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# Shifts in mid- to late-Holocene anion composition in Elk Lake (Grant County, Minnesota): Comparison of diatom and ostracode inferences

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## Abstract

The fossil diatom record from Elk Lake (Grant County, Minnesota) was used to reconstruct salinity and brine type between 2640 and 4645 <sup>14</sup>C yr BP. This lake was selected for a brine-type reconstruction because a previous study using fossil-ostracode assemblages indicated a shift in anion composition during the mid-Holocene (Smith et al., 1997). Salinity was reconstructed using a transfer function developed for the Northern Great Plains (NGP) of North America; the reconstruction revealed that salinity was higher (1.5–6.2 g l<sup>-1</sup>) between ~4000 and 4645 <sup>14</sup>C yr BP and dropped to 0.35–1.2 g l<sup>-1</sup> after 4000 <sup>14</sup>C yr BP. The anion composition of the system was investigated by passively plotting fossil diatom assemblages onto a canonical correspondence analysis (CCA) biplot of the NGP modern samples to determine where core assemblages fell with respect to brine type. The biplot suggests that Elk Lake was mainly a bicarbonate system, but temporarily shifted to sulfate domination at 4080 <sup>14</sup>C yr BP. Both the salinity and brine-type reconstructions essentially agree with results from Smith et al. (1997), but the diatom record provides less-definitive information on anion proportions as compared to anion concentrations. Because shifts in the relative abundances of anion-associated diatom taxa generally tracked the ostracode-inferred changes in brine type, we conclude that fossil diatom assemblages can reveal information on shifts in brine type over time and provide insight into brine evolution and groundwater behavior in a lake system.

## 1. Introduction

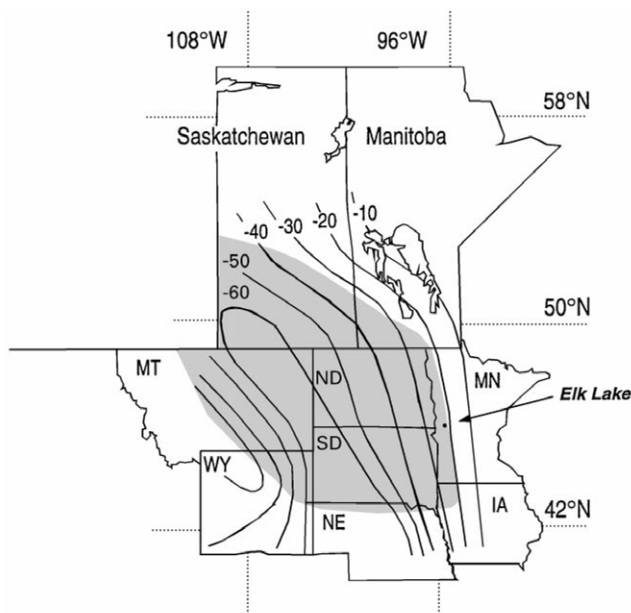
Diatom distributions in closed-basin lakes are highly correlated with salinity and anion composition (Wilson et al., 1994; Blinn, 1993; Fritz et al., 1993; Gasse et al., 1995). This relationship has been applied to sedimentary diatom assemblages to reconstruct salinity and to infer regional paleoclimate (Fritz et al., 1991; Laird et al., 1998; Bradbury et al., 1989; Gasse et al., 1987; Metcalfe, 1995). The correlation of diatom distributions with brine type can also potentially reveal paleolimnological trends in brine evolution and groundwater inputs, providing additional insight into past climate change. During evaporative concentration, solute fractionation mechanisms, such as mineral precipitation and degassing, lead to shifts in brine composition. Brine evolution follows a predictable pathway, with calcite precipitating first during evaporative concentration.

The removal of calcite can lead to the depletion of calcium or bicarbonate. Thus, the relative proportion of HCO<sub>3</sub> to (Ca + Mg) determines the eventual pathway of brine evolution (Eugster and Jones, 1979). The proportion of these ionic species in lakewater is dependent on the composition of dilute inflow to the system. Thus, both the extent of evaporative concentration, controlled by the effective moisture balance in the region, and the composition of dilute inflow shape the ionic composition of lakewater.

The chemistry and flow rate of groundwater into a lake can affect the course of brine evolution, and these are a function of topographic gradients. During droughts, local and regional groundwater flow patterns can shift, which can alter the quantity and/or solute composition of inflowing groundwater. Webster et al. (1996) examined the response of a set of northern Wisconsin lakes to a 4-yr drought in relation to their landscape position. Chemical responses to

drought differed in groundwater versus precipitation-dominated systems, with cation mass increasing in groundwater-dominated systems as flowpath length increased due to desiccation of up-gradient basins and capture of their catchments. In contrast, cation mass declined in precipitation-dominated systems due to diminished inputs of solute-rich groundwater. Reconstructing changes in ion composition can thus potentially enhance our understanding of differential responses of systems to climate change.

Although diatom distributions exhibit a correlation with brine type, this relationship is based on observations from spatially arrayed sets of modern samples, and the extent to which diatoms respond to changes in ion dominance within a single system is thus far uncertain. In saline lakes located in the Northern Great Plains of North America, diatom taxa such as *Campylodiscus clypeus*, *Anomoeoneis costata*, and *Gomphoneis olivaceum* are characteristic of bicarbonate-dominated systems, whereas *Nitzschia constricta*, *Navicula cincta*, *Cocconeis pediculus*, and *Chaetoceros elmorei/muelleri* are mainly found in high sulfate lakes (Fritz et al., 1993). Sulfate-associated taxa are found in bicarbonate-dominated systems but in much lower abundances than in sulfate systems, and vice versa for bicarbonate-associated taxa. Although certain taxa are associated with a particular brine type, it is presently unclear whether diatoms actually respond to changes in anion composition or exhibit this correlation due to factors that covary with brine type, such as phosphorus concentrations (Caraco et al., 1989), molybdate availability (Cole et al., 1986), and nitrogen : phosphorus ratios (Saros and Fritz, 2000a).



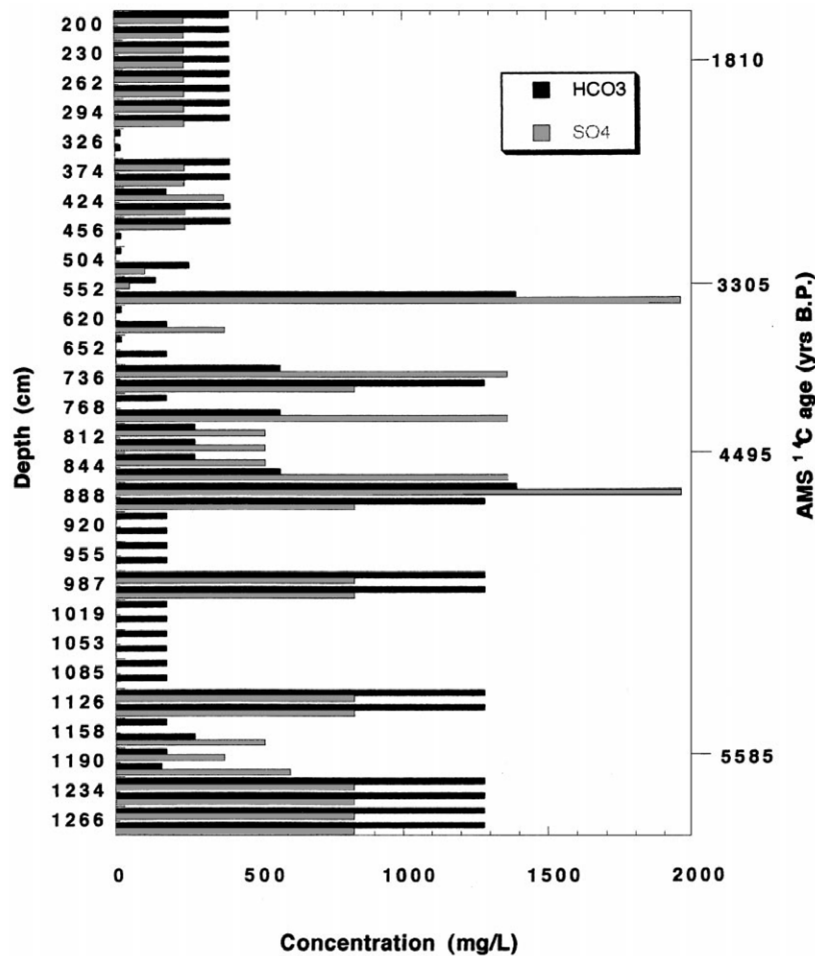
**Figure 1.** Map of the Northern Great Plains (shaded area) showing location of Elk Lake. Isolines indicate precipitation minus evaporation ( $\text{cm yr}^{-1}$ ).

To examine this question, we determined the diatom profile of Elk Lake (Grant County, Minnesota; Figure 1), which, based on fossil ostracode assemblages, experienced shifts in anion composition during the Holocene (Figure 2). The ostracode reconstruction suggests that the lake shifted from bicarbonate to sulfate domination around 4700  $^{14}\text{C}$  yr BP (888 cm), with a return to bicarbonate domination at  $\sim$ 3300 yr BP (552 cm). We plotted fossil diatom assemblages passively onto a canonical correspondence analysis (CCA) biplot of the NGP modern samples (Fritz et al., 1993) to determine whether or not switches in diatoms characteristic of sulfate versus bicarbonate brines occurred coincident with changes in brine type as indicated by ostracode reconstruction methods. We also reconstructed salinity using a transfer function (Fritz et al., 1993), which allowed us to compare diatom- and ostracode-inferred salinity, as well as to assess whether diatom assemblages from the modern data set provided good analogues for the fossil samples.

## 2. Site description and previous work

Elk Lake, located in west-central Minnesota (Figure 1), is presently a freshwater  $\text{Mg-Ca-HCO}_3$  system with a concentration of total dissolved solids (TDS) of  $\sim$ 1000  $\text{mg l}^{-1}$ . It receives groundwater that is generally  $\text{Mg-Ca-SO}_4$  dominated with a TDS up to 2500  $\text{mg l}^{-1}$ . A complete description of the hydrologic setting of Elk Lake is provided by Smith et al. (1997).

Smith et al. (1997) described changes in Holocene lake-water chemistry based on fossil ostracode assemblages (Figure 3), ostracode shell chemistry, and groundwater modeling. Ostracode abundances are influenced in part by ionic concentration and composition, and thus can be used to infer changes in these parameters. For example, *Limnocythere staplini* is a halophilic species found in bicarbonate-depleted sulfate-dominated waters, whereas *Candona rawsoni* is a eurytopic species found in both bicarbonate-enriched and bicarbonate-depleted sulfate-dominated waters (Smith, 1993). *Cytherissa lacustris* and *Candona ohioensis* also found in the Elk Lake record, inhabit bicarbonate-dominated fresh water (Smith, 1993; Smith et al., 1997). Smith et al. (1997) inferred that in the early Holocene (zone A of the core), Elk Lake was a dilute,  $\text{Ca-Mg-HCO}_3$  system with TDS concentrations less than 500  $\text{mg l}^{-1}$ . The bottom of zone B represents a period of more concentrated waters, enriched in bicarbonate relative to calcium. By the mid-Holocene, the lake became depleted in bicarbonate relative to calcium (sulfate dominated), with the highest salinities of the Holocene at the top of zone B. After the mid-Holocene, lake water became more dilute and was once again enriched in bicarbonate relative to calcium (zones C and D), similar to conditions



**Figure 2.** Concentrations ( $\text{mg l}^{-1}$ ) of bicarbonate and sulfate in Elk Lake from  $\sim 6700$   $^{14}\text{C}$  yr BP to present, as inferred from fossil ostracode assemblages. Values were reconstructed using the matching analogue technique.

in the lake today. Because Elk is the deepest in a series of lakes, its hydrological and chemical budgets were, at times, strongly influenced by sulfate-rich groundwater inputs. Thus, the response of this system to climate change was not solely controlled by processes confined to the lake.

Although Mg/Ca values indicated higher salinity in Elk Lake during the mid-Holocene,  $\delta^{18}\text{O}$  values of ostracode calcite were lighter at this time, contrary to what would be expected during evaporative concentration. This apparent anomaly can be explained in terms of groundwater influences. During severe droughts, water levels in shallower lakes in the chain dropped, and groundwater flowing into Elk Lake was no longer concentrated by evaporation in these systems before reaching Elk. Thus, influent groundwater would be isotopically lighter during droughts than during intervals of higher effective moisture. In contrast, longer flow paths and thus enhanced water-rock interactions could increase groundwater salinity, as well as sulfate flux to the lake.

### 3. Materials and methods

Sediment samples were collected from the same core and at the same core depths as were sampled by Smith et al. (1997) between 408 and 1274 cm (2640–6680  $^{14}\text{C}$  yr BP). Core depths represent the mid-point of a 2-cm increment, with a sampling interval of 8 or 16 cm. Each sample integrates approximately 10 yr of sediment accumulation. After homogenizing a 5 cc sample, 1 cc was subsampled and processed with 35% hydrogen peroxide to oxidize organic matter, then rinsed with distilled water to remove peroxide. The processed samples were settled onto coverslips and mounted onto slides with Naphrax<sup>®</sup>. A minimum of 300 valves per slide was counted under oil immersion on an Olympus BH-2 bright-field microscope (numerical aperture=1.4). Diatom taxonomy was based primarily on Patrick and Reimer (1966, 1975) and Krammer and Lange-Bertalot (1986, 1988, 1991a, 1991b).

The calibration set of environmental and species data collected by Fritz et al. (1993) for the NGP, originally

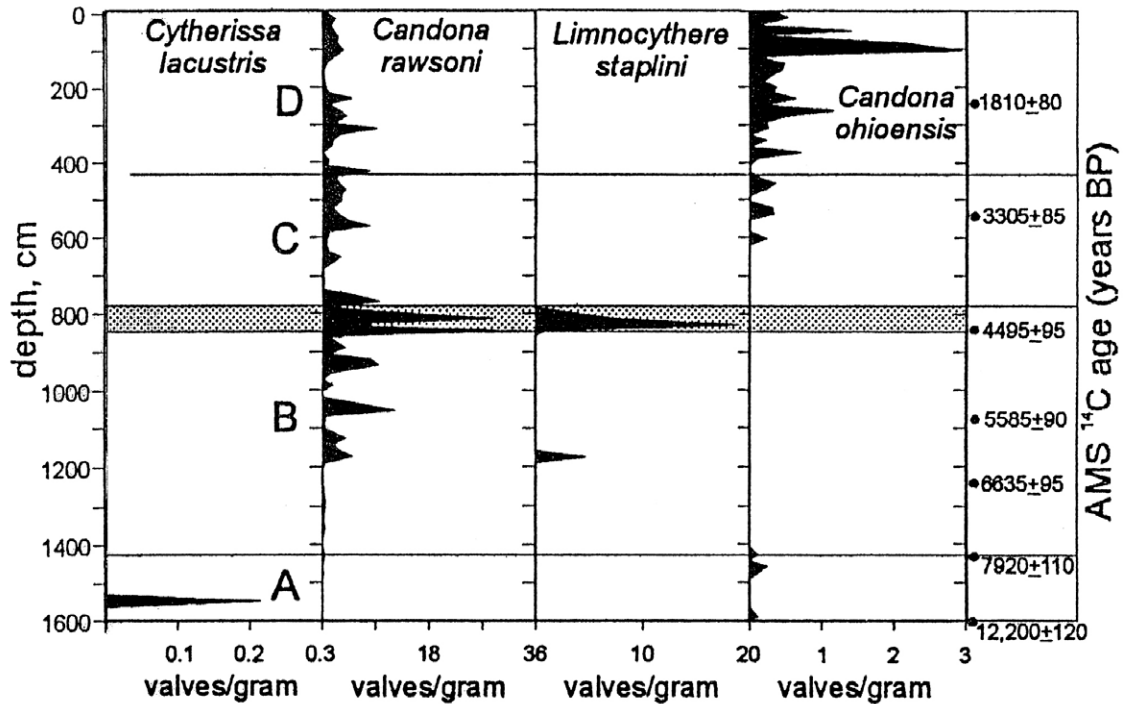


Figure 3. Ostracode record and zonation for Elk Lake (From Smith et al., 1997).

consisting of 53 lakes, was enlarged with data from 26 additional NGP lakes. These lakes expanded the salinity gradient covered by this calibration set, as most of these additional lakes fall in the range of 0.1–3.0 g l<sup>-1</sup>. Canonical correspondence analysis (CCA) was performed on the expanded data set using the computer program CANOCO (version 3.12, Ter Braak, 1988a and Ter Braak, 1990) with downweighting of rare taxa. Because many of the environmental variables in this set are highly inter-correlated, we used forward selection to test the significance of each environmental variable in influencing species composition. Variance partitioning was also employed to separate the effects of ionic composition from those of salinity/conductivity. Fossil assemblages were plotted passively onto a CCA biplot of anion composition, as well as salinity.

The transfer function developed by Fritz et al. (1993) was modified with the additional NGP data and used to reconstruct salinity. The program CALIBRATE (version 0.82, Juggins and Ter Braak, 1998) was used to perform weighted-averaging regression (with jackknifing) and calibration. No-analog samples were identified using the computer program MAT (Modern Analog Technique, version 1.1, unpublished program. S. Juggins, Department of Geography, University of Newcastle, UK), which provides a measure of dissimilarity by calculating the squared chi-squared distance between a fossil sample and the closest

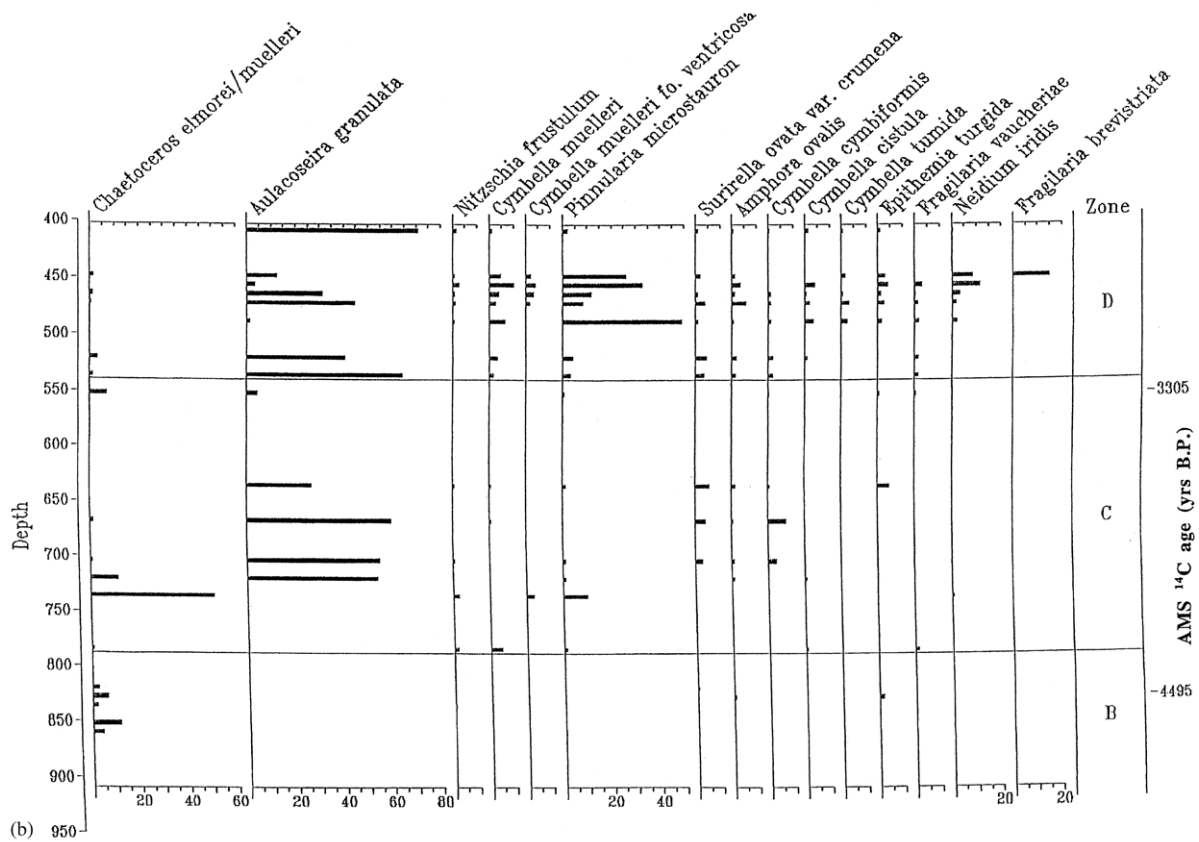
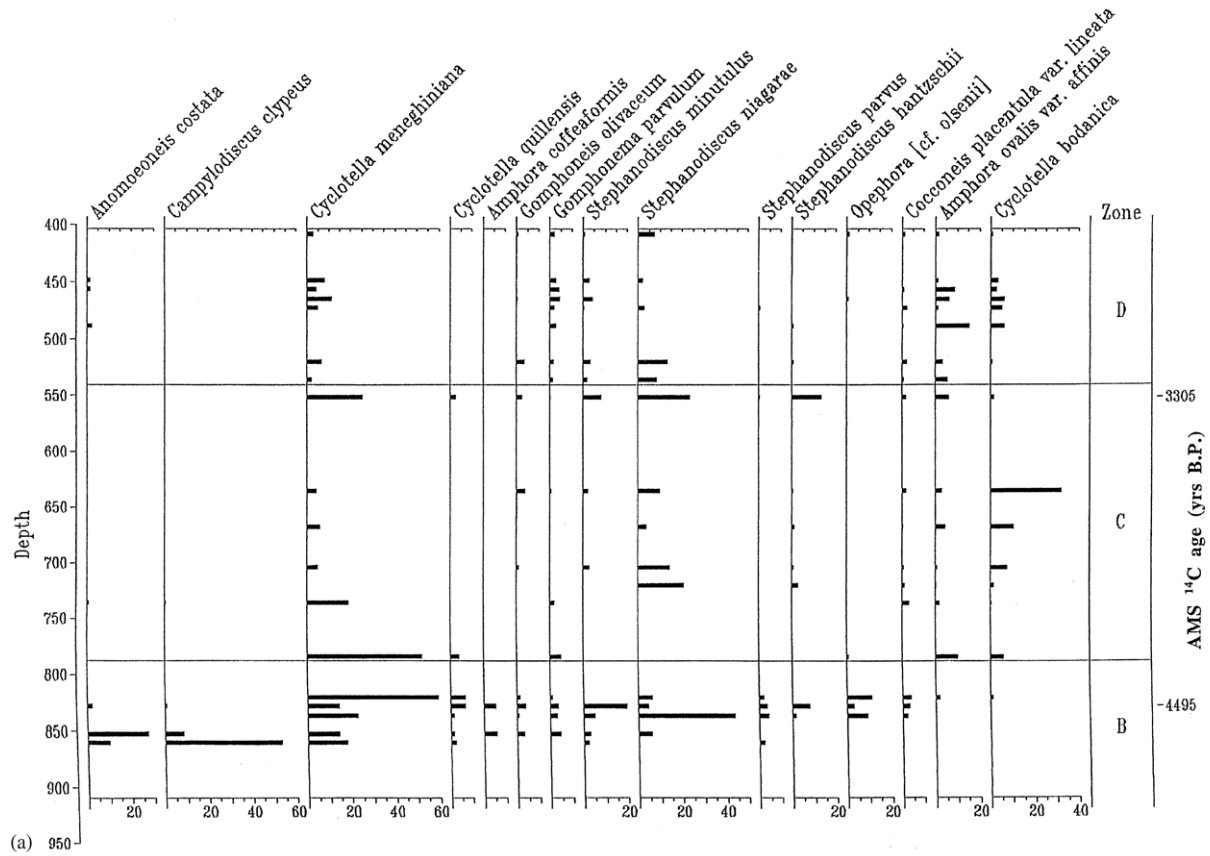
modern assemblage. A fossil sample with a minimum dissimilarity coefficient (DC) <0.900, which is the fifth percentile of the distribution of distances among all modern samples (Bartlein and Whitlock, 1993), was defined as a good analogue.

## 4. Results

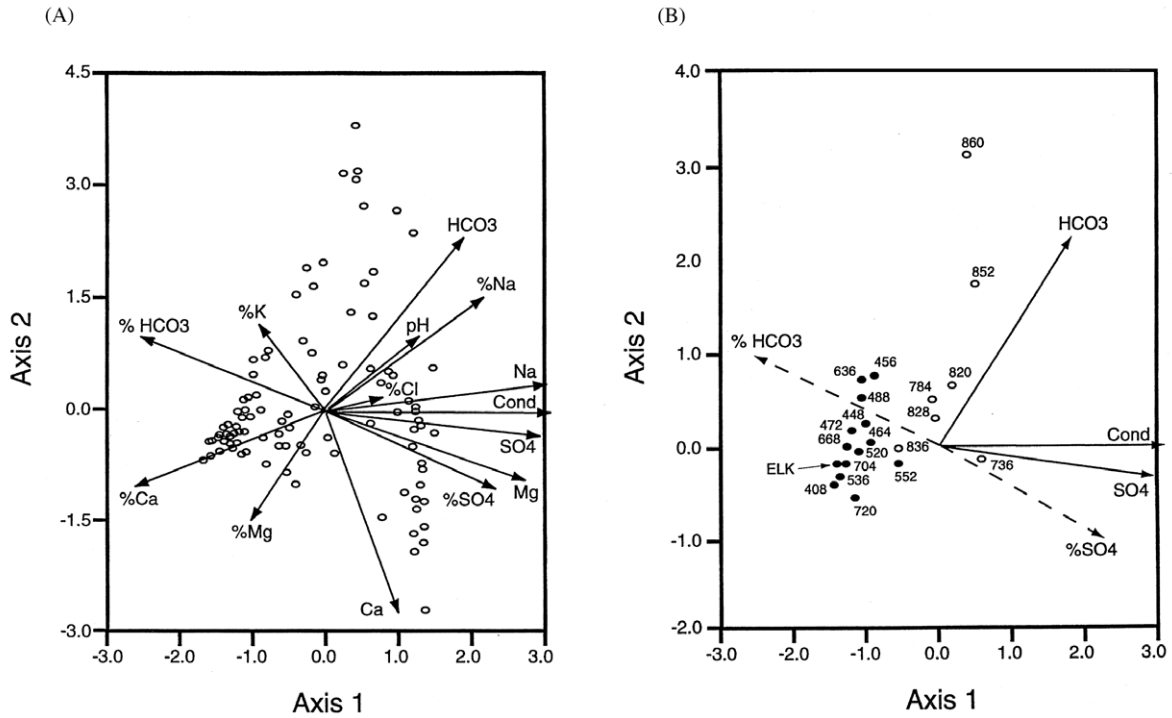
### 4.1. Diatom stratigraphy

In general, diatom preservation was rather poor, with diatoms present between 408 and 860 cm (approximately 2640–4645 <sup>14</sup>C yr BP), but absent from 860 to 1274 cm. The diatom profile for this section of the core is displayed in Figure 4, with the taxa arranged roughly in order of appearance and zone boundaries as in Smith et al. (1997). *Cyclotella meneghiniana*, *Stephanodiscus niagarae*, and *Gomphonema parvulum* are present throughout this section, whereas *Anomoeoneis costata*, *Campylodiscus clypeus*, *Cyclotella quillensis*, *Amphora coffeaeformis*, and *Opephora cf. olseni* are found mainly in zone B. *Amphora ovalis var. affinis*, *Cyclotella bodanica*, and *Aulacoseira granulata* are abundant in zones C and D, while *Pinnularia microstauron* comprises a large fraction of many of the assemblages in zone D. *Chaetoceros elmorei* is interspersed throughout the core and dominates the assemblage at 736 cm, comprising 51% of the total.





**Figure 4.** Diatom profile of Elk Lake from ~4645 to 2640 <sup>14</sup>C yr BP. Taxon abundance is expressed as percent of the total valves, with taxa comprising less than a maximum of 5% excluded here. Zone delineation follows that of Smith et al. (1997).



**Figure 5.** (A) CCA ordination of 79 lakes (indicated by open circles) from the Northern Great Plains. Environmental vectors show the direction of maximum variation of the given variable across the diagram, with vector length indicating relative importance. Conductivity is denoted by "Cond". Vectors for conductivity, concentrations of  $\text{SO}_4$ ,  $\text{HCO}_3$ , Ca, Mg, and %Na are the only ones plotted actively here (i.e. the only variables included in the CCA to determine the position of samples on the biplot). Forward selection revealed that all other variables did not have a significant independent influence on species distributions. Bicarbonate-dominated lakes plot from the upper central area down to the left, opposite the conductivity vector. Sulfate-dominated lakes also fall opposite the conductivity vector, as well as on the lower right of the plot. Both sulfate- and bicarbonate-dominated lakes fall opposite the conductivity vector because the position of these lakes on the biplot results from the influence of both conductivity and anion composition, and this group of lakes is low in conductivity. (B) Positions of Elk Lake fossil assemblages (plotted passively) with respect to brine type and conductivity vectors. Samples from the ostracode-inferred period of higher sulfate proportions are plotted as open circles, while filled circles represent samples from the ostracode-inferred period of bicarbonate domination. The modern Elk Lake assemblage is denoted by "Elk".

#### 4.2. Ordination analysis

The results of the CCA with the expanded NGP data set (Figure 5A) are slightly different from those in Fritz et al. (1993), but the significant axes and variables remain the same. Forward selection, which separates the effects of co-varying variables, revealed that conductivity,  $\text{SO}_4$ ,  $\text{HCO}_3$ , Ca, Mg, and %Na explain the species data almost as well as the full set of variables. Therefore, all other variables were removed from the CCA and are only plotted passively in Figure 5A. We attempted to statistically separate the effects of salinity and brine type using a partial CCA (Ter Braak, 1988b) with salinity and conductivity removed, but only cation variables were significant after partitioning out salinity and conductivity. Thus, the effects of salinity and brine type could not be statistically separated in this dataset.

Conductivity is highly correlated with axis 1, with higher salinity lakes plotting to the right of Figure 5A and relatively freshwater sites on the left. Samples also separate out based on % $\text{HCO}_3$  and % $\text{SO}_4$ , as in Fritz et al. (1993). Almost all fossil assemblages, plotted passively in Fig-

ure 5B, fall in the area of the biplot characterized by high proportions of  $\text{HCO}_3$ , whereas assemblages from 860 and 852 cm are located near lakes with the highest  $\text{HCO}_3$  concentrations. The 736 cm sample is the only one that plots along the positive portion of the % $\text{SO}_4$  vector, as a consequence of domination of the sample by the sulfate-associated *Chaetoceros elmorei*. The positions of fossil samples are also influenced by the conductivity vector. Samples above 736 cm plot to the left in the biplot in the freshwater region and cluster near the modern Elk Lake assemblage, while those from 736 cm and lower in the core fall to the right of the freshwater samples, indicating increased salinity during this period.

#### 4.3. Salinity reconstruction

The diatom-based salinity reconstruction summarizes the ordination results (Figure 6), and indicates that salinity values above 736 cm were  $<1 \text{ g l}^{-1}$ . Lakewater was generally more saline between 736 and 860 cm, with greater fluctuations in salinity during this period. The highest salinity values occurred at 736, 852, and 860 cm (4081, 4607,

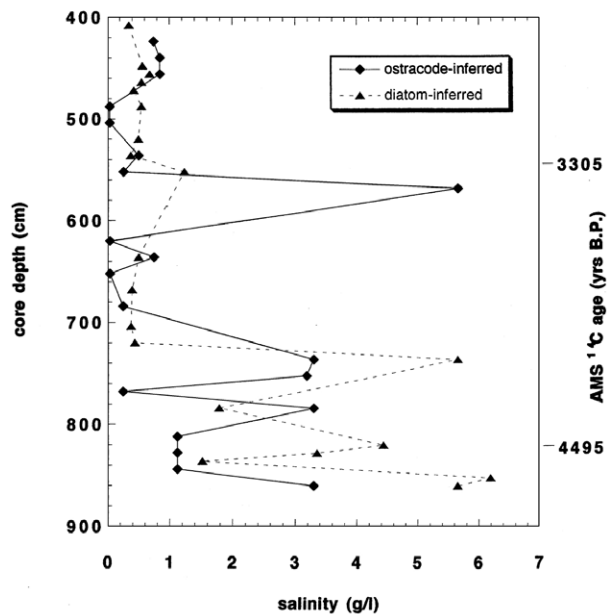


Figure 6. Comparison of diatom- and ostracode-inferred salinity from ~4645 to 2640  $^{14}\text{C}$  yr BP.

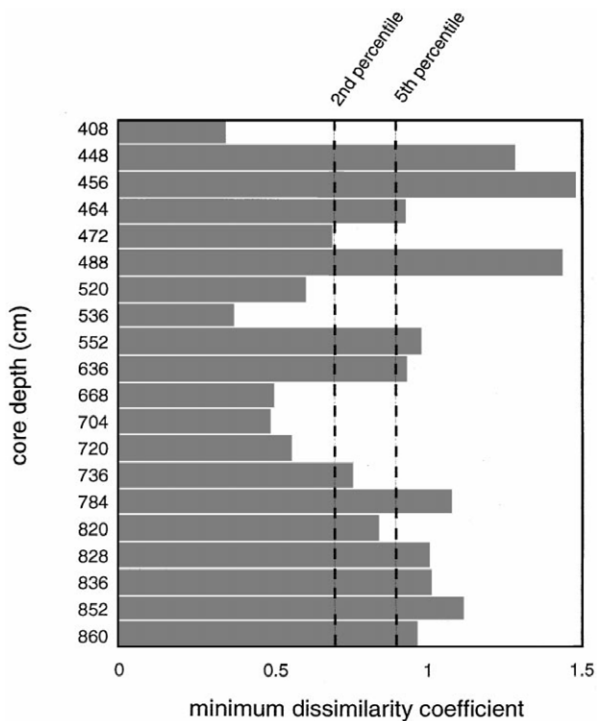


Figure 7. Analog analysis of fossil diatom samples, based on calculated squared chi squared distances between fossil samples and the closest ten modern samples. Fossil samples with a minimum dissimilarity coefficient  $<0.900$  (which is the fifth percentile of the distribution of distances among all modern samples) were defined as having good analogs in the NGP calibration set.

and 4645  $^{14}\text{C}$  yr BP, respectively), with a maximum of  $6.2 \text{ g l}^{-1}$  at 852 cm. About half of the fossil assemblages had poor analogs in the calibration set from Fritz et al. (1993), as their minimum DC values were greater than

0.900 (Figure 7). At 568 cm, the ostracode record indicates a brief peak in salinity that is not recorded by the diatom profile. However, diatoms were absent from this particular sample, possibly due to greater dissolution of valves at the higher salinity and/or high bicarbonate concentrations.

## 5. Discussion

The diatom-inferred salinity, spanning 2640–4645  $^{14}\text{C}$  yr BP, indicates that the most saline conditions occurred in the basal portion (mid-Holocene) of this record. After approximately 4080  $^{14}\text{C}$  yr BP, lakewater salinity was relatively low. Ostracode-inferred salinity shows the same general pattern (Figure 6), with more saline conditions prior to 4080  $^{14}\text{C}$  yr BP, although one exception occurs around 3300  $^{14}\text{C}$  yr BP (568 cm). The overall shift from high salinity to low salinity after 4000  $^{14}\text{C}$  yr BP at Elk Lake is consistent with other regional sites, which similarly show a decrease in salinity and thus an inferred increase in moisture sometime between 5000 and 4000  $^{14}\text{C}$  yr BP (reviewed in Laird et al., 1996a; see also Bradbury and Dean, 1993; Schwab et al., 1995; Smith et al., 1997; Xia et al., 1997).

In most locations, conditions moister than those of the mid-Holocene persisted until modern times, consistent with the pattern seen here. At the sites that are hydrochemically most sensitive to climate variation, the data do suggest large fluctuations between wet and dry conditions during the late Holocene, especially after 2200  $^{14}\text{C}$  yr BP (Laird et al., 1996b; Schwab and Dean, 1998), and these fluctuations are manifest as the generally smaller scale variation evident in the upper part of the Elk Lake record (see also Smith et al., 1997). The zone of high salinity (as inferred from the ostracodes) and poor diatom preservation around 3300  $^{14}\text{C}$  yr BP (568 cm) in Elk Lake is similar to patterns at Moon Lake, N.D., to the west, where diatom preservation is poor during this time interval (Laird et al., 1996a), presumably because of high salinity during an arid interval.

The absence of diatom fossils below 860 cm is consistent with ostracode reconstructions, which suggest a period of high salinity,  $\text{HCO}_3$ -dominated lakewater. Bicarbonate brines typically promote the highest degree of frustule dissolution (Barker et al., 1994; Flower, 1993). This may explain the absence of diatoms in the lower section of the core, and it may also have affected the quality of diatom preservation in the rest of the core. Barker et al. (1994) monitored the dissolution of diatoms in various solutions and found changes in assemblage composition in bicarbonate solutions, with taxa having high valve surface area : volume ratios exhibiting the greatest susceptibility to dissolution. High bicarbonate concentrations in Elk Lake may have affected the integrity of the extant diatom record, as many samples consisted mainly of large, heavily silic-



ified taxa, such as *Stephanodiscus niagarae*, *Aulacoseira granulata*, *Pinnularia microstauron*, and *Campylodiscus clypeus*, and preservation of valves was poor in general.

Although the diatom- and ostracode-inferred salinity reconstructions show the same trends, certain differences are apparent. As mentioned above, diatoms were not present in the sample at 568 cm, thus a diatom-inferred salinity is not available for comparison with the high ostracode-inferred value. Between 736 and 860 cm, the two records are somewhat offset and the diatom-inferred salinity is generally greater. This may be the result of differences in the methods used in these reconstructions, with the ostracode-inferred values determined with the matching analogue technique and the diatom-inferred salinity with a transfer function. With the matching analogue technique, the salinity of a modern lake with an assemblage most similar to the fossil one becomes the inferred value. This method is based on presence-absence data, due to the patchy nature of ostracode populations. In this case, the use of percentage data would be less accurate. In contrast, diatom distributions are generally more homogeneous than those of ostracodes, thus a transfer function using percentage data is appropriate. A salinity value is obtained by summing the salinity optima of individual taxa, weighted by their relative abundances in the sample.

About half of the fossil diatom assemblages had poor analogues in the NGP calibration set (Figure 7), which could affect the accuracy of salinity reconstructions for these sample depths. Samples in the lower section of the core, as well as those from 552 and 636 cm, had poor analogues because *Cyclotella bodanica*, *Stephanodiscus niagarae*, *Campylodiscus clypeus*, and *Anomoeoneis costata* comprised larger fractions of these assemblages than of any samples in the modern data set. Higher percentages of these relatively large diatoms may reflect dissolution of smaller taxa during these periods. Good analogues for assemblages at 448, 456, 464, and 488 cm were unavailable, because these samples contained large percentages of *Pinnularia microstauron*, which is not currently found in any of the 79 lakes in the NGP data set. In North America, this taxon inhabits waters with broad ranges of pH and mineral content (Patrick and Reimer, 1966), and in East Africa, Gasse (1986) found this taxon mainly in bicarbonate-dominated systems of low conductivity ( $<300 \mu\text{Siemens cm}^{-1}$ ), which is consistent with the ecological traits of other taxa found in fossil samples with *P. microstauron*.

In general, the positions of fossil samples on the CCA biplot indicate that Elk Lake was mainly a bicarbonate-dominated system between 2640 and 4645  $^{14}\text{C}$  yr BP, with only one assemblage (736 cm) plotting along the positive portions of the  $\% \text{SO}_4$  and  $\text{SO}_4$  vectors. Because we were unable to statistically separate the effects of salinity from brine type on the ordination, the position of samples is in-

fluenced by both variables, which makes it somewhat difficult to clearly resolve shifts in anion composition based on the diatom record. However, it is evident that samples from 860 and 852 cm plot in the same region as modern systems with high bicarbonate concentrations, having assemblages dominated by *Anomoeoneis costata* and *Campylodiscus clypeus*. Samples from 784, 820, and 828 cm also plot in the region with relatively high bicarbonate concentrations. Their positions also suggest that the proportion of sulfate is higher in these samples than in subsequent ones, but the relative proportion of sulfate to bicarbonate is unclear. The ostracode record indicates that sulfate proportions exceeded those of bicarbonate during this period (Figure 2), although both sulfate and bicarbonate concentrations were high during this period. The data suggest that sulfate proportions relative to bicarbonate are not sufficiently great to affect diatoms, and/or that diatoms in subsaline and saline systems are responding to anion concentrations, not proportions. The response of diatom assemblages to changing  $\text{HCO}_3^-$  concentration is supported by the assemblage at 860 cm, which is dominated by taxa strongly associated with bicarbonate systems and is the only preserved diatom sample with  $>1000 \text{ mg l}^{-1} \text{ HCO}_3^-$  (as inferred from the ostracode record). In addition, results of culturing experiments also indicate that  $\text{HCO}_3^-$  concentrations affect diatom physiology. The maximum growth rates of bicarbonate-associated taxa, such as *Cymbella pusilla* and *Anomoeoneis costata*, were higher in bicarbonate-dominated media compared to sulfate-dominated media (Saros and Fritz, 2000b). The results of this culturing work, as well as the reconstructions presented here, suggest that the direct influence of  $\text{HCO}_3^-$  concentration on diatom physiology may be one mechanism behind the correlation between diatom distributions and anion composition.

Above 784 cm, both records indicate the same shifts in anion composition, with both ostracode and diatom assemblages reflecting bicarbonate domination in all samples except 736 cm, in which they indicate sulfate domination. The ostracode record also suggests high sulfate concentrations at 568 cm; as mentioned above, diatoms were absent from this sample.

In conclusion, both the diatom- and ostracode-inferred salinity and brine-type reconstructions are in general agreement. The diatom record provides information on ionic proportions, but also suggests that diatoms respond strongly to bicarbonate concentrations. Both records indicate higher salinity between  $\sim 4000$  and  $4600 \text{ }^{14}\text{C}$  yr BP (which is the oldest portion of the diatom record) and brine shifts at some point during this period.

We infer from this study that diatoms respond to shifts in anion composition and concentrations, as the relative abundances of anion-associated taxa generally tracked the ostracode-inferred changes in brine type. This type of re-

construction can be particularly insightful in systems such as Elk Lake, where the anion composition of ground water differs from that of lakewater. Shifts in brine type may thus reveal changes in groundwater behavior over time, potentially providing additional information on the impact of regional climate.

### Acknowledgements

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