

The controls on phosphorus availability in a Boreal lake ecosystem since deglaciation

Stephen A. Norton · Randall H. Perry · Jasmine E. Saros ·
George L. Jacobson Jr. · Ivan J. Fernandez · Jiří Kopáček ·
Tiffany A. Wilson · Michael D. SanClements

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Abstract The sediment record from a 5.3-m core from Sargent Mountain Pond, Maine USA indicates strong co-evolutionary relationships among climate, vegetation, soil development, runoff chemistry, lake processes, diatom community, and water and sediment chemistry. Early post-glacial time (16,600–12,500 Cal

Yr BP) was dominated by deposition of mineral-rich sediment, low in organic matter and secondary hydroxides of Al and Fe; pollen indicate tundra conditions; diatom taxa indicate pH between 7.5 and 8, and total P concentrations of about $25 \mu\text{g L}^{-1}$, favoring higher productivity. Chemical weathering was rapid, with high alkalinity, pH, Ca, and P in runoff. As climate ameliorated, about 12,500 Cal Yr BP, forest vegetation became established; soils would have developed vertical zonation, including organic matter accumulation, and incipient podzolic horizons, with accumulating secondary hydroxides of Al and Fe that sequestered P in the soils. Labile minerals (primarily apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$) became depleted in the soil, further reducing the supply of P to the lake. Dissolved organic carbon (DOC) from soil organic matter mobilized Al and Fe to the lake where $\text{Al}(\text{OH})_3$ (primarily) and $\text{Fe}(\text{OH})_3$ (minor) were precipitated. The sedimenting hydroxides adsorbed P from the water column, further reducing bioavailable P. These long-term trends of moderating climate, and changing terrestrial biology, soils, and aquatic chemistry and phytoplankton were interrupted by the 1,000-year long Younger Dryas cooling, which led to a temporary reversal of these processes, a period that ended with the major onset of Holocene warming. The sequestration of P by soils would have strengthened because of long-term soil acidification and pedogenesis. The lake was transformed from a more productive, high P, high pH, low DOC system into an oligotrophic, relatively low P, acidic, humic lake over a period of 16,600 years, a

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S. A. Norton (✉) · R. H. Perry
Department of Earth Sciences, University of Maine,
Orono, ME 04469-5790, USA
e-mail: Norton@Maine.edu

J. E. Saros · G. L. Jacobson Jr.
School of Biology and Ecology, University of Maine,
Orono, ME 04469, USA

S. A. Norton · J. E. Saros · G. L. Jacobson Jr. ·
I. J. Fernandez · T. A. Wilson
Climate Change Institute, University of Maine, Orono,
ME 04469, USA

I. J. Fernandez
Department of Plant, Soil, and Environmental Sciences,
University of Maine, Orono, ME 04469, USA

J. Kopáček
Biology Centre ASCR, Institute of Hydrobiology,
České Budějovice 37005, Czech Republic

M. D. SanClements
Institute of Arctic and Alpine Research, University
of Colorado, Boulder, CO 80303, USA

natural trend that continues. In contrast to many human-affected lakes that become increasingly eutrophic, many lakes become more oligotrophic during their history. The precursors for that are: (1) absence of human land-use in watersheds, (2) bedrock lithology and soil with a paucity of soluble Ca-rich minerals, and (3) vegetation that promotes the accumulation of soil organic matter, podzolization, and increased export of metal-DOC complexes, particularly Al.

Keywords Oligotrophication · Phosphorus · Sediment · Aluminum · Post-glacial weathering · Watershed evolution · Climate change

Introduction

Lake-sediment chemistry provides insights about catchment till/soil mineralogy (Engstrom and Wright 1984). Studies of lake chronosequences (Engstrom et al. 2000; Engstrom and Fritz 2004), landscape evolution (Cooper 1923a, b; Crocker and Major 1955; Jacobson and Birks 1980; Chapin et al. 1994; Fastie 1995), and lake cores have revealed trends in chemical weathering and lake productivity in landscapes exposed since the Little Ice Age (LIA). Long-term (post-Last Glacial Maximum) trends in lake acidification and productivity have also been reconstructed using sediment records (Whitehead et al. 1973, 1986; Ford 1990; Renberg 1990; Kopáček et al. 2007). Multi-proxy paleoecological studies have supplemented the pioneering insights of the earlier single-variable records (Birks and Birks 2006). The interpretation of sediment chemical and biological records is strengthened by laboratory-based, whole-rock weathering experiments, single mineral weathering experiments, and studies of mineral depletion in soil profiles. Together, these different lines of evidence indicate rapid declines in pH of runoff as a result of rapid weathering of carbonate and phosphate minerals, declining nutrients in runoff (especially phosphorus, P), and declining ionic strength as soluble minerals become depleted (Boyle 2007a).

After reaching its maximum areal extent about 22,000 years before present (y BP), the Laurentide Ice Sheet margin retreated across the Gulf of Maine, reaching the present Maine, USA coastline between 17,000 and 16,000 Cal Yr BP (Borns et al. 2004). Mount Desert Island (the site of this work), is 1 km

offshore, forming a rounded island with a diameter of about 30 km, and a maximum elevation of 470 m. Sargent Mountain Pond (SMP) (elevation 336 masl) lies on the flank of Sargent Mountain (elevation 417 masl). The lake basin was exposed at approximately 16,600 (± 500) Cal Yr BP and was likely the first post-glacial lake in Maine; it subsequently remained above the inland marine limit (approximately 80 masl; Thompson and Borns 1985), collecting a continuous post-glacial sediment record of ecosystem development.

We used ^{14}C -dated stratigraphy of sediment chemical speciation, and diatom and pollen enumeration within a 5.3 m long core from SMP to infer lake water chemistry and soil development since deglaciation. These changes are in the context of variations in climate and vegetation. Our objective was to document the evolution of chemical and biological events and processes that link the terrestrial system with the aquatic system, and that control the millennial-scale productivity of a lake in a simple geologic setting. This understanding contributes to the understanding of lake ontogeny and long-term acidification.

Location and lake description

Sargent Mountain Pond (44.334°N, 68.270°W, 336 masl) is an approximately 0.75-ha lake draining an approximately 1.3-ha spruce-fir forested catchment in Acadia National Park, Maine, USA (ESM 1). The watershed is underlain nearly exclusively by Cadillac Mountain Granite (abbr. CMG; Gilman et al. 1988) of Devonian age (Osberg et al. 1985). It contains feldspar, quartz, and hornblende, with minor apatite and monazite. Basalt dikes underlie less than 0.1% of the watershed. About 20% of the catchment is exposed bedrock. The remainder is underlain with thin pockets of till, typically less than 0.5 m thick, consisting mostly of local bedrock detritus. Soil is coarse-loamy, mixed, frigid, Aquic Haplorthods developed on till. The catchment has high relief ($\sim 20\%$ slope). Recharge is dominated by precipitation and surface runoff. Some groundwater may enter through bedrock joints. The pond has no permanent surface inlets; it drains through a fen to the southeast. The modern lake is acidic (pH = 4.96), because of acidic rain, dissolved organic carbon (4.4 mg L^{-1}), and slowly weathering bedrock and thin till ($\text{Ca} = 16 \text{ } \mu\text{eq L}^{-1}$ (ESM 1). The catchment has no roads or

other development, and is accessible only by a 3-km foot trail. Human impact, other than long-range atmospheric transport of pollutants, is negligible. Temperature ranges from about -15°C to $+35^{\circ}\text{C}$, with an annual mean of about 6°C . Precipitation averages about 1.4 m year^{-1} , with about 75% occurring as rain. The lake is ice covered from December until April.

Methods

Coring and sectioning

We retrieved a 5.3-m core in March 2007, through 80 cm of ice, from the deepest part (approximately 4 m) of SMP using a 10-cm diameter square-rod piston corer (Wright 1991). The upper-most watery 11 cm of the core was discarded because of disturbance. We sectioned sediment in the laboratory at 2-cm intervals. We collected a separate 30-cm core, 5 cm in diameter, near the same locality in March 2004 using a gravity corer and sectioned it at 1-cm intervals. The ^{210}Pb dating profile of the short core was the basis for the upper portion of the age-depth model developed for this paper (Norton et al. 2007).

Sediment processing

We determined water (% H_2O) and organic matter (% loss on ignition = LOI) of the sediment sequentially on homogenized aliquots from every depth interval. Wet sediment was weighed, dried at $103\text{--}105^{\circ}\text{C}$ for 16 h, cooled in a dessicator, and reweighed to determine the moisture content. The procedure was repeated until a constant weight was obtained. Dried sediment was heated in a muffle furnace at 550°C for 4 h and reweighed to determine LOI.

We obtained 14 radiocarbon (^{14}C) accelerator mass spectrometer (AMS) sediment dates from depths ranging from 116.5 to 525 cm. We combined data from laboratories at National Ocean Sciences Accelerator Mass Spectrometer Facility at Woods Hole Oceanographic Institution, Woods Hole, MA, USA ($n = 11$) and Beta Analytic, Inc., Miami, FL, USA ($n = 3$). We applied two approaches to derive the core chronology. The major changes and mechanisms described in this paper are not dependent on which model is correct.

Linear age-depth relationships: Based on the obvious dramatic increase in LOI at sediment dated between 12,000 and 11,000 Cal Yr BP and the relatively constant LOI above and below this period, we developed a two-segment linear age model (ESM 2). The oldest AMS ^{14}C -date was $15,718 \pm 363$ Cal Yr BP at 523 cm, and the youngest was $3,069 \pm 100$ Cal Yr BP at 116.5 cm. We rejected two dates. One was from a log that the core penetrated. It dated young compared to its neighboring dates and may have represented a tree fragment that had penetrated into deeper sediment during sedimentation. The other rejected date was from the bottom of the core where the LOI was low, the counting error was high, and the material dated more than 3,000 years younger than its neighbor dates. We converted ^{14}C ages to Cal Yr BP using the CALIB 5.10 program (Stuiver and Reimer 1993) to produce calendar age-depth model (ESM 2, Figs. 1, 2, 3).

Best fit of the data: We applied the non-Bayesian ‘CLAM’ model of Blaauw and Christen (2005) and Blaauw (2010) to our complete ^{14}C data set. This approach rejected one ^{14}C date. The strengths of this approach are in having calculated ages for all sediment intervals and error bars for any of the calculated ages. We rejected the results of this model because of the calculated huge peak in the sediment mass accumulation rate, centered on about 4,000 Yr BP (ESM 3, Figs. 1, 2). There is no change in the sediment physical and chemical properties (ESM 4, Figs. 1, 2, 3), or LOI (Fig. 2) to indicate the calculated dramatic change.

Speciation of metals

We used sequential extraction (modified after Psenner et al. 1988) to characterize the chemical components of the lake sediment. One to two grams of wet sediment from each interval was homogenized and sequentially treated with increasingly aggressive reagents to release progressively the elements of interest from their various phases. Each extract was centrifuged at $\sim 3,000$ rpm for 15 min and filtered (glass-fiber filters, pore size of $0.45\text{ }\mu\text{m}$). We determined concentrations of P, Al, Fe, and Ca in the filtrate of each of the five extractions by inductively coupled plasma atomic emission spectrometry (ICP-AES; Perkin-Elmer model 3300XL). Total extractable concentration is the sum of the five fractions, as in Al_{tot} .

Fig. 1 Age-Depth Model for the Sargent Mountain Pond sediment core: The deeper line (Line 1) fits Samples 9–11 and 13. The shallower line (Line 2) fits Samples 1–10 and was forced through age zero at 11 cm depth. Samples 12 and 14 were excluded. The deepest age (530 cm) = 16,653 Cal Yr BP. The curves intersect at 460 cm

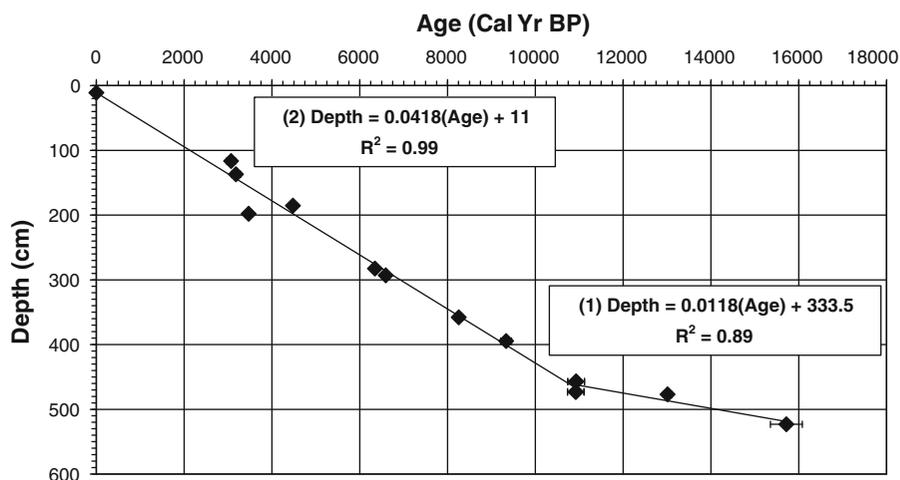
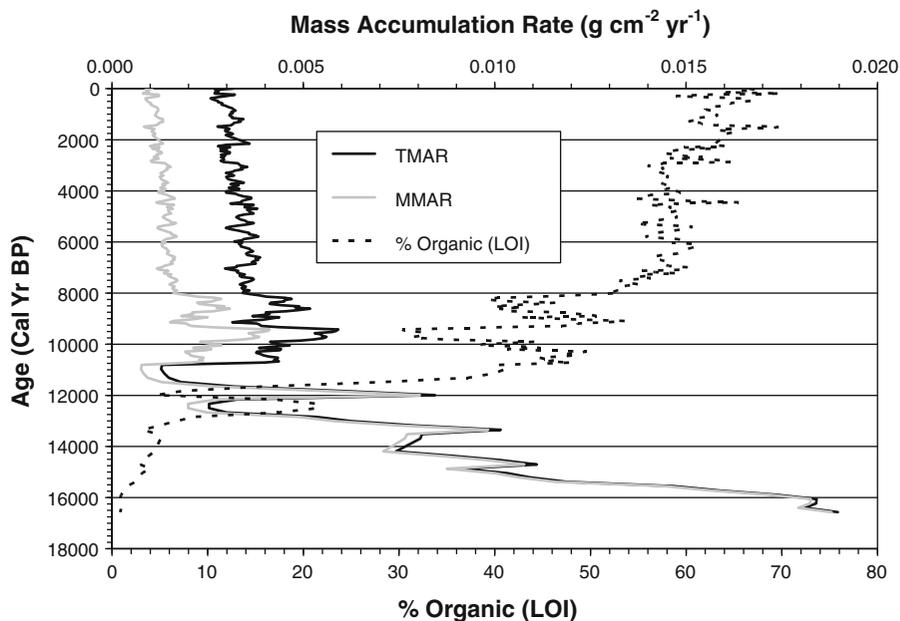


Fig. 2 Mass accumulation rate and LOI in the Sargent Mountain Pond sediment core. The dashed black line is LOI. The solid black line is Total Mass Accumulation Rate (TMAR), including organic matter, and the solid gray line is Mineral Mass Accumulation Rate (MMAR)

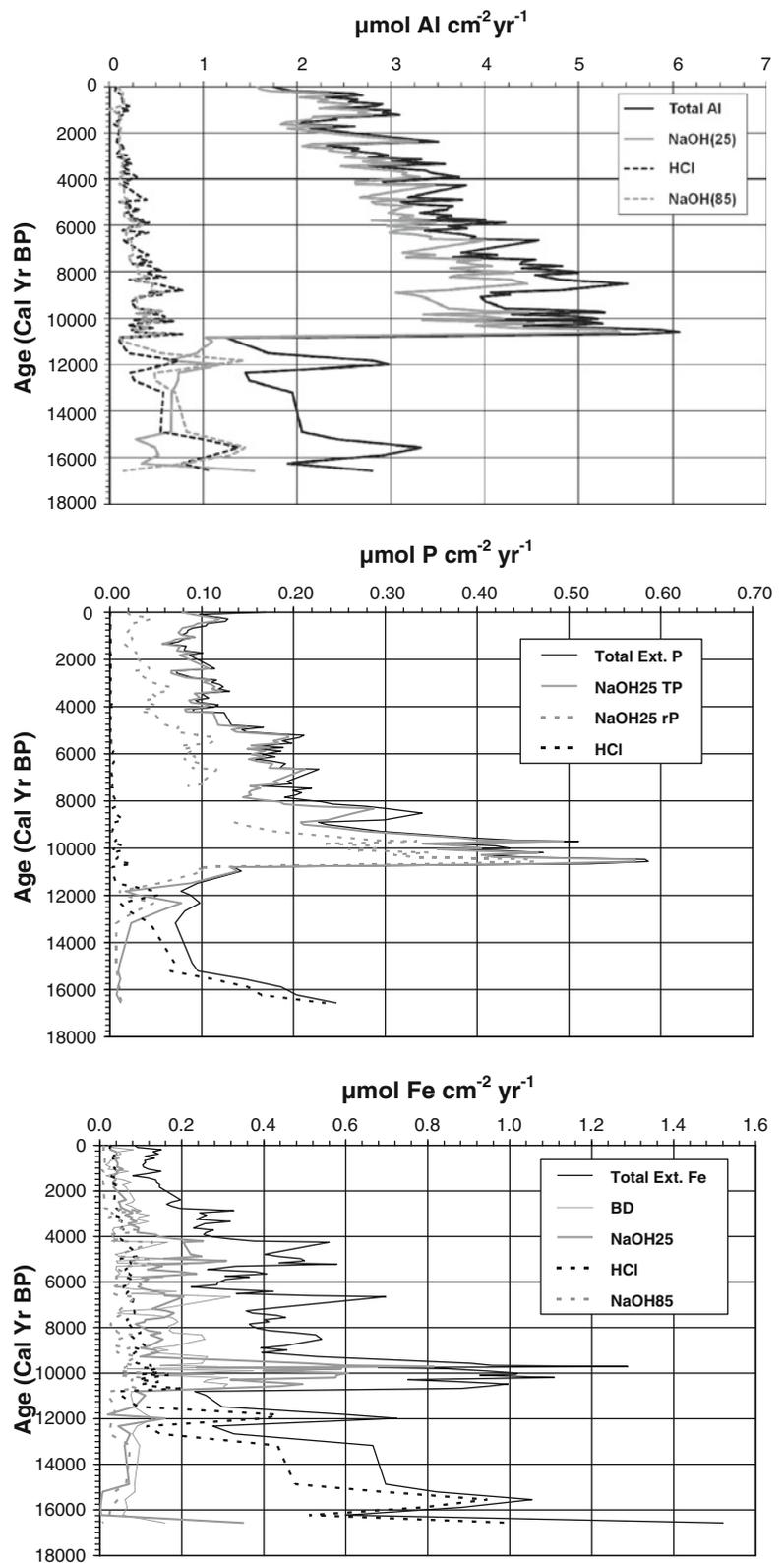


The sequential extractions are:

- (1) 1 M NH_4Cl , pH 7, at 25°C for 1 h to obtain the *exchangeable fraction*, e.g., Ca_{ex} .
- (2) 0.1 M $\text{NaHCO}_3\text{-Na}_2\text{S}_2\text{O}_4$ (abb. BD) at 40°C for 30 min to dissolve the *reducible fraction* that is primarily Fe ($\text{Fe}(\text{OH})_3$ and $\text{FeO}(\text{OH})$) hydroxides and associated P, e.g., Fe_{BD} .
- (3) 0.1 M NaOH at 25°C for 16 h to dissolve the *NaOH-extractable fraction*, e.g., $\text{Al}_{\text{NaOH}25}$. This fraction contains Al hydroxide ($\text{Al}(\text{OH})_3$) (primarily) and Fe^{III} hydroxides and associated P (including organic-P). We used 0.1 molar NaOH

solution, rather than 1.0 molar (Hieltjes and Lijklema 1980). Within the NaOH extraction, we determined PO_4 directly, called reactive P (P_r), using the molybdate blue method (Murphy and Riley 1962). The difference between total extractable P in the NaOH fraction (determined by ICP-AES) and P_r is defined as non-reactive P (P_{nr}), and equated with organic P and bacteria-incorporated P. Wilson et al. (2010) found that approximately half of the $\text{P}_{\text{NaOH}25}$ is organically-bound after substantial burial time (approximately 100 year) and diagenesis.

Fig. 3 (a) Aluminum species fluxes in the Sargent Mountain Pond sediment core. For clarity, Al values for the NH_4Cl and bicarbonate-dithionite fractions are not shown because they are so low. Total extractable Al is the sum of all five extractions. (b) P species fluxes. The P values for the NH_4Cl , bicarbonate-dithionite, and NaOH_{85} fractions are not shown because of they are so low. Total extractable P is the sum of all five extractions. (c) Iron species fluxes. For clarity, Fe values in the NH_4Cl and NaOH_{85} fractions are not shown because they are so low. Total extractable Fe is the sum of all five extractions



- (4) 0.5 M HCl at 25°C for 16 h to dissolve acid-soluble minerals (including apatite), the *acid soluble fraction*, e.g., P_{HCl} .
- (5) 1 M NaOH at 85°C for ≥ 24 h to dissolve “residual” material, the *residual fraction*, e.g., $Al_{\text{NaOH}85}$. Our experience is that the true total P (by HF/aqua regia dissolution) is typically nearly the same as the sum of the five extractions (P_{tot}).

Sediment chemical data analysis

We report accumulation rates (mol or mass cm^{-2} year $^{-1}$) (ESM 5). Using accumulation rates, rather than concentrations (shown in ESM 4, Figs. 1, 2, 3, 4), avoids the problems of dilution because of variations in the flux of major components, such as biogenic Si.

Diatom enumeration

We selected 16 intervals, after determination of the chemical stratigraphy and chronology, from 150 cm (3,325 Cal Yr BP) to 512 cm (15,127 Cal Yr BP) depth. Our goal was to emphasize the early evolution of the lake and evaluate major changes in pH and (possibly) P. Ten of 16 samples focused on early post-glacial conditions to just younger than the Younger Dryas (YD). Sediments were digested with 30% H_2O_2 , and then settled onto cover slips and mounted onto slides with Naphrax[®]. A minimum of 300 valves per slide were counted under oil

immersion on an Olympus BX51 microscope with differential interference contrast under oil immersion at 1,000 \times magnification. Diatom taxonomy was based primarily on Camburn and Charles (2000) and Krammer and Lange-Bertalot (1986–1991).

Lake water concentrations of total phosphorus (TP) and pH inferred from sedimentary diatom assemblages using the maximum-likelihood (ML) model (Birks 1995) applied to the calibration set from Ginn et al. (2007). The ML model estimates optima and tolerances from the calibration set by fitting species-environment response curves to the limnological gradient of interest. We used these curves to calculate a most probable TP or pH value for the fossil species assemblage. With this method, the root mean squared error of prediction (RMSEP) for TP is 0.46 on the log-transformed data; the RMSEP for pH is 0.45 (Ginn et al. 2007). While the absolute values of reconstructed pH and P concentration may be incorrect because of co-varying P and pH, we believe the trends are correct.

Pollen enumeration

We selected nine levels of sediment for pollen identification, after determination of the chemical stratigraphy and chronology, to document major vegetation change around the YD. YD time was significant in the evolution of the sequestration of P by $Al(\text{OH})_3$. The nine samples range from 526 to 420 cm, spanning 16,600–9,800 y BP. Post-glacial vegetation succession is well known for Maine (Davis and Jacobson 1985, Schauffler and Jacobson 2002).

Samples for pollen identification were prepared following standard procedures (Fægri et al. 1989) and mounted in silicone oil. Pollen of upland types were identified with a Leitz microscope. Because SMP is small (0.75 ha), the pollen source area is relatively small, but still well beyond the immediate watershed (Jacobson and Bradshaw 1981). In this case, the likely source region would be the surrounding area on Mt. Desert Island.

Results

Chronology

After exclusion of two apparently erroneous dates, the chronology model yields two distinct linear

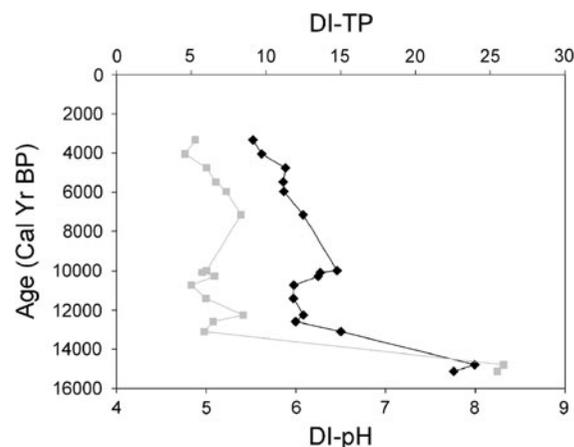


Fig. 4 Diatom-inferred pH (black diamonds) and P (gray squares) from the Sargent Mountain Pond sediment core

segments (Fig. 1). The lower segment fits the sediment with low organic sediment, deposited largely in the first 5,000 years of the lake history. LOI increases dramatically at the intersection of the two chronology segments, abruptly increasing the sediment accumulation rate (cm year^{-1}). The age at 11 cm of the long core was set to be 1950 (zero in ^{14}C age). The short sediment core was dated by ^{210}Pb at 1950 at 8.5 cm. Each 2-cm interval in the upper part of the long core represents about 40 years, the level of resolution for chemistry, H_2O , and LOI. For the lower part of the core, resolution was about 150 years/interval.

Lowell (1980) determined a bottom date of $15,669 \pm 738$ Cal Yr BP, from organic material 1.33 m above the base of a core taken at SMP in the 1970s, in agreement with our bottom date of $15,718 \pm 363$ Cal Yr BP, 7 cm above corer refusal. He found fresh water diatoms in the organic-poor sediment below the lowest dated horizon. Regionally, the Laurentide Ice Sheet margin passed through the Sargent Mountain locality about $15,919 \pm 380$ Cal Yr BP (Borns et al. 2004). Thus, the SMP core represents all or nearly all of the post-glacial record.

LOI and mass accumulation rate

A small percentage of LOI is attributable to loss of water during dehydration of secondary Al and Fe hydroxide phases in the sediment. The organic matter concentration (assumed to be equal to LOI) (Fig. 2) is inversely related to the mineral mass accumulation rate (see below). Organic sedimentation first peaked approximately 12,700–12,300 Cal Yr BP, before declining sharply from $\sim 25\%$ to $\sim 5\%$ from ca. 12,000 to nearly 11,000 Cal Yr BP, and then resuming its generally upward trend toward present-day values. Two less distinct declines occurred at approximately 9,500 ($\Delta\text{LOI} = -20\%$) and 8,200 ($\Delta\text{LOI} = -10\%$) Cal Yr BP. The linear age-depth model was applied to estimate mass accumulation rates (MAR) in SMP through time (Fig. 2).

Overall, total MAR (TMAR) decreased from $\sim 0.0190 \text{ g cm}^{-2} \text{ year}^{-1}$ at the initial time of lake exposure ($>16,600$ Cal Yr BP) to $\sim 0.0025 \text{ g cm}^{-2} \text{ year}^{-1}$ at the top of the core (ca. 1950), a decline of 87%. The sediment was predominantly minerogenic until approximately 11,000 Cal Yr BP, when the input of organic material rapidly became important, typically comprising more than 50% of the mass. A

short-lived approximately four-fold increase of TMAR occurred at $\sim 12,000$ Cal Yr BP, and several distinct but less-pronounced peaks occurred before and after the major 12,000 Cal Yr event. This major abrupt change for all measured parameters is contemporaneous with the YD cooling in this region, initiated about 12,000 Cal Yr BP and lasting for approximately 1,000 years (Borns et al. 2004).

Chemical speciation

The history of Al speciation is divisible into the periods before and after 13,000 Cal Yr BP (Fig. 3a). Al_{ex} and Al_{BD} are both small contributors to Al_{tot} throughout the core. Prior to 13,000 Cal Yr BP, the $\text{Al}_{\text{NaOH}25}$ (interpreted to be $\text{Al}(\text{OH})_3$), Al_{HCl} , and $\text{Al}_{\text{NaOH}85}$ were low. Just prior to the beginning of the YD, $\text{Al}_{\text{NaOH}25}$ rapidly increased, then sharply decreased in the YD, and finally increased to a peak at about 10,400 Cal Yr BP. At that time, $\text{Al}_{\text{NaOH}25}$ was approximately 90% of Al_{tot} . This relationship is maintained to the present, even as the flux of Al_{tot} declined 50%, from 5 to $2.5 \mu\text{mol cm}^{-2} \text{ year}^{-1}$.

The P speciation trends appear grossly similar to those of Al, with important exceptions (Fig. 3b). Prior to the YD, most extractable P occurs as P_{HCl} , consistent with its being from acid-soluble apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F})$). By the start of the YD, P_{HCl} had declined and remained low, approaching undetectable, in post-YD sediment. $\text{P}_{\text{NaOH}25}$ increased slightly just prior to the YD, in phase with $\text{Al}_{\text{NaOH}25}$. $\text{P}_{\text{NaOH}25}$ comprises 90–95% of the total extractable P, suggesting a strong linkage between $\text{Al}(\text{OH})_3$ and P. Both $\text{P}_{\text{NaOH}25}$ and $\text{Al}_{\text{NaOH}25}$ declined sharply in the YD and then increased dramatically coming out of the YD to a maximum about 10,400 Cal Yr BP, followed by an exponential decrease for $\text{P}_{\text{NaOH}25}$ to the present. Reactive P (= PO_4 ; P_r), at deposition now, is approximately 25–30% of $\text{P}_{\text{NaOH}25}$, and increases to about 80% at 10,000 Cal Yr BP (Fig. 3b). As diagenesis of organic P (P_{nr}) occurs, released PO_4 is sorbed onto $\text{Al}(\text{OH})_3$ in the sediment (Wilson et al. 2010). The $\text{Al}_{(\text{NaOH})}:\text{P}_{(\text{NaOH})}$ ratio is about 20:1 in recent sediment, decreasing to 10:1 in early post-YD sediment, close to the theoretical limit for adsorption of P by $\text{Al}(\text{OH})_3$ (de Vincente et al. 2008). This change in ratio parallels changes in the proportions of P_{nr} and P_r in the NaOH extract.

The Fe speciation is much more complex than Al and P, but can also be divided into pre- and post-YD phases (Fig. 3c). Prior to the YD, extractable Fe is largely Fe_{HCl} , probably derived from hornblende, the principal Fe-bearing phase in the bedrock and till. During the Holocene, this component declined to 5% of the maximum pre-YD flux. Concurrent with the pre-YD increase for $\text{Al}_{\text{NaOH25}}$, Fe_{BD} and $\text{Fe}_{\text{NaOH25}}$ increased but the flux of Fe_{tot} is only 20% of that of Al_{tot} and twice that of P_{tot} . Throughout the Holocene, Fe_{BD} and $\text{Fe}_{\text{NaOH25}}$ varied irregularly, but generally declined to the present. The $\text{Al}_{\text{NaOH25}}/\text{Fe}_{\text{BD}}$ ratio (essentially $\text{Al}(\text{OH})_3:\text{Fe}(\text{OH})_3$) ranged between 10 and 20 during the Holocene.

Diatoms

Diatom assemblages at the base of the core are dominated by *Staurosira construens* (Ehrenberg) Williams and Round and *Staurisirella pinnata* (Ehrenberg) Williams and Round (ESM 6). These two species rapidly decreased in abundance by 13,000 Cal Yr BP, while taxa such as *Fragilaria exigua* (Grunow) Krammer and Lange-Bertalot, *Discostella stelligera* (Cleve and Grunow) Houk and Klee, and *Aulacoseira perglabra* versus *florinae* (Camburn) E.Y. Haw dominated assemblages between 13,000 and 9,000 Cal Yr BP. After 9,000 Cal Yr BP, a diverse set of diatom taxa comprise the assemblages, primarily including several *Eunotia*, *Cymbella*, and *Frustulia* taxa. No major changes in diatom taxa are apparent after 9,000 Cal Yr BP.

The diatom-inferred pH declined rapidly from 7.99 ± 0.45 to near 6 by the beginning of the YD, and then declined more gradually to 5.52 ± 0.45 by 3,300 Cal Yr BP (Fig. 4). The 2007–2009 field pH ($n = 5$) averaged 4.9. The current lower pH results from: (1) slowly weathering bedrock and till, (2) continued slow acidification of the soil as base cations from labile phases become more depleted, (3) anthropogenic atmospheric input of excess SO_4 (largely as H_2SO_4), and (4) dissolved organic carbon that ranges from 3 to 7 mg L^{-1} . Atmospheric SO_4 is currently declining (National Atmospheric Deposition Program, <http://nadp.sws.uiuc.edu/>) while DOC may be increasing (Monteith et al. 2007), producing a partial offsetting effect on pH.

Diatom-inferred Total P (TP) was 25 $\mu\text{g L}^{-1}$ at the base of the core. By 13,000 Cal Yr BP, diatom-

inferred TP rapidly dropped to 6 $\mu\text{g L}^{-1}$; inferred values from 13,000 to 3,300 Cal Yr BP only varied between 4.6 and 8.5 $\mu\text{g L}^{-1}$ TP. The TP inferences from the diatom record suggest that the biological availability of P was much higher prior to 13,000 Cal Yr BP than after. Modern TP in the water column ($n = 5$) averages 7 $\mu\text{g L}^{-1}$, ranging from 5.1 to 7.9 $\mu\text{g L}^{-1}$. Ginn et al. (2007) point out that P and pH co-vary for diatom reconstructions. Unfortunately, there are no taxa represented in the sediment that are specific to P concentration, regardless of pH. The declines of diatom-inferred pH, TP, and P_{HCl} are concurrent.

Pollen

Early post-glacial sediment had very low concentrations of pollen and spores. The concentrations and fluxes were evaluated using a modified version of guidelines in Davis and Jacobson (1985) to differentiate among tundra ($<1,000$ grains/ cm^2/year), open forest ($6,000 \geq X \geq 1,000$ grains/ cm^2/year), and closed forest (>6000 grains/ cm^2/year). However, early in SMP's history (ca. 17,000 Cal Yr BP), the high portion of Mt. Desert Island would have been a nunatak near the margin of the Laurentide Ice Sheet, with the rising Atlantic Ocean nearby on the south side. After the margin of the ice sheet retreated, the site would have been an island surrounded by the de Geer Sea, the arm of the Atlantic Ocean that flooded central-interior Maine for nearly 4,000 years (Davis and Jacobson 1985). In both cases, few opportunities existed for vegetation to be growing in the nearby landscapes that later would provide abundant pollen to the site. Nearly all of the pollen deposited in the sediment would have originated within the catchment, which had abundant exposed bedrock with fringing vegetation around the lake. Consequently, pollen-influx values were <0.5 of those at nearby mainland terrestrial sites, and the boundaries for tundra-open forest-closed forest were halved.

Immediately after deglaciation, probably just prior to 16,600 Cal Yr BP, the site had little vegetation and what little pollen reached the sediments likely was carried considerable distance by winds. Sometime in the next 1,000 years (by 14,960 Cal Yr BP), scattered vegetation was present in the area, with willows (*Salix*), shrub birches (*Betula*), sedges (Cyperaceae), and various herbaceous taxa common in tundra. By

13,090 Cal Yr BP, the vegetation of the area had become much more developed, with scattered pine (*Pinus*) and spruce (*Picea*) trees, along with abundant poplars (*Populus*), shrub birches, and willows. The vegetative cover at the time could be described as woodland, while sedges and sage (*Artemisia*) also remained common, indicating a landscape with tundra-like conditions among scattered trees. By about 12,250 Cal Yr BP, conifer forest cover was complete, with spruces more common than pines. The spruces likely included both white and black (*Picea glauca* and *P. mariana*). Red spruce (*P. mariana*), which is now so abundant in Maine forests, was not present in the late-glacial (Lindbladh et al. 2003). By 11,900 Cal Yr BP, the onset of the YD had led to a reduced abundance of spruce and pine; at that same time, shrub birches, alders (*Alnus*), Ericaceae, and various herbaceous taxa were again common, indicating colder conditions. The onset of the Holocene warming at the end of the YD produced dramatic changes in the vegetation, initially with highly abundant spruce and a lesser amount of pine; white pine (*Pinus strobus*) occurred in the area for the first time. By 11,060 Cal Yr BP, pine was increasing in abundance, with white pine having an increasing share. The forest became considerably more diverse by 10,650 Cal Yr BP, with balsam fir (*Abies balsamea*), oak (*Quercus*), aspen (*Populus*), ironwood (*Ostrya/Carpinus*), and alder all gaining in importance. The effects of a warming climate continued for the next few centuries, with white pine becoming dominant; mixed hardwoods (oak, birch, alder) were also becoming common, while spruce was declining sharply. By 10,310 Cal Yr BP, white pine and balsam fir were highly abundant. Balsam fir remained even as spruce almost disappeared by 9,780 Cal Yr BP. By that time, hardwoods present included oak, birch, maple (*Acer*), and walnut (*Juglans*)—all common elements of the thermophilous Holocene forests of Maine that became established about 11,000 Cal Yr BP. This history of change is consistent with that of Davis and Jacobson (1985).

Discussion

We characterized water concentration, LOI, AMS ^{14}C age, sediment chemistry from sequential extraction, and diatom and pollen populations from the

sediment core from SMP, Maine, USA. Data indicate two distinct periods in the evolution of the landscape. From deglaciation (ca. 16,600 Cal Yr BP) to nearly the beginning of the YD (ca. 12,000 Cal Yr BP), the sediment is mineral-rich, including apatite, and poor in secondary Al and Fe phases. Secondary Al and Fe phases appeared in the sediment just prior to the YD. Almost concurrently, the concentration and mass rate of deposition for apatite declined. YD sediment partially returns to earlier post-glacial characteristics, with lower water concentration, LOI, and secondary Al and Fe. At the end of the YD the chemistry of the sediment changes abruptly; vegetation changes suggest warmer climate. Diatom-inferred PH increased slightly while P was constant. The Holocene was characterized by gradual changes in chemistry, and little change in diatom communities.

Phosphorus (P) biogeochemistry

Phosphorus and Ca biogeochemistry are linked initially. Prior to the YD (>12,000 Cal Yr BP), P and Ca occur predominantly as P_{HCl} and Ca_{HCl} (Fig. 3; ESM 4, Figs. 2 and 4). The $\text{Ca}_{\text{HCl}}:\text{P}_{\text{HCl}}$ molar ratio (2.17 ± 0.32 , $n = 9$ intervals) (ESM 7) is similar to that of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F})$) ($5:3 = 1.67$), suggesting strong control of this mineral on sediment extractable Ca. Dissolution of hornblende likely also contributes to Ca_{HCl} . Ca_{HCl} declines from 0.4 to $0.02 \mu\text{mol cm}^{-2} \text{ year}^{-1}$ between 16,600 and 11,000 Cal Yr BP. In post-YD sediment, the molar ratio of $\text{Ca}_{\text{HCl}}/\text{P}_{\text{HCl}}$ is $\gg 5:3$, the stoichiometry expected from congruent dissolution of apatite. Post-YD, most of the Ca_{tot} is $\text{Ca}_{\text{NH}_4\text{Cl}}$, varying between 0.45 and $0.25 \mu\text{mol cm}^{-2} \text{ year}^{-1}$, which we interpret as being controlled by the cation exchange capacity of organic matter in the sediment. The $\text{Ca}_{\text{NH}_4\text{Cl}}$ in the upper sediment corresponds to approximately $13 \text{ cmol}_c \text{ kg}^{-1}$ sediment.

These trends imply that apatite delivery to the lake declined substantially, although apatite in sediment may not be extractable if it is occluded within feldspar and quartz (SanClements et al. 2009). This decline is supported by three lines of independent data: (1) There is virtually no Ca_{HCl} and P_{HCl} in post-Little Ice Age sediment in five oligotrophic lakes studied in Maine (SanClements et al. 2009; Wilson et al. 2008; and Norton et al. 2008), in sharp contrast to the early post-glacial sediment from SMP. (2)

Preliminary SEM observation of B-horizon soil on till about 500 m to the west (but out of the watershed) found no apatite. (3) Lead isotope data from the SMP sediment (Norton et al. 2010) suggested that most of the apatite (with a very high $^{208/207}\text{Pb}$ value and a very low $^{207/206}\text{Pb}$ value) was depleted by the YD.

Currently, the Ca/P molar ratio in SMP water is $\gg 5:3$, indicating that Ca concentration is controlled by silicate weathering, and P is depleted from and retained in soil. If Ca were still from apatite, the concentration of P (assuming no retention by soil) in entering surface and groundwater would have to be about 150 ug P L^{-1} , an unrealistically high value. The P accumulation rate in the sediment does not support such a high flux of P into the lake.

Just prior to the YD, $\text{P}_{\text{NaOH}25}$ increased concurrently with $\text{Al}_{\text{NaOH}25}$, declined through the YD, and then dramatically increased to a peak value about 10,500 Cal Yr BP, before declining by 80% to the present. At the peak of $\text{P}_{\text{NaOH}25}$, the annual accumulation rate of P (P_r plus P_{nr}) in the sediment was approximately $0.6 \text{ umoles cm}^{-2}$. If precipitation and runoff were unchanged through the Holocene, and the P accumulation rate at the core site was twice that of the lake area average, the sediment P accumulation represents 25 ug P L^{-1} removed on a sustained basis. Greater sediment focusing would reduce this value. Ambient P in the lake would be some unknown amount higher, prior to the advent of the $\text{Al}(\text{OH})_3$ scavenging mechanism. However, the pre-YD climate was colder and dryer, likely with lower runoff. Consequently, the dissolution rate of apatite may have been lower, but dilution of P would also have been lower. $\text{Al}_{\text{NaOH}25}$ flux declined from the 10,500 Yr BP peak to about 50% of maximum value during the Holocene. Concurrently, the $\text{P}_{\text{NaOH}25}/\text{Al}_{\text{NaOH}25}$ ratio declined from 1:10 to 1:20. The decline of sediment P, relative to Al, is likely caused by three processes: (1) depletion of apatite in soils as a result of chemical weathering, prior to erosion and sedimentation, (2) increasing retention (adsorption) of anionic P in soils as pedogenesis in the catchment produced an increasing illuvial accumulation of secondary $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ (Lundström et al. 2000), and (3) increased anion adsorption capacity of the $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ as a consequence of long-term soil acidification (Nodvin et al. 1986; Navrátil et al. 2009). Processes (2) and (3) are well understood but probably are less important than apatite depletion.

During the decline of $\text{Al}_{\text{NaOH}25}$ and $\text{P}_{\text{NaOH}25}$, P_{HCl} declined to virtually zero. The “half life” ($t_{1/2}$) of the concentration of P_{HCl} since the YD is about 2,500 year. For $\text{P}_{\text{NaOH}25}$, it is about 5,000 year, while for $\text{Al}_{\text{NaOH}25}$ it is between 10,000 and 30,000 year. That $t_{1/2}$ for $\text{P}_{\text{NaOH}25}$ is shorter than for $\text{Al}(\text{OH})_3(\text{NaOH}25)$ is consistent with a limited and declining source of P from the watershed. The strong relationship between Al and P occurs for a similarly long sediment record from Plesné Lake, southwestern Czech Republic (Kopáček et al. 2006, 2007, 2009). They did not differentiate P speciation within the $\text{NaOH}25$ extract (P_r and P_{nr}), but the observed relationship between P_{NaOH} and Al_{NaOH} was equally strong. They attributed the relationship to adsorption of $\text{H}_2\text{PO}_4^{1-}$ and HPO_4^{2-} by freshly precipitated $\text{Al}(\text{OH})_3$ in the water column.

The pH of SMP, except for probably the last 100+ years, was likely above 5.2, based on diatom-inferred pH. This suggests that most ionic Al in the water column would precipitate to the sediment. The source of the $\text{Al}(\text{OH})_3$ in sediment would have been either from ionic Al precipitation in emerging groundwater (unlikely) or from photo-dissociation of Al-DOC complexes in the lake. The photo-dissociation would release inorganic ionic Al, which would precipitate in the higher pH environment of the lake. The $\text{Al}(\text{OH})_3$ precipitate would adsorb P and carry it irreversibly to the accumulating sediment. Reactive P (P_r) released during diagenesis of P_{nr} would be sorbed by already precipitated $\text{Al}(\text{OH})_3$. Currently (ESM 1), organically-bound Al is about half of the dissolved Al in SMP, and dissolved P is about 6 ug L^{-1} .

The Al-DOC complex originates in a terrestrial environment where DOC, produced in organic-rich, freely-drained soils, encounters mineral soil prior to entering the lake (Jacobson and Birks 1980). Modern surface soil $\text{pH}_{\text{H}_2\text{O}}$ values in this forest type range between ~ 3.5 and 4, and DOC of soil water can range up to $>50 \text{ mg L}^{-1}$, conditions suitable for the mobilization of organically-bound Al and equilibrium concentrations of ionic Al. Pollen data from SMP indicate the establishment of conifer forest cover, dominated by spruce, by about 12,250 Cal Yr BP. Some of this Al would reach surface waters; the rest is translocated from upper mineral soils to the B horizon. Freshly precipitated amorphous $\text{Al}(\text{OH})_3$ has a strong affinity for adsorbing anionic P (Navrátil et al. 2009) making adsorption irreversible at circum-

neutral pH, even during hypolimnetic anoxia or after sediment burial. Fe would also be mobilized from catchment soil, as for Al, but the Fe_{BD} values indicate that much less Fe was translocated from soil to the lake sediment (Fig. 3c). Sediment Al_{NaOH25} molar concentrations are approximately 20 times Fe_{BD} concentrations, precluding the release of P from lake sediment during any anoxia (Kopáček et al. 2005). The Al:Fe molar ratio for the granite bedrock is approximately 6:1, indicating that Al was, and still is, mobilized preferentially over Fe from the soils.

The YD resulted in a reduced abundance of spruce and pine. Concurrently, shrub birches, alders, Ericaceae, and various herbaceous taxa were again common, indicating colder conditions. These vegetation, lower temperature, and less humid conditions likely reduced production of DOC, thereby decreasing the terrestrial export of Al-DOC to the lake, reducing in-lake precipitation of amorphous $Al(OH)_3$ and the sequestration of P in the water column and sediment. The increased mass accumulation rate during the YD is largely from increased flux of primary minerals, and is accompanied by declines in % LOI and the rate of sedimentation of organic matter. These alterations in sediment composition may have been caused partly by cryoturbation and erosion of soil, coupled with decreased soil stabilization by vegetation. With post-YD warming, forest vegetation returned to late pre-YD conditions and the fluxes of Al_{NaOH25} and P_{NaOH25} peaked. Part of the decline of fluxes of elements in the sediment core is probably related to decreased sediment focusing (the lake shallowed from 10 to <5 m over 16,600 years), and increased stabilization of soils.

By inference from the chemical evidence, different mechanisms controlled dissolved P in the lake at different times. During the pre-YD period, weathering of abundant apatite in the sediment and soils would have contributed substantially more dissolved P to soil water, runoff, and lake water. Over time, exposed apatite in soil and sediment particles would become depleted, and secondary $Al(OH)_3$ accumulation in both substrates would have resulted in increasing P adsorption starting about 13,000 Cal Yr BP. This would result in decreasing dissolved P concentrations in the lake. Inferred total dissolved P concentrations from diatoms indicate this pattern was evident, with timing consistent with the sediment chemical evidence. The inferences about dissolved P are also consistent with the evidence

and interpretation of the long sediment core from Plešné Lake, in the Czech Republic (Kopáček et al. 2007). That site, an alpine cirque, also has a continental climate and likely remained cold for several 1,000 years after deglaciation.

Other water chemistry variables

Weathering of apatite involves H^+ consumption. Consequently, during periods of maximum weathering of apatite (and possibly calcite ($CaCO_3$) in the till), the pH of runoff water should have been relatively high. The rapid decline in diatom-inferred pH during the first 3,000 years of watershed evolution was likely caused largely by the rapid weathering of apatite (Boyle 2007a), as well as finely comminuted silicate minerals in the till (Schott et al. 1981). Pierret-Neboit and Lesser (personal commun.) observed free and occluded apatite by SEM in the pre-YD sediment. No calcite occurred in the sediment, at any level. The pH would decline after depletion of apatite, and become dominated by CO_2 - H_2O -silicate weathering. The pH would decline further with the addition of DOC, as vegetation increasingly dominated terrestrial biogeochemical cycling and organic soils developed.

Diatoms give indirect evidence for the concentration of Ca in the water column, through Ca's close correlation with pH and alkalinity. It is likely that Ca concentration declined through time, as soluble phases (especially apatite) became depleted in the soil (Engstrom et al. 2000; Boyle 2007a) and sorption by accumulating organic matter increased. In pre-YD time in SMP, diatoms suggest $pH > 7.5$, consistent with rapid weathering of Ca-phases and little DOC (implied by the lack of secondary $Al(OH)_3$). In post-YD time, sediment P_{HCl} indicates a nearly complete loss of non-occluded apatite (Fig. 3, ESM 7) and lack of a Ca:P molar stoichiometry close to 5:3. However, Ca_{tot} increased dramatically, concurrent with LOI. Sixty to 80% of this Ca is associated with Ca_{NH4Cl} . Ca_{NH4Cl} is about $13 \text{ cmol}_c \text{ kg}^{-1}$ of sediment; for 70% organic matter, equating to $20 \text{ cmol}_c \text{ kg}^{-1}$ organic matter, a reasonable value for organic matter in equilibrium with the lake water.

Lake Ontogeny and Chemical Weathering

Attempts to model the interaction of the atmosphere with Earth's crust after the start of deglaciation of the

northern hemisphere, starting about 22,000 years ago, focus on the impact of chemical weathering on the CO₂ cycle. The drawdown of CO₂ from chemical weathering was accelerated during the period immediately after exhumation of glaciated terrane, providing a negative feedback to climate warming. Empirical chemical studies such as the lake chronosequence by Engstrom et al. (2000), and long-term sediment chemical studies such as Kopáček et al. (2009) and this study provide useful information about kinetics of chemical weathering amelioration of climate warming since the Wisconsinan glaciation. More biological studies (Renberg 1990), coupled with modeling (Boyle 2007a, Boyle 2007b), also help constrain the kinetics of response to deglaciation. The pattern of lake ontogeny at SMP and at lakes of Glacier Bay, Alaska (Engstrom et al. 2000; Fritz et al. 2004), are similar in some respects, but different in (1) the evolution of nutrient status and productivity at the two sites, and (2) the time scale of their trajectory of increasing acidification and increasing DOC.

At Glacier Bay, newly formed lakes have low total nitrogen (TN). As alder (and other plants) occupy the watershed, lake-water total TN increases and reaches a peak approximately 100 years after lake formation, after which TN levels decline. Lake productivity, based on chlorophyll *a*, follows the same trends, reaching a maximum when TN levels are highest. However, in the Glacier Bay chronosequence of lakes, TP concentrations do not change substantially with lake age. In contrast, biologically available P was highest in SMP early in the successional sequence, and dropped over several 1,000 years during depletion of apatite, and then dropped further from sorption by Al(OH)₃. The decline in pH in the Alaskan lakes, occurring largely between 100 and 1,000 year, may be caused by the loss of free carbonate (as calcite) in the watersheds, not apatite. It is possible that the weathering of calcite caused saturation with respect to apatite reducing the weathering rate of apatite, delaying the release of P from the new soil. Glacier Bay catchment tills are relatively enriched in calcite (~4 wt. %; Crocker and Major 1955) and have little apatite.

The second major difference between the Alaskan chronosequence and SMP's history is the time over which dramatic chemical evolution occurs. The Alaskan lakes, as a group, developed lower pH, Ca,

and alkalinity, and higher DOC within several 100–1,000 years. The same transition in Maine occurred over a 3,000–5,000 year period. Phosphorus remains relatively constant within the Alaskan lakes over time, whereas at SMP, P declined dramatically only after apatite was selectively removed, by weathering, from the watershed soil, and sequestration of P by precipitating Al(OH)₃ and Fe(OH)₃ in soils, and Al(OH)₃ in the lake. The latter became important only after the development of terrestrial vegetation that produced organic-rich soils, leading to higher DOC production, DOC complexation of Al in soil solutions, and eventual delivery of the Al-DOC complex to the lake water column.

The temporal difference in behavior between the chronosequence lakes and SMP is likely a consequence of the dramatic differences in climate immediately after deglaciation, and the till mineralogy. Calcite weathers orders of magnitude more rapidly than apatite (Guidry and Mackenzie 2003), becoming depleted from soils within 200–300 year at Glacier Bay, while apatite weathers more slowly, persisting for >5,000 year at SMP, consistent with modeling results of Boyle (2007a).

The environment at the time of deglaciation in northern New England and the Canadian maritimes was significantly different from that of the Northwest. The western glacial border was strongly influenced by relatively temperate air masses from the Pacific, so much so that scattered spruce trees were able to live at the ice margin in Minnesota, even at the glacial maximum (Jacobson et al. 1987). In contrast, freshly deglaciated landscapes in Maine and the Canadian Maritimes were blocked from those temperate western air masses by the remaining Laurentide ice in the Midwestern USA and north-central region (Denton and Hughes 1981). The northeastern USA received mostly south-flowing air masses that originated from the large remaining portion of the Laurentide Ice Sheet. Thus, after deglaciation, there were several 1,000 years of tundra vegetation, before the first trees entered the landscapes (Davis and Jacobson 1985). Closed forests were delayed even longer.

Deglaciation near the Alaskan coast at the end of the Little Ice Age exposed fresh till and bedrock surfaces with neighboring forested landscapes and a wealth of seed sources for re-colonization of vegetation and soil development. The temperate wet

climate there promoted rapid changes in the vegetation and soils. In contrast, SMP was farther from seed sources and the moisture that would help to drive weathering of soils. Climatically, at least, the late-glacial conditions in Maine were probably much more similar to those present at the soil and vegetation (Jacobson and Birks 1980) chronosequences studied in the cold interior of the Yukon Territory, Canada.

These contrasting watershed-scale responses to deglaciation likely represent near end members of response—virtually instantaneous and delayed. As such, they represent important end members for reconstruction of the evolution of surface waters at a sub-continental to continental scale, after deglaciation. The time scale of “rapid” chemical response ranges from a few 100 to 1,000 years in Alaska (Engstrom et al., 2000) but 3,000–4,000 years at SMP, Maine, USA and Plesné Lake, Czech Republic (Kopáček et al. 2009). The SMP and Plesné records are probably more typical of response to continental climate. The processes demonstrated here and at the Alaskan sites are averaged in space and smeared over time as ice sheet margins retreat, exposing new landscape. The paleolimnological record of co-evolution of climate, soil, vegetation, surface water runoff chemistry, and lake ontogeny is a demonstration of the need to study ecosystems as an integrating unit, rather than parts of the system.

The controls on the flux of P to lakes are varied and include climate, bedrock type, soil development, and accumulation of organic matter. Bedrock that yields high alkalinity runoff commonly has higher dissolved P. Poorly-drained soils typically yield higher dissolved P in runoff than well-drained soils. After delivery to the lake, P may be removed from the water column by biological uptake and sedimentation (organic-P), formation of insoluble precipitates with essential P (e.g., apatite = $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), co-precipitated (e.g., in calcite = CaCO_3 , or other carbonate minerals), or adsorbed by sedimenting sesquioxides (Al, Fe, Mn) or particulate organic matter. Once in the sediment, diagenesis may result in mineralization of organic matter (Wilson et al. 2010), reductive dissolution of Fe and Mn hydroxides (Mortimer 1941) and related mobilization of P to deeper sediment or to the hypolimnion, and precipitation of various phosphate phases such as variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), apatite, or vivianite ($\text{Fe}_2(\text{PO}_4)_2$).

Release of P from sediment back to the water column during anoxia is repressed when the sediment $\text{Al}(\text{OH})_3\text{:Fe}(\text{OH})_3$ ratio is greater than 3 (Kopáček et al. 2005). This situation has been documented in short sediment cores (spanning no more than 500 years) of the six oligotrophic lakes we have evaluated in Maine and in many surface sediments of oligotrophic lakes and reservoirs (Kopáček et al. 2005). It is clear that the processes responsible for inactivation of dissolved P in sediment, thereby short-circuiting most P-regeneration mechanisms, are the production of dissolved Al by either terrestrially-derived DOC or anthropogenic acidification and subsequent precipitation of the Al as $\text{Al}(\text{OH})_3$ in the lake. The process in deglaciated terrane starts with the establishment of forest vegetation, which may follow deglaciation nearly immediately in maritime climates, or be delayed for thousands of years in more continental climates such as occurred in Maine and the Czech Republic. It is highly likely that most oligotrophic lakes (P-limited) result from these processes.

Summary

We documented the sequence of chemical and biological events and processes after deglaciation that link the terrestrial system with the aquatic system, and that control the millennial-scale productivity of a lake in a simple geologic setting. Our goal was to contribute to the understanding of linkages between the terrestrial and aquatic systems, their co-evolution, lake ontogeny, and long-term acidification. The sediment record from a 5.3-m core from SMP, Maine USA indicates strong co-evolutionary relationships among climate, vegetation, soil development, runoff chemistry, lake processes, and the lake diatom community.

Early post-glacial time (16,600 to 12,500 Cal Yr BP) was dominated by deposition of mineral-rich sediment, low in organic matter and secondary phases of Al and Fe; pollen indicate tundra conditions; diatom taxa indicate pH between 7.5 and 8, and total diatom-inferred P concentrations were on the order of $25 \mu\text{g L}^{-1}$, favoring higher productivity. Chemical weathering was rapid, probably dominated by weathering of apatite, producing high alkalinity, pH, Ca, and P. As climate ameliorated, about 12,500 Cal Yr

BP, forest vegetation became established and soils developed horizonation, including organic accumulations and incipient podzolic horizons, with accumulating secondary hydroxides of Al and Fe that would have sequestered P in the soils. Labile minerals (primarily apatite) became depleted in the soil, reducing the supply of P to the lake. Dissolved organic carbon from soil organic matter mobilized Al and Fe to the lake where the organic metal complexes were photo-oxidized, releasing ionic Al and Fe, which precipitated as $\text{Al}(\text{OH})_3$ (abundant) and $\text{Fe}(\text{OH})_3$ (minor). The sedimenting hydroxides adsorbed P from the water column, further reducing available P in the lake. Sedimented $\text{Al}(\text{OH})_3$ would retain PO_4 as it was diagenetically produced from organic-P. The retention of P by soils strengthened as a consequence of long-term acidification and pedogenesis, including accumulation of secondary $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. The lake was transformed from a more productive, high P, high pH, low DOC system to an oligotrophic, relatively low P, acidic, humic lake over a period of 16,600 years, a trend that continues. This long-term trend of changing climate, terrestrial biology, soils, and aquatic chemistry and phytoplankton was interrupted by the approximately 1,000-year long YD cooling, which led to a temporary cessation of these processes, a period that ended with the major onset of Holocene warming. The processes inferred from this multi-proxy study suggest that currently oligotrophic lakes may have their productivity limited by P retention in soils and P sedimentation by precipitating Al hydroxide, in addition to sequestration by sedimenting organic material.

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