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Physical and chemical predictors of diatom dissolution in freshwater and saline lake sediments in North America and West Greenland

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Abstract

Diatom dissolution in surface sediment samples from two regional lake datasets in the Northern Great Plains (NGP; $n = 64$) and West Greenland ($n = 40$) is assessed using a morphological approach categorizing valves during routine diatom analysis. Two dissolution indices are derived to parameterize diatom dissolution, and, when compared between two analysts in a blind test, show good correspondence and are closely correlated to diatom fragmentation. We explore the relationships between hydrochemical and physical lake parameters (including meromixis) on dissolution within both lake regions using multivariate methods and modeled with logistic regression. Salinity is the sole significant predictor of dissolution in West Greenland but salinity, carbonate concentration ($[CO_3^{2-}]$) and meromixis are significant predictors in the NGP. Limnological parameters explain 40–59% of variation in dissolution in both regions for both dissolution indices. The dissolution index methodology is applied to a short sediment sequence from Devils Lake (North Dakota), where diatom-inferred salinity inferences can be compared with a historical record of salinity fluctuations over the 20th century. Absolute errors in paleosalinity estimates are strongly correlated with diatom dissolution, with salinity overestimated in 8 out of 11 poorly preserved samples. Preservation does appear to constrain the reliability of the inferred paleosalinity at this site and may also affect the quality of diatom-based paleoenvironmental inferences elsewhere (including estimates of biogenic silica), where preservation state is often not explicitly considered.

The value of lake sediments as paleoenvironmental archives is widely recognized for studies of long-term environmental change (e.g., Smol 2002; Fritz 2003). In arid and semiarid regions of the United States, Africa, Europe, and West Greenland, diatom models have been developed for quantitative reconstructions of salinity as a direct proxy for effective moisture (e.g., Fritz 1990; Gasse et al. 1995; Ryves et al. 2002) and applied to sedimentary fossil assemblages to infer the nature and variability of climate during the Holocene (Verschuren et al. 2000; Laird et al. 2003; McGowan et al. 2003). Poor preservation of diatoms as a result of silica dissolution and valve fragmentation occurs in both freshwater and saline systems, although the latter are particularly susceptible (Barker 1992; Gasse et al. 1997; Ryves et al. 2003). Recent work on both freshwater and saline lake assemblages has shown that effects are differential between species (Barker et al. 1994; Ryves et al. 2001; Battarbee et al. 2005) and can lead to unpredictable error in quantitative reconstructions (Barker 1992). While dissolution can result in the complete destruction of the diatom silica record in sedimentary sequences, partial diatom dissolution can bias assemblages to more resistant taxa with profound, but often overlooked, implications for reconstructing environmental and ecological change. Dissolution and diagenesis may also cause significant distortion to isotopic proxy records being developed from diatom silica. Understanding the information loss associated with poor microfossil preservation is fundamental to assessing the quality of such paleoenvironmental inferences.

Acknowledgments

We thank Emily Bradshaw, Robert Hecky, and two reviewers for many constructive comments on the manuscript. We dedicate this paper to the memory of our diatomist colleagues, John Kingston and Platt Bradbury, both of whom contributed to the early development of our work on the NGP lakes. Part of this work was carried out within NERC grant GR9/02033 to D.B.R. and R.W.B., and additionally during an NERC studentship to D.B.R. (GT4/90/ALS/28).

Diatoms are key to understanding the geochemical cycling of silica in lacustrine and marine systems (Lund 1950; Bailey-Watts 1976; Reynolds 1986). In particular, diatom dissolution has important implications for silica recycling and the extent to which silica is sequestered in sediments. In deeper, stratifying lakes, long-term epilimnetic silica concentrations have been shown to decline following eutrophication, as diatom productivity increases (Conley et al. 1993), when silica exported from the epilimnion is not efficiently recycled to the photic zone. Diatom community structure can alter to favor those species competitive at low Si concentrations, which are often less robust forms requiring less silica incorporated into their frustules. Low silica levels in epilimnetic waters are associated with the rise in dominance of nonsiliceous algae as primary producers and concomitant changes in zooplankton community structure and can have implications for whole-lake functioning.

Diatom preservation in lake sediments has been linked to aspects of water chemistry and physical limnology, often through anecdotal evidence. Laboratory experiments on diatom dissolution have shown that pH, temperature, salinity, and ionic strength are all important factors (e.g., Lewin 1961; Barker et al. 1994; Bidle et al. 2002). In many natural systems, taphonomic processes (and valve preservation) may be dominated by biological interactions, for example, bacterial dissolution (Bidle and Azam 1999; Bidle et al. 2003), bioturbation (Covich et al. 1999; Gibson et al. 2000), grazing and fecal pelletization (Haberyan 1985; Buck and Newton 1995), although the importance of zooplankton as agents of sedimentation has recently been challenged (Turner 2002). Physical characteristics of lakes may also be important, especially where long-term stratification develops (meromixis; Meriläinen 1971). Water depth may play a role where surface sediments are subject to physical resuspension from wind (Flower and Nicholson 1987), and dissolution of finer taxa can occur during sedimentation over deeper water columns (Haberyan 1990; Ryves et al. 2003). Water-body permanence has been shown to be important among saline lakes in Spain (Reed 1998) and experimentally (Flower 1993). The organic content of sediments has been invoked to explain good preservation in tropical, alkaline lakes (Hecky and Kilham 1973).

A simple and robust method for assessing diatom dissolution has recently been developed, based on the morphological appearance of diatom valves under light microscopy (Ryves et al. 2001), and applied to taphonomic problems in a variety of lake types (Ryves et al. 2001, 2003; Verleyen et al. 2004). Here we develop a second diatom dissolution index and contrast diatom dissolution across two regional surface sediment lake datasets from the Northern Great Plains (Fritz et al. 1993) and West Greenland (Ryves et al. 2002). We examine the controls on diatom dissolution in natural systems by relating these dissolution indices to measured physical and chemical lake parameters and consider the implications of these relationships for silica cycling and paleoenvironmental inferences more widely. In particular, we explore the effect of dissolution on quantitative diatom-based reconstructions with an example from Devils Lake, North Dakota.

Study sites

The northern Great Plains—The northern Great Plains of North America (hereafter the NGP) are located within the continental interior, approximately bounded from 96° to 106°W and from 42° to 52°N. Rainfall decreases from northeast to southwest, while temperatures increase from north to south, creating a strong gradient of negative effective moisture (P-E < 0) and strong continentality, with temperatures ranging from less than -10°C in January to greater than +20°C in July throughout the region (Fritz et al. 1993). Lake basins, many endorheic, are widely developed throughout the glaciated parts of the Plains, ranging from ephemeral, prairie potholes ($\sim 10^{-2}$ km^2) to permanent, large lakes ($\sim 10^2$ km^2). The dataset of 64 lakes (Fritz et al. 1993) includes water bodies from 0.1 to 28 m deep and covers the salinity spectrum from subsaline (0.5–3 g L^{-1} total dissolved solids [TDS]) to hypersaline ($>$260 g L^{-1} TDS), with a mean salinity around 24 g L^{-1} TDS (Table 1). Due to preferential precipitation of carbonate with increasing total salinity (Eugster and Jones 1979), overall lake chemistry is predominantly Na-$MgSO_4$, although carbonate-rich lakes are found at lower salinity. Chloride is the dominant anion in only one lake (Reflex) and is abundant in nine others (Table 1).

West Greenland—The ice-free margin of West Greenland, between 66° and 67°N and from 50° to 53°W, contains several thousand lakes. The lakes range in size from 10^{-2} to 10^2 km^2 and $<$2 m to $>$100 m deep and are found from sea level to $\sim$600 m altitude. Climate is low arctic, with mean annual temperature -6°C and continuous permafrost. The climate is increasingly continental away from the coast, with precipitation $<$150 mm yr^{-1} inland. A limited number of subsaline lakes (0.5–3 g L^{-1} TDS) above the local marine limit have developed inland from evaporative concentration, a process that has been important since the early–mid Holocene (McGowan et al. 2003; Anderson and Leng 2004). A study of over 80 lakes in this region has shown the importance of the longitudinal position and local geology in determining lake-water chemistry, which essentially reflects the climatic gradient from coast to ice sheet (Anderson et al. 2001). Lakes are predominantly oligosaline ($<$0.5 g L^{-1} TDS; Table 1), with Ca, Mg, Na, and K the dominant cations, and alkalinity (mainly bicarbonate) and Cl the most important anions, although SO_4 is significant in rare cases (e.g., subsaline lakes SS70 and SS71). Carbonate precipitation occurs in more concentrated lakes (Anderson et al. 2001). Forty lakes used in the diatom-conductivity transfer function of Ryves et al. (2002) are included in the present study.

Diatom dissolution indices

Individual diatom valves were examined under the light microscope (LM) and assigned to a dissolution category. Between 2 and 4 dissolution categories were identified for different taxa, depending on the number of identifiable states (dissolution stages) each taxon passes through as dissolution progresses. Dissolution stages for common taxa

Table 1. Summary of physicochemical and geographical variables and diatom dissolution indices across 64 lakes in the NGP and 40 lakes in the West Greenland datasets. Trans. = transformation ($\log_{10}$, square root, logit, or none) applied in numerical analyses. Code = abbreviated code (see Figs. 3, 4). a: based on 30 lakes.

		NGP			West Greenland				
Variable	Unit	Mean	Max.	Min.	Mean	Max.	Min.	Trans.	Code
Salinity	g L^{-1} TDS	24.4	268	0.7	0.53	3.13	0.01	log(x)	Salinity
Conductivity	μS cm^{-1} (20°C; 25°C for NGP)	17,762	101,000	800	721	4,072	24	log(x)	Cond
Ionic strength	M	0.61	6.69	0.02	0.01	0.06	0.0003	log(x)	IonicS
Sodium	Na^+, mg L^{-1}	4,959	58,700	20	80	590	0.9	log(x)	Na
Potassium	K^+, mg L^{-1}	231	1,130	14	33	191	0.2	log(x)	K
Magnesium	Mg^{2+}, mg L^{-1}	1,860	18,000	31	41	251	0.5	log(x)	Mg
Calcium	Ca^{2+}, mg L^{-1}	116	551	4.7	17	74	1.9	log(x)	Ca
Sulfate	SO_4^{2-}, mg L^{-1}	14,943	178,000	119	45	501	0	log(x+1)	SO_4
Chloride	Cl^-, mg L^{-1}	1,510	17,280	7.3	103	720	2.0	log(x)	Cl
Strontium	Sr, μg L^{-1}	1,070	19,500	9	—	—	—	log(x)	Sr
Barium	Ba, μg L^{-1}	40.8	247	7	—	—	—	log(x)	Ba
% Sodium	Na^+, % of cations	50.1	98.6	9.4	23.5	49.7	7.0	None	%Na
% Potassium	K^+, % of cations	3.1	7.1	0.5	7.2	13.4	2.3	None	%K
% Magnesium	Mg^{2+}, % of cations	40.1	79.3	0.5	36.3	49.5	15.9	None	%Mg
% Calcium	Ca^{2+}, % of cations	6.8	40.5	0.1	33.0	54.4	1.7	None	%Ca
% Sulfate	SO_4^{2-}, % of anions	69.9	97.0	6.9	7.8	85.1	0	None	%SO_4
% Chloride	Cl^-, % of anions	11.7	71.9	1.2	20.7	46.6	7.2	None	%Cl
Anion ratio	Total alkalinity : (Cl + SO_4)	0.6	5.7	0.005	3.25	7.15	0.06	log(x)	MolAn-R
Cation ratio	(Na + K) : (Mg + Ca)	10.6	333.4	0.3	1.03	2.81	0.31	log(x)	MolCat-R
Carbonate	CO_3^{2-}, mg L^{-1}	168	4,204	2	—	—	—	log(x)	CO_3
Bicarbonate	HCO_3^-, mg L^{-1}	647	2,461	35	—	—	—	log(x)	HCO_3
Total alkalinity	HCO_3^- + CO_3^{2-}, mg L^{-1}	814	6,665	50.6	192	1,046	3.8	log(x)	TotAlk
% Carbonate	CO_3^{2-}, % of anions	1.3	8.4	0.1	—	—	—	None	%CO_3
% Bicarbonate	HCO_3^-, % of anions	15.9	68.9	0.2	—	—	—	None	%HCO_3
% Alkalinity	HCO_3^- + CO_3^{2-}, % of anions	17.2	74.8	0.3	57.2	80.9	3.3	None	%TotAlk
pH	pH units	8.9	9.9	8.3	7.8[a]	9.2[a]	6.6[a]	None	pH
Altitude	m.a.s.l.	—	—	—	312	540	70	None	Altitude
Lake area	km^2	—	—	—	0.33	1.84	0.02	log(x)	Area
Lake depth	Maximum (m)	4.7	28.0	0.1	16	47	2	Square root	Depth
Area : depth	Ratio	—	—	—	0.022	0.088	0.002	log(x)	Area : Depth
Salinity : depth	Ratio	70.86	2,680.36	0.12	0.037	0.207	0.001	log(x)	Sal : Depth
F index	Ratio ($0 \leq x \leq 1$)	0.400	0.856	0	0.679	0.886	0.373	logit(x)	F
DDI	Ratio ($0 \leq x \leq 1$)	0.393	1	0.060	0.175	0.545	0.051	logit(x)	DDI

from NGP lakes are illustrated in Ryves (1994). The F (fractional) index estimates the proportion of pristine valves (stage 1) to all valves that can be classed (see Ryves et al. 2001). The index varies from 0 to 1, with $F = 1$ implying all valves perfectly preserved, to $F = 0$, where all valves are appreciably dissolved under LM. Experimental results on diatom assemblages showed that this index is strongly correlated with a decline of both valve abundance and biogenic silica content (Ryves et al. 2001). However, as the F index is relatively insensitive in poorly preserved assemblages, another index to capture changes within the higher dissolution stages was developed. This index is termed the diatom dissolution index (DDI) and estimates the proportion of valves in an assemblage that are in the most dissolved state possible, as follows:

$$\mathrm{DDI} = \frac{\sum_{s=1}^{s=4} n_s \cdot (S - 1)}{N \cdot (S_{\max} - 1)} \quad (1)$$

where n is the number of valves in stage S, and N is the total number of valves classified. $S_{\max}$ is the highest stage that valves in the assemblage could reach if dissolution progressed to its end point; $S_{\max}$ thus varies between 2 and 4. $S_{\max}$ is highly correlated with species' relative resistance to dissolution ($r = 0.97$ for 23 taxa grouped into five susceptibility classes; $p < 0.001$; from data in Ryves et al. 2001). The formulation of Eq. 1 optimizes the balance between ease of use and maximizing dissolution information, and implicitly emphasizes taxa with fewer dissolution stages, which are, on average, more susceptible to dissolution (see previous) and, thus, evidence of better sample preservation.

In practice, as almost all assemblages contain at least one valve from a species with four dissolution stages, $S_{\max}$ is based on species comprising at least 5% of the observed assemblage, to reduce the variability in assemblage $S_{\max}$ purely due to count sum. As with the F index, valves in girdle view are not classified (and so take no part in evaluating the dissolution index). DDI also varies from 0 to 1, DDI = 0 indicating perfect preservation (exactly equivalent to $F = 1$), and DDI = 1 indicating maximum dissolution possible (all valves in the maximum dissolution stage for the assemblage).

Although strongly inversely related to F, DDI exploits more dissolution information from assemblages. Recalculating the experimental dissolution data from fresh material in Ryves et al. (2001) in terms of DDI shows that there is a similarly strong relationship between DDI and diatom abundance (as percentage of number of valves at t_0), as with the F index (F: $r = 0.92$, DDI = -0.26 ln[%abundance] + 1.2, $r = 0.93$; $n = 32$, $p < 0.001$). The relationship is almost as strong as with assemblage biogenic silica loss (percentage of initial BiSi at t_0; DDI: $r = 0.91$, F: $r = 0.94$; $n = 32$, $p < 0.001$). Moreover, using DDI enables these relationships to be applied in a wider range of situations where dissolution is poor ($F \approx 0$). For example, from experimental dissolution data (*see* fig. 4a in Ryves et al. 2001), when $F = 0$, predicted diatom abundance is ≈10% of initial number at t_0, while when DDI = 1, predicted diatom abundance is ≈2% of initial number. The methodology for assessing dissolution was compared between two analysts (D. B. Ryves and R. W. Battarbee) for 27 NGP lakes in a blind test.

Diatom analysis

Original slides from the NGP (Fritz et al. 1993) and the West Greenland (Ryves et al. 2002) surface sediment diatom training sets were examined by the same analyst (D. B. Ryves) to assess diatom dissolution of assemblages. All 40 lakes from the West Greenland training set were included in the study, with at least 400 valves counted per sample (mean 425; Ryves et al. 2002). Counts were made under phase-contrast LM at ×1,000 magnification. All surface sediments in the West Greenland dataset contained diatoms.

For the NGP, dissolution indices were based on reexamination of diatom slides from 53 of the 64 lakes with (i) full water chemistry data and (ii) preserved diatoms, as reported in Fritz et al. (1993). For 46 of these slides, a minimum of 299 valves was counted (mean 314), with poor preservation reducing count sums to between 100 and 250 for five lakes, and to <100 valves for two lakes (Shinbone and Horseshoe). A further two assemblages (East Stump and Alkaline, North Dakota), which were originally classed as having very poor preservation, were also included, although count sums were low (29 and 17, respectively). Dissolution indices for these two samples were based on a dissolution assessment from original count sheets (R. W. Battarbee, unpubl. data). Low count sums are less critical for assessing diatom dissolution as opposed to assemblage species composition, as valves need only be placed in 2–4 categories of preservation, compared with classification into many individual species. No diatoms were found in the remaining nine NGP surface samples (Fritz et al. 1993) and were considered to represent maximum diatom dissolution ($F = 0$, DDI = 1) for subsequent analyses.

Numerical methods

The original water chemistry and physical data from the NGP (Fritz et al. 1993) and West Greenland (Anderson et al. 2001; Ryves et al. 2002) datasets were used as predictor variables in multivariate analyses to explain diatom dissolution, estimated by F and DDI indices (Table 1). Major cation and anion concentrations (including Na, K, Mg, Ca, SO_4, Cl, and both molar anion and cation ratio), conductivity, salinity, alkalinity, and depth are available for both datasets. Alkalinity was measured as total alkalinity in West Greenland and as HCO_3, CO_3, and (HCO_3 + CO_3) in the NGP. Additionally, Ba and Sr concentrations are available for the NGP lakes and several other catchment parameters are included for West Greenland lakes (altitude, lake area, area:depth). Individual ions were also expressed as their relative contribution (% μeq L^{-1}) to total anions or cations as appropriate for both datasets. Most variables were log transformed to reduce the

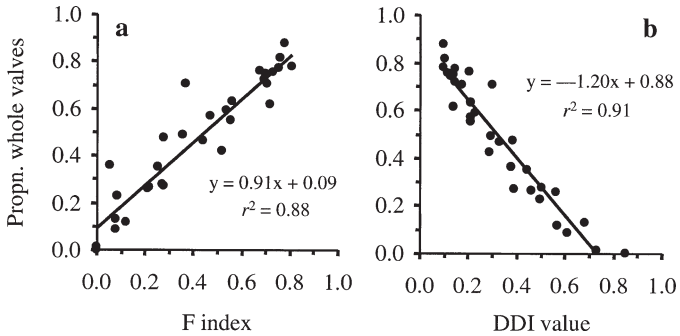

Fig. 1. Relationship between (a) *F* index and (b) DDI and valve fragmentation (the proportion of whole valves in each sample) for 32 NGP slides analyzed by R. W. Battarbee.

effect of skewed distributions, as reported in Fritz et al. (1993) and Ryves et al. (2002), except for depth (square root). Percent Ca, %Cl, %HCO_3, %CO_3, and %(HCO_3 + CO_3) were also log transformed in the NGP dataset (Table 1). Methods used for chemical analysis are given in Fritz et al. (1993) for the NGP and in Anderson et al. (2001) for West Greenland.

Information on lake stratification (meromixis) was also incorporated into the analyses, in the form of a dummy (0/1) variable. Six lakes in the NGP (Basin, Deadmoose, George, Medicine, Sayer, and Waldsea) and five in West Greenland (SS4 [Braya Sø], SS6, SS17 [Store Saltsø], SS42, and SS70) are known to be chemically stratified. For many lakes, however, the stratification regime is not known.

As a number of the predictor variables (chemistry, morphometric, and stratification parameters) were strongly intercorrelated, principal components analysis (PCA) was used to explore the relationships between predictor variables, and between predictors and diatom dissolution indices. The significance of the PCA axes was tested using a broken stick model (Jolliffe 1986). As both diatom dissolution indices (*F* and DDI) vary between 0 and 1, they were logit transformed ($f(x) = \ln[x/(1 - x)]$) prior to PCA analyses.

Subsequently, multiple logistic regression was used to model the relationship between the dissolution indices and one or more physical and chemical lake parameters. Backward elimination was used to select the most parsimonious model for each index in each dataset and its significance tested using a Monte Carlo permutation test (999 random permutations). For each model, we estimated the goodness of fit using a pseudo r^2. This measure is analogous to the r^2 value in least-squares regression and is calculated as the squared Pearson correlation coefficient of the observed index with the predicted value (Mittlböck and Schemper 1996). PCA was carried out using CANOCO 4.51 software (ter Braak and Šmilauer 1998), and logistic regression was carried out in R (R Development Core Team 2004).

Results

Assessing dissolution and fragmentation—There is very good agreement between the dissolution indices (*F* and DDI) calculated by two analysts from the same slides (*F*: $r = 0.94$, DDI: $r = 0.96$, $n = 27$, $p < 0.001$). Despite errors arising from the use of different microscopes, count transects, and techniques (for example, in the treatment of enumerating partial specimens), assessment of dissolution is not statistically distinguishable between analysts for either index ($p > 0.15$; Wilcoxon rank test). Results of the blind test support the idea that the criteria for classification are robust and that the methodology presented here can be used more generally for assessing dissolution.

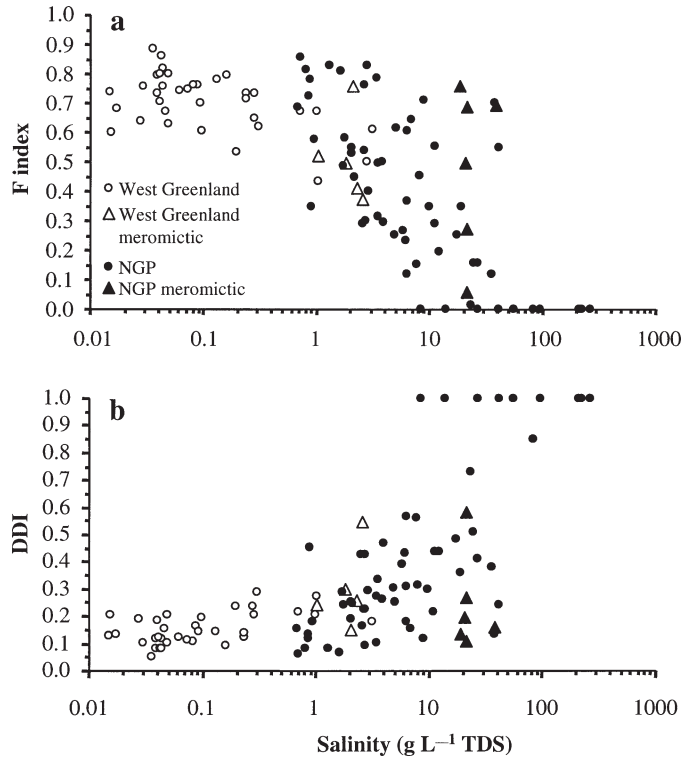

Fig. 2. Relationship between (a) *F* index and (b) DDI and salinity (TDS, log g L^{-1}) for West Greenland and NGP lakes. Known meromictic lakes are indicated.

Analysis of the fragmentation data associated with 32 NGP samples (Fig. 1a,b) demonstrates the strong covariance between dissolution and fragmentation (*F* index: $r = 0.94$, DDI: $r = 0.95$; $n = 32$, $p < 0.0001$), as expected from the well-known control that specific surface area exerts on dissolution rate (cf. Barker et al. 1994).

Dissolution within lake regions—Dissolution is markedly lower within the West Greenland ($F_{mean} = 0.68$, $DDI_{mean} = 0.17$, $n = 40$) than the NGP dataset ($F_{mean} = 0.4$, $DDI_{mean} = 0.39$, $n = 64$; Table 1). The two lake groups, however, overlap to form a taphonomic continuum when plotted along a salinity gradient, with dissolution generally increasing as salinity increases (Fig. 2a,b). The relationship is not simple, however, with significant scatter (especially at higher salinity) and a sudden drop in preservation at salinity >1 g L^{-1}. Dissolution varies substantially within each group of meromictic lakes in the two lake regions, despite an offset of about an order of magnitude in the

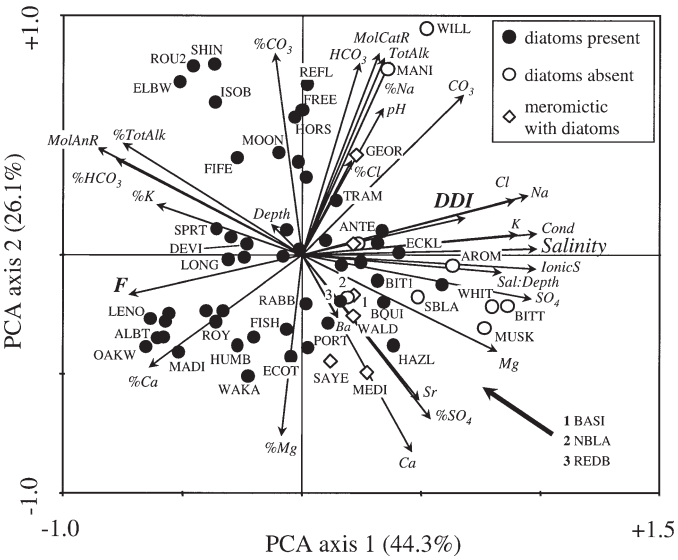

Fig. 3. Principal components analysis (PCA) biplot for sites (symbols) and limnological variables (vectors in italics; Table 1) for the 64 NGP sites. Known meromictic lakes and samples without diatoms in the surface sediments are indicated. Sites (in upper case) are coded according to Fritz et al. (1993). Amount of variance captured by axes 1 and 2 is shown.

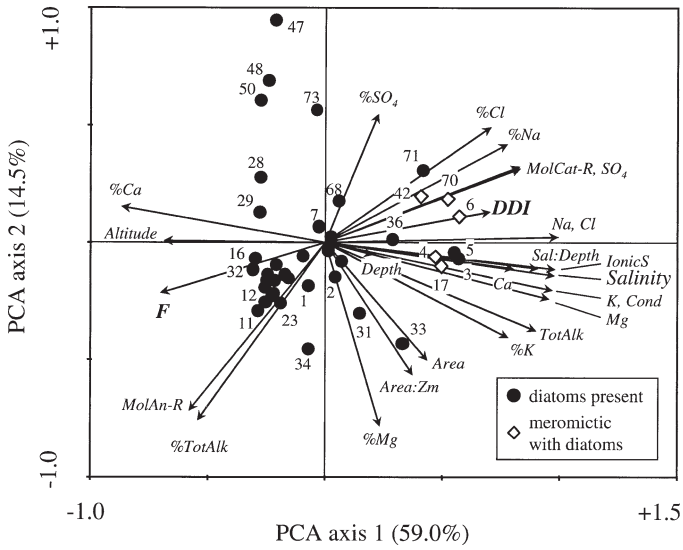

Fig. 4. Principal components analysis (PCA) biplot for sites (symbols) and limnological variables (vectors in italics; Table 1) for the 40 West Greenland sites. Known meromictic lakes are indicated. Sites (in upper case) are coded according to Anderson et al. (2001) and Ryves et al. (2002). Amount of variance captured by axes 1 and 2 is shown.

salinity range of known meromictic lakes in West Greenland (1–3 g L^{-1}) and the NGP (20–30 g L^{-1}).

Relationships between dissolution indices and physicochemical parameters (listed in Table 1) within each lake region are summarized in PCA biplots (NGP: Fig. 3, West Greenland: Fig. 4). Axes 1 and 2 are significant for both plots, capturing about 70% (NGP) and 74% (West Greenland) of variation between them. In both cases, axis 1 is dominated by an overall salinity (conductivity) gradient, increasing from left to right, and highly correlated with Na, Cl, K, Mg, and SO_4. Among the lower salinity lakes of West Greenland, axis 1 is also correlated with total alkalinity, while this is largely expressed along axis 2 within the NGP, as carbonates are progressively removed among the higher salinity lakes, a process that also occurs within the more concentrated West Greenland lakes (Anderson et al. 2001).

Lake positions reflect these chemical gradients, with freshwater lakes found to the left and more saline sites plotting to the right along axis 1, and axis 2 separating different ion types within broadly similar salinity in both regions. Low alkalinity freshwater lakes within the NGP (e.g., Oakwood, Albert, Lenore, and Roy; Fig. 3) are separated from higher alkalinity, subsaline (<3 g L^{-1}) sites along axis 2 (e.g., Elbow, Shinbone, and Isobel). Meromictic lakes plot at similar axis 1 scores, as expected from their similar salinity (cf. Fig. 2), with George unusual in having high alkalinity. Sites without diatoms present in surface sediments, which include the most saline lakes in the dataset, are found to the right of axis 1 (e.g., Bitter (Sask.), Whiteshore, and Muskiki). Similar overall patterns are found within West Greenland, where there is an inverse relationship between altitude and salinity along axis 1. Axis 2 separates lakes with low alkalinity (notably the low pH sites SS47, SS48, and SS50; Fig. 4) and those with high proportions of sulfate (e.g., SS73). Meromictic lakes plot within a similar range of values along axis 1.

Diatom dissolution vectors (*F* and DDI) plot in a similar position in both datasets, along the salinity gradient of axis 1 (Figs. 3, 4), in opposite directions as expected. Values of *F* increase as salinity decreases, while the opposite is true for DDI. Morphometric parameters are generally less important along axes 1 and 2, notably depth, which shows opposite trends in the two regions, tending to decrease in the NGP, and increase in West Greenland, with increasing salinity.

Logistic regression—Results of stepwise logistic regression for each lake region show that only salinity is a significant predictor of DDI and *F* in Greenland (Fig. 5), but that salinity, carbonate concentration ($[CO_3^{2-}]$), and meromixis are significant predictors in the NGP (Fig. 6; $p \leq 0.001$ in all cases). Around 40% of the variance in dissolution indices in West Greenland, and 51–59% in the NGP, is explained by observed limnological parameters. Increasing salinity is associated with greater diatom dissolution in both the NGP and West Greenland, despite the very different range of lake salinity in each lake region. Additionally, $[CO_3^{2-}]$ is positively linked with enhanced dissolution and meromixis with reduced dissolution in the NGP surface samples (Fig. 6).

Discussion

Fragmentation—While many diatom analysts routinely count valve fragments (see Battarbee 1986), relatively few diatom studies have been made on fragmentation, the other major facet of preservation (e.g., Haberyan 1985). Higher

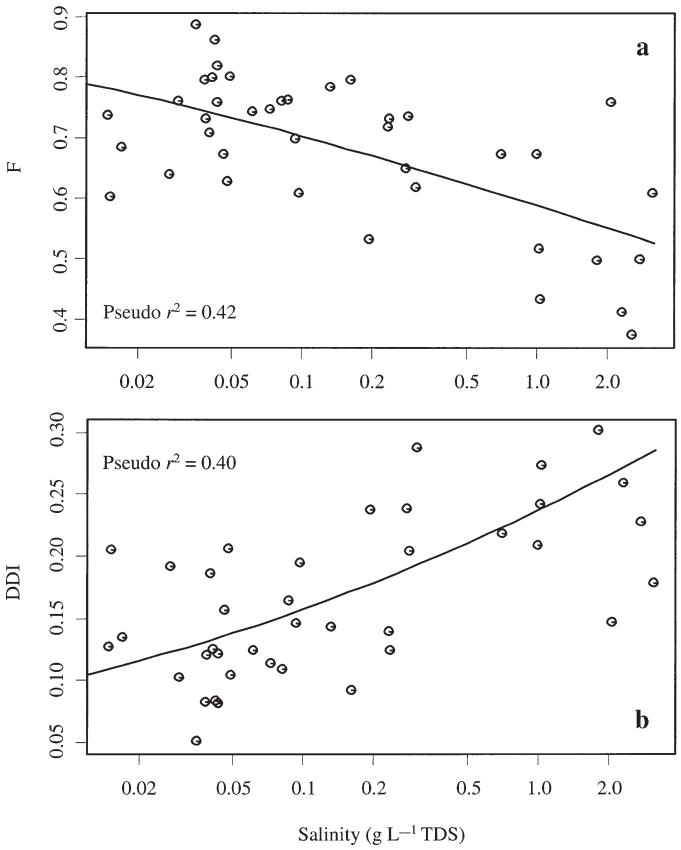

Fig. 5. Logistic regression of salinity (TDS, log g L^{-1}) against dissolution indices (a) *F* index and (b) DDI for West Greenland lakes. For explanation of pseudo r^2 values, see text.

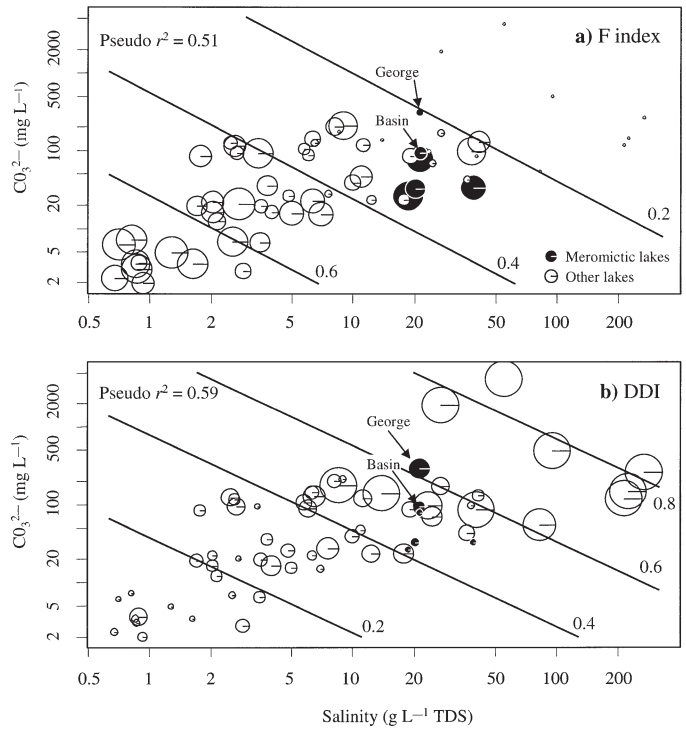

Fig. 6. Logistic regression (as dissolution trend surfaces) of salinity (TDS, log g L^{-1}) and carbonate concentration (log mg L^{-1}) against dissolution indices (a) *F* index and (b) DDI for NGP lakes. Samples are sized according to dissolution index. Meromictic lakes are indicated and two with poor preservation (George, Basin) labeled. For explanation of pseudo r^2 values, see text.

energy environments (e.g., nearshore shallows and wave-mixed zones within lakes; Round 1964; Flower and Nicholson 1987) may play an important role in promoting dissolution through initial breakage of valves, implying a role for water depth, wind speed, and fetch on dissolution. In this study, poor preservation in some relatively low-alkalinity and low-salinity shallow lakes (<3 m deep; e.g., Long, Madison, and Twin within the NGP and SS47 in West Greenland), may be due in part to turbulent mixing of the uppermost sediments. Such turbulence might enhance dissolution from a combination of physical breakage of valves, and the resuspension of valves into Si-undersaturated waters. Frequent resuspension would also inhibit the buildup of dissolved silica in upper sedimentary pore waters, which might slow or halt dissolution of a sedimented valve (though good preservation in sediments has been reported despite low pore-water silica concentrations; Hecky and Kilham 1973).

Controls on diatom dissolution—Salinity is the most important variable affecting dissolution within each dataset, despite the much reduced salinity gradient within the West Greenland dataset (Table 1). In contrast, Marshall and Warakomski (1980) found the solubility of particulate silica gel at 25°C decreased with increasing salinity (or ionic concentration) in a variety of salt solutions up to 6 mol L^{-1} (including 2 mol L^{-1} Na_2SO_4 and 3 mol L^{-1} $MgSO_4$), with the reduction greatest in solutions of bivalent metal salts, correlated with hydration number of the cation. However, experiments on natural surface-sediment diatom assemblages, fresh diatom valves, and pure quartz found that the kinetics of silica dissolution in solutions of different metal salts diverge unpredictably from theoretical behavior (Barker et al. 1994), with dissolution rates varying among different electrolytes at both the same molarity and ionic strength. With natural sediment assemblages, Barker et al. (1994) found that solubility in pH-neutral NaCl solutions reached a maximum between 0.6 mol L^{-1} and 3 mol L^{-1} (equivalent to 35 and 176 g L^{-1}, respectively). Dissolution rates were also higher in 3 mol L^{-1} Li^+, K^+, and Na^+ solutions than in distilled water, and greater for 3 mol L^{-1} solutions of these monovalent cations than solutions of bivalent cations (for 3 mol L^{-1} $MgCl_2$ and $CaCl_2$).

Although the relationship between the activity coefficient of $Si(OH)_4$ (silicic acid) and ionic strength (I) is unclear (Marshall 1980), this behavior may result from a minimum in activity coefficients (and thus maximum solubility of corresponding compounds) between 0.5–1 I (Garrels and Christ 1965; Barker et al. 1994). Above ~3 I (equivalent to 142 g L^{-1} Na_2SO_4 and 90 g L^{-1} $MgSO_4$), activity coefficients generally increase, and compound solubilities decrease (Garrels and Christ 1965), which may also hold true for $Si(OH)_4$. The presence of other mineral

silicates with different solubility (e.g., quartz) within the sediment matrix may also have important consequences for dissolution kinetics (Barker et al. 1994) and may be involved with more complex diagenetic processes of Si precipitation–dissolution (e.g., Flower 1993). Such complications may explain the discrepancies between the results of controlled laboratory experiments on nonbiogenic amorphous silica and dissolution observed in sediments under natural conditions of silica dissolution where a range of silica species is present.

Results here suggest that brine (electrolyte) type does influence diatom dissolution independent of salinity in more concentrated waters, with carbonate important in the NGP but not in West Greenland. Within the NGP, salinity and $[CO_3^{2-}]$ are fairly closely correlated ($r = 0.69$, $n = 64$, $p < 0.001$), although there is considerable scatter across the salinity gradient (Fig. 6), reflecting both local geology and (at higher salinity) selective carbonate precipitation (Eugster and Jones 1979). No lake with $[CO_3^{2-}]$ above ~250 mg L^{-1} contained well-preserved diatoms, including meromictic George Lake (Fig. 6). High alkalinity in freshwaters has been linked with greater dissolution in some Late Glacial sediments from the English Lake District (Round 1964) and in early deglacial sediments from West Greenland (SS2; D. B. Ryves, unpubl. data). Anecdotal evidence exists for both good and poor preservation in alkaline lakes in Ireland (Round 1964; N. J. Anderson, unpubl. data) and Denmark (Anderson and Odgaard 1994). Poor preservation of frustules in early Holocene sections from a core taken from Little Round Lake, Ontario, coincides with high sedimentary carbonate content (Smol and Boucherle 1985). Newberry and Schelske (1986) speculate that enhanced dissolution during this period at this site is linked to the higher lake-water pH at the time of carbonate deposition. Highly alkaline (and high pH) lakes in East Africa are often associated with poor diatom preservation (e.g., Barker 1992), but by no means in all cases (Round 1964; Hecky and Kilham 1973). Diatoms (but not sponge spicules) are poorly preserved in calcareous sediments from Lake Malawi (core M86-12P, collected at 143 m, in the mixolimnion of this meromictic lake; Gasse et al. 2002). In ephemeral lakes, sediment desiccation may be especially destructive in carbonate-rich sediments (Flower 1993). $[CO_3^{2-}]$ is closely related to pH within the NGP ($r = 0.78$, $n = 64$, $p < 0.001$) but pH is less effective as a predictor of diatom dissolution (see following).

Ionic strength was also less effective as a predictor of dissolution than total salinity, though closely correlated with it (Figs. 3, 4). It has been hypothesized that, in otherwise similar carbonate-rich systems, dissolution should increase as the activity of the metal species increases, in the sequence Ca-Mg-Na (Flower 1993). Monovalent to bivalent cation ratio (Na + K : Mg + Ca) was not found to be significant, in agreement with a study of diatom preservation in surface sediment assemblages in Spanish saline lakes (Reed 1998).

As kinetic theory argues against greater dissolution with increased salinity, other factors linked to salinity may be responsible for the patterns observed across the NGP and West Greenland lake regions. In contrast with carbonate, salinity has only a weak positive correlation to pH and total alkalinity in the NGP ($r < 0.39$ for both, $p > 0.01$), but is strongly correlated with total alkalinity among the generally dilute West Greenland lakes ($r = 0.94$, $p < 0.001$). High pH may have a nonlinear effect on diatom preservation as silica dissolution increases exponentially above pH 9 (Krauskopf 1982), even in concentrated salt solutions (Marshall and Warakomski 1980). In very alkaline waters (e.g., in some East African rift lakes; Barker 1992, and *see* following), pH may be the dominant factor involved in diatom dissolution and silicate mineral diagenesis, but this is not apparent here, where maximum pH is 9.9. Results of the multiple logistic regressions indicate that pH has no effect independent of salinity, nor are the interaction terms (salinity × pH, pH × pH) significant ($p > 0.05$). Similarly, pH (varying between 6.3 and 9.9) was not important within a Spanish dataset (Reed 1998), and substantial dissolution does occur in circumneutral freshwaters, both shallow (e.g., Devils Lake during high stands; Lent and Lyons 2001) and deep (e.g., Lake Baikal; Ryves et al. 2003). Within the NGP, sites with high pH may have excellent preservation (e.g., Free People: $F = 0.71$, pH = 9.2), while the converse is also true (e.g., Lake Lenore: $F = 0.35$, pH = 8.25). In a study of 26 sodium carbonate-dominated alkaline lakes in East Africa, diatoms were found well preserved in surface sediments in 21 lakes (10 meromictic), despite pH often above 10, with diatoms too sparse to be counted in five lakes (Hecky and Kilham 1973). While the authors favored dilution by inorganic detrital material as explaining low diatom concentrations in these five lakes, all were shallow, with alkalinity >80,000 μeq L^{-1} $HCO_3 + CO_3$, and they included the two most saline (57,400 and 95,100 μS cm^{-1}) and alkaline (>925,000 μeq L^{-1} $HCO_3 + CO_3$) lakes in the dataset. In the light of results from the present study, these observations suggest that dissolution played at least a part in this pattern.

Salinity and depth show only weak inverse (NGP: $r = -0.26$, $p = 0.05$) or nonsignificant positive relationships (West Greenland: $r = 0.28$, $p > 0.05$) across each lake region. Changes in water depth may alter taphonomic processes, exposing valves to, or protecting them from, physical breakage (and so affecting dissolution). In semiarid areas, shallow (often saline) lakes are also more prone to periodic desiccation, which may destroy the diatom record completely, as shown by observations in the laboratory (Flower 1993) and the field (Reed 1998); salt crystal growth itself might fracture diatom valves during precipitation events. The diatom assemblages of some shallow, highly saline lakes within the NGP dataset may thus not represent the local living community, but the reworking of older, dried sediments from littoral areas during seasonal or interannual lake-level fluctuations. Conversely, increasing water depth might be expected to have a positive effect on preservation where physical mixing is reduced, as in many freshwaters, relatively little dissolution occurs during sedimentation, even over deep, oxic water columns (Schelske et al. 1984; Ryves et al. 2003). Dissolution in upper sediments may also be enhanced in

some shallow NGP lakes from seasonal thermal instability of interstitial waters, leading to a flux of pore water Si to the overlying water column, as has been observed in late summer in shallow, unstratified Canadian lakes (Hecky et al. 1986). In the present study, neither depth, area : depth, nor the ratio salinity : depth was significant in any analyses. In fact, depth produces opposite preservation patterns in the two regions (Figs. 3, 4). Depth is likely to be more important in large, shallow systems, however.

Despite the limnological differences between lakes in West Greenland and the NGP, salinity is the dominant factor explaining dissolution in surface sediments in both systems. Dissolution rates might be expected to be lower in West Greenland lakes, as average temperatures are lower, affecting silica solubility (Krauskopf 1982) and bacterial efficiency (Bidle et al. 2002). Longer ice cover reduces the opportunity for turbulent mixing. As productivity is lower (due to a shorter, less intense growing season and lower nutrient levels) and catchment inwash events rare, sedimentation rates are also low in Greenland (mean of six lakes = 0.06 cm yr^{-1} for the last 40 yr; Bindler et al. 2001; McGowan et al. 2003). The presence of permafrost in West Greenland simplifies lake hydrology, as regional groundwater movements can be ignored. In contrast, subsurface flows are extremely important in understanding the fine-scale spatial heterogeneity of water chemistry among NGP lakes (e.g., Schwalb and Dean 2002).

Meromixis—Meromixis was positively correlated with reduced diatom dissolution in the NGP dataset. Meromixis has previously been linked to poor preservation of sedimentary diatoms in freshwaters (Meriläinen 1971, 1973) but good preservation in marine systems (McMinn 1995; Verleyen et al. 2004). Meromixis may contribute to good preservation in East African soda lakes (as only shallow lakes had low diatom concentrations in surface sediments; *see* above, Hecky and Kilham 1973). Meriläinen (1971) found that appreciable dissolution of diatoms occurred in recent sediments from the monimolimnion of four of the six meromictic lakes he examined in Scandinavia and the United States. Conditions in the monimolimnion can improve diatom preservation by a number of mechanisms. Hypoxia or anoxia promotes lower pH, while salinity is higher, reducing silica saturation concentrations. Silica that does dissolve has a long residence time in the monimolimnion, thereby increasing silica concentrations and reducing further dissolution, while silica concentrations may quickly reach saturation within the sediments (Meriläinen 1971; cf. Hecky and Kilham 1973). In a study from Lake Lugano, Hofmann et al. (2002) found that <20% of the Si exported to the nonmixed layer was resupplied to the surface waters, with the bottom waters acting as a large, permanent sink for Si. Although diatom dissolution is recognized as a major problem in marine systems where a global average of 3% of surface production is incorporated into the sediment record (Tréguer et al. 1995), good diatom preservation has been reported from anoxic basins (McMinn 1995; Verleyen et al. 2004). Sediments deposited under alternating marine and freshwater conditions in a coastal lake on Antarctica show better preservation during anoxic marine than oxic freshwater phases (Verleyen et al. 2004), in contrast with dissolution patterns found across (oxic) freshwater/marine transitions in a shallow coastal fjord in Denmark (Ryves et al. 2004).

Biological processes will also be affected by meromixis. Bacterial degradation of organic coatings of diatom valves may be reduced under hypoxic or anaerobic conditions, although anaerobic bacterial activity can be high in meromictic lakes (Humayoun et al. 2003; Egli et al. 2004). Bioturbation is reduced in the monimolimnion of meromictic lakes, enhancing preservation through a reduction in physical breakage and by the maintenance of high pore-water concentrations of silica (cf. Gibson et al. 2000).

Meriläinen (1971) noted that Fe concentrations were high in the monimolimnia of all four lakes with poor diatom preservation, and not in the two others. Diatom preservation improved in the sediments of Little Round Lake, Ontario, after the inferred onset of meromixis (Smol and Boucherle 1985), where Fe concentrations are also low in the monimolimnion (Newberry and Schelske 1986). Conditions in the monimolimnion are often conducive to dissolution of Fe species under reduced pH and redox potential, often leading to bottom waters enriched in Fe (e.g., Albéric et al. 2000). Iron and other trace metal ions (e.g., Al), which retard dissolution of diatom frustules (Lewin 1961), might thus be stripped away from silica cell walls (Dixit et al. 2001). Geochemical conditions in the monimolimnion might therefore exacerbate dissolution under certain conditions, depending on pH and the degree of anoxia that develops.

Results from the present study suggest that meromixis itself is not a sufficient condition to guarantee good diatom preservation, as dissolution was poor in two meromictic lakes in the NGP (George, Basin; Fig. 6), and meromixis was not linked to better preservation in (subsaline) West Greenland lakes (Fig. 2). More knowledge of the limnology of these saline lakes is needed before the true importance of mixing regime can be evaluated, including studies on the duration and stability of meromictic episodes, geochemical conditions in the monimolimnion, and patterns of seasonal sedimentation.

Other factors—Trace metal ions within the diatom silica matrix are known to be important in reducing silica dissolution of diatom frustules, especially Fe and Al (e.g., Lewin 1961; Dixit et al. 2001). Even if Ba or Sr might be incorporated into silica frustules in a similar way (or are correlated with other species that are), neither variable had a significant effect on dissolution state, and had little clear pattern with salinity.

As only between 40% and 59% of the variance in dissolution indices among these datasets is explained by physicochemical variables, clearly other factors that have not been included are important. Given the importance of biological factors, such as the role of bacteria (both directly dissolving silica and removing the protective organic coatings to frustules; Bidle and Azam 1999; Bidle et al. 2003) and invertebrate bioturbation and grazing (Rippey

and Jewson 1982; Covich et al. 1999; but see Turner 2002), it is likely that these influence dissolution, although the intensity of their effect may covary with salinity and biogeographical region. Large-scale bioirrigation of upper sediments is generally associated with larger invertebrates (e.g., amphipods) in large freshwater lakes and the marine realm.

Sedimentation rate is also likely to have a role. It can be hypothesized that, where sediments are not being resuspended into overlying waters and where biogenic silica production is high enough to saturate pore waters, dissolution is reduced as sedimentation rate increases (Conley and Schelske 1989), as frustules will be removed more quickly from the sediment–water interface and uppermost sediment layers, where most dissolution occurs (e.g., Ryves et al. 2003). At higher productivity, high sedimentation rates have been invoked to explain good preservation in otherwise corrosive environments, especially where anaerobic decomposition of organic material can reduce pore-water pH and so reduce silica saturation concentrations in the absence of groundwater movements (Flower 1993). Hecky and Kilham (1973) linked excellent preservation in sediment cores from two alkaline lakes (one meromictic) in Tanzania to organic matter content, as pore-water silica concentrations (<10 mg L^{-1}) were undersaturated by about an order of magnitude despite sediment pH values over 9. Unfortunately, sedimentation rates for most lakes in the present study are not known.

Comparison with other lake types—While salinity, $[CO_3^{2-}]$, and meromixis are important in explaining the pattern of diatom dissolution within one or both lake regions studied here, other factors may dominate in different limnological settings, although studies in which diatom preservation has been assessed are rare. In shallow, coastal lakes (salinity 0.2–18 g L^{-1}) in Denmark, where salinity is related to marine connectivity rather than evaporative concentration, surface sediment preservation (as assessed using the *F* index) is positively correlated with (log) salinity ($r = 0.64$, $n = 25$, $p < 0.001$; data from Ryves et al. 2004). In many freshwater lakes with deep water columns, although most biogenic silica reaches the sediment surface (Schelske et al. 1984; Ryves et al. 2003), selective dissolution of susceptible taxa can be severe and appears unrelated to salinity. Among the great lakes of East Africa, for example, fine *Nitzschia* spp. are well preserved in surface sediments of Lake Kivu ($z_{max} \approx$ 485 m, surface conductivity ($cond_{surf}$) = 1,240 μS cm^{-1}) and Lake Tanganyika ($z_{max} \approx$ 1,470 m, $cond_{surf}$ = 610 μS cm^{-1}), yet are underrepresented compared with abundance in the plankton in surface sediments of the more dilute and lower alkalinity Lake Malawi ($z_{max} \approx$ 705 m, $cond_{surf} \approx$ 250 μS cm^{-1}; Haberyan and Hecky 1987; Haberyan 1990). Similarly, fine *Nitzschia* and *Synedra* spp. are preferentially dissolved in the deep water column of Lake Baikal (Ryves et al. 2003). Rapidity of sedimentation may be decisive, perhaps through floc formation and mass sedimentation events rather than zooplankton pelletization, as copepods selectively avoid these long forms here (Haberyan 1985).

Anecdotal evidence suggests that meromixis (and/or anoxia) plays an important role in silica cycling and long-term burial in these large lakes. Lakes Kivu, Tanganyika, and Malawi are all meromictic, with deep waters of Lake Kivu unusual in being both saline (~5,000 μS cm^{-1}) and acidic, conditions especially conducive to long-term silica preservation. Diatom preservation is reported as excellent in Kivu sediments (Haberyan and Hecky 1987; R. Hecky pers. comm.), while fine *Nitzschia,* though fragmented, are prominent throughout the Holocene record of Tanganyika (Haberyan and Hecky 1987). In contrast, while fine *Nitzschia* reach the deep-water sediment of Lake Victoria ($z_{max} \approx$ 68 m, $cond_{surf} \approx$ 96 μS cm^{-1}), they are not well preserved in subfossil sediments (Verschuren et al. 2002), despite anoxia for up to 10 months of the year and the absence of bioturbation at depths over 65 m, although wave-induced mixing is frequent offshore at depths less than 50 m and can rarely occur to the lake floor (Verschuren et al. 2002). In Lake Malawi (anoxic below ~250 m), preservation can be poor in the mixolimnion (Gasse et al. 2002), although on a whole-lake basis, 7–11% of diatom production is permanently buried (Bootsma et al. 2003), compared with 5% or less in Lake Michigan (Schelske 1985) and ~1% (by valve abundance) in Lake Baikal (Ryves et al. 2003; cf. oceanic preservation of 3%; Tréguer et al. 1995). The importance of diatom dissolution as a control on silica cycling (Reynolds 1986) justifies further research to elucidate the complex and multifactorial processes involved across different limnological systems.

Paleolimnological implications—By predicting diatom dissolution, paleolimnological effort and expense of core collection can be saved by avoiding certain lake types altogether. High salinity (>20 g L^{-1} TDS) and carbonate-rich lakes, especially, are unlikely to contain a good diatom (and so biogenic silica) record. Meromixis (and anoxia) can help preserve the biogenic silica reaching the sediment surface, but substantial losses can occur during sedimentation in deeper water columns, particularly of finer taxa. Surface sediment dissolution state, however, may not be a guide to preservation in deeper sediments (Flower 1993; Reed 1998).

Dissolution profiles themselves, as taphonomic histories, can be used to help interpret limnological change in terms of sedimentation processes. In saline systems, periods of enhanced dissolution can indicate higher salinity and alkalinity, although it is clear that lake-level change is an important component of such changes in closed basin lakes (e.g., Fritz 1990). Diatom preservation should respond to lake-level fall in such systems as dissolution is enhanced both by rising salinity (and alkalinity), the greater incidence of turbulent mixing in reduced water depth, and the possible breakdown of stratification in meromictic systems. On lake-level rise, preservation should improve, although the taphonomic signal may be distorted by reworking of littoral sediments (which will likely be less well preserved). In freshwater systems, where lake-level lowering and littoral erosion may leave a similar benthic assemblage at a pelagic site, greater diatom dissolution and fragmentation might be expected from the latter taphonomic pathway

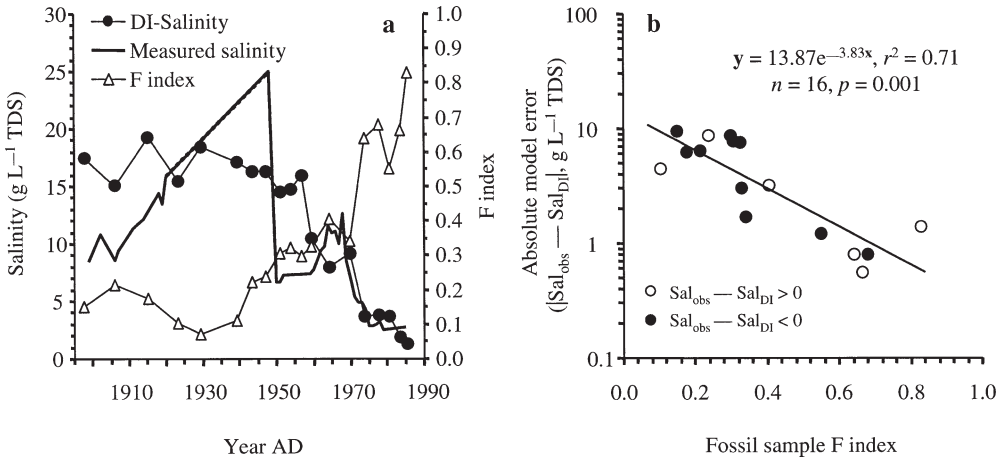

Fig. 7. (a) Comparison of diatom-inferred salinity, measured salinity (TDS, g L^{-1}) and *F* index at Devils Lake over the 20th century (redrawn from Fritz 1990 and Ryves et al. 2001). (b) Relationship between dissolution index, *F*, and absolute error (TDS, log g L^{-1}) in diatom-inferred salinity reconstructions for Devils Lake, North Dakota, from a short core covering the last ~100 years (Fritz 1990). Samples are coded according to whether inferred salinity is underestimated or overestimated.

(with evidence of particle fining upcore if a true turbidite deposit; Mackay et al. 1998).

Stratigraphic patterns of diatom preservation might also improve inference of past diatom productivity from measures based on sedimentary diatom abundance (including BiSi wt % or flux), and it may be a useful comparison with other measures of diatom productivity (e.g., fossil pigments; Verleyen et al. 2004). In Devils Lake, North Dakota, which has fluctuated in historical times between fresh and saline, diatom biomass from phytoplankton sampling was estimated as ~3 times higher in saline than freshwater periods, but the partially dissolved sedimentary BiSi record suggests the opposite (Lent and Lyons 2001). As a corollary to this, changes in dissolution state viewed as an indicator of sedimentary BiSi loss may provide a link to silica cycling (cf. Stoermer et al. 1985). In Devils Lake, Lent and Lyons (2001) estimate that BiSi accumulation in sediments in freshwater periods is ~3 times higher than in low-stand, saline periods. These shifts are reflected in the diatom dissolution profile in a short core (Fig. 7a; Ryves et al. 2001), which can potentially be applied to investigate changes in long-term biogeochemical cycling of silica in this system, and linked to changes in salinity, alkalinity, stratification and perhaps other factors.

Changes in diatom community, following nutrient enrichment, for example, may leave a distinct dissolution signal in the stratigraphic record. More silicified and so resistant taxa (e.g., larger *Cyclotella* and *Aulacoseira* spp.) are often replaced by finer forms (e.g., *Stephanodiscus* and *Nitzschia* spp.), as has been observed among morphotypes within a species (e.g., *A. islandica* and *S. niagarae* in Lake Ontario; Stoermer et al. 1985, 1989) as sedimentary burial rates increase. During the transition to finer forms, overall preservation should deteriorate and more fragile taxa may be significantly underrepresented, while the replacement of more robust by more dissolution-susceptible species promotes more efficient recycling of reduced silica stocks in upper waters. This stratigraphic pattern of dissolution has been noted in Lake Ontario sediments spanning eutrophication from the late 1800s (Stoermer et al. 1985), while in both Lake Victoria and Lake Baikal, increases of the fine *Nitzschia acicularis* in the plankton community over the last decades are underestimated by the fossil record (Verschuren et al. 2002; Ryves et al. 2003, and see previous discussion). In some situations, changes in the intensity of bioturbation could be linked to variations in diatom dissolution and might provide a test of the bioturbation hypothesis as a factor in diatom preservation and silica recycling (for example, at Lough Neagh where sediment records imply up to a 10-fold increase in chironomid populations from 1960; Gibson et al. 2000).

Diatom dissolution also has an impact on qualitative and quantitative inferences based on species-assemblage composition, as dissolution rates are differential between species (Barker et al. 1994; Ryves et al. 2003; Battarbee et al. 2005). Salinity transfer functions may be especially prone to errors from this effect, as relative abundance data are used to calculate the species parameters (optima, tolerances) that define the models from the surface sediment training set and in the fossil samples on which reconstructions are made. Model and fossil data may thus be affected by unequal dissolution between taxa, across the environmental gradient (in space), and over depth (time) within a core.

Devils Lake provides the opportunity to test the effects of diatom dissolution on transfer function performance, as historical records of salinity covering much of the 20th century exist at this site, and can be compared with diatom-salinity model reconstructions over this period (Fig. 7a; Fritz 1990). The absolute size of model errors (|inferred − observed salinity|) over this period are directly related to the dissolution index, *F*, of the fossil samples (Fig. 7b).

While dissolution tends to result in overestimation of salinity (10 cases out of 16), especially in more dissolved samples (8 out of 11 where $F < 0.5$), overestimation or underestimation both occur right across the dissolution gradient. Thus, while increasing dissolution cannot be linked to systematic overestimation or underestimation (bias) of salinity, it does appear to constrain the reliability of the inferred values, at this site at least. While the Devils Lake record may also be subject to ^{210}Pb dating errors and taphonomic effects from sediment reworking due to lake-level fluctuations in step with salinity changes (Fritz 1990), fossil preservation clearly has an important effect on model error. Elsewhere, progressive dissolution has been shown to affect inferences for a pH transfer function unpredictably (Barker 1992), while poor preservation has been implicated as an important source of model error in a salinity transfer function for shallow coastal sites (Ryves et al. 2004). An assessment of preservation can therefore be a useful measure of the confidence that should be placed in any given reconstruction, in addition to other diagnostics (goodness of fit, whole-model and sample-specific errors) that can be generated for transfer functions, as well as providing taphonomic information that may have direct paleoenvironmental and paleolimnological relevance.

References

Albéric, P., E. Viollier, D. Jézéquel, C. Grosbois, and G. Michard. 2000. Interactions between trace elements and dissolved organic matter in the stagnant anoxic deep layer of a meromictic lake. Limnol. Oceanogr. **45:** 1088–1096.

Anderson, N. J., R. Harriman, D. B. Ryves, and S. T. Patrick. 2001. Dominant factors controlling variability in the ionic composition of West Greenland lakes. Arctic, Antarctic and Alpine Res. **33:** 418–425.

———, and M. J. Leng. 2004. Increased aridity during the early Holocene in West Greenland inferred from stable isotopes in laminated-lake sediments. Quaternary Sci. Rev. **23:** 841–849.

———, and B. V. Odgaard. 1994. Recent palaeolimnology of three shallow Danish lakes. Hydrobiologia **256/257:** 411–422.

Bailey-Watts, A. E. 1976. Planktonic diatoms and some diatom–silica relations in a shallow eutrophic loch. Freshw. Biol. **6:** 69–80.

Barker, P. 1992. Differential diatom dissolution in Late Quaternary sediments from Lake Manyara, Tanzania: An experimental approach. J. Paleolimnol. **7:** 235–251.

———, J.-C. Fontes, F. Gasse, and J.-C. Druart. 1994. Experimental dissolution of diatom silica in concentrated salt solutions and implications for paleoenvironmental reconstruction. Limnol. Oceanogr. **39:** 99–110.

Battarbee, R. W. 1986. Diatom analysis, p. 527–570. *In* B. E. Berglund [ed.], Handbook of Holocene palaeoecology and palaeohydrology. Wiley.

———, A. W. Mackay, D. Jewson, D. B. Ryves, and M. Sturm. 2005. Differential dissolution of Lake Baikal diatoms: Correction factors and implications for palaeoclimatic reconstruction. Global Planetary Change **46:** 75–86.

Bidle, K. D., and F. Azam. 1999. Accelerated dissolution of diatom silica by marine bacterial assemblages. Nature **397:** 508–512.

———, M. A. Brzezinski, R. A. Long, J. L. Jones, and F. Azam. 2003. Diminished efficiency in the oceanic silica pump caused by bacteria-mediated silica dissolution. Limnol. Oceanogr. **48:** 1855–1868.

———, M. Manganelli, and F. Azam. 2002. Regulation of oceanic silicon and carbon preservation by temperature control on bacteria. Science **298:** 1980–1984.

Bindler, R., I. Renberg, P. G. Appleby, N. J. Anderson, and N. L. Rose. 2001. Mercury accumulation rates and spatial patterns in lake sediments from west Greenland: A coast to ice margin transect. Environ. Sci. Technol. **35:** 1736–1741.

Bootsma, H. A., R. E. Hecky, T. C. Johnson, H. J. Kling, and J. Mwita. 2003. Inputs, outputs, and internal cycling of silica in a large, tropical lake. J. Great Lakes Res. **29:** 121–138.

Buck, K. R., and J. Newton. 1995. Fecal pellet flux in Dabob Bay during a diatom bloom: Contribution of microzooplankton. Limnol. Oceanogr. **40:** 306–315.

Conley, D. J., and C. L. Schelske. 1989. Processes controlling the benthic regeneration and sedimentary accumulation of biogenic silica in Lake Michigan. Arch. Hydrobiol. **116:** 23–43.

———, ———, and E. F. Stoermer. 1993. Modification of silica biogeochemistry with eutrophication in aquatic systems. Mar. Ecol. Prog. Ser. **101:** 179–192.

Covich, A. P., M. A. Palmer, and T. A. Crowl. 1999. The role of benthic invertebrate species in freshwater ecosystems: Zoobenthic species influence energy flows and nutrient cycling. Bioscience **49:** 119–127.

Dixit, S., P. Van Cappellen, and A. J. van Bennekom. 2001. Processes controlling solubility of biogenic silica and pore water build-up of silicic acid in marine sediments. Mar. Chem. **73:** 333–352.

Egli, K., M. Wiggli, M. Fritz, J. Klug, J. Gerss, and R. Bachofen. 2004. Spatial and temporal dynamics of a plume of phototrophic microorganisms in a meromictic alpine lake using turbidity as a measure of cell density. Aquatic Microbial Ecol. **35:** 105–113.

Eugster, H. P., and B. F. Jones. 1979. Behavior of major solutes during closed-basin brine evolution. Am. J. Sci. **279:** 609–631.

Flower, R. J. 1993. Diatom preservation: Experiments and observations on dissolution and breakage in modern and fossil material. Hydrobiologia **269/270:** 473–484.

———, and A. J. Nicholson. 1987. Relationships between bathymetry, water quality and diatoms in some Hebridean lochs. Freshw. Biol. **18:** 71–85.

Fritz, S. C. 1990. Twentieth-century salinity and water-level fluctuations in Devil's Lake, North Dakota: Test of a diatom-based transfer function. Limnol. Oceanogr. **35:** 1771–1781.

———. 2003. Lacustrine perspectives on Holocene climate, p. 227–241. *In* R. W. Battarbee, A. W. Mackay, H. J. B. Birks and F. Oldfield [eds.], Global change in the Holocene: Approaches to reconstructing fine-resolution climate change. Edward Arnold.

———, S. Juggins, and R. W. Battarbee. 1993. Diatom assemblages and ionic characterization of lakes of the northern Great Plains, North America: A tool for reconstructing past salinity and climate fluctuations. Can. J. Fisheries Aquat. Sci. **50:** 1844–1856.

Garrels, R. M., and C. L. Christ. 1965. Solutions, minerals and equilibria. Freeman.

Gasse, F., P. Barker, P. A. Gell, S. C. Fritz, and F. Chalié. 1997. Diatom inferred salinity in palaeolakes: An indirect tracer of climate change. Quat. Sci. Rev. **16:** 547–563.

———, ———, and T. C. Johnson. 2002. A 24,000 yr diatom record from the northern basin of Lake Malawi, p. 393–414. *In* E. O. Odada and D. O. Olago [eds.], The East African Great Lakes: Limnology, palaeolimnology and biodiversity. Advances in Global Change Research. Kluwer.

———, S. Juggins, and L. B. Khelifa. 1995. Diatom-based transfer functions for inferring past hydrochemical characteristics of African lakes. Palaeogeogr. Palaeoclim. Palaeoecol. **117:** 31–54.

Gibson, C. E., G. Wang, and R. H. Foy. 2000. Silica and diatom growth in Lough Neagh: The importance of internal cycling. Freshw. Biol. **45:** 285–293.

Haberyan, K. A. 1985. The role of copepod fecal pellets in the deposition of diatoms in Lake Tanganyika. Limnol. Oceanogr. **30:** 1010–1023.

———. 1990. The misrepresentation of the planktonic diatom assemblage in traps and sediments: Southern Lake Malawi, Africa. J. Paleolimnol. **3:** 35–44.

———, and R. E. Hecky. 1987. The late Pleistocene and Holocene stratigraphy and paleolimnology of Lakes Kivu and Tanganyika. Palaeogeogr. Palaeoclim. Palaeoecol. **61:** 169–197.

Hecky, R. E., and P. Kilham. 1973. Diatoms in alkaline, saline lakes: Ecology and geochemical implications. Limnol. Oceanogr. **18:** 53–71.

———, H. J. Kling, and G. J. Brunskill. 1986. Seasonality of phytoplankton in relation to silicon cycling and interstitial water circulation in large, shallow lakes of central Canada. Hydrobiologia **138:** 117–126.

Hofmann, A., D. Roussy, and M. Filella. 2002. Dissolved silica budget in the north basin of Lake Lugano. Chem. Geol. **182:** 35–55.

Humayoun, S. B., N. Bano, and J. T. Hollibaugh. 2003. Depth distribution of microbial diversity in Mono Lake, a meromictic soda lake in California. Appl. Environ, Microbiol, **69:** 1030–1042.

Jolliffe, I. T. 1986. Principal component analysis. Springer-Verlag.

Krauskopf, K. 1982. Introduction to Geochemistry, 2nd ed. McGraw-Hill.

Laird, K. R., B. F. Cumming, S. Wunsam, J. A. Rusak, R. J. Oglesby, S. C. Fritz, and P. R. Leavitt. 2003. Lake sediments record large-scale shifts in moisture regimes across the northern prairies of North America during the past two millennia. PNAS **100:** 2483–2488.

Lent, R. M., and W. B. Lyons. 2001. Biogeochemistry of silica in Devils Lake: Implications for diatom preservation. J. Paleolimnol. **26:** 53–66.

Lewin, J. C. 1961. The dissolution of silica from diatom walls. Geochim. Cosmochim. Acta **21:** 182–198.

Lund, J. W. G. 1950. Studies on *Asterionella formosa* Hass. II. Nutrient depletion and the spring maximum. J. Ecol. **38:** 1–35.

Mackay, A. W., and others. 1998. Diatom succession and pollution trends in recent sediments from Lake Baikal and their relation to atmospheric pollution and to climate change. Phil. Trans. R. Soc. Lond. B **353:** 1011–1055.

Marshall, W. L. 1980. Amorphous silica solubilities—III. Activity coefficient relations and predictions of solubility behavior in salt solutions, 0–350°C. Geochim. Acta **44:** 925–931.

———, and J. M. Warakomski. 1980. Amorphous silica solubilities—II. Effect of aqueous salt solutions at 25°C. Geochim. Cosmochim. Acta **44:** 915–924.

McGowan, S., D. B. Ryves, and N. J. Anderson. 2003. Holocene records of effective precipitation in West Greenland. The Holocene **13:** 239–249.

McMinn, A. 1995. Comparison of diatom preservation between oxic and anoxic basins in Ellis Fjord, Antarctica. Diat. Res. **10:** 145–151.

Meriläinen, J. 1971. The recent sedimentation of diatom frustules in four meromictic lakes. Ann. Bot. Fennici **8:** 160–176.

———. 1973. The dissolution of diatom frustules and its palaeoecological interpretation. Univ. of Lund.

Mittlböck, M., and M. Schemper. 1996. Explained variance for logistic regression. Stat. Med. **15:** 1987–1997.

Newberry, T. L., and C. L. Schelske. 1986. Biogenic silica record in the sediments of Little Round Lake, Ontario. Hydrobiologia **143:** 293–300.

R Development Core Team. 2004. R: A language and environment for statistical computing. R Foundation for Statistical Computing.

Reed, J. M. 1998. Diatom preservation in the recent sediment record of Spanish saline lakes: Implications for palaeoclimate study. J. Paleolimnol. **19:** 129–137.

Reynolds, C. S. 1986. Diatoms and the geochemical cycling of silica, p. 269–289. *In* B. S. C. Leadbeater and R. S. Ridings [eds.], Biomineralization in the lower plants and animals. Oxford Univ. Press.

Rippey, B., and D. H. Jewson. 1982. The rates of sediment–water exchange of oxygen and sediment bioturbation in Lough Neagh, Northern-Ireland. Hydrobiologia **91–2:** 377–382.

Round, F. E. 1964. The diatom sequence in lake deposits, some problems of interpretation. Verhandlungen Internationale Vereinigung für Theoretische und angewandte Limnologie **15:** 1012–1020.

Ryves, D. B. 1994. Diatom dissolution in saline lake sediments: an experimental study in the Great Plains of North America. Ph.D. dissertation, Univ. College London.

———, A. L. Clarke, P. G. Appleby, S. L. Amsinck, E. Jeppesen, F. Landkildehus, and N. J. Anderson. 2004. Reconstructing the salinity and environment of the Limfjord and Vejlerne Nature Reserve, Denmark, using a diatom model for brackish lakes and fjords. Can. J. Fish. Aquat. Sci. **61:** 1988–2006.

———, D. H. Jewson, M. Sturm, R. W. Battarbee, R. J. Flower, A. W. Mackay, and N. Granin. 2003. Quantitative and qualitative relationships between planktonic diatom communities and diatom assemblages in sedimenting material and surface sediments in Lake Baikal, Siberia. Limnol. Oceanogr. **48:** 1643–1661.

———, S. Juggins, S. C. Fritz, and R. W. Battarbee. 2001. Experimental diatom dissolution and the quantification of microfossil preservation in sediments. Palaeogeogr. Palaeoclim. Palaeoecol. **172:** 99–113.

———, S. McGowan, and N. J. Anderson. 2002. Development and evaluation of a diatom-conductivity model from lakes in West Greenland. Freshw. Biol. **47:** 995–1014.

Schelske, C. L. 1985. Biogeochemical silica mass balances in Lake Michigan and Lake Superior. Biogeochemistry **1:** 197–218.

———, B. J. Eadie, and G. L. Krausse. 1984. Measured and predicted fluxes of biogenic silica in Lake Michigan. Limnol. Oceanogr. **29:** 99–110.

Schwalb, A., and W. E. Dean. 2002. Reconstruction of hydrological changes and response to effective moisture variations from North-Central USA lake sediments. Quat. Sci. Rev. **21:** 1541–1554.

Smol, J. P. 2002. Pollution of lakes and rivers. Arnold.

———, and M. M. Boucherle. 1985. Postglacial changes in algal and cladocerans assemblages in Little Round Lake, Ontario. Hydrobiologia **103:** 25–49.

Stoermer, E. F., G. Emmert, and C. L. Schelske. 1989. Morphological variation of *Stephanodiscus niagarae* Ehrenb. (Bacillariophyta) in a Lake Ontario sediment core. J. Paleolimnol. **2:** 227–236.

———, J. A. Wolin, C. L. Schelske, and D. J. Conley. 1985. Variations in *Melosira islandica* valve morphology in Lake Ontario sediments related to eutrophication and silica depletion. Limnol. Oceanogr. **30:** 414–418.

ter Braak, C. J. F., and P. Šmilauer. 1998. Canoco for Windows. Centre for Biometry.

Tréguer, P., D. M. Nelson, A. J. Van Bennekom, D. J. DeMaster, A. Leynaert, and B. Quéguiner. 1995. The silica balance in the world ocean: A reestimate. Science **268:** 375–379.

Turner, J. T. 2002. Zooplankton fecal pellets, marine snow and sinking phytoplankton blooms. Aquat. Microbial Ecol. **27:** 57–102.

Verleyen, E., D. A. Hodgson, P. R. Leavitt, K. Sabbe, and W. Vyverman. 2004. Quantifying habitat-specific diatom production: A critical assessment using morphological and biogeochemical markers in Antarctic marine and lake sediments. Limnol. Oceanogr. **49:** 1528–1539.

Verschuren, D., and others. 2002. History and timing of human impact on Lake Victoria, East Africa. Proc. Royal Soc. Lond. B **269:** 289–294.

———, K. R. Laird, and B. F. Cumming. 2000. Rainfall and drought in equatorial east Africa during the past 1,100 years. Nature **403:** 410–41.

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