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ORIGINAL PAPER

Algal-silica cycling and pigment diagenesis in recent alpine lake sediments: mechanisms and paleoecological implications

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Abstract The quality and interpretability of the paleobiological record depends on the preservation of morphological and geochemical fossils. Siliceous microfossils and sedimentary pigments are often cornerstones in paleoecology, although the microbial and geochemical processes conducive to their preservation remain poorly constrained. We examined sediments from an alpine lake in Banff National Park (Alberta, Canada) where diatom frustules are completely dissolved within 50 years of deposition. Diatom dissolution, silica recycling, and diagenetic alteration of algal pigments were investigated, in conjunction with pore-water geochemistry and microelectrode profiling of the sediment–water interface. Analysis of sediment trap material showed ~90% of biogenic silica (BSi) production is lost prior to burial. Silica flux calculations, based on dissolved silica (as H_4SiO_4) in pore-waters, show a further ~6% of total BSi is returned to the water column from the upper 4 cm of sediments, implying that only ~4% of total BSi is permanently archived in sediments. In situ sediment pH and O_2 profiles reveal that aerobic respiration by bacteria fully consumes oxygen by a depth of 4 mm into the sediment, with associated strong pH and redox gradients. During sedimentation and early diagenesis, diatoms undergo loss of extracellular polymeric substances that coat their frustules, promoting silica dissolution and leading to the loss of the microfossil record by a depth of 3.25 cm. Sedimentary pigments similarly undergo rapid degradation, but diatom-related carotenoids persist below the depth of silica dissolution. This work provides new insights on diagenetic processes in lakes, with broad implications for the interpretation of sedimentary proxies for algal production.

Keywords Dissolution · Diatoms · Alpine lake · Algal pigments · Biogenic silica · Extracellular polymeric substances

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Introduction

Diatoms primarily biomineralize orthosilicic acid (H_4SiO_4) to construct the solid portion of their cell walls, called frustules. It is the preservation of frustules as amorphous biogenic silica ($nH_2O{\cdot}SiO_2$, hereafter BSi) in lake sediments that has led to their common use in freshwater paleoecology (Smol 2008;

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Stoermer and Smol 1999). However, the dissolution of diatoms within lake sediments may compromise interpretations of the sediment record (Ryves et al. 2006), making the full understanding of conditions for dissolution imperative. A number of experimental studies have examined conditions that promote diatom dissolution revealing important roles for pH, ionic strength, temperature, silica concentration, alkalinity and alkali metals (Lewin 1961; Barker et al. 1994; Flower 1993). In general, warm, alkaline and saline lakes have the lowest preservation potential for diatom frustules. However, the recycling of diatom silica also occurs in cold and chemically dilute lakes, both from lake sediments into the water column or within the water column (Schelske et al. 1984; Conley and Schelske (1989); Battarbee et al. 2005).

Diatoms are encased in extracellular polymeric substances (EPS), which are produced during cell formation by the cytoplasm and composed mainly of amino acids and polysaccharides (Hecky et al. 1973). Although the thickness of EPS can vary between diatom taxa, its biochemical composition is fairly consistent (Duke and Reimann 1977). Under appropriate conditions, diatom EPS also provide a suitable substrate for heterotrophic microbial communities. In the marine environment, microbial processes are directly linked to the dissolution of diatom frustules and the recycling of silica in the photic zone (Bidle and Azam 1999). The importance of analogous processes has not previously been considered in lakes, despite experimental results that suggest this very possibility. For example, the early observations of Lewin (1961) showed that freshwater diatom dissolution was greater for acid-cleaned frustules relative to either living or dead counterparts retaining EPS coatings.

Photoautotrophic pigments are another important component of lake-sediment organic matter, providing a biochemical record of primary production and the degree of diagenesis. Sedimentary chlorophylls, carotenoids, and their derivatives are readily quantified using high pressure liquid chromatography (HPLC), and used to reconstruct historical changes in whole-lake photoautotrophic abundance and community composition (Leavitt and Hodgson 2001). The preservation of pigments in lake sediments has previously been explored (Buchaca and Catalan 2008; Leavitt 1993; Leavitt and Findlay 1994; Verleyen et al. 2004). The majority (>95%) of primary algal pigments degrade in the water column within days. In alpine lakes, low concentrations of light-attenuating dissolved organic carbon (DOC) and high ultraviolet radiation irradiance (UVR) are common (Vinebrooke and Leavitt 2005), implying high rates of pigment photodegredation during sedimentation. Post-depositional alterations occur on longer timescales (years to decades), leaving a more stable inventory of derivative compounds.

Understanding the processes influencing preservation of algal biomass in alpine lakes is especially important due to the sensitivity of these ecosystems with respect to climate change and anthropogenic nutrient deposition. In many cases, paleoecological and geochemical investigations of recent sediments have proven important in demonstrating the ecological consequences of human stressors (Baron et al. 2000; Battarbee et al. 2002; Wolfe et al. 2003). For the most part, these studies have assumed that sediment proxies of algal production, including BSi, are well-preserved due to cold water temperatures, prolonged winter ice cover, and dilute, oligotrophic water chemistries.

In this study, we investigate the mechanisms responsible for rapid diatom dissolution and pigment diagenesis in a small alpine lake. We present the first investigation into the importance of BSi regeneration within an alpine lake. In so doing, we evaluate the hypotheses that: (1) diatom frustule dissolution is accelerated by microbial activity that degrades diatom EPS; (2) pore-water pH transients associated with organic matter degradation drive diagenetic processes affecting diatoms and pigments; and (3) diatom pigments can provide an indication of diatom production despite the loss of the frustule.

Site description

Pipit Lake is located in Banff National Park, Alberta, Canada (2217 masl; 51°36′59″N, 115°51′42″W; Fig. 1a). The lake is 10.6 ha with a catchment area of 254 ha, and a maximum and mean depth of 20.6 and 12.6 m, respectively. It is situated just above alpine tree-line within a northeast facing cirque containing a number of perennial snow-packs that feed the lake (Fig. 1b). Bedrock geology of the catchment is Upper Paleozoic dark grey argillaceous limestone and dolomite with some black shales and trace lignite seams. The basin is primarily talus and bedrock, with

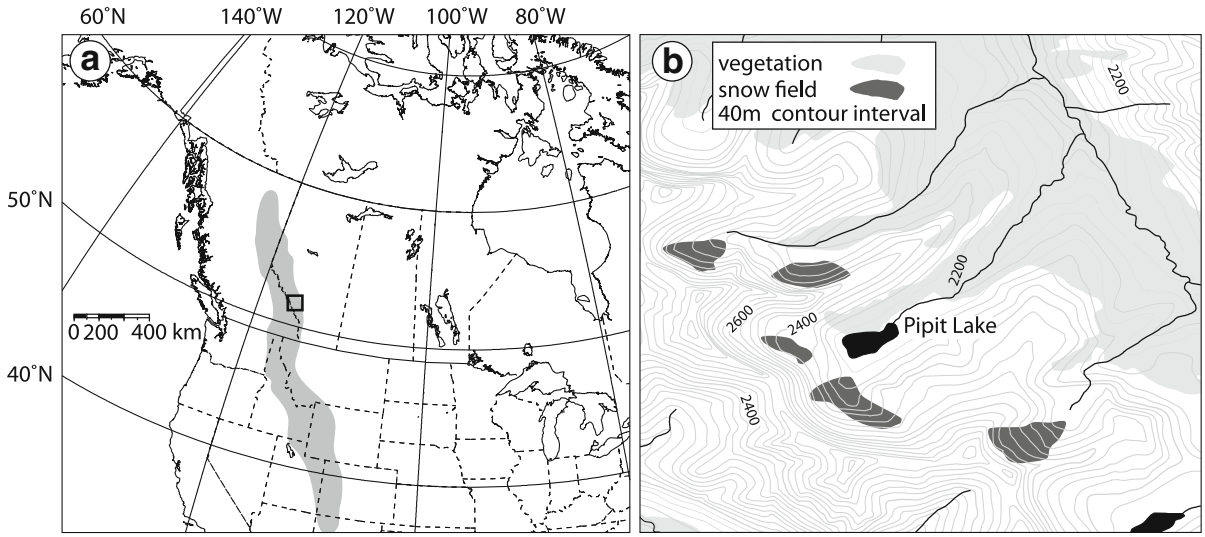

Fig. 1 Location of study site. **a** The North American continent, where the *shaded area* represents the extent of the Rocky Mountains. **b** Topographic map of the Pipit Lake catchment

some vegetated areas (<10% of the catchment) that include grasses, mosses, and a copse of subalpine fir immediately north of the lake. The lake waters are alkaline with a mean pH of 8.1, and high concentrations of Mg^{2+} and Ca^{2+} (Table 1). The lake is clear, oligotrophic, and currently fishless (Parker and Schindler 2006). The water column becomes weakly stratified for a short period (~4 weeks) during summer, and the flushing rate is in the order of months. Pipit Lake was stocked from 1964 to 1966 with rainbow trout (*Onchorhynchus mykiss*) and brook trout (*Salvelinus fontinalis*) as part of the greater stocking program of alpine lakes in Banff (Donald 1987). Introduced salmonids failed to reproduce and Pipit was fishless after 1977. Zooplankton typical of fishless alpine lakes (*Hesperodiaptomus arcticus* and *Daphnia middendorffiana*) are present, in addition to a pelagic macroinvertebrate, *Gammarus lacustris* (Donald 1987; Parker and Schindler 2006; Wilhelm et al. 1998).

Bi-weekly to monthly limnological monitoring of Pipit Lake has taken place during the summer since 1991, as summarized in Table 1 (Schindler, unpublished data). The water quality data reveal no obvious temporal trends over this period. Water chemistry is representative of alpine lakes in this region: low dissolved organic carbon, total dissolved P, NO_3^-, and relatively high conductivity, alkalinity, and pH.

Methods

Sediment collection, pore-waters and geochronology

Two sediment cores were retrieved from the deepest section of the lake (~20 m) on August 16, 2007 using a Glew-type gravity corer (Glew et al. 2001). Both cores were sealed in hypolimnetic water for transport, unsealed immediately prior to in situ pH and dissolved O_2 (DO) profiles being generated by microelectrode on the undisturbed cores, and analyzed within 6 h of collection. Microelectrodes, with a tip diameter of ~50 µm, were inserted vertically into the sediment cores using a Unisense MM33-2 micromanipulator operating in 100 µm intervals. The probes included a Clark-type O_2 microelectrode (OX50, Unisense, Århus, Denmark) calibrated to atmospheric oxygen and zeroed in 0.1 M ascorbic acid, and a pH microelectrode (PH50, Unisense) calibrated using commercial pH buffers (pH 4, 7, and 10). Microsensor data was collected using a Unisense PA2000 picoammeter, a high impedance pH meter (Radiometer Analytical SAS, Villeurbanne, France), and a PC data acquisition system. Immediately thereafter (within 8 h of collection), both cores were sub-sampled directly into 50-ml centrifuge tubes at 0.25-cm intervals for the first 10.0 and 0.5 cm from then on. Pore-waters were

Table 1 Pipit Lake summer mean water chemistry (1991–2007)

	Hypolimnion			Epilimnion			Inflow 1			Inflow 2			Outflow
	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	Mean	SD	*n*	
NO_3 (μg l^{-1})	55.66	23.17	83	71.66	37.84	94	131.64	49.95	40	125.89	31.43	34	127.00
NH_3 (μg l^{-1})	14.17	32.91	65	6.57	7.32	59	5.08	3.76	29	4.32	4.01	22	5.00
Total dissolved N (μg l^{-1})	157.64	168.34	81	134.61	88.06	93	180.05	93.75	40	167.39	81.65	34	171.00
Particulate N (μg l^{-1})	52.46	25.08	41	25.93	14.30	48	15.56	26.79	31	7.94	6.80	27	16.80
Total P (μg l^{-1})	9.17	4.50	83	5.19	4.39	92	6.00	4.94	40	4.32	1.47	34	5.10
Total dissolved P (μg l^{-1})	4.58	3.71	82	2.92	1.89	90	3.96	0.91	40	4.20	1.55	34	2.10
Dissolved organic C (μg l^{-1})	2.13	3.25	79	2.27	3.81	91	0.50	0.35	31	0.50	0.43	28	0.40
Particulate C (μg l^{-1})	405.85	171.01	41	252.30	183.71	49	463.40	1,165.68	32	120.15	51.52	28	142.23
Dissolved Si (mg l^{-1})	1.90	0.50	82	1.10	0.27	96	0.68	0.19	40	1.05	0.16	34	1.04
Cl^- (mg l^{-1})	0.36	0.24	73	0.37	0.30	86	0.18	0.09	38	0.16	0.09	33	0.12
SO_4^{2-} (mg l^{-1})	17.55	4.74	81	12.59	4.56	94	10.69	8.81	40	5.14	1.30	34	8.91
Na^+ (mg l^{-1})	3.07	4.83	77	1.29	0.42	90	0.19	0.09	40	0.24	0.07	34	0.86
K^+ (mg l^{-1})	0.39	0.10	77	0.28	0.08	90	0.14	0.03	40	0.17	0.03	34	0.22
Ca^{2+} (mg l^{-1})	35.54	4.93	77	27.59	2.90	90	21.73	3.55	40	21.76	1.39	34	25.20
Mg^{2+} (mg l^{-1})	14.73	2.34	77	10.53	2.35	90	5.97	1.24	40	5.75	0.45	34	8.65
Conductivity (μS cm^{-1})	283.62	34.79	82	214.85	28.65	95	155.05	29.29	40	149.07	10.15	34	182.00
pH	7.98	0.22	83	8.11	0.22	96	8.05	0.14	40	8.08	0.12	34	8.16
Alkalinity (mg l^{-1} $CaCO_3$)	130.34	15.97	83	97.34	11.01	96	68.29	7.29	40	71.28	4.38	34	88.63
HCO_3^- (mg l^{-1})	158.68	19.71	83	118.20	12.77	96	83.26	8.89	40	86.92	5.34	34	108.05
CO_3^{2-} (mg l^{-1})	0.11	0.72	83	0.30	1.05	96	NA	NA	NA	NA	NA	NA	0
Absorbance (350 nm)	0.04	0.02	81	0.04	0.09	94	0.02	0.02	38	0.02	0.02	33	MDL
Turbidity (NTU)	0.88	0.40	81	0.55	0.28	92	0.72	0.96	40	0.18	0.11	33	0.30

Outflow data is based on a single sample

NA not analyzed, *MDL* method detection limit

immediately extracted on one core by centrifugation at 1,500 rpm for 10 min. The supernatant was collected using a syringe and immediately filtered through 0.45-μm Teflon syringe filters and acidified with 1 M HCl. Samples were also kept out of natural light to avoid photo-degradation of fossil pigments. Both cores were frozen within 24 h of collection and freeze-dried.

Geochronology was established through ^{210}Pb decay (measured as ^{210}Po) by alpha-spectroscopy on a single core. The constant rate of supply (CRS) model was used to estimate ages and sedimentation rate based on the radioactive decay of excess (or unsupported) ^{210}Pb above the background (or supported) ^{210}Pb activity (Appleby and Oldfield 1978). In order to infer estimated CRS ages within the second core, downcore % organic matter (%OM) measurements were correlated, confirming consistent sedimentation between the two adjacent cores.

A sediment trap was deployed between October 2005–July 2007 at a depth of 19.5 m (0.5 m above the deepest point of the lake) and emptied approximately every 9 months. Locating the trap near the deepest point of the lake enables measurement of materials destined for the immediate region of the two cores. The trap had a length:width aspect ratio of 2:1, with an active area of 100 cm^2.

Diatom analysis

Slides for diatom frustule enumeration were prepared by digesting ~100 mg of dry sediment in 30% H_2O_2 to oxidize labile organic matter. Diluted slurries were spiked with a known quantity of exotic pollen grains for calculating absolute microfossil concentration (Wolfe 1997), and permanently mounted using Naphrax® (Battarbee et al. 2001). Diatoms and chrysophyte cysts were enumerated with differential interface contrast light microscopy at 1,000× and also examined by scanning electron microscopy (SEM) with a JEOL-6301F field emission system. Untreated sediment trap material was also examined under SEM.

Biogenic and pore-water silica

The analysis of biogenic silica (BSi) in sediments provides a quantification of the total production of siliceous algal fossils (diatoms and chrysophyte cysts). We used a modified wet alkali digestion method from DeMaster (1991) on approximately 30 mg of freeze-dried sediment (Conley and Schelske 2001). Sediments were digested in a 1% Na_2CO_3 solution, while in a shaking water bath at 85°C, and aliquots were removed at 3, 4, and 5 h for analysis of dissolved Si. This method allows for the sequential digestion and separation of BSi and the aluminosilicate fraction. The concentration of dissolved silica (as H_4SiO_4 and abbreviated herein as DSi) in the extract and pore-water was then analyzed using the heteropoly blue method (Clescerl et al. 1999) with a Beckman DU 520 spectrophotometer operating at 815 nm. All BSi results are expressed as wt% SiO_2.

The BSi method precision for triplicate digestions gave a coefficient of variation of 6.8%, while duplicate analysis on all the extracts gave relative percent differences (RPDs) <10% for those samples above the method detection limit (~0.5 wt% SiO_2 for 30 mg of sediment). Pore-water DSi samples were run in duplicate with most intervals showing <4% RPD, those which were outside an acceptable RPD (>10%) were re-run giving a coefficient of variation (CV%) <4% for each sample. All method blanks were below detection limits.

Metals, loss on ignition, and X-ray diffraction

Analysis of labile Fe and Mn within sediments was carried out using acid digestion and inductively-coupled plasma mass spectrometry (ICP-MS) on a Perkin Elmer Elan 6000. Sediments were digested in 10 ml of 1.6 M trace element grade HNO_3 at room temperature for 24 h, which targets loosely bound elements and not those hosted within the mineral lattices. Both sediment eluates and pore-water samples were injected into the ICP-MS for measurements of [Fe] and [Mn]. Duplicate analyses, carried out on 10% of the samples, were <3% RPD. Method blanks were below method detection limits.

Freeze-dried sediments were analyzed for % organic matter (% OM) and % carbonate-C (% CO_3) using the loss-on-ignition technique at 550 and 950°C, respectively (Heiri et al. 2001). Freeze-dried sediments above and below the noted depth of complete diatom dissolution were also analyzed for mineral composition through X-ray diffraction using a Rigaku Geigerflex Power Diffractometer with a Co tube and a graphite monochromator.

Sedimentary pigments

Pigment concentrations were quantified using reverse-phase high pressure liquid chromatography (HPLC) (Vinebrooke et al. 2002). Pigments were first extracted from freeze-dried sediments using an acetone:methanol solution. Extracts were then filtered (0.2-μm pore nylon), dried under N_2, and reconstituted using a precise volume of injection solution. Chromatographic separation was performed with an Agilent 1100 Series HPLC equipped with a Varian Microsorb 100Å C18 column, and pigment detection using in-line diode array and fluorescence detectors. Pigment concentrations were quantified via calibration equations and an electronic spectral library constructed using standards purchased from DHI Water and Environment, Denmark. Jeffrey et al. (2005) was consulted as a key reference for taxonomically diagnostic pigments. All concentrations are expressed by mass normalized to sediment organic matter.

Sedimentary silica flux

Solute flux from sediments have been estimated and measured in a number of studies (Calvert 1983; Hofmann et al. 2002). Estimations of fluxes are based on Ficks Law of diffusion, assuming a steady-state relationship, and the observed dissolved concentration gradient in the pore-waters. We used the following relationship to calculate flux (F) in g m^{-2} $year^{-1}$:

$$F = -D_e \phi (\partial C/\partial z), \quad (1)$$

where D_e is the effective solute diffusion coefficient (cm^2 s^{-1}), ϕ is the sediment porosity in the upper 3 cm (calculated from dry bulk density) and $\partial C/\partial z$ is the concentration gradient as calculated from pore-water analysis. The slope of the interstitial [DSi] linear model ($r = 0.89$; $p \ll 0.001$) is used as the concentration gradient. We adjusted the molecular diffusion coefficient (D) of silica in free solution, 5.5×10^{-6} cm^2 s^{-1} (Wollast and Garrels 1971) for tortuosity, accounting for the porosity of sediment at the surface, using the formula (Ullman and Aller 1982):

$$D_e = \phi^2 D \quad (2)$$

The estimation of permanently buried silica is based on measured BSi concentrations (a mean of 0.45 ± 0.05 wt% SiO_2 below the depth of complete dissolution) and the ^{210}Pb calculated sedimentation rate (g m^{-2} $year^{-1}$).

Results

Contemporary limnology

There are two notable features of the long-term limnological data: (1) the DSi concentrations in hypolimnetic waters (mean 1.9 mg l^{-1}) are consistently and significantly ($p < 0.001$) higher than epilimnetic (mean 1.1 mg l^{-1}) and inflowing stream waters (mean 0.7 and 1.1 mg l^{-1}) (Table 1), and (2) there is a significant negative relationship between hypolimnetic DSi and plankton diatom biomass ($r = -0.48$; $df = 35$; $p = 0.002$), while the same is not true of epilimnetic DSi and plankton diatom biomass ($r = 0.05$; $df = 34$; $p = 0.76$). These observations provide a first-order indication that sediments are acting as a net source of DSi to the hypolimnion and the standing diatom crop.

Lake sedimentation

Supported ^{210}Pb activities were reached at a depth of 5 cm in the Pipit Lake core (Fig. 2a). Unsupported ^{210}Pb decays near-exponentially from surface activities of 0.53 Bq g^{-1} to a mean supported activity of 0.05 Bq g^{-1}. The stability of the sedimentation rate through the unsupported ^{210}Pb section of the core is confirmed by the linear relationship between cumulative dry mass and log ^{210}Pb activity (Fig. 2b). The mean mass accumulation rate of Pipit Lake is estimated to be 252 ± 30 g m^{-2} $year^{-1}$. Similarly, from a core collected in 1991, Leavitt et al. (1994) found the estimated ^{210}Pb mass accumulation rate in Pipit to be 290 ± 27 g m^{-2} $year^{-1}$. Estimated CRS ages in the section of the core where dissolution is taking place (0–3.25 cm) are well constrained with low dating errors (Fig. 2c). The correlation of %OM between the two cores is highly significant ($r = 0.8$; $p < 0.001$; $df = 32$), confirming similar sediment accumulation between them (Fig. 2d). However, we should acknowledge that sediment focusing is an unknown factor in our calculation of sedimentation rates. We were unable to quantify reliable sedimentation rates from the sediment traps. A single trap near the bottom of the lake has the potential to continuously

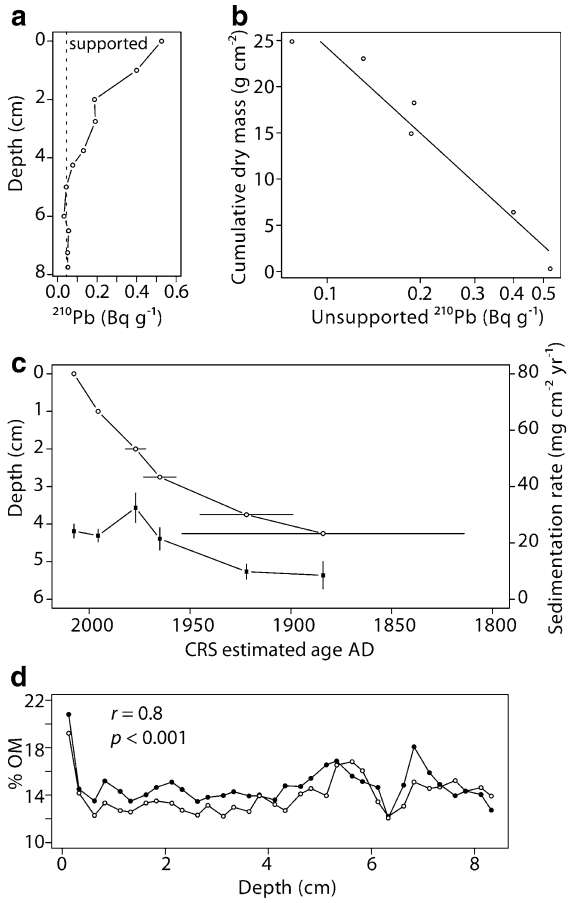

Fig. 2 ^{210}Pb chronology of the sediment core. **a** ^{210}Pb activity (Bq g^{-1}) with depth; the depth of background or supported amount of ^{210}Pb is shown with the *dashed line*. **b** Linear relationship between the log of unsupported ^{210}Pb (Bq g^{-1}) and cumulative dry mass (g cm^{-2}), which establishes a constant sedimentation rate in this portion of the core. **c** CRS estimated ages with depth (cm) and sedimentation rate (mg cm^{-2} year^{-1}) over the estimated dates. **d** The correlation of % organic matter between the two cores taken from Pipit Lake, where the dated core (*open circles*) is significantly similar to the core which pore-waters were extracted from (*black circles*)

trap resuspended settling material and not reflect the true settling rate or sediment flux to the lake bottom (Nuhfer et al. 1993). However, this does not preclude measurements of the relative composition of the settling material.

Diatom analysis

Micrographs of the uncleaned sediment collected from the sediment trap during the summer showed an abundance of littoral periphytic diatoms (*Gomphonema* spp., *Achnanthes* spp., *Cocconeis* spp.) with *Cyclotella* cf. *comensis* being the dominant planktonic form (Fig. 3). The EPS coating and microbial activity is evident on a number of benthic diatoms (Fig. 3a, b), while many of the *C.* cf. *comensis* specimens have preserved siliceous nodules on the cell face (Fig. 3c), a characteristic feature among many representatives of this genus (Round et al. 1990).

Peroxide-cleaned surface-sediment diatoms clearly show signs of dissolution (pitting or etching of the cell wall) on a number of specimens, particularly on *C.* cf *comensis*. Tracking *C.* cf. *comensis* with depth in the cleaned sediment core shows the progressive loss of silica beginning at the valve margins and ending with the central area before dissolution is complete (Fig. 4).

The absolute diatom concentrations from the Pipit lake sediments show a loss of frustules at a depth of 3.25 cm (Fig. 5), corresponding to sediment accumulation of the past ~50 years. The thicker and less ornamented siliceous cysts of chrysophytes persist to ~5 cm, at which point they too are lost to dissolution.

Biogenic silica and XRD

BSi within the sediment trap averaged 16.2 ± 1.7% BSi over the period Oct. 2005–July 2007 (Table 2). Summer abundance of BSi was greater than the winter collections. The loss of BSi from the sediment trap to the surface sediment is ~90% (16.2–1.5%). Sediment core BSi reflects the same profile seen in the diatom concentrations, with a 66% decrease in the upper 1.5 cm, from 1.5 to ~0.5% (Fig. 5). Measurable amounts of BSi persist beyond the depth of complete frustule dissolution, indicating that some fraction of the solid-phase silica must be present as highly degraded frustules or authigenic silica-containing minerals that are not discernable by light microscopy; X-ray diffraction analysis (data not shown) shows no change in sediment mineral composition above and below the depth of complete frustule dissolution, indicating that solid phase silica was present in amorphous form (e.g., as lepispheres) as opposed to crystalline aluminosilicates such as illite or smectite. This 'background' amount of BSi is roughly 0.5% and represents the approximate method detection limit.

The measured BSi in sediments and corresponding DSi in pore-waters are inversely correlated ($r = -0.51$; $p = 0.011$; $n = 24$). The dissolution of BSi

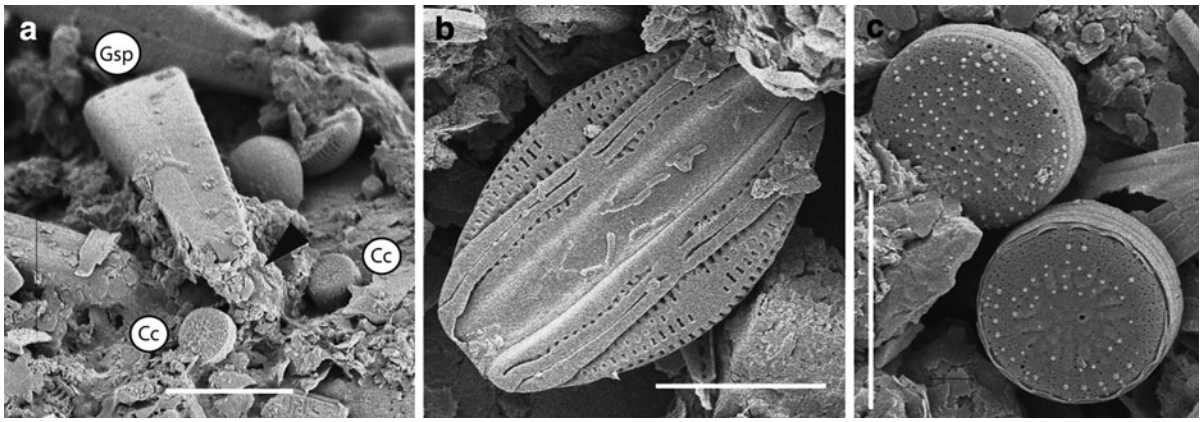

Fig. 3 Scanning electron micrographs of sediment trap material. **a** An epiphytic diatom *Gomphonema sp*. (Gsp) can be seen with an EPS coating and mucilage stalk (*arrow*) and complete cells of *Cyclotella* cf. *comensis* (Cc). **b** EPS coated *Amphora sp*. with bacterial cells present on the surface. **c** Complete *C*. cf *comensis* cells with no EPS evident, but silica nodules evident on the valve face. *Scale bars* are 10 μm in *a* and 5 μm in *b* and *c*

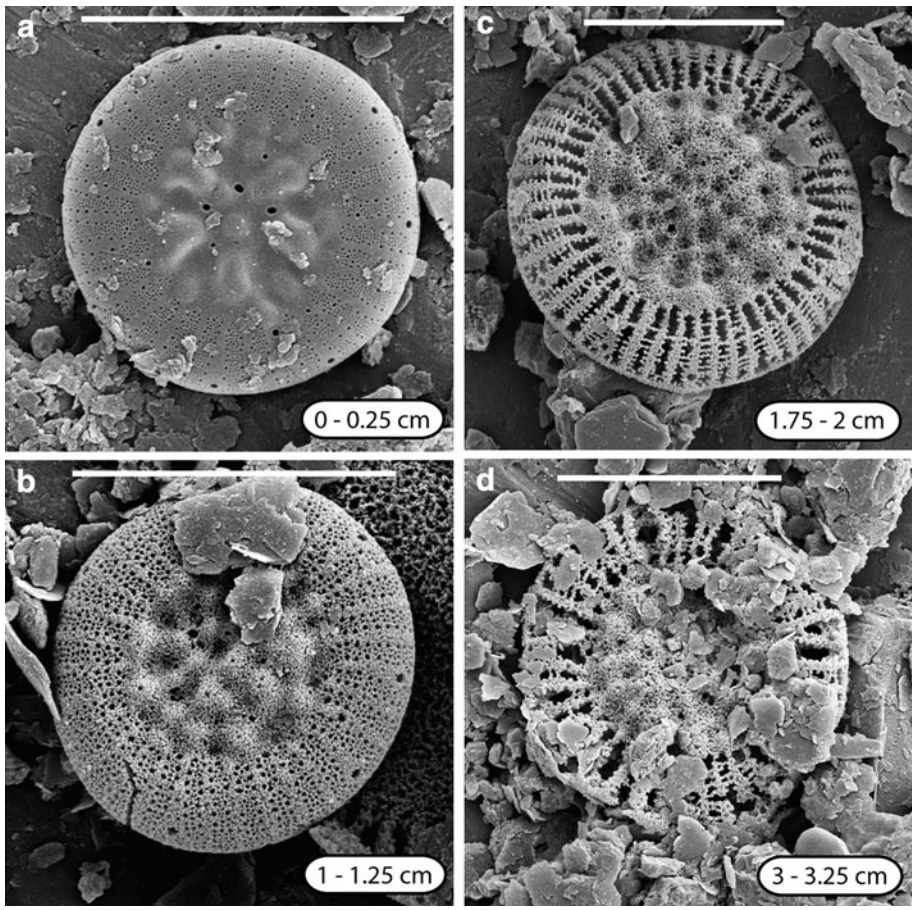

Fig. 4 **a** A cleaned valve from the surface sediment, no pitting or nodules are evident. **b** At 1 cm depth pitting and etching become more evident; **c** dissolution of puncta on the valve margins at 1.75–2 cm; **d** leaving the straie, before complete dissolution. All *scale bars* are 5 μm

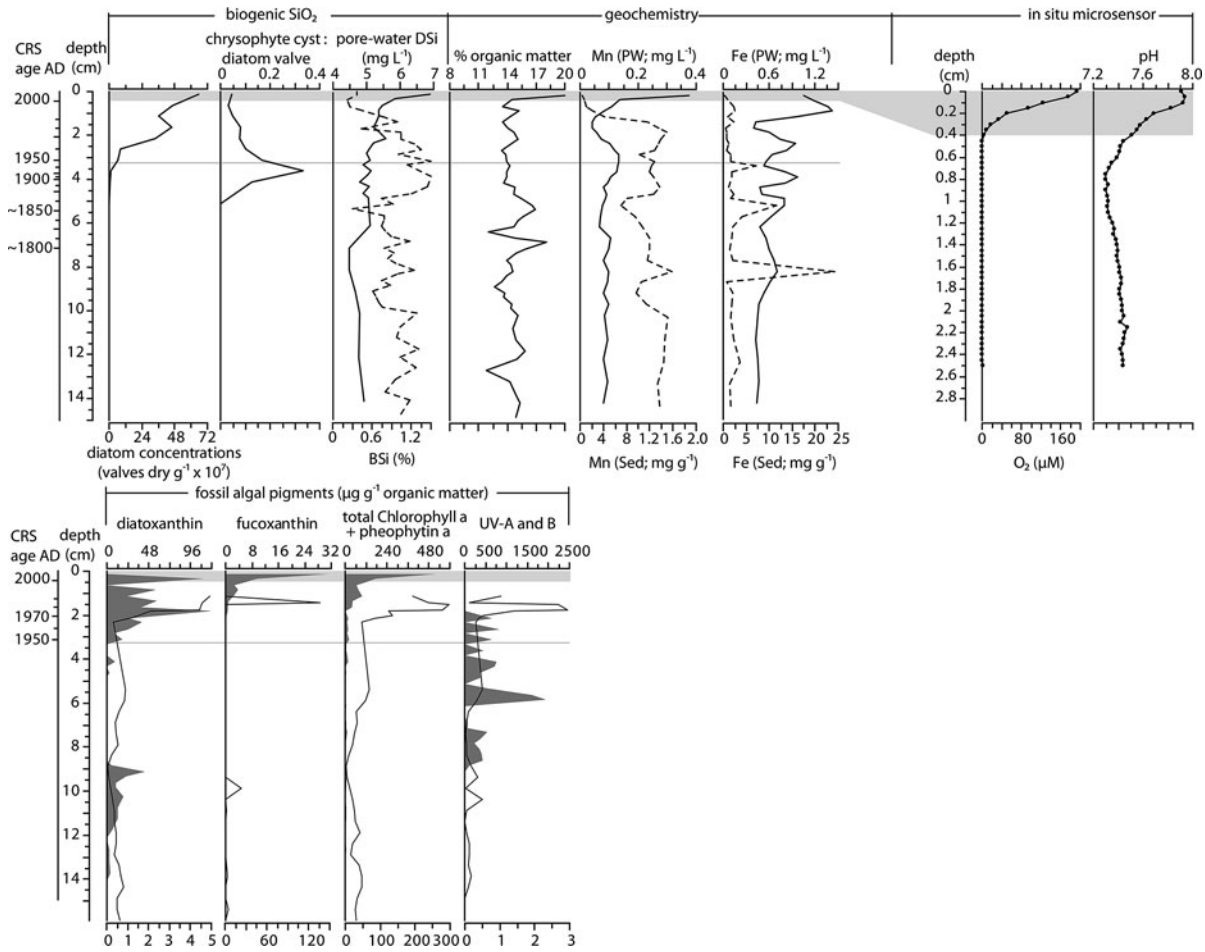

Fig. 5 Profile of the biogenic SiO_2, geochemistry, and fossil pigments. The oxic zone of the sediments is *shaded grey* and the depth of complete diatom dissolution is marked by the *grey line* (3.25 cm). Estimated ^{210}Pb CRS age (extrapolated dates in *italics*) and depth on *y*-axis. *Dashed lines* are pore-water concentrations while *solid lines* are labile solid phase concentrations. BSi proxies include diatom concentrations (valves dry $g^{-1} \times 10^7$), chrysophyte cyst: diatom valve ratio, and extracted BSi (wt% SiO_2) and pore-water DSi (mg l^{-1}). Geochemical analyses include OM, Mn, and Fe. In situ microprobe O_2 and pH are blown-up and shown on the *right*, where the maximum depth of analysis is 2.8 cm. Fossil pigments (µg pigment g^{-1} OM) from this study (*shaded silhouettes*) include the diatom carotenoids, fucoxanthin and diatoxanthin, the total chlorophyll *a* pigments (chlorophyll *a* and pheophytin *a*), and the UV-radiation-specific compounds A and B. Sedimentary pigment analyses from the 1991 core collected by Leavitt et al. (1994) are shown as *lines*. The 1991 and 2007 cores are aligned temporally for the upper 3 cm, where dating uncertainty is low and sediments are unconsolidated, and by depth of sample (adjusted for the time difference between cores) for the remaining consolidated portion of the cores. Axis scales differ between the 1991 and 2007 due to differences in the absorption coefficients of the HPLC units used, which does not affect the comparison of temporal trends

begins to level off at ~3.5 cm, where the buried amount of BSi is at or below the method detection limit below this depth. Dissolved Si in the pore-waters increases from the sediment water interface to a maximum concentration of 6.9 mg l^{-1} at a depth of 3.75 cm, which is just below the point of complete dissolution. Below the point of frustule dissolution, DSi concentrations reach a relatively stable background of 5.7 ± 0.2 mg l^{-1}.

The diffusional dissolved silica flux from the interstitial waters is 0.86 g SiO_2 m^{-2} $year^{-1}$ to the water column. This flux is consistent with other estimates from pore-waters in oligotrophic lake sediments (Hofmann et al. 2002). Biogenic silica flux in this portion of the sediments is 1.71 g SiO_2 m^{-2} $year^{-1}$, and 1.13 g SiO_2 m^{-2} $year^{-1}$ is permanently buried in sediments. Therefore, there is a total of 1.44 g SiO_2 m^{-2} $year^{-1}$ above background

Table 2 Summary of sediment geochemistry from Pipit Lake trap and core

Interval	OM (% d.w.)	CO_3 (% d.w.)	BSi (% d.w.)	% Clastics (residual)	Total diatom carotenoids (μg g^{-1} OM)	Total Chl *a* (μg g^{-1} OM)
11-Aug-05–13-Jul-06	18.3 ± 4.7	19.7 ± 3.5	15.4 ± 1.1	46.6 ± 6.0	2,003.0	2,539.8
13-Jul-06–19-Oct-06	19.1 ± 1.9	13.5 ± 1.0	18.9	48.5 ± 2.1	1,057.1	1,668.1
19-Oct-06–15-Jul-07	12.8 ± 0.5	17.2 ± 1.0	15.8	54.2 ± 1.1	2,499.6	3,429.2
0–0.25 cm	20.8	12.8	1.48	64.9	169.8	257.4
0.25–3.5 cm	14.2 ± 0.6	12.9 ± 1.4	0.68 ± 0.07	72.7 ± 1.5	12.3	24.8
3.5–15 cm	14.6 ± 1.2	11.9 ± 1.9	0.45 ± 0.05	73.3 ± 2.2	0.2	1.7

Values expressed as mean ± standard deviation

burial, of which the dissolved silica flux to the water column represents ~60%.

Organic matter and redox sensitive metals

The organic content of the sediment trap material averaged 16.5 ± 4.0%, while carbonate mineral content inferred from LOI is 17.1 ± 3.3%. The summer sediment trap sample has higher OM content (Table 2). Surface sediment OM from the core is 20.8%, while carbonates comprise 12.8%. The organic content of the sediment decreases extremely rapidly from 0 to 0.5 cm and remains relatively stable for the remainder of the core (mean 14.5 ± 0.3%) (Fig. 5).

Solid-phase Mn, most likely present as Mn(IV) oxyhydroxides, declines rapidly in near-surface sediments (0–1 cm), and solid-phase Fe, similarly presumed to reflect Fe(III) oxyhydroxides, decreases immediately below at 1–2 cm, indicative of Mn and Fe reduction zones, respectively. Pore-water Mn(II) increases accordingly from 0.009 mg l^{-1} at the surface to 0.300 mg l^{-1} at 1.75 cm (Fig. 5), however pore-water Fe(II) does not appear to increase. As no solid-phase ferrous iron minerals were indicated by XRD, it is likely that some Fe loss from porewaters occurred due to rapid oxidation and precipitation after porewater extraction. Aerobic respiration of organic matter in the surface sediments is evident by the loss of %OM concomitant with declining O_2 (zero at 4 mm) and decreasing pH (reduction of 0.8 pH units at 4 mm) (Fig. 5). The solid-phase Mn and Fe profiles, along with the porewater O_2 and Mn profiles, are wholly consistent with typical biogeochemical zonation where O_2 is the preferred electron acceptor, followed in turn by Mn(IV) and Fe(III), respectively.

Sedimentary pigments

Diatoms produce chlorophylls *a* and *c*, as well as xanthophylls fucoxanthin and diatoxanthin. Fucoxanthin is a relatively labile compound, while diatoxanthin is more stable (Leavitt and Hodgson 2001). There is a dramatic decrease of both fucoxanthin and diatoxanthin by 3.25 cm, consistent with the depth where diatoms are completely dissolved (Fig. 5). Trace amounts of diatoxanthin are present deeper in the core (9–15 cm) despite the absence of diatoms, suggesting that residual diatoxanthin is preserved despite complete diatom dissolution. Coincident with the loss of diatom pigments is the presence of pigments analogous to compounds A and B of Leavitt et al. (1997). These compounds are suggested to be UV-photoprotective pigments. They are carotenoid-like structures similar to scytonemin, which is produced in cyanobacterial sheaths to protect against UVR (Leavitt et al. 1997). These compounds were not found in the sediment trap material or in the upper sediments. Within the upper 3.25 cm the total concentration of primary chlorophyll *a* (chl *a*) and its more stable derivative, pheophytin *a* are completely lost from the sediment record, confirming the importance of diagenetic processes in Pipit Lake sediments (Fig. 5).

Discussion

Biological mechanisms for diatom dissolution

In Pipit Lake a concurrent decrease in pH and %OM within the upper half centimeter of sediment reflects the heterotrophic production of dissolved CO_2 and

hence of carbonic acid (H_2CO_3) through hydrolysis. The microelectrode profiles reveal aerobic respiration of OM by microorganisms, marked by pore-water DO declining in the upper few millimeters of the core and achieving anoxia at 4.0 mm (Fig. 5). Diagenetic loss of organic matter from the upper sediments (0–0.5 cm) is approximately 30%. This is slightly greater than the estimates of Gälman et al. (2008), who showed that up to 20% of new organic matter is lost from lake sediments within 5 years of deposition. Further microbial reduction of OM below the depth of anoxia is confirmed by the solid-phase profiles of Mn and Fe, whose decline is best attributed to Fe- and Mn-reducing heterotrophy (Fig. 5). The depths of these redox transitions in alpine lake sediments have not been studied, but it is generally accepted that in most lakes, these transitions occur within the uppermost few centimeters of sediment (Engstrom and Wright 1984). It is clear that the surface sediments of Pipit Lake are strongly altered by heterotrophic metabolism.

SEM images of sediment-trap material reveal intact diatom cells with organic coatings and attached epiphytic species (Fig. 3a). Some specimens also show the traces of microbial degradation of EPS, with no signs of chemical dissolution (Fig. 3b). Loss of EPS and the first signs of dissolution, including pitting and etching, become immediately evident on surface-sediment frustules, and progress rapidly down-core (Fig. 4). A quantitative measure of this progressive dissolution is captured by the absolute diatom concentrations down-core (Fig. 5). Diatom frustules disappear below 3.5 cm, and chrysophyte cysts at 5 cm (Fig. 5). The latter are slightly less susceptible to dissolution due to their spherical and inaperturate morphology. These observations on the loss of EPS and frustule dissolution soon after deposition and potentially during sedimentation correlate well with experimental and field based studies that indicate frustules exposed by the microbial degradation of EPS are more susceptible to chemical dissolution than counterparts with intact EPS (Lewin 1961; Bidle and Azam 1999). We must also acknowledge the possibility of frustule breakage and exposure of surfaces from grazing by daphnids (*Daphnia middendorffiana*) and bioturbation by benthic invertebrates (*Gammarus lacustris*) near the sediment–water interface as a secondary factor (Wilhelm et al. 1998; Wilhelm and Schindler 1999).

Chemical mechanisms for diatom dissolution

The solubility of amorphous silica is largely insensitive to changes in pH below 9.5, above which it increases significantly (Langmuir 1997). At the lower pH values characteristic of Pipit and other lakes (pH ~8–9; Ryves et al. 2006), pH-dependence of BSi solubility cannot be the prominent mechanism driving frustule dissolution: disequilibrium of DSi in natural waters becomes a more likely mechanism for dissolution, as suggested decades ago by Lewin (1961). DSi saturation in natural waters is 122 mg l^{-1} at pH 8 (Langmuir 1997), while lake water DSi concentrations across the Canadian Rocky Mountain lakes range from 0.5 to 5.5 mg l^{-1} (Anderson 1969; Anderson and Donald 1976, 1978). This degree of undersaturation is driven by the combination of low catchment DSi production, which results from slow weathering of silica-poor lithologies, and rapid biological uptake by diatoms and chrysophytes.

Laboratory experiments have shown that dissolution is promoted by the presence and dissociation of alkali metals in carbonate waters, such that rates of dissolution favour the sequence Na > Mg > Ca (Barker et al. 1994; Flower 1993; Ryves et al. 2006). However, the concentrations of alkali metals in the hypolimnetic waters of Pipit are well below those used in laboratory experiments and while they are comparable to those found by Ryves et al. (2006) for a number of lakes in West Greenland, the authors showed that neither the metals nor carbonate were statistically important in diatom dissolution. We also found that the concentrations of alkali metals in the pore water are similar to the lake water, suggesting that there is no increase in the pore water alkalinity. While we are unable to explicitly state that alkali metal concentrations are not sufficient enough to influence diatom dissolution, it does not appear to be a dominant driver in Pipit Lake.

Alpine lakes and silica recycling

Our observations of diatom dissolution in Pipit Lake are not isolated within the Canadian Rocky Mountain Range. We have observed the loss of diatom microfossils from recent alpine lake sediments in 9 of 13 lakes sampled in the Rocky Mountains of Alberta (spanning 51.4°N to 53.6°N), suggesting that reliable diatom preservation is the exception rather than the

Table 3 Summary of diatom dissolution depths in sediments from Canadian Rocky Mountain Lakes

Lake	Dissolution depth in sediments (cm)	Latitude (°N)	Longitude (°W)	Altittude (m asl)	Maximum depth (m)	pH	Conductivity (μS/cm)	$NO_2 + NO_3$ (μg/l)	TN (μg/l)	SRP (μg/l)	TP (μg/l)
Lower Snow[a]	2.5	53.620286	−118.835285	2,024	4	7.97	300	18.1	188	1.0	8.7
Upper Snow[a]	2	53.617742	−118.843608	2,193	11.3	8.3	220	2.64	127	1.0	5.8
Jack-knife[a]	4	53.582364	−118.806483	2,046	16	8.22	210	6.61	100	0.3	3.9
Curator	Preserved	52.792055	−117.862727	2,232	25	8.4	220	66.5	269	<MDL	4.0
Caribou	4	52.738981	−117.795416	2,200	10.5	7.7	80	22.2	123	<MDL	4.3
Caribou #2	10	52.685902	−118.011384	2,220	6.3	8.45	240	44	211	1.9	9.1
Upper Geraldine[a]	2	52.558832	−117.933171	2,280	11	8.23	150	59	196.2	1.3	2.0
Upper Devon	Preserved	51.722571	−116.240989	2,200	24	8.3	195	14	174	4	3
McConnell	Preserved	51.638162	−115.977579	2,390	28	8	unk	129	184	2	3
Pipit	3.25	51.616915	−115.863622	2,217	20.6	8.1	214.8	134.6	25.9	2.9	5.2
Goat	Preserved	51.447013	−115.858658	2,438	43	8.2	150	75	279	6	10
David	4	51.507745	−116.522488	2,200	22	8.1	227	44	170	2	6
Sue	4	50.586362	−115.379498	2,371	29.5	7.8	158	65	230	4	4

Water chemistry are single summer measurements, with the exception of Upper Geraldine, Pipit, and Upper Devon Lakes where mean values over multiple years are given. Dissolution depths in sediments are established from short (11–45 cm) gravity type cores

[a] Unofficial name

<MDL = less than method detection limit

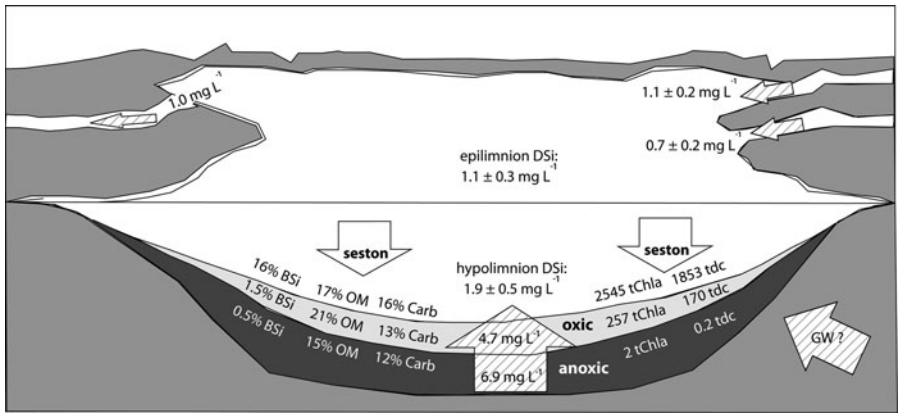

Fig. 6 Deposition and loss of sedimentary biogenic silica, organic matter, carbonates, and algal pigments. Pigments are expressed as total diatom carotenoids (tdc; fucoxanthin and diatoxanthin) and total chlorophyll *a* (tChl*a*; chlorophyll *a* and pheophytin *a*), measured in μg g^{-1} organic matter. All other values are expressed as % mass. Aqueous dissolved silica concentrations for inputs and outflows from Pipit Lake expressed in mg l^{-1} (mean 1995–2007) and highlighted by *line-filled arrows*

rule in this region (Table 3). No clear predictive lake characteristics (e.g. depth) of faithful diatom preservation are observed. Rapid dissolution has not been documented in several other Canadian alpine lakes, which instead present discrete intervals of diatom dissolution during the Holocene (Hickman and Reasoner 1998; Karst-Riddoch et al. 2005). The inference from these studies is that conditions which obliterate the diatom record are potentially episodic and associated with increases in lake water alkalinity during anoxic periods of extended ice cover.

The regeneration of silica from the sediments of Pipit Lake appears to be both biologically and chemically mediated. BSi recycling is initiated between hypolimnetic waters and surface sediment. The BSi content of the sediment trap material is 16.2 wt% SiO_2 compared to 1.5 wt% SiO_2 at the sediment surface, meaning only an estimated 10% arrives at the sediment surface or is rapidly dissolved within the surface sediments (Fig. 6). In addition, the flux of DSi from the sediments represents a further return of ~60% of the sedimentary silica pool from the interstitial waters back to the water column, where it can be re-utilized or exported in outflow. Therefore, only ~4% of the original BSi standing crop is buried permanently within the sediments. Alternatively, if we only look at the loss of BSi from the sediment trap to permanent burial (16.2–0.45 wt% SiO_2), it appears that ~3% of the total is buried. In comparison, Conley and Schelske (1989) reported that only 5% of the BSi produced in Lake Michigan accumulates in sediments based on a complete silica budget. We are unable to comment on the net DSi budget for Pipit Lake because groundwater DSi contributions and stream discharge rates are not constrained. Internally, the magnitude of recycled DSi from the sediments suggests this is a greater source for siliceous algae than DSi derived from the sum of catchment inputs (Fig. 6; Table 1).

Sedimentary pigments

As a component of the sediment organic matrix, fossil pigments are predicted to be affected by the processes outlined above. Indeed, the progressive diagenetic loss and alteration of pigments begins during sedimentation of the seston (Table 2). Degradation of chlorophyll *a* during algal senescence has been studied extensively and often involves the loss of the Mg^{2+} atom, producing pheophytin *a* (Leavitt 1993). The most important factors regulating the deposition of pigments within lakes appears to be the size of the phytoplankton standing crop, the sinking rate, and herbivory (Cuddington and Leavitt 1999). Physical lake characteristics, such as lake depth and resulting photic zone depth also bear on the oxidation of pigments. There is a substantial degradation of labile pigments within the bottom 0.5 m of Pipit Lake (i.e. from sediment trap to lake bottom; Fig. 6). Here, potential degradative mechanisms include oxidation and digestion by large, suprabenthic daphnids (Wilhelm et al. 1998).

Within the lake sediments, diagenetic loss of fucoxanthin and total chlorophyll *a* and pheophytin *a* is complete by a depth of 2 cm. Diatoxanthin and the UV-absorbing compounds A and B of Leavitt et al. (1997) appear to have stratigraphic trends that are inverse to one another and which persist below the zone of diatom dissolution (Fig. 5). Given limits on the present characterization of compounds A and B we offer two possible explanations for this stratigraphic pattern: (1) they represent periods of increased UVR penetration and benthic production by scytonemin-containing cyanobacteria (Leavitt et al. 1997); or (2) the UV-protective compounds are chemical by-products of pigment diagenesis. These two potential mechanisms are not mutually exclusive because exposure to UVR favors both increased benthic cyanobacterial abundance (Leavitt et al. 1997) as well as the potential for photodegradation of pigments. However, we find a lack of compounds A and B in 2 years of summer (and winter) sediment trap material, suggesting a diagenetic provenance for these compounds within the lake sediments. We have also shown that the total chlorophyll *a* profile (i.e. including pheophytin *a*) demonstrates that rapid diagenesis shapes the recent sedimentary pigment record and not historical algal standing crop (Fig. 6).

We examined the individual diode-array fluorescence spectra for chl *a*, fucoxanthin, diatoxanthin, and the UV-B compound from selected intervals. Although there is some indication of isomerization of structures, wavelengths of maximum absorption remained consistent between samples for each pigment, implying that structures remained intact while pigment was present, and that degradation did not involve transient moieties.

Comparison of our results with the pigment stratigraphy from a core recovered from Pipit Lake in 1991 confirms that pigment diagenesis is highly dynamic in Pipit Lake (Fig. 5; Leavitt et al. 1994). Down-core profiles of the more labile total chlorophyll *a* and fucoxanthin are all very similar, despite being offset by 15 years of sediment accumulation. This comparison suggests that these pigment records are largely the product of post-depositional diagenesis rather than ecological changes among algal communities. On the other hand, an increase in diatoxanthin concentrations is compatible between both profiles ($\sim$1970) and there is evidence of preservation at depth in both the 1991 and 2007 cores, which indicates that diatom-specific carotenoids have the potential to survive despite complete dissolution of their microfossil record.

Implications for paleoecology

The results from Pipit Lake challenge the assumption that sediments from cold oligotrophic lakes faithfully archive trends of primary production. For example, the use of BSi as a proxy for siliceous algal production assumes *a priori* that the preservation of BSi in sediments is proportional to diatom production. Given the importance of recycled silica in Pipit Lake, caution should be exercised when interpreting this proxy, especially if microfossils are not examined in parallel. This is particularly important on longer timescales (i.e. Holocene records) where diatom microfossils can intermittently disappear from stratigraphic records (Hickman and Reasoner 1998; Karst-Riddoch et al. 2005). It is possible that episodes of pervasive dissolution are being recorded, analogous to conditions in Pipit Lake, rather than the absence or decline of diatom communities from algal standing crops.

Variable states of pigment preservation are present in the Pipit Lake sediment core. While the labile chlorophyll *a* and fucoxanthin are being lost diagenetically in the surface sediments, the more recalcitrant diatom carotenoid, diatoxanthin, appears to persist through this zone. This suggests sedimentary pigments can be a reliable proxy of algal production despite active diagenesis in the upper sediments. In support of this, sediment records from additional lakes in the Canadian Rocky Mountains where complete diatom dissolution is occurring retain sedimentary pigments and do not appear to be affected by diagenesis (Vinebrooke, unpublished data).

Conclusion

Despite the importance of diatom taphonomy in freshwater paleoecology, few studies seem to acknowledge or discuss the extent of early diagenesis. Our work shows that the degradation of diatom cells and fossil pigments in alpine lake sediments can occur rapidly and as a result of a number of factors acting in concert. In Pipit Lake, microbial activity in a very shallow ($\sim$4 mm) oxic layer is the locus for organic

matter remineralization, affecting both diatom EPS and photoactive pigments. Decreases in pore-water pH and DO result from this metabolism, ultimately freeing cells of EPS and facilitating the chemical dissolution of unprotected frustules. The hydrolysis of BSi then proceeds rapidly at the sediment surface down to 3 cm because of strong DSi undersaturation in lake and pore waters. The vast majority ($\sim$90%) of BSi is lost during sedimentation, with an additional $\sim$6% recycled back to the water column from the sediments through the diffusion of DSi. Pigment diagenesis occurs equally rapidly, with major transformations in the upper 3.5 cm, before a more stable inventory of recalcitrant carotenoids is reached. The results from Pipit Lake highlight how important diagenetic processes can be in shaping the lake-sediment record, even in cold, low-nutrient, and undisturbed environments.

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