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## Diatom-rich sediment formation in lakes

Zahajská, Petra

2021

*Document Version:*  
Publisher's PDF, also known as Version of record

[Link to publication](#)

*Citation for published version (APA):*  
Zahajská, P. (2021). *Diatom-rich sediment formation in lakes*. Lund University (Media-Tryck).

*Total number of authors:*  
1

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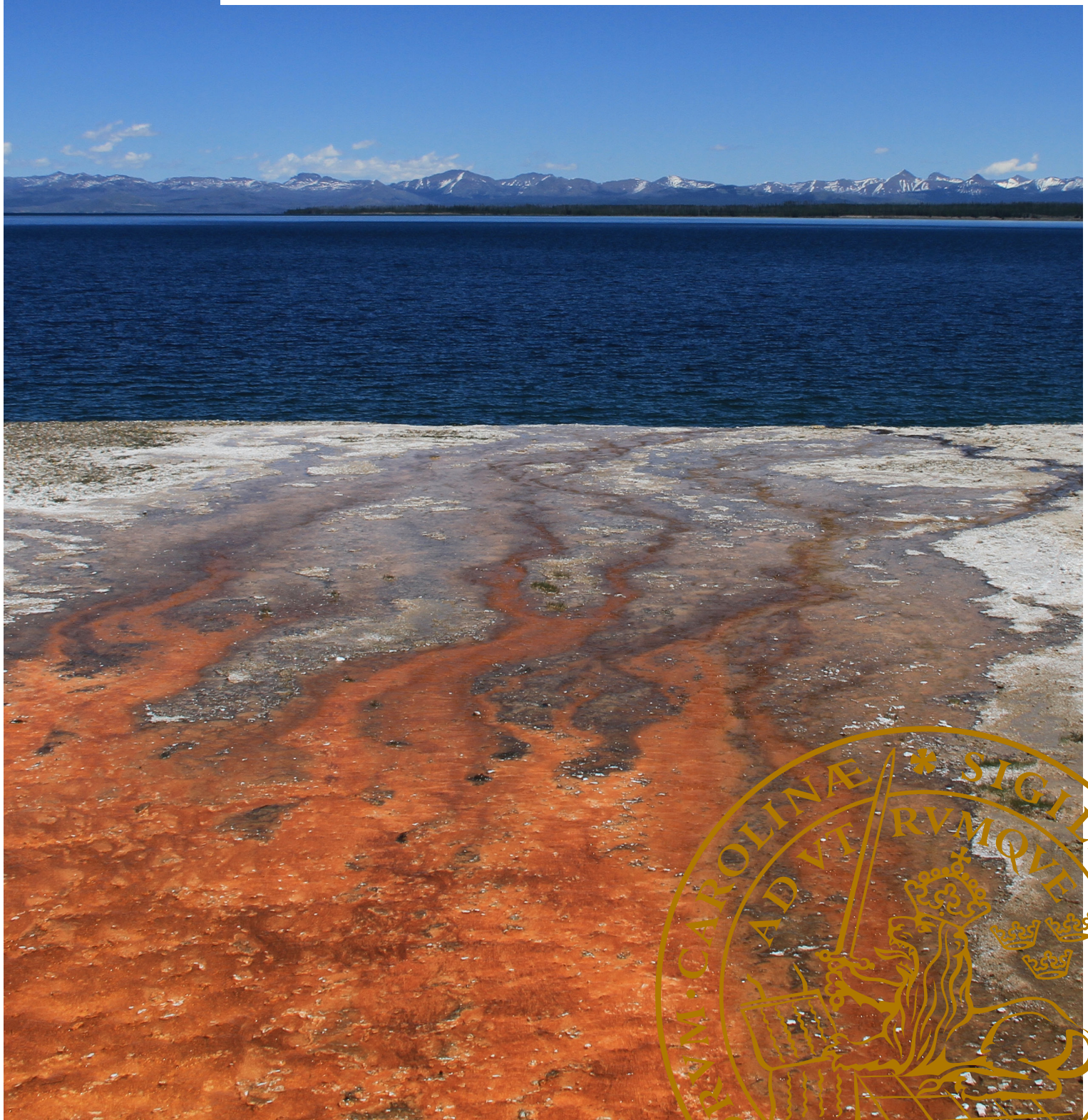
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# Diatom-rich sediment formation in lakes

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QUATERNARY SCIENCES | DEPARTMENT OF GEOLOGY | LUND UNIVERSITY 2021





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ISSN 0281-3033  
ISBN 978-91-87847-56-1

LUNDQUA THESIS 91

# Diatom-rich sediment formation in lakes

Petra Zahajská



**LUND**  
UNIVERSITY

Quaternary Sciences  
Department of Geology

**DOCTORAL DISSERTATION**

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To be defended at Pangea, Geocentrum II, Sölvegatan 12 and via Zoom. Date 2021-03-05 at time 13:15.

*Faculty opponent*

Prof. Anson W. Mackay  
University College London

**Cover illustration front:** Hydrothermal fluids delivery to Yellowstone Lake from West Thumb Geyser Basin in June 2017, Yellowstone National Park, Wyoming, USA. (Credits: Petra Zahajská)

**Cover illustration back:** View across Isfjorden from Longyearbyen seaside in March 2017, Svalbard, Norway. Photo taken during winter Arctic limnology course. (Credits: Petra Zahajská)

**Funding information:** The thesis was financially supported by several grants from the Royal Physiographic Society in Lund and by the Swedish Research Council.

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Faculty of Science, Department of Geology

ISBN: 978-91-87847-56-1 (print)

ISBN: 978-91-87847-57-8 (pdf)

ISSN: 0281-3033

Printed in Sweden by Media-Tryck, Lund University, Lund 2021



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**MADE IN SWEDEN** 

Organization <b>LUND UNIVERSITY</b> Department of Geology Sölvegatan 12 SE-22362 LUND Sweden	Document name <b>DOCTORAL DISSERTATION</b>	
	Date of disputation 2021-03-05	
	Sponsoring organization	
Author(s) Petra Zahajská		
Title and subtitle Diatom-rich sediment formation in lakes		
Abstract Unicellular photosynthetic golden-green algae called diatoms are one of the most abundant silicifying organisms. Diatoms take up silicon and build their frustules, in the form of biogenic silica (BSi), which have high preservation potential, and thus are found in sediments. Around 27 % of the annual dissolved silicon (DSi) delivery from the land to the ocean is retained in lakes and reservoirs in the form of BSi. Therefore, diatom production in lakes creates silicon sinks and influences the Si cycle. However, the processes driving and regulating lacustrine diatom-rich sedimentation are poorly constrained. This dissertation investigates two lakes in very different settings to evaluate the major factors governing diatom-rich sediment accumulation. The first study site is a small subarctic, high-latitude lake, Lake 850 in Northern Sweden, and the other study site is in the hydrothermally active and DSi-rich Yellowstone Lake in Yellowstone National Park, Wyoming, U.S.A. The study of the recent Si cycle in Lake 850 revealed the importance of groundwater input to the lake's Si budget. Groundwater brings 3 times more DSi compared to the stream inlet and thus is the main source of DSi for diatom production. Low sedimentation rates in the last 150 years are responsible for BSi accumulation as high as 20 dry weight%. The Holocene sedimentary record shows that the lake had low detrital input throughout the last 7400 years, likely due to low-relief geomorphology and a stable environment in the lake's watershed. The stable Si isotopes of fossil diatoms suggest a stable DSi supply for the lake, where only the relative proportion of stream influx and groundwater influx of DSi are driving isotopic changes. The BSi accumulation in the sediment of Lake 850, as high as 46 dry weight% throughout the Holocene, is driven by a combination of sufficient DSi supply from groundwater and the stream inlet, low detrital input and good preservation of diatoms in the sediment. In Yellowstone Lake the importance of hydrothermal vents bringing DSi into the lake was shown. The impact of hydrothermal DSi supply is observed in the sedimentary record over the last 9800 years as elevated Ge/Si ratios (up to 37 $\mu\text{mol/mol}$ ). Holocene hydrothermal input is responsible for a long-term stable lake DSi concentration and its Si isotopic signature, reflected in the fossil diatoms. The high sustained input of DSi masks the effects of the sublacustrine Elliott's Crater hydrothermal explosion -8500 years ago. The relative proportion of the DSi sources from hydrothermal fluids and stream inlets, diatom production and dissolution are concurrent processes responsible for the variation of the Si isotopic signal. The BSi accumulation is accounted for by low accumulation rates with limited amounts of detrital input and high diatom preservation, which results in BSi concentrations in the sediment of up to 52 dry weight%. On Holocene timescales, neither lake was DSi limited, which resulted from presence of the additional sources of DSi – groundwater or hydrothermal fluids. The unlimited DSi is partly responsible for BSi accumulation. Additionally, low sediment accumulation rates due to low detrital input, often driven by changes in climate and hydrology, are factors contributing to high BSi concentration. Finally, a fine balance between diatom production and dissolution may influence BSi accumulation. These studies suggest that diatom-rich sediments are likely to accumulate in lakes situated on silicon-rich bedrock and regions influenced by volcanic and hydrothermal activity if accompanied by low clastic sediment inputs. High-latitude lakes, which may have high groundwater input also are candidates for high BSi accumulation. Lakes with low-relief watershed morphology and with limited stream input bringing only fine-grained clastic input have the potential to accumulate BSi.		
Key words Silicon, silica, diatom, biogenic silica, lakes, sediment, stable Si isotopes, Ge/Si, Yellowstone, Northern Sweden		
Classification system and/or index terms (if any)		
Supplementary bibliographical information		Language English
ISSN and key title 0281-3033 LUNDQUA thesis		ISBN 978-91-87847-56-1 (print) 978-91-87847-57-8 (pdf)
Recipient's notes	Number of pages 132	Price
	Security classification	

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*“In wilderness I sense the miracle of life, and behind it our scientific accomplishments fade to trivia.”*

Charles Lindbergh

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## List of publications

This thesis is based on the following publications, referred to by their Roman numerals:

**I What is diatomite?**

Zahajská, P., Opfergelt, S., Fritz, S. C., Stadmark, J. and Conley, D. J.  
*Quaternary Research*, vol. 96, pp. 48-52. DOI: 10.1017/qua.2020.14.

**II Modern silicon dynamics of a small high-latitude subarctic lake**

Zahajská, P., Olid, C. G., Stadmark, J., Fritz, S. C., Opfergelt, S. and Conley, D. J.  
*In review in Biogeosciences*. DOI: 10.5194/bg-2020-441.

**III Impact of Holocene changes in climate on silicon cycling in Lake 850, Northern Sweden**

Zahajská, P., Cartier, R., Fritz, S. C., Stadmark, J., Opfergelt, S., Yam, R., Shemesh, A. and Conley, D. J.  
*Submitted to The Holocene*.

**IV Impact of Holocene sub-lacustrine hydrothermal activity on the Si cycle and diatom-rich sediment accumulation in Yellowstone Lake**

Zahajská, P., Frings, P. J., Gaspard, F., Cartier, R., Opfergelt, S., Fritz, S. C., Stadmark, J., and Conley, D. J.  
*Manuscript*.

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Publications not included in this thesis:

**Yellowstone Lake Coring Projects: Research with a History**

Spanbauer, T. L., Brown, S.R., Cartier, R., Conley, D. J., Fritz, S. C., Schiller, C. M., Theriot, E. C., Whitlock, C., Zahajská, P.  
*Limnology and Oceanography Bulletin*, vol. 27, pp. 6-10. DOI: 10.1002/lob.10229.

**Multi-proxy record of Holocene paleoenvironmental conditions from Yellowstone Lake, Wyoming, USA**

Brown, S.R., Cartier, R., Schiller, C. M., Zahajská, P., Fritz, S. C., Morgan, L. A., Whitlock, C., Conley, D. J., Lacey, J. H, Leng, M. J. and Shanks III, W. C.  
*To be submitted to Quaternary Science Reviews*.

## Acknowledgements

*“What I see here is nothing but a shell. What is most important is invisible...”* – Antoine de Saint Exupery, The Little Prince

This thesis is just a brief suitcase that wraps my PhD student journey, which was much more than a thesis. My PhD studies were full of diverse joyful and fruitful activities, which brought me to this point. I have learnt a tremendous amount of new things, I've experienced four years of intensive research work as an individual, but also as part of bigger research groups, which I always dreamt of. I've met many passionate, enthusiastic, amiable colleagues, researchers, and people. I was always surrounded by terrific friends, whom all I would like to express my gratitude in a few following lines.

I want to thank all of my supervisors, Daniel, Johanna, Sophie and Sheri, for being here for me, listening and answering my questions, repeating the answers, again and again, discussing new ideas, reading and improving my manuscripts, proposals and supporting me in almost everything that I came with.

Thanks to Magnus Mörth, Christian Bigler, Hans Schöberg for great ideas, help, and connecting with new people. Thanks to my co-authors Carolina and Patrick for discussing and improving the manuscripts, even in short time notice. I also want to thank the HD-YLake group, Sabrina, Chris, Lisa, Pat, Rob and all others for allowing me to be part of a big team of smart people working on Yellowstone. It was an honour for me to meet and work with you all.

Thanks to Honor, my mentor, for being a patient listener, thoughtful mentor, and for still looking after me. Further, I want to thank all of you at the Department of Geology here in Lund, for creating a friendly working environment very opened to international PhD students. I thank Mats, Helena and Mikael for an opportunity to gain some teaching skills. Also, big thanks to Gert for keeping the electronic world well functioning all the time and to whole Kansli for being so great to help anytime.

My thanks go to all my colleagues and friends, who made my days enjoyable. Thanks to all PhD students for coming out for PhD dinners, having PhD fikas and having fun together. I would also like to thank people at the Université Louvain-la-Neuve for being so inviting and open to newcomers, thanks to François, Elisabeth, Arthur, Catherine, Maxime and everybody else. I enjoyed the time in Louvain. I want to thank Chris, Jessica, Jacob and Rosine to going with me to “the grizzly land” in Yellowstone. I couldn't do this without you!

Carla, thanks for being here to talk about anything anytime, for joining the very cold fieldwork and for having all the fun, which we had. Thanks to Zhouling for spreading the

good mood and laugh through the department. Thank you, Guillaume and Billy, for answering all my questions about simple things and making Friday beers even more fun. Big thanks go to Bingjie for keeping me in the biomarkers' world updated and for having good times with good food. Thanks to Maria for always having a solution for any situation and patience during our kiteboarding time :-). It was so much fun! Geert, thanks for encouraging me to climb more challenging routes and climb higher than my limits. Laurie, thanks for being such a good listener and having patience with me.

Huge thanks go to Franzi for reading, discussing, suggesting and helping out, because I don't know how this would have ended up if you hadn't come here. I also thank Karola, Tjördis and Ethan for being always a lovely company and for “just chatting” or playing board games with a glass of beverage. Thanks to Yuhao, Isa, Rebecca and Rosine for reading my texts, for bringing new ideas and approaches into the discussions. Thanks to Cindy, Ingrid, Chiara and Sofia for being on the online PhD meetings almost every time and keeping some PhD social life still on even in corona times. This list can go on, so in short, thanks to all of you reading these acknowledgements because if you read them, it means that you've earned my gratitude for something. Thank you all! Tack allihopa!

Since I started my PhD studies here in Lund, many things in my life have changed, but my good old friends were always there for me. Thus, I would like to thank Venca, Fazole, Káťa, Klárka, Péťa, Adél, Adéla, Terka, Anička and many others for being always ready to meet for a cup of tea and cake when I came back to Prague or even online. I also want to thank Sebastian, my good friend, for supplying me with spectacular photos of northern lights and for making me always laugh after reading his messages. Thank you Max, for all the nice days in Lomma! I cannot forget to thank Pällsboll, the cutest cat ever, for keeping a strict, but closed eye on me when writing during the corona times.

I want to thank my esteemed smarties Lukáš, Filip, Míra and Honza who (indirectly) motivated me to try harder, learn more, and they made a creative space for any kind of ideas during our trips. Thank you guys for being still here, even though we are now all over Europe.

Finally, I would like to thank my whole family. Mami, tati děkuji, že jste mě vždy podporovali v mé zvědavosti a že mě stále podporujete v mých bláznivých rozhodnutích dělat vědu a cestovat po světě. Ségra a bráchové, je s vámi sranda a mám vás ráda. Nakonec děkuju šamákovi, že má se mnou trpělivost, učí mě věci dělat lépe a pořádně, že jezdí na dovolenou sbírat vzorky místo válení se na pláži a že mě podporuje v tom pokračovat dál, i když sama dál už nemůžu. Děkuji, že jste!

$$x^2 + \left(\frac{5y}{4} - \sqrt{|x|}\right)^2 = 1$$

## I Introduction

The Earth's crust is composed of large quantities of silicate minerals, which are chemically weathered once exposed to exogenous processes. Both macro- and micro-nutrients are released during the mineral weathering and distributed to the ecosystem where they are utilized, recycled and buried. Those processes are part of elemental cycling, which is responsible for the Earth's evolution. To understand the distribution of different elements, biogeochemical models are established based on observational data. Here we focus on an essential element for single-cell silicifying algae – *silicon* (Si).

The Si cycle is characterized by two sub-cycles: the continental cycle and the oceanic cycle. These sub-cycles are connected through rivers, which transport the silicon from land to oceans. Diatoms are the most prevalent silicifying organism in aquatic environments (Battarbee et al., 2002; Opfergelt et al., 2011), and marine diatom production accounts for one quarter of the world's entire net primary productivity (Armbrust, 2009; Simpson and Volcani, 1981) and one fifth of world oxygen production. Oceanic diatom production is fully dependent on dissolved silicon delivery from the continental cycle. However, processes in the continental cycle – such as diatom production and accumulation – affect the Si delivery to the oceans as shown by several Si mass-balance studies (Frings et al., 2016, 2014b; Sutton et al., 2018; Tréguer and De La Rocha, 2013). These studies identified knowledge gaps in the Si cycle, particularly the need to better constrain sinks and sources in the continental cycle to better understand Si delivery to the ocean. An example of those sinks or sources is the lacustrine diatom-rich sediments, which can retain silicon on long timescales, but they can also release the silicon if conditions change.

This PhD project aims to investigate the processes governing diatom-rich sediment formation

in lakes in order to enhance our understanding of the functioning of continental silicon sinks.

## 2 Aims of the thesis

The aim of this thesis is to improve current understanding of retention of Si in lakes and factors governing diatom-rich sediment formation during the Holocene. Its main research questions are as follows:

- What nomenclature should be used to name diatom-rich sediment?
- What are the processes responsible for high diatom accumulation in high-latitude lakes?
- How do hydrothermal inputs affect sediment accumulation of diatoms ?
- Do hydrothermal processes during the Holocene affect diatom accumulation in Yellowstone Lake?
- What are the general processes responsible for Holocene diatom-rich sedimentation in lakes?

## 3 Background

### 3.1 What is diatom-rich sediment?

Diatom-rich sediment is mainly composed of diatom frustules and accumulates worldwide. *Diatoms* are single-cell golden algae, with an external skeleton made of *biogenic silica* (*BSi*), known as a *frustule*. All aquatic environments, such as lakes, rivers, oceans, but also soils, host conditions for diatom growth. Accumulation of diatoms in sediment is known in all aquatic environments including wetlands, lakes, and the oceans

(Clarke, 2003). Furthermore, diatom sensitivity to changes in water temperature, pH, dissolved oxygen, nitrogen, phosphorus, and other nutrients make diatoms often used as a proxy in paleoenvironmental reconstructions (Battarbee et al., 2002). *Dissolved silicon (DSi)* concentrations in the environment are essential for diatoms to grow, as diatoms take up DSi to build their frustules. Therefore, to investigate factors driving freshwater diatom production and then accumulation, we need to understand what is driving changes in DSi concentrations. Essential understanding of silicon behavior, coupled with constraining the processes affecting DSi concentration in the environment, is part of global Si cycle studies.

### 3.2 Silicon behavior

In natural waters, only small amounts of silicon are found in the form of *orthosilicic acid* ( $\text{H}_4\text{SiO}_4$ ), which acts as a weak acid. Orthosilicic acid does not dissociate below pH 9, and Si is soluble at basic pH ranges (Oelze, 2015). Silica solubility in hydrous fluids and soils increases with pH and temperature (Albarède, 2009). The highest silica solubility occurs under alkaline conditions at a pH higher than 9 (Oelze, 2015). Additionally, formation of silicate complexes with Fe and Al hydroxides decreases solubility of silicates in sediment and decreases silicate solubility in waters at  $\text{pH} > 7$  (Wetzel, 1975). Thus, the presence of clay minerals rich in Al and Fe can influence silica solubility.

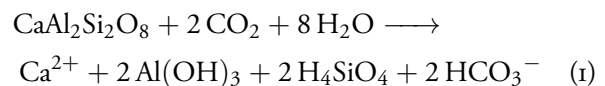
### 3.3 The global Si cycle

The biogeochemical cycle of Si occurs in both terrestrial and aquatic environments. A simplified model of the Si cycle shows how DSi released by weathering directly enters the fluvial system via surficial run-off or groundwater (Figure 1). The DSi delivered by rivers into the ocean accounts

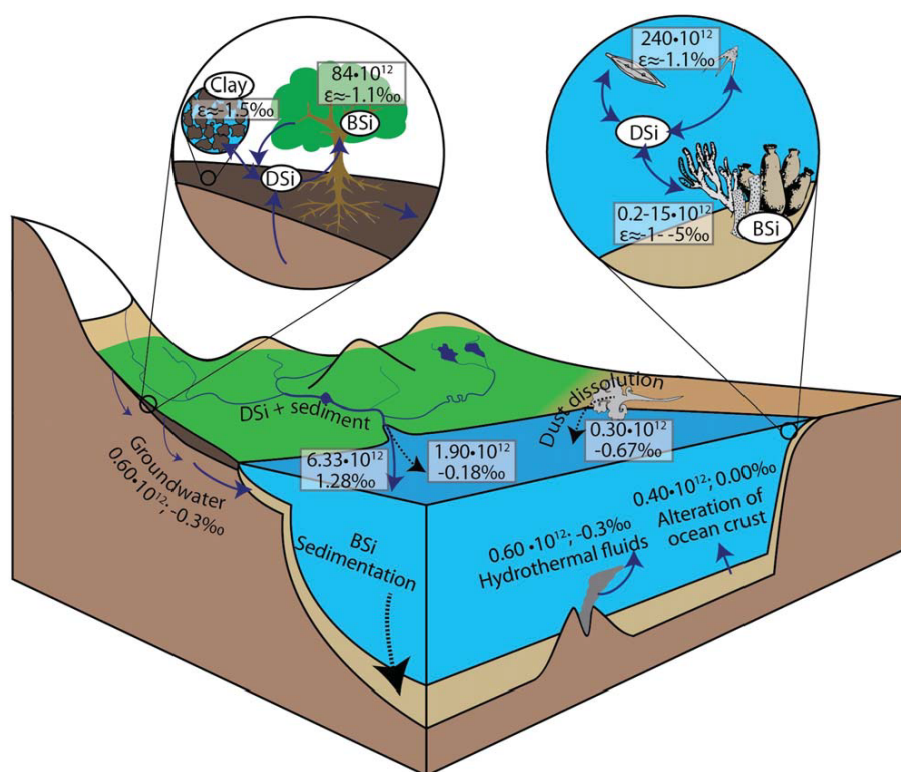
for 80 % of the total annual DSi delivery to the ocean (Frings et al., 2016; Sutton et al., 2018). Therefore, processes in the watershed are studied to understand the DSi fluxes. Several sinks and sources of DSi, such as soils, lakes and reservoirs (e.g., damming), were identified as important in regulating DSi delivery (Frings et al., 2016).

Dissolved silicon is delivered from weathered bedrock. The Earth's crust is composed primarily of Si, Al and O in the form of aluminosilicates. Silicon occurs as 1. a crystalline form of *lithogenic silica* in soils, minerals and rocks (LSi), 2. poorly ordered crystalline *amorphous silica* (ASi), which includes *biogenic silica* (BSi) produced by organisms, and 3. *dissolved silicon* (DSi) available in waters (McKeague and Cline, 1963). Quartz, feldspar and chalcedony are the predominant forms of crystalline lithogenic silica that are weathered and supply the system with DSi (McKeague and Cline, 1963).

The silicon release to the environment by chemical weathering of igneous silicate rocks and minerals is accompanied by  $\text{CO}_2$  consumption (Sommer et al., 2006):



Silicate weathering produces *orthosilicic acid* ( $\text{H}_4\text{SiO}_4$ ), also reported as *dissolved silicon (DSi)*, which is transported by rivers to the ocean. The global mean of DSi concentration in natural waters is  $9.5 \text{ mg SiO}_2 \text{ l}^{-1}$  ( $\sim 160 \mu\text{M}$ ) (Dürr et al., 2011). The highest DSi concentrations (up to  $125 \text{ mg SiO}_2 \text{ l}^{-1}$ ) occur in groundwaters and hydrothermal fluids ( $580 \text{ mg SiO}_2 \text{ l}^{-1}$ ) that are in contact with volcanic rock (Fowler et al., 2019b; Georg et al., 2009; Schopka and Derry, 2012; Wetzel, 1975). Intermediate concentrations are associated with plutonic rocks, sediments containing feldspar, and volcanic rock fragments. Carbonates and marine sandstones are generally associated with a lower amount of DSi (Wetzel,



**Figure 1:** Schematic figure of the modern day global Si cycle by Frings et al. (2016). Values show the magnitudes of the fluxes (in  $\text{mol yr}^{-1}$ ) and also  $\delta^{30}\text{Si}$  values (in ‰). The values of fractionation ( $\varepsilon$ , ‰) showed in the inset panels are associated with BSi production and clay minerals.

1975). On its pathway to the ocean, DSi cycles through continental filters, such as soils, lakes and reservoirs, which can efficiently remove DSi from the water and retain it for a long time (Frings et al., 2014b).

### 3.3.1 Terrestrial Si filters

Most of the DSi passes through a terrestrial filter before it is exported into river systems (Derry et al., 2005; Struyf et al., 2009). In many terrestrial ecosystems the soil-plant ASi pool stores more Si than the DSi released annually by weathering; therefore, the soil-plant system acts as a filter (Clymans et al., 2011; Frings et al., 2016; Struyf et al., 2010). Soils can retain DSi as it is taken up by vascular plants to build supportive siliceous structures – *phytoliths* (Piperno, 2001). Those silica

bodies are precipitated in roots, stems, branches, leaves or needles as biogenic silica (BSi) and can be recycled in litterfall after the plant dies.

The phytolith BSi can be structurally or chemically altered by dissolution and precipitation processes in soils (Barão et al., 2014; Cornelis et al., 2011; Sommer et al., 2006), forming pedogenic silica. Due to loss of water during dissolution and precipitation processes, the pedogenic silica can gain more structural order, and thus its solubility and reactivity decreases compared to the original BSi and ASi (Saccone et al., 2007). Under acidic conditions in soils, the ASi and pedogenic silica are lost slowly, because they are insoluble (McKeague and Cline, 1963). Hence, soils can store large Si stocks, but they are particularly susceptible to human perturbation connected to changes in pH (Clymans et al., 2011).

### 3.3.2 Lacustrine continental Si sink

Not only soils, but also lakes and reservoirs (damming) can store silicon. Lakes are considered to store 21–27 % of the annual global DSi delivery to the ocean in lake sediments (Frings et al., 2014b). Diatoms act as a silicon sink, as they grow in all aquatic environments and take up DSi to build their frustules, which are deposited in the sediment in the form of biogenic silica (BSi) after their death. The BSi accumulation depends on several factors:

1. Favorable conditions for diatoms to grow, such as light and nutrients. Diatoms are limited by the DSi concentration in the environment. Therefore, continuous DSi supply or Si recycling in the water column are crucial for sustaining diatom production and thus BSi accumulation (Ragueneau et al., 2006).
2. The DSi supply must be higher than the DSi removal by an outlet in order to accumulate BSi. An excessive supply of DSi or fast

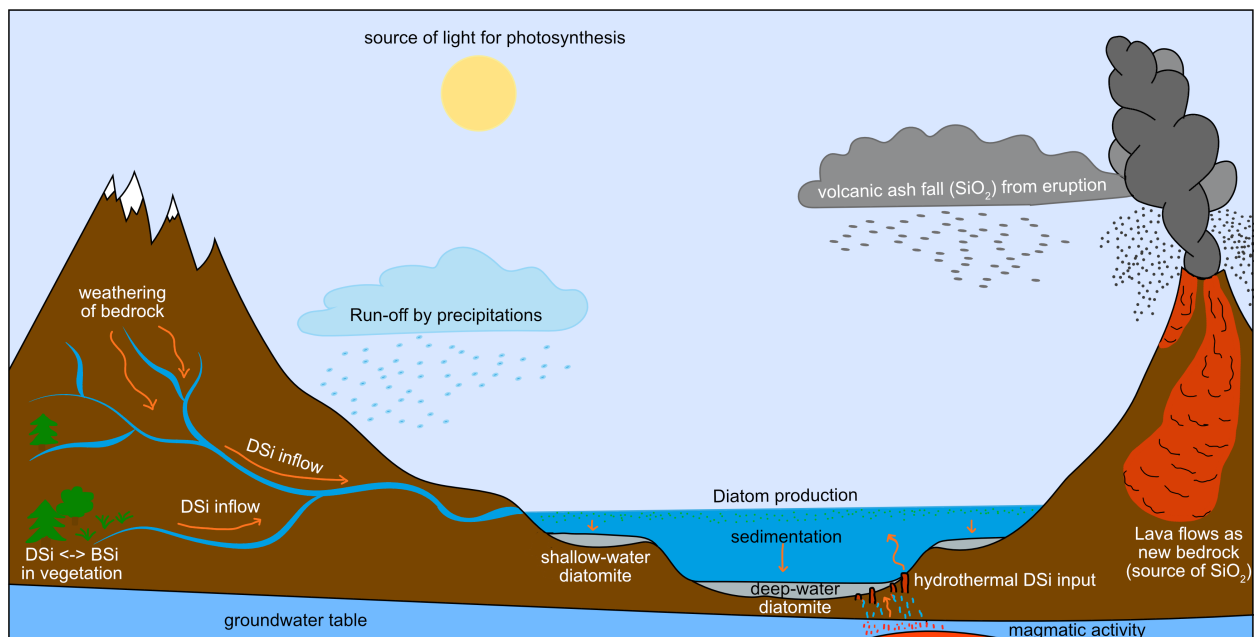
sedimentation rates prevent diatom dissolution in the water column and diatom-rich sediments are formed.

3. Lakes with low detrital input (Conger, 1942) have the potential to accumulate BSi in the sediment.
4. Volcanic and hydrothermal lakes enriched in DSi may accumulate BSi (Conley, 1998).

A conceptual model was created to illustrate all the above mentioned factors influencing diatom-rich sediment formation in volcanic and non-volcanic settings, which were both studied for their silicon cycle (Figure 2).

### 3.4 Stable Si isotopes

Stable silicon isotopes have previously been used as a tool to constrain different biological and chemical processes influencing DSi concentrations in the global Si cycle. Silicon has three stable isotopes, which have different relative abundances in nature:  $^{28}\text{Si}$  (92.18 %),  $^{29}\text{Si}$  (4.71 %), and  $^{30}\text{Si}$  (3.12 %) (Reynolds, 1953). Due to different masses of the



**Figure 2:** A conceptual model of diatom-rich sediment formation.

isotopes –  $^{28}\text{Si}$  (27.976927),  $^{29}\text{Si}$  (28.976495),  $^{30}\text{Si}$  (29.973770) – there is mass-dependent fractionation, which occurs during physical, chemical, and biological processes. Two main isotopic fractionation types are distinguished: 1. kinetic fractionation, and 2. equilibrium fractionation. Kinetic fractionation occurs during an irreversible chemical reaction of physical processes and preferentially enriches the product in lighter isotopes. One example of kinetic fractionation is the uptake and incorporation of Si by diatoms or plants. Equilibrium fractionation is associated with reversible chemical reactions and physical processes (when the chemical reaction is in equilibrium) (Opfergelt et al., 2011; Wiederhold, 2015).

Because mass spectrometric methods allow the difference in isotopic ratio of two stable isotopes to be measured much more precisely than their absolute abundance (Poitrasson, 2017), the isotopic composition is expressed as a ratio of two isotopes. Additionally, to compare the isotopic composition of different materials, the measured isotopic ratios in the materials are normalized by comparing them with an international reference standard.

The Si isotopic fractionation between the sample and the standard is then expressed in ‰ as:

$$\delta^{30}\text{Si}(\text{‰}) = \left( \frac{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{standard}}} - 1 \right) \cdot 1000. \quad (2)$$

Different reference materials are used as standards, most often NBS-28, now registered as RM-8546, a reference for silicate solid samples or secondary standard diatomite (Reynolds et al., 2007). To describe the degree of isotopic fractionation between two materials, e.g.,  $A$  and  $B$ , we use the *fractionation factor*  $\alpha_{A-B}$ :

$$\alpha_{A-B} = \frac{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_A}{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_B}. \quad (3)$$

In natural environments,  $\alpha_{A-B}$  is very close to 1; hence, the discrimination between two materials

$A$  and  $B$  is presented in permille as

$$^{30}\epsilon_{A-B} = (\alpha_{A-B} - 1) \cdot 1000. \quad (4)$$

Because of a small Si isotope fractionation, the discrimination between two materials  $A$  and  $B$  can be expressed as  $\Delta^{30}\text{Si}_{A-B}$ , which gives us a good approximation for the fractionation ( $^{30}\epsilon$ ):

$$^{30}\epsilon_{A-B} \approx 10^3 \ln(\alpha_{A-B}) \approx \Delta^{30}\text{Si}_{A-B}, \quad (5)$$

$$^{30}\epsilon_{A-B} = \delta^{30}\text{Si}_A - \delta^{30}\text{Si}_B. \quad (6)$$

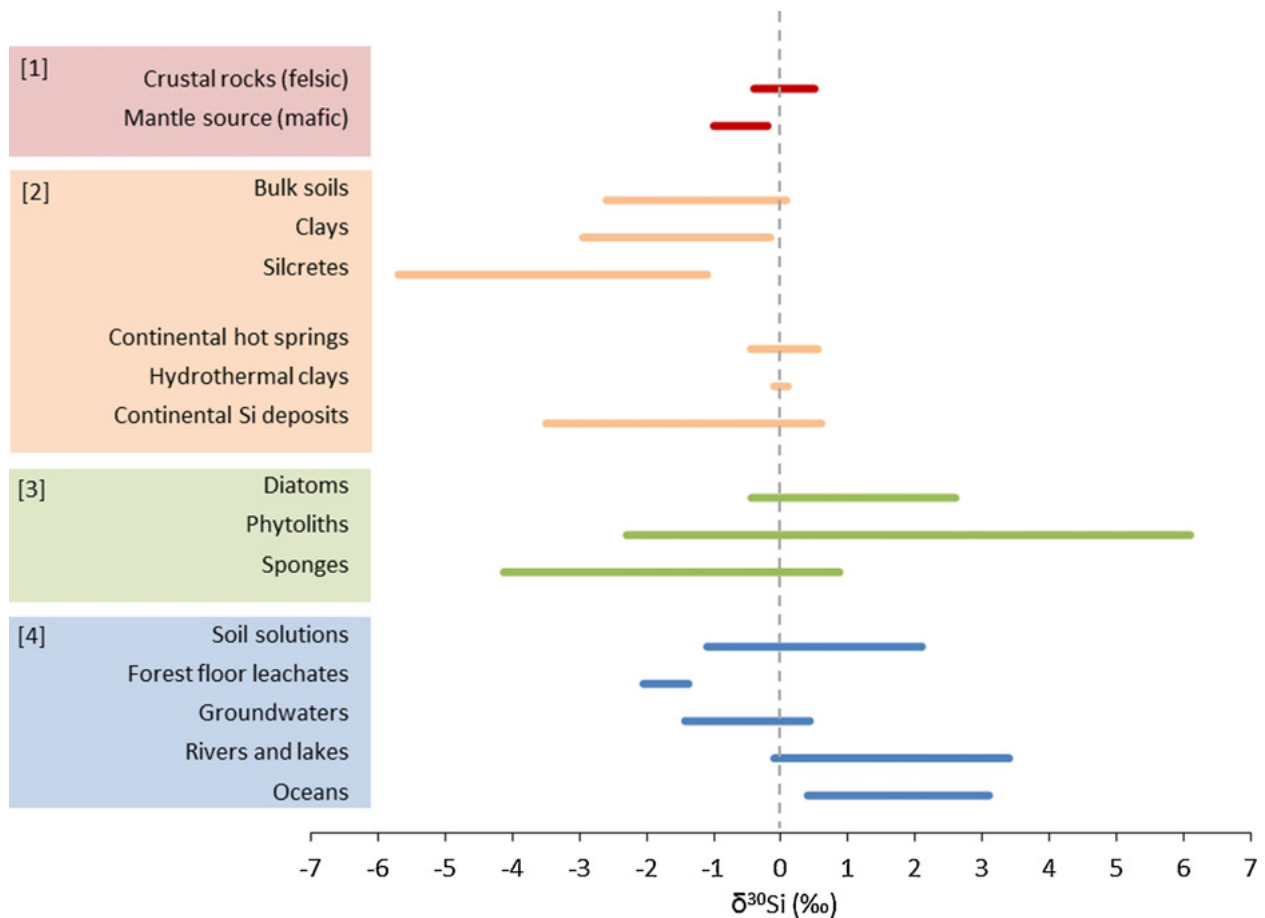
In general, Si isotopes have a tendency to fractionate in association with the formation of a solid form from a solution and preferentially incorporate the lighter isotopes into the newly formed solid.

Fractionation results in the residual solution being enriched in the heavier isotopes (De La Rocha et al., 2000, 1997; Opfergelt and Delmelle, 2012; Ziegler et al., 2005). There are three main processes observed in the Si cycle that fractionate the Si isotopes: rock forming processes, water-rock interaction processes, and biological processes (Figure 3).

Rock forming processes happen on longer geological timescales and thus are not in the scope of this thesis. The water-rock interaction processes are of two types: firstly, the formation of secondary minerals and soils, and secondly, the hydrothermal fluids and deposits. In all cases the light isotopes are preferentially incorporated into the clay, hydrothermal fluid or deposit, and the residual water DSi carries a heavier isotopic signature (Figure 3).

Finally, biological processes are represented by silicifying organisms, which come from different phylogenetic branches, such as the stramenopiles (e.g., diatoms), rhizarians (e.g., radiolarians), opisthokonts (e.g., sponges), land plants, and cyanobacteria. They all take up DSi and deposit it in the form of biogenic silica (Marron et al., 2016). The BSi formed by diatoms, sponges, radiolarians and plants will show a lighter isotopic signature





**Figure 3:** Variation of  $\delta^{30}\text{Si}$  in the different materials. [1] are rock forming processes, [2] water-rock interactions, [3] biological processes, [4] water reservoir by Opfergelt and Delmelle (2012).

than the DSi source, and fractionates differently (Figure 3).

### 3.5 Si isotope fractionation models

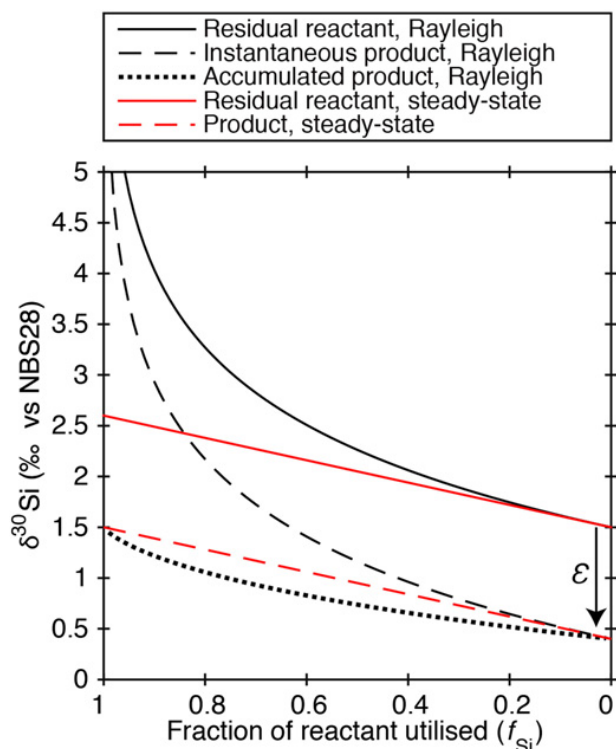
The effect of the discrimination of the heavier Si isotopes during DSi utilization by diatoms is described in *isotopic fractionation models*. Such models follow one of two approaches.

The first approach uses the Rayleigh model of isotope distillation and predicts the Si isotopes behavior in a closed system (see Box 1 and Figure 4). This model assumes a finite silicon reservoir without any external sources (De La Rocha et al., 1997). It is often used in systems with a limited

DSi source, such as well stratified lakes and oceans, where the evolution of the Si isotopic signature reflects DSi utilization. The more DSi is consumed, the smaller the fractionation  $\epsilon$  (Figure 4, black lines). The second approach is a steady-state model describing an open system where a continuous supply of DSi from the same external source is assumed (Varela et al., 2004) (see Box 1, Figure 4).

Lakes with high DSi concentrations and large BSi accumulation are considered to have an infinite pool, and hence the open system model is used. As the isotopic signature of BSi does not reflect the DSi utilization in open DSi-unlimited systems, the interpretation of stable Si isotopes in these cases includes more variables, such as DSi sources and in-lake processes. Therefore, knowledge of

current lake DSi and BSi concentrations is an important starting point for defining all variables potentially driving BSi accumulation and Si isotopic signatures.



**Figure 4:** Two fractionation models showing the evolution of the Si isotopic signature during the formation of BSi from DSi by organisms by Frings et al. (2016). On the  $x$ -axis is the fraction of DSi used from 1 to 0, where 1 represents the situation when no DSi is left in the system. The open system model is shown by red lines, whereas the Rayleigh closed system is in black. The  $y$ -axis shows the Si isotopic composition. The dashed lines represent the  $\delta^{30}\text{Si}$  BSi product, solid lines show the  $\delta^{30}\text{Si}$  of the residual DSi and the dotted line represents the accumulated product of the closed system model. The fractionation factor ( $\epsilon$ ) is the difference between the dashed and solid lines.

### 3.6 Current state of knowledge of lake Si budgets

Some lake sediments have a BSi concentration as high as 60 weight percent (wt%) of  $\text{SiO}_2$  (Frings et al., 2014b; Rosén et al., 2010), but no mechanism or pattern has been proposed for such high values. Frings et al. (2014b) demonstrated that surface sediment BSi concentration in lakes shows no correlation with pH, DSi concentration, lake size and depth, latitude, altitude, vegetation type or lithology. Nevertheless, high BSi accumulations tend to be found in high latitudes, low-nutrient lake systems (Rosén et al., 2010), which would require sufficient DSi concentration, low detrital input (Conger, 1942) and additionally limited dissolution and low competition by other organisms (Egge and Aksnes, 1992; Panizzo et al., 2016; Swann et al., 2010).

Stable Si isotopes have been used to constrain DSi utilization by diatoms and identification of DSi sources; however, only a limited number of studies on Si mass balances and/or stable Si isotopes in lakes have been published. Studies on Si mass balance have been done on Lake Superior and Lake Michigan in the USA (Johnson and Eisenreich, 1979; Schelske, 1985), Lake Tanganyika in the East African Rift (Alleman et al., 2005), Lake Kasumigaura in Japan (Arai and Fukushima, 2012), Lake Myvattn in Iceland (Opfergelt et al., 2011), and Lake Baikal in Russia (Panizzo et al., 2017). In addition, estimated mass balance of 34 lakes and reservoirs has been done on datasets from Frings et al. (2014b). However, from all of the studies mentioned above, only few include stable Si isotope balance.

Isotopic signature from fossil diatoms has been used as a proxy in oceanic and continental systems for changes in climate (De La Rocha et al., 1998; Hendry and Brzezinski, 2014; Opfergelt and Delmelle, 2012), changes in vegetation (Frings et al., 2016, 2014a; Leng et al., 2009; Sun et al.,

**Box 1: Silicon fractionation models****The Rayleigh model**

The Rayleigh model for closed systems describes the post-production DSi ( $\delta^{30}\text{Si}_{\text{postDSi}}$ ) as:

$$\delta^{30}\text{Si}_{\text{postDSi}} = {}^{30}\epsilon_{\text{DSi-BSi}} \cdot \ln(f_{\text{Si}}), \quad (7)$$

where  ${}^{30}\epsilon_{\text{DSi-BSi}}$  is the fractionation factor between the solid and the aqueous DSi isotopic signature and  $f_{\text{Si}}$  is the fraction of utilized DSi.

Furthermore, the accumulated BSi signature is modeled as (De La Rocha et al., 1997; Frings et al., 2016; Opfergelt and Delmelle, 2012):

$$\delta^{30}\text{Si}_{\text{BSi}} = \delta^{30}\text{Si}_{\text{in}} - \left( \frac{f_{\text{Si}}}{1 - f_{\text{Si}}} \right) \cdot {}^{30}\epsilon_{\text{DSi-BSi}} \cdot \ln(f_{\text{Si}}), \quad (8)$$

where  $\delta^{30}\text{Si}_{\text{in}}$  is the Si isotopic signature of the initial DSi before uptake (Mariotti et al., 1981).

**Steady-state model**

The open system model is used for systems with constant supply of DSi and the expected post-production  $\delta^{30}\text{Si}_{\text{postDSi}}$  is modeled as (Frings et al., 2016; Varela et al., 2004):

$$\delta^{30}\text{Si}_{\text{postDSi}} = {}^{30}\epsilon_{\text{DSi-BSi}} \cdot (1 - f_{\text{Si}}), \quad (9)$$

and the expected BSi signature  $\delta^{30}\text{Si}_{\text{BSi}}$  is calculated as:

$$\delta^{30}\text{Si}_{\text{BSi}} = \delta^{30}\text{Si}_{\text{in}} + {}^{30}\epsilon_{\text{DSi-BSi}} \cdot f_{\text{Si}}, \quad (10)$$

where  $\delta^{30}\text{Si}_{\text{in}}$  is the isotopic signature of the initial DSi source, and  ${}^{30}\epsilon_{\text{DSi-BSi}}$  is the fractionation factor. For marine diatoms,  ${}^{30}\epsilon_{\text{DSi-BSi}} = 1.1\text{‰} \pm 0.41\text{‰}$  (De La Rocha et al., 1997), whereas for freshwater diatoms,  ${}^{30}\epsilon_{\text{DSi-BSi}} = 1.61\text{‰}$  (Panizzo et al., 2016). Most paleoenvironmental studies use the fractionation factor of marine diatoms since there are few data for the fractionation factor by freshwater diatoms. Moreover, the species-specific fractionation is still discussed in the Si isotope community.

2011), and changes in DSi sources (Nantke et al., 2019; Vandevenne et al., 2015). Nevertheless, in lacustrine sediments the  $\delta^{30}\text{Si}_{\text{BSi}}$  method is still not widely used, with only a few published studies. These studies have shown that  $\delta^{30}\text{Si}_{\text{BSi}}$  in lake environments is related to processes in the watershed and to regional climate systems, e.g., Lake Victoria and Lake Edward in East Africa (Cockerton et al., 2015). Moreover, in-lake biogeochemical processes, such as diatom production and dissolution, were shown to drive the  $\delta^{30}\text{Si}_{\text{BSi}}$  in Lake Rutundu

(Street-Perrott et al., 2008) and Lake Huguangyan (Chen et al., 2012). In ultra-oligotrophic Lake El'gygytgyn,  $\delta^{30}\text{Si}_{\text{BSi}}$  reflects changes in nutrient supply directly linked to diatom DSi utilization (Swann et al., 2010).

Additionally, in the dammed river Changjiang, changes in  $\delta^{30}\text{Si}_{\text{BSi}}$  are related to the co-occurrence of clay mineral formation and seasonal diatom DSi uptake (Zhang et al., 2020). The complexity of long-term changes in the isotopic composition

and several simultaneous processes is also demonstrated in Lake Baikal (Panizzo et al., 2016).

Based on current knowledge of lake Si cycling, I investigate two lakes in this thesis for the key controlling factors, such as sedimentation rates, detrital input, continuous DSi sources, including groundwater and hydrothermalism that influence lake Si cycles in order to better constrain BSi accumulation.

### 3.6.1 Groundwater responsible for the high BSi accumulation

Groundwater is one of the poorly understood parts of lake systems, as measurements of groundwater discharges and chemistry are very complex. Submarine groundwater discharge is an important component in the ocean nutrient budget (Johannes, 1980; Moore, 2010; Null et al., 2012). High DSi concentrations have been identified in groundwaters worldwide (Georg et al., 2006a, 2009; Hurley et al., 1985; Luijendijk et al., 2020; Maavara et al., 2018). However, only a few studies on groundwater influences on lake and river Si cycle have been carried out, even though it has been shown that the contribution of groundwater input is substantial, especially into alpine and mountain lakes (Clow et al., 2003; Hood et al., 2006; Huth

et al., 2004; Liu et al., 2004). The distinctive characteristic of the influx of groundwater DSi into lakes compared to surface waters is the low amount of detrital material carried. Therefore, groundwaters can contribute to BSi accumulation by keeping the sedimentation undiluted by clastics.

The first task is to identify the presence of substantial groundwater into the lake. For this purpose, several methods can be used. Water mass-balance calculations have been used (Box 3), where all influxes and outfluxes were well constrained (Hood et al., 2006). A method of hydrograph separation using stable oxygen isotopes to identify the contribution of different end-members' inflowing water into a lake has been used in several mountain lakes (Huth et al., 2004; Liu et al., 2004). Additionally, silicon concentrations have been used to identify how much snow meltwater has been delivered through subsurface paths (Huth et al., 2004).

Another approach to track and quantify groundwater is to use  $^{222}\text{Rn}$  balance (Paper II) (Dimova et al., 2013). Radon is released from radium-bearing minerals present in bedrock, soils, and sediments. Released radon is the product of radioactive decay of  $^{226}\text{Ra}$ . Therefore, radon is more concentrated in subsurface waters compared to surface waters. A quantification of groundwater

#### Box 2: Groundwater quantification

##### Radon fluxes

Radon concentration measurements are used in Paper II for the construction of a radon mass balance and calculation of groundwater fluxes into the lake (Dimova and Burnett, 2011; Dimova et al., 2013). Radon ( $^{222}\text{Rn}$ ) is produced during the radioactive decay of  $^{226}\text{Ra}$ , which is present in rocks, soils, and sediments. Radon released from radium (Ra) bearing minerals enters the groundwater and is transported through aquifers. Groundwaters usually contain Rn concentrations orders of magnitude higher than surface waters. Thus, groundwater discharging into lakes can be detected by measuring the Rn in the lake water and end-members from sediment (the groundwater). Further, by using the steady-state  $^{222}\text{Rn}$ , mass balance the Rn enrichment of the lake water is quantified, as well as the groundwater flux (Burnett and Dulaiova, 2003; Dimova and Burnett, 2011; Dimova et al., 2013).

influx is then calculated by radon mass balance knowing all radon sources and sinks (Box 2; Dimova and Burnett, 2011).

### 3.6.2 Hydrothermalism as a driver of high BSi accumulation

One of the study sites is the silicon-rich volcanic Yellowstone Lake, partly situated in the Yellowstone Caldera, which was formed by the last cataclysmic eruption 640 000 years ago (Christiansen, 2001). The Yellowstone Plateau Volcanic Field is still active mainly with on-land hydrothermalism (Hurwitz and Lowenstern, 2014).

However, two types of sublacustrine hydrothermal vents have been found within Yellowstone Lake (Balistrieri et al., 2007; Fowler et al., 2019b; Gemery-Hill et al., 2007; Morgan et al., 2003; Shanks et al., 2007). One of the vent systems in the west of Yellowstone Lake is of neutral to alkaline chemistry, and those vents bring high DSi concentration ( $\sim 200 \text{ mg SiO}_2 \text{ l}^{-1}$ ) water into the lake (Fowler et al., 2019b). The other venting system in the northern part of the lake is of acidic, steam-heated character, and does not contribute much to the lake Si budget (Fowler et al., 2019a).

Steam vents have a fluid chemistry close to the lake chemistry, which suggests that the steam heats up groundwater or pore water in the sediment, and those fluids are percolating upwards through the sediment and subsequently mix with the lake bottom waters. Those vents bring fluids with a DSi concentration of around  $15 \text{ mg SiO}_2 \text{ l}^{-1}$  (Fowler et al., 2019a).

A result of the combination of on-land hydrothermal vents feeding lake tributaries with the sublacustrine hydrothermalism and the weathering of the silica-rich bedrock in the watershed is that the DSi concentration of Yellowstone Lake is high, around  $12 \text{ mg SiO}_2 \text{ l}^{-1}$  (Balistrieri et al., 2007; Gemery-Hill et al., 2007), which is above the

world's river mean (Frings et al., 2016). Those increased DSi concentrations are responsible for unlimited diatom growth and limited dissolution of diatom valves, which together create favorable conditions for massive BSi accumulation. The Yellowstone Lake system demonstrates the importance of hydrothermalism for diatom-rich sedimentation. However, studies on sublacustrine hydrothermalism and its impact on Si budgets are very sparse. To untangle the sources of DSi in Yellowstone Lake, a trace element, germanium, is used together with silicon to identify the relative importance of processes, such as hydrothermalism or weathering of bedrock in the watershed.

### 3.6.3 Using germanium as a trace element

Germanium (Ge) is a trace element, which mimics the behavior of Si in natural processes. Due to the very similar atom ionic sizes, covalent Si-O and Ge-O bond lengths, and identical outer electronic structures, Ge behaves like stable Si isotopes (Froelich et al., 1992). Similarly to DSi, dissolved Ge (DGe) originates ultimately from silicate rock weathering (Froelich et al., 1989). Ge/Si ratios are used as a tracer of sources and silicon behavior in exogenic processes, such as chemical weathering, biological uptake or secondary mineral formation (Froelich et al., 1992; Kurtz et al., 2002, 2011; Murnane and Stallard, 1990). The Ge/Si ratios characteristic for bedrock range between 1.5 and  $6.8 \mu\text{mol/mol}$  (Mortlock and Frohlich, 1987; Tribovillard, 2013), the riverine Ge/Si ratios are within a range of 0.1 to  $1.3 \mu\text{mol/mol}$ , and hydrothermal fluids have Ge/Si ratios ranging from 2 to  $1000 \mu\text{mol/mol}$  (Arnórsson, 1984; Evans and Derry, 2002; Mortlock et al., 1993).

Because of the large difference between riverine and hydrothermal Ge/Si ratios, Ge/Si ratios have a high potential to trace hydrothermal inputs. However, to distinguish processes driving changes in Ge/Si ratios, where both hydrothermalism and

**Box 3: Balance models**

The effect of lakes on the Si cycle can be quantified through BSi accumulation, where mass balance is used to quantify all Si fluxes and BSi sinks. DSi is brought by rivers and tributaries, as well as by groundwater. Diatoms form BSi, which is partly preserved in the sediment. The flux of BSi into the sediment is a sign of higher DSi influxes relative to outfluxes. To constrain DSi fluxes, the water balance must be constructed prior to the Si mass balance. When the lake water balance is in steady-state, the Si mass balance can be calculated. The lake water (eq. 11) or DSi mass balance (eq. 12) is calculated using balance equations:

$$\Delta V = Q_{in} + Q_{GWin} + P - Q_{out} - Q_{GWout} - E, \quad (11)$$

where  $\Delta V$  is the change in lake water volume,  $Q_{in}$  is stream inflow,  $Q_{GWin}$  is groundwater inflow,  $P$  is precipitation,  $Q_{out}$  is stream outflow,  $Q_{GWout}$  is out-flowing groundwater, and  $E$  is evaporation. Groundwater can be replaced or complemented with hydrothermal fluid discharges.

The DSi flux is calculated as  $F = Q \cdot c$ , where  $Q$  is discharge and  $c$  is DSi concentration. The DSi balance is then calculated as:

$$\Delta DSi = F_{in} + F_{GWin} - F_{out} - F_{GWout} - F_{BSi}, \quad (12)$$

where  $\Delta DSi$  is the change of lake DSi,  $F_{in}$  is the stream DSi influx,  $F_{out}$  is the stream DSi outflux,  $F_{GWin}$  is the incoming groundwater DSi flux, and finally  $F_{GWout}$  is the DSi outflux via groundwater. Groundwater fluxes can be replaced or complemented with hydrothermal fluid fluxes.  $F_{BSi}$  is flux of BSi into the sediment calculated as:

$$F_{BSi} = SR \cdot \rho_{dry} \cdot BSi \text{ wt}\%, \quad (13)$$

where  $SR$  is sedimentation rate,  $\rho_{dry}$  is dry bulk sediment density, and  $BSi \text{ wt}\%$  is the BSi concentration in sediment.

A positive Si mass balance is defined as  $F_{BSi} > 0$ , which occurs in condition where  $F_{in} > F_{out}$ . Hence, if steady-state is reached,  $\Delta DSi = 0$ .

Based on the water and Si mass-balance models, stable Si isotope balance models (Section 3.5) can be used to calculate the DSi utilization, the DSi source isotopic composition or the BSi isotopic composition, depending on known variables.

clay mineral formation show enrichment in Ge, stable Si isotopes are used. The stable Si isotopes are typically isotopically lighter in hydrothermal fluids compared to the remaining DSi after clay mineral formation; therefore, the processes responsible for the Ge/Si ratio and  $\delta^{30}\text{Si}$  signature

can be identified. A combination of these two proxies is a useful tool for studying the influence of hydrothermal inputs into Yellowstone Lake. Additionally,  $\delta^{30}\text{Si}$  combined with Ge/Si in diatom frustules has the potential to identify the relative proportion of the effects of diatom production

versus hydrothermal inputs on the diatom isotopic signature.

## 4 Methods

### 4.1 Dissolved silicon

Silicon dissolved in water is present as orthosilicic acid ( $\text{H}_4\text{SiO}_4$ ), with an assumption that most of the DSi is a monomer. Polymerization occurs only at extreme pH and temperatures (Dietzel, 2000; Wonisch et al., 2008) and in the presence of a high concentration of organics (Coradin and Livage, 2001). Therefore, natural samples from organic-rich environments or hydrothermal fluid samples with extreme pH, both high and low, and extreme temperatures need to be treated cautiously in order to deliver accurate DSi concentrations. Water samples measured in this thesis originate from oligotrophic lakes and streams, therefore, the risk of polymerization is low. Hydrothermal vent fluid were sampled by a specialized sampling system developed by Wu et al. (2011) and diluted to lower DSi concentrations (described in Fowler et al. (2019a,b) to prevent effects of fractionation during the sampling process.

All river and lake water samples were filtered directly in the field through a  $0.45\ \mu\text{m}$  cellulose Sterivex™-HV Durapore filter and acidified with HCl to pH 2 in the laboratory before the analysis of DSi concentrations. An automated molybdate-blue method (Grasshoff, 1999; Hansen and Grasshoff, 1983) was used for DSi measurements with a Smartchem 200 (AMS System) discrete analyzer with an instrumental error of  $\pm 3.7\%$ . The molybdate-blue method is based on the reaction of monomeric silicic acid with ammonium molybdate forming a yellow molybdosilicic acid complex. This complex is reduced from Mo(IV) to Mo(V) by ascorbic acid to heteropoly-molybdenum, which is measured

spectrophotometrically at 660 nm.

### 4.2 Sedimentary biogenic silica

The quantification of BSi is done through a conversion of BSi into DSi via weak-alkaline extraction (Conley and Schelske, 2001; DeMaster, 1981). This method is based on slower dissolution rates of minerals compared to the dissolution rates of BSi in a weak alkaline reagent. Thus, the extraction is done by digesting 30 mg of freeze-dried homogenized sediment in  $0.1\ \text{M}\ \text{Na}_2\text{CO}_3$  for 5 hours with sub-sampling of 0.1 ml after 3, 4, and 5 hours.

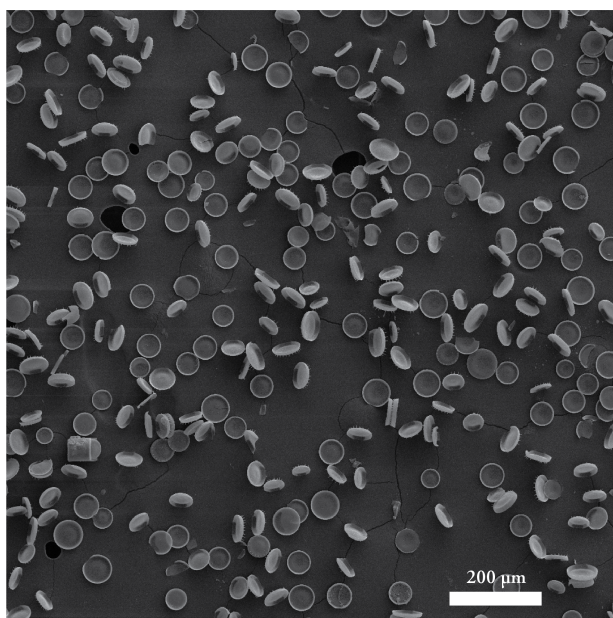
A limited number of samples ( $\sim 5\%$ ) was tested for dissolution of  $\text{SiO}_2$  by prolonged digestion over 24 hours with sub-sampling after 3, 4, 5, 9, 10, 11, 20, 22, and 24 hours of the digestion. Based on those samples, no distinguishable minerogenic  $\text{SiO}_2$  dissolution occurred during the digestion. Therefore, weight percentages of biogenic  $\text{SiO}_2$  were calculated as the mean value of extracted  $\text{SiO}_2$  during the first five hours. DSi concentrations were measured as described in Section 4.1.

### 4.3 Stable silicon isotopes

#### 4.3.1 Sample preparation

Stable silicon isotope analyses are done on pure diatoms, opaline silica materials, or waters. To gain clean diatoms, secondary minerals, organic matter, and carbonates have to be removed from the sample by a combination of chemical, physical, and mechanical separations. Organic matter and carbonates are removed using  $33\%$   $\text{H}_2\text{O}_2$  and  $5\%$  to  $30\%$  HCl, respectively (Morley et al., 2004). The mineral fraction is separated by using density differences between the mineral fraction ( $2.6\ \text{g cm}^{-3}$ ) and the biogenic silica ( $2.0\ \text{g cm}^{-3}$ ). The method of heavy liquid separation using sodium polytungstate at densities of 2.05 to

$2.1 \text{ g cm}^{-3}$  is used to separate the floating opaline silica from the settled mineral fraction. Clusters of secondary minerals often have similar densities as biogenic silica. Therefore, 0.05 M sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) is used to disintegrate fine grain-size clay clusters, and the sample is then sieved at 53 and/or 25  $\mu\text{m}$  for the final removal of clay particles (grain size  $< 53 \mu\text{m}$ ). The sample purity is always confirmed by using first light microscopy and further by using a scanning electron microscope (SEM) (Figure 5) with the possible extension of energy-dispersive X-ray spectroscopy (EDS) to map possible contaminants.



**Figure 5:** An example of cleaned diatoms from Yellowstone Lake

Cleaned opaline material – diatoms – is transformed into solution by dissolution in 0.5 to 1 ml of 0.4 M NaOH (analytical purity) at 50 °C for at least 48 hours. After 48 hours of dissolution, samples are diluted with Milli-Q® water to prevent amorphous silica precipitation and artificially caused fractionation. The samples are further neutralized by 0.5 to 1 ml of 0.4 M suprapur® HCl. The DSi concentration of the produced solutions is analyzed (Section 4.1) to obtain Si recovery, which must be between 90 and 100 %.

Water samples are usually filtered directly in the field and later acidified to prevent any processes causing fractionation. For most of the water samples no additional cleaning is needed. Only samples with excessive concentrations of sulfates or chlorides must be additionally pre-cleaned by using anion-chromatographic separation (Gaspard et al., 2020) or overcome by doping with  $\text{H}_2\text{SO}_4$  before isotope measurements (Chen et al., 2020; Hughes et al., 2011; Oelze et al., 2016).

Sample solutions are further purified before silicon analysis by a cation-chromatographic separation, which removes any contaminants left and results in a solution of pure Si (Georg et al., 2006b). The international Si standard NIST reference material RM-8546 (former NBS-28) and the laboratory standard Diatomite are both cleaned along the sample purification to constrain the cleaning process, and full chemical column blanks are also included.

#### 4.3.2 Silicon isotopic composition determination

Stable Si isotopes are commonly measured by multi-collector inductively coupled plasma mass-spectrometers (MC-IPC-MS, Box 4). Our measurements were performed on a NuPlasma (II) HR MC-ICP-MS (Nu Instruments™) in dry plasma mode using an Apex HF desolvation nebulizer at the Vegacenter, Swedish Museum of Natural History, Stockholm.

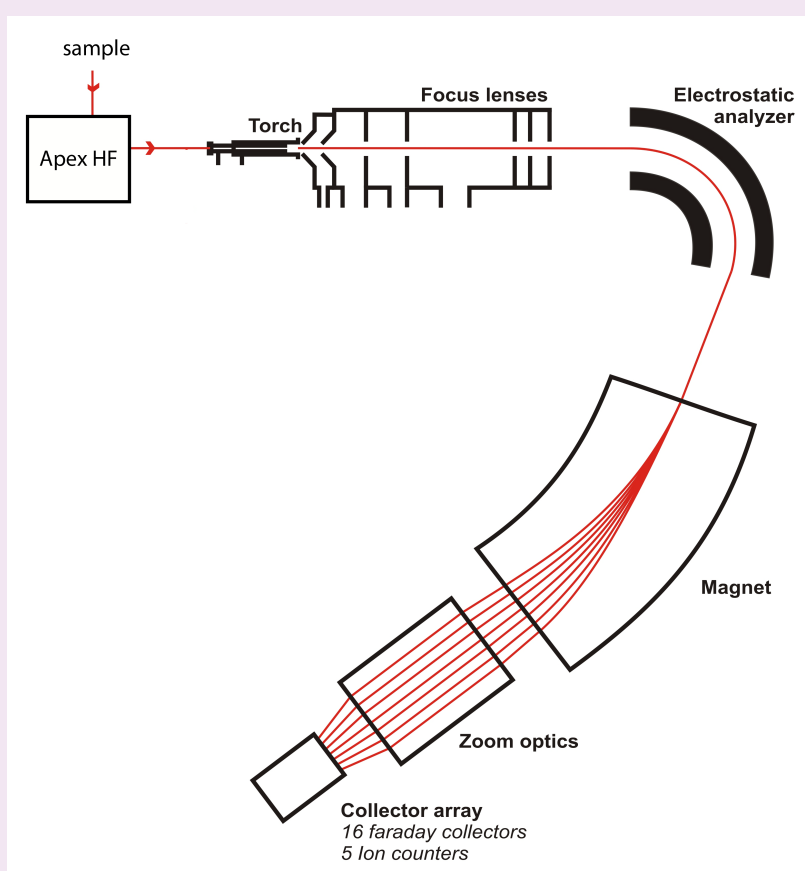
All samples were spiked with Li to match the standard matrix (see Box 5). The instrumental mass bias is constrained by using the sample–standard bracketing technique. The  $^{28}\text{Si}$  signal of full procedural blanks is always determined in order to identify possible sample contamination.

Silicon isotopes data are reported as deviations of  $\frac{^{30}\text{Si}}{^{28}\text{Si}}$  and  $\frac{^{29}\text{Si}}{^{28}\text{Si}}$  from the RM-8546 in ‰, denoted  $\delta^{30}\text{Si}$  as shown in equation 2. Full chemical sample



**Box 4: MC-ICP-MS**

**Multi-collector inductively-coupled plasma mass-spectrometers** are nowadays commonly used for Si isotope measurements. The principal mechanisms behind the measurements are that a solution is introduced, in our case through Apex HF, into an inductively-coupled plasma created by a torch, where electrons are removed and positively charged ions are formed. These ions are accelerated across an electrical potential gradient up to 10 kV, focused into a beam using a series of slits and focus lenses, and passed through an energy filter (electrostatic analyzer). A consistent energy spectrum is created by the energy filter and further passes through a magnetic field, which separates ions based on their mass-to-charge ratio. Finally, the beams of sorted ions are collected by multiple collectors simultaneously, where the ions are converted to voltage. The isotope ratios are then calculated by comparing voltages from different collectors.



A simplified scheme of MC-ICP-MS NuPlasma instrument in Vegacenter, Swedish Museum of Natural History, Stockholm. Modified from the original Vegacenter scheme (Vegacenter, 2020).

replicates are measured in order to determine the natural variability of the sample, whereas analytical replicates are used to quantify the measurement deviation.

**Box 5: Standard preparation**

The sample isotopic ratio is always normalized to a standard material. Therefore, the international Si standard NIST reference material RM-8546 (former NBS-28), as well as laboratory standards are prepared via NaOH fusion (Georg et al., 2006b).

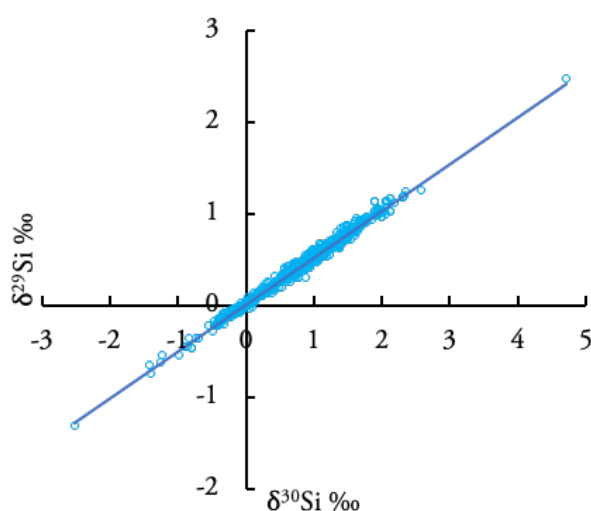
Another way of standard preparation is used in the Vegacenter facilities, where Si isotopes were measured. The laboratory standards IRMM-018, Big-Batch, Diatomite, and the international Si standard RM-8546 were prepared by fusion with  $\text{LiBO}_2$  (Sun et al., 2010), and thus the standard matrix contains Li.

Therefore, our alkaline NaOH fused RM-8546 and Diatomite standards, cleaned along with the sample purification, were matrix matched to contain  $3 \text{ mg l}^{-1}$  Li IPC-MS standard. Similarly, all purified samples were diluted to a concentration of  $3 \text{ mg l}^{-1}$  of Si in a 0.12 M Seastar™ HCl matrix and doped with Li to contain  $3 \text{ mg l}^{-1}$  of Li to match the Vegacenter standard matrix.

A three-isotope plot  $\delta^{30}\text{Si}$  vs  $\delta^{29}\text{Si}$  is used to ensure that there are no polyatomic interferences present during mass spectrometry measurements. All measured samples should fall on the expected mass-dependent fractionation line with a slope of 0.5092 (Figure 6, Reynolds et al., 2007).

The secondary reference materials Diatomite, Big-Batch, and IRMM-018 are measured throughout all measuring sessions. Our measuring sessions (over 3 years) resulted in means of  $\delta^{30}\text{Si} = 1.26 \pm 0.19 \text{ ‰}$  ( $2\text{SD}_{\text{repeated}}$ ,  $n = 219$ ) for Diatomite,  $\delta^{30}\text{Si} = -10.64 \pm 0.18 \text{ ‰}$  ( $2\text{SD}_{\text{repeated}}$ ,  $n = 77$ ) for Big-Batch, and  $\delta^{30}\text{Si} = -1.77 \pm 0.18 \text{ ‰}$  ( $2\text{SD}_{\text{repeated}}$ ,  $n = 100$ ) for IRMM-018. All secondary reference material values are in good agree-

ment with values from previous inter-laboratory comparisons (Reynolds et al., 2007). The reproducibility and repeatability of all samples is 0.2 ‰. In the Vegacenter laboratory long-term precision was determined to be 0.15 ‰ (expressed as 2SD).



**Figure 6:** Three-isotopes plot of all Si isotope measurements in this thesis. Data plotted without error bars, however, all data follow the expected mass-dependent fractionation line with slope 0.5092 (blue line) (Reynolds et al., 2007),  $\delta^{29}\text{Si} = 0.51 \cdot \delta^{30}\text{Si}$ ,  $R^2 = 0.99$ ,  $n = 986$ .

**4.4 Ge/Si ratios determination**

Ge/Si mole ratios can be determined using several techniques, but in general, concentrations of DGe and DSi are measured, and the Ge/Si ratios are calculated from those values. To measure Si concentrations, the molybdate-blue method can be used, as well as inductively-coupled plasma-optical emission spectrometry (ICP-OES) or inductively-coupled plasma mass spectrometry (ICP-MS). Due to its low natural abundance, germanium needs to be measured by an ICP-MS through measuring the most abundant  $^{74}\text{Ge}$  isotope (35.9%). In case of measuring both DSi and DGe concentrations on an ICP-MS, the two

isotopes  $^{74}\text{Ge}$  and  $^{29}\text{Si}$  are monitored. Polyatomic interferences (e.g.,  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$  on  $^{74}\text{Ge}$ ) are removed by a collision cell with He as reaction gas. Then, the Ge/Si ratios are calculated directly from the ratio of beam intensities.

#### 4.5 Total organic carbon and nitrogen – TOC and TN

Total organic carbon (TOC) and total nitrogen (TN) analyses are used to better constrain the sediment composition by quantification of organic matter (Papers II, III, and IV). To measure TOC and TN, a COSTECH ECS4010 elemental analyzer was used. Samples of dried homogenized sediment are packed in tin capsules and introduced into an ignition chamber, where the capsules are combusted. During this combustion, nitrogen and carbon gasses are released and carried by a carrier gas (He) to a pre-packed reaction column. The pre-packed column contains copper wires to remove any oxygen which was not consumed during the initial combustion and converts any oxides of nitrogen into  $\text{N}_2$  gas. Further, the de-oxidized gasses pass through a gas-chromatographic (GC) column placed in an oven and heated up; thus the carbon and nitrogen are separated. After the separation, the C and N are quantified by a thermal conductivity detector. TOC and TN are measured simultaneously and the C/N ratio is calculated to identify the organic matter source (Meyers, 2003).

If a sediment contains calcium carbonate, the TOC measurements would be biased. Therefore, samples are tested for carbonate ( $\text{CaCO}_3$ ) content by comparing bulk sediment TOC with the de-calcified replicate. The de-calcification is done before the TOC measurements by adding HCl and heating to  $60^\circ\text{C}$  in silver capsules (Brodie et al., 2011). Both replicates are measured, and the carbonate content is calculated as the difference in TOC between the de-calcified sample and the bulk sample.

#### 4.6 ITRAX $\mu\text{X}$ -ray fluorescence – XRF

All long cores (Papers III and IV) were scanned by ITRAX  $\mu\text{XRF}$  analyzer using the X-Ray Fluorescence principle. The technique of X-Ray Fluorescence is used to determine the elemental composition of sediment. The principle of this method is to expose the sediment to X-rays, which causes ionization of the atoms, excitation of electrons from the atomic inner orbit. When an electron is excited, the atom becomes unstable, and electrons from higher orbitals must stabilize the atom by filling the gap left by the excited electron. As these electrons are moving from higher energy orbitals to lower ones, the excessive energy is released in the form of photons. The energy released is equal to the energy difference between two orbitals, which is element-specific, and thus, the element is identified. The ITRAX is an automated multi-function core-scanning instrument recording elemental variations in the sediment cores with a resolution of up to  $100\ \mu\text{m}$ . We have used data from X-ray-fluorescence analysis and from the integrated magnetic susceptibility sensor to constrain the detrital input through the elements Ti and Fe or through magnetic susceptibility (Davies et al., 2015). Ti and Fe are elements released during bedrock weathering and are part of the minerals brought by rivers or run-off into the sedimentary basins. Further, elements such as Cl and As, which are characteristic for some hydrothermal fluids in Yellowstone Lake (Balistrieri et al., 2007; Gemery-Hill et al., 2007; Shanks et al., 2007), were used for detection of past hydrothermal activity.

## 5 Summary of papers

### Paper I

Zahajská, P., Opfergelt, S., Fritz, S. C., Stadmark, J., & Conley, D. J. (2020). *What is diatomite?* *Quaternary Research*, Vol. 96, pp. 48–52. doi:10.1017/qua.2020.14

Widespread inconsistencies in the use of the word “diatomite” in the literature were the motivation for bringing clarity into diatom-rich sediment nomenclature. In order to stimulate scientific dis-

cussion and communicate our research efficiently, a clear definition of diatom-rich sediment was proposed.

Paper I is a literature review on sediment nomenclature and suggests unification of variability in the naming of diatom-rich sediment. We defined the principal name diatomite to be used for a siliceous/opaline consolidated sediment composed of more than 50 % of diatom biogenic silica, with a porosity higher than 70 % and formed in temperatures below 50 °C and at burial depths of 0 to 600 m. The stand-alone word *diatomite* is used

Table 1: Authors' contribution to the papers

	Paper I	Paper II	Paper III	Paper IV
Planning and study design	P. Zahajská, D. J. Conley	P. Zahajská	P. Zahajská	P. Zahajská, D. J. Conley
Literature review	P. Zahajská	n/a	n/a	n/a
Fieldwork and data collection	n/a	P. Zahajská, C. G. Olid	P. Zahajská	P. Zahajská, R. Cartier, D. J. Conley, S. Fritz, HD-YLake team*
Labwork, sample preparation	n/a	P. Zahajská, C. G. Olid	P. Zahajská	P. Zahajská, R. Cartier
Analysis	n/a	P. Zahajská, C. G. Olid	P. Zahajská	P. Zahajská, F. Gaspard, P. Frings
Figures	P. Zahajská	P. Zahajská	P. Zahajská	P. Zahajská, R. Cartier, L. Morgan*
Data interpretation and discussion	All authors	All authors	All authors	All authors
Lead author(s)	P. Zahajská	P. Zahajská, C. G. Olid	P. Zahajská	P. Zahajská
Comments and editing of manuscript	All authors	All authors	All authors	All authors

\* contributors who are not co-authors

specifically for sediment composed of more than 80 % of diatom biogenic silica.

Unconsolidated sediments with a content higher than 50 % of diatom biogenic silica are called *diatomaceous ooze*. Consolidated sediments with a content of diatom biogenic silica from 10 to 50 % are called *diatomaceous sediment* combined with the prevailing sediment name. Burial depth, low temperatures and diatom content are three main classifiers in the naming of diatom-rich sediment.

Paper I aims to bring awareness about the inconsistencies in terminology used for diatom-rich sediment and proposes a solid classification system.

## Paper II

Zahajská, P., Olid, C. G., Stadmark, J., Fritz, S. C., Opfergelt, S., & Conley, D. J. (2020). *Modern silicon dynamics of a small high-latitude subarctic lake*. *Biogeosciences Discuss., in review*. doi:10.5194/bg-2020-441

Several lakes in northern Sweden have high BSi concentrations, up to 60 wt% (Frings et al., 2014b; Rosén et al., 2010). Paper II focuses on finding the sources of the silica and conditions leading to diatom-rich sedimentation in a small, high-latitude subarctic lake. Factors responsible for the high BSi concentration in the sediment (up to 46 wt% of SiO<sub>2</sub>) of Lake 850 are explored using water, Si, and stable Si isotope mass-balance models.

The water balance revealed the importance of groundwater supply, which was quantified by using a <sup>222</sup>Rn mass-balance model. Strong seasonality in the stream inlets and outlet was observed. The water balance models showed lake-level changes of ± 0.95 m annually due to the seasonality of inputs, despite the presence of groundwater supply. Additionally, the water and Si mass-balance models suggest that groundwater brings three times more water and DSi into the

lake than the ephemeral stream inlets. The Si and stable Si isotope mass balances revealed groundwater input to be a potential Si source for diatom production.

Furthermore, sedimentation rates of 0.08 cm yr<sup>-1</sup> and high diatom preservation suggest low residence time of diatoms in the water column, which results in high BSi accumulation. When including all sources and the total BSi burden into the mass- and Si isotopic model, diatom production consumes up to 79 % of the lake DSi. The stable Si isotopic signature of sediment diatoms reflects the DSi sources and diatom production. Groundwater supply and mass accumulation rates justify the good preservation of diatoms in the sediment. BSi accumulation during the last 150 years is driven by sufficient DSi supply with relatively light isotopic signature and by accumulation rates, which are responsible for good diatom preservation.

## Paper III

Zahajská, P., Cartier, R., Fritz, S. C., Stadmark, J., Opfergelt, S., Yam, R., Shemesh, A. & Conley, D. J. *Impact of Holocene changes in climate on silicon cycling in Lake 850, Northern Sweden*. Submitted to *The Holocene*, 2021.

Although the continental silicon cycle has been intensively studied during the last 20 years, the diatom δ<sup>30</sup>Si records from lake sediments are still sparse. Moreover, the interpretation of those data is usually complex and site specific. The individual factors driving changes in lake DSi concentrations are often poorly understood. The study in Paper III contributes to the understanding of the functioning of continental silicon cycle sinks on long-term scales.

Diatoms have a high preservation potential and their frustules carry an isotopic signature of the source DSi. Climate, diatom productivity, DSi availability, detrital input, and weathering rates are potential factors influencing the variability in

diatom BSi deposits.

In Paper III the Holocene variability in BSi deposits and their stable Si isotopes in Lake 850 are studied to identify factors driving diatom-rich sediment formation. Stable silicon isotopes were used as a tracer of changes in DSi sources and processes in the last 9400 cal. yr BP. Changes in sedimentation due to allochthonous detrital input were identified through sediment elemental composition.

Paper III suggests that the lake was mainly influenced by changes in summer temperatures and by hydrological fluctuations during the last 9400 cal. yr BP. The diatom  $\delta^{30}\text{Si}$  in Lake 850 suggests the presence of a sufficient, isotopically light DSi source, such as groundwater or freshly weathered primary minerals. Moreover, the  $\delta^{30}\text{Si}$  shows a linkage to changes in regional climate, where lighter isotopic values coincide with continental climate during the mid-Holocene, and a heavier Si isotopic signature shows a connection to the oceanic climate in the early and late Holocene. The BSi accumulation ranges between 0.28 and 1.50 mg cm<sup>2</sup> yr<sup>-1</sup> of SiO<sub>2</sub> during the Holocene. Good preservation, where sedimentary diatoms show no sign of dissolution, combined with low sedimentation rates induced by low detrital input leads to a BSi concentration as high as 42 wt% of SiO<sub>2</sub>. However, correlations of proxies showed that both the BSi concentrations and the  $\delta^{30}\text{Si}$  values result from several concurrent processes.

## Paper IV

Zahajská, P., Frings, P., Gaspard, F., Cartier, R., Opfergelt, S., Fritz, S. C., Stadmark, J., & Conley, D. J. *Impact of Holocene sub-lacustrine hydrothermal activity on the Si cycle and diatom-rich sediment accumulation in Yellowstone Lake. Manuscript.*

Yellowstone Caldera is one of the largest active silicic volcanoes in the world (Mason et al.,

2004). Yellowstone Lake is situated within the Yellowstone Caldera, which results in lake water enriched in DSi compared to other freshwater environments. The elevated DSi concentrations are driving diatom production, which results in sedimentary BSi.

Sub-lacustrine hydrothermal activity has previously been identified in Yellowstone Lake, and Paper IV is focusing on the impact of hydrothermal events on the lake Si cycle and diatom BSi accumulation. Stable silicon isotopes ( $\delta^{30}\text{Si}$ ) together with Ge/Si ratios are used to study a single fossil diatom species *Stephanodiscus yellowstonensis*, as well as recent water DSi sources. Recent lake water, tributaries, and hydrothermal vent fluids samples were studied to better constrain the impact of Holocene hydrothermal events on the sedimentary BSi record.

An undisturbed deep basin sedimentary record and a hydrothermally affected record were both studied for their elemental composition, BSi concentration,  $\delta^{30}\text{Si}$ , and Ge/Si ratios. A series of hydrothermal explosions and the Mazama ash layer originating from the Mazama volcano explosion (~7700 cal. yr BP) were present in both studied cores, and, together with lithological units (Tiller, 1995), those were used for correlation between the two cores.

The hydrothermal explosions showed no identifiable impact on BSi accumulation,  $\delta^{30}\text{Si}$  signature, and thus on the lake DSi budget. Both cores show several similarities, which suggest a stable and homogeneous DSi source within the entire lake. Additionally, the ranges of  $\delta^{30}\text{Si}$  and Ge/Si values of the diatom *Stephanodiscus yellowstonensis* suggest that the productive layer of the lake where the diatoms live was well mixed and biogeochemically very stable, with a large hydrothermal background, which limits the impact of most of the disturbances during the last 9800 cal. yr BP. BSi, stable Si isotopes, Ge/Si ratios, the elemental composition of the sediment and lithology data

all suggest that Yellowstone Lake is a stable, well-buffered system on long timescales.

The variation of BSi is partly connected to changes in production reflected in the  $\delta^{30}\text{Si}$  fossil diatom record. However, the variation in the  $\delta^{30}\text{Si}$  likely shows changes in the relative proportion of DSi sources (hydrothermal to rivers) combined with effects of production and potentially dissolution. All those processes occur concurrently.

A shift of 0.6 ‰ toward heavier  $\delta^{30}\text{Si}$  throughout both cores reflects changes in diatom production associated with changes in Holocene climate, specifically summer temperatures and lake water column mixing. An alternative explanation of this systematic isotopic shift toward heavier  $\delta^{30}\text{Si}$  is a gradual shift in the relative proportion of hydrothermal DSi input and riverine DSi supply. Relatively larger contribution of heavier  $\delta^{30}\text{Si}$  brought by increased run-off from watershed could explain the trend in  $\delta^{30}\text{Si}$ . Likely both explanations are plausible.

These results illustrate that hydrothermal activity has a significant impact on the lake Si cycle and on BSi accumulation. However, hydrothermal explosions are masked by the high long-term hydrothermal background inputs to the lake. Long-term stability of large lake systems, such as Yellowstone Lake, results in a significant sink of Si in the Si cycle; however, quantification of those sinks is still needed for improved understanding of the global Si cycle.

## 6 Discussion

### 6.1 Diatomite in society

Diatomite is a widely used word, as well as a material used in everyday production. Due to its high porosity, large surface area, high permeability, and chemical inertness, diatomite is used for filtering

inorganic and organic chemicals, pharmaceuticals, but also beer, wine, whiskey, and fruit and vegetable juices (Inglethorpe, 1993). Diatomite filtering removes fine-grained particles from fluids. There are many other industrial applications of diatomite, such as fillers, insulators, abrasives, fertilizers or absorbent powders with potential use for heavy metals and oil water contamination removal (Bakr, 2010). Thus, diatomite is of great importance for society. But what is diatomite actually? Materials used in those industrial processes are sediments with more than 80 % of diatoms.

When investigating diatom-rich sediment formation, a clear definition of the sedimentary content of diatom  $\text{SiO}_2$  is needed. In order to draw general conclusions about what factors are crucial for diatom-rich sediment formation, the comparison of several sedimentary records is essential. Inconsistencies in the present use of the term diatomite and diatomaceous sediment throughout literature were the motivation to clarify nomenclature.

Paper I describes the inconsistency of usage of the word diatomite in the scientific literature and suggest a classification of consolidated and unconsolidated diatom-rich sediments.

### 6.2 Constraining the modern Si cycle in lakes

Estimates of the global Si fluxes usually require simplification or assumptions due to the lack of data on lakes and rivers, which introduces high uncertainties into models of Si dynamics. Stable Si isotopes can be used to constrain the DSi utilization by processes within the lake and the watershed. Building a detailed Si or Si isotope mass-balance model requires monitoring data on discharge, DSi concentration, and  $\delta^{30}\text{Si}$  from all inlets and outlets, as well as lake water. Moreover, other elements, such as sulfur, chloride or sodium are important to monitor, as those elements can

modify the  $\delta^{30}\text{Si}$  if they are not removed from the matrix (Hughes et al., 2011). An important part of Si and Si isotope mass-balance models is to test the presence of additional DSi sources, such as groundwater, hydrothermal input or dissolution of secondary minerals. Groundwater and hydrothermal vents were investigated in our studies on Lake 850 (Paper II) and Yellowstone Lake (unpublished data, Figure 8).

Additionally, knowledge about BSi production and accumulation is also essential for building a mass balance. Finally, processes, such as clay mineral formation or dissolution, can also play an important roles in the Si budget. Information about the bathymetry and annual lake volume dynamics is needed in order to quantify water and DSi residence times. With all these data, a very detailed model describing the lake system and its functioning can be constructed and forecasting of BSi accumulation or release can be calculated. In the case of missing data, they can be modeled, which brings uncertainties into the mass balances. In this thesis, I have constrained most of the factors and processes influencing the DSi and BSi variation, and I modeled missing data, as suggested above.

Previous Si mass balances have been constructed on Lake Michigan and Lake Superior (Schelske, 1985), the African Great Lakes (Hecky et al., 1996), Williams Lake (LaBaugh et al., 1995), Lake Kasumigaura (Arai and Fukushima, 2012), and many more (Frings et al., 2014b); however, only some of those studies constrained all the influxes and outfluxes, as we did in our study (Paper II). Based on our results, the mass balances need to be conducted cautiously, as all DSi sources need to be constrained to evaluate whether the lake acts as Si sink or source.

Studies on Si isotope mass balances are more sparse and have been conducted on Lake Baikal (Panizzo et al., 2017), Lake Tanganyika (Alleman et al., 2005), and lakes of the Taupo Volcanic

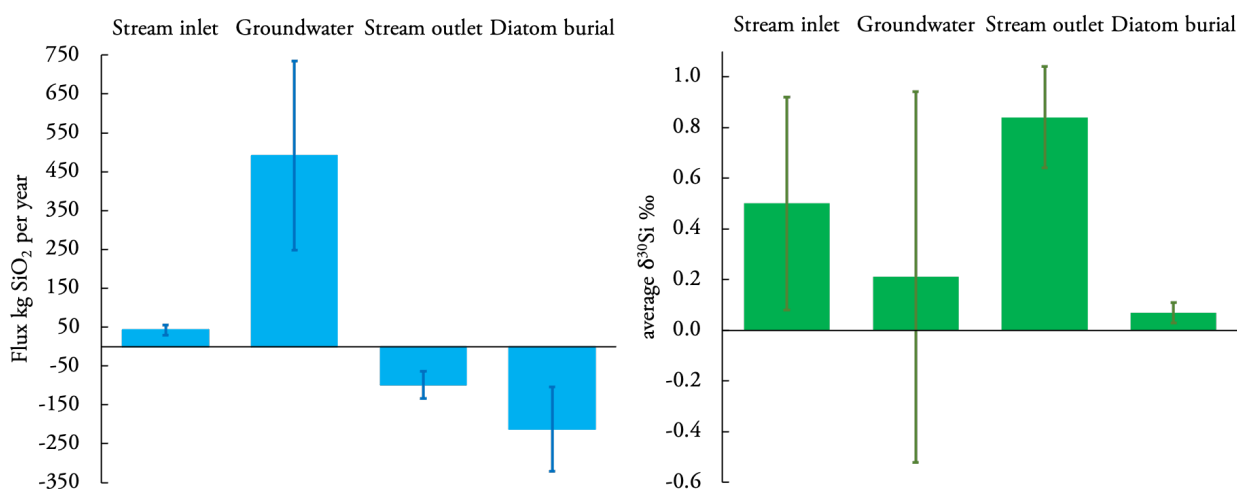
Zone (Pearson et al., 2016). In Lake Baikal it was shown that one-fourth of the inflowing DSi during the last century is stored in the sediment as BSi (Panizzo et al., 2017). The  $\delta^{30}\text{Si}$  long-term trend indicated the complexity of the Lake Baikal system, where several co-occurring processes affect the isotopic composition. A similar phenomenon is observed in Yellowstone Lake (Paper IV). In Lake Tanganyika the mass balance resulted in a non-steady state Si cycle in the lake, where the DSi concentration has been increasing in the last 30 years, and diatom production has decreased as a response to the lowering of N and P supply (Alleman et al., 2005). In contrast, our models assume steady-state in order to quantify missing DSi sources and further interpret the sedimentary data. One of the potential DSi sources was demonstrated in several Taupo Volcanic lakes, where an Si efflux from the sediment to the lake water is present even at high lake DSi concentrations often due to hydrothermal input (Pearson et al., 2016). Thus, similar processes are expected in Yellowstone Lake, however, no data for identification of Si efflux had yet been measured.

All those studies together indicate that the Si cycle in lakes reflects local processes and that it is site specific. Therefore, to understand and later quantify the importance of continental DSi filters and BSi sinks in lakes and reservoirs, more complex models that include lake balance data must be used, including the potential effects of bedrock, groundwater, hydrothermal inputs and weathering rates.

### 6.3 The role of groundwater in lake Si cycles

Lakes, reservoirs, and processes in the watersheds of rivers regulate the DSi concentration and stable Si signature exported into the ocean (Cockerton et al., 2015; Phillips and Cowling, 2019). Groundwater has been identified to be an important





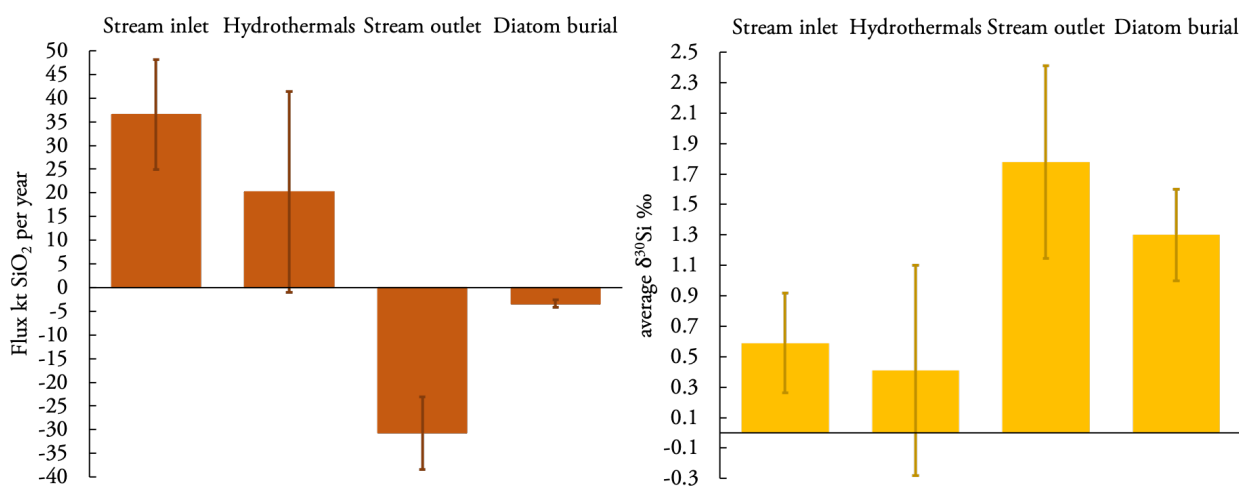
**Figure 7:** Mean annual Si and stable Si mass balance of Lake 850 (based on data from Paper II).

water source in mountain lakes (Clow et al., 2003; Hood et al., 2006; Huth et al., 2004; Liu et al., 2004). Groundwaters are not only a water source, they also provide the lakes and rivers with DSi (Paper II) (Hurley et al., 1985; Maavara et al., 2018; Opfergelt and Delmelle, 2012). However, mass balances conducted for the global Si cycle have not accounted for this additional source of DSi into lakes, which contributes to BSi accumulation, and therefore the BSi retention in the continental cycle is likely underestimated.

Papers II and III show an example of the impact of groundwater on BSi accumulation in an oligotrophic mountain and high-latitude lake in northern Sweden. Lake 850 is situated above the treeline and is not in steep terrain. No substantive impact on the DSi budget is likely caused by vegetation, as no developed soils are acting as a DSi pool; only bare bedrock with mosses, lichens and grasses are found in the lake watershed. Additionally, low sedimentation rates and DSi brought into the lake by groundwater are contributing to high BSi accumulation (Papers II and III). The groundwater brings 3 times more DSi into the lake than the ephemeral streams during the ice-free period. If a simplified mass balance using only the stream inlet DSi flux and

the outlet DSi flux were made, this lake would act as a DSi source (Figure 7). However, if the BSi accumulation rate and groundwater are accounted for in the mass-balance model, the lake becomes a DSi sink, which is in agreement with observations in sediment cores (Figure 9).

Paper II used a short gravity core to quantify the BSi accumulation, which resulted in a slightly lower BSi concentration (mean 18.8 wt%) than we found in a long piston core (mean 32.3 wt%) presented in Paper III. Additionally, the uppermost 6 cm of the sediment from Lake 850 sampled in 1999 (Bigler and Hall, 2003) showed BSi as high as 40 wt% of diatom SiO<sub>2</sub> (Frings et al., 2014b; Rosén et al., 2010). Therefore, despite the small sedimentation area of the lake basin (7300 m<sup>2</sup>) a great heterogeneity of sediment composition is observed. This brings us to the conclusion that more than one core should be used to study lake sediments in order to constrain lake sedimentation as suggested by Anderson (1990). As observed here, the heterogeneity of sediment and BSi accumulation can greatly increase the uncertainties in the model.



**Figure 8:** A schematic Si and Si isotope mass balance of Yellowstone Lake (preliminary unpublished data).

#### 6.4 Is hydrothermalism affecting BSi accumulation?

An example of an environment with a high potential for BSi accumulation is Yellowstone Lake. The lake and Yellowstone River outlet DSi concentrations are higher than the world river mean, and the lake diatom production does not show DSi depletion. The rhyolitic bedrock surrounding Yellowstone Lake in combination with hydrothermal vents is suggested to contribute greatly to the lake DSi budget. Further, the oligotrophic conditions in Yellowstone Lake along with deep mixing make the lake ideal for diatom growth without being out-competed by other organisms. If the hydrothermal input into the lake was not included in a Si budget, the lake would act as DSi source rather than DSi sink. However, the Si mass balance (preliminary data, Figure 8) and the lake sediment BSi accumulation (Paper IV) both indicate that the lake is acting as a DSi sink.

Hydrothermalism in Yellowstone Lake was previously quantified to contribute with around 1% of the lake water inflow (Balistrieri et al., 2007), but the DSi concentration in those hydrothermal fluids can be 10 times higher compared to the inlets. A preliminary Yellowstone Lake annual

Si and Si isotope mass balance based on 6 and 2 years of data, respectively (Figure 8) reveals the importance of hydrothermal vent fluids, which were likely underestimated in the previous balance model (Balistrieri et al., 2007). However, great uncertainties of those mass-balance models arose from the lack of monitoring data to constrain the budget. Therefore, a simplification of the annual water fluxes, DSi concentration and  $\delta^{30}\text{Si}$  fluxes is needed to account for variability in the two seasons defined by the rivers' flow regime: high flow inputs in the spring, and low flow during the late summer. These results bring initial insights into the Yellowstone Lake  $\delta^{30}\text{Si}$  mass balance. To improve the preliminary  $\delta^{30}\text{Si}$  model, samples of living diatoms, sediment pore water samples, and annual monitoring of the lake diatom production and dissolution in the water column are prospects for future studies.

Another approach to investigate the importance of hydrothermalism is to focus on the sediment  $\delta^{30}\text{Si}$  (Paper IV). In volcanic systems, such as Yellowstone, a continuous, long-term hydrothermal influence is demonstrated in the thermal features on land, such as hot springs or geysers (Hurwitz and Lowenstern, 2014). However, Yellowstone Lake is a large water body situated on the Yellowstone

Caldera rim, remote ~10 km to 50 km from the main hydrothermalism. The main Yellowstone Lake water input is the Yellowstone River with its watershed outside the Yellowstone Caldera. All these factors suggest that hydrothermal input into the lake will be rather local. Nevertheless, diatom Ge/Si ratios in the sediment showed that the lake has a high hydrothermal background input during the last 9800 years. This background is large enough that it masks the hydrothermal explosion of Elliott's Crater (Paper IV), which created a 1 m thick hydrothermal deposits within the lake.

The results of these analyses suggest the answer to the question whether hydrothermalism is responsible for BSi accumulation is likely yes. Even though we do not see the direct impact of the hydrothermal explosion in the sedimentary BSi and  $\delta^{30}\text{Si}$  (Paper IV), the long-term hydrothermal input shows long-term biogeochemical lake stability. Additionally, the fossil diatom  $\delta^{30}\text{Si}$  is likely influenced by relative changes in DSi sources. Thus, a combination of our preliminary mass-balance models together with the fossil diatom record (Paper IV) highlighted the importance of including an additional source of DSi, e.g., hydrothermal inputs, for mass-balance models.

## 6.5 Factors driving BSi accumulation in pristine lakes

To understand which lakes have the potential to accumulate large amounts of BSi, several factors must be taken into account. The DSi source, which is often connected to the bedrock type and further depends on the presence of vegetation and soils, influences the DSi budget of a lake. Areas with exposed igneous bedrock combined with a lack of vegetation and developed soils have large potential to deliver high DSi concentrations originating from bedrock weathering into a lake (Paper II). Further, the importance of groundwater can be often neglected, even though it can play

a crucial role in some lakes (Paper II, Figure 7). We have studied mass balances of a small high-latitude lake in northern Sweden (Paper II) and of one of the largest high-altitude lakes in the USA, Yellowstone Lake. Groundwater or hydrothermal fluids (Figures 7 and 8) are distinct sources of DSi into Lake 850 and Yellowstone Lake, respectively, which are not traditionally measured.

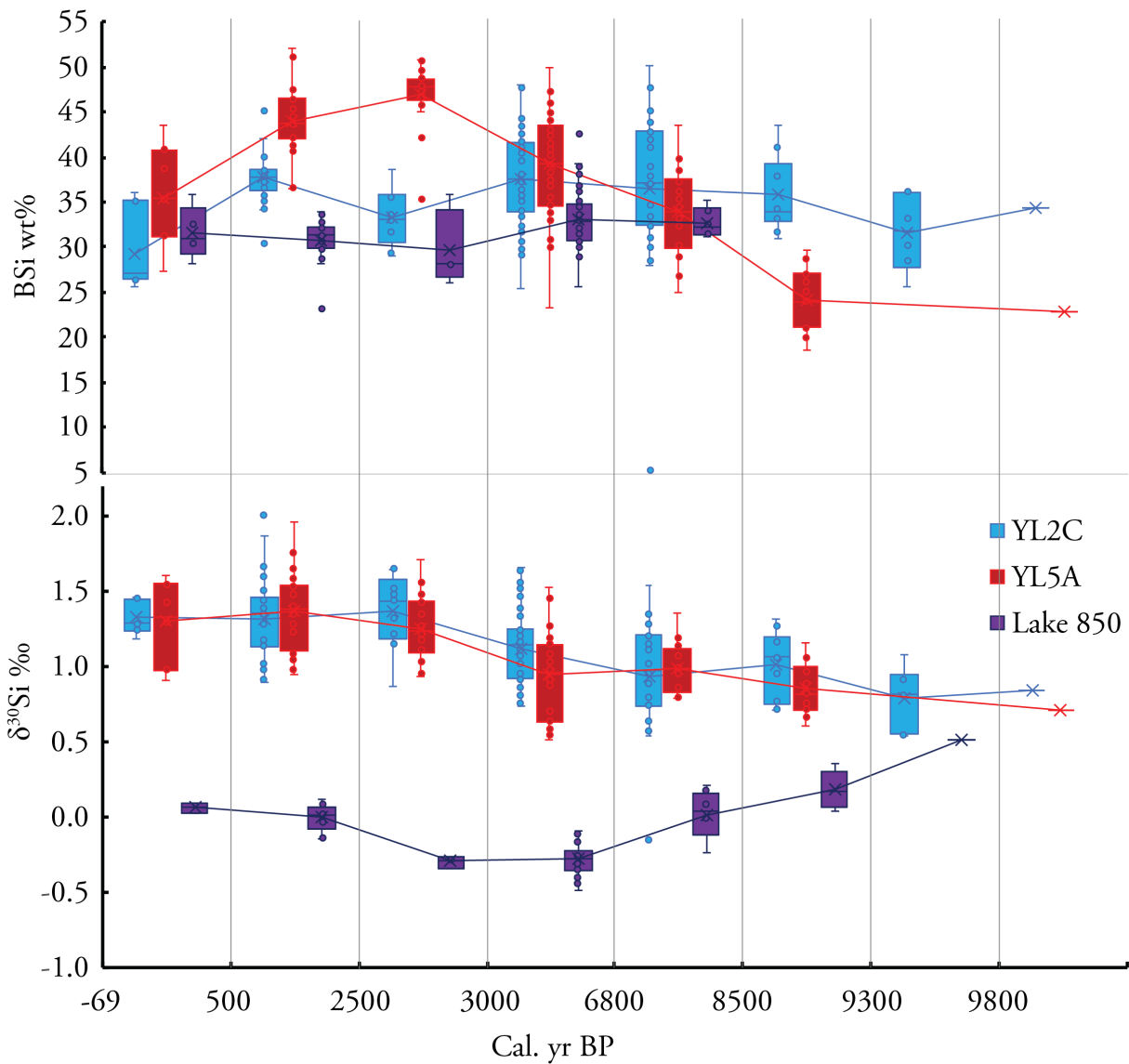
By comparing our two study sites some similarities are found. The DSi concentration of the outlets in both models (not shown, Paper II) is lower than the concentration in the inlets. The first explanation for this observation is diatom production and DSi uptake. Using only these two variables for the mass balance suggests that the lakes act as sinks. However, when comparing the DSi fluxes (Figures 7 and 8), both lakes rather act as sources of DSi. When adding BSi flux to the sediment into the mass balance, the inlet is not sufficient to feed both the outlet DSi flux and the BSi accumulation. Therefore, if a mass balance needs to be simplified, the BSi accumulation to the sediment is a more robust characterization of mass balance than the DSi concentrations of the stream inlets and outlets in determining whether the lake acts as a source or a sink in the Si cycle.

Both lakes show relatively light isotopic values of the inlets (Figures 7 and 8), which are likely connected to the transport of DSi originating from freshly weathered bedrock. Both transport over a short distance (Lake 850) and the oligotrophic status of high-altitude rivers (Yellowstone tributaries) can account for the relatively light  $\delta^{30}\text{Si}$  of DSi observed in inlets. Another similarity observed is the additional DSi sources, the groundwater and the hydrothermal fluids, that both bring lighter  $\delta^{30}\text{Si}$  and a substantial DSi flux compared to the inlets. The difference in the  $\delta^{30}\text{Si}$  of the DSi in the outlet waters of both lakes is caused by great differences in lake size. In Yellowstone Lake several concurrent processes, such as diatom production and dissolution, amorphous silica precipitation or

clay mineral formation may influence the lake  $\delta^{30}\text{Si}$ , whereas in Lake 850, the lake  $\delta^{30}\text{Si}$  is mostly affected by DSi sources and diatom production.

The mass accumulation rates and BSi fluxes to the sediment studied here (Papers II, III, IV) differ considerably. Yellowstone Lake has about five times larger BSi accumulation rates compared to Lake 850, but both lakes show BSi concentrations

over 30 wt% of diatom  $\text{SiO}_2$  in the sediment. Therefore, low or high sediment mass accumulation rates stand-alone do not guarantee high or low BSi accumulation, respectively, which is consistent with the great variability of mass accumulation rates and BSi concentrations demonstrated in this thesis and in other lakes (Arai and Fukushima, 2012; Conley, 1988; Kaplan et al., 2002; McKay



**Figure 9:** Box-plot showing BSi concentration and  $\delta^{30}\text{Si}_{\text{BSi}}$  variability in all three sedimentary cores from Papers III and IV aligned by ages. YL2C is a core from Yellowstone Lake deep sedimentary basin, YL5A is a core from Yellowstone Lake in the distal part of Elliott’s crater, and Lake 850 is a core from Lake 850 in northern Sweden.

et al., 2008; Newberry and Schelske, 1986; Opfergelt et al., 2011; Schelske et al., 1987). BSi accumulation always depends on a combination of factors, such as higher diatom production than diatom dissolution, higher DSi influx than DSi outflux, and low detrital flux.

As demonstrated by two lakes in very different settings, multiple factors act simultaneously and drive BSi accumulation. The results support previous suggestions that high-latitude, low-nutrient lakes tend to accumulate a large amount of BSi in the sediment (Frings et al., 2014b). Further, the data support the generalization that high BSi accumulation is dependent on low detrital input (Conger, 1942).

I have also confirmed that sedimentation rates play a role in the BSi accumulation (Panizzo et al., 2016; Ryves et al., 2003), but are dependent on other factors, such as detrital input and DSi concentration in the water column influencing BSi preservation. Indirectly, we have shown that watershed vegetation and length of transport of weathered DSi is affecting the DSi isotopic composition. Additionally, places with silicic volcanism or hydrothermalism are good candidates for high BSi accumulation.

## 6.6 Lake diatom $\delta^{30}\text{Si}$ proxy interpretation

Only a limited number of studies on freshwater diatom Si isotopic records have been published (Chen et al., 2012; Cockerton et al., 2015; Panizzo et al., 2016; Street-Perrott et al., 2008; Swann et al., 2010; Zhang et al., 2020). Our results in Papers III and IV add data sets of lakes where the diatom  $\delta^{30}\text{Si}$  is affected by several simultaneous processes, such as changes in DSi sources, DSi utilization, and diatom dissolution. The sedimentary diatom  $\delta^{30}\text{Si}$  of Yellowstone Lake is comparable to values from Lake El'gygytyn (Swann et al., 2010), Lake

Baikal (Panizzo et al., 2016) and Lake Edward (Cockerton et al., 2015), whereas sedimentary diatom  $\delta^{30}\text{Si}$  from Lake 850 is relatively lighter compared to the world mean of 0.63 ‰ for diatoms buried in sediments (Frings et al., 2016; Sutton et al., 2018).

With a combination of the BSi concentration and stable Si isotopes, the variation in DSi supply and changes in DSi sources can be tracked. In Lake 850 the BSi concentration is pretty stable throughout the core (Figure 9), and the  $\delta^{30}\text{Si}$  shows lighter values in the period from ca 9400 until ca 3000 cal. yr BP. As BSi is stable, an explanation of the Si isotopic behavior is that the relative proportion of DSi sources has changed towards isotopically lighter sources. In the last 3000 years another change in the relative proportion of DSi sources (larger surficial stream contribution), groundwater residence time or increased DSi utilization by diatom production is recorded in the  $\delta^{30}\text{Si}$ , this time towards heavier sources.

In Yellowstone Lake the data record several co-occurring processes (changes in DSi sources, DSi utilization, diatom dissolution) driving the  $\delta^{30}\text{Si}$ . Moreover, the Yellowstone cores vary in BSi concentrations at a given time (Figure 9), which indicates a DSi-unlimited system, where shifts in relative proportion of several processes, such as production, dissolution and detrital input, result in variation of BSi in the sediment. Additionally, a considerable heterogeneity of the sediment composition within one lake is demonstrated.

The  $\delta^{30}\text{Si}$  in both Yellowstone Lake cores show similar trends (Figure 9), which suggest that the lake DSi sources is homogeneous. The systematic shift towards heavier  $\delta^{30}\text{Si}$  through time is likely connected to production as influenced by Holocene climate development (Brown, 2019), relative changes in the proportions of DSi sources and diatom dissolution in the water column. Disentangling of those processes would require additional data on recent functioning and other proxies,

such as Ge/Si ratios or other trace elements when building mass-balance models and reconstructing Si cycling through the past. Ge/Si ratios can be used as a tracer for weathering rates (Filippelli et al., 2000; Froelich et al., 1992; Kurtz et al., 2002; Lugolobi et al., 2010; Shemesh et al., 1989), as well as for hydrothermal input when studying fossil diatoms and thus bring another perspective into data interpretation. Our  $\delta^{30}\text{Si}$  and Ge/Si data demonstrate the impact of local DSi sources on  $\delta^{30}\text{Si}$ , which indicates that knowledge of the lake or river watershed is crucial for estimating BSi accumulation, as well as DSi export into the ocean.

The comparison of the diatom  $\delta^{30}\text{Si}$  of Yellowstone Lake and Lake 850 (Figure 9) shows a dependency of the  $\delta^{30}\text{Si}$  on the signature of the source DSi. The  $\delta^{30}\text{Si}$  in Yellowstone Lake is rather related in to in-lake processes, whereas diatom  $\delta^{30}\text{Si}$  of Lake 850 reflects the lighter DSi sources. Likely, the water and Si residence time plays a role in the diatom  $\delta^{30}\text{Si}$ . Yellowstone Lake with longer water and Si residence times has higher potential for Si recycling compared to Lake 850.

## 6.7 Future research perspectives

The global stable Si isotope cycle is built on available data, which for some continental systems, especially lakes, are still sparse (Frings et al., 2016; Sutton et al., 2018). The processes in watersheds of rivers and lakes drive Si fluxes. The rates of these processes contribute to the size of pools, which act as sources and sinks of silicon. However, these watershed processes are still understudied (Frings et al., 2014b; Phillips, 2020). By studying more individual lake Si cycles, Si flux estimates can be specified in more detail by taking into account different site-specific factors. Moreover, by studying processes that influence the DSi concentration in lakes and rivers, we will get a better understanding of the Si cycle, which can then be better constrained on longer timescales.

The coupling of silicon and carbon cycles has previously been shown to be important for the  $\text{CO}_2$  drawdown on a geological timescale through weathering (Street-Perrott et al., 2008). Moreover, chemical weathering determines the nutrient supply to rivers, lakes, and the ocean. Weathering processes are connected to climate and vegetation changes and influence ecosystems development. Therefore, tracing chemical weathering by using different elemental and isotopic proxies can help us better understand past changes in ecosystems. Germanium and silicon, but also aluminum, zinc or lithium (Sutton et al., 2018) are elements that can be used individually or coupled to trace chemical weathering and the processes in global elemental cycles (Kurtz et al., 2002; Mortlock and Frohlich, 1987; Murnane and Stallard, 1990).

## 7 Conclusions

- A diatom-rich sediment nomenclature has been proposed for more clarity. Diatom-rich sediments should be evaluated based on BSi concentration. Diatomite was defined as consolidated sediment with more than 50 wt% of diatom SiO<sub>2</sub> accompanied with the name of the remainder of the sediment. The stand-alone word “diatomite” is composed of more than 80 wt% of diatom SiO<sub>2</sub>. Unconsolidated sediment with diatom content above 50 wt% is called “diatomaceous ooze”, with similar rules as for diatomite applied.
- Diatom-rich sediment tends to accumulate in lakes situated on silicon rich bedrock, volcanic and hydrothermal areas. Further, diatom-rich sediment can accumulate in high-latitude lakes with significant groundwater input. Moreover, lakes with low-relief watershed morphology and with low stream inlet resulting in low and fine-grained clastic input are potential places for high BSi concentration in the sediment. All those water bodies with potentially high BSi accumulation are acting as sinks of Si in the global silicon cycle.
- The groundwater supplying Lake 850 with DSi was shown to be an important factor for high BSi concentration in this high-latitude subarctic lake. Generally, groundwater can be an important source of DSi in lakes and should not be overlooked in mass-balance models and when building global elemental cycles.
- The  $\delta^{30}\text{Si}$  in Lake 850 reflects the isotopically light DSi sources – weathered bedrock and groundwater. Both sources experience very few processes that fractionate Si, likely due to poor soil development and sparse vegetation.
- The variations in fossil diatom  $\delta^{30}\text{Si}$  in Lake 850 indicate changes in the relative proportion of DSi sources. The DSi sources are influenced by Holocene summer temperature and precipitation changes.
- Continuous Holocene hydrothermal input supplies Yellowstone Lake with high DSi and DGe concentrations that is reflected in the high BSi concentrations and high Ge/Si ratios in a single fossil species, the diatom *Stephanodiscus yellowstonensis*.
- The  $\delta^{30}\text{Si}$  of *Stephanodiscus yellowstonensis* shows a gradual shift of +0.6 ‰ throughout the Holocene, which is either connected with the Holocene summer temperature increase driving diatom production, or to changes in the relative proportion of DSi sources. Increased stream input brings isotopically heavier DSi from the watershed compared to the hydrothermal input. Alternatively, an increase of hydrothermal source could supply the lake with even more DSi, which would fertilize the diatom production. Increased production would lead to an increase of the  $\delta^{30}\text{Si}$ .
- The understanding whether a lake acts as a source or a sink of Si requires constraint of BSi accumulation, which depends on sufficient DSi concentrations for diatom production and further on diatom dissolution and detrital input. Using inlet and outlet DSi fluxes to estimate the BSi accumulation in a lake is not sufficient as other substantial DSi sources, such as groundwater or hydrothermalism, can be present.

## Populärvetenskaplig sammanfattning

Kiselalgsrika sediment är vanligtvis en blandning av mineraler och encelliga fotosyntetiserande alger, där de största är ca 0.0025 mm och de minsta är mindre än 0.0005 mm. Dessa alger har ett ytterskal av kisel-dioxid ( $\text{SiO}_2$ ), vilket gör att de är helt beroende av att det finns löst kisel (Si) i deras miljö, eftersom kisel behövs för att bygga deras skal. Kiselalger lever i alla vattenmiljöer så som sjöar, floder och hav, men även i jord. Om det finns en stor mängd löst kisel och tillräckligt med näring i vattnet och låg konkurrens från andra organismer, kan kiselalger växa i stora mängder och när de dör bildas kiselrika sediment som kiselgur.

Kiselgur består till största del av kisel-dioxid och är ett material med många olika användningsområden i samhället. Det används exempelvis för att filtrera oorganiska och organiska kemikalier och läkemedel, eller som filter vid framställning av öl, vin, whisky och frukt- och grönsaksjuicer. Många av oss har faktiskt stött på produkter som innehåller kiselgur då det t.ex. används som milt slipmedel i tandkräm. Kiselgur undersöks även som ett möjligt och relativt billigt sätt att absorbera tungmetaller och oljespill i vatten. Användningsområdena är alltså många, men det är inte helt klart hur det kiselrika sedimentet bildas och vilka förhållanden och faktorer som leder till de massiva ansamlingarna av kiselalger.

Även om kisel är det näst vanligaste grundämnet i jordskorpan är det mesta bundet i bergarter, i en form som organismer inte kan använda. De flesta organismer kan endast ta upp ämnen i flytande eller gasform och därför måste kisel först frigöras från bergarterna, vilket kan ske genom så kallad kemisk vittring. Kemisk vittring är en process där koldioxid och vatten reagerar med bergarten och löser upp den. Det tidigare bundna kisel är nu löst

i vatten och kan transporteras via floder till haven. På vägen från det vittrade berget till havet kan dock jord, växter eller sjöar fungera som filter och fånga upp och lagra det lösta kisel och därmed minska mängden löst kisel i vattnet nedströms, vilket i sin tur begränsar kiselalgstillväxten.

I denna avhandling har olika kiselrika sediment definierats genom andelen kiselalger i sedimentet. För att utforska vilka faktorer som möjliggör ansamlingar av kiselalger har två sjöar med kiselrika sediment studerats. Den ena sjön är en liten sjö (Lake 850) i ett fjällområde som ligger ovanför polcirkeln, nära Abisko nationalpark i norra Sverige. Den andra sjön är Yellowstone Lake, den största fjällsjön i USA, belägen i Yellowstone National Park, som är känd för sin vulkaniska och hydrotermiska aktivitet. Båda sjöarna är istäckta under vintern och på grund av det sker större delen av kiselinbindningen i alger under en mycket kort växtsäsong på sommaren.

För att identifiera vilka faktorer som leder till stora mängder kiselalger i vattnet och som ansamling i sedimenten, undersöktes först hur förhållandena i sjöarna varit de senaste åren. Detta gjordes genom att studera vattenflöden och analysera mängden löst kisel i vattendragen som leder till och från sjöarna, och mängden kisel i själva sjövattnet. Sedimentet i sjöarna undersöktes också och från det har vi kunnat beräkna hur stor del av sedimentets vikt som utgjordes av kisel-dioxid bundet i kiselalger. För att uppskatta hur gammalt sedimentet var på olika djup och för att avgöra hur mycket kiselalgs-kisel som varje år fastlagts i sjöbotten har två dateringsmetoder ( $\text{KOL-14}$  och  $\text{BLY-210}$ ) använts. Tillsammans har alla dessa mätningar och beräkningar visat att det saknas någon kiselkälla för att halten kisel med de kända flödena ska gå ihop i de i de båda sjöarna.

För att identifiera varifrån det ”förlorade” lösta kisel kommer från användes en metod där stabila kiselisotoper analyseras. Metoden baseras på det faktum att kiselatomen kan ha olika antal



neutroner i sin kärna. Den vanligaste och mest utbredda kiselisotopen (92 procent) är  $^{28}\text{Si}$  som har 14 neutroner och 14 protoner och således en atomvikt på 28. Det finns ytterligare två isotoper,  $^{29}\text{Si}$  (5 procent) och  $^{30}\text{Si}$  (3 procent), som har 15 respektive 16 neutroner och som på grund av deras högre atomvikt inte används lika frekvent i kemiska, fysiska och biologiska processer. Med andra ord föredras den lätta isotopen,  $^{28}\text{Si}$ , av kiselalger, och det är också den isotopen som främst släpps ut vid vittring av berg och mineraler. På grund av dessa olika egenskaper kan de stabila kiselisotoperna därför berätta var det lösta kiset kommer ifrån, om det funnits någon kiselalgs- eller växtproduktion på dess väg eller hur stor mängd kisel som var tillgänglig i vattnet när kiselalger växte.

Med alla dessa verktyg har vi upptäckt att det i Lake 850 finns en stor mängd grundvatten som bidrar med löst kisel till sjön och dess kiselalgsproduktion. Vi har också sett att sjöförhållandena har varit stabila under de senaste 9400 åren och att växtsäsongens längd och förändringar i fördelningen av tillförseln från grundvatten och vattendrag påverkat ansamlingen av kiselalger. Undersökningarna tyder på att det var mindre tillförsel av mineraler från vattendrag som rinner in i sjön i tider då klimatet var varmare och torrare. Eftersom det var en mindre mängd mineraler som spädde ut sedimentet under de varmare klimatförhållandena bestod sedimentet då till 40 procent av kiselalger. Vi fick också reda på att det mesta av det lösta kisel som togs upp av kiselalger under den varmare perioden kom från grundvattnet eller från nyligen vittrad kisel.

På samma sätt observerade vi att den extra källan till löst kisel i Yellowstone Lake är hydrotermiska utflöden från botten av sjön. Dessa utflöden har bidragit med löst kisel till sjön under de senaste 9800 åren och det är anledningen till att sjön har ett väldigt högt kiselinnehåll. Mängden löst kisel i sjön är så hög att hela 50 procent av sedimentet består av kiselalger. Dessutom observerade vi att

en hydrotermisk explosion inträffade för omkring 8000 år sedan, men som inte påverkade sedimentationen av kiselalger. Denna observation leder oss till slutsatsen att Yellowstone Lake har varit ett mycket stabilt sjösystem de senaste 9800 åren.

I den här avhandlingen visar jag att både grundvatten och hydrotermiska utflöden är viktiga källor till löst kisel i sjöar som bidrar till bildningen av kiselalgsrika sediment. Våra studier tyder på att kiselalgsrika sediment kommer att bildas i sjöar belägna på kiselrik berggrund, i vulkaniska och hydrotermiska områden samt i sjöar på höga breddgrader som tenderar att ha ett påtagligt grundvatteninflöde. Vattendrag i relativt platta områden med ett lågt vattenflöde kan leda till en låg tillförsel av lera och sand till sjöar och därför bidra till sediment med en hög andel kiselalger. Alla dessa vattensystem som ansamlar stora mängder kisel bundet i kiselalger, fungerar som kiselsänkor i den globala kiselomsättningen.

## Popular summary

Diatom-rich sediment is an accumulation of a single-cell photosynthetic algae of size from 0.005 mm to less than 0.0005 mm usually mixed with minerals. These microscopic organisms with an external skeleton of silica, known as a frustule, live in all aquatic environments, such as lakes, rivers, oceans, but also in soils. They account for one fourth of the world's entire net primary productivity and one fifth of world oxygen production. However, diatoms are fully dependent on the presence of dissolved silicon in the environment, because it is an essential element for building their frustules. If there is a great amount of dissolved silicon in the water and favorable conditions (high nutrients and low competition) are met, diatoms can grow in large abundance and then diatom-rich sediments can be formed and composed of more than 80 % of diatoms.

Diatomite is a material with wide socio-economical utilization. It is used for filtering inorganic and organic chemicals, pharmaceuticals, beer, wine, whiskey, and fruit and vegetable juices. Many of us might have come across products containing diatomite regularly, such as a mild abrasive in toothpaste. Diatomite is further used in construction as insulators, metal polish, fillers, absorbents or as concrete additive abrasives. Diatomaceous silica is also used to improve plastic properties, as well as a stabilizing agent in explosives. Last but not least, diatomites are used as economically affordable absorbent powders for heavy metals and oil water contamination removal. To be able to use diatomite for all those purposes, first we need to know how the diatom-rich sediment is formed and what are the conditions and factors leading to the massive diatom-rich accumulation.

Even though silicon is the second most abundant element in the Earth's crust, most of it is bound in rocks, which is a form unavailable for organisms to use. Most organisms can use only elements

in liquid or gaseous form; therefore, silicon must be released from rocks via chemical weathering. During this process, CO<sub>2</sub> and water react with the source rock and dissolve it. The silicon is dissolved in water and transported through rivers to the ocean. In rivers, lakes and in the ocean, the dissolved silicon can be taken up by diatoms, which after their death sink down to the bottom and accumulate. However, on the way from the weathered rock to the ocean there are other filters, such as in soils or through plant uptake, which catch and store dissolved silicon and thus, decrease the dissolved silicon in the waters, which limits diatom growth.

This thesis starts by defining different diatom-rich sediments by the relative contribution of diatom silica. Then, two lakes with diatom-rich sediment were studied to explore factors responsible for diatom accumulation. Two different lake systems were investigated; one is a small lake (Lake 850) in a mountainous area situated above the polar circle in Northern Sweden close to Abisko National Park. The other lake is Yellowstone Lake, the biggest mountain lake in the United States, situated in Yellowstone National Park, which is well known for its volcanic and hydrothermal activity. Both lakes are ice-covered during winter, and thus most of the diatom production happens during a very short growing season in summer.

To identify factors responsible for diatom production and accumulation, the functioning of lakes during recent years was examined first. I measured water fluxes and the amount of dissolved silicon in rivers and streams entering and leaving the lakes, as well as the amount of dissolved silicon in the lake water and calculated how much silicon contained in diatoms is retained in the lakes. Furthermore, I looked into the deposits from the bottom of the lakes and measured the percent of diatom silica. Dating methods (<sup>14</sup>C and <sup>210</sup>Pb) were used to estimate the ages of those deposits, and I calculated how much diatom silica

is deposited into the lake bottom for one year. From all those measurements, I could see that I have not accounted for an important dissolved silicon source in both lakes.

Therefore, I used stable silicon isotopes to identify sources of dissolved silicon to reveal what is the missing source. The measurement of stable silicon isotopes is a method based on the different number of neutrons in the atomic nucleus. Due to one or two additional neutrons in the atomic core, the whole atom differs in weight. The most common and widespread silicon isotope (comprising 92 %, of all Si) is  $^{28}\text{Si}$ , which has 14 neutrons and 14 protons, and has an atomic weight of 28. There are two more isotopes,  $^{29}\text{Si}$  (5 %) and  $^{30}\text{Si}$  (3 %), which have 15 and 16 neutrons, respectively, and due to their increased atomic weight, they are discriminated against during chemical, physical, and biological processes. In other words, the light isotope  $^{28}\text{Si}$  is preferred by diatoms and it is preferentially released during rock and mineral weathering. Therefore, the stable silicon isotopes can tell us where the dissolved silicon comes from, or if there was some diatom or plant production on its pathway, or the amount of available silicon in water when the diatoms were growing.

Using all those tools, I found that in Lake 850 there is substantial groundwater input bringing a lot of dissolved silicon into the lake and supplying diatom production. I also observed that lake conditions were relatively stable over the last 9400 years, and that the length of the growing season and changes in the relative proportion of groundwater input and river input influenced diatom accumulation. The data suggest that in times when the climate was warmer and drier, there was less stream input, which is also bringing minerals. Therefore, more diatoms (40 %) were found in the sediment, because there was a reduced input of minerals diluting the sediment during warmer climate conditions. I also found that during this warmer period, most of the dissolved silicon taken

up by diatoms was brought by groundwater or from freshly released dissolved silicon from the rocks.

Similarly, in Yellowstone Lake, it was observed that the additional source of dissolved silicon is hydrothermal vents situated on the lake bottom. Those vents have contributed dissolved silicon into the lake for the last 9800 years, and this is the reason for the really high content of silicon in the lake. The amount of dissolved silicon in the lake is so high that 50 % of the sediment is composed of diatoms. Additionally, it was observed that a hydrothermal explosion that happened around 8000 years ago did not affect diatom sedimentation, which brings us to a conclusion that Yellowstone Lake has been a stable lake system for the last 9800 years.

In this thesis it has been shown that groundwater and hydrothermal vents are both important sources of dissolved silicon in lakes and are partly responsible for diatom-rich sediment formation. Three listed studies suggest that diatom-rich sediments are likely to form in lakes situated on silicon rich bedrock, volcanic and hydrothermal areas, as well as in lakes at high latitudes with pronounced groundwater input. Furthermore, lakes with low-relief watershed morphology and with low stream inflow resulting in low and fine-grained clastic input, such as mud and sand, are potential places for diatom-rich sediment formation. All those water bodies with potentially high BSi accumulation are acting as sinks of Si in the global silicon cycle.

## Populárně-vědecký souhrn

Sediment s vysokým obsahem rozsivek je usazenina složená z jednobuněčných fotosyntetických řas – rozsivek – o velikosti 0.005 až 0.0005 mm a minerálů. Rozsivky si tvoří křemičitou schránku, která se nazývá frustula, a žijí ve všech vodních prostředích, jako jsou jezera, řeky, moře a oceány, ale také v půdě. Představují čtvrtinu celé primární produkce v oceánech a pětinu světové produkce kyslíku. Nicméně rozsivky jsou plně závislé na přítomnosti rozpuštěného křemíku v prostředí, jelikož ten je základním prvkem pro budování jejich schránek. Za příznivých podmínek (dosatek živin a nízká konkurence), a pokud je ve vodě velké množství rozpuštěného křemíku, mohou rozsivky růst v hojném počtu. Za těchto podmínek mohou vznikat sedimenty bohaté na rozsivky jako je křemelina, v níž se vyskytuje více než 80 % rozsivek.

Křemelina je materiál s širokým socioekonomickým využitím. Používá se pro filtraci anorganických a organických chemických látek nebo léčiv. Mnozí z nás se již setkali s výrobky, které obsahují křemelinu s funkcí jemného brusiva například v zubních pastách. Křemelina se dále používá během výroby piva, vína, whisky či ovocných a zeleninových šťáv jako filtr. Dále se používá ve stavebnictví jako izolant, při leštění kovů, jako plnivo, absorbent nebo jako aditivum do betonu. Křemelina se také používá ke zlepšení vlastností plastů a jako stabilizační činidlo ve výbušninách. V neposlední řadě je křemelina používána v cenově dostupných sypkých sorbentech pro odstraňování kontaminace těžkými kovy a při úniku ropy. Abychom mohli používat křemelinu pro všechny tyto účely, nejprve potřebujeme vědět, jak a za jakých podmínek vzniká.

Přestože je křemík druhým nejhojnějším prvkem zemské kůry, většina je vázána v horninách a minerálech, což je forma, kterou organismy nedokáží využít. Většina organismů je schopna využívat

pouze prvky rozpuštěné v kapalině nebo prvky v plynné formě; proto musí být křemík uvolněn z hornin a minerálů chemickým zvětráváním. Během chemického zvětrávání dochází k reakci oxidu uhličitého a vody s horninou, jež je takto rozpouštěna. Křemík rozpuštěný tímto způsobem je dále odnášen vodními toky až do oceánu. V řekách, jezerech a v oceánech je rozpuštěný křemík spotřebováván rozsivkami, které po svém úhynu klesnou na dno, kde se hromadí. Nicméně na cestě od zvětrávání hornin a minerálů až do oceánu se nacházejí místa, která mohou zadržovat rozpuštěný křemík a tím snižovat koncentraci a dostupnost rozpuštěného křemíku ve vodách, což omezuje růst rozsivek. Těmito filtry jsou například půdy, rostliny nebo jezera.

V této dizertaci se nejprve podíváme na systém určování jmen rozsivkových sedimentů, založený na procentuálním podílu rozsivek. Následně prezentujeme studie dvou jezer, které disponují vysokým obsahem rozsivek v sedimentu. V těchto studiích zkoumáme faktory vedoucí k akumulaci rozsivek. Podíváme se do dvou různých jezerních systémů. Prvním z nich je malé jezero (Lake 850) za polárním kruhem v severním Švédsku v blízkosti národního parku Abisko. Druhým jezerem je Yellowstoneské jezero, jež je největší horské jezero ve Spojených státech amerických nacházející se v Yellowstone národním parku, dobře známým pro svou sopečnou a hydrotermální aktivitu. Obě jezera jsou v zimě pokryta ledem, a proto většina rozsivek roste jen během velmi krátkého vegetačního období v létě.

Abychom našli faktory odpovědné za tvorbu a akumulaci rozsivek, nejprve musíme znát současné fungování jezer. Proto jsme změřili množství rozpuštěného křemíku v řekách a potocích, které vtékají a vytékají z jezera, stejně jako množství křemíku v jezeře. Z usazenin ze dna jezera jsme změřili, kolik procent rozsivek je v usazeninách. Poté jsme použili metody datování usazenin (metoda radioaktivního uhlíku  $^{14}\text{C}$  a pomocí olova  $^{210}\text{Pb}$ ),

abychom odhadli stáří usazenin a vypočítali tak, kolik křemíku sedimentuje na dno jezera za jeden rok. Ze všech těchto měření jsme zjistili, že nám chybí nějaký dodatečný zdroj křemíku v obou jezerech.

Proto jsme použili analýzu izotopů křemíku, která umožňuje identifikovat zdroje rozpuštěného křemíku a odhalit původ chybějícího zdroje. Měření stabilních izotopů křemíku je metoda založená na rozdílných atomových hmotnostech křemíku. Izotopy křemíku jsou atomy křemíku lišící se počtem neutronů v atomovém jádře, a tedy i atomovou hmotností. Nejběžnější a nejrozšířenější izotop křemíku (92 %),  $^{28}\text{Si}$ , má 14 neutronů a 14 protonů, a tedy jeho atomová hmotnost je 28. Existují další dva izotopy,  $^{29}\text{Si}$  (5 %) a  $^{30}\text{Si}$  (3 %), které mají 15 a 16 neutronů. Vzhledem k jejich zvýšené atomové hmotnosti jsou během chemických, fyzikálních a biologických procesů diskriminovány. Jinými slovy, lehký izotop  $^{28}\text{Si}$  je upřenostňován rozsivkami, ale zároveň je přednostně uvolňován během zvětrávání. Proto nám stabilní izotopy křemíku mohou poskytnout informaci o původu rozpuštěného křemíku a o procesech, které mohou křemík odebírat během jeho transportu do oceánu, jako jsou například růst rozsivek či rostlin. Zároveň lze v některých případech rekonstruovat množství dostupného křemíku ve vodě v době růstu rozsivek.

Za použití všech těchto nástrojů jsme zjistili, že v jezeře Lake 850 je velké množství podzemní vody, která přináší do jezera spoustu rozpuštěného křemíku a podporuje růst rozsivek. Také jsme zjistili, že podmínky v jezeře byly stabilní v posledních 9400 letech. Délka vegetačního období, změny v relativním podílu podzemní vody a přítoku pramene do jezera ovlivnily akumulaci rozsivek. Naše data naznačují, že v době, kdy bylo klima teplejší a sušší, přitékalo méně vody skrze povrchové toky, které by jinak přinášely písek a jíl, což by nařadilo usazování rozsivek. Proto jsme našli více rozsivek (40 %) v usazenině během teplejších klimatických

podmínek. Také jsme zjistili, že v tomto teplejším období byla většina rozpuštěného křemíku, který byl spotřebován rozsivkami, přinesena podzemní vodou.

Podobně jsme zjistili, že hydrotermální prameny umístěné na dně Yellowstonekého jezera jsou dodatečným zdrojem rozpuštěného křemíku. Za posledních 9800 let tyto prameny přinášely dostatek rozpuštěného křemíku, a z toho důvodu má jezerní usazenina opravdu vysoký obsah rozsivek. Množství rozpuštěného křemíku v jezeře je tak vysoké, že umožňuje nalézt usazeniny tvořené až z 50 % rozsivkami. Kromě toho jsme zjistili, že hydrotermální exploze, ke které došlo asi před 8000 lety, neovlivnila usazování rozsivek, což nás přivádí k závěru, že Yellowstoneké jezero je velmi stabilní jezerní systém v posledních 9800 letech.

V této studii jsme ukázali, že podzemní voda a hydrotermální prameny jsou důležitým zdrojem rozpuštěného křemíku v jezerech a jsou částečně zodpovědné za tvorbu rozsivkových usazenin. Naše studie naznačují, že rozsivkové usazeniny se pravděpodobně vytvoří v jezerech vzniklých na křemičitých horninách, či ve vulkanických a hydrotermálních oblastech. Podobně jezera ve vysokých zeměpisných šířkách, která mají přítok podzemních vod, ukládají rozsivkové usazeniny. Jezera situovaná v mírném reliéfu bez strmých svahů v povodí a s nízkým přítokem jsou potenciální místa pro tvorbu rozsivkových usazenin. Všechny tyto vodní plochy s vysokým potenciálem akumulovat rozsivky působí jako uložisko křemíku v globálním křemíkovém cyklu.

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