Reconstruction of past changes in salinity and climate using a diatom-based transfer function

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THE prospect of global warming has focused attention on the role of palaeoecology in testing the accuracy and sensitivity of climate-model predictions, in identifying past analogues for future climate change, and in placing model-predicted climate responses in the context of natural climate variability[1,2]. Proxy data for climate reconstruction can be derived from many sources, including the palaeolimnological record[3,4]. In closed-basin lakes in arid and semi-arid regions, shifts in effective moisture lead to the concentration or dilution of dissolved salts, and these changes in salinity are clearly reflected in the composition of lacustrine diatom assemblages[5-8]. Here we refine a previously published[9] diatom-based transfer function for the reconstruction of past changes in salinity of lakes in the northern Great Plains region of North America, and apply the refined transfer function to a late-glacial and Holocene sediment record from Devils Lake, North Dakota. Our results show that there were a number of alternations between fresh and saline conditions during the Holocene and hence demonstrate the utility of the technique in reconstructing past changes in regional climate.

Our transfer function for salinity reconstruction is based on the statistical relationship between regional modern diatom assemblages in surface sediments and lakewater chemistry. We collected surface-sediment samples for diatom analysis and associated data on water chemistry in 1982 and 1985 from 39 sites in North and South Dakota, USA and from 27 lakes in Saskatchewan, Canada. The lakes had salinity ranging from 0.7‰ to 270‰ and the sites had a strong gradient from east to west in their precipitation minus evaporation gradient (Fig. 1). Standard techniques were used for diatom analysis[10]. In most cases diatom counts were 400-600 valves, but in samples where diatoms were scarce or poorly preserved, fewer were counted. Cation concentrations were measured by d.c.-plasma atomic emission spectrometry, anions by ion chromatography and inorganic carbon by automated coulometric titration. Statistical analysis of the data on water chemistry and diatoms was carried out using principal-component analysis, detrended correspondence analysis and canonical correspondence analysis[11-13]. In all ordinations the first axis was strongly related to total salinity and many of its associated ionic components, and the second axis related to differences in brine type, in particular the difference between systems dominated by CO_3/HCO_3 and those dominated by SO_4. The combined data set was screened, and 11 samples where diatoms were absent or poorly preserved were omitted from further analysis.

On the basis of the strong first-axis relationship between diatom composition and salinity, we used weighted-averaging regression[14] of the log-transformed salinity data to estimate the salinity optima and tolerances of all taxa that occurred with at least 2% abundance in any one sample. We subsequently used weighted-average calibration with an inverse deshrinking regression[15] to estimate the diatom-inferred modern salinity for each site in the data set. A previously published transfer function[9], derived from canonical correspondence analysis[16], was based on classical regression, which produces larger root-mean-square errors and pulls inferred values away from the mean[15]. Optima

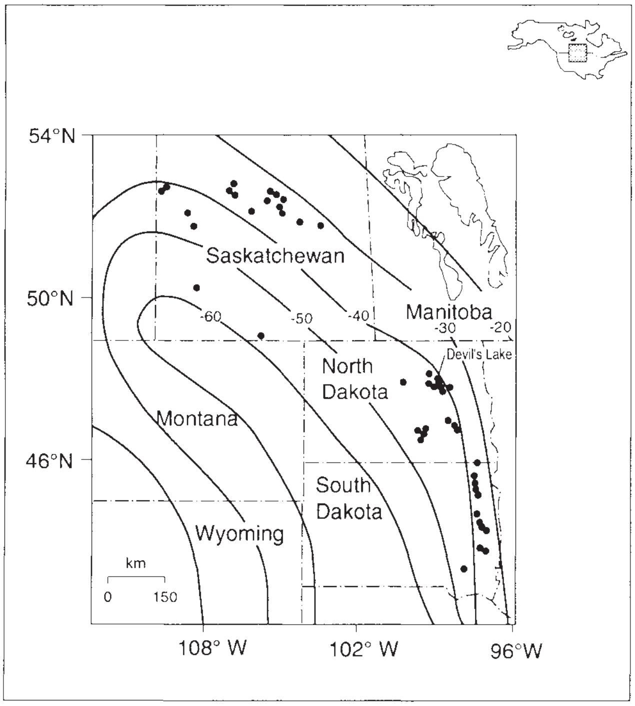

FIG. 1 Map of the northern Great Plains showing the location of surface-sample sites and Devils Lake. The contours are lines of equal precipitation minus evaporation, measured in cm yr^{-1} (ref. 18).

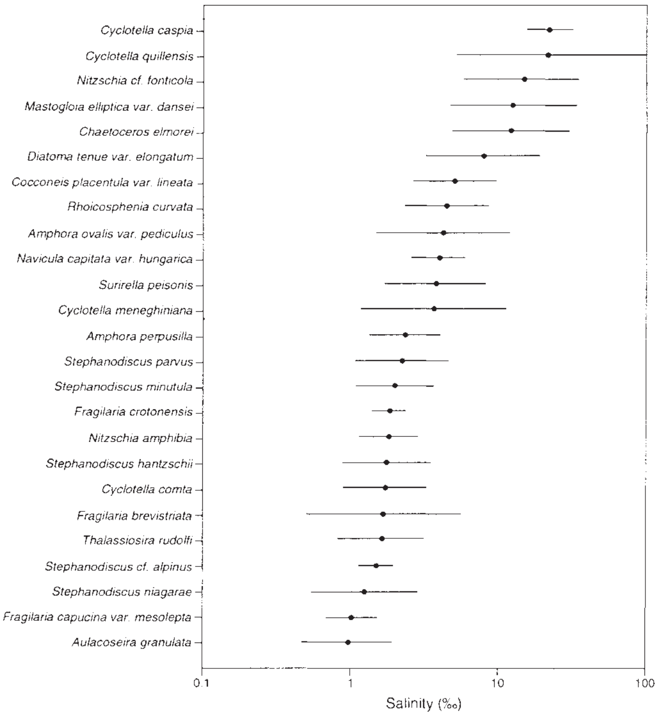

FIG. 2 Estimated optima (abundance-weighted means) and tolerances (abundance-weighted standard deviations) of taxa in the Devils Lake core with maximum abundance >5% and occurrences in five or more samples.

$$\hat{u}_k = \sum_{i=1}^{m} y_{ik}x_i \Big/ \sum_{i=1}^{n} y_{ik} \qquad \hat{t}_k = \left[\sum_{i=1}^{n} y_{ik}(x_i - \hat{u}_k)^2 \Big/ \sum_{i=1}^{n} y_{ik} \right]^{1/2}$$

where y_{ik} is the abundance of taxon k in sample i, x_i is the observed salinity of sample i, and $\hat{u}_k$, $\hat{t}_k$ are the optimum and tolerance of species k, respectively.

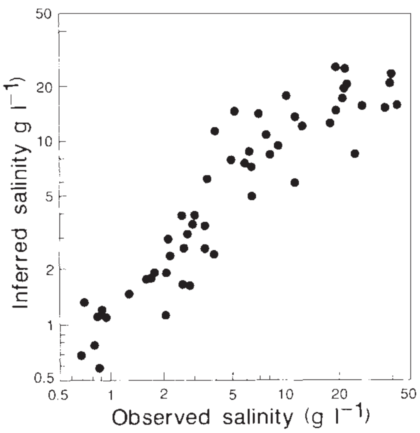

FIG. 3 Observed salinity against diatom-inferred salinity (derived from weighted-averaging regression) for the 55 surface-sample sites ($r=0.91$).

$$\hat{x}_i = \sum_{k=1}^{m} y_{ik}\hat{u}_k \Big/ \sum_{k=1}^{m} y_{ik} \qquad \dot{\hat{x}}_i = a + b\hat{x}_i$$

where y_{ik} is the abundance of taxon k in sample i, $\hat{u}_k$ is the optimum of species k, $\hat{x}_i$ is the inferred salinity, and a and b are the coefficients of the deshrinking regression of observed salinity x_i on $\hat{x}_i$ (ref. 72 in ref. 15).

and tolerances of selected diatom taxa and a comparison between inferred and measured salinity for each site are shown in Figs 2 and 3, respectively. The data indicate a very close agreement between inferred and measured salinity with no apparent outliers, despite the variable state of diatom preservation in the surface-sediment samples. These results suggest that diatom preservation is not significantly biased towards either the fresh or saline ends of the spectrum or that differential loss of entire valves is small.

To evaluate the use of the transfer function, we took cores from Devils Lake, North Dakota (48°05′ N 98°56′ W), where historical records show a strong hydrological response to climate change in the past century[17]. Lake levels fell and salinity rose from the late nineteenth century through the drought years of the 1930s and 1940s. Thereafter levels rose and salinity decreased to the present day (modern salinity is 2.8‰). This cycle of water-level change is recorded in the uppermost 30 cm of sediment by changes in the diatom composition. The recent freshwater phases are characterized by *Stephanodiscus minutulus* Kütz. Cleve and Moller and *S. niagarae* Ehr., whereas *Cyclotella quillensis* Bailey and resting spores of *Chaetoceros elmorei* Boyer dominate earlier saline periods. The highly saline low-water stands of the 1930s to 1940s also contain increased percentages of benthic diatoms and the meso-polysaline taxon *Cyclotella caspia* Grun. Application of both the preliminary[9] and the revised transfer functions to this time period showed that the salinity history could be accurately reproduced for periods of fresh water and low salinity (<10‰) and that high-salinity intervals could be clearly distinguished from those of low to moderate salinity. Discrepancies between the measured and diatom-inferred salinity during high-salinity episodes for Devils Lake probably result from problems with the sedimentary

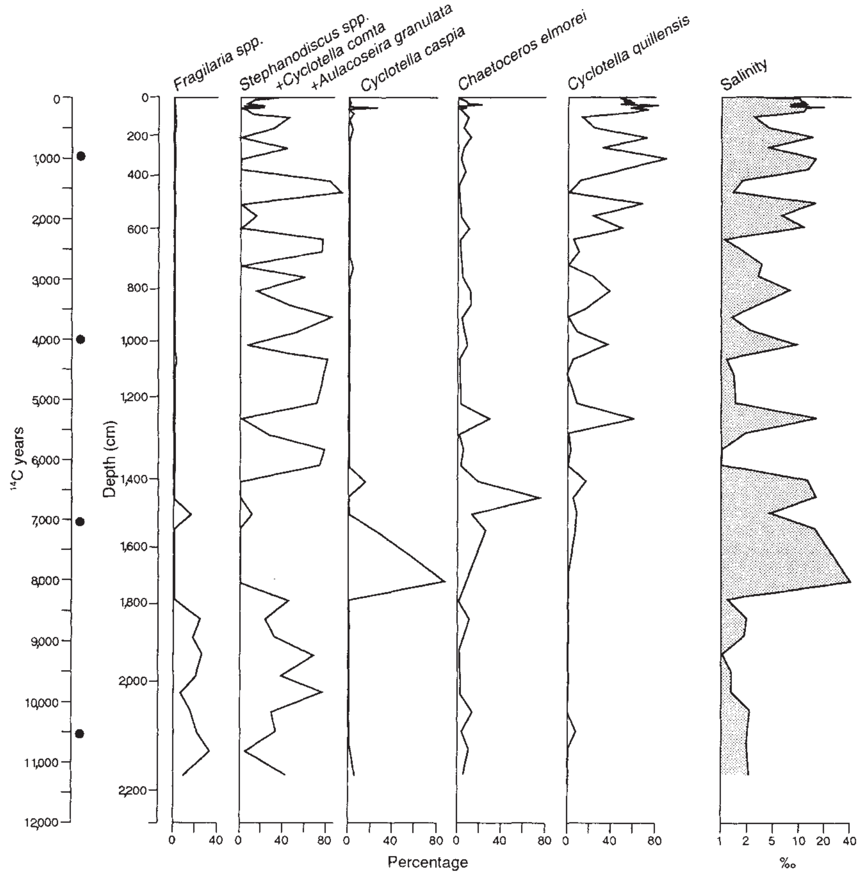

FIG. 4 Summary diatom diagram and diatom-inferred salinity for the late-glacial and Holocene record of Devils Lake, North Dakota. Core depth is measured from the sediment surface. Dates on the y-axis are derived from an age–depth relationship based on four AMS radiocarbon dates: Beta-21193/ETH-3022, 108–116 cm (woody fragment), 955 ± 120 BP; beta 21023/ETH-3009, 995–1003 cm (woody fragment), 3,950 ± 150 BP; beta-20471/ETH-2925, 1507–1515 cm (woody fragment), 6,855 ± 110 BP; beta-20472/ETH-2926, 2131–2139 cm (conifer twig), 10,580 ± 160 BP. The dating uncertainty limits represent 1 s.d. from counting statistics; dates are corrected by ^{13}C for total isotope effects; •, position of dates.

record, such as poor diatom preservation, sediment mixing and reworking, or dating inaccuracies, rather than from inadequacies in the inference method itself.

Diatom analysis of a 24-m-long, ^{14}C-dated by accelerator mass spectrometry (AMS) core from Devils Lake (Fig. 4) showed that the late-Wisconsin/early-Holocene was characterized by freshwater taxa, such as *S. minutulus*, *S. niagarae*, *Cyclotella comta* (Ehr.) Kütz. and *Fragilaria* sp. These freshwater species were abruptly replaced ~8,000 yr BP by *Cyclotella caspia* and other euryhaline species indicating a phase of low water level and high salinity that persisted until ~7,000 yr BP. A series of oscillations between fresh and saline episodes then followed, as shown by the alternation of freshwater *S. niagarae*, *S. minutulus* and *Aulacoseira granulata* (Ehr.) Ralfs. with the saline *C. quillensis* and *C. elmorei.*

Application of the transfer function to the Holocene stratigraphy suggests that salinities in the lake have fluctuated from ~1 to 40‰, with highest salinities in the early Holocene (Fig. 4). These oscillations in salinity, if repeated synchronously at other sites in the region, suggest that maximum aridity occurred ~8,000 yr BP, and that effective moisture fluctuated cyclicly throughout the remainder of the Holocene. At least seven oscillations are indicated by the Devils Lake data. The data further suggest that the lake was much more saline and conditions much drier in the past than the present day.

Because of high rates of sediment accumulation in many endorheic basins and a rapid chemical response to hydrological change, the diatom stratigraphy of saline-lake sediments can provide a sensitive, high-resolution record of climate change, without the lags characteristic of many other palaeoclimate proxies. We still need to extend our calibration data set at both ends of the salinity gradient to describe the weighted-averaged salinity optima of some taxa more accurately and to assess further the importance of variable diatom preservation in both the calibration data set and the core samples. Moreover, the relationship of salinity to water level and climate is complex and varies from lake to lake depending on hydrological and morphometric features of the lake and its watershed, as well as on geochemical characteristics of the lake water. For the northern Great Plains, where greenhouse warming could have a considerable impact on water availability and the agricultural economy, a series of accurately dated cores from additional sites are needed to substantiate the inferences that we have drawn here about effects on the climate. We can then use the pattern of events thus indicated to validate and refine moisture simulations from general circulation models, and to predict regional responses to climate change. ☐

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Nanometre-size diamonds in the Cretaceous/Tertiary boundary clay of Alberta

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STARTING with the discovery of an iridium anomaly at the Cretaceous/Tertiary boundary in Italy[1], the idea that a large asteroid or comet struck the Earth at the end of the Cretaceous period has gained wide acceptance[2–4] although some workers suggest that massive volcanic eruptions can also explain the observations[5]. The abundance of small diamonds, 3–5 nm in size, in chondritic meteorites[6,7] prompted us to search for such diamonds in the Cretaceous/Tertiary boundary clay of the Red Deer Valley of Alberta (the 'Knudsen's farm' locality). Dissolution and oxidation of this clay yielded 45 ng g^{-1} of a white fraction, consisting of more than 97% carbon, which was absent from rocks above and below the boundary layer. We present evidence that this material is indeed diamond, which strengthens further the case for an extraterrestrial impact. The diamond/iridium ratio in the boundary clay may constrain the type of impactor; our estimate (1.22 : 1) is close to the value found in type C2 chondritic meteorites[2].

The stratigraphy and palaeontology of the 'Knudsen's farm' section, located along the Red Deer Valley (51° 54′ 10″ N, 113° 00′ 50″ E) in Alberta, Canada, have been much studied[4,8–13]. The K/T boundary lies within the Scollard formation, the sediments of which were laid down in terrestrial, not marine environments. The 1-cm-thick boundary claystone overlies many metres of sandstones and mudstones and is capped by a coal seam half a metre thick, followed by more mudstones, both with Tertiary microflora. The sampled boundary clay is a medium grey claystone and is equivalent to the 'fireball layer' of the compound boundary layer described by Hildebrand and Boynton[4].

Following the procedure adopted by Lewis *et al*[1], we dissolved the major minerals from a 20-g sample with HF and HCl. The residue, consisting of 114 mg of solids, was suspended in distilled water and the supernatant colloid decanted off. After washing and repeated decanting, the discarded residue consisted chiefly of spinel and chromite. Spinels and chromite have previously been noted in the boundary claystone at other localities[14–16]. The colloidal supernatant fraction was oxidized by successive treatment with 20 M HNO_3 (16 h at 70 °C) and concentrated $HClO_4$ (2 h at 140 °C). This is adequate to dissolve amorphous carbon and graphite as well as coal macerals[17]. A final washing with HF and HCl, to remove any remaining silicates, yielded 0.90 mg of a white residue. On the unlikely supposition that this represents almost 100% recovery from the original 20-g sample then the concentration in the rock is at least 45 ng g^{-1}, or, integrated over the rock section, 129 ng cm^{-2}.

Energy-dispersive X-ray analysis of the white residue fraction in the scanning electron microscope showed no element of higher mass than silicon. Magnesium, aluminium and silicon together accounted for ~2% of the total mass with the remainder composed of carbon. X-ray diffraction showed three broad diffuse lines which matched the three principal lines of diamond. In the transmission electron microscope, the grains were found to be ~3–5 nm in size and, wherever any morphology could be discerned, octahedral in form, rather than the hexagonal plates of graphite. Electron diffraction (ring powder) gave spacings characteristic of diamond: 2.06, 1.26, 1.08, 0.891, 0.819, 0.73 and 0.68 Å (Fig. 1). We conclude that this material is indeed diamond.

Similar samples prepared from the coal seam 2 cm above the boundary clay, and from the mudstones 3 cm below and 1 m