Title: Linking silicon isotopic signatures with diatom communities

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Diatom silicon isotope ratios in Lassen Volcanic National Park

**Linking silicon isotopic signatures with diatom communities**

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**Abstract**

The use of silicon isotope ratios (expressed as \(\delta^{30}\)Si) as a paleolimnological proxy in lacustrine systems requires a better understanding of the role of lake processes in setting the \(\delta^{30}\)Si values of dissolved Si (dSi) in water and in diatom biogenic silica (bSi). We determined the \(\delta^{30}\)Si of modern dSi (\(\delta^{30}\)Si\(_{\text{dSi}}\)) and bSi (\(\delta^{30}\)Si\(_{\text{bSi}}\)) in three lakes in Lassen Volcanic National Park (LAVO), California (USA), and produced diatom assemblage compositional data from the modern system and from sediment core samples. In the modern systems, we observe the largest magnitude diatom Si isotope fractionations yet reported, at -3.4 and -3.9‰ for Fragilaria dominated samples. Using statistical approaches designed to condense multivariate ecological data, we can deconvolve assemblage-specific Si isotope fractionations from the combined diatom assemblage-\(\delta^{30}\)Si data. For example, samples dominated by generally deeper water
euplanktic species have low $\delta^{30}$Si$_{bSi}$ values (< -1.10‰). Conversely, samples dominated by shallow water planktic or benthic periphyton have higher $\delta^{30}$Si$_{bSi}$ values (> -0.14‰). These data suggest that $\delta^{30}$Si records from LAVO lakes reflect species specific Si isotope fractionations and thus act as paleolimnological proxy for the aquatic-habitat of bSi production. Silicon isotope analysis should be coupled with diatom community composition data and other geochemical proxies for the most robust paleolimnological interpretations. We also construct a Si mass-balance for Manzanita Lake based on elemental fluxes. Despite a short residence time of ~4 months, it is an efficient Si sink: about 30% of inflowing Si is retained in the lake sediments. An entirely independent Si isotope-based estimate agrees remarkably well. Burial fluxes of bSi derived from radiometrically dated sediment cores yield retention rates of about a factor of three higher, which might suggest groundwater is an important term in the lake Si budget.
1. Introduction

Diatoms, through their prodigious uptake of dissolved Si (dSi) and rapid mineralization of biogenic Si (bSi), are central to freshwater Si cycling. Understanding diatom uptake and recycling of this often limiting nutrient therefore shines light on the continental Si cycle (Frings et al., 2014) and lake phytoplankton ecology (e.g. Kilham, 1971). Silicic acid is delivered to lakes from either surface water or groundwater, and ultimately derives from the weathering of silicate minerals. Within-lake recycling of biogenic silica is also important, as most freshwater systems are strongly undersaturated with respect to bSi, particularly during periods of enhanced biological activity where Si is removed from the water column. Given its role as a key nutrient in lake ecology, and its coupling to the carbon cycle via the silicate-weathering feedback (Frings, 2019), there is considerable incentive to be able to reconstruct aspects of the past Si cycle. As integrators of catchment biogeochemistry, lake sediment archives are ideally placed to achieve this, but estimates of bSi concentrations or accumulation rates can paint an incomplete or misleading picture (Nantke et al., 2021).

Silicon isotope ratios (expressed as $\delta^{30}\text{Si}$) are emerging as a powerful tool to trace Si biogeochemistry. Differences in $\delta^{30}\text{Si}$ between two phases result from isotope fractionation, that can be expressed as a fractionation factor $\alpha$, defined as $\alpha_{A,B} = R_A/R_B$, where $R$ is the ratio $^{30}\text{Si}/^{28}\text{Si}$ in phase A and B. Since $\alpha_{A,B}$ is typically very close to unity it can also be presented in $\varepsilon$ notation (Coplen, 2011), where $\varepsilon_{A,B} = \alpha_{A,B} - 1$ and is typically given in per mille. Si is incorporated in the diatom frustule as bSi (a hydrated, amorphous silicon oxide or SiO$_2$·nH$_2$O; De La Rocha et al. 1998). This typically occurs with a discrimination against the heavier isotopes. This leaves the residual dissolved Si enriched in the heavier Si isotopes (i.e. higher $\delta^{30}\text{Si}$), while the bSi in the diatom frustule...
becomes isotopically lighter (De La Rocha et al., 1997). In other words, $\varepsilon_{A-B} < 0$ or $\alpha_A < 1$ (De La Rocha et al., 1997; Frings et al., 2016; Opfergelt and Delmelle, 2012).

Estimates of the fractionation $\varepsilon$ associated with the biological uptake of Si by freshwater diatoms, as compiled by (Frings et al., 2016), are around -2.0 to -1.0‰.

To our knowledge, no laboratory investigations of freshwater taxa Si isotope fractionation have been performed. The limited field-based data that exist include estimates of $\varepsilon = -1.61$‰ in Lake Baikal (Panizzo et al., 2016), -1.10‰ in Lake Tanganyika (Alleman et al., 2005) and -1.04‰ in Icelandic Lake Myvatn (Opfergelt et al., 2011). Sun et al. (2018) interpret a downstream increase in $\delta^{30}$Si of dSi in the Lena River as reflecting diatom activity, and derive a Si isotope fractionation $\varepsilon = -1.40$‰. A similar value was derived for diatoms blooming in the eutrophic Oder River (Sun et al., 2013). While these values are broadly consistent with each other, and with marine taxa, the variability hints at environmental controls, species-specific isotope fractionations, or habitat-specific variability that are not yet fully understood.

Two simple models can be used to predict and interpret the evolution of silicon isotope compositions as a function of the fraction of the available dSi converted to diatom bSi, with an associated isotope fractionation $\varepsilon_{A-B}$. The first considers the evolution of isotope ratios in a finite pool of dSi that is converted to bSi with no reverse reaction. This is commonly referred to as a “closed” system or Rayleigh model. Under the conditions of this model, as bSi is produced and dSi is consumed, both $\delta^{30}$Si$_{bSi}$ and $\delta^{30}$Si$_{dSi}$ evolve towards higher values when $\varepsilon$ is negative:

$$\delta^{30}\text{Si}_{dSi} = \delta^{30}\text{Si}_{init} + \varepsilon_{dSi-bSi} \cdot \ln f$$  \hspace{1cm} \text{Eqn. 1a}

$$\delta^{30}\text{Si}_{bSi} = \delta^{30}\text{Si}_{dSi} + \varepsilon$$  \hspace{1cm} \text{Eqn. 1b}

$$\delta^{30}\text{Si}_{bSi} = \delta^{30}\text{Si}_{init} - \varepsilon (f \ln f / f - 1 - f)$$  \hspace{1cm} \text{Eqn. 1c}
Where the subscript ‘init’ denotes the $\delta^{30}\text{Si}$ of the dSi initially supplied (e.g. of the river flow into a lake), and $f$ is the fraction of initial dSi remaining (i.e. at $f = 1$, no diatom growth has occurred, and at $f \to 0$, all available dSi has been used). $\delta^{30}\text{Si}_{bSi}$ indicates the instantaneously produced bSi, which is always one fractionation offset from the coeval dSi. The cumulative product is given in Eqn. 1c. The alternative model is a steady-state or “open” system where there is a constant supply of new dSi with constant $\delta^{30}\text{Si}$ into the system, of which a fraction is converted to bSi:

$$\delta^{30}\text{Si}_{dSi} = \delta^{30}\text{Si}_{\text{init}} - \epsilon(1 - f)$$

Eqn. 2a

$$\delta^{30}\text{Si}_{bSi} = \delta^{30}\text{Si}_{\text{init}} + \epsilon f$$

Eqn. 2b

Again, both $\delta^{30}\text{Si}_{bSi}$ and $\delta^{30}\text{Si}_{dSi}$ will evolve towards higher values, but along different trajectories than that of the Rayleigh model. In this model, the bSi instantaneously produced and the cumulative product have the same composition. Note that evolution of $\delta^{30}\text{Si}$ as a function of reaction completeness in a closed system but where both forward and reverse reactions occur at equilibrium has the same mathematical form as the ‘steady-state’ model. For this reason, we use ‘Rayleigh’ and ‘steady-state’ to distinguish between the two models. Two endmember possibilities for the bSi produced are shared by both models. Firstly, at 0% utilization (i.e. $f = 1$) an infinitesimally small amount of diatom Si uptake will produce bSi offset by exactly one fractionation from the source dSi. Secondly, at 100% Si utilization (i.e. $f = 0$) the bSi must have the same $\delta^{30}\text{Si}$ as the source dSi ($\delta^{30}\text{Si}_{\text{init}}$). The models differ in their predictions for intermediate utilizations, but crucially both predict increasing $\delta^{30}\text{Si}_{bSi}$ with increasing dSi utilization. This forms the basis of silicon isotope ratios as a paleoproductivity proxy (De La Rocha et al., 1998). From this simple framework, the source pool dSi isotope composition (i.e. $\delta^{30}\text{Si}_{\text{init}}$), and the Si isotope fractionation $\epsilon$
associated with diatom production, emerge as key parameters. If these are constrained, then we are able to quantitatively interpret diatom $\delta^{30}$Si in terms of Si utilization (i.e. $f$).

There is a growing body of research using Si isotopes as proxies for diatom productivity in freshwater systems (Chen et al., 2012; Swann et al., 2010), or for interpreting environmental change more generally (Cockerton et al., 2015; Nantke et al., 2021; Nantke et al., 2019; Street-Perrott et al., 2008). These depend on a robust understanding of Si cycling in modern settings (Alleman et al., 2005; Panizzo et al., 2017; Sun et al., 2014), though knowledge gaps exist. For example, the range of plausible Si isotope fractionations and the potential for species-specific fractionations (‘vital effects’) is poorly constrained, though marine studies offer some guidance. The first laboratory study of three marine diatom taxa yielded consistent Si isotope fractionations of -1.1‰ (De La Rocha et al., 1997). Subsequent work broadly corroborated the magnitude of fractionation, but also indicated that marine diatom Si isotope fractionation is more variable. Published estimates for both freshwater and marine diatoms range from -2.09 to -0.54‰ (Sutton et al., 2013). As well as intrinsic differences in Si processing by different taxa, variability in the isotope fractionation, could also plausibly be influenced by environmental conditions including (micro-)nutrient availability, temperature, or growth rate. Superimposed on this, diatom habitat in the water column or seasonality of growth can affect the final measured $\delta^{30}$Si if the source pool $\delta^{30}$Si is spatially or temporally variable. Whether the system is best described by a steady-state or Rayleigh model further complicates interpretation of the measured ratio (e.g. Closset et al., 2016; Varela et al., 2004).

Here, we explore the influence of diatom community composition and lake
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characteristics on $\delta^{30}\text{Si}_\text{bSi}$ in three diatom-dominated lakes in Lassen Volcanic National Park (LAVO), California. These wilderness-area aquatic systems are of management concern because they are keystone aquatic resources in LAVO, and as such these lakes are well-studied with respect to other nutrients and anthropogenic impacts. These lake systems also have wider significance, in that they are potential recorders of regional hydroclimate (Howard and Noble, 2018). A diversity of microhabitats and susceptibility of ecosystem functioning to anthropogenic perturbation means that observations here are easily translated to other small lake systems around the world.

Here, we present Si isotope data in combination with analysis of diatom community composition and limnological parameters from these three lakes. Our objectives are to investigate links between $\delta^{30}\text{Si}_\text{bSi}$ values and diatom communities in LAVO lakes to better guide interpretations of down-core $\delta^{30}\text{Si}_\text{bSi}$ in lake systems.

2. Study sites

The locations and catchment areas of Manzanita Lake (ML), Butte Lake (BL), and Widow Lake (WL) in LAVO are presented in Figure 1. Lakes in this region tend to polymictic to dimictic (i.e. exhibiting vertical stratification on ephemeral- to seasonal-timescales). The combined catchment area of these three lakes comprises approximately 33% of LAVO, and also includes a small area outside the park boundary.

2.1 Manzanita lake

Manzanita Lake, located in the northwestern corner of the park (Figure 1), is fed by Upper Manzanita Creek with headwaters located on the northwestern flank of Lassen Peak. Manzanita Lake has a maximum depth of 9-10 m and was formed approximately 350 years ago when a series of landslides (Chaos Jumbles) broke off
Chaos Crags and flowed approximately 6 km damming Manzanita Creek (Clynne et al., 2008; Clynne and Muffler, 2010). Upper Manzanita Creek (UMC) drains Chaos Crags lava domes, which were emplaced approximately 1050 years ago (Clynne et al., 2008). The bedrock geology of the ML watershed is dominated by rhyodacite and other easily erodible high-Si extrusive igneous rocks. ML was artificially dammed in 1913, which raised the lake level by ~0.6 m (Clynne et al., 2012). Lower Manzanita Creek (LMC) continues past the dam and serves as the only outlet to ML.

2.2 Butte Lake

Butte Lake, in the northeastern region of the park (Figure 1), is situated amidst the Fantastic Lava Beds near the Cinder Cone. This area of the park is dominated by extrusive igneous rocks of andesitic composition. Butte Lake is a remnant of a larger lake that was partly filled by lava flows during the eruption of the Cinder Cone approximately 350 years ago (A.D. 1666) (Clynne et al., 2000). The maximum depth of the lake is 13-15 m, and the lake is thermally stratified during summer months (Howard and Noble, 2018). Butte Lake is mainly supplied by water seeping beneath the Fantastic Lava Beds from Snag Lake, which was formed when the Painted Dunes lava flow (Cinder Cone) blocked Grassy Creek, a stream draining the central highland of LAVO (Clynne et al., 2000). Ephemeral surface outflow from BL is into Butte Creek and is directly related to inter-annual fluctuations in precipitation and snowpack. Butte Lake is hydrologically interesting site because it oscillates between being a hydrologically open and closed system for surface water flows (Howard and Noble, 2018), depending on the degree of winter precipitation.

2.3 Widow Lake
Widow Lake is located in the northeastern region of the park, approximately 2 km from the southeastern margin of BL (Figure 1) and sits on a volcanic highland beyond a ridge about 234 m above BL. Widow Lake lies within the Butte Lake watershed, occupying about 4% of BL catchment. The bedrock geology is dominated by extrusive igneous rocks of basaltic-andesitic composition. The maximum lake depth of WL is 9-10 m, and because no permanent surface water inflow landforms are present, the lake is likely supported mainly by groundwater and surface runoff from snow melt in the spring. Widow Lake is surrounded by locally derived glacial sediments (Clynne and Muffler, 2010) and is therefore likely a post-glacial lake, formed in a topographic low or in a kettle hole (a pit formed by a detached ice block during glacial retreat).

3. Materials and Methods

3.1 Field sampling and initial sample preparation

Physical and chemical characteristics (described below) were measured, and water/phytoplankton samples were taken around the same time of day (early afternoon) and in the same location in ML and WL during monthly sampling trips in the summer months of 2012, 2013, and 2014, giving sequential snapshots of lake structure. Sediment samples for diatom community composition, bSi concentrations, and silicon isotope analyses were taken from three (<1m) continuous lake-sediment cores with an intact sediment-water interface that were collected in 2012 (WL), 2013 (ML), and 2014 (BL). The WL core was taken using a Multi-Use Coring Kit (MUCK) gravity coring device, and the ML and BL cores were taken using a Livingstone type push-corining device (Glew et al., 2001).

3.1.1 Physical measurements
Surveys to determine maximum depth (m) and identify sampling locations for each lake were performed using a sonar depth finder. Thermal and chemical profiles (temperature, dissolved oxygen, conductivity) were measured at each sampling location with a YSI-85 multiparameter instrument (Xylem Incorporated) that was calibrated in the lab before being taken to the field on each sampling date. Thermal and chemical profiles were then used as a determinant of lake structure and to define the locations of the epi-, meta-, and hypo-limnia at each sampling location. Water clarity was measured using a Secchi disk. Discharge was estimated at a location above ML in UMC and at a location in LMC below ML using Manning’s equation and the slope-area method of discharge estimation (Dalrymple and Benson, 1968; Online Supplementary Material). These estimates were then coupled with an estimate of lake volume to calculate a range of hydraulic residence times for ML, where the hydraulic residence time (HRT) is defined as the time required to fill an empty lake with its natural inflow and can be calculated by dividing lake volume by inflow or outflow rate. Mean and median discharges calculated from discharges measured in LMC from August 1979-September 1981 at a USGS stream gauge (site #11376038) were also used to estimate an average HRT for ML. Various catchment and lake characteristics were also determined, including lake volume, surface area, drainage ratio, curve number (a measure of surface runoff potential) following methods described in (Howard and Noble, 2018).

3.1.2 Chemical and phytoplankton samples

Water and phytoplankton samples from ML, UMC, LMC, BL, and WL were collected in the spring, summer, and fall of 2014 for silicon isotope analyses, chlorophyll-α (Chl-α) and diatom analyses. Water was sampled using a Van Dorn sampler at several predetermined depths to capture of snapshot values from the epi-,
meta-, and hypolimnion of each lake, and from the surface (0 m) in UMC and LMC. (Epilimnion, metalimnion and hypolimnion refer to the upper, intermediate and lower thermal layers in a stratified lake). Samples for $\delta^{30}$Si analysis of ca. 100 ml were filtered in the field through 0.4 μm polycarbonate (PC) filters (Whatman-Nuclepore) and stored in acid-cleaned, opaque, polyphenylene ether (PPE) plastic bottles and kept cool in the dark until return from LAVO. Chl-α and pheophytin were measured from 100 mL of water via fluorometry (Turner Designs model 10AU Fluorometer) using methanol as a solvent to determine algal biomass (Welschmeyer, 1994). Calibration was conducted using a spectrophotometric method (Parsons et al., 1984) and a standard, Chl-α from *Anacystis nidulans* (Sigma Corp.). Samples of lake diatoms for identification, enumeration, and silicon isotope analysis were taken from: 1) surface tows (~300 m) using a 20 μm plankton net; and 2) from substrate scrapes at the lake margin, and 3) near surface inflow and outflow (ML only). The plankton tow and substrate scrape samples were stored in acid-cleaned PPE bottles and kept on ice and then refrigerated before sample preparation.

3.1.3 Sediment core samples

Lake cores were stabilized with Zorbitrol (sodium polyacrylate absorbent powder) upon recovery in the field and then refrigerated before being sent to the National Lacustrine Core facility (LacCore) in Minnesota, USA. At LacCore, the cores were split and subsampled at a 0.5 cm or 1 cm resolution. Sediment samples from the cores were freeze-dried and stored in opaque polyethylene containers before further sample preparation and analysis. Age-depth models of the BL, ML, and WL cores were established by $^{210}$Pb and $^{137}$Cs dating at Flett Research Ltd (Canada), using a gamma spectroscopy technique for $^{137}$Cs and an alpha spectrometry method modified from
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(Eakins and Morrison, 1978) for $^{210}\text{Pb}$. Radioisotope data from BL and ML were analyzed using the slope-regression and constant rate of supply (CRS) models (Appleby, 2001; Appleby and Oldfield, 1978; Pourchet et al., 1989). Radioisotope data for WL were analyzed using a linear slope-regression model (Appleby, 2001; Appleby and Oldfield, 1978; Pourchet et al., 1989). A CRS model could not be applied to WL $^{210}\text{Pb}$ data, because bulk density was not measured during core sampling. Analysis for percent bSi was conducted at the Sedimentary Records of Environmental Change Laboratory (Northern Arizona University) using a wet-alkaline method of extraction (Mortlock and Froelich, 1989). Briefly, ~20 mg of crushed freeze-dried sediment is leached for 5 hr in 40 ml of 2M Na$_2$CO$_3$, then neutralized and analyzed for dissolved Si concentration spectrophotometrically.

3.2 Diatom enumeration

Prior to cleaning, “boil-and-burn” mount slides were made from all samples to examine the algal communities, including colony formation. Preparation of modern and sediment samples for diatom enumeration followed protocols described in Battarbee et al. (2001) and Stoermer et al. (1995). Diatom community enumeration was carried out on samples also analyzed for $\delta^{30}\text{Si}_\text{bSi}$, including modern plankton, periphyton, and sediment. Permanent slide mounts were made using ZRAX and were used to determine relative abundance counts ($n = 500$). Samples were also examined during counting for presence of chrysophytes and sponge spicules and presence was recorded in count data. They were rare in all cleaned samples (<1% of counts) and are not discussed further. Diatoms were identified and counted at 1000x using an oil immersion lens with DIC (differential interference contrast) on an Olympus BX51 microscope.
### 3.3 Si isotope preparation and analysis

Following the method described by De La Rocha et al. (1996), a solution of acidified Triethylamine molybdate (TEA-Moly) was added to the lake water samples and dSi was precipitated overnight. This protocol aims to purify Si from all components of the sample matrix (cationic, anionic, organic). The precipitate (triethylamine silicomolybdate) in each sample was collected by vacuum filtration onto a 0.2 μm polycarbonate filter and placed into a platinum crucible. The crucibles were placed into a muffle furnace and sequentially combusted at 350 °C for 30 minutes to remove residual water, 500 °C for 2 hours to remove organics; and 1000 °C for 10 hours to volatilize the molybdenum. The relatively pure silica (SiO$_2$) left in each crucible was weighted and then dissolved in an excess of 40% HF. A molar Si:F ratio of 1:100 was targeted to avoid the formation of volatile SiF$_4$, and diluted to a target Si concentration of 229.9 mM. Any loss of Si during the processing is physical, i.e. without the potential for isotope fractionation. Next, following the anion exchange protocol outlined in Engström et al. (2005), samples were loaded onto anion exchange columns filled with 1.5 ml AG 1-X8 resin (100–200 mesh; Eichrom). Matrix elements were eluted with 95 mM HCl and 22.6 mM HF, and Si was eluted with a solution of 0.15 M HNO$_3$ and 5.5 mM HF. Complete recovery was verified by colourimetric determination of dSi concentrations in the elutant after complexing the fluoride ions with boric acid. Matrix matched standards were used for the colourimetry.

Diatom surface tow samples, substrate scrape samples, and selected sediment samples from cores were processed using techniques described in Morley et al. (2004). First, several grams of bulk sediment and substrate scrape sample (several milliliters for each surface tow sample) were cleaned with H$_2$O$_2$ and HCl to remove organic matter.
and any trace carbonates. The bSi was then separated from other detrital material in the samples by heavy liquid separation using sodium polytungstate (SPT) at a density of ca. 2.26 g cm$^{-3}$. The resulting bSi material was inspected under SEM for any contamination (e.g. mineral material); no obvious contamination was observed in checks of modern or sediment samples. Coupled with the negligible presence of non-diatom biosilicifiers (see below) observed in relative abundance counts under light microscopy demonstrates that the $\delta^{30}\text{Si}_{\text{bSi}}$ data generated reflects diatom biomass. As reported above for water samples, the resulting cleaned and separated bSi fractions were then dissolved in an excess of HF and processed via anion exchange chromatography as above.

Silicon isotope ratios of the samples were measured on a Neptune (Thermo Scientific) multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at the Pole Spectrométrie Océan (PSO, Ifremer, Brest). The Neptune was operating in medium-resolution mode with a mass-resolution (m/Δm) of $> 3500$ at 5 and 95% peak height. All solutions were doped with a matching Mg concentration and the $^{24}\text{Mg}/^{26}\text{Mg}$ ratio was monitored dynamically in order to monitor and correct the Si isotope ratios for instrumental mass-fractionation, assuming an exponential fractionation law (Cardinal et al., 2003). The corrected ratios are then used to calculate the $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ values, i.e. the deviation in the $^{30}\text{Si}/^{28}\text{Si}$ or $^{29}\text{Si}/^{28}\text{Si}$ ratios in per mil from bracketing analyses of the NBS28 standard, a reference material of quartz grains distributed by the National Institute of Standards (NIST):

$$\delta^{30}\text{Si} = \left(\frac{x^{30}\text{Si}}{x^{28}\text{Si}_{\text{SMP}}} - 1\right) \quad \text{Eqn. 3}$$

where $x^{30}\text{Si}/^{28}\text{Si}$ are the Mg-corrected isotope ratios of the sample and the
average of the bracketing NBS28 standards, with $x = 29$ or 30. Secondary reference materials (Diatomite, and Big-Batch) were prepared as described above and measured in the same analytical sessions. The results (Big Batch = -10.35±0.31; Diatomite = 1.20±0.06) were in good agreement with previously published values (Oelze et al., 2016; Reynolds et al., 2007). The mean absolute deviation between full procedural replicates ($n = 15$) was 0.08±0.05%. A three-isotope plot of all samples (Figure 2) defines the relationship $\delta^{30}\text{Si} = 1.93 \delta^{29}\text{Si} \ (r^2 = 0.99, n = 77)$, equivalent to an expected kinetic or equilibrium mass-dependent fractionation line, and confirming the successful removal of potential polyatomic interferences during preparation and measurement.

3.4 Diatom numerical analyses

Non-metric multidimensional scaling (NMDS) was conducted on the diatom count data set for all modern and sediment core samples (PC-Ord 6, Autopilot mode, Sorensen distance measure, 250 iterations (McCune and Grace, 2002)). NMDS is an ordination technique well-suited to count-data that condenses multivariate datasets (e.g. diatom count data) to a small number of Cartesian axes in such a way that distance between samples is maintained. $\delta^{30}\text{Si}_{\text{bsi}}$ values were plotted as an environmental variable overlay vector on the NMDS ordination.

Samples were subjected to constrained clustering using $\delta^{30}\text{Si}_{\text{bsi}}$ values from modern and down-core samples using the Rioja R package (Juggins and Juggins, 2020; https://github.com/nsj3/rioja). An optimal number of clusters was determined using a Mantel (Pearson) method of correlation between the original distance matrix and binary matrices computed from the dendrogram cut at various levels (Borcard et al., 2018). Indicator species analysis was conducted on each cluster group (PC-Ord 6, Dufrêne and
Legendre (1997) method, 4999 permutations in the Monte Carlo test). Finally, a multi-response permutation procedure (MRPP) was conducted as a significance test for differences between/within the cluster groups based on within-group diatom taxa similarities (PC-Ord 6, Sorensen distance measure; Peck (2016)). The output of MRPP includes the test statistic $T$, which indicates separation among groups, and an effect size $A$, that refers to the chance-corrected, within-group agreement. When $A = 1$ there is homogeneity within groups and when $A = 0$ there is heterogeneity within groups (McCune and Grace, 2002). P-values are produced using permutation, and indicate how likely an observed difference between groups is as a result of chance (McCune and Grace, 2002). $A \leq 0.4$ is considered a ‘large’ effect size (Peck, 2016), though this may change as our understanding of this novel statistic improves (Peck, 2016).

4. Results

4.1 Lake characteristics

A summary of catchment characteristics and lake physicochemical parameters are reported in Table 1 for ML, WL, and BL. An in-depth discussion of catchment characteristics, lake physicochemical parameters, modern diatom community succession, and Chl-$a$ values for Butte Lake (BL) is presented in Howard and Noble (2018). Table 2 presents the modern water samples and phytoplankton silicon isotope compositions and Chl-$a$ concentrations (a proxy for phytoplankton biomass). All lake characteristic data (e.g. oxygen, chlorophyll, temperature, conductivity) are given in the online supplementary data file. Diatom relative abundance counts, sediment core bSi contents and sediment $\delta^{30}$Si$_{\text{Si}}$ values are given in the online Supplementary Data. Diatoms dominate the phytoplankton samples from all lakes, though BL and WL have
higher mean Chl-α values than ML (Table 2). Both ML and WL appear to have a subsurface Chl-α maximum in the summer. As with BL (Howard and Noble, 2018), ML and WL have a consistent, planktic diatom succession following ice-out in the spring, through to the fall, although the community composition differs between the lakes.

4.1.1 Manzanita lake

Vertical profiles of temperature, conductivity, and dissolved oxygen across three years of monitoring are shown in Figure 3A. In ML, the seasonal progression of stratification was similar during each year of the monitoring period as was the mixing depth (~3-4 m) during stratification. The vertical profiles reflect a stratified structure, where hypolimnetic temperatures increased through the period of stratification. Estimated average hydraulic retention time for ML is ~4 months. Manzanita Lake is distinguished hydrologically from either BL or WL by the influence of Manzanita Creek, with surface water inflows and outflows observed over the algal growing seasons in 2012-2014.

The δ^{30}Si_{dSi} values for ML, and ML’s inflow and outflows at upper and lower Manzanita Creek, respectively, are reported in Table 2 and plotted in Figure 4. Inflow δ^{30}Si_{dSi} values in Upper Manzanita Creek are lower than ML or LMC (outflow) δ^{30}Si_{dSi} values. ML δ^{30}Si_{dSi} values are variable in the epilimnion over the growing season, with the highest value was observed in September 2014 (+2.79 %o). ML δ^{30}Si_{dSi} values of the meta- and hypo-limnia in 2014 are similar and near to the baseline level of UMC inflow (+1.01%) (Figure 4). In ML, δ^{30}Si_{dSi} varies seasonally, and between phytoplankton and periphyton (Table 3; Figure 5). In general, periphyton diatom δ^{30}Si values were higher than plankton diatom δ^{30}Si values (Table 3). In ML, Chl-α values
suggest that the greatest productivity occurs in the meta- and hypo-limnia with the exception of September 2014, when the highest productivity occurred in epilimnion (Table 2).

In ML, *Asterionella formosa* is abundant in May and June, transitions to *Fragilaria crotonensis* dominance in August, and finally to a mixed *F. crotonensis* and *Aulacoseira granulata* var. *angustissima* assemblage in the fall. The UMC periphyton spring and fall communities differ slightly. There is a greater relative abundance of araphids such as *Diatoma aniceps*, *Diatoma mesodon*, *Fragilaria vaucheriae* as well as *Gomphonema* spp in June 2014, whereas the fall community was dominated by monoraphids *Achnanthidium minutissimum* and *Planothidium lanceolatum* and *Nitzschia* spp. (i.e., *Nitzschia dissipata*).

4.1.2 Butte Lake

BL limnological characteristics were reported previously (Howard and Noble, 2018) and outlined in section 2.2. Briefly, the lake undergoes summer stratification following ice-out, persisting into the early fall, with a mixing depth of 5-6 m. Surface dSi concentrations ranged from 2.4 to 3.6 mg/L. Concentrations at 6m depth ranged from 2.6-4.5 mg/L and increased throughout the seasonal succession (Table 2). Epilimnetic $\delta^{30}$Si$_{dSi}$ values in BL are generally lower than ML and range from +1.30 ‰ (fall) to +1.60 ‰ (summer) (Table 3; Figure 4). The summer hypolimnetic silicon isotope composition of dSi in BL is also enriched in $^{30}$Si, with $\delta^{30}$Si similar to that of the epilimnion (+1.6 ‰), while the other $\delta^{30}$Si$_{dSi}$ values from the meta- and hypo-limnia are broadly unfractionated relative to inputs, assuming that surface water inflow value of UMC (+1.01‰) is representative of the total Si influx.

Planktic diatom $\delta^{30}$Si$_{bSi}$ values in BL hint at seasonality with a ~0.13 ‰
difference between spring and summer 2014. Spring 2014 had a $\delta^{30}\text{Si}_{\text{bSi}}$ value of -0.74% during the time it was dominated by the species *F. crotonensis* (Howard and Noble, 2018). In summer 2014 $\delta^{30}\text{Si}_{\text{bSi}}$ was -0.9%, with the assemblage dominated by *Staurosira construens* var. *binodis* (Howard and Noble, 2018). In addition to species differences, total diatom productivity differed between seasons; total planktic diatom biovolume decreased by ~50% between spring and summer 2014 (Howard and Noble, 2018).

### 4.1.3 Widow Lake

In contrast to ML and BL, the smaller WL does not exhibit sustained stratification, and was nearly isothermal at all sampling dates with the exception of June 2012 (Figure 3B). Vertical profiles of conductivity and DO also suggest that WL is a polymictic system where frequent mixing is interspersed with short-term stratification. dSi concentrations are relatively consistent across the sampling period, at 2.4 to 3 mg/L. With a mean of 1.25%, WL has the lowest epilimnetic $\delta^{30}\text{Si}_{\text{dSi}}$ values of the three lakes (Table 3). Widow Lake has a different diatom succession than its neighboring lakes; *Tabellaria flocculosa* and *Fragilaria tenera-nanana* group dominate in spring, followed by *F. crotonensis* and *T. flocculosa* in the summer, and *F. tenera-nanana* group in the fall.

### 4.2 LAVO lake sediment cores

#### 4.2.1 Manzanita Lake

Down-core $\delta^{30}\text{Si}_{\text{bSi}}$ values, percent bSi, and diatom data are shown in Figure 5A. Around 1942 CE (Common Era), percent bSi is relatively low (<10%) and a relatively high $\delta^{30}\text{Si}_{\text{bSi}}$ value (-0.60‰) is observed (Figure 5A). Percent bSi increases
and $\delta^{30}\text{Si}_{\text{bsi}}$ decreases slightly until ~1968 CE. The diatom community composition during this same period is dominated by benthic periphyton (Navicula and Nitzschia spp), epilithic periphyton (i.e., Fragilaria vaucheriae), and meroplankton taxa (Aulacoseira spp). From ~1968 CE until 1986 CE, the relative abundances of tychoplankton (i.e., Staurosira construens var. venter) and euplanktic taxa (Stephanodiscus spp., F. crotonensis, F. mesolepta) begin to increase. A simultaneous increase in percent bSi (up to ~20%) and decrease in $\delta^{30}\text{Si}_{\text{bsi}}$ values (to around -1.0‰) is also observed. From 1986 CE to 1998 CE, there is a slight decrease in percent bSi coincident with an increase in $\delta^{30}\text{Si}_{\text{bsi}}$ values (up to around -0.70‰). Relative abundances of euplanktic taxa decrease slightly while relative abundances of tychoplankton (i.e., Pseudostaurosira brevistiata, Staurosira construens var. binodis), meroplankton (i.e., Aulacoseira granulata var. angustissima) and periphyton taxa (i.e., Pseudostaurosira pseudoconstruens, Navicula spp) increase slightly over this period. From 1998 CE to the present, the relative abundances of euplanktic (F. crotonensis, F. mesolepta, A. formosa) and tychoplanktic taxa (S. construens var. venter, S. construens var. binodis) increase dramatically, concurrently with increases in percent bSi (up to ~30%) and constant $\delta^{30}\text{Si}_{\text{bsi}}$ values around -0.90‰.

4.2.2 Butte Lake sediment core

In the BL core (Figure 5B), prior to the dated section, $\delta^{30}\text{Si}_{\text{bsi}}$ values are around -0.2‰, and decrease upwards to values of -0.9‰, tracking consistently with increasing (up to ~70%) and then decreasing (to ~50%) percent bSi. Decreasing values prior to 1932 CE are coincident with increasing relative abundances of euplanktic taxa (Asterionella formosa, Fragilaria crotonensis, Fragilaria grunowii). In the dated
section, from ~1932 CE to 2014 CE, there is no correlation between $\delta^{30}\text{Si}_{\text{bSi}}$ values and percent bSi values is observed: percent bSi remains relatively consistent during this period (at ~50%), while $\delta^{30}\text{Si}_{\text{bSi}}$ values fluctuate about a trend towards increasing values (around ~0.3%). A major change in diatom community composition occurs in the period from 1932 CE to present, with a decline in the relative abundance of euplanktic taxa and an increase in the relative abundance of small araphid tychoplanktic taxa (i.e., *Staurosira construens var. binodis*).

### 4.2.3 Widow lake sediment core

WL sediment $\delta^{30}\text{Si}_{\text{bSi}}$ values vary from -0.5 % to about -0.1 % (Fig 5C). Distinct trends are apparent both below and above the tephra layer (Figure 5C). The highest percent bSi concentrations occur below the tephra layer (beyond the age model), and are correlated with high $\delta^{30}\text{Si}_{\text{bSi}}$ values. This period is associated with benthic periphyton taxa (i.e., *Sellaphora pupula*, *Pinnularia* spp., *Stauroneis* spp.) and *Discostella stelligera*. Above the tephra layer (~1881 CE to present), the direction of relationship between percent bSi and $\delta^{30}\text{Si}_{\text{bSi}}$ values change, with higher percent bSi coincident with lower $\delta^{30}\text{Si}_{\text{bSi}}$ values. This change is also coincident with a change in diatom community composition where euplanktic taxa (i.e., *Fragilaria crotonensis*, *Tabellaria flocculosa*), and tychoplanktic taxa (i.e., *Pseudostaurosira brevistriata*) become dominant. A slight decrease in percent bSi with coincident higher $\delta^{30}\text{Si}_{\text{bSi}}$ values is noted around 1946 CE and is consistent with an increased relative abundance of *Nitzschia perminuta*, *Achnanthidium minutissimum*, and *Lindavia* spp. Sediment $\delta^{30}\text{Si}_{\text{bSi}}$ values correlate with percent bSi and phosphorus below the tephra layer in zones 2 and 3, but deviate in zone 1 (Figure 5C), where values become anticorrelated.
with total P and percent bSi. Similar temporal patterns for $\delta^{30}\text{Si}_{\text{bSi}}$ values are also observed in BL.

### 4.3 Numerical analyses

A $\delta^{30}\text{Si}$-constrained cluster analysis yielded six statistically significant sample groups, based on Mantel (Pearson) correlation. One of the groups had only one sample so a total of five groups was chosen for the final analysis. NMDS analysis resulted in a stable solution and stress = 9.44. Axis 1 explains 43% of the variance, Axis 2 explains 25% of the variance and Axis 3 explains 18% of the variance. Values of $\delta^{30}\text{Si}$ correlate best with axis 3 ($r = 0.593$) and axis 1 ($r = 0.339$). Figure 6 shows an NMDS ordination biplot (axes 1 and 3) of all lake core and modern samples with convex hulls delineating the $\delta^{30}\text{Si}$-constrained cluster groups and the overlay vector for $\delta^{30}\text{Si}_{\text{bSi}}$. MRPP among all $\delta^{30}\text{Si}_{\text{bSi}}$ groups is significant ($p < 0.001$; $\alpha = 0.05$), with a within-group homogeneity effect size of $A = 0.26$ (Supplementary Material). Significant MRPP p-values and associated A-values (Supplementary Material) indicate that the grouping structure (i.e. clusters produced by the NMDS analysis, constrained by $\delta^{30}\text{Si}_{\text{bSi}}$) explains a portion of the variation in the response (diatom taxa) distribution and is corroborated by $\delta^{30}\text{Si}$ values correlating with Axes 1 and 3 in the NMDS ordination (section 4.3) and specific, significant indicator taxa (Table 3). Most pairwise comparisons between the groups are also significant (adjusted $P$; Holm-Bonferroni correction) at the $\alpha = 0.05$ level (Supplementary Material). Associated significant ($\alpha = 0.05$) indicator taxa were identified for 4 of these 5 groups (Group 2 did not yield any significant indicator taxa at the $\alpha = 0.05$ level) and are given in Table 3.
5. Discussion

5.1 Patterns of Si utilization in LAVO lakes

Relatively high dSi concentrations (~16 mg/L Si at the UMC inflow, and ~12 mg/L at the LMC outflow; Table 3) compared to the other lakes likely reflect a large drainage ratio, large capacity for surface water runoff (curve number = 63), and the dominant rhyodacite bedrock (Table 1). Beyond these factors, the high dSi concentrations hint at hydrothermal processes seen in the catchment, as reported in general for the LAVO park (Ingebritsen et al., 2016). These values agree well with historical USGS monitoring data for LMC collected in 1979-1981 (mean outflow = 14.8 mg/L Si, no correlation with discharge, USGS site 11376038).

In ML, lower concentrations of dSi in the epilimnion relative to the inflow (~12 mg/L vs. ~17 mg/L, respectively), and higher δ³⁰Si_{dSi} values (~2.20 ‰ vs. ~1.00 ‰, respectively) suggest utilization of Si throughout the growing season (Table 2, Figure 4). The pattern of higher lake water than inflow water values is consistent amongst all lake studies to date (Alleman et al., 2005; Opfergelt et al., 2011; Panizzo et al., 2017; Zahajská et al., 2021), and is a clear indicator of biological Si uptake. Outflow δ³⁰Si_{dSi} values in LMC are around +1.86 ‰ (Table 3), lower than epilimnetic values and likely reflect mixing of dSi pools from the metalimnion, hypolimnion, or groundwater into outflow water. High epilimnion δ³⁰Si suggests most biosiliceous production occurs in the upper water column. Chl-a values are a general measure of productivity for all algae groups, and in ML are higher in the meta- and hypolimnia compared to the surface (Table 2). Higher Chl-a at depth in ML may result from non-diatom algal groups (e.g., chlorophytes or cyanophytes). Alternatively, the values might reflect export or migration of surface diatom production from the epilimnion to deeper depths. The
Diatom silicon isotope ratios in Lassen Volcanic National Park

$\delta^{30}$Si$_{dSi}$ values of the deeper water samples in ML are lower than the epilimnion either because of lower diatom productivity at depth, the progressive dissolution of diatoms exported from overlying layers or mixing with less $^{30}$Si enriched dSi pools (i.e., groundwater or a diffusive flux across the sediment-water interface).

In BL dSi concentrations and $\delta^{30}$Si$_{dSi}$ values also suggest Si utilization in the epilimnion under stratified conditions (Table 3; Figure 4), with surface waters being ca. 0.3 %o heavier than deeper waters in May and August 2014. In September 2014, surface water $\delta^{30}$Si$_{dSi}$ in BL decreased to 1.27‰, indistinguishable to the hypolimnetic value, which we attribute to rigorous vertical mixing after a breakdown in stratification towards the end of the summer season due to decreased air temperatures and storms (see Figure 4 in Howard and Noble (2018)).

Unlike ML and BL, WL appears to be continuously mixed and only develops weak stratification on the scale of days (Figure 3). WL only has ephemeral surface water inflow and outflow and has overall lower dSi concentrations (lowest observed was 2.4 mg/L; Table 2), which may reflect a lower weighted curve number for the catchment, smaller drainage ratio, and dominant catchment geology perhaps with a differently reactive suite of minerals than the rhyodacite and andesite underlying ML and BL catchments (Table 1). Chl-$\alpha$ values in WL differ between top and bottom under stratified conditions (Table 2) suggesting higher diatom productivity and Si utilization at depth than in the surface water. The one date during which WL exhibited strong stratification, June 21, 2012, shows the greatest variation in epilimnetic (1.29 µg/l) vs hypolimnetic (13.33 µg/l) Chl-$\alpha$ values (Table 2). Other sampling dates exhibit much higher Chl-$\alpha$ values from surface waters (Table 2) indicating frequent mingling of surface and deeper water in this polymictic system. Unfortunately, dSi concentration
and δ³⁰Siᵃᵦ data were not collected for multiple depths in WL so we cannot verify whether increased productivity at depth in WL is linked to enriched δ³⁰Siᵃᵦ. Epilimnetic δ³⁰Siᵃᵦ values and dSi concentrations vary slightly over the growing season in WL, suggesting changes in dSi utilization and very weak or short-term stratification (Table 3, Figure 3B).

5.1.1 Distinguishing between fractionation models

By plotting δ³⁰Siᵃᵦ and δ³⁰Siᵦᵦ as a function of Si utilized for ML, we can attempt to distinguish between the two endmember fractionation models (see introduction; Figure 7). The x-axis in this plot, i.e. the degree of dSi utilization, is hard to constrain. We take \( f = 1 - C/C₀ \) as an approximation, where \( C₀ \) is the Si concentration of inflows to ML via UMC at the time of sampling and \( C \) is the Si concentration of the epilimnion in ML. Accurately accounting for groundwater is not possible, since no wells exist within the park (water supply for consumption is surface water sourced), so we assume the groundwater has the same dSi concentration as UMC. The groundwater dSi should be measured in future work. UMC is thus used as the closest proxy available for background Si concentration of inflows in the absence of biological Si isotope fractionation. Figure 7 shows that the overall range of Si utilization (ca. 19 – 35%; see also section 5.4 below) is not large enough to be able to distinguish Rayleigh-style system evolution (Eqn. 1) from a steady-state model (Eqn. 2). The reality likely falls somewhere between these two endmember scenarios; for much of the growing season, diatom growth rates exceed dSi supply, causing a transient depletion in lake water Si inventory. This lack of balance between supply and removal invalidates the steady-state assumption of Eqn. 2. On the other hand, the non-zero supply of new or recycled dSi, invalidates the assumptions inherent in a Rayleigh
model. Where a system behavior falls between these two models will depend on the rate of bSi production relative to supply; when it is much greater, a Rayleigh model (Eqn. 1) will be closer to the truth, but when they are more closely matched, a Steady-State model (Eqn. 2) may best capture the dynamics of the system. Overall, even simple lake ecosystems cannot be condensed to the models typically used. Seasonal imbalances between supply and demand, combined with variable Si isotope fractionation factors (Section 5.2 below), suggest more nuanced models that capture time-dependence, are required if we are to fully describe system behavior.

5.2 Diatom silicon isotope fractionations

Diatom Si isotope fractionation factors, degree of Si utilization, and degree of system openness combine to define $\delta^{30}_{\text{Si}} \text{bSi}$ and residual dSi $\delta^{30}_{\text{Si}} \text{diatom}$ (Section 2). From our LAVO data, we can get a snapshot of the magnitude of the isotope fractionation for diatoms by comparing $\delta^{30}_{\text{Si}} \text{bSi}$ values with $\delta^{30}_{\text{Si}} \text{diatom}$ values for diatom samples collected simultaneously, i.e. $\varepsilon_{\text{diatom}} \approx \Delta^{30}_{\text{Si}} \text{water-diatom} = \delta^{30}_{\text{Si}} \text{water} - \delta^{30}_{\text{Si}} \text{diatom}$. Using this approach, we can calculate a Si isotope fractionation for ML planktic diatoms in spring 2014 of -3.4‰ (dominated by A. formosa and F. crotonensis) and -3.9‰ in fall of 2014 (F. crotonensis and A. granulata var anugustissima dominant) (Figure 7). We can also derive fractionations for BL from 2 paired samplings; in spring of 2014 (-2.29‰, dominated by F. crotonensis), summer of 2014 (-2.51 ‰, dominated by S. construens var. binodis), and for WL in summer of 2014 (-1.58‰, dominated by F. crotonensis and T. flocculosa). Finally, we can estimate Si isotope fractionations associated with the periphyton taxa growing on ML inflow and outflows (Table 2). This yields a mean value of -1.63 ‰ for three samples. This is an imperfect approach: calculated
fractionations may include bias introduced by a mismatch in the timeframe the two pools represent. Dissolved Si $\delta^{30}$Si is effectively an instantaneous value, but diatom bSi $\delta^{30}$Si will integrate over a few lifespans, i.e. days to 10s of days. In general, the estimates for BL and ML fall outside the range of marine diatom taxa Si isotope fractionations presented by Sutton et al. (2013) of -2.09 to -0.53‰, but within the range of Si isotope fractionation observed for marine sponges of ca. -6.75 to – 0.50‰ (Cassarino et al., 2018; Hendry and Robinson, 2012). This is an interesting result that warrants deeper investigation.

It is well established that marine sponges have variable Si isotope fractionations that exhibit a relationship with the dSi concentrations of the water they grow in (Hendry and Robinson, 2012; Wille et al., 2010). This is thought to be caused by the variable expression of isotope fractionation at different stages of sponge biomineralization (uptake, polymerization, and efflux), in a manner that is governed by mass-balance (cf. Eqn. 2). The presence of various transport proteins is also believed to play a role. Previously, Milligan et al. (2004) have argued that the only fractionating step in diatom biosilicification is the uptake of dSi into the cell. This might suggest that the relationship between ambient dSi concentrations and isotope fractionation seen for sponges would not hold for diatoms. Nevertheless, in compiled marine data, there is a subtle hint of a trend towards larger magnitude Si isotope fractionations at higher dSi concentrations (see Figure 2B in Abelmann et al. (2015)), albeit for ocean surface waters < ~2.2 mg/L Si. In general, the range of dSi concentrations seen in surface waters of the ocean is lower than for lacustrine systems: ML lake waters, for example, reach ~18 mg/L (> 600 µM; Table 2). Lake systems thus offer a chance to investigate a potential dSi concentration dependency of diatom Si isotope fractionation. Figure 8
compiles diatom fractionations from this study and the published literature as a function of water dSi concentration and temperatures. Two conclusions can be drawn. First, our isotope fractionations estimated from coupled bSi-dSi $\delta^{30}$Si for ML are the largest magnitude reported to date. Note that they are also corroborated by the suite of water samples alone (Figure 7; Table 2), which plot on a line defined by a fractionation of ca. -3.5%. Second, although these are also the datapoints at the highest dSi concentration, there is no relationship between dSi concentration and the magnitude of diatom Si isotope fractionation across the entirety of the data (Figure 8A). This corroborates earlier conclusions in the marine realm (Sutton et al., 2013). Considering just the freshwater estimates, a negative trend emerges but is strongly influenced by the two ML datapoints. Future work could investigate diatom Si isotope fractionation in other high dSi lacustrine environments. Most of the studies compiled in Figure 8 do not generate diatom relative abundance counts. In the following, we explore the extent to which we can exploit diatom assemblage data to yield insight into Si isotope geochemistry.

Culturing experiments provide evidence that diatom silicon isotope fractionation is not a constant value, even for the same taxa grown in similar (though not identical) conditions (De La Rocha et al., 1997; Meyerink et al., 2017; Milligan et al., 2004; Sutton et al., 2013). In the modern ocean, there are latitudinal gradients in marine diatom Si isotope fractionation (Cardinal et al., 2007), which may reflect species effects. There is also evidence that diatom fractionations at a single site change as the community composition changes (e.g. Annett et al., 2017). Why different taxa have different fractionations, or why the same species can exhibit different fractionations is unclear, but some of the variability in natural settings may be related to trace-element
avaliability. For example, Fe availability has been shown to alter diatom Si isotope fractionation in some cases (Meyerink et al., 2017). There is also evidence that micronutrient (Fe, Zn, Cu, etc.) availability affects diatom cell stoichiometry (e.g. Baines et al., 2011) or frustule structure (e.g. Boutorh et al., 2016). Deconvolving intrinsic differences in Si metabolism between taxa, from changes induced by environmental variables, is important for accurate interpretation of paleoenvironmental records. Given that the high dSi concentrations in ML are indicative of hydrothermal fluids in the lake catchment, it is plausible that there is also an enhanced supply of trace-elements that may be enriched in hydrothermal fluids. We thus speculate that the large fractionations are linked to some facet of the water chemistry, and to hydrothermalism in the region (Ingebritsen et al., 2016).

Our modern and downcore assemblage data allows us to explore the role of diatom community composition in setting the net Si isotope fractionation factor. NMDS and indicator species analyses on all samples (from all three lakes) demonstrate that systematic and statistically significant relationships can be drawn between diatom assemblages and their $\delta^{30}$Si$_{bSi}$ (Figure 6, Table 3). Samples with the lowest $\delta^{30}$Si$_{bSi}$ values (< -1.1‰) are associated with Group 5, composed of araphid euplankton taxa $F$. crotonensis, F. mesolepta, such as seen in the Manzanita Lake plankton samples, and the Spring 2014 Butte Lake plankton sample. Samples with $\delta^{30}$Si$_{bSi}$ values -0.69 to -1.1‰ are associated mainly with Group 4, composed of araphid tychoplanktic taxa (i.e., S. construens var venter, Pseudostaurosira brevistriata), which are common throughout the Manzanita Lake core and the upper 45 cm of the Butte Lake core (Figure 5). Samples with moderate $\delta^{30}$Si$_{bSi}$ values (-0.55 to -0.66 ‰) are mainly associated with Group 3, a mixed group of attached periphyton, consisting of monoraphid taxa (i.e.,
Karayevia clevei, Achnanthidium exiguum) and araphid taxa (i.e., Pseudostaurosira parasitica, Staurosirella pinnata), found in greatest abundance in a subset of Butte Lake core samples (Figure 5). Samples with the highest $\delta^{30}{\text{Si}}_{\text{bSi}}$ values (> -0.14 %o) are mainly associated with Group 1, that comprise unattached, motile benthic, biraphid taxa (i.e., Navicula spp, Encyonopsis spp, Stauroneis spp), and a few centric, euplanktic taxa (i.e., Discostella stelligera and Lindavia spp), found in modern samples from Lower Manzanita Creek and well as a subset of the Widow Lake core samples and Widow Lake modern plankton sample (Figures 5,6). Although not significant at the $\alpha = 0.05$ level, araphid, needle-like Fragilaroid taxa are associated with low to moderate $\delta^{30}{\text{Si}}_{\text{bSi}}$ values (-0.21 to -0.51 %o) (Table 3).

A-values for significant MRPP tests (Supplementary Material) reflect moderate to large effects ranging from 0.095 to 0.455 for group separation, and within group heterogeneity since dispersion within groups is variable (Figure 6). Thus, samples in a given group (samples with similar range of $\delta^{30}{\text{Si}}_{\text{bSi}}$ values) are more like one another in terms of specific diatom taxa than if they belonged to a different group (samples with a different range of $\delta^{30}{\text{Si}}_{\text{bSi}}$ values). Pairwise comparisons of adjacent groups are not significant at the $\alpha = 0.05$ level (1 v. 2, 2 v. 3, 3 v. 4) suggesting a degree of gradation between these adjacent groups. Pairwise comparisons of non-adjacent groups (e.g. Group 1 v. Group 3), which are separated by more than ~0.4%o variation in $\delta^{30}{\text{Si}}$ value, are significant at the $\alpha = 0.05$ level, indicating a clear distinction in their taxonomic composition and demonstrating that species-specific isotope effects for different functional groups can be teased out of whole-assemblage data in a quantitative manner. Because these functional groups can be related to specific habitats (see above), the contribution of potential micro-habitat effects on diatom Si isotope fractionation – for
example, via micronutrient availability, growth rate, ecological interactions, etc. - rather than intrinsic species-specific effects – cannot be strictly ruled out.

5.3 Si mass-balance for Manzanita Lake

Manzanita Lake is an efficient Si sink, removing approximately 30% of inflowing dSi. This conclusion is based on three independent lines of evidence: 1) the construction of elemental Si mass balance calculations (Figure 9, see below); 2) the isotope ratio difference between inflows and outflows and 3) sediment accumulation rates of bSi.

dSi concentration data and stream discharge data (Supplementary Material) allow the total mass of Si retained in the system to be derived (Figure 9). The reduction in fluvial dSi concentrations between upper and lower Manzanita Creeks is approximately 35%. Combined with an estimate of UMC discharge (Supplementary Material), this suggests a basin wide accumulation rate of ~0.008 g/m²/yr. We measured δ³⁰Si = 1.01‰ in UMC and δ³⁰Si = 1.86‰ in LMC (Table 2). If we take an estimate ε₃₀Si ≈ -2.5‰, based on isotope differences of the LAVO dSi-bSi sample pairs (section 5.2), this produces an estimate of 34% retention under the steady-state model and 29% for the Rayleigh model (Eqn. 1 and Eqn. 2, respectively). This agrees remarkably well with the estimate based on element fluxes alone (ca. 35%, see above and Figure 9). One implication is that any unaccounted for dSi inputs to the system (notably groundwater or soil-interflow water, plus potential direct hydrothermal fluid recirculation, though we have no evidence for this) has the same dSi concentration and δ³⁰Si as UMC waters. Were this not the case, the good agreement between the two methods would be unlikely.

Down-core percent bSi and average mass accumulation rates (based on core chronology data presented in Howard (2018)), produce an average bSi mass
accumulation rate (MAR) for recent ML lake sediments of ~0.023 g/m²/yr (Figure 9). This is approximately a factor of three higher than the estimate based on Si concentrations. Two aspects may contribute to this discrepancy. Firstly, the fluvial dSi flux does not represent 100% of the inputs of Si to ML. Other potential Si sources were not quantified and therefore could contribute to the ‘missing’ dSi (see Figure 9). Groundwater is likely the most important non-quantified flux, as it has been shown to have high Si concentrations – often over 25 mg/L Si – in volcanic regions (Rosen, 2001; Schopka and Derry, 2012). Although the groundwater flux (implicitly including Si derived from hydrothermal activity) is unknown for ML, it is expected to be an important component of ML hydrology and as a source of Si for this system. The input of amorphous Si phases in UMC sediments and via dust deposition could also contribute Si to the system, though this is likely to be small (Frings et al., 2014). There is no evidence for direct hydrothermal vent features in the lakes, though this cannot be conclusively ruled out. Secondly, we do not attempt to correct for sediment focusing – the tendency of sediment to move to deeper areas of a lake. In other words, the bSi MAR is likely overestimated here since the core derives from the lakes depocenter. Work elsewhere has shown that single cores can distort estimates of mass-accumulation rates (Dillon and Evans, 2001; Hilton, 1985; Likens and Davis, 1975).

Recent work has highlighted how not accounting for groundwater can give extremely misleading or nonsensical lake Si mass-balances (Zahajská et al., 2021). One benefit of silicon-isotope based estimates of lake Si retention is that they can help reconcile the divergent Si burial rates derived from elemental mass-balance (0.008 g/m²/yr) with those from burial rates (0.023 g/m²/yr). Assuming other sources of Si are limited (e.g. within-lake sediment dissolution), it suggests that groundwater is
supplying about two-thirds of the lake dSi, corroborating the work of (Zahajská et al., 2021) who argue it should be considered in lake budgets more widely. One of the few lake Si mass-balances that explicitly consider groundwater Si reported a groundwater contribution of 70% for an Argentine pampean lake (Miretzky and Cirelli, 2004).

Elsewhere, (Hofmann et al., 2002) have acknowledged their Si mass-balance for Lake Lugano, on the Swiss/Italian border, may be biased by the lack of groundwater data. In a French crater lake, (Michard et al., 1994) have shown that groundwater supplies ca. 90% of dSi to the system. We thus suggest that analogously to the attention submarine groundwater discharge is receiving for its importance to ocean element and isotopic budgets (Mayfield et al., 2021; Rahman et al., 2019), the role of groundwater in supplying nutrients to lake ecosystems should be more widely considered.

Harrison et al. (2012) and Frings et al. (2014) previously demonstrated that lake hydraulic residence time is the most important control on lake Si retention efficiency. There are several lake or reservoir systems with similar residence times to ML that have established Si budgets. These include the reservoirs Alexandrina, Australia (ca. 3.6 months; Cook et al., 2010), Aube and Marne, France (ca. 4.8 and 5.5 months; Garnier et al., 1999) and the natural systems Loch Leven, Scotland (ca. 5 months; Bailey-Watts et al., 1989) and Southern Indian Lake, Canada (ca. 2.75 months; Hecky et al., 1986)). These systems all have dSi retention efficiencies of a similar magnitude (mean ± 1σ = 44 ± 17%). Elsewhere, silicon isotopes have been used to quantify Si retention in Lake Myvatn, Iceland (Opfergelt et al., 2011). Here, an elevated δ³⁰Si of lake outflow dSi, by 0.2 – 0.9‰, relative to the dSi sources, was interpreted to reflect substantial Si retention, even in a system with a water residence time of ~27 days (Opfergelt et al., 2011). Zahajská et al. (2021) present a similar Si isotope mass-balance for the high
latitude, subarctic Lake 850 in northern Sweden, which retains ca. 79% of inflowing dSi. These studies all point to the remarkable ability of lakes to quickly and efficiently sequester dSi in their sediments as bSi. Seen in the context of this previous work, the retention efficiency of Si in the sediments of ML, while large, is entirely in line with other systems, both man-made and natural. Overall, this underscores the importance of lacustrine systems in modifying both the riverine dSi flux and its silicon isotope composition. It also demonstrates that silicon isotope geochemistry is a powerful tool to quantify lake Si retention efficiency (Opfergelt et al., 2011; Zahajská et al., 2021).

Frings et al. (2014) estimated that lakes retain, as bSi in their sediments, about 25% of the Si flux released to the fluvial system from silicate weathering reactions. Assuming the canonical diatom Si isotope fractionation of -1.1‰, this was sufficient to raise riverine δ^{30}Si by 0.3‰ and arguably require consideration in paleoceanographic studies. If the mean fractionation is actually closer to those observed in the LAVO systems (-3.90 - -1.58‰; see above) then the impact on river δ^{30}Si would be correspondingly greater and the δ^{30}Si of dSi delivered to the ocean on glacial-interglacial timescales more sensitive to changing lake Si retention efficiency (Frings et al., 2016).

### 6. Conclusions

Lakes act as biogeochemical reactors in the continental Si cycle, and efficiently retain dSi in their sediments. Here, we used geochemical and (paleo)ecological approaches to investigate Si cycling in three lakes in Lassen Volcanic National Park, California. We generated data on lake characteristics, silicon isotope compositions, and diatom abundances from modern and sediment core samples for Manzanita, Butte, and Widow Lakes. These systems exhibit a range of diatom Si isotope fractionations,
including the largest reported to date. There are strong, significant relationships
between diatom species composition and diatom silicon isotope composition that were
revealed by ecological dimension-reducing statistical approaches. Samples that are
dominated by specific diatom functional groups tend to cluster within a specific range
of $\delta^{30}\text{Si}_{\text{bs}}$ values. These functional groups can be related to specific habitats. The
possibility of micro-habitat effects thus cannot be excluded as an explanation for
differences in $\delta^{30}\text{Si}_{\text{bs}}$ values between species, rather than species-specific Si isotope
fractionation factors *sensu stricto*. Data from LAVO lake cores suggest that diatom
species composition most closely covaries with $\delta^{30}\text{Si}_{\text{bs}}$ values over the past century.
While nutrient supply does play a role, the relationship between productivity and
$\delta^{30}\text{Si}_{\text{bs}}$ is likely more indirect, mediated by the effects nutrient concentration and
stoichiometry have on the species composition of the sample. Finally, a Si mass-balance
for Manzanita Lake highlights the Si retention efficiency of lacustrine systems and
suggests an understudied role for groundwater in lake dSi supply.

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8. Figure captions
Figure 1: Locations of Manzanita, Butte, and Widow Lakes and catchment areas in Lassen Volcanic National Park, California.

Figure 2: Three isotope plot of $\delta^{30}$Si and $\delta^{29}$Si values of water, modern diatom samples, and bulk sediment core biogenic silica (diatom) for LAVO lakes. The gradient of the linear regression between $\delta^{30}$Si and $\delta^{29}$Si agrees with theoretical predictions of the mass-dependency of Si isotopes, indicating the successful removal of polyatomic interferences during sample preparation and measurement (see main text for details). A long-term reproducibility of $\pm 0.15 \%$ (2sd) is shown; typical internal measurement precisions are better.

Figure 3: Vertical profiles of temperature ($^\circ$C), dissolved oxygen (mg/L), and specific conductance ($\mu$S/cm), taken on 7 sampling dates in 2012-2014 for: Column A) Manzanita Lake, and Column B) Widow Lake. Colors indicate the months that samples were collected in each year.

Figure 4: Down-core plots of sediment core $\delta^{30}$Si$_{bSi}$, sedimentary bSi concentrations, and diatom taxa relative abundances for Manzanita, Widow, and Butte lakes. Vertical axes are: calendar year per $^{210}$Pb age model, and cm below lake floor. Age models for each core can be found in the online Supplementary Material. Epi = Epilithic, Ben = Benthic, Peri = Periphyton. Diatom taxa abbreviations, corresponding to those in Howard (2018), are ACHN = Achnanthidium spp., AMIN = Achnanthidium minutissimum, ADLA = Adlafia spp., AGVA = Aulacoseira granulata var. angustissima, AULA = Aulacoseira spp. 4, AFOR = Asterionella formosa, DIAT = Diatoma mesodon, DINC = Distriionella incognita, DSTE = Discostella stelligera, ENPS1 = Encyonopsis spp. 4, FCRO = Fragilaria crotonensis, FGRU = Fragilaria grunowii, FMES = Fragilaria mesolepta, FPED = Fragilaria perdelicatissima, FTEU = Fragilaria tenuissima, FVAU = Fragilaria vaucheriae, GOMP1 = Gomphonema spp. 1, KCLE = Karayevia clevei, LIND = Lindavia spp., NAVI1 = Navicula spp. 1, NITZ = Nitzschia spp., NLIE = Nitzschia liebertruthii, NPER = Nitzschia perminuta, PINN3 = Pinnularia spp. 3, PINN4 = Pinnularia spp. 4, PBRE = Pseudostaurosira brevistriata, PPAR = Pseudostaurosira parasitica, PSEU = Pseudostaurosira pseudoconstruens, REIS = Reimeria simuata, SPUP = Sellaphora pupula, SCVB = Staurosira construens var. binodis, SCVV = Staurosira construens var. venter, SPIN = Staurosirella pinnata, SNEO = Stauroneis neohyalina, SANC = Stauroneis aniceps, STEP = Stephanodiscus spp., STEPH1 = Stephanodiscus sp. 1, STEPH2 = Stephanodiscus sp. 2, TFLO = Tabellaria flocculosa.

Figure 5: Vertical profiles of lake $\delta^{30}$Si$_{bSi}$ values for Manzanita and Butte lakes in 2014. Consistently higher lake $\delta^{30}$Si than inflow values for ML indicates biological utilization of dSi. Generally higher surface water $\delta^{30}$Si than deeper waters indicates biosiliceous production at the surface and progressive dissolution in the water column or sediments, though vertical mixing occasionally obscures this general pattern. A long-term reproducibility of $\pm 0.15 \%$ (2sd) is shown; typical internal measurement precisions are better.

Figure 6: NMDS biplot of Axis 1 v. Axis 3 for modern and down-core samples overlain
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with convex hulls of five groups of $\delta^{30}$Si$_{bSi}$ values (determined by constrained clustering). The samples assigned to each group are plotted by symbol. The range of $\delta^{30}$Si$_{bSi}$ values for each of the groups is found in Table 3, as are the indicator taxa associated with each group. Axis 1 explains 43% of the variance, Axis 3 explains 18% of the variance. The statistical analyses indicate that approaches designed for the analysis of noisy, ecological data can be used to deconvolve species-specific isotope effects from bulk samples.

**Figure 7:** Evolution of silicon isotope ratios in Manzanita Lake in samples from 2014 as a function of fraction of dSi converted to bSi by diatom growth. The x-axis $(C/C_0)$ is taken as a proxy for relative fraction of reactant (dSi) remaining, where $C$ is the dSi concentration ML waters, and $C_0$ the initial concentration in inflow UMC waters (see values in Table 2 and main text for details). Vertical arrows indicate the isotope difference between bSi and dSi samples collected simultaneously. Black and red lines indicate the predicted evolution of $\delta^{30}$Si as a function of $f_{bSi}$ for the Rayleigh (Eqn. 1) and Steady-State (Eqn. 2) models, respectively. A long-term reproducibility of ±0.15‰ (2σ) is shown; typical internal measurement precisions are better.

**Figure 8:** A compilation of diatom Si isotope fractionations from the literature for freshwater (green symbols), estuarine/brackish (light blue symbols), and marine (dark blue symbols) environments, as a function of A) dSi concentration and B) temperature. Symbol shape indicates study type: laboratory/culturing experiment (squares); mesocosm experiment (diamonds), and empirical field measurements (circles). Many of the field-based studies are displayed as two symbols if the original study did not or could not differentiate between Rayleigh and Steady-State models. The lack of a correlation between magnitude of isotope fractionation and either dSi concentration or temperature indicates the variation in fractionation remains to be explained and may be partially related to species specific Si processing pathways. DLR97 refers to the De La Rocha et al. (1997) canonical value for diatom Si isotope fractionation of -1.1‰. Data from this study and literature (Alleman et al., 2005; Annett et al., 2017; Beucher et al., 2008; Beucher et al., 2011; Cao et al., 2015; Cao et al., 2012; Cassarino et al., 2017; Closset et al., 2015; Cloisot et al., 2019; Coffineau et al., 2014; De La Rocha et al., 1997; Doering et al., 2016; Egan et al., 2012; Ehlert et al., 2012; Fripiat et al., 2007; Meyerink et al., 2017; Meyerink et al., 2019; Milligan et al., 2004; Opfergelt et al., 2011; Panizzo et al., 2017; Reynolds et al., 2006; Sun et al., 2013; Sun et al., 2018; Sun et al., 2014; Sutton et al., 2013; Varela et al., 2016; Varela et al., 2004; Weiss et al., 2015; Zhang et al., 2015; Zhang et al., 2020).

**Figure 9:** Simple mass-balance model for Si in Manzanita Lake, as described in main text. Retention efficiency based on Si concentrations observed in surface inflow and outflow in 2014, and agrees well with isotope-based estimate (see main text and Figure 7). These can be scaled to burial fluxes by using field measurements (2014) of surface inflow/outflow rate (slope-area method; Supplementary Material) and/or historical USGS gauging data (1979-81 Lower Manzanita Creek; Supplementary Material). For comparison, an estimate of average bSi (from down-core bSi concentrations) mass accumulation rate (based on $^{210}$Pb and $^{137}$Cs-derived sediment accumulation rate for ML lake gravity core, data from Howard (2018)) is presented. Sediment-core derived burial fluxes are a factor of three higher than lake mass-balance derived fluxes, which
may be due to groundwater dSi supply, to sediment focusing, or to a combination.

10. Table captions

Table 1: Table 1: Summary of Manzanita, Butte, and Widow lakes catchment characteristics and morphometry. For closed or semi-closed lakes (BL, WL), size metrics calculated based on GIS data representing full-lake conditions (see Howard and Noble 2018). Curve Number is an empirical parameter that predicts the likelihood of overland runoff for a rainfall event; Shoreline Development is shoreline length relative to a circle of the same area. Notes: 1 Small ephemeral stream; a dry stream bed indicated a potential inflow, but no flow was observed during the 2012-2014 sampling period. 2 Lower Manzanita Creek sampled by USGS 1979-1981, data accessed via NWIS portal, site number: 11376038. 3 Outflow in Butte Creek was observed May-September in 2012. In 2013/2014, Butte Lake level dropped below the outflow level and outflow ceased. 4 Although a dry creek/stream bed indicated a possible inflow path; no flow was observed during sampling activities 2012-2014. 5 See discussion in Howard and Noble (2018).

Table 2: Table 2: Modern silicon concentrations (mg/l) and $\delta^{30}$Si values for lake water dSi and diatom bSi, and observed Chl-a and Secchi depth values for BL, ML, and WL on sampling dates in 2012-2014. Range, Mean, and SD for ML do not include UMC and LMC values. Long term typical reproducibility on $\delta^{30}$Si data is ±0.15 (2σ). Notes: *Secchi depth was estimated by measuring visible depth to white 2L Van Dorn water sampler. $^{15}$Si$bSi$ values presented for 2014-05-29 and 2014-09-26 are for periphyton taxa collected from surface scrapes.

Table 3: Significant ($\alpha < 0.05$) indicator taxa for Groups 1, 3, 4, 5 (Groups based on groupings determined from $\delta^{30}$Si values). Although not significant, top taxa for Group 2 are also given. IV = indicator value. Taxa listed in this table also are shown in figure 4, along with their habitat associations.

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| LAVO Lake | Total Watershed Area (km²) | Drainage Ratio | Inflow | Outflow | Dominant Watershed Lithology | Estimated Curve Number | Lake Surface Area (km²) | Shoreline Length (km) | Shore Development | Lake Volume (x10⁵ m³) | Average Depth (m) | Maximum Depth (m) | Hydraulic Retention Time (HRT; years) |
|-----------|---------------------------|----------------|--------|---------|-----------------------------|------------------------|------------------------|-----------------------|-------------------|---------------------|-------------------|-------------------|-----------------------------|
| Manzanita | 29.5                      | 164            | Upper Manzanita Creek, Little Manzanita Creek¹ | Lower Manzanita Creek² | Rhyodacite                  | 63                     | 0.18                   | 2.48                  | 1.65              | ~1.0                | ~5.3              | ~10               | 0.33                        |
| Butte     | 113.7                     | 135            | None observed | Butte Creek³ | Andesite                    | 58                     | 0.84                   | 11.3                  | 3.8               | ~60                 | ~7.3              | ~15               | 2 - 6¹                    |
| Widow     | 4.1                       | 34             | None observed | Lower Widow Creek⁴ | Basalt                      | 33                     | 0.12                   | 1.81                  | 1.48              | ~5.0                | ~3.8              | ~10               | --                         |

Table 1: Summary of Manzanita, Butte, and Widow lakes catchment characteristics and morphometry. For closed or semi-closed lakes (BL, WL), size metrics calculated based on GIS data representing full-lake conditions (see Howard and Noble 2018). Curve Number is an empirical parameter that predicts the likelihood of overland runoff for a rainfall event; Shoreline Development is shoreline length relative to a circle of the same area.

¹Small ephemeral stream; a dry stream bed indicated a potential inflow, but no flow was observed during the 2012-2014 sampling period.

²Lower Manzanita Creek sampled by USGS 1979-1981, data accessed via NWIS portal, site number: 11376038

³Outflow in Butte Creek was observed May-September in 2012. In 2013/2014, Butte Lake level dropped below the outflow level and outflow ceased.

⁴Although a dry creek/stream bed indicated a possible inflow path; no flow was observed during sampling activities 2012-2014.

⁵See discussion in Howard and Noble (2018)
| Date       | Sample location | Dissolved Si concentration (mg/L) | Chlorophyll-a concentration (μg/L) | Secchi depth (m) | $\delta^{30}$Si$_{d}$ (% vs. NBS28) | $\delta^{30}$Si$_{b}$ (% vs. NBS28) |
|------------|-----------------|-----------------------------------|-----------------------------------|------------------|-----------------------------------|-----------------------------------|
| Butte Lake | 2012-08-08      | 0 m                               | --                               | 1.1              | 5.9                               | --                               |
|            | 4 m             | --                                | 3.4                               |                  | --                                | --                               |
|            | 9 m             | --                                | 4.8                               |                  | --                                | --                               |
|            | 2013-08-09      | 0 m                               | 3.6                               | 4.3              | 5.5                               | --                               |
|            | 7.5 m           | 4.5                               | 21                                |                  | --                                | --                               |
|            | 10.5 m          | 4.4                               | 18.2                              |                  | --                                | --                               |
|            | 2014-05-31      | 0 m                               | 2.4                               | 4.1              | 5                                 | 1.55                             | -0.74                            |
|            | 6 m             | 2.6                               | 4.9                               |                  | 1.34                              | --                               |
|            | 10 m            | 3.2                               | 18.8                              |                  | 1.57                              | --                               |
|            | 2014-08-06      | 0 m                               | 2.7                               | 8.4              | < 3*                              | 1.63                             | --                               |
|            | 7 m             | 3.9                               | 80.4                              |                  | 1.3                               | --                               |
|            | 9 m             | 4.2                               | 17                                |                  | 1.57                              | --                               |
|            | 2014-09-27      | 0 m                               | 3                                 | 16.9             | 3                                 | 1.27                             | --                               |
|            | 9.5 m           | 2.8                               | --                                |                  | 1.21                              | --                               |
|            | Range           |                                   |                                   |                  |                                   |                                   | 2.1                               | 79.3                             | 0.48                             |
|            | Mean            |                                   |                                   |                  |                                   |                                   | 3.4                               | 15.6                             | 1.38                             |
|            | SD              |                                   |                                   |                  |                                   |                                   | 0.8                               | 20.7                             | 0.18                             |
| Manzanita Lake | 2014-05-29  | Inflow (UMC)                       | 16                               |                  | 1.01                             | -0.4                             |
|            | 2014-09-26      |                                  | 18                               |                  | 1.01                             | -0.81                            |
|            | 2014-05-29      | 0 m                               | 12                               |                  | 1.94                             | 0.27                             |
|            | 2014-09-26      | Outflow (LMC)                     | 12                               |                  | --                                | --                               |
|            | 2014-09-29      | --                                | --                                |                  | 1.78                             | --                               |
|            | 2012-06-24      | 0 m                               | --                                | 0.31             | 7.75                             | --                               |
|            | 4 m             | --                                | 0.48                              |                  | --                                | --                               |
|            | 7 m             | --                                | 0.6                               |                  | --                                | --                               |
|            | 2012-08-12      | 0 m                               | --                                | 0.71             | 7                                 | --                               | -0.96                            |
|            | 4.5 m           | --                                | 1.3                               |                  | --                                | --                               |
|            | 7.5 m           | --                                | 0.98                              |                  | --                                | --                               |
|            | 2012-09-29      | 0 m                               | --                                | 0.37             | 9.7                               | --                               |
|            | 4 m             | --                                | 2.2                               |                  | --                                | --                               |
|            | 9 m             | --                                | 0.49                              |                  | --                                | --                               |
|            | 2013-08-13      | 0 m                               | 11                                | 2.07             | 7.5                               | --                               | -1.59                            |
|            | 3.5 m           | 14                                | 4.41                              |                  | --                                | --                               |
|            | 8 m             | 13                                | 2.66                              |                  | --                                | --                               |
|            | 2014-06-01      | 0 m                               | 13                                | 0.58             | 9.3                               | 2.1                               | -1.3                             |
|            | 4 m             | 12                                | 1.18                              |                  | 1.29                              | --                               |
|            | 8 m             | 13                                | 2.26                              |                  | 1.37                              | --                               |
|            | 2014-08-16      | 0 m                               | 12                                | 2.98             | --                                | 1.71                             | --                               |
|            | 5 m             | 14                                | 5.01                              |                  | 1.43                              | --                               |
|            | 8 m             | 14                                | 6.04                              |                  | 1.56                              | --                               |
|            | 2014-09-29      | 0 m                               | 12                                | 7.4              | 6.5                               | 2.79                             | -1.11                            |
|            | 7 m             | 14                                | 1.7                               |                  | 1.42                              | --                               |
|            | Range ML        |                                   |                                   |                  |                                   |                                   | 3.5                               | 5.73                             | 1.5                              |
|            | Mean ML         |                                   |                                   |                  |                                   |                                   | 3.4                               | 2.19                             | 1.71                             |
|            | SD ML           |                                   |                                   |                  |                                   |                                   | 0.8                               | 20.7                             | 0.18                             |
| Widow Lake | 2012-06-21      | 0 m                               | --                                | 1.28             | 7.75                             | --                               |
|            | 9 m             | --                                | 13.33                             |                  | --                                | --                               |
|            | 2012-08-10      | 0 m                               | --                                | 3.3              | 7                                 | --                               |
|            | 2012-09-29      | 0 m                               | --                                | 5                 | 8                                 | --                               |
|            | 9 m             | --                                | 5.37                              |                  | --                                | --                               |
|            | 2013-08-10      | 0 m                               | 3                                 | 22.78            | 5                                 | --                               |
|            | 9 m             | 2.8                               | 42.07                             |                  | --                                | --                               |
|            | 2014-05-31      | 0 m                               | 2.4                               | 6.76             | 8                                 | 0.94                             | --                               |
|            | 2014-08-15      | 0 m                               | 2.9                               | 12.29            | 1.5                               | -0.08                            |
|            | 2014-09-27      | 0 m                               | 3                                 | 36.12            | 6.5                               | 1.31                             | --                               |
|            | Range           |                                   |                                   |                  |                                   |                                   | 0.6                               | 40.79                            |
|            | Mean            |                                   |                                   |                  |                                   |                                   | 2.8                               | 17.19                            |
|            | SD              |                                   |                                   |                  |                                   |                                   | 0.2                               | 14.28                            |
| Group 1 (δ²⁹Siₛᵢ > -0.14 ‰) | Group 2 (-0.21 < δ²⁹Siₛᵢ < -0.51 ‰)¹ | Group 3 (-0.55 < δ²⁹Siₛᵢ < -0.66 ‰) | Group 4 (-0.69 < δ²⁹Siₛᵢ < -1.1 ‰) | Group 5 (δ²⁹Siₛᵢ < -1.1 ‰) |
|---------------------------|-------------------------------------|-------------------------------------|-------------------------------------|----------------------------|
| Tabellaria flocculosa 79  | Stephanodiscus spp 3 21             | Karayevia clevei 73                | Reimeria sinuata 45                | Fragilaria crotonensis 73  |
| Navicula spp 1 63        | Distriomella incognita 20           | Pseudostaurosira parasitica 56     | S. construens var venter 42        | Fragilaria mesolepta 60    |
| Discostella stelligera 56| Fragilaria grunowii 18              | Staurosirella pinnata 52           | Diatoma mesodon 42                 |
| Nitzschia perminuta 55   | Fragilaria perdelicatissima 15      | Pseudostaurosira confusa 50        | Stephanodiscus spp 2 40            |
| Encyonopsis spp 1 54     | Fragilaria tenuissima 15            | Nitzschia liebertruthii 50         | Pseudostaurosira brevistriata 36   |
| Encyonopsis spp 5 52     |                                    |                                    |                                    |
| Navicula spp 2 51        |                                    |                                    |                                    |
| Encyonopsis spp 4 51     |                                    |                                    |                                    |
| Lindavia spp 46          |                                    |                                    |                                    |
| Stauroneis neohyalina 44 |                                    |                                    |                                    |
| Encyonema lange-bertalotii 41 |                        |                                    |                                    |
| Stauroneis phoenicenturii 41 |                           |                                    |                                    |
| Gomphonema acuminatum 40 |                                    |                                    |                                    |
| Encyonopsis spp 3 37     |                                    |                                    |                                    |
| Gomphonema brebissonii 36|                                    |                                    |                                    |
| Pinnularia spp 3 35      |                                    |                                    |                                    |

Significant (γ < 0.05) indicator taxa for Groups 1, 3, 4, 5 (Groups based on groupings determined from δ³⁰Siₛᵢ values). IV = indicator value

¹Although not significant, top taxa for Group 2 are also given.
Mass-dependent fractionation line

Water samples

Modern diatoms

Sediment diatoms

Typical 2σ uncertainty
Figure 4

A graph showing the relationship between depth (m) and δ³⁰Si (%) for different lakes and creek flows.

- Blue squares represent Butte Lake.
- Green circles represent Manzanita Lake.
- Star symbols represent Manzanite Creek inflow.
- Star symbols with a green outline represent Manzanita Creek outflow.

The graph indicates typical 2σ uncertainty in the δ³⁰Si measurements.

Legend:
- Blue = spring sample
- Green = summer sample
- Wine = autumn sample
A. Manzanita Lake

Euplankton
Typhoplankton
Meroplankton
Epilithic Periphyton
Benthic Periphyton

B. Butte Lake

Euplankton
Typhoplankton
Epilithic Periphyton
Benthic Periphyton

C. Widow Lake

Euplankton
Typhoplankton
Epilithic Periphyton
Benthic Periphyton

Tephra Layer
Figure 7

- dSi
- bSi, instantaneous
- bSi, cumulative

Rayleigh Model (Eqn. 1)

Steady-State Model (Eqn. 2)

Surface waters
Diatoms

Typical 2σ uncertainty

June 2014 $\varepsilon = -3.4\%$
Sept 2014 $\varepsilon = -3.9\%$
Manzanita Lake—Si Retention

Inflow
DSi in, BSi in

Spring: Si = 16 mg/L
Flow rate: ~0.2 m³/s (7 ft³/s)
Mass Si: 1.0 x 10^4 kg/yr

Fall: Si = 18 mg/L
Flow rate: ~0.1 m³/s (3 ft³/s)
Mass Si: ~3.2 x 10⁴ kg/yr

Energy (quantified) Si Sources/Sinks:
-River inflow/outflow (fluvial flux DSI)
-Bulk sediment BSI

Mean DSI = 12 mg/L
BSi production/dissolution

Epilimnion

Mean DSI = 13 mg/L
BSi production/dissolution

Metalimnion

Mean DSI = 14 mg/L

BSi mass accumulation in sediment = ~0.023 g/m²/yr
From Fluvial flux DSI = ~0.008 g/m²/yr (5%)

Hypolimnion

Outflow
DSi out, BSi out

Spring: Si = 12 mg/L
Flow rate: ~0.11 m³/s (4 ft³/s)
Mass Si: ~6.4 x 10^4 kg/yr

Fall: Si = 12 mg/L
Flow rate: ~0.01 m³/s (1 ft³/s)
Mass Si: ~1.1 x 10⁴ kg/yr

Un-quantified Si Sources:
-Groundwater DSI
-Dust
-Precipitation
-BSi in/out
-Others?