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Diatom oxygen isotopes: Evidence of a species effect in the sediment record

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[1] Diatom oxygen isotope measurements are commonly made on bulk mixed species assemblages due to the difficulty in purifying and separating individual taxa. As such, it is essential to understand processes in diatoms which may lead to isotope offsets both between and within individual species. Existing studies have suggested that mechanisms which may lead to isotopes offset in diatoms, such as vital effects, are either nonexistent or negligible. Here, we present a suite of diatom oxygen isotope data from the onset of major Northern Hemisphere Glaciation at ODP site 882 in the northwest Pacific Ocean which display large offsets (mean = 1.23‰, max = 3.51‰, error = 0.84‰) between two different size fractions (75–150 μm and >150 μm) that are dominated by only two species: *Coscinodiscus marginatus* and *Coscinodiscus radiatus*. These offsets are most likely size related, although additional interspecies and intraspecies effects may also be important in determining the exact magnitude of the offsets. Consequently, considerable care is needed when interpreting bulk diatom oxygen isotope data in relation to paleoenvironmental change, especially when the amount of stratigraphical change within the isotopes is small.

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1. Introduction

[2] Diatom silica represents an important and increasingly viable option for obtaining isotope records from the numerous lacustrine and marine sites devoid of carbonates. Many studies have demonstrated the potential for $\delta^{18}O_{diatom}$ in paleoenvironmental reconstructions, both as a standalone technique (see *Leng and Barker* [2006] for a review) and alongside carbonate isotope records [*Shemesh et al.*, 1992; *Leng et al.*, 2001; *Lamb et al.*, 2005; *Swann et al.*, 2006]. Further work has also clarified that the diatom-temperature coefficient most likely lies at approximately −0.2‰/°C [*Brandriss et al.*, 1998; *Moschen et al.*, 2005] rather than the higher values proposed in earlier studies [*Shemesh et al.*, 1992; *Juillet-Leclerc and Labeyrie*, 1987].

[3] Despite recent advances, there remain a number of uncertainties over the use of $\delta^{18}O_{diatom}$ for paleoenvironmental reconstructions. One is the potential for isotope exchange during burial and early diagenesis, which may act to remove much of the surface water paleoenvironmental isotope signal [*Shemesh et al.*, 1992; *Schmidt et al.*, 1997, 2001; *Moschen et al.*, 2006]. Second is the possibility for interspecies and intraspecies offsets in $\delta^{18}O_{diatom}$. Diatoms are assumed to precipitate in isotope equilibrium. However, many biological organisms display significant isotope deviations from isotope equilibrium. These so-called vital effects have been attributed to a range of processes including variations in the micro-environment, incorporation of metabolic fluids, vertical migration in the water column, changes in pH and changes in the rate of precipitation [*Leng and Marshall*, 2004]. In freshwater ostracods these effects can range from 0.3–2.5‰ for $\delta^{18}O$ [*Xia et al.*, 1997; *von Grafenstein et al.*, 1999; *Chivas et al.*, 2002; *Holmes and Chivas*, 2002]. Within marine organisms, vital effects have been most widely studied in foraminifera with $\delta^{18}O$ variations of up to 6‰ being documented [*Duplessy et al.*, 1970; *Wefer and Berger*, 1991; *Spero and Lea*, 1993, 1996; *Spero et al.*, 1997; *Bemis et al.*, 1998].

[4] To date, a range of culture experiments [*Binz*, 1987; *Schmidt et al.*, 2001] and down-core studies [*Juillet-Leclerc and Labeyrie*, 1987; *Shemesh et al.*, 1995; *Swann et al.*, 2006] have found little or no evidence to indicate that vital or other species effects exist in diatoms. In particular, *Moschen et al.* [2005] found no isotope offset between three size fractions of diatoms collected from Lake Holzmaar, Germany. While the data of *Brandriss et al.* [1998] do indicate a 0.6‰ difference between two laboratory cultured species and while *Shemesh et al.* [1995] found a 0.2‰ offset between two size fractions of diatoms, such offsets are within the range of reproducibility routinely achieved using fluorination based techniques. As such, interspecies and intraspecies offsets in $\delta^{18}O_{diatom}$ have hitherto been regarded to be either nonexistent or within analytical reproducibility. However, this assumption is currently based on a limited data set, highlighting the need for further investigation. This is important since, in contrast to biogenic carbonates such as ostracods and foraminifera, single species diatom valves cannot easily be picked out to create mono-specific species samples due to their smaller size. While in some instances it has proven possible to isolate different sized taxa using SPLITT [see *Rings et al.*, 2004] or by sieving at different size fractions [*Swann et al.*, 2006], in the majority of cases $\delta^{18}O_{diatom}$ data are derived from samples composed of multiple species.

[5] Here we reexamine the issue of interspecies and intraspecies offsets in $\delta^{18}O_{diatom}$ using sediment core material from ODP site 882, a site at which it has previously proven possible to separate different sized taxa. Previous comparisons made at only three levels between 2.83 Ma and 2.73 Ma suggested the absence of $\delta^{18}O_{diatom}$ vital or species effects at this site [*Swann et al.*, 2006]. Further extraction of an additional 22 pure diatom samples which are dominated by only two taxa, however, show that there is a mean offset of 1.23‰ between the two size fractions (75–150 μm and >150 μm).

2. Methodology

[6] Sediment samples corresponding to the onset of major Northern Hemisphere Glaciation (NHG), 2.84-2.57 Ma (MIS 116 (G12)–102) were collected from the northwest Pacific Ocean at Ocean Drilling Project (ODP) site 882, situated on the western section of the Detroit Seamounts (50°22′N,

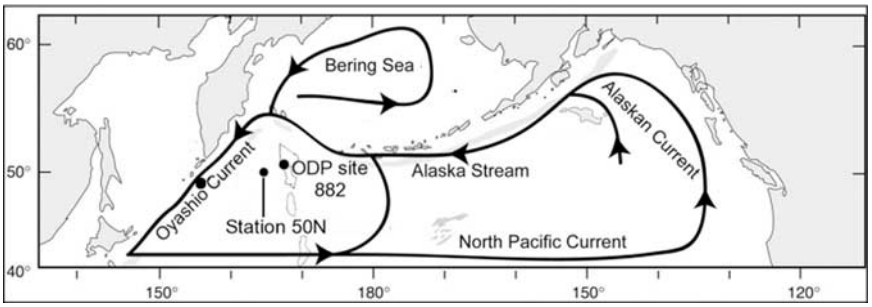

Figure 1. Location of ODP site 882 (50°22′N, 167°36′E) northwest Pacific Ocean together with diatom monitoring station 50N (50.01°N, 165.01°E) and major ocean surface currents in the North Pacific Ocean.

167°36′E) at a water depth of 3,244 m (Figure 1) [*Rea et al.*, 1995]. High resolution GRAPE density and magnetic susceptibility measurements were astronomical calibrated with linear interpolation of sedimentation rates between tie-points to calculate sample ages [*Tiedemann and Haug*, 1995]. Samples for $\delta^{18}O_{diatom}$ were prepared using the three-stage methodology detailed by *Swann et al.* [2006] with material sieved at 75 μm and 150 μm and both size fractions (75–150 μm and >150 μm) retained for isotope analysis. Visual inspection of the diatom flora prior to this stage showed these size fractions as being optimal to minimize diatom species diversity. Subsamples of the final purified material were mounted on a coverslip using a Naphrax® mounting media and visually checked for contamination under a light microscope at ×1000 magnification using thirty randomly selected quadrants on a 100 μm × 100 μm grid graticule with further SEM analyses undertaken to ensure diatom purity. Random quadrants were selected in such a way that the whole coverslip was sampled, including the edge of the coverslip where more contamination may be present. All samples containing more than a few percent of nondiatom material were disregarded for isotope analysis.

[7] Diatoms were analyzed for oxygen isotopes using a stepwise fluorination method to dissociate the silica and liberate the oxygen [*Leng and Barker*, 2006]. In brief, the diatom hydrous layers were stripped during a prefluorination outgassing stage in nickel reaction tubes using a stoichiometric deficiency of BrF_5 reagent at low temperature before full reaction with an excess of reagent at high temperature. Oxygen was converted to CO_2 following the methodology of *Clayton and Mayeda* [1963] with $\delta^{18}O_{diatom}$ measured on an Optima dual inlet mass spectrometer. $\delta^{18}O_{diatom}$ values were converted to the SMOW scale using a within-run laboratory standard (BFC_{mod}) calibrated against NBS28. Diatom species biovolumes were calculated following the recommendations of *Hillebrand et al.* [1999] on the final purified unreacted sample with the assumption that relative hydroxyl layer thicknesses were constant across all diatoms. While measurements of diatom biovolume record the volume rather than the mass of diatoms, the values remain a valuable tool for identifying the relative contribution of individual diatom species to an isotope measurement.

[8] While the range of the size fractions analyzed for $\delta^{18}O_{diatom}$ would ideally have been reduced to create more sieve bins, e.g., 75–100 μm, 100–125 μm, 125–150 μm and 150–175 μm, this was not possible due to the necessity of extracting sufficient material for isotope analysis (5 mg). Smaller size fractions, e.g., 10–38 μm and 38–75 μm, were not suitable for isotope analysis due to the increased numbers of diatom species in these samples, which also bloom across different seasons, and due to the multiple fragments of larger *C. radiatus* and *C. marginatus* diatom frustules that were present in these samples.

3. Results

[9] All diatoms within the analyzed samples appear pristine and do not appear to have undergone any diagenesis (Figure 2). In addition, levels of nondiatom contamination in both size fractions are minimal (Figure 3a). Sample biovolumes for the >150 μm fraction are dominated by *Coscinodiscus marginatus* (Ehrenb.) and *Coscinodiscus radiatus* (Ehrenb.), which are approximately equally distributed throughout with neither contributing more than 65% of any sample biovolume (Figure 3b). Biovolumes in the 75–150 μm fraction are dominated solely by *C. radiatus* until 2.69 Ma after which *C. marginatus* becomes dominant (Figure 3b).

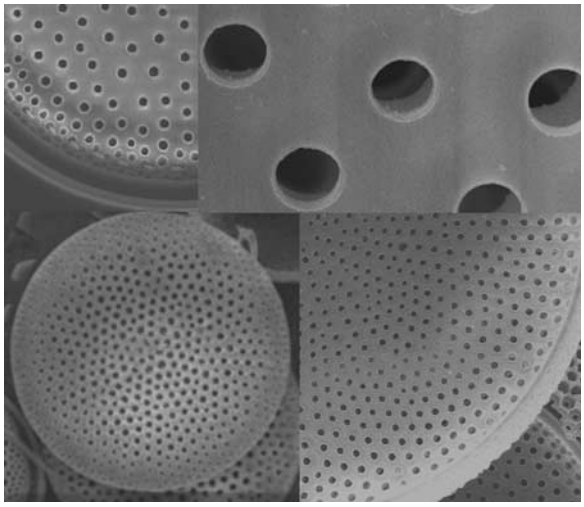

Figure 2. SEM images of diatoms analyzed for $\delta^{18}O$ from ODP site 882.

[10] Comparisons indicate the presence of large $\delta^{18}O_{diatom}$ offsets between the two size fractions with a mean offset of 1.23‰ and a maximum offset of 3.51‰ (Figures 3c and 4 and Table 1). Replicate analyses indicate a mean $\delta^{18}O_{diatom}$ standard deviation of 0.44‰ in the 75–150 μm fraction, 0.71‰ in the >150 μm fraction and 0.41‰ for BFC_{mod}, the NIGL laboratory diatom standard. Of the 25 analyzed levels, including the three samples previously published by *Swann et al.* [2006], 18 contain offsets which are beyond the combined square root sum of squares analytical reproducibility for the two size fractions (0.84‰). With the exception of three levels, the smaller 75–150 μm fraction has a higher $\delta^{18}O_{diatom}$ relative to the >150 μm fraction ($p < 0.001$). After the onset of major Northern Hemisphere Glaciation (NHG) at 2.73 Ma when the region undergoes major paleoenvironmental change [*Haug et al.*, 2005; *Swann et al.*, 2006], $\delta^{18}O_{diatom}$ values in 75–150 μm fraction remain statistically higher than the >150 μm fraction, but at a lower confidence interval ($p = 0.08$).

4. Discussion

4.1. Reliability of the $\delta^{18}O_{(diatom)}$ Record

[11] $\delta^{18}O_{diatom}$ measurements from the 75–150 μm fraction have previously been used to indicate the development of a stratified water column in the northwest Pacific Ocean at the onset of major NHG, circa 2.73 Ma [*Haug et al.*, 2005; *Swann et al.*, 2006]. While measurements between the two size fractions at three levels from 2.83 Ma to 2.73 Ma produced similar results within the limits of analytical reproducibility [*Swann et al.*, 2006], 18 out of 25 levels in the extended data set presented

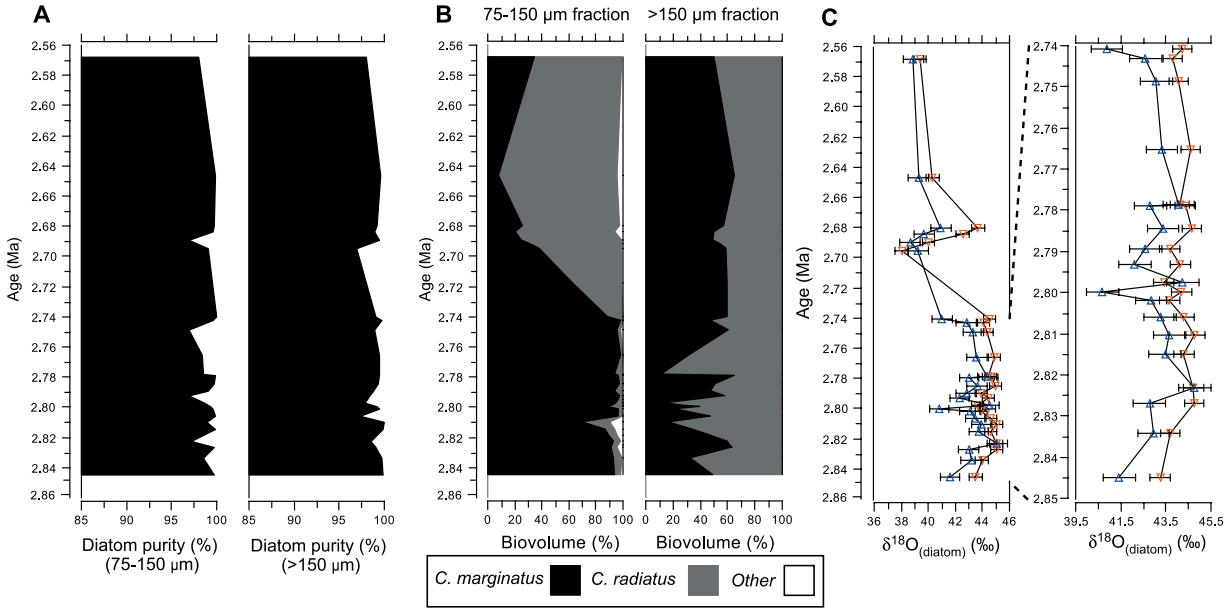

Figure 3. (a) Sample purity, percentage of diatom material relative to all other material. (b) Relative diatom species biovolume in purified samples analyzed for $\delta^{18}O_{diatom}$. (c) Comparison of $\delta^{18}O_{diatom}$ measurements from the 75–150 μm fraction (red down triangle) and >150 μm fraction (blue up triangle) between 2.86 Ma and 2.56 Ma. Error bars represent mean, 1σ, analytical reproducibility of 0.44‰ in the 75–150 μm fraction and 0.71‰ in the >150 μm fraction.

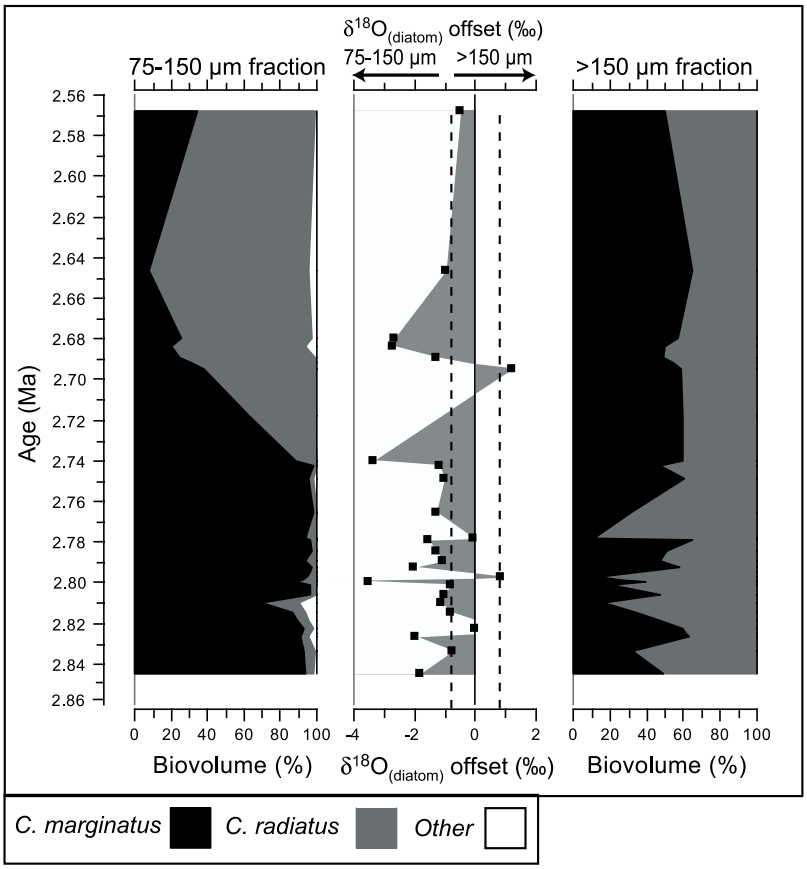

Figure 4. Relative diatom species biovolume in purified samples analyzed for $\delta^{18}O_{diatom}$ alongside the magnitude and direction of the $\delta^{18}O_{diatom}$ offsets (>150 μm fraction minus 75–150 μm fraction) between the two size fractions (dashed lines represent the combined analytical reproducibility of 0.84‰ for the two size fractions).

here display significant offsets beyond the combined analytical reproducibility for the two size fractions of 0.84‰.

[12] As detailed above, all analyzed diatom samples are considered pristine with minimal nondiatom contamination and dissolution (Figures 2 and 3a). Furthermore, no evidence of diagenesis exists either within the sediment or the analyzed diatoms. Evidence to support the lack of contamination in these samples is present within the $\delta^{18}O_{diatom}$ data themselves. First, high $\delta^{18}O_{diatom}$ values in all samples makes it unlikely that contamination is an issue since the $\delta^{18}O$ of clays and silts are usually significantly lower than $\delta^{18}O_{diatom}$, although no clay isotope values are available from ODP site 882 over the analyzed interval. Secondly, it would be expected that if contamination was an issue, the relative amount of any contamination, particularly from clays, would be greater in the 75–150 μm fraction due to the fraction's smaller size. This would then lead to $\delta^{18}O_{diatom}$ values in the 75–150 μm fraction being lower than the >150 μm fraction. In practice, the 75–150 μm fraction displays higher $\delta^{18}O_{diatom}$ values in almost all samples (Figures 3c and 4).

[13] An important finding in recent years is evidence for secondary isotope exchange in diatoms, caused by silica maturation, which increases fossil/subfossil values of $\delta^{18}O_{diatom}$ relative to diatoms in the water column [*Schmidt et al.*, 1997, 2001; *Brandriss et al.*, 1998; *Moschen et al.*, 2006]. Checking for silica maturation in diatoms is difficult as it does not always visibly alter the diatom frustule and so cannot be assessed under a light microscope or SEM. However, the role of silica maturation on $\delta^{18}O_{diatom}$ at this site and over this interval has previously been ruled out by comparing changes in $\delta^{18}O_{diatom}$ to changes in bottom water $\delta^{18}O$, as indicated by benthic foraminifera [*Swann et al.*, 2006]. In addition, it would be expected that any secondary isotope exchange caused by silica maturation would be constant across both size

Table 1. $\delta^{18}O_{diatom}$ Data for the 75–150 μm and >150 μm Size Fractions[a]

Age, Ma	$\delta^{18}O_{diatom}$, ‰ 75–150 μm	$\delta^{18}O_{diatom}$, ‰ >150 μm	Offset, ‰ (150 μm – 75–150 μm)
2.568	39.33	38.82	+0.51
2.647	40.20	39.21	*+0.99*
2.680	43.42	40.77	*+2.65*
2.683	42.33	39.58	*+2.75*
2.690	39.90	38.59	*+1.30*
2.695	38.00	39.18	*−1.18*
2.740	44.23	40.87	*+3.36*
2.743	43.81	42.60	*+1.21*
2.749	44.07	43.06	*+1.00*
2.765	44.59	43.32	*+1.27*
2.779	44.13	44.06	+0.07
2.779	44.37	42.81	*+1.56*
2.784	44.66	43.37	*+1.29*
2.789	43.67	42.59	*+1.08*
2.793	44.14	42.12	*+2.02*
2.797	43.41	44.25	−0.84
2.800	44.19	40.68	*+3.51*
2.802	43.67	42.85	+0.82
2.806	44.30	43.25	*+1.05*
2.810	44.77	43.66	*+1.11*
2.815	44.30	43.47	+0.83
2.823	44.72	44.77	−0.05
2.827	44.75	42.77	*+1.98*
2.834	43.70	42.95	+0.75
2.845	43.25	41.43	*+1.82*
Mean			**+1.23**

[a] Offsets are difference in $\delta^{18}O_{diatom}$ between the two size fractions (italic values indicate offsets beyond the combined analytical reproducibility for the two size fractions of 0.84‰).

fractions. As such, silica maturation should not be the cause of the isotope offsets observed here.

4.2. Seasonality/Temporal Effect

[14] Details on the spatial and temporal distribution of *C. marginatus* and *C. radiatus* at station 50N in the northwest Pacific Ocean, situated close to ODP site 882 (see Figure 1), are described by *Onodera et al.* [2005]. This, together with other studies on *C. marginatus* and *C. radiatus* in the North Pacific, shows that peak fluxes of these taxa occur in autumn/winter [*Takahashi*, 1986; *Takahashi et al.*, 1996]. Counts also show the relative seasonal flux of *C. marginatus* and *C. radiatus* frustules in the 75–150 μm range to be similar through the year (Table 2). No data are available on the temporal flux of >150 μm frustules, due to their near complete absence in the samples collected at station 50N by *Onodera et al.* [2005] and due to a lack of other studies investigating the temporal and ecological characteristics of very large frustules for these taxa. However, since all available evidence from the North Pacific Ocean shows peak fluxes of these taxa during autumn/winter, it is reasonable to assume that similar patterns also occur for >150 μm sized frustules. Consequently, it is unlikely that the isotope offsets are related to different taxa or different sized diatoms growing in different seasons.

[15] Given that each sample represents on average an approximately 2000–3000 year interval, it is possible that different conditions within the time interval covered by each sample may have favored different sized diatoms. For example, diatoms from the 75–150 μm fraction may have predominantly originated from periods of higher salinity/lower temperatures and diatoms in the >150 μm fraction from periods of lower salinity/higher temperatures. However, even if this occurred, it is hard to envisage that environmental conditions could have varied sufficiently at ODP site 882 to explain the entire magnitude of these offsets. Assuming a diatom-temperature coefficient of approximately −0.2‰/°C, for which increasing evidence exists is the true diatom-temperature coefficient [*Brandriss et al.*, 1998; *Moschen et al.*, 2005], the mean isotope offset between the two size fractions of 1.23‰ becomes equivalent to a Sea Surface Temperatures (SST) change of 6.15°C with the maximum offset of 3.51‰ equivalent to a change of 17.55°C. These compare with a relatively small mean SST fluctuations of 0.28°C/kyr over the analyzed interval [*Haug et al.*, 2005]. Similarly, if a record of Sea Surface Salinity (SSS) is calculated, mean rates of change are equivalent to ~0.10‰/kyr in the analyzed samples when using a SSS:$\delta^{18}O$ relationship of 1 and ~0.20‰/kyr with a SSS:$\delta^{18}O$ relationship of 2 [*Swann et al.*, 2006]. Consequently it is

Table 2. Modern-Day Relative Seasonal Flux of *C. marginatus* and *C. radiatus* Frustules Between 75 μm and 150 μm at Station 50N in the Subarctic Northwest Pacific Ocean From January 1999 to December 1999[a]

Season	75–150 μm Fraction *C. marginatus*, %	75–150 μm Fraction *C. radiatus*, %
JFM	38.9	50.51
AMJ	22.66	16.22
JAS	15.35	10.81
OND	23.08	22.46

[a] See Figure 1 for Station 50N location. Only minimal numbers of >150 μm frustules were present in the analyzed samples (n = 5 for *C. marginatus* and n = 0 for *C. radiatus*). Samples from *Onodera et al.* [2005].

unlikely that the isotope offsets are related to different sized diatoms growing in separate intervals of different paleoenvironmental conditions. This is particularly true from 2.73 Ma to 2.81 Ma when environmental conditions were relatively stable with SST of ~8°C [*Maslin et al.*, 1995, 1996; *Haug et al.*, 1999, 2005]. Despite this, 11 out of 14 samples from this period display a $\delta^{18}O_{diatom}$ offset beyond the combined analytical reproducibility with a mean offset of 1.5‰ (Figures 3 and 4).

4.3. Evidence of an Interspecies Effect in $\delta^{18}O_{diatom}$

[16] Given the existence of only two dominant taxa within the analyzed samples, the $\delta^{18}O_{diatom}$ offsets could reflect an interspecies effect between *C. marginatus* and *C. radiatus*. Visual comparisons, however, only provide evidence for a weak, largely unclear, relationship between the offsets and differences in diatom species biovolumes between the two fractions (Figure 4). From 2.86 Ma to 2.74 Ma, when biovolumes in the 75–150 μm fraction contain >90% *C. marginatus*, increases in *C. marginatus*/*C. radiatus* in the >150 μm fraction are broadly associated with higher/lower $\delta^{18}O_{diatom}$ offsets between the two size fractions (r = +0.49 and −0.49, respectively) (Figure 4). However, from 2.69 Ma onward, when biovolumes in the >150 μm fraction are constant and biovolumes vary in the 75–150 μm fraction, the relationship reverses with increases in *C. marginatus*/*C. radiatus* in the 75–150 μm fraction associated with lower/higher $\delta^{18}O_{diatom}$ offsets (r = −0.53 and +0.46, respectively).

4.4. Evidence of a Size Effect in $\delta^{18}O_{diatom}$

[17] With all but one of the significant offsets marked by higher $\delta^{18}O_{diatom}$ measurements in the smaller 75–150 μm fraction, it is possible that the offsets reflect a size related species effect. Determining the processes which might cause a size effect, however, are not straightforward and can only be truly investigated through culturing experiments in addition to diatom monitoring and sediment core top studies. Within foraminifera, size related vital effects arise from their vertical migration in the water column at different stages in their life cycle [*Sautter and Thunell*, 1991]. This is unlikely to be an issue for diatoms which primarily bloom and take up oxygen into the inner tetrahedrally bonded -Si-O-Si layer within the photic zone. Evidence from the modern North Pacific Ocean suggests all diatoms except *Thalassiosira trifulta* and *Thalassiosira gravida* bloom within the upper 50 m of the water column [*Katsuki and Takahashi*, 2005]. Water column profiles from close to ODP site 882 show salinity gradient through the year in the upper 50 m of the water column to be 0.2 psu [*Boyer et al.*, 2002]. As such, any salinity effect on the $\delta^{18}O_{diatom}$ offsets would be minimal and within the analytical reproducibility of the $\delta^{18}O_{diatom}$ measurements. Water temperature profiles from the same site also show the gradient between the surface and 50 m to be negligible, less than 1°C, through most of the year [*Stephens et al.*, 2002]. Consequently, if modern-day SST and diatom growth patterns are used as an analogue for the past, differences in diatom depth habitats for different sized frustules could only result in an offset of ~0.1‰ when using a diatom-temperature coefficient of −0.2‰/°C. Although the temperature gradient increases to 5–6°C between July and September [*Stephens et al.*, 2002], the blooms of *C. marginatus* and *C. radiatus* over this interval account for only 19.4% and 29.0% of the total annual diatom flux [*Onodera et al.*, 2005] or 13.1% and 6.2% of the 75–150 μm fraction annual diatom flux, respectively (Table 2). It is also likely that the majority of frustules bloom nearer the surface where light penetration is higher and where differences in the temperature gradient are further reduced. While a proportion of the offsets could be explained if all 75–150 μm diatoms bloomed in spring and all >150 μm diatoms bloomed in autumn, this appears unlikely in light of the aforementioned contemporary studies showing peak fluxes of *C. marginatus* and *C. radiatus* in autumn/early winter (Table 2) [*Takahashi*, 1986; *Takahashi et al.*, 1996; *Onodera et al.*, 2005]. Furthermore, 19 out of the 25 levels originate prior to the development of the halocline in the region at 2.73 Ma when the seasonal SST gradient would have been significantly reduced relative to today [*Haug et al.*, 1999, 2005].

[18] *Schmidt et al.* [2001] have previously suggested that $\delta^{18}O_{diatom}$ may be partially governed by diatom growth rates with less isotope fractionation occurring in fast-growing diatoms. Today, much of the northwest Pacific Ocean is believed to be under Fe limitation with respect to diatom growth [*Harrison et al.*, 1999; *Tsuda et al.*, 2003; *Yuan and Zhang*, 2006]. Consequently, changes in Fe deposition, particularly variations in line with glacial (high Fe aeolian deposition) and interglacial (low Fe aeolian deposition) cycles, and the subsequent impact on diatom growth rates and

cell chemistry (see review by *de Baar et al.* [2005]) may be initiating the offsets. However, no relationship is apparent between glacial and interglacial intervals, as indicated by a global stacked benthic foraminifera $\delta^{18}O$ record [*Lisiecki and Raymo*, 2005], and the magnitude of the $\delta^{18}O_{diatom}$ offsets.

[19] The availability of nutrients such as N, Si and P may be important in explaining the offsets after circa 2.73 Ma following the development of a stratified system in the region, which significantly limited deep water delivery of nutrients into the photic zone and lowered opal accumulation rates within the sediment [*Haug et al.*, 1999, 2005]. For example, the extent to which $\delta^{18}O_{diatom}$ in the 75–150 μm fraction is significantly higher than the >150 μm fraction decreases at this juncture ($p = 0.08$ compared to $p < 0.001$ prior to 2.73 Ma). In addition, the transition from *C. marginatus* being associated with larger to smaller $\delta^{18}O_{diatom}$ offset (see section 4.3) also occurs over this interval. However, N, Si, and P are unlikely to be significant in explaining the offsets prior to circa 2.73 Ma (a period including 19 of the 25 analyzed levels) when a mixed water column was marked by extremely high opal accumulation rates and high nutrient availability [*Haug et al.*, 1999, 2005]. It is also unclear whether issues of diatom growth rates and nutrient availability are relevant issues for explaining the isotope offsets since the effects of growth rates/nutrient availability would presumably be constant across all diatoms, regardless of size, at a given level. However, it is possible that the growth effect identified by *Schmidt et al.* [2001] influences larger diatoms to a greater extent than smaller diatoms.

4.5. Future Work

[20] Above, we have exhausted many of the possible mechanisms which have the potential to explain the large $\delta^{18}O_{diatom}$ offsets between the two size fractions. Due to the uncertainties which currently exist with regards to the fractionation of oxygen by diatoms, we will not speculate further as to the processes which may be causing the offsets. Given that all but one of the levels are marked by higher values in the smaller 75–150 μm fraction, a size related species effect may be present. However, on the basis of the available data no one mechanism can be confidently attributed to explain the entire magnitude of the offsets. From the above, a clear need exists for further sediment trap, core top and culture studies on $\delta^{18}O_{diatom}$. Such work on both marine and freshwater diatoms should consider the interspecies and intraspecies variations in $\delta^{18}O_{diatom}$ that might arise following changes in diatom growth rates, cell chemistry, deep water upwelling, nutrient availability and other physiological and environmental conditions.

[21] In section 4.1 the role of silica maturation was discounted as a factor in explaining the isotope offsets on the basis of evidence from *Swann et al.* [2006] and by assuming that the magnitude of any silica maturation would be constant across both size fractions at a given level. Theoretically, however, it is conceivable that the $\delta^{18}O_{diatom}$ offsets may reflect a size related difference in the extent to which silica maturation occurs in diatoms with greater silica maturation occurring in the smaller 75–150 μm fraction. At present, though, no evidence exists to indicate that interspecies and intraspecies variations exist in the magnitude of isotope exchange during silica maturation. Consequently, on the basis of current scientific knowledge, issues of silica maturation cannot be attributed to explain the $\delta^{18}O_{diatom}$ offsets presented within this paper. However, given the uncertainties that currently exist with regards to the operation of silica maturation in diatoms, experiments are required to better understand silica maturation and to investigate possible variations in silica maturation between and within individual diatom taxa.

4.6. Impact on Existing Paleoceanographic Reconstructions

[22] It is important to note that the offsets presented here do not affect the reliability of the paleoenvironmental reconstructions of *Haug et al.* [2005] and *Swann et al.* [2006] with regards to the development of a halocline in the region from 2.73 Ma. First, these paleoenvironmental interpretations were based upon, among other lines of evidence, a 4.6‰ decrease in $\delta^{18}O_{diatom}$ which is significantly greater than any of the offsets observed here. In addition the $\delta^{18}O_{diatom}$ record in these studies is generated solely from the 75–150 μm fraction, minimizing any potential size or other species effect. While the 75–150 μm fraction is marked by a shift in diatom species biovolume from *C. marginatus* to *C. radiatus* [see *Swann et al.*, 2006, Figure 4b] this change occurs much later at 2.71 Ma (102.66 meters below seafloor (mbsf)) than the 4.6‰ decreases in $\delta^{18}O_{diatom}$ which occurs at 2.73 Ma (102.99 mbsf). Consequently, while a species effect may be partially influencing the

isotope shift observed in these studies, we remain certain that the large $\delta^{18}O_{diatom}$ decrease at circa 2.73 Ma reflects the development of a halocline as detailed by *Haug et al.* [2005] and *Swann et al.* [2006].

5. Conclusion

[23] The presence of large $\delta^{18}O_{diatom}$ offsets between two size fractions at ODP site 882 represents a notable problem for future uses of $\delta^{18}O_{diatom}$ in marine sediment cores, except in instances where species relative biovolumes and size ranges are constant or where the amount of change in $\delta^{18}O_{diatom}$ between samples is sufficiently high as to rule out any species effect. Both taxa which dominate the two size fractions analyzed here are primarily autumn/winter blooming. With all but one of the offsets marked by higher values in the 75–150 μm fraction, a size related species effect may be present. Identifying the mechanisms behind such an effect though is problematic. Given that the magnitude of the offsets varies throughout, it remains possible that the offsets are also controlled by a combination of other interspecies and intraspecies effects. Consequently, we are currently unable to conclusively attribute the causes of these offsets to any single process. Further studies are required to investigate and understand the $\delta^{18}O_{diatom}$ signal with respect to intraspecies and interspecies offsets and the extent to which similar offsets may exist outside of *C. marginatus* and *C. radiatus*. In the meanwhile, it is essential that samples analyzed for $\delta^{18}O_{diatom}$ be as size and species specific as possible in order to minimize or eliminate the species effects/offsets observed here. This is particularly important in instances where the expected magnitude of isotope change in a stratigraphical sequence is low.

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