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Diatom-inference models for acid neutralizing capacity and nitrate based on 41 calibration lakes in the Sierra Nevada, California, USA

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Abstract We investigated relationships among modern diatom species composition and physical and chemical characteristics of high-elevation lakes of the Sierra Nevada (California), to develop transfer functions that can be used to infer historic lake conditions. Data were collected from 50 lakes in National Parks and Forests of the central and southern Sierra Nevada. Multivariate statistical methods revealed that acid neutralizing capacity (ANC) and nitrate accounted for significant variation in diatom taxa. A training set with 242 modern diatom taxa from a subset of 41 lakes was used to develop transfer functions for ANC and nitrate using weighted averaging techniques. ANC and nitrate calibration ranges were 23.0–137 µEq/L and 0.18–9.5 µM, respectively. Coefficients of determination for the models were: ANC: $R^2 = 0.76$, and $R^2_{jackknife} = 0.44$; NO_3: $R^2 = 0.67$, and $R^2_{jackknife} = 0.27$. The ANC model was applied to the top 50 cm of sediments in Moat Lake to reconstruct ANC from *ca.* AD 350 to 2005. The reconstruction suggests that ANC declined by about 40 % (101–60 µEq/L) between the 1920s and the 1960s and then recovered to pre-1920s levels during 1980–2000. The magnitude of this ANC excursion was the largest observed during the past 1,600 years. We hypothesize that temporal variations in ANC were influenced by: (1) changes in rates of acid deposition, especially nitric acid and (2) variations in the timing and magnitude of snowmelt runoff.

Introduction

Global climate models indicate that future warming will be most pronounced in high-latitude and mountain

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regions (IPCC 2007), however, understanding the effects of climate change represents a challenge because of the broad range of factors that modulate responses to climate variability within arctic and alpine ecosystems. Lakes are excellent bellwethers of regional environmental change (Smol 2010), owing to their environmental sensitivity, and can function as early warning systems, indicating effects from global change on mountain ecosystems (Elser et al. 2009). The sensitivity of mountain lakes is attributable, in part, to dilute water chemistry, low primary production, and high flushing rates associated with snowmelt hydrological regimes (Hobbs et al. 2010).

In many mountainous regions, climate warming is occurring against a backdrop of increasing long-range transport of air pollutants (Cooper et al. 2010). In North America, the ecological responses to warming may be confounded by inputs of reactive compounds delivered by atmospheric deposition, including acid rain and nutrients (Fenn et al. 2003). Currently, the higher elevations of the Sierra Nevada (California) receive an average deposition of 3–4 kg ha^{-1} year^{-1} of inorganic nitrogen, with maximum rates of about 6–7 kg ha^{-1} year^{-1}; preindustrial rates of N deposition are estimated to have been in the range of 0.5–1.0 kg ha^{-1} year^{-1} (Baron 2006). Current rates of N deposition equal or exceed proposed critical loads for N in Rocky Mountain Lakes (Baron 2006). Lakes near the crest of the Sierra Nevada above 3,500 m have exceptionally low N retention capacity and several are exhibiting symptoms of N saturation (Sickman et al. 2003). With the exception of Lake Tahoe, long-term hydrochemical and limnological records for the Sierra Nevada began only in the 1980s, which raises the question of whether high-elevation lakes of the Sierra Nevada had been affected by atmospheric deposition earlier in the twentieth century, before routine monitoring began.

One approach to answering this question is the use of diatoms as indicators of lake chemistry and trophic state conditions. Ecological studies on diatoms in mountain lakes have been conducted in Europe (Catalan et al. 2009) and parts of the United States (Saros et al. 2011). There have been, however, few diatom-based calibration and paleo reconstructions for lakes in California's Sierra Nevada (Bloom et al. 2003; Holmes et al. 1989; Whiting et al. 1989). Holmes et al. (1989) evaluated the pH and acid neutralizing capacity of Emerald Lake over the past

150 years using multiple linear regressions of broad ecological groups of diatoms, and Index B, a ratio of pH ecological categories with coefficients developed for Swedish lakes. More recent diatom studies utilized statistical methods, such as weighted-averaging calibration and regression (Birks 1998; ter Braak 1995). Weighted-averaging regression calculates optimal environmental conditions for individual species by regressing their abundance values in a large set of lakes, and then estimates past water quality for historic samples based on the average of optima for species that are present in a sample, weighted by their abundance. Weighted-averaging calibration has strong predictive capability, and it provides realistic error estimates for inferences using a resampling method called bootstrapping.

In this study, we used diatoms preserved in lake sediments to better understand the effects of global change on Sierra Nevada lakes during the twentieth century. We performed canonical correspondence analysis (CCA) to quantify the relationships among diatom species composition and the physical and chemical characteristics of 50 Sierra Nevada lakes (California, USA) sampled during the summers of 2007 and 2008. We used multivariate ordinations to fully explore relationships among lakes and diatom assemblages and developed diatom transfer models for acid neutralizing capacity (ANC) and nitrate (NO$_3^-$) based on weighted-averaging with data from 41 of the 50 lakes. We explored the utility of the ANC transfer model in Moat Lake, a subalpine lake on the eastern slope of the Sierra Nevada, to detect changes in lake chemistry caused by climate change and atmospheric deposition. We augmented these analyses by investigating the relationship between lake ANC and snowpack conditions using a long-term record of watershed measurements from Emerald Lake (Sequoia and Kings Canyon National Parks) and discuss the relative importance of climate and atmospheric deposition in modulating ANC changes in Sierra Nevada lakes.

Materials and methods

The calibration lakes

Water samples and short sediment cores were collected from 50 high-elevation lakes ("calibration lakes") in the central Sierra Nevada (Electronic

Supplementary Material, ESM Table 1) during the summers of 2007 and 2008. The calibration lakes were chosen from a database of Sierra Nevada lake chemistry that contains records from >500 lakes sampled since 1980 by resource agencies and scientific investigators (J. Sickman, unpublished data). Calibration lakes were situated between 2,198 and 3,791 m above sea level and their surface area ranged from 0.55 to 83.6 ha, depth from 3 to 35 m and watershed area varied from 40.1 to 944 ha. Thirty-five of the lakes had non-native fish populations when sampled.

Moat Lake (elevation 3,224 m) is a subalpine lake located 12.5 km WNW of Mono Lake in the Humboldt-Toiyabe National Forest. It was one of four lakes from which we collected long sediment cores, but the only one with a sedimentation rate sufficient to provide a high-resolution history of the twentieth century. The lake has a maximum depth of 7 m, area of 2.8 ha and lies within a 59.1-ha watershed. A majority of the watershed is comprised of the western flank of Dunderberg Peak (elevation 3,772 m), a rock and scree-covered slope with a mean angle of 35°. The bedrock geology of the watershed is dominated by metasedimentary rocks including quartzite and argillite. Less than 10 % of the watershed is vegetated.

Lake sampling procedures

All sediment and water samples were collected from an inflatable raft at a station overlying the deepest part of the lakes, which was located after performing a coarse bathymetric survey using a hand-held echo-sounder. Vertical profiles of dissolved oxygen and temperature (meter intervals) were measured to assess lake stratification, using a portable meter equipped with a polarographic oxygen electrode and thermistor. The lakes were sampled between late July and early October 2007 (n = 42) and 2008 (n = 8). Surface sediment samples were collected with a gravity corer (Aquatic Research Instruments). We collected four replicate cores from all lakes along transects spaced at 10-m intervals. With care, the sediment–water interface of the cores was collected without disturbance, which allowed us to obtain samples of the most recent sediment deposition. Each of these cores was sectioned in the field using an extruding tool and metal blade. The upper 0–1-cm sections were placed into Whirl–Pak bags and were kept cool in the field and transported to the laboratory at UC Riverside on ice. In the laboratory, sediment samples were kept at 5 °C until analyzed.

At Moat Lake, we used a rod-corer to collect a single 210-cm core, which was sectioned every cm. All core sectioning was done in the field immediately after collection and samples were placed in Whirl-Pak bags. Samples were kept cool during transport and were held at 5 °C until analyzed. Diatom counting was restricted to the top 50 cm of the core.

Water samples were collected at depths of 1 m and 7 m using a hand-operated peristaltic pump and a graduated length of silicon tubing. Samples for dissolved nutrients [nitrate, soluble-reactive phosphorus (SRP), total dissolved N (TDN), total dissolved P (TDP), dissolved silica, major cations and anions (Ca, Mg, Na, K, Fe, Cl, SO_4)] were filtered into clean HDPE bottles using 1.0-μm polycarbonate membrane filters (47-mm diameter). Samples for pH, ANC and specific conductance were collected, unfiltered, in HDPE bottles. Prior to use, all filtering apparatus and bottles were soaked in 18-megaohm deionized water for several days. All bottles were rinsed three times with sample prior to filling.

Samples for particulate carbon (PC), particulate nitrogen (PN) and particulate phosphorus (PP) were collected on pre-combusted, 47-mm Pall-Gelman A/E, glass-fiber filters. The filters were used with a magnetic filter tower, side-arm flask and hand vacuum pump. Four filters were collected from each depth of the lake by gently drawing water through the filters using vacuum less than 0.5 bar. After collection, the filters were folded in half (sample side in) and placed into small petri dishes and kept cool during transport. In the lab, seston samples were stored at −20 °C until analyzed.

Laboratory analyses

A high-quality pH meter and Ross combination electrode were used to measure pH and ANC using the Gran titration method. The meter was calibrated using pH 7 and 4 buffers and the calibration was checked by measurements of two weak acid solutions: 10^{-4}N HCl (theoretical pH = 4.0) and 10^{-5}N HCl (theoretical pH = 5.0). Specific conductance was measured with a conductivity meter and electrode (cell constant = 1.0) and readings corrected to 25 °C. Chloride, nitrate and sulfate were measured by

chemically suppressed ion chromatography on a Dionex ion chromatograph. Calcium, magnesium, sodium, potassium and iron were measured by inductively coupled plasma, atomic emission spectroscopy (ICP-AES). Total dissolved nitrogen and phosphorus (TDN and TDP) and PP were determined after persulfate digestion using the cadmium reduction and the molybdenum blue-ascorbate methods, respectively. Silica was determined on a filtered subsample using the silico-molybdate method. Filters containing PC and PN were dried and analyzed for carbon and nitrogen mass on an elemental analyzer.

The carbon and nitrogen elemental and isotopic composition of freeze-dried sediments was measured using a Delta V isotope ratio mass spectrometer interfaced with an elemental analyzer. National Institutes for Standards and Technology (NIST) glutamic acid standards (RM 8573 and 8574) were included in all runs and isotope values are reported in per mil units (‰) relative to Pee Dee Belemnite ($\delta^{13}C$) and atmospheric N_2 ($\delta^{15}N$). Prior to analysis of $\delta^{13}C$, the filters were acid fumigated to remove trace amounts of inorganic carbon. Nitrogen isotope measurements were conducted on un-fumigated sediments.

The chronology of the top 50 cm of the Moat Lake sediment core was established with ^{210}Pb (1–19 cm) and ^{14}C dating (25–50 cm). Radiometric measurements (^{210}Pb and ^{226}Ra) were made using low-background gamma counting with well-type intrinsic germanium detectors at the Florida Institute of Paleoenvironmental Research at the University of Florida (Schelske et al. 1994). Sediment ages were calculated using the constant rate of supply (CRS) model (Appleby and Oldfield 1983; Oldfield and Appleby 1984). Age errors were propagated using first-order approximations and calculated according to Binford (1990). The Moat Lake core had a total unsupported ^{210}Pb inventory of >30 dpm cm^{-2} and there was good agreement between ^{210}Pb dates and ^{137}Cs dates, indicating that the core was collected from an accumulation zone.

Radiocarbon measurements were conducted on humin fractions isolated from sediment using acid and base pretreatment (Olsson 1986). Because the Moat Lake watershed is almost devoid of vegetation, we did not find any macrofossils in the sediment core above 50 cm and were forced to use bulk sediments for dating. The humin isolates were prepared using standard combustion, extraction and graphitization

procedures and the ^{14}C abundances were measured by accelerator mass spectrometry. Raw radiocarbon ages were converted using IntCal09 (http://ac.uk/oxcal/OxCal.html; Reimer et al. 2010). An age-depth model was fitted to the ^{210}Pb and ^{14}C dates using a sixth-order polynomial equation (Fig. 1). Because of the overall greater uncertainty of the ^{14}C dates (Fig. 1), we restricted the use of the age-depth model to estimating sediment chronology below a depth of 15 cm in the sediment core; at the 15 cm level and above we used the ^{210}Pb dates directly.

Diatom taxonomy, enumeration and data transformations

All diatom slides were prepared using techniques described in Weckstrom et al. (1997). A minimum of 500 diatom valves were identified and enumerated from each sample under oil immersion using an Olympus BHS microscope (1,000× magnification). The 49- and 50-cm sediment layers consisted of volcanic ash and low diatom abundance and poor preservation prevented counting of these samples. Diatom taxonomy followed Hustedt (1930), Patrick
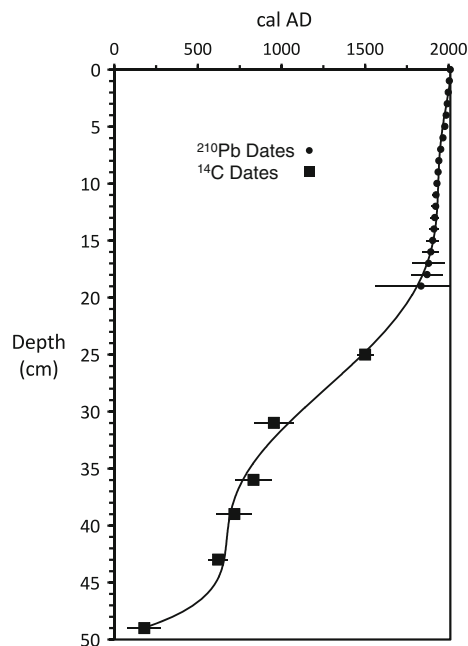
Fig. 1 Age-depth model for the top 50 cm of the Moat Lake long core. *Error bars* for ^{210}Pb dates denote the 1s model error. *Error bars* for ^{14}C dates denote the 95.4 % confidence intervals derived from IntCal09 (Reimer et al. 2010)

and Reimer (1966) and Krammer and Lange-Bertalot (1986) and more recent literature (Kociolek and Stoermer 1993; Potapova and Hamilton 2007).

The diatoms preserved in the surface lake sediments and the measured geographic (8), major ion (14), nutrient and trace element (10), and sediment variables (5) (ESM Tables 1 and 2) were used to develop a calibration dataset to estimate the environmental optima and tolerances of the diatom taxa. Our study employed transfer-function inference models such as weighted averaging (WA) (Birks 1998) and weighted averaging partial least squares (WA-PLS) (ter Braak and Juggins 1993). Prior to model development, the species and environmental data were screened to identify and eliminate outliers. In cases for which the distributions of environmental variables were found to be strongly skewed (e.g. nitrate), transformations were applied to the data (ln(x), log(x + 10) or Box–Cox) (Box and Cox 1964).

Relationships between diatoms and environmental data were investigated using CCA (Fig. 2a). CCA with manual forward selection (analogous to stepwise selection in multiple regressions) and partial CCA (pCCA) were run for each variable individually and with other significant variables as conditional co-variables (Fig. 2b). Manual forward selection among individually significant variables was conducted using permutation testing to determine those variables with significant explanatory power (Monte Carlo tests with 99 unrestricted permutations, $p < 0.05$; ter Braak 1986). Additionally, to assess whether each individually significant variable explained a unique fraction of the variance in the diatom species assemblages, pCCA was run for each variable individually and with other significant variables as conditional co-variables.

Weighted-average modeling

Transfer functions were tested using partial least squares (PLS), WA with inverse and classical deshrinking, and WA-PLS (ter Braak 1995). The gradient lengths in the diatom data DCCA were less than 2 SD for each variable of interest, suggesting there could be linear relationships between the diatom composition and the environmental variables (ter Braak 1995). However, because WA-PLS has been shown to be a better calibration method than PLS when dealing with diatom species and environmental data, even when the floristic gradient length was less that 2 SD (Rosén et al.

2000), we used unimodal methods to develop the diatom transfer functions (ter Braak and Juggins 1993; ter Braak and Smilauer 1998). In addition, commonly used methods of weighted averaging with and without tolerance weighting and/or deshrinking were compared with the WA-PLS technique for all three variables. As a result of comprehensive data analyses from all tested models, final regression models were developed for ANC and nitrate using the WA method with classical deshrinking.

Model performance was assessed by examining; (1) the coefficient of determination (R^2) between diatom-inferred (predicted) and observed chemistry, (2) the root mean square error (RMSE), and (3) the distribution of residual values (observed-inferred) (Birks 1998; Birks et al. 1990). Since these performance assessments use the same data to generate and evaluate the model, we also employed the statistical approach of jackknifing (Miller 1974) to generate a jackknifed coefficient of determination ($R^2_{jackknife}$) and a root mean square error of prediction (RMSEP), which is a measure of the overall predictive abilities of the training set. Models with an $R^2_{jackknife}$ greater than 0.35 and an R^2 greater than 0.5, were accepted. Models with $R^2_{jack-knife}$ less than 0.35, but an R^2 greater than 0.6, were allocated a 'low' utility ranking. Our thresholds are commensurate with those published elsewhere (Philibert et al. 2006; Chen et al. 2008; Reavie et al. 2009). All transfer functions were computed using C2 software version 1.5 (Juggins 2007). Additionally, species optima and tolerances were calculated for physical and chemical variables with significant explanatory power.

Results

Modern diatom distribution

Over 240 taxa were identified in the calibration lakes, and the most common and noteworthy species and their distributions are contained in ESM Table 2. The floristic composition of the Sierra Nevada lakes was characterized by the dominance of small species typical of dilute, oligotrophic lakes. *Staurosirella pinnata* (Ehr.) Williams and Round (30 lakes) and planktonic *Discostella stelligera* (Cl. & Grun.) Houk & Klee (37 lakes) often co-dominated with acidophilic species from the *Pinnularia* group (>40 lakes), and
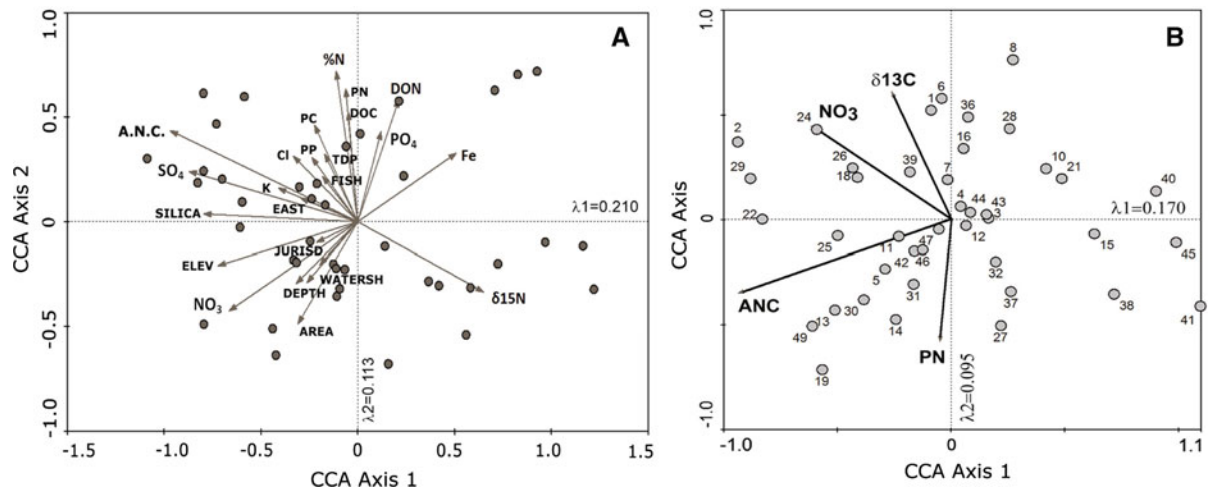
Fig. 2 Canonical correspondence analysis (CCA) of the 41-lake data set and 24 environmental variables (*symbols* denote individual lakes). **a** Full CCA with all 24 environmental variables. *Arrows* indicate environmental variables that exert significant and independent influence on diatom distribution.

b CCA with forward selection identifying the most significant variables in our datasets (ANC, NO_3, sediment $\delta^{13}C$ and PN). The *numbers* in this *panel* correspond to the lake descriptions contained in ESM Table 1

Tabellaria flocculosa (Roth) Kütz. (40 lakes). More than 20 species each of the genera *Eunotia* and *Pinnularia* were identified in our samples.

Among the identified species, 91 % were benthic and only 9 % were considered planktonic. The majority of the common benthic taxa in the lakes were *Pinnularia mesolepta* (Ehr.) W. Sm. (45 lakes, mean abundance = 4.8 %, maximum abundance = 20 %), *Tabellaria flocculosa* (40 lakes, mean = 3.4 %, maximum = 21 %), *Achnanthidium minutissimum* (Kütz.) Czarnecki (37 lakes, mean = 3.7 %, maximum = 36 %), and *Encyonema minutum* (Hilse) Mann, *Sellaphora pupula* (Kützing) Meresch. (both 36 lakes). Species of the genus *Psammothidium* (mostly *P. levanderi* (Hust.) Bukht. & Round) were present in a majority of the lakes (45 lakes, relative abundance >5 %). There were only 7 lakes in which planktonic diatom species made up more than 50 % of the taxa, and in these cases the populations were largely composed of *Discostella stelligera* (mean abundance = 9.5 %, maximum abundance = 70 %), *Asterionella formosa* Hass. (mean abundance = 1.8 %, maximum abundance = 27 %), *Aulacoseira alpigena* (Grun.) Kram. (mean abundance = 5.5 %, maximum abundance = 39 %), *Aulacoseira distans sensu lato* (mean abundance = 5.7 %, maximum abundance = 62 %) and *Fragilaria crotonensis* Kitton (mean

abundance = 10 %, maximum abundance = 27 %). Six lakes had a ratio of planktonic to benthic species higher than 1, with the highest ratio observed in Bingaman Lake (ratio P/B = 18).

Species common in lakes with higher concentrations of nitrate (>5 μM) and ANC (>120 μEq L^{-1}) were *Discostella stelligera*, *Fragilaria construens* (Ehr.) Grun. and *Psammothidium sensu lato*. Lakes with lower ANC (<20) were dominated by species from the genus *Pinnularia* and *Aulacoseira distans sensu lato*, with a significant presence of *Psammothidium* and *Eunotia*. The Simpson's diversity index typically ranged from 0.7 to 0.9. Lower diversity index values (0.3 and 0.5) were often observed in the lakes with the highest nitrate values (e.g. Arctic 5 and Hamilton).

Species previously identified as potential indicators of nitrogen-deposition effects in high-elevation lakes were not abundant in most calibration lakes (Saros et al. 2005); *Asterionella formosa* was found in 12 lakes and *Fragilaria crotonensis* occurred in 19 lakes (Table ESM 2). Of the 24 lakes containing at least one of these two taxa, only three of the lakes did not contain fish when sampled (two of these three lakes, Eastern Brook Lake and Amphitheatre Lake, had non-native fish populations earlier in the twentieth century). The highest *Fragilaria crotonensis* densities were recorded in Upper Rae (9.3 %), a lake deemed an

outlier because it possessed the highest conductivity in our dataset (39 µS/cm). *Asterionella formosa* was most abundant in Kearsarge Lake (27 %).

Selection of environmental variables and lakes

Because the original set of 37 environmental data included redundant information and outliers, we selected only those variables that either: (1) were not significantly correlated to other environmental variables (correlation coefficient <0.6) or (2) exerted an independent influence on diatom distributions. In addition, we excluded variables for which the inflation factor produced by canonical correspondence analysis (CCA) was >20, meaning that a variable was strongly correlated with other variables and therefore had no unique contribution to the regression (Birks et al. 1990). Variables that are ratios (e.g. the Redfield ratio) were not included in the models, owing to high covariance with other variables. Based on the exploratory CCA of the original 50 lakes, lakes were deleted from future analyses if: (1) the lake score was outside the 95 % confidence limits around the sample core means in analyses of both species and environmental data for the full calibration set (Gauch 1982), or (2) the lake had an environmental variable with extreme values (>3 standard deviations from the mean; Birks et al. 1990). The final calibration data set consisted of 41 lakes and 24 environmental variables (Table ESM 1). All diatoms from surface sediment samples were included in constructing the final models.

An initial PCA using all 37 environmental variables from the calibration lakes indicated good separation of lakes along major environmental gradients (graph not shown). The first axis was strongly correlated with indices of weathering (ANC, conductivity, silica) and some nutrients, principally TP and TN. The second axis correlated with nitrate and PO_4 and the DIN:TP ratio. Detrended correspondence analysis, based on the dominant diatoms showed some separation of lakes based on diatom assemblages at each site (graph not shown). *Staurosira construens* Ehr. and *Staurosirella pinnata* were common in lakes at the highest elevations. Although there was no clear elevational separation among middle- and low-elevation lakes, some of the low-elevation lakes were dominated by species of the genus *Aulacoseira*. The major outlier was Bingaman Lake, which showed a very distinct diatom population dominated by *Synedra parasitica*

and *Aulacoseira alpigena.* Neither water depth, nor lake surface area, showed a statistically significant effect on lake grouping among major environmental gradients or diatoms.

Axes 1 and 2 of the final CCA (Fig. 2a), using only the selected 24 environmental variables (eigenvalues of $\lambda 1 = 0.210$ and $\lambda 2 = 0.113$), accounted for 37.6 % of the cumulative variance of the diatom data. The diatom-environmental correlations for axes 1 and 2 were relatively high, with values of 0.87 and 0.93, respectively, indicating a strong relationship between the diatom species and the 24 environmental variables selected.

Results of CCA with forward selection with unrestricted Monte Carlo permutation testing (Fig. 2b) and pCCA (in which each of the selected variables was assessed for significance with the remaining variables used as conditional co-variables) demonstrated that four environmental variables, ANC, nitrate, sediment $\delta^{13}C$ and water-column PN, explained a significant proportion (17.6 %, $p \leq 0.05$) of the variance in the diatom species data for the 41-lake dataset, and consistently showed a significant and independent relationship with the diatom assemblages. Of these four variables, ANC alone explained the greatest amount of variance in the diatom communities (6.9 %), followed by nitrate (4.7 %), $\delta^{13}C$ (3.9 %) and PN (3.6 %) (Table 1). When analyzed in constrained and partially constrained CCA, ANC yielded highly significant relationships with canonical axes ($p \leq 0.001$) and showed a $\lambda 1/\lambda 2$ ratio of 0.7. Nitrate also showed significant values ($p \leq 0.05$) with a $\lambda 1/\lambda 2$ ratio of 0.4. In contrast, $\delta^{13}C$ and PN were not used for model development because: (1) the CCA analyses showed lower $\lambda 1/\lambda 2$ ($p \leq 0.05$, ratio of 0.2), and only slightly higher $\lambda 1/\lambda 2$ (0.04) in partially constrained CCA, and (2) both variables were significantly correlated to CCA axis 1 (Table 1).

Diatom-inference models

Because the exploratory analyses revealed that ANC and nitrate were the most important characteristics for explaining diatom species composition of Sierra Nevada lakes, we developed diatom-inference models for ANC and nitrate using the final 41-lakes/24-environmental-variables dataset (Fig. 3). Each of these models potentially reflects some aspect of atmospheric

Table 1 Summary of canonical correspondence analysis (CCA) for the training set in relation to the main environmental variables identified by forward selection

Variable	Constrained CCA			Partially constrained CCA			Detrended CA
	Total explained variance	Correlation to axis $\lambda 1$	$\lambda 1/\lambda 2$	Unique explained variance	Correlation to axis $\lambda 1$	$\lambda 1/\lambda 2$	Length of gradient
ANC	6.89 ($p < 0.005$)	−0.79	0.70	6.07 ($p < 0.001$)	−0.81	0.79	1.47
NO$_3$	4.70 ($p < 0.01$)	0.71	0.41	3.33 ($p < 0.05$)	0.76	0.43	1.04
Sediment δ^{13}C	3.88 ($p < 0.05$)	0.81	0.30	3.24 ($p < 0.05$)	0.88	0.42	1.08
PN	3.60 ($p < 0.05$)	0.81	0.27	3.24 ($p < 0.05$)	0.73	0.42	1.14

Percentage variance of species data explained by the variable on axis 1 are from constrained and partially constrained CCA, the correlation of each variable to axis 1 and the ratio between eigenvalues for axis 1 and axis 2 ($\lambda 1/\lambda 2$). Significance is given in parentheses

N deposition and climate variability on lake chemistry and ecology. When applied to sediment cores, a nitrate model (Fig. 3c, d) could potentially reveal changes in nutrient supply rates arising from atmospheric deposition of N or changes in the N assimilation of terrestrial ecosystems caused by climate change. Similarly, an ANC model (Fig. 3a, b) can potentially reveal changes in catchment weathering rates brought on by acid deposition and interannual variability in the volume of snowmelt runoff.

Among the models tested, the WA method with classical deshrinking best represented both the diatom-ANC and the diatom-nitrate relationships. The $R^2_{jackknife}$ and RMSEP for ANC models developed with WA and WA-PLS were very similar, however for nitrate, the $R^2_{jackknife}$ derived from the WA models were superior to those derived from the WA-PLS method (0.27 vs. 0.069). The WA method is known to be less vulnerable to data dimensionality and outliers (Hastie and Tibshirani 1990), which allowed us to use more diatom species in the model (important because the differences in diatom assemblages among lakes were greater than typically observed in temperate lakes), without degrading the $R^2_{jackknife}$ statistic. Other advantages of the WA method include that it does not assume linearity, as does multiple regression, and it is not hindered by multi-collinearity. Overall, the WA method performed better with our species-rich dataset and relatively large environmental gradients (Hill and Gauch 1980; ter Braak and Juggins 1993).

ANC produced relatively robust models with relatively high coefficients of determination ($R^2 = 0.76$, $R^2_{jackknife} = 0.44$) and relatively small errors (RMSE = 18.4 µEq/L, RMSEP = 25.0 µEq/L)

compared to the measured range of ANC in our calibration dataset (23.0–137 µEq/L). The model for nitrate had lower predictive ability ($R^2 = 0.67$, $R^2_{jackknife} = 0.27$, Table 2) and also exhibited a weak trend in the residuals ($R^2 = 0.04$). The nitrate model underestimated the highest values of the reconstructed spectrum. This error can be attributed to the fact that only lakes with low to moderate nitrate (range 0.18–9.5 µM) were included in the transfer function, because we had to exclude the highest-nitrate lakes (up to 38 µM) to achieve a normal distribution in our dataset.

The WA model allowed calculation of ANC and nitrate optima and tolerances and the effective number of occurrences of the diatom species (Fig. 4). For diatom species found in more than 10 lakes and at least in two lakes with relative abundance more than 5 %, the WA optima for ANC ranged from 53.5 µEq/L (*Aulacoseira distans sensu lato*) to 93.8 µEq/L (*Cavinula pseudoscutiformis* (Hust.) Mann and Stickle). When all diatom species were included, the ANC optima ranged from 23.0 to 131 µEq/L. Nitrate optima for common species (in transformed µM units) ranged from 0.28 (∼0.4 µM untransformed) (*Frustulia rhomboides* (Ehr.) De Toni) to 0.46 (∼1 µM untransformed) (*Achnanthidium minutissimum*) (Fig. 4). For all diatom species the nitrate optima ranged from 0.25 to 0.50 in transformed µM units, equal to a nitrate range of approximately 0.25–1.2 µM.

ANC reconstruction for Moat Lake

Using the ANC model, ^{210}Pb dating and age-depth model, we reconstructed ANC in Moat Lake for the
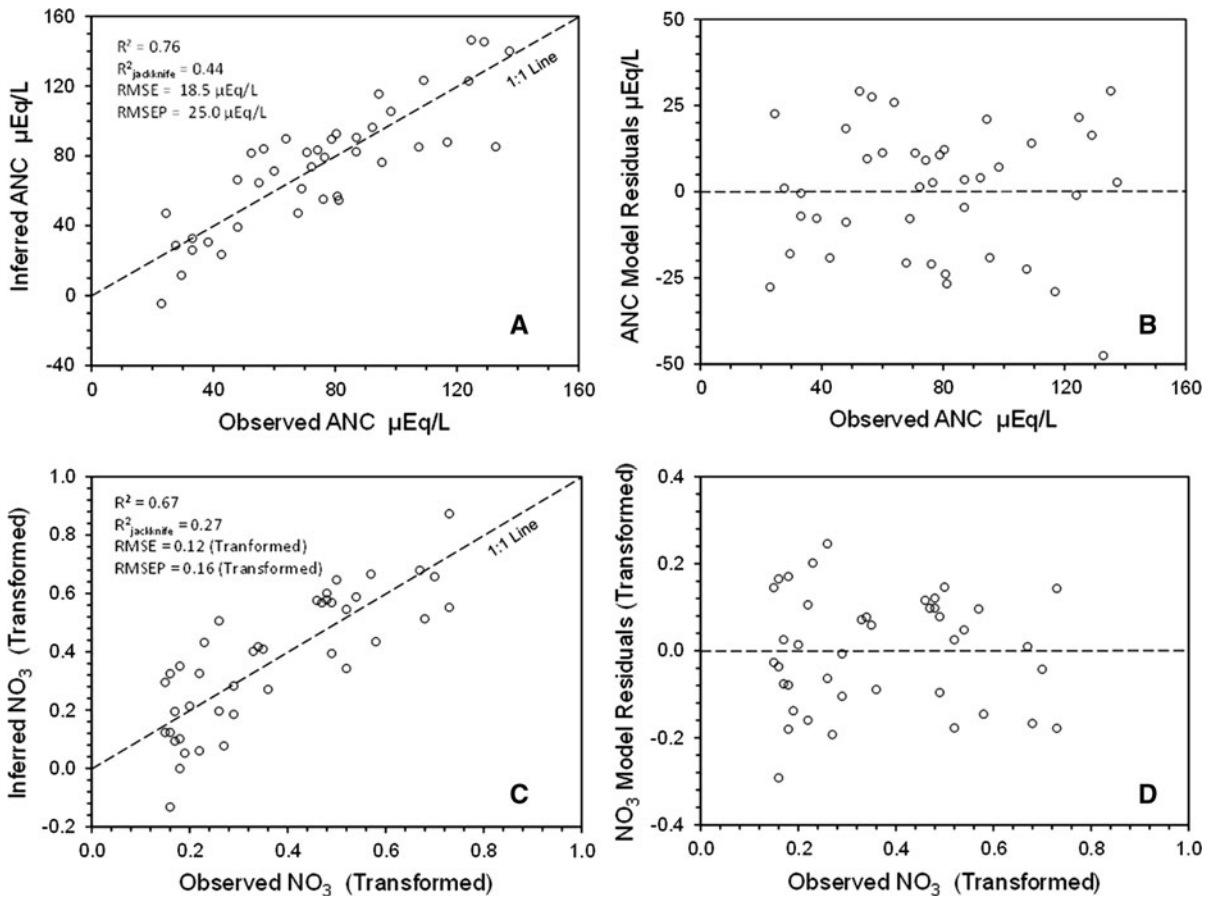
Fig. 3 Regression model plots of diatom-inferred versus observed **a** ANC and **b** NO_3 using the weighted averaging method with classical deshrinking for ANC (untransformed data) and NO_3 (transformed data). **c**, **d** Show the model residuals (inferred values minus observed values)

Table 2 Main statistics for transfer functions for ANC and NO_3

Model	$R^2_{apparent}$	RMSE	$R^2_{jackknife}$	RMSEP	Mean bias	Max. bias	Pattern in residual	Number of diatoms included	Number of lakes included	Data transform	Data range for included lakes
ANC	0.76	18.5	0.44	25.0	0.06	27.3	0.004	242	41	No	23–137 µEq/L
NO_3	0.67	0.13	0.27	0.17	0.00	0.10	0.040	242	41	Box–Cox	0.18–9.5 µM

Jackknife R^2 is the coefficient of determination between predicted and observed values using leave-one-out cross validation. RMSEP is the root mean square error of prediction based on Jackknifing. Mean and maximum bias are measures of systematic errors in the predictions. Error and bias terms are expressed in concentration units for ANC and in transformed concentration units for NO_3. Pattern in Residual is the R^2 value for the model residuals

period *ca.* AD 350–2005 (Fig. 5). With the exception of relatively low ANC levels in the fifth and sixth centuries AD, ANC in Moat Lake varied between 85 and 115 µEq/L from *ca.* 600 AD until the early part of the twentieth century. In the eighteenth and nineteenth centuries, variations in reconstructed

ANC fell within an even smaller range, 105–115 µEq/L. Beginning in the 1920s, however, we observed a multi-decadal decline in ANC, with a minimum occurring in the 1960s and early 1970s that was about 60 % of the ANC values observed in the first decades of the twentieth century. The most rapid
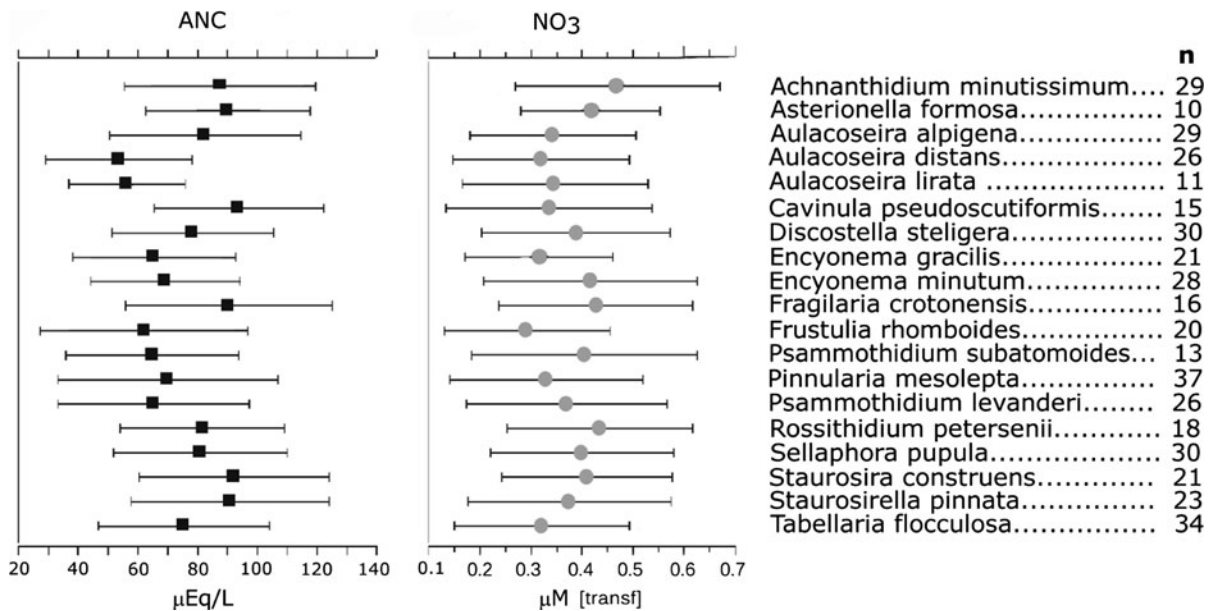
Fig. 4 The optima and tolerances for diatom species found in a minimum of 10 lakes in our dataset, with a relative abundance above 5 % in at least two lakes

period of ANC decline at Moat Lake occurred in the 1950s. Following the ANC minima there was a strong increase in ANC during the 1980s and 1990s. By the beginning of the twenty-first century, ANC values had recovered to levels observed in the early twentieth century.

The diatom stratigraphy revealed that the 1920–1960 ANC decline was associated with a strong increase in the relative abundance of *Fragilaria crotonensis* and moderate increases in *Aulacoseira distans sensu lato* and *Psammothidium subatomoides* (Fig. 5). During the recovery of ANC in the 1980s and 1990s, the relative abundance of *Fragilaria crotonensis* stabilized at about 2 %, whereas *Aulacoseira distans sensu lato* and *Psammothidium subatomoides* relative abundances returned to pre-1920s levels. The abundance of two taxa, *Sellaphora pupula* and *Navicula disjuncta* declined beginning in the 1920s and these species became very rare or disappeared in the late twentieth century, despite representing about 1–3 % of the diatom assemblage in Moat Lake for more than 1,500 years (Fig. 5). It is possible that both species passed their ANC tolerance threshold and, despite the recovery of ANC, were outcompeted by other diatoms. At the time of the lowest ANC, we also noted a short period of *Discostella stelligera* increase.

Discussion

We sought to use diatom assemblages in two ways to assess the effects of atmospheric deposition and climate variation on Sierra Nevada lakes. In the first approach we assessed whether the lakes with the highest nitrate concentrations or lowest ANC levels (putatively the lakes most likely to be affected by atmospheric deposition) contained similar diatom species. In the second approach, we attempted to use diatom stratigraphy and a reconstruction within a single lake (Moat) to test the hypothesis that Sierra Nevada lakes had already been affected by atmospheric deposition before routine limnological monitoring began in the 1980s.

Diatom indicators of atmospheric deposition in the Sierra Nevada

Of the five lakes with the highest nitrate concentrations (10217, Arctic 4, Gem, Hamilton and Maclure; all values >5 μM), two diatom species occurred in relative abundance >10 % in more than one of these lakes: *Psammothidium subatomoides* and *Staurosirella pinnata* (both are benthic species). Of these species, *Psammothidium subatomoides* also exhibited an
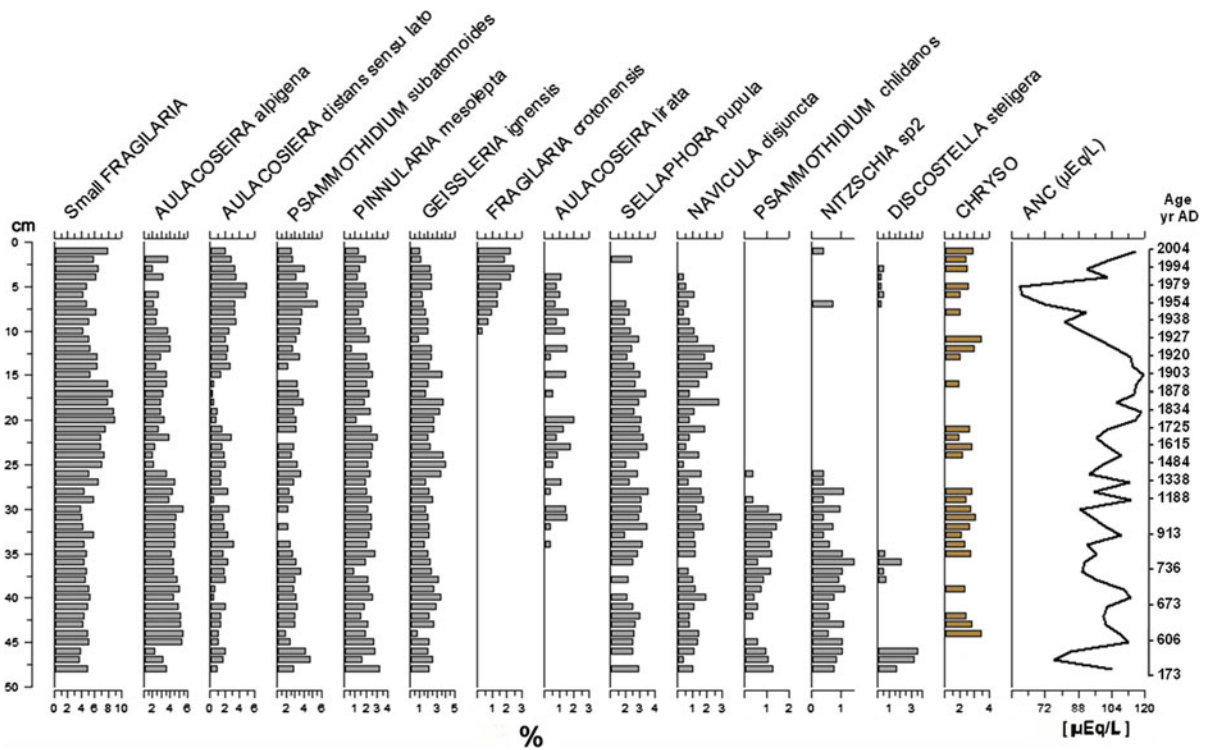
Fig. 5 Stratigraphy of selected diatom species and reconstruction of ANC in Moat Lake spanning the period of *ca.* AD 350–2005

increase in abundance as ANC declined during the twentieth century in Moat Lake (Fig. 5). *Staurosirella pinnata* (a benthic diatom), however, did not have a high nitrate optimum relative to other common taxa (Fig. 4), suggesting that it is not a broadly nitrophilic species in the Sierra Nevada. Recent investigations in the Rocky Mountains have identified two planktonic diatom species associated with increased nitrogen deposition, *Asterionella formosa* and *Fragilaria crotonensis,* but these mesotrophic, planktonic species are relatively uncommon in the Sierra Nevada, limiting their use for identifying N-affected lakes in synoptic surveys such as ours. In Moat Lake, however, *Fragilaria crotonensis* did strongly respond to decreasing ANC, suggesting that its stratigraphy in short sediment cores may have utility for identifying individual Sierra Nevada lakes affected by nitric acid deposition during the twentieth century (Saros et al. 2011).

Five calibration lakes had ANC <30 µEq/L: Amphitheatre, Nydiver, Powell, Topaz and Maclure. Two diatom species occurred in relative abundance of >10 % in three of these lakes: *Aulacoseira distans*

sensu lato and *Pinnularia mesolepta*. In Moat Lake we observed increases in relative abundance of *Aulacoseira distans sensu lato* around the time of the 1960s ANC minimum, but no trend in *Pinnularia mesolepta* abundance was detectable (Fig. 5). The most common planktonic species in our data set was *Discostella stelligera* and increases in its relative abundance have been associated with lake acidification (Battarbee et al. 1999) and oligotrophic conditions (Clerk et al. 2000; Leahy et al. 2005). In Moat Lake we noted three periods of increased relative abundance of *Discostella stelligera* that were associated with declines in reconstructed ANC: *ca.* AD 170–470, AD 700–800 and AD 1950–1980 (Fig. 5). In the calibration lakes, however, *Discostella stelligera* showed relatively wide ANC tolerance (Fig. 4).

Overall, the diatom assemblages of Sierra Nevada lakes are defined by a variety of cosmopolitan species adapted to oligotrophic habitats. A majority of the calibration lakes were dominated by benthic species and only a few lakes had communities dominated by planktonic diatoms. A similar scarcity of planktonic diatoms in apparently suitable, high-elevation lakes

has been observed in previous studies (Cameron et al. 1999). The predominance of benthic diatom species in the Sierra Nevada may be problematic from the standpoint of using individual taxa as indicators of nitrogen deposition in synoptic surveys. Because the nitrogen demands of benthic diatoms are partially met by fluxes of ammonium and nitrate from lake sediments, we speculate that their response to allochthonous inputs of nitrogen may be weaker than those for planktonic diatom species.

Problems with nitrate reconstructions

Reconstructions of nitrate in individual lakes using diatom inference models provide an alternative method for identifying lakes affected by atmospheric deposition, however there are challenges to using this approach. The predictive ability of our nitrate model ($R^2_{jackknife} = 0.27$) was weaker than that of the ANC model ($R^2_{jackknife} = 0.44$), which can be attributed to the relatively short nitrate gradient incorporated in our model, owing to the fact that high-nitrate lakes (e.g. Hamilton and Arctic 4; Table ESM 1) were underrepresented in our dataset. Our nitrate model showed a relatively high slope in the residuals ($R^2 = 0.04$), suggesting that the model underestimates the highest values of the reconstructed spectrum. As a result, nitrate reconstructions using our model would be most accurate within ultra-oligotrophic and oligotrophic Sierra Nevada lakes, but would have limited ability to reconstruct nitrate levels in lakes like Hamilton and Arctic 4. The effect of uneven sampling of the environmental gradient on species optima, predicted by ter Braak and Looman (1986), has been noted previously (Cameron et al. 1999; Telford and Birks 2011). This type of error and lower predictive ability appears to be common in nutrient models in North America (Siver 1999). Although the reconstructive power based on $R^2_{jackknife}$ and errors of prediction for our nitrate model is in the typical range for nutrient models in the literature (Siver 1999), we believe the actual utility is low and we therefore chose not to present the nitrate reconstruction at Moat Lake.

It will likely be difficult to substantially reduce errors in a nitrate inference model for Sierra Nevada lakes. There is a scarcity of high-nitrate lakes in the Sierra Nevada, and many of the lakes with nitrate >10 μM lie in watersheds with N-bearing bedrock, making them unsuitable for a general nitrate model

(Bradford et al. 1994). Nitrogen-limited lakes present a special problem because any additions of anthropogenic nitrogen during the growing season could be totally assimilated and not expressed in water chemistry measurements. Nitrogen-limited diatoms could also shift to limitation by phosphorus, creating additional problems. Arnett et al. (2012) observed that under conditions of nitrogen limitation, *Asterionella formosa* and *Fragilaria crotonensis* can be pushed into P limitation with small additions of nitrogen, at which point these species decline in abundance as a consequence of suboptimal N:P ratios and competition from more eutrophic diatom species. These observations may help explain why previous synoptic studies have been unable to show a meaningful correlation between N deposition rates and nitrate concentrations in Sierra Nevada lakes (Clow et al. 2010; Sickman et al. 2001).

Factors controlling long-term variation of ANC in Sierra Nevada lakes

ANC emerged as the primary environmental variable explaining variations in diatom populations in the Sierra Nevada and the coefficients of determination ($R^2 = 0.76$, $R^2_{jackknife} = 0.44$) derived for the ANC inference model compare favorably with results from other lake studies in North America (Siver 1999). Our findings support previous research suggesting that ANC and pH are important factors controlling distribution and changes in diatom composition in the Sierra Nevada (Holmes et al. 1989; Whiting et al. 1989). ANC is generally accepted as a useful criterion for lake response to acid deposition (Lien et al. 1996; Wilander 2001) and relative intra-annual variations of ANC at high elevations are less pronounced than those for nitrate, making ANC a less ambiguous environmental index. Because nitrate and sulfate are the most important acid anions in precipitation in the Sierra Nevada (Sickman et al. 2001), reconstructions of ANC may partially reflect the effects of changing nitric and sulfuric acid deposition. Thus, we hypothesize that reconstructions of ANC can be useful in developing critical loads for atmospheric deposition in the Sierra Nevada.

The ANC reconstruction at Moat Lake suggests roles for both atmospheric deposition and climate variability in the control of ANC variations over the past 1,600 years (Fig. 5). Prior to the twentieth century, multiple observed fluctuations in lake ANC

could have been the effect of climate variation, including trends in the timing and magnitude of snowmelt, as we argue below. In the twentieth-century record, we observed a pronounced ANC decline beginning in the 1920s, with a bottoming out of ANC in the 1960s and 1970s followed by a strong increase in ANC during the period 1980–2000. The most rapid decline in ANC occurred in the 1950s, coincident with a period of accelerating use of fossil fuels, synthetic fertilizers and rapid population growth, noted in assessments of twentieth-century global change (Steffen et al. 2004). Assuming that the ANC time series at Moat is a result of acid deposition, our supposition that Sierra Nevada lakes had already responded to global change prior to routine monitoring in the 1980s is confirmed. However, pH reconstructions for four Sierra Nevada lakes (Harriet, Lake 45, Emerald and Eastern Brook) developed by Whiting et al. (1989), suggest that acid–base changes during the twentieth century are not consistent across all lakes. Harriet Lake had no significant trend in pH over the past 250 years and the Eastern Brook Lake reconstruction showed evidence for alkalization over the twentieth century. Patterns of pH change in Lake 45, however, are similar to the ANC trends we observed at Moat Lake: (1) acidification beginning in 1915, with greatest pH decline occurring from 1915 to 1950 and (2) a pH minimum in the 1970s. The latest date in the Lake 45 reconstruction was in the early 1980s and yielded a pH that was higher than the 1970s pH minimum, suggesting that pH recovery might have begun in the 1980s. In Emerald Lake, there were no strong patterns in pH over most of the twentieth century, but Whiting et al. (1989) did identify a statistically significant increase in pH after 1976. Together, these observations suggest that thresholds for acid deposition may have been crossed for some, but not all Sierra Nevada lakes during the twentieth century, and that more research is needed to identify acid-affected lakes.

Long-term changes in Sierra Nevada climate complicate the interpretation of acid–base chemistry of Sierra Nevada lakes and offer an alternative driver for some of the changes in pH and ANC observed in the twentieth century. Porinchu et al. (2007) developed a chironomid-based inference model for lake temperature and applied it to three Sierra Nevada lakes: McGee, Rocky Bottom and Moat Lake. They noted strong warming in all three lakes after the 1970s, with

lake water temperatures rising 0.5–1.0 degrees above the long-term average. The inferred warming observed in Moat Lake corresponds closely with the recovery of ANC in Moat Lake noted in our study. We hypothesize that the warming trend detected in Moat Lake by Porinchu et al. (2007) could be the result of decreasing snowpack or earlier snowmelt, which would also lead to an increase in summer/autumn ANC as our reconstruction demonstrates.

Testing this hypothesis requires long-term observations of lake chemistry and snowpack dynamics, which are lacking for Moat Lake. Our multi-decadal research program on other Sierra Nevada lakes, however, has identified strong linkages between lake chemistry and snowpack variability. During years with deep snowpacks, most lakes have higher nitrate concentrations, lower ANC and are colder during the growing season (Leydecker et al. 1999; Sickman et al. 2003). Importantly, snowmelt depression of ANC persists for many weeks and is detectable even at the end of the summer. As a result, long-term data from Emerald Lake (1983–2011) show that September ANC is positively correlated with maximum summer lake temperature ($r = 0.61$) and negatively correlated with snowpack water content ($r = -0.88$) (Fig. 6). The correlation between lake temperature and snowpack water content ($r = -0.65$) was weaker than the correlation between ANC and snowpack. These observations suggest that decreasing snowmelt volume or earlier snowmelt would result in warmer lake temperature and higher ANC levels, as was observed in the Moat Lake reconstructions after the 1970s.

Assuming that Moat Lake exhibits a strong inverse relationship between ANC and snowmelt (Fig. 6b), we can then interpret ANC variations prior to the twentieth century as changes in the timing and magnitude of snowmelt runoff. We are currently comparing the ANC reconstruction at Moat to instrumental and paleo-records of climate in the Sierra Nevada to quantify their coherence. Intriguingly, ANC reconstructions produced for intensively studied lakes like Emerald may provide a tool for reconstructing past snowpack variability in the Sierra Nevada (i.e. reconstructed ANC, Fig. 5, could be transformed into a snowpack reconstruction using a relationship like that in Fig. 6b). This new paleo-proxy could potentially augment existing climate proxies in regions above treeline in the Sierra Nevada, albeit at a
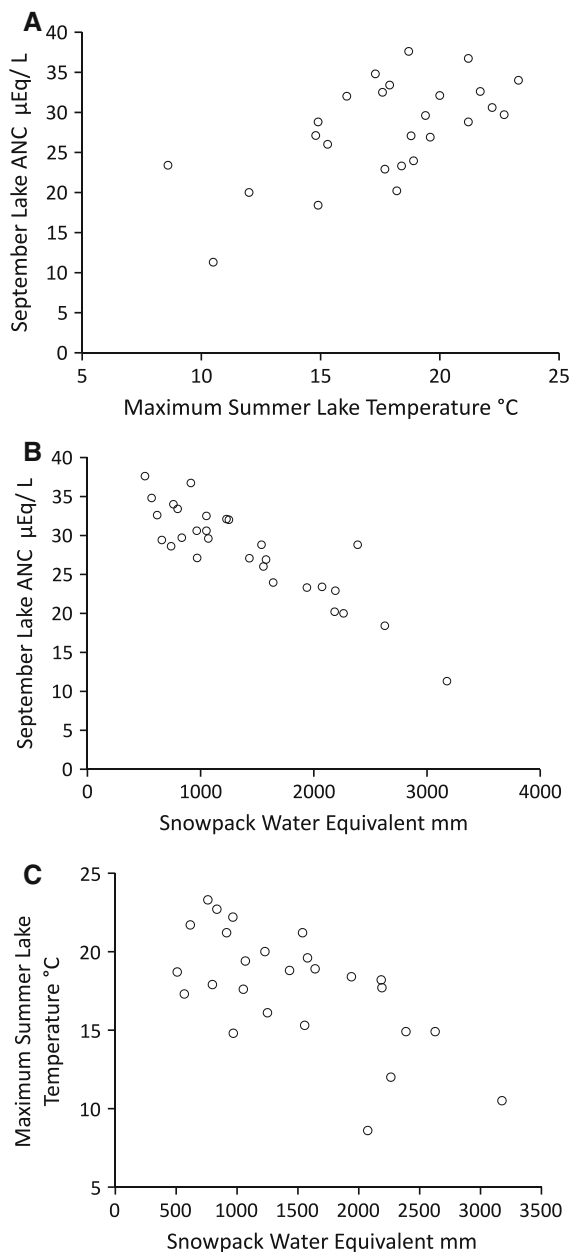
Fig. 6 Relationships among ANC, water temperature, and spring snowpack for the Emerald Lake watershed for the years 1983 to 2011. **a** September lake ANC (volume-weighted mean of all depths) versus maximum summer lake temperature. **b** September lake ANC versus April snow water equivalent and **c** maximum summer lake temperature versus April snow water equivalent

resolution coarser than tree-ring records and applicable over shorter time horizons (centuries vs. millennia). We are investigating relationships between lake

chemistry and snow survey records to determine if the tight coupling between ANC and snowpack observed at Emerald Lake is a quantifiable feature of high-elevation lakes throughout the Sierra Nevada.

We did not include water temperature in the development of the inference models, although successful temperature models were previously developed for other Sierra Nevada lakes (Bloom et al. 2003). Diatom-based temperature reconstructions, using summer surface water temperature or July air temperature, have been criticized, especially under conditions of changing acid–base conditions (Anderson 2000). Challenges to diatom-temperature models are based on the observation that climate change may affect lake ecosystems more strongly through alterations in lake chemistry and that diatom populations are generally less sensitive to temperature change than to variations in pH, ANC and nutrient levels. The data from Emerald Lake suggest that summer lake temperature in the Sierra Nevada is controlled, almost equally, by two factors: (1) the magnitude and timing of snowmelt runoff and (2) summer climate forcing, including variation in lake energy balance (Fig. 6c). Thus, we cannot clearly distinguish the causes for the apparent depletion and recovery of ANC in Moat Lake during the late twentieth century and more data and analyses are needed. We are in the process of making additional sediment geochemical analyses, including measurements of nitrogen isotopes (Wolfe et al. 2007) and spheroidal carbonaceous particles (Rose et al. 1994), with the goal of developing better proxies of twentieth century atmospheric deposition in the Sierra Nevada.

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