly enough circumstantial evidence points to elevated phosphate concentrations in the surface water in association with increased crystal size and isotopically depleted calcite precipitates, the mechanism linking these three parameters can be debated. Various studies have suggested that PO_4^{2-} ions can inhibit calcite crystal growth (Kunz and Stumm 1984; Dove and Hochella 1993). Under this assumption, high $[PO_4^{2-}]$ in the Baldeggersee spring surface waters, after winter turnover, could initially inhibit calcite growth, thereby increasing supersaturation of carbonate in the lake. As soon as $[PO_4^{2-}]$ is reduced through assimilation by algal productivity, calcite precipitation ensues at greatly accelerated rates, leading to larger crystals and isotopic depletions.

McConnaughey and Whelan (1997) have proposed an alternative explanation for the role of phosphorous in isotopic disequilibrium reactions. They reason that, because the protons generated through calcification are necessary for bicarbonate and nutrient assimilation by organisms, calcification is best seen as a product of a proton-generating process, rather than vice versa. Based on observations in Fayetteville Green Lake, New York, Thompson et al. (1997) demonstrated that calcite precipitation can be mediated by the photosynthetic activity of cyanobacterial picoplankton, which cre-
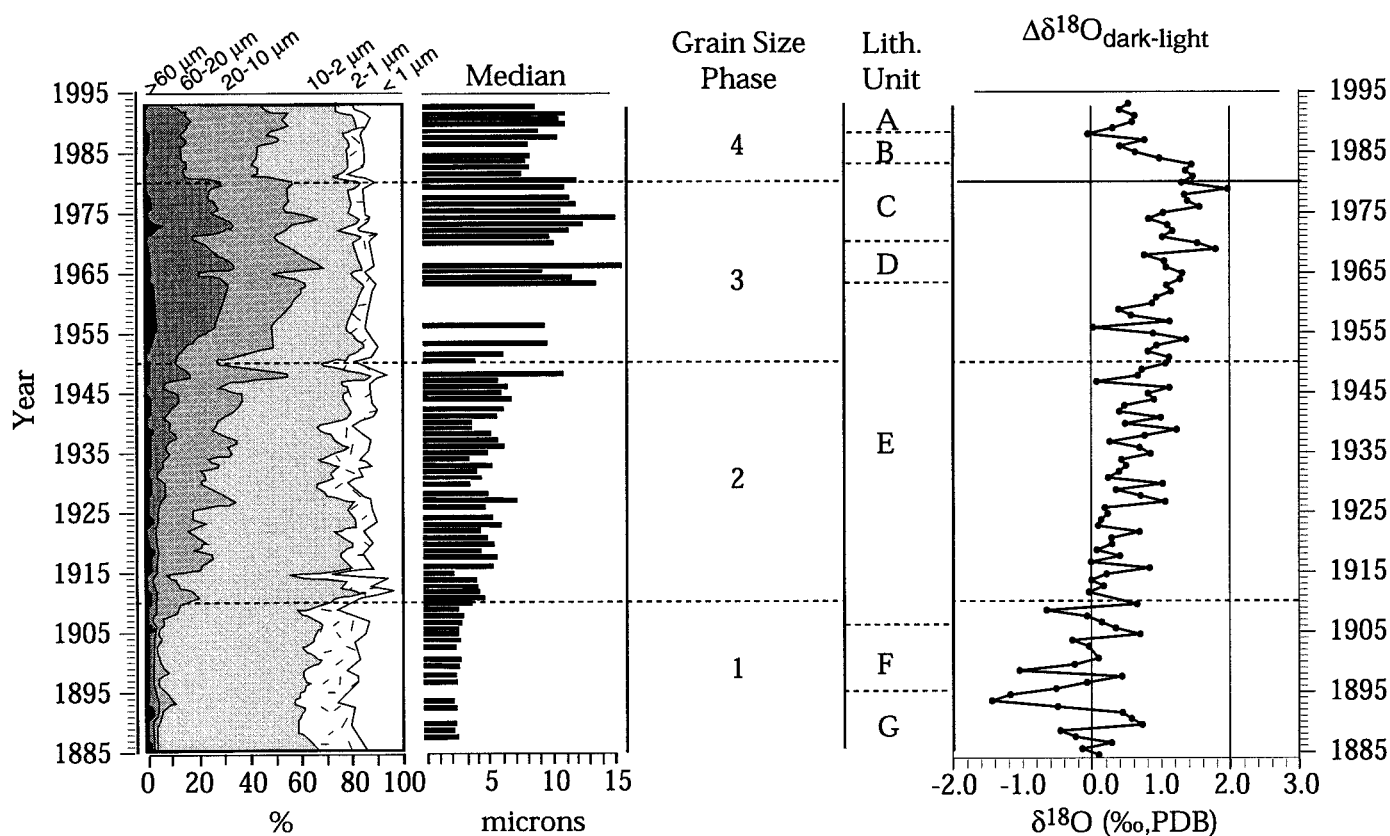
Fig. 9. Stratigraphic plots of grain size distribution, adapted from Lotter et al. (1997b), and the calculated difference in oxygen isotopic values between the dark and light layers ($\Delta\delta^{18}O_{dark-light}$) in the Baldeggersee core. An increase in calcite grain size, coincident with phosphate loading throughout the 1950s, 1960s, and early 1970s, correlates with a relative decrease in the light-layer $\delta^{18}O$ value with respect to the dark-layer value. Total phosphate concentration decreased after 1976 in response to restrictions on nutrient loading and initiation of the lake restoration program in 1982. Calcite grain size and the ^{18}O depletion in the light layers decrease correspondingly.

ates a high pH microenvironment around their cells, leading to epicellular precipitation of calcite. Under these assumptions, calcite precipitation in Baldeggersee would be a biologically mediated process where spring "whiting events" would be induced, at greatly accelerated rates, either to generate protons in the increasingly alkaline environment to facilitate bicarbonate and phosphate assimilation by organisms and/or in response to carbonate ion disequilibrium in the high pH microenvironment surrounding the cyanobacterial picoplankton cells.

As oxygen isotope depletions and larger grain size are associated with increased primary productivity, and thus relatively higher surface-water pH values and $[CO_3^{2-}]$, we propose that the observed isotopic depletions are most likely the result of varying oxygen fractionation factors as a function of the changes in the major carbonate component equilibrium in the surface waters accompanying increased primary productivity. Calculated oxygen isotope fractionation factors between aqueous CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-} with respect to H_2O have been demonstrated to vary with pH (Usdowski et al. 1991). Specifically, fractionation experiments by Usdowski and Hoefs (1986, 1993) and Usdowski et al. (1991) indicate that the hydration of CO_2 ($CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$) yields values for the equilibrium fractionation of the oxygen isotopes that are significantly different

from those for reactions involving the hydroxylation of CO_2 ($CO_2 + OH^- \leftrightarrow HCO_3^-$). At higher pH values, hydroxylation is the dominant process over hydration of the CO_2. The final result is more depleted $\delta^{18}O$ values in systems with higher pH (Usdowski et al. 1991).

Isotopic investigations of daily sediment trap material from Baldeggersee reveal that high phosphate concentrations can lead to temporarily elevated carbonate ion concentration in the spring surface water, thus creating a supersaturated system with respect to calcite (Teranes et al. in press). The first calcite grains to precipitate from this supersaturated water are relatively large, anhedral calcite grains, >30 microns in diameter (*see* Fig. 3). Sediment trap isotopic data show that the resulting large spring calcite grains are depleted in ^{18}O. During the late summer and into the autumn, when phosphorous concentrations remain low, creating temporary "oligotrophic" conditions in the epilimnion (Fig. 2), smaller calcite grains precipitate at a relatively slower rate. (Compare spring/summer and late summer/autumn calcite grain sizes in Fig. 3.) Sediment trap isotopic data show that calcite precipitated in the late summer/autumn is in isotopic equilibrium with the ambient water (Teranes et al. in press).

Depending on the phosphate concentrations in the spring epilimnion, which, in turn, vary with anthropogenic nutrient loading, the apparent oxygen isotopic nonequilibrium in the

spring calcite might be severe enough to overprint the isotopic equilibrium record of the light layer (composed of spring through midsummer calcite precipitate) in the Baldeggersee core. A plot of the historical phosphate concentrations with the calculated offset between the dark and light layers (Fig. 8) graphically displays the positive correlation between lake trophic level and ^{18}O-depleted light-layer calcite values.

In summary, the response of oxygen isotope values in Baldeggersee calcite to distinct long-term and seasonal environmental factors is manifested in the Baldeggersee sediment core isotopic record. Oxygen isotopic values from the light layers are increasingly depleted in ^{18}O in response to increased productivity in the lake. δ^{18}O values from the dark sedimentary layers, in contrast, do not correlate with any productivity proxy in the lake, but they do respond to changes in the isotopic composition of the lake water, which is in turn determined by the isotopic composition of precipitation supplying the catchment area.

Both productivity level of the lake and ^{13}C depletions, as explained above, influence the carbon isotopic composition of calcite precipitated in the spring. These two factors compete as P loading in the lake increases and, in fact, appear to cancel out the effects of each other. In contrast, the carbon isotopic composition of calcite precipitated in autumn is in isotopic equilibrium and is primarily influenced by the productivity in the lake. There is a significant negative correlation between dark-layer δ^{13}C and light-layer δ^{18}O values as the productivity in the lake increases (Fig. 6).

Alternative hypotheses—Other oxygen isotopic studies from lacustrine sedimentary sequences have suggested that anomalous light δ^{18}O values were not caused by isotopic disequilibrium effects but rather, could be explained by longer periods of productivity-induced disequilibrium in the bicarbonate system, resulting in continuous precipitation of calcite extending longer and at greater rates into the warmer summer months (McKenzie 1985; Schelske and Hodell 1991; Hodell et al. 1998). Based on data from Greifensee, a small eutrophic lake in central Switzerland located 35 km NE of Baldeggersee, McKenzie (1985) proposed that a delay in timing of spring calcite precipitation was linked to the lake's trophic state, i.e., more phosphate in the surface waters increased the calcite precipitation inhibiting effect, thereby forcing calcite to precipitate later in the spring and thus, at higher ambient water temperature. Based on a study from Lake Ontario, Schelske and Hodell (1991) proposed that interannual climate variability, through phasing of thermal stratification, primarily influences the quantity and isotopic composition of biologically induced calcite precipitate. Hodell et al. (1998) further documented that calcite production in Lake Ontario is dependent on the timing of seasonal water stratification, in addition to primary productivity and abundance of picoplankton and therefore, is highly correlated to lake temperature. Maxima in δ^{13}C values and minima δ^{18}O values were found to be associated with carbonate production peaks, evidence that the duration of epilimnetic production was longer and at relatively higher water temperatures in years with longer periods of lake stratification (i.e., warmer spring temperatures; Hodell et al. 1998).

Both of the above hypotheses are incompatible with the Baldeggersee oxygen isotopic results. To explain the large negative shift in Baldeggersee δ^{18}O values in terms of a change in water temperature would require a 10°C increase in average surface-water temperatures (assuming a 1°C temperature change is represented by a 0.24‰ change in δ^{18}O; Epstein et al. 1953). Regardless of whether the cause of the temperature change is due to delayed seasonal precipitation of calcite or earlier seasonal warming of the surface water, the required temperature increase, amounting to an average surface-water temperature of 24°C, is clearly unrealistic in Baldeggersee. Long-term records of monthly water temperatures only rarely register temperatures in excess of 23°C (data from EAWAG Limnological Research Center, Kastanienbaum). Additionally, there is no lithologic evidence for significantly delayed calcite precipitation. McKenzie and Hollander (1993) also concluded, based on further examination of a high-resolution Greifensee sequence, that the amount of change in the average water temperature at the time of precipitation would have to be unrealistically large to be solely responsible for δ^{18}O changes in the Greifensee record. Schelske and Hodell (1991) calculated that only a 3°C average water temperature change would be necessary to explain the stratigraphic δ^{18}O deviations observed in Lake Ontario. Lake Ontario is a bigger system, phosphorous concentrations are lower, and the negative trends in δ^{18}O are not as pronounced as in the two Swiss lakes, and therefore, phasing of thermal stratification may indeed play an important role in calcite production and its isotopic composition in Lake Ontario.

The lack of evidence to show either a major variation in the timing of calcite precipitation or a 10°C change in average surface waters renders ambient water temperature change an unlikely cause of observed negative shifts in δ^{18}O values. Additionally, there is no petrographic evidence to suggest that the epilimnion calcite has been diagenetically altered after deposition. Instead, we favor the hypothesis that changes in the major carbonate component equilibrium values in the spring surface water result in varying oxygen fractionation factors that lead to ^{18}O depletions in the calcite of the light layers in Baldeggersee and Greifensee. In fact, the magnitude of the changes in the calcite δ^{18}O values in the light layers in Baldeggersee and Greifensee sediments is remarkably similar, thus implying a similar isotopic response to nutrient loading in the lakes' respective watersheds.

Conclusion

Data from high-resolution (seasonal) samples presented here are evidence of the distinct seasonal responses of carbon and oxygen isotopes in lacustrine calcites. In eutrophic lakes, elevated surface-water phosphorus and carbonate ion concentrations in the spring affect major carbonate component equilibrium and are linked to ^{18}O depletions in the sedimented light-layer calcite. Nutrient loading in the lake largely determines the degree and duration of isotopic depletion in the spring calcite and can, during hypertrophic conditions (TP > 0.1 mg liter^{-1}), destroy the utility of the resulting bulk carbonate signal as a paleoclimate proxy. In

contrast, from late summer through autumn, when the epilimnion is essentially "oligotrophic," calcite precipitates in predicted isotopic equilibration. Thus, the resulting $\delta^{13}C$ and $\delta^{18}O$ stratigraphies produced from calcite in the dark laminae of a sequence such as the annually laminated Baldeggersee sediment core provide better proxies for climatic information.

These findings build on other studies (Fronval et al. 1995; Gat and Lister 1995; Spero et al. 1997) in warning that apparent oxygen isotope nonequilibrium in precipitated calcite can overprint climatic trends. Rather than dismissing valuable data stored in oxygen isotope sequences, however, our findings stress the importance of high-resolution sampling of laminated lacustrine sequences. High-resolution sampling of the annually laminated Baldeggersee sediment was essential to obtain an accurate understanding of seasonal variations in isotope fractionation. However, not all lake archives are annually laminated, nor are eutrophic conditions known in advance from longer lake archives. Therefore, we offer the following four guidelines, based on observations in Baldeggersee, for evaluating isotopic signals that are dominated by variable isotopic depletions as a result of nonequilibrium calcite precipitation. (1) Characteristics of the calcite grains, when viewed with SEM, are probably the most helpful for distinguishing the rate of precipitation in ancient lacustrine sequences, i.e., large, irregular, anhedral calcite crystals could indicate that the calcite precipitated quickly and therefore, may be isotopically depleted relative to equilibrium fractionation values (*see* Fig. 4). (2) As outlined above, isotopic depletion often occurs intermittently throughout the seasonal cycle, and, depending on the degree and duration, isotopic depletion might not significantly affect the utility of the resulting bulk carbonate signal. For example, today in Baldeggersee, isotopic depletions are only noted for the first few days of calcite production in the spring; the rest of the calcite production in late summer and autumn precipitates under equilibrium conditions. Therefore, an isotopic signal of the bulk lacustrine sediment would essentially measure in isotopic equilibrium, i.e., $\delta^{18}O$ depletions < 0.3–$0.4‰$ relative to isotopic equilibrium values (Teranes et al. in press). (3) Apparent oxygen isotopic nonequilibrium often occurs only intermittently throughout the seasonal cycle, and the resulting large anhedral calcite grains are easily recognizable. Therefore, physical removal of these grains (i.e., sieving or grain size separation techniques) before isotopic analysis of the sediment would avoid spurious measurements. Finally, (4) our findings associate apparent isotopic nonequilibrium calcite precipitation with eutrophic lakes when primary productivity is high. Therefore, caution is required when analyzing inorganic carbonates from lacustrine sequences where organic matter preservation and/or $\delta^{13}C$ values point to times of high paleoproductivity.

In conclusion, Baldeggersee data demonstrate that, with prudence in sampling, carbon and oxygen stable isotopic results from lacustrine calcite, even from eutrophic systems, provide useful paleoenvironmental proxies. For example, by concentrating on late summer to autumn Baldeggersee calcite precipitate, it was possible to obtain a 108-yr record of environmental and regional climate changes. Stratigraphic trends in the carbon isotopic composition of calcite in the dark laminae, precipitated in isotopic equilibrium, are primarily influenced by the productivity level of the lake, as DIC of the lake becomes enriched in ^{13}C with increasing organic carbon burial (and therefore removal of ^{12}C from the system).

Finally, this calibration allows recognition of a genuine climatological signal from isotopic shifts in the Baldeggersee dark laminae. The oxygen isotopic composition of calcite in the dark laminae is independent of the amount of primary productivity in the lake and precipitates at approximately the same water temperature each year. Thus, $\delta^{18}O$ values are exclusively a function of changes in the isotopic composition of the lake water and can be used as a proxy for the isotopic composition of the regional paleoprecipitation.

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