Diatom preservation: experiments and observations on dissolution and breakage in modern and fossil material

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Abstract

Selected aspects of diatom preservation in both laboratory and field environments are examined with a view to improving techniques and to help understand why only some lake sediments have good diatom preservation.

Laboratory measurements of biogenic silica following diatom dissolution by alkali digestion are questioned because results are shown to be dependant on initial sample size . Diatom breakage experiments identified drying carbonate rich sediment as a major cause of fragmentation of the large robust diatom Campylodiscus clypeus Ehrenb. Diatom dissolution experiments in carbonate media indicated that carbonate rich lakes should preserve diatoms better in order of the particular alkali metal type $(Ca > Mg > Na)$. A preliminary assessment of the role of depth in diatom preservation is made for Lake Baikal where partly dissolved Cyclotella are more common in deep water surface sediments . The effect of time on diatom dissolution is examined in a saline lake sediment core and by comparing dissolution rates of recent and geologically old diatom samples in the laboratory . A simple link between diatom dissolution and sample age was not established . Factors thought to be important in controlling diatom preservation in lake sediments are discussed .

Introduction

Diatom analysis of sediments is a major palaeoecological technique for reconstructing past environmental changes. Pre-requisites are that changes in the composition and abundance of living diatom communities are faithfully recorded in sediments and that these changes can be accurately revealed by subsequent analysis. Transformation of modern diatom communities into the fossil record is controlled by a complex array of often site specific taphonomic processes that operate both in the water column and in sediments, promoting mixing, dissolution and breakage. Laboratory studies have shown that diatom dissolution is largely pH, temperature and time dependant (e.g. Jørgensen, 1955; Krauskopf, 1959). Precise dissolutions rates are, however, affected by a wide range of external and internal factors (Lewin, 1961; Hurd & Birdwhistell, 1983). Cell breakage can result from a variety of natural processes such as invertebrate grazing (Turner, 1991) but partial dissolution makes cells more prone to fracturing (Mikkelsen, 1980). Despite the amount of information available from laboratory studies of diatom preservation, predicting lakes with good sedimentary diatom preservation remains difficult.

Although natural processes can profoundly affect the quality of sedimentary diatom records, taphonomic considerations also extend to the effects of laboratory procedures on diatom preservation (Behrensmeyer & Kidwell, 1985). In this paper, simple experiments and observations were made on diatom material from different environments to examine some of the important factors thought to influence diatom preservation in laboratory and field environments . Six specific experiments were conducted on a variety of diatom samples in order to address the following questions: Is measurement of diatom biogenic silica in sediments by alkali-digestion methods reliable? $(Experiment 1)$. Can routine sample preparation techniques damage robust diatoms? (Experiment 2). Can diatom dissolution be related to water depth? (*Experiment 3*). Does the nature of sedimentary carbonates affect diatom preservation? (*Experiment 4*). Is diatom resistance to dissolution related to sample age? (*Experiment 5*). How quickly can diatoms dissolve in a particular lake sediment? (Experiment 6).

Experiments and methods

Unless otherwise stated all diatom samples were prepared in H_2O_2 and dispersed in distilled water (Battarbee, 1986; Flower, 1980). All dissolution experiments were carried out at between ambient temperature (overnight) and 50° C, with occasional stirring. Cell/valve numbers were counted directly in aqueous samples. Relative diatom concentrations were monitored during dissolution experiments by counting coverslip transects of three replicate 30 μ l subsamples of suspension at \times 400 magnification.

Experiment 1. Measuring increases in dissolved silica, typically following alkali digestion (Krause et al., 1983), is intuitively an attractive method because it is sensitive and quick and the contribution of small fragments is measured. The method assumes that the digestion removes biogenic silica quantitatively from sediment samples .

Portions (2 to 100 mg) of previously dried dia-

tom rich lake sediment were digested in 250m1 polypropylene flasks containing an excess of 5% $Na₂CO₃$ solution with shaking for 2 hours at 85 'C. After cooling, samples were neutralized with HCl and 1 ml subsamples were diluted (\times 20) before Si concentration was measured colorimetrically (Krause et al., 1983).

Experiment 2. Campylodiscus clypeus Ehr. is a large robust diatom common in shallow saline lakes such as Sidi bou Rhaba (Morocco). Routinely prepared sediment samples for diatom analysis from this lake revealed excessive valve breakage. This must have occurred during slide preparation or by natural processes in the lake.

The effect of two different sediment cleaning methods was checked, one following Battarbee (1986) involving quick $(< 2 h)$, vigorous peroxide and strong acid cleaning at 90° C; the other (Renberg, 1990) involving slow (8 days) cold peroxide cleaning with dilute acid treatment. The methods were applied to fresh wet sediment and to sediment dried overnight at 50 \degree C, and with and without sample centrifuging. Some effects of sample treatments were examined in SEM and diatom breakage was assessed by counting whole valves (100) and large fragments (25% of valve area) of C. clypeus under LM.

Experiment 3. In Lake Baikal diatoms such as Cyclotella and Aulacoseira taxa are frequently poorly preserved in deep water sediment (R. Flower unpubl.). If water depth is a factor then diatom preservation should be better in shallow rather than indeep water sediment.

Counts of whole, partly dissolved, and broken Cyclotella valves were made on surface sediment (0-Imm depth) samples from two depths, 1320 m and 130 m in southern Lake Baikal (see Flower, 1993).

Experiment 4. Some carbonate rich lakes contain good diatom records while others do not. Alkali and alkali earth metal carbonates commonly present in hard-water lake sediments are those of calcium and magnesium; sodium carbonate often predominates in some saline lakes .

Diatom-rich sediment samples (200 mg) from Sidi bou Rhaba were treated with sodium, magnesium and calcium carbonates. 10g of each salt

were added to 100 ml of distilled water. Of these, only sodium carbonate dissolves easily and the other two salts were present as white suspensions. The pH of each sample was measured. All samples were kept at 40 °C and at constant volume and occasionally stirred with a magnetic stirrer. At appropriate intervals, valves were counted. Supernatants were changed daily.

Experiment 5. Geologically old diatomites are more resistant to dissolution than fresh diatom samples (Lewin, 1961). If dissolution is related to the degree of silica crystallization then resistance to dissolution could be directly related to sample age. To test this, dissolution rates of diatom samples representing a range of different ages was measured. Surface sediment (0-5 yr old) (from an acid lake, Corrie an Lochan) was compared with 90 yr old sediment (dates from $210Pb$ analysis). From eutrophic Lough Neagh, sediment trap material $(< 1$ yr old) was compared with samples from 7000 yr BP (Flower, 1980; Smith, 1984, respectively). Two diatomites of differing geological age, from Lomo Camastra, Costa Rica (2.5) Myr BP, Mathers et al., 1991) and from Toro Road, California (6-8 Myr BP, Barron, 1976) were compared.

Sample weights were adjusted to give counts of around 100-200 diatoms per coverslip transect, typically 0.1 g sediment was made up in 50 ml 10% sodium carbonate. One sample (Corrie an Lochan) was used as a control, distilled water replacing the carbonate solution . All samples were cleaned to assist sample dispersion .

Experiment 6. One aspect of the seemingly intractable question of diatom dissolution rates in natural sediment can be tackled by using sediment dating methods. Natural dissolution rates are relatively slow but can be determined over a period of decades by $2^{10}Pb$ dating of sediment cores (Parker & Edgington, 1976).

Diatoms are sometimes poorly preserved in saline lakes, one such site is Lac Ichkeul, a shallow Tunisian lake. In situ diatom dissolution is this lake was examined by subsampling a short core and analyzing for diatoms over a $2^{10}Pb$ time scale established using the CRS model (Appleby & Oldfield, 1978; Appleby et al., 1986).

Results

Experiment 1. The amount of dissolved silica in solution after the experiment was dependent on the initial sample size (Fig. 1). There was a difference of 60% between the amount of $SiO₂$ dissolved from the smallest and largest samples, the latter producing relatively less $SiO₂$ per mg of lake sediment. This is probably because dissolved silica is partially reabsorbed by undissolved sediment (B. Rippey, pers. comm.).

Experiment 2. Irrespective of the cleaning method used, all the pre-dried samples between 99 and 100% of all valves were broken. In all preparations of fresh wet sediment about 50% of the valves remained unbroken. Neither vigorous cleaning nor centrifuging had any appreciable effect on the proportion of broken valves of C . clypeus.

SEM examination of a wet sediment (20 cm core depth), following cleaning in dilute acid and distilled water before drying, demonstrates the abundance of intact cells and valves (Fig. 2) and the excellent state of preservation (Fig. 4), with girdle bands and epiphytic Achnanthes marina Hustedt still in situ. Fragmentation in a pre-dried but otherwise similarly treated sediment sample is shown in Fig. 3. Partial dissolution in alkaline solution shows that valves remain largely intact

Fig. 1. Variation of dissolved silica concentration with sediment sample weight (Data from B. Rippey & H. McGrogan).

Figs 2-5. Campylodiscus clypeus in sediment (20 cm depth, age ca 10 yr.) from Sidi bou Rhaba, a saline lake in Morocco. Fig. 2. Predominantly intact valves and cells obtained from undried sediment. Fig. 3. Highly fragmented valves in pre-dried sediment. Fig . 4 . Diatom preservation is generally excellent in the wet sediment as indicated by the persistence of delicate girdle bands and epiphytic diatoms . Fig. 5 . A partly dissolved valve showing loss of central area and inter costae (see text) .

species of *Cyclotella* (Table 1) clearly show that at the deep-water site there were relatively fewer in-

despite loss of the central area and inter-costae tact valves and partial dissolution was frequent. (Fig. 5).

Experiment 3. Percentage abundances of two

Flower was also more frequent at this site. Al-*Experiment 3*. Percentage abundances of two Flower was also more frequent at this site. Al-
ecies of *Cyclotella* (Table 1) clearly show that at though broken *C. minuta* (Skvortzov) Antipova were very infrequent, intact valves without signs

Figs 6-11. Stages of sequential dissolution of Cyclotella minuta in deep water (1320 m) surface sediment from Lake Baikal. Fig. 6. Stage 1, the morphology not significantly altered by dissolution. Fig. 7. Stage 2, corrosion of radiate striae clearly visible. Fig. 8. Stage 3, the mantle has become detached from the valve face and corrosion of the striated zone is progressing. Fig. 9. Stage 4, inter striae costae become shorter and striae lost . Fig. 10 . Stage 5, inter striae costae almost lost and central area processes have fallen away leaving holes (arrowed). Fig. 11. Stage 6, the valve is reduced to a deeply corroded central disc of silica.

Table 1. Percentage abundances of whole, partly dissolved and broken valves of Cyclotella taxa in surface sediment (0- 1 mm depth) from shallow water (130 m) and deep water locations (1320 m) in Lake Baikal. Percentages were calculated from counts of 150 valves.

Taxon and valve condition	Sample depth (m)	
	134	1320
Cyclotella minuta:		
whole	69	36
partly dissolved	34	64
broken	0	0
Cyclotella ornata:		
whole	50	25
partly dissolved	42	50
broken	8	25

of dissolution were almost 50% less frequent in the deep-water sample.

Dissolution effects on valve structure of C. minuta in the deep-water sample were examined in SEM and six preservation stages of C . minuta were identified (Figs 6-11) . Dissolution preceded progressively and centripetally and by the final stage only the corroded silica matrix of the central area remained. This preliminary assessment of diatom preservation from two locations in Lake Baikal indicates that valve dissolution is more frequent in deep water than shallow water surface sediment.

Experiment 4. Diatoms in $Na₂CO₃$ were quickly dissolved, with over 90% of valves in all samples disappearing within three days (Fig. 12). With $MgCO₃$, 90% of valves disappeared within 7 days and with $CaCO₃$, valves disappeared irregularly with 90% loss after 13 days. These results initially support the hypothesis that metal carbonate type does control diatom dissolution rate. However, this may be an indirect consequence of solution pH rather than of the particular cations present. In water, these alkali metal carbonates undergo hydrolysis, producing different strength alkaline solutions; the initial pH values of the solutions were 11.3, 10.0 and 9.9, respectively. The order of increasing alkali metal activities $(Na > Mg > Ca)$ corresponds with the observed dissolution sequence.

Fig. 12. Effects of different alkali and alkali earth metal carbonates on dissolution of sedimentary diatoms. Error was indicate count standard deviations, where $n = 3$.

Experiment 5. All the diatoms in the fresh recent samples dissolved within four hours, with those from Lough Neagh dissolving most rapidly (Fig. 13). Diatoms in the older samples from this site and from Corrie an Lochan dissolved more slowly and after two days less than 20% remained. In the ca 90 yr old Corrie an Lochan sample all the diatoms were dissolved after 4 days. Counting of the Lough Neagh diatomite sample was stopped after two days (the fragmented material was difficult to count). Diatom dissolution was undetected in the control sample.

Of the two geologically old diatomite samples, both initially dissolved quickly but Toro Road was rather slower than the Lomo Camastra diatomite. All diatoms in the latter material dissolved within 7 days but a few diatoms in the Toro Road material remained after 11 days .

The diatom species were similar in the different aged samples from Lough Neagh and Corrie an Lochan and so the results offer direct evidence of a time-related increasing valve resistance to dissolution. Diatom concentrations apparently increased in the control sample as dispersion and valve separation increased (SEM checks showed no signs of increasing valve ultra-structure dissolution after 3 weeks).

Species differences make comparisons between the dissolution behaviour of the two geologically old diatomites difficult. However, both samples dissolved relatively rapidly, 90% of valves dis-

Fig. 13. Effects of diatom sample age on dissolution rates of different sedimentary diatoms and diatomites. All experiments were carried out using 10% sodium carbonate solution. Error was as for Fig. 12.

solving within 2 days although a few valves re-
mained in the Toro Road material. These obser-
(ca 1980) was dominated by Cyclotella cf. atomus vations suggest that there is no simple relationship between diatom dissolution rate and sample age.

(ca 1980) was dominated by Cyclotella cf. atomus
and Cocconeis placentula Ehrenb. (Fig. 14). Below this level the percentage frequencies of large

Fig. 14. Percentage abundances of dominant diatoms in a core from Lac Ichkeul (1982), a saline lake in Tunisia. + present

strongly silicified diatoms, Diploneis gruendleri (A. Smidt) Cleve and Nitzschia punctata (W. Smith) Grun., increased as relative diatom concentration declined. The $15-16$ cm level (ca 1930) was an exception as frequencies of C. placentula and C. cf. atomus increased. At 20-21 cm depth (ca 1892) all diatoms were very scarce, only a few very poorly preserved valves of D. gruendleri and N. punctata remained; no diatoms occurred below this depth.

The sediment accumulation rate in this core declined with depth and concentrations of nondiatom microfossils remained essentially unchanged between 10-23 cm depth (Stevenson & Battarbee, 1991). These observations indicate that past changes in sediment sources or water quality cannot wholly account for the down-core decline in diatom abundance nor for their absence below 20 cm sediment depth. Differential diatom dissolution seems the most likely explanation for at least some of the species abundances changes recorded in the core .

Discussion

Unfavourable preservational conditions in either the laboratory or field environments will destroy or diminish the palaeoecological value of sedimentary diatom records. Of these, unreliable laboratory techniques for measuring diatom silica and for preparing diatoms can be the most misleading.

Laboratory errors

Results presented here indicate that sedimentary diatom biogenic silica determinations by alkali digestion can be unreliable due to silica reabsorption on undissolved sediment. Although method error can be reduced by rigorous standardization of analysis (Mortlock & Froelich, 1989; D. J. Conley, pers . comm.) it is unlikely that the method will give consistent results for multi-component sediment samples of variable composition and mass. Where such measurements are used to estimate silica fluxes (e.g. Parker $et al., 1977;$ Flower, 1980; Schelske et al., 1984) results will probably underestimate true values . Additionally, method error will be further exaggerated by natural dissolution processes . These can deplete biogenic silica in even apparently well preserved sedimentary diatom assemblages by over 30% (Flower, 1980) . Accurate measurements of sedimentary biogenic silica concentrations are nevertheless important and other methods of determination such as alkali fusion (Barker, 1992) or X-ray diffraction (Goldberg, 1958) should be evaluated in inter-calibration studies .

Inappropriate preparatory techniques, such as vigorous acid oxidation of samples, are well known not only to destroy delicate diatom valves (Round, 1964; Hürlimann, 1992) but also to make valves more prone to dissolution (Barker, 1992). Likewise, rapid centrifuging and drying of samples during cleaning will break long delicate diatoms, such as Synedra and Asterionella taxa. Robust diatoms are normally considered resistant to sediment drying and most cleaning processes . This study has shown, however, that sediment pre-drying alone is sufficient to cause excessive breakage of Campylodiscus clypeus. The sediment tested was high in authigenic carbonates (60–70% dry weight, Flower & Appleby, 1992) and sediment shrinkage was the likely cause of cell breakage . Excessive breakage of Fragilaria crotonensis on drying of marl lake sediments has been noted elsewhere (R. W. Battarbee, pers. comm.) and implies that carbonates, as well as organic matter, can cause sediment shrinkage and diatom preservation problems.

Sediment dynamics and morphometric **Characteristics**

In the field, diatom breakage without extensive dissolution is generally associated with high energy environments (Round, 1964; Flower, 1990). Diatoms in shallow costal environments are often highly fragmented (Beyens & Denys, 1982). In shallow exposed lakes in NW Scotland (Flower & Nicholson, 1986) surface sediment abundances of intact Cocconeis placentula valves were threefold greater in those sites which contained Potomogeton stands (R. Flower, unpubl.). As well as enhancing diatom accumulation rate, the macrophyte stands probably reduced wind-induced water turbulence and so minimized physical breakage of cells. Grazing and bioturbation can also affect preservation of diatoms but these processes are considered elsewhere (e.g. Rippey, 1983; Jewson et al., 1981; Turner, 1991).

In deep alkaline lakes, such as Lake Michigan, diatom breakage increases with depth (Glover, 1982) and pelletization is largely responsible for delivering diatoms to the sediment (Ferrante & Parker, 1977). In the deeper and less alkaline Lake Baikal, preliminary results indicate that cell dissolution is more important than breakage and that dissolution effects are greater in deep than in shallow water surface sediment. Cell size seems important too, of the two Cyclotella taxa examined, the smaller C. minuta was always the better preserved. Dissolution of finely silicified diatoms occurs in the Lake Baikal water column (Jouse, 1966) and this process is known in other lakes (Round, 1964; Haberyan, 1990). Poor preservation of more robust diatoms in Lake Baikal deepwater surface sediment could be linked both with the low sediment accumulation rate (Edgington et al., 1991), bioturbation, and with the lake's great depth. Diatom preservation does not, however, appear to deteriorate markedly with depth in surficial sediment in this lake (R. Flower, unpubl.).

Dissolution in carbonate rich systems

Irrespective of lake depth, it is broadly true that diatom preservation is better in acid than in alkaline lakes. However, high pH sites can contain good diatom records (e.g . Hecky & Kilham, 1973) and this is particularly true for some carbonate precipitating lakes (Moss, 1979; Lotter, 1988). Experimental results presented here indicate that the form of carbonate present is an important factor in diatom dissolution. They suggest that, other conditions being constant, preservation in carbonate sediments should decline as activity of the metal species increases . Dissolution is caused

by hydrolysis of the metal carbonates which produces hydroxyl ions and, in turn, these attack Si-O bonds (Stumm & Morgan, 1970) in the diatom cell wall. Hence, as proportions of metals with higher dissociation constants increase, preservation should become progressively poorer. Preservation should, therefore, deteriorate from calcium, through magnesium to sodium carbonate dominated systems. This hypothesis requires field testing but it is partially supported by observations in several African lakes where sodium carbonate rich waters transform diatom assemblages into minerals such as magadiite and zeolites (Barker et al., 1990).

Time and resistance to dissolution

Whilst not changing the morphology of sedimentary diatoms, some diagenetic changes must affect the diatom silica wall making it more resistant (Lewin, 1961) . Sediments tested here indicate that is no simple link between resistance to dissolution and sample age. The older sedimentary diatom samples from Corrie an Lochan and Lough Neagh, dominated respectively by Achnanthes taxa and Aulacoseira subarctica (Müller) Haworth, showed a greater resistance to dissolution. However, despite species differences and a time difference of ca 7000 yr, dissolution rates of material from these two sites were essentially the same. Similarly, dissolution of Lomo Camastra diatomite was not markedly different from that of much older Toro Road material nor from the 90 and 7000 yr old material from Corrie an Lochan and Lough Neagh . In addition to species differences between the diatomite samples, the oldest material (Toro Road) was also different because a few valves persisted throughout the dissolution experiment. This could indicate increased resistance caused by partial crystallization of the silica in this material.

Overall, these observations on dissolution rates indicate that the first few decades following deposition are the most important in conferring diatom resistance to dissolution and that there are no marked dissolution differences in samples between ca. 90 and 7.5 Myr old. However, an age482

resistance relationship cannot be ruled out unless more diatom samples of different ages are tested in less aggressive dissolving media.

Some general considerations concerning diatom preservation

Despite many studies on diatom preservation, it is not possible to predict confidently recent lake sediments which have poor diatom preservation. Moreover, partial dissolution of sedimentary assemblages produces differential preservation of taxa, so making interpretation of fossil assemblages more difficult (Shemesh et al., 1989). Poor preservation occurs in lakes as strikingly different as Lac Ichkeul and Lake Michigan (Parker & Edgington, 1976) where the diatom records are entirely lost by dissolution within 100 yr . In other lake sediments the diatom record is frequently interrupted by periods of excessive dissolution (Meriläinen, 1973; Fritz, 1989). External factors known to affect dissolution include ionic concentration (Marshall & Warakomski, 1980) and composition (Kamatani, 1971) of dissolving media as well as pH, temperature, dissolved silica diffusion rates (Rippey, 1983) and diagenesis (Berner, 1980) . Meromictic lakes are special cases where preservation is often poor (Merilainen, 1971) and past variations in lake water circulation could be linked with down-core diatom dissolution phases (Meriläinen, 1973). Internal factors affecting the diatom cell wall include organic layers (Hecky & Kilham, 1973), inorganic ions (Lewin, 1961) and the nature of the silica frustule (Hurd & Birdwhistell, 1983) . However, over time periods pertinent to the sedimentary record, field observations indicate that the major considerations are water quality and the nature of the sedimentary environment. Consequently, any process which speeds up removal of diatoms from dissolving or high energy environments will promote preservation but diatoms will continue to dissolve in any lake sediment, if pore waters remain undersaturated with regard to silica.

Based on a consideration of a variety of lakes, it is clear that diatom preservation declines with increasing pH, temperature, coarseness of sediment, grazing and bioturbation, water depth and exposure. Preservation generally increases with diatom robustness, diatom and sediment accumulation rate and diatom concentration . Relationships between these variables are complex and some can mitigate the effects of others. For example, comparing two high pH saline lakes, Sidi bou Rhaba and Lac Ichkeul, preservation is good only in the former because the high dissolution potential of the lake water is minimized. This lake is shallow and sheltered and the sediment accumulation rate is high (ca 2 cm yr, Flower & Appleby, 1992) and benthic invertebrates are few. These conditions result in rapid burial so that deposited diatoms are quickly removed from the lake water environment. Furthermore, most of the diatoms are robust and abundant so that sediment pore waters probably become saturated with regard to silica without extensive diatom dissolution of values. Conversely, deep fresh water lakes with low sediment accumulation and high pH will promote dissolution and breakage in both the water column and sediment (Parker & Edgington, 1976). In Lake Baikal, a deep water column and a low sediment accumulation rate mean that diatoms spend a long period exposed to lake water undersaturated in dissolved silica. Invertebrate grazing and bioturbation at the sediment surface must exacerbate dissolution by promoting breakage and diffusion of dissolved silica (Rippey, 1983) but breakage without significant dissolution can be expected in shallow exposed lakes irrespective of pH. Low pH does not necessarily indicate good preservation and where suspected ground water movements occur, diatom dissolution is extensive (Flower et al., 1988). The preservational role of sediment organic matter is less clear but any anaerobic decomposition must generate acidity which should reduce the dissolved silica saturation concentration in pore water.

In conclusion, it is clear that understanding and predicting diatom preservation in lake sediment is a complex multivariate problem of profound importance to palaeoecology. With present knowledge it is only possible to produce a very incomplete account of diatom preservation and more systematic study of the subject is required .

Taphonomic changes affect every stage of diatom preservation and include the effects of laboratory and sampling techiques. The latter can be major sources of error that not only devalue modern diatom calibrational data sets but also make diatom influx estimates and diatom based lake water quality reconstructions unsound.

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