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MOUNTAIN LAKES

Diatom changes in two Uinta mountain lakes, Utah, USA: responses to anthropogenic and natural atmospheric inputs

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Abstract Diatom assemblages in sediments from two subalpine lakes in the Uinta Mountains, Utah, show asynchronous changes that are related to both anthropogenic and natural inputs of dust. These lakes are downwind of sources of atmospheric inputs originating from mining, industrial, urban, agricultural and natural sources that are distributed within tens to hundreds of kilometers west and south of the Uinta Mountains. Sediment cores were retrieved from Marshall and Hidden lakes to determine the impacts of atmospheric pollution, especially metals. Paleolimnological techniques, including elemental analyses and ^{210}Pb and $^{239+240}$Pu dating, indicate that both lakes began receiving eolian inputs from anthropogenic sources in the late 1800s with the greatest increases occurring after the early 1900s. Over the last century, sediments in Marshall Lake, which is closer to the Wasatch Front and receives more precipitation than Hidden Lake, received twice the concentrations of metals and phosphorus as Hidden Lake. Comparison of diatom and elemental data reveals coeval changes in geochemistry and diatom assemblages at Marshall Lake, but not at Hidden Lake; however, a major shift in diatom assemblages occurs at Hidden Lake in the seventeenth century. The change in diatoms at Marshall Lake is marked by the near disappearance of *Cyclotella stelligera* and *C. pseudostelligera* and an increase in benthic, metal-tolerant diatoms. This change is similar to changes in other lakes that have been attributed to metal pollution. The marked change in diatom assemblages at Hidden Lake indicates a shift in lake-water pH from somewhat acidic to circumneutral. We hypothesize that this change in pH is related to drought-induced changes in input of carbonate-rich desert dust.

Keywords Diatom · Metals · Dust · Eolian · Geochemistry · Alpine

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Introduction

Mountain lakes are commonly considered to be pristine because of limited human activity in their catchments; however, dust and aerosols originating from human activities thousands of kilometers upwind can potentially have deleterious impacts on these lakes. Lake-sediment records commonly archive changes in atmospheric deposition (Smol, 2002), and previous research has shown that lakes far distant from urban and industrialized areas have been affected by atmospheric contributions associated with industrialization (e.g., Battarbee et al., 1999; Dixit et al., 1999; Neff et al., 2008). Typically, atmospheric emissions from mining and/or fossil-fuel combustion increase metal concentrations and lower pH (Keller & Gunn, 1995), and these changes have negative effects on aquatic vegetation, fish, and waterfowl (Schindler, 1988; Keller & Gunn, 1995). Although many lakes in the eastern United States have been affected by acid deposition (Dixit et al., 1999), mountain lakes in the west do not appear to be significantly acidified (Baron et al., 1986; Charles, 1990). Here we use a multi-proxy, paleolimnological approach to determine the downwind effects of human activities, including mining, industry, agriculture, and urbanization, on lake ecosystems in the Uinta Mountains, Utah (USA). The Uinta Mountains are an east–west trending mountain range located approximately 100 km downwind of the Wasatch Front, a densely populated area located just west of the Wasatch Range (Fig. 1). Previous study has shown that these lakes are not acidic (Christensen & Jewell, 1998), allowing us to test whether increased metal deposition has impacted mountain lake ecosystems.

Beginning in the late nineteenth century, human activities have increased air pollution and decreased air quality along the Wasatch Front (Lamborn & Peterson, 1985). Mining activities in this region

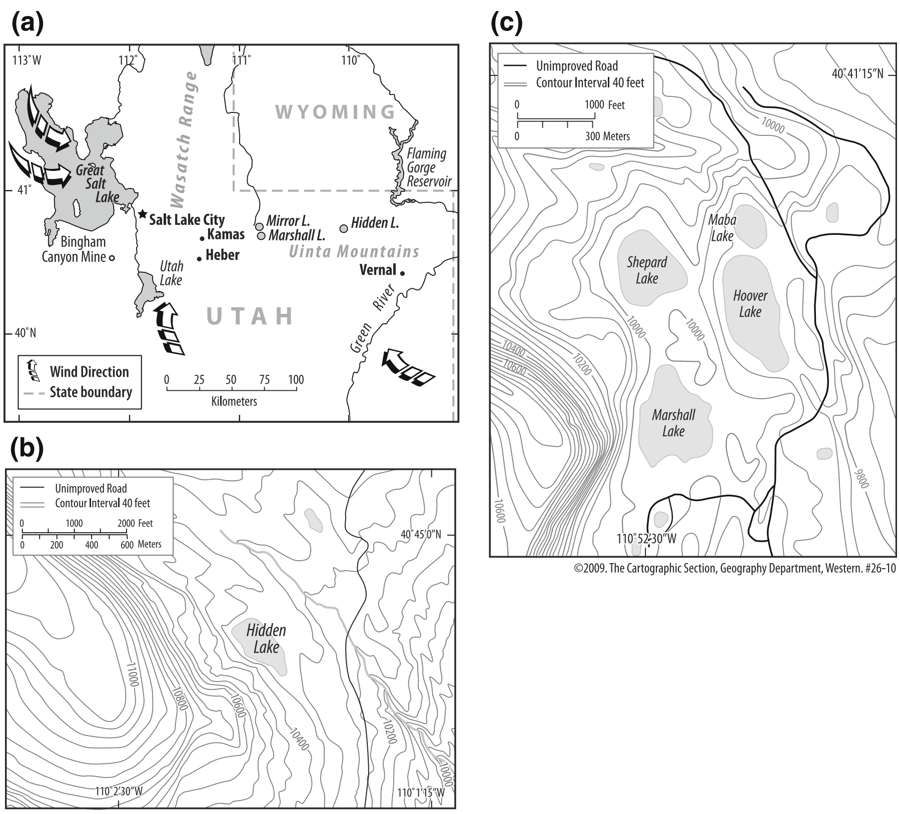


Fig. 1 Location maps of study areas. **a** Map showing the location of the Uinta Mountains at the border of Utah, Colorado and Wyoming. The arrows indicate the main wind directions. **b**, **c** Maps showing surrounding area of Marshall Lake and Hidden Lake, respectively

began about 1863 (McPhee, 1977). The Bingham Canyon Mine (Fig. 1), one of the largest mining operations in the United States, opened in 1865 and has produced more copper than any other mine (approximately 18 million tons) (Voynick, 1998; Kennecott Utah Copper, 2008). Open-pit mining continues at this site today.

Land disturbance associated with urbanization and agriculture also increases dust and atmospheric pollution (Wetzel, 2001; Neff et al., 2008). The first settlers arrived along the Wasatch Front in 1847, and sheep and cattle grazing were prevalent by 1890 (Sillitoe, 1996). Agriculture was the primary industry along the Wasatch Front for nearly a century. Although agriculture continues to be important, the conversion of farmland to residential or industrial uses began as early as 1940. During the early part of the twentieth century, industry began contributing significantly to atmospheric pollution (Environmental Protection Agency, 2002; Utah Department of Environmental Quality, 2006).

We used elemental analyses of sediments from two subalpine lakes, Marshall and Hidden Lake, in the Uinta Mountains (Fig. 1) to track atmospheric deposition including metals, rare earth elements, and phosphorus, and diatom analyses to determine changes in lake ecosystems. Chemical analyses of lake sediments can provide information about mineralogic sources and environmental change (Boyle, 2001). A previous lake-sediment record from Mirror Lake, located approximately 3 km north of Marshall Lake (Fig. 1), indicates increased metal deposition, including Pb, Zn, Cu, and Cd, beginning in the early 1900s (Kada et al., 1994).

Diatoms (*Bacillariophyceae*), microscopic, unicellular algae with siliceous cell walls that exist in most aquatic environments, give information regarding lake-ecosystem health (Smol, 2002). Diatoms are widely used bioindicators, because they are abundant, diverse, and commonly well preserved in the sediment record (Moser, 2004). Diatom species have specific ecological tolerances, and short life spans that enable them to respond rapidly to environmental change (Reid et al., 1995; Moser et al., 1996). Previous paleolimnological research has shown that diatom community composition (Ruggiu et al., 1998; Cattaneo et al., 2004; Kamenik et al., 2005; Salonen et al., 2006), diatom size (Cattaneo et al., 1998), the abundance of deformed diatoms (Ruggiu et al., 1998; Cattaneo et al., 2004), diatom diversity (Ruggiu et al., 1998), and diatom bioaccumulation (Cattaneo et al., 2008) are sensitive to metal pollution. Most of these studies were conducted on lakes with extremely elevated metal concentrations owing to nearby point sources of pollution. Here, we determine the effects of atmospherically deposited metals in mountain lakes.

Study area

The Uinta Mountains are located in northeastern Utah between 109° to 111°W and 40° to 41°N, near the Utah-Colorado and Utah-Wyoming borders (Fig. 1). Most lakes in the Uinta Mountains were formed by glacial processes and lie above 3,050 m. For this research, two lakes were selected: Marshall Lake, near the west end of the Uinta Mountains and ~90 km east of the Wasatch Front, and Hidden Lake, near the east end of the Uinta Mountains ~160 km from the Wasatch Front (Fig. 1). These sites are similar in all aspects except distance to the Wasatch Front, thereby allowing us to examine the effect of distance from potential pollution sources (Table S1, Electronic supplementary material).

Both lakes are surrounded by subalpine forest, comprised mainly of the arboreal species *Picea engelmannii* (Englemann spruce) and *Abies lasiocarpa* (subalpine fir). Precambrain rocks of the Mount Watson and Hades Peak units of the Uinta Mountain Group underlie Marshall and Hidden lakes, respectively. Both geologic units are comprised mainly of quartzites and arkoses with some shales (Bryant, 1992), which have extremely limited buffering capacities (Christensen & Jewell, 1998). Field observations indicate that the lake catchments are mainly sandstones with little shale. Overlying the bedrock are glacial deposits, and both lakes are situated in late Pleistocene (Smiths Fork) till. Soils in the subalpine zone of the southeastern Uinta Mountains near Hidden Lake are Dystrocryepts and Cryorthents that are characterized by Ca-enriched silt caps of eolian origin (Bockheim et al., 2000). No information is available for soils of the southwestern region of the Uinta Mountains where Marshall Lake is located, although they are likely comparable given the similar parent material. It is not known whether Ca-enriched soil caps exist in the Marshall Lake catchment.

Climate of the Uinta Mountains varies with elevation and from east to west. Precipitation increases with elevation (Table S2 in Electronic supplementary material). For example, the Chepeta SNOTEL site, which is at relatively high elevation, receives almost four times as much snow as a lower elevation site at Vernal, UT. Orographic uplift of humid air from the west generally results in more precipitation on the western half of the range than on the eastern half (Munroe & Mickelson, 2002). Sites in the western Uinta Mountains receive, on average, approximately twice the yearly precipitation of eastern sites (Table S2, Electronic supplementary material). The timing of maximum precipitation also varies across the range; highest monthly precipitation in Vernal occurs during the Spring (April, May) and Fall (September, October), and lowest values occur in winter months. In contrast, maximum precipitation in Heber occurs during the cold season (October to March, Western Regional Climate Center, 2006). The variation in timing of maximum precipitation may be related to variations in the importance of monsoon precipitation (MacDonald & Tingstad, 2007). Owing to the rugged topography and paucity of weather stations, wind directions for this region are difficult to characterize; however, the dominant wind directions affecting the Uinta Mountains are from the west and northwest and the south and southeast (Klink, 1999; Western Regional Climate Center, 2006) (Fig. 1).

Methods

Methods for sediment sampling, limnological measurements, and water chemistry

In 2001, a K-B gravity corer (Glew et al., 2001) was used to retrieve two ~50-cm-long cores from the deepest part of each of the lakes. Two cores from each lake were required to provide enough sediment for the anticipated analyses. Core 1 was used for ^{210}Pb and diatom analyses, and core 2 was used for all other analyses, including $^{239+240}$Pu. At each lake cores were collected within a few meters of each other and carefully transported back to shore where they were extruded vertically and sampled at 0.5-cm contiguous intervals.

Limnological measurements and water samples were obtained during a single sampling day in July 2002. Given the extreme variability of climate conditions in this environment, measurements and samples collected on one day may not be representative of the range of limnological conditions, particularly metal concentrations, which occur over a year. For example, during peak meltwater flows, metals may be more concentrated (Malinovsky et al., 2002).

Temperature and specific conductivity were measured using a YSI-M85 meter; a minimum of three pH readings were obtained with multiple hand-held Hanna pHep 2 meter. Water was sampled approximately 0.5 m below the lake surface near the core sites using a pre-cleaned polyethylene bottle. The water was filtered through a 0.45 μm Millipore filter and divided into two 30 ml samples, one for anions and one for cations and trace metals. The sample for cations and trace metals was adjusted to a pH of 2 by addition of concentrated nitric acid. Samples were kept cool and in the dark until they were shipped to the aqueous geochemistry lab in the University of Minnesota Department of Geology and Geophysics. Samples were analyzed for cations, anions and trace metals using a ThermoElemental PQ ExCell Inductively Coupled Plasma Mass Spectrometer.

Chronology

The chronologic data have been presented previously in Reynolds et al. (2009), so the chronologic methods and results are only briefly presented here. The upper parts of the lake-sediment cores were dated using ^{210}Pb and $^{239+240}$Pu techniques. Twenty samples from core 1 at each lake (at 0.5-cm intervals in the uppermost 10 cm) were analyzed for ^{210}Pb. Samples were dried, ground to pass through a 100-mesh screen, and then analyzed by alpha spectrometry at MyCore Scientific (Deep River, Canada). The depth-age profile was determined using the constant rate of supply (CRS) model that assumes a constant influx of unsupported, atmospheric ^{210}Pb to the site (Appleby, 2001).

Measurable $^{239+240}$Pu in lake sediments is the result of nuclear-weapon testing that began in the 1950s, peaked in 1963 and ceased in 1972. Concentrations of such bomb products provide a dating tool. The Pu-based age analysis was made on the basis of 17 samples (15 from the upper 10.5 cm) from Marshall Lake core 2 The results strengthen the correlation between cores 1 and 2 (Reynolds et al., 2009). A similar analysis was not possible at Hidden Lake owing to insufficient sediments. The analysis of $^{239+240}$Pu followed methods described by Ketterer et al. (2004).

Elemental geochemistry

Reynolds et al. (2009) previously presented the elemental geochemical data, so the methods are only briefly explained here. Twenty samples from core 2 at each lake were analyzed for 50 major and trace elements using inductively coupled plasma emission- and mass-spectrometry at SGS Mineral Services (Toronto, Canada). Analyses from Marshall and Hidden Lakes were obtained at 1-cm increments for the top 10 cm of the cores. Additional analyses were made at 3–4 cm intervals from the remainder of the cores. Elemental concentrations were calculated on an organic-matter-free basis using loss-on-ignition data. We did not analyze or correct for possible dilutional effects from endogenic carbonate and biogenic silica. Forty elements were chosen for having possible bearing on issues related to sediment sources, biogeochemical cycling in the watersheds, and effects of dust on air and water quality.

Diatom analysis

Samples were prepared for diatom analysis using the method described by Battarbee et al. (2001). Approximately 1 ml of sediment was mixed with a 50:50 M solution of concentrated sulphuric and nitric acid to remove organic material. After 24 h the samples were heated to 80–90°C for 2 h. Samples were allowed to settle for 24 h and then acids were aspirated. Samples were then washed repeatedly with distilled water until neutralized. A small aliquot of each slurry was evaporated on a coverslip and the coverslip was mounted to a glass slide using Naphrax®. For each sample, a minimum of 600 diatom valves were identified and enumerated along transects using a Nikon Eclipse E6000 microscope equipped with Nomarski differential interference contrast (DIC) optics and a 100× oil-immersion objective (total magnification = 1,000×). Diatom identifications were based on (Kramer & Lange-Bertalot, 1986–1991b; Cumming et al., 1995; Fallu et al., 2000; Moser et al., 2004). Samples were counted at 1-cm increments for the top 10 cm of the cores, and at 2–5 cm increments thereafter, for a total of 20+ samples per lake.

Data analyses

Following Salomons & Förstner (1984) enrichment factors (EFs) for several metals and P were calculated to determine anthropogenic inputs separate from natural variations due to changes in chemical weathering and erosion. Enrichment factors (EFs) were calculated by relating the metal to Ti ratio in samples to the average metal to Ti ratio in cored sediment deposited prior to AD 1860 (i.e., pre-mining background levels).

Principal components analysis (PCA), a linear, direct gradient analysis, was performed on the elemental and diatom data in order to identify the main stratigraphic changes and to more easily compare the two data sets. Principal components analysis (PCA) was done with the program CANOCO (ter Braak & Šmilauer, 1998). The geochemical data were centered and standardized as the units of measurement were not always the same, whereas the species data were transformed by square root to reduce the importance of dominant species. A detrended correspondence analysis (DCA) was performed in order to determine Hill's N2, a measure of diversity equivalent to the inverse of the Simpson's diversity measure (Hill, 1973), and the magnitude of species turnover by scaling the sample scores to be standard deviation units of compositional change (Hill & Gauch, 1980; Birks, 1998).

Results

Water chemistry

Both lakes were circumneutral and had low specific conductivity (Table S1, Electronic supplementary material). Trace metal concentrations, including Cu, Pb, Cd, and Zn, were generally two to three orders of magnitude lower at the Uinta Mountain sites than at Lake Orijärvi (Finland) (Salonen et al., 2006) and Lake Dufault (Quebec, Canada) (Cattaneo et al., 2008), both of which have point sources for metal contamination in their catchments (Table 1). Values were more similar, but still an order of magnitude less

Table 1 Water chemistry for Marshall and Hidden lake sediments compared to lakes affected by point source metal pollution

	Marshall Lake	Hidden Lake	Lake Orijarvi	Lake Dufault	Lake Vandrey
Cu	0.470	0.390	20–50	8.1	3.0
Pb	0.043	0.068	1–3	n/a	n/a
Cd	0.004	0.007	2–8	0.330	0.067
Zn	1.730	0.640	600–1,200	27	1.8

The units for all measurements are μg/l. Values for Lake Orijarvi (Finland) are from Ruggiu et al. (1998) and for Lake Dufault and Lake Vandrey (Quebec, Canada) are from Cattaneo et al. (2008)

for Cu, Pb, and Cd than values from Lake Vaudray (Quebec Canada), which received metals atmospherically from the Rouyn Noranda smelter approximately 30 km away (Cattaneo et al., 2008).

Core description, chronology, and correlation

Sediments varied from light to medium to dark brown hues, contained ~30% organic material and lacked visible laminations (Walsh, 2002). On the basis of ^{210}Pb results, sediments below 9 cm at both lakes were deposited prior to AD 1870 (Reynolds et al., 2009; Fig. S1, Electronic supplementary material). Activity of ^{210}Pb decreases exponentially with depth until background levels are reached (Fig. S1a-b, Electronic supplementary material). Dating uncertainty increases toward the bottom of both cores so that large age uncertainties overlap at and below depths of 8.5 cm (Fig. S1c-d, Electronic supplementary material).

A maximum $^{239+240}$Pu activity of 87 ± 2 Bq/kg occurs in the 3.5–4.0 cm interval in the Marshall Lake core (Reynolds et al., 2009). These results indicate that the 1963-deposition peak is between 3.0- and 4.5-cm depths. Assuming that a depth of 3.75 cm represents the 1963 peak, the average sedimentation rate since 1963 is ~1 mm/year. The year 1963 is represented by the 3.9-cm depth in core 1 using the ^{210}Pb age model, indicating that depths in cores 1 and 2 are time equivalent.

In order to estimate the timing of changes in diatom community composition prior to AD 1850, a straight line was fitted to the ^{210}Pb dates, giving ages of ~AD 1340 for 44.25 cm at Marshall Lake and ~AD 1070 for 48.75 cm at Hidden Lake. In the absence of several ^{14}C ages, these models are tenuous. The models used for determining ages of sediments below the ^{210}Pb dates for Marshall Lake and Hidden Lake are $y = -15.25x + 2015.9$ ($r^2 = 0.88$) and $y = -19.424x + 2018.8$ ($r^2 = 0.98$), respectively (where y is the date in years AD and x is the depth in centimeters).

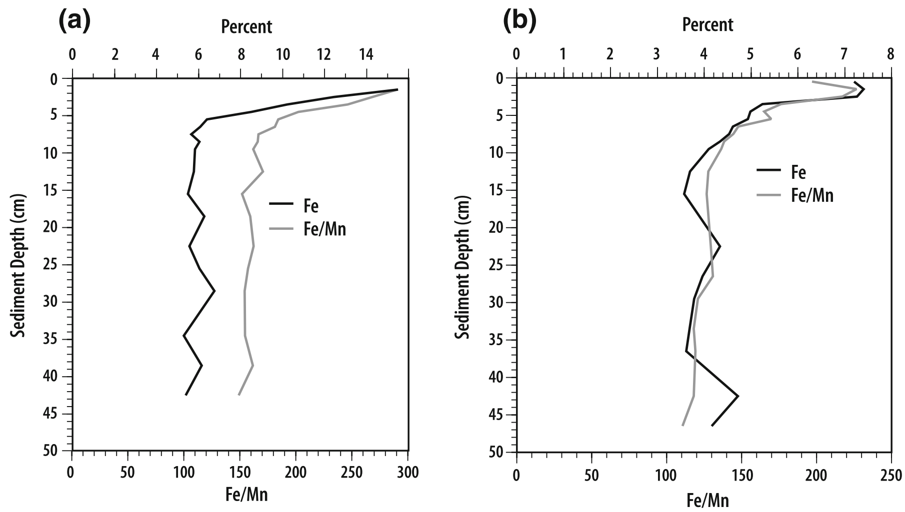
Table 2 Maximum enrichment factors (EFs) for selected metals in Marshall and Hidden Lake sediments

	Marshall Lake	Hidden Lake
Pb	13	8
Cu	3	2
Cd	7	2
Zn	2	1
Bi	9	4
Sb	6	3
Ag	4	1
As	5	5
Sn	3	2
Fe	3	2
Co	2	1

Elemental geochemistry

Previous interpretations of geochemical and magnetic-property data indicate that a component of the sediment originates from outside the lakes' catchments and is delivered to the lakes atmospherically as dust (Reynolds et al., 2009). The post-mining metal concentrations in Marshall Lake are generally twice as much as in Hidden Lake sediments (Reynolds et al., 2009). Enrichment factors for metals related to mining range from 2 to 13 at Marshall Lake and from 1 to 8 at Hidden Lake (Table 2). Maximum enrichment factors for Pb are 13 and 8 at Marshall and Hidden Lake, respectively, which are greater than values between 3 and 4 reported from alpine sites in Europe (Kamenik et al., 2005).

Fig. 2 Plots showing Fe/Mn and Fe against depth for **a** Marshall Lake and **b** Hidden Lake



Principal components analysis (PCA) of the geochemical data supports the findings of Reynolds et al. (2009). For the geochemical data, eigenvalues for the first and second axes of the PCA are, respectively, 0.58 and 0.18 for Marshall Lake, and 0.52 and 0.20 for Hidden Lake, indicating that the first axes explain most of the variance in the data sets. The PCA biplots illustrate the relations among different chemical variables (Fig. S2a and S3a, Electronic supplementary material) and show that the composition of the sediments has changed over time (Fig. S2b and S3b, Electronic supplementary material). The first PCA axis primarily represents the sediment source, with negative values reflecting a natural or unchanged source (mainly from the catchment), and positive values indicating a changing source (i.e., atmospheric input). Based on comparisons to chemical analyses of the underlying bedrock (Condie et al., 2001), variables that plotted in the upper left portion of PCA plots predominately originated from the catchment and were unchanged over time. Elements that plotted to the right with low angles to axis 1 increased upwards. The most likely explanation is that these elements originated from outside the catchment and were delivered atmospherically, although some of these elements, could become enriched due to changes in redox potential (Reynolds et al., 2009). To test the influence of redox potential on the geochemistry of the lake sediments, we plotted Fe/Mn with Fe (Fig. 2), and found that these variables covaried. Covariation between these variables can indicate that changes in Fe and Mn are not related to redox, but to changes in allochthonous inputs (Mackereth, 1966). This is, however, a simplistic view of the relationships between Fe and Mn because many other factors affect these elements (Engstrom & Wright, 1984; Boyle, 2001). For example, it has been shown that Fe/Mn and Fe can covary in very reducing environments where iron sulfides are precipitating (Engstrom & Wright, 1984); however, no iron sulfides were observed during petrographic observations of these sediments. Although we cannot rule out some role of redox potential, we interpret changes in atmospheric deposition as the main cause of the observed changes in elemental concentrations.

In Marshall Lake, elements such as U, Rb, Ta, Zr, Ni, and Yb, which plot in the upper left (Fig. S2a, Electronic supplementary material), have sediment concentrations that are similar to, or less than in UMG rocks. In contrast, elements such as Pb and La, which plot on the right with small angles to axis 1, have concentrations in the upper sediments that are 10–100× greater than in UMG rocks. Many of the elements plotting to the right side of the diagram close to axis 1, including Bi, Sb, Pb, Cd, As, Ag, Sn, Fe, Cu, Co, and P, are commonly associated with anthropogenic activities, including mining, industry, fossil-fuel burning, and agriculture. Generally, elements plotting in the upper left quadrant of the plot are common in rock-forming minerals, including K, Mg, Na, and Al.

Sample scores on the first axis, therefore, largely reflect the degree to which a sample has been influenced by materials originating from human

Table 3 Main diatom species found at Marshall Lake

Species #	Species name	Authority
1	*Fragilaria construens* var. *venter*	(Ehrenberg) Grunow in Van Heurck
2	*Fragilaria pinnata*	Ehrenberg
3	*Tabellaria flocculosa*	(Roth) Kützing
4	*Asterionella formosa*	Hassall
5	*Navicula pupula*	Kützing
6	*Achnanthes minutissima*	Kützing
7	*Achnanthes pusilla*	Grunow in Cleve & Grunow
8	*Fragilaria brevistriata*	Grunow in Van Heurck
9	*Fragilaria capucina*	Desmazières
10	*Pinnularia mesolepta*	(Ehrenberg) W. Smith
11	*Achnanthes curtissima*	Carter
12	*Stauroneis anceps*	Ehrenberg
13	*Achnanthes nodosa*	Cleve
14	*Navicula cryptocephala*	Kützing
15	*Achnanthes subatomoides*	(Hustedt) Lange-Bertalot & Archibald
16	*Achnanthes levanderi*	Hustedt
17	*Cyclotella glomerata*	Bachmann
18	*Cyclotella pseudostelligera*	Hustedt
19	*Cyclotella stelligera*	Cleve & Grunow in Van Heurck
20	*Aulacoseira alpigena*	(Grunow) Krammer
21	*Nitzschia palea*	(Kützing) W. Smith
22	*Achnanthes didyma*	Hustedt
23	*Cymbella microcephala*	Grunow (in Van Heurck)
24	*Fragilaria exigua*	Grunow
25	*Achnanthes suchlandtii*	Hustedt
26	*Fragilaria tenera*	(W. Smith) Lange-Bertalot
27	*Fragilaria nanana*	Lange-Bertalot
28	*Achnanthes carissima*	Lange-Bertalot

Species numbers correspond to numbers on PCA of Marshall Lake diatom data (Fig. 3)

activity outside the catchment. Higher positive scores indicate higher contents of these atmospherically delivered materials.

Sediments from 46.5–7.5 cm to 46.5–6.5 cm from Marshall and Hidden lakes, respectively, plot to the left (Fig. S2b and S3b, Electronic supplementary material), indicating that these samples contained relatively high concentrations of catchment-derived elements. A shift of samples from the left to the right of the plots for Marshall and Hidden Lake begins above 9.5 cm (the late 1800s). By $\sim$6 cm (the early 1900s) samples were enriched in anthropogenically derived elements. This enrichment continued to the present, and is similar to that observed at nearby Mirror Lake (Kada et al., 1994).

Diatom analysis

A total of 217 diatom taxa were identified and enumerated from Marshall and Hidden Lakes. Species that accounted for $\geq$1% relative abundance, and were present in at least two intervals were plotted for each lake (Fig. S4, Electronic supplementary material). Twenty-nine and 43 diatom taxa met these criteria in Marshall and Hidden Lake, respectively. Only these taxa were used in further analyses. Authority names are not included in the text but are provided in Tables 3 and 4.

A major shift in diatom species composition occurs at 6.5 cm (early 1900s) in Marshall Lake (Fig. S4a, Electronic supplementary material). This

Table 4 Diatom species identified at Hidden Lake

Species #	Species name	Authority
1	*Aulacoseira ambigua*	(Grunow in Van Heurck) Simonsen
2	*Aulacoseira alpigena*	(Grunow) Krammer
3	*Aulacoseira distans*	(Ehrenberg) Simonsen
4	*Aulacoseira lirata*	(Ehrenberg) Ross
5	*Cyclotella pseudostelligera*	Hustedt
6	*Cyclotella stelligera*	Cleve & Grunow in Van Heurck
7	*Tabellaria flocculosa*	(Roth) Kützing
8	*Cymbella silesiaca*	Bleisch
9	*Eunotia exigua*	(Brébisson) Rabenhorst
10	*Fragilaria construens* var. *venter*	(Ehrenberg) Grunow in Van Heurck
11	*Fragilaria brevistriata*	Grunow in Van Heurck
12	*Frustulia rhomboides*	(Ehrenberg) De Toni
13	*Achnanthes levanderi*	Hustedt
14	*Achnanthes subatomoides*	(Hustedt) Lange-Bertalot & Archibald
15	*Nitzschia fonticola*	Grunow (in Van Heurck)
16	*Brachysira brebissonii*	Ross
17	*Cymbella minuta*	Hilse ex. Rabenhorst
18	*Nitzschia palea*	(Kützing) W. Smith
19	*Fragilaria capucina*	Desmazières
20	*Fragilaria exigua*	Grunow
21	*Achnanthes carissima*	Lange-Bertalot
22	*Cymbella gracilis*	(Ehrenberg) Kützing
23	*Cymbella gaeumannii*	Meister
24	*Pinnularia mesolepta*	(Ehrenberg) W. Smith
25	*Achnanthes minutissima*	Kützing
26	*Brachysira intermedia*	Lange-Bertalot in Lange-Bertalot & Moser
27	*Brachysira neoexilis*	Lange-Bertalot in Lange-Bertalot & Moser
28	*Achnanthes marginulata*	Grunow
29	*Eunotia incisa*	Gregory
30	*Eunotia paludosa*	Grunow
31	*Gomphonema parvulum*	Kützing
32	*Eunotia flexuosa*	
33	*Cymbella microcephala*	Grunow (in Van Heurck)
34	*Cymbella hebridica*	(Grunow) Cleve
35	*Navicula pseudoscutiformis*	Hustedt
36	*Nitzschia perminuta*	(Grunow) M. Peragallo
37	*Diatoma anceps*	(Ehrenberg) Grunow
38	*Eunotia faba*	(Ehrenberg) Grunow
39	*Navicula angusta*	Grunow
40	*Eunotia sp.*	
41	*Achnanthes curtissima*	Carter
42	*Achnanthes pusilla*	Grunow in Cleve & Grunow
43	*Brachysira styriaca*	(Grunow in Van Heurck) Ross in Hartley

Species numbers correspond to numbers on PCA biplot Hidden Lake diatom data (Fig. 4)

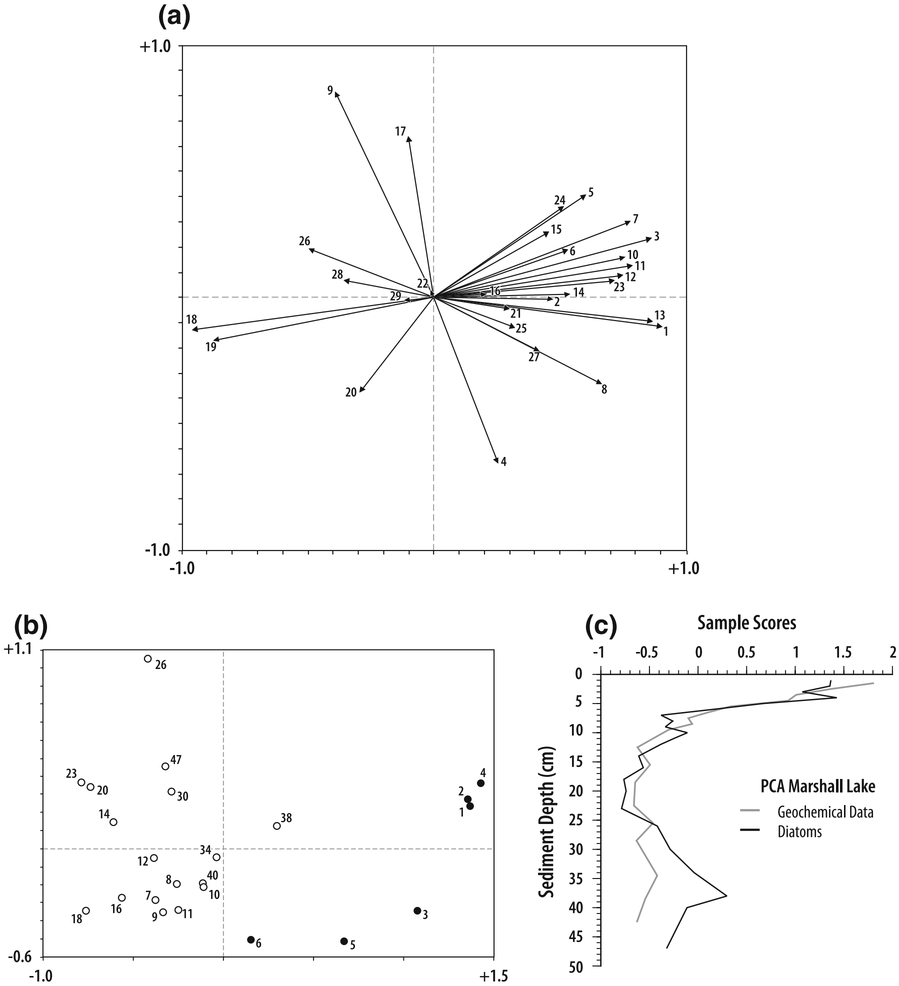


Fig. 3 Principal components analysis of diatom species abundance data for Marshall Lake. **a** shows diatom species. Each diatom species is shown by a number and the diatom species that corresponds to that number is provided in Table 3. Each species is represented by a numbered arrow, such that the smaller the angle between the arrows the more strongly correlated the two diatom species. Arrows at 90° to one another are uncorrelated, whereas arrows that plot in opposite directions are negatively correlated. **b** is a plot of samples and shows how the diatom assemblages have changed with time. Each point represents a different sediment depth and the distance between points estimates Euclidean distance, so that less distance indicates greater similarity. Samples that plot close to the end of an arrow have relatively high abundances of that species. **c**) is a comparison of the sample scores on the first axis of the PCA of the geochemical data compared to the sample scores on the first axis of the PCA of the diatom data

shift occurred at about the same time as the geochemical shift toward greater concentrations of atmospherically derived elements (Fig. 3c). The shift in diatom community composition is marked by a decrease in *Cyclotella* species and an increase in small, periphytic diatoms, including several *Fragilaria* and *Achnanthes* species (Fig. S4a, Electronic supplementary material). *Cyclotella* species, particularly *C. pseudostelligera* and *C. stelligera* dominate from ∼47 to 7 cm, accounting for ∼50% of the diatom assemblages. A number of other taxa appear in abundance in the top 5 cm of sediment, including *Tabellaria flocculosa,* and large pennate diatoms such as *Pinnularia mesolepta* and *Stauroneis anceps*. Several periphytic diatoms, including several *Achnanthes*, *Navicula* and *Nitzschia* species, occur consistently only in the top 5–7 cm.

PCA plots (Fig. 3a, b) of the diatom species in Marshall Lake show similar trends to the diatom stratigraphy (Fig. S4a, Electronic supplementary material). The eigenvalues for axes 1 and 2 are 0.47 and 0.14, respectively, so most of the explained variance is represented by axis 1. Planktonic and thycoplanktonic diatoms, including *Cyclotella* species and *Fragilaria tenera* were negatively correlated with axis 1, whereas non-planktonic taxa, such as *Achnanthes nodosa*, *A. pusilla*, *A. curtissima*, *Pinnularia mesolepta*, *Tabellaria flocculosa*, *Navicula pupula*, *Nitzchia palea*, and *Fragilaria brevistriata* are positively correlated with axis 1. From 0 to 6 cm, samples plot to the right of the plot indicating higher amounts of non-planktonic diatoms. The greatest amount of species turnover occurs between 7 and 4 cm, and diatom diversity is greatest in the upper 5 cm of sediment (Fig. 5).

The timing and direction of major change in diatom assemblages at Hidden Lake is different from Marshall Lake (Fig. S4b, Electronic supplementary material, and Fig. 4). The change at Hidden Lake occurs at ~17.5 cm, which based on the ^{210}Pb-age model, represents an age of ~AD 1680. Below 17.5 cm, the diatom community composition is more diverse and characterized by abundant *Tabellaria flocculosa* and *Frustulia rhomboides* and by several periphytic species, such as, *Eunotia incisa*, *E. exigua*, *E. flexuosa*, *Cymbella hebridica*, *C. silesiaca*, *Brachysira brebissoni*, *B. intermedia*, *B. styriaca*, *Gomphenema parvulum*, *Navicula angusta*, and *Nitzschia fonticola*, that are rare or absent in more recent sediments. Above ~17.5 cm, the diatom assemblage is dominated (>60%) by *Cyclotella*, mainly *C. pseudostelligera* and *C. stelligera* species.

Principal components analysis (PCA) yields eigenvalues of 0.57 and 0.09, for the first and second axes, respectively. Therefore, most of the explained variance is described by the first axis. As at Marshall Lake, the first axis was positively correlated to non-planktonic diatoms, including *Eunotia incisa*, *Fragilaria exigua*, *F. rhomboides*, *Tabellaria flocculosa*, *Brachysira brebissoni*, *B. intermedia*, *B. neoexilis*, *Achnanthes minuitissima*, *Cymbella gracilis*, *Pinnularia mesolepta*, and negatively correlated to planktonic diatoms, such as *Cyclotella stelligera* and *C. pseudostelligera* (Fig. 4a). In contrast to Marshall Lake, *Cyclotella* increased toward the top of the core. In fact, samples from above ~17.5 cm plot to the far left of the diagram indicating high amounts of *Cyclotella* species, whereas samples from below ~17.5 cm plot to the far right of the diagram indicating greater abundance of non-planktonic diatoms (Fig. 4b). The first axis PCA scores plotted against depth indicate a long-term decrease in sample score beginning at ~17.5 cm, reflecting decline in diatom diversity and increase in planktonic *Cyclotella* species (Fig. 4c). The interval between 20 and 14 cm is characterized by the greatest amount of species turnover and diatom diversity is greatest below 17.5 cm (Fig. 5).

Discussion

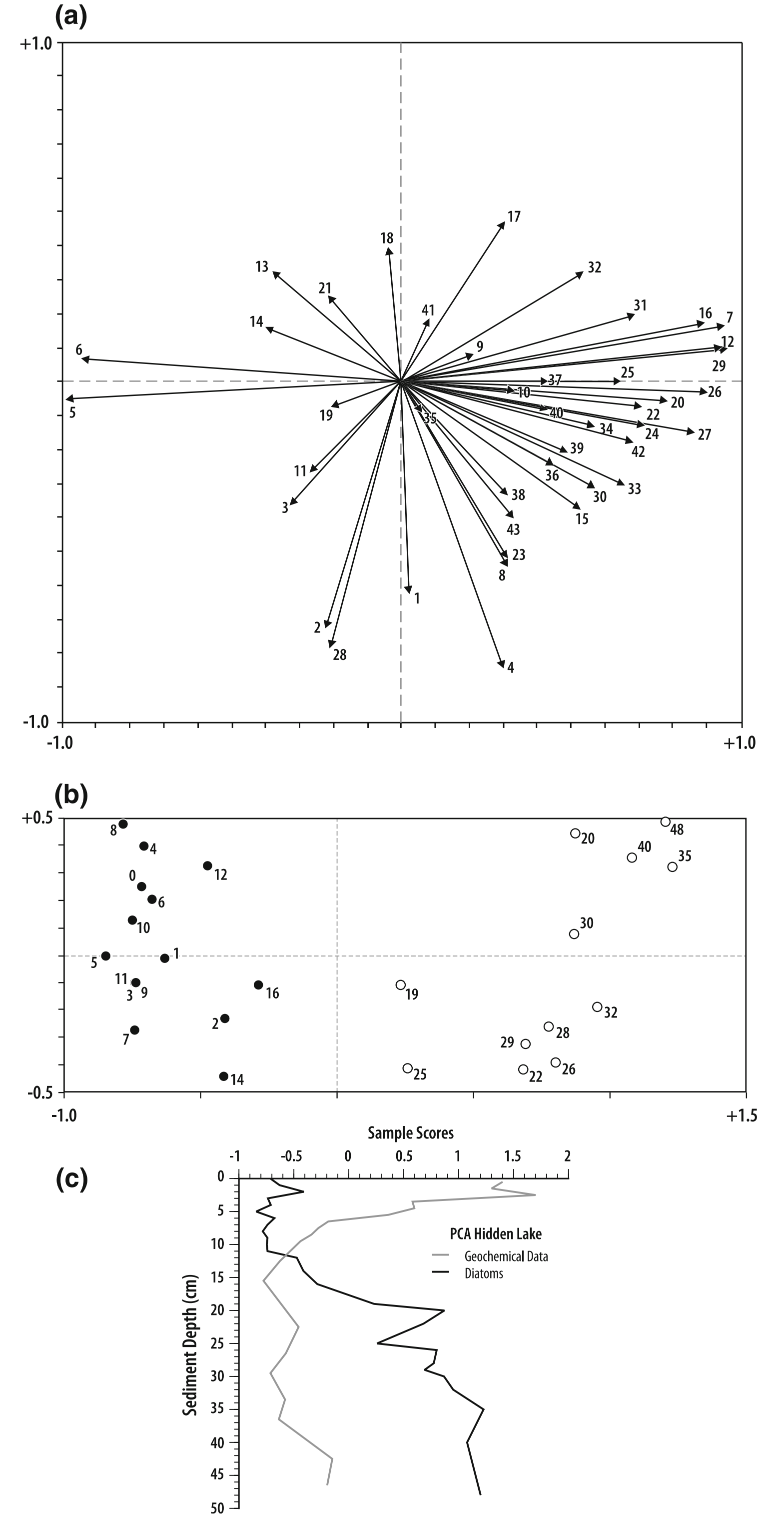
Biological response to metal enrichment

At Marshall Lake, the main change in diatom community composition was approximately coeval with increased metal deposition in the early 1900s (Fig. 3c). However, it is impossible to determine which metal(s) caused the changes in diatom community composition because of the high correlations among many of the metals (Fig. S2a, Electronic supplementary material). Metal enrichment at Hidden Lake did not reach large enough values to cause a diatom response.

At Marshall Lake, diatom assemblages dominated by planktonic diatoms, mainly *Cyclotella stelligera* and *C. pseudostelligera*, were replaced by assemblages dominated by benthic species, including several species of *Achnanthes* and small fragilaroids. The shift in diatom species composition at Marshall Lake could have been driven by changes in nutrients or temperature; however, the trends in diatom community composition observed at Marshall Lake are most similar to changes in metal enrichment (Fig. 6). The changes in diatom community composition at Marshall Lake are also similar to changes observed in lakes directly affected by metal pollution.

The shift in diatom species composition at Marshall Lake does not appear to be related to increased phosphorus. Previous study by Reynolds et al. (2009) indicates that the onset of increasing phosphorous in Marshall and Hidden lakes corresponds approximately in time to the beginning of extensive phosphate extraction and its use in agriculture in the western United States. Recent increases in phosphorus, interpreted as agricultural phosphorus, have been found in other alpine areas of the western United States (Neff et al., 2008). A comparison of the

Fig. 4 Principal components analysis of Hidden Lake diatom data. See Fig. 3 for an explanation. Numbers on arrows represent diatom species listed in Table 4



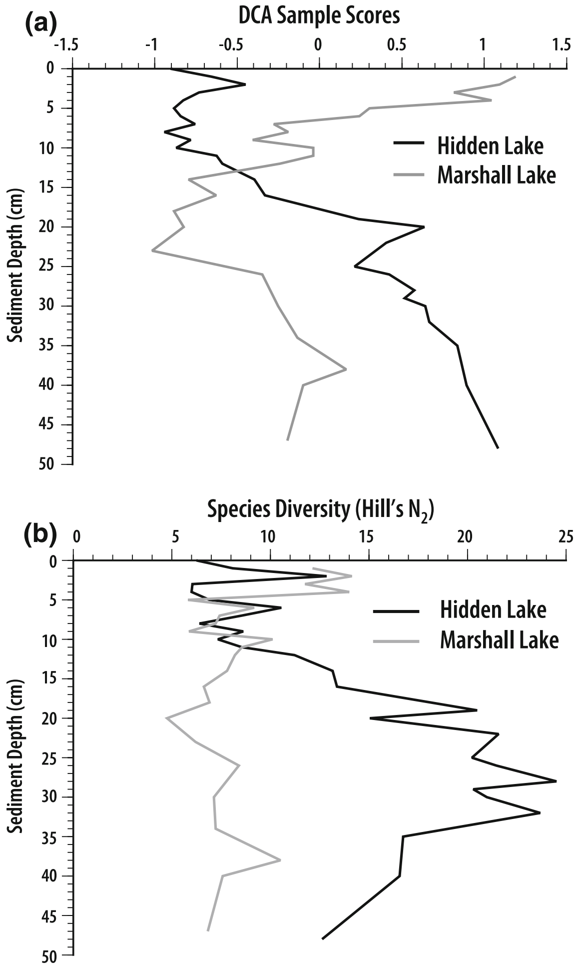


Fig. 5 A comparison of **a** species turnover and **b** species diversity (Hill's N2) determined using detrended correspondence analysis (DCA) for Marshall and Hidden Lake

diatom PCA scores to the phosphorus enrichment factors at Marshall Lake shows little covariation between these variables. Furthermore, the observed changes in diatom assemblages at Marshall Lake are unlike those typically associated with increases in phosphorus. An increase in nutrients generally results in an increase in planktonic diatoms rather than a decrease (Brugam, 1988). Experimental work on alpine diatoms shows that *Asterionella formosa* increase in abundance when phosphorus is low and nitrogen is high and *Fragilaria pinnata* increase in abundance when both nitrogen and phosphorus are low, further indicating that the changes at Marshall Lake are unlikely related to an increase in phosphorus (Saros et al., 2005).

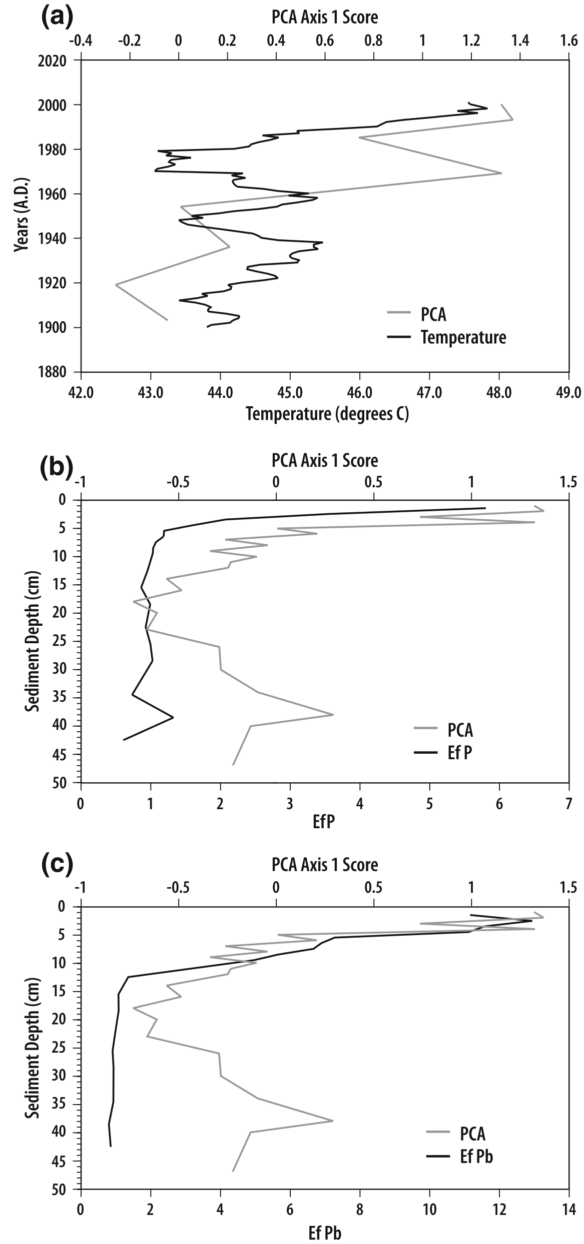


Fig. 6 Marshall Lake diatom PCA sample scores on axis 1 compared to **a** 10-year running- mean of annual temperature from Heber, Utah (Western Regional Climate Center), **b** enrichment factors (Ef) for Phosphorous, and **c** Ef for Pb

There is evidence that warming temperatures, which result in reduced ice cover and increased nutrient cycling, have caused changes in diatom assemblages elsewhere. *Cyclotella* and small, fragilarioid species have been observed to increase and decrease, respectively, in alpine and arctic lakes from around the world in response to recent warming (Rühland et al., 2008). The observed decreases in *Cyclotella* and increases in small, fragilarioid species in Marshall Lake would thus suggest cooling if water temperature were the primary control on changes in diatom community composition. However, evidence is lacking that temperatures are decreasing in the Uinta Mountains. By contrast, a recent report shows that dramatic warming throughout the western USA, which began in the 1970s and continues today, has profoundly impacted alpine ecosystems (Saunders et al., 2008). A comparison of diatom PCA scores and a 10-year running average of summer temperatures from Heber, just west of Marshall Lake (Fig. 1), shows little covariation between these variables (Fig. 6b). However, this comparison is not perfect owing to the dating errors and the few data points available from the sediment record that overlap with the instrumental temperature record. The relation between changes in diatom taxa and changing temperatures, therefore, should be explored further.

Changes in diatom community composition at Marshall Lake correspond with metal enrichment, as illustrated by a comparison of the diatom PCA scores to the Pb-enrichment factors (Fig. 6c). The changes in diatom assemblages observed at Marshall Lake are also similar to those previously reported as a result of increased metal concentrations, mainly from point sources (Ruggiu et al., 1998; Salonen et al., 2006; Cattaneo et al., 2004, 2008). *Cyclotella stelligera* has frequently been described as metal-sensitive (Takamura et al., 1990; Ruggiu et al., 1998; Nakanishi et al., 2004) and has been found to disappear shortly after metal contamination (Ruggiu et al., 1998; Cattaneo et al., 2004, 2008). *Achnanthes* species, particularly *A. minutissima*, have been shown to be metal-tolerant (Takamura et al., 1990; Ruggiu et al., 1998; Nakanishi et al., 2004) and to increase, sometimes dramatically, following metal contamination. Many studies have also noted a shift from planktonic to benthic species with increasing metals (Ruggiu et al., 1998), but the reason for this remains unclear. It is possible that littoral organisms, which are adapted to living in environments that experience greater variability, have superior plasticity, and therefore, greater tolerance to contaminants (Ruggiu et al., 1998). Another possibility is that the shift from planktonic to non-planktonic species is related to biofilms, which are frequently observed in littoral environments and can greatly alter metal bioavailability (Ivorra et al., 2000).

Our findings indicate that even relatively small changes in metals above natural background levels can cause significant changes in diatom community composition, as has been noted in other alpine lakes receiving relatively small inputs of atmospheric metals (Kamenik et al., 2005). Research on boreal lakes in Russia with metal concentrations in the sediments comparable to Marshall and Hidden Lake, however, shows no relationship between diatom assemblages and sediment geochemistry (Michelutti et al., 2001). These researchers indicated that the absence of diatom response was due to low bioavailability of metals as a result of high alkalinity (pH range = 7.53–9.03) of the lakewaters. Alkaline waters result in the formation of metallic complexes, which are incorporated into lake sediments (de Philippis & Pallaghy, 1994). Unlike the Russian lakes, both Marshall and Hidden Lake have circumneutral waters of low alkalinity (Table S1, Electronic supplementary material). Although the concentrations of metals in Marshall and Hidden lakes were low when the water samples were taken (Table 1), the values may have been higher at other times in the year, for example during spring melt, when runoff is greatest and pH lowest.

The difference between the Russian and Uinta lakes may also be explained by dissolved organic carbon (DOC), which can affect the bioavailability of metals and, therefore, diatom response. Metals will adsorb to DOC, decreasing the free and labile metal concentration, and perhaps, the metals available for organism uptake. Lakes having low DOC values, therefore, may have greater bioavailability of metals.

The response of diatoms at Marshall Lake differs from those of other lakes where metal concentrations were greater. Diatom diversity, as measured by Hills N2, increases with metal concentration, whereas previous research shows a decrease in diversity (Ruggiu et al., 1998). Low-level metal pollution could be described as an "intermediate" disturbance, different from the more extreme disturbance resulting from point-source pollution. It has been hypothesized that an extreme disturbance results in extinction of species adapted to pre-disturbance conditions and decreases diversity, whereas an intermediate disturbance allows for new species to establish without extinction events and increases diversity (Connell, 1978).

Cattaneo et al. (1998, 2004) indicate a shift to smaller diatoms, a finding not observed in Marshall Lake where several large pennate diatom species appear following increase in sediment-metal concentrations. The shift to small diatoms may only result with greater metal concentrations.

Hidden Lake diatom assemblages and changes in pH

The change in diatom assemblages at Hidden Lake at ~AD 1680 is similar to observations at lakes recovering from acid rain (e.g., Dixit et al., 1988). Many diatom species, including *Eunotia incisa*, *E. exigua*, *E. flexulosa*, *Cymbella hebridica*, and *Frustulia rhomboides*, present in Hidden Lake before ~AD 1680 are acidophilous, whereas diatoms that dominate the lake after ~AD 1680 are more common in circumneutral waters (Dixit et al., 1988; Jones et al., 1990; Camburn & Charles, 2000).

Several factors could have caused an increase in pH at Hidden Lake. Previous research has shown that fire can produce short-lived (~30–40 years) increases in pH (Rhodes & Davis, 1995; Korhola et al., 1996). Charcoal analyses at Hidden Lake show that as many as eight fires occurred in the catchment during the period spanned by the sediment and that three of these occurred in the sixteenth and seventeenth century (Walsh, 2002). However, given that fires occurred prior to the seventeenth century with no change in diatoms and given the persistence of the diatom change (several hundred years), it is unlikely that fire caused the inferred increase in pH.

Another possibility is that surface water entering the lake originated from a different source. Air-photo analysis indicates that wetlands are located to the northeast of Hidden Lake. Water from these areas bypass Hidden Lake today, but if they entered Hidden Lake in the past they may have caused lake waters to be more acidic. No evidence of a past inflow connecting the wetlands to the lake has been observed, so this too is unlikely.

We speculate that severe drought caused increased input of carbonate-rich dust from the Uinta Basin (Bockheim & Koerner, 1997), south of the Uinta Mountains, resulting in increased lake-water pH. Such a change in lake chemistry could be sustained by re-deposition of carbonate-rich dust that was first deposited in the catchment. Buffering of Uinta Mountain lake systems by desert dust has been invoked by others (Messer et al., 1982; Ellis, 1986) to explain the relatively high pH of these lakes. Our monitoring of pH in 60 Uinta Mountain lakes indicates that the lakes are neutral to alkaline (Moser, unpublished data).

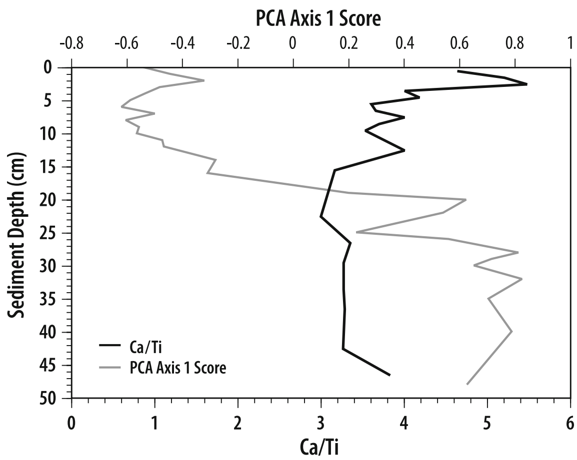


Fig. 7 Hidden Lake Ca/Ti plotted against depth compared to Hidden Lake diatom PCA sample scores on axis 1

A plot of Ca/Ti values provides evidence that Ca in Hidden Lake sediments has been atmospherically enriched beginning at about 22 cm sediment depth, just prior to the shift in diatom assemblage from more acidic to more alkaline taxa (Fig. 7).

Evidence for eolian dust reaching the Uinta Mountains is provided by soil-science research. In the Chepeta Basin, where Hidden Lake is located, the soils are characterized by a Ca-enriched silt cap of eolian origin (Bockheim et al., 2000). Perhaps the conditions responsible for this cap also delivered calcium carbonate to Hidden Lake.

The age of the eolian silt deposit is uncertain. Bockheim et al. (2000) speculated that the cap was formed during the late glacial or mid-Holcoene. Recent studies indicate that although much of the western United States was exceptionally dry during the mid-Holocene, an area that encompasses the eastern Uinta Mountains may have been wet as a result of increased monsoonal flow (e.g., Poore et al., 2005). Tree-ring research suggests that the southwestern United Sates, including the south eastern section of the Uinta Mountains, were dramatically affected by severe droughts in the seventeenth century (Fye et al., 2003). Tree-ring data suggest that a sixteenth-century megadrought was the most sustained severe drought in North America in the past 500 to 1,000 years (Stahle et al., 2000). Although these droughts occurred well before the change in lake-water pH, the uncertainty of the lake-sediment dating is large enough that the deposition of an eolian silt cap and a sustained drought may have been synchronous. To test the hypothesis that the change in pH was the result of natural eolian inputs of calcium carbonate from deserts to the south, well-dated sediment records from several Uinta Mountain and other southwestern alpine lakes are required.

Conclusions

Changes in diatom community composition were recorded in a Uinta Mountain lake over the last 120 years. Our evidence indicates that these changes were due to atmospheric metal pollution; however, increased nutrients and warming temperatures may also have played a role. The ecological health of mountain lakes, such as Marshall Lake, also may be threatened by the synergistic effects of multiple stressors, which are presently not well understood in the western alpine areas of the United States.

Eolian transport and deposition of dust from desert environments may be protecting some lakes in the Uinta Mountains from acid rain. Many lakes in the Uinta Mountains are underlain by siliciclastic rock with extremely limited buffering capacity, which should make these lakes susceptible to pollution and acid rain caused by upwind industry. However, most lakes in the Uinta Mountains are neutral to alkaline. Our research suggests that carbonate-rich dust may have increased pH and alkalinity in Hidden Lake beginning in the seventeenth century, protecting such lakes from recent acid rain.

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