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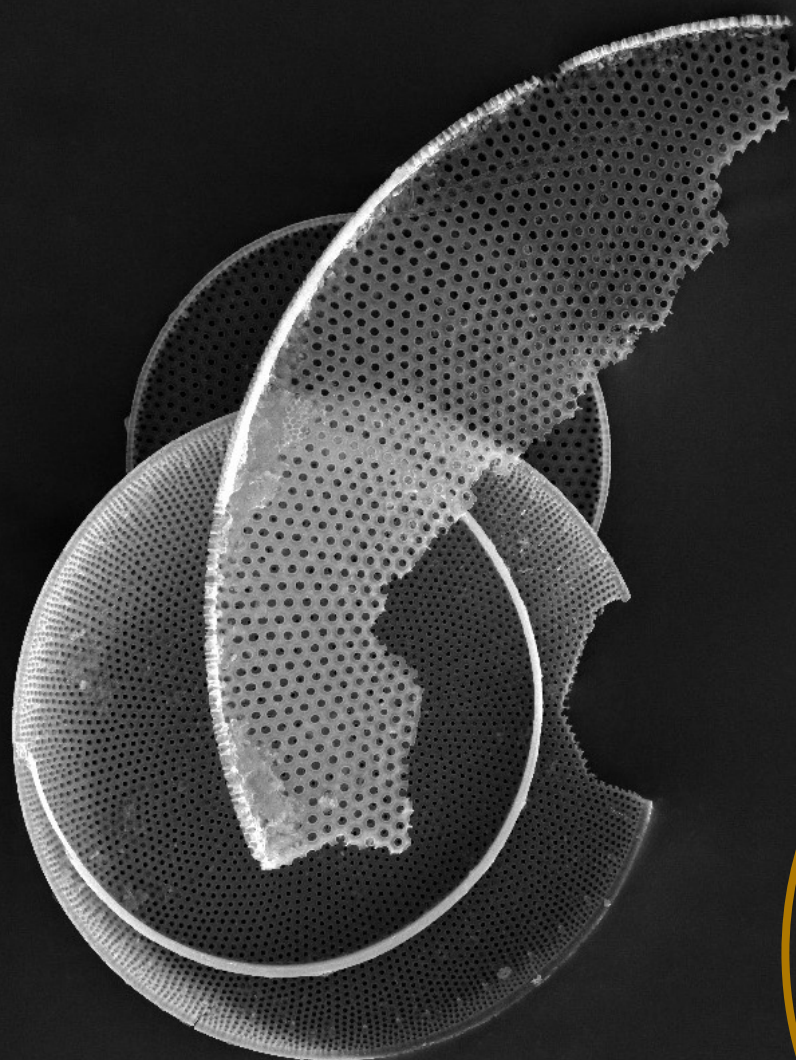
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Abstract

Global biogeochemical cycles and their interactions are an important parts of climate research. Investigations during the last decades emphasize the key role of diatoms – siliceous phytoplankton – in the silicon (Si) cycle as they are important carbon sequesters in both marine and lacustrine environments. Terrestrial Si cycling and especially fluxes across the vegetation-soil interface are highly variable but important for the global Si budget. Shifts from natural vegetation to cultivated soils have been shown to impact the Si cycle in modern soil systems. Coastal zones and lake sediments provide suitable archives to investigate how human land use modified the terrestrial Si cycle in the past.

The aim of this PhD project is to further constrain changes in the continental Si budget and link them to environmental factors such as land cultivation, deforestation, and salinity. Our study sites, Chesapeake Bay (East coast of the United States) and Tiefer See (north-eastern Germany) record climate and vegetation changes as well as human settlements during the Holocene. The measurement of biogenic Si (BSi) fluxes and Si isotopes in diatom frustules ($\delta^{30}Si_{diatom}$) separated from sediment cores, create a record of terrestrial Si cycling back in time, which then can be linked to the factors mentioned above.

Our results show that increasing human activity, especially deforestation and crop harvest impact the terrestrial Si cycle on geologically short time scales (decades-centuries). Changes in dissolved Si inputs from the catchment area dominate the variation in Si cycling in terrestrial freshwater systems; in contrast to marine environments where $\delta^{30}Si_{diatom}$ is a proxy for Si utilization. On a local scale, Si inputs can alter the budget of lake within decades.

Overall this thesis investigates how climate and human activity influence the so called 'terrestrial Si loop' determining the amount of Si delivered to the ocean.

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Contents

List of Papers

This thesis is based on three papers listed below, which have been appended to this thesis. Paper I is published in *Biogeochemistry*, Paper II has been submitted to *Quaternary Science Reviews* and is in revision, Paper III is a manuscript.

Paper I: Si cycling in transition zones

Nantke, C.K.M., Frings, P.J., Stadmark, J., Czymzik, M. and Conley, D.J. (2019).
Si cycling in transition zones – a study of Si isotopes and biogenic silica accumulation in the Chesapeake Bay through the Holocene.
Biogeochemistry 146, 145-170. https://doi.org/10.1007/s10533-019-00613-1.

Paper II: The influence of land use changes on continental Si fluxes

Nantke, C.K.M., Brauer, A. Frings, P.J., Czymzik, M., Hübener, T, Stadmark, J., Dellwig, O., Roeser, P. and Conley, D.J.(in review). Human influence on the continental Si budget during the last 4300 years: $\delta^{30}Si_{diatom}$ in varved lake sediments (Tiefer See, NE Germany),
Submitted to *Quaternary Science Reviews*, in review.

Paper III: Si isotopes in lake pore waters

Nantke, C.K.M., Frings, P.J., Stamm, F., Dellwig, O., Roeser, P., Czymzik, M., Brauer, A., and Conley, D.J. (manuscript). Si cycling in lake sediments – Si isotopes and dissolved Si concentrations in pore waters from Tiefer See (TSK), northeastern Germany, manuscript.

Acknowledgements

Introduction

The cycling of elements on Earth, e.g. the so-called biogeochemical cycles (e.g. C, N, P, Si, Fe, ...), are key processes governing the Earth's evolution and describe the global transport and transformation of elements. Chemical, physical and biological processes determine the distribution of elements forming compounds. These elements or compounds accumulate in the environment in soils, lakes, and oceans, and they are transported and cycled between them. Studies, especially within the last two decades, aim to reconstruct and analyze these reservoirs and fluxes, to provide information about processes influencing and altering their pathways.

We have greatly deepened our understanding of the global silicon (Si) cycle with the first comprehensive mass-balance of the modern ocean in the mid-1990s (Tréguer et al. 1995). Previous work has focused on the variability of Si fluxes within one of the two main Si sub-cycles: the terrestrial environment and the marine Si cycle (Fig. 1) (e.g. Frings et al. 2016). However, there are still knowledge gaps concerning Si connectivity between the cycles and the storage of biogenic silica (BSi) in aquatic sediments.

Today the majority of continental ecosystems are over-exploited and influenced by humans: deforestation, intensive land use, increasing nutrient loads and damming are only a few of the processes by which modern societies impact global nutrient cycles. Additionally, changes in terrestrial ecosystems (e.g. vegetation, land use) can have an effect on Si distributions and export.

The primary aim of this PhD project is to better understand the pathway between the continental environments and the aquatic Si cycle. Terrestrial Si fluxes from soils to rivers and lakes are the most important Si sources to the ocean Potentially influenced by natural and anthropogenic vegetation changes as well as climate shifts, these fluxes are currently poorly constrained.

Transition zones, including coastal areas and lakes, are suitable archives to investigate Si fluxes from the continents to the ocean due to their location between these realms. Sediment cores record changes in terrestrial Si cycling but also climate and vegetation shifts, allowing multi-proxy studies. By measuring Si isotopes in deposited diatom frustules, we have a tool to disentangle different processes.

potentially influencing the Si availability (Si source) and Si uptake (diatom production) in an ecosystem.

2. Background

2.1 The global Si cycle

Biogeochemical cycles describe the exchange of material and energy on the Earth's surface, influencing the functioning of ecosystems on different temporal and spatial scales (Hedges 1992). Fueled by geophysical forcing and thermal energy, the transfer of elements determines the distribution of nutrients and is closely linked to ecological processes (Van Cappellen 2003).

Silicon is the second most abundant element in the Earth's crust (28.8%) (Rudnick and Gao 2003). It is widely distributed and occurs naturally in three broadly defined structural phases: as mineral, crystalline silicates in the lithosphere of the Earth (LSi); as amorphous silica (ASi) including incorporated in organisms (biogenic silica, BSi) and found in soils and sediments; and as dissolved silica (ortho-silicic acid, $Si(OH)_4$, hereafter termed dissolved silica = DSi) that is dissolved in water (e.g

rivers, groundwater, oceans).

The global Si cycle consists of two main sub-cycles: the terrestrial and the marine Si cycles (Fig. 1). Chemical weathering processes cause the mobilization of Si from minerals in the lithosphere and the release of DSi. For example:

$$CaSiO_3 + 3H_2O + 2CO_2 \rightarrow 2HCO_3^- + Ca^{2+} + Si(OH)_4 \quad \textbf{(1)}$$
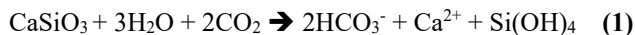
Here, wollastonite is hydrolyzed to produce bicarbonate and calcium ions in solution, releasing DSi. Note that this reaction results in the conversion of CO_2 to a form that can ultimately be precipitated as carbonate minerals. It enters the soil/regolith solution where it can be taken up by plants and fixed as phytoliths (in the form of BSi), precipitated as a secondary phase, or exported in rivers and groundwater to the ocean. DSi is used by siliceous organisms, most importantly the diatoms, radiolarians and sponges. Recycling in the water column and the storage of BSi in sediments are the main processes controlling the aquatic Si pool. Diagenetic and tectonic processes ultimately transform the deposited BSi into more stable (alumino-)silicates, closing the cycle and returning Si from the marine environment to the lithosphere.

Recent models have estimated a DSi load of 9.4 Tmol Si a^{-1} delivered to the oceans, of which river
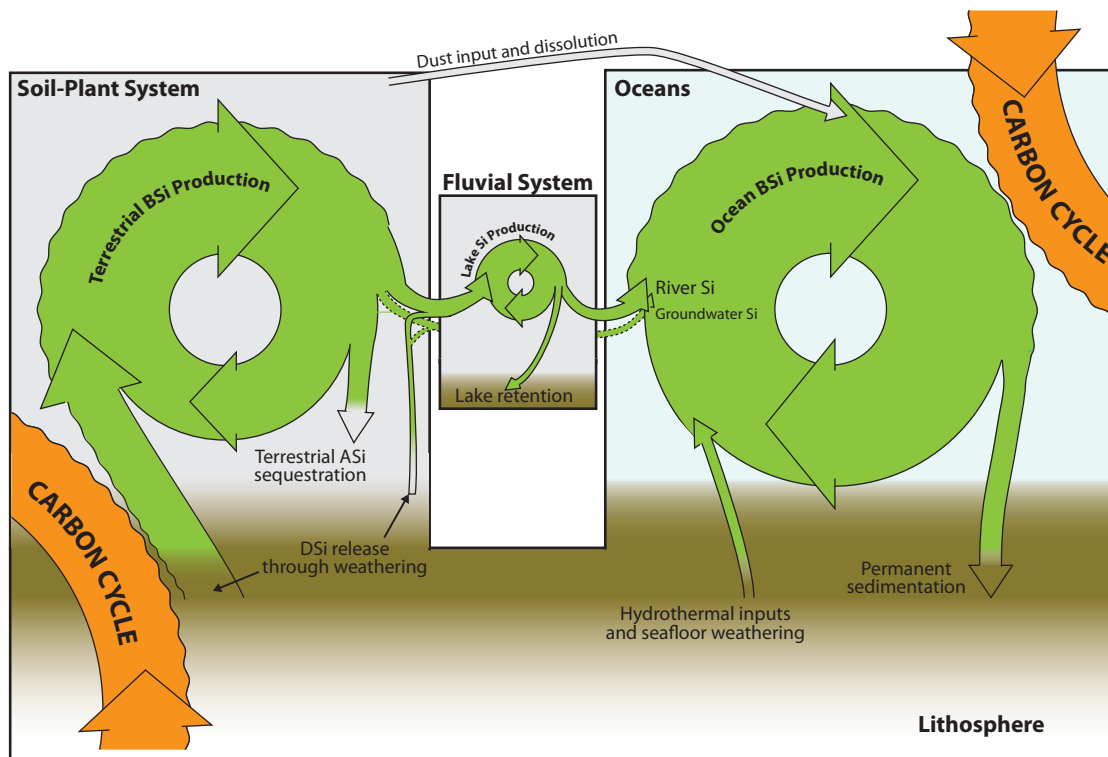
Figure 1: Schematic figure of the global Si cycle. The thickness of the arrows approximates the magnitude of the fluxes (Frings et al. 2014).

discharge is the most important source (around 64%). The DSi is transported with a mean stable isotope composition (expressed as $\delta^{30}Si$, the deviation of the $^{30}Si/^{28}Si$ ratio from that of the reference material NBS28) of 1.28‰ (n = 544) (Frings et al. 2016). This value is influenced by lithology, biotic and abiotic conditions and the water residence time of rivers, lakes and estuaries. With longer residence times favouring recycling processes in the water column and sediments that are an important control on the amount of DSi available for utilization by organisms (diatoms, radiolarians, sponges). A mean accumulation rate of 6.3 Tmol Si a^{-1} (of which coastal areas comprise around 3.3 ± 2.1 Tmol Si a^{-1}) makes the ocean the main Si sink (Tréguer and De La Rocha 2013).

2.2 Importance of Si and connection to other biogeochemical cycles

The Si cycle is coupled to the long-term (or 'geologic') carbon cycle. On long time scales (>106 yrs) chemical weathering of siliceous rocks consumes a considerable amount (~12 Tmol a^{-1}) of carbon dioxide (CO_2) (see equation 1) by the production of bicarbonate (Gaillardet et al. 1999; Moon et al. 2014), which is ultimately deposited in the sediments. High atmospheric CO_2 concentrations are related to high temperatures and global precipitation rates and, therefore, increasing weathering rates, which act as a negative feedback on atmospheric pCO_2. On shorter time scales, the contribution of siliceous phytoplankton (especially diatoms) to carbon sequestration in marine environments is of greater importance (Struyf et al. 2009). Due to their robust Si frustules or shells diatoms have high sinking rates and longer dissolution times than other phytoplankton, which makes them relevant in the export of Si and C to the sea floor. Recent studies suggested that not only diatoms in the marine environment, but also Si depositing organisms in terrestrial ecosystems can significantly influence CO_2 levels (Carey and Fulweiler 2012). Grasslands and crops both store a large amount of Si in their tissues and are thus potentially efficient in carbon sequestration in terrestrial ecosystems, similar to the role of diatoms in the oceans.

A system of global mass transfer processes directly and/or indirectly connects Si to the other main

nutrient cycles: carbon (C), phosphorus (P) and nitrogen (N). The increase of N and P loading to marine environments caused by human activities has had a major influence on ecological functions and community structure. Changes in nutrient availability can cause shifts in food chains and trophic cascades. Major shifts of pools and fluxes within the Si cycle thus can alter the availability of other nutrients. Together the balance of biogeochemical cycles determines the structure and function of biotic communities and can influence the Earth's climate on regional and global scales.

3. Silica in diatoms

Diatoms - siliceous phytoplankton – are a key group of aquatic primary producers and often dominate the springbloom. The species composition and population size are dependent on the specific environmental tolerances of the taxa to variables such as water temperature, salinity, food web community and nutrient supply (Carstensen et al. 2015). Due to their sensitivity and their ability to remain preserved in sediments, diatoms are often used as indicators of paleo-environmental change. Furthermore, diatoms sequester around 25.8 Gton (2322 Tmol) C a^{-1}, comprising 43% of the total oceanic net primary production (Tréguer et al. 2020).
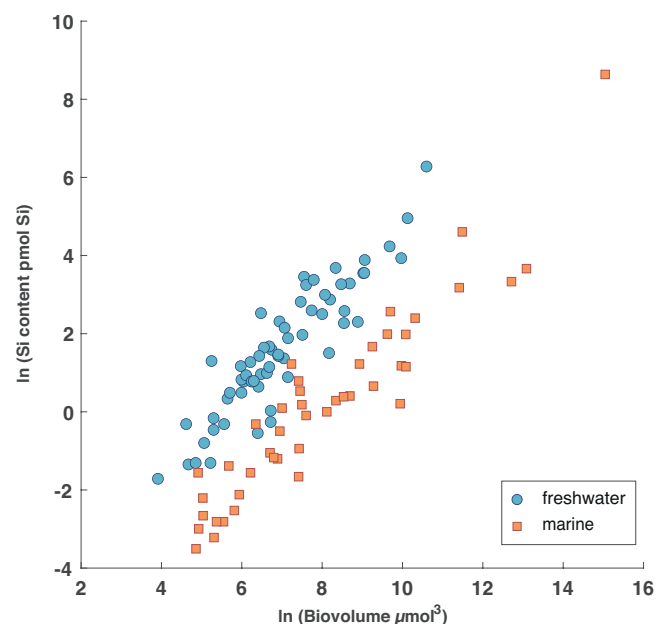
Figure 2: The relationship of Si content (pmol Si) to biovolume of freshwater diatoms (blue circles) and marine diatoms (orange squares) (Conley et al. 1989)

The transport of C from surface waters to the sediments makes them important contributors in the so called "biological pump" absorbing CO_2 from the atmosphere (Sun et al. 2014). Their requirement for DSi often makes it the limiting nutrient for the production of diatom populations (Conley et al. 1993).

The BSi content bound in diatom frustules varies with the diatom composition (Sutton et al. 2013). Findings of Conley et al. (1989) showed positive correlation to size and differences in orders of magnitude between diatom species. In general, marine diatom species (orange squares in Fig. 2) build less heavily silicified frustules than freshwater species (blue circles, Fig. 2). Due to relatively low DSi concentrations in ocean waters, the majority of marine diatoms adapt to these conditions by lowering their reuirement for silica as a nutrient (Conley et al. 1989). Differences in size distributions could be explained by nitrogen vs. phosphorus limitation, nutrient fluctuations and mixed layer depth differences between freshwater and marine ecosystems (Litchman et al. 2009).

Complex competition conditions have been observed for diatoms in aquatic ecosystems, where different water masses meet. Distinctive fractionation factors (see section 3.1) for DSi uptake between species may also occur (Sutton et al. 2013), but species dependent fractionation is difficult to observe because single species are hard to separate due to their small size and often overlapping size ranges between different species. Addressing this challenge, for our studies we decided to hand-pick single diatom frustules from pre-cleaned samples (see method section). There are several advantages here: this approach provides the opportunity to look into every sample in detail and assess the diatom composition. The purity of the samples increases by choosing single frustules individually. For example, remains of organic matter or clays potentially attached to diatom frustules in the sediment could be detected and removed if necessary. Secondly, a single species or genus diatom record is possible to measure. This avoids the potential influence of species-specific fractionation. The comparability within the record over time increases. Further, the picked species/genus can be described and discussed in context of the diatom population in the ecosystem. For example bloom forming taxa are expected to record a different signal than those which grow in high DSi situations. Constrained by

the availability of single-species diatom frustules through a sediment core nevertheless, this would enhance the comparability of isotope data by minimizing the uncertainty associated with species/ genera specific fractionation. Small cell sizes in freshwater systems, however, limit the possibility of hand-picking samples. Diatom frustules <50 μm are difficult to identify with light microscopy and to hand-pick properly.

3.1 Measurement of Si isotope ratios in diatoms

Silicon has three naturally occurring stable isotopes with different abundances (^{28}Si = 92.23%, ^{29}Si = 4.67%, ^{30}Si = 3.10%) (Faure and Mensing 2005). The mass difference between the three nuclides causes slight differences in reaction rate constants or partition coefficients between the individual isotopes that induces isotope fractionation as Si is cycled in the natural environment. Due to the bigger mass difference often the ratio of ^{28}Si and ^{30}Si is measured and expressed in the δ-notation (in ‰). $\delta^{30}Si$ is defined as follows:

$$\delta^{30}Si = [(^{30}Si/^{28}Si_{sample})/(^{30}Si/^{28}Si_{standard*})-1] \times 1000 \quad (2)$$

*the accepted standard is NBS28 (National Institute of Standard and Technology RM#8546 (Carignan et al. 2004)).

The fractionation factor (α) is determined by isotope effects (kinetic or equilibrium). Kinetic fractionation is unidirectional with the product not reacting with the substrate. Equilibrium fractionation, by contrast describes the condition when the chemical reactions are in equilibrium and the reactants interact with each other.

$$^x\alpha_{substrate-product} = R_{substrate}\Big/R_{product} \quad (3)$$

where R is the ratio of $^{29}Si/^{28}Si$ or $^{30}Si/^{28}Si$.

Since α is close to one the fractionation ε is often conveniently presented in permille (‰) notation as epsilon:

$$^x\varepsilon_{substrate-product} = 10^3 \left(^x\alpha_{substrate-product} - 1 \right) \quad (4)$$

The relationship between $\delta^{30}Si$ and $\delta^{29}Si$ is a predictable function of the mass dependence of the fractionation factors and is used to track potential polyatomic interferences during mass spectrometry, where especially $^{14}H^{16}O^+$ have been reported to cause potential molecular interferences (Cardinal et al. 2003).

$\delta^{30}Si$ values measured in diatom frustules are increasingly used for paleoenvironmental interpretation. Diatoms take up Si from the surrounding water and discriminate against the heavier Si isotopes ^{30}Si and ^{29}Si. This selective utilization leads to a relative depletion of light ^{28}Si isotopes in the remaining DSi, i.e. a shift towards higher $\delta^{30}Si$. Two different models describe the evolution of Si isotope ratios as diatoms progressively deplete a pool of available DSi: the Rayleigh model (eq. 5) and the steady-state model (eq. 6) (de la Rocha et al. 1997; Varela et al. 2004).

$$\delta^{30}Si_{product} = \delta^{30}Si_{initial\ substrate} - \left(f_{Si}/1 - f_{Si}\right) \times \varepsilon^{30}_{substrate-product} \times \ln(f_{Si}) \quad (5)$$

$$\delta^{30}Si_{product} = \delta^{30}Si_{initial\ substrate} + \varepsilon^{30}_{substrate-product} \times f_{Si} \quad (6)$$

The Rayleigh model (Fig. 3) describes the isotope fractionation of Si during the uptake of DSi by diatoms under the assumption of a fixed pool of silica with a certain initial isotope composition assuming the diatoms do not re-dissolve. Because diatoms favour the lighter ^{28}Si, the surrounding water becomes depleted in light isotopes with a fractionation factor of -1.1 ± 0.4‰ (De la Rocha et al. 1997). Conversely, the steady-state model assumes an open system with a continuous Si supply from a steady external source. Both approaches define a mass balance model constrained within 0 and 100% of Si utilization. The fractionation factor is defined as the fractionation between the dissolved and the solid Si phase. The fractionation (ε) is constant in both models and determines the shape of the curve dependent on the DSi supply (Varela et al. 2004). When the Si utilization is 100% the $\delta^{30}Si_{diatom}$ must equal $\delta^{30}Si_{water}$. However, when it comes to paleo-climatic interpretation of Si isotope data the difference between the models is generally small, since the $\delta^{30}Si$ of the accumulated diatoms in the sediment in both models are quite similar considering proportional loss of biogenic opal along
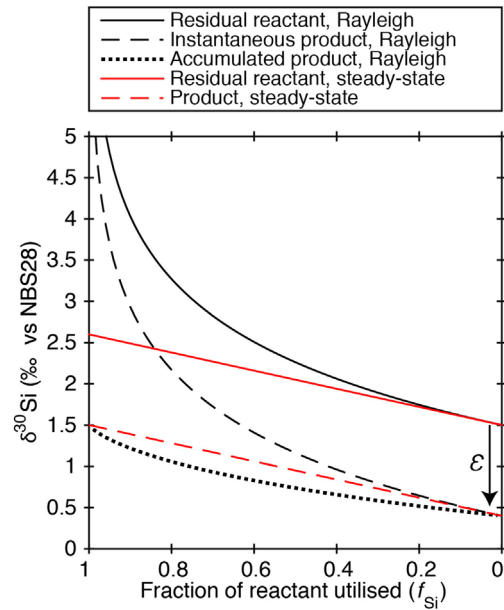
Figure 3: Rayleigh Model (black lines) and steady-state model (red lines) display the utilization of DSi by diatoms and the associated fractionation factors in a closed and open system respectively (Frings et al. 2016). The initial $\delta^{30}Si$ of the water (solid line) and the $\delta^{30}Si_{diatom}$ (broken line) are plotted on the y-axes along a Si utilization factor plotted on the x-axis.

the Si utilization gradient (Fig. 3, compare dotted black line and broken red line) (De la Rocha et al. 1997).

Si isotope measurements in diatom frustules provide a tool to reconstruct the relative Si utilization if the initial composition and the fractionation associated with biogenic silica production are known. Assuming the fractionation is known and constant, $\delta^{30}Si_{diatom}$ is controlled by two main parameters (Fig. 3): $\delta^{30}Si$ of the ambient water ($\delta^{30}Si_{DSi}$) during diatom growth and the relative amount of DSi utilization, i.e. the ratio of biogenic silica production to DSi supply (related to the BSi burial flux). This leads to two contrasting endmember interpretations. Most commonly, as a paleo-proxy diatom $\delta^{30}Si$ is used to infer relative changes in Si utilization and thus to interpret changes in Si cycling through time (De La Rocha et al. 1998). Alternatively, diatom $\delta^{30}Si$ can be interpreted as yielding information about the changes in DSi supply from the terrestrial ecosystem. This allows conclusions about abiotic and biotic controls of the Si fluxes from the continents to be drawn (Opfergelt and Delmelle 2012). To distinguish between these two processes is the most important challenge for interpreting Si isotope records.

The measurement of $\delta^{30}Si_{diatom}$ requires special attention because other compounds/organisms
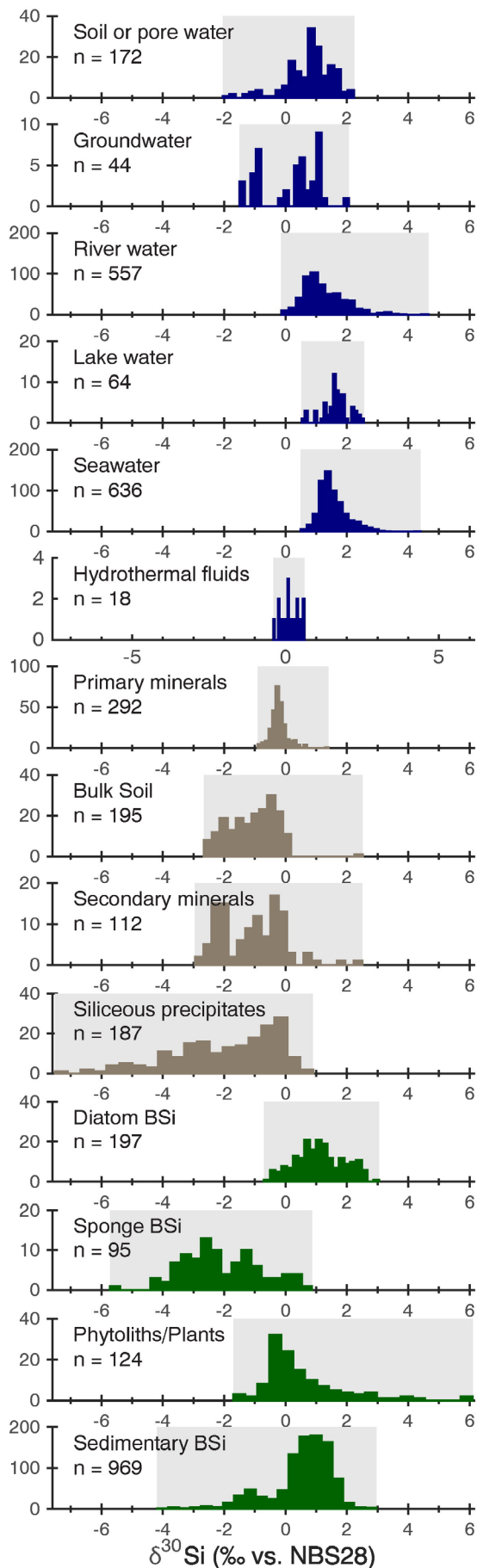
Figure 4: The range of Si isotope values measured on different material (Frings et al., 2016).

containing Si create the potential for contamination that can influence $\delta^{30}Si_{diatom}$ if the sample is not properly prepared (Egan et al. 2012). Typical $\delta^{30}Si$ values for different natural materials are shown in Figure 4 (Frings et al. 2016). In particular, contamination of a diatom sample with secondary clay minerals or sponge spicules, with generally low isotope values, would shift the measured $\delta^{30}Si_{diatom}$ and make it invalid. Such an effect has been shown for the oxygen isotope composition of diatoms (Mackay et al. 2011) Finally, the fractionation cannot always be assumed constant through time in a natural system. Possible changes due to species shifts are a challenge measuring diatom bulk samples, especially in dynamic ecosystems as coasts and lakes. However, hand-picking individual diatom frustules from specific species or genera tackles these challenges providing a tool for paleo-studies in complex ecosystems.

4. Transition zones

The transition zone between the continents and the ocean is particularly important for global nutrient cycles. A variety of sources and processes determine material fluxes and therefore geochemical processes. A growing number of studies have highlighted the role of net land–ocean inputs of dissolved and solid material (Jeandel 2016). River inputs are identified as one of the most important material sources transporting dissolved, colloid or solid forms. Peucker-Ehrenbrink (2009) estimated a freshwater runoff of approximately 38900 km^3 a^{-1} and suspended sediment delivery to the coastal ocean of ~19 Gtons a^{-1} summarising 19 large scale drainage regions. Due to imbalances between sources and sinks in the land-ocean system, recent studies proposed sources and sinks along the margins to play a key role and explain these gaps, the so-called 'boundary exchange' processes (Jeandel 2016). Si sinks like BSi formation and reverse weathering for example can be balanced with submarine groundwater discharge in shallow coastal aquifers, recently estimated to around 3 Tmol a^{-1} proposed by Rahman et al. (2019).

These 'boundary effects' describe the interactions between elements and sediment (Fig. 5): Elements can get scavenged particulates, dissolved and/or be buried in the sediments. All of these processes can occur several times within the coastal zone and
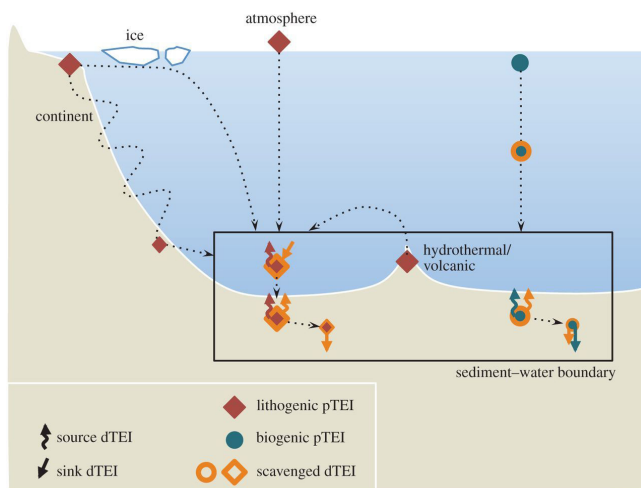
Figure 5: Potential sources and sinks of dissolved elements and isotopes (dTEI) (Homoky et al. 2016)

determine the element ocean budget (Homoky et al. 2016). Paleo-studies comparing element fluxes and isotope ratios are helpful to assess changes and process links through time. Further measurements of pore water profiles can help to better understand the complex system of nutrient (re)cycling in the sediments of transition zones.

4.1 State of the Art: The continental Si cycle

The biogeochemical cycle of Si in soil ecosystems has been intensively investigated during the last decade, raising new questions. Terrestrial ecosystems act as a filter that controls the amount of Si exported to the marine Si cycle. This concept of the 'ecosystem Si filter' (Struyf and Conley 2012) describes the fixation and recycling processes in the terrestrial Si cycle (Fig. 6). The annual fixation of Si in terrestrial vegetation amounts to approximately 84 Tmol and exceeds the yearly export of DSi to the coastal zone by more than 10 times (6.18 Tmol DSi export)(Carey and Fulweiler 2012; Frings et al. 2016).

The weathering of primary silicates is the ultimate source of DSi. However, the importance of the silicate mineral fraction for the Si nutrient cycle can differ according to the geology on a regional scale. Weathering rates are influenced by temperature, hydrology, solution chemistry and the exposure of new reactive surfaces by erosion. In addition, the composition and availability of primary silicates (e.g. feldspar, olivine) and rates of secondary mineral formation modify DSi availability and the isotope

signature ($\delta^{30}Si_{DSi}$) of the soil waters and can vary on very local scales (catchment scale).

Part of the DSi released from weathering is stored in Si soil pools (amorphous silica pools, ASi pools) that can differ naturally depending upon vegetation and climate (e.g. temperature, precipitation) and range typically between 15000 and 105000 kg SiO_2 ha^{-1} (Struyf and Conley 2011). In an undisturbed landscape the uptake of DSi from the soils follows the natural seasonality of the vegetation. During the vegetation growth period, the plants take up DSi from the soils, store it in their tissues as phytoliths and return it during their decay. Consequently, the ASi pool consists primarily of biogenic Si (BSi) mainly as plant phytoliths but also terrigenous forms e.g. Si adsorbed to soil particles especially Al and Fe oxides/hydroxides (Sauer et al. 2006; Clymans et al. 2011b). Physical conditions such as temperature, salinity and pH influence the reactivity/dissolution rates of ASi in soils, waters and sediments. The size of the ASi pool stored in soils is also dependent on the occurrence of organisms specialized in the uptake and utilization of silica. In terrestrial ecosystems, grasses are known to be efficient accumulators of silica influencing the DSi fluxes in the surrounding soil (Cooke and Leishman 2012). Altogether the continental Si cycle is a complex system with various sources and sinks that can be altered by natural and anthropogenic processes already on very local scales. Especially the more reactive ASi pool has been shown to be vulnerable to disturbances (see section 4.3).

4.2 Aquatic filters: Si in lakes and coastal zones

Global models estimate the amount and variability of Si cycling through ecosystems. Uncertainties arise from the transition zones (rivers, lakes and coastal zones) where a part of the mobilized Si in soils accumulate in their sediments, largely as biogenic silica remains, before the remainder is transported to the oceans. Within the last two decades most studies focused on the Si cycle in the open ocean and terrestrial soils, considering the transition zones (river, lakes, estuaries) to be a rather passive connection between them. However recent studies (e.g. Hughes et al. 2012; Cockerton et al. 2015; Rahman et al. 2017) started to highlight the role of continental margins and lakes suggesting
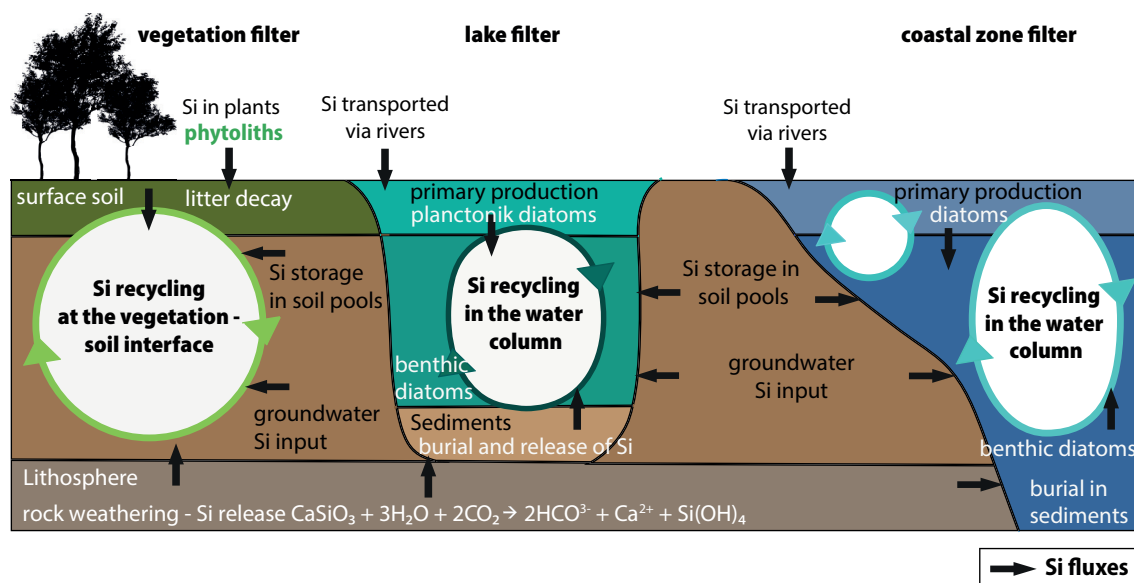
Figure 6: Conceptual model of the continental Si cycle including the terrestrial Si subcycle and the transition zone: lakes and coastal areas.

potential Si effluxes and sinks that can change the Si isotope composition in the transition zones before reaching the open ocean. However, further studies are required to investigate the suite of climate and land use parameters that together determine terrestrial Si cycling and consequently $\delta^{30}Si_{DSi}$ values in adjacent aquatic ecosystems.

Coastal zones

Coastal marine areas are among the most productive ecosystems worldwide and often have a long history of human disturbance (Jickells 1998). Nutrient replete conditions favour high productivity and typically, the dominance of diatoms. Relatively short water residence times (from weeks to months) make them sensitive to environmental changes on geologically short timescales (years to centuries) (Jickells 1998) that might be difficult to resolve in more buffered ocean waters. Major Si inputs to coastal areas from terrestrial ecosystems are transported via tributaries, groundwater flow and direct overland flow (Laruelle et al. 2009; Tréguer and De La Rocha 2013).

Mangalaa et al. (2017) identified four major factors that influence the Si cycle in coastal areas: (i) lithogenic supply through changing weathering rates, (ii) diatom uptake related to population size and composition, (iii) mixing ratios of sea water and freshwater and (iv) land use changes (related to changes in vegetation, soil system and hydrology). Further, reverse weathering has been suggested to

enhance the preservation efficiency of Si in coastal zones (Aller 2014; Frings et al. 2016; Rahman et al. 2017).

DSi concentrations along the salinity gradient have been investigated to better understand recent Si dynamics in coastal areas (Dürr et al. 2011; Barão et al. 2015; Mangalaa et al. 2017). A 14-year monitoring period in the Rhode River sub-watersheds of the Chesapeake Bay (hereafter 'CB') revealed inter-annual variations in Si fluxes, that could be linked to precipitation changes and water discharge (Correll et al. 2000). Dry winters were found to cause low DSi discharge and subsequent Si limitation in the RhodeRiver estuary (Correll et al. 2000). Seasonality in DSi supply and uptake (through diatoms in the dry season) along the pH and salinity gradient in Indian estuaries highlight the importance of freshwater/ seawater mixing ratios on the Si cycle in estuaries (Mangalaa et al. 2017).

Lakes

Freshwater lakes - as a part of the continental Si cycle - are net sinks for Si and retain on average 30% of inflowing DSi (Frings et al. 2014). At the global scale, estimation of Si retention in rivers and lakes varies between 1.15 Tmol Si a^{-1} to 2.4 Tmol Si a^{-1} (Laruelle et al. 2009; Clymans et al. 2011b; Dürr et al. 2011). Previous studies were able to calculate the importance of different Si sources: groundwater, river input, atmospheric inputs and re-supply from the sediments in Lake Lugano (Switzerland) in

modern waters (Hofmann et al. 2002) and theoretically in a box model based on global data from oceans and continents (Laruelle et al. 2009). Frings et al. (2014) estimated the global storage of Si in lake sediments, using a dataset of 34 lakes with different environmental properties: pH, latitude, elevation and surface area. However, it was shown that the Si retention in different lakes cannot be explained with only these parameters but depends on a variety of distinctive conditions in the lake and the catchment .

The Si residence time (Si inventory/Si input) of lakes provides information about reactivity and recycling rates in an ecosystem. Long residence times make the inventory important in sustaining production and buffering against short-term perturbations in supply, but can lead to Si depletion over longer time scales (e.g. Great Lakes) (Schelske et al. 1983). Short residence times are typical for coastal zones and small lakes, which make the system more dependent on Si inputs. On longer time scales (longer than the Si residence time) the influences of BSi recycling in the water column on the $\delta^{30}Si_{diatom}$ can be neglected.

Lake water Si isotope data are limited. Available datasets include the lakes Tanganyika (East Africa) (Alleman et al. 2005), lake Baikal (Russia) (Panizzo et al. 2017; Swann et al. 2020) and Myvatn (Iceland) (Opfergelt et al. 2011), examining the seasonal and spatial variations in DSi utilization and export. Published values range from 0.7‰ in Myvatn to 2.28‰ in lake Baikal.

Lake diatom paleo-environmental records are similarly scarce. The first studies of silicon isotopes measured in lacustrine diatoms were published for lake Rutundu (Kenya) (Street-Perrott et al. 2008), lake El'gygytgyn (Russia) (Swann et al. 2010) and lakes Victoria and Edward (East Africa)(Cockerton et al. 2015). All three studies discuss them together with $\delta^{18}O_{diatom}$ to investigate the role of climate shifts on Si cycling and emphasize the potential of $\delta^{30}Si_{diatom}$ in lakes. $\delta^{30}Si$ data (0.9 - 1.4‰) spanning the last 23000 years in Siberian Lake El'gygytgyn indicate the importance of large-scale temperature changes and nutrient inputs for controlling $\delta^{30}Si_{diatom}$ values in an oligotrophic lake in the absence of human activity (Swann et al. 2010). Increasing temperatures favour water column mixing and the recycling of nutrients from bottom waters consequently increase DSi availability and lower $\delta^{30}Si_{diatom}$. Cockerton et al. (2015) show the influence of enhanced monsoon rainfall and vegetation changes on weathering rates,

DSi export and consequently $\delta^{30}Si_{diatom}$ on glacial/interglacial time scales. In Lake Rutundu only a few $\delta^{30}Si_{diatom}$ data points varying between -1.3 and 0.5‰ are interpreted as changes in input, source and/or recycling of Si in an open system. A recent study from Lake Baikal suggests the main process predominating the $\delta^{30}Si_{diatom}$ variation to shift from Si utilization (during the last 2000 years) to Si supply in the 20th and 21st – century (Swann et al. 2020).

Given the shorter residence time, $\delta^{30}Si_{diatom}$ in lakes is generally a proxy for Si supply, unlike in the ocean, where it is largely seen as a Si utilization proxy. Due to the seasonal total depletion of DSi in the surface water after spring bloom, the isotope ratio captures the signal of the lake water and Si inputs. However, due to the dynamic of lake systems with a variety of processes, the interpretation of $\delta^{30}Si_{diatom}$ as a 'primary' signal without any secondary isotope fractionations is still a concern. Results from lake Baikal however, measured on sediment trap material present a stable isotope signal through the water column indicating the absence of isotope fractionation during potential dissolution processes (Panizzo et al. 2015).

The results of very different lake systems (Tanganyika, Myvatn and Baikal) reveal the variation of Si cycling in lake ecosystems and the importance of individual site studies to better understand the conditions and processes. Questions about key controls on the lake Si cycle dominated by lake internal processes like changes in water overturning, nutrient distribution and Si recycling or inputs from the watershed of the lake controlled by Si soil pools, erosion and vegetation changes need to be answered.

Si in pore waters

The recycling rate of Si at the water-sediment interface is still understudied and poorly investigated in natural ecosystems. Chemical conditions in the topmost sediment are potentially influencing the dissolution rate of accumulated BSi and silicate minerals control the DSi flux from the sediment. Recent studies focus on pore waters in marine ecosystems using Si isotopes ($\delta^{30}Si_{PW}$) to assess (re)cycling processes (Ehlert et al. 2016; Geilert et al. 2020, Ng et al. 2020; Fig. 7).

The DSi (silicic acid) concentration in sediment pore waters most critically depend on the dissolution

rate of particulate Si influenced by: (i) pH, (ii) temperature, (iii) type and concentration of other Si species (polymers and complexes) and (iv) the availability of additional minerals (Williams and Crerar 1985). Also, the rate of DSi diffusing through the sediment is of importance where a low rate increases the residence time of the fluid and therefore the reactivity. Here temperature and porosity play a major role and need to be considered in natural archives. Previous studies reporting laboratory experiments, showed that the Si dissolution rate increases with temperature, pressure and alkalinity of the solution (Williams and Crerar 1985). Additionally Fe and Al released by detrital minerals can influence (reduce) the solubility of Si (Dixit et al. 2001). Anoxic conditions have been suggested to reduce the release of Si from the sediments (Siipola et al. 2016). However, the investigation of natural archives will help to discuss the interplay of these factors.

Si isotope ratios measured in marine pore waters from the Peruvian upwelling region varies between 1.1 and 1.9‰. Around 25% of the accumulated BSi dissolves and acts as a source of light Si. The authors suggest the importance of the authigenic re-precipitation of previously dissolved BSi in the topmost centimetres of the sediment (Ehlert et al. 2016). A recent study from the Gulf of California, however, found $\delta^{30}Si_{PW}$ values much lower (around 0‰), implicating the dissolution of Si minerals (clays) as one dominant process in the topmost sediment (Geilert et al. 2020). More field studies are needed to constrain and better understand the

processes controlling the recycling of Si in the top-most sediment layers.

4.3 Human impact on the Si cycle

In addition to the natural variability of Si fluxes, there are different anthropogenic influences that can impact the Si transfers in the global Si cycle. The land-ocean interface is especially vulnerable to human influences. Perturbations to the terrestrial Si cycle by agriculture and changes in hydrology have large effects on Si fluxes (Conley et al. 1993; Clymans et al. 2011b). Land use, deforestation and cultivation of landscapes, urbanization and sealing of soils, and the utilization of hydropower through dams all alter ecosystem Si budgets. In general, the preference of plants to take up the lighter ^{28}Si leads to a soil-water depletion of the light isotopes. In undisturbed environments this lighter Si is returned to the soil system during plant decay processes at the end of the growing season.

Disturbances to the terrestrial Si filter cause changes in Si fluxes at the soil-vegetation interface: Deforestation leads to a declining recycling of Si in soils and a decrease in the ASi pool causing an increase in $\delta^{30}Si_{soil\ water}$ (early deforested, Fig. 8). Additional landscape cultivation also alters Si pools and fluxes. Removing plant tissues (and phytoliths) during harvest inhibits the return of light Si isotopes to the soil ASi pool (Vandevenne et al. 2012). This leads to a depletion of the lighter Si isotopes in the soil system and a drawdown in pool size
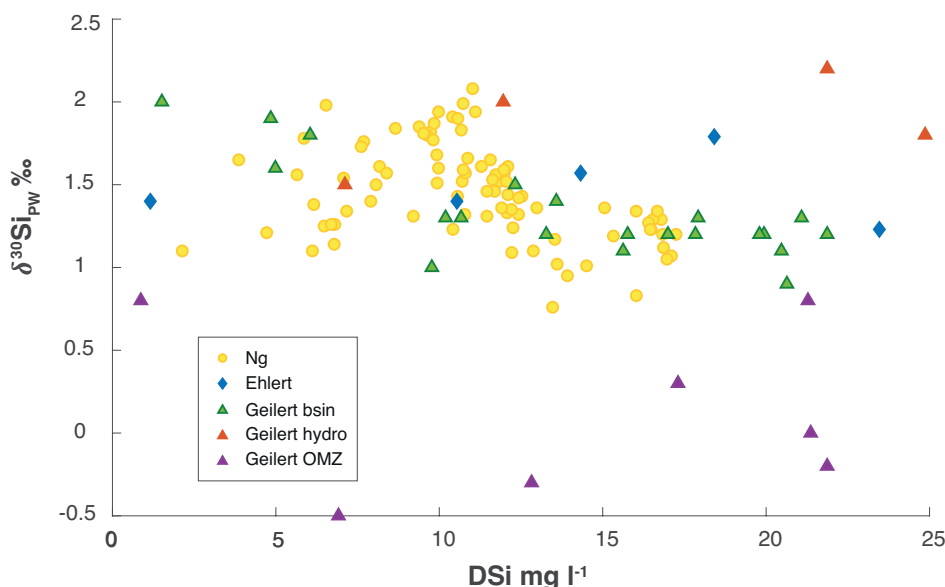
Figure 7: Published $\delta^{30}Si_{PW}$ data plotted against DSi (mg l^{-1}) (Yellow dots Ng et al., 2020, blue diamonds Ehlert et al., 2016, green, red and purple triangles Geilert et al., 2020).
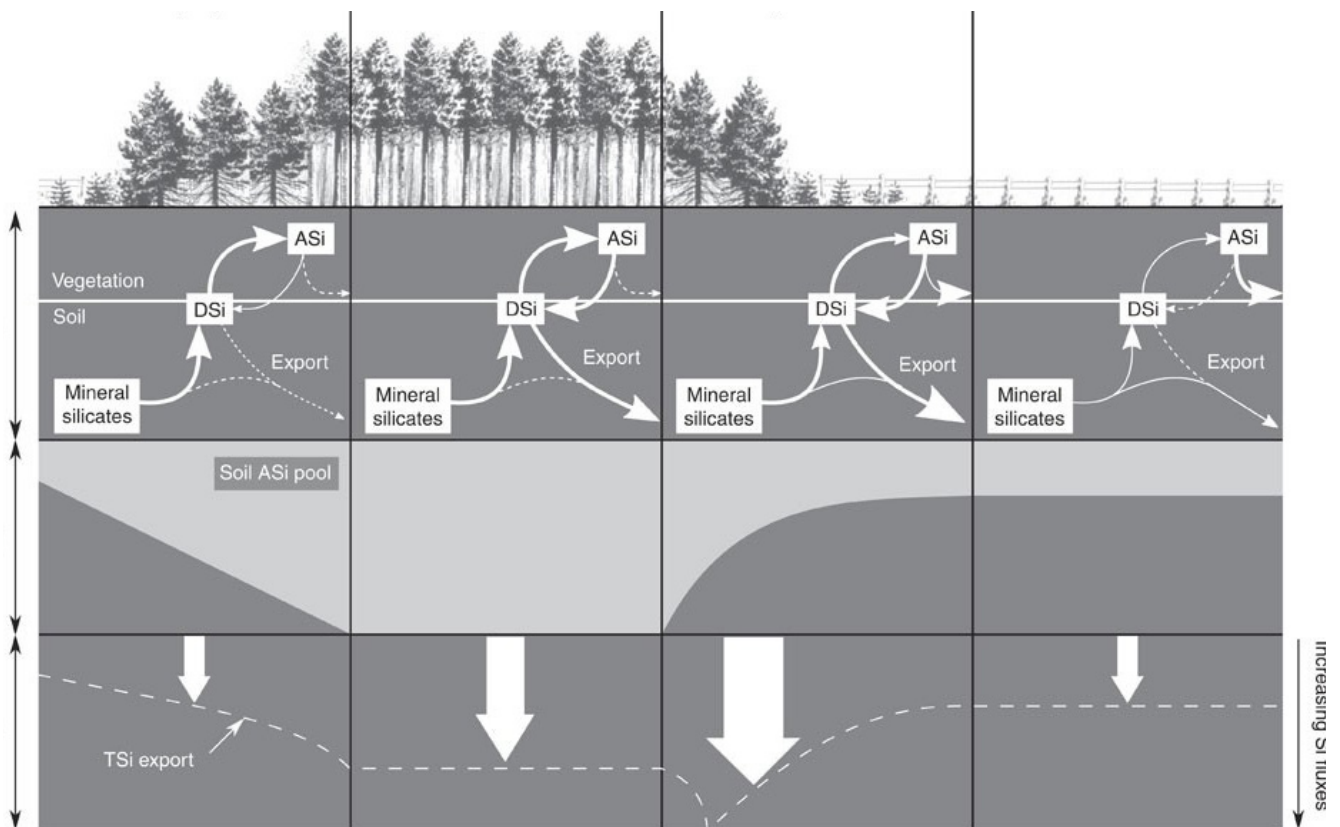
Figure 8: Conceptual model of variations in Si pools and fluxes in an ecosystem undergoing land use change (from Struyf et al. 2010).

(climax cultivated, Fig. 8) (Vandevenne et al. 2015). Considering the range of published $\delta^{30}Si_{diatom}$ (Fig. 4) and based on findings of this PhD thesis a decrease in $\delta^{30}Si_{DSi}$ by ~0.5-1‰ is conceivable. The dependence on the ASi pool size, make this estimation vague. The concurrent increase of soil erosion also enhances DSi export from soils (Struyf et al. 2010; Clymans et al. 2011b). Thus, the pool of ASi stored in the soil system further declines (Fig. 8).

Altered Si fluxes from soils reach the fluvial system and influence the amount of Si transported to the ocean as well as its isotope composition. Changes of the hydrology through damming or straightening of rivers additionally influence Si fluxes. Slowing down of rivers through dams can enhance diatom production by creating a lake situation with lower turbidity, higher sedimentation rates and longer Si residence times. Accumulated nutrients enhance the diatom production and the utilization of DSi in rivers expected with damming, observed in the Black Sea and the Baltic Sea (Humborg et al. 2000; Conley et al. 2008). Since aquatic ecosystems are strongly dependent on DSi loads delivered through river inputs, the fluvial Si cycle is not considered to be independent, but highly sensitive to changes

in the terrestrial cycle. Increased nutrient fluxes represent another potential impact on the Si cycle. Large scale exports of nitrogen and phosphorus to ecosystems has visible effects on food webs, favouring organisms with higher nutrient requirements and faster growth rates. As DSi availability is limiting the diatom population, shifts in trophic levels and species composition could be the consequence. An increase in BSi flux caused by a higher nutrient availability would first lead to an increase in $\delta^{30}Si_{diatom}$, due to a higher demand for DSi favoring a smaller expression of fractionation (Fig. 3). When DSi is nearly totally depleted, mass-balance dictates that $\delta^{30}Si_{diatom}$ records the isotope signal of the source water with an isotope difference around zero.

5. Aims and research questions

The aim of this PhD thesis is to improve the understanding of the pathways by which Si is transported from the continents to the oceanic Si cycle. To achieve that, the investigation of Si mobilization and recycling rates in the transition zone is necessary. Diatoms accumulated in aquatic sediments (lakes and coastal zones) provide us the opportunity to reconstruct Si cycling on geologically short time scales (decades to centuries) and to resolve the potential impact of human activity. Paleo-studies help us to constrain the temporal scales on which Si cycling can be altered. The investigation of sediment archives through the Holocene provides an insight into the filter capacity of aquatic freshwater systems and their importance in controlling Si fluxes towards the ocean. Simultaneously, the increasing human impact during the Holocene allows us to reconstruct the influence of land use on the terrestrial Si budget as suggested by observational studies of modern systems (e.g. monitoring rivers for a few years) and chronosequences so far (Clymans et al. 2011b).

This thesis is addressing the following research questions:

1. What are the specific influences on the Si loads transported from the continents to the oceans?

2. Can we distinguish between natural and anthropogenic processes changing Si accumulation in freshwater ecosystems?

3. Which processes are most dominant in altering Si cycling in aquatic freshwater systems?

4. Is it possible to separate different Si sources (fluvial, groundwater, BSi recycling) to aquatic ecosystems?

As research sites we investigated the Chesapeake Bay located at the East coast of North America (Paper I) and Tiefer See, a lake in northeastern Germany (Papers II and III). Maps of both locations and site descriptions can be found in the papers.

6. Methods

6.1 Water samples

Since the availability and isotopic composition of dissolved silica (DSi) in aquatic systems plays an important role for the interpretation of $\delta^{30}Si_{diatom}$ (see 3.1/Figure 3), monitoring of the modern water DSi helps to constrain the paleo-interpretation of aquatic Si cycling. In this thesis water samples from Tiefer See (TSK) (Papers II and III) were taken monthly between January and December 2019. The samples were filtered through 0.45 µm Nucleopore filters, acidified to approximately pH 2 immediately after collection and stored in a fridge at ~4℃. A water profile at the deepest part of TSK (~52 m water depth) as well as the inlet and outlet were sampled to monitor the Si inputs and fluxes of the modern lake system. Pore water samples (Paper III) were taken from two short cores in October 2019 using Rhizon samplers (described in Seeberg-Elverfeldt et al. 2005; Shotbolt 2010) and acidified to ~ pH 2. The DSi concentrations of the water were measured on a SmartChem 200 discrete chemical analyzer as described in Galhardo and Masini (2000) see section 6.3.

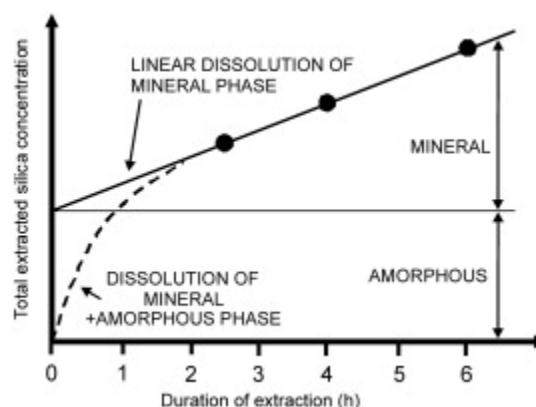Figure 9: Hypothetical diagram of Si extraction from sediments (Clymans et al. 2011a).

6.2 Investigation of the diatom community

The optical investigation of the diatom frustules in the sample material helped to constrain the preparation steps. The aim was to determine the size and the dominant species species of the diatoms, to adjust the preparation steps and get the most reliable isotope signal. The composition of the

diatom community was examined down core for Chesapeake Bay and Tiefer See, analyzing smear slides with an Olympus BX41 microscope at 600x magnification. Additionally, scanning electronic microscopy (SEM) was used to identify specific genera of diatoms in the sediments.

6.3 BSi measurements

Biogenic silica (BSi) measurements in sediment archives are a commonly used method to assess variations in diatom accumulation (Clymans et al. 2011a; Alfredsson et al. 2015; Barão et al. 2015). In this study the BSi concentration of sediment samples (n = 383) was determined using the sequential alkaline extraction method with 0.1 M Na_2CO_3 as developed by DeMaster in 1981 (DeMaster 1981). The method is based on the assumption that aluminosilicate minerals dissolve in a linear way over time, whereas biogenic silica dissolves completely after a treatment of 2 hours. The continuous subsampling after 3, 4 and 5 hours is carried out to track the dissolution of the silica in the sample and to be able to correct for aluminosilicate dissolution (Fig. 9) (DeMaster 1996; Clymans et al. 2011a). The extracted Si was measured on a SmartChem 200 discrete chemical analyzer: Ammonium molybdate reacts with the silicic acid in the sample and forms a molybdosilicic acid complex. Ascorbic acid reduces Mo(IV) to Mo(V) and creates a molybdenum blue compound which is then determined spectrophotometrically (Galhardo and Masini 2000).

6.4 Seperation of diatoms

For Si isotope measurements by MC ICP-MS (multi-collector inductively coupled plasma mass-spectrometry) in natural samples it is necessary to separate and purify the siliceous material carefully. Three main steps include separation, purification and dilution of the Si fraction. The separation of Si from natural samples depends on sample composition, amount of sample and siliceous material (BSi). The purification is based on alkaline dissolution followed by ion-exchange chromatography (Georg et al. 2006).

The separation of biogenic silica (BSi) is a method widely used over the last decades (e.g. Shemesh et al. 1988; de la Rocha et al. 1997; Leng et al. 2009).

For the separation of bulk diatom frustules in the current project, an extraction with three different preparation steps was used:

1. Chemical dissolution of organic matter and carbonates with H_2O_2 and HCl, respectively

2. Density separation (heavy liquid separation) with sodium polytungstate (SPT) at densities between 2.0 and 2.3 g cm^{-3}.

3. Division into three different size fractions by sieving (5-25μm, 25-53μm, >53μm)

Due to high organic matter and low BSi contents (<5%) in the samples, the method was adapted to get optimal results: a relatively large amount of sediment (~3 g) was used for the separation to increase the likelihood of sufficient diatom material in the end. Each sample was covered with 30 ml of H_2O_2 (30%) in a beaker and placed on a hotplate (50°C) to speed up the reaction. The reaction times varied related to sediment compositions between 5 days and 1 month. To separate further contaminants (minerals and clays) several steps of heavy liquid separation with densities of 2.3, 2.2 and 2.0 g cm^{-3} were performed. Microplate sieves were used to divide the diatom fraction in three size fractions: 5-25 μm, 25-53 μm and >53 μm. The "large" diatom fraction (>53μm) was prepared for hand-picking under a stereo microscope with a magnification of 50x. From each sample 400-500 diatom frustules were hand-picked and dissolved in 0.5 ml 0.4M NaOH before cation exchange chromatography (see section 6.5).

6.5 Isotope measurements ($\delta^{30}Si_{diatom}$)

After extracting the diatoms from the sediment (see section 6.4) the frustules were dissolved in 0.4ml 0.4 M NaOH and neutralized with HCl creating 1 ml DSi samples for isotope measurements. Cation exchange chromatography (Georg et al. 2006) was performed to separate the Si from further contaminants. Standards, NBS and Diatomite, were prepared in an identical way during the same analytical sessions. All samples and standards were checked for complete removal of potential contaminants (e.g. Al, Na) with an ICP-OES (inductively coupled plasma optical emission spectroscopy). The final Si solutions as well as the standards (NBS28, Diatomite, Big Batch) were diluted to 0.4, 0.5 or 0.6 ppm Si in a 0.1 M HCl

matrix and doped with Mg accordingly for mass-spectrometry. $\delta^{30}Si_{diatom}$ was assessed on a Neptune MC ICP-MS (multi collector inductively coupled plasma mass spectrometer) using matrix-matched sample-standard bracketing at the German Research Centre for Geosciences Potsdam (GFZ) following standard protocols (Oelze et al. 2016). Mg isotopes were monitored in dynamic mode to improve the precision of $\delta^{30}Si$ measurements by correcting for instrumental mass-bias following Cardinal et al. (2003). The corrected ratio of ^{30}Si to ^{28}Si is:

$$\left(\frac{^{30}Si}{^{28}Si}\right)_{corr} = \left(\frac{^{30}Si}{^{28}Si}\right)_{meas} \times \left(\frac{^{30}Si_{AM}}{^{28}Si_{AM}}\right)^{fMg} \quad (7)$$

where $(^{30}Si/^{28}Si)meas$ is the measured ratio and $(^{30}Si_{AM}/^{28}Si_{AM})$ are the atomic masses of ^{30}Si and ^{28}Si. fMg was determined using the beam intensities on masses 24 and 25:

$$fMg = \ln\left(\frac{\left[\frac{^{25}Mg}{^{24}Mg}\right]_{true}}{\left[\frac{^{25}Mg}{^{24}Mg}\right]_{measured}}\right) / \ln\frac{^{25}Mg_{AM}}{^{24}Mg_{AM}} \quad (8)$$

with 'true' being the theoretical expected value of ^{25}Mg and ^{24}Mg, and 'measured' the measured ratio of both isotopes.

The corrected values are used to calculate the Si isotope value relative to the NBS28 standard (see 2.1). Three individual bracketed measurements (standard-sample-standard) were averaged for $\delta^{30}Si$ and $\delta^{29}Si$, respectively.

Author contributions to Papers I to III:

	Paper I	Paper II	Paper III
Concept and study design	D.J. Conley P.J. Frings C.K.M. Nantke	P.J. Frings C.K.M. Nantke D.J. Conley	C.K.M. Nantke P.J. Frings D.J. Conley
Sample preparation	C.K.M. Nantke	C.K.M. Nantke	C.K.M. Nantke P.J. Frings
Measurements and data analysis	C.K.M. Nantke P.J. Frings	C.K.M. Nantke P.J. Frings	C.K.M. Nantke P.J. Frings
Discussion of results	C.K.M. Nantke P.J. Frings J. Stadmark D.J. Conley	C.K.M. Nantke P.J. Frings D.J. Conley M. Czymzik	C.K.M. Nantke F. Stamm P.J. Frings P. Roeser
Writing	C.K.M. Nantke	C.K.M. Nantke	C.K.M. Nantke
Comments and feedback	All authors	All authors	All authors

7. Summary of Papers

Paper I: Si cycling in transition zones

Nantke, C.K.M., Frings, P.J., Stadmark, J., Czymzik, M. and Conley, D.J. (2019)

Si cycling in transition zones – a study of Si isotopes and biogenic silica accumulation in the Chesapeake Bay through the Holocene.

Biogeochemistry, 146: 145-170.
https://doi.org/10.1007/s10533-019-00613-1.

This research article provides the first study of Si isotopes in estuarine diatoms through time. The main aim was to investigate changes and variations of supply, accumulation and recycling rates of Si through the Holocene in the Chesapeake Bay. Processes, both natural and anthropogenic, potentially influencing the Si cycle were considered and discussed (Table 1). The study uses previously measured datasets including vegetation composition (pollen counts), modern DSi monitoring data and proxies characterizing water-mixing conditions ($\delta^{18}O$, authigenic Rhenium) to support the discussion.

The study site, the Chesapeake Bay (North America), is the largest estuary in the US and has a strong salinity gradient. Two sediment cores, one located

Table 1: Summary of the hypothesized processes influencing $\delta^{30}Si_{diatom}$ in coastal ecosystems (Nantke et al. 2019).

Climate shift	Process	$\delta^{30}Si_{diatom}$
Enhanced precipitation	Enhanced discharge and enhanced DSi transport to the coastal zone via rivers and ground water flows. Enhanced runoff and erosion of the Si soil pool.	Decrease in $\delta^{30}Si_{diatom}$
Natural vegetation changes	Changes in uptake and export rates of Si in the terrestrial watershed larger export of soil stored ASi.	Decrease in $\delta^{30}Si_{diatom}$
	High demands of Si by plants can reduce the Si released to tributaries, ground waters and coastal zones.	Increase in $\delta^{30}Si_{diatom}$
Water mixing conditions	Precipitation and freshwater delivery influences the mixing conditions in and the distribution of Si (DSi and PSi) in the water column. Marine waters have a relatively high $\delta^{30}Si_{water}$.	Depending on the location: $\delta^{30}Si_{diatom}$ increase or decrease
Human impact	**Process**	$\delta^{30}Si_{diatom}$
Deforestation	Increase in Si export from the relatively light ASi pool in soils.	Decrease in $\delta^{30}Si_{diatom}$
Land-use changes	Crops have a high Si demand and leave the soil depleted in light Si isotopes. Harvest of crops reduces the release of relatively light Si stored in phytoliths back to the soil system.	Increase in $\delta^{30}Si_{diatom}$
Damming	Slows down the discharge rate and the flow speed of the tributaries which leads to more diatom production in the river water and less DSi reaching the coastal zone.	Increase in $\delta^{30}Si_{diatom}$
Nutrient inputs	Changes the N:P:Si ratio in an ecosystem and leads to diatom blooms or shifts in phytoplacton communities (eg. shifts from a Si saturated to a Si limited system).	Depending on the nutrient and foodweb increase or decrease in $\delta^{30}Si_{diatom}$

in the northern part near the main tributary (freshwater influenced) and one further south influenced by marine water masses, showed distinct differences in $\delta^{30}Si_{diatom}$.

As a main result we showed the influence of land use changes in the catchment area on Si fluxes in the northern Chesapeake Bay. Deforestation events since European settlement (since 250 a BP) increased the export of light ^{28}Si, visible in the $\delta^{30}Si_{diatom}$ record. The second sediment core, more distal from the main tributary, seemed to be buffered through Atlantic waters and displayed an increase in water level around 7000 a BP changing the former fluvial system into an estuary. Furthermore, an estimated retention rate of Si around 90% for the Chesapeake Bay exceeds all former suggestions for estuarine systems (up to 50%).

The result of this study revealed the need for more detailed analyses in simpler systems with fewer variables that change concurrently (climate, vegetation changes, circulation, anthropogenic impacts, etc.).

Paper II: The influence of land use changes on continental Si fluxes

Nantke, C.K.M., Brauer, A. Frings, P.J., Czymzik, M., Hübener, T., Stadmark, J., Dellwig, O., Roeser, P. and Conley, D.J. (in review)

Human influence on the continental Si budget during the last 4300 years: $\delta^{30}Si_{diatom}$ in varved lake sediments (Tiefer See, NE Germany).

submitted to Quaternary Science Reviews

Based on the findings in Paper I we investigated the sed iments of a lake (Tiefer See, TSK) located in northeastern Germany. The advantage of a well-dated (varved) sediment record, a small catchment area (5.5 km^2) and only one outlet draining the lake provides a more direct $\delta^{30}Si$ signal. Data availability including diatom productivity, geochemistry and vegetation changes (pollen counts) build a suitable foundation for a detailed analysis of changes in Si cycling through time.
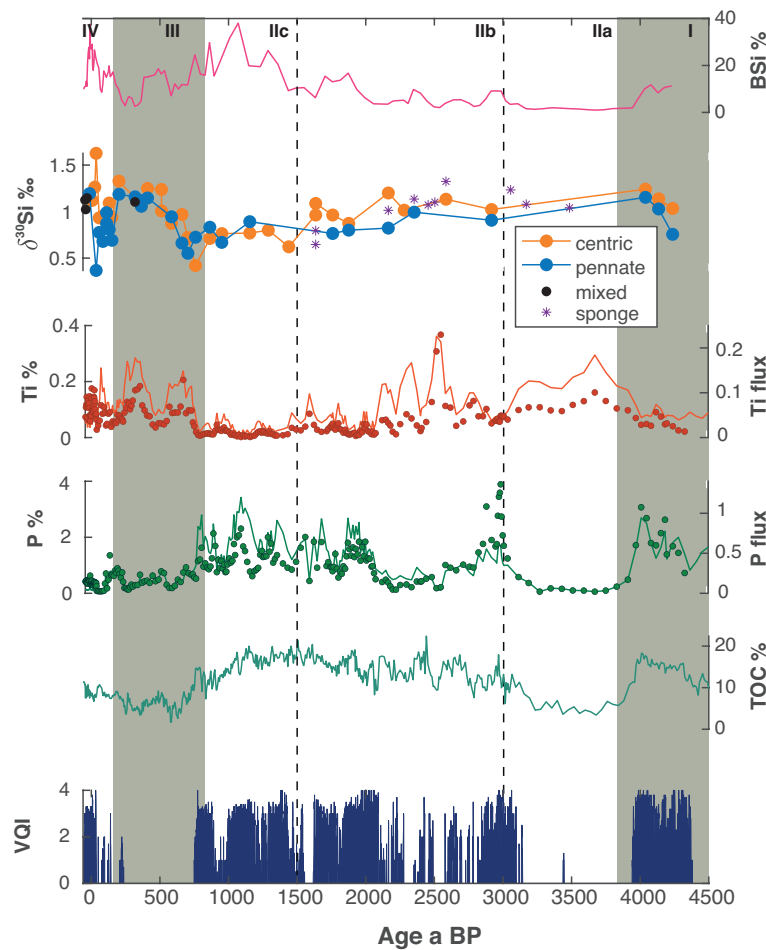

Figure 10: BSi concentration (%), $\delta^{30}Si$ in ‰ (centric diatoms, orange circles), pennate diatoms (blue circles), mixed diatoms (black circles) and sponge spicules (purple stars), titanium cps and %, phosphorus cps and %, TOC (%), and varve quality index (VQI) in Tiefer See (TSK) plotted for the last 4300 years.

The main aim was to link the variability in $\delta^{30}Si_{diatom}$ directly to processes both in the lake and changes in the catchment area. Diatom frustules were separated into planktonic (centric) and benthic (pennate) diatoms by hand-picking. A similar trend in planktonic and benthic diatoms within the period suggests a well-mixed ecosystem during the spring diatom bloom.

The results of this article show that changes in the catchment area, especially the vegetation, have a significant influence on the Si cycle. Both, the Si source and the uptake (BSi), vary systematically and were linked to environmental changes. A decrease in $\delta^{30}Si_{diatom}$ since around 4000 a BP coincides with deforestation and increasing diatom production (BSi) suggesting DSi inputs as the dominant control (Fig. 10). As Si source we interpret an increased export of light [28]Si from the watershed ASi pool and potentially an increase in terrigenous Si dissolution (also associated with a low $\delta^{30}Si$) caused by enhanced soil erosion. An abrupt increase in $\delta^{30}Si_{diatom}$ at ~750 a BP could be linked to intensified landscape cultivation and harvest, leading to a removal of light [28]Si from the soil ecosystem in the catchment.

Paper III: Si isotopes in lake pore waters

Nantke, C.K.M., Frings, P.J., Stamm, F.M., Dellwig, O., Roeser, P., Czymzik, M., Brauer, A., and Conley, D.J. (manuscript)

Si cycling in lake sediments – Si isotopes and dissolved Si concentrations in pore waters from Tiefer See (TSK), Northeastern Germany.

Based on the findings in Paper II we investigated Si cycling in the topmost part of the sediments from Tiefer See. The dissolution of accumulated BSi, secondary minerals and/or (oxyhydr)oxides and the formation of secondary clay minerals are the potential processes controlling Si fluxes from the uppermost layers of sediments, suggested by findings in marine systems. DSi concentrations in the pore waters of the sediment depend on the biogenic Si (BSi) and/or terrigenous Si contents and their reactivity. This again is determined by physical conditions including pH, oxygen concentration and the presence of. elements like Al and Fe with the potential to scavenge Si.

Two sediment cores for the measurement of pore waters were retrieved in October 2019 from the deepest part of Tiefer See capturing the uppermost 50 and 90 cm respectively. Si isotopes in pore water samples ($\delta^{30}Si_{PW}$) were measured on a MC ICP-MS (GFZ Potsdam) to investigate Si cycling in the uppermost sediment of a freshwater ecosystem. We tested for the potential of matrix effects induced by components of the porewaters not removed by the cation exchange protocol. A doping experiment with oxalic acid (OA), with OA/Si ratios up to 10, suggests the absence of substantial matrix effects resulting from high dissolved organic carbon concentrations on our $\delta^{30}Si_{PW}$ data.

The results from both pore water profiles show a decrease in Si isotopes of about 1‰ through both pore water profiles. A negative correlation between DSi concentrations and $\delta^{30}Si$ in the pore waters suggest the dissolution of a siliceous material with a low Si isotope ratio as the main control of the decrease (Fig. 11). We considered the influence of BSi, secondary mineral and iron-oxide dissolution. With the comparison to our $\delta^{30}Si_{diatom}$ from Paper II we could conclude that diatom dissolution is not the sole process, since the $\delta^{30}Si_{PW}$ is too low. Although secondary clay minerals are associated with a light Si isotope signature (approximately between -3 and 1‰) their reactivity is low, especially at pH 6-7 and saturated DSi conditions as measured in Tiefer See pore waters. Consequently, the dissolution of iron-oxides is the most likely Si source supported by high Fe concentrations in Tiefer See pore waters.
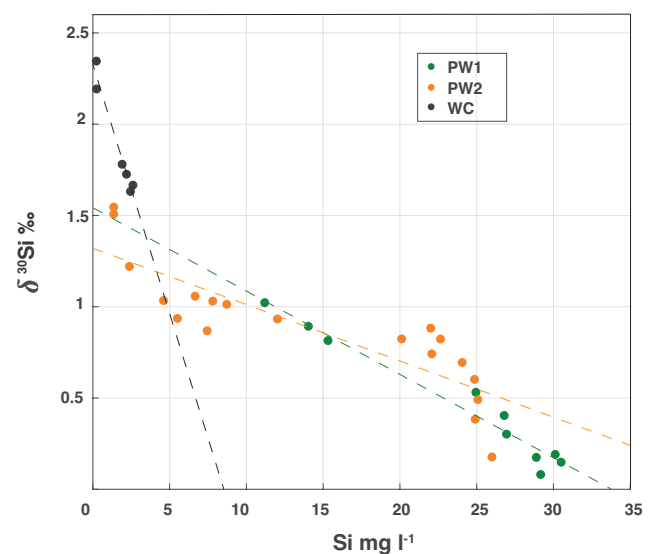

Figure 11: Si (mg l^{-1}) plotted against $\delta^{30}Si_{PW}$ in both pore water cores and water samples from Tiefer See. PW1 = pore water core 1, PW2 = pore water core 2, WC = water column of TSK in October 2019.

The quantification of this Fe–Si shuttle and the contribution to the low $\delta^{30}Si_{PW}$ values in pore fluids at the oxygen minimum zone (OMZ) remains difficult given that Fe undergoes multiple cycles of dissolution and re-precipitation.

8. Discussion

8.1 The potential of investigating coastal sediments

The 'ecosystem Si filter' including the terrestrial Si pool and the circulation and recycling of Si (DSi and BSi) in soils, lakes and estuaries, control the amount of Si transported to the ocean (Dürr et al. 2011; Struyf and Conley 2011). A complex system of natural and anthropogenic processes has the potential to influence these Si fluxes on different time scales. In this thesis three key components of the continental Si cycle – i.e., estuaries, lakes and pore waters – were investigated to improve our understanding of its variation on short geological time scales (years to centuries). Coastal zones and lakes are both vulnerable systems and provide archives for the investigation of short-term Si flux variability. Si recycling in the uppermost sediments is still poorly investigated and its contribution to the DSi budget, especially in freshwater systems, is

an unknown. Coastal zones are dynamic ecosystems with high nutrient concentrations (N, P and DSi) favouring the growth of diatoms (Jickells 1998). Their role in the global Si cycle is widely discussed but poorly constrained (e.g. Tréguer and De La Rocha 2013; Frings et al. 2016). Large amounts of Si transported as DSi, ASi or minerals via rivers, groundwater and overland flow reach the ocean margins with regional differences. There are a variety of sources, sinks and processes that can alter the amount of Si supply on relatively short annual to centennial timescales. To gain an improved understanding of the 'coastal filter' investigating different coastal ecosystems is necessary. Paleo-studies on siliceous organisms (diatoms, sponges) are especially helpful since they provide insight in how Si cycling changed through time and which processes are the main controls. To be able to compare different case studies in the future it is important to reduce the complexity of the ecosystem and create a generally valid conceptual model of how to analyse and interpret changes in $\delta^{30}Si_{diatom}$. In the papers comprising this thesis, we argue that the seasonal Si depletion makes $\delta^{30}Si_{diatom}$ in coastal areas a proxy for the $\delta^{30}Si$ of Si supply to the system, which is again influenced by climate and vegetation changes (Fig. 12). It was our aim to distinguish these two factors in Papers I and II. For coastal areas we could show the influence of climate variability and salinity in the Chesapeake Bay and the increasing land use in the watershed to
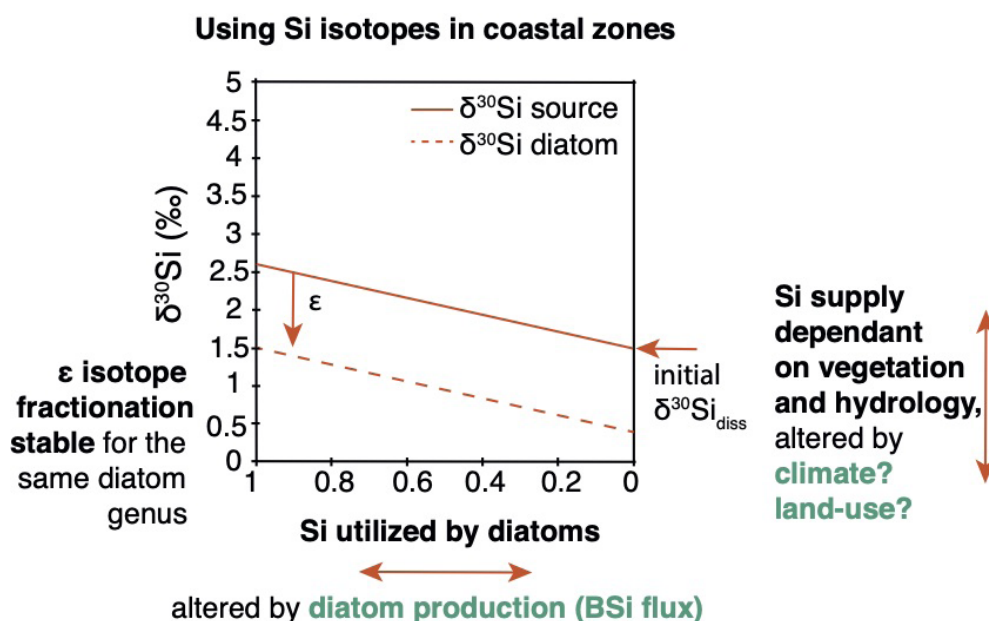

Figure 12: Steady-state model explaining the influence of $\delta^{30}Si_{DSi}$ and BSi flux on the $\delta^{30}Si_{diatom}$ signal in a system with a steady supply of DSi (Nantke et al. 2019).

cause changes in $\delta^{30}Si_{diatom}$. However, to differentiate the interplay of processes and Si sources was especially challenging. The large size of the study site and the complexity of the watershed made the interpretation complicated. A proxy for DSi or $\delta^{30}Si_{DSi}$ would help to constrain and improve the analysis of Si isotopes in coastal areas. To calculate the 'Si filter' capacity, it is necessary to constrain the inputs and outputs of the ecosystem. The mass balance for the Chesapeake Bay (Paper I), however, revealed the need for more comprehensive datasets to better constrain the Si budget. The monitoring of inputs (tributaries, groundwater, pore water) as well as the outputs (BSi and terrigenous Si fluxes) are essential for a detailed investigation. For most of the coastal areas it would be of advantage to measure the BSi concentration at different locations with varying conditions to calculate a mean value for the ecosystem. Submarine groundwater discharge, however, has recently been shown to be rather influenced by lithogenic dissolution (Rahman et al. 2019). We showed in Paper I that local differences, especially in relatively large estuaries have to be considered.

8.2 Coastal zones and lakes as archives of the continental Si cycle

The continental Si cycle has been investigated in a growing number of studies within the last two decades revealing the importance of the 'terrestrial loop'. The filter capacity of terrestrial ecosystems and their role in controlling Si fluxes to the ocean are a key result that emphasize the importance of ecosystem dynamics (Struyf and Conley 2011). Changes in vegetation, hydrology and Si reactivity all have the potential to alter Si fluxes and are vulnerable to changes induced by climate shifts or human activity. To understand these dynamics and the time scales they are influencing the Si cycle on, paleo-studies are essential. Freshwater systems such as estuaries (Paper I) and lakes (Paper II) have suitable sediment archives recording changes in nutrient cycling through time. They are fast-changing ecosystems globally distributed with the opportunity to build a comprehensive database. Using multi-proxy studies to characterize the site allows us to link changes in $\delta^{30}Si_{diatom}$ to processes in these ecosystems. The results of Paper I revealed the challenge of superimposed processes in the large Chesapeake Bay ecosystem: a shift from a

lake to an estuarine system with increasing salinities as well as a changing vegetation (both natural and human induced) during the Holocene overlay each other. The influence of these processes on the terrestrial Si cycle could be shown but to disentangle their effects on the $\delta^{30}Si_{diatom}$ has turned out to be challenging. However, differences between the two sediment cores, located proximal and distal to the main freshwater tributary provide insight into the dominant processes associated with the local conditions of salinity, productivity, oxygen and DSi flux from the watershed. The investigation of a relatively small freshwater lake in Paper II highlights the potential of a more constrained ecosystem. A systematic change in $\delta^{30}Si_{diatom}$ linked to shifts in vegetation and water overturning in the lake, could be observed with a relatively high data resolution based on an annually resolved varve-based age model of the sediment core.

8.3 The variation in BSi fluxes

Variations in biogenic Si fluxes (BSi fluxes) are interpreted as a proxy for productivity changes. Since diatoms play a key role in most freshwater ecosystems, changes in populations can influence the entire food web and water conditions including nutrient (re)cycling. As described above, variation in diatom growth rates depend on a variety of factors such as e.g. temperature, nutrient availability (DSi, N and P) and competition with other phytoplankton (Sun et al. 2014). Assuming a correlation between deposited BSi and diatom population size, BSi fluxes provide a paleo-archive for DSi uptake and productivity.

Coastal zones and lakes are generally high productivity archives with diatoms dominating the primary production sensitive to eutrophication (Schelske et al. 1983; Kemp et al. 2005), with decreasing diatom diversity correlated with increasing BSi flux. Our results from the Chesapeake Bay (Paper I), however, showed differences between the proximal and the distal core: the BSi flux in the proximal core location, near the main tributary, is twice as high as measured in the distal core. The main observed impacts are sea level rise around 7000 a BP and the intensifying cultivation after European settlement since ~250 a BP, both associated with additional nutrient inputs leading to an increased BSi flux. Thus, the distal core location seems to be less influenced by nutrient inputs from the

catchment. Our mass balance calculation for the Chesapeake Bay suggest a Si retention efficiency of around 90%, much higher than previous studies arrived at (global mean: 20%) (e.g. DeMaster 2002; Tréguer and De La Rocha 2013), implying a much larger buffer function of coastal zones than previously expected.

In Tiefer See (Paper II) the BSi flux is predominantly linked to lake overturning triggered by wind stress with high BSi contents when the lake stratification is more dominant indicated by varved sediments (Fig. 11). Here low turbidity could favour larger blooms. The nutrient supply has a minor impact, at least until land use intensifies around 150 a BP. The preservation efficiency also is likely enhanced during times of more stable stratification: the dissolution of diatom frustules in the water column is decreased causing larger and faster BSi deposition in the sediments. A lack of bioturbation, due to anoxic bottom waters could have a further positive effect on frustule preservation.

Overall, we could show that diatom production and Si uptake has only a minor influence on the $\delta^{30}Si_{diatom}$ in our study sites. Unlike marine environments,

where $\delta^{30}Si_{diatom}$ is a proxy for DSi uptake, in our studies BSi flux and $\delta^{30}Si_{diatom}$ are not correlated and DSi supply is most likely the dominant control on the Si cycle.

8.4 DSi supply

Papers I and II showed the importance of changing DSi fluxes from soils for the Si budget of freshwater systems and, thus, $\delta^{30}Si_{diatom}$. Paleo-changes in the magnitude of DSi fluxes and its $\delta^{30}Si_{DSi}$ in freshwater ecosystemsare yet determined only indirectly through the absence of a $\delta^{30}Si_{diatom}$ and BSi flux correlation (Papers I and II) or calculated as a relative value (Swann et al. 2020). Especially for short term changes, a direct proxy would improve the interpretation and identification of the dominant processes on Si (re)cycling rates.

Si isotope ratios in freshwater sponges hold the potential to reflect DSi concentrations. This hypothesis is based on findings from Hendry and Robinson (2012) showing the negative relationship between marine $\delta^{30}Si_{sponge}$ and DSi concentrations in the ocean. The first reported measurements of
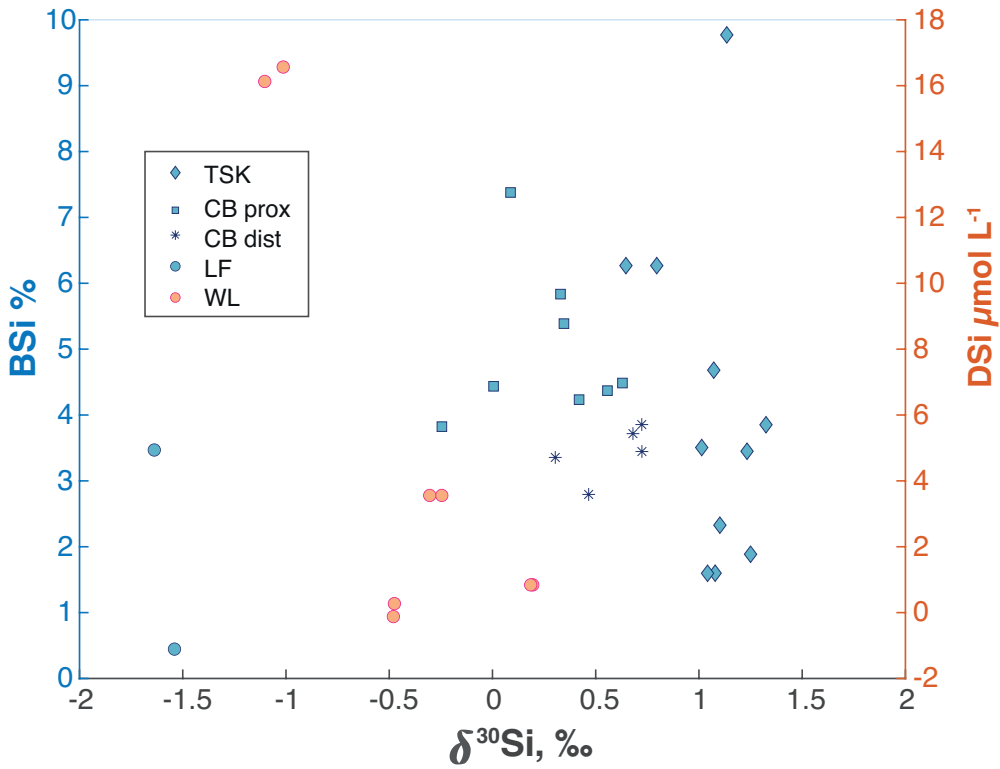

Figure 13: $\delta^{30}Si$ measured on freshwater sponge spicules from different archives: TSK = Tiefer See (NE Germany), CB = Chesapeake Bay (NE America); prox: core near the main tributary (freshwater); dist: core influenced by fresh and marine water masses, LF = Limfjord (Denmark) and WL = Wisconsin lakes (North America).

freshwater sponges were carried out within this thesis in samples from the Chesapeake Bay (NE America), Tiefer See (NE Germany) and Limfjord (Denmark) as well as 4 lakes from Wisconsin (Grassy Lake, Mystery Lake, Trout Bog and Crystal Bog). The results however show a rather complex picture and no consistent relationships (Fig. 13). A study of freshwater sponges in a variety of different lakes and estuaries would help to constrain this potential relationship.

8.5 Human impact on continental Si fluxes

One of the main focuses of this PhD thesis was the investigation of the human impact on the terrestrial Si cycle through time. Previous studies showed significant differences in Si budgets between forested and cultivated land (Clymans et al. 2011b; Vandevenne et al. 2015). The conceptualization of Struyf et al (2010), provides a framework for changes in Si (re)cycling along a land use gradient and the foundation for our investigations.

Papers I and II use Si isotopes to show how variations in climate, vegetation, land use and crop harvest can alter the Si cycle in dynamic freshwater systems on relatively short time scales. For the first time paleo-records have shown that changes in terrestrial Si cycling could be observed through time and linked to processes in the specific archives. In both ecosystems, the Chesapeake Bay (Paper I) and the Tiefer See (Paper II) we found the importance of DSi supply influenced by vegetation changes, in the catchment controlling the $\delta^{30}Si_{diatom}$. In periods of increased land cultivation, more rapid changes in $\delta^{30}Si_{diatom}$ suggested the impact of abrupt land use changes. Especially large-scale deforestation seems to trigger the export of DSi from the adjacent soils to the freshwater ecosystem. In Tiefer See (Paper II), however, our results point to a systematic shift of Si cycling in the soil system as a consequence of increased export of light DSi from ASi soil pools: a long-term decrease in $\delta^{30}Si_{diatom}$ over ~2500 years infer additional processes like the dissolution of terrigenous Si by changes in weathering processes (Fig. 14). For example, below ground pCO_2, organic acid concentrations, soil-solutionchemistry, and the presence and abundance of mycorrhiza fungal networks all affect the rate at which primary silicate minerals are attacked, and secondary minerals precipitate. A decrease in $\delta^{30}Si_{DSi}$, as we interpret from our diatom records, therefore infers that progressively more clay Si dissolves. This would mean that weathering beneath cropland and meadows produces more Si-poor clays than forests.

Increasing cultivation and crop harvest were suggested to change the terrestrial Si cycle by decreasing the availability of light Si in the soil and ultimately the local ecosystem (see 4.3, Vandevenne et al. 2015). We could confirm this for Tiefer See (Paper II): the increase in cultivation in the catchment area since ~ 750 a BP here led to a shift towards higher $\delta^{30}Si_{diatom}$, suggested as a central impact on the Si cycle in Paper I (Table 1).
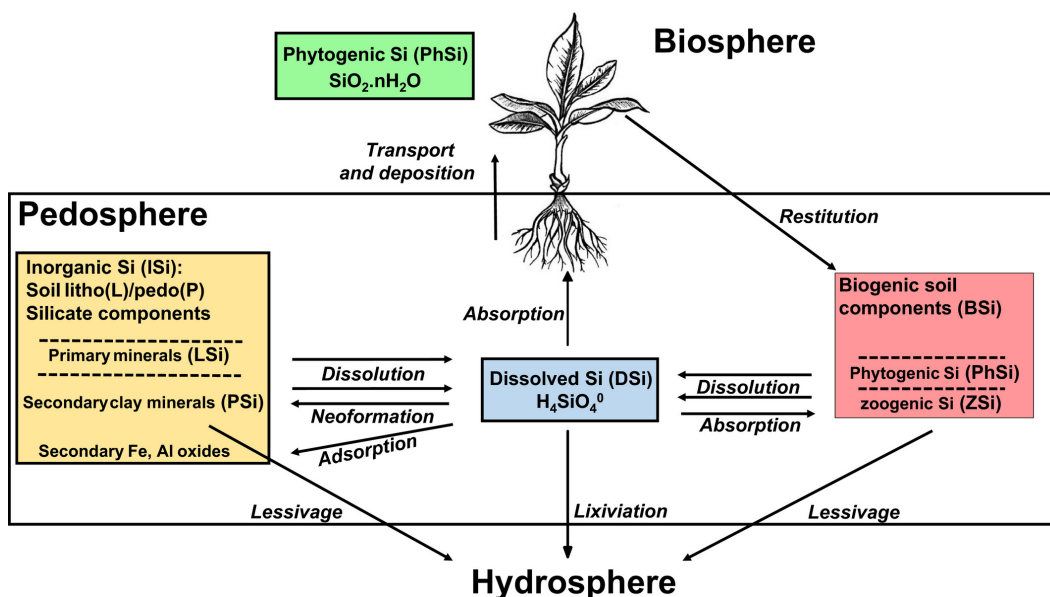

Figure 14: Conceptual scheme of Si pools at the soil/vegetation interface (Cornelis and Delvaux 2016).
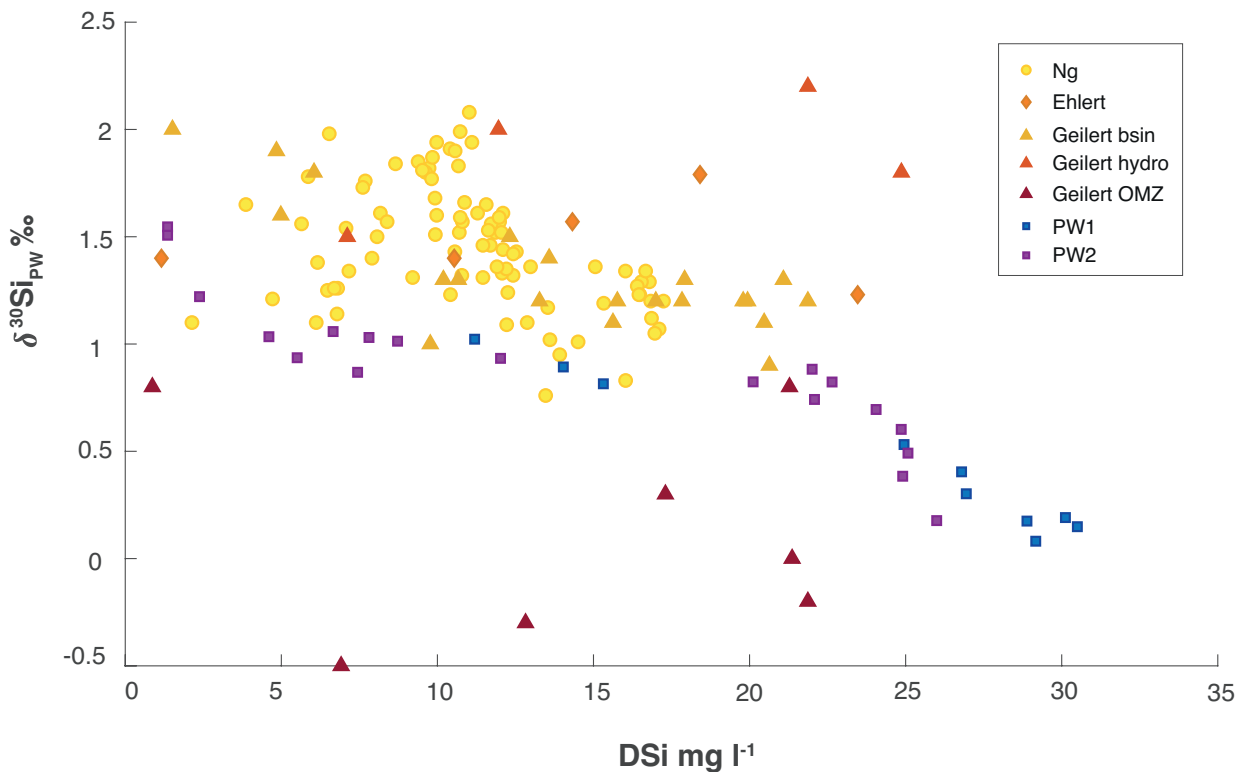
Figure 15: Pore water $\delta^{30}Si$ (‰) against DSi (mg l^{-1}) from marine sediments: yellow dots: Greenland margin (Ng et al. 2020), orange diamonds: Peruvian margin (Ehlert et al. 2016) and yellow, orange and red triangles: Gulf of California (Geilert et al. 2020) plotted together with data from Tiefer See (Paper III): blue and purple squares.

8.6 Controls on Si (re)cycling in lake sediments

Previous studies have shown that most of the diatom frustules already re-dissolve in the water column (up to 97% in marine systems and up to 80% in lakes) and only a small amount gets preserved in the sediments (Tréguer and De La Rocha 2013; Frings et al. 2014). Potential diatom dissolution in the topmost centimeters of the sediments, might act as an additional input changing the Si budget in the lake water. The recycling of BSi in the uppermost sediment (of diatoms after deposition), however, is still poorly investigated and constrained. Studies in marine environments (Ehlert et al. 2016; Geilert et al. 2020; Ng et al. 2020) suggest the importance of BSi dissolution and secondary clay formation in the topmost part of the sediments to be dependent on pH conditions, DSi concentrations and metals such as Al and Fe which have the potential to scavenge Si. Paper III uses for the first time Si isotopes in pore water samples of a freshwater lake (Tiefer See, NE Germany) to investigate Si cycling and fluxes from the sediment.

Our results show a distinct decrease in $\delta^{30}Si_{PW}$ and increasing trend in DSi with depth in the sediment column. This negative correlation fits well with the already published data from marine pore water sites (Fig. 15). The face value interpretation is the input of isotopically light DSi to the pore water solution. However, a more constrained relationship and very high Si concentrations in 90 cm sediment depth in TSK (Fig. 15, PW1) also suggest process differences. Pore water $\delta^{30}Si$ show a systematic decrease by about 1.5 ‰ in the topmost 30 to 90 cm of sediment implying the dissolution of particulate Si in the uppermost 1 m of the sediment to be the dominant process. Interestingly, deviations between the two retrieved pore water cores suggest local differences, perhaps linked to oxygen saturation in the bottom waters.

To explain our $\delta^{30}Si_{PW}$ profiles the dissolution of a light Si source is required as described e.g. for the Gulf of California by Geilert et al. (2020). Si-rich precipitates, biogenic Si assimilated by diatoms and clay-sized components (terrigenous Si: secondary minerals, secondary oxides) all preferentially sequester light Si isotopes (Opfergelt et al. 2009). Based on our $\delta^{30}Si_{diatom}$ measured in TSK for Paper II we are able to preclude the diatom dissolution as the only control on $\delta^{30}Si_{PW}$. However, the similarity between $\delta^{30}Si_{PW}$ to $\delta^{30}Si_{diatom}$ in the topmost 20 cm

make diatom dissolution as a DSi source in TSK possible. The large-scale dissolution of secondary minerals is unlikely due to a pH between 6 and 7 and high Si concentrations between 1.3 and 30 ppm (48 – 1090 µmol l^{-1}).

Based on high iron concentrations of 0.029 – 98 mg l^{-1} in both pore water profiles, the transport and dissolution of Si bound to iron oxides is the most likely scenario. Delstanche et al. (2009) describes the preferential absorbance of light ^{28}Si to iron oxides with a Si isotope fractionation estimated between -1.06 and -1.59‰. Anoxic conditions in the sediments then favour their dissolution by reducing Fe III to Fe II. The supply of light DSi to the pore waters due to Fe-oxide dissolution as described for the oxygen minimum zone (OMZ) in the Gulf of California (Geilert 2020) is likely the dominant source in TSK given the anoxic to sulfidic conditions within the last 200 years.

It is still to be analysed to what degree the dissolution of former solid-bound Si in pore waters of TSK, impacts the water column and the DSi budget of the lake. A brief Si dissolution model suggests a DSi flux at the sediment water interface of 0.12 mol m^{-2} a^{-1} in agreement with benthic fluxes calculated for different marine environments ranging from 0.0017 to 3.35 mol m^{-2} a^{-1} (Frings 2017). Scaled to the size of the lake (0.75 km^2) a total flux of 5.4 t SiO$_2$ a^{-1} can be estimated. Altogether the dissolution of BSi and terrigenous Si is a potential but poorly investigated Si flux which could alter the Si budget especially in small lakes. Further studies are necessary to explore the influence.

9. Conclusions and future perspectives

This PhD thesis highlights the potential of Si isotopes in freshwater ecosystems as a paleo-proxy for terrestrial Si cycling. I was able to link changes in Si (re)cycling to distinct processes such as vegetation and salinity (climate) changes and human impact.

My results from Paper I and II provide knowledge on the timing and amplitude of changes in Si cycling in different freshwater systems that can be linked to changes in the watershed. This is observed in both records from the Chesapeake Bay (Paper I) and Tiefer See (Paper II). Human impact has

been shown to have a distinct influence on Si (re)cycling in the transition zone between the terrestrial and the marine realm. Increasing land use enhances DSi export rates from soils to rivers, lakes and coastal zones. The harvest of vegetation and crops also impacts the Si availability in terrestrial ecosystems and on long time scales, in the ocean. The results from Paper II in particular show how fast terrestrial Si cycling can react to land use changes. Within a few decades an ecosystem can change from Si replete to Si limited. Si fluxes from concentrations and Si isotopes in the pore waters suggests the dissolution of particulate Si in the uppermost sediments. Iron-oxides are the most likely Si source in the deeper part od the sediment indicated by high Fe concentrations and the range of $\delta^{30}Si_{PW}$ precluding the extensive dissolution of diatom BSi as the only source. A brief calculation suggests a medium Si flux across the sediment water interface of 0.12 mol m^{-2} a^{-1}.

However, the results of this thesis also revealed knowledge gaps and challenges that need further investigation:

- Paleo-studies in estuaries and lakes are necessary to improve our knowledge about timing and amplitude of changes in terrestrial Si cycling through time. To be able to quantify the filter capacity of transition zones on a global scale it would be important to investigate sites from different climate regions and with varying physical conditions. Superimposing processes influencing the Si cycle, especially observed in the Chesapeake Bay, could be disentangled by comparing small catchments (lakes) with different biogeochemical conditions and with limited nutrient pathways constraining DSi fluxes from terrestrial environments.

- The input and sources of DSi in freshwater environments seem to be controlling Si cycling in freshwater systems and need more attention in future research. Constraining the impact of groundwater inputs, especially in lakes, could help to distinguish different lake ecosystems. The development of a paleo-proxy for DSi concentrations or $\delta^{30}Si_{DSi}$ would help to interpret changes in $\delta^{30}Si_{diatom}$ through time and improve mass balance calculations. Freshwater sponges are currently poorly investigated, but hold the potential to serve as a proxy for Si concentrations in freshwater systems, similar to that developed for marine sponges.

- To increase the data resolution, it would be necessary to decrease the preparation time of the freshwater diatom samples. Hand-picking diatoms has certain advantages but is time consuming and limited by small frustule sizes (<50 μm). An improved cleaning protocol or the development of an alternative method to measure Si isotopes (e.g. measurements of single diatom frustules with SIMS) could help to make the preparation more efficient and increase the data resolution.

- Si (re)cycling in sediment pore waters is poorly investigated. A potential Si source through dissolving BSi, secondary clays or iron oxides may change the Si budget of some ecosystems. In particular, isolated lakes without tributaries could be influenced by Si fluxes from the sediments depending on pH, oxygen and DSi concentrations.

Svensk sammanfattning

Den globala omsättningen av ämnen i biologiska, geologiska, kemiska och fysiskaliska processer och samspelet mellan olika ämnens omsättning är viktiga att förstå då dessa samband används i klimatforskningen. Undersökningar de senaste decennierna har betonat nyckelrollen som kiselomsättningen har eftersom kiselalger – växtplankton med kiselinnehåll - är viktiga kolbindare i både salta och söta vattenmiljöer. Genom att studera kiselalger som har bevarats i sedimentet kan man förstå hur tillförseln och exporten av kisel har varierat i systemet över tid. Under de senaste årtiondena har undersökningar visat på stora variationer i kiselflödena mellan växtlighet och mark som kan kopplas till förändringar i markanvändning orsakad av människan. Skiftet från naturlig växtlighet till odlade marker har till exempel visats påverka kiselomsättningen i moderna jordar och växter. Sediment i kustzonen och i sjöar är lämpliga som arkiv för att undersöka hur människans markanvändning förändrat kiselomsättningen på land genom tiderna.

Det huvudsakliga syftet med detta doktorandprojekt är att bättre förstå samspelet mellan källor och sänkor av kisel i landbaserade ekosystem. För att bättre kunna förstå förändringar i den kontinentala kiselbudgeten undersökte vi två platser, Chesapeake Bay, en flodmynning på USA: s östkust och Tiefer See, en sjö i nordöstra Tyskland. Båda platserna har sediment som visar på förändringar i klimat och vegetation sedan den senaste istiden och även spår som kan kopplas till människans aktiviteter i området. Mätningar av flöden av biologiskt bundet kisel (BSi) och av kiselisotoper i nedfallna kiselalgsskal ($\delta^{30}Si_{diatom}$), som tagits fram från sedimentkärnor, skapar en bild av omsättningen av kisel på land genom tiderna. Denna bild kan sedan jämföras med miljömässiga faktorer som uppodling av mark, avskogning och salthalt.

Denna doktorsavhandling belyser möjligheten att använda kiselisotoper i sötvattensekosystem för att kunna skapa en bild av tidigare landbaserad omsättning av kisel. Vi kunde koppla förändringar i kiselomsättning till vegetation, salinitet (klimat) och mänsklig aktivitet. Våra resultat visar att ökad mänsklig aktivitet, särskilt avskogning och skörd av grödor, påverkar den markbundna kiselomsättningen på geologiskt korta tidsskalor (årtionden-århundraden). Till skillnad från i marina miljöer beror variationen i kiselomsättningen främst på förändringar i inflödet av löst kisel från avrinningsområdet. Våra resultat från prov på porvattnet i sedimentet i Tiefer See väcker frågan hur viktig upplösningen av biologiskt bundet kisel och grundvatteninflöden är för sjöars kiselbudgetar.

Sammantaget undersöker denna avhandling hur klimat och mänsklig aktivitet påverkar den så kallade "markbundna kisel-loopen", ett naturligt filter som avgör hur stor mängd kisel som når havet.

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