Climate and CO_2 saturation in an alpine lake throughout the Holocene

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Abstract

This study shows that diatom sediment records can be used to investigate the long-term inorganic carbon dynamics in oligotrophic and poorly acid-buffered lakes. Using a training set of 115 high-mountain lakes in the Pyrenees, we found that both alkalinity and potential hydrogen (pH) independently explained some of the variability in diatom assemblages. Transfer functions for both variables were developed and applied to a Holocene record from Lake Redon and CO_2 changes calculated. CO_2 saturation broadly followed alkalinity, which in turn was related to summer and autumn air-temperature fluctuations. In general, warmer climate during the ice-free period led to higher supersaturation, due to increased alkalinity, which facilitated retention of CO_2 from respiration, and decreased primary production (assessed by diatom fluxes). Only during the early Holocene, there were periods of extreme undersaturation, corresponding to cold periods of low alkalinity (<20 micro-equivalents per liter [μeq L^{-1}]), and suggesting carbon limitation of primary production. The winter and spring climate, which determines the ice cover duration, appears to be relevant for CO_2 saturation only during periods when the organic-matter content of the sediments was low (<22%). Longer periods of ice cover led to lower lake CO_2 saturation, suggesting that the ice cover influence on internal nutrient loading may regulate lake productivity fluctuations under low allochthonous nutrient and organic-matter inputs. Alkalinity $\sim$20 μeq L^{-1} and sediment organic matter $\sim$22% appear as critical thresholds in the way lake CO_2 levels respond to climate fluctuations.

The dissolved inorganic carbon system (DIC) plays a pivotal role in lake biogeochemistry, because it is involved in several key processes including primary production, respiration, decomposition, and acid-buffering. Temporal DIC fluctuations depend on changes in three main factors: (1) DIC water storage capacity, which is related to alkalinity (i.e., excess of base cations over strong acid anions); (2) the biological consumption and release balance, because DIC is the carbon source for primary production and the final byproduct of organic-matter oxidation; and (3) air–water gas exchange, because CO_2 transport between the atmosphere and water is not immediate and the water column is commonly stratified; thus, a departure from equilibrium between air and water phases is common and occasionally severe (Cole et al. 1994). Each of these factors may vary according to watershed and in-lake processes (Psenner and Catalan 1994). Watershed alkalinity sources, including rock weathering, soil base exchanges, and dust deposition, are usually quantitatively more relevant than within-lake processes (e.g., anaerobic oxidation). However, the latter cannot always be ignored and can become the dominant source if relatively persistent, and large anaerobic layers occur in lakes on crystalline bedrocks (Psenner 1988). Biological CO_2 balance is also highly affected by loadings from the watershed; nutrients increase the CO_2 demand by photosynthetic organisms, whereas organic matter in dissolved (DOC) or particulate (POC) forms increases the lake's heterotrophic nature and eventual CO_2 imbalance (Kortelainen et al. 2006). Internal nutrient loading from sediments and organic matter produced within the lake may also play

a role, depending on the lake volume and water renewal time. The higher the lake volume and the slower the water renewal, the more relevant the internal loadings and demands become. Finally, air–water exchange depends on water-column stratification, ice cover duration, runoff, and any other processes that stir the lake water.

Many of the processes quoted above, if not all of them, are directly or indirectly affected by climate. Climate drives soil and vegetation dynamics in the watershed and stratification and mixing patterns in lakes. Thus, matter transport from the catchments and mechanical energy input into the lakes are ultimately under climatic control and the whole lake ecosystem is climate-dependent (Catalan and Fee 1994). However, climate is a single word but not a single variable: its multivariate nature (i.e., seasonal patterns, temperature and moisture components) makes it even more difficult to disentangle the complex relationships (Fritz 2008; Schmidt et al. 2008). For particular types of lakes, or for a specific site, the picture can be simplified, because only some processes may be of interest. By definition, climate implies at least decadal time scales. Observational time series may be too short to infer conclusive relations between climate and fluctuations in inorganic carbon components, beyond some exceptional cases involving strong sources of variability (e.g., Northern Atlantic Oscillation (NAO) [Blenckner et al. 2007]). Lake manipulations, which have been very successful in other aspects (i.e., eutrophication, acidification [Findlay et al. 1999]), are difficult to apply to climate issues (Lydersen et al. 2008). Studies on climate–lake-process relationships use alternative approaches, such as space-for-time substitutions, numerical modeling and short time series to observe climate-shift effects (Magnuson 1990). Paleolimnology can

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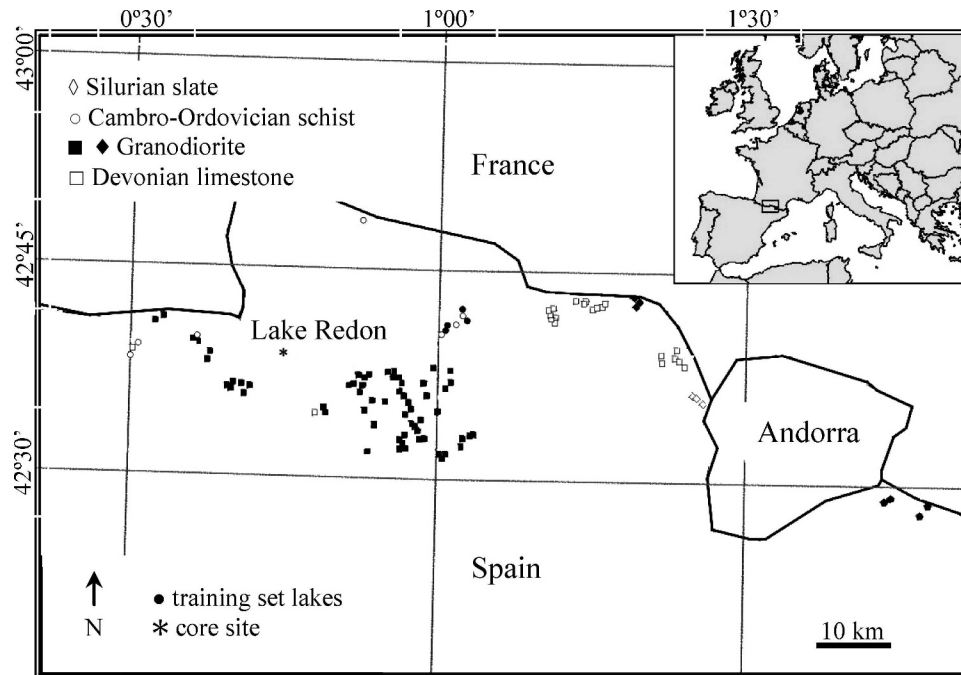*Corresponding author: catalan@ceab.csic.es

Fig. 1. Map showing the location of the Pyrenean lakes used as diatom training set for developing alkalinity and pH transfer functions and the coring site where CO$_2$ saturation reconstructions have been applied.

offer a complementary approach, because different proxies can be used to reconstruct climate forcing and lake processes independently. Here, we present a study of the relationship between climate and CO$_2$-saturation over the last 10,000 yr.

Diatoms have been extensively used to reconstruct lake-water pH with excellent results, particularly concerning atmospheric acid deposition in sensitive areas (Battarbee 2001). These reconstructions implicitly assume that pH is related to fluctuations in acid neutralizing capacity (ANC). They tacitly admit that pH deviations due to lack of equilibrium with atmospheric CO$_2$ are of minor relevance or simply cannot be differentiated from true changes in ANC using the available techniques (Anderson 2000). As a consequence, pH, ANC, DIC, and alkalinity are used synonymously in the paleolimnological literature. However, if diatoms do not respond identically to pH and alkalinity, both variables can be reconstructed separately. This would open paleolimnological investigations to new aspects of Global Change investigations and carbon cycling, particularly to CO$_2$ dynamics.

The present paper is divided into two sections. First, we show that pH and water alkalinity are factors that can explain certain diatom assemblage variation independently. Consequently, diatom-based pH and alkalinity transfer functions can be developed and water CO$_2$ levels estimated. In the second section, we apply this method to reconstruct CO$_2$ saturation in an alpine lake throughout the Holocene, as a case study for investigating long-term CO$_2$ dynamics in a poorly acid-buffered, oligotrophic lake that is highly influenced by climate. Fluctuations in CO$_2$ are considered in terms of CO$_2$ storage capacity, potential carbon productivity limitations and links to nutrient and organic-matter loadings in the context of the climatic changes that occurred during the Holocene.

Methods

Training data set—The study of pH and alkalinity effects on diatom distribution and the development of transfer functions for both variables were based on data from 115 lakes in the Central and Eastern Pyrenees (North East Spain; Fig. 1). Nine lakes were sampled several times in different years; thus, the total sample No. was 124. The lakes were selected from >500 lakes in the area to include a broad range in altitude (1615–2954 m above sea level [a.s.l.]), size (0.007–0.454 km^2), chemistry, and trophic status (Pla et al. 2003). Most lakes were situated on granodioritic bedrock distributed among four batholiths (Maladeta, Bassiers, Andorra-Montlluís, and Marimanha) that cover ~70% of the total lake watersheds. The remaining lakes were on Cambro-Ordovician schist and phyllite, except for a few located on Silurian slate rich in sulfides, and others situated on Devonian limestone. Vegetation was generally poorly developed. Occasional summer pasturing was the most common human disturbance to these lakes. Ten lakes had some minor modifications (a small dam, channel, or pipeline) for water use in hydroelectric power stations located down the valley. These modifications did not significantly change water-level fluctuations.

The data set amalgamates four survey campaigns (1987, 1995, 1996, and 1998) carried out during July or August. In the 1987 and 1995 surveys, sediment samples from 2 m and 6 m depths were collected by diving for diatom analysis. Approximately the first centimeter of this sediment was

analyzed. In the remaining surveys, sampling was carried out using a gravity core in the deepest part of the lake, and the upper 0.5 cm was analyzed.

The chemical characteristics of Pyrenean lakes were studied by Catalan et al. (1993). The lakes generally have a low ionic content and buffering capacity, but have not been acidified by atmospheric industrial pollution. Most chemical variance is related to the nature of the bedrock. The lakes in watersheds rich in carbonates (Devonian limestone) or materials rich in sulfides (Silurian slate and Cambro-Ordovician schist) differed from those on granodioritic watersheds; and even some granodioritic batholiths were distinguishable from others (e.g., lakes on Bassiers batholith had the lowest ion content). Lakes with very low pH and negative alkalinity were scarce; they were located on slate and schist bedrock, and characterized by a high sulfate and magnesium content. The phosphorus content of all lakes was low, indicating the oligotrophic nature of these lakes. However, nitrogen compounds, and particularly nitrate, were usually abundant because of atmospheric depositions. The lakes are not dystrophic, because of the scarce vegetation development in most of the watershed. DOC is generally low ($\sim$ <1 mg L^{-1}).

Lake Redon core (RCA94)—The coring site was Lake Redon (formerly Redó; 42°38′33″N, 0°46′13″E), located in the central Pyrenees at 2240 m a.s.l. It has a surface area of 0.24 km², a maximum depth of 73 m, and a mean depth of 32 m. Average water residence time is >4 yr. The watershed area is a small granodiorite basin (1.55 km²). Land cover consists of poorly developed soil (74%), generally <30 cm deep, supporting grasslands. The rest of the area is bare rock. The lake occupies an intermediate position within the range of lakes surveyed, in terms of altitude and chemistry. In August 1994, a sediment core (RCA94) was taken from the deepest part of the lake using a gravity corer (Pla and Catalan 2005). The total length of the core was 56 cm, and it was extruded immediately and sliced into 3-mm sections. Dating (*see* below) showed that the core covered the last 10,000 yr, reflecting the low sedimentation rate in the lake, due to the oligotrophy and a relatively small watershed compared to the lake volume.

Chemistry—Water samples were collected either at the outflow or the central part of each lake, and kept in cool and dark conditions until analysis. No air space was left in the bottles and pH measurements were performed without CO_2 air equilibrium. A low-ionic-strength filling solution was used in the pH-electrode and the recommendations of Neal and Thomas (1985) for pH measurements in low-ionic-strength waters were followed. In the 1987 survey, alkalinity was measured by reverse titration on the same day as the samples were taken. In the rest of the surveys, it was measured by Gran acidic titration. In order to check the alkalinity measurements, we also determined conductivity, major anions (sulfate, nitrate, and chloride; analyzed by ion chromatography or capillary electrophoresis), major cations (calcium, magnesium, sodium, and potassium; atomic absorption spectrometry, inductively coupled plasma or capillary electrophoresis), and ammonium (molecu-

lar spectrophotometry by the indophenol method). The charge balance and a comparison of measured against calculated conductivity were carried out as analytical quality controls.

Diatoms—After sediment digestion with hydrogen peroxide, diatom samples were mounted on slides using Naphrax© and ~500 valves were counted per sample using a light microscope with an ×100 phase objective. The taxonomy used in the AL:PE (Cameron et al. 1999) project was followed. Diatom flux was estimated by weighing dry sediment samples before digestion and adding known quantities of latex microspheres to the samples in order to determine the valve concentration. Then, matter accumulation rates, based on sample density and age, were used to estimate fluxes.

Core dating and characterization—The top 8 cm were ^{210}Pb dated (Camarero et al. 1998). Samples for AMS ^{14}C dating were selected by performing a stratigraphically constrained cluster analysis from previous diatom analysis. The cluster results indicated five zones with significant changes in their species assemblages (Fig. 2). Thus, nine bulk sediment samples were selected, because wood or other terrestrial vegetation remains were not available. Beta Analytica processed the samples. The INTCAL98 calibration procedure was followed for dates calibration (Stuiver et al. 1998). A pollen analysis was performed to check the agreement of ^{14}C dating with the established pollen chronology in the Central Pyrenees (Pla and Catalan 2005). Loss on ignition (LOI) at 550°C was carried out as an estimation of the organic content (Heiri et al. 2001).

Variance partition—The explicative capacity of pH and the alkalinity of the diatom assemblage compositions were evaluated using the training-set data. We performed several partial redundancy analyses (pRDA), using the Hellinger distance to obtain a variance partition indicative of the unique and shared contribution of pH and alkalinity in explaining diatom distribution. The Hellinger distance was used for the ordination because it has more suitable properties, as shown by Rao (1995). Alternative techniques, such as canonical correspondence analysis (CCA) using the chi-square distance provided similar results, although the variance explained was slightly less and rare species had a greater influence on the results. We obtained the Hellinger distance by square-root transformation of the original taxon proportions in the samples, combined with the Euclidean distance of a common redundancy analysis (Legendre and Gallagher 2001). Using each environmental variable (i.e., pH and alkalinity) as a sole constraining variable and the other as a covariable in pRDA, we showed that both variables had a significant marginal effect ($p <$ 0.001), as assessed by Monte-Carlo permutation tests. The relative strength and statistical independence of the variables was assessed using the pRDA results to partition the total variance in the diatom data into components representing: (1) the unique or marginal effects of each variable, (2) the conditional or shared effects between
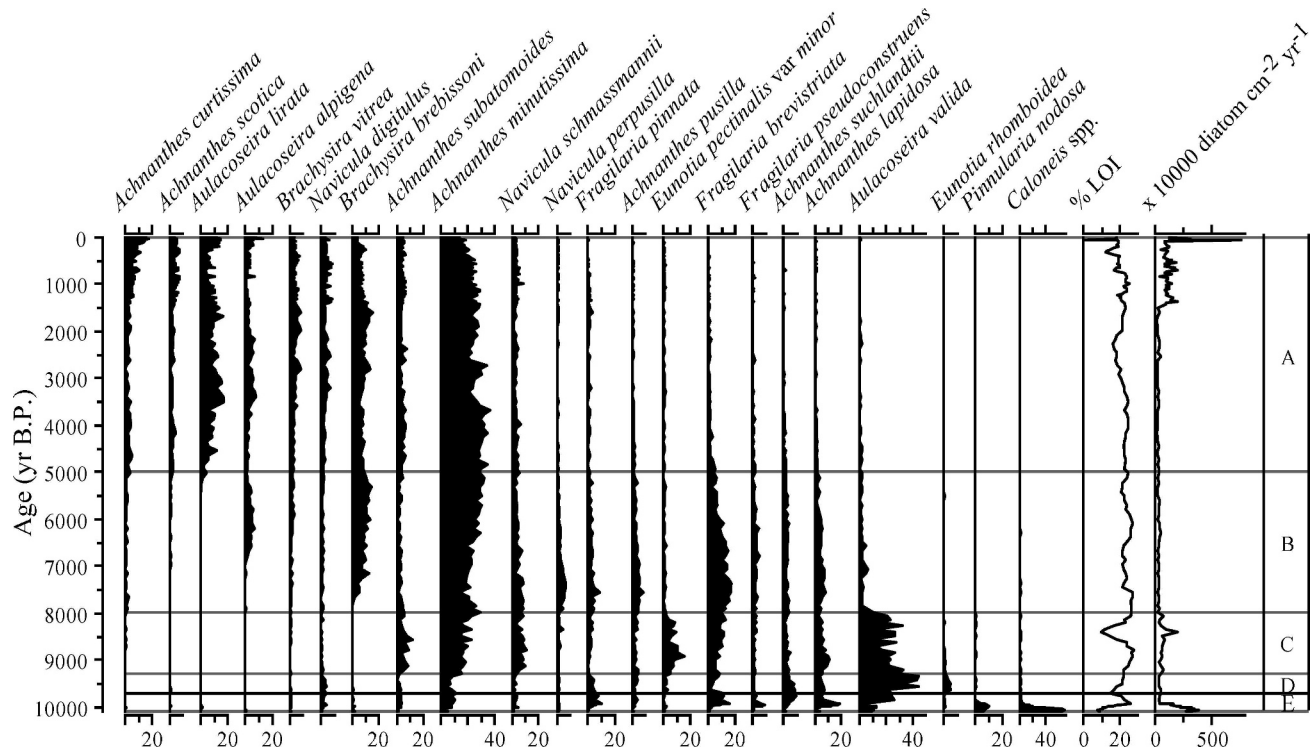
Fig. 2. Stratigraphical changes (zones A–E) of the most relevant diatom taxa in the sediment record of Lake Redon (RCA94). Values indicate relative abundance (%). Changes in loss on ignition (LOI) and total diatom flux are also indicated.

variables, and (3) unexplained variance (Borcard et al. 1992).

Transfer functions—The extent of the variability in the lake diatom assemblages was assessed using detrended canonical analysis (DCA). After confirming the large gradient in taxon distribution, we used training-set data to construct transfer functions for pH and alkalinity, using weighted-averaging partial least-squares (WAPLS; Birks et al. 1990; ter Braak and Juggins 1993). The predictive ability of the resulting models was assessed using bootstrap validation (1000 permutation cycles [Birks et al. 1990]). For alkalinity, we recoded negative values as zero values and used log transformation [log (alkalinity + 1]. This produces less noisy reconstructions and, in addition, it is closer to the expression as alkalinity enters the CO_2 calculations, because 'log CO_2' is proportional to 'log (Alkalinity) − pH'. The transfer functions were applied to the RCA94 core diatom data to reconstruct pH and alkalinity throughout the Holocene in Lake Redon.

CO_2 concentration and saturation—CO_2 concentrations throughout the Holocene in Lake Redon were calculated using reconstructed pH and alkalinity (Stumm and Morgan 1996) and equilibrium constants for 5°C. We used atmospheric values from Indermühle et al. (1999) to estimate CO_2 saturation values for most of the Holocene and measured CO_2 values for the most recent period (Keeling and Whorf 2005). We assumed atmospheric and water-vapor pressures of 77.16 kiloPascals (kPa) and 1.01 kPa, respectively.

Climate references—Climate references were only used in the present study to analyze fluctuations in CO_2 saturation. Lake ice-free (i.e., summer and autumn), and ice-covered (i.e., winter and spring) climatic conditions were distinguished, according to the reconstructions made in Pla and Catalan (2005) using, respectively, pollen and chrysophyte cyst records from the same core (RCA94). The winter and spring climatic signal was considered by recoding the altitudinal anomalies reconstructed by Pla and Catalan (2005) into ice cover duration (Fig. 3). We followed the close relationship between altitude and mean ice cover duration in lakes found by Thompson et al. (2005).

Results

Variance partition—Broad ranges of pH and alkalinity were considered (Fig. 4A), and the diatom data set included 233 taxa. Detrended canonical analysis indicated a main distribution gradient encompassing >4 standard deviations. Therefore, the diatom data had a large potential for environmental reconstructions. Partial RDAs indicated that both pH (8.7%) and alkalinity (5.6%) had significant ($p < 0.001$) independent explicative value, regarding the diatom assemblages from Pyrenean lakes. The shared explicative value (5.9%) was similar to the marginal capacity of each one. Consequently, we would not expect the marginal explicative capacity to be obscured by a mutually conditioned effect. The remaining unexplained variance was large (79.8%), but similar to that obtained for large data sets with many species. Species that were highly dependent on pH (e.g., *Cymbella aequalis*, *C. hebridica*,
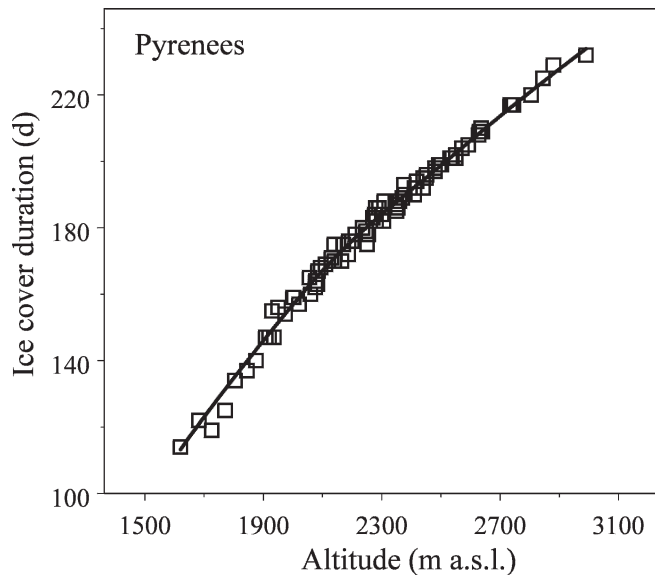
Fig. 3. Relationship between altitude and ice cover duration estimated according to Thompson et al. (2005) for the lakes of the Pyrenees. The LOESS interpolation shown was used to recode chrysophyte-based altitude anomalies (Pla and Catalan 1995) into ice cover duration in Lake Redon throughout the Holocene (Fig. 5).

Aulacoseira pfaffiana, Achnanthes austriaca var. *minor, A. marginulata, A. levanderi, A. austriaca* var. *helvetica*), differ from species that were highly dependent on alkalinity (e.g., *Achnanthes curtissima, Diploneis ovalis, Navicula schmassmannii, Tabellaria flocculosa, Fragilaria pinnata*), as indicated by the individual species variance explained by the marginal influence of pH and alkalinity, respectively (Fig. 4B). Taxa that are closely linked to pH tended to present optima at low pH (Fig. 4B). A comparison of the respective taxon optima for pH and alkalinity showed that taxa differentiated mainly by pH below alkalinity = 100 micro-equivalents per liter (μeq L^{-1}) and by alkalinity above pH = 6.8 (Fig. 4C). Therefore, we could expect that the respective transfer functions would not reconstruct similar patterns for pH and alkalinity.

Transfer functions—Transfer functions for both pH and alkalinity showed a high predictive capacity, as assessed by bootstrap root mean-squared error and the correlation coefficient (Table 1). For both transfer functions, the third component of the WAPLS provided the best results, but they do not significantly differ from the second components. As a consequence, we used the second-component reconstructions for further calculations. We also tried to develop a transfer function to reconstruct directly CO_2 concentrations. However, although estimated r^2 and root mean-square errors were acceptable (i.e., $r^2 = 0.73$), when tested for prediction using cross-validation the performance become very poor (i.e., jack-knifed $r^2 = 0.03$). This droop indicated that the apparent direct relationship between diatom composition and CO_2 was due to a spurious effect determined by the CO_2 dependence on
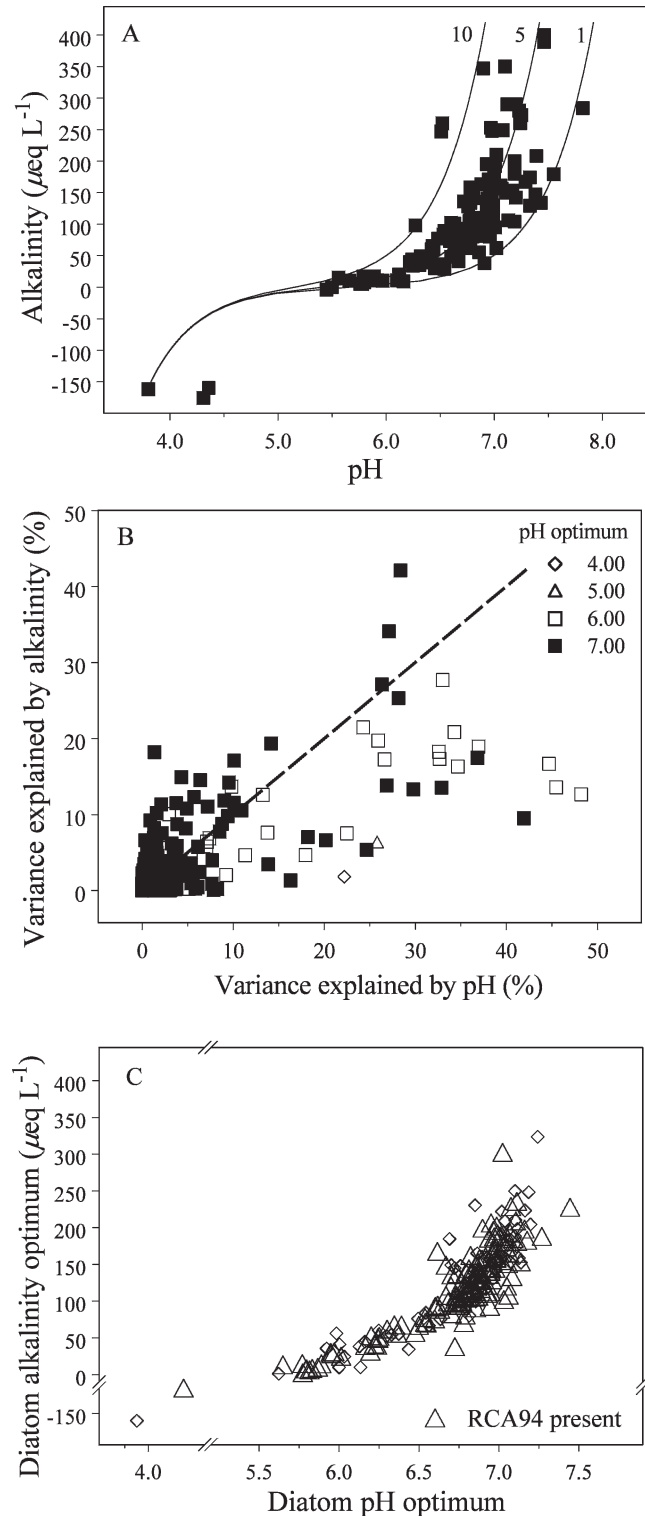

Fig. 4. (A) Relationship between alkalinity and pH in the training-set lakes. The reference lines indicate pH and alkalinity relationships for CO_2 in equilibrium with the atmosphere and at 5- and 10-fold saturation levels, respectively. (B) Relationship between the variance explained by pH and alkalinity for diatom taxa of the Pyrenean training set. Range of taxon pH optima is indicated by symbol style. (C) Relationship between pH and alkalinity optima for the 233 taxa considered in the training set. Taxa present in the Lake Redon (RCA94) record are indicated.

Table 1. Characteristics of the diatom transfer functions developed to reconstruct pH and alkalinity based on a Pyrenean lake training set.

	pH	Alkalinity
No. of samples	124	124
Descriptive statistics		(μeq L^{-1})
Minimum	3.8	0 ($-$176)
Maximum	7.82	400
Mean	6.68	113
Median	6.81	102
SD	0.61	89
WAPLS prediction model		
Data transformation		log(X+1)
Best component	2	2
Apparent r^2	0.883	0.907
Bootstrap r^2	0.748	0.817
Root mean-square error	0.210	0.169
Bootstrap root mean-square error	0.331	0.254
Bootstrap mean bias	-0.018	-0.011
Bootstrap maximum bias	1.258	0.683

alkalinity and pH and the respective relationships of some diatom species with these variables.

RCA94 diatom record—The record was rich in species (201 taxa), most of which were present in the training set (Fig. 4C), particularly the most common and abundant. Changes in assemblage composition throughout the Holocene included fluctuations in many taxa (Fig. 2). In order to summarize the observed changes, five zones were distinguished: Zone E, (10,085–9680 yr before present (B.P.); year 1950 considered as present) was characterized by very rapid changes in diatom assemblages. *Caloneis* spp. (e.g., *C. bacillum*) and *Pinnularia nodosa* were the most characteristic species, and markedly decreased at the end of this zone; *Fragilaria pinnata*, *F. brevistriata*, and *Achnanthes lapidosa* were also common. Zone D, (9680–9300 yr B.P.) was characterized by an increase in *Aulacoseira valida* and *Eunotia rhomboidea*. Zone C, (9300–8000 yr B.P.) was characterized by dominance of *A. valida* and a marked increase in epilithic diatoms such as *Achnanthes minutissima*, *Eunotia pectinalis* var. *minor*, *A. suchlandtii*, *Navicula digitulus*, *A. lapidosa*, and the small *Fragilaria brevistriata*, while *F. pinnata* declined. Zone B, (8000–5000 yr B.P.) was characterized by the disappearance of *A. valida* and stable proportions of a large No. of typical epilithic diatoms (*Achnanthes pusilla*, *Brachysira brebissonii*, *N. schmassmannii*, *A. curtissima*, *Navicula perpusilla*). Zone A, (5000 yr B.P.–present) was characterized by the emergence of *Aulacoseira lirata* and a decline in *A. lapidosa* and *F. brevistriata*.

According to diatom flux, Lake Redon primary production was higher both at the beginning of the Holocene (10,000–8000 yr B.P.) and from 1900 yr B.P. to the present. During the rest of the Holocene, production was lower and scarcely fluctuated (Fig. 2). Other proxies that were not included in this study, such as chrysophyte cysts or photosynthetic pigments (T. Buchaca unpubl.), confirm this general pattern.

The organic nature of the sediment (i.e., LOI) did not follow diatom flux changes (Fig. 2) or other primary production indicators (S. Pla pers. comm.). Therefore, LOI fluctuations can mainly be attributed to fluctuations in materials exported from the watershed, either because of changes in organic loading itself or due to its dilution with mineral particles.

Alkalinity and pH reconstructions—Alkalinity and pH fluctuation patterns reconstructed from the diatom record of Lake Redon clearly varied throughout the Holocene (Fig. 5A). Alkalinity was extremely low ($\sim$10 μeq L^{-1}) in the early Holocene ($\sim$10,000 yr B.P.), coinciding with the period of the highest pH recorded. Alkalinity progressively increased until $\sim$8000 yr B.P., thereafter fluctuating in a plateau of high values until 6000 yr B.P. In the following 500 yr, alkalinity values sharply declined from $\sim$80 μeq L^{-1} to 50 μeq L^{-1}. This decline continued gently during the next 3000 yr, down to values of $\sim$40 μeq L^{-1}. Thereafter, alkalinity fluctuated around this value until the present, with the exception of the period between 1400 yr and 1600 yr B.P., when values were lower ($\sim$30 μeq L^{-1}). Initially, pH values abruptly declined following the increase in alkalinity in the early Holocene, but from 9000 yr B.P. to the present there was a gentle decline from $\sim$7.1 to $\sim$6.8. In that tendency, there were oscillations of <0.2 pH units, with the exception of a marked increase around 1600 yr B.P. and a single-sample extreme decline at $\sim$834 yr B.P.

CO$_2$ fluctuations—We used pH and alkalinity values to calculate CO$_2$ water concentration and degree of saturation with respect to CO$_2$ atmospheric partial pressure throughout the Holocene (Fig. 5B). During the early Holocene, CO$_2$ values were quite low as a result of low alkalinity (<20 μeq L^{-1}) and relatively high pH (Fig. 5B). When compared with atmospheric levels at that time (Indermühle et al. 1999), the water CO$_2$ levels reflected a clear undersaturation (Fig. 5C), indicating higher in-lake CO$_2$-uptake than release. Undersaturation lasted until 9000 yr B.P., when the alkalinity increased above 40 μeq L^{-1}. The lake water progressively became supersaturated, reaching a plateau of around 200% from 8000 yr to 6000 yr B.P. Supersaturation dropped to $\sim$150% with the abrupt decline in alkalinity in the mid-Holocene, and oscillated around this value until 2000 yr B.P. From 2000 yr to 1500 yr B.P., water CO$_2$ was almost at equilibrium with atmospheric gas. Since then to the present day, the trend has been an increase in supersaturation. This trend varied in the last decades, when CO$_2$ values increased, but saturation did not, due to the comparatively higher rate of atmospheric CO$_2$ increase. In the latter historical period, there was a large peak in supersaturation (Fig. 5C), which corresponded to a single sample.

Discussion

Diatom-based CO$_2$ reconstructions—To date, alkalinity and pH have generally been considered as synonyms in
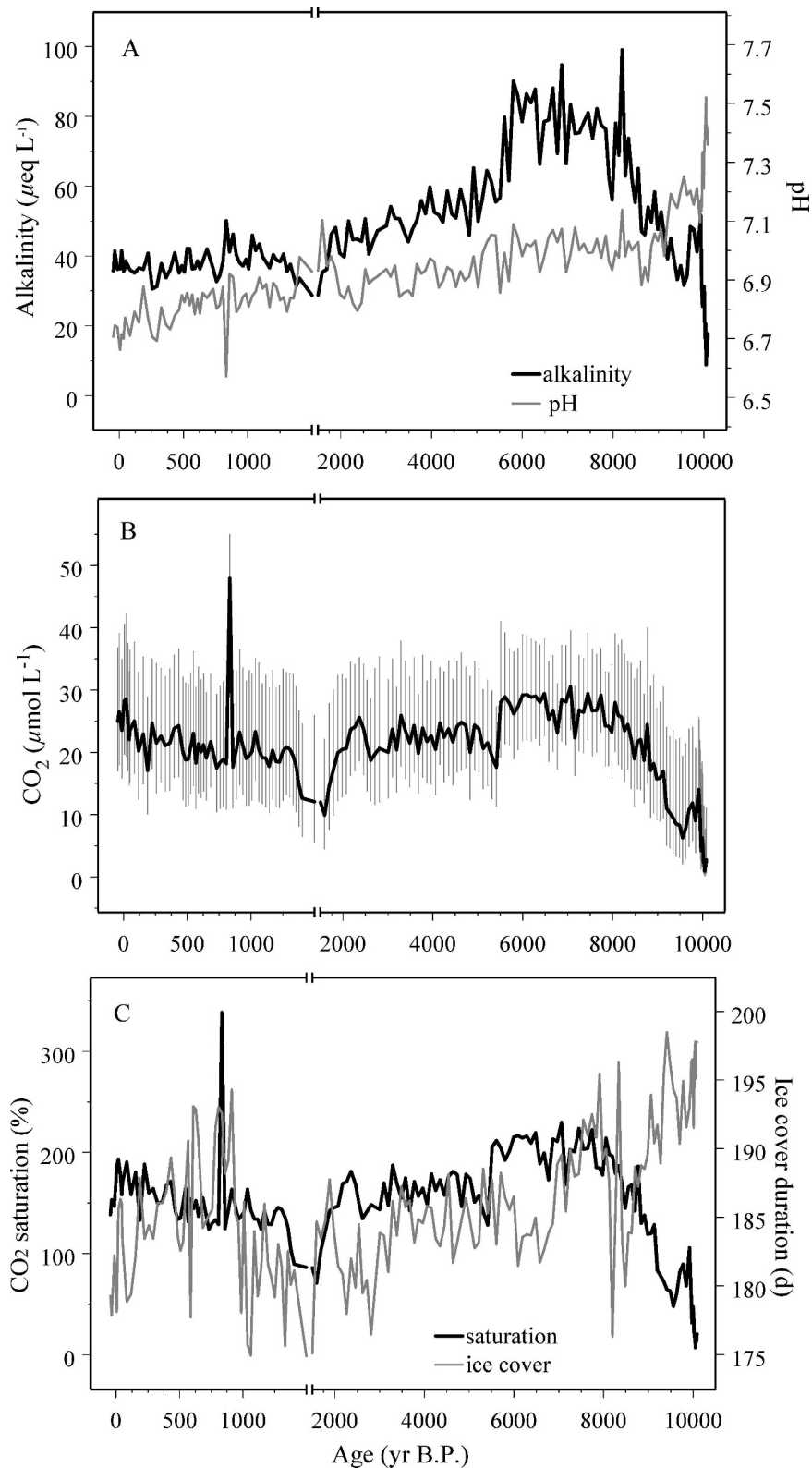
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Fig. 5. Lake Redon diatom-based reconstructions throughout the Holocene. (A) pH and alkalinity. (B) CO_2 concentration estimated by combining pH and alkalinity reconstructions on (A). Error bars were estimated from bootstrap-estimated standard errors for alkalinity and pH. (C) Comparison between CO_2 saturation and ice cover duration (Pla and Catalan 2005). The X-axis break indicates a change in the plotting scale because of higher temporal resolution of the data due to an increase in the sedimentation rate during the last ~2000 yr.
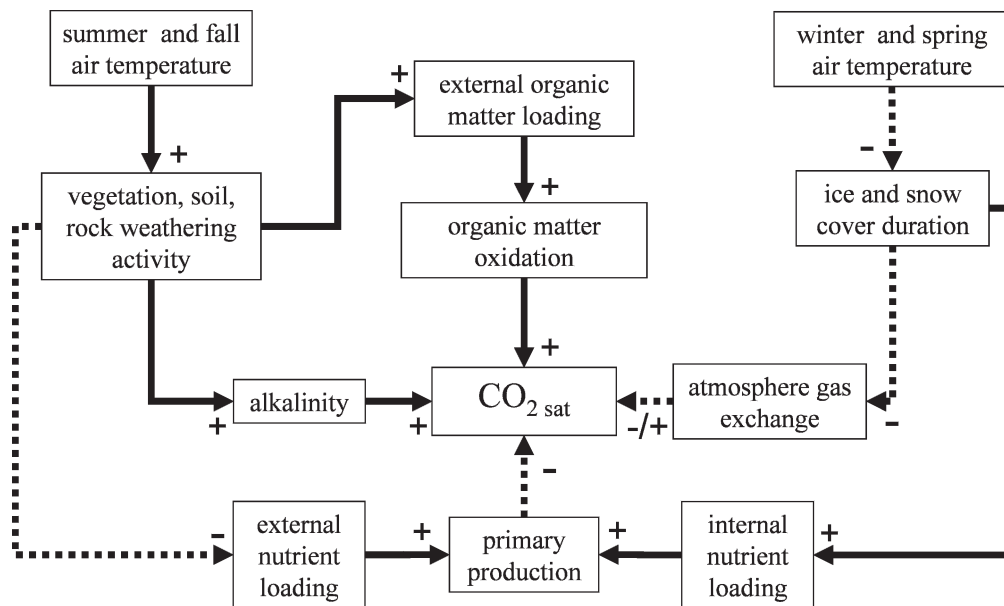
Fig. 6. Conceptual model of the process affecting CO_2 saturation levels in lake Redon and their relation with climate for ice-free (summer and autumn) and ice-covered (winter and spring) periods. The latter becomes more relevant when organic matter in sediments is low (LOI <22%). Solid and dotted arrows indicate positive and negative feedbacks, respectively.

paleolimnological studies. However, our results indicate that pH and alkalinity reconstructions showing distinct temporal patterns, and thus complementary information, can be obtained from a common diatom record. At least, two requirements are necessary in order to succeed in differentiating the two variables. First, pH for the training set must be measured with no CO_2 equilibration with the surrounding atmosphere. Second, the pH and alkalinity ranges in the training set have to be very broad, covering extremes both in acidity and well–acid-buffered waters. In that way, the optima for taxa with preference for extreme conditions will be more accurately estimated. At circumneutral pH, as in our case study and in many poorly acid-buffered lakes, the deviations between alkalinity and pH patterns are precisely reflected by diatom taxa with their optima in the respective extreme conditions. The optimum ranges of the taxa present in the Lake Redon record go far beyond the actual lake oscillations in both variables (Fig. 4C). In fact, if we restricted the lakes in the training set to granitic bedrock, the pH and alkalinity reconstructions hardly differed. Only when including bedrocks resulting in more acidic (i.e., Silurian slate and Cambro-Ordovician schist) and more basic waters (i.e., Devonian limestone), we succeeded in estimating the optima for those key indicative species.

With some exception, CO_2 has not been the subject of much direct interest in paleolimnological studies to date (Philibert and Prairie 2002). Our results indicate that an opportunity to reconstruct CO_2 levels and the whole carbonate system exists for paleolimnological studies. Accuracy and precision of the reconstructions may be a matter of debate, which is a recurrent but non-trivial issue in reconstructions based on fossil remains. Our pH and alkalinity transfer functions are excellent judging by comparison with well-accepted transfer functions (Cameron et al. 1999; Battarbee 2001). Unavoidably, the CO_2 calculations accumulate the uncertainties of the two functions. Direct CO_2 reconstruction could mitigate the error, but it proved unreliable, because diatom species do not segregate according to CO_2 but respond with different intensity to pH and/or alkalinity (Fig. 4B). All in all, precision of the reconstructions merit some considerations. First, estimated bootstrap standard errors for each sample in the record are lower than the average errors for the training-set samples. For instance, in our case, the reconstructed standard error for pH was generally <0.2, whereas the root mean-squared error of prediction in the training set was 0.33. Second, diatom composition throughout the core is not independent from sample to sample. Trends at certain time scales are more reliable than it would be for series of randomly selected independent samples from the training set, for instance. Therefore, error bars in our reconstructed CO_2 values are likely overestimations of the true uncertainties. Finally, concerning accuracy, it can be questioned to what extent CO_2 values can be estimated from pH and alkalinity in low-alkalinity waters (Herczeg and Hesslein 1984), regardless of its application in more buffered waters (Cole et al. 1994). The main point of concern may be the interference of DOC in the pH measurements; however, Lake Redon and the training-set lakes have DOC values far below 5 mg L^{-1}, which was found as a threshold for significant interference (Herczeg and Hesslein 1984). Low DOC is the case for most alpine lakes and many oligotrophic lakes. In any case, it remains a matter of further research to assess the degree of concordance between directly measured CO_2 concentrations and estimations from pH and alkalinity in alpine lakes.

CO_2 saturation and Holocene climate—From our case study, two climate-related aspects are worthy of discussion,
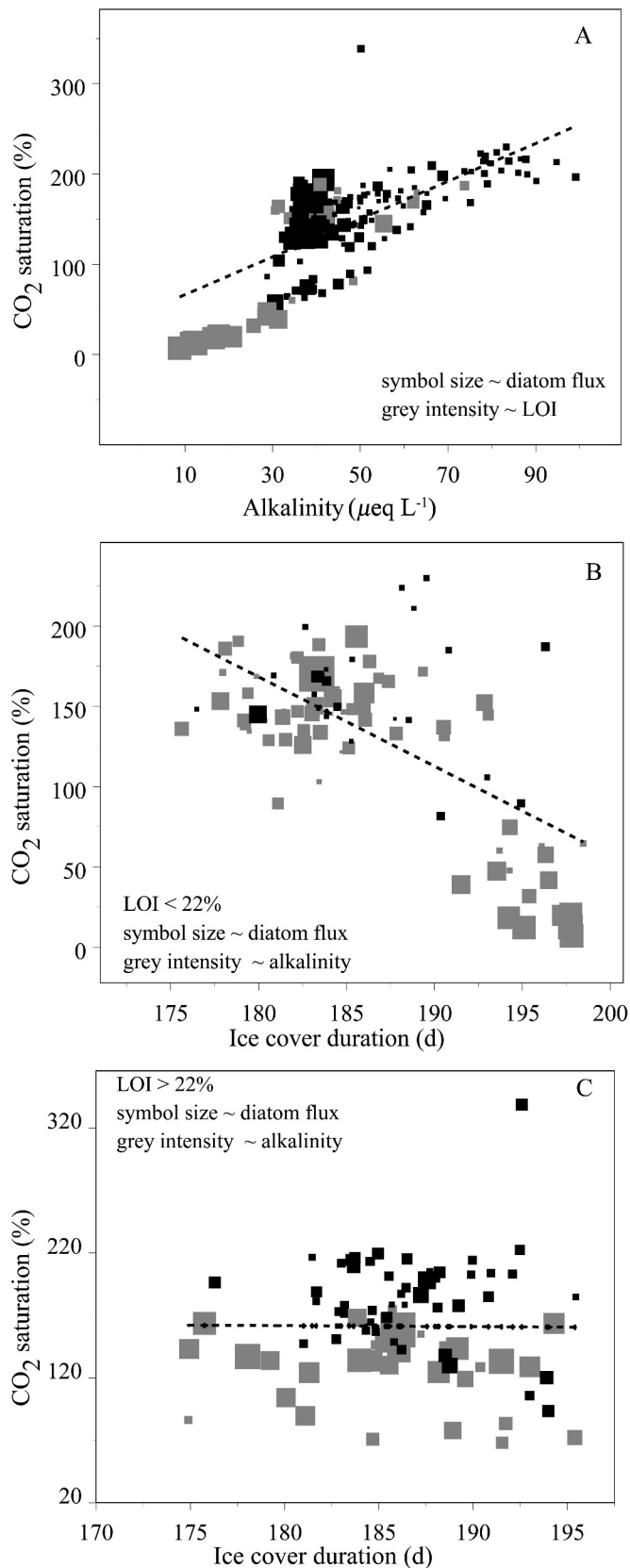
Fig. 7. (A) Relationship between alkalinity and CO_2 satura-
tion in Lake Redon throughout the Holocene. LOI values, as a
proxy for organic matter in the sediments, are indicated using a

those related to climate during the ice-free period (summer
and autumn) and the ice-covered period (winter and
spring), respectively. Pla and Catalan (2005) used pollen
(ice-free) and chrysophyte cysts (ice-covered) to show that
the main fluctuations in climate during these two periods of
the year followed decoupled seasonal patterns in the
Pyrenees throughout the Holocene. The summer tempera-
ture followed the pattern commonly found in many climate
reconstructions in Europe using pollen records, with a
climatic optimum between 8000 and 6000 yr B.P. and a
following decline during the late-Holocene (Reille and
Lowe 1993; Schmidt et al. 2006). Winter and spring
temperature patterns were, however, low during the early
Holocene and progressively increased towards late Holo-
cene. Therefore, the first part of the Holocene was more
continental than the second. What do these two contrasting
climate patterns mean in terms of lake CO_2 saturation?
(Fig. 6).

Alkalinity fluctuations during the Holocene in Lake
Redon followed ice-free period temperatures (Pla and
Catalan 2005) and were related to changes in rock
weathering (J. Catalan, J. Garcia, S. Pla and L. Camarero
unpubl.). It confirmed the hypothesis about pH and
temperature relationship in alpine lakes (Psenner and
Schmidt 1992). However, our results here add a new aspect
to the climate–carbon-cycle relationship, because they show
a dependency between alkalinity and the capacity for CO_2
saturation in the lake (Fig. 7A). CO_2 saturation can vary
according to alkalinity due to the slowing down effect in
the flux of water CO_2 towards the atmosphere that a higher
bicarbonate reserve determines (Broecker and Peng 1982).
Furthermore, according to our results (Fig. 7A), additional
mechanisms enhancing CO_2 saturation in warmer periods
can be an increase in both organic-matter export and
nutrient retention by watershed vegetation (Fig. 6), which
finally result in higher LOI and lower productivity (e.g.,
diatom flux). The increase in rock weathering implies a net
sink for atmospheric CO_2, because eventually carbonates
will precipitate in the sea (Kump et al. 2000). The capacity
to increase CO_2 supersaturation with increasing alkalinity
may appear as an additional, but spurious, retention of
CO_2 out of the atmosphere. However, the final net balance
may depend on how much of this CO_2 is finally
incorporated into organic matter and permanently buried.
These relationships are worth exploring in a larger No. of
systems, using both instrumental measurements of present
trends and reconstructions using the method proposed
here.

At the beginning of the Holocene, water was character-
ized by very low alkalinity (<20 μeq L^{-1}) and relatively

←

grey color scale, the lighter the color the lower the LOI level. (B)
Relationship between ice cover duration and CO_2 saturation for
periods with LOI <22%. Symbol size indicates diatom flux
intensity as a proxy for primary productivity in the lake. Grey and
black symbol colors distinguish between alkalinity values lower
and higher than 40 μeq L^{-1}, respectively. (C) As (B), but for
LOI >22%.

high pH (Fig. 5A). CO$_2$ saturation was lower than expected according the general relationship with alkalinity found for the whole Holocene period (Fig. 7A). According to the diatom flux and LOI, lake productivity was relatively high and organic-matter accumulation low during this initial Holocene period (Fig. 7A). It was probably due to the lack of watershed vegetation at that time, which resulted in low organic-matter export and nutrient (i.e., phosphorus) retention in the watershed. Water was undersaturated in CO$_2$, indicating the likelihood of severe carbon-limited primary production conditions, which at present only occasionally occur in deep chlorophyll maxima below the summer thermocline in some alpine lakes. This situation may be characteristic of early stages of cirque lake after glacier retreat.

The winter and spring climate determines ice cover duration (Livingstone 1997), which can affect CO$_2$ saturation by (1) physically limiting gas exchange with the atmosphere, and (2) favoring internal nutrient loading as decrease in oxygen in the deep parts of the lake facilitates phosphorus release from the sediments. The higher internal loading of phosphorus will eventually increase productivity and CO$_2$ take up during the ice-free period. Therefore, in principle, ice cover duration can favor both supersaturation and undersaturation (Fig. 6). Lower degassing enhances the CO$_2$ trend determined by ice-free processes (external nutrient and organic-matter loadings), whereas higher internal nutrient loading will tend to decrease CO$_2$ saturation. When comparing ice cover duration and CO$_2$ saturation patterns (Fig. 5C), at first glance it seems that the two variables fluctuated in opposite ways, at least during the first 8000 yr of the Holocene. However, the amount of organic carbon in the sediments (i.e., LOI) modulates the relationship. When LOI <22%, there is a negative relationship between the length of ice cover and CO$_2$ saturation. It indicates that the enhancement of internal nutrient loading with longer lasting ice covers increases primary production in the lake, thus reducing CO$_2$ saturation (Fig. 7B). However, when LOI >22% such a relationship does not exist (Fig. 7C), and higher or lower saturation mainly reflects productivity, as assessed by diatom flux. In general, high saturation values tend to match low diatom flux and high alkalinity, suggesting that the pattern is driven by summer climate (Fig. 6). Therefore, the effect of ice cover duration, and thus internal loadings, is hidden by large LOI values (high respiration potential). External loadings of nutrients and organic matter mainly may drive CO$_2$ fluctuations during these periods (Karlsson et al. 2008). However, when external organic-matter influx is low, ice cover duration becomes a more relevant source of variability for CO$_2$ levels. The unusually high value of CO$_2$ saturation found at 834 year B.P. is probably not an outlier (Fig. 5C); error bars do not indicate higher uncertainty in the estimation. It may result from a sequence of long ice cover periods, due to very harsh winters occurring at the beginning of the XII century (Pfister et al. 1998) that limited CO$_2$ exchange with the atmosphere.

In conclusion, our study shows that diatom reconstructions can be used to fully explore DIC system fluctuations in poorly acid-buffered and low DOC lakes at long-term temporal scales. Combined with other proxies, they can be useful for addressing questions of climate effects on lakes and particularly concerning CO$_2$ storage capacity, lake trophic dynamics and seasonality effects on air–water gas exchange. Quantitatively, changes in storage capacity (i.e., alkalinity) due to the link between rock weathering and air temperature during the summer and autumn period are probably the most remarkable. However, we showed that there are critical thresholds for certain state variables (e.g., alkalinity ~20 μeq L^{-1}; LOI ~22%) where sensitivity of CO$_2$ levels to climate-related ice cover duration and primary production fluctuations changes. Evidence of higher CO$_2$ retention capacity with increasing alkalinity has direct implications in the present global warming context (Sobek et al. 2005). DIC in freshwaters may not only increase because of higher rock weathering, but higher alkalinity may imply higher supersaturation capacity. The fate of this higher DIC concentration whether as buried organic matter, precipitated carbonate or degassed to the atmosphere becomes critical for the role of freshwater ecosystems in the global carbon balance (Cole et al. 2007).

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