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A review of diatom $\delta^{18}O$ in palaeoceanography

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Abstract

Measurements of diatom oxygen isotopes ($\delta^{18}O_{diatom}$) hold the potential to provide an important additional source of palaeoceanographic information in regions depleted in carbonates. However, despite analyses of $\delta^{18}O_{diatom}$ being carried out since the 1970's and the increasingly widespread use of $\delta^{18}O_{diatom}$ in palaeolimnology since the 1990's, to date only a handful of studies have applied $\delta^{18}O_{diatom}$ in marine reconstructions. Here the historical development and current state of affairs concerning the usage of $\delta^{18}O_{diatom}$ in palaeoceanography is reviewed. This includes a summary of:

1. sample purification and analytical techniques for $\delta^{18}O_{diatom}$;
2. existing palaeoceanographic reconstructions with an emphasis on sites at which both diatoms and foraminifera have been analysed for $\delta^{18}O$;
3. uncertainties associated with $\delta^{18}O_{diatom}$ including the presence of isotope vital effects and secondary isotope exchanges;
4. a review of the current and future developments required to improve the reliability of $\delta^{18}O_{diatom}$ based reconstructions in palaeoceanography.

Keywords: opal, silica, oxygen isotopes, oceanography, paleoceanography

1. Introduction

One of the most widely used palaeoceanographic techniques is the oxygen isotope analysis of foraminifera ($\delta^{18}O_{foram}$), a $CaCO_3$ organism which fractionates oxygen either in equilibrium with the ambient seawater or with a known vital effect which can be quantitatively accounted for (e.g., Emiliani, 1955; Lisiecki and Raymo, 2007). Using $\delta^{18}O_{foram}$ in conjunction with other proxies it has proven possible to reconstruct, amongst other variables, changes in deep water formation, surface and bottom water temperature, salinity, global ice volume and water column stratification (e.g., Mulitza et al., 1997; Barrera and Johnson, 1999; Niebler et al., 1999; Ravelo and Andreasen 1999; Zachos et al., 2001; Simstich et al., 2003; Rohling et al., 2004). In particular, records of $\delta^{18}O_{foram}$ have enabled palaeoenvironmental reconstructions over both geological timescales (e.g.,

Zachos et al., 2001), as well as over shorter, millennial-scale, intervals such as those studies investigating Heinrich and Dansgaard-Oeschger events (e.g., Skinner et al., 2003). Similarly, the analysis of other isotopes in marine carbonates, including $\delta^{11}B$, $\delta^{13}C$ and $\delta^{15}N$, have allowed the reconstruction of other parameters including surface water pCO_2, ocean circulation, nutrient utilisation and palaeoproductivity (e.g., Duplessy et al., 1988; Kroon and Ganssen, 1989; Pearson and Palmer, 1999, 2000).

A significant caveat in the use of foraminifera and other carbonates in palaeoceanography is their scarcity or complete absence in sediment records for large sections of the globe, particularly in high latitude regions (Fig. 1). This is most notable in areas such as the North Pacific Ocean and the Southern Ocean, which are increasing viewed to be both sensitive to and potential drivers of global climatic change (e.g., Shackleton, 2000; Brzezinski et al., 2002; Galbraith et al., 2007). Fortunately cores extracted from these regions are often dominated by diatom microfossils, unicellular siliceous eukaryotic algae, which have been widely analysed through the use of transfer functions, taxonomy and bulk concentrations to reconstruct changes in Sea Surface Temperatures (SST), sea-ice extent and palaeoproductivity (e.g., Romero et al., 2003; Crosta et al., 2004; Gersonde et al., 2005; Kienast et al., 2006). Although these records have significantly improved our understanding of high latitude palaeoceanography (e.g., Bianchi and Gersonde, 2004; Kohfeld et al., 2005), it remains desirable to derive biogenic $\delta^{18}O$ records from these non-carbonate regions. One important reason for this is that the incorporation of palaeoenvironmental information is different for both isotope and non-isotope proxies. For example, as well as changes in palaeoceanographic conditions, fossil assemblages may also be affected by processes such as inter- and intra-species competition, migration, dissolution and taxonomic evolution. Furthermore, any reconstruction may also be dependent on the mathematical uncertainties associated with the use of transfer functions (e.g., Birks, 1998; Telford et al., 2004; Telford and Birks, 2005). In contrast, the $\delta^{18}O$ signal of biogenic material is generally a direct function of both local and global changes in temperature, mineralisation/calcification processes, habitat, global ice volume and other regional/local processes (Hoefs, 1997; Criss, 1999; Rohling and Cooke, 1999). While it is not possible to state that any one approach, isotope or species analysis, is superior, the notably different mechanisms and uncertainties behind these techniques makes it possible to minimise the errors of any reconstruction if both are used together in a multi-proxy study. In addition, the availability of non-carbonate $\delta^{18}O$ records in high latitude regions will complement existing carbonate $\delta^{18}O$ records from mid/low latitudes, allowing an increased comparison of environmental events over latitudinal gradients.

Recent years have witnessed considerable advancements in the development of techniques for analysing stable isotopes in biogenic silica, including $\delta^{13}C$, $\delta^{15}N$ and $\delta^{30}Si$ as well as $\delta^{18}O$ (e.g., De La Rocha, 2002; Robinson et al., 2004; Lücke et al., 2005; Leng and Sloane, 2008) The majority of $\delta^{18}O$ work, however, has focused on diatoms ($\delta^{18}O_{diatom}$). This is due to the $\delta^{18}O$ of other siliceous organisms being considerably less well understood. For example, evidence exists that radiolaria may become isotopically equilibrated with bottom waters over

long, millennial, timescales (Mopper and Garlick, 1971; Matheney and Knauth, 1989). Similarly, studies have found an absence of any significant systematic or thermodynamic isotope fractionation between siliceous sponges and the surrounding water (Matheney and Knauth, 1989). While the development and first applications of $\delta^{18}O_{diatom}$ as a palaeoenvironmental proxy occurred in marine systems in the 1970's, in recent years $\delta^{18}O_{diatom}$ has been almost solely applied in lacustrine systems (see review in Leng and Barker, 2006). Here, we review the historical development and current state of $\delta^{18}O_{diatom}$ in palaeoceanography. We first describe the isotopic structure of diatom frustules before examining the methodological and analytical techniques for $\delta^{18}O_{diatom}$. Subsequently we describe existing palaeoceanographic reconstructions using $\delta^{18}O_{diatom}$ with an emphasis on studies in which $\delta^{18}O_{diatom}$ and $\delta^{18}O_{foram}$ have been analysed together from the same core. The current uncertainties and limitations of $\delta^{18}O_{diatom}$ are then described together with the future directions that are required in order to further develop $\delta^{18}O_{diatom}$ and it usage in palaeoceanographic reconstructions. As increasing numbers of laboratories set up facilities to analyse $\delta^{18}O_{diatom}$, we hope that this review will re-focus attention on the potential that exists in using $\delta^{18}O_{diatom}$ in palaeoceanography.

2. Oxygen isotope composition of diatom frustules

All silicates, including diatom silica, are composed of silica tetrahedrons. Following the uptake and fractionation of oxygen, covalent -Si-O-Si bonds are formed in the diatom frustule through the condensation of two Si-OH groups to form $(SiO_2)_n$:

$$\text{-Si-OH + -Si-OH} \rightarrow \text{-Si-O-Si + } H_2O \qquad \text{(Eq. 1)}$$

Within the centre of the diatom frustule the -Si-O-Si bonds form an isotopically homogeneous dense layer of silica, the $\delta^{18}O$ of which is assumed to reflect the $\delta^{18}O$ of the water in which the silica precipitated at a given temperature (Julliet, 1980a,b) (Fig. 2). Similar to $\delta^{18}O_{foram}$, measurements of $\delta^{18}O_{diatom}$ therefore reflect the isotopic composition of the ambient seawater ($\delta^{18}O_{water}$), which is a function of changes in global ice volume ($\delta^{18}O_{GIV}$) as well as local changes in evaporation, freshwater inputs, salinity and changes in water mass or ocean circulation ($\delta^{18}O_{local}$), the temperature of the water in which the diatom is precipitated (δ_T) and the presence of any isotope vital effects that may exist in diatoms. An important distinction between $\delta^{18}O_{diatom}$ and $\delta^{18}O_{foram}$ is that $\delta^{18}O_{diatom}$ should only be representative of changes in the photic zone of the water column due to the need for diatoms to photosynthesise. In contrast, planktonic $\delta^{18}O_{foram}$ is often derived from taxa living at much more variable water depths, both inside and outside of the photic zone whilst benthic $\delta^{18}O_{foram}$ is reflective of deep/bottom water changes in $\delta^{18}O_{water}$, $\delta^{18}O_{GIV}$ and δ_T. By analysing $\delta^{18}O_{diatom}$, planktonic $\delta^{18}O_{foram}$ and benthic $\delta^{18}O_{foram}$ in conjunction with each other, the opportunity therefore exists to obtain detailed insights into the vertical structure of the water column, particularly over periods of abrupt change such as onset of glaciations and terminations.

Around the tetrahedrally bonded -Si-O-Si layer of the diatom frustule, a series of loosely bonded -Si-O species exist which rapidly exchange with water in the photic zone after silica precipitation to form a -Si-OH molecule (Fig. 2) (Labeyrie and Juillet, 1982; Fröhlich, 1989). This less dense, hydrous, layer of the frustule represents a notable problem for analysing $\delta^{18}O_{diatom}$. Although the assumption is that the $\delta^{18}O$ composition of both the -Si-O-Si and -Si-OH molecules will be identical in the photic zone during a diatoms life cycle, the relatively high porosity of diatoms (Lewin, 1961; Hurd et al., 1979, 1981) results in continual exchange between the -Si-OH layer and any water the frustule is exposed to both during and after sedimentation. As such, the $\delta^{18}O$ composition of the Si-OH layer at the point of isotope analysis will reflect a combination of dehydroxylation and hydroxylation isotope exchanges with sediment pore water, laboratory water used during sample preparation and atmospheric moisture. Results indicate that between 7% and 40% of all the oxygen in a diatom frustule may originate post depositionally (Knauth, 1973; Labeyrie, 1979; Labeyrie and Juillet, 1982; Leng et al., 2001; Leng and Sloane, 2008; Swann et al., 2008). To date, the presence of such a large degree of variability in -Si-OH layer thickness remains unexplained. While it is well established that the porosity of diatoms, and so the amount of -Si-OH bonds, decreases in response to dissolution over long (>5-10 Ma) timescales (Hurd et al., 1981), this does not explain why such large variability is observed in well preserved frustules over more recent (0-5 Ma) periods. One possible, as yet unconfirmed, explanation is that the relative size of the -Si-OH layer varies between and/or within individual taxa in line with changes in the surface area, morphology and size of the diatom frustule (Swann et al., 2008). However, provided that the -Si-OH layer is fully removed/accounted for, such issues do not affect the application of $\delta^{18}O_{diatom}$ in palaeoceanography. In the sections below the methodologies for completing this prior to analysing the $\delta^{18}O$ of the -Si-O-Si layer are described.

3. Methods

3.1. Bulk extraction and cleaning of diatom frustules

A key pre-requisite of diatom isotope analysis is the necessity of ensuring that samples are free from all sources of non-diatom contamination as most contaminants contain oxygen and/or will interfere in the isotope analysis. Existing work has demonstrated $\delta^{18}O_{diatom}$ to be highly sensitive to the level of non-diatom material within the sample, particularly when sample purity falls below 90% (Morley et al., 2004). Obtaining pure diatom material can be challenging with diatoms intermixed with similar sized silt, clay (common in Ice Rafted Debris [IRD]), tephra, carbonates and organic matter (Fig. 3). To remove these "contaminants", a number of clean-up methodologies have been used, each involving a series of chemical and physical preparation stages (e.g., Juillet-Leclerc, 1986; Shemesh et al., 1995; Morley et al., 2004; Rings et al., 2004; Swann et al., 2006; Tyler et al., 2007). These generally involve the use of HCl to remove carbonates and disaggregate the sediment before prolonged digestion with H_2O_2 and/or HNO_3 to remove organic matter attached to the frustule. The removal of organic material can be complemented by heating the samples in air at up to 550°C (Tyler et al., 2007). Clay, silts and other remaining contaminants are then separated by sieving at a size fraction of ≥ 10 μm, the exact size

of which can be adjusted according to the size of the diatom frustules and contaminants in the sediment assemblage. A number of studies have also reported using HF as well as alkaline solutions such as $KMnO_4$, NaF and $(NaPO_3)_6$ in order to "etch" diatoms and so further remove any contaminants, in particular clays and tephra, which may be adhering to the frustule by electrostatic charge. However, caution should be applied in using any reagent which has the potential to cause any dissolution to the frustule due to the risk of isotopic fractionation in the -Si-O-Si layer. Although the exact extent to which individual chemicals can alter $\delta^{18}O_{diatom}$ remains unknown, a small-scale study carried out by Moschen et al. (2006) indicates that these processes can result in isotopic alterations of up to c. 7‰ if the organic coating around the diatom frustule is absent/removed. Further work is therefore required into the detrimental effects of individual chemicals and length of digestion period on $\delta^{18}O_{diatom}$.

In addition to any chemical dissolution and physical separation, the clean-up procedure can be further complemented by the use of settling techniques involving water or a heavy liquid such as sodium polytungstate (SPT) (see Morley et al., 2004). In the later, samples are mixed with SPT and then centrifuged at 2,500 rpm at specific gravities ranging from c. 2.10-2.25 g/ml for up to 20 minutes. In addition, or as an alternative to the use of a heavy liquid, a gravitational split-flow thin fractionation (SPLITT) can be employed to separate particles of different densities, and consequently diatoms from contaminants, in a laminar flow [see Giddings (1985); Rings et al. (2004) and method description in Leng and Barker (2006)]. The improvement achieved with each individual clean-up stage in improving the quality of the $\delta^{18}O_{diatom}$ signal was first quantified by Morley et al. (2004). Although conducted on lacustrine samples from Lake Baikal (Russia) and Lochnagar (Scotland) the results remain relevant for marine samples and highlight the progressive increase in $\delta^{18}O_{diatom}$ as contaminants are removed and the concentration of isotopically heavy diatom frustules increases. Based on our own observations as well as those of others, however, it is apparent that no single method is suitable for all sediment samples. Instead, the clean-up methodology should be adapted to fit each set of samples with the optimal procedure usually found by a combination of trial and error using the various techniques described above combined with microscopy observations at each stage.

3.2. Extraction of species-specific taxa

In addition to the need to fully clean/purify samples before isotope analysis, consideration should also be given to the modern and palaeoenvironmental conditions occupied by individual taxa. In instances where analysed samples contain a large number of taxa, or even where samples are comprised of a single taxa, a habitat or seasonality effect may exist in measurements of $\delta^{18}O_{diatom}$. A habitat/seasonality effect is defined here as an $\delta^{18}O_{diatom}$ offset either within or between individual taxa which occurs despite diatom isotope fractionation occurring in equilibrium with the surrounding water. A habitat effect refers to the different depth habitats in the water column at which a taxa may bloom and consequently the different conditions and $\delta^{18}O_{water}$ encountered at these depths, the signals of which will be incorporated into an organism during calcification/silicification.

Within foraminifera, habitat effects most commonly arise from the different depths individual taxa live at, or from the significant vertical migration which an organism may undertake through the water column at different stages in their life cycle (Sautter and Thunell, 1991). In marine systems any diatom based habitat effect is likely to be significantly smaller than that occurring in foraminifera due to the need for diatoms to bloom in the photic zone close to the surface. As such, the possibility of a habitat effect has generally been ignored in previous $\delta^{18}O_{diatom}$ studies, particularly in marine systems where photic zone variations in temperature and $\delta^{18}O_{water}$ are often assumed to be small. This may be unwise given that photic zone depths can at many sites extend down to c. 100 m; depths which can display markedly different $\delta^{18}O_{water}$ and environmental conditions relative to those present at the surface (Schmidt et al., 1999; Antonov et al., 2006; Locarnini et al., 2006).

A seasonality effect refers to instance where individual species bloom in different seasons e.g., spring and autumn, at a single location. With each season possibly marked by different environmental conditions and $\delta^{18}O_{water}$ values (e.g., due to changes in temperature or meltwater input), large inter-species offsets in $\delta^{18}O_{diatom}$ may exist between different taxa collected over a year. The issue of inter-species seasonality effects may be particularly prominent in diatoms due to analysed samples usually containing a mixture of taxa that bloom across different seasons (Raubitschek et al., 1999; Leng et al., 2001). However, even if a single species sample is successfully extracted, an intra-species seasonality effect may exist if that taxa also blooms across different seasons. As such, there is a high potential for $\delta^{18}O_{diatom}$ records to be distorted by bloom-signal dilution/seasonality effects, unless bloom specific samples can be obtained. Indeed, given that the temporal resolution of a single sample analysed for $\delta^{18}O_{diatom}$ may range from decades to centuries, consideration should also be given to the extent to which a taxa's habitat/seasonality may vary with time, for example in response to changes in climatic conditions, ocean circulation or nutrient availability.

Ideally, therefore, in order to ensure that records of $\delta^{18}O_{diatom}$ are entirely unaffected by seasonality/habitat effects, as well as any inter/intra-species vital effect (Section 5.4), $\delta^{18}O_{diatom}$ samples need to be comprised of a single taxa which primarily blooms within a single season. Although in some instances it has proven possible to create mono- or near mono-species specific samples using SPLITT, due to the different densities of individual taxa (Leng and Barker, 2006), or by sieving at different size fractions (e.g., Swann et al., 2006) in the majority of cases $\delta^{18}O_{diatom}$ data are derived from samples comprised of multiple species that may make a significant contribution to the isotope measurement. Whilst species-specific samples can be obtained with carbonates such as foraminifera by hand-picking samples, for diatoms this is generally not feasible due to static effects in addition to the smaller size of diatom frustules (usually c. 2-200 μm in diameter/length), which result in anywhere from a few hundred to several thousand individual frustules, depending on the volume and analytical technique employed, being required for a single analysis. Given this constraint, the potential of a seasonality/habitat effect being the dominant signal in any stratigraphical record should be assessed, for example by calculating the relative biovolume of individual tax within the analysed sample (see Hillebrand et

al., 1999). Although only a crude measure which fails to consider pore spaces, variations in -Si-OH layer thicknesses, voids and other irregulars in the frustule, biovolume measurements based on the final purified material provide an important step for accounting for size variations between and within individual taxa as well as assessing the relative contribution of each taxa to the $\delta^{18}O_{diatom}$ measurement. By combining this information in relation to modern day (and palaeo-) diatom habitats from the core location, the results provide a simple means for better understanding the origin of the $\delta^{18}O_{diatom}$ signal as well as checking for possible intra- and inter-species habitat/seasonality effects in $\delta^{18}O_{diatom}$ (e.g., Swann et al., 2007, 2008).

3.3. Contamination assessment

Despite the wide range of possible clean-up techniques (Section 3.1), Brewer et al. (2008) has shown that some samples may become impossible to fully purify due to contaminants becoming trapped within or electro-statically charge to the frustule. Furthermore while the use of heavy liquids, such as SPT, often enable the separation of diatoms from non-diatom material, in many cases the similar densities between diatoms and clays/silicates can prevent complete separation (ibid). This problem may be exacerbated in the marine environment by the presence of other siliceous organisms such as radiolarians, sponges or phytoliths, the $\delta^{18}O$ of which remains poorly understood (Mopper and Garlick, 1971; Matheney and Knauth, 1989; Webb and Longstaffe, 2003; Hodson et al., 2008).

In order to account for the possible impact of non-diatom contaminants on the measured $\delta^{18}O$ signal, it is necessary for the level of contamination to be individually assessed for each cleaned sample. In practice, however, few studies actually conduct any quantitative assessment of sample purity. Until recently most checks employed a point-counting methodology in which the sample is examined using a grid graticule on a light microscope in order to calculate the relative proportion of diatom to non-diatom material (Morley et al., 2004). Recent work, however, has shown that these techniques, while providing a useful indication of sample contamination, may be overly simplistic due to the absence of any consideration for diatom pore spaces, differences in biovolumes between diatoms and minerals/other contaminants and contaminants trapped within the diatom structure (Lamb et al., 2007; Brewer et al., 2008). Furthermore, since such measurements are derived from only a limited proportion of the purified material, point counting estimates of contamination may not be representative of the sample as a whole. Due to these limitation, Brewer et al. (2008) have suggested that more reliable estimates of contamination can be obtained by analysing the trace element geochemistry of purified samples, for example using Scanning Electron Microscope (SEM) plus Energy Dispersive X-ray Spectroscopy (EDS), X-ray Fluorescence (XRF) or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). By measuring the concentrations of compounds such as Al_2O_3 and CaO and comparing these to published diatom and clay minerals elemental concentrations, the relative proportion and type of residual contamination can be established across the sample being analysed (Lamb et al., 2007; Brewer et al., 2008). Regardless of whether a point-counting or geochemical method is used to check sample purity,

samples containing more than a few percent contamination should be re-cleaned. Where further cleaning does not improve the level of cleanliness, however, mass-balance corrections can be employed to correct for the effects of non-diatom contaminants following isotope analysis (Section 3.5).

3.4. Analysis of $\delta^{18}O_{diatom}$

Historically, $\delta^{18}O$ records from waters and silicates are quoted relative to V-SMOW (Vienna – Standard Mean Oceanic Water) rather than the V-PDB (Vienna – PeeDee Belemnite) which is used for reporting $\delta^{18}O$ from carbonates and organic matter (Gonfiantini, 1978, 1984; Coplen et al., 1983; Coplen, 1996). As described in Section 2, prior to analysis it is essential to remove or account for the -Si-OH layer of the diatom frustule when attempting to obtain environmental records from $\delta^{18}O_{diatom}$. Extraction of the -Si-OH layer however, which may require the removal of 7-40% of all oxygen within diatoms (Knauth, 1973; Labeyrie, 1979; Labeyrie and Juillet, 1982; Leng et al., 2001; Leng and Sloane, 2008; Swann et al., 2008), is technically challenging requiring specialised equipment, hazardous reagents and highly trained operators. Early attempts to remove the oxygen in the -Si-OH layer involved dehydrating samples under vacuum at 800-1000ºC with the molecules energised by the heating (Mopper and Garlick, 1971; Labeyrie, 1974, 1979). Although the vacuum dehydration method improved analytical reproducibility and accuracy, the $\delta^{18}O_{diatom}$ signal remained contaminated due to a small proportion of the exchangeable oxygen remaining in the frustule after dehydration (Labeyrie, 1979; Labeyrie and Juillet, 1980, 1982). At present, three reliable techniques have been established which fully account for the -Si-OH layer and permit palaeoenvironmental reconstructions from $\delta^{18}O_{diatom}$: Controlled Isotope Exchange (CIE) followed by fluorination (Labeyrie and Juillet, 1982; Juillet-Leclerc and Labeyrie, 1987), Stepwise Fluorination (SWF) (Haimson and Knauth 1983; Matheney and Knauth 1989) and inductive High-Temperature carbon Reduction (iHTR) (Lücke et al., 2005). The amount of diatom material required for each technique varies according to the employed methodology and its setup, whether the mass spectrometer is online or offline and, in theory, the relative size of the diatom -Si-OH layer. Typically between 1.5 mg and 6.5 mg of material is required for a single analysis, which is large compared to the 10-100 μg normally required for measuring $\delta^{18}O$ in foraminifera.

Under CIE, oxygen in the -Si-OH layer of the diatom is exchanged either once or twice with water containing a known $\delta^{18}O$ at 200ºC for six hours (Labeyrie and Juillet, 1982; Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1995; Crespin et al., 2008). After vacuum heating at 1000ºC to remove as much of the oxygen in the -Si-OH layer as possible, samples are reacted with a fluorine regent such as F_2, ClF_3 BrF_5 to dissociated the remaining oxygen within the diatom frustules before analysis using standard gas source Isotope Ratio Mass Spectrometry (IRMS) techniques. Mass-balance corrections are then applied to correct for any of the labelled water not removed under vacuum:

$$\delta^{18}O_{measured} = x\delta^{18}O_{water} + (1 - x)\ \delta^{18}O_{non\text{-}exch}$$

(Eq. 2)

where $\delta^{18}O_{measured}$ is the measured $\delta^{18}O$ of the sample after vacuum heating, $\delta^{18}O_{non\text{-}exch}$ is the $\delta^{18}O$ of the -Si-O-Si layer within the diatom, $\delta^{18}O_{water}$ is the $\delta^{18}O$ of the labelled water and *x* the fraction of oxygen exchanged. By varying the value of the $\delta^{18}O_{water}$ used in CIE, *x* can be calculated for a given temperature and exchange time as the gradient in a regression of $\delta^{18}O_{measured}$ against $\delta^{18}O_{water}$.

SWF techniques involve the use of a fluorine reagent to extract the oxygen from the different layers of the diatom frustule in separate stages, thereby avoiding contamination between the oxygen in the -Si-OH and -Si-O-Si layers (Haimson and Knauth, 1983; Thorliefson and Knauth, 1984; Matheney and Knauth, 1989). Using adaptations of the fluorination procedures established by Taylor and Epstein (1962) and Epstein and Taylor (1971), the -Si-OH layer is initially stripped away leaving behind the inner -Si-O-Si layer which contains the fossil $\delta^{18}O$ signal. Measurements of the oxygen released during this process indicate an increasing $\delta^{18}O$ signal with time, reflecting the progressive removal of the -Si-OH layer. Complete removal of the -Si-OH layer is subsequently reflected by a plateauing and development of constant $\delta^{18}O$ values, indicating that only the isotopically homogeneous -Si-O-Si layer remains unreacted (Haimson and Knauth, 1983; Matheney and Knauth, 1989; Leng et al., 2001). A second fluorination stage is subsequently used to liberate oxygen from the -Si-O-Si layer. A recent advancement in this method field is the development of a SWF technique which allows for the $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ signal to be collected simultaneously from the same sample (Leng and Sloane, 2008). Following liberation and collection of the oxygen, the silicon can be collected as a by-product of the fluorination reaction as SiF_4:

$$SiO_2 + BrF_5 \rightarrow O2 + SiF_4 + ...$$

(Eq. 3)

This is an important step given the large (milligrams) amounts of material normally required for $\delta^{18}O_{diatom}$ analysis and opens the possibility of combining information on surface water oceanographic and climate conditions ($\delta^{18}O_{diatom}$) with information on photic zone nutrient utilisation ($\delta^{30}Si_{diatom}$) (see De la Rocha (2006) for a review on $\delta^{30}Si_{diatom}$).

Whilst both CIE and SWF have produced comparable results, using either conventional furnace or laser heating, it has been suggested that measurements from CIE have to be calibrated against SWF due to concerns over incomplete oxygen exchanges between the -Si-OH layer and the labelled water under CIE (Schmidt et al., 1997). Such a process would result in contaminant oxygen from the -Si-OH layer, not accounted for in Equation 2, potentially remaining in the diatom during vacuum heating and isotope analyses. In contrast the SWF technique will remove all oxygen within the -Si-OH layer regardless of diatom size or age, although the timing of the pre-fluorination stage may need to be calibrated and adjusted by the operator to ensure complete removal of the -Si-OH layer (Leng and Barker, 2006). In addition, since the the first fluorination stage of the

SWF methodology will remove a proportion of any non-diatom contamination in the sample (Matheney and Knauth, 1989), the SWF method will provide $\delta^{18}O_{diatom}$ data that is less distorted by contamination when sample purity is below 100% (see also Section 3.5).

A significant problem of both the CIE and SWF techniques is the requirement for fluorine based oxidising reagents, which represent a notable problem for many institutions due to "health and safety" implications. However recently a new inductive High Temperature carbon Reduction (iHTR) method for analysing $\delta^{18}O_{diatom}$ was demonstrated, which eliminates the need for a fluorine based reagent (Lücke et al., 2005). In iHTR, diatoms are mixed with graphite and heated under vacuum to 850°C-1,050°C to volatilise any sample contaminants and remove the -Si-OH layer. Further heating of the sample to 1,550°C results in oxygen from the -Si-O-Si bonds being converted to CO for either continuous or offline mass spectrometry:

$$SiO_2 + 3C \rightarrow SiC + 2CO \quad \text{(Eq. 4)}$$

To date, iHTR has only been used in one laboratory with the method yet to be replicated elsewhere. However, given the potential for more precise $\delta^{18}O_{diatom}$ measurements, the absence of fluorine reagents and the use of continuous flow mass spectrometry to increase throughput, it is likely that the number of laboratories adopting the iHTR method to analyse $\delta^{18}O_{diatom}$, over more traditional fluorine-based methods, will increase with time. Whilst $\delta^{18}O_{diatom}$ can also be analysed using an ion microprobe, difficulties in obtaining the larger amounts of material required for this may limit the application of this technique (Alexandre *et al*., 2006). Regardless, though, of whether CIE, SWF or iHTR is used, it should be noted that the magnitude of analytical reproducibility for $\delta^{18}O_{diatom}$, ±0.2-0.5‰, compares unfavourable to that achieved with $\delta^{18}O$ analyses of carbonates (±0.05-0.10‰). This suggests that if diatom-temperature coefficients are as low as −0.2‰/°C (see Section 5.1) (Brandriss et al., 1998; Moschen et al., 2005), SST changes of up to 2.5°C may be undetectable in the sediment record.

3.5. Mass balance corrections

Given that values of $\delta^{18}O_{diatom}$ are typically very high (c. +30‰ to +45‰ for marine samples) whilst the $\delta^{18}O$ of contaminants such as clay ($\delta^{18}O_{contamination}$) are generally lower, the exact value will vary in line with the origin and composition of the contamination (Sheppard and Gilg, 1996), a very small amount of contamination can significantly distort the record of $\delta^{18}O_{diatom}$. For example, a sample containing 5% contamination will result in a 2‰ shift in measured $\delta^{18}O$ when $\delta^{18}O_{contamination}$ is +10‰ and true $\delta^{18}O_{diatom}$ is +30‰. Such an alteration is significantly greater than analytical reproducibility for $\delta^{18}O_{diatom}$ ±0.2-0.5‰) and is equivalent to a temperature change of 10°C when using a diatom-temperature coefficients of −0.2‰/°C (see Section 5.1). In instances where small amounts of contamination are present, the effects of contamination can be accounted for through mass balance corrections:

$$\delta^{18}O_{corrected} = \frac{\delta^{18}O_{measured} - \frac{\%\,Contamination}{100} \bullet \delta^{18}O_{contamination}}{\frac{\%\,Purity}{100}}$$

(Eq. 5)

where $\delta^{18}O_{corrected}$ is measured $\delta^{18}O$ corrected for contamination, $\delta^{18}O_{measured}$ the original $\delta^{18}O$ of the analysed sample and %Contamination and %Purity are the percentage of contamination and diatom material respectively within the analysed sample as assessed using either the point-counting or geochemical methods described in Section 3.3. The potential importance of mass-balance corrections is highlighted in Brewer et al. (2008) who applied XRF estimates of contamination to calculated $\delta^{18}O_{corrected}$ values for previously published $\delta^{18}O_{diatom}$ records from Lake Baikal, Russia (Morley et al., 2005) and Lake Tilo, Eithiopia (Lamb et al., 2007). Values of $\delta^{18}O_{corrected}$ at these sites vary significantly, both in terms of magnitude and even the direction of the isotope shift, from the original (uncorrected) $\delta^{18}O_{diatom}$ data (Fig. 4). Whilst based on lacustrine samples, the results are equally relevant to marine measurements of $\delta^{18}O_{diatom}$ and highlight the need to adequately account for non-diatom contamination in order to avoid erroneous palaeoenvironmental reconstructions. It should be noted, however, that obtaining accurate estimates of %Contamination and %Purity is not straight forward due to the absence of a standard method for their determination (see Section 3.3). Although the use of geochemical, as opposed to point-counting, methods are likely to reduce this uncertainty in future (c.f. Brewer et al., 2008), establishing accurate values of %Contamination and %Purity is not possible when using the SWF technique due to the small, but unknown, proportion of contamination removed during the first fluorination stage (Section 3.4).

4. Palaeoceanographic reconstructions

4.1. Pre-1990 vacuum dehydration studies

Prior to c. 1990, many palaeoceanographic studies analysing $\delta^{18}O_{diatom}$ were compromised by the difficulties in accounting for the contaminant oxygen within the -Si-OH layer of the diatom frustule (e.g., Labeyrie, 1974; Mikkelsen et al., 1978; Wang and Yeh, 1985). Despite this, changes in $\delta^{18}O_{diatom}$ within these vacuum dehydration studies do appear to provide meaningful palaeoceanographic reconstructions. For example, results from a box-core in the Eastern Equatorial Pacific Ocean indicate approximately similar magnitude changes between $\delta^{18}O_{diatom}$ and $\delta^{18}O_{foram}$ over the last 20 ka BP (Mikkelsen et al., 1978). Although differences exist between the magnitude and direction of change in the two records, such contrasts can be plausibly related to the different depth habitats and seasonal variations in the timing of individual diatom and foraminifera blooms within the water column. Similarly, Wang and Yeh (1985) analysed $\delta^{18}O_{diatom}$ at DSDP Site 480 in the Gulf of California. Results from this are again broadly coherent with changes in benthic $\delta^{18}O_{foram}$ measured in the uppermost sections of the core where foraminifera were preserved in the sediment record. By confirming that changes in $\delta^{18}O_{diatom}$ were primarily reflecting changes in $\delta^{18}O_{water}$, caused by alternations in global ice volume,

measurements of $\delta^{18}O_{diatom}$ aided in the development of a chronology and oxygen isotope stratigraphical back to Marine Isotope Stage 7 (Wang and Yeh, 1985). The fact that qualitative changes in $\delta^{18}O_{diatom}$ vary in line with other palaeoceanographic data should not be surprising within these early studies, despite the inability of vacuum dehydration to fully remove or account of the -Si-OH layer. The majority of the contaminant oxygen in the -Si-OH layer is likely to originate from laboratory water/chemicals. If the quantity and weighted averaged $\delta^{18}O$ of the contaminant oxygen incorporated into the -Si-OH layer during sample preparation can be assumed to be constant, together with the impact of vacuum dehydration on removing oxygen from the -Si-OH layer, then stratigraphical changes in $\delta^{18}O_{diatom}$ should be related to the $\delta^{18}O$ of the -Si-O-Si layer and so palaeoenvironmental change within the water column. However, ultimately the unknown impact of vacuum dehydration techniques on the -Si-OH layer makes it problematic to either use or infer the true potential of using $\delta^{18}O_{diatom}$ in palaeoceanography from these early studies.

4.2. Pre-1990 CIE studies

The first marine $\delta^{18}O_{diatom}$ studies unaffected by the presence of the -Si-OH layer occurred following the development of the CIE technique in the 1980's. Sancetta et al. (1985) related changes in $\delta^{18}O_{diatom}$ within the Bering Sea to shifts in the bulk sediment assemblage diatom flora in order to infer and distinguish between changes in SST and Sea Surface Salinity (SSS). By using these two records together, the large 5-10‰ variations in $\delta^{18}O_{diatom}$ were successfully constrained to reconstruct past changes in sea-ice history and meltwater events despite the absence of a foraminifera $\delta^{18}O$ record. Indeed, by using estimates from global records of benthic $\delta^{18}O_{foram}$ to account for changes in $\delta^{18}O_{GIV}$, measurements of $\delta^{18}O_{diatom}$ were shown to display a 1.85‰ increase in SST between the last glacial and the present day. Depending on the $\delta^{18}O_{diatom}$-temperature calibration, this equates to a change of 3.7-9.3ºC (see Section 5.1). However, given the presence of varying concentrations of individual taxa in these samples which are orientated to blooming in different seasons, it is uncertain to what extent change in $\delta^{18}O_{diatom}$ may reflect some form of seasonality effect.

Similarly, Juillet-Leclerc and Schrader (1987) used measurements of $\delta^{18}O_{diatom}$ in cores from the Gulf of California to investigate palaeoceanographic changes in the region that may be linked to past El Niño events over the last 3 ka BP. By using modern day oceanographic data to account for localised changes in $\delta^{18}O_{water}$ and assuming that the net contribution of changes in $\delta^{18}O_{GIV}$ are minimal over the time interval, records of $\delta^{18}O_{diatom}$ indicated changes in SST of up to 8ºC over the interval. In turn, and in conjunction with diatom taxonomic studies, unusually cold SST over the timeframe were interpreted to reflect changes in upwelling and upwelling intensity within the region, which could be tied to changes in atmospheric patterns related to the occurrence of El Niño events. Results from this, for example, make it clear that an enhanced period of upwelling and intensified trade winds in the North Pacific Ocean existed between 1.5 and 2.0 ka BP, suggesting a phase of reduced El Niño events. Further work at the same site covering the last century has revealed a strong relationship between changes in $\delta^{18}O_{diatom}$ and historical El Niño records with recent increases in the amplitude

of El Niño events accompanied by inferred increases in SST and decreases in upwelling intensity (Juillet-Leclerc et al. 1991).

4.3. Post-1990: diatom/foraminifera comparisons

Since the 1990's palaeoceanographic studies utilising records of $\delta^{18}O_{diatom}$ have shifted to sites where planktonic foraminifera are preserved in the sediment record, thereby allowing direct comparisons of $\delta^{18}O_{foram}$ and $\delta^{18}O_{diatom}$. Although the number of locations containing sufficient numbers of foraminifera and diatoms for isotope analysis is limited, such work permits a far greater range of variables to be reconstructed than could be reasonable achieved when using either isotope record on their own. This largely originates from the different positions that exist between diatoms and foraminifera in the water column. Diatoms, as a photosynthesising organism, are required to bloom and uptake both silica and oxygen within the photic zone within the uppermost section of the water column. Whilst the depth of the photic zone varies seasonally and spatially across the globe, photic zone depths typically extend down to a depth of c. 100 m. Indeed within this, diatoms are likely to be disproportionately distributed to focus on the uppermost few metres of the water column due to the increased light penetration at these depth. In contrast individual foraminifera taxa are likely to occupy a much larger range of depths within the water column. If the depth habitats of the analysed planktonic and benthic foraminifera and diatoms can be established, it becomes possible to reconstruct vertical changes in $\delta^{18}O$, similar to the more coarse comparisons that can be achieved from solely analysing planktonic and benthic $\delta^{18}O_{foram}$.

4.3.1. Southern Ocean

Analysing material from a core in the South Atlantic Ocean, Shemesh et al. (1992) combined $\delta^{18}O_{diatom}$ with planktonic $\delta^{18}O_{foram}$ (*Neogloboquadrina pachyderma* (dextral)) to reconstruct changes in surface $\delta^{18}O_{water}$ and SST over the last 30,000 years:

$$\Delta T = T_1 - T_2 = 3.85[(\delta^{18}O_{diatom2} - \delta^{18}O_{diatom1}) - (\delta^{18}O_{foram2} - \delta^{18}O_{foram1})] \quad \text{(Eq. 6)}$$

and

$$\Delta\delta^{18}O_{water} = \delta^{18}O_{water1} - \delta^{18}O_{water2} = 0.89[(\delta^{18}O_{diatom2} - \delta^{18}O_{diatom1}) - 1.9(\delta^{18}O_{foram2} - \delta^{18}O_{foram1})] \quad \text{(Eq. 7)}$$

where subscripts 1 and 2 refer to the lower and upper data points of the interval respectively. By combining the two records in this way, whole ocean variations in $\delta^{18}O_{water}$ related to changes in $\delta^{18}O_{GIV}$ were solved for without the need for benthic $\delta^{18}O_{foram}$ or $\delta^{18}O_{porewater}$. From this, Shemesh et al. (1992) reconstructed changes in SST and $\delta^{18}O_{water}$ with a 2.0ºC increase in SST observed over the glacial-Holocene transition and a concordant 1.2‰ decrease in $\delta^{18}O_{water}$.

Integrated within equations 6 and 7, however, is a $\delta^{18}O_{diatom}$-temperature calibration of c. 0.5‰/°C. The debate over the validity of this and other $\delta^{18}O_{diatom}$-temperature calibrations is described in detail in Section 5.1. In addition, a further assumption made within Equations 6 and 7 is that the incorporation of oxygen into both diatoms and foraminifera occurred in the same season and at the same water depth. Even if it is valid to assume that both organisms bloom in the same season, given the potentially different depth positions of diatoms and foraminifera within the water column, it seems reasonable to assume that the reconstructed values of SST and $\delta^{18}O_{water}$ in this study are indicative of the broad rather than specific direction of change. Evidence for this is supported by other cores from the Southern Ocean containing both diatoms and planktonic foraminifera. While records of $\delta^{18}O_{diatom}$ and planktonic $\delta^{18}O_{foram}$ at these sites capture large scale palaeoceanographic events, for example the Antarctica Cold Reversal (ACR) at c. 14.5 ka BP, the magnitude of change in planktonic $\delta^{18}O_{foram}$ is significantly more muted compared to $\delta^{18}O_{diatom}$ (Hodell et al., 2001; Shemesh et al., 2002). This has been interpreted to suggest that the analysed foraminifera (*N. pachyderma* (dextral)) resided outside of the surface water during intervals of increased meltwater influx and enhanced stratification that accompany events such as the ACR. Rather than being a limitation, the different depth habitats of these two organisms during these periods provides an insight into changes in $\delta^{18}O_{water}$ through the uppermost section of the water column both above and below any possible stratification boundary.

Subsequent work on the Southern Ocean has focused on interpreting the raw $\delta^{18}O_{diatom}$ data rather than deriving SST or any other quantitative palaeoenvironmental reconstructions. Results from the Atlantic Sector of the Southern Ocean, for example, have indicated a progressive lowering in $\delta^{18}O_{diatom}$ through the Holocene, on which are superimposed oscillations of c. 1‰ (Shemesh et al., 1995; 2002; Hodell et al., 2001). Analyses over longer timescales across three cores from the Atlantic and Indian sectors of the Southern Ocean south of the Polar front have also indicated periodic decreases in $\delta^{18}O_{diatom}$ of up to 2-3‰ during the last glacial (Shemesh et al., 1994). Relating such changes to glacial increases in SST contradicts other palaeotemperature records from the region, from diatom transfer functions and other palaeoceanographic data, which suggest that the oceans were much cooler relative to the modern day. Accordingly, these shorter timescale fluctuations in $\delta^{18}O_{diatom}$ have been attributed to periodic large meltwater influxes from icebergs and/or Antarctica (ibid). Measurements of $\delta^{18}O_{diatom}$ from a further core from the Atlantic Sector of the Southern Ocean where planktonic $\delta^{18}O_{foram}$ and the $\delta^{13}C$ and $\delta^{15}N$ of intrinsic organic matter within diatom frustules have also been analysed, has provided further insight into the significance of these Southern Ocean deviations in $\delta^{18}O_{diatom}$ over the last deglaciation and in particular the ACR, reiterating the sensitivity of the region to meltwater influxes originating from Antarctica (Shemesh et al., 2002). In order to investigate the occurrence of these events in greater detail, Shemesh et al. (1995) analysed a total of eight cores from the Atlantic Sector of the Southern Ocean over the last 430,000 years. Results from this document similar periodic decreases in $\delta^{18}O_{diatom}$ of up to c. 5‰ (Fig. 6). However, due to the low resolution nature of the $\delta^{18}O_{diatom}$ records at these sites, it is not currently possible to fully understand the timing, mechanism or implication of these meltwater releases from Antarctica: for example their

relationship to possible changes in the North Atlantic Ocean. However, the results provide an intriguing insight into possible changes in the Southern Ocean in near-polar regions where carbonates are not well preserved within the sediment record and should provide the focus of further research.

4.3.2. North West Pacific Ocean

Recent research has resulted in the analysis of $\delta^{18}O_{diatom}$ at ODP Site 882, situated in the high latitude waters of the North West Pacific Ocean were both planktonic and benthic foraminifera shells remain preserved in the sediment record. A notable event in the region is the documentation of an abrupt decrease in biogenic productivity at c. 2.73 Ma over the onset of major Northern Hemisphere Glaciation (NHG) when large ice-sheets began to develop across Eurasia and the North American continent (Haug et al., 1999, Sigman et al., 2004). In order to provide further insights into the nature and palaeoenvironmental significance of these changes, measurements of $\delta^{18}O_{diatom}$ were analysed in conjunction with U^{k}_{37} inferred estimates of SST (Haug et al., 2005; Swann et al., 2006). In conjunction with existing proxy records including planktonic and benthic $\delta^{18}O_{foram}$, bulk sediment $\delta^{15}N$, opal concentrations and magnetic susceptibility, these results confirmed that the region underwent a significant transition over the onset of major NHG. In particular, the combined evidence of a significant decrease in productivity (opal and bulk sediment $\delta^{15}N$), increase in SST (U^{k}_{37}), IRD (magnetic susceptibility) and freshwater input to the region ($\delta^{18}O_{diatom}$) confirmed the development of a halocline (salinity) driven stratification system marked by unusually fresh and warm surface waters overlying much cooler and saltier deep waters (Fig. 7). In turn, this evidence was used to suggest that the North West Pacific Ocean may have acted as an important source of moisture for the advancing ice sheets across North America (ibid).

One unusual feature of this multi-proxy record is the divergent nature of the planktonic $\delta^{18}O_{foram}$ and $\delta^{18}O_{diatom}$ records (Fig. 7). Whereas $\delta^{18}O_{diatom}$ decreases by 4.6‰ from 2.73 Ma, indicating both fresher and warmer waters in line with U^{k}_{37} inferred SST (Haug et al., 2005; Swann et al., 2006), planktonic $\delta^{18}O_{foram}$ increases by 2.6‰, indicating a large decrease in SST (Maslin et al., 1995, 1996). However, whilst the U^{k}_{37} and $\delta^{18}O_{diatom}$ are derived from taxa which live in the stratified photic zone during the autumn/winter months, the analysed foraminifera (*Globigerina bulloides* and *N. pachyderma* (dextral)) are likely to be indicating conditions during the spring months at depths below the halocline (see discuss in Swann et al., 2006). As such, whereas the uppermost parts of the water column in the North West Pacific Ocean became warmer over the onset of major NHG, sub-surface waters immediately below the stratification boundary became significantly cooler: reflecting the climatic cooling observed in other marine cores over this timeframe (e.g., Mudelsee and Raymo, 2005 and reference within).

This anomaly highlights an important advantage in analysing, where possible, both $\delta^{18}O_{diatom}$ as well as planktonic and benthic $\delta^{18}O_{foram}$. Provided that the temporal and depth habitat of each taxa can be estimated from modern day studies and be assumed to be representative of past conditions, it becomes possible to obtain a

detailed perspective into the vertical structure of the water column from the uppermost section of the surface waters in the photic zone ($\delta^{18}O_{diatom}$), other depths of the surface/sub-surface waters (planktonic $\delta^{18}O_{foram}$) through to deep/bottom waters (benthic $\delta^{18}O_{foram}$). For this to be achieved in future studies it will become necessary to routinely extract both season and species specific diatoms samples for isotope analysis, which can be both challenging and time-consuming (see Section 3.2).

5. $\delta^{18}O_{diatom}$ uncertainties

Although, as highlighted above, considerable potential exists in using records of $\delta^{18}O_{diatom}$ to complement and extend existing carbonate records of $\delta^{18}O$, a number of uncertainties remain to be resolved. These include the:

1) uncertainty over the $\delta^{18}O_{diatom}$-temperature calibration (Section 5.1);
2) impact of secondary isotope exchange/silica maturation on $\delta^{18}O_{diatom}$ (Section 5.2);
3) effects of dissolution on $\delta^{18}O_{diatom}$ (Section 5.3);
4) presence of isotope vital effects in $\delta^{18}O_{diatom}$ (Section 5.4).

5.1. $\delta^{18}O_{diatom}$-temperature calibration

Early attempts to develop a marine $\delta^{18}O_{diatom}$-temperature calibration suggested that a similar isotope equilibrium curve existed between diatoms and calcite (e.g., Epstein et al., 1953; Labeyrie, 1974). These calibrations, however, were derived using dehydroxylation techniques which are now known to not sufficiently account for contaminant oxygen in the -Si-OH layer (Section 3.4). This has been verified by other work using CIE and SWF analytical techniques in which it was shown that the gradients between the diatom/calcite curves differ by up to a factor of two (Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992). Despite this, the exact magnitude of the $\delta^{18}O_{diatom}$-temperature coefficient derived in these three studies varies widely. For example, a global calibration of SST, $\delta^{18}O_{water}$ and marine $\delta^{18}O_{diatom}$ in surface sediment assemblages produced a palaeotemperature calibration between 1.5°C and 24°C of

$$1000 \ln \alpha = 3.26 \frac{10^6}{T^2} + 0.45 \qquad \text{[In Kelvin]} \qquad \text{(Eq. 8)}$$

where α is the fractionation coefficient between diatoms and ambient water and T is temperature (Juillet-Leclerc and Labeyrie, 1987). Although this calibration, equivalent to c. −0.3‰/°C, is supported by data in Matheney and Knauth (1989), Shemesh et al. (1992) have suggested the calibration to be inaccurate in high latitude waters where localised upwelling imparts a significant control on the diatom-water oxygen isotope equilibrium. Support for this originates from the Southern Ocean where core-top $\delta^{18}O_{diatom}$ data suggests a SST of 8.8°C under the calibration of Juillet-Leclerc and Labeyrie (1987), whereas observed SST in the region peak at below 4°C (Shemesh et al., 1992). Based on core-top samples from the Southern Ocean, Shemesh et al.

(1992) therefore proposed a SST calibration equivalent to c. −0.5‰/ºC for high latitude regions.

However, even after consideration of analytical error, neither of these marine based coefficients are in agreement with recent lacustrine calibrations which show a $\delta^{18}O_{diatom}$ coefficient closer to −0.2‰/ºC (Brandriss et al., 1998; Moschen et al., 2005). The marked difference between the two environments may reflect recent improvements in the analytical procedures for measuring $\delta^{18}O_{diatom}$. With all marine calibrations conducted over 15 years ago, compared to lacustrine calibrations calculated in the last 10 years, the lacustrine-based coefficient of −0.2‰/ºC may be more accurate. Alternatively, the different coefficients may indicate a systematic vital effect between lacustrine and marine diatoms. At present therefore, due to the absence of further calibration work on marine diatoms, it remains unknown whether the lower, freshwater based, or higher, marine based, coefficient is most suitable for use in palaeoceanographic research. Although not ideal, in the interim it is suggested that both the −0.5‰/ºC and −0.2‰/ºC coefficients be used as two possible end-members when attempting to constrain past changes in SST. Determining the correct coefficient is important not only for future work, but also in assessing the accuracy of the palaeoceanographic interpretations made in previous studies.

5.2. Secondary isotope exchange/silica maturation

A key assumption of analysing $\delta^{18}O_{diatom}$ is that no isotope exchange occurs between the inner, -Si-O-Si, layer and the hydrous layer or surrounding water during or after sedimentation (Julliet, 1980a,b). Culture experiments of marine and lacustrine diatoms, however, have demonstrated $\delta^{18}O_{diatom}$ fractionation factors of between 2‰ and 10‰ below those observed for fossil diatoms (Schmidt et al., 1997, 2001; Brandriss et al., 1998; Moschen et al., 2006). Initially these deviations were attributed to partial dissolution of the diatom frustule during sedimentation (Brandriss et al., 1998). Other work, however, has made it clear that these isotopic changes are instead related to silica maturation in the diatom frustule during sedimentation/burial with isotopically light ^{16}O from the -Si-OH layer released and the remaining, heaver, ^{18}O forming isotopically enriched -Si-O-Si linkages in the -Si-O-Si layer of the frustule (Schmidt et al., 1997; 2001; Moschen et al., 2006):

$$Si\text{-}^{18}OH + H^{16}O\text{-}Si \rightarrow Si\text{-}^{18}O\text{-}Si + H_2{}^{16}O \quad \text{(Eq. 9)}$$

At present the implication of these exchanges and the extent to which silica maturation affects the use of $\delta^{18}O_{diatom}$ in palaeoenvironmental reconstructions remains unknown. On the one hand deviations from equilibrium of 2‰ to 10‰ could erode any environmental signal in $\delta^{18}O_{diatom}$. However, based on the isotopic exchanges in Equation 9, measured $\delta^{18}O_{diatom}$ can be expressed as a weighted linear combination of the pre-silica maturation -Si-O-Si layer ($\delta^{18}O_{\text{-Si-O-Si}}$) and the -Si-O-Si linkages formed during silica maturation after dehydroxylation ($\delta^{18}O_{dehydroxyl}$):

$$\delta^{18}O_{diatom} = \delta^{18}O_{\text{-Si-O-Si}} + \delta^{18}O_{dehydroxyl}$$

(Eq. 10)

in turn, $\delta^{18}O_{dehydroxyl}$ can be regarded as a function of the isotope fractionation, governed by the fractionation factor "*f*", that occurs between the pre-dehydroxylation -Si-OH layer ($\delta^{18}O_{\text{-Si-OH}}$) and $\delta^{18}O_{dehydroxyl}$ during silica maturation

$$\delta^{18}O_{dehydroxyl} = f[\delta^{18}O_{\text{-Si-OH}}]$$

(Eq. 11)

Since the isotope composition of $\delta^{18}O_{\text{-Si-OH}}$ at the point of silica maturation will be representative of the $\delta^{18}O$ of the water it last came into contact with, due to the readily exchangeable nature of the oxygen within the -Si-OH layer, the $\delta^{18}O_{dehydroxyl}$ component in $\delta^{18}O_{diatom}$ should reflect the isotopic composition of bottom water and/or sediment porewater. As such, even if silica maturation exerts a significant impact on measured $\delta^{18}O_{diatom}$, as long as these isotope exchanges are systematic and predictable, i.e., *f* is constant spatially and temporally as well as within and between individual taxa, values of $\delta^{18}O_{diatom}$ should, at the very least, provide important information on deep/bottom water palaeoceanographic conditions. However, in practise it is important to stress that numerous studies have demonstrated strong correlations between sediment records of $\delta^{18}O_{diatom}$ and other surface water $\delta^{18}O$/proxy records (Leng and Barker, 2006; Tyler et al., 2008). Indeed comparisons of $\delta^{18}O_{diatom}$ and benthic $\delta^{18}O_{foram}$ have shown contrasting stratigraphical changes (e.g., Swann et al., 2006). Such a feature would not be expected were $\delta^{18}O_{diatom}$ predominantly controlled by silica maturation and suggests that silica maturation does not significantly distort the $\delta^{18}O$ of -Si-O-Si layer. Accordingly, it is reasonable too assume that stratigraphical changes in $\delta^{18}O_{diatom}$ can be safely used in reconstructing quantitative changes in surface/photic zone water conditions.

In order to advance our understanding, however, further laboratory and in-field studies are urgently required to fully assess the extent to which silica maturation has a detrimental impact on the use of $\delta^{18}O_{diatom}$ in both palaeoceanography and palaeolimnology. One significant advancement would be the routine assessment of silica maturation in samples analysed for $\delta^{18}O_{diatom}$, which may eventually allow the effects of silica maturation to be quantitatively accounted for. The extent to which silica maturation has occurred is most easily checked through infra-red spectroscopy which measures the magnitude of the -Si-OH and -Si-O-Si layers in the diatom sample (e.g., Schmidt et al., 2001). By comparing samples against a diatom standard comprised of living taxa that have not undergone silica maturation, the composition of which is representative of taxa in the sediment sample, variations in silica maturation between individual samples can be assessed (Fig 5). If the extent of silica maturation varies considerable over a stratigraphical section, caution would be required in the interpretation of $\delta^{18}O_{diatom}$ in terms of palaeoceanographic change.

5.3. Dissolution/diagenesis

Due to the majority of marine locations being unsaturated with respect to silica, most diatoms living in the water column will be subjected to some form of dissolution. While the number of measurements are low, it is estimated that only 1-10% (mean = 3%) of all living diatoms in the marine system are preserved within the sediment (Tréguer et al., 1995). The extent to which dissolution occurs depends on a range of parameters including, but not restricted to, temperature (Hurd, 1972; Natori et al., 2006), sedimentation rate (Ragueneau et al., 2000), alkalinity (Barker, 1992; Ryves et al., 2006; Loucaides et al., 2008), trace metals (van Bennekom et al., 1989, 1991; Barker et al., 1994; Dixit et al., 2001; Dixit and van Cappellen, 2002; Koning et al., 2007), organic coating, bacterial and other biological communities (Lewin, 1961; Jacobson and Anderson, 1986 Sullivan et al., 1975; Miller et al., 1990; Cowie and Hedges 1996; Bidle and Azam, 1999; Bidle et al., 2002, 2003) as well as the size, morphology, aggregation and silicification of individual frustules (Lewin, 1961; Lawson et al., 1978; Nelson et al., 1995; Ragueneau et al., 2000). Diatom dissolution will continue at the surface-sediment interface and during incorporation/burial into the sedimentary record. The rates at which dissolution occurs in the sediment is generally dependent on pH, temperature and silica concentrations in the pore water of the silica asymptotic concentration zone, which generally lies within the upper 30 cm of the sediment. Below this dissolution is reduced, although diagenesis may continue through either the re-precipitation or diagenetic alterations of the diatom silica (Kastner et al., 1977; Hurd et al., 1981).

Given that diatoms can not usually be hand-picked for isotope analysis due to their small size, it is reasonable to assume that a proportion of frustules within an otherwise well preserved sample will have undergone some form of dissolution/diagenesis. At present it remains unknown to what extent these processes may alter the analysed $\delta^{18}O$ within the -Si-O-Si layer, although it would be expected that the chemical and biological dissolution of diatom frustules, particularly in alkaline waters, would alter $\delta^{18}O_{diatom}$. Such an assumption is reinforced by a limited number of laboratory dissolution experiments carried out by Moschen et al. (2006) who observed isotope deviations of up to 7‰ following the removal of the protective organic matter coating around the frustule. Although further experiments are needed to replicate these results and to cover a greater range of variables, in the interim the results highlight the need to only analyse pristine fossilised diatoms free of dissolution and diagenesis, which must be assessed through both SEM and light microscopy.

5.4. Vital effects

As with other organisms, diatoms are assumed to be precipitated in isotope equilibrium as predicted by thermodynamic fractionation. However, it has been widely shown in carbonates that offsets from isotope equilibrium may arise in response to variations in kinetic or metabolic processes within and between individual taxa, e.g., changes in growth rates, nutrient availability or rates of calcification/silicification (Duplessy et al., 1970; Wefer and Berger, 1991; Spero and Lea, 1993, 1996; Spero et al., 1997; Bemis et al., 1998). For biogenic carbonates, such as ostracods and foraminifera, the impact of these processes can be negated by picking single species samples for isotope analysis. This is not generally feasible for diatoms due to their smaller size (Section

3.2). A number of culture (Binz, 1987; Brandriss et al., 1998; Schmidt et al., 2001), sediment trap (Moschen et al., 2005) and down-core studies (Sancetta et al., 1985; Juillet-Leclerc and Labeyrie, 1987; Shemesh et al., 1995; Schiff et al., In review) in marine and lacustrine systems have failed to find any conclusive evidence to indicate that a similar vital effect exists in $\delta^{18}O_{diatom}$. While data in Brandriss et al. (1998) display a 0.6‰ difference between two laboratory cultured diatom taxa and Shemesh et al. (1995) found a 0.2‰ offset between two different size fractions of diatoms, offsets of this magnitude are within the range of reproducibility routinely achieved when analysing $\delta^{18}O_{diatom}$. As such, most studies suggest that $\delta^{18}O_{diatom}$ vital effects are either non-existent or within the analytical reproducibility of $\delta^{18}O_{diatom}$ measurements.

More recently, however, results from ODP Site 882 in the North West Pacific Ocean between 2.86 Ma and the modern day have been shown to display large isotope offsets of up to 3.5‰ between different size fractions of purified diatoms (Fig. 8) (Swann et al., 2007; 2008). At present the mechanisms behind these offsets remain unresolved, opening the possibility that some form of inter/intra-species vital effect may be present. Possible candidates for such a process could include, amongst others, changes in nutrient availability, growth rate, life cycle stage, environmental conditions and variations in silica maturation (Swann et al., 2008). At present insufficient evidence exists to advocate any one process over another. However, evidence of a possible growth rate effect has previously been observed by Schmidt et al. (2001) with less isotope fractionation suggested to occur in fast-growing diatoms. If verified elsewhere, caution would be required when interpreting records of $\delta^{18}O_{diatom}$ in areas where growth rates vary spatially/temporally. This is particularly relevant in High Nutrient Low Chlorophyll (HNLC) areas such as the Southern Ocean where changes in Fe fertilisation/availability lead to significant changes in the geochemical composition of diatoms and their growth rates on a variety of short to long-term timescales (see Hutchins and Bruland (1998); Takeda (1998) and reviews in de Baar et al. (2005) and Ragueneau et al. (2006)).

Given that down-core changes in $\delta^{18}O_{diatom}$ greater than a few per mille are the exception rather than the norm, particularly if marine diatom-temperature coefficients are as low as −0.2‰/°C, there is an urgent need for greater in-field studies and laboratory culture experiments in order to improve our understanding of these offsets and the possible presence of an isotope vital effects in $\delta^{18}O_{diatom}$. If evidence of other large $\delta^{18}O_{diatom}$ offsets are detected, it would introduce significant uncertainty as to the reliability of quantitative reconstructions derived from $\delta^{18}O_{diatom}$ unless species specific samples can be successfully extracted for isotope analysis. Given the complexity in achieving this in most sequences, it becomes essential in future to consider the species biovolume composition of each sample analysed for $\delta^{18}O_{diatom}$.

6. Conclusions and future directions

Measurements of $\delta^{18}O_{diatom}$ provide a potentially important source of palaeoceanographic information, equivalent to that from $\delta^{18}O_{foram}$, which can extend our understanding of palaeoceanographic changes in both

high latitude regions and other sites containing diatoms. Recent years have been marked by several advances with regards to method development and our understanding of the $\delta^{18}O_{diatom}$ signal (e.g., Moschen et al., 2006; Brewer et al., 2008; Leng and Sloane, 2008). However, in addition to resolving the issues raised above in Section 5, a number of other areas need to be addressed in order to improve the accuracy of $\delta^{18}O_{diatom}$ based reconstructions. This first includes the development of techniques for extracting size, species and season specific diatom frustules from sediment samples. As well as circumnavigating the issue of vital effects in $\delta^{18}O_{diatom}$, such an advancement will allow season-specific $\delta^{18}O_{diatom}$ reconstructions and an insight into the seasonal evolution of palaeoceanographic events. Secondly, there is a need to further develop existing/new analytical procedures for analysing $\delta^{18}O_{diatom}$ which do not require fluorine reagents (e.g., iHTR). Such a step will likely lead to increased numbers of laboratories developing analytical lines for $\delta^{18}O_{diatom}$ and subsequently the widespread application of $\delta^{18}O_{diatom}$ in palaeoceanography.

At present, despite the considerable potential in using records of $\delta^{18}O_{diatom}$ to provide further insights into the nature of climatic/oceanographic changes in carbonate free regions, to date only a limited number of studies have been carried out on marine sediment cores. While this can be attributed to the issues raised above and in Section 5, existing studies have shown that records of $\delta^{18}O_{diatom}$ can provide detailed information on photic zone processes and changes in both the Southern Ocean and North Pacific Ocean. To date, the rapid expansion of $\delta^{18}O_{diatom}$ in palaeolimnology (Leng and Barker, 2006) has not been matched in marine systems. However, it should be expected that this will change in the future, particularly at sites where measurements of both $\delta^{18}O_{diatom}$ and $\delta^{18}O_{foram}$ are feasible in conjunction with other isotope and non-isotope methods. As shown in Shemesh et al. (1992, 1995, 1995, 2002), Haug et al. (2005) and Swann et al. (2006), such studies are able to increase the range of palaeoceanographic information and allow an overall holistic understanding of the water column to be reconstructed on seasonal timescales. This is likely to be further advanced by the development of a combined methodology for analysing $\delta^{18}O_{diatom}$ and $\delta^{30}Si_{diatom}$ on the same sample (Leng and Sloane, 2008). In conjunction with separate analyses on the $\delta^{13}C$ and $\delta^{15}N$ of intrinsic organic matter within diatoms, this will permit a more detailed, isotope based, reconstruction of photic zone conditions than has hitherto been possible (De La Rocha, 2002, 2006; Robinson et al., 2004). To date no study has taken advantage of this to analyse $\delta^{18}O_{diatom}$, $\delta^{30}Si_{diatom}$, $\delta^{13}C_{diatom}$ and $\delta^{15}N_{diatom}$ at the same site. However, as long as sufficient material can be extracted, the provision of a complete suite of diatom isotope data, in conjunction with other geochemical and biological proxy data, should enable a more in-depth interpretation of palaeoceanographic change in both carbonate and carbonate-free locations.

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Figures

Figure 1: Global distribution of marine sediment types. Adapted from Open University (1989)

Figure 2: Schematic structure of diatom silica showing the isotopically homogeneous inner -Si-O-Si layer and the outer -Si-O layer which forms a -Si-OH hydroxyl bond.

Figure 3: SEM images of: A, B, C, D) diatoms surrounded by clay particles and other non-diatom contaminant including tephra (D) which can prove difficult to remove even after the use of SPT; E) cleaned diatom material showing the presence of other siliceous organisms, such as radiolaria, which may be problematic to fully

separate; F) cleaned material showing the multiple broken fragments of diatom frustules that can occur following multiple centrifugation stages; G & H) fully cleaned diatom material showing no evidence of adhering clays or other contaminants. Images in C and D reproduced with permission by Cathy Stickley and Warren Eastwood.

Figure 4: Original $\delta^{18}O_{diatom}$ data from Lake Baikal, Russia, with no correction for non-diatom contaminants (black line) (Morley et al., 2005) and $\delta^{18}O_{diatom}$ corrected ($\delta^{18}O_{corrected}$) for contamination based on XRF analysis (grey line) (Brewer et al., 2008). Whilst both records shows similar changes, the magnitude of change in $\delta^{18}O_{corrected}$ is significantly reduced and more realistic when compared to other proxy data from the lake.

Figure 5: Infra-red absorption spectra of diatoms from a laboratory culture and from Lake Holzmaar, Germany, showing the progressive loss of -Si-OH groups and the creation of -Si-O-Si bonds as the frustules undergo silica maturation during sedimentation/burial. Graph of *Cyclotella meneghiniana* represent the absorption spectra of a laboratory culture which is similar in transmission to that of sediment-trap material. Figure reprinted from Geochimica et Cosmochimica Acta, 70, Moschen, R., Lücke, A. , Parplies, J., Radtke, U., Schleser, G.H., Transfer and early diagenesis of biogenic silica oxygen isotope signals during settling and sedimentation of diatoms in a temperate freshwater lake (Lake Holzmaar, Germany), 4367–4379, 2006, with permisson from Elsevier.

Figure 6: Changes in $\delta^{18}O_{diatom}$ (black triangles) from the Atlantic Sector of the Southern Ocean. Changes in $\delta^{18}O_{foram}$ (grey circles) are shown for core RCM13-259 where corresponding $\delta^{18}O_{diatom}$ measurements have been made. Data from Shemesh et al. (1995). Arrows indicate position of the LGM, see Shemesh et al., (1995) for details.

Figure 7: $\delta^{18}O_{diatom}$ (black triangles) and $\delta^{18}O_{foram}$ (*Globigerina bulloides*) (grey circles) from ODP Site 882 in the North West Pacific Ocean over the onset of major Northern Hemisphere Glaciation (Haug et al., 2005; Swann et al., 2006).

Figure 8: Observed $\delta^{18}O_{diatom}$ vital effects/offsets between different size fractions of diatoms at ODP Site 882 for A) the interval covering the onset of major Northern Hemisphere Glaciation (2.84-2.57 Ma) (>150 μm fraction minus 75-150 μm fraction) and B) the interval from 0-200 ka BP (>100 μm fraction minus 38-75 μm fraction). Dashed lines on each graph represent the Root Mean Squared Error (RMSE) based on the analytical reproducibility for the separate size fractions (Swann et al., 2007, 2008).

Tables

Table 1: Summary of modern and fossil marine $\delta^{18}O_{diatom}$ studies. VD = Vacuum Dehyrdation, CIE = Controlled

Isotope Exchange, SWF = Stepwise Fluorination.

Study	Study Type	Location	Method
Labeyrie, (1974)	Calibration	Global	VD
Mikkelsen et al. (1978)	Reconstruction	Equatorial Pacific Ocean	VD
Labeyrie, (1979)	PhD Thesis	Southern Ocean	VD
Sancetta et al. (1985)	Reconstruction	Bering Sea	CIE
Wang and Yeh, (1985)	Reconstruction	Gulf of California	VD
Juillet-Leclerc and Labeyrie, (1987)	Calibration	Global	CIE
Juillet-Leclerc and Schrader, (1987)	Reconstruction	Gulf of California	CIE
Juillet-Leclerc et al. (1991)	Reconstruction	Gulf of California	CIE
Shemesh et al. (1992)	Reconstruction	Southern Ocean	CIE
Shemesh et al. (1994)	Reconstruction	Southern Ocean	CIE
Shemesh et al. (1995)	Reconstruction	Southern Ocean	CIE
Schmidt et al. (1997)	Surface water and culture	Global	CIE
Hodell et al. (2001)	Reconstruction	Southern Ocean	CIE
Schmidt et al. (2001)	Surface water, core tops and culture	Global	CIE
Shemesh et al. (2002)	Reconstruction	Southern Ocean	CIE
Haug et al. (2005)	Reconstruction	North Pacific Ocean	SWF
Swann et al. (2006)	Reconstruction	North Pacific Ocean	SWF
Swann et al. (2007)	Vital effects	North Pacific Ocean	SWF
Swann et al. (2008)	Vital effects	North Pacific Ocean	SWF

Figure 1

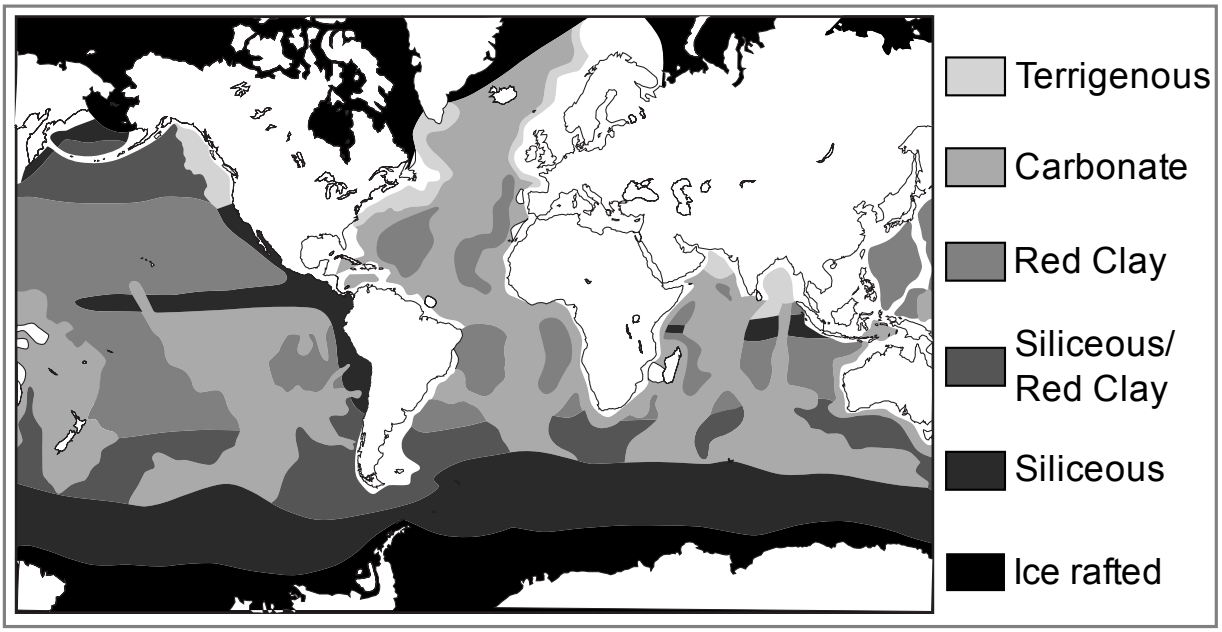

Terrigenous
Carbonate
Red Clay
Siliceous/
Red Clay
Siliceous
Ice rafted

Figure 2

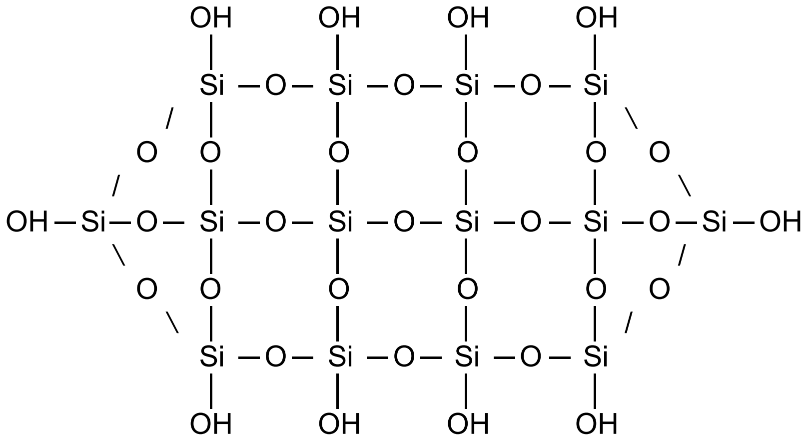


Figure 3

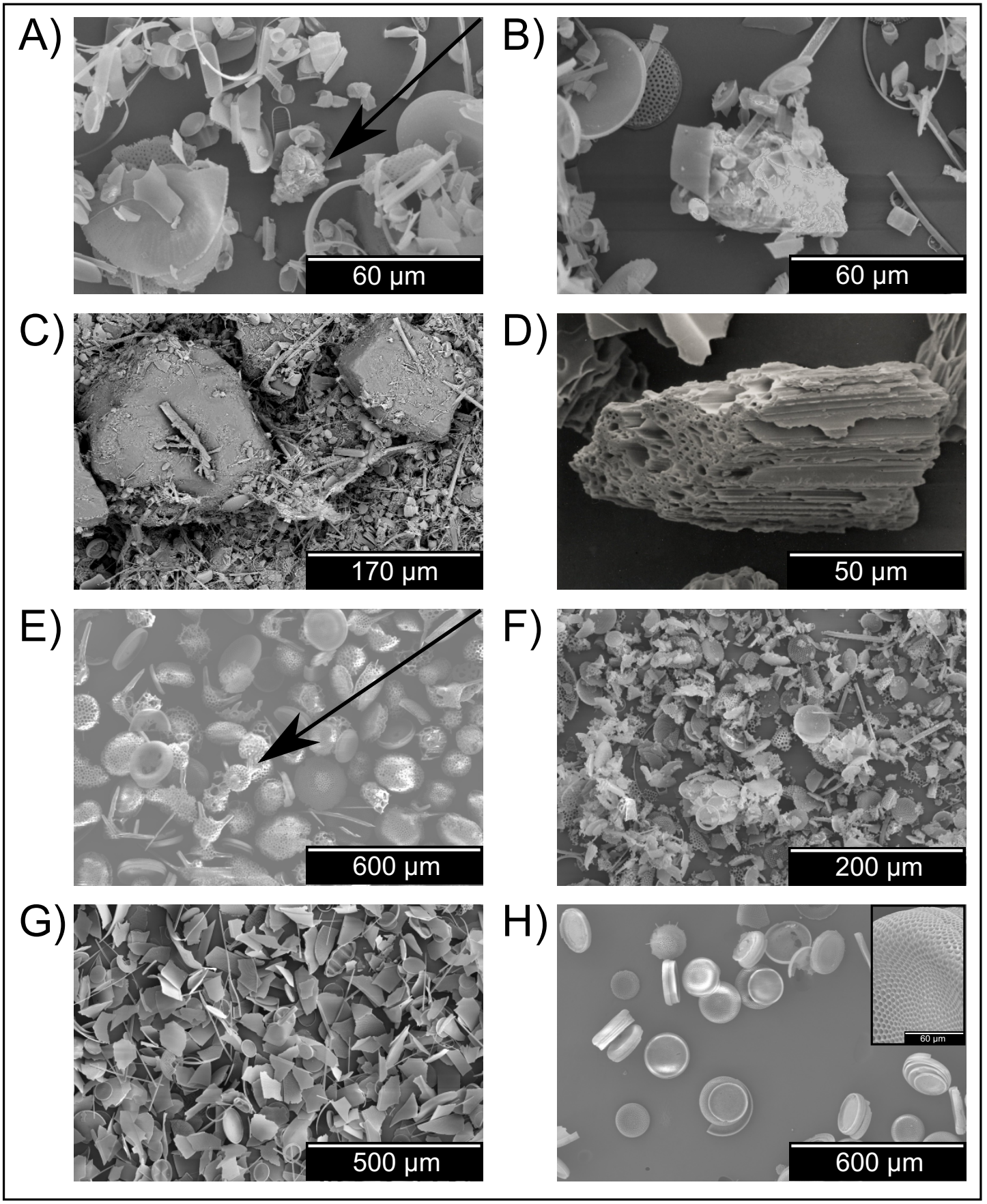


Figure 4

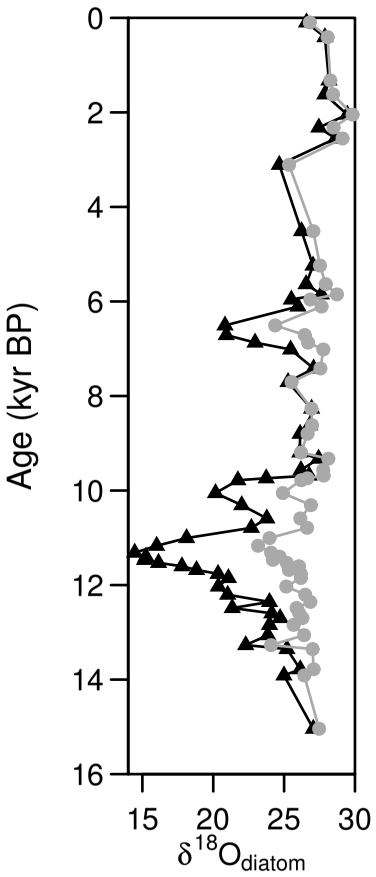


Figure 5

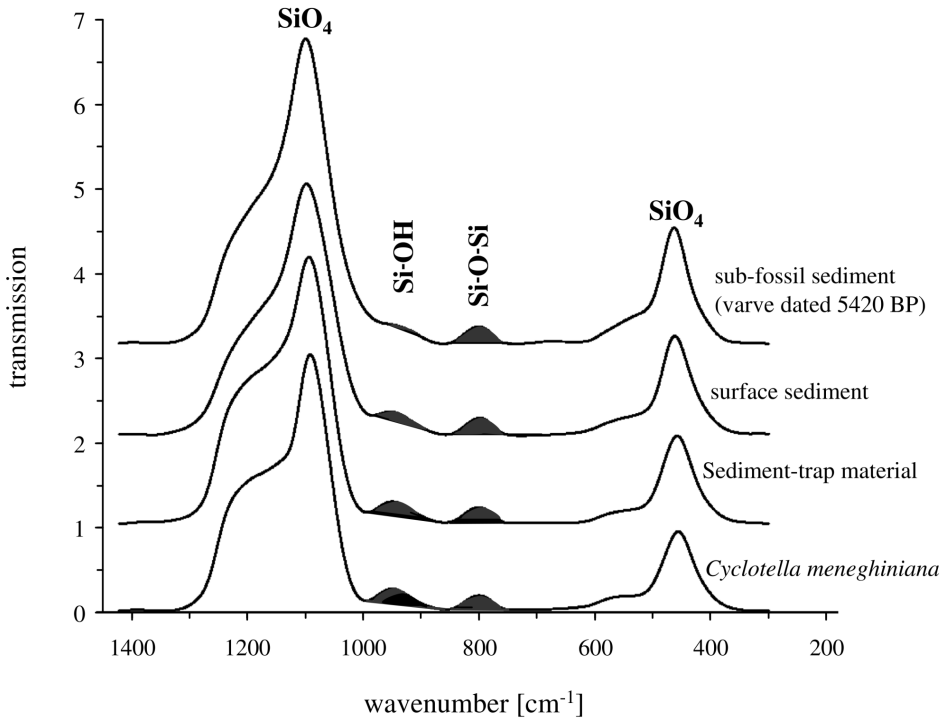

SiO4
Si-OH
Si-O-Si
SiO4
sub-fossil sediment
(varve dated 5420 BP)
surface sediment
Sediment-trap material
Cyclotella meneghiniana
transmission
wavenumber [cm-1]
0
1
2
3
4
5
6
7
1400
1200
1000
800
600
400
200

Figure 6

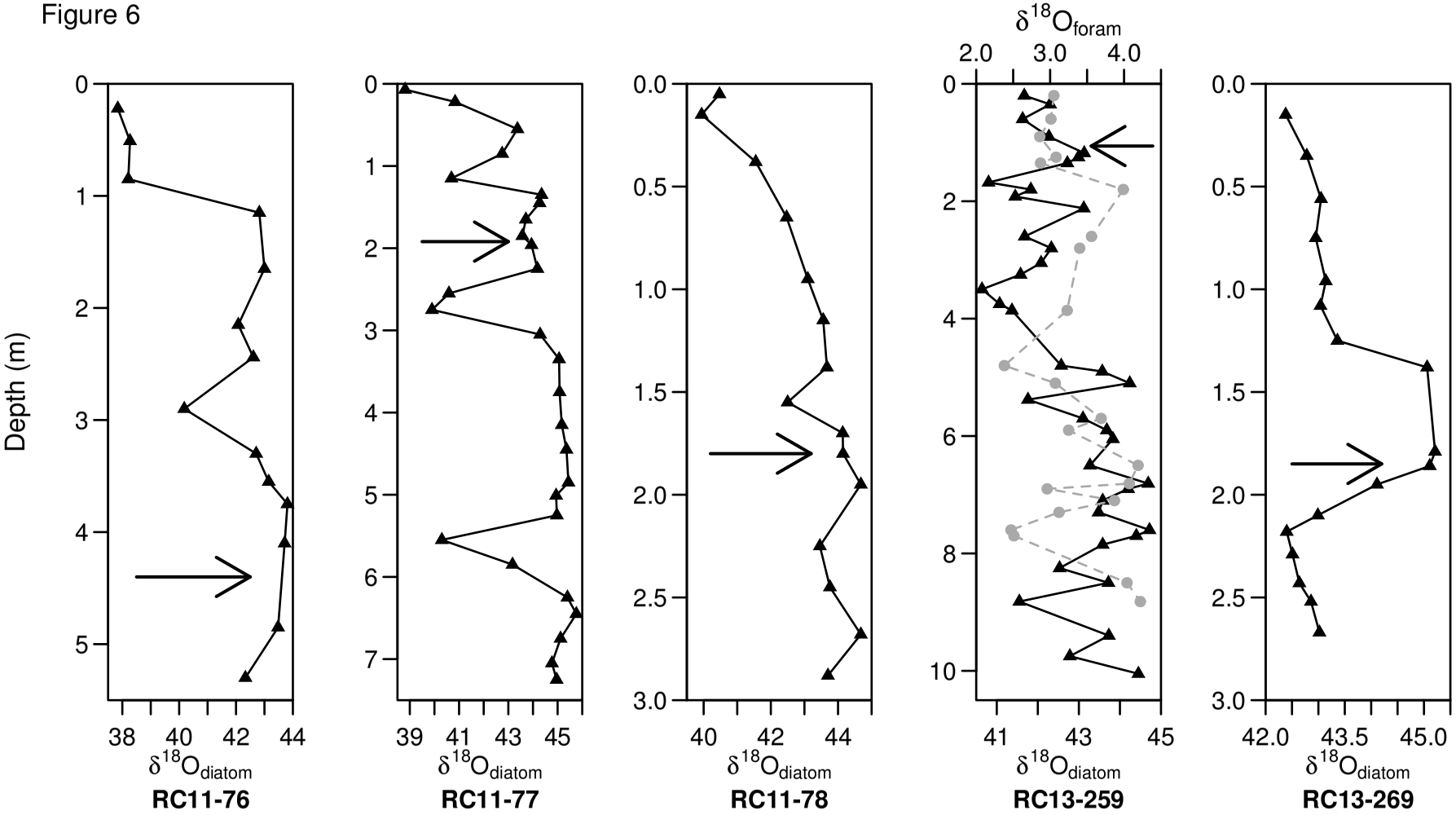

Depth (m)
δ18Odiatom
δ18Oforam
RC11-76
RC11-77
RC11-78
RC13-259
RC13-269

Figure 7

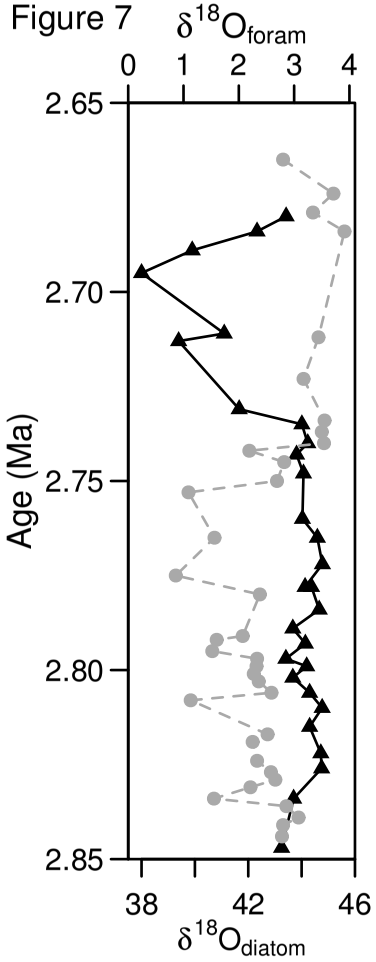
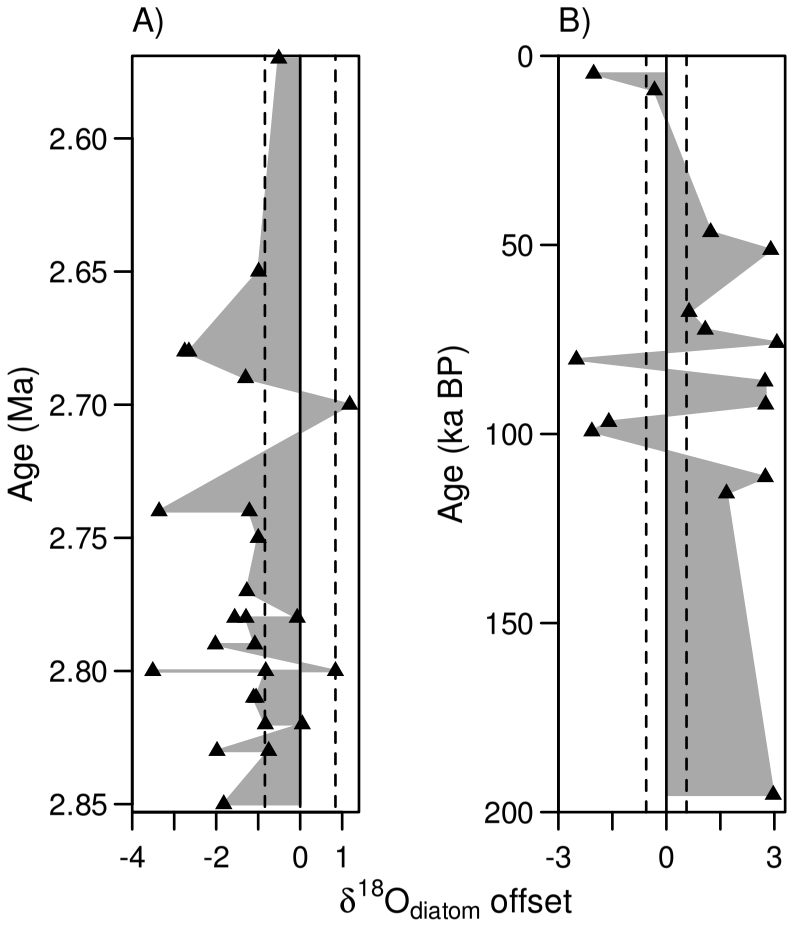

δ18Oforam
0
1
2
3
4
2.65
2.70
2.75
2.80
2.85
Age (Ma)
38
42
46
δ18Odiatom

Figure 8


A)
B)
Age (Ma)
2.60
2.65
2.70
2.75
2.80
2.85
-4
-2
0
1
Age (ka BP)
0
50
100
150
200
-3
0
3
δ18Odiatom offset