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Quantifying the impact of freshwater diatom productivity on silicon isotopes and silicon fluxes: Lake Myvatn, Iceland

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ABSTRACT

Diatom productivity in the oceans plays a crucial role in the carbon cycle, but is strongly dependent upon the continental silicon supply. However, the relative influence of weathering and biological processes on continental Si fluxes remains poorly constrained. This study aims to quantify the impact of terrestrial diatom productivity on Si fluxes to the ocean. Lake Myvatn in North Iceland is one of the most productive lakes in the Northern Hemisphere, with nutrient-rich waters almost uniquely sourced by groundwater. The primary production is mainly controlled by diatom growth but also by cyanobacteria, and the lake output is via a single river, thereby providing a relatively simple natural laboratory to quantify the impact of diatom growth on the chemistry and Si budget of lake waters. Silicon stable isotopes (δ^{30}Si) provide a tracer of this biocycling, and have been measured in groundwater inputs to the lake, and in time-series monitoring of waters at the lake outlet. The δ^{30}Si values at the outlet range from $+0.70 \pm 0.08$ to $+1.42 \pm 0.06$‰, which is significantly heavier than the groundwater input (average cold and hot springs: $+0.50 \pm 0.17$‰, 2SD) and consistent with the preferential uptake of light Si isotopes by diatoms. The δ^{30}Si value at the outlet increases by up to 0.9‰ in spring and autumn relative to the Si isotope composition of the inflow. These seasonal diatom blooms can be modeled by an open system of Si uptake and affect Si fluxes at the outlet of the lake by up to 79%, or 53% integrated over the year. In the summer a shift to lighter δ^{30}Si values is correlated with a higher pH, which results in dissolution of diatoms releasing light Si isotopes. From mass balance, this seasonal diatom dissolution affects Si fluxes by up to 33%, but is limited to 3.7% integrated over the year. These results clearly illustrate that biological activity can have a significant impact on both isotope composition and elemental abundance of continental derived Si. They also demonstrate the pH dependency of diatom dissolution and/or preservation, which is likely to affect not only the continental Si fluxes to the ocean but also the Si recycling in the oceans themselves.

1. Introduction

On geological timescales the chemical weathering of silicates provides a natural means of regulating global climate (e.g. Berner, 1995; Kump et al., 2000; Walker et al., 1981), by converting atmospheric CO_2 to bicarbonate ions, which along with metals, are transported to the oceans by rivers where the CO_2 is fixed by formation of carbonates. On millennial timescales changes in the flux of alkalinity and nutrients to the ocean from continental weathering can also affect biological productivity and carbonate sedimentation (e.g. Archer et al., 2000), which can in turn influence atmospheric CO_2.

Diatom growth is a major process controlling the capacity of the ocean to store CO_2 (Ittekkot et al., 2006; Smetacek, 1999). These are the most prevalent silicifying organisms in oceans, using silica as rigid structural material for their cell walls (frustules). Biogenic silica (BSi) production by diatoms in the ocean has been estimated at around 240 Tmol yr^{-1} (Tréguer et al., 1995), with diatoms also constituting ~45% of total marine primary production. Diatoms are extremely sensitive to Si limitation and consume silicon from both continental input and Si recycling in the ocean (Ragueneau et al., 2006). Recycling of Si in the water column and at the sediment–water interface plays a crucial role in sustaining production (Ragueneau et al., 2006). Globally, ~50% of the BSi produced by diatoms redissolves in surface waters (Nelson et al., 1995), and up to ~90% may redissolve prior to reaching the seafloor (Nelson and Brzezinski, 1997; Tréguer et al., 1995). The dissolution of biogenic opal is mostly driven by the

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undersaturation of the ocean with respect to silicic acid concentrations (Brzezinski et al., 2003), and is affected by a number of factors including temperature, pH, specific surface area, aluminum concentrations, and organic material coating (Van Cappellen and Qiu, 1997; Van Cappellen et al., 2002).

Chemical weathering of the continents is thought to contribute some 85% of the dissolved silicon in the oceans (Tréguer et al., 1995), sourced by rivers, groundwaters and aeolian dust. Recent studies have indicated a marked decline in riverine Si fluxes (Humborg et al., 2000, 2002; Ittekkot et al., 2006; Laruelle et al., 2009) that may have severe consequences for oceanic diatom production. However, the relative influence of inorganic and biological processes on the continental weathering signal remains poorly constrained. Silicon isotopes potentially provide key information on these biogeochemical processes because they are fractionated both by inorganic chemical weathering processes on the continents, and by biological processes, in particular diatom growth in the marine and terrestrial environment. In fresh waters (rivers and lakes), Si stable isotopes have been shown to be a promising tracer for quantifying the impact of biological activity on the Si budget (Alleman et al., 2005; De La Rocha et al., 2000; Ding et al., 2004; Georg et al., 2006a, 2007). Likewise, in the oceans Si isotope fractionation has been related to diatom activity (Cardinal et al., 2005, 2007; Fripiat et al., 2007; Reynolds et al., 2006; Varela et al., 2004). Indeed, Si isotopes appear to be strongly fractionated during incorporation into diatoms, with no dependence on temperature or species (De La Rocha et al., 1997), pH (Milligan et al., 2004) or salinity (Alleman et al., 2005).

The sub-Arctic Lake Myvatn is one of the most productive lakes in the Northern Hemisphere. The lake is unique in that almost all of the inflow is supplied through groundwater (both high- and low-temperatures) fed through artesian springs, and negligible surface water enters the lake because the area is covered by young and porous lava fields and cross cut by faults (Kristmannsdóttir and Ármannsson, 2004; Ólafsson, 1979a). Therefore, the inflow of water to the lake and its chemistry is remarkably stable (Kristmannsdóttir and Ármannsson, 2004). Moreover, the residence time of water in the lake is short (27 days) and there is a single outflow from the lake, via three channels to a single major river (Ólafsson, 1979a). Consequently, temporal variations in the chemistry of the waters can be readily monitored and Lake Myvatn, therefore, constitutes a remarkable natural laboratory to study the impact of terrestrial biogeochemical processes on Si fluxes to the ocean. The high productivity of Lake Myvatn is dominated by the growth of diatoms, therefore it can be anticipated that this will result in the preferential incorporation of light Si isotopes into the diatoms imparting a distinctive heavy Si isotope signal to the residual lake waters.

This study aims to assess the impact of diatom productivity on Si stable isotopes in lake waters relative to the composition of groundwater input, the principal source of Si in the waters of Lake Myvatn, and to further quantify the impact of diatom growth on Si fluxes from the lake. Silicon isotope compositions have been measured on the groundwaters and bottom sediments. The impact of seasonal diatom blooms has been assessed through time-series monitoring of Si isotope compositions of the outflow from the lake. These results contribute to a better understanding of the impact that lake biogeochemistry has on continental Si fluxes from rivers to oceans. Since 16% of the gross riverine Si load is delivered to the ocean as BSi (Conley, 1997), diatom uptake and dissolution in continental rivers and lakes have a potentially significant impact on silicon fluxes to the ocean, and hence the carbon storage capacity of the ocean.

2. Environmental setting

Lake Myvatn is located in northeast Iceland (65°35′N and 17°00′W) just below the Arctic circle, and is at 278 m above sea level. The lake is relatively shallow with a maximum depth of 4.2 m and is well-mixed over the entire water column during the ice free period (Kjaran et al., 2004). The area of the lake is 37 km^2 and comprises two basins, Ytrifloi (North Basin) and Sydrifloi (South Basin). Average sediment thickness in the South Basin is about 4.3 m. Diatom frustules comprise about 55% and rock derived material, mostly volcanic ash, about 30% of the dry weight of the sediments in the North Basin (Lindal 1959). The lake is mainly fed by groundwater, with cold springs emerging into the Sydrifloi basin and tepid springs into the Ytrifloi basin, the latter originating from the Namafjall and Krafla geothermal fields (Kristmannsdóttir and Ármannsson, 2004; Ólafsson, 1979b). The main outflow of the lake into the river Laxa has a discharge rate of some 33 $m^3 s^{-1}$, yielding a residence time for the water in the lake of about 27 days (Ólafsson, 1979a). Evaporation in the summer is negligible compared to the lake volume and the water renewal period (Ólafsson, 1979a).

Lake Myvatn was formed around 2300 years ago following a major volcanic eruption, at the same site where another lake existed before the eruption, as recorded in core sediment (Einarsson, 1982). The underlying geology of the Myvatn area is characterized by basaltic lavas greatly faulted with open fissures, explosive craters, pseudo-craters and numerous crater rows (Thorarinsson, 1979). Several volcanic episodes occurred during the Holocene, including recently at Krafla 10 km north during the 1975–1984 “fires”.

The climate in this area is characterized by low rainfall (mean annual precipitation 468 mm) peaking in July–August, a daily temperature ranging from −20 °C to +20 °C (mean annual temperature of 1.8 °C), high solar radiation (79 kcal $cm^{-2} yr^{-1}$), and a number of sunlight hours ranging from a few in December up to 18 h in June (Björnsson and Jónsson, 2004).

The lake is one of the most productive in the Northern Hemisphere despite being covered with ice from late October until early May. This high productivity of the lake is related to the relatively high solar radiation, inflow waters rich in macro- and micro-nutrients, N_2 fixation by cyanobacteria and intense internal nutrient loading (Einarsson et al., 2004; Gíslason et al., 2004; Jonasson, 1979). Most of the primary production takes place on the bottom of the lake where diatoms dominate the overall productivity inducing a net primary production of ~222 g C $m^{-2} yr^{-1}$ (Ólafsson, 1979b; Thorbergsdóttir et al., 2004). Green algae and cyanobacteria (*Anabaena*) also contribute to the productivity but do not affect the Si budget.

The concentrations of dissolved metals in the lake itself are largely controlled by biological activity. During the winter, when the lake is ice-covered, the top sediment pore water is enriched in nutrients (more than a hundredfold greater than in the lake water). These nutrients are then released during the ice-free period by resuspension of the sediment, diffusion, bioturbation and recycling, leading to increases in nutrients in the spring. The lake sediment thus constitutes both a source and sink of solutes (Einarsson et al. 2004; Gíslason et al., 2004; Thorbergsdóttir and Gíslason, 2004; Thorbergsdóttir et al., 2004).

3. Methods

3.1. Sampling

3.1.1. Groundwaters, lake waters and sediments

Samples were collected on 26–27 August 2009, including groundwater from cold (MY01 to MY07) and hot springs (MY08 to MY11), middle lake water (MY12) and water from the outlet of the lake (MY13) (Fig. 1). Water was collected in acid pre-cleaned polypropylene bottles and stored in the dark at 5 °C. At each sampling site, temperature, pH, and conductivity were measured *in situ*. Lake and outlet water samples were filtered in the field within 24 h through 0.2 μm cellulose acetate membranes. Filters were dried at 60 °C to recover suspended particulate material. A core sample (5 cm diameter) from the top 10 cm of diatomite sediment was also

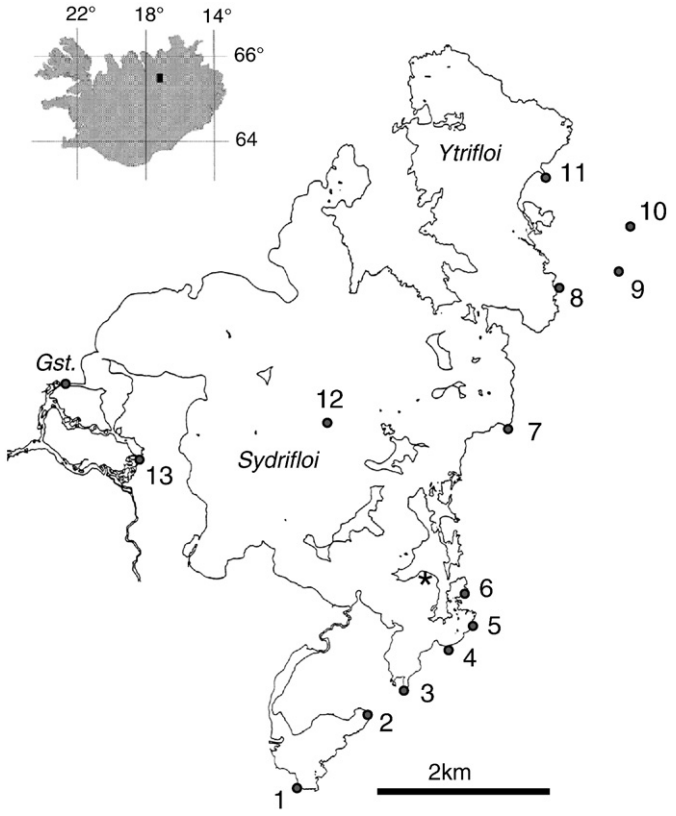

Fig. 1. Sample location map of Lake Myvatn with the two main basins (Ytrifloi and Sydrifloi): cold springs (MY01 to 07), hot springs (MY08 to 11), middle lake water (MY12) and outlet (MY13). The monitoring over 2000–2001 was made at the outlet Geirastadaskurdur (Gst.). The diatomaceous sediment core was sampled at Kalfastrond (star).

taken at Kalfastrond, dried at 60 °C, and ashed at 450 °C to remove organic matter. The diatomite sediment and the suspended particulate material from the outlet water (MY13 SPM) were observed as bulk sample by scanning electron microscopy (SEM, JEOL JSM-840A).

3.1.2. Lake outlet time series

Sample monitoring was undertaken at the outlet of the lake at Geirastadaskurdur (Gst., Fig. 1) over the year 2000–2001 (Eiriksdottir et al., 2008). Lake Myvatn was covered with ice when the research started in March 2000. The ice began to break up around the middle of April and was completely gone on 9th May 2000. Due to low particulate organic matter in the summer 2000 (Eiriksdottir et al., 2008), the lake was clear throughout the summer when the research took place. Eleven water samples were collected over a period of 12 months. Around one month elapsed between sampling during the summertime, but a little more during the winter. Temperature, conductivity and discharge were measured at the site. Samples were taken for particulate and dissolved constituents. The samples for dissolved constituents were immediately filtered through 0.2 µm cellulose acetate membranes and the samples stabilized at the site. Alkalinity and pH were measured at room temperature (23 °C) from air tight glass bottles the following day or days after sampling, and the rest of the dissolved and particulate constituents measured after the monitoring period (Eiriksdottir et al., 2008). Charge balance, the activity of various chemical species, pH *in situ*, and CO_2 partial pressure were then calculated using the PHREEQC speciation code (Parkhurst and Appelo 1999). The average charge imbalances of major elements in the outlet water samples were less than 2% of the total ionic strength.

3.2. Major and trace element analyses in waters

For the groundwater samples from 2009, dissolved major and trace element concentrations were measured by quadrupole ICP-MS (Agilent, Open University, UK) in 2% HNO_3. The accuracy was assessed by using a water reference material SLRS-4 (Yeghicheyan et al., 2001). The analytical precision is ±6% for major and ±7% for trace elements, with a detection limit better than 0.01 mM for major and than 0.01 µM for trace elements. Silicon concentrations (±2%) were analyzed by photospectrometry (Hach DR2800, University of Oxford). For the outlet time-series 2000–2001, most major and trace elements were measured from filtered and acidified samples by ICP-AES, and some trace elements (Fe and Al) were measured by ICP-QMS (Analytica-SGAB, Luleå, Sweden, ±5%). The NO_3 content was measured by colorimetry with an Alpkem autoanalyser (Institute of Earth Science, University of Iceland, IES), and major anions (other than bicarbonate and carbonate) by ion chromatography (IC2000, IES, ±5%). The sample for NO_3 was filtered on site and kept frozen until the time of analysis.

3.3. Silicon isotope analysis

Silicon isotope compositions were measured on groundwaters, time-series samples, suspended load and diatomite sediment. Diatomaceous sediment was dissolved by NaOH fusion at 720 °C in a silver crucible (Georg et al., 2006b). Given the small amount of material, suspended loads were dissolved by 0.2 M NaOH leaching of filters at 100 °C (Ragueneau et al., 2005). Solutions were then acidified to pH 2 using distilled HNO_3. Dissolved samples and water samples were purified for isotopic measurements through cation exchange resin (BioRad AG50W-X12; Georg et al., 2006b).

Silicon isotope compositions were determined on a Nu Plasma HR-MC-ICP-MS (Nu Instruments, Wrexham, UK) at the Department of Earth Sciences, University of Oxford (UK), in dry plasma mode using a desolvating system Cetac AridusII, in pseudo-high ("medium") resolution mode. The instrumental mass bias was corrected for by the sample-standard bracketing technique, and data are expressed in relative deviations of $^{30}Si/^{28}Si$ ratios from NBS-28 silica sand standard using the common δ-notation (‰): where $\delta^{30}Si = [(^{30}Si/^{28}Si_{sample})/(^{30}Si/^{28}Si_{NBS28}) - 1] \times 1000$. Each sample was analyzed 9 times, where each single δ-value (n) represents one sample run and two bracketed standard runs. Accuracy and reproducibility ($\delta^{30}Si$) were checked over a period of 12 months on reference material diatomite (+1.25 ± 0.09‰, 2SD, n = 132), Quartz Merck (−0.05 ± 0.06‰, 2SD, n = 45) and USGS rock standard BHVO-2 (−0.26 ± 0.09‰, 2SD, n = 124), which yielded isotope compositions indistinguishable from previously published values (Abraham et al., 2008; Reynolds et al., 2007). Quality control of mass bias was checked by confirming that the measured isotopic values fell on a straight line on a $\delta^{29}Si$ vs. $\delta^{30}Si$ plot, corresponding to a mass-dependent fractionation curve (Fig. 2).

4. Results

4.1. Groundwaters: major and trace elements and Si isotope analysis

Two major types of groundwater can be distinguished from the inflow to Lake Myvatn: the cold springs (MY01 to 07) from the south east, and the hot springs (MY08 to 11) from the north east. Despite the significant chemical differences between cold and hot springs, the silicon isotope composition of groundwater is nearly constant among these sources. The former are characterized by a mean temperature of 6.2 ± 1.4 °C, pH of 9.4 ± 0.2, and a low conductivity (134 ± 14 µS cm^{-1}) (Table 1). The latter display a higher mean temperature of 30.5 ± 12.4 °C, lower pH of 8.3 ± 0.2, and higher conductivity of 424 ± 63 µS cm^{-1} (Table 1). Cold waters generally display lower Na, K and Ca contents (Na 0.72 ± 0.12 mM, K 0.03 ±

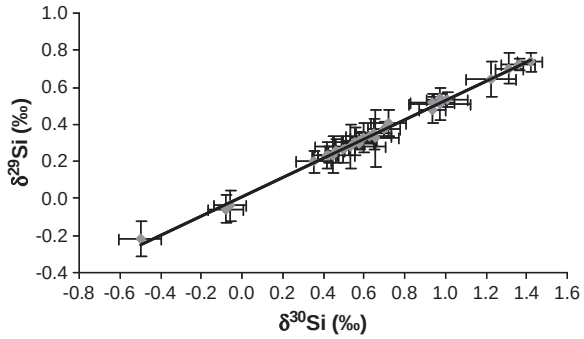

Fig. 2. Silicon isotope measurements of all samples fit onto a mass-dependent fractionation array δ^{30}Si vs. δ^{29}Si (y = 0.5199, x + 0.0108, R^2 = 0.996). The slope of 0.5199 ± 0.0064 corresponds within error to the theorical 0.5178 slope for equilibrium mass-dependent fractionation. This supports the interference-free determination of all three Si isotopes via MC-ICP-MS Nu Plasma HR.

0.01 mM, Ca 0.13 ± 0.02 mM; Table 1) than the hot waters (Na 2.43 ± 0.71 mM, K 0.12 ± 0.03 mM, Ca 0.36 ± 0.10 mM, respectively; Table 1) (Fig. 3). In contrast, Mg and Al contents are similar in both cold and hot waters (respectively, Mg 0.11 ± 0.03 and 0.12 ± 0.04 mM, Al 0.52 ± 0.08 and 0.55 ± 0.38 μM). Cold and hot springs differ strongly in their Si content which is much lower in cold waters (0.31 ± 0.02 mM) than hot waters (1.76 ± 0.55 mM) (Fig. 3). Crucially however, δ^{30}Si values display no difference (+0.50 ± 0.08 and +0.51 ± 0.12‰, respectively), with an average value for cold and hot springs of +0.50 ± 0.17‰ (Fig. 3).

Relative to the groundwaters, the lake (MY12) and outlet (MY13) water samples from August 2009 are characterized by an intermediate temperature 10.5 ± 0.4 °C, higher pH 9.9 ± 0.1, and intermediate conductivity 160 ± 4 μS cm^{-1}. The Na, K, Ca, and Mg contents are similar to the cold springs, whereas the Al content is lower than both cold and hot springs (Table 1). In the lake and at the outlet, the Si content is lower (average 0.14 ± 0.02 mM) and the δ^{30}Si value is much heavier by ~0.47‰ (average +0.97 ± 0.05‰) than the spring waters (Fig. 3). The suspended particulate material from the lake and the outlet displays a similar δ^{30}Si value of −0.08 ± 0.09 and −0.06 ± 0.08‰ (Table 1), heavier than the diatomaceous sediment from the bottom of the lake (−0.50 ± 0.11‰). The sediment from Lake Myvatn dominantly comprises opal-A (as determined by X-ray diffraction) from diatom frustules, and particles of volcanic tephra, as seen in SEM observations (Fig. 4).

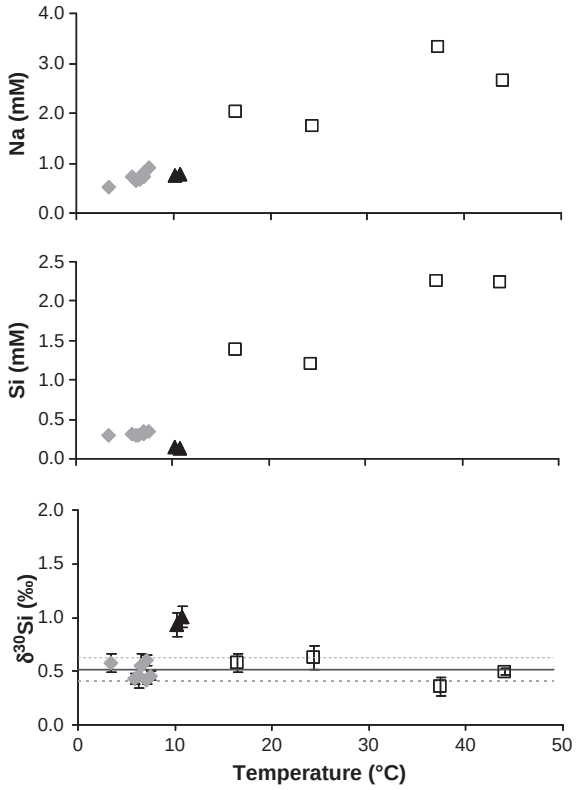

Fig. 3. Distinction between cold and hot springs based on temperature, Na content (similar for K, Ca), and Si content. Distinction between groundwater input (full line is average δ^{30}Si value: +0.52 ± 0.11‰, dotted lines 2SD; Section 5.2) and lake waters based on Si isotope composition. Cold springs: gray diamond — hot springs: open square — lake and outlet water: black triangle.

4.2. Outlet: major and trace elements and Si isotope analysis

Over the year 2000–2001 at the outlet of Lake Myvatn, temperature varied from 0 to 15.7 °C with a maximum in July–August (Table 2). The pH was also at a maximum value during these months with pH at room temperature ranging over the year between 8.08 and 9.86, and pH *in situ* between 8.32 and 9.93 (Table 2). The NO_3 concentration ranged between 0.15 and 2.75 μM with two declines over the year, during the spring (April–May) and the autumn

Table 1
Major characteristics of groundwaters input into Lake Myvatn: temperature (*T*), pH, conductivity (Cond.), major and trace elements, Si concentrations, and Si isotope signatures (δ^{30}Si, 2SD, n measurements).

Sample	Name		Latitude	Longitude	*T* (°C)	pH	Cond. (μS cm^{-1})	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Fe (μM)	Al (μM)	Si (mM)	δ^{30}Si (‰)	2SD	n
Dissolved																	
MY01	Graenavatn South End	Cold	N65°32′12.9″	W17°00′29.0″	3.4	9.27	–	0.53	0.02	0.07	0.11	–	0.45	0.29	0.57	0.09	9
MY02	Graenavatn North End	Cold	N65°32′54.4″	W16°58′54.4″	7	9.4	130	0.72	0.03	0.11	0.12	–	0.53	0.31	0.60	0.05	9
MY03	Gardur, by main road	Cold	N65°33′09.3″	W16°58′0.85″	6.5	9.21	141	0.67	0.03	0.15	0.15	–	0.50	0.30	0.55	0.10	9
MY04	Kilklettar	Cold	N65°33′34.0″	W16°57′10.7″	6.2	9.23	129	0.64	0.03	0.14	0.14	–	0.45	0.30	0.45	0.11	9
MY05	Grjotavogur	Cold	N65°33′46.4″	W16°56′37.6″	5.8	9.6	115	0.74	0.02	0.07	0.11	–	0.67	0.31	0.43	0.05	9
MY06		Cold	N65°34′05.3″	W16°56′49.4″	7	9.6	134	0.81	0.02	0.08	0.11	–	0.59	0.34	0.42	0.05	9
MY07		Cold	N65°35′43.1″	W16°56′01.0″	7.5	9.29	156	0.90	0.03	0.13	0.16	–	0.48	0.35	0.46	0.05	9
MY08		Hot	N65°37′00.8″	W16°54′59.6″	16.5	8.68	359	2.02	0.10	0.16	0.30	0.09	0.62	1.38	0.57	0.08	9
MY09	Leynigja	Hot			37.3	8.29	505	3.32	0.15	0.08	0.35	0.10	1.06	2.25	0.35	0.09	9
MY10	Grjotagja	Hot	N65°37′34.6″	W16°53′03.4″	44	8.1	437	2.65	0.15	0.09	0.28	–	0.20	2.23	0.50	0.03	9
MY11		Hot	N65°38′01.2″	W16°55′21.1″	24.3	8.29	396	1.73	0.10	0.16	0.51	0.13	0.32	1.20	0.62	0.11	9
MY12	Middle Lake, station 33	Lake	N65°35′38.4″	W17°00′08.7″	10.2	9.82	157	0.77	0.03	0.11	0.15	0.03	0.39	0.15	0.93	0.11	9
MY13	Geirastadaskurdur	Outlet	N65°35′14.3″	W17°04′20.3″	10.7	10	162	0.79	0.03	0.12	0.15	0.06	0.31	0.13	1.01	0.10	9
Suspended load and sediment																	
MY12 SPM	Lake suspended load														−0.08	0.09	9
MY13 SPM	Outlet suspended load														−0.06	0.08	9
Diatomite	Kalfastrond														−0.50	0.11	9

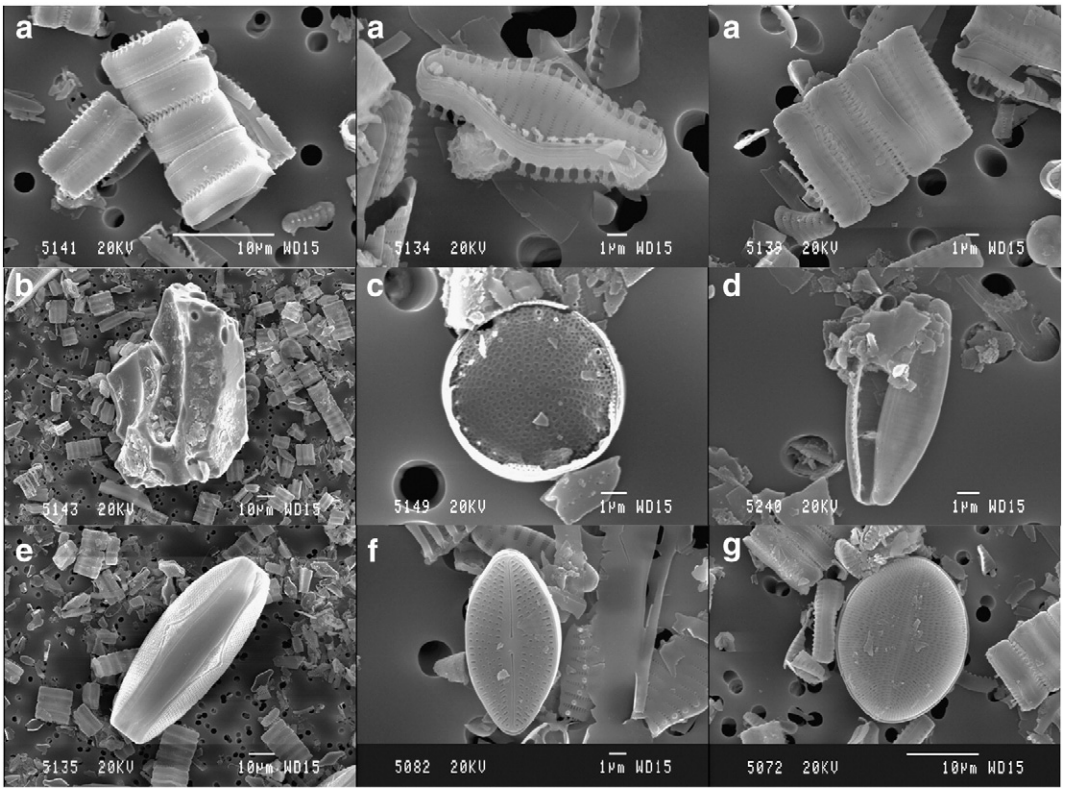

Fig. 4. Scanning electron microscope images of diatoms species and volcanic tephra in the diatomaceous sediment from Lake Myvatn (a,b,e,f,g) and in the suspended particulate matter at the outlet in September 2009 (MY13 SPM) (c,d): (a) *Fragilaria construens*, (b) Volcanic tephra slightly eroded with *Fragilaria construens* in the background, (c) *Stephanodiscus hantzschii*, (d) *Nitzschia* sp., (e) *Epithemia turgida*, (f) *Achnanthes* sp., (g) *Cocconeis placentula*.

(September–October; Fig. 5). The Na, K, Mg and Ca contents ranged between 0.75 and 1.04 mM, 0.03 to 0.04 mM, 0.13 to 0.17 mM, 0.15 to 0.20 mM, respectively, with a significant decline in the spring resulting in a minimum value in May and a maximum value in August (Table 2). The Fe and Al concentrations varied between 0.18 to 0.64 µM and 0.15 to 1.08 µM, respectively, with maxima in July (Al) and August (Fe). The Si contents show a significant and systematic decline from March to July and increase from July to January (Fig. 5), ranging from 0.05 to 0.41 mM. The δ^{30}Si values at the outlet are generally heavier than that of the groundwater (April to November 2000) or within the range of groundwater values (March 2000, January and March 2001) (Fig. 5). This trend is characterized by an initial increase in δ^{30}Si value from March to June (0.70 to 1.42‰) followed by a significant decline towards lighter isotope composition in July nearly reaching the δ^{30}Si value of the groundwater, and a second increase in δ^{30}Si from July to October (0.72 to 1.36‰; Table 2, Fig. 5).

5. Discussion

5.1. Seasonal variations of chemistry and Si content in Lake Myvatn

The chemistry of the groundwater samples studied here is consistent with previous studies where both the temperatures and pH are similar (Kristmannsdóttir and Ármannsson, 2004; Ólafsson, 1979b). The Si concentrations in the cold groundwaters (0.31 ± 0.02 mM; Table 1) are within the narrow range of published values from 0.30 to 0.37 mM (Kristmannsdóttir and Ármannsson, 2004; Ólafsson, 1979b; respectively) (Fig. 6). In contrast, the Si content of the hot springs displays a much larger range (1.76 ± 0.55 mM; Table 1; Fig. 6). However, groundwater samples MY09 and MY10 (with the highest temperature and Si concentrations) originate from fissures located northeast of the lake, and are not direct inputs to the lake itself (Fig. 1). Therefore, in order to make the most representative estimate for the Si input from groundwater into the lake, average Si

Table 2
Major characteristics of the monitoring at the outlet Geirastadaskurdur (Gst., Fig. 1) of Lake Myvatn (2000–2001): temperature (*T*), pH at room temperature (23 °C), pH *in situ* (calculated with PHREEQC; Parkhurst and Appelo, 1999), major and trace elements, Si concentrations, and Si isotope signatures (δ^{30}Si, 2SD, n measurements).

Sample	Month	*T* (°C)	pH (23 °C)	pH *in situ*	NO_3 (µM)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	Fe (µM)	Al (µM)	Si (mM)	δ^{30}Si (‰)	2SD	n
00A013	Mar-00	1.2	8.14	8.37	2.06	1.01	0.04	0.16	0.20	0.41	0.33	0.41	0.70	0.08	9
00A023	Apr-00	0.0	8.69	9.03	0.35	0.78	0.03	0.15	0.16	0.39	0.33	0.30	0.94	0.07	9
00A031	May-00	6.0	8.31	8.52	0.15	0.75	0.03	0.13	0.15	0.33	0.30	0.22	1.31	0.07	9
00A044	Jun-00	12.3	9.45	9.63	0.98	0.88	0.03	0.15	0.18	0.25	0.40	0.10	1.42	0.06	9
00A053	Jul-00	15.7	9.86	9.93	1.01	0.95	0.03	0.14	0.18	0.28	1.08	0.05	0.72	0.09	9
00A062	Aug-00	15.5	9.67	9.78	0.17	1.04	0.04	0.17	0.20	0.64	0.49	0.09	0.97	0.03	9
00A071	Sep-00	8.3	9.15	9.35	0.17	0.94	0.04	0.15	0.18	0.41	0.26	0.10	1.22	0.12	9
00A080	Oct-00	1.4	8.43	8.73	0.15	0.95	0.04	0.16	0.18	0.18	0.15	0.16	1.36	0.08	9
00A089	Nov-00	0.6	8.08	8.32	0.51	0.97	0.04	0.16	0.19	0.22	0.18	0.31	0.97	0.15	9
01A006	Jan-01	0.9	8.11	8.34	2.75	0.97	0.04	0.16	0.19	0.52	0.47	0.41	0.65	0.12	9
01A015	Mar-01	0.5	8.18	8.43	0.89	0.88	0.04	0.14	0.16	0.49	0.38	0.34	0.53	0.17	9

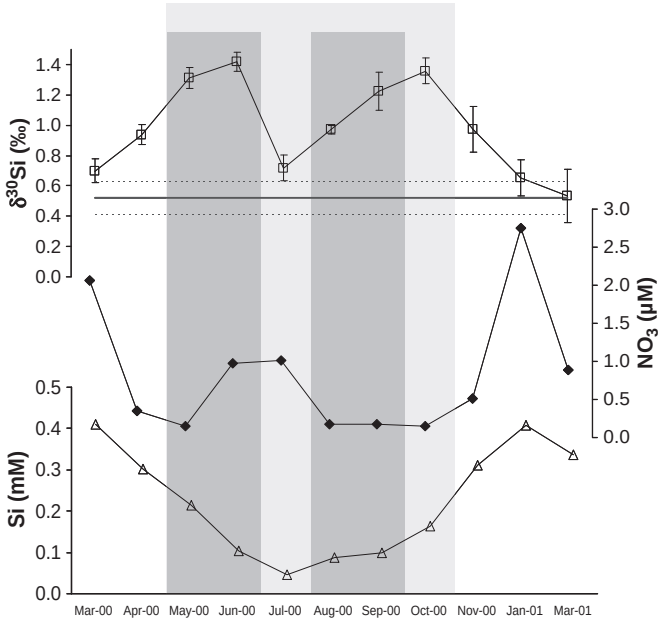

Fig. 5. Variation of the chemistry of Lake Myvatn over the 2000–2001 monitoring at the outlet: dissolved Si content (open triangle), NO_3 content (black diamond), and Si isotope composition (open square). The groundwater input ($\delta^{30}Si$) is represented by the full line (2SD, dotted lines). The lake is without ice cover during all the period highlighted in gray. The spring and autumn diatom blooms are marked in dark gray.

concentrations were calculated for the cold and hot springs located directly around the lake from the present and previous studies (excluding MY09 and MY10), giving values of 0.32 ± 0.04 mM Si for cold waters, and 1.07 ± 0.19 mM Si for hot waters. Groundwater is considered to act as a constant source of dissolved nutrients (Thorbergsdóttir and Gíslason, 2004) with a discharge of 26 $m^3 s^{-1}$ for cold springs and 7 $m^3 s^{-1}$ for the hot springs, corresponding to 79% and 21% of the input, respectively. The discharge was calculated from the integrated mean concentration in the lake for Na, K, Ca, Cl, corresponding to a mixture from the concentrations of these elements in the cold and hot springs (Ólafsson, 1979b). Based on the average Si content for cold and hot waters (0.32 and 1.07 mM, respectively), a mean Si concentration of the inflow to the Lake Myvatn can be estimated from the balance of discharge of both water types into the lake: 0.48 mM Si.

The seasonal variations of NO_3 over the year 2000–2001 can be related to the primary production, which is mainly controlled by diatom growth but also by the growth of green algae and cyanobacteria. The seasonal succession of phytoplankton growth is

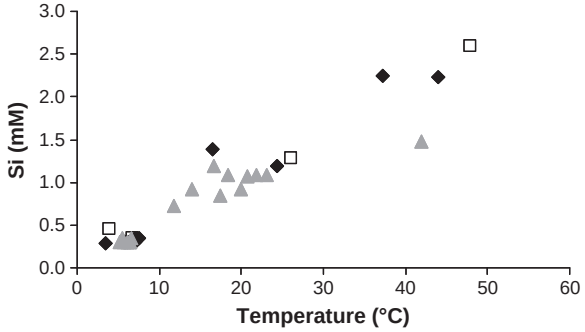

Fig. 6. Comparison of the groundwater samples from 2009 (this study; black diamond) with samples from 1971 to 1974 (Ólafsson, 1979a,b; gray triangle) and samples from 1997 to 1999 (Kristmannsdóttir and Ármannsson, 2004; open square) on a dissolved Si concentration vs. temperature plot to distinguish cold (below 10 °C) from hot springs (above 10 °C).

usually characterized by a diatom peak during the month following the break up of ice, cyanobacteria during the summer, and another diatom peak in the autumn (Gíslason and Jóhannsson, 1991; Jonasson and Adalsteinsson, 1979). Most of the diatoms in Lake Myvatn, in terms of both species and biomass, are benthic. These diatoms are dominated by *Fragilaria* sp. (Fig. 4a) and growth takes place at the muddy bottom surface of the lake (Einarsson et al., 2004). They are more specifically termed "tychoplanktonic", in that they are suspended during storm events. The fraction of the planktonic species, represented by *Stephanodiscus* sp. (Fig. 4c) and small *Nitzschia* sp. (Fig. 4d), is very small and has been estimated from a surface sediment sample containing both living and dead diatoms (Einarsson, 1982). Other diatom species contribute in smaller amounts to the diatomaceous sediment (Fig. 4e,f,g). *Fragilaria* sp. constitutes 97% of the total diatom frustules, while the pure planktonic species make up just 0.6% of the residual material. There is a clear decline in diatom growth in the summer, which has been ascribed to N-limitation (Ólafsson, 1979b). The two main periods of diatom bloom in the spring and in the autumn can be seen by a decline on each occasion in NO_3 (Fig. 5), since N is the limiting nutrient for primary production.

Silicon concentrations at the outlet of the lake decrease from April to July, and then increase from August to November (Fig. 5). Even if two seasonal diatom blooms are marked by the NO_3 variations in the lake (in the spring and in the autumn), the low Si concentrations in July also support the observation that some diatoms grow in the summer, as shown by Thorbergsdóttir et al. (2004). Low Si concentrations in the summer were also reported by Ólafsson (1979b). Between the two diatom blooms in the spring and in the autumn, the nutrient level is governed by internal loading from the lake sediment (Gíslason et al., 2004; Thorbergsdóttir and Gíslason, 2004). The diatom growth in the summer is supplied by an NH_4^+ benthic flux from the sediments (Gíslason et al., 2004) arising from the decomposition of organic matter, which is at a maximum during midsummer during the period of highest temperatures (Thorbergsdóttir et al., 2004). In addition, low particulate organic matter in the summer 2000 (Eiriksdottir et al., 2008) provided favorable light conditions for benthic diatoms growth through the summer.

Overall, diatom productivity (by Si uptake) affects the Si flux at the outlet of the lake by up to 79% (53% on average over the year) relative to the average Si inflow from cold and hot waters into the lake (0.48 mM Si). Considering the groundwater input with a discharge of 33 $m^3 s^{-1}$ (Ólafsson, 1979a) and the mean Si concentration of groundwater of 0.48 mM, the monthly Si input in the lake is 1.17×10^6 kg Si. Taking the Si concentration at the outlet (e.g. for July 2000: 0.05 mM; Table 2) and a discharge at the outlet of 33 $m^3 s^{-1}$ (Ólafsson, 1979a), the Si output from the system in July 2000 is 0.11×10^6 kg Si, indicating a net Si fixation of 1.05×10^6 kg Si in the lake in July 2000 (monthly gross silica production in Fig. 7). Applying the same calculation for each month produces an average net Si fixation of 7.42×10^6 kg Si $yr.^{-1}$. This value is 12% higher than the net fixation calculated for the summer of 1974 (6.64×10^6 kg Si $yr.^{-1}$), which was based on a lower estimate for Si input (0.44 mM Si; Ólafsson, 1979b). The value of Si input used in the present calculation (0.48 mM) is based on a larger range of samples of cold and hot springs located directly around the lake (1971–1974, 1997–1999 and 2009; Fig. 6), which is likely to provide a better constraint on the Si input to the Lake.

5.2. Seasonal variations of Si isotope in Lake Myvatn

The 10 cm core diatomite sample represents about 50 years of sedimentation, based on the accumulation rate of 2.1 mm $yr.^{-1}$ (Einarsson et al., 2004). The diatomaceous sediment comprises some 55% diatoms (mainly *Fragilaria* sp.; Fig. 4a) and 30% tephra (air borne volcanic tephra; Fig. 4b), on a dry weight basis (Einarsson et al., 2004). The bulk $\delta^{30}Si$ value of this sediment is −0.50‰ (Table 1). Fresh

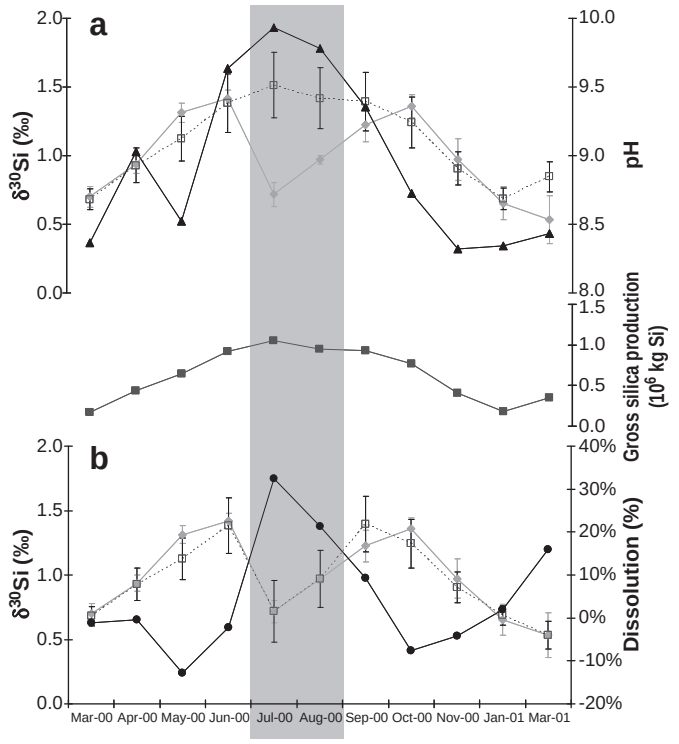

Fig. 7. Modeling δ^{30}Si variations at the outlet of Lake Myvatn over the year 2000–2001: plot of δ^{30}Si measured (gray diamond) vs. δ^{30}Si predicted (open square) by (a) the steady state model for uptake (following Eq. (1)) and (b) the uptake model including 33% and 21% Si from dissolution in July and August 2000, respectively, and 16% Si from internal loading in March 2001 (see Section 5.4 for details). Over the year, variations of pH *in situ* (black triangle; Table 2), monthly gross silica production (full square; see calculation Section 5.1), and the proportion of Si from dissolution (black dots; Table 3) are illustrated in support of the given interpretation.

diatoms are characterized by δ^{30}Si value close to −0.1‰ (suspended load: -0.08 ± 0.09 and -0.06 ± 0.08‰ for the lake and outlet waters, respectively; Table 1) and tephra is likely to possess a typical δ^{30}Si value of Icelandic basalt (−0.35‰; Georg et al., 2007). Isotope mass balance calculations suggest that a Si pool characterized by a δ^{30}Si value close to −2.2‰ is contributing about ~15% to the global sediment signature. This indicates a minor contribution from weathered material such as clay minerals in the sediment, since secondary clay minerals preferentially incorporate light Si isotopes relative to the parental basalt (Opfergelt et al., 2010; Ziegler et al., 2005).

A mean value of the Si isotope composition of the Si inflow to the Myvatn lake (δ^{30}Si +0.52‰) can be estimated from the balance of discharge of both cold (79%) and hot (21%) waters into the lake, based on the average δ^{30}Si value for cold and hot waters located directly around the lake (excluding the springs not located directly around the lake MY09 and MY10). The Si isotope signatures at the outlet are generally heavier than the groundwater input, displaying two increases towards heavier isotope composition from April to June, and from August to October (where Δ^{30}Si, the difference between δ^{30}Si at the outlet and average δ^{30}Si of the Si inflow, is up to 0.9‰). Note that the outlet δ^{30}Si value in August 2009 (MY13: 1.01 ± 0.10‰; Table 1) is in very good agreement with the δ^{30}Si value in August 2000 (00A062: 0.97 ± 0.03‰; Table 2). These heavier isotope compositions in the dissolved Si can be attributed to the preferential uptake of light Si isotopes by diatoms (De La Rocha et al., 1997). However, given the low Si concentrations in July, diatoms also grow in the summer, so the δ^{30}Si value of the dissolved Si should, in principle, remain heavier than the groundwater input. The lighter Si isotope compositions in July point to a different process occurring in the summer, which is masked by the change in the Si concentration. The isotopic approach adopted here provides a unique means of quantifying the processes impacting Si fluxes at the outlet of the lake.

5.3. Modeling Si isotope variations in Lake Myvatn

The key utility of the Lake Myvatn system for understanding the Si cycle is that inflow and outflow are both extremely well characterized. This allows quantification of the evolution of the δ^{30}Si value of the lake through the year, to better understand the processes governing the Si isotope variations at the outlet, and thereby provide some insight into the factors controlling Si fluxes to the oceans.

Biologically driven Si isotopic fractionation can be described by either closed (Rayleigh) or open (steady state) models. The former assumes that nutrient consumption is not replenished by external sources, whereas the latter presumes a continuous supply of nutrients from the same external source. In the case of Lake Myvatn, a constant input from groundwater and outflow from the lake can be assumed, and hence an open system model is more appropriate to describe the evolution of Si isotopes.

The open system steady state model (e.g., Sigman et al., 1999; Varela et al., 2004) can be used to describe the evolution of the dissolved Si isotope composition at the outlet of the lake induced by diatom Si uptake ($\delta^{30}Si_{postuptake}$) following:

$$\delta^{30}Si_{postuptake} = \delta^{30}Si_{input} - {}^{30}\varepsilon_{uptake}(1-f) \quad (1)$$

where f is the fraction of Si remaining (the ratio of the Si concentration at the outlet vs. that of the initial Si concentration estimated from the groundwater input) and ${}^{30}\varepsilon_{uptake}$ is the fractionation resulting from diatom uptake of silicic acid to produce BSi which has been experimentally determined to be -1.1 ± 0.41‰ (De La Rocha et al. 1997). This ${}^{30}\varepsilon_{uptake}$ determined for marine diatoms is similar to that observed for freshwater diatoms (Alleman et al., 2005), and is also confirmed by the difference between the δ^{30}Si compositions of the dissolved Si and of the suspended silica at the outlet (August 2009: -1.04 ± 0.08‰). The $\delta^{30}Si_{input}$ and the initial Si concentration are taken to be representative of the input to the lake before any Si consumption has taken place.

For each concentration measured at the outlet of the lake over the year 2000–2001, f can be calculated, and therefore, the Si isotope composition at the outlet $\delta^{30}Si_{postuptake}$ can be predicted from Eq. (1). The measured δ^{30}Si ratios at the outlet are then compared with the predicted values (Fig. 7a). The δ^{30}Si predicted by the steady state model is in good agreement with the δ^{30}Si measured at the outlet (within analytical uncertainty), except in July–August 2000 and March 2001. These results provide evidence that diatom uptake is the major process controlling δ^{30}Si at the outlet from March to June 2000, and from September 2000 to January 2001. However, it is apparent from the model that during the months of July, August 2000 and March 2001, the Si isotope variations in the lake are not related to diatom uptake alone, but rather have been influenced by some other process as the measured Si isotope compositions are significantly lighter than those predicted by the model (Fig. 7a).

A particular phenomenon that occurs in July–August is the rise of pH *in situ* to values up to 9.8–9.9 or greater (Table 2; Fig. 7a). The primary production results in consumption of CO_2, Si and an ensuing increase in pH. The solubility of BSi changes dramatically around the pH 9.5, when the pH of the water is equal to or higher than the pK1 of the monosilicic acid (dissociation constant at 25 °C pK1 = 9.51) (Van Cappellen and Qiu 1997). The solubility of the diatom frustules increases with temperature and there is a drastic increase in the solubility above the pH of 9.8 at 25 °C. Crucially, the dissolution rate is rapid because of high temperature, high pH, and maximum Si undersaturation (Gíslason et al., 2004; Thorbergsdóttir and Gíslason, 2004). Additionally, the cyanobacteria (*Anabaena*) bloom will push pH even higher without consuming silica, resulting in faster

dissolution rates and therefore higher recycling rates of both dead diatoms, and likely some living diatoms in the lake (Thorbergsdóttir and Gíslason, 2004). The lighter Si isotope composition during cyanobacteria bloom in July can thus be attributed to diatom dissolution with higher pH. The difference between the predicted and the measured δ^{30}Si curve in July–August can thus be used to quantify the impact of diatom dissolution (Fig. 7a).

5.4. Quantifying the impact of dissolution

To quantify the impact of dissolution on the Si budget in Lake Myvatn, the dissolved Si isotope composition measured at the outlet ($\delta^{30}Si_{outlet}$) of the lake is considered as an isotope mass balance between dissolved Si affected by diatom uptake predicted by the steady state model following Eq. (1) ($\delta^{30}Si_{postuptake}$) and dissolved Si affected by dissolution of fresh diatoms ($\delta^{30}Si_{dissolution}$) following:

$$\delta^{30}Si_{outlet} = \delta^{30}Si_{postuptake}x + \delta^{30}Si_{dissolution}(1-x). \quad (2)$$

In this equation, $(1-x)$ represents the proportion of dissolved Si from dissolution. In order to determine $(1-x)$, the $\delta^{30}Si_{dissolution}$ is calculated based on the fractionation factor $^{30}\varepsilon_{dissolution}$ of diatom dissolution. Indeed, diatom dissolution has been experimentally shown to preferentially release light Si isotopes, producing a dissolved Si 0.55‰ lighter than the parental BSi ($^{30}\varepsilon_{dissolution} = -0.55$‰; Demarest et al., 2009). For small Si isotope fractionations, $^{30}\varepsilon$ offers a good approximation of the difference between the δ^{30}Si value of the dissolved and the solid phase if an isotope equilibrium has been reached between those phases (Alleman et al., 2005; De La Rocha et al., 1997; Varela et al., 2004). Consequently, the Si isotope composition of the dissolved phase derived from diatom dissolution ($\delta^{30}Si_{dissolution}$) can be recalculated from the δ^{30}Si value of the solid phase (BSi in diatom frustules) following:

$$\delta^{30}Si_{dissolution} = {}^{30}\varepsilon_{dissolution} + \delta^{30}Si_{biogenic}. \quad (3)$$

The Si isotope composition of the solid phase ($\delta^{30}Si_{biogenic}$) was directly measured on samples of suspended load from the lake (MY12) and the outlet (MY13) in August 2009 (-0.08 ± 0.09 and -0.06 ± 0.08‰, respectively; Table 1). The Si isotope composition of the living diatoms ($\delta^{30}Si_{biogenic}$) can also be predicted from the dissolved Si isotope composition measured at the outlet ($\delta^{30}Si_{outlet}$) using the uptake fractionation factor $^{30}\varepsilon_{uptake} = -1.1$‰ (De La Rocha et al., 1997) following:

$$\delta^{30}Si_{biogenic} = {}^{30}\varepsilon_{uptake} + \delta^{30}Si_{outlet}. \quad (4)$$

Following Eq. (4), the calculated $\delta^{30}Si_{biogenic}$ for MY12 and MY13 are -0.17 ± 0.11‰ and -0.09 ± 0.10‰, respectively. This is in very good agreement with the δ^{30}Si values measured on the suspended load from those samples (-0.08 ± 0.09 and -0.06 ± 0.08‰, respectively; Table 1). This supports the hypothesis that the $\delta^{30}Si_{biogenic}$ produced monthly can be accurately predicted following Eq. (4).

Therefore, $\delta^{30}Si_{biogenic}$ can be calculated for each monthly value from Eq. (4), and used in Eq. (3) to calculate $\delta^{30}Si_{dissolution}$ for each month. Finally, $\delta^{30}Si_{dissolution}$ is used in Eq. (2) together with $\delta^{30}Si_{postuptake}$ predicted from Eq. (1) to determine $(1-x)$, the proportion of dissolved Si from dissolution. This calculation predicts that 33% and 21% of Si are derived from diatom dissolution in July and August, respectively (Table 3; Fig. 7). Dissolution above ~20% should have an isotope effect large enough to be detected with the current precision limits on the δ^{30}Si measurement (more than ~0.1‰). From March to June 2000 and from September 2000 to January 2001, dissolution does not impact the Si budget (≤10%; Table 3; Fig. 7). In March 2001, contrary to March 2000, the model predicts that 16% of the Si is derived from dissolution. However, the pH *in situ* in March 2001 has a value of 8.43 (Table 2) in which case dissolution is less likely to occur relative to the higher pH values in the summer. In March 2001, the additional Si contribution is probably related to a spike of internal loading and diffusive fluxes of nutrient derived from the bottom sediment of the lake, since the interstitial pore water of the sediment was shown to reach Si concentration of 700 μM in the winter (Gíslason et al., 2004). Dissolution of the diatomaceous sediment can provide a lighter δ^{30}Si value since the sediment is at −0.50‰ (Table 1). From mass balance calculations, it appears that 16% of the Si dissolved in March 2001 can be derived from internal loading providing a signature representative of diatomite dissolution (involving the dissolution fractionation factor $^{30}\varepsilon_{dissolution}$ of −0.55‰). However, this diffusive flux from sediments is rather an occasional event since it did not occur in March 2000. This process cannot explain the change in the isotope composition in July–August since the estimated annual diffusive flux of H_4SiO_4 is 1.3 g Si $m^{-2}yr^{-1}$, which is less than 1% of both the input (340 g Si $m^{-2}yr^{-1}$) and the annual net Si fixation by diatoms (178 g Si $m^{-2}yr^{-1}$) within the lake (Gíslason et al., 2004).

Table 3
Quantification of the impact of dissolution on Si fluxes at the outlet of the Lake Myvatn (see details of calculation in the text; Section 5.4).

Month	$\delta^{30}Si_{outlet}$ [a] (‰)	$\delta^{30}Si_{postuptake}$ [b] (‰)	$^{30}\varepsilon_{uptake}$ [c] (‰)	$\delta^{30}Si_{biogenic}$ [d] (‰)	$^{30}\varepsilon_{dissolution}$ [e] (‰)	$\delta^{30}Si_{dissolution}$ [f] (‰)	% dissolution [g] (1 − x)
Mar-00	0.70	0.68	−1.1	−0.40	−0.55	−0.95	−1%
Apr-00	0.94	0.93	−1.1	−0.16	−0.55	−0.71	0%
May-00	1.31	1.13	−1.1	0.21	−0.55	−0.34	−13%
Jun-00	1.42	1.38	−1.1	0.32	−0.55	−0.23	−2%
Jul-00	0.72	1.51	−1.1	−0.38	−0.55	−0.93	33%
Aug-00	0.97	1.42	−1.1	−0.13	−0.55	−0.68	21%
Sep-00	1.22	1.39	−1.1	0.12	−0.55	−0.43	9%
Oct-00	1.36	1.24	−1.1	0.26	−0.55	−0.29	−8%
Nov-00	0.97	0.91	−1.1	−0.13	−0.55	−0.68	−4%
Jan-01	0.65	0.69	−1.1	−0.45	−0.55	−1.00	2%
Mar-01	0.53	0.85	−1.1	−0.57	−0.55	−1.12	16%

[a] Measured on dissolved Si from the outlet (Table 2).
[b] Predicted by the steady state model (Eq. (1)).
[c] De La Rocha et al. (1997).
[d] Calculated from Eq. (4).
[e] Demarest et al. (2009).
[f] Calculated from Eq. (3).
[g] Proportion of Si from dissolution (Eq. (2)).

The Si isotope variations measured at the outlet of Lake Myvatn can thus be explained by an uptake and dissolution model (Fig. 7b), in which the variations are governed by Si uptake (following Eq. (1)) from March to June and from September to January, significantly affected by dissolution in July and August when pH rises (Table 3), and occasionally influenced by the diffusive flux of H_4SiO_4 from the bottom sediment, such as in March 2001.

5.5. Implications

The range of Si isotope variations (δ^{30}Si) controlled by diatoms at the outlet of Lake Myvatn over the year 2000–2001 (0.70 to 1.42‰; Table 2) is within the range reported for Icelandic rivers (−0.08 to 1.46‰) related to basalt weathering and secondary mineral formation (Georg et al., 2007). However, the Icelandic rivers sampled in June 2001 displayed a mean value of 0.63 ± 0.38‰ (Georg et al., 2007) which is significantly lighter than the Si isotope signature at the outlet of the lake in June 2000 (1.42 ± 0.06‰; Table 2). This suggests that the seasonal impact of diatom production can drive Si isotopes to significantly heavier values at the outlet of the lake, which can be distinguished from the signatures of many of the rivers the chemistry of which simply reflect basalt weathering, and secondary mineral formation. However, some rivers possess δ^{30}Si values that are indistinguishable from those seen at Lake Myvatn (Georg et al., 2007) which highlights the difficulties of deconvolving the signal from inorganic and biological processes particularly in areas surrounding lakes. This difficulty arises largely because for both Si incorporation into secondary weathering phases and biological uptake of Si the sense of isotope fractionation is the same.

Given that 85% of the Si input to oceans is carried by rivers (Tréguer et al., 1995), and that 16% of the gross riverine Si load is delivered to ocean as BSi (Conley, 1997), diatom uptake and dissolution in rivers and lakes on continents will inevitably affect the Si isotope signal to the oceans. The average net Si fixation by diatoms in Lake Myvatn (7.42×10^6 kg Si yr.$^{-1}$; Section 5.1) is underestimated since the Si concentration at the outlet of the lake includes both processes of Si uptake and dissolution. Using Si isotopes (Table 3), the monthly proportion of Si from dissolution can be subtracted from the outlet Si concentration. In this case, the average net Si fixation through uptake by diatoms (excluding dissolution) is 7.70×10^6 kg Si yr.$^{-1}$. In this study, the impact of diatom dissolution on Si fluxes is significant on a seasonal basis (up to 33% in the summer) but remains limited to just 3.7% over the course of a year.

This study provides evidence of Si recycling in Lake Myvatn with a link between pH forcing and recycling rates of BSi. This is supported by increasing BSi dissolution with an increasing pH (from pH 6 to 9) over the entire range of undersaturation (Van Cappellen and Qiu, 1997). At high pH and primary production rates, the phytoplankton increase the recycling efficiency of Si in the water column (Gíslason et al., 2004), and the present isotope mass balance provides evidence that up to 33% of the Si can be recycled in the summer months characterized by the highest pH values, consistent with diatom productivity relying strongly on Si input from BSi recycling.

In the oceans, anthropogenic CO_2 is absorbed, and at the current rate of CO_2 uptake, it has been postulated that the average surface ocean pH will drop from the pre-industrial revolution value of 8.2 to 7.8 by the end of 2100 (Caldeira and Wickett, 2005). This represents a shift in seawater pH to levels below those experienced by marine organisms during the last several million years (Pearson and Palmer, 2000). Based on the results from Myvatn Lake and on the pH dependence of diatom dissolution (Van Cappellen and Qiu 1997), such an ocean acidification could significantly reduce BSi dissolution. This would reduce the Si supply for diatoms, affecting their productivity and severely affecting the carbon storage capacity of the ocean (Smetacek, 1999).

6. Conclusions

This is the first study using silicon isotopes to estimate biogeochemically relevant rates for Si cycling dynamics. Moreover, this work provides some insight into an important, but largely unquantified, aspect of the global silicon cycle, namely processes that occur at the terrestrial/marine interface. The objective of this study was to assess the impact of diatom productivity on Si stable isotopes in Lake Myvatn relative to the groundwater input, the principal Si source in the lake. The Si isotope compositions of both cold and hot springs were shown to be similar. Based on the δ^{30}Si variations in the outflow of the lake over one year, the impact of diatom uptake and diatom dissolution was quantified. Diatom productivity, characterized by two seasonal blooms in spring and autumn, can affect the Si flux at the outlet of the lake up to 79% by Si uptake (53% on average over the year) resulting in a shift to heavier δ^{30}Si compositions of up to 0.9‰ relative to the Si isotope signature of the inflow from cold and hot waters into the lake. A shift to lighter δ^{30}Si compositions at the outlet in the summer correlates with pH rises and provides evidence of diatom dissolution with a preferential release of light Si isotopes in July–August. The Si isotope budget at the outlet of the lake is thus governed by groundwater input in the winter, by diatom uptake in the spring and the autumn, and by diatom dissolution in the summer. Quantitatively, diatom dissolution affects the total Si fluxes from the lake up to 33% in the summer, and averages 3.7% over the year. The link between pH forcing and recycling rates of BSi in lakes provided in this study is potentially crucial for the Si supply for diatoms in oceans. In the oceans themselves acidification is likely to reduce Si supply from BSi recycling for diatoms, reducing diatom productivity and thereby the oceanic carbon storage capacity.

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