A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction

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Abstract

Diatom silica (frustules) are a form of biogenic opal and contain oxygen isotopes that are being increasingly used in palaeoclimate studies. Frustules are comprised of an inner tetrahedrally bonded silica skeleton (Si–O–Si) with an outer, hydrous layer. The hydrous layer is freely exchangeable and must be removed prior to oxygen isotope measurement using oxidising reagents and/or high temperatures. Analysis of the oxygen isotope composition of diatom silica requires samples that are almost pure diatomite since extraction techniques will liberate oxygen from all the components in the sediment. There is a generally acceptable protocol involving chemistry, sieving and settling techniques and more recently laminar flow separation. Recent studies of lacustrine diatoms have shown that even a small proportion of contaminant can have a significant influence on the oxygen isotope value. All lake sediments require their own specific procedure and every sample must be scrutinised by microscopy to check for the level of contamination prior to analysis. Where sediment cannot be purified sufficiently, a semi-quantitative assessment of the diatom content can facilitate mass balance techniques. When robust preparation methods are used, diatom silica offers an important palaeoclimate proxy, providing an additional complementary, rather than an alternative, host of oxygen isotopes in carbonates.

In lacustrine isotope studies it is often assumed, but rarely proven, that diatom silica form in isotope equilibrium and hence empirically derived palaeotemperature equations, usually made in vitro, can be used. Most studies lack the detailed investigation of contemporaneous materials from natural waters of the region under study to test these equations. Further investigations need to be conducted in order to understand the systematic relationship between temperature, water isotope composition and diatom isotope composition to enable quantitative interpretation of the sediment record. Experiments to test for vital effects and inter-specific differences have so far revealed little variation. It is useful to know when and where the diatom silica is formed in the modern environment, so details of diatom ecology are important in the interpretation of isotope data.

Here we show that valuable palaeoclimate data can be gained from the oxygen isotope composition of diatom silica ($\delta^{18}O_{diatom}$), especially since diatoms are abundant in many lakes sensitive to climate variation where other hosts (e.g., carbonates) are absent. To date the most successful studies have been conducted in areas where the $\delta^{18}O_{diatom}$ registers changes in the oxygen isotope composition of the lake water (rather than temperature) which is then related to other aspects of climate. In these studies, the range of values obtained is often greater than the error introduced by contaminating materials.

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1. Introduction

Stratigraphic changes in the oxygen isotope composition of authigenic minerals in lakes are routinely used to reconstruct palaeoclimate (see reviews in Buchardt and Fritz, 1980; Siegenthaler and Eicher, 1986; and more recently Ito, 2001; Schwalb, 2003; and Leng and Marshall, 2004). Carbonates (e.g., marl, ostracods, molluscs) are the most commonly used material and the technique is now well established, but in non-alkaline, dilute, and/or open lakes, carbonates may be rare or absent. Such lakes are common at high-altitudes and are ideal for investigating climate change using oxygen isotopes because the isotope composition of the lake water is often similar to the composition of meteoric water (on either an annual or seasonal basis). These lakes nearly always contain diatom silica, which can be used as an alternative to carbonates in isotope studies. In simple systems, the oxygen isotope composition of diatom silica ($\delta^{18}O_{diatom}$) is controlled by water temperature and by the isotope composition of the lake water from which the diatom frustule is formed (Fig. 1). If diatom silica is precipitated in isotope equilibrium with the lake water, then mineral–water fractionation equations (often referred to as palaeotemperature equations after Craig, 1965) can be used to estimate varia-

tions in past temperatures providing there is no change in the oxygen isotope composition of the lake water. The interpretation of oxygen isotope compositions, in practice however, is complicated because the oxygen isotope composition of the water can be affected by changes in hydrology and climate. Knowledge of the factors that may have influenced the isotope composition of the lake water ($\delta^{18}O_{lakewater}$ on Fig. 1) is vital to the interpretation of the $\delta^{18}O_{diatom}$ signal. Perhaps the most critical control on a lake's isotope hydrology is the extent to which the lake is open (has an outflow and a short residence time) or closed (no effective outflow, and a long lake water residence time). The oxygen isotope composition of water in hydrologically open lakes usually reflects the isotope composition of precipitation, both rain and snowfall, received by the lake ($\delta^{18}O_{precipitation}$ or δp). Whereas closed lakes tend to have $\delta^{18}O$ that respond predominantly to the balance between precipitation (P) and evaporation (E). Although closed lake basins can be important in terms of area, the majority of lakes are open to some extent and their relative sensitivity to changes in P and E will depend on their water residence time. If a lake has a low P/E, then the isotope signal will record P/E changes since the amount of change due to temperature fluctuation will be small in comparison to the potential
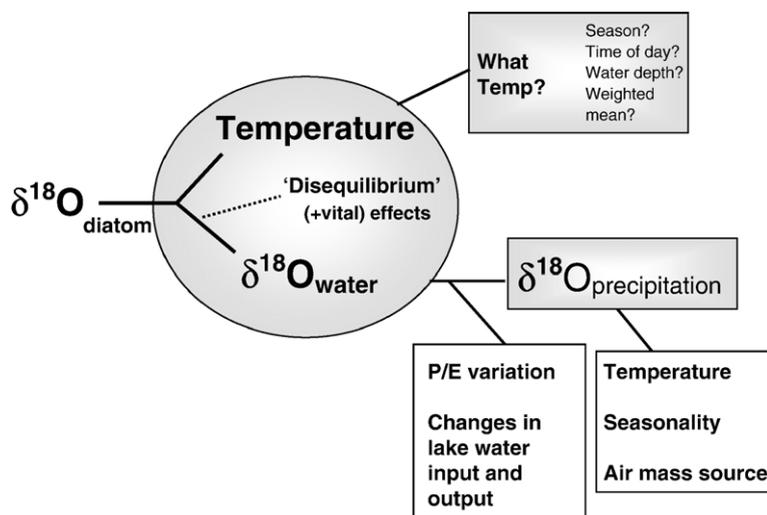
Fig. 1. Controls on the oxygen isotope composition of lacustrine diatom silica ($\delta^{18}O_{diatom}$). If diatom silica is precipitated in isotopic equilibrium, $\delta^{18}O_{diatom}$ depends entirely on temperature and the isotope composition of the lake water ($\delta^{18}O_{water}$). Disequilibrium effects, commonly known as 'vital effects' in biogenic precipitates, caused by local changes in microenvironment or rate of precipitation can induce systematic or non-systematic offsets in the $\delta^{18}O_{diatom}$ signal. Interpretation of $\delta^{18}O_{diatom}$ signal in terms of temperature depends on knowledge of the environment and time of year in which the diatom silica forms. For example, at high-latitude sites, diatoms typically grow in the summer months in the surface waters. Quantitative interpretation similarly demands an understanding of the local controls on the isotope composition of lake water ($\delta^{18}O_{lakewater}$). In some lakes, there is a simple relationship to $\delta^{18}O_{precipitation}$ but in others, the water composition is strongly influenced by processes such as evaporation within the catchment and within the lake itself. $\delta^{18}O_{precipitation}$ is increasingly being shown to be an important indicator of climate change: it typically changes with mean annual temperature but non-linear responses to climate change are increasingly being recognised. See text for more discussion of this figure. Modified from Leng and Marshall (2004).

change due to changes in the *P/E* balance (see Table 1 in Leng and Marshall, 2004).

Research on diatom-based oxygen isotopes was developed by oceanographers (Labeyrie, 1974; Labeyrie and Juillet, 1982; Labeyrie et al., 1984) and has produced many notable records, especially from the opal-rich sediments of the Southern Ocean (Shemesh et al., 1993, 1995). Sustained work on lacustrine diatoms is a more recent development, in part because of even more challenging methodological considerations (Binz, 1987), and also because the application of stable isotope methods to lakes has developed more slowly than in the oceans. This review of the rapid expansion of the literature in this field during the last decade seeks to highlight the factors that influence the measured isotope composition of lacustrine diatom silica and the assumptions that need to be made in using isotope variation to indicate past changes in climate. The most important considerations are the need to analyse a pure diatom sample, to measure the oxygen isotope ratio incorporated at the time of formation, and the need to calibrate the isotope records using studies of the isotope systematics of the modern lake system and the link to climate. We describe a number of studies from late Quaternary lake sediments to illustrate how the oxygen isotope composition of diatom silica has been successfully used to demonstrate climate change.

2. Diatoms in lakes

Diatoms are photosynthetic algae (2–200 μm) that form a shell, or frustule, composed of opalline or biogenic silica ($SiO_2 \cdot nH_2O$) (Round et al., 1990). The precise method of formation is still not fully understood but most models propose the formation of a matrix of organic fibrils and microtubules onto which the silica is deposited. More recently, Sumper and Kröger (2004) have suggested that silica formation takes place in intracellular compartments termed silica deposition vesicles (SDVs). The SDV grows during cell division, until valve formation is complete and the SDV fuses with the cell membrane. Some workers have suggested that the building blocks of the frustule are fused, 3–50 nm in diameter, and that silica spheres (Volcani, 1981) and fibrils found within the SDV might be chains of these nanospheres (Sumper and Kröger, 2004). Pores created by the packing of the spheres may be partially in-filled as the frustule grows but the process would lead to density differences within the frustule as has been observed with electron microscopy (Hurd et al., 1981). The formation of nano-scale patterns on diatoms may be controlled by long-

chain polyamines that have been found within diatom silica. The physicochemical properties of polyamines promote a hexagonal honeycomb like structure that has been recognised in a model of *Coscinodiscus* valve formation (Sumper, 2002). Traces of the organic matrix will be preserved in the frustule and is a potential contaminant of the structural oxygen (Hurd et al., 1981; Kröger et al., 2002).

Diatoms are ubiquitous in most lakes wherever the macronutrients of Si, N and P are sufficient to sustain productivity. They can be out-competed by other algal groups in eutrophic waters where Si/P and Si/N ratios are low. Notwithstanding these stoichiometric considerations, diatoms are also successful in well mixed environments where their buoyant cells, often augmented by chitin threads or colonial adaptions, enable them to keep within the photic zone better than many other algae. Moreover, some species are able to withstand deep mixing and low light levels (Kilham et al., 1986). A further survival strategy used by diatoms is to produce long lived resting spores to buffer environmental deterioration (Round et al., 1990), although these only occur in small quantities in sediments. Diatoms are found in a variety of life forms including free-floating planktonic, benthic and attached forms (e.g., epiphytic and epilithic). Water depth, photon penetration, vertical mixing, and micro-substrate conditions determine the relative importance of each habitat. An important consideration is that different species will be exposed to different water conditions, and if a lake has spatially distinct inflows or is strongly vertically stratified, this could theoretically introduce a species/habitat effect into the oxygen isotope signal, although this has not yet been demonstrated.

Diatom productivity follows a seasonal pattern in most lakes, controlled by the variability of climate, nutrient supply, mixing regimes, and in northern latitudes the period of ice cover. For example, many temperate lakes mix twice a year (spring and autumn) when epilimnion and hypolimnion temperature and density are similar, thereby creating conditions where diatoms can exploit nutrient-rich waters, whereas the strong mixing would exclude other algae. In large tropical lakes, the majority of diatom productivity often takes place in the well mixed dry season (Bootsma, 1993). In smaller polymictic lakes, seasonal productivity differences can also arise from nutrient and temperature variations (King et al., 2002). Therefore, diatoms will acquire their isotope signature during their major growing seasons and this will be specific to the lake under consideration.

The majority of diatom silica is recycled through dissolution within the water column but a fraction,

typically 5–20%, is incorporated into lake sediments (Bootsma et al., 2003). The size of the sedimentary diatom pool depends on vertical mixing, water depth, export, and lake water chemistry (Gallinari et al., 2002). Most natural waters are strongly under saturated with respect to silica and dissolution will progress at a rate defined by temperature (Hurd, 1972; Lawson et al.,
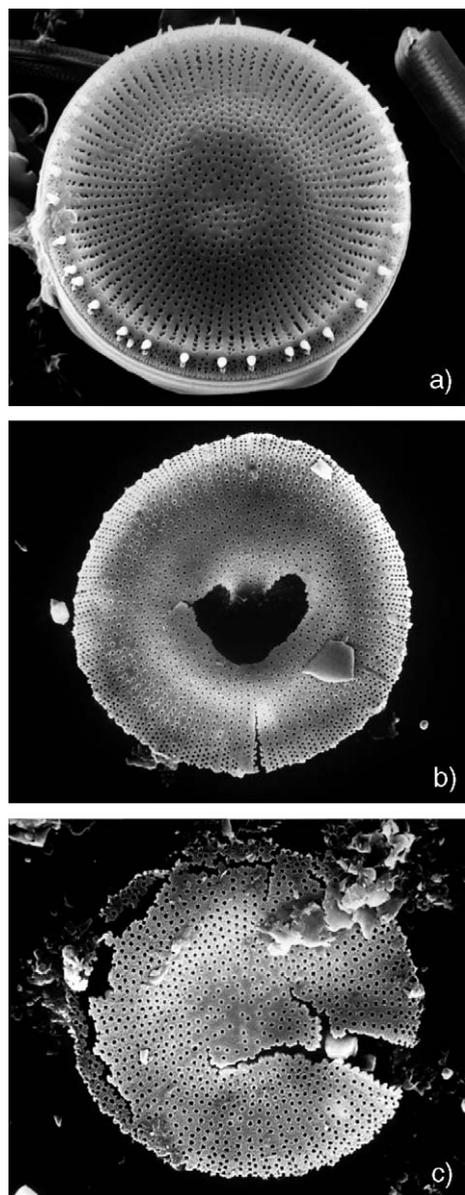
Fig. 2. Once the diatoms are incorporated into the sediment the dissolution rate will tend to slow but does not cease while pore waters are under-saturated with silica, and further diagenesis occurs. Diatom silica is highly adorned (a) and dissolution will preferentially exploit structural ornamentation and lines of fracture (b). Further dissolution will enlarge structural holes and increase the overall porosity of the diatom (c).

1978), alkalinity (becomes exponential above pH 9.0) (Iler, 1979), redox (Kato, 1969), and the presence of retardants such as Al and Fe (Lewin, 1961; van Bennekom, 1981). The organic membrane that covers the frustules also protects living diatoms and helps to adsorb metals but this decomposes on death and through bacterial activity (Lewin, 1961; Bidle et al., 2003). Without this protection, rapid dissolution of the fresh frustule begins with the weakest and least dense parts of the frustule being lost first. The most important factor controlling the dissolution rate is the specific surface area of the constituent parts (silicon spheres and nanometre-scale structures) and also the morphology of the whole diatom, which can lead to differential preservation of certain species (Hurd et al., 1981; Barker, 1992; Ryves et al., 2001; 2003; Battarbee et al., 2005).

Once the diatoms are incorporated into the sediment the dissolution rate will tend to slow but diagenesis does not cease while pore waters are under-saturated with silica. Diatom silica is highly adorned and dissolution will preferentially exploit structural ornamentation and lines of fracture (Fig. 2). Less obvious under optical microscopy is that the frustule itself is porous, possibly due to stacked spherical silicon building blocks, and that the pore spacing is generally lower with depth into the frustule. One consequence of this is that the densities of diatom frustules change with age as easily dissolved parts are lost and others are in filled by re-precipitated silica (Hurd et al., 1981). Over long time scales, amorphous diatom silica can be diagenetically altered to crystoballite (Kastner et al., 1977). In extreme circumstances, zeolites and clay structures can be observed growing on diatom frustules from re-precipitated silica (Gasse and Seyve, 1987; Barker et al., 1994; Gasse et al., 1997). Such diagenetic changes have important implications for the acquisition of oxygen isotope data as discussed below.

3. Analytical methodologies

3.1. Purification techniques

Nearly pure samples of diatom frustules from naturally occurring diatomite deposits, or artificially concentrated sediment samples, are required for oxygen isotope analysis, since the method generally used (i.e., fluorination techniques following Clayton and Mayeda, 1963) will liberate oxygen from all the components in the sediment; for example, silt, clay, tephra, carbonates and organic matter (Juillet-Leclerc, 1986). Natural diatomites are relatively rare, although careful choice of

sites can improve the likelihood of high sediment diatom concentration. Near diatomites are more common in spring-fed lakes, crater lakes with small catchments, cascading lakes where those upstream are a sediment trap, and large deep lakes where cores can be taken away from the influence of shorelines or fluvial inputs. Conversely, lakes with highly eroded catchments, or those fed by large rivers are generally less suitable as they often contain a high proportion of clay and silt. The vital importance of removing contaminants is shown in Fig. 3 and was demonstrated through analysis of material from a core covering the Eemian to early Holocene from Lake Baikal, where bulk sediment had been assumed to be pure diatomite (Fig. 4). These data show a similarity between diatom concentration and $\delta^{18}O_{bulk}$ (bulk sediment including diatoms), clearly indicating that the contaminants (mostly silt in this case) have low $\delta^{18}O$ compared to $\delta^{18}O_{diatom}$. Published methods of removing contamination involve various stages of chemical attack (HCl, NaOH·Cl, H_2O_2, HNO_3), sieving and differential settling (e.g. Shemesh et al., 1988). Carbonates and organic materials are generally removed by chemical methods, clay and fine silt by sieving at 5 or 10 μm, and coarser silt grains by differential settling techniques. Shemesh et al. (1995 and subsequent papers) describe a similar methodology but added a heavy liquid settling stage to separate diatoms from remaining clastic grains. In addition, sometimes potassium permanganate and nitric acid are used to remove organic material and etch the surficial silica layer assuming this will disassociate any adsorbed

clay which adheres to the diatoms (e.g., van Bennekom and van der Gaast, 1976; Juillet-Leclerc, 1986).

More recently, Morley et al. (2004) described a method for purification of diatoms which involves a series of structured 'clean-up' stages (Fig. 5). This was the first attempt at quantifying the preparation method and involved a semi-quantitative assessment of the diatom content at each stage of the cleaning process and comparison to the bulk sediment $\delta^{18}O$ values. Subsequently, Morley et al. (2005) show that even after purification, diatom concentration in Lake Baikal sediments range from 33% to 99% and have isotope values between $+14.4‰$ and $+34.3‰$ (Fig. 6). It appears that in these sediments it is currently virtually impossible to get 100% pure diatom samples when silt of a similar size to the diatoms is the major contaminant. Throughout the Lake Baikal sequence, it is evident that silt has a major influence on $\delta^{18}O$, since samples containing most silt have correspondingly lower $\delta^{18}O$ values. To compensate for this contamination problem, the authors decided to omit all samples of less than 90% diatom content, and used a mass balance calculation to mathematically remove the effect of the silt contamination. The bulk $\delta^{18}O$ value was considered as a linear mixture of oxygen from silt and diatoms, taking the $\delta^{18}O$ value of silt as $+12.3‰$ (the "silt" oxygen isotope value was taken as an average of rock fragments and silt found in the core). An adjusted silt-free value of $\delta^{18}O_{diatom}$ was then estimated using the relative proportions of diatoms and silt (based on point counting). This study was the first to use a mass balance
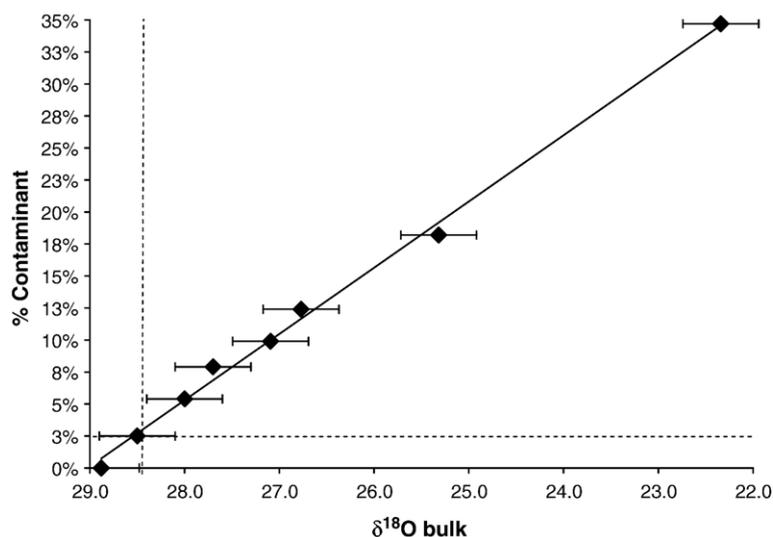
Fig. 3. Data showing the importance of removing clays and silts from a diatom sample prior to oxygen isotope extraction. The data shows the effect of a typical contaminant (in this case, NBS27, an international quartz standard, has a $\delta^{18}O$ value of $+9.64‰$) on a diatomite (NIGL laboratory standard BFC $\delta^{18}O=+28.9\pm0.4‰$). In this case, <3% contaminant in the BFC material provides data within analytical error.
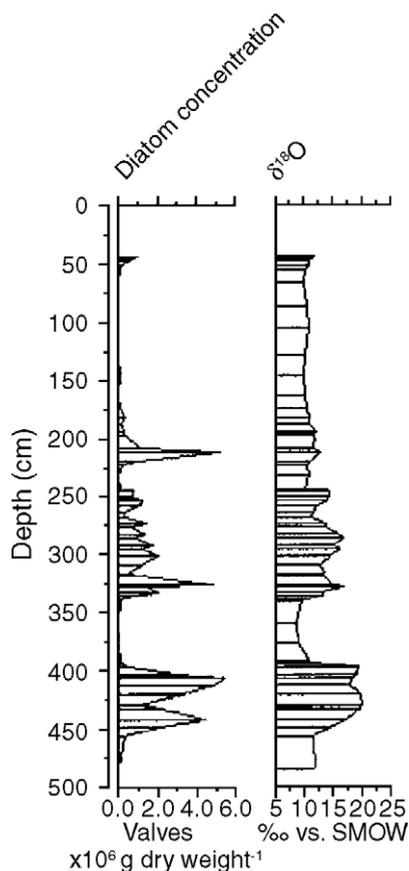
Fig. 4. Diatom concentration and bulk $\delta^{18}O$ for a core representing the Eemian to Early Holocene from the Academician Ridge, Lake Baikal. Clay and silt with $\delta^{18}O \sim +10\permil$ provide a signal in the parts of the core where diatoms are essentially absent and must influence the $\delta^{18}O$ from other parts where diatom concentrations can be variable. Reproduced with permission from Morley et al. (2004).

correction to compensate for the effect of silt on $\delta^{18}O_{diatom}$ although others have recognised the problems associated with silt (Juillet-Leclerc, 1986).

The recalculated $\delta^{18}O_{diatom}$ composition of the purified samples from Lake Baikal display a trend of gradually lowering values throughout the late glacial (Fig. 6). During the latter part of the Younger Dryas and early Holocene (c. 11.5–10 cal kyrs BP) pure samples could not be obtained due to low diatom abundance and the presence of small or fragmented diatoms. During the Holocene, $\delta^{18}O$ gradually switched to higher values and remained relatively stable throughout this period varying between +24.7‰ and +30.0‰ apart from a large excursion of one sample at c. 8000 BP to +32.0‰. There are problems with this approach that should be acknowledged; for example, during the mid-Holocene, an increase in silt content 5.5–7 ka BP is not concordant with a similar drop in sediment diatom concentration.

The dominant diatoms present at this level are easily fragmented needle like forms, and also small circular diatoms which have diameters of less than 10 μm (Morley et al., 2005). The authors attribute the resultant drop in $\delta^{18}O_{diatom}$ to an overestimate of the diatom content, as the cleaning method would have removed many of these smaller diatoms and diatom fragments. In addition, the mass balance approach used to calculate the amount of silt to diatom used by Morley et al. (2004) assumes that each grain (silt/diatom) contains the same amount of oxygen, whereas in reality the volume and density will vary. If the silt grains are predominantly silica, then they will contain significantly more oxygen due to the greater mass of silt compared to diatoms. The mass balance approach without consideration of volume and density of the point counts will underestimate the effect of silt $\delta^{18}O$ on the overall oxygen isotope composition, but is one of the few non-destructive ways of correcting for the influence of contaminants.

Lake sediments in volcanic regions will contain shards of tephra which have similar chemical and physical properties to diatom silica. Tephra shards within the size range of diatom frustules are difficult to separate from diatom frustules (Fig. 7). Lamb et al. (2005) found that it was impossible to completely remove tephra deposited in samples from an Ethiopian lake, where large amounts of tephra were reworked from the catchment into the sediments for 100 yrs or more after the main tephra fall. As in the detrital silicates of Baikal, very small amounts of tephra can have a significant effect on the $\delta^{18}O_{diatom}$ of samples. Lamb et al. (2005) showed that this tephra had an average $\delta^{18}O$ value of +11‰ and typically the diatomites had values of +35‰, so only 4–5% contamination (by weight) would be needed to reduce the sample value by 1‰ (i.e. 2 to 4 times typical analytical error). It is thought that low $\delta^{18}O$ values in some parts of the Ethiopian core are the result of tephra remaining after the cleaning procedure and not being distinguished by optical means. Both Morley et al. (2005) and Lamb et al. (2005) emphasise the need for petrological examination of every sample and a cleaning method that is individually tailored to the material being analysed.

An alternative approach to heavy liquid separation for cleaning diatom samples, is gravitational split-flow lateral-transport thin (SPLITT) developed by J.C. Giddings at the University of Utah (Giddings, 1985) and first applied to the separation of diatoms at the University of Jülich (Schleser et al., 2001; Rings et al., 2004). SPLITT works by introducing a sample (A′) into a thin channel 371 μm high where it meets a carrier fluid (B′,
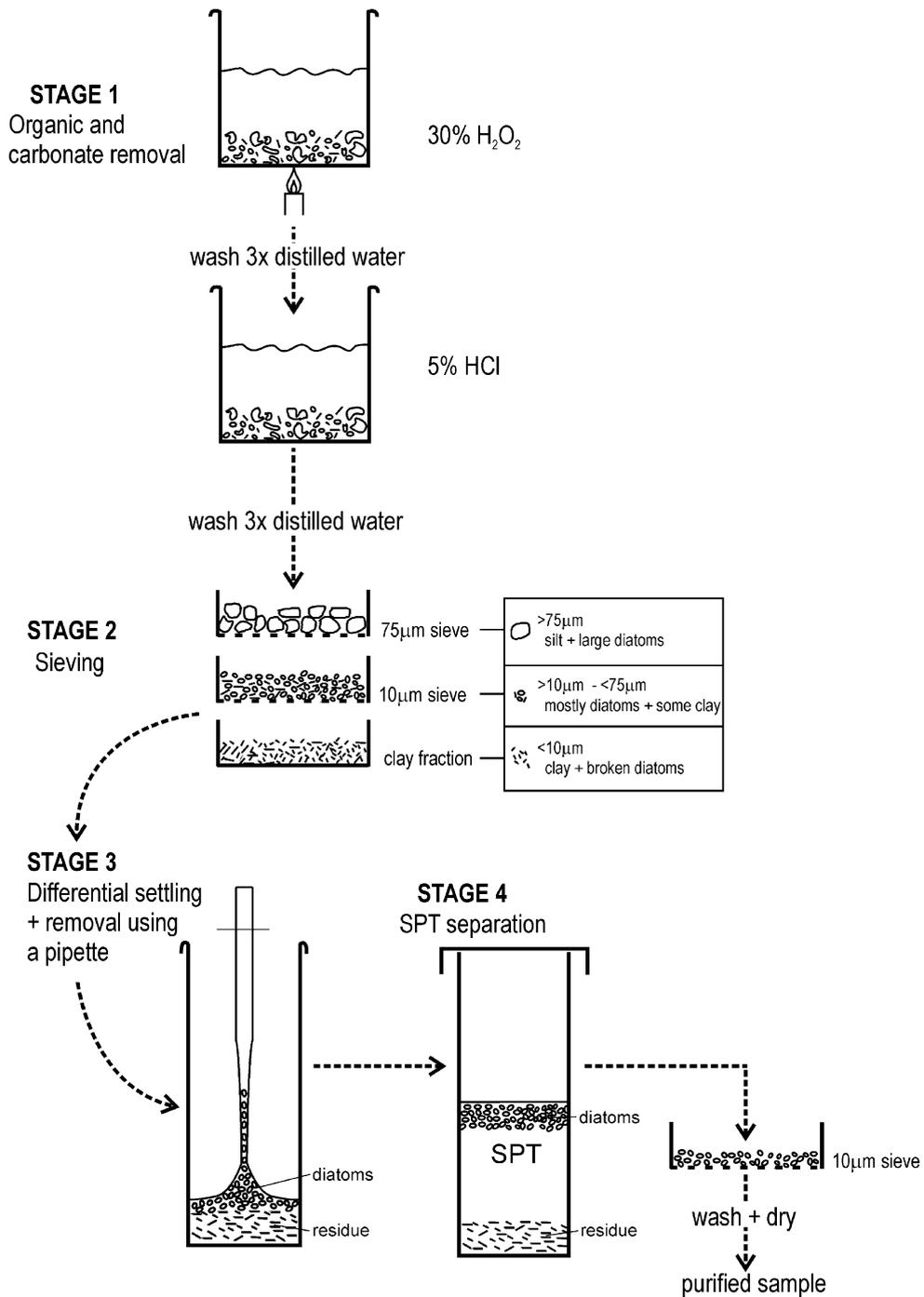
Fig. 5. Flow diagram showing the four-stage cleaning method for concentrating diatom for oxygen isotope analysis from lake sediments. Reproduced with permission from Morley et al. (2004).

usually water for diatom samples) in a laminar flow (Fig. 8). The velocity of the two flows is controlled to separate the sample into two streams; an upper A sample containing finer, less dense and more hydrodynamic particles passes through one outlet (A), while the remaining particles are collected through a lower outlet B. Rings et al. (2004) described in detail the conditions they used to separate mineral grains from diatoms in Lake Holzmaar. Experiments with SPLITT at Lancaster University have established the following procedure,
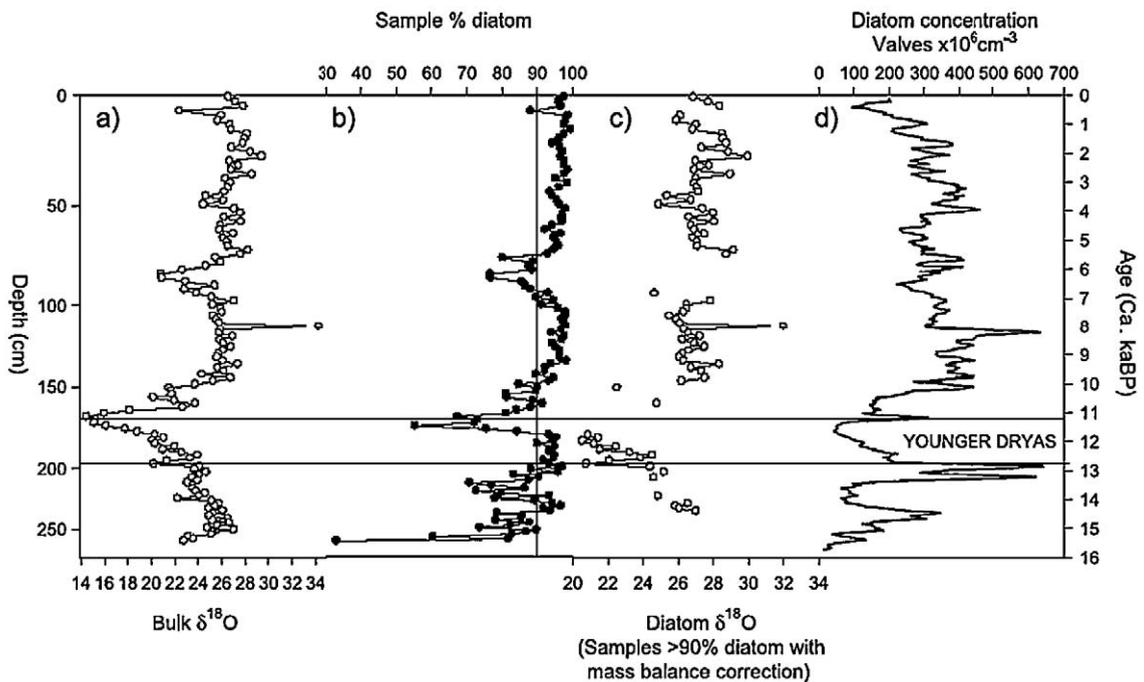
Fig. 6. (a) $\delta^{18}O$ vs. age for a core taken from the Vydrino Shoulder, Lake Baikal. (b) Estimated sample percentage diatom content with marked limit of 90% purity. (c) Mass balanced $\delta^{18}O$ calculated using samples >90% purity and a mass balance correction to remove the effects of small amounts of silt still present after cleaning. Reproduced with permission from Morley et al. (2005).

for materials from crater lakes in East Africa, controlled at every stage by optical microscopy (Fig. 9). Firstly the sample is cleaned using hot 30% H_2O_2, 10% HCl and concentrated HNO_3. The treatment is repeated until no trace of organic material remains. Secondly the sample is sieved at 63, 38, 20 and 10 μm. The fraction containing the greatest proportion of diatoms is selected for SPLITT but in general the method is most successful with fractions greater than 20 μm. Typical initial settings for the 20–38 μm fraction would be 10 ml/min for A and 20 ml/min for B, and for the <20 μm fraction, 5 ml/min for A and 15 ml/min for B. This high rate of throughput allows relatively high concentrations to be processed. The particles are then inspected and if they contain components other than diatoms then the A and B samples are re-processed through SPLITT at slower sample flow rates enabling greater discrimination. Once a near pure sample is obtained it is washed again across a 10 or 20 :m sieve, collected and dried. Samples can be recombined if unsuccessful or if a larger sample is needed for analysis. Some results of SPLITT separation are shown in Fig. 10. The main disadvantage of SPLITT is the need for repetition since no two samples are identical and there is a requirement to clean the channel thoroughly between batches. The advantages of

SPLITT fractionation are high throughput, small losses, and sometimes the ability to isolate specific taxa (where they have different size, density and/or shape). It also avoids the need to introduce products other than water into the sample. For example, Morley et al. (2004) show that the heavy liquid can contaminate diatom oxygen isotope ratios. Using the staged clean-up approach they removed the heavy liquid, sodium polytungstate (SPT), by rinsing the sample over a 10-μm sieve because they found that centrifuge washing alone tended to retain a proportion of the SPT with the sample. When testing the method using standard laboratory diatomite, the standard material yielded a $\delta^{18}O$ value 6.5‰ lower than expected without this final sieve stage which they attribute to insufficient removal of the SPT.

3.2. Oxygen isotope extraction techniques

The common view is that diatom frustules consist of an inner tetrahedrally bonded silica skeleton (Si–O–Si) with an outer, hydrous layer (Labeyrie and Juillet, 1982) (Fig. 11). The distribution of these components is more complex than simple layering and is related to the mode of formation of the frustule and its differen-
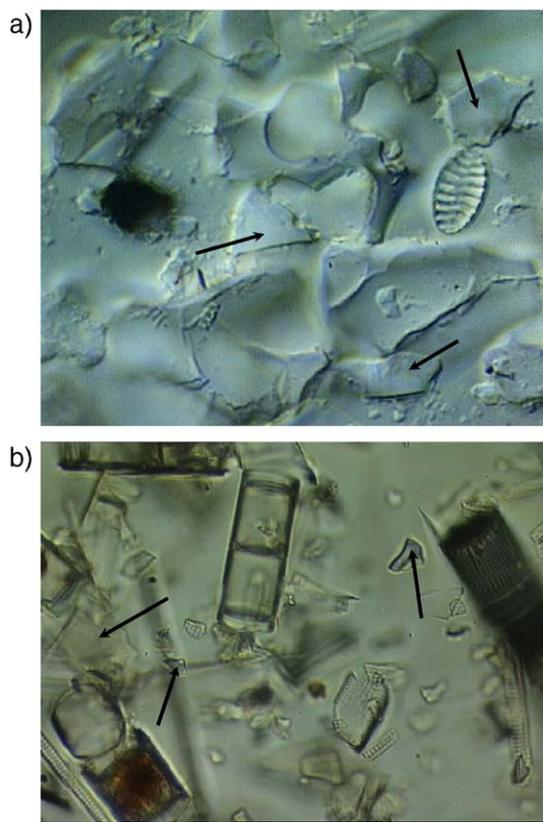
Fig. 7. Lake sediment in volcanic regions will contain shards of tephra which have similar physical and chemical properties to diatom silica. Tephra shards within the size range of diatom frustules are difficult to remove from the sediments. (a) This example is from Lake Massoko, Tanzania taken under light microscope using Nomarski phase contrast with a 1000× objective. (b) A sample from Lake Tilo, Ethiopia showing whole diatoms and broken fragments of diatoms mixed with similarly shaped tephra, 40× objective. (Arrows point to tephra shards).

tial porosity. Through dissolution of the hydrous parts of the frustule, Juillet (1980a,b) demonstrated that this internal dense silica is isotopically homogenous, while the outer hydrous layer freely exchanges with any water the diatom silica comes into contact with. Knauth (1973) considered that biogenic opal has 7–12 wt.% water, compared to 1 wt.% for quartz, although Leng et al. (2001) suggested that 20–30% of diatom oxygen needs to be removed before stable values for $\delta^{18}O$ are reached. There may be different types of structural oxygen preserved depending on the age of the diatom due to diagenesis and porosity changes. For example, Schmidt et al. (2001) found little relationship between diatom $\delta^{18}O$ from sediment traps and diatom $\delta^{18}O$ from the sediment itself, probably due to the more hydrated nature of fresh diatom silica. The internal Si–O bond requires considerably

energy to break, and necessitates the use of an extremely powerful oxidising reagent (i.e., a fluorine-based compound such as ClF_3 or BrF_5; see Fig. 12) or high temperatures. The difficulty of both the purification of the material as well as the extraction of formation water oxygen (described below) means that the analytical reproducibility of diatom silica oxygen isotope ratios is generally quoted as 0.15‰ to 0.3‰ (1σ), although some studies suggest that this can be considerably higher (e.g. Schmidt et al., 2001). The precision is significantly lower than for carbonate oxygen which has a precision generally in the range of 0.05‰ for pure carbonate minerals to 0.1‰ (1σ) for authigenic carbonates within lake sediments.

To date, there are three main methods that have been used to remove the hydrous layer from the biogenic silica and disassociate the silicon and oxygen. These are vacuum dehydration, isotope exchange and stepped fluorination techniques. Degens and Epstein (1962), Mopper and Garlick (1971), and Labeyrie (1972, 1974) reported the initial vacuum dehydration experiments. Pore waters were volatilised by heating above 100 °C in vacuum, and the hydrated silica was disassociated by heating above 1000 °C under vacuum (Labeyrie, 1974). Labeyrie (1974) suggested that for marine sponge spicules it is possible to remove the hydrous component, leaving the formation silica. This preparation technique was subsequently applied to marine sediments in the eastern Pacific (Mikkelsen et al., 1978), the Gulf of California (Wang and Yeh, 1985), and to modern cultures (Brandriss et al., 1998). However, there is the possibility of isotope exchange by atomic diffusion at high temperatures although this may be reproducible (Brandriss et al., 1998). Few laboratories currently undertake the vacuum dehydration method for silicates, although recently, a dehydration technique based on the reduction of silica by carbon at high temperatures (1550 °C for biogenic silica) has been described (inductive high temperature carbon reduction, iHTR) by Lücke et al. (2005). Silica is mixed with graphite and heated under vacuum until conversion to CO. Weakly bonded oxygen and some contaminants, like hydroxyl groups, are volatilised under vacuum at lower temperatures (850–1050 °C) before the reduction of the silica. The authors describe the advantages of the iHTR as being a relatively simple technique, much faster, and with a higher overall precision than traditional vacuum dehydration techniques. Although the results from the materials reported in Lücke et al. (2005) look promising, application of this methodology to sediment archive material is needed to assess these long-term applicability of this meth-
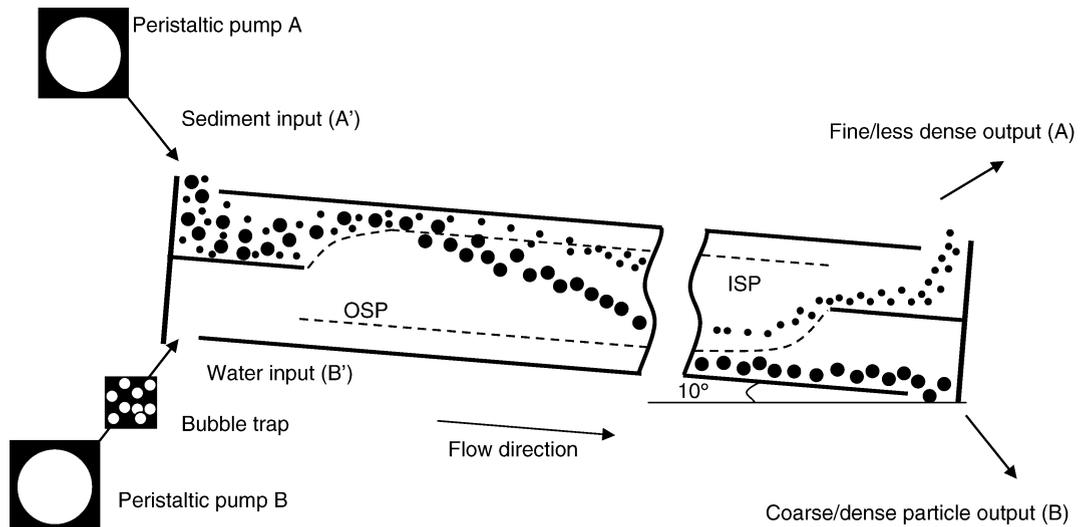
Fig. 8. An alternative approach to heavy liquid separation for cleaning diatom samples is gravitational split-flow lateral-transport thin (SPLITT) developed by J.C. Giddings at the University of Utah (Giddings, 1985) and first applied to the separation of diatoms at the University of Jülich (Schleser et al., 2001; Rings et al., 2004). SPLITT works by introducing a sample (A′) into a thin channel (380 μm high × 4 cm wide × 20 cm long) where it meets a carrier fluid (B′, usually water for diatom samples) in a laminar flow. The inlet splitter plane (ISP) and outlet splitter plane (OSP) divide the flow. The velocity of the two flows is controlled to separate the sample into two streams; an upper A sample containing finer, less dense and more hydrodynamic particles passes through one outlet (A), while the remaining particles are collected through a lower outlet B. The SPLITT cell is inclined to reduce deposition of sediment onto the splitter plate at low flows.

odology in palaeoclimate research in view of the identification of atomic diffusion at high temperatures.

The surficial hydrous silica (SiOH) is reactive under much lower energy conditions than the inner bound silica, which allows exchange of oxygen atoms of known isotope composition with the unstable hydrous material whilst leaving the skeletal silica intact. Labeyrie and Juillet (1982) used this to derive the controlled isotope exchange method (CIE). This method allows exchange of the hydrous oxygen with oxygen of a known isotope value, and then through mass balance calculations determine the composition of the non-exchangeable silicate oxygen after fluorination (see below). Juillet-Leclerc and Labeyrie (1987) applied CIE to diatom silica from marine and lacustrine surface sediments.

As an alternative to the CIE, a method that reacts the silica with a fluorine compound in steps was first described by Haimson and Knauth (1983), and subsequently by Thorliefson (1984) and Thorliefson and Knauth (1984). The so-called stepwise fluorination (SWF) method involves reacting the biogenic silica in steps involving a stoicheometric deficiency of reagent. The first oxygen fractions released from the hydrous silica usually have a low $\delta^{18}O$ compared with oxygen recovered in subsequent reactions, which eventually stabilise at a 'plateau' value (Matheney and Knauth, 1989). Based on this pattern of isotope variations,

Matheney and Knauth argued that the first reaction involved the hydrous component of the biogenic silica leaving the anhydrous silica for subsequent reactions. Matheney and Knauth (1989) used the SWF method in the analysis of modern and recent biogenic silica deposits for comparison with measured temperature and isotope composition of ambient water. To a certain degree, the data of Matheney and Knauth (1989) compare favourably to those measured using CIE by Juillet-Leclerc and Labeyrie (1987), suggesting that the two methods measure the same 'non-exchangeable' fraction, and that any oxygen atoms available for isotope re-labelling are eliminated early on in the SWF approach (Matheney and Knauth, 1989). CIE and SWF have different advantages, SWF has the potential of removing differing amounts of the hydrous layer (which might be species-/age-specific), but it is not known which structural oxygen atoms are being removed at each stage (Brandriss et al., 1998). However, the advantage of the method is that some very fine fraction clays remaining in the sample are removed (Matheney and Knauth, 1989) although the disadvantage is that the stable $\delta^{18}O$ plateau may need to be determined for different diatom assemblages. With the CIE method there is the potential that not all exchangeable oxygen reacts completely, especially for fresh sediments, where the proportion of hydrous silica is high (Juillet, 1980a,b; Schmidt et al., 1997; Brandriss et

1. Original diatom sample prepared using hot H_2O_2. Diatom ~12% of silt-sized particles

2. 38-20 μm fraction collected by sieving ~diatoms 42% (not shown)

3. Sieved fraction processed with SPLITT

SPLITT fraction A ~diatoms 95%

SPLITT fraction B ~diatoms 17%

Sample reprocessed with SPLITT at different settings to collect diatoms

4. Samples checked for purity and dried for isotope analysis

Fig. 9. Some results of SPLITT separation from Lake Rutundu, Mount Kenya. SPLITT separation is repeated at different flow rates until diatoms are separated in sufficient quantity for analysis.

al., 1998). Both CIE and SWF methods require fluorination to disassociate the silicon and oxygen. Schmidt et al. (1997) compared the two methods on marine diatoms and came to the conclusion that both produced reliable results, although with the CIE method the exchangeability of the silica was variable. They recommended calibration of the CIE method using results from SWF to select a water vapour of an appropriate isotope composition for the equilibration.

Classical fluorination with the step wise approach is employed at the NERC Isotope Geosciences Laboratory, UK. The method involves a three stage process. Stage one involves 'outgassing' to remove surficial and loosely bound water in nickel reaction tubes at room temperature. Stage two involves a prefluorination step involving a stoichiometric deficiency of the reagent, either chlorine trifluoride (ClF_3) or bromine pentafluoride (BrF_5), at low temperature. The third stage is a full

reaction at high temperature for an extended period with an excess of reagent. The oxygen liberated is then converted to CO_2 by exposure to graphite (see procedure outlined by Clayton and Mayeda, 1963). Oxygen yields are monitored by comparison with the calculated theoretical yield for SiO_2. Using this method, Quaternary and recent diatom samples have an average yield of 74% of their theoretical yield based on silica suggesting that on average around 26%, including hydroxyl and loosely bonded water (both OH^- and H_2O), of the material is removed during prefluorination.

The oxygen isotope composition of diatom silica is expressed on the delta-scale in terms of per mille (or per mil) (‰):

$$\delta = \left[\left(R_{sample}/R_{reference}\right) - 1\right]1000 \qquad (1)$$

where R is $^{18}O/^{16}O$, and 'reference' means the appropriate universally accepted reference material. The 'δ'
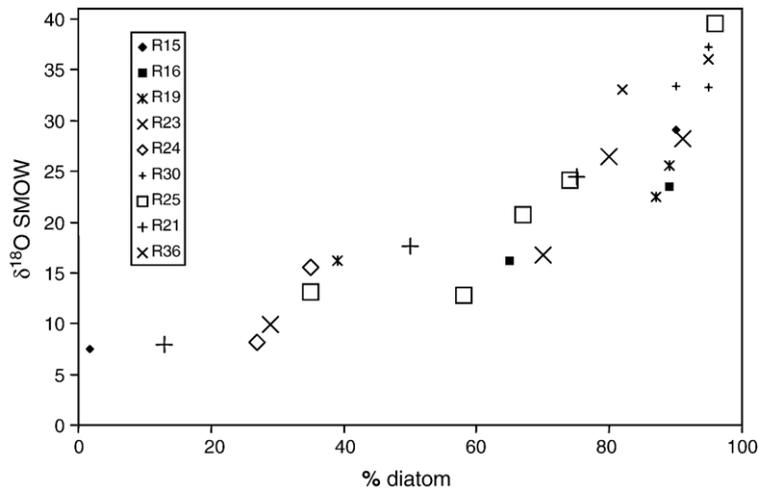
Fig. 10. SPLITT separation was used to produce different concentrations of diatoms and silt from sediments of Lake Rutundu, Kenya. For each sample, $\delta^{18}O$ increased with the percentage diatoms. Silt end members of this site have values of 8‰ (based on the value for R15 which has the least diatoms). While different equations could be constructed for each sample, overall for Lake Rutundu, every 1% of silt reduces the value by 0.3‰. This relationship can be used to give a mass balance correction to $\delta^{18}O$ values. R15–R36 refer to specific depths from Lake Rutundu core R1 285–735 cm, 12.5–37 ka.

for each element takes its name from the heavy isotope, thus $\delta^{18}O$. For diatom oxygen, the reference is VSMOW (Vienna Standard Mean Ocean Water, a specially prepared distilled seawater). There is no universally accepted standard material for diatom silica although most laboratories analyse it alongside the NBS27 (quartz) and their own standard diatomites. VSMOW and NBS27 are held and distributed by the IAEA (International Atomic Energy Agency) in Vienna.

4. Diatom oxygen systematics

Changes in the oxygen isotope composition of diatom silica can be used to infer changes in either tem-

Fig. 11. Amorphous silica (here used as an analogue for diatom silica). A schematic illustration of the structure of amorphous hydrated silica showing the inner tetrahedrally bonded silica and the outer (readily exchangeable) hydrous layer. Modified from Perry (1989).

perature or the oxygen isotope composition of lake water, although both are affected by climate dynamics and lake hydrology.

4.1. Temperature

A number of studies have determined the empirical relationship between temperature and the oxygen isotope composition of carbonate minerals and the composition of the water from which they formed (e.g., Epstein et al., 1953; Craig, 1965; Kim and O'Neil, 1997). However, the temperature dependence of oxygen isotope fractionation between diatom silica and water has not been so rigorously derived, although the relationship has been estimated from analyses of diatoms from marine and freshwater sediments, coupled with estimates of the temperatures and isotope compositions of coexisting waters during silica formation (Labeyrie, 1974; Wang and Yeh, 1985; Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992; Brandriss et al., 1998). The data from these calibration studies are limited, and are mainly based on bulk samples not individual diatom species (although Brandriss et al., 1998 used individual species). The estimates of the average temperature dependence based on these bulk samples ranges from -0.2‰/°C to -0.5‰/°C (Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1992). More recently, controlled diatom culturing experiments (marine diatoms) by Brandriss et al. (1998) and planktonic diatoms from Lake Holzmaar (Moschen et al., 2005)

Fig. 12. Schematic of the fluorination line used at the NERC Isotope Geosciences Laboratory for the extraction of oxygen from diatom silica for isotope analysis.

have shown that the diatom–temperature coefficient is around $-0.2‰/°C$. However, questions regarding the diatom–temperature fractionation have been raised by Schmidt et al. (1997). They analysed the oxygen isotope composition of diatom frustules collected live from the oceans and found no regular correlation between temperature and the oxygen isotope fractionation between diatom silica and water. These results led to the hypothesis that the temperature-dependent oxygen isotope fractionation preserved in some biogenic opaline sediments may have been established during early diagenesis rather than acquired during growth. It is certainly true that the nature of the silica will change rapidly after death as dissolution begins and pores within the frustule are infilled with re-precipitated silica. The dissolution/diagenesis rate will be high in the water column and will continue at the sediment interface, but will usually slow when the most easily soluble parts of the frustule are removed and equilibrium with pore waters is approached. It seems unlikely that a significant lag will be introduced into the acquisition of the oxygen, especially that derived from the densest parts of the frustule analysed after step-wise fluorination. Moreover, near synchronous changes in $\delta^{18}O_{diatom}$ and $\delta^{18}O_{calcite}$ have been observed in a recent study of Lake Tilo, Ethiopia (Lamb et al., 2005), here at least the major part of the $\delta^{18}O_{diatom}$ signal must be acquired within decades rather than millennia.

The equation of Juillet-Leclerc and Labeyrie (1987) is comparable with an extrapolation to low temperatures of non-biogenic silica fractionation models (Clayton, 1992).

$$T°C = 17.2 - 2.4(\delta^{18}O_{diatom} - \delta^{18}O_{water} - 40) - 0.2(\delta^{18}O_{diatom} - \delta^{18}O_{water} - 40)^2 \quad (2)$$

Shemesh et al. (1992) assessed the silica–water temperature fractionation Eq. (2) of Juillet-Leclerc and

Labeyrie (1987), and reported that it overestimates temperatures for polar oceanic regions and produced an alternative equation which has subsequently been used for many high latitude sites:

$$T°C = 11.03 - 2.03(\delta^{18}O_{diatom} - \delta^{18}O_{water} - 40) \quad (3)$$

In these equations, $\delta^{18}O$ of the diatom silica and water are compared to the SMOW international standard.

The interpretation of the measured oxygen isotope data from diatom silica in terms of palaeotemperatures requires an understanding of two temperature effects that have opposing effects on the composition of diatom silica. There is the fractionation between diatom silica and water described above, which has a gradient of between $-0.5‰/°C$ to $-0.2‰/°C$. There is also the relationship between precipitation and temperature of approximately $+0.6‰/°C$ (the so-called Dansgaard relationship $\delta p/dT$; Dansgaard, 1964) at intermediate and high latitudes, and a worldwide range between $+0.2‰/°C$ and $+0.7‰/°C$ (Dansgaard, 1964). Ideally, it is important to establish the relationship between precipitation and temperature at each site (see Leng et al., 2005a and the IAEA–WMO GNIP database); it is worth noting here that a Dansgaard relationship is not common in coastal or monsoonal regions or where rainfall comes from two air masses.

For many lake records the diatom oxygen isotope response to temperature will be dominated by the change in the isotope composition of precipitation and effectively 'damped' by the opposing effect of mineral–water fractionation. For diatoms the measured isotope composition will, therefore, covary with temperature — with an increase of $\sim0.1‰/°C$ to $0.4‰/°C$ (cf., Eicher and Siegenthaler, 1976). This assumes that $\delta p/dT$ always changes according to the Dansgaard relationship. For example, a non-evaporating lake in southwestern Alaska is thought to contain precipitation from only one source of moisture, $\delta^{18}O$ records are likely to represent some aspect of temperature, both changes in δp and

changes due to the temperature dependent diatom–water fractionation (Hu and Shemesh, 2003). This record shows that at the end of the last glaciation, $\delta^{18}O$ increased by 4.5‰ between 12.3 and 11 ka ^{14}C then fell by 1.7‰ at the onset of the Younger Dryas (YD) before climate recovered at the end of the YD. If this is the case then the data show a YD reversal in this region. In another application of the temperature equation from Linsley pond, Connecticut, a 12 °C temperature drop marked the onset of the YD in just 200 yrs, although the average fall through this period was 6 °C. Although large, these changes are comparable to changes seem in other proxies for this region (Shemesh and Peteet, 1998).

In the only late glacial to middle Holocene lacustrine record available from the Southern Ocean (island of South Georgia), the oxygen isotope record of diatom silica was interpreted largely in terms of temperature change (Rosqvist et al., 1999). It shows that deglaciation on South Georgia commenced prior to 18.6 ka. Colder conditions were reinstated shortly after 14 ka and lasted across the YD. The transition to postglacial conditions occurred between 8.4 and 6.5 ka was interrupted by a 400-yr cold event that began ca. 7.8 ka.

Quantitative information on temperature from a $\delta^{18}O_{diatom}$ lake record can only be gained if there were no changes in the temperature or isotope composition of the seawater undergoing evaporation or changes in the long-distance trajectory of air-masses since both affect the isotope composition of precipitation (δp). A number of recent studies have demonstrated significant short term deviation from the classic Dansgaard relationship in the sediment records and have highlighted important shifts in the Holocene climate system. Isotope studies of lake sediments that attempt to interpret oxygen isotope records solely in terms of temperature change at the site, potentially ignore the possible effects of changes in δp that are related to more distant climatic processes (cf., von Grafenstein et al., 1999; Teranes and McKenzie, 2001). δp can really only be unravelled where there is an independent temperature estimate (see Hammarlund et al., 2002).

The relationship between temperature and δp still has considerable uncertainties. It is usually very difficult to derive quantitative palaeo-temperature/δp data with any certainty. It might be more realistic to use $\delta^{18}O_{diatom}$ in areas where there are likely to have been significant changes in the isotope composition of the lake water due to changes in the precipitation/evaporation balance or in the source of precipitation (see below). The change in $\delta^{18}O_{diatom}$ due to these factors is normally far greater than temperature alone.

4.2. Changes in the oxygen isotope composition of lake water

4.2.1. The P/E balance

In closed (or terminal) lakes, changes in $\delta^{18}O_{lakewater}$ will usually be far greater than changes due to temperature or δp. $\delta^{18}O_{lakewater}$ depends on the balance between the isotope composition of inputs (including the source and amount of precipitation, surface runoff and groundwater inflow) and outputs (evaporation and groundwater loss). Unless there is significant groundwater seepage, most closed lakes will lose water primarily through evaporation, the rate of which is controlled by wind speed, temperature and humidity. The phase change of evaporation results in light isotopes of oxygen (^{16}O) being preferentially evaporated from water bodies leaving water that is relatively enriched in the heavier isotope (^{18}O). Any effects of varying precipitation source or temperature on $\delta^{18}O$ are often small in comparison to evaporative concentration and measured $\delta^{18}O$ (and δD) values become elevated above those of ambient precipitation (Gat, 1980; Gasse and Fontes, 1992). In extreme circumstances, evaporation in the lake catchment area or from the surface of a lake can lead to significantly elevated $\delta^{18}O_{water}$ values.

The degree to which evaporation will increase $\delta^{18}O_{lakewater}$ depends on the residence time of the lake (lake volume/throughput rate). Changes to a lake's residence time, caused by changes in basin hydrology or varying groundwater fluxes, will also influence the degree of enrichment, as will changes in the nature of catchment vegetation and soils. These factors have been considered important in the interpretation of a $\delta^{18}O_{diatom}$ record from Ribains Crater Lake in the Massif Central region of France (Rioual et al., 2001; Shemesh et al., 2001a,b). Although some temperature changes were noted, variations in the isotope composition of lake water related to the isotope composition of precipitation and evaporation dominate the record. An even more striking example of the dominance of $\delta^{18}O_{lakewater}$ comes from a sediment record from Lake Tilo in East Africa that reveals changes in diatom oxygen from a dominantly evaporative lake system (Lamb et al., 2005; Fig. 13). They compared $\delta^{18}O_{diatom}$ and $\delta^{18}O_{calcite}$ from a small crater lake where it was assumed that the high temperatures encourage diatoms to grow throughout the year. In a previous study, Lamb et al. (2000) showed from the calcite isotope record that the early Holocene lake had a high solute input due to hydrothermal groundwater inflow and the lake-level was close to the crater rim. The alkaline lake had a constant solute supply which
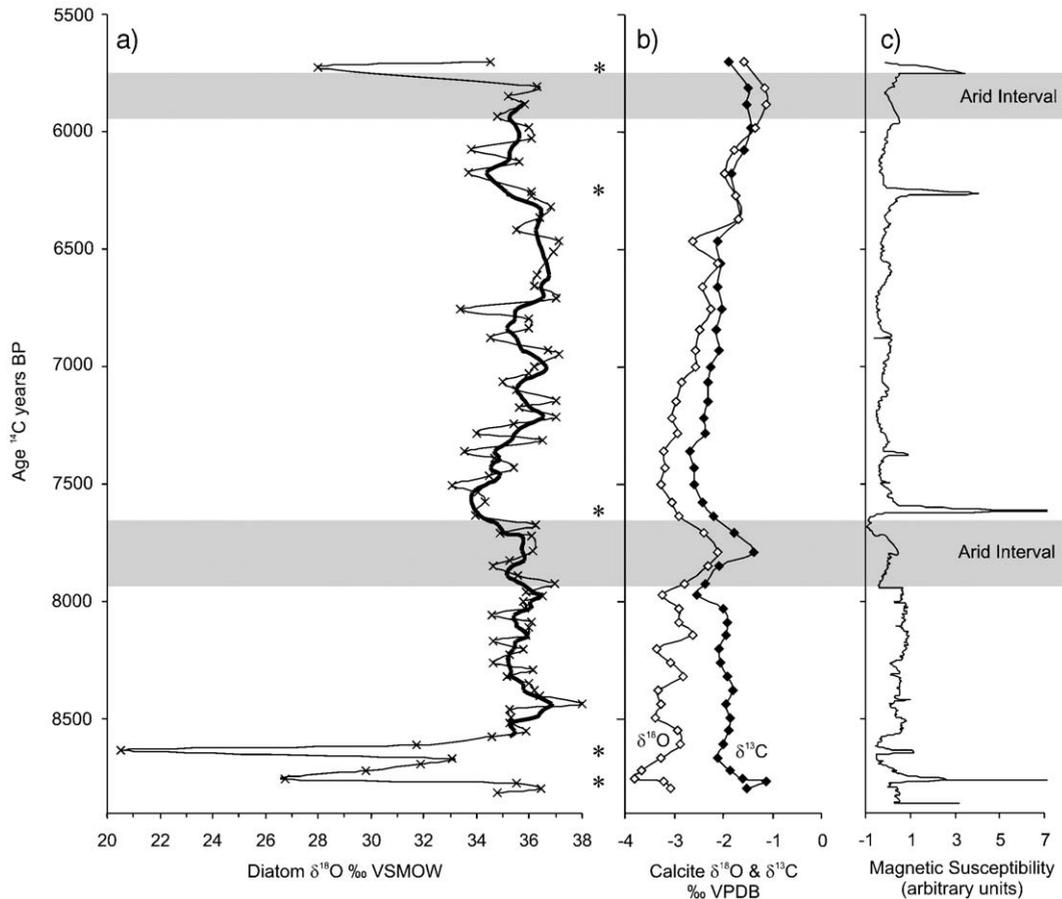
Fig. 13. (a) $\delta^{18}O_{diatom}$ from Lake Tilo (8800–5500 yrs BP). Solid line is 3-point running mean and stars represent position of tephra deposits, (b) $\delta^{18}O_{calcite}$ and $\delta^{13}C_{calcite}$ from Lake Tilo (8800–5500 yrs BP), (c) magnetic susceptibility—peaks indicate high concentrations of tephra. Note: $\delta^{18}O/\delta^{13}C_{calcite}$ and $\delta^{18}O_{diatom}$ are on VPDB and VSMOW scales respectively. The early Holocene arid intervals are indicated by grey shading. Reproduced with permission from Lamb et al. (2005).

meant that both diatom and calcite production was high. The comparison between the $\delta^{18}O_{diatom}$ and $\delta^{18}O_{calcite}$ from the early Holocene is similar and thus they may provide a suitable alternative proxy for each other. However, this study highlights the larger errors associated with $\delta^{18}O_{diatom}$. In particular the diatom isotope data is more variable than the calcite oxygen isotope data and does not record all the fluctuations in $\delta^{18}O_{calcite}$. Especially note worthy is the fact that the $\delta^{18}O_{diatom}$ data do not record the well documented 7800 yrs BP arid interval found in neighbouring Ethiopian lakes. The authors suggest the lack of modern limnological and seasonal ecological information, the larger errors associated with the $\delta^{18}O_{diatom}$ method than $\delta^{18}O_{calcite}$, and the incomplete removal of tephra shards could all be contributing factors.

Oxygen isotope records in tropical regions have also been shown to be sensitive to the amount of precipitation (Cole et al., 1999) and it is likely that this strong

relationship will be important in tropical lake records. For example, abrupt shifts of up to 18‰ in $\delta^{18}O_{diatom}$ have been found in a 14-ka-long record from two alpine lakes on Mount Kenya (Barker et al., 2001; Fig. 14). The most important potential causes of isotope variation on Mount Kenya since the late glacial were investigated using GCM simulations. For the last glacial maximum (LGM) it is suggested that the $\delta^{18}O$ values of rainfall ($\delta^{18}O_{precip}$) at low altitudes in the tropics were probably 1–3‰ higher than today (Hoffmann and Heimann, 1997; Jouzel et al., 2000), the net effect of a 1.6‰ increase in the ^{18}O content of mean ocean water, the lowering of tropical SSTs, resulting in a smaller temperature gradient between the vapour source and the site of condensation, and the weakening of the African and Asian monsoons (reduced amount effect). The same factors have been attributed to the high values of $\delta^{18}O_{diatom}$ (maximum +36.7‰) recorded on Mount Kenya during the late-glacial (14–11.2 ka). In
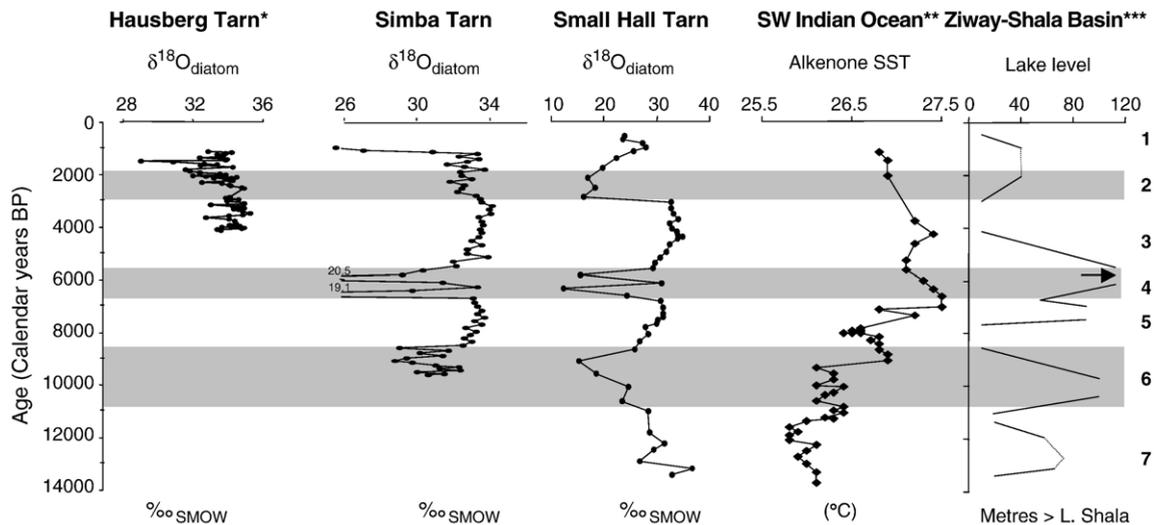
Fig. 14. Diatom silica is especially useful in acidic lakes with no authigenic or biogenic carbonates. In three high-altitude, freshwater lakes on Mount Kenya, the oxygen isotope composition of biogenic silica is useful because the lake-water oxygen isotope composition records lake moisture balance. The diatom oxygen isotope data from Simba Tarn, Small Hall Tarn, and Hausberg Tarn (Mount Kenya) are compared to lake levels in the Ziway-Shala Basin, Ethiopia, derived from ^{14}C dated shorelines. Abrupt shifts of up to 18‰ in diatom silica are thought to represent lake moisture balance. Episodes of heavy convective precipitation dated ~11.1–8.6, 6.7–5.6, 2.9–1.9, and <1.3 thousand Cal BP, were linked to enhanced soil erosion, neoglacial ice advances, and forest expansion on Mt. Kenya. Numbers 1 to 7 down right hand margin refer to wet–dry phases. Zones 2, 4 and 6 refer to high lake levels. Reproduced with permission from Barker et al. (2001).

the Holocene, the authors looked at modern precipitation data to understand the variations in the curve. Modern records of the isotope composition of precipitation in the Kenyan Highlands show the most negative isotope values occurring during the wet season, suggesting that rainfall amount has a controlling influence on $\delta^{18}O$. During wetter intervals in the past, the mean isotope values of lake water would have been lowered by increases in precipitation and decreased evaporation and possibly by lake overflow. Barker et al. (2001) suggest that lake moisture balance best explains Holocene variations in $\delta^{18}O$, and that the sedimentary record from Mount Kenya shows episodes of heavy convective precipitation that are linked to enhanced soil erosion, neoglacial ice advances, and vegetation changes on Mount Kenya. Elsewhere on the mountain, Rietti-Shati et al. (1998) based their $\delta^{18}O_{diatom}$ interpretation of changes during the last 4 ka in a lake at the terminus of the Hausberg glacier as primarily resulting from temperature changes and inferred shifts of up to 6 °C during this period.

4.2.2. Changes in the source or at the source of precipitation (δP)

There have been several studies of $\delta^{18}O_{diatom}$ from lakes in Northern Europe. These lakes have similarities, in that many are open, through-flow systems with minimal evaporation. Changes in the stratigraphic re-

cord of $\delta^{18}O_{diatom}$ are interpreted as changes in the summer isotope composition of the lake water. In a pro-glacial lake covering the last 5000 yrs in Northern Sweden, a $\delta^{18}O_{diatom}$ record combined with a sedimentary proxy for glacier fluctuations reflects changes in the isotope composition of summer precipitation (Rosqvist et al., 2004). They found a general lowering trend of 3.5‰ with spikes (>1‰) to lower values on a c. 1000-yr cyclicity. Climate simultaneously sustained a positive glacier mass balance, that caused the catchment glacier to advance. The authors suggest that a persistent change in the atmospheric circulation pattern could potentially have caused the changes in $\delta^{18}O_{diatom}$ because different air masses influence this area and these air masses have characteristic $\delta^{18}O$ signatures of their precipitation. They infer a steady increase but fluctuating dominance of colder and $\delta^{18}O$-depleted air masses from the north/northeast. The $\delta^{18}O_{diatom}$ depletion and glacier events occur at times of relative ice-rafted-debris maxima in the North Atlantic, consistent with cold conditions and changes in surface wind directions (Fig. 15). A second $\delta^{18}O_{diatom}$ record from Swedish Lapland from a non glacial lake in the Abisko region was also interpreted in terms of changes in the summer isotope composition of the lake water. The overall +3.5‰ lowering of $\delta^{18}O_{diatom}$ from the early Holocene is thought to represent an increasing influence of the Arctic polar continental air mass
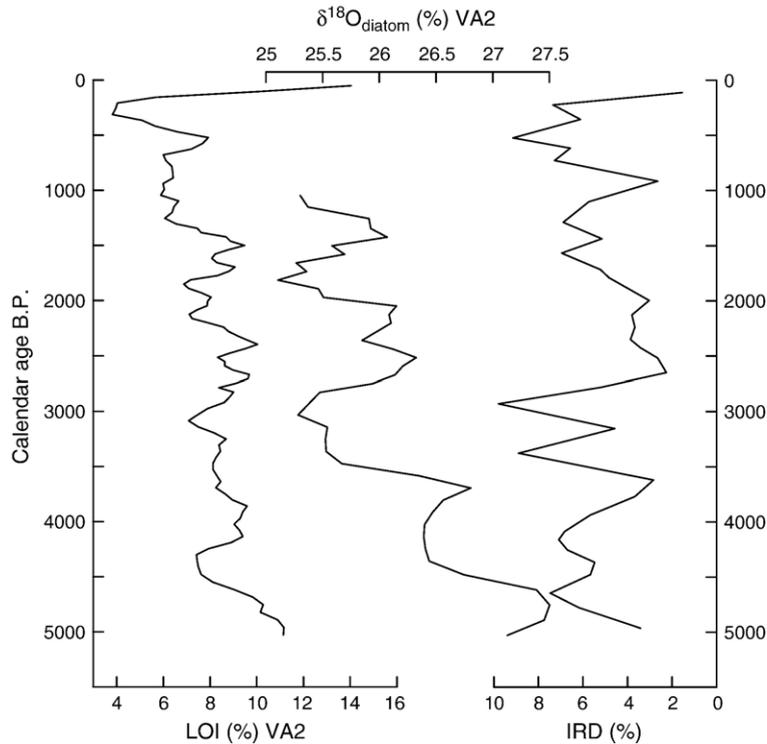
Fig. 15. In a pro-glacial lake covering the last 5000 years in Northern Sweden, the oxygen isotope record of diatom silica ($\delta^{18}O_{diatom}$), combined with a sedimentary proxy for glacier fluctuations, reflects changes in the isotope composition of summer precipitation. The $\delta^{18}O_{diatom}$ depletion and glacier events occur at times of relative ice-rafted-debris maxima in the North Atlantic. Reproduced with permission from Rosqvist et al. (2004).

that has lower $\delta^{18}O_{precipitation}$ compared to rain derived from the Atlantic (Shemesh et al., 2001a,b). A third site on the Kola Peninsula in NW Russia has recently been analysed for $\delta^{18}O_{diatom}$ through the Holocene (Jones et al., 2004). Lake Chuna is a through-flow lake and the $\delta^{18}O_{diatom}$ is thought to record the predominance of polar Arctic air masses bringing relatively cold summer air temperatures immediately after the last glaciation and again after 4000 cal. BP to the present time. Here the Atlantic maritime air mass is thought to have supplied relatively warm summer rainfall especially around the mid-Holocene. These conclusions are supported by vegetation changes using pollen (Jones et al., 2004). In particular, after c. 8000 cal. BP, the $\delta^{18}O_{diatom}$ results suggest that the summer contribution of warmer Atlantic air had increased and this is consistent with the Holocene temperature optimum (to 5500 cal. BP) shown by the pollen record. Both the $\delta^{18}O_{diatom}$ and pollen reconstructions show an abrupt event after at 4700 cal. BP. The $\delta^{18}O_{diatom}$ event at c. 4700 cal. BP is associated with catchment erosion and probably high precipitation while the pollen reconstruction shows a sharp decrease in temperature and a gradual increase in

precipitation over this period. Both isotopes and pollen show lower temperatures from c. 4000 cal. BP onwards, reflecting an increase in the influence of colder summer Arctic air. Overall, the Kola and Lapland studies show some similarities in the diatom isotope records, in particular a late-Holocene cooling, although there are regional differences; notably the relatively cold early Holocene is not seen in the records from Northern Sweden.

Changes in the source of precipitation have also been suggested as one reason for variations in $\delta^{18}O_{diatom}$ in a small, spring fed lake in the Central Mexican highlands (Leng et al., 2005b). The lake has shallowed, and today is at one of its lowest lake levels, but the modern isotope data suggest that the modern water is not evaporated, indicating that hydrology or recharge rates, rather than evaporation are controlling lake level. Two main possibilities might have controlled variations in $\delta^{18}O$ in the past. Since Central Mexico gets rainfall that originates from the tropical Atlantic/Gulf of Mexico and also from both the tropical and extra-tropical Pacific (in summer and winter, respectively), the authors postulate that changes in $\delta^{18}O_{precipitation}$ are connected to temperature and salinity variations in the

Gulf of Mexico and/or changing contributions from these two different air masses (Gulf of Mexico vs. Pacific-derived hurricanes). However, this is a good example of where it is difficult to identify the controls on $\delta^{18}O_{diatom}$. For example, it is difficult to correlate $\delta^{18}O_{diatom}$ changes with evidence for changes in the Gulf of Mexico because of the limited dating control for these sediments compared to the marine sediments. It is also impossible to relate $\delta^{18}O_{diatom}$ to changes in the Pacific hurricane frequency, because there are no comparable records.

5. Vital effects

Disequilibrium effects (Fig. 1) (commonly known as 'vital' effects in the case of biogenic carbonates) include a variety of rate effects and micro-environment induced changes that cause the mineral to have an isotope composition that is different from that predicted purely by thermodynamics (cf., Holmes and Chivas, 2002 show a table of ostracod species effects). In one of the earliest studies of lacustrine $\delta^{18}O_{diatom}$, Binz (1987) found little difference in fractionation between three cultured diatoms. Shemesh et al. (2001a,b, and references therein) states that marine diatoms do not exhibit an isotope species effect and that species effects have not been observed in freshwater diatoms. Brandriss et al. (1998) suggest that species fractionations may explain some of the variations in multi-specific phytoplankton assemblages described by Juillet-Leclerc and Labeyrie (1987). Indeed, from a rather limited data set, Brandriss et al. (1998, their Table 5) show a small species-dependent fractionation in two species of cultured diatoms. Shemesh et al. (1995) analysed two different size fractions of a diatom sample in which species abundances varied, they found only a variation of 0.2‰, which is within typical analytical error of fluorination techniques. Schmidt et al. (2001) in culturing experiments showed that marine diatoms grown at constant temperatures showed little isotope variation. They explained the variation in terms of the growth stage and speed of bloom of the diatom. The integration of diatoms that occurs within a sediment sample would offset considerations of growth rate. Because lacustrine diatoms are physically difficult to separate into species, bulk samples are normally analysed for $\delta^{18}O_{diatom}$. There are no studies which show consistent stratigraphical similarities between diatom species changes and $\delta^{18}O_{diatom}$ changes leading most authors to suggest that variations due to different vital effects are smaller than the overall analytical error (e.g., Leng et al., 2001).

6. Comparison between carbonate and diatom silica records

Combining isotope analysis of different authigenic minerals offers the possibility of obtaining seasonally specific information. For example, where carbonates and diatom silica co-occur they may provide different, yet complementary, oxygen isotope signatures weighted by different seasonal biological productivities. This has been undertaken in the marine environment, and a recent example from the NW Pacific showed that combining $\delta^{18}O$ from foraminifera and diatoms provided inter seasonal ocean water temperatures. Different responses in the two data sets across the onset of the Northern Hemisphere Glaciation boundary (2.7 Ma) help unravel the trigger. The onset of a halocline and an increase in sea surface temperatures, which enabled an adequate supply of moisture to the North American ice sheets in the summer months, are recorded in $\delta^{18}O_{diatom}$ while $\delta^{18}O_{foram}$ record cooler conditions in the late winter/early spring (Haug et al., 2005).

In the lacustrine environment, the information that can be obtained from multi-isotope analysis is dependent on both season of precipitation/formation and the hydrology of the lake. In most temperate regions, planktonic diatom production follows a well-defined seasonal cycle, peaking first in the spring and then in autumn (Reynolds, 1984), although some diatom species can grow from spring to autumn. In low-latitude lakes, higher temperatures can encourage diatoms to grow throughout the year, although other mechanisms may control algal blooms such as lake-water mixing and nutrient availability (Kifle and Belay, 1990). In some lakes, species specific blooms can also occur at different times of year (Raubitschek et al., 1999) and in different parts of large lakes (e.g., Lake Baikal, A. Mackay, personal communication, 2005). Knowledge of species ecology is vital in deriving accurate interpretation of the diatom isotope signal. Oxygen isotope data from diatoms will contain components of different seasonal growth, but bulk analysis will be weighted towards the major growth periods. Biogenic carbonate (ostracods, mollusc) will also be weighted towards ecological preferences (Holmes and Chivas, 2002), although authigenic calcite precipitation mainly occurs when nutrient availability, enhanced light regime and warmer temperatures contribute to enhanced algal productivity (Reynolds, 1984). In temperate areas with strong seasonality, authigenic calcite production and its isotope signature will usually be weighted toward summer conditions. Therefore, depending on the period of diatom growth, a comparison of $\delta^{18}O_{calcite}$ and

$\delta^{18}O_{diatom}$ may provide information on seasonality (i.e., spring to summer). A comparison of the $\delta^{18}O$ of calcite (summer) and diatom silica (predominantly spring) in a small, open groundwater fed lake in Turkey shows differences in the two $\delta^{18}O$ curves and confirms diatom silica will not always provide a direct substitute for carbonate based analysis in acid lakes (Fig. 16). In this case, the strong seasonality probably caused authigenic calcite precipitation to be temporally limited to a few summer months while the diatom silica was limited to early spring due to enhanced nutrient supply brought in by the spring thaw of winter snow. Therefore, changes in summer temperatures are thought to be mainly recorded by the calcite record, whereas different amounts of snowmelt in the spring are thought to influence the diatom record (Leng et al., 2001). In

contrast, in Lake Tilo in the Ethiopian Rift Valley (described earlier), Lamb et al. (2005) showed that the $\delta^{18}O_{diatom}$ and $\delta^{18}O_{calcite}$ records from the early Holocene are similar and thus the minerals provide a suitable alternative proxy for each other. However, this study highlights the larger errors associated with $\delta^{18}O_{diatom}$ and all the information from $\delta^{18}O_{calcite}$ may not been seen in $\delta^{18}O_{diatom}$.

7. Summary

Analysis of the oxygen isotope composition of diatom silica requires samples that are almost pure diatomite since fluorination and other analytical techniques will liberate oxygen from all the components in the sediment. There is a generally acceptable protocol in-
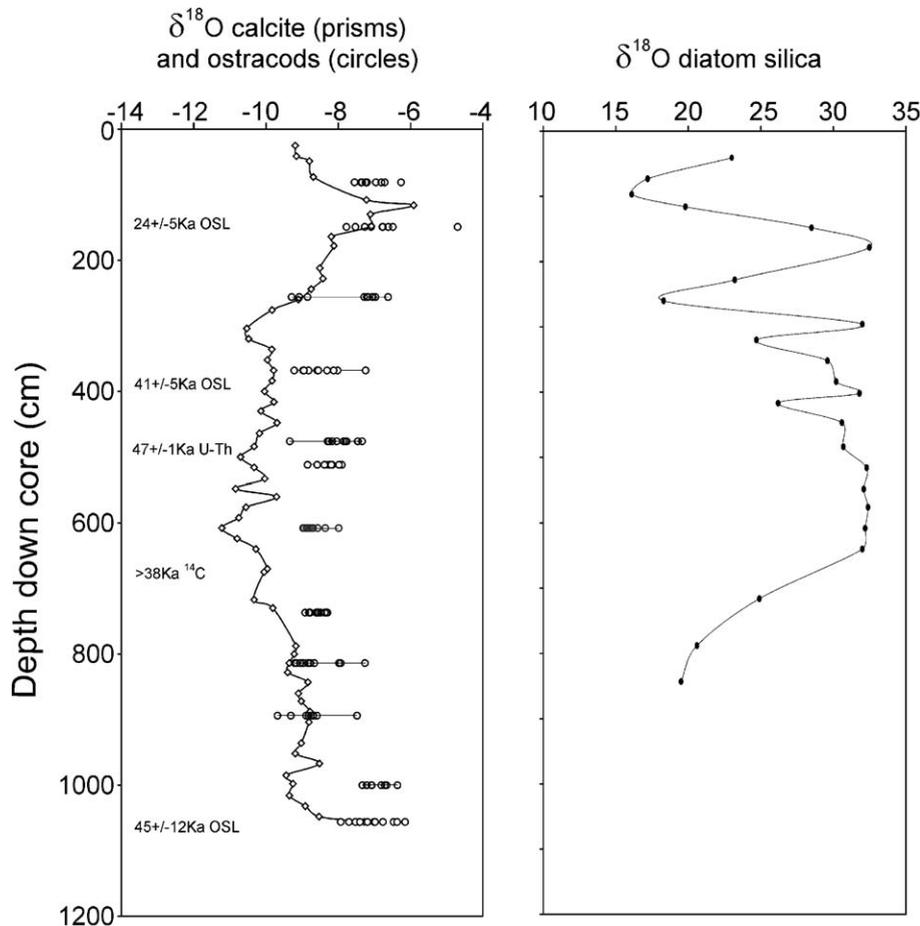
Fig. 16. Comparing isotope data from authigenic and ostracod carbonate and diatom silica from a small, hydrologically open, high-altitude lake in southern Turkey. Authigenic and ostracod carbonates are thought to precipitate in the summer months, while the diatoms are thought to grow predominately in the spring months. The strong seasonality (spring–summer) of this region allows the materials to capture different climatic conditions. The dating control is relatively poor, but the data seems to show that the warmer interglacial summers in the calcite record correspond to enhanced amounts of snow melt in the spring seen in parts of the diatom record. In the glacial, cooler summer months are associated with arid winters with little snow. Modified from Leng et al. (2001).

volving chemistry, sieving and settling techniques and more recently laminar flow separation. However, all lakes require a dedicated procedure and every sample must be scrutinised with microscopy. Where sediments cannot be purified sufficiently, a semi-quantitative assessment of the diatom content can facilitate mass balance techniques.

Diatom silica is comprised of an inner tetrahedrally bonded silica skeleton (Si–O–Si) with an outer, hydrous layer. The hydrous layer is freely exchangeable and must be removed prior to oxygen isotope measurement. To date there are three main methods to do this. These are vacuum dehydration, isotope exchange and stepped fluorination techniques. A comparison of the controlled isotope exchange (CIE) and stepwise fluorination (SWF) methods showed that both yield good results although the SWF method may also eliminate some very fine fraction clays remaining in the sample. With the CIE method, there is the potential that not all exchangeable oxygen reacts completely, especially for fresh sediments, where the proportion of hydrous silica is high. Future inter-laboratory comparisons are needed to test these methodologies.

In lake studies, it is often assumed, but not proven, that diatom silica (and carbonates) form in isotope equilibrium and hence palaeotemperature equations can be used. However, all studies to date using $\delta^{18}O_{diatom}$ lack the detailed investigation of contemporaneous materials to prove this. Ideally, any palaeoclimate study of $\delta^{18}O_{diatom}$ from a lacustrine sequence should include a study of the contemporary lake water and the modern diatom silica. As in other uses of isotopes as a 'palaeothermometer', regional regression lines, or ones relevant to subsets of lakes might be required. The presence of a systematic relationship between temperature, water isotope composition and diatom isotope composition for the modern lake enables quantitative interpretation of the sediment record. It is particularly useful to know when and where the diatom silica 'bloom' in the modern environment, so details of diatom ecology are important. This type of information will tell us whether the diatom record reflects specific seasons or year round conditions. A calibration may not be feasible, especially in isolated geographical regions. Where such a calibration is not possible assumptions have to be made based on evidence from both a multi-proxy approach using isotope signals from different materials as well as using other palaeolimnological techniques.

This review has aimed at showing that useful palaeoenvironmental data can be gained from $\delta^{18}O_{diatom}$, especially since diatoms are abundant in the type of lakes that are sensitive to climate variation. However, the relationship between temperature and δp still has considerable uncertainties. It is usually very difficult to derive quantitative palaeotemperature data with any certainty apart from over major climatic boundaries. It might be more realistic to use $\delta^{18}O_{diatom}$ in areas where there are likely to have been large changes in the isotope composition of the lake water due to changes in the precipitation/evaporation balance or in the source of precipitation. The change in $\delta^{18}O_{diatom}$ due to these factors is normally greater than temperature and the range of values obtained is often far greater than methodological errors.

Acknowledgements

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