Oxygen isotopes in diatom silica: a new understanding of silica-water oxygen isotope fractionation in diatom frustules and an application of diatom d18O values as a record of paleohydrologic variability in a middle-Pleistocene lacrustine core from the Valles Caldera, New Mexico

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Justin Paul Dodd  
Candidate

Earth and Planetary Sciences  
Department

This dissertation is approved, and it is acceptable in quality and form for publication:

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[Signatures of committee members]

[Signatures of committee members]

[Signatures of committee members]
OXYGEN ISOTOPES IN DIATOM SILICA: A NEW UNDERSTANDING OF SILICA-WATER OXYGEN ISOTOPE FRACTIONATION IN DIATOM FRUSTULES AND AN APPLICATION OF DIATOM δ\(^{18}\)O VALUES AS A RECORD OF PALEOHYDROLOGIC VARIABILITY IN A MIDDLE-PLEISTOCENE LACustrine CORE FROM THE VALLES CALDERA, NEW MEXICO

BY

JUSTIN PAUL DODD

B.S., Geology, B.S. Anthropology, Beloit College, 2003
M.S., Geological Sciences, University of Saskatchewan, 2006

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY IN EARTH AND PLANETARY SCIENCES

The University of New Mexico
Albuquerque, New Mexico

June 2011
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OXYGEN ISOTOPES IN DIATOM SILICA: A NEW UNDERSTANDING OF SILICA-WATER OXYGEN ISOTOPE FRACTIONATION IN DIATOM FRUSTULES AND AN APPLICATION OF DIATOM δ¹⁸O VALUES AS A RECORD OF PALEOHYDROLOGIC VARIABILITY IN A MIDDLE-PLEISTOCENE LACUSTRINE CORE FROM THE VALLES CALDERA, NEW MEXICO

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ABSTRACT OF DISSERTATION

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I present oxygen isotope data from modern diatom frustules that were collected from freshwater systems in the Jemez Mountains of northern New Mexico. The frustules display a constant silica-water fractionation over the measured temperature range (5.1 to 37.8°C) regardless of species. This relationship is in close agreement with other published silica-water fractionation factors for laboratory cultured diatom samples;
however, it is as much as 8‰ lower than equilibrium quartz-water fractionations and 3-4‰ lower than observed silica-water fractionations in diatomaceous silica collected from sediment traps and sediment cores.

Post mortem loss of organic material results in an alteration or 'maturation' of diatom silica in which silica reequilibrates with a silica-water fractionation closer to the equilibrium quartz-water fractionation. Post-mortem alteration of silica $\delta^{18}O$ values occurs within 0.5 years in diatom frustules from a lacustrine setting in the Valles Caldera, New Mexico resulting in an increase of ~7.4‰ in the $\delta^{18}O$ values. The rapid post-mortem alteration of diatom $\delta^{18}O$ values explains much of the disparate data regarding silica-water fractionation for diatom silica and has profound implications for the use of diatom silica $\delta^{18}O$ values as a paleoclimate proxy. In the setting of open basin lacustrine environments where bottom temperatures are nearly constant at 4ºC, the maturation effect may facilitate reconstruction of variations in paleowater $\delta^{18}O$ values without the confounding influence of fluctuating water temperature and variable $\delta^{18}O$ water values that occur at the surface.

Lastly, I present $\delta^{18}O$ values of diatom silica from a middle-Pleistocene lacustrine core (VC-3) from the Valles Caldera, northern New Mexico, which record considerable (>25‰) variability in lake water $\delta^{18}O$ values during interglacial Marine Isotope Stage 11 (MIS 11) and glacial MIS 12. There is a strong correspondence between the $\delta^{18}O$ values of diatoms throughout the VC-3 core and mean annual temperatures recorded by MBT/CBT indices in the core. Average $\delta^{18}O$ values of diatom silica for MIS 11 and MIS 12 are 26.5‰ (± 5.3; n=62) and 18.5‰ (± 6.3; n= 27), respectively. At the MIS 12 termination at ~430 kya, there is abrupt (<2 ka) increase in the $\delta^{18}O$ values of the diatom
silica from ~11 to ~34 ‰. Throughout the core the $\delta^{18}O$ values of the diatom silica are strongly correlated with mean annual temperature (MAT) reconstructed from MBT/CBT indices in the VC-3 core on orbital (precessional) and millennial time scales. Rapid changes in the $\delta^{18}O$ values during both MIS 11 and the millennial scale variations in MIS 12 termination indicate the extreme hydroclimatological sensitivity of this region, and present a strong argument linking long term aridity in the southwestern United States to decreases in summer precipitation.
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CHAPTER 1. INTRODUCTION

Diatoms are a major group of algae and are one of the most prevalent primary producers in both marine and nonmarine environments. Diatoms belong to the class Bacillariophyceae and are mostly unicellular, but they often exist as colonies and can form a brown to green mucous-like film during blooms (Figure 1.1). Diatoms are unique in that they produce silica (hydrated SiO$_2$) tests or frustules (e.g. Round et al., 2007). Silica frustules from diatoms are widely distributed throughout marine and nonmarine environments and are abundantly preserved throughout the past 70 Ma of Earth history (e.g. Chacón-Baca, et al., 2002; Falkowski et al., 2004; Leng and Barker, 2006). Additionally, diatoms exist and thrive in low temperature environments where other algae and calcite-precipitating organisms cannot (i.e. subglacial lakes, high altitude lakes, high latitude fresh and marine waters; Patrick, 1977; Round et al., 2007). Due to their prevalence in a wide variety of marine and non-marine environments, diatoms are of particular interest as paleoclimatic and paleohydrologic proxies (e.g. Patrick, 1977, Stoermer and Smol, 1999).

Oxygen isotope values preserved by authigenic minerals in lacustrine sediments have been widely used as a proxy for paleoclimate and paleohydrologic variability; however, studies that make use of oxygen isotope values of diatom silica from lacustrine sediments have been relatively sparse (e.g. Leng and Marshall, 2004; Leng and Barker, 2006). The paucity of diatom oxygen isotope data from lacustrine environments is partially due to analytical constraints; however, a poor understanding of the mechanisms that control oxygen isotopes in diatom silica has also precluded their widespread use as
indicators of paleoclimate (e.g. Leng and Barker, 2006; Dodd and Sharp, 2010). Diatom frustule silica is hydrous amorphous opal A (Figure 1.2), and to successfully measure the oxygen isotope values of the oxygen in silica tetrahedra, the hydroxol oxygen must be removed prior to oxygen isotope analysis (Labeyrie and Juillet 1982; Leng et al., 2001; Leng and Barker, 2006). To facilitate analyses of diatom silica oxygen isotopes, I have developed a new method of laser fluorination that completely removes the hydroxol oxygen and allows relatively rapid analysis of small (~1mg) samples of diatom silica (Figure 1.3). Using this laser fluorination technique, I have developed a new empirical calculation of oxygen isotope silica-water fractionation during diatom growth (Chapter 2). Also, I provide evidence of post mortem alteration of diatom silica δ¹⁸O values (Chapter 3). Lastly, I present an application of diatom silica δ¹⁸O values as a record of paleohydrologic variability in a middle-Pleistocene lacustrine core from the Valles Caldera of northern New Mexico (Chapter 4).

Chapter 2 of this dissertation was originally submitted as Dodd and Sharp, 2010. Chapter 3 and Chapter 4 of this dissertation will be submitted to Palaeogeography, Palaeoclimatology, Palaeoecology and Earth and Planetary Science Letters, respectively. The author list for the Chapter 3 manuscript includes Justin P. Dodd, Dr. Zachary D. Sharp, Dr. Peter J. Fawcett, and Dr. Adrian J. Brearley. For Chapter 4, authors are Justin P. Dodd, Dr. Peter J. Fawcett, Dr. Zachary D. Sharp, and Dr. Toti Larson. In Chapter 5, I present general conclusions on oxygen isotopes in diatom silica, closing remarks, and possibilities for future diatom silica research.
Figure 1.1. Living diatom culture of *Pinnularia gastrum* collected from the Valles Caldera Headquarters Pond May 20, 2011.
**Figure 1.2** This schematic illustration of the structure of amorphous hydrated silica (i.e. diatom frustules) shows the oxygen molecules in the adsorbed water and exchangeable hydrous layer that must be removed prior to oxygen isotope analysis of the silica tetrahedra (modified from Perry, 1989).
Figure 1.3. Schematic of the laser fluorination set-up described by Dodd and Sharp (2010). Batches of 10-18 samples of <2mg of pure diatom silica and standards are loaded into a nickel sample holder in the laser chamber and kept under vacuum for 24 to 36 hours. Subsequently, pure F2 gas is admitted to the chamber at room temperature to remove remaining absorbed H2O and exchangeable hydroxyl oxygen atoms. Silica is then heated with a CO2 laser in the presence of 100 mbar BrF5 to produce SiF4 and O2 gas following the protocol of Sharp (1990). SiF4 and remaining BrF5 are frozen in liquid nitrogen (LN2) traps while the O2 gas is frozen in a zeolite trap before being transferred to a Finnigan MAT Delta Plus mass spectrometer for analysis. Pressure is monitored along the line (P).
CHAPTER 1. REFERENCES


Dodd, J.P. Sharp, Z.D., Fawcett, P.J., and Brearley, A.J., in prep.a, Maturation of diatom silica δ¹⁸O values within one growing season: implications for diatom silica isotopes as paleoclimate proxies: Palaeogeography, Palaeoclimatology, Palaeoecology.


CHAPTER 2. A LASER FLUORINATION METHOD FOR OXYGEN ISOTOPE ANALYSIS OF BIOGENIC SILICA AND A NEW OXYGEN ISOTOPE CALIBRATION OF MODERN DIATOMS IN FRESHWATER ENVIRONMENTS

ABSTRACT

An empirical calibration for the oxygen isotope fractionation between biogenic silica and water was determined for diatom frustules sampled from living diatom communities in the Jemez Mountains of northern New Mexico, USA. Over a temperature range from 5.1 to 37.8°C, the silica-water fractionation is defined by the equation

\[ 1000 \ln \alpha_{(\text{silica-water})} = 2.39(\pm0.13) \times 10^6 T^{-2} + 4.23(\pm1.49) \]

This relationship is in close agreement with other published silica-water fractionation factors for laboratory cultured diatom samples; however, it is as much as 8‰ lower than equilibrium quartz-water fractionations and 3-4‰ lower than observed silica-water fractionations in diatomaceous silica collected from sediment traps and sediment cores. There are three possible explanations for the disparate silica-water fractionation factors observed in diatom silica: 1) silica does not precipitate in equilibrium with ambient water, 2) silica does precipitate in equilibrium with ambient water, but the silica-water fractionation factor for diatom silica is considerably less than the equilibrium fractionation factor for quartz-water, or 3) silica precipitation is influenced by a ‘vital’ effect, where the \( \delta^{18}O \) value of the water inside the diatom cell walls is lower than the \( \delta^{18}O \) values of ambient water.

Post mortem loss of organic material results in an alteration or 'maturation' of diatom silica in which silica reequilibrates with a silica-water fractionation closer to the equilibrium quartz-water fractionation. Alteration is likely to occur rapidly after the diatom frustule loses its organic coating, either as it settles through the water column or at
the sediment-water interface; δ¹⁸O values recorded by paleo-diatom silica therefore do not record growing conditions but more likely record conditions at the sediment-water interface. In the case of lacustrine environments, where the bottom water remains at a nearly constant 4°C, the reequilibration of diatom silica with bottom conditions could reduce or remove the confounding effects of temperature on δ¹⁸O values recorded by paleo-diatom silica and provide direct information on the δ¹⁸O value of the lake water.

2.1 INTRODUCTION

Oxygen isotope values of biogenic silica from diatom frustules are a commonly used proxy in freshwater and marine environments that provide a valuable archive of paleoclimatic information such as temperature and variations in the hydrologic cycle (e.g. Leng and Barker, 2006, Swann and Leng 2009). Advances in analytical techniques have made oxygen isotope measurements of diatom silica more accurate; however, to date, there are multiple published fractionation factors for biogenic silica with no general consensus on which is ‘correct’ (Matheney and Knauth, et al., 1989; Brandriss et al., 1998; Schmidt et al., 2001, Moschen et al., 2005). There is a strong temperature dependence of the silica-water fractionation factor observed in laboratory cultured diatoms samples (e.g. Brandriss et al., 1998, Schmidt et al., 2001); however, the fractionations are not in agreement with other published silica-water fractionation factors for silica in marine and freshwater environments (e.g Clayton et al., 1972; Becker and Clayton, 1976; Knauth and Epstein, 1976; Shiro and Sakai, 1972; Kita et al., 1985; Juillet-Leclerc and Labeyrie, 1987; Matheney and Knaueth, 1989; Shemesh et al., 1992). The fractionation factors that have been published are based on a wide range of methods, including cultured diatoms in a controlled setting, empirical estimates from sedimentary
samples, and extrapolation of high temperature quartz-water fractionation experiments (Clayton et al., 1972; Labeyrie, 1974; Becker and Clayton, 1976; Knauth and Epstein, 1976; Shiro and Sakai, 1972; Kita et al., 1985; Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992; Lücke et al., 2005). Without knowing which calibration is applicable to natural samples, the utility of diatoms for temperature reconstruction is limited. In order to effectively use $\delta^{18}$O$_{\text{diatom}}$ values as a climate proxy, it is necessary to understand how oxygen isotopes fractionate during silica frustule formation and identify potential errors in $\delta^{18}$O$_{\text{diatom}}$ values obtained through different analytic/purification processes (Leng and Barker, 2006). Here I have used a laser fluorination technique to produce an oxygen isotope calibration for modern diatoms from a wide variety of natural freshwater environments in northern New Mexico, USA. I demonstrate that the silica-water fractionation observed in modern diatoms is strongly temperature dependent and is in very good agreement with a published temperature coefficient of -0.2‰/°C (Brandriss et al., 1998; Moschen et al., 2001); however, the modern silica-water fractionation cannot be used to explain the apparent silica-water fractionation observed in sub-fossil diatoms. The $\delta^{18}$O values of mature diatom silica are therefore altered from the initial $\delta^{18}$O values recorded by growing diatoms.

2.2 BACKGROUND

The silica-water fractionation observed in cultured (modern) diatoms and quartz-water fractionation experiments comprise the lower and upper extremes, and the discrepancy between the different end members is over 8‰ from 0°C to 40°C (Matheney and Knauth, 1989; Sharp and Kirschner, 1994; Brandriss et al. 1998; Schmidt et al., 2001). Studies in which diatoms were collected in sediment traps in the water column
record a silica-water fractionation that is 3 to 4‰ higher than the laboratory culture studies (Moschen et al. 2005, Moschen et al., 2006). This offset in the silica-water fractionation factor has been attributed to a 'silica maturation' process that occurs between the death of the diatom cell and the incorporation of the frustule into the sediment (Matheney and Knauth, 1989, Schmidt et al., 2001; Moschen et al., 2006). An inherent difficulty in using of diatoms from sediments and sediment traps is that it is not possible to directly measure the water temperature or δ^{18}O_{H2O} values where the diatoms were growing, thus assumptions must be made about the growing conditions. For this reason, attempts to constrain the silica-water fractionation have made use of cultured diatoms (e.g. Brandriss et al., 1998; Schmidt et al., 1991); however, the discrepancy between δ^{18}O_{diatom} values observed in these studies and other published silica-water fractionation factors from natural environments has left considerable ambiguity in determining the exact magnitude of offset in δ^{18}O values between diatom silica and the water in which they formed.

2.3 METHODS

Diatom Collection

In order to calculate the silica-water fractionation factor for diatom silica, it is necessary to know the temperature and δ^{18}O value of the water in which the diatom frustules were formed. In this study, living diatoms were collected from four shallow freshwater locations in northern New Mexico where water temperature and δ^{18}O_{H2O} could be easily measured. Samples were collected from two locations on the East Fork of the Jemez River and its tributary, Jaramillo Creek. Water depth was less than 1 meter and the primary substrate was vegetation along the stream banks. Samples growing in a high-
temperature (29 to 38°C) environment were collected from a hot-spring-fed pool in the area of Soda Dam on the Jemez River where abundant cyanobacteria also contained diatom communities. Samples were also collected from a spring-fed pond in the Valles Caldera, approximately 5m in diameter and 2m deep. In the pond samples, diatoms were collected from the surface of vegetation near the perimeter of the water body, with care taken to avoid the shallow margin of the lake where the temperature variations could be significant. Samples were collected over a twelve month period from April 2008 to April 2009.

_Diatom Purification_

Multiple studies have demonstrated that oxygen isotope analyses of diatoms require pure silica samples, as even minor contamination can significantly alter the measured $\delta^{18}O_{\text{diatom}}$ values (e.g. Juillet-Leclerc, 1984; Morley et al., 2004; Leng and Barker 2006). Diatoms were cleaned following the procedures in Morley et al. (2004). Organic material and carbonate were removed from fresh diatom samples using H$_2$O$_2$, HCl, and HNO$_3$ treatments at room temperature and then at 90°C (Battarbee et al., 2001; Morley et al., 2004; Ming and Wang, 2007). Initial cleaning with 30% H$_2$O$_2$ at room temperature was dependent on the amount of organic matter associated with the sample, and this step generally took from 12 to 48 hours. Once the sample stopped reacting vigorously with H$_2$O$_2$, the sample was heated in a water bath or on a hot plate at 90°C until the remaining visible organic material was removed. Samples were rinsed in deionized water and then reacted with 5% HCl at room temperature for 12 hours to remove carbonate minerals. After 12 hours, the HCl was heated to 90°C. Samples were then reacted with 15M HNO$_3$ at 90°C until remaining organic material had been removed.
(~12 hours). Physical cleaning (removal of clay and other detritus) was accomplished by wet sieving and differential settling/heavy liquid separation.

Diatom samples were inspected for visual and elemental purity with a scanning electron microscope/microprobe to insure that pure silica was used for $\delta^{18}$O analyses (e.g. Brewer et al, 2008). Organic content following treatment with 15M HNO$_3$ was measured with an elemental analyzer and diatoms were considered to be pure SiO$_2$ once carbon content dropped below 0.01 wt. %.

**Evaluation of potential isotopic effects during chemical treatment**

Unlike diatoms collected in sediments, modern (live) diatoms contain a considerable amount of organic matter that is difficult to remove even after reaction with aggressive acids and/or oxidants at room temperature. Removal of the recalcitrant organic matter requires a high-temperature acid treatment of ~90°C. In order to evaluate whether high-temperature acid treatments alter the $\delta^{18}$O values of the frustules, 10mg of diatom sample (VT-8C) were reacted with 1L of 15 molar nitric acid spiked with $^{18}$O-enriched water to bring the $\delta^{18}$O value of the acid to ~1000‰ (vs. VSMOW) for ~12 hours at 90°C.

**Oxygen Isotope Analysis**

Diatom frustules are composed of biogenic opal A (hydrated silica) and can contain up to 15 wt. % H$_2$O, meaning that as much as 20-30% of the diatom oxygen must be removed in order to obtain reproducible $\delta^{18}$O$_{\text{diatom}}$ values (Labeyrie and Juillet 1982; Leng et al., 2001; Leng and Barker, 2006). Removal of the hydroxyl oxygen is required prior to $\delta^{18}$O analysis, as oxygen in the hydrated portion of the frustule freely exchanges with the environment (e.g. Mopper and Garlick, 1971; Juillet-Leclerc and Labeyrie,
1987; Leng and Barker, 2006). In this study, I combined the stepwise fluorination procedure of Matheney and Knauth (1989) with laser fluorination (Sharp, 1990). Batches of 10-18 samples of <2mg of pure diatom silica and standards are loaded into a nickel sample holder and evacuated in the laser chamber for 24 to 36 hours. Subsequently, 100 mbar of pure F₂ gas was admitted to the chamber at room temperature to remove remaining absorbed H₂O and exchangeable hydroxyl oxygen atoms (e.g. Haimson and Knauth, 1983; Matheney and Knauth, 1989). Fluorine gas was chosen over BrF₅ as a prefluorinating agent because it is less likely to cause an isotopic fractionation during partial fluorination (Garlick and Epstein, 1967). In addition to dehydrating the diatom samples, prefluorination provided a visual check of diatom purity, as samples that still contained greater than 0.5 wt. % carbon reacted violently with the F₂ gas.

The water content varies considerably between species and between samples of different ages (Kamatani, 1971); therefore, the amount of F₂ required to completely dehydrate the sample yet not completely dissolve the silica varies greatly between samples (Leng and Baker, 2006). Following the initial fluorination with 100 mbar of F₂ gas for 1 hour, fluorination is repeated with 50 mbars of F₂ gas for approximately 1 hour an additional one to five times. Internal laboratory diatom "standards" SR2-1B (\(\delta^{18}O_{\text{diatom}} = 32.2 \pm 0.2\%o, n=13\)) and VT-8C (\(\delta^{18}O_{\text{diatom}} = 28.6 \pm 0.2\%o, n=10\)) were analyzed with each batch of samples as monitors of the prefluorination procedure. As diatom samples were subjected to increasing degrees of prefluorination, the \(\delta^{18}O_{\text{diatom}}\) values increased due to the removal of the hydroxyl oxygen that has relatively lower \(^{18}O/^{16}O\) ratios (Figure 2.1). Prefluorination was considered complete when the \(\delta^{18}O_{\text{diatom}}\) values of the in-house-
Figure 2.1. Plot of $\delta^{18}O_{\text{diatom}}$ values (SR2-1B) vs. degree of prefluorination. Once hydrated material has been completely removed, the $\delta^{18}O_{\text{diatom}}$ values plateau on a consistent value $\delta^{18}O_{\text{diatom}} = 32.2 \pm 0.2\%$o (n=13; horizontal bar). Continued fluorination does not change the $\delta^{18}O$ value of the sample, but will eventually remove the entire sample. Following the initial fluorination with 100 mbar of F$_2$ gas for 1 hour, fluorination is repeated with 50 mbar of F$_2$ gas for approximately 1 hour each. Symbols indicate different analytical sessions.
diatom 'standard' reached a plateau and were within 0.2‰ of the known $\delta^{18}O_{\text{diatom}}$ value for that standard (e.g. Matheney and Knauth, 1989 Schmidt et al., 1997). During prefluorination, HF and SiF$_4$ gas were produced and continuously frozen in a liquid nitrogen trap. Although the F$_2$ gas reacts with the silica, it does not alter the $\delta^{18}O$ value of the remaining diatom silica (Garlick and Epstein, 1967).

Once all hydroxyl oxygen has been removed at room temperature by prefluorination, samples are heated with a CO$_2$ laser in the presence of 100 mbar BrF$_5$ to produce SiF$_4$ and O$_2$ gas (e.g. Sharp, 1990). Each sample is heated by the CO$_2$ laser on low power (1 to 2% of total 20W beam power) with a defocused beam for approximately 60s. This initial heating causes individual frustules to begin to fuse, thus limiting sample ejection when the laser power is increased (Kirschner and Sharp, 1997). Laser power is then rapidly increased to 30 to 40% full beam power and focused to a beam diameter of ~100 µm and the sample is heated until it completely is converted to a gas (~120s). O$_2$ is transferred cryogenically by adsorption on a zeolite trap. The trap is heated and the O$_2$ gas is expanded into the dual inlet of a Finnigan MAT Delta Plus mass spectrometer. The O$_2$ gas is then analyzed for the $\delta^{18}O$ value of the initial diatom SiO$_2$. The ability of the laser ablation method to analyze relatively small sample sizes (<2mg) makes this method broadly applicable for reconstruction of paleoclimate records from lacustrine and marine diatom sedimentary sequences where low diatom abundances limit sample availability (Leng and Barker, 2006).


2.4 RESULTS

Chemical Purification Results

When diatoms were treated with 30% hydrogen peroxide (H₂O₂) alone, significant organic material (>5 weight percent carbon) remained, and required the additional use of a strong chemical treatment as per previous studies (e.g. Juillet-Leclerc, 1984). When samples with >5 weight percent carbon where exposed to F₂ gas they combusted and produced an ash like substance. The δ¹⁸O_{diatom} value of samples analyzed after combustion varied by more than 50‰ indicating that the reaction significantly altered the δ¹⁸O_{diatom} value. Elemental analysis of these samples indicate the carbon, most likely in the form of residual organic material, is only impurity and therefore is the cause of this violent reaction. Treatment of diatom samples with nitric acid (HNO₃) at room temperature did not completely remove organic material (>0.5 weight percent carbon) in agreement with Crespin et al. (2008). Organic material was successfully removed from diatom frustules only by treatment with 15M HNO₃ at 90°C for 12h. Visual inspection of diatom frustules with a scanning electron microscope before and after treatment with HNO₃ indicated no physical alteration of the frustule structure (Figure 2.2). Oxygen isotope exchange does not occur between the hot acid and diatom, as demonstrated by treatment of diatom samples VT-8C and VC09-01 with ¹⁸O-enriched HNO₃ at 90°C. Sample VT-8C was collected from a nearly pure Pleistocene diatomite in the Valles Caldera (VT-8C) and has a δ¹⁸O_{diatom} value of 28.6 ± 0.2‰ (n= 10). Sample VC09-01 is a modern diatom from a small pond in the Valles Caldera with a δ¹⁸O_{diatom} value of 22.2± 0.3‰ (n=7). After initial prefluorination treatment with a stoichiometric deficiency of F₂ gas, the δ¹⁸O values of the diatom frustules in the VT-8C sample treated with ¹⁸O-
Figure 2.2. Diatom frustules of middle Pleistocene age VT-8C sample before (A) and after (B) treatment with HNO₃ show no signs of dissolution.
enriched HNO₃ were approximately 10‰ higher than those treated with normal HNO₃ while the δ¹⁸O_diatom values in the VC09-01 sample were approximately 70‰ higher. This is due to remaining hydroxyl oxygen which had exchanged with the nitric acid and, which also demonstrates the greater amount of hydroxyl oxygen in modern verses sub-fossil diatom silica. With increasing degrees of prefluorination, however, the δ¹⁸O values of diatoms treated with the ¹⁸O-enriched HNO₃ were the same, within error, as those treated with regular HNO₃ (Figure 2.3A&B). The only significant difference between the two samples is that the modern diatom sample (VC09-01) required twice as much F₂ gas as the sub-fossil sample, which is in agreement with results published by Juillet (1980) that indicate modern diatoms have approximately twice the exchangeable oxygen as sub-fossil diatoms.

Our experiments with ¹⁸O-enriched HNO₃ clearly demonstrate that treatment of the diatoms with 15 molar nitric acid at 90°C for 12hrs does not affect the δ¹⁸O value of the oxygen in the diatom silica. This is in contrast to the results of Crespin et al. (2008), who noted that at treatment temperatures greater than 60°C, measured δ¹⁸O_diatom values were approximately 1‰ higher than diatoms treated between 50°C and 60°C. One possibility for the discrepancy is that our nitric-acid treatment did alter the δ¹⁸O values of the diatoms, but that the prefluorination step removed the altered silica prior to δ¹⁸O analysis. A more likely explanation for the discrepancy is that Crespin et al. (2008) did not remove all hydroxyl oxygen during prefluorination. A similar offset in measured δ¹⁸O_diatom values occurred in this study when samples were not sufficiently prefluorinated (Figure 2.3), thus demonstrating that the prefluorination step is critical and must remove all hydrated material in order to obtain accurate δ¹⁸O_diatom values.
Diatom Isotope Data

The $\delta^{18}$O values measured using our stepwise fluorination laser ablation method are highly reproducible. For our internal laboratory diatom standards SR2-1B and VT-8C, the 1σ standard deviation of multiple samples is ± 0.2‰ (Table 2.1). As a further test of the accuracy of our method, a sample analyzed by Brandriss et al. (1998) was generously provided for an inter-laboratory comparison. This sample yielded a $\delta^{18}$O$_{\text{diatom}}$ value of 30.1‰ (± 0.1‰ VSMOW, n=3), compared to the value of 30.4‰ obtained by Brandriss et al. (1998) through stepwise fluorination using conventional nickel bombs (Clayton and Mayeda, 1963). All data are reported relative to VSMOW, defined by NBS-28 = 9.65‰.

Sample information for the modern (live) freshwater diatoms used in this study is given in Table 2.2. There is a clear relationship between oxygen isotope (1000ln$\alpha$$_{\text{diatom-water}}$) and the water (growth) temperatures ($T_w$ in Kelvin) of a range of 5.1°C to 37.8°C (Figure 2.4), which is represented by the following equation:

$$1000\ln\alpha_{\text{silica-water}} = 2.39(\pm 0.13) \times 10^6T_w^{-2} + 4.23(\pm 1.49) \quad (2.1)$$

where $\alpha_{\text{silica-water}} = (1000 + \delta^{18}$O$_{\text{diatom}})/(1000 + \delta^{18}$O$_{\text{H2O}})$. This relationship is nearly identical that presented by Brandriss et al. (1998) where

$$1000\ln\alpha_{\text{silica-water}} = 2.21(10^6T_w^{-2}) + 6.42 \quad (2.2)$$

This is equivalent to a temperature coefficient of -0.2‰/°C, which is identical to temperature coefficients obtained by Brandriss et al. (1998) and Moschen et al. (2005).

2.5 COMPARISON WITH PREVIOUS STUDIES

Diatom Isotope Data

The $\delta^{18}$O$_{\text{diatom}}$ values in this study are in agreement with silica-water fractionation reported by previous studies (Brandriss et al., 1998; Schmidt et al., 2001; Moschen et al.,
Figure 2.3. (A) $\delta^{18}O_{\text{diatom}}$ values vs. degree of prefluorination for samples reacted with $^{18}$O-enriched nitric acid. 10 mg of diatom sample (VT-8C) were reacted for ~12 hrs at 90°C with 1 liter of 15 molar nitric acid which had been spiked with $^{18}$O-enriched water to bring the $\delta^{18}$O value of the acid to ~1000‰ (vs. VSMOW). The sample treated with the $^{18}$O-enriched nitric acid (X) initially displayed values that were 10‰ higher than those treated with normal nitric acid ($\delta^{18}$O ~ 0‰; closed circles); however, these two samples converged on the known value of VT-8C of 28.6‰ (± 0.2‰ VSMOW) once fluorination is complete (arrow). Initial fluorination was with 100 mbar of F$_2$ for 1 hour. The two subsequent fluorination treatments were with 50 mbar of F$_2$ for 1 hour. After the third treatment, there was essentially no difference (within error) between the two batches of samples. (B) The same procedure was repeated with a modern diatom sample (VC09-01) that has a reproducible $\delta^{18}O_{\text{diatom}}$ value of 22.2‰ (± 0.2‰ VSMOW). The $\delta^{18}O_{\text{diatom}}$ values initially measured in the VC09-2 frustules treated with the $^{18}$O-enriched nitric acid was considerably larger than with VT-8C, and gave a $\delta^{18}O_{\text{diatom}}$ value of 90.85‰ VSMOW. The modern frustules also required more extensive prefluorination than VT-8C; however a $\delta^{18}O_{\text{diatom}}$ value of 22.3‰ was ultimately obtained (arrow).
Table 2.1. Reproducibility of stepwise fluorination laser ablation method with subfossil diatoms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>$\delta^{18}$O</th>
<th>Date Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR2-1B</td>
<td>2.5</td>
<td>32.5</td>
<td>3/12/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
<td>3.4</td>
<td>32.4</td>
<td>3/12/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
<td>2.6</td>
<td>32.5</td>
<td>3/30/2007</td>
</tr>
<tr>
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<td>2.7</td>
<td>32.5</td>
<td>3/30/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
<td>1.0</td>
<td>31.8</td>
<td>6/30/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
<td>2.0</td>
<td>32.2</td>
<td>6/30/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
<td>1.3</td>
<td>32.2</td>
<td>7/2/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
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<td>32.3</td>
<td>8/26/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
<td>1.5</td>
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<td>SR2-1B</td>
<td>2.0</td>
<td>32.1</td>
<td>9/19/2007</td>
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<tr>
<td>SR2-1B</td>
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<td>32.3</td>
<td>9/19/2007</td>
</tr>
<tr>
<td>SR2-1B</td>
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</tr>
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<td>Average</td>
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<td></td>
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<td>VT-8C</td>
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</tr>
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<td>3/12/2007</td>
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<td>3/12/2007</td>
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<td>5/11/2009</td>
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<td></td>
</tr>
<tr>
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<td>Location</td>
<td>Diatom Taxonomy</td>
<td>Substrate</td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
<td>----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>VC08-03</td>
<td>E. Fork Jemez River</td>
<td><em>Pinnularia</em> sp., <em>Synedra</em> sp., <em>Synedra</em> sp</td>
<td>vegetation</td>
</tr>
<tr>
<td>VC08-07</td>
<td>Jaramillo Creek</td>
<td><em>Pinnularia</em> sp., <em>Synedra</em> sp</td>
<td>sediment/streambed</td>
</tr>
<tr>
<td>VC08-05</td>
<td>Soda Dam Hot Spring</td>
<td><em>Cymbella</em> sp.</td>
<td>cyanobacteria mats</td>
</tr>
<tr>
<td>VC08-13</td>
<td>Soda Dam Hot Spring</td>
<td><em>Cymbella</em> sp.</td>
<td>cyanobacteria mats</td>
</tr>
<tr>
<td>VC09-00</td>
<td>Soda Dam Hot Spring</td>
<td><em>Cymbella</em> sp.</td>
<td>cyanobacteria mats</td>
</tr>
<tr>
<td>VC09-03</td>
<td>Soda Dam Hot Spring</td>
<td><em>Cymbella</em> sp.</td>
<td>cyanobacteria mats</td>
</tr>
<tr>
<td>VC08-02</td>
<td>Valles Caldera Pond</td>
<td><em>Pinnularia gastrum</em></td>
<td>vegetation</td>
</tr>
<tr>
<td>VC08-10</td>
<td>Valles Caldera Pond</td>
<td><em>Pinnularia</em> sp., <em>Gomphonema</em> sp., <em>Pinnularia</em> sp., <em>Pinnularia</em> sp., <em>Pinnularia</em> sp., <em>Gomphonema</em> sp., <em>Synedra</em> sp</td>
<td>vegetation</td>
</tr>
<tr>
<td>VC08-11</td>
<td>Valles Caldera Pond</td>
<td><em>Fraularia</em> sp., <em>Gomphonema</em> sp., <em>Synedra</em> sp</td>
<td>vegetation</td>
</tr>
<tr>
<td>VC09-01</td>
<td>Valles Caldera Pond</td>
<td><em>Pinnularia gastrum</em></td>
<td>vegetation</td>
</tr>
</tbody>
</table>
$1000 \ln \alpha_{\text{SiO}_2 - \text{H}_2\text{O}} = 2.39 \times (10^6/T^2) + 4.23$

$r^2 = 0.98$

This Study
Figure 2.4. $\delta^{18}O_{\text{diatom}}$ values from this study (solid circles), plotted in $1000/\Delta_{\text{silica-water}}$ vs. $10^6 T^{-2}$ space, display a silica-water fractionation defined by (red line) $1000/\Delta_{\text{silica-water}} = 2.39 (\pm 0.13) \times 10^6 T_w^{-2} + 4.23 (\pm 1.49)$. $\delta^{18}O_{\text{diatom}}$ values with repeat analyses are shown as an average value with vertical error bars. This fractionation is almost identical to that published by Brandriss et al. (1998) for cultured diatom silica (A; open circles) and similar to a silica-water fractionation curve published by Moschen et al. (2005) for diatoms in a freshwater lake (B; open triangles). $\delta^{18}O_{\text{diatom}}$ values from cultured studies by Schmidt et al. (2001; +) generally fall below a silica-water fractionation determined from our study and may be explained by incomplete removal of hydroxyl oxygen. One sample from this study (VC08-7; denoted by a star) collected from the sediment surface, as well as other sediment trap $\delta^{18}O_{\text{diatom}}$ data (Schmidt et al., 2001; X) approach the silica-water fractionation published by Moschen et al. (2005). Additional $\delta^{18}O_{\text{diatom}}$ data from sediment samples from Matheney and Knauth (1989; solid boxes) and Schmidt et al. (2001; open boxes) fall closer to the equilibrium silica-water fractionation factor (Sharp and Kirshner, 1994; C). Other published fractionation factors shown here are Juillet-Leclerc and Labeyrie (1987; D), Kita et al. (1985; E), Clayton et al. (1972; F), Becker and Clayton (1976; G) and Knauth and Epstein (1976; H). Some of these lines have been extrapolated beyond the original temperature ranges and may therefore include large uncertainties.
and demonstrate that the isotopic fractionation between modern (cultured or collected as living specimens) diatoms and water is strongly temperature dependent and record a consistent silica-water oxygen isotope fractionation (Figure 2.4). As with any samples collected from a natural system, there is no assurance that the temperatures and \( \delta^{18}O_{H2O} \) measured during sample collection are truly representative of the total growth period of the diatom frustules. However, individual diatoms have relatively short life spans; by sampling living diatom communities the time averaging of water temperature and \( \delta^{18}O_{H2O} \) values recorded by the diatom silica is reduced to less than a week (e.g. Patrick, 1977; Lotter et al., 1999). The sites reported here are from a high altitude (~3000m) alpine region where the dominant water source is spring snow-melt via runoff and infiltration. Temperature and \( \delta^{18}O_{H2O} \) variations in the sample locations were relatively small on a weekly time frame. In particular, the \( \delta^{18}O_{H2O} \) values of the Valles Caldera Pond were very consistent over the entire sample period, with a total variability of only 1.2‰ over a 12-month period and were essentially constant over a 10 day period (equal to the growth period of individual diatom frustules). Water temperature of Jaramillo Creek and the East Fork of the Jemez River varied by less than 2°C over any 10 day period during the sample period.

Four genera of diatoms (Table 2.2) are included in this study and display no systematic species-dependent variation in the silica-water fractionation. These data support results of previous studies in which no significant species effects were found (e.g. Brandriss et al., 1998; Moschen et al., 2005). Other studies have demonstrated a possible species effect as high as 3.5‰ on the \( \delta^{18}O_{diatom} \) values observed in different size fractions.
of diatom frustules in marine sediments; however, the explanation for these offsets is not clear (e.g. Swann, 2007).

Comparison with older sediment samples

A nearly identical temperature-dependent diatom-water fractionation for living diatoms has now been obtained from three independent studies. However, the measured fractionations are significantly smaller than any published curve for equilibrium quartz-water fractionation (Figure 2.4; Sharp and Kirschner, 1994). When the silica-water fractionation observed in this study or by other modern diatom studies (Brandriss et al., 1998; Moshcen et al., 2005) is applied to diatoms collected from sediments, unrealistically low temperatures and/or $\delta^{18}O_{H_2O}$ reconstructions are obtained. For example, if our silica water fractionation equation is applied to $\delta^{18}O$ values of diatoms collected from sediment traps and from core-tops in Alaskan lakes (Schiff, 2007), temperatures between -29 and -11°C are obtained. Although water temperatures at these locations were not measured, the projected temperatures using our silica-water fractionation are well below possible water temperatures. Far more reasonable temperature estimates are obtained using silica-water fractionations closer to equilibrium quartz-water fractionation (Table 2.3). The silica-water fractionation recorded by modern diatom silica is therefore not the same as that recorded by sub-fossil diatoms.

Three possibilities are considered to explain the discrepancy between living and sediment-derived samples. The first is that the silica does not precipitate in equilibrium with ambient water but is modified in post mortem digenesis. Such effects are seen for rapidly growing calcite (McCrea, 1950; O'Neil et al., 1969) and have been seen for rapid, non-equilibrium $SiO_2$ crystallization (Sharp and Kirschner, 1994). Alternatively, the
Table 2.3. Temperature estimates for sediment trap samples from Alaskan lakes (Schiff, 2007). Estimates using modern diatom samples are unreasonably low. Instead, these samples more closely represent fractionations for quartz-water.

<table>
<thead>
<tr>
<th>Location</th>
<th>(\delta^{18}O_{H2O})</th>
<th>(\delta^{18}O_{\text{diatom}})</th>
<th>Estimated (T^\circ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee's Lake</td>
<td>-16.1</td>
<td>26.9</td>
<td>-23.9</td>
</tr>
<tr>
<td>Mica Lake</td>
<td>-13.2</td>
<td>29.8</td>
<td>-23.2</td>
</tr>
<tr>
<td>Shrode Lake</td>
<td>-14.0</td>
<td>26.7</td>
<td>-16.3</td>
</tr>
<tr>
<td>Milliard Lake</td>
<td>-15.3</td>
<td>24.7</td>
<td>-14.0</td>
</tr>
<tr>
<td>Cascade Lake</td>
<td>-15.2</td>
<td>25.7</td>
<td>-17.1</td>
</tr>
<tr>
<td>Bear Lake</td>
<td>-14.0</td>
<td>25.8</td>
<td>-13.2</td>
</tr>
</tbody>
</table>
silica does precipitate in equilibrium with ambient water, but the silica-water fractionation factor for diatom silica is considerably less than the equilibrium fractionation factor for quartz-water. Finally, the discrepancy could relate to a ‘vital’ effect, where the $\delta^{18}$O value of the water inside the diatom cell walls has a lower $\delta^{18}$O value than the ambient stream water. In this case, the $\delta^{18}$O value of the diatom frustules would be in equilibrium with the intercellular water with the same fractionation as quartz-water, but would give an apparent offset due to the difference in the $\delta^{18}$O value of the intracellular and ambient water. This could be caused by the production of silicic acid within the diatom cells and the preferential incorporation of $^{18}$O by the silica frustules, which would result in a concomitant depletion in the $\delta^{18}$O value of the intercellular water. Any additional silica precipitation will occur in equilibrium with the lighter intercellular water resulting in an apparent $\ln$ silica-water that is less than the equilibrium quartz-water fractionation factor.

In this study, one sample (VC08-07) was collected from the sediment surface in Jaramillo Creek. The silica-water fractionation observed in this sample falls well above the silica-water fractionation line derived from the other modern samples and is nearly identical to that observed in diatoms collected from sediment traps (Figure 2.4; Moschen et al., 2005). I believe that this sample contained a significant amount of diatom frustules which had undergone post-mortem diagenesis, and therefore the $\delta^{18}$O$_{\text{diatom}}$ value of this sample is likely the result of silica maturation.

Schmidt et al. (2001) demonstrated that there is not a differential dissolution of $^{18}$O and $^{16}$O in the Si-O bonds of diatom silica. The change in $\delta^{18}$O$_{\text{diatom}}$ values between living and sub-fossil diatoms cannot therefore be attributed solely to preferential
dissolution of $^{16}$O-rich material (Lewin, 1961; Mayer et al., 1991; Schmidt et al., 2001). Rather, the discrepancy between silica-water fractionation factors observed in modern and sub-fossil diatom silica is due to maturation as the diatom frustules sink through the water column or at the sediment water interface (Matheney and Knauth, 1989; Schmidt et al., 2001). I believe diatom silica reequilibrates with ambient water according to an abiogenic silica-water fractionation that is higher than that observed in modern (live) diatom samples. The silica-water fractionation factors for sub-fossil diatom frustules collected from sediments are closer to theoretical and measured quartz-water equilibrium fractionation factors (Matheney and Knauth, 1989; Sharp and Kirschner, 1994). Thus, the maturation of diatom silica by condensation of new silica could explain the discrepancies observed in published silica-water fractionation in diatoms (e.g. Brandriss et al., 1998; Schmidt et al., 2001).

Although no explanation for this diagenesis and alteration of $\delta^{18}$O$_{\text{silica}}$ values in the diatom cells has been observed, it is possible that it is a result of bacterial consumption of organic matter in the diatom cell. Since the bulk of reequilibration of $\delta^{18}$O$_{\text{diatom}}$ values likely takes place at depth in the water column or at the sediment water interface, the $\delta^{18}$O$_{\text{diatom}}$ values of sediment samples do not record water temperatures and $\delta^{18}$O$_{\text{H2O}}$ values of diatom growth. Rather, $\delta^{18}$O$_{\text{diatom}}$ values record the equilibrium quartz-water fractionation at or just below the sediment-water interface.

The $\delta^{18}$O values of diatoms are a function of both temperature and the isotopic composition of water. While this complicates the interpretation of the isotope data, many lakes, particularly deep lakes, have a nearly constant bottom temperature (~4°C) (Vallentyne, 1957). If $\delta^{18}$O$_{\text{diatom}}$ values reequilibrate at the sediment water interface,
variations in atmospheric temperature are not recorded by mature diatom silica. This, in effect, means that $\delta^{18}O_{\text{diatom}}$ values from paleo-diatoms will generally provide direct information on the $\delta^{18}O$ value of the lake water. I propose that this reequilibration of diatom silica $\delta^{18}O$ values occurs relatively quickly, as several recent studies of diatoms in lacustrine sediments have noted that there is a strong relationship between changes in the $\delta^{18}O$ values of precipitation and the $\delta^{18}O_{\text{diatom}}$ values (e.g. Schiff et al. 2008, Taylor et al., 2008). Although it is unlikely that the diatom silica entirely reequilibrates, the 8‰ shift in $1000\ln\alpha_{\text{diatom-water}}$ indicates that the $\delta^{18}O$ values recorded by the reequilibrated silica appear to overwrite the initial $\delta^{18}O_{\text{diatom}}$ values. I also argue that the reequilibration of diatom oxygen does not limit the utility of this paleoclimate proxy; in fact, it increases it because lacustrine $\delta^{18}O_{\text{diatom}}$ values would therefore record variations in paleoprecipitation. Changes in the $\delta^{18}O$ values of the water would result in a nearly one-to-one change in the diatom $\delta^{18}O$ values, where as a change of 5°C only equates to ~1‰ variability in diatom $\delta^{18}O$ values. There is no evidence that freshwater and marine diatoms behave differently in life or during the maturation process; therefore, the maturation of diatom silica in marine environments, though beyond the scope of this paper, has significant implications for the environmental information recorded by marine $\delta^{18}O_{\text{diatom}}$ values.

### 2.6 CONCLUSIONS

Oxygen isotope studies of diatom frustules have indicated an apparent discrepancy in the silica-water fractionation factor between modern or cultured diatoms and sediment derived diatom records (e.g. Schmidt et al. 2001; Moschen et al, 2005, Moschen et al., 2006; Tyler et al., 2008). The $\delta^{18}O$ values of modern diatoms collected as
living specimens from natural, freshwater environments record a temperature dependent, silica-water fractionation nearly identical to that reported by Brandriss et al. (1998) and Moschen from cultured diatom samples. It is promising that the temperature coefficient of -0.2‰/°C observed in this study is identical to other studies involving modern diatom silica (Brandriss et al., 1998; Moschen et al., 2005).

This strong temperature correlation observed in modern diatoms does not, however, solve the conundrum presented by the discrepancies observed in the silica-water fractionation factors of modern and sub-fossil diatoms. When the silica-water fractionation from modern samples is applied to sediment-based $\delta^{18}O_{\text{diatom}}$ values, unrealistic temperature and/or water values are obtained. The explanation for this apparent discrepancy is that $\delta^{18}O_{\text{diatom}}$ values are subject to alteration during the maturation process as diatom frustules are incorporated in the sediment. Since sediment-based $\delta^{18}O_{\text{diatom}}$ values do appear to record changes in the $\delta^{18}O$ composition of the water, it appears that this maturation process occurs relatively quickly once the organic coating of diatom frustules has begun to decay. Despite this alteration – or in fact, because of it – sediment-based diatom $\delta^{18}O_{\text{silica}}$ values do record valuable environmental information, namely the $\delta^{18}O$ value of lake water.

The results of this study indicate that the $\delta^{18}O$ values of diatoms collected in sediments most likely do not record the conditions during diatom growth in the water column. While this conclusion initially appears to limit the utility of paleoclimate reconstruction from oxygen isotope values of diatoms, this is not the case. In fact, if $\delta^{18}O_{\text{diatom}}$ values are recording the temperature and $\delta^{18}O_{\text{H}_2\text{O}}$ values of the sediment-water interface, particularly in the case of lacustrine diatoms where bottom temperatures are
often ~4°C, it dramatically simplifies interpretation of sub-diatom δ¹⁸O values. The δ¹⁸O_diatom values in that case will be directly related to isotopic composition of the lake water (at constant temperature). Rapid temperature fluctuations and local evaporation effects occur in the uppermost layers of a lake and are essentially eliminated as a variable, giving a signal that is representative of a time-integrated average lake water δ¹⁸O values. Further research is required to elucidate the silica-water fractionation observed in mature diatom silica; however, the implication is that lacustrine δ¹⁸O_diatom values can potentially be used to reconstruct high-resolution variations in paleoprecipitation.

Acknowledgements

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CHAPTER 3 MATURATION OF DIATOM SILICA $\delta^{18}O$ VALUES WITHIN ONE GROWING SEASON: IMPLICATIONS FOR DIATOM SILICA ISOTOPES AS PALEOClimATE PROXIES

ABSTRACT

Post-mortem alteration of silica $\delta^{18}O$ values occurs within one growing season in diatom frustules from a lacustrine setting in the Valles Caldera, New Mexico. Diatom silica collected antemortem from the Valles Caldera headquarters pond have $\delta^{18}O$ values of 21.5‰ (VSMOW, $2\sigma = 1.3$, $n = 23$); whereas diatom silica from two sediment cores from the same pond record significantly higher $\delta^{18}O$ values (28.9‰, $2\sigma = 0.8$, $n = 13$), indicating post-mortem alteration of diatom silica $\delta^{18}O$ values that results in an $\sim 7.4$‰ increase in $\delta^{18}O$ values. The diatom silica $\delta^{18}O$ values from the Valles Caldera Pond reach mature values within 0.5 years of frustule death. Similar effects of silica maturation on $\delta^{18}O$ values and frustule reactivity have been noted by other studies; however, this study demonstrates that initial diatom $\delta^{18}O$ values that record growing conditions are rapidly and completely overwritten during silica maturation and that the mature diatom $\delta^{18}O$ values approach isotopic equilibrium for quartz-water. Despite the significant change in silica $\delta^{18}O$ values, high resolution SEM and TEM imaging of diatom frustules collected ante- and post-mortem show no significant alteration of silica structures or crystallography. The rapid post-mortem alteration of diatom $\delta^{18}O$ values explains much of the disparate data regarding silica-water fractionation for diatom silica and has a profound effect on the use of diatom silica $\delta^{18}O$ values as a paleoclimate proxy. In the setting of open basin lacustrine environments where bottom temperatures are nearly constant at 4°C, the maturation effect may facilitate reconstruction of variations in
paleowater $\delta^{18}O$ values without the conflating influence of fluctuating water temperature and variable $\delta^{18}O_{\text{water}}$ values that occur at the surface.

### 3.1 INTRODUCTION

Silica frustules from diatoms are widely distributed throughout marine and nonmarine environments and are abundantly preserved throughout the past 70 Ma of Earth history (e.g. Chacón-Baca et al., 2002; Falkowski et al., 2004; Leng and Barker, 2006). Oxygen isotope ratios preserved in the silica of diatom frustules have great potential as paleoclimate proxies; however, there is considerable variation in published silica-water oxygen isotope fractionation for diatom frustules, with a discrepancy up to 8‰ between measured fractionations of diatom frustules and coexisting water collected from living specimens (cultured and natural settings) and those expected based on published quartz-water equilibrium fractionation factors (e.g. Matheney and Knauth, 1989; Sharp and Kirschner 1994; Schmidt et al., 2001; Moschen et al., 2006; Brandriss et al., 1998; Dodd and Sharp, 2010). X-ray diffraction, infrared-absorption, and transmission electron microscopy have been used to examine the crystallographic properties of diatom silica and demonstrate that there is no regular ordering of the atomic lattice and that diatom silica is amorphous silica (e.g. Kamatani, 1971; Volcani, 1981; Robinson and Sullivan, 1987). Additionally, modern diatom silica has been shown to be more susceptible to dissolution and alteration of $\delta^{18}O$ values than ancient diatom silica (Moschen et al., 2006; Labeyrie and Juillet, 1982; Kamatani, 1971).

Diatom frustules from fresh water environments in northern New Mexico were used by Dodd and Sharp (2010) to produce a silica-water fractionation for antemortem diatoms given by the following equation:
1000lnα_{silica-water} = 2.39 \times 10^6 T^{-2} + 4.23 \quad (3.1)

However, this equation does not appear to explain the $\delta^{18}O$ values of diatoms extracted from sediments, suggesting that some form of maturation and oxygen isotope reequilibration occurs post-mortem (e.g. Matheney and Knauth, 1989; Brandriss et al., 1998; Schmidt et al., 2001; Moschen et al., 2006; Dodd and Sharp, 2010). Silica-water fractionation factors for marine diatoms (Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992) are up to 8‰ higher than silica-water fractionation factors for diatoms collected antemortem (Brandriss et al., 1998; Dodd and Sharp, 2010). Additionally, the higher diatom silica-water fractionation factors approach the quartz-water equilibrium fractionation of Sharp and Kirschner (1994), which represents the high end member of silica-water fractionation factors.

While it is clear that there is some degree of post-mortem reequilibration, the timing and extent of the reequilibration and the fractionation factors governing this reequilibration have not been well established (Schmidt et al., 2001; Moschen et al., 2006), nor have there been any detailed comparisons between changes in the $\delta^{18}O$ values and fine-scale crystallographic modifications. Errors imparted by various analytical methods and limited data about the water temperature and $\delta^{18}O_{H2O}$ values recorded by diatom silica have obscured which silica-water fractionation equation is most appropriate for reconstructing temperature and/or water $\delta^{18}O$ values from diatom silica in a paleoclimate context (e.g. Matheney and Knauth, 1989; Dodd and Sharp, 2010).

Here I present diatom silica maturation data that reconcile the disparate diatom silica-water fractionation relationships in the literature and demonstrate that post-mortem alteration of diatom silica $\delta^{18}O$ values occurs in a lacustrine environment within one
growing season (~0.5 years). Initial δ^{18}O values of the diatom silica are overwritten by those that record water conditions and temperature of diagenesis and reequilibration with bottom water or pore waters at the sediment-water interface and approach quartz-water equilibrium fractionation. δ^{18}O values preserved in subfossil diatom silica, particularly from some lacustrine environments, can therefore be used as paleoclimate proxies of precipitation δ^{18}O values.

3.2 GEOLOGIC BACKGROUND

Diatom samples were collected from a small artificial pond in the Valles Caldera in the Jemez Mountains of northern New Mexico. The caldera floor was covered by large shallow lakes during several periods between 1.25 Ma and 55ka, where the abundance of silica and other nutrients allowed for high diatom productivity (Reneau et al., 2007; Fawcett et al., 2007). In the modern setting, there are no longer large lakes in the Valles Caldera; however, waters in the caldera remain a productive location for diatom growth. The pond, which is located near the park headquarters (35° 51' 54.6"N, 106° 31' 02.95"W; 2669 m asl), lies on a tributary of the East Fork of the Jemez River and provides an ideal natural environment to investigate diatom growth conditions and δ^{18}O values in a modern setting.

The pond has a maximum diameter of ~20 m and a maximum depth of ~2 m and is ice-covered from November to early April. Growing season (April – November) diatom populations, diatom δ^{18}O values, water δ^{18}O values, and water temperatures have been monitored at the Valles Caldera headquarters pond from April 2008 through September 2010 (Table 3.1; Dodd and Sharp, 2010). The period of maximum diatom
Table 3.1. Antemortem and post-mortem $\delta^{18}O_{\text{diatom}}$ values, $\delta^{18}O_{\text{water}}$ values, water temperatures, and calculated silica-water fractionation data

<table>
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<tr>
<th>Sample ID</th>
<th>Depth (m)</th>
<th>Sample Type</th>
<th>Sample Date</th>
<th>$\delta^{18}O_{\n{HDO}}$ water (°C)</th>
<th>$\delta^{18}O_{\text{diatom}}$ Measured Ave n 2σ</th>
<th>$10^6/T^2$ (K)</th>
<th>1000 ln a</th>
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<td>VC08-02*</td>
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<td>4/21/2008</td>
<td>-12.8 5.5</td>
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Post-Mortem – Sediment Core VC09-06

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<th>Sample ID</th>
<th>Depth (m)</th>
<th>Sample Type</th>
<th>Sample Date</th>
<th>$\delta^{18}O_{\n{HDO}}$ water (°C)</th>
<th>$\delta^{18}O_{\text{diatom}}$ Measured Ave n 2σ</th>
<th>$10^6/T^2$ (K)</th>
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* from Dodd and Sharp (2010)
† The average $\delta^{18}O_{\text{water}}$ value for growing season months (April-October) of the Valles Caldera Pond between April 2008 and September 2010 is -13.0 (2σ = 0.62; n=11).
§ temperature calculated using silica-water fractionation of Dodd and Sharp (2010) for modern diatom silica
# temperature calculated using silica-water fractionation of Becker and Clayton (1976), representing intermediate silica maturation
** temperature calculated using silica-water fractionation of Juillet-Leclerc and Labeyrie (1987) for complete silica maturation
Note: Remaining samples are stored in the collections of the University of New Mexico Department of Earth and Planetary Sciences, Albuquerque, New Mexico, 87131. All $\delta^{18}O$ values are reported relative to VSMOW.
growth in the pond corresponds with spring runoff in late April/ early May and is consistent with published data indicating that diatom species can tolerate a wide range of growth temperatures and can thrive at low temperatures (e.g. Patrick, 1971; King et al., 2002). Diatom communities in the pond are dominantly *Pinnularia gastrum*, although *Pinnularia* sp., *Fragilaria* sp., *Gomphonema* sp., and *Synedra* sp. are present as well. The pond has a nearly constant water δ¹⁸O value of -13.0‰ (2σ =0.6, n=11) between April 2008 and September 2010 (Table 3.1). The pH of the pond is circum neutral with an average of 7.3 over the study period. A 0.58 m core collected in September 2010 terminates in basal gravel, and represents 9 years of sedimentation based historical data that indicates a most recent dredging of the pond in 2001. The pond has a constant through-flow that brings significant sand, silt, clay, and organic detritus which results in a relatively high sedimentation rate ~0.06 m/yr. Nine annual layers in the sediment core recorded by increases in diatom frustules and course silt/ sand were used to calculate the sedimentation rate. Mean annual air temperature at the Valles Caldera headquarters is 4.8°C (ISIS, 2010).

### 3.3 SAMPLE COLLECTION AND DIATOM OXYGEN ISOTOPE VALUES

Diatom silica analyzed in this study includes samples collected from living diatom populations and from two sediment cores from the Valles Caldera park-headquarters pond. Living samples in this study and in Dodd and Sharp (2010) were collected from floating and submerged substrates near the rim of the pond between April 2008 and September 2010 (Table 3.1). Sediment cores were collected in October 2009 (VC09-06) and September 2010 (VC10-2) from a boat in ~ 1.6m of water with a push core and a Livingstone corer. Sediment cores were extruded into PVC pipe, frozen, and
sliced. Isolation and cleaning of diatom frustules was accomplished following the procedure of Morley et al. (2004). δ^{18}O analyses were conducted using a laser fluorination technique (Dodd and Sharp, 2010). Diatom δ^{18}O values are reported in per mil (‰) relative to VSMOW defined by NBS-28 = 9.65‰.

Diatom silica collected antemortem in this study and by Dodd and Sharp (2010) as well as frustules from the upper 0.3m of the VC09-06 core have an average δ^{18}O_{diatom} value of 21.5‰ (2σ = 1.3, n=23). Diatom silica from 0.4m and below in both sediment cores have higher δ^{18}O values with an average value of 28.9‰ (2σ = 0.8, n=13). Intermediate δ^{18}O_{diatom} values were displayed by two samples (one from each core) and have an average δ^{18}O_{diatom} value of 24.9 ‰ (2σ = 0.4, n=2; Figure 3.1).

3.4 DIATOM FRUSTULE STRUCTURE

In contrast to the dramatic isotopic changes that occur during maturation, there are no structural/crystallographic changes observable by either scanning electron microscopy (SEM) or high resolution transmission electron microscopy (HRTEM). High magnification SEM images of antemortem diatom frustules (VC09-01; Figure 3.2A) and frustules from the sediment (VC09-06-05; Figure 3.2B) indicate no significant difference in the structure of the diatom frustules with the possible exception of what appear to be silica nodes on the frustule of the sample collected from the sediment core. HRTEM shows no difference in frustule structure and demonstrates that both the modern and sediment samples are completely amorphous (including silica nodes) as shown by a fast Fourier transform analysis diffraction pattern of the HRTEM image (Figure 3.3).
Figure 3.1 Diatom silica $\delta^{18}O$ values display a bimodal distribution. Unaltered silica from frustules collected antemortem and the uppermost layers of the sediment have $\delta^{18}O$ values <24.0‰ (green). Post-mortem altered frustules that are older than 0.5 years have $\delta^{18}O$ values >27‰ (brown); while intermediate $\delta^{18}O$ values (24-27‰; orange) as a result of partial maturation or a combination of mature and immature silica at the sediment surface. Variation in the $\delta^{18}O_{\text{diatom}}$ values of the mature diatom silica display variation of ~1‰ consistent with natural variation in the $\delta^{18}O_{\text{water}}$ values.
Figure 3.2. SEM images of diatom frustules collected from living diatoms (VC09-01; A) and from the 5cm interval of the VC09-06 core (B) show slight changes in diatom structure. Higher magnification (inset) shows the presence of silica nodules in the VC09-06-05 diatom that are not present in the diatom when collected as a living specimen.
Figure 3.3. HRTEM images show no apparent difference between diatoms collected antemortem from the water surface (VC09-01; A) and post-mortem from the sediment core (VC09-06-06; B). Fast Fourier transform analysis shows a diffuse ring characteristic of amorphous materials, thus indicating no ordered arrangement of the silica structure in either antemortem (VC09-01; C) or post-mortem silica (VC09-06-05; D).
TEM based X-ray analysis of the diatom frustules using energy dispersive spectroscopy demonstrates that some chemical changes occur between diatoms collected ante- and post-mortem. Antemortem diatom frustules (VC09-01) have a small amount of P and undetectable Ca. The reverse is true in the post-mortem sediment sample (VC09-06-05) where Ca reaches a concentration of 1-1.5% and P is absent. Additionally, trace amounts of Na, Cl, and K are found in VC09-06-05. The TEM images show that the analyzed areas are completely homogeneous demonstrating that the Na, Cl, K, Ca and P are within the amorphous silica structure rather than as distinct localized inclusions. The homogenous distribution of these trace elements within the silica structure indicates significant post-mortem elemental exchange between the fluid and diatom silica.

3.5 DISCUSSION

Assuming the 0.06 m/yr sedimentation rate recorded by peaks in the coarse silt/fine sand size fraction, the ~7.4‰ increase in $\delta^{18}O_{\text{diatom}}$ values represents a significant post-mortem alteration of the diatom silica within 0.5 years of sediment burial. Therefore, maturation of diatom silica $\delta^{18}O$ values occurs within 0.5 years, April through October. The growing season is also when bacterial activity and frustule diagenesis is greatest; thus, the rapid post-mortem alteration of diatom silica $\delta^{18}O$ values is most likely driven by bacterial consumption of organic matter in the frustule (e.g. Lewin, 1961; Gallinari et al., 2002; Bidle et al., 2003). Sediment samples less than 0.5 years old display a range of $\delta^{18}O$ values from antemortem values to intermediate values as a result of partial reequilibration or mixing of antemortem and post-mortem samples. Complete alteration of diatom silica $\delta^{18}O$ values results in a silica-water fractionation that approaches those determined empirically for equilibrium quartz-water fractionation (Sharp and Kirschner,
1994) and is nearly identical to silica-water fractionation factors observed in mature marine diatoms (Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992; Figure 3.4).

A number of studies have shown post-mortem alteration or maturation of diatom $\delta^{18}O$ values (e.g. Matheney and Knauth, 1989; Schmidt et al., 2001; Moschen et al., 2006). Although the mechanism of silicification is not well known, diatom silica is initially deposited as amorphous hydrated silica in the form of nanosized spheres (e.g. Volcani, 1981; Schmid and Schulz, 1979; Kröger et al., 1999; Crawford et al., 2001). Additionally, living diatoms likely precipitate amorphous silica in disequilibrium as a result of preferential uptake of $^{16}O$ during photosynthesis (Eisenstadt et al., 2010). The $\sim 7.4\%$ change in diatom silica $\delta^{18}O$ values seen in this study represents reequilibration to quartz-water equilibrium conditions as predicted by empirical studies of silica-water fractionation in marine diatoms (e.g. Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh et al., 1992). To perpetuate the changes in the $\delta^{18}O_{\text{diatom}}$ values of the magnitude seen in this and other studies, the initial oxygen atoms must completely exchange during maturation. Complete exchange of oxygen in the diatom silica can occur because a lower activation energy is required to cause exchange between oxygen atoms in the amorphous silica and in water in the form of silanol (SiOH) as it diffuses through the silica framework (Bakos et al., 2002). Silaffins, the primary organic proteins responsible for silica biomineralization in diatoms, have been shown to cause spontaneous silica precipitation of nanosized particles in a solution of silicic acid (Kröger et al., 1999; Noll et al., 2002). Diatom maturation occurs with no major morphological or crystallographic changes of the amorphous, yet intricate, silica structures; however,
Dodd and Sharp (2010)

$1000 \ln \alpha_{\text{SiO}_2-\text{H}_2\text{O}} = 2.39 \times (10^9/T^2) + 4.23$

$r^2 = 0.98$
Figure 3.4. $\delta^{18}O_{\text{diatom}}$ values vs. temperature with a range of published silica-fractionation curves. The diatom frustules collected antemortem from the Valles Caldera Pond (red circles) as well as sediment samples collected post-mortem from the upper sediment that are less than one growing season old (purple circles) fall on the silica-water fractionation lines for modern diatom silica defined by Dodd and Sharp (2010) and Brandriss et al. (1998; A). Frustules from the sediment traps display a rapid increase $\delta^{18}O$ values, with an intermediate silica-water fractionation values (Moschen et al., 2005; B) and ultimately mature samples with a silica-water fractionation that are in close agreement with quartz-water equilibrium fractionation factors Sharp and Kirschner (1994; C). The empirically derived silica-water fractionation factor of Juillet-Leclerc and Labeyrie (1987; D) is the best fit mature samples (solid blue squares), which are shown here with calculated temperatures of silica maturation for the sediment samples 0.5 years and older with measured $\delta^{18}O_{\text{diatom}}$ values and an average $\delta^{18}O_{\text{water}}$ value of -13.0‰. The range of published silica-water fractionation factors including Kita et al. (1985; E), Clayton et al. (1972; F), Becker and Clayton (1976; G), and Knauth and Epstein (1976; H) are also likely the result of varying degrees of silica maturation. The post-mortem alteration of diatom silica $\delta^{18}O$ values therefore accounts for much of the disparate silica-water fractionations in the literature.
exchange of oxygen atoms and perhaps precipitation of additional nanospheres of silica from residual silaffins result in mature diatom silica that is at or near isotopic equilibrium for quartz-water as defined by the published fractionation curves. The degree of post-mortem alteration necessary to produce the observed shift in the silica-water fractionation means that the original antemortem $\delta^{18}O$ values of the diatom silica are reset.

Since reequilibration is relatively rapid, it most likely occurs at the sediment-water interface in lacustrine environments. Seasonal overturning in many lacustrine environments produces a nearly constant bottom temperature of approximately 4°C. Under those conditions, diatom silica $\delta^{18}O$ values record information about the lake water $\delta^{18}O$ values at a nearly constant temperature. Additionally, in open basin lacustrine environments, the waters where diagenesis occurs will not be subjected to high evaporative rates present in surface waters where diatom growth occurs. The timing of diatom maturation in very large lakes or marine environments will depend on the rate of bacterially moderated diagenesis as well as a number of water conditions such as sedimentation rate, temperature, alkalinity, and trace metal concentration (e.g. Swann and Leng, 2009); however, there is no reason to assume that silica maturation will be significantly different in marine environments.

### 3.6 CONCLUSIONS

Diatom silica $\delta^{18}O$ values from the modern Valles Caldera headquarters pond sediments demonstrates that significant (~7.4‰) post-mortem alteration occurs within 0.5 years. The discrepancy between measured antemortem silica-water fractionation and the expected quartz-water equilibrium demonstrates that diatoms initially precipitate silica out of oxygen isotope equilibrium with the surrounding water (Dodd and Sharp,
During post-mortem alteration oxygen atoms in the diatom structure undergo essentially complete exchange with ambient water to isotopic values at/or near quartz-water equilibrium conditions. Additionally, this study supports the silica-water fractionation equations published by Juillet-Leclerc and Labeyrie (1987) and Matheney and Knauth (1989) for use with diatoms that are collected more than a few months post-mortem.

The rapid post-mortem alteration of diatom silica $\delta^{18}$O values has profound implications for the use of diatom silica $\delta^{18}$O values in calculations of paleotemperature and paleowater $\delta^{18}$O values in both lacustrine and marine environments. In lacustrine sediments, the $\delta^{18}$O values of diatoms reflect equilibrium fractionation following the quartz-water equilibration at the sediment water interface or within the upper centimeters of the sediment. This is particularly significant in open basin temperate lakes where seasonal mixing produces bottom water temperatures of a nearly constant ~4°C and $\delta^{18}$O values of the bottom water represent the average annual $\delta^{18}$O value of the lake. Diatom silica $\delta^{18}$O values from lacustrine environments thus provide direct records of changes in lake water $\delta^{18}$O values and facilitate high-resolution reconstruction of paleoprecipitation $\delta^{18}$O values.

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CHAPTER 4. EVIDENCE FOR PRECIPITATION VARIABILITY DURING INTERGLACIAL AND GLACIAL PERIODS MIS 11 AND 12 AS RECORDED BY DIATOM SILICA $\delta^{18}O$ VALUES FROM THE VALLES CALDERA, NEW MEXICO

ABSTRACT

Diatom frustules are nearly ubiquitous in lacustrine sediment archives and $\delta^{18}O$ values of diatom silica from lacustrine environments are common proxies of paleoclimate and paleohydrologic variability. Diatom silica $\delta^{18}O$ values from a middle-Pleistocene lacustrine core (VC-3) from the Valles Caldera record considerable (>25‰) variability in the paleolake water $\delta^{18}O$ values during interglacial Marine Isotope Stage 11 (MIS 11) and glacial MIS 12. Average $\delta^{18}O$ values of diatom silica for MIS 11 and MIS 12 are 26.5‰ ($\pm$ 5.3; n=62) and 18.5‰ ($\pm$ 6.3; n= 27), respectively. At the MIS 12 termination at ~430 kya, there is abrupt (~2 ky) increase in the $\delta^{18}O$ values of the diatom silica from ~11 to ~34 ‰.

Throughout the core, the $\delta^{18}O$ values of the diatom silica are strongly correlated with mean annual temperature (MAT) reconstructed from MBT/CBT indices in the VC-3 core on orbital (precessional) and millennial time scales (Fawcett et al., 2011). During MIS 12, millennial scale variations on the order of 10‰ in the $\delta^{18}O$ values of diatom silica are likely driven by changes in the $\delta^{18}O$ values of precipitation as a result of north south migration of the polar front jet stream and generally correspond to similar scale variations in MAT recorded by the MBT/CBT indices. A millennial peak in $\delta^{18}O$ diatom values at ~438 kya records an increase of > 22‰ from the lowest values observed during
MIS 12 and is likely a conflation of millennial scale and longer (precessional) scale forcings. During MIS 11, three periods of generally higher $\delta^{18}O$ values correspond with precessional scale variability seen in other proxies from the core (Fawcett et al., 2011). The highest $\delta^{18}O$ values of diatom silica ($\sim36\%$) occur during the warmest period in MIS 11 and reflect summer dominated precipitation and increased evaporation of lake waters; however, there are several periods of rapid decreases ($\sim12\%$) in the $\delta^{18}O$ values during MIS 11 that record a collapse of the summer monsoon and extreme decreases in the summer precipitation. These periods coincide with extremely arid conditions recorded by other proxy data in the VC-3 core and present a strong argument linking middle-Pleistocene aridity in the southwestern United States to decreases in summer precipitation. MIS 11 is a potential pre-industrial analog to the present interglacial climate; therefore, such extreme variations in precipitation as recorded by the $\delta^{18}O$ diatom values in the VC-3 core have significant implications for present and future precipitation variability in the southwestern United States.
4.1 INTRODUCTION

Climate models have predicted increased aridity in the southwestern United States coincident with future warming as a result of large scale changes in atmospheric circulation and an expansion of subtropical dry zones (Seager et al., 2007). Similarly, paleoclimate records from the region also indicate pervasive dry conditions during warm periods in geologic history (e.g. Anderson et al., 2008; Woodhouse et al., 2010; Fawcett et al., 2011). One such record is a lacustrine sediment core from the Valles Caldera in northern New Mexico that includes interglacial periods Marine Isotope Stage 11 (MIS 11) and MIS 13 and contains multiple proxies that indicate prolonged periods of aridity accompanied these warm periods (Fawcett et al., 2011). It is unclear, however, how changes in the source region and seasonal distribution of precipitation relate to middle-Pleistocene hydroclimatic variability.

Here I present oxygen isotope values of diatom silica from a lacustrine core (VC-3) as a new long record of hydroclimatological variability during the middle-Pleistocene in the southwestern United States. The $\delta^{18}$O values of diatom silica ($\delta^{18}$O$_{\text{diatom}}$) in the VC-3 core record >25‰ of variation in the $\delta^{18}$O value of the paleolake water ($\delta^{18}$O$_{\text{lake}}$). Changes in the $\delta^{18}$O$_{\text{lake}}$ reflect changes in the seasonality of precipitation and/or precipitation source combined with variable evaporative flux from the lake during MIS 11 and 12 (~470 to ~380 kya). Interglacial MIS 11 is a long interglacial with low orbital eccentricity, similar to today and is a possible analog to the present interglacial (e.g. Loutre and Berger, 2003). The rapid precipitation changes recorded by $\delta^{18}$O$_{\text{diatom}}$ values in the VC-3 core have dramatic implications for future changes in the hydroclimatology of the southwest United States.
4.2 GEOLOGIC BACKGROUND

The Valles Caldera is a volcanic caldera in the Jemez volcanic field of northern New Mexico (Figure 4.1; 35.87°N, 106.46°W, 2,594 m ASL). The Valles Caldera has contained multiple lakes since the formation of the resurgent dome at ~1.2 Ma as a result of damming of drainages during the three youngest episodes of volcanism (Reneau et al., 2007). An 82-m core from the Valles Caldera (VC-3) contains middle-Pleistocene lacustrine sediment which spans two glacial cycles from MIS 14 to MIS 10 (552 kya to ~368 kya; Fawcett et al, 2011). Estimates of Mean Annual Temperature (MAT) in the Valles Caldera have been reconstructed from the index of Methylation of Branched Tetraethers (MBT) and Cyclization of Branched Tetraethers (CBT) contained in lipids in the VC-3 core (Fawcett et al., 2011). MAT during the warmest parts of the interglacial periods (MIS 11 and 13) are similar to modern MAT (~5°C) and range from ~0 to 7°C. During glacial periods (MIS 12 and MIS 14), MAT range from -5 to 2°C. Multiple climate proxies including total organic carbon (TOC), \( \delta^{13}C_{org} \) values, and pollen concentration from a number of terrestrial plant species in the VC-3 core record considerable climate variability during the middle Pleistocene including prolonged periods of aridity during the warmest points of the interglacial periods (Fawcett et al, 2011).

The modern climate displays a strong seasonal distribution of precipitation sources in the portions of the southwest United States in the North American Monsoon region (Douglas et al., 1993; Adams and Comrie, 1997; Higgins et al., 2001; Wright et al., 2001; Vera et al., 2006). Generally, winter precipitation is derived from Pacific Ocean sources and summer precipitation is dominated by more southern sources in the Gulf of
Figure 4.1. A Landsat image of Valles Caldera in northern New Mexico shows the VC-3 drill site (red circle) in the Valle Grande. The South Mountain rhyolite (red triangle) blocked the southern drainage and allowed the formation of a middle-Pleistocene lake. Los Alamos (red square) is ~15 km to the northeast of the drill site (USGS).
Mexico and the Gulf of California (Adams and Comrie, 1997). At present, the Valles Caldera is at the general boundary between North American Monsoon and westerly dominated precipitation sources, resulting in pronounced seasonal variation in the $\delta^{18}O$ values of precipitation ($\delta^{18}O_{\text{precip}}$), with more positive $\delta^{18}O_{\text{precip}}$ values in the summer and more negative $\delta^{18}O_{\text{precip}}$ in the winter (Hoy and Gross, 1982; Metcalfe et al., 1997; Wright et al., 2001; Strong et al., 2007). Precipitation collected at Los Alamos (~15 km NE of the Valles Caldera) between 2005 and 2010 displayed an average $\delta^{18}O$ value of -11‰. Average summer (-7‰) and winter (-16‰) $\delta^{18}O_{\text{precip}}$ values for the 5 year period display an interseasonal range of ~9‰ (Figure 4.2).

### 4.3 OXYGEN ISOTOPES IN DIATOM SILICA

Oxygen isotope values preserved by authigenic minerals in lacustrine sediments are a function of the $\delta^{18}O$ values of the lake water ($\delta^{18}O_{\text{lake}}$) and temperature and have been widely used as paleoclimatic and paleohydrologic proxies (e.g. Leng and Marshall, 2004; Leng and Barker, 2006). Despite the abundance of paleoclimate proxy material in the VC-3 core, there is a lack of carbonates or other authigenic minerals from which to reconstruct $\delta^{18}O_{\text{lake}}$ and the $\delta^{18}O$ values of preceding precipitation ($\delta^{18}O_{\text{precip}}$). However, diatom frustules are abundant throughout Valle Grande lacustrine sediments with localized zones of nearly pure diatomite (Reneau et al., 2007; Fawcett et al., 2007; Fawcett et al., 2011). Within the diatomite and throughout the core, *Stephanodiscus niagareae* are the dominant species with localized species variations that include *Navicula* sp., *Cymbella* sp., *Sceptroneis* sp., *Campylodiscus* sp., and *Ellerbeckia* sp. (Round et al., 2007; Figure 4.3).
Figure 4.2. Seasonal variations in the monthly weighted average $\delta^{18}$O$_{\text{precip}}$ values at Los Alamos, NM have a total range of $\sim$15‰ (-20.5 to -4.0‰) between 2005 and 2010. The black line represents the average for each month during the 5-year period. The $\delta^{18}$O$_{\text{precip}}$ values are generally lowest during winter months (November to April), although there is considerable variability in the range of $\delta^{18}$O$_{\text{precip}}$ values (vertical bars) for each month.
Figure 4.3. Examples of diatom frustules from the VC-3 core: *Navicula* sp., *Cymbella* sp., *Sceptroneis* sp., *Stephanodiscus niagareae* (A), *Stephanodiscus niagareae* are the dominant species throughout the core (B), *Campylodiscus* sp., (C), and *Ellerbeckia* sp. (D).
Unlike carbonate biominerals, diatom frustule $\delta^{18}O$ values undergo rapid post-mortem alteration (Dodd et al., *in prep. a*). As a result, the $\delta^{18}O_{\text{diatom}}$ values in lacustrine sediments record conditions at the sediment-water interface (i.e. lake bottom) rather than the near-surface conditions under which the diatoms grew (Schmidt et al., 2001; Moschen et al., 2006; Dodd et al., *in prep. a*). In open basin temperate lakes where seasonal mixing produces bottom water temperatures of a nearly constant $\sim 4^\circ\text{C}$, the $\delta^{18}O$ values of the bottom water represent the average annual $\delta^{18}O$ value of the lake without the conflating influence on large temperature variations that might be experienced in surface waters (Dodd et al., *in prep. a*). Once this initial alteration occurs, diatom silica is not significantly altered by diagenesis (Dodd et al., *in prep. a*; Moschen et al., 2006).

The $\delta^{18}O_{\text{silica}}$ values record the $\delta^{18}O$ value of the lake water as per the silica-water fractionation relationship of Juillet-Leclerc and Labeyrie (1987) given by the following equation, where $T$ is water temperature in Kelvin:

$$1000 \ln \alpha = 3.26 \cdot 10^6/T^2 + 0.45 \quad (4.1)$$

*Analytical Methods*

Approximately $2 \text{ cm}^3$ of sediment were collected at each sampling location from the middle 1 cm of the 10-cm diameter VC-3 core. Therefore, each sample represents $\sim 1\text{cm}$ of accumulation ($<100\text{ yr}$). Oxygen isotope analyses of diatoms require pure silica samples since contamination from organic material or other silicates can alter the measured $\delta^{18}O_{\text{diatom}}$ values (e.g. Juillet-Leclerc, 1986; Morley et al., 2004; Leng and Barker 2006). Initial isolation of diatoms included a series of chemical treatments (e.g. Battarbee et al., 2001; Morley et al., 2004; Meng et al., 2007). Organic removal was performed on approximately $1 \text{ cm}^3$ of sediment with $30\% \text{ H}_2\text{O}_2$ at room temperature until
the sample stopped reacting vigorously, at which point the sample was heated in a convection oven at 90°C. Samples were then rinsed in deionized water and reacted with 5% HCl at room temperature to remove carbonate minerals. Previous studies have demonstrated that an additional chemical treatment with 15M HNO₃ at 90°C was necessary to completely remove organic material, and the chemical treatment does not alter the δ¹⁸O value of the diatom silica (Dodd and Sharp, 2010). Physical cleaning (removal of other detritus) was accomplished by wet sieving at 100 µm and 50µm, differential settling, and heavy liquid (sodium polytungstate, ρ=2.1 to 2.3) density separation. Visual inspection with a scanning electron microscope (SEM) showed that fine silt and clay particles adhered to the diatom frustules following both chemical and physical treatments, but these particles were successfully removed with an ultrasonic probe. Diatom samples were inspected for visual and elemental purity with a SEM/microprobe to insure that pure silica was used for δ¹⁸O analyses (e.g. Brewer et al, 2008).

Oxygen isotope (δ¹⁸O) analyses were performed using a laser fluorination method which requires relatively small sample sizes of 1 to 2 mg of pure diatoms (Sharp, 1990; Dodd and Sharp, 2010). Diatom frustules are composed of biogenic opal A (hydrated silica) and can contain up to 15 wt. % H₂O, which must be removed in order to obtain reproducible δ¹⁸O_diatom values (Labeyrie and Juillet 1982; Leng et al., 2001; Leng and Barker, 2006). Diatom silica was dehydrated by reaction with 100 mbar of F₂ gas for 1 hour, and the reaction was repeated with 50 mbars of F₂ gas for approximately 1 hour an additional one to five times. Prefluorination was considered complete when the δ¹⁸O_diatom values of the in-house-diatom 'standard' reached a plateau and were within 0.2‰ of the
known $\delta^{18}O_{\text{diatom}}$ value for that standard (e.g. Matheney and Knauth, 1989; Schmidt et al., 1997; Dodd and Sharp, 2010). Diatom samples were then heated with a CO$_2$ laser in the presence of 100 mbar BrF$_5$ to produce SiF$_4$ and O$_2$ gas, the latter of which was transferred cryogenically by adsorption on a zeolite trap to the dual inlet of a Finnigan MAT Delta Plus mass spectrometer. The O$_2$ gas was then analyzed for the $\delta^{18}O$ value of the initial diatom SiO$_2$ (e.g. Sharp, 1990). Internal laboratory diatom "standards" from a middle-Pleistocene diatomite in the Valles Caldera SR2-1B ($\delta^{18}O_{\text{diatom}} = 32.2 \pm 0.2\%_o$, n=23) and VT-8C ($\delta^{18}O_{\text{diatom}} = 28.6 \pm 0.2\%_o$, n= 19) were analyzed with each batch of samples as monitors of the prefluorination procedure (Dodd and Sharp, 2010). Internal quartz standards Gee Whiz ($\delta^{18}O = 12.55\%_o$) and Lausanne 1 ($\delta^{18}O =18.16\%_o$) were used as a check for reproducibility. Internal standards were calibrated with international quartz standard NBS-28 ($\delta^{18}O = 9.57\%_o$) and all $\delta^{18}O$ values were reported relative to VSMOW. An interlaboratory comparison of $\delta^{18}O_{\text{diatom}}$ analyses demonstrated that other methods of $\delta^{18}O_{\text{diatom}}$ analyses are in good agreement the Dodd and Sharp (2010) method (Chapligin et al., in press).

$\delta^{18}O$ Values of VC-3 Diatom Silica

Diatom silica from the VC-3 core between 11.9 m depth (~383 kya) and 55.37 m depth (~538 kya) were analyzed in this study and have a total range in $\delta^{18}O_{\text{diatom}}$ values of 25.4\%o and display a strong correspondence with MAT ($r^2=0.3$). There is considerable variation in the $\delta^{18}O_{\text{diatom}}$ values throughout the core, with several periods of large scale and rapid changes (Figure 4.4). The $\delta^{18}O_{\text{diatom}}$ values record significant changes on
Figure 4.4. Comparison of $\delta^{18}O_{\text{diatom}}$ values with other proxies from the VC-3 core and June insolation at 30°N (A). The $\delta^{18}O_{\text{diatom}}$ values (B; blue) from this study and with other proxy data from the VC-3 core (Fawcett et al., 2011). High Ca concentration (C, black) indicates periods when the lake basin is closed and evaporation is high. MAT (D, red) reconstructed from MBT/CBT indices. Pollen content of *Juniperus* (E, purple) and *Picea* + *Abies* (F, green) indicate dryer conditions during MIS 11 and also record millennial scale variation during MIS 12 (B1-B7). TOC (G) and $\delta^{13}C_{\text{org}}$ (H) reflect changes in C3/C4 plant abundance and productivity, respectively.
millennial and longer (orbital) time scales. During interglacial MIS 11 (11.90 m to 27.35 m depth) the average $\delta^{18}$O$_{dijom}$ value is 26.5‰ ($\pm$ 5.3; n=62) and during glacial MIS 12 (27.58 m to 41.52 m depth), the average $\delta^{18}$O$_{dijom}$ value is 18.5‰ ($\pm$ 6.3; n=27). At the glacial/interglacial transition between MIS 12 and MIS 11 (~29 m and ~430 kya) $\delta^{18}$O$_{dijom}$ values increase by ~20‰ within 2 ky.

Within MIS 11, there are three general periods of high $\delta^{18}$O$_{dijom}$ values (11a, 11c, and 11e; Figure 4.4) separated by periods of generally lower or highly variable $\delta^{18}$O$_{dijom}$ values. These sub-stage variations are also observed in other proxies in the VC-3 core and are probably associated with precessional cycles (Fawcett et al., 2011). Within MIS 11e, a notable high point in $\delta^{18}$O$_{dijom}$ values (36.5‰) occurs at ~25 m depth (420 kya), which represents the highest $\delta^{18}$O$_{dijom}$ values reported here for the VC-3 core and corresponds with the highest MAT (6.8ºC) in the MBT/CBT record. Similarly, the highest $\delta^{18}$O$_{dijom}$ values and MAT during MIS 11a (27.1‰/2.0ºC) and MIS 11c (32.4‰/4.1ºC) are temporally equivalent. During the cooler sub-stages of MIS 11 (b and d), the $\delta^{18}$O$_{dijom}$ values are more variable and lower, and again show a general agreement with MAT (~17‰/-1.0ºC and ~20‰/0.5ºC for 11b and 11d, respectively).

Within MIS 12, $\delta^{18}$O$_{dijom}$ values are much lower than during MIS 11; however, there are notable variations in the $\delta^{18}$O$_{dijom}$ values. Generally, variations in the $\delta^{18}$O$_{dijom}$ values on the order of 10‰ (~12‰ to ~23‰) correspond to millennial scale variations in MAT (B1 through B7; Figure 4.4). A period of rapid increase in $\delta^{18}$O$_{dijom}$ values of ~18‰ is associated with a 0.15 m thick diatomite containing nearly pure *Stephanodiscus niagareae* at ~438 kya (~32 m depth) and silty sediments preceding the diatomite. This peak corresponds with a millennial peak (B1) in other proxies, but is of much greater
magnitude than other variations in $\delta^{18}O_{\text{diatom}}$ values within MIS 12 and represents an increase in $\delta^{18}O_{\text{diatom}}$ values to interglacial like values (~32‰). A similar diatomite with high $\delta^{18}O_{\text{diatom}}$ values (~30‰) occurs in MIS 14 at ~538 kya. Repeat analyses of diatom samples and of different size fractions (<100 μm and 50<<100 μm) from the same sample interval indicate that the reproducibility of the VC-3 $\delta^{18}O_{\text{diatom}}$ values is better than ±0.6‰.

4.4 DISCUSSION

Variations in $\delta^{18}O$ Values of VC-3 Diatom Silica

It is likely that the diatom silica from the VC-3 core formed under a nearly constant temperature of 4°C (Dodd et al., in prep. a); however, if the lake did not have a well established thermocline, then bottom temperatures may not have been constant. In the case that the lake bottom temperature was variable, the mean annual temperature (MAT; °C) derived from the MBT/CBT proxy represents the maximum possible temperature effect on the $\delta^{18}O_{\text{diatom}}$ values (Fawcett et al., 2011). Using the silica-water fractionation relationship defined by Juillet-Leclerc and Labeyrie (1987; Eq. 4.1) and the measured $\delta^{18}O_{\text{diatom}}$ values, I have calculated the $\delta^{18}O_{\text{lake}}$ values in which the diatom silica formed at both a constant 4°C and using a variable temperature as recorded by the MBT/CBT temperature proxy (Figure 4.5; Fawcett et al., 2011). The difference between the two temperature estimates can account for up to ~2.9‰ of variation in the calculation of the $\delta^{18}O_{\text{lake}}$ value, which is an order of magnitude less than the changes >25‰ seen in the overall core. In other words, while the temperature dependence of the silica–water oxygen isotope fractionation may have an effect, it is minor in terms of the overall
Figure 4.5. Reconstructed $\delta^{18}O_{\text{lake}}$ values using the silica-water fractionation equation of Juillet-Leclerc and Labeyrie (1987; Eq. 4.1). The $\delta^{18}O_{\text{lake}}$ values have been calculated at a constant 4°C (blue) and using the MAT recorded the MBT (gray). The annual and seasonal $\delta^{18}O_{\text{precip}}$ values from Los Alamos (dashed lines) are higher than most of the $\delta^{18}O_{\text{lake}}$ values except where temperatures are the highest during MIS 11 and associated with the diatomite in MIS 12. Mudcracks (red triangle) are present at ~23 m depth, indicating desiccation of the lake.
variability in the core (Eq. 4.1). Additionally, the difference in the \( \delta^{18}O_{\text{lake}} \) calculations using constant and variable temperatures is most notable during the periods when MAT is very low and it is unlikely that the diatoms record temperatures below 0ºC. Therefore, the bulk of the observed variations in the \( \delta^{18}O_{\text{diatom}} \) values from the VC-3 core must represent changes in the \( \delta^{18}O \) value of the lake water (\( \delta^{18}O_{\text{lake}} \)).

The \( \delta^{18}O_{\text{lake}} \) values are dependent on the \( \delta^{18}O \) value of the initial water that enters the lake (precipitation, runoff, groundwater seepage, etc.) versus the amount of water lost to evaporation (e.g. Gonfiantini, 1983; Gat and Lister, 1995; Gat, 2010). Changes in the \( \delta^{18}O_{\text{precip}} \) values reflect the temperature of precipitation (air temperature), the transport path (e.g. path length and topographic variations along the path), and the \( \delta^{18}O \) value of the initial water vapor (e.g. Pacific Ocean or Gulf of Mexico/ Gulf of California source region). The relationship between MAT (\( T_a \) in ºC) and the \( \delta^{18}O_{\text{precip}} \) values is given by the following equation (Dansgaard, 1964):

\[
\delta^{18}O_{\text{precip}} = 0.695 \ T_a + 13.6 \%
\]  

(4.2)

Using this relationship, changes in MAT between glacial (MIS 12) and interglacial (MIS 11) temperatures account for \( \sim 8 \% \) variation in the \( \delta^{18}O_{\text{precip}} \). Although on geologic time scales the temperature coefficient can vary from 0.3 to 0.7 because of large scale changes in atmospheric processes, it does serve as a reference point for interpreting the observed variations in \( \delta^{18}O_{\text{lake}} \) values in (Fricke and O’Neil, 1999). The effect of MAT on \( \delta^{18}O_{\text{precip}} \) values and subsequent \( \delta^{18}O_{\text{lake}} \) values is significant and can be seen in the general agreement of the MAT and \( \delta^{18}O_{\text{diatom}} \) values; however, the temperature effect on the \( \delta^{18}O_{\text{precip}} \) values is insufficient to describe the total variation in the \( \delta^{18}O_{\text{diatom}} \) values in the VC-3 core.
Changes in the seasonal distribution of the precipitation and different source regions and storm trajectories also have a major effect on $\delta^{18}O_{\text{precip}}$; however, these effects are more difficult to quantify than other precipitation effects (e.g. Cole et al., 1999). At present, seasonality in northern New Mexico results in ~9‰ of variation in the $\delta^{18}O_{\text{precip}}$ values (Figure 4.2). However, during MIS 12 and parts of MIS 11, $\delta^{18}O_{\text{lake}}$ values (-30‰ to -20‰) were as much as 19‰ lower than the current average $\delta^{18}O_{\text{precip}}$ values (-11‰), and even lower than current winter season $\delta^{18}O_{\text{precip}}$ values (-16‰). Similar values are seen today in extreme northern regions of North America and in high altitudes (>3 km) throughout the Rocky Mountains (e.g. Yonge et al., 1989; Bowen and Wilkinson, 2002; Kendall and Coplen, 2002; Bowen and Revenaugh, 2003; Dutton et al., 2005). Additionally, snow-fed rivers throughout the Rocky Mountains often have values < -20‰ (Kendall and Coplen, 2002; Dutton et al., 2005). In order for extremely low $\delta^{18}O_{\text{precip}}$ values such as these to persist in northern New Mexico long enough to be recorded by the $\delta^{18}O_{\text{diatom}}$ values in the VC-3 core, the $\delta^{18}O_{\text{lake}}$ values in the Valles Caldera basin must be dominantly derived from snow melt runoff (cf. Dutton et al., 2005). A southward deflection of the winter polar-front jet stream relative to its present position and an increase in winter precipitation produces lower $\delta^{18}O_{\text{precip}}$ as a result of 1) storm trajectories that are strongly continental and reflect extreme depletion of $^{18}O$ in the precipitation waters, 2) precipitation that has a source in the north Pacific Ocean, and 3) colder air temperatures associated with precipitation events (Hoy and Gross, 1982; Barry and Chorley, 1987). Although the atmospheric conditions that affect the $\delta^{18}O_{\text{precip}}$ values (MAT, precipitation source, seasonality of precipitation), are not mutually exclusive (e.g.
covariability of seasonality of precipitation and air temperature), combining the precipitation effects results in a maximum change in the $\delta^{18}O_{\text{precip}}$ of $\sim 20\%$.

If the residence time of water in the lake is long or during closed basin conditions, a large potential source variation in the $\delta^{18}O_{\text{lake}}$ values in high altitude temperate regions such as the Valles Caldera is changes in the evaporative balance in the lake (Gonfiantini, 1986). I have used the following equation to calculate the variable enrichment of $^{18}$O in the lake water as a result of evaporation (Gat, 2010):

$$
\delta^{18}O_{\text{lake}} = \frac{(\delta^{18}O_{\text{atm}} - \delta^{18}O_{\text{atm}}) + \frac{\varepsilon}{h} + (1 - h) \cdot \Delta \varepsilon}{1 + \frac{F_{\text{in}}}{E} \cdot \frac{(1 - h)}{h}} + \delta^{18}O_{\text{in}} \tag{4.3}
$$

where $h$ is relative humidity, $\delta^{18}O_{\text{atm}}$ and $\delta^{18}O_{\text{in}}$ are respectively the $\delta^{18}$O values of the atmospheric water vapor and the water entering the lake, and $\varepsilon$ and $\Delta \varepsilon$ are the equilibrium and kinetic liquid – vapor fractionation factors. In this case $\varepsilon = (1 - \alpha) \cdot 1000$, where $\alpha$ is $<1$ and $\Delta \varepsilon = 14.2\cdot(h-1)$ as is often the case in natural systems (Gonfiantini, 1986; Horita and Wesolowski, 1994). When the flux of water into the lake ($F_{\text{in}}$) equals the amount of lake water lost to evaporation ($E$), all of the lake has evaporated. As $E$ approaches 0, the $\delta^{18}O_{\text{lake}}$ value approaches the original $\delta^{18}$O value of the water entering the lake ($\delta^{18}O_{\text{lake}} = \delta^{18}O_{\text{in}}$), which is demonstrated here for different values of $\delta^{18}O_{\text{in}}$ and can result in increases of $\sim 20\%$ in the $\delta^{18}O_{\text{lake}}$ values if evaporation progresses to total evaporation of the lake (Figure 4.6). Weather stations in the Valles Caldera that make continuous measurements of humidity in the Valles Caldera indicate that $h = 0.15$ is a typical low relative humidity value; therefore, this value has been used to represent the most extreme evaporative effects on the reconstructed $\delta^{18}O_{\text{lake}}$ values (NCDC, 2011).
Figure 4.6. Evaporative effect on the $\delta^{18}O_{\text{lake}}$ value from different initial $\delta^{18}O$ values at a humidity 0.15 as the fraction of the lake water lost to evaporation from no evaporative effect ($E = 0$) progresses to completion ($E=1$) calculated at different initial $\delta^{18}O_{\text{lake}}$ values from Eq. 3 (Gat, 2010). The $\delta^{18}O_{\text{lake}}$ value resulting from total evaporation of the lake is ~23‰ higher than the initial $\delta^{18}O$ value of the water.
The total combined effects of precipitation, evaporation, and silica-water fractionation would result in >40‰ variation in the δ18O_diatom values; however, many of these effects are covariant and the reconstructed δ18O_lake values are therefore the result of multiple correlated variables. In the case of the Valles Caldera lake, changes in the δ18O_in (i.e. δ18O_precip) and the evaporative budget of the lake are the dominant controls on the δ18O_lake values. Since it is impossible to separate the contribution of these two factors, it is difficult to attribute the changes in the δ18O_lake values to a single variable. In fact, both almost certainly have an effect on the δ18O_lake values.

However, by using other proxies from VC-3 core it is possible to better constrain the environmental parameters that produced changes in the δ18O_lake values. Maximum evaporation occurs when the lake is a closed basin and the water lost to evaporation approaches 100%. Under such conditions, calcium concentrations increase dramatically (Fawcett et al., 2011). High calcium concentrations are preserved in the VC-3 core during MIS 11 from ~413 to ~420 kya (25.48 m to 22.94 m depth) and during much of MIS 13, but notably not during the rapid change at the MIS 12 termination (Figure 4.4). Significant evaporative alteration of δ18O_lake is still likely to occur during open basin conditions; however in order to produce the observed variation in the δ18O_lake values around the MIS 12 termination by evaporation alone, the lake must completely evaporate (F_inc = E). The only indication for complete desiccation of the lake is a mudcrack at 23 m depth (~415 kya ) and does not coincide with the period of most rapid change at the MIS 12 termination or the highest δ18O_lake values during MIS 11 (Figure 4.5). In fact, the mudcrack at 23 m depth corresponds with a low decrease in the δ18O_diatom values and likely represent a δ18O_lake value that reflects dominantly winter precipitation.
Specific Variations in $\delta^{18}O$ Values of VC-3 Diatom Silica

During MIS 11, there are several rapid (<0.5 ky) decreases in the $\delta^{18}O_{\text{lake}}$ values despite closed basin conditions during sub-stages 11b and 11d, and less frequently late in 11e and 11c. It is likely that the loss of water to evaporation remains high since calcium concentration remains high, but the $\delta^{18}O_{\text{lake}}$ values decrease as a result of reduced summer monsoon precipitation and annual $\delta^{18}O_{\text{precip}}$ values that more closely correspond to winter precipitation. This effect is most apparent in the area of the prominent mudcrack where there is physical evidence of extreme desiccation of the lake that could result in an evaporative increase in the $\delta^{18}O_{\text{lake}}$ values of >15‰, yet the $\delta^{18}O_{\text{lake}}$ values remain very low (-23.2‰). Additionally, pollen and $\delta^{13}C_{\text{org}}$ values in the VC-3 sediments indicate several periods of prolonged period of aridity during MIS 11 that coincide with low $\delta^{18}O_{\text{lake}}$ values (Fawcett et al., 2011) For example, low $\delta^{13}C$ values reflect an increase in the amount of dry climate C$_4$ plants relative to the amount of C$_3$ (wet climate) vegetation (e.g. Deines, 1980).

Within MIS 12, Fawcett et al. (2011) have noted at least seven millennial scale cycles in other VC-3 core proxies. These six of the cycles (B1 through B6) also appear in the $\delta^{18}O_{\text{diatom}}$ values (Figure 4.5) and are consistent with a strong covariance of $\delta^{18}O_{\text{precip}}$ values with temperature. One of these millennial scale peaks (B2) records an anomalous period of rapid increase in $\delta^{18}O_{\text{diatom}}$ values associated with the diatomite layer. This occurs at ~438 kya and lags an insolation maxima by ~6 ky (Figure 4.5). A similar diatomite to the one seen in MIS 12 is present in MIS 14 (~538 kya), and although only a
few analyses of diatom silica from this interval have been done, the high $\delta^{18}O_{\text{diatom}}$ values for the MIS 14 diatomite indicate that a similar event occurred during the previous glacial interval.

Despite the potential for significant evaporation-driven increases in the $\delta^{18}O_{\text{lake}}$ values relative to the $\delta^{18}O_{\text{precip}}$ values, the calculated $\delta^{18}O_{\text{lake}}$ values during MIS 11 and MIS 12 are considerably lower than present day annual average $\delta^{18}O_{\text{precip}}$ for Los Alamos (Figure 4.5). Only during the warmest points of the interglacial (MIS 11) and within the diatomites are $\delta^{18}O_{\text{lake}}$ values equivalent to modern $\delta^{18}O_{\text{precip}}$ values. Additionally, several periods of low $\delta^{18}O_{\text{lake}}$ values during MIS 11 indicate that there must be significant decreases in the $\delta^{18}O_{\text{precip}}$ value and this can only be the result of 1) an extreme decrease in the amount of summer precipitation and/or 2) an increased input of non-monsoon/Pacific Ocean precipitation source. Millennial scale variations in the $\delta^{18}O_{\text{lake}}$ values during MIS 12 (B1-B7) are similar to variations observed in the TOC, MAT, and pollen ($Picea + Abies$) content, and are most likely the result of variations in the $\delta^{18}O_{\text{precip}}$ values as a result of north/south migration of the winter polar-jet stream and correlate with changes in MAT of as much as 6°C (Fawcett et al., 2011).

4.5 CONCLUSIONS

The $\delta^{18}O_{\text{diatom}}$ values of the VC-3 core record considerable variation in $\delta^{18}O_{\text{lake}}$ values as a result of changes in the seasonality of precipitation, source of precipitation, and enhanced evaporation in the southwestern United States during the middle-Pleistocene. The variations in $\delta^{18}O_{\text{lake}}$ values of > 25‰ observed during MIS 11 and MIS 12 in the VC-3 core are greater than in any other records for this period (e.g. Devils Hole vein calcite; Winograd et al., 1992; Imbrie et al., 1993). Additionally, $\delta^{18}O$ calcite
records from other time periods such as lacustrine carbonates from Death Valley from MIS 1 to MIS 5 (Yang et al., 2005) or speleothems the southwest United States (Asmerom et al., 2010; Wagner, et al., 2010) display less than 10‰ total variation in $\delta^{18}$O values.

High $\delta^{18}$O$_{lake}$ values in the VC-3 core are consistent with an increase in monsoon precipitation at the MIS 12 - 11 transition; however, continued warming during MIS 11 culminated in a collapse of the monsoon and extreme decreases in summer precipitation during MIS 11, which coincide with prolonged periods of aridity recorded by other proxy data in the VC-3 core. Additionally, millennial scale variations in the $\delta^{18}$O$_{lake}$ values during MIS 12 (B1 through B7) and the prominence of sub-stages, particularly MIS 11a and MIS 11e, provide evidence of paleoclimate variability not seen in other terrestrial (e.g. Winograd et al., 1992; Imbrie et al., 1993) or marine (e.g. Imbrie et al., 1984) records. Changes in the $\delta^{18}$O$_{lake}$ values during both MIS 11 and the millennial scale variations in the MIS 12 termination indicate the extreme hydroclimatological sensitivity of this region, and present a strong argument linking long-term aridity in the southwestern United States to decreases in summer precipitation.

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CHAPETER 4. REFERENCES


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CHAPTER 5. CONCLUSIONS, CLOSING REMARKS, AND FUTURE RESEARCH

5.1 CONCLUSIONS

I have developed a new laser fluorination technique for the analysis of diatom silica $\delta^{18}O$ values and produced a new silica-water fractionation for diatom silica growth (Dodd and Sharp, 2010); however, subsequent analyses of post-mortem diatom silica indicates a rapid (<0.5 yr) alteration of diatom silica $\delta^{18}O$ values. Although the exact mechanism of this alteration is not known, I have shown that the rapid post-mortem reequilibration that occurs completely overwrites the initial $\delta^{18}O$ values of the diatom silica; therefore, diatom silica from lacustrine and marine sediment archives likely does not represent the growing conditions (temperature and $\delta^{18}O$ water values). Instead $\delta^{18}O$ diatom values record the water in which the final reequilibration occurred. In the case of many lacustrine environments, this means that the $\delta^{18}O$ values of diatom silica represent the $\delta^{18}O$ values of the annual average lake water and constant bottom temperatures of 4°C (Dodd et al., in prep. a).

I have then presented an application of $\delta^{18}O$ values of diatom silica as a proxy of paleohydrologic variability in a middle-Pleistocene lacustrine core from the Valles Caldera. The $\delta^{18}O_{\text{diatom}}$ values of the VC-3 core record considerable variation (> 25‰) in $\delta^{18}O_{\text{lake}}$ values as a result of changes in the seasonality of precipitation, precipitation source region, and enhanced evaporation in the southwestern United States during the middle-Pleistocene (Dodd et al., in prep. b). There is a strong correspondence between the $\delta^{18}O$ values of diatoms throughout the VC-3 core and mean annual temperatures recorded by MBT/CBT indices in the core (Fawcett et al., 2011). High $\delta^{18}O_{\text{lake}}$ values in
the VC-3 core record an increase in monsoon precipitation at the MIS 12 transition, yet continued warming during MIS 11 culminated in a collapse of the monsoon and extreme decreases in summer precipitation during MIS 11, which coincide with prolonged aridity recorded by other proxy data in the VC-3 core (Fawcett et al., 2011).

The $\delta^{18}O$ values of diatom silica from the VC-3 core also demonstrate significant hydroclimate variability in the southwestern United States during the middle-Pleistocene. Millennial scale variations in the $\delta^{18}O_{lake}$ values during MIS 12 (B1 through B7) and the prominence of sub-stages, particularly MIS 11a and MIS 11e, provide evidence of paleoclimatic variability not seen in other terrestrial (e.g. Winograd et al., 1992; Imbrie et al., 1993) or marine (e.g. Imbrie et al., 1984) records. It might be that the past is the key to the future (Doe, 1983); the large magnitude and rapid (millennial scale) changes recorded in the $\delta^{18}O$ values of diatom silica southwestern United States have significant implications for future climate change. Additionally, if MIS 11 is truly an analog for the present interglacial (Seager et al., 2007), the prevalence of prolonged arid conditions associated with a decline in summer precipitation in the VC-3 has dramatic implications for future water availability in the region.

5.2 CLOSING REMARKS

The data on oxygen isotopes in diatom silica that I have presented here demonstrate that $\delta^{18}O$ values of diatom silica have excellent potential as archives of paleoclimatic and paleohydrologic variability; however, they are not without their limitations. Although I have demonstrated that diatom silica $\delta^{18}O$ values do not appear to change once the initial post mortem alteration is complete, I have not presented any direct or quantifiable mechanism by which the $\delta^{18}O$ values are altered. Additionally, as with
any lacustrine proxy, the $\delta^{18}$O value of the lake water is not a direct record of changes in the $\delta^{18}$O values of precipitation.

5.3 FUTURE RESEARCH

There are several directions for future research that could greatly benefit both our general understanding of oxygen isotopes in diatom silica as well as the hydroclimatic variability recorded by the $\delta^{18}$O values of diatom silica from the VC-3 core. Two main questions need to be addressed to better quantify the $\delta^{18}$O values of diatom silica in general: 1) what is driving the post mortem alteration (Schmidt et al., 2001, Moschen et al., 2006), and 2) how long does this alteration continue after the frustules are incorporated into the sediment (Matheney and Knauth, 1989; Schmidt et al., 2006). I have speculated that bacterial activity is the driving force behind the initial rapid reequilibration of diatom silica $\delta^{18}$O values (Moschen et al., 2006). To test this hypothesis, diatom cultures could be used to monitor the $\delta^{18}$O values of diatom silica antemortem and post mortem (in the presence and absence of bacteria). Quantifying the timing of the post mortem alteration is not so straightforward; however, silicon isotopes ($\delta^{30}$Si) of diatom silica present interesting possibilities (Ziegler et al., 2011).

CHAPTER 5. REFERENCES


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