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The Role of Autotrophic Picocyanobacteria in Calcite Precipitation in an Oligotrophic Lake

Maria Dittrich,[1] Philipp Kurz,[2] and Bernhard Wehrli[1]
[1]*Swiss Federal Institute for Environmental Science and Technology, EAWAG, Limnological Research Center, Kastanienbaum, Switzerland*
[2]*University of Zurich, Zurich, Switzerland*

A 1-year field study monitoring depth profiles of picoplankton and physicochemical data in the oligotrophic Lake Lucerne (Switzerland) showed that picocyanobacteria play an important role in the $CaCO_3$ precipitation process. Laboratory experiments with *Mychonastes* and *Chlorella*, isolated from Lake Lucerne and *Synechococcus* using ion selective electrodes, scanning electron microscopy and X-ray powder diffraction clearly demonstrated the potential of picoplankton for fast and effective $CaCO_3$ precipitation. The combination of a field study with laboratory experiments confirmed the previous reports of picocyanobacteria triggering the $CaCO_3$ precipitation in hardwater oligotrophic lakes. Electron micrographs of particles from the water column often reveal the size and shape of picoplankton cells covered by calcite. In addition the results from the laboratory approach indicated that algae and bacteria induced different precipitation mechanisms. Experiments with *Mychonastes* and *Chlorella* produced crystalline calcite completely covering the cells. Experiments with the cyanobacteria *Synechococcus*, however, yielded amorphous, micritic $CaCO_3$, indicating a different precipitation process.

Keywords ion selective electrodes, calcite precipitation, oligotrophic lake, picocyanobacteria

INTRODUCTION

The unicellular autotrophic picoplankton (APP) is an ubiquitous component of pelagic ecosystems (Stockner, Callieri, and Cronberg 2000) that dominates the total phytoplankton biomass and production in both oligotrophic lakes and oceans (Weisse 1993), but has often been overlooked due to its small cell size of 0.2 μm to 2 μm in diameter. Considerable efforts have been made to study the ecology and population dynamics of APP (Weisse 1993; Stockner et al. 2000). Cyanobacteria dominate the picoplankton community in most oligotrophic systems and are often more abundant than the larger components of the phytoplankton (Weisse 1993; Agawin et al. 2000; Stockner et al. 2000; Bell and Kalff 2001).

Relatively little is known about the interaction between APP and abiotic processes in ecosystems. Both laboratory experiments (Thompson and Ferris 1990; Schultze-Lam et al. 1992; Yates and Robbins 1999; Merz-Preiss 2000) and field observations (Robbins et al. 1996; Thompson et al. 1997; Hodell et al. 1998) suggest that APP may play an important role in calcite precipitation. Because of the small cell size and its high abundance picoplankton provides large surface areas for adsorption and heterogeneous nucleation.

However, so far no laboratory experiments were performed to investigate these biogenic precipitation processes over time, or to compare precipitation mechanisms induced by two types of picoplankton, eukaryotic green phytoplankton and prokaryotic cyanobacteria. In the present paper we combine field observations with laboratory experiments in order to correlate spatial and temporal patterns of picoplankton abundance and calcite precipitation in lake and to provide mechanistic information about calcite precipitation triggered by different kind of APP.

METHODS

Study Site, Sampling, and Chemical Analysis

Lake Lucerne is an oligotrophic hardwater lake in Central Switzerland that has been studied intensively from 1961 to 1992 (Bührer and Ambühl 1996). At a station located at 47°00′36.8″N/8°25′58.5″E we collected water samples from five depths (0, 5,

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Address correspondence to Maria Dittrich, EAWAG, Limnological Research Center, CH-6047, Kastanienbaum, Switzerland. E-mail: dittrich@eawag.ch

10, 15, and 20 m) by means of nonmetallic Van Dorn samplers and measured Secchi depth. Water samples were taken in biweekly intervals during spring and summer 2000 and on a monthly basis during late autumn and winter. Temperature and conductivity were measured in situ with a WTW-sensor and the alkalinity was analyzed by titration to pH = 4.2 (Titroprozessor 686, Metrohm) in the laboratory immediately after sampling. The pH was obtained before the titration started. For the determination of $CaCO_3$, aliquots were filtered through 0.45 μm cellulose acetate filters that were subjected to coulometric analysis assuming that all inorganic carbon was present as calcite (Lotter et al. 1997).

Dissolved calcium was determined in filtrated samples (0.45 μm, cellulose acetate) using an ion chromatograph (Metrohm 690). Particulate matter was collected on 0.2 μm polycarbonate Nucleopore filters that were air-dried for observation by scanning electron microscopy (SEM, Philips XL30). Subsequently these samples were analyzed by energy dispersive X-ray spectroscopy (EDX) for element analysis. The filters (0.2 μm black polycarbonate Nucleopore) prepared for cell counting were frozen immediately after filtration and picoplankton was counted as described by MacIsaac and Stockner (1993) within 1 month. Replicate filters were examined on an epifluorescence microscope (Zeiss Axiolab with a total magnification of 1600×) by counting 300 to 400 cells.

We calculated the $CaCO_3$ saturation index SI = IAP/K_{sp} where IAP is the observed ion activity product and K_{sp} represents the solubility constant. Activities of calcium and carbonate ions were obtained from measured concentrations and the activity coefficients calculated by the extended Debye-Hueckel equation (Stumm and Morgan 1996). The ionic strength, I, was calculated from conductivity data with the empirical relationship by Howard, Skirrow, and House (1984)

$$I = 0.0152\,\kappa_{20} * 10^{-3} + 0.162 * 10^{-3} \qquad [1]$$

where κ_{20} represents the conductivity [μS cm^{-1}] at 20°C.

Laboratory Experiments

For the laboratory experiments we used cyanobacteria *Synechococcus* PCC 7942 obtained from the Pasteur Institute, Paris, France (Rippka et al. 1981) and two eukaryotic picoplankton strains *Mychonastes* sp. and *Chlorella* sp. isolated from Lake Lucerne, which were identified by 18rDNA sequencing (Hepperle et al. 1998). Precipitation experiments were carried out at 20°C in duplicate for each picoplankton species in a 750-ml five-necked vessel placed in a transparent water bath in front of a fluorescent tube (Osram L36W/12-950) providing 20 μE m^{-2} s^{-1} to the culture. A supersaturated $CaCO_3$ solution prepared by the dropwise addition of 350 ml 6 mM $NaHCO_3$ to 350 ml 6 mM $CaCl_2 \cdot 2H_2O$ was added to the vessel which remained closed during the later experiment. The electrodes were inserted through the 45-mm portal and the setup was equilibrated for 1 h prior to the addition of picoplankton suspensions to the magnetically stirred supersaturated solution of $CaCO_3$. After the start of each experiment, two samples of the reaction mixture were taken for the picoplankton counts.

Calcite precipitation was monitored with a pH electrode and ion-selective electrode for CO_3^{2-} (Müller et al. 1998). The solutions of Tris buffered (pH = 8.4) $NaHCO_3$ and pH standards were used for calibration of CO_3^{2-} and the pH electrodes, respectively. The internal reference of the pH electrodes served as the reference for CO_3^{2-} electrodes. Electrode signals were transformed with an impedance converter and mean values of 600 measurements per min were recorded by a Lab View computer program (National Instruments).

The morphology of precipitates was characterized by SEM and the crystal structure was determined by X-ray powder diffraction (STADI P; STOE with monochromatic Cu Kα_1 X-ray radiation and a curved position sensitive detector). At the end of each experiment the chlorophyll-a concentration was analyzed using HPLC (JASCO with a UV-970 detector) measuring absorption at 430 nm. The dissolved Ca concentration was determined by ion chromatography.

RESULTS

Field Observations

The thermal stratification started in April and ended in November. Secchi disk readings remained constant from April to July at about six meters and declined to three meters in August within two weeks (Figure 1a). This decline in transparency was associated with decreasing concentrations of dissolved calcium (Figure 1c) and the increasing abundance of picocyanobacteria (Figure 2a) and centric diatoms (Bürgi, personal communication). The pH values of the surface water started to increase with the onset of the stratification in April (Figure 1b). The pH maxima were 8.20 and 8.32 in May and July, respectively.

The alkalinity at 0–5 m depth declined throughout the summer stratification and reached a minimum in September (Figure 1b). The concentration of the dissolved calcium at the surface (0–5 m depth) decreased from 1 mM in June to 0.5 mM in July. The saturation index for $CaCO_3$ peaked in May and August and declined below 1 afterwards. Calcite concentration, saturation index, and abundance of picocyanobacteria simultaneously peaked, while dissolved calcium concentration reached a minimum in August (Figures 1c, 2a).

In the water layer (0–10 m) cyanobacteria (annual mean 1.2×10^5 cells ml^{-1}) dominated the eukaryotic picoplankton (annual mean 3.0×10^4 cells ml^{-1}) during the whole year. The highest average abundance (3.4×10^5 cells ml^{-1}) was found at a depth of ten meters at the beginning of July (Figures 2b, 5b). Later, the abundance leveled off to about 7.0×10^4 cells ml^{-1}. In the upper layer (0–5 m) picoplankton cell numbers reached maxima in August (Figure 2a). Afterwards the population remained constant about 7.0×10^4 cells ml^{-1}. In the deeper water (10–20 m) the abundance increased in July and declined to a constant value of 1.8×10^4 cells ml^{-1} in October (Figure 2b). Figure 3(a, b) shows SEM photographs from a sample, which

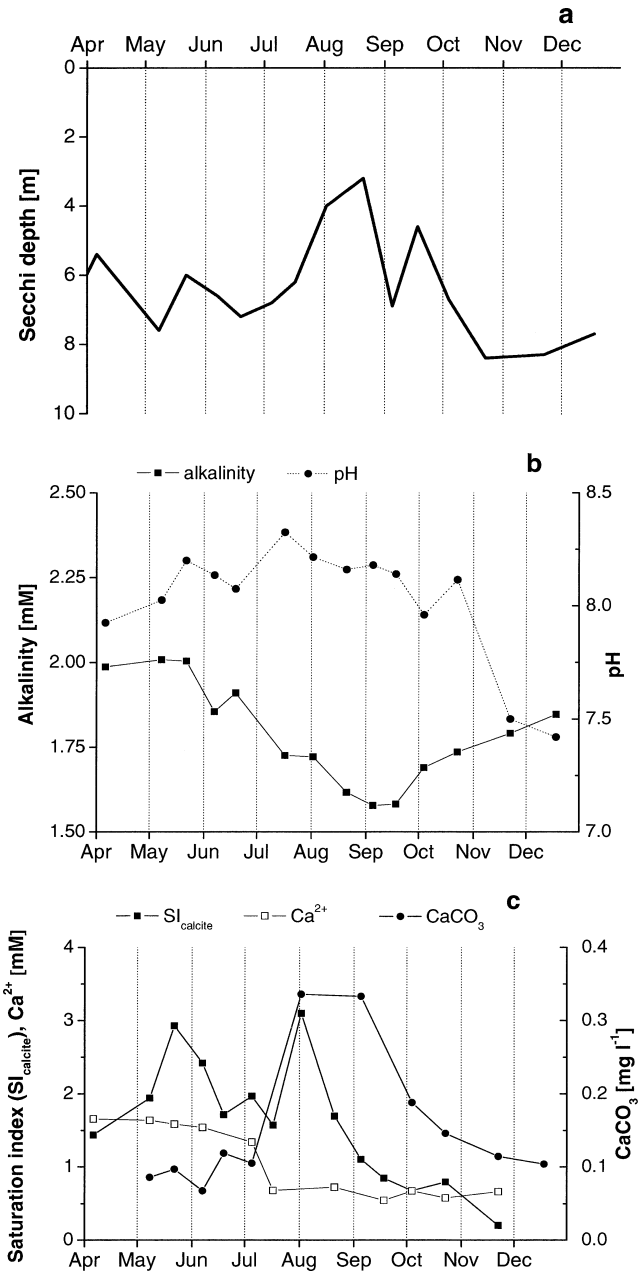

Figure 1. Seasonal trends in physicochemical data during the year 2000. (a) Secchi depth in Lake Lucerne. (b) Seasonal trends in pH and alkalinity for the 0–5 m depth interval. (c) Seasonal trends in the calcite saturation index, dissolved calcium, and calcite concentrations at 0–5 m depth.

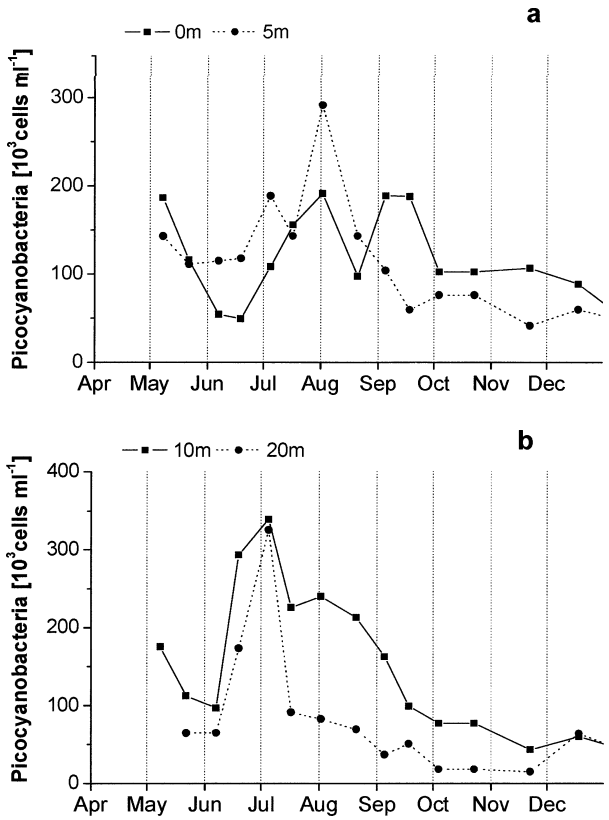

Figure 2. Picocyanobacteria cell abundance at four different water depths. Shallow water cell abundance represented by the 0- and 5-m curves (a) and deeper water cell abundance at 15- and 20-m depth (b).

was taken at maximum calcite concentration on August 2nd. The crystal-covered rods, which looked like the picocyanobacteria cells, consisted of $CaCO_3$ according to the EDX analyses.

The abundance of picocyanobacteria peaked twice, in late spring and summer. This bimodal pattern is typical for temperate lakes and was also observed in Lago Maggiore (Stockner et al. 2000). Temperature and the onset of stratification were identified as triggering variables for the spring peak of picoplankton, while zooplankton grazing is largely responsible for the early summer decline (Weisse 1993; Stockner et al. 2000).

LABORATORY EXPERIMENTS

Experiments with Eukaryotic Picoplankton

At the beginning of the experiments, the pH increased to approximately 9 due to the photosynthetic activity of the organisms (Figure 4a). We refer to this interval as the pH-drift time. In the experiments with 1.3×10^4 and 2.3×10^4 cell ml^{-1} of *Mychonastes*, the pH-drift time varied from 18 to 45 h. After this phase the precipitation started and pH and CO_3^{2-} dropped. The precipitation took approximately 20 h. At the end of a typical experiment, over a third of the dissolved calcium was precipitated from the solution corresponding to 0.045–0.1 mg of Ca for 10^6 cells (Table 1). According to the SEM images, the precipitated material consisted of aggregates of rhomboidal crystals as expected for calcite crystals (Figure 4b). Round and elliptic holes corresponding to picoplankton cells were present in many crystals. These crystals were identified as calcite by XRD. The experiments with *Chlorella* showed similar results.

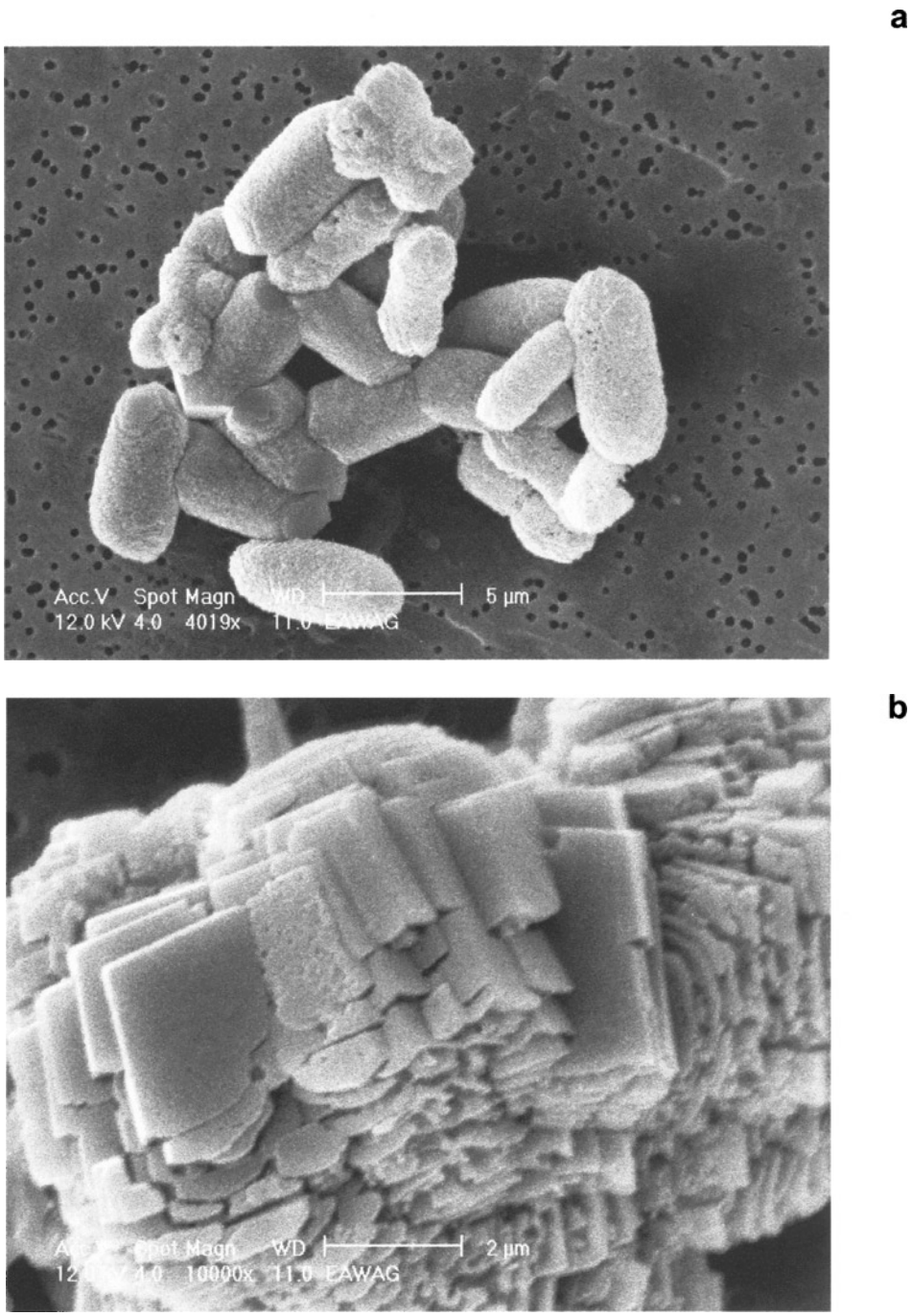

Figure 3. SEM photographs of calcite of Lake Lucerne in surface water on August 2, 2000 (a). Rod shaped particles like picocyanobacteria covered with $CaCO_3$ crystals (b).

Experiments with Picocyanobacteria

The concentrations of cyanobacteria ranged from 3×10^4 to 9×10^4 cells ml^{-1} in the experiments Syn1 and Syn2, respectively. In the first experiment the pH increased for 40 h and attained a maximum value of 8.95. During $CaCO_3$ precipitation, the pH dropped to 8.85. In the second experiment with the higher cell density, the pH rose more quickly and reached 9.05 after only 30 h. Subsequently it decreased to 8.30 (Figure 4c, Table 1).

In the first experiment only 13% of the initially dissolved calcium was removed from the solution whereas in the second experiment nearly a third of the calcium was precipitated.

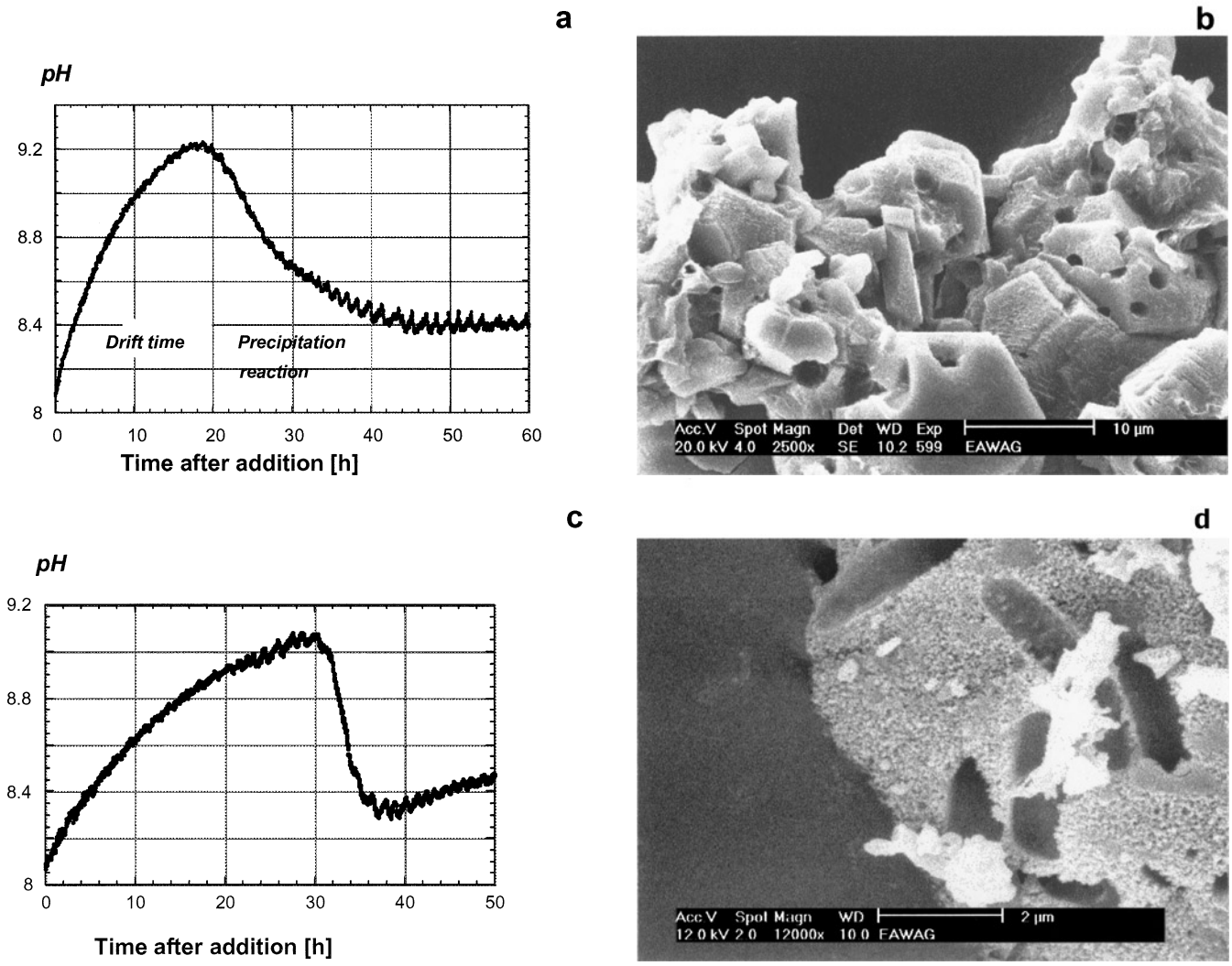

Figure 4. Changes of pH and CO_3^{2-} acquired with ISEs during an experiment with eukaryotic picoplankton *Mychonastes* (a) and picocyanobacteria *Synechococcus* (c), SEM photograph of carbonate precipitates in presence of eukaryotic picoplankton, holes in the carbonate structure correspond to picoplankton cells (b) and picocyanobacteria (d).

Calculated on a per-cell basis, equal amounts of $CaCO_3$ were produced in both experiments (Table 1). The precipitates consisted of very fine grains (<1 μm in diameter) that formed aggregates of up to 100 μm in diameter (Figure 4d). The electron micrographs show the shapes of the *Synechococcus* cells imprinted on the surfaces of these particles. The X-ray diffraction showed no distinct features, which is characteristic for fine-grained amorphous material.

Table 1
Precipitations experiments

Experiment	Cell abundance [10^3 cells·ml^{-1}]	Chlorophyll a [μg·l^{-1}]	pH drift time [h]	pH at start of prec.	Length of prec. [h]	% of Ca^{2+} precip.
Myc 1	13.2	142	45	9.05	50	41
Myc 2	22.9	448	18	9.20	30	34
Chl 1	6.85	222	25	9.00	10	26
Chl 2	8.71	379	11	8.95	4	29
Syn 1	33.4	130	40	8.95	40	13
Syn 2	94.1	324	30	9.05	8	32

DISCUSSION

Field Observation

Saturation Index and Picoplankton Abundance. Lake Lucerne is a typical hard-water lake in which calcite precipitation occurs regularly during times of high primary productivity. Bloesch (1974) quantified the calcium sedimentation rate for Lake Lucerne as 110 g Ca m^{-2} a^{-1}, which is lower than values like 180 and 160 g Ca m^{-2} a^{-1} observed in the eutrophic lakes Sempachersee and Lago Lugano, respectively (Ramisch et al. 1999). Calcite accumulated in the sediment of Lake Lucerne contributing between 34% and 17% to the total dry weight in the surface layer and at 45-cm depth (Staub 1981). Both the accumulation rate obtained from measurements of sediment cores (100 g Ca m^{-2} a^{-1}) and the sedimentation rate indicated that some dissolution (10 g Ca m^{-2} a^{-1}) was occurring in the hypolimnion of Lake Lucerne. The smaller calcite dissolution flux in Lake Lucerne compared to Sempachersee (60 g Ca m^{-2} a^{-1}) or Lago di Lugano (170 g Ca m^{-2} a^{-1}) corresponds to the less intensive mineralization processes in the hypolimnion of Lake Lucerne.

Based on the qualitative model of Bell and Kalff (2001) we estimated for Lake Lucerne that the picoplankton contributed almost half (48%) to the total biomass. This is consistent with results on fractionated phytoplankton samples obtained for Lake Lucerne by Uehlinger and Bloesch (1989). The size fraction of 0.8–3 μm contributed 33% (range 3–63 %) to the total primary production in Lake Lucerne significantly affecting pH values in the euphotic zone.

Despite the oversaturation in May no calcite precipitation was evident from the calcite concentration curve and the Secchi depth observations (Figure 1a). Dissolved ions such as orthophosphate and dissolved organic matter may inhibit crystal growth (House 1987; Kleiner 1990) and prevent calcite precipitation. Inhibition of $CaCO_3$ precipitation was also observed in other field studies such as in Lake Constance, where Stabel (1986) found no correlation between high saturation indices and $CaCO_3$ sedimentation rates. However, it seems unlikely that phosphate and DOM at the low concentration of <1 to 7 μg P l^{-1} and 1 mg DOM l^{-1} really could inhibit $CaCO_3$ precipitation in May 2000.

The second peak of the saturation index in August occurred simultaneously with the maximum of the calcite concentration, the maximum of picocyanobacteria and the decline of the Secchi depth (Figures 1c, 5a). At the beginning of August, the cyanobacteria population (3×10^5 cells l^{-1}) outnumbered the larger phytoplankton with cell size >10 μm (5×10^3 cells l^{-1}, Bürgi, personal communication) by two orders of magnitude. In June the cell numbers of cyanobacteria and phytoplankton were similar (6×10^4 and 8×10^4 cells l^{-1}, respectively) and no peak of the larger phytoplankton was observed at that time. This suggests that a saturation index exceeding 1 is not sufficient to induce the precipitation of calcite in surface water, if picocyanobacteria are not dominant.

In addition to the synchronous timing of a picoplankton bloom and calcite precipitation in August also a spatial correlation was observed. The calcite concentration in the water column was highest at 10 m depth on July 5th, which corresponded to the maximum in the cyanobacteria cell abundance (Figure 5b). In order to check whether this feature was related to a local calcite production, we estimated the sedimentation velocity of calcite particles of different size. Following Stokes' law the sedimentation velocities of calcite with 5, 10, 20, and 30 μm diameter are 1, 5, 21, and 48 m d^{-1}, respectively. To reach the 10 m water depth at the sampling time of 10 a.m., large calcite crystals (20–30 μm) should have formed during the night, which is rather improbable. Small calcites of 5–10 μm could have formed during several days before the sampling date, but this would lead to a rather uniform profile. The fact that the largest fraction of calcite particles were agglomerated to a size of more than 10 μm supports the interpretation of a local source of biogenic calcite at the depth of the picoplankton maximum.

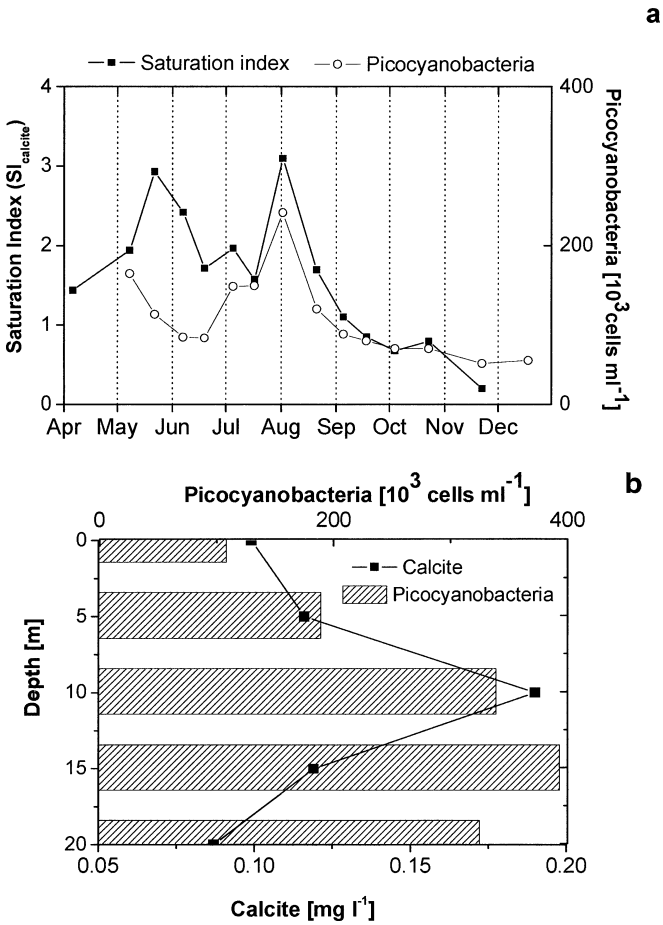

Figure 5. Seasonal trends in saturation indices and picocyanobacteria abundance in 0–5-m depth (a) and depth profiles of picocyanobacteria abundance and calcite concentration on July 5, 2000 (b).

Similar evidence for a calcite precipitation by picoplankton at greater depths was reported in two recent studies. Ohlendorf and Sturm (2001) observed highest calcite concentration between 6 and 9 m water depth in the high-altitude Lake Hagelseewli (2,339 m a. s. l.). The authors suggested that calcite precipitation was related to the occurrence of picoplankton. Also in Fayetteville Green Lake, highest calcite concentrations occurred at 8 m water depth and were related to the growth of the cyanobacterial picoplankton *Synechococcus* (Thompson et al. 1997).

Laboratory Experiments

Dynamics of Calcite Precipitation. The calcification potential of a number of phytoplankton species has been demonstrated and general trends for the kinetics of planktogenic calcification have already been evaluated (Küchler-Krischun 1990; Hartley et al. 1995; Heath et al. 1995; Yates and Robbins 1998). In this study not only pH but also carbonate was monitored in experiments with both cyanobacteria and algae, thus providing more detailed information. Both types of picoplankton, *Synechococcus* cyanobacteria and the eukaryotic *Mychonastes* sp. and *Chlorella* sp., were found to induce the precipitation of $CaCO_3$. In all experiments the precipitation process developed in three stages: (1) a pH-drift period, (2) the actual precipitation reaction, and (3) an equilibration phase. The time intervals of the stages as well as the concentration changes found in this work were comparable to the results of other experimental studies on $CaCO_3$ precipitation by algae (Hartley et al. 1995; Heath et al. 1995). During the first phase, conditions for $CaCO_3$ nucleation, particularly a pH increase from $\approx$8.1 to $\approx$9 were created by the photosynthetic activity of the cells. The rate of this pH shift varied from one picoplankton species to the other. As a general trend there was a correlation between the pH-drift time and the cell number in the suspension.

The pH drift occurs in our experiments as a consequence of CO_2 uptake by the growing picoplankton in the closed vessel. By combining data from the pH and the carbonate records we may elucidate the processes occurring in the first stage of the experiments. For the pH increase from 8.2 to 9.2 a CO_3^{2-}-shift of 21×10^{-5} M was calculated for an equilibrium speciation. The measured concentration of CO_3^{2-} increased by only 13×10^{-5} M in the experiments indicating a loss of alkalinity by nucleation processes at the cell surfaces. Similar calculations can be performed for the pH decrease associated with calcite precipitation. Equilibrium calculations based on changes of dissolved calcium (Table 1) predict a pH drop to 7.2, while the observed pH value was 8.4, indicating that the CO_2 consumption by growing algae still prevailed even during the precipitation phase. However, in the equilibration phase a large part of the cells seems to have been covered by $CaCO_3$ so that only limited photosynthesis remained possible.

Mechanisms of Precipitation. In the microenvironment close to the picoplankton cell walls the pH might be higher than in the bulk solution because some cells release OH^- as a result of the uptake of HCO_3^- during photosynthesis (Borowitzka 1989). Therefore, the over-saturation of the surface layer around the cells most likely exceeds that of the bulk phase and nucleation at a significant rate becomes possible. If this happened, the whole mineralization process could be classified as biologically induced (Borowitzka 1989).

On the other side, heterogeneous nucleation might be promoted on the cell surface of microorganisms, where negatively charged macromolecules acting as nucleation sites are able to bind and accumulate significant quantities of metal ions such as Ca^{2+} (Beveridge and Fyfe 1985). If this were the case, the $CaCO_3$ biomineralization by picoplankton would follow a "biologically controlled" mineralization process according to the terminology of Borowitzka (1989).

No detailed studies on the cell membranes or the microenvironments of any of these three picoplankton species have been carried out so far. The two mechanisms of $CaCO_3$-nucleation by an unspecific supersaturation or by specific nucleation at the cell wall can therefore not be conclusively resolved with the existing data. However, the SEM pictures from the experiments with three picoplankton species provide some indirect evidence for the unspecific mechanism. The precipitated material shows either aggregates of small crystals at random orientation, which are X-ray amorphous, or the precipitated $CaCO_3$ crystals contain marks and holes of the same shape and size as the cells used in the experiments.

Crystals with similar marks and holes have also been found in other experiments on $CaCO_3$ precipitation by algae, as well as in field studies (Stabel 1986; Küchler-Krischun and Kleiner 1990). This suggests that $CaCO_3$ precipitation mediated by freshwater algae often starts in the microenvironment close to the outer cell membrane. Micritic $CaCO_3$ has been seen as the product of precipitation processes at extremely high saturation (Küchler-Krischun 1990). In the *Synechococcus* experiments presented here there is no obvious reason for micrite formation. Similar pH values as in the cases of *Mychonastes* and *Chlorella* were reached at the start of precipitation, so the bulk solutions reached a comparable saturation index of $SI = 10$. Therefore, the micritic $CaCO_3$ in the *Synechococcus* experiments probably has its origin in the special microenvironment of the *Synechococcus* cells.

Comparison between Laboratory Experiments and Field Observations

The crystals precipitated in experiments with *Mychonastes* and *Chlorella* were well formed and large enough in size to be clearly identified as calcite by XRD. Similar looking crystals, nucleated by *Chlorella* and other algae, were found in Lake Constance (Stabel 1986) and Lake Michigan (Strong and Eadie 1978). The morphology of the precipitate found in the laboratory experiments with *Synechococcus* was rather unexpected and no micritic aggregates were observed in Lake Lucerne. However, rod shaped particles like picocyanobacteria covered with $CaCO_3$

crystallites were found in lake samples by electron microcopy (Figure 3a).

This morphological difference could be caused either by different strains present in the lake and in the laboratory experiments or by the higher concentrations of dissolved calcium in the experiment compared to the lake (3 and 1 mmol l^{-1}, respectively). The pH values observed during the experiments were higher than those measured in the field study in 2000, but the long-term observation in Lake Lucerne showed pH values up to 8.9 in lake water (Bührer and Ambühl 1996). The duration and magnitude of precipitation may be critical to understanding the process. Biologically induced precipitation of calcite may contribute significantly to the lake carbonate budget. A suspension of 10^4 cells ml^{-1} of *Synechococcus* precipitated about 30% of calcite in the laboratory experiments. The annual abundance of picocyanobacteria in the lake was around 10^5 cells ml^{-1} and the alkalinity decreased during summer by about 22% from 2 mmol l^{-1} to 1.55 mmol l^{-1} (Figure 2c). The laboratory experiments therefore support the view that the picoplankton activity might be responsible for an important fraction of the calcite precipitation during the summer stratification in Lake Lucerne.

SUMMARY AND CONCLUSIONS

Our field study combining chemical data of the water column with picoplankton abundance showed that APP is an important part of the phytoplankton community in Lake Lucerne and peaked simultaneously with calcite concentration. Temporal and spatial correlations of cyanobacteria and solid calcite, as well as images of bacterial shape particles, which were covered with calcite crystals, indicated that picoplankton plays an important role in calcite precipitation in Lake Lucerne. This class of phytoplankton has to be considered in studying the biogeochemical cycling of oligotrophic hardwater lakes.

The laboratory experiments showed that picoplankton is able to precipitate calcite very effectively within a couple of days. The crystals precipitated by cyanobacterial and eukaryotic picoplankton showed different morphological structure. We observed small calcite crystals and micritic carbonate during the experiments with eukaryotic and cyanobacterial picoplankton, respectively. These first observations indicate that different cells may induce distinct precipitation processes.

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