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STABLE SILICON ISOTOPES AS A TRACER FOR THE BIOLOGICAL PUMP

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**Curriculum Vitæ**
Summary

The exchange of CO$_2$ between the surface ocean and the atmosphere is significantly influenced by the uptake of CO$_2$ by marine photosynthesising microorganisms. Their uptake of carbon, and their subsequent sinking to depth after death, results in CO$_2$ transport away from the ocean-atmosphere interface, and ultimately its sequestration in the deep ocean for hundreds to thousands of years. This process, known as the biological pump, has been hypothesised to have been more efficient during the last ice age, and thus to have contributed to the lowering of atmospheric CO$_2$ levels. One of the most important organisms in this context are diatoms, unicellular algae that utilise dissolved silicon to build an opal cell wall. Owing to their superior ecological strategies diatoms dominate the uptake of nutrients such as carbon, nitrogen, and silicon in dynamic parts of the ocean, where carbon and nutrient-rich deep waters are upwelled to the surface. Diatoms, thus establish a strong link between the marine cycles of silicon and carbon.

The silicon isotope composition of the sedimentary remains of diatom opal is a promising store of information on changes in the marine carbon cycle during cold and warm intervals. The robust application of this geochemical fingerprint is, however, dependent on the preservation of the opal’s silicon isotope composition during sinking through the water column, and in the sedimentary environment. Two important processes that may disturb the pristine silicon isotopic signal of the opal are examined in this thesis. Furthermore, the silicon isotope composition of diatom opal is used to reconstruct physical and biogeochemical changes in the ice age Southern Ocean.

First, this thesis investigates whether dissolution of sedimentary opal is associated with silicon isotope fractionation. Dissolution of fresh diatom opal has previously been shown to fractionate silicon isotopes, but in terms of mass balance with no effect on the silicon isotope composition of the usually very well preserved opal. Here, it was found that dissolution of mature sedimentary opal does not fractionate silicon isotopes. The results were reproducible across different temperatures, degrees of undersaturation, age, and specific surface area, providing further evidence for the integrity of the diatom silicon isotope composition against dissolution.

In the second part of the thesis the potential for the diatom opal silicon isotope fingerprint to become compromised by isotopic disequilibrium in the temperature range 5-22ºC is examined. In the sedimentary environment opal is buried, compacted and heated up along with other sediment
constituents, such as silicate minerals. This sequence of processes may give rise to silicon isotope exchange and, thus, the alteration of the original isotope signal of the opal. It is found here that silicon isotope exchange rates with a solution strongly spiked in one silicon isotope are very low over the temperature range 5-22°C for time periods up to 482 days. Other processes, such as dissolution of the opal and adsorption of dissolved silicon onto the opal surfaces exerted a proportionally much stronger control on the mass balance of the system, and thus the silicon isotope composition of the opal and the solution. Since these other processes camouflaged silicon isotope exchange, a quantitative assessment of silicon isotope exchange rates was inhibited. However, the information the experiment provides, and the analytical setup that was developed for accurate and precise measurements of non-natural silicon isotope compositions, help to define the boundary conditions for an experiment that is more sensitive to silicon isotope exchange.

In the last part of this thesis, new silicon isotope data for sediment core diatom opal from the Atlantic sector of the Southern Ocean are presented. The Southern Ocean exhibits a strong control on the nutrient distribution in the global thermocline, such that the reconstruction of past silicon utilisation in the surface Southern Ocean provides important information on biogeochemical changes in the glacial Southern Ocean, and potentially the global ocean. The silicon isotope data are used to provide model calculations of the relative amount of silicon that was not taken up by diatoms through the past 80,000 years. These calculations take account of variations in the sample’s diatom species composition, which has most recently been discovered to potentially influence such calculations. Moreover, variations in the silicon isotope composition of the silicic acid taken up by diatoms are considered in the model. This parameter is unknown for the past, and its potential variability has not been sufficiently addressed in the literature so far. It is found that the glacial Southern Ocean is likely to have had 20-70% excess silicon, a substantial proportion of which may have been transported into lower latitudes to induce diatom blooms. The exact amount of excess silicic acid available for export to the global thermocline is associated with a large uncertainty. Both the species composition of the sediments and the assumed value for the silicon isotope composition of the supplied silicic acid exert a strong influence on the calculated amounts. While the species composition can be taken care of, a large portion of uncertainty stems from the unknown silicon isotope composition of the supplied silicic acid. A sensitivity study shows that changes in the silicon isotope composition of silicic acid cannot explain the full variability of the silicon isotope compositions observed for diatom opal, but that consideration of transient changes within the source isotopic composition, accompanied by changes in the residence time of water masses in the Southern Ocean, yield a large range of calculated excess silicic acid.

The results presented in this thesis provide evidence for the integrity of the silicon isotope composition of diatom opal against post-mortem alteration, and supports its utilisation and usefulness for the reconstruction of glacial-interglacial marine silicon cycling.
Zusammenfassung

Der Austausch von CO\textsubscript{2} zwischen der Atmosphäre und dem Oberflächenozean wird massgeblich durch Photosynthese und der damit verbundenen Aufnahme von CO\textsubscript{2} durch Mikroorganismen beeinflusst. Die Aufnahme von Kohlenstoff durch Mikroorganismen im Oberflächenozean sowie deren Absinken in die Tiefsee nach dem Tod führen dazu, dass CO\textsubscript{2} von der Grenzschicht zur Atmosphäre abtransportiert und schliesslich für hunderte bis tausende Jahre in der Tiefsee gespeichert wird. Es wird vermutet, dass dieser Prozess, bekannt als biologische Pumpe, während der letzten Eiszeit effizienter war als heute und zu einer Reduktion der CO\textsubscript{2} Konzentration in der Atmosphäre geführt hat. Eine der in diesem Kontext wichtigsten Organismen sind Diatomeen, einzellige Algen, welche im Meerwasser gelöstes Silizium aufnehmen um eine Zellwand aus Opal zu bilden. Diatomeen besitzen eine ausgezeichnete Fähigkeit Nährstoffe wie Kohlenstoff, Stickstoff und Silizium aufzunehmen und sind daher in dynamischen Regionen des Ozeans, in denen CO\textsubscript{2} und nährstoffreiche Tiefenwässer an den Oberflächenozean transportiert werden, vertreten. Diatomeen verknüpfen somit die marinen Kreisläufe von Silizium und Kohlenstoff.


Temperatur- und Sättigungsbedingungen, sowie für unterschiedliche spezifische Oberflächen und Opalalter reproduziert und liefert einen weiteren Beleg für die Integrität der Siliziumisotopenzusammensetzung des Opals nach dem Tod der Diatomeen.

Im zweiten Teil der Arbeit wird untersucht, inwiefern ein Isotopenungleichgewicht im Temperaturbereich 5-22°C die ursprüngliche Isotopenzusammensetzung des Opal verändert. Der Diatomeen Opal ist mit anderen siliziumhaltigen Phasen wie Silikatmineralen Versenkung, Kompaktion und erhöhten Temperaturen während der Diagenese ausgesetzt, was ein isotopisches Ungleichgewicht zur Folge haben kann und zu einer Veränderung der ursprünglichen Siliziumisotopenzusammensetzung führen kann. In dieser Arbeit wurde herausgefunden, dass der Austausch von Siliziumisotopen zwischen Opal und einer mit einem Siliziumisotope angereicherten Lösung im Temperaturbereich 5-22°C und einer Reaktionszeit von bis zu 482 Tagen sehr langsam ist. Andere Prozesse wie die Auflösung des Opals und Adsorption von gelöstem Silizium an Opal hatten im Rahmen des Experiments einen grösseren Einfluss auf die Isotopenzusammensetzung der Lösungen und des Opals. Da diese Prozesse höhere Reaktionsraten als Siliziumisotopenaustausch hatten und diesen überlagerten, war eine Quantifizierung von Austauschprozessen nicht möglich. Dennoch lassen die gewonnenen Informationen, sowie das für das Experiment entwickelte analytische Verfahren, von präzisen Messungen von Unnatürlichen Siliziumisotopenzusammensetzungen, genutzt werden um ein Folgeexperiment zu entwickeln, welches in der Lage ist Siliziumisotopenaustauschprozesse zu bestimmen.

Veränderungen der Siliziumisotopenzusammensetzung des gelösten Siliziums die Siliziumisotopenzusammensetzung des Opals nicht komplett erklären kann. Allerdings kann die Berücksichtigung von vorübergehenden Veränderungen der Siliziumisotopenzusammensetzung des gelösten Siliziums, welche in Verbindung mit Veränderungen der Residenzzeit von Wassermassen im Südozean stehen, in berechneten Siliziumüberschüssen resultieren, die eine deutlich unterschiedliche Interpretation der Ergebnisse zur Folge haben.

The fields of paleoclimatology and paleoceanography have experienced a boost in the last two decades due to methodological and analytical advances that have made it possible to develop more and more geochemical fingerprints of past climate and environmental change. The resultant information on historic changes within the environment is encrypted in geological records such as ice cores, ocean sediments, speleothems, or soils. The objective of this thesis is to contribute to the decryption of the environmentally relevant information held by one of the most prominent groups of marine algae: diatoms. Diatoms are unicellular, photosynthesising, and major primary producing organisms that form a siliceous cell wall, such that they uniquely link the carbon cycle and the silicon cycle. In contrast to carbon, the silicon cycle has no atmospheric component, silicon does not participate in redox reactions, and it is present in the ocean almost entirely as silicic acid, $\text{H}_2\text{SiO}_4$, which is taken up by diatoms to form their sophisticated opaline cell walls. Pioneering studies in the late 1990s suggested that the silicon stable isotope composition of diatom opal could be used to indirectly infer past changes in the carbon cycle, and hence climate. However, key ground-truthing work about the exact information provided by the silicon isotope composition of diatoms is still lacking. This thesis aims to remedy this.

The introduction that follows provides the conceptual ideas that underpin the diatom silicon isotope fingerprint. At first, the marine silicon cycle and its singularity due to diatom production is introduced (1.1). Then, the silicon isotope systematics of diatom opal are outlined, along with previous constraints on its reliability as well as on glacial-interglacial silicon cycling (1.2). Finally, the aims of this thesis are outlined (1.3).
1.1 The marine silicon cycle

This section provides a general overview of how silicon is delivered to, cycled within, and removed from the ocean. Input and output fluxes are small compared to biological cycling, which is dominated by one single group of phytoplankton: diatoms (Nelson et al., 1995; Treguer et al., 1995). Being one the most important primary producers in the ocean (Nelson et al., 1995), diatoms tightly couple the marine silicon and carbon cycle, by building a protective opal cell wall around their organic tissue. However, the link is not straightforward as biomineral and organic tissue have different physical and chemical properties. The combination of the fact that diatoms are the only significant utilisers of silicon in the ocean, the differential regeneration of organic tissue and biogenic opal, and ocean circulation results in a subsequent decoupling of the silicon cycle from that of classical macronutrients such as carbon and nitrogen (e.g. Dugdale et al., 1995; Ragueneau et al., 2002). During ice ages the (de-)coupling of silicon from carbon and nitrogen, as we know it today, might have changed and ultimately impacted the atmospheric CO$_2$ content (Brzezinski et al., 2002).

1.1.1 The marine silicon balance

Silicon is mainly supplied to the ocean via rivers from continental weathering (78%), with the remainder being delivered by seafloor weathering, biogenic silica in rivers, hydrothermal activity, groundwaters, and aeolian dust (Tréguer and De La Rocha, 2013). In the ocean, silicon exists in dissolved form as silicic acid (H$_4$SiO$_4$; henceforth also called simply silicon) with a minor contribution, of about 4%, from anionic H$_3$SiO$_4^-$. Silicic acid is utilised by several types of organism to form amorphous opal (henceforth also called biogenic silica/opal) hard parts, of which the most important groups are diatoms (unicellular phytoplankton), radiolaria (unicellular zooplankton), siliceous sponges (multicellular benthos), and silicoflagellates (unicellular phytoplankton). This biological utilisation results in annual intra-oceanic cycling of silicon that is about 25 times higher than the total input or output flux (Tréguer and De La Rocha, 2013). About 44% of the biologically fixed silicon is exported from the surface mixed layer to the deep ocean, most of which is resupplied as regenerated silicic acid to the surface mixed layer through mixing and water mass advection. The only significant sink of silicon from the ocean as a whole is the burial of biogenic opal (Nelson et al., 1995; Tréguer and De La Rocha, 2013). Based on recent estimates, the silicon cycle can be assumed to be in steady-state – though an anthropogenic perturbation is to be expected (Laruelle et al., 2009) – such that the whole-ocean residence time for silicon is estimated to be between 10,000 and 17,000 years (Laruelle et al., 2009; Tréguer and De La Rocha, 2013). Given a whole-ocean overturning time scale of 1000-2000 years, the residence time of silicon in the ocean implies that, without biological activity, silicon would be homogeneously distributed in the water column. Instead, given the gross biogenic opal production into account (Tréguer and De La
each silicon atom entering the ocean is cycled approximately 20-70 times via biological uptake and dissolution before it is eventually buried. From this, it follows that the distribution of silicon within the ocean must be governed by a combination of physical and biogeochemical processes.

1.1.2 The decoupling of silicon from other nutrients

The distribution of silicon in the ocean is set by a complex interplay of utilisation by organisms in the surface, dissolution of biogenic opal at all depths, and ocean circulation. As silicon is only used for the construction of biogenic opal by marine organisms, its marine distribution and cycling is distinctly different from that of the nutrients that are needed in organic tissue, such as carbon and nitrogen. Figure 1.1 shows the concentrations of silicon and nitrate in the surface ocean. Both nutrients are depleted in most surface regions, and generally show very similar distributions. The major exception from this trend is in the Southern Ocean between 40-60ºS, where nitrate concentrations remain high, but silicon is almost entirely depleted. As the low-latitude thermocline is fed by Southern Ocean-derived waters (Antarctic Intermediate Water AAIW, Subantarctic Mode Water SAMW; Sarmiento et al., 2004; Marinov et al., 2006), surface nutrient uptake in the Southern Ocean has an important influence on the global distribution of silicon and nitrogen. Figure 1.2 shows vertical sections of silicon and nitrate from the Atlantic Ocean to the Pacific Ocean via the Southern Ocean. Two striking differences are obvious: first, global thermocline waters (<1000 m) are much more strongly depleted in silicon than in nitrate and, second, the vertical concentration gradient of silicon is much stronger than that of nitrate. These differences originate from the preferential uptake of silicon over nitrogen by diatoms in the surface Southern Ocean (Pondaven et al., 2000; Smith et al., 2000; Sarmiento et al., 2004; see 2.2.3), and the more efficient transport of opal compared to organic tissue into the deep ocean (Broecker and Peng, 1982; Dugdale et al., 1995; Ragueneau et al., 2002; Brzezinski et al., 2003). The preferential depletion of silicon over nitrate in the surface Southern Ocean explains both the high surface nitrate concentrations in the 40-60ºS band compared to those of silicon (Fig. 1.1), and the low silicon concentrations in the global thermocline (Fig. 1.2). The strong depth gradient in silicon concentrations results from the primarily vertical silicate transport in the Southern Ocean, consisting of the sinking of opal, and upwelling of regenerated silicate through Circumpolar Deep Water (CDW; Fig. 1.2). Thus, through the interaction of physical and biogeochemical processes silicon becomes ‘trapped’ in the Southern Ocean, inhibiting the production of biogenic silica in large parts of the ocean outside it (Fig. 1.1).
Figure 1.1: Surface ocean silicon ($\text{H}_4\text{SiO}_4$) and nitrate ($\text{HNO}_3$) concentrations in $\mu$mol kg$^{-1}$. Nitrate is a major limiting nutrient throughout most of the ocean, visible in very low concentrations in the low- and mid-latitudes. The Southern Ocean has very high surface nitrate concentrations due to incomplete utilisation, the excess being exported to the low-latitudes through intermediate and mode water formation (see Fig. 1.2). In equatorial upwelling regions, such as the equatorial Pacific, the Southern Ocean-derived nitrate is upwelled and partly consumed by primary producers. Data provided by World Ocean Atlas 2009 (available under odv.awi.de; Garcia et al., 2010) and compiled using Ocean Data View (ODV; odv.awi.de).
Figure 1.2: Vertical sections, starting from the North Atlantic (left), via the Southern Ocean and ending in the North Pacific (right) of global silicon (a) and nitrate (b) concentrations, as well as a schematic representation of the meridional overturning circulation based on Sarmiento & Gruber (2006) and Toggweiler et al. (2006). Red and blue colours represent the upper and warmer, as well as the deep and colder loops of ocean circulation, respectively (Toggweiler et al., 2006). These sections clearly show that silicon and nitrate distributions are distinctly different. Silicon concentrations are remarkably low in the uppermost 1000 m, and vertical and lateral concentration gradients are much higher than for nitrate. An important control on this difference is that the Southern Ocean exports nitrate, but virtually no silicon, to the lower latitudes via intermediate and mode waters, which has important consequences for the primary productivity in the Southern Ocean and the lower latitudes. NADW: North Atlantic Deep Water; CDW: Circumpolar Deep Water; AABW: Antarctic Bottom Water; AAIW: Antarctic Intermediate Water; SAMW: Subantarctic Mode Water; NPIW: North Pacific Intermediate Water.
The unique impact of the Southern Ocean on global nutrient cycles makes it a key study area for paleoceanography and paleoclimatology. Any changes in the uptake of silicon and nitrate in the surface Southern Ocean over glacial-interglacial transitions could potentially have global impacts on primary productivity and the regional efficiency of the sequestration of CO$_2$ to the deep ocean by the biological pump (e.g. Kohfeld et al., 2005; Sigman et al., 2010).

1.1.3 The dominance of diatoms

Diatoms are unicellular photoautotrophs that utilise H$_4$SiO$_4$ to form opaline (SiO$_2$ · nH$_2$O) cell walls, called the frustule (Del Amo and Brzezinski, 1999). The frustule is encased in organic tissue, which prevents the dissolution of the opal in pervasively silica-undersaturated ocean water (Volcani, 1981; Van Bennekom et al., 1991; Treguer et al., 1995). Due to their comparatively large size, and thus surface-to-volume ratio, diatoms have high nutrient demands. Phytoplankton communities in dynamic oceanographic settings that are characterised by pulsed supply of nutrients, such as the equatorial Pacific or the Southern Ocean, thus tend to be dominated by diatoms (Ragueneau et al., 2000; Armbrust, 2009). Their competitive advantage over other organisms has been suggested to be based on the reduced energy requirements for silicification compared to the construction of other minerals, and to high nutrient uptake and growth rates combined with the ability to internally store nutrients (Raven, 1983; Martin-Jezequel et al., 2000). Furthermore, because they are equipped with large vacuoles diatoms are able to regulate their buoyancy, which allows them to move vertically within the euphotic zone, for instance to depth levels that are less depleted in nutrients (Round et al., 1990). It also been observed that a very few diatom species are able to grow under dark conditions for very short periods (24 hours), as it appears that the energy required for growth can be sourced from aerobic respiration rather than photosynthesis (Martin-Jezequel et al., 2000, and references therein). Apart from competitive advantages in nutrient acquisition and growth, it has also been proposed that diatoms have a reduced mortality owing to their comparatively large size and protective frustule, which make it harder for grazing zooplankton to cope with them (Smetacek, 1999; Hamm et al., 2003, and references therein).

Owing to their superior strategies in nutrient acquisition, in combination with their dynamic marine habitats, diatoms express a strong bloom behaviour (Ragueneau et al., 2000). After exhaustion of nutrients, the dead matter flocculates and sinks (Smetacek, 1985). Diatom-dominated food webs, such as the Southern Ocean or equatorial Pacific, appear to transport a disproportionately large amount of organic matter into the deep ocean (Buesseler, 1998; Smetacek, 1999; Kemp et al., 2000; Dunne et al., 2005), though large uncertainties are associated with field measurements and model results (cf. Francois et al., 2002; Klaas and Archer, 2002; Ragueneau et al., 2006). In total, diatoms contribute 35-75% of marine primary productivity, therefore being responsible for about one fifth of photosynthesis on Earth (Nelson et al., 1995). The transport of particulate organic carbon into the deep ocean (i.e. the mechanism of the biological pump) removes it from chemical equilibrium with the atmosphere and contributes to lowering atmospheric
Though the silicon flux associated with silicification of radiolarians, sponges, and silicoflagellates is poorly constrained, it is widely accepted that diatoms exert the primary control on the marine silicon cycle (Nelson et al., 1995; Treguer et al., 1995; Ragueneau et al., 2000). The uncertainty is partly based on limited field data, and partly on the technical difficulty of quantitatively separating the individual silicon pools of the different species in biogenic silica-rich sediments. Except for some equatorial regions, suspended particulate biogenic silica in the surface ocean is 70-90% of diatom opal (Lisitzin, 1972), emphasising the dominant role of diatoms in silicon cycling. Relative abundances in pelagic sediments are more difficult to interpret, as the preservation and export efficiencies of the various types of opal are different due to their different sizes and architectures. For instance, silicoflagellate abundances are minor in the surface, but can comprise up to 2% of the total biogenic silica in the sediment (Lisitzin, 1972). Radiolarian opal can reach significant abundances in sediments of the equatorial Pacific (Lisitzin, 1972), but productivity is largely dominated by diatoms (e.g. Bruland et al., 2012). According to recent estimates, siliceous sponges may indeed comprise much larger standing stocks than previously thought, but their growth rates (and thus the associated silicon cycling) are much slower compared to diatoms (Maldonado et al., 2010; Maldonado et al., 2011; Chu et al., 2011; Tréguer and De La Rocha, 2013).

In summary, the marine silicon cycle is well constrained by external and internal fluxes, with diatoms being the dominant cyclers. The preferential uptake of silicon over nitrogen by diatoms in surface waters of the Southern Ocean has important consequences for nutrient regimes in the other ocean basins as well as the regional biological pumps. In order to study potential changes in this nutrient (de-)coupling over glacial-interglacial transitions, a geochemical tool is introduced that records the degree of silicon depletion in the surface ocean: the silicon isotope composition of diatom opal.

1.2 The silicon isotope composition of diatom opal

This section introduces how diatoms fractionate silicon isotopes, and how their isotopic composition is likely to reflect the degree of silicon depletion in the surface ocean. In order to reconstruct past silicon utilisation in the surface ocean, however, it has to be demonstrated that the silicon isotope composition of the opal is systematically related to the amount of silicic acid consumption. The section ends with an introduction to literature studies that have used the isotopic fingerprint to reconstruct the nutrient status of the glacial ocean.

1.2.1 Silicon isotope fractionation by diatoms

Silicon has three stable isotopes, with masses 28, 29, and 30 and natural abundances of 92.23%, 4.68%, and 3.09%. A chemical reaction in which isotopes are fractionated in a mass-
dependent fashion has a characteristic fractionation factor defined as: $\alpha = R_p / R_e$, where $R_p$ is the isotope ratio of the product, and $R_e$ the isotope ratio of the reactant. The difference in the isotope ratios, i.e. the degree of isotope fractionation, is small, such that the difference is also commonly expressed as an isotope effect or enrichment factor $\varepsilon$ in per mil [$‰$] defined as: $\varepsilon = 1000 \ln \alpha \approx 1000 (\alpha - 1)$. In order to compare the silicon isotope compositions of various materials with each other, the silicon isotope ratios of the samples are normalised to a reference standard, NBS28, and expressed in per mil deviations from this standard using the delta-notation:

$$\delta^{30}\text{Si} = \left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}} - 1 \times 1000$$

From this equation it becomes obvious that samples enriched in $^{30}$Si (or depleted in $^{28}$Si) compared to the reference material have positive $\delta^{30}$Si values. Figure 1.3 illustrates the range of $\delta^{30}$Si values found for terrestrial materials, including seawater silicic acid and diatoms. Seawater is generally enriched in the heavier silicon isotopes, such that $\delta^{30}$Si values range between $+0.6‰$ and $+3.3‰$. Marine diatoms from sediments and the water column show lighter $\delta^{30}$Si values than seawater, ranging between $-0.7‰$ and $+2.8‰$.

**Figure 1.3:** Observed range of $\delta^{30}$Si values in terrestrial materials (Ding et al., 1996; Wu et al., 1997; Varela et al., 2004; Basile-Doelsch, 2006; Cardinal et al., 2007; Cavagna et al., 2011; Reynolds, 2011; Fripiat et al., 2011; Cao et al., 2012; Ehler et al., 2012; Hendry and Robinson, 2012; Egan et al., 2012). The solid line indicates the $\delta^{30}$Si of the bulk silicate Earth (Savage et al., 2010).
De La Rocha et al. (1997) presented the first systematic study of silicon isotope uptake by diatoms. They found that three different diatom species preferentially utilise isotopically lighter silicic acid to form their opaline frustules, with a fractionation factor of 0.9989 corresponding to an isotope effect of -1.1‰. As a result, both, remaining silicic acid and diatom opal become progressively heavier during subsequent silicic acid consumption. If this effect is constant, the silicon isotope composition of the diatom opal will record the relative degree of silicic acid depletion/utilisation (De La Rocha et al., 1997; De La Rocha et al., 1998). As the interpretation of the silicon isotope composition of diatom opal relies on the isotope effect to be constant, or at least well known, several factors have to be considered, and are discussed in the following section.

1.2.2 What controls the silicon isotope composition of diatom opal?

In order to interpret the silicon isotope composition of diatom opal as the degree of silicic acid depletion, the isotope effect during uptake must be well known. Several factors might cause variability in the isotope effect, or modify the silicon isotope composition of the opal after silicification:

1. Species-dependent isotope fractionation (due to vital effects);
2. Variable uptake rates (temperature and concentration dependent);
3. Variable silicon isotope composition of the silicic acid source;
4. Silicon isotope fractionation in the water column and sedimentary environment.

Species-dependent isotope fractionation

Most recently, new culturing experiments found substantial variability in the isotope effect for different diatom species (Sutton et al., 2013). In particular, *F. kerguelensis* and *C. brevis*, two very common Southern Ocean species, showed isotope effects of -0.54‰ and -2.09‰, respectively. While these results are in agreement with the preferential uptake of lighter silicon isotopes (De La Rocha et al., 1997; Milligan et al., 2004), this finding requires that the taxonomic composition of diatom samples must be known in order to correct for species-dependent isotope effects (Sutton et al., 2013). Field-studies that have measured both the silicon isotope composition of surface waters and that of diatom opal have shown that the local natural diatom assemblages fractionate silicon isotopes to a degree that is in broad agreement with the isotope effect of -1.1‰ found for cultured diatom assemblages (De La Rocha et al., 1997; Varela et al., 2004; Fripiat et al., 2011). Additionally, a recent core-top calibration did not show any significant impact of the species composition (Egan et al., 2012). Therefore, the impact of species-dependent isotope fractionation appears to be at least partly balanced by mixed-species systems that show stronger and weaker isotope effects than -1.1‰.
Variable uptake rates

In principle, the isotope effect that is expressed between opal and seawater can be considered as a net effect of isotope fractionation associated with silicon influx into the cell, polymerisation, and efflux of silicon out of the cell. Hence, variable influx:efflux ratios may influence the net isotope effect. Milligan et al. (2004) cultured diatoms under variable $p\text{CO}_2$ conditions and found higher silicon influx:efflux ratios under low $p\text{CO}_2$ conditions (100 ppm) compared to high $p\text{CO}_2$ conditions (750 ppm). However, the variability of influx:efflux ratios did not affect the net fractionation, which suggests that silicon isotope fractionation occurs during uptake and not during efflux or polymerisation. The implication of this is that the concentration of ambient silicic acid does not influence the magnitude of isotope fractionation, even though it might influence uptake rates. This finding would also explain the fact that silicon isotope fractionation has been found to be insensitive to temperature (De La Rocha et al., 1997). All culturing experiments that have systematically examined silicon isotope fractionation by the most common marine diatom species did not find any influence of the ambient silicic acid concentration on the isotope effect (De La Rocha et al., 1997; Milligan et al., 2004; Sutton et al., 2013).

Variable silicon isotope composition of the silicic acid source

Changes in the silicon isotope composition of opal might not reflect the degree of silicic acid utilisation, but a change in the isotopic composition of the silicic acid that is supplied. Considering that in most parts of the surface ocean silicic acid is almost entirely depleted (Fig. 1.1), and that most of the ocean’s silicon inventory is found in the deep ocean (>1000 m), mass balance arguments would strongly suggest that the silicon isotope composition of the deep ocean is likely to be invariant. On time scales that exceed the residence time of silicon in the ocean, however, the average silicon concentration and silicon isotope composition of the ocean will change if there is a change in inputs and outputs. Given a residence time of 10,000-17,000 (see 1.1.1), and in the simple case of a step change in the silicon concentrations and isotope compositions of the riverine inputs, the whole ocean will be 95% equilibrated with the new inputs after three residence times (30,000-51,000 years). Hence, it is in principle conceivable that the whole ocean silicon concentration and isotopic composition varies during a full glacial cycle (i.e. over 100,000 years). A recent study estimated that the input of silicon during glacial times was reduced and that the silicon isotope composition of glacial and interglacial rivers is very similar (Opfergelt et al., 2013). Therefore, the changes in the oceanic inventory can be expected to be small. Furthermore, the transition from glacial to interglacial climate states occurs in <10,000 years, such that a change in whole ocean $\delta^{30}\text{Si}$ cannot explain the previously observed differences in the silicon isotope composition of diatom opal of about 0.5-1‰ over this transition (De La Rocha et al., 1998; Brzezinski et al., 2002; Beucher et al., 2007; Pichevin et al., 2009; Horn et al., 2011; Sutton et al., 2013; Ehlert et al., 2013; this study chapter 5).

On a yearly basis, the silicon isotope composition of the surface ocean is largely determined by the properties of the winter-mixed layer that bears the characteristics of the strongly fractionated surface mixed layer and the deeper water column (Fripiat et al., 2011; de Souza et al., 2012).
Transient changes in the water column structure (such as the bipolar seesaw mechanism; Broecker, 1998), may significantly influence the properties of the winter-mixed layer, and thus the overall silicon isotope composition of the diatom opal. In the paleoceanographic context, such transient changes in the isotopic composition of the source have not yet been addressed properly. In chapter 5 of this thesis, it is discussed whether this effect could have contributed to the deglacial variability observed in diatom opal $\delta^{30}\text{Si}$ from Southern Ocean sediments.

**Silicon isotope fractionation in the water column and sedimentary environment**

The silicon isotope composition of diatom opal might become modified by several processes that occur in the water column or in the sedimentary environment. For instance, if dissolution fractionates silicon isotopes, then the bulk silicon isotope composition of the opal will change. Demarest et al. (2009) found that silicon isotopes are fractionated during dissolution of diatom opal collected from the sea surface with an isotope effect of $-0.55\%$. The authors, however, point out that the observed effect is small, and that the excellent preservation of diatom frustules in the sediment, make it unlikely that such a process would change the diatom $\delta^{30}\text{Si}$ value significantly. Nonetheless, the magnitude of fractionation might be sensitive to the dissolution rate, and thus be a function of temperature, specific surface area, and grain size (Van Cappellen et al., 2002; Loucaides et al., 2012). It is also well known that the reactivity of the opal (and thus the dissolution rate) significantly decreases during sinking and in the sedimentary environment, in particular due to the incorporation of aluminium into the frustule (Van Cappellen et al., 2002, and references therein). Whether silicon isotope fractionation during dissolution of sediment core diatom opal under variable conditions can change the silicon isotope composition of the opal has not yet been resolved, and will be addressed in chapter 3.

Strong evidence for the preservation of the silicon isotope fingerprint of relative silicic acid consumption comes from core-top studies (Ehlert et al., 2012; Egan et al., 2012). These studies found that diatom $\delta^{30}\text{Si}$ values of the uppermost sediment in the Southern Ocean and equatorial Pacific are well-matched by $\delta^{30}\text{Si}$ values of fresh mixed-layer diatoms and waters, suggesting that the $\delta^{30}\text{Si}$ signature of the opal is not disturbed by water column or early diagenetic processes. However, these studies point out that $\delta^{30}\text{Si}$ values can be severely biased if diatom separation does not successfully remove all clay minerals, or radiolarian and sponge opal, all of which have different $\delta^{30}\text{Si}$ values from diatoms (Ehlert et al., 2012; Egan et al., 2012; Fig. 1.3, see also chapter 3).

The application of the diatom $\delta^{30}\text{Si}$ fingerprint is ultimately limited by the diagenetic temperature and pressure range at which the opal undergoes the phase transition to cryptocrystalline opal (within 1 km of sediment depth) and eventually chert (Williams and Crerar, 1985; Williams et al., 1985). These phase transitions involve dissolution and reprecipitation processes and diffusional silicon transport along grain boundaries (Williams and Crerar, 1985), therefore determining the ultimate fate of the pristine silicon isotope fingerprint. A sediment layer of 1 km thickness corresponds to several million years of sedimentation in the Southern Ocean (Gersonde et al. 1999), such that somewhere within these spatial and temporal boundaries a threshold integrity of the opal
\( \delta^{30}\text{Si} \) can be expected. No study in the literature has so far addressed this issue. In chapter 4 of this thesis, the first constraints on silicon isotope exchange between diatom opal and the environment are presented.

Though some uncertainties remain (species-dependent isotope fractionation by species not yet examined, isotope fractionation during dissolution, diagenetic effects), there is compelling evidence that the diatom opal collected in the surface ocean and recovered from sediment cores indeed records the relative degree of silicic acid utilisation in the surface ocean. This promising result enables the utilisation of the \( \delta^{30}\text{Si} \) value of diatom opal for the reconstruction of silicic acid utilisation over the most recent glacial-interglacial cycles.

### 1.2.3 Previous observations of glacial-interglacial silicon utilisation

The first sedimentary records analysed for diatom opal \( \delta^{30}\text{Si} \) were three cores from the Atlantic and Indian sector of the Southern Ocean south of the Antarctic Polar Front (APF; De La Rocha et al., 1998). The data showed \( \delta^{30}\text{Si} \) values during the Last Glacial Maximum (LGM) that were 0.7‰ (Atlantic sector) and 0.3-0.6‰ (Indian sector) lighter than Holocene \( \delta^{30}\text{Si} \) values, indicating less silicic acid utilisation in the LGM surface Southern Ocean than today. This was a rather surprising discovery, as it had previously been suggested that nitrate utilisation in the surface Southern Ocean, by the bulk phytoplankton assemblage including diatoms, was enhanced compared to today (Francois et al., 1997; Sigman et al., 1999). Enhanced nitrate consumption by diatoms would intuitively suggest enhanced silicon consumption as well, since the demand for nitrogen and silicon by diatoms under nutrient replete conditions is about 1:1 (Brzezinski, 1985). The higher nitrate consumption in the surface Southern Ocean during the LGM has been interpreted as due to reduced nutrient supply through upwelling (i.e. enhanced water column stratification; Francois et al., 1997; Sigman et al., 1999; Sigman et al., 2004). However, the reduced silicon utilisation would not be consistent with reduced silicon supply through upwelling and was used as a counter-argument for the stratification hypothesis (De La Rocha et al., 1998). These unexpected opposite trends posed a challenge, as higher nutrient utilisation in the Southern Ocean would increase the efficiency of the biological pump and thus contribute to lower atmospheric CO\(_2\) values during the LGM (Volk and Hoffert, 1985; Sigman and Boyle, 2000).

At around this time, the first field and culturing studies systematically examined the uptake ratios of silicon and nitrogen by diatoms (Hutchins and Bruland, 1998; Takeda, 1998; Franck et al., 2000; Brzezinski et al., 2003). These studies found that diatoms respond physiologically to iron-limitation by preferential uptake of silicon over nitrogen (Fig. 1.4). Since Si:N supply ratios are about 2:1, and uptake ratios by diatoms about 4:1 under conditions of iron limitation, today’s surface Southern Ocean in the Atlantic sector is preferentially depleted in silicon over nitrogen (Martin et al., 1990; Pondaven et al., 2000; Smith et al., 2000; Boyd et al., 2000; Sarmiento et al., 2004; Moore et al.,
The decoupling of surface silicon and nitrate concentrations is further enhanced due to the preferential regeneration of organic matter over opal in the shallow ocean, resulting in preferential export of silicon over nitrogen to depth (Dugdale et al., 1995; Buesseler, 1998; Ragueneau et al., 2002; Brzezinski et al., 2003).

**Figure 1.4:** Average mixed layer iron concentrations (Measures and Vink, 2001; A) and silicon:nitrate uptake ratios during a diatom bloom in the Pacific sector of the Southern Ocean (Franck et al., 2000; B). Panel A shows progressive iron consumption as the waters are transported from the region of upwelling in the south towards the north. Panel B illustrates the strong sensitivity of silicon:nitrate uptake ratios by diatoms to low levels of iron. The horizontal bar indicates the observed range of mixed-layer iron concentrations and the dashed line marks the stoichiometric Si:N uptake ratio of 1:1 under iron-replete conditions.

These findings have important consequences for the global carbon cycle and biological productivity (Archer et al., 2000; Sarmiento et al., 2004; Kohfeld et al., 2005; Marinov et al., 2006; Sigman et al., 2010). Brzezinski et al. (2002) presented diatom opal $\delta^{30}$Si from the Antarctic Zone of Southern Ocean (ODP 1094) over three full glacial-interglacial cycles, showing systematically lower $\delta^{30}$Si values (by about 0.7‰) in glacial times compared to interglacial times (Fig. 1.5). At the same time, a nearby site (RC13-259) showed a systematic opposite trend for nitrate utilisation, with higher degrees of utilisation in glacial times (Rau and Froelich, 1993). Based on the previous findings of the variability of Si:N uptake ratios by diatoms under iron-limited/replete conditions, and elevated dust deposition (and thus iron supply to the surface ocean; Wolff et al., 2006) during glacial times (Petit et al., 1999; Fig. 1.5), Brzezinski et al. (2002) interpreted the opposite isotope patterns as a transition from nitrate-depleted (glacial) to silicon-depleted (interglacial) regimes. They pictured an essentially opposite pattern for today’s Southern Ocean nutrient status (Fig. 1.1). This picture is also coherent with the Southern Ocean stratification hypothesis: low supply rates of silicon and nitrate to the surface ocean during glacials, as well as relief from iron stress and the correspondingly lower Si:N demand by diatoms, results in reduced silicon utilisation (or excess silicon) and more complete nitrogen utilisation, and hence a more efficient biological pump (Fig. 1.5). The authors note that, analogous to the excess nitrate export into lower latitudes via intermediate and mode waters today
excess silicon might have been transported towards the lower latitudes in glacial times. The potential export of excess (unutilised) silicon from the Southern Ocean gave rise to the silicic acid leakage hypothesis (SALH; Brzezinski et al., 2002; Matsumoto et al., 2002; Matsumoto and Sarmiento, 2008), according to which the exported silicon supports diatom growth in the lower latitudes. The low-latitude ocean is typically dominated by growth of calcifying organisms such as coccolithophorids and foraminifera. Increased diatom growth would thus lower the CaCO$_3$/organic carbon ratio of exported materials, constituting a powerful climate feedback through whole-ocean alkalinity increase, leading to enhanced uptake of atmospheric CO$_2$ (Broecker and Peng, 1987; Archer and Maier-Reimer, 1994; Sigman and Boyle, 2000).

**Figure 1.5:** Evolution of atmospheric CO$_2$ (Luthi et al., 2008), diatom $\delta^{30}$Si (Brzezinski et al., 2002), diatom $\delta^{15}$N (Crosta and Shemesh, 2002), and atmospheric dust (EPICA Community Members, 2004) from the Last Glacial Maximum (LGM) to the Holocene. Low $\delta^{30}$Si and high $\delta^{15}$N values during the LGM indicate less silicon and higher nitrate utilisation in the surface Southern Ocean (note the reverse scale for $\delta^{15}$N). This situation is reversed during the Holocene, when atmospheric dust levels are low. Note that $\delta^{15}$N data are on a relative time scale only and shown against sediment core depth.

Since this early work, several studies have attempted to constrain the potential for silicic acid
leakage to support higher low-latitude productivity during glacial times, and a concurrent positive feedback mechanism that would contribute to lowering atmospheric CO₂ concentrations. An indicator that might support SALH is increased opal productivity in the equatorial regions, fed by the excess silicon exported from the Southern Ocean. Several studies, however, found no, or only unconvincing evidence for an increase in low-latitude opal production during the LGM, at a time when silicic acid leakage is predicted to be strongest (e.g. Higgison and Altabet, 2004; Crosta et al., 2005; Kienast et al., 2006; Bradtmiller et al., 2006; Beucher et al., 2007; Crosta et al., 2007). On the other hand, Matsumoto and Sarmiento (2008) pointed out that opal productivity could even decline as long as production of biogenic opal successfully competes with calcifying organisms for nutrients, such that the CaCO₃/organic carbon export ratio declines. Dubois et al. (2010) found evidence for both, opal production peaks and opal preservation peaks in eastern equatorial Pacific sediments, suggesting that the link between silicic acid leakage and low-latitude productivity and export is more complex than previously thought. For instance, nitrogen in the modern eastern equatorial Pacific is only incompletely consumed, but during the LGM bulk sediment data indicate even lower nitrate consumption, which can only be explained by a change of the source waters supplying nitrate to the eastern equatorial Pacific (Robinson et al., 2009). Recently, Meckler et al. (2013) found distinct opal production peaks in subtropical sediments from North Atlantic during the last six deglaciations. They interpreted the increased opal production to be the result of increased silicon supply from the deep Atlantic rather than supply through Intermediate and Mode waters.

Despite the difficulties in finding direct evidence in the lower latitudes for a reduced CaCO₃/organic carbon rain ratio, subsequent studies of diatom opal δ³⁰Si in the Southern Ocean consistently showed lower silicon utilisation during glacial times (Beucher et al., 2007; Horn et al., 2011), supporting the potential for silicic acid leakage. Similarly, there is broad consistency of nitrogen isotope records from diatom-bound nitrogen or bulk organic sediment, showing that nitrogen was a more limiting nutrient in the Southern Ocean during the LGM than today (Francois et al., 1997; Sigman et al., 1999; Shemesh et al., 2002; Crosta and Shemesh, 2002; Robinson et al., 2005; Combes et al., 2008; Robinson and Sigman, 2008; Schneider-Mor et al., 2008; Horn et al., 2011). Strong support for a switch from nitrate to silicon depletion during the transition from the LGM to the Holocene was provided by Horn et al. (2011), who presented the first coupled silicon and nitrogen isotope record of the same diatom opal samples from the Southern Ocean, with previously unprecedented age resolution. While their records confirmed the previously postulated transition from nitrate depletion in the LGM to silicon depletion in the Holocene, their high-resolution record revealed new details about the potential origin of the transition. As previously suggested by Anderson et al. (2009), at the glacial termination the deep Southern Ocean was ventilated in two intervals, which resulted in enhanced nutrient supply and CO₂ evasion into the atmosphere. During these intervals, Horn et al. (2011) found incomplete nitrate and silicon utilisation in the surface Southern Ocean, suggesting that nutrient supply exceeded the demand. Moreover, the second of the two intervals of upwelling was associated with higher silicon utilisation compared to the earlier interval. Horn et al. (2011) interpreted this feature as the result of a contemporaneous decrease in atmospheric iron fertilisation and thus an increased demand for silicon (Wolff et al., 2006).
If this result can be confirmed for other oceanic sites, it would provide strong evidence for the overall picture that has emerged in recent years. Nitrate consumption during the LGM was enhanced due to low vertical mixing rates in the Southern Ocean and thus low nutrient supply rates (Francois et al., 1997; Sigman et al., 1999; Sigman et al., 2004), as indicated by lower excess nitrate in the surface. As a result, the biological pump in the Southern Ocean was more efficient and contributed to atmospheric CO\textsubscript{2} drawdown (Archer et al., 2000; Sigman et al., 2010). Silicon utilisation at the LGM was reduced due to natural iron fertilisation and thus relief from iron-stress (Brzezinski et al., 2002; Wolff et al., 2006). Then, the re-invigoration of vertical mixing in the Southern Ocean at the glacial termination supplied more nutrients than were consumed, resulting in CO\textsubscript{2} release to the atmosphere (Anderson et al., 2009; Horn et al., 2011). During the glacial-to-Holocene transition, decreasing atmospheric iron deposition may have caused, or at least contributed to, a switch from a nitrate-depleted towards a silicon-depleted surface Southern Ocean due to an increased Si:N demand by diatoms (Hutchins and Bruland, 1998; Takeda, 1998; Pondaven et al., 2000; Brzezinski et al., 2002; Brzezinski et al., 2003).

Though the silicon and nitrogen isotope records of diatom opal from the Southern Ocean are coherent and can be explained with the physiological responses of diatoms to changing environmental conditions, several uncertainties are still to be overcome. One includes the correction of older silicon isotope records for species-specific isotope effects. Sutton et al. (2013) corrected the data of Horn et al. (2011) for the species effect, which smoothed out the aforementioned details from the glacial termination. The overall trend towards lower glacial $\delta^{30}$Si values than the Holocene remained, but decreased from 0.7‰ to 0.5‰. The species-specific isotope effect for 20-40% of the species in that core is, however, still unknown such that an uncorrected fraction remains. The effect could, however, both increase or decrease the glacial-interglacial offset. Other uncertainties are addressed in this thesis and will be introduced in the following section.

1.3 Aims and outline of the thesis

In this thesis, I provide a systematic analysis of the robustness of the silicon isotope composition of diatom opal against post-mortem modification, which has previously not been investigated in detail, followed by application of the proxy to a sedimentary record from the Southern Ocean.

In chapter 2 of this thesis, the methods are introduced that have been applied in order to prepare the samples and acquire precise and robust data. Egan et al. (2012) performed a systematic study of the relationship between sample grain size and the bulk sample $\delta^{30}$Si values. The results show that an ideal and virtually contamination-free grain size is provided by the 2-20 µm fraction, whereas other grain size fractions introduce bias from clay minerals or radiolarian opal, both of which have significantly different silicon isotope compositions. The same conclusion is reached here, and it is demonstrated that the grain size fraction 20-62 µm is not reliable as it is contaminated with radiolarian opal.

In chapter 3, the potential for silicon isotope fractionation of sediment core diatom opal is
experimentally determined. Demarest et al. (2009) found that silicon isotopes are fractionated during dissolution of diatom opal collected from the water column. Since the effect was found to be small, and given the excellent preservation of opal frustules in sediment, there is a strong mass-balance argument for the insignificance of this effect. However, the chemical and physical properties of the opal change while settling through the water column and during early diagenesis, including a change in surface area, incorporation of, for instance, aluminium into the frustule and in reactivity (Van Cappellen et al., 2002). The effect of these changes on silicon isotope fractionation of diatom opal remains to be tested.

In chapter 4, an experiment is presented that aims at measuring silicon isotope exchange rates between a solution and diatom opal, in order to obtain constraints on the threshold integrity of the silicon isotope composition of the opal in the sedimentary environment. Diatom opal forms in the uppermost parts of the ocean, where chemical and physical properties are significantly different from the deep ocean (temperature, pressure, density, pH, salinity, silicic acid concentrations) or the sedimentary environment. As the opal leaves the surface and enters the deep ocean and ultimately the sediment, chemical and isotopic disequilibrium develops. Moreover, in the sedimentary environment silicic acid-rich pore-fluids percolate and secondary silicate minerals form. Ultimately, during burial, compaction, and diagenesis the opal will experience phase transformations and will probably lose the original isotope signature, as the newly formed crystals will have silicon isotope compositions in equilibrium with the ambient pressure-temperature conditions. The effect of this isotopic disequilibrium on the silicon isotope composition of the opal has never been researched.

In chapter 5, new diatom opal δ^{30}Si data are presented for a down-core record from the Atlantic sector of the Southern Ocean. The data are used to provide a detailed reconstruction of the amount of silicic acid that was consumed by diatoms in order to constrain the potential for excess silicic to feed lower latitude productivity. The reconstruction will consider species-dependent silicon isotope fractionation, which has been shown to influence the interpretation of diatom opal δ^{30}Si values (Sutton et al., 2013). As outlined in 1.2.2, a further influential parameter on diatom opal δ^{30}Si is the silicon isotope composition of the source silicic acid. Changes associated with this value have so far been insufficiently addressed in the literature, though it can be assumed that this value changed in association with substantial physical changes that occurred in the Southern Ocean over glacial-interglacial time scales (Oppo and Curry, 2012). Thus, in chapter 5 a model is presented that considers transient changes of the silicon isotope composition of the source silicic acid and their impacts on the calculated amount of excess silicic acid, such that the results should provide upper and lower bounds of excess silicic acid in the Southern Ocean.

Lastly, this thesis finishes with a synthesis of the results, and an outlook that provides a basis for future research directions.
References


CHAPTER 1 – INTRODUCTION

Observatory, Columbia University, Palisades, New York.


mechanistic models for the particle export ratio. Global Biogeochemical Cycles 19, GB4026.


Chapter 2 – Methods

High-precision silicon isotope analysis is a comparatively young field, since the analytical demands are very high. First, the silicon isotope compositions of terrestrial samples span a narrow range, such that precise measurements are required in order to resolve differences. Second, several isobaric interferences require a high mass resolving power from the mass-spectrometer. These hurdles have been overcome in the past decade with the advent of multi-collector inductively coupled plasma mass-spectrometers (MC-ICP-MS). For the silicon isotope analysis of diatom opal, technical improvements and increasing precision have led to a shift in the methodological focus, from purely analytical considerations towards sample preparation. In the following, the recent history of silicon isotope analysis of diatom opal is briefly reviewed. Subsequently, the methodological procedures for this thesis are introduced. Part of this PhD was aimed at fine-tuning a method that Ben Reynolds had set up at ETH Zurich, a method that avoids the use of hazardous chemicals such as hydrofluoric acid (HF), and allows accurate, precise, reproducible, and rapid analysis of the silicon isotope composition of biogenic opal.
2.1 Existing methods for diatom opal analysis

Traditionally, silicon has been extracted from minerals using hydrofluoric acid (Reynolds and Verhoogen, 1953). This technique, however, is impractical for ocean sediments, since silicon from both mineral and biogenic sources is leached out. De La Rocha et al. (1996) introduced the first systematic method for silicon isotope measurements of diatom opal, and applied it to cultured diatoms (De La Rocha et al., 1997) and down-core sedimentary diatoms (De La Rocha et al., 1998). While the cultured diatoms were dissolved directly in HF, sedimentary diatoms were separated from radiolaria, minerals, mineral coatings and organics by an elaborate method that involved sieving, differential settling, sonication, and cleaning with strong acids, following the procedure given by Shemesh et al. (1988). After HF digestion, the dissolved silicic acid was re-precipitated using a triethylamine-molybdate complex to avoid loss of volatile SiF$_6$ and to isolate the silicon from the bulk matrix. The complex is combusted to SiO$_2$ polymorphs at temperatures as high as 1000°C, at which the triethylamine-molybdate complex evaporates. Afterwards, the SiO$_2$ is fluorinated with BrF$_5$ or F$_2$ in a vacuum line and introduced as SiF$_4$ into an isotope-ratio mass-spectrometer (IRMS). Later, this technique was adjusted using CsCl to re-precipitate the dissolved silica as Cs$_2$SiF$_6$, which is then decomposed in vacuo with sulphuric acid, and measured as SiF$_4$ (Brzezinski et al., 2006). This technique was found to increase the silicon yields and to improve analytical precision by 200% (Brzezinski et al., 2006). The major drawbacks of these techniques are the utilisation of hazardous chemicals such as HF, BrF$_5$, and F$_2$, and the long and elaborate methodological and analytical protocol. The digestion of silica with HF produces volatile SiF$_6$, the loss of which may result in silicon isotope fractionation, and the labs containing BrF$_5$ or F$_2$ gas bottles must obey special security requirements.

With the advent of plasma instruments in the late 1990s, it became possible to measure silicon without the need for hazardous fluorine gases. Also, the sample introduction system of plasma instruments differs from that of IRMS, such that new and faster sample processing protocols could be developed. De La Rocha (2002) treated opal with mild HCl and H$_2$O$_2$ to remove organics following the method of Mortlock and Froelich (1989), dissolved it in HF, and diluted the solution with HCl and water. This solution had to be analysed in wet-plasma mode to avoid the formation of the volatile SiF$_{4g}$ gas that would have formed if the sample had been desolvated. Wet-plasma conditions, however, cause a significant reduction in beam intensity and stability. Cardinal et al. (2003) used a slightly different setup, and diluted the final HF-HCl-sample mixture more to inhibit the formation of volatile SiF$_{4g}$. As a result, they were able to measure in dry-plasma mode, and obtained increased beam intensity and stability. However, Georg et al. (2006) found that significant amounts of silicon are still lost through the formation of SiF$_{4g}$.

In subsequent years, studies adapted techniques that had traditionally been designed to determine the total biogenic silica content in sediments. These techniques used dissolved Na$_2$CO$_3$ or NaOH to leach biogenic opal out of sediment (Mortlock and Froelich, 1989; Ragueneau et al., 2005). Such a solution is, however, unsuitable for silicon isotope analyses as the matrix of the
dissolved phase contains unwanted by-products, such as silicate mineral-sourced silicon, organic matter, and a poorly defined mixture of anions and cations. A possible work-around was introduced by Cardinal et al. (2007), who digested the opal in 0.2 M NaOH, isolated the silicon by reprecipitating the dissolved silicic using the triethylamine-molydate complex (De La Rocha et al., 1996), and redigested the sample using an HF–HCl mixture (Cardinal et al., 2003). This integrated approach, however, still uses HF for the final digestion. In addition, most ICP-MS instruments were not able to fully resolve all polyatomic interferences, such that $^{30}$Si could not be measured.

In recent years, an augmented interest in the isotope compositions of such diatom-associated elements as carbon, nitrogen, silicon, and oxygen, as well as the enhanced instrumental precision, has led to increasing demands on samples and their preparation. Compared to the earlier studies, the overall workload has clearly shifted from analytics to sample preparation, while the overall time consumption remained comparable. As a result, highly specialised microseparation and cleaning procedures were developed (Shemesh et al., 1988; Ellwood and Hunter, 1999; Morley et al., 2004; Robinson et al., 2004; Minoletti et al., 2009), such that the starting sample material is basically a pure opal powder that can be quickly dissolved. This circumstance eventually allowed the complete avoidance of HF and the use of NaOH for dissolution medium, such that the digested sample has a well-defined and simple matrix. The alkaline dissolution utilises the fact that opal dissolution rates are greatly increased at high temperatures and above pH 8.5 (Iler, 1979). Egan et al. (2012), dissolved the opal in 0.2 M NaOH for 40 minutes at 100°C. Ehrlert et al. (2012), and Etourneau et al. (2012) used 0.1 M NaOH and temperatures of 130°C. Afterwards they included an additional step of organic matter oxidation by adding H$_2$O$_2$ to the samples, which was found to improve beam stability and reproducibility (Ehrlert et al., 2012). Reynolds et al. (2008) pre-treated the opal before dissolution with HClO$_4$ but did not find any influence on the measurements if this step was not included. The use of 0.2 M NaOH, however, results in solutions that either require a comparatively large amount of cation exchange chromatographic medium, substantially increasing elution times, or a dilution step, resulting in additional requirements for sample beakers and storage space. It has also been observed that the basic sample solution can react with polypropylene bottles, causing the formation of organic polymers that are visible as a white “fog” (Brzezinski and Nelson, 1995; C. Baah and Baah, 2002).

2.2 Methodological setup and developments of this thesis

The method for silicon isotope analysis of diatom opal in this thesis consists of three major steps:

1. Separation of diatom opal from the sediment and chemical cleaning;
2. Dissolution of the opal and subsequent purification of the solution through cation exchange chromatography;
3. Mass-spectrometric analysis of the purified solutions;
The separation and cleaning of diatom opal was not part of the PhD and was done in the Department of Environmental Sciences and Energy Research, Weizman Institute of Science, Rehovot, Israel (courtesy of Aldo Shemesh and Aya Schneider-Mor). Unless otherwise stated, dissolution, purification, and analysis of the opal in this thesis followed the protocol as described in the following section, where the methodological developments that have been achieved during the PhD are also highlighted.

2.2.1 Separation of diatom opal from the sediment and chemical cleaning

All samples for this PhD were provided by Prof. Dr. Aldo Shemesh Department of Environmental Sciences and Energy Research, Weizman Institute of Science, Rehovot, Israel. They were collected in the course of the Ocean Drilling Program (ODP) Leg 177, Site 1093. The site is at 3624 m depth and located in the Atlantic sector of the Southern Ocean at S49°58'35, E5°51'55. Micro-separation of diatoms is necessary in order to filter out other silicon-bearing sediment components such as radiolaria, sponges, and silicate minerals. After this enrichment, diatom opal is chemically cleaned in order to remove organic tissues, and to leach off, oxidise and/or complex any surface coatings such as authigenic clays and adhesively bound Fe or Al. The method applied here is based on Shemesh et al. (1988) and Singer and Shemesh (1995), and described in detail in Schneider-Mor (2006). Four major steps are involved: first, the sediment is treated with H$_2$O$_2$ to oxidise organic matter, and then with HCl to dissolve carbonates; second, the sediment is sieved into grain size fractions $>$63 µm, 20-62 µm, and $<$20 µm, to pre-concentrate diatom opal and separate it from radiolarian opal, whereas the $>$62 µm fraction is rejected; third, the enriched diatom opal is separated from the matrix by heavy liquid separation using sodium polytungstate ($\rho\approx2.3$ g/cm$^3$); fourth, in order to remove the outermost opal layer containing adsorbed ions and metals, clays, and secondary precipitates the opal surfaces are leached and oxidised with a 1:1 mixture of HNO$_3$ and HClO$_4$ ($<$20 µm, 20-62 µm) and CH$_3$COOH and HONH$_2\cdot$HCl ($>$20-62 µm).

For this thesis, the grain size fraction $<$20 µm was preferred where enough sample material was available, as this fraction contains the most enriched diatom opal, and only minor impurities as verified by microscopic inspection (Fig. 2.1a, b). A recent study by Egan et al. (2012) used a microfiltration technique to obtain narrow grain sizes, demonstrating that the sample grain size is indeed the most suitable fraction for diatom silicon isotope analysis. Based on mass-balance, a 5% abundance of radiolarian opal with a $\delta^{30}$Si of -1.5‰, and assuming a diatom $\delta^{30}$Si of +1.5‰, results in a bulk $\delta^{30}$Si of +1.35‰, a difference that is just above the external reproducibility of $\delta^{30}$Si values ($\pm0.14$‰, 2SD) in this thesis (see 2.3.1). From Figure 2.1a, b, however, a radiolarian abundance of 5% in the $<$20 µm is very unlikely. As not all samples have been checked for their purity with a secondary electron microscope, it may be possible that some $<$20 µm samples are unusually rich in fragments of radiolarian opal. In rare cases where duplicate measurements of the samples were unusually ambiguous, new sample splits were dissolved and measured in order to narrow down the most representative diatom opal silicon isotope composition. The grain size fraction 20-62 µm from
the available sediment core contains significant amounts of radiolarian opal (Fig. 2c, d), and was sampled when not enough material of the size fraction <20 µm was available, but also to compare the silicon isotope composition of both fractions.

![Secondary electron images of separated and chemically cleaned opal samples used in this thesis. A and B are samples from the grain size fraction <20 µm and are the most enriched in diatom opal. C and D are samples from the size fraction 20-62 µm and contain substantial amounts of radiolarian opal.](image)

**Figure 2.1:** Secondary electron images of separated and chemically cleaned opal samples used in this thesis. A and B are samples from the grain size fraction <20 µm and are the most enriched in diatom opal. C and D are samples from the size fraction 20-62 µm and contain substantial amounts of radiolarian opal.

### 2.2.2 Dissolution of opal and purification using cation exchange chromatography

Experiments on opal dissolution with diluted (5 mM) NaOH solution had been performed previously at ETH (B. Reynolds, unpublished). The low concentration of cations in this solution requires a low volume of chromatographic cation exchange medium for purification of solutions, reducing the elution time and allowing for higher sample throughput. Compared to 0.2 M NaOH, the concentration is 40 times more diluted, but dissolution rates are only 3 times lower (Brady and Walther, 1989). The pH of 11.7 combined with temperatures of about 100°C should allow the
complete dissolution of the opal overnight. During this PhD, the ability of this method to dissolve the opal completely was tested.

Throughout this PhD, reagent-grade NaOH (Merck, KGaA, Germany) pellets were used to prepare stock solutions of NaOH. The silicon blank in the solid was 1 ppm, corresponding to a maximum contribution of 0.005% to the silicon in samples. Typically, 0.47-0.90 mg of opal was weighed using a micro-scale balance and added to 40-50 ml of NaOH, such that the final silicon concentrations were between 156-374 µM, well-below the solubility of acid-cleaned sediment core diatom opal of 828-924 µM (Van Cappellen et al., 2002).

For dissolution, a thermo-mixer (HLC Ditabis, Germany) capable of reaching temperatures up to 130±0.1°C, and shaking frequencies of 1300 rpm, was used. The agitation of the liquid supports dissolution while at the same time ensuring that the solution is well mixed. As opal powders constitute an integrated silicon isotope signal, and to avoid potential effects of silicon isotope fractionation during dissolution (see chapter 3), complete dissolution is required. The opal was usually dissolved for a minimum of 24 hours, though less time might also achieve full dissolution. As visual confirmation of complete dissolution is difficult due to the small sample grain sizes of <20 µm, complete dissolution has to be confirmed through mass balance considerations, as detailed in the following paragraph.

During this PhD, a total of 108 samples have been specifically monitored for their degree of dissolution during sample preparation, based on the amount of opal that was weighed. The range of measured degrees of dissolution varied between 50% and 116%, with an average of 79±12% (1SD). Thus, the evaluation suggests that on average 21% of the opal remained undissolved. However, two possible sources of error contribute to uncertainties in the calculated degrees of dissolution.

First, the amount of silicon in 1 mg opal is uncertain and variable. For instance, 1 mg of SiO$_2$ contains 467 µg silicon, whereas opal is reported as SiO$_2$·nH$_2$O (Jones and Segnit, 1971), such that the same mass of opal can be assumed to have <467 µg silicon. The hydroxylated opal surface is usually greatly removed by chemical cleaning of the opal (Labeyrie and Juillet, 1982), such that silicon contents of 440 µg have been reported for 1 mg of opal (De La Rocha, 2006). Assuming that the 21% of silicon found here to be missing is due to uncertainty in stoichiometry, however, would require a silicon content of only 374 µg per mg opal.

Second, weighing errors could introduce systematic errors in the calculated degrees of dissolution. During this PhD, it was observed that on humid days the weight of diatom opal progressively increased during weighing, suggesting that ambient water vapour adsorbs onto the opal. Next to loss due to electrostatic repulsion from the sample beaker during transfer, adsorption of ambient water contributed substantially to balancing uncertainties. An estimate of the increase in weight due to ambient water adsorption is provided by two weight measurements with a nano-scale balance built at ETH, which was used to measure BET surface areas of the opal samples (see chapter 3). The two samples were first weighed using a micro-scale balance, giving weights of 1.1 and 1.2 mg. Then, the samples were baked to remove adsorbatively-bound molecules. The subsequent measured dry weights were 0.74 and 0.97 mg, respectively, which is an offset of 32%
and 19% compared to the wet weights, encompassing the observed mean of 21% apparently undissolved opal. This example shows that it is likely that an underestimation of the opal weight due to ambient water adsorption is the major source of variability in the observed theoretical degrees of dissolution. Therefore, it can essentially be assumed that complete dissolution is achieved throughout this thesis. In cases where the calculated degree of dissolution was observed to be unusually low, the sample was dissolved for longer or a replicate sample was dissolved.

The purification of the solutions after dissolution was achieved by ion-exchange chromatography. At pH 11.7, silicon is dominantly present as $\text{H}_3\text{SiO}_4^-$ with minor abundances of uncharged $\text{H}_4\text{SiO}_4^0$, which allows the separation of the $\text{Na}^+$ ions using a cation-exchange medium. Due to the simple matrix chemistry, the final solutions are free of any anions that could cause matrix effects during mass-spectrometric analysis. The chromatographic method is based on Georg et al. (2006), who showed that a 12% cross-linkage cation-exchange resin (AG50W-X12, Bio-Rad Laboratories, USA) results in quantitative silicon elution without isotope fractionation. As shown by de Souza (2011), the use of an 8% cross-linkage medium (AG50W-X8, Bio-Rad Laboratories, USA) is able to provide the same results, while reducing the time for chromatography by roughly 25%. The low concentrations of cations (0.005 meq/ml) requires only a low volume of cation-exchange resin AG50W-X8, which has a retention capacity of 1.7 meq/ml. A resin volume of 0.75 ml (1.3 meq) is therefore easily able to retain all cations of the sample solution. The chromatographic separation was carried out in 4 ml BioSpin PP columns with a polyethylene frit (Bio-Rad Laboratories, USA). Before loading the samples, the resin was cleaned with acids and afterwards rinsed with Milli-Q Element water (MQe, 18.2 MΩ · cm) and checked for neutral pH. The detailed chromatographic procedure is summarised in Table 2.1.

Table 2.1: Detailed procedure for the chromatographic purification of silicon from 5 mM NaOH solutions. A resin volume (AG50W—X8) of 0.75 ml (1.3 meq) is used. Sample volume was always chosen such that 2.4 µg of silicon were loaded resulting in final solutions with 600 ppb silicon.

<table>
<thead>
<tr>
<th>Step</th>
<th>Volume [ml]</th>
<th>Concentration [mol/L]</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean</td>
<td>1</td>
<td>3</td>
<td>HCl</td>
</tr>
<tr>
<td>Fill</td>
<td>6</td>
<td></td>
<td>HCl</td>
</tr>
<tr>
<td>Fill</td>
<td>0.3 conc</td>
<td></td>
<td>$\text{HNO}_3$</td>
</tr>
<tr>
<td>Fill</td>
<td>6</td>
<td>1</td>
<td>HCl</td>
</tr>
<tr>
<td>Rinse</td>
<td>1</td>
<td>-</td>
<td>MQe</td>
</tr>
</tbody>
</table>

check if pH=7, otherwise continue rinsing

Sample load

<table>
<thead>
<tr>
<th>Volume [ml]</th>
<th>Concentration [mol/L]</th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24-0.7</td>
<td></td>
<td>MQe</td>
</tr>
<tr>
<td>0.3-0.76</td>
<td></td>
<td>MQe</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>MQe</td>
</tr>
</tbody>
</table>
Throughout this thesis, silicon concentrations of the samples after dissolution were measured using a photospectrometer following the molybdate-blue method (Strickland and Parsons, 1968). Depending on the measured concentration, about 240-700 µL of sample solution, but always 2.4 µg silicon, were loaded onto the cation-exchange resin. The final purified solutions had a volume of 4 ml and a silicon concentration of 600 ppb (21.4 µM).

2.2.3 Mass-spectrometric analysis of silicon isotopes

Silicon isotope analysis has been performed using a double-focusing multi-collector inductively coupled plasma mass-spectrometer (MC-ICP-MS) Nu Plasma 1700 (Nu Instruments, UK) at ETH. The instrument is unique in having a high mass resolving power, so that all polyatomic interferences on the three isotopes $^{28}\text{Si}^+$, $^{29}\text{Si}^+$, and $^{30}\text{Si}^+$ are fully resolved, while maintaining peak flatness. A mass-resolution of $\sim$1900 ($m/\Delta m$ at 10% peak level) is required to separate the major polyatomic interferences ($^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}^{14}\text{N}^+$, $^{14}\text{N}^{15}\text{N}^+$, $^{14}\text{N}^{15}\text{N}^{1}\text{H}^+$, $^{14}\text{N}^{16}\text{O}^+$) from the ion beam (Fig. 2.2).

The samples are aspirated with a PFA nebuliser at a rate of 50-100 µL/min and introduced into the plasma through a desolvating unit (DSN-100; Nu Instruments, UK). Silicon isotope ratios $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ are measured in static mode against the standard reference material NBS28. The difference between sample and standard is reported using the delta notation in parts per thousand:

$$\delta^{x}\text{Si} = \left( \frac{^{x}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}} \cdot 1000$$

where $x$ stands for the respective isotope masses 29 or 30. Throughout the thesis only $\delta^{30}\text{Si}$ values are reported, unless explicitly mentioned (chapter 4). Monitoring $^{29}\text{Si}/^{28}\text{Si}$ ratios only served as proof of mass-dependency of the isotope ratios (a result of instrumental fractionation), and hence the successful resolution of polyatomic interferences. Instrumental mass bias is corrected by standard-sample-standard bracketing (Albarède and Beard, 2004). Each $\delta^{30}\text{Si}$ value represents the average of 5 bracketed measurements of the sample (36 integrations for 5 s per standard and sample measurement), such that about 2 ml (~43 nmol silicon) of sample solution are consumed. After each standard and sample measurement, a 5 or 50 mM HCl wash solution was aspirated for 120 s. Prior to each standard and sample measurement, electronic backgrounds of the Faraday cups were collected for 30 s by deflection of the ion beam using the electrostatic analyser (ESA).
2.3 Method evaluation

2.3.1 Accuracy and precision

Accuracy of the measurements has been monitored throughout the PhD using the secondary standard Diatomite (Brzezinski et al., 2006) and later also the sponge standard LMG08 (Hendry et al., 2011). Inter-laboratory comparisons using different methodological procedures yielded $\delta^{30}$Si values of $1.26 \pm 0.02\%$ (2SEM, $n=82$) for Diatomite (Reynolds et al., 2007) and $-3.37 \pm 0.04\%$ (2SEM, $n=22$) for LMG08 (Hendry et al., 2011), respectively. During this PhD, $\delta^{30}$Si values of $1.27 \pm 0.01\%$ (2SEM, $n=104$, 2.8 years) were obtained for Diatomite (Reynolds et al., 2007) and $-3.39 \pm 0.02\%$ (2SEM, $n=11$, 1.4 years) for LMG08 (Hendry et al., 2011). Both are in excellent agreement with the inter-calibrated values.

The achieved precision is given by the variance of the data. Figure 2.3 shows the probability-density function of the bulk data ($n=104$) for Diatomite accumulated over 2.8 years. It is nicely demonstrated that the data are normally distributed, having a mean $\delta^{30}$Si of $1.27\%$ and an associated standard deviation of $0.07\%$, such that the long-term external reproducibility of $\delta^{30}$Si values in this thesis is $\pm 0.14\%$ (2SD). This value is comparable to the reproducibilities of $0.14\%$ and $0.12\%$ as reported by (Reynolds et al., 2008) and de Souza et al. (2012), respectively, using different sample preparation techniques but the same mass-spectrometer. Other laboratories that use similar methods and standard-sample-standard bracketing protocols report 2SD external
reproducibilities of 0.25‰ (Ehlert et al., 2013), 0.24‰ (Egan et al., 2012), 0.20‰ (Fripiat et al., 2012), and 0.15‰ (Hendry and L. F. Robinson, 2012).

Figure 2.3: Cumulative probability-density function (red curve) of all (n=104) Diatomite measurements within this PhD with a mean (black line) of 1.27±0.01‰ (2SEM) and a standard deviation of ±0.07‰. The grey curve represents the probability-density function of a perfectly normally distributed data set. The similarity of measured and theoretical distribution provides strong evidence that the standard deviation of ±0.07‰ represents the long-term external reproducibility of δ³⁰Si values. The plot has been created using Isoplot (K. R. Ludwig, Berkeley Geochronological Center).

2.3.2 Background acquisition

All raw sample ratios were corrected for electronic baseline by deflecting the ion beam away from the Faraday cups using the ESA. This method neglects the overall instrumental silicon background of the sample matrix, desolvator, torch, injector, cones, and lenses, while allowing for about 50% faster measurements, as no additional blank solution is measured after samples and standards. In addition, the time between standard and sample measurements is kept as short as possible, thus increasing the accuracy of the mass bias correction through standard-sample-standard bracketing (Albarède and Beard, 2004). The application of this acquisition method, however, has critical pre-requisites: (1) the overall silicon background signals must be significantly lower than the intensities of sample silicon, and/or, (2) the isotopic composition of the silicon background must be comparable to the samples. Throughout this thesis sample/background intensity ratios were between 101-1182 with a median of 275. Based on a sample/background intensity ratio of 275 and a typical sample δ³⁰Si value 1.5‰, a mass-balance calculation shows that
the background $\delta^{30}\text{Si}$ would need to be as high/low as $+42\%_\circ/-39\%_\circ$ in order to create bias that is larger than the external reproducibility of $0.14\%_\circ$.

**Figure 2.4:** Cumulative probability-density function (red curve) of instrumental background measurements. The black lines represent the mean ($n=18$) of $\delta^{30}\text{Si}$ ($0.96\pm 20.39\%_\circ$) and $\delta^{29}\text{Si}$ values ($0.10\pm 11.48\%_\circ$) values. The grey curve represents the probability-density function of a perfectly normally distributed data set. The large scatter of the data is due to the poor counting statistics on a low background silicon signal of 15 mV, which is about a factor of 300 smaller than for common silicon samples. As background intensities are very low compared to samples and the isotopic composition similar to that of natural samples, the pre-requisites for silicon isotope measurements in ESA beam deflection mode are met. The plots have been created using *Isoplot* (K. R. Ludwig, Berkeley Geochronological Center).

In order to assess the potential for the background to bias the measurements, background measurements have been acquired over one night using the same analytical protocol as for regular samples. Thus, each $\delta$-value consisted of 5 bracketed background measurements, each measured 36 times for 5 s, which resulted in a total sample acquisition time of 15 min. The mean silicon background intensity was 15 mV. Values obtained for $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ were $0.96\pm 9.64\%_\circ$ (SD; $n=18$) and $0.10\pm 6.80\%_\circ$ (SD; $n=18$). Figure 2.4 demonstrates that the data are normally distributed and that the mean silicon isotope composition approximates zero. This observation provides evidence that the background has a natural silicon isotope composition close to the average crust (Fig. 1.3) and that the scatter of background $\delta$-values is based on poor counting statistics on a small background signal. For instance, in order to achieve the same precision for the background as for Diatomite (SEM = $0.01\%_\circ$; see 2.3.1) the number of measurements using the same analytical setup would need to be approximately as high as 1,000,000. Furthermore, the excellent precision and reproducibility achieved for Diatomite measurements (2.3.1) strongly argues for the instrumental background to be insignificant. Thus, it can be concluded that the instrumental silicon background of the *Nu1700* at ETH has no significant impact on the silicon isotope composition of the samples and can be neglected. It is, however, necessary to assure for every analytical session that the pre-
requisites for the method are still met.

In chapter 4 of this thesis, this issue is addressed in more detail. There, a data acquisition scheme for samples with non-natural silicon isotope composition is presented. It is demonstrated that the instrumental silicon background systematically biases measurements in ESA beam deflection mode, such that the background must be accounted for.

2.3.3 Sample heterogeneities

The question of how representative an opal subsample is of the bulk is hard to quantify. In general, it is desired that the sample is heterogeneous in the sense that one sample represents the diatom silicon isotope utilisation signal of different species integrated over several years, such that seasonal effects are averaged out. This heterogeneity is defined as mixture of seasonally blooming diatom species, excluding opal from other biogenic sources such as sponge or radiolarian opal. As mentioned in 2.2.1, sample grain sizes available for this PhD were <20 µm and 20-62 µm, where the fraction 20-62 µm can contain substantial amounts of radiolarian opal. The impact of radiolarian-sourced silicon on the silicon isotope composition of samples containing diatom-radiolaria mixtures is illustrated in Figure 2.5. Plotted are the δ^{30}Si values of all samples available for this PhD, separated according to their grain size fractions. While the overall amplitude of δ^{30}Si values for the grain size fraction <20 µm is about 0.8‰, it is 1.8‰ for the size fraction 20-62 µm. Moreover, trends and absolute values of δ^{30}Si values are mostly not coherent between the two grain size fractions, such that the interpretations of both records would be significantly different. The different habitats of diatoms and radiolaria imply that a mixture of both would represent a silicon isotope signal with no environmental meaning. As there are no systematic studies yet on silicon isotope fractionation by radiolaria, δ^{30}Si values cannot be corrected for radiolarian-derived silicon. Consequently, for this thesis the sample grain size fraction 20-62 µm is of no further use (see also chapter 3). For the grain size fraction <20 µm, a diatom purity of 100% is generally impossible to establish by microseparation techniques, but microscopic tools allow increased confidence in the insignificance of impurities.

A further possible source of heterogeneity could be that the bulk opal sample is not well mixed prior to subsampling. Due to the strongly electrostatic properties of dry opal, clusters tend to form in the opal powder that may or may not be enriched in individual diatom species, such that subsampling would not be representative for the bulk sample. This issue was monitored by dissolving replicate subsamples, with the result that all eight replicates were indistinguishable in their δ^{30}Si values, within the external reproducibility of 0.14‰, from the previous values. While an influence of this cannot generally be ruled out, it appears that the bias is less than the analytical precision.
Figure 2.5: Comparison of $\delta^{30}$Si values (with associated measurement errors) of the grain size fractions <20 µm (dark grey) and 20-62 µm (light grey). It is demonstrated that the two grain size fractions are distinctly different in their silicon isotope composition, which can be ascribed to significant amounts of radiolarian opal in samples of the size fraction 20-62 µm (Fig. 2.1c, d). Thus, $\delta^{30}$Si values of this size fraction have no environmental/paleoceanographic significance.
References


Chapter 3 – Silicon isotope partitioning in response to diatom dissolution*

Abstract

The silicon isotope composition of opal frustules from photosynthesising diatoms is a promising tool for studying past changes in the marine silicon cycle, and indirectly that of carbon. Dissolution of this opal has recently been shown to fractionate silicon isotopes, adding complexity to the understanding of marine silicon cycling and the diatom opal isotope fingerprint. Here, we aim to assess the sensitivity of silicon isotope fractionation during opal dissolution to various factors, such as temperature, specific surface area, grain size, and opal age.

Our results demonstrate either insignificant or no clearly resolvable isotope fractionation for a sample grain size fraction that has previously been shown to be the most indicative for diatom opal, suggesting that silicon isotope fractionation during dissolution of sediment core diatom opal is absent, or different than during dissolution of fresh diatom opal. Experiment variables such as temperature, degree of undersaturation, sediment age, or opal specific surface area were not observed to have a significant effect on isotope fractionation, although they did influence dissolution rates. Instead, we observe a striking sensitivity of silicon isotope evolution during dissolution to sample heterogeneities. Dissolution of a larger grain size fraction results in mixing of silicon isotope signatures from different silicon sources such as radiolaria, producing an artificial apparent isotope effect. With a simple model we show that dissolution of a heterogeneous sample can create isotope effects that mimic isotope fractionation. We discuss the potential influence of sample age, dissolution medium, and sorption on silicon isotope fractionation during opal dissolution. Overall, the findings of our study agree with the previous findings that silicon isotope fractionation during diatom dissolution does not significantly alter the opal's original silicon isotope fingerprint, which is considered to be a valuable proxy for the degree of silicic acid utilisation in the past.

*submitted to Geochimica et Cosmochimica Acta as F. Wetzel, G. F. de Souza, and B. C. Reynolds: “Silicon isotope effects during diatom dissolution and their sensitivity to sample composition”.
3.1 Introduction

Diatoms are unicellular phototrophs that utilise silicon to form sophisticated opal cell walls. On a global scale diatoms are responsible for about one-fifth of the photosynthetically fixed carbon (Nelson et al., 1995). In the ocean, they play a major role in atmosphere-ocean CO$_2$ equilibrium via the biological carbon pump (Volk and Hoffert, 1985). After death, sinking diatoms efficiently transport organic carbon to the deep ocean (Buesseler, 1998), making it inaccessible to the atmosphere for hundreds to thousands of years. Changes in a surface water's productivity, community structure, or nutrient stocks may strongly affect the regional efficiency of the biological pump, and ultimately climate. It has been hypothesised that at glacial times the ratio of carbon export-to-supply was closer to unity than today, resulting in an efficient biological pump and hence a carbon-enriched deep ocean and CO$_2$-poorer atmosphere (Francois et al., 1997; Sigman and Boyle, 2000; Anderson et al., 2002; Kohfeld et al., 2005). A mechanistic and integrated picture of how and why the efficiency of the biological pump changes has not yet been achieved. Reliable and robust nutrient proxies are required to study past changes in nutrient dynamics.

In the oceanic water column, silicon geochemistry is relatively simple and well understood, since it exists almost entirely as silicic acid (H$_4$SiO$_4$) has no atmospheric cycle and is not involved in redox reactions. The discovery that diatoms fractionate silicon isotopes during uptake offered the possibility to trace both the modern marine biogeochemical cycle of silicon as well as potential changes in the past (De La Rocha et al., 1997). Silicon has three stable isotopes with atomic masses 28, 29, and 30. During uptake by diatoms, the lighter isotopes are preferred, leaving behind an isotopically heavier dissolved Si (dSi) pool. Since the effect of isotope fractionation on stable isotope ratios is small, deviations are commonly expressed in per mil relative to an established standard reference material, NBS28 quartz sand, using the delta-notation:

$$\delta^{x}Si = \left( \frac{^{x}Si}{^{28}Si} \right)_{\text{sample}} \times \left( \frac{^{28}Si}{^{28}Si} \right)_{\text{standard}} - 1 \times 1000 \quad \text{eq. (3.1)}$$

where x denotes the isotopes of mass 29, or 30.

Early systematic studies (De La Rocha et al., 1997; Milligan et al., 2004), indicated that uptake by diatoms fractionates silicon isotopes with a constant magnitude that is independent of temperature, species, and ambient $p$CO$_2$. Therefore, any variability in the $\delta^{30}$Si of recent and sediment core diatoms has been interpreted as variability in the utilised fraction of dSi (De La Rocha et al., 1998; Varela et al., 2004). This information has then been used to trace changes in nutrient limitation, efficiency of the biological pump, and water column stratification on various temporal and spatial scales (e.g. Brzezinski et al., 2002; Beucher et al., 2007; Cardinal et al., 2007; Reynolds et al., 2008; Pichevin et al., 2009; Swann et al., 2010; Fripiat et al., 2011; Fripiat et al., 2012).
The application of the diatom $\delta^{30}$Si proxy for paleoreconstructions has recently been facilitated through several studies. First, Egan et al. (2012) showed that sedimentary core-top diatoms conserve their surface silicon isotope utilisation fingerprint into the sediment. They also demonstrated that even small amounts of radiolarian and sponge opal, as well as clay minerals, can have a substantial impact on the bulk diatom $\delta^{30}$Si, and point out the importance of a well-established sample cleaning and separation procedure. In particular, the choice of a single, specific, sample grain size fraction can greatly reduce the amount of non-diatom silicon sources. Second, Sutton et al. (2013) found a significant dependence of the magnitude of silicon isotope fractionation on the taxonomic composition, complicating the interpretation of diatom silicon isotope variations.

A third potential issue addressed here is that the pristine diatom $\delta^{30}$Si signal might be compromised by silicon isotope fractionation during dissolution. Since biogenic silica (bSi) is undersaturated throughout the entire ocean, it is constantly prone to dissolution, especially once its protective organic coating has been removed (Bidle et al., 1999). A study by Demarest et al. (2009) has found silicon isotope fractionation during dissolution of diatom opal. The authors, however, point out that the observed effect is small, and that considering the excellent preservation of diatom frustules in the sediment, it is unlikely to change the diatom $\delta^{30}$Si value significantly. A rather surprising feature of their dissolution experiments is the observed linear evolution of isotope compositions. Such a trend would be expected if reactant (bSi) and product (dSi) are continuously in isotopic equilibrium, or if reactant and product are constantly separated and removed from the system. While the latter is excluded by the experimental setup, isotopic equilibrium throughout the reaction implies bidirectional exchange, in which the back-reaction might influence the net (apparent) isotope fractionation. This raises the questions of to what extent - or if at all - the observed isotope fractionation is explained by dissolution only, i.e. if the results are reproducible when back-reactions are restricted. Currently, no study in the literature has systematically addressed potential silicon isotope effects associated with dSi sorption or reprecipitation onto bSi. If associated with isotope fractionation, reprecipitation and/or sorption could explain the observed isotope effect. Fresh impetus for the re-examination of silicon isotope effects during diatom dissolution also comes from the above-mentioned findings of Egan et al. (2012), which demonstrate the susceptibility of diatom $\delta^{30}$Si to sample impurities, that can largely be avoided if the sample’s grain size is between 2 and 20 µm. For their experiment, Demarest et al. (2009) used plankton tow and sediment trap samples, for which the exact grain size fraction was poorly known (M. Brzezinski, pers. comm.), though it is stated that no significant non-diatom silicon sources were identifiable.

The goal of this study is to examine potential silicon isotope effects during dissolution of diatom opal and their sensitivity to several external parameters. By using a much more corrosive dissolution environment, we try to exclude competing processes in order to approximate a unidirectional dissolution reaction. Additionally, instead of fresh diatom opal we use sediment core material. As observed in previous studies, the reactivity of diatom opal progressively decreases with age (McManus et al., 1995; Van Cappellen and Qiu, 1997b; Van Cappellen et al., 2002). As is the case
for opal dissolution rates (Van Cappellen et al., 2002 and references therein; Loucaides et al., 2011), silicon isotope partitioning during dissolution might be sensitive to the age of opal surfaces and dissolution environments. The observed isotope effect is surprisingly sensitive to opal grain size, which we attribute to parallel dissolution of radiolarian and diatom opal. This observation supports the finding of Egan et al. (2012) that, depending on the chosen sample grain size fraction, diatom silicon isotope analyses can easily be biased by other silicon-bearing impurities. Our purest diatom samples show almost no resolvable isotope effects, suggesting that silicon isotope fractionation during dissolution of sediment core opal is absent, or at least different from fresh water column opal.

3.2 Methods

3.2.1 Experimental rationale & design

In their dissolution experiments, Demarest et al. (2009) found that the δ³⁰Si values of bSi and dSi show a constant offset of -0.55‰ (the isotope effect ε), meaning that dSi released by dissolution is isotopically lighter than bSi throughout the reaction. Such constant isotope offsets are characteristic of equilibrium reactions in closed or open systems (Figure 3.1a). If an ε-value of -0.55‰ is characteristic for the forward (dissolution) reaction, it should be reproducible under unidirectional conditions. At given thermodynamic boundary conditions for a unidirectional chemical reaction, the magnitude and sign of ε are characteristic for this particular reaction. In equilibrium reactions, both forward and backward reaction might be associated with an isotope effect ε_{for} and ε_{back}, creating a net isotope effect ε_{net}, the magnitude and sign of which depends on the relative forward and backward reaction rates. Since we are particularly interested in the isotope effect of the forward reaction (the dissolution reaction) only, our experiments are designed such that they drastically increase the forward reaction rate. For experimental simplicity we conduct dissolution in closed system containers, which might, however, create an environment that allows for reaction of bSi and dSi and with a tendency of forward and backward reactions to reach equilibrium after some time (saturation of the dissolution medium with dSi). Therefore, in addition to enhancing forward reaction rates, we interrupt dissolution at early stages, when the possible backward reaction rate is still negligible. Figure 3.1b illustrates the evolution of silicon isotope compositions of bSi and dSi during dissolution in a unidirectional system (Rayleigh-type fractionation). We calculate ε_{uni} based on the relationship:
CHAPTER 3 – SILICON ISOTOPE PARTITIONING DURING DISSOLUTION OF SEDIMENTARY DIATOM OPAL

\[ \varepsilon_{uni} = -f \times \frac{(\delta^{30}S_{\text{dSi}} - \delta^{30}S_{\text{bSi}})}{(1-f) \ln(1-f)} \]  

where \( f \) is the fraction dissolved, \( \delta^{30}S_{\text{bSi}} \) the bulk opal value, and \( \delta^{30}S_{\text{dSi}} \) the measured dSi isotope composition. If back-reactions are indeed occurring, \( \varepsilon_{bi} \) is simply derived by the difference in \( \delta^{30}S \) of bSi and dSi (Fig. 3.1a):

\[ \varepsilon_{bi} = \delta^{30}S_{\text{dSi}} - \delta^{30}S_{\text{bSi}} \]  

eq (3.3)

We limit our observations to within the first 10% of the dissolution progress, where the uncertainty on \( \varepsilon \) is small and the evolution of bSi and dSi \( \delta^{30}S \) values are very similar in bidirectional and unidirectional systems (Fig. 3.1).

**Figure 3.1:** Evolution of \( \delta^{30}S \) of reactant (bSi) and product (dSi) in the case of (a) bSi-dSi isotope exchange during dissolution and (b) unidirectional dissolution only. An initial \( \delta^{30}S \) of 1‰ and an isotopic effect due to dissolution of \( \varepsilon = -0.55\% \) are assumed. In (b) the isotopic effect \( \varepsilon \), which is characteristic and constant for the reaction, is only visible in the compositional difference of residual bSi and instantaneously formed dSi. Since the instantaneous product mixes with the accumulated product, a continuously increasing apparent isotope effect \( \varepsilon_{app} \) is expressed between residue and product. The following formula were used for calculation: (a) \( \delta^{30}S_{\text{bSi residual}} = \delta^{30}S_{\text{initial}} - \varepsilon_{bi} f; \) \( \delta^{30}S_{\text{dSi accumulated}} = \delta^{30}S_{\text{initial}} + \varepsilon_{bi} (1-f); \) (b) \( \delta^{30}S_{\text{bSi residual}} = \delta^{30}S_{\text{initial}} + \varepsilon_{uni} \ln(1-f); \) \( \delta^{30}S_{\text{dSi instantaneous}} = \delta^{30}S_{\text{bSi residual}} + \varepsilon_{uni}; \) \( \delta^{30}S_{\text{dSi accumulated}} = \delta^{30}S_{\text{initial}} - \varepsilon_{uni} \ln(1-f) (1-f) / f. \)
In order to understand the controls on silicon isotope partitioning during bSi dissolution, we vary several parameters that influence dissolution kinetics and introduce compositional variation (Table 3.1). To approach unidirectional conditions we use 5 mM NaOH (pH=11.7, semi-conductor grade) as the dissolution medium in every experiment, since from pH 9 to 10.7 the dissolution rate of amorphous silica has been shown to increase manifold (Iler, 1979). In addition, based on its strong impact on the reaction rate (Van Cappellen et al., 2002), the degree of undersaturation in our experiments is kept high by stopping the reaction after ~10% reaction progress. By varying the amount of opal dissolved (~0.5-2 mg) and medium volume (20-40 ml), the degree of undersaturation is altered. Temperatures are set to 20°C and 100°C, thereby varying the dissolution rate of opal substantially (Van Cappellen and Qiu, 1997a). Compositional controls on isotope partitioning are captured by using samples with variable grain sizes and sample ages. As shown by Egan et al. (2012), grain size can have a substantial impact on the bulk sample silicon isotope composition. While the grain size fraction 2-20 µm contains the most contamination-free diatom opal, grain size fractions >20 µm can contain substantial amounts of biogenic opal from other sources, e.g. radiolaria. Here we use samples having the grain size fractions <20 µm and 20-62 µm. As shown in Figure 3.2, the sample of grain size 20-62 µm (8044) contains a substantial amount of radiolarian opal, which is not detectable in the <20 µm samples. The 20-62 µm sample thus allows for an assessment of the influence on isotopic evolution during dissolution of multiple silicon sources in the sample. On the other hand, the two samples of grain size <20 µm have different specific surface areas and are of different age, so that any difference in the dissolution behaviour of samples 8036 and 8062 could give insights into sample-related factors that control silicon isotope fractionation during diatom dissolution. Sample aging involves the loss of reactive surface sites and incorporation of Al into the structure of bSi (Van Bennekom et al., 1991; Van Cappellen et al., 2002; Gehlen et al., 2002). Both specific surface area and sample age can substantially influence dissolution rates by a factor of 5 (Van Cappellen et al., 2002).

Figure 3.2: Secondary electron microscope images of cleaned biogenic opal samples from ODP core 1093. 8036 and 8062 have a grain size of <20 µm, whilst that of 8044 is 20-62 µm.
Table 3.1: Summary of the basic experimental parameters and their influence on diatom dissolution. Abbrev.: mcd=metres composite depth.

<table>
<thead>
<tr>
<th>Sample</th>
<th>8036</th>
<th>8044</th>
<th>8062</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mM NaOH</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>Increased reaction rate (with respect to seawater)</td>
</tr>
<tr>
<td>$m_{\text{opal}}$ [mg]</td>
<td>0.5, 2</td>
<td>2</td>
<td>2</td>
<td>Variable degrees of undersaturation</td>
</tr>
<tr>
<td>T [°C]</td>
<td>20, 100</td>
<td>20</td>
<td>20, 100</td>
<td>Variable reaction rates</td>
</tr>
<tr>
<td>grain size [μm]</td>
<td>&lt;20</td>
<td>20-62</td>
<td>&lt;20</td>
<td>Tracing sample heterogeneities</td>
</tr>
<tr>
<td>spec. surface area [m$^2$/g]</td>
<td>8.8</td>
<td>unknown</td>
<td>24.8</td>
<td>Variable reaction rates</td>
</tr>
<tr>
<td>core depth [mcd]</td>
<td>9.28</td>
<td>11.18</td>
<td>15.68</td>
<td>Tracing age-related sample properties</td>
</tr>
<tr>
<td>approx. age [ka]</td>
<td>14.7</td>
<td>26.8</td>
<td>53.9</td>
<td></td>
</tr>
</tbody>
</table>

3.2.2 Sample processing and mass spectrometric $\delta^{30}$Si analyses

We conducted dissolution experiments using down-core sediment opal from the opal belt in the Atlantic sector of the Southern Ocean (ODP Leg 177, Site 1093). The samples (courtesy of A. Shemesh) were prepared at the Weizmann Institute of Science, Rehovot, Israel, with the aim of removing organic coatings and tissues and of separating diatom opal from other opal and clays. The preparation procedure, introduced by Shemesh et al. (1988) and refined according to Shemesh et al. (1995) and Singer and Shemesh (1995), involves $\text{H}_2\text{O}_2$ and HCl treatment to remove organic tissues and carbonates respectively, heavy liquid separation to remove clastics and clays, sieving into grain size fractions <20 μm and 20-62 μm to remove radiolaria and concentrate diatoms, and chemical leaching using HNO$_3$ and HClO$_4$ to remove any natural or method-based surface alteration and contamination. During this process, and after the final step, samples were quality-controlled for the accuracy of the preparation method and purity, with smear slide light microscopy and scanning electron microscopy. Fig. 3.2 shows the composition of the grain size fractions <20 μm and 20-62 μm after preparation. While the <20 μm fraction consists of diatoms only (mainly shards of *F. kerguelensis*, *Thalassiothrix spp.*, and *Thalassiosira lentiginosa*), the 20-62 μm fraction contains less fragmented frustules and a substantial amount of radiolarian opal. Since it has been shown that the surface area of *F. kerguelensis* is larger in sediment of glacial age compared to interglacial (Cortese et al., 2012), we determined BET specific surface areas for samples 8036 and 8062 (Table 3.1). We used a magnetically levitated nano-scale balance, built at ETH Zurich, that is capable of resolving nanogram-level variations in mass following N$_2$ gas adsorption. The method is non-destructive and allows samples to be processed after BET measurements. The detailed functionality is described in Aciego et al. (2011).

The dissolution experiments follow the technique of Reynolds et al. (2008), in which the opal is digested in an alkaline solution (NaOH). This method aims at avoiding both use of hazardous HF
and the formation of the volatile SiF₄. In order to obtain an aqueous silicic acid solution for mass spectrometric analysis, sodium ions must be removed chromatographically with a cation exchange resin. While concentrations higher than 5 mM require more resin volume and therefore longer elution times, this concentration allows us to load the entire solution directly onto a small amount of resin bed (0.75 ml), substantially increasing sample throughput per unit time.

As dissolution vessels we used acid-cleaned 60 ml FEP bottles containing 20 or 40 ml of 5 mM NaOH. Each sample (8036, 8044, 8062) was split into fractions of 0.56-2.08 mg and added to the vessels, either at 20°C (room temperature) or at 100°C. The solution at 100°C was agitated using a thermal shaker (MHL 23, HLC BioTech). After 2, 4, and 8 minutes (100°C), or 390 and 2880 minutes (20°C), dissolution was terminated by filtering the solution through a PTFE filter (0.2 µm pore size). We chose to use new sample material for each time step in order to avoid undesired manipulation of the dissolution environment, acknowledging that this method might introduce biases due to sample heterogeneity. We collected dSi in a Teflon vial, while the remaining bSi filtrate was recovered from the filter by rinsing with Milli-Q Element water (>18.2 MΩ) into an acid-cleaned 60 ml FEP bottle. Subsequently, 5 mM NaOH was added to the bSi samples, which were then dissolved for at least 48 hours at 100°C. A split of each sample was furthermore dissolved for at least 48 hours in 5 mM NaOH at 100°C to obtain the bulk silicon isotope composition (‘100% dissolved’). After filtration and dissolution, the [Si] of all residual bSi and dSi solutions was determined photometrically, using the molybdate blue technique (Strickland and Parsons, 1968). Sample solutions were then directly loaded onto a cation exchange column (using AG50W-X8 resin, BioRad Laboratories) to separate the negatively charged Si species (mainly H₃SiO₄⁻) from the Na⁺ matrix. The sample volume loaded onto the resin was dependent on [Si] in the sample solutions and adjusted to obtain 4 ml of 600 ppb Si solutions. A detailed description of the chromatographic protocol is given by Georg et al. (2006).

The solutions were analysed for silicon isotope composition using a NuPlasma 1700 high-resolution multicollector inductively coupled plasma mass spectrometer (Nu Instruments, UK). We applied standard-sample bracketing, such that each δ³⁰Si value represents the average of 5 bracketed measurements of the sample (36 x 5 s integrations each). Analytical accuracy was monitored using two secondary standards, Diatomite and LMG08 (Hendry et al., 2011; Reynolds et al., 2007). The long-term external reproducibility for both Diatomite (n=88, 2.5 years) and LMG08 (n=11, 2 years) is ±0.14‰ (2SD) and best represents the reproducibility of our data. The average δ³⁰Si values measured for Diatomite and LMG08 are 1.27±0.02‰ (2SEM) and -3.39±0.04‰ (2SEM), respectively, consistent with the inter-laboratory comparisons of Reynolds et al. (2007) and Hendry et al. (2011). A detailed description of the analytical protocol can be found in Georg et al. (2006).
CHAPTER 3 – SILICON ISOTOPE PARTITIONING DURING DISSOLUTION OF SEDIMENTARY DIATOM OPAL

3.3. Results

3.3.1 Dissolution rates

Dissolution rates have been calculated by linear interpolation between a zero concentration at the start of the experiment and the silicon concentration at a given time. In closed systems dissolution rates typically decrease in a parabolic fashion, but since we did not exceed 12% of dissolution in any experiment we argue that the short time scale of interest can be approximated by linear interpolation. Dissolution rates of 0.9-2.3% bSi dissolved per minute have been achieved for the 100°C runs and 0.003-0.009% for the 20°C runs. The rates observed at 20°C are surprisingly similar to those of Demarest et al. (2009), considering the roughly 3.5 units higher pH in our experiments.

3.3.2 Silicon isotope partitioning

With one exception, \( \delta^{30}\text{Si} \) values of dSi are higher throughout the experiment than \( \delta^{30}\text{Si} \) of the residual bSi, resulting in positive \( \epsilon \) values (Table 3.2, Figure 3.3). This observation is at odds with an \( \epsilon \) value of -0.55±0.05‰ (SD), with dSi being lighter, estimated by Demarest et al. (2009). As listed in Table 3.2, the estimated \( \epsilon_{uni} \) (the isotope effect assuming Rayleigh fractionation) and \( \epsilon_{bi} \) (the isotope effect assuming equilibrium isotope fractionation) values span very similar ranges, from 0.04‰ to 0.83‰ for \( \epsilon_{uni} \), and from 0.00‰ to 0.91‰ for \( \epsilon_{bi} \). Based on their propagated uncertainties, which are between 0.06‰ and 0.18‰ (SD), \( \epsilon_{uni} \) and \( \epsilon_{bi} \) are indistinguishable from each other for a specific sample (data not shown).

Taken at face value, \( \epsilon_{uni} \) and \( \epsilon_{bi} \) are variable across multiple experiments on the same sample. For example, \( \epsilon_{bi} \) for sample 8062 varies from 0.00‰ to 0.27‰. However, both values have propagated uncertainties of 0.15‰ (SD), again questioning the statistical significance of this variability. In the following, we address the effects of sample amount, temperature, specific surface area, and age separately.
Figure 3.3: Silicon isotope compositions of dissolved (white) and biogenic (black) phases. A-C are shown on equal scales to visualise inter-specific isotope effects, while D and E are scaled to illustrate the detailed intra-specific differences in dSi and bSi. All data point error bars are external (0.14‰). Black lines represent the bulk sample isotope compositions, with the grey area marking the mean uncertainty as given by two standard errors of the (Table 3.1).
Table 3.2: Silicon isotope compositions of dissolved product and remaining biogenic silica. Note that [Si] at t=0 is 0. Fraction dissolved (f) was calculated based on volume of the dissolution medium (20 or 40 ml), its silicon concentration, and the assumption that diatom opal has SiO₂ stoichiometry. The long-term external reproducibility of samples is 0.14‰ (2σSD). The isotope effect ε is given for the case of Rayleigh-type isotope fractionation (unidirectional; eq. 3.2) and equilibrium isotope fractionation (bidirectional; eq. 3.3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size [μm]</th>
<th>T [°C]</th>
<th>t [min]</th>
<th>m opal [mg]</th>
<th>[Si]f [μM]</th>
<th>f</th>
<th>δ³⁰Si[dSi] STD [%‰]</th>
<th>δ³⁰Si[bSi] STD [%‰]</th>
<th>ε uni [%‰]</th>
<th>ε bi [%‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8036</td>
<td>&lt;20</td>
<td>100</td>
<td>4</td>
<td>0.56</td>
<td>20.9</td>
<td>0.04</td>
<td>1.89</td>
<td>0.04</td>
<td>1.69</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>100</td>
<td>8</td>
<td>0.66</td>
<td>38.5</td>
<td>0.07</td>
<td>1.86</td>
<td>0.05</td>
<td>1.70</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>100</td>
<td>2</td>
<td>2.02</td>
<td>55.9</td>
<td>0.03</td>
<td>1.86</td>
<td>0.06</td>
<td>1.70</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>100</td>
<td>4</td>
<td>2.06</td>
<td>64.1</td>
<td>0.04</td>
<td>1.82</td>
<td>0.03</td>
<td>1.73</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>20</td>
<td>390</td>
<td>1.89</td>
<td>32.8</td>
<td>0.02</td>
<td>1.79</td>
<td>0.06</td>
<td>1.71</td>
<td>0.13</td>
</tr>
<tr>
<td>weighted mean (with 1SEM errors)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.84</td>
<td>0.02</td>
<td>1.70</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.65 ± 0.05 (2SEM), n=7</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8044</td>
<td>20-63</td>
<td>20</td>
<td>390</td>
<td>2.08</td>
<td>18.2</td>
<td>0.01</td>
<td>1.63</td>
<td>0.09</td>
<td>0.72</td>
<td>0.14</td>
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<tr>
<td></td>
<td>20-63</td>
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<td>2.00</td>
<td>38.3</td>
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<td>1.48</td>
<td>0.08</td>
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<td>0.09</td>
</tr>
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<td>weighted mean (with 1SEM errors)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.55</td>
<td>0.06</td>
<td>0.84</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
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<td>0.81 ± 0.05 (2SEM), n=3</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>8062</td>
<td>&lt;20</td>
<td>100</td>
<td>2</td>
<td>1.87</td>
<td>70.6</td>
<td>0.05</td>
<td>1.58</td>
<td>0.08</td>
<td>1.56</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
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<td>4</td>
<td>1.95</td>
<td>115.8</td>
<td>0.07</td>
<td>1.64</td>
<td>0.13</td>
<td>1.64</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>20</td>
<td>390</td>
<td>1.95</td>
<td>59.1</td>
<td>0.04</td>
<td>1.62</td>
<td>0.10</td>
<td>1.60</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>&lt;20</td>
<td>20</td>
<td>2880</td>
<td>1.93</td>
<td>94.4</td>
<td>0.12</td>
<td>1.74</td>
<td>0.11</td>
<td>1.47</td>
<td>0.10</td>
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<tr>
<td>weighted mean (with 1SEM errors)</td>
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<td></td>
<td></td>
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<td>1.63</td>
<td>0.05</td>
<td>1.58</td>
<td>0.04</td>
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<tr>
<td></td>
<td>1</td>
<td>1.54 ± 0.10 (2SEM), n=5</td>
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</tr>
</tbody>
</table>
Effect of sample amount and temperature
Sample 8036 is of grain size <20 µm and most representative of diatom opal (Egan et al., 2012). It was dissolved using variable temperature and sample amounts. All dSi samples are systematically heavier in their isotopic composition by 0.08-0.21‰ (0.14‰ on average) than their corresponding bSi residues, but indistinguishable from each other within error (Fig. 3.3a, d). Accordingly, neither temperature nor sample amount had an analytically resolvable impact on the isotope compositions of dSi and bSi. Though, given the analytical uncertainties, dSi samples partly overlap with those of bSi and the bulk mean (Fig. 3.3d), the offset appears systematic and reproducible. The weighted means of dSi and bSi yield values of 1.84±0.04‰ (2SEM) and 1.70±0.05‰ (2SEM), respectively, suggesting a statistically significant difference between the two populations. A Student’s t-test (two-sided, equal variances) reveals that dSi and bSi are significantly different at the 95% confidence level.

Furthermore, all bSi data are systematically heavier, by up to 0.08‰, compared to the mean bulk sample value, resulting in consistently larger calculated \( \epsilon_{\text{uni}} \) over \( \epsilon_{\text{bi}} \) values, since \( \epsilon_{\text{uni}} \) values depend on the bulk sample \( \delta^{30}\text{Si} \). As individual data have been reproduced across measurement sessions and the observed offset is absent in the other two data sets, we can rule out a systematic methodological or analytical bias. A potential explanation could be that bSi fractions were not completely dissolved after termination of the experiment. Consequently, the bSi data would in fact represent the 80-90% accumulated dissolved fraction in Fig. 3.3a/d. However, this does not affect the main observation that the observed apparent isotope effect is of opposite sign from that previously observed (Demarest et al., 2009). Since dSi data are not affected by this bias, the only consequence would be that the average difference of dSi and bSi is not ~0.14‰, but rather ~0.2‰.

Effect of opal grain size
Sample 8044 contains diatom and radiolarian opal of the grain size 20-62 µm (Fig. 3.2). Dissolution of this sample results in the largest difference between \( \delta^{30}\text{Si} \) values of dSi and residual bSi in our experiments, with values for \( \epsilon_{\text{bi}} \) ranging up to 0.91‰. As can be seen from Figure 3.2, sample 8044 contains radiolarian and diatom opal that strongly differ in their geometries and might form enriched aggregates in the sample. Since they may differ significantly in their silicon isotope composition, small sub-sampling biases can potentially result in large bulk isotope composition differences (Egan et al., 2012). If the observed positive \( \delta^{30}\text{Si} \) offset of dSi were related to isotope fractionation alone, both dSi and bSi would be expected to become isotopically lighter with advancing dissolution. However, the bSi sample at 5% dissolution is 0.17‰ heavier than the bSi sample at 1%, implying that the two sample splits did not have the same bulk isotope composition (see discussion in section 4).

Effect of specific surface area and sample age
As shown in Table 3.1, the specific BET surface area of sample 8062 is significantly higher than
that of sample 8036, which resulted in the highest observed dissolution rate of 2.3% per minute. Both samples contain highly enriched diatom opal but with slightly different species composition. Additionally, sample 8062 is roughly 40 ka older and originates from greater core depths. Figures 3.3c and 3.3e show that all bSi and dSi data for sample 8062 are analytically indistinguishable from each other and the bulk mean. Weighted means of dSi and bSi are 1.63±0.10‰ (2SD) and 1.58±0.08‰ (2SD), respectively, and therefore statistically indistinguishable; a Student’s t-test (two-sided, equal variances) yields no significant difference at the 95% confidence level. The data pair at 12% dissolution progress seems to be at odds with the previous data. Though isotope discrimination against the lighter isotopes would result in residual bSi becoming isotopically lighter, the corresponding dSi value should do so as well. We observed a similar discrepancy for sample 8044, which is characterised by strong compositional heterogeneity.

3.4 Discussion

The two major observations described in section 3 are that (1) we observe $\epsilon$ values for dissolution different from those observed by Demarest et al. (2009) and (2) the three samples subjected to dissolution do not share a common $\epsilon$ value. The sample-specific variability of $\epsilon$ values is within analytical uncertainty, but given that every dSi-bSi data pair represents a new sample split, sample heterogeneities need to be considered. Sample 8044 is obviously compositionally heterogeneous (Fig. 3.2), containing radiolarian and diatom opal. In this sample, we observe large and variable $\epsilon$ values of 0.91‰ and 0.59‰ (Table 3.2).

In the following, we argue that these observed isotope effects could be related to mixing of individual silicon reservoirs (in essence diatoms and radiolaria), with distinctly different isotope compositions and that undergo differential dissolution, without the need for isotope fractionation during dissolution. We suggest that this compositional bias dominates the isotope compositions of dSi and bSi during dissolution, potentially camouflaging any thermodynamic or kinetic isotope fractionation. Acknowledging that we cannot completely rule out isotope fractionation, we conclude by discussing its potential existence in conjunction with the experimental setup (dissolution medium) and opal properties (age, reactivity).

3.4.1 The influence of sample heterogeneities on the apparent isotope fractionation

The largest apparent isotope fractionation was observed during dissolution of sample 8044. As shown in Fig. 3.2, this sample contains a considerable abundance of radiolarian opal of unknown silicon isotope composition. If radiolarian and diatom opal have different solubilities and isotope compositions, the difference in dSi and bSi $\delta^{30}$Si can easily be explained by binary mixing of silicon
derived from these two sources. Unfortunately, for sample 8044 the grain size fraction <20 µm is not available, and the limited amount of material for the 20-62 µm fraction prevents us from testing this hypothesis by isolating the two potential end-members for δ30Si analysis. Hurd (1973) and Hurd and Theyer (1975) observed very similar solubilities for acid-cleaned radiolaria and diatoms, suggesting that the differences are minor and challenging to resolve experimentally. In cases of very similar solubilities, the respective surface areas might control the relative dissolution rates of radiolarian versus diatom opal and the resultant release of silicon. Though the solubilities and silicon isotope compositions of the end-members are unknown, we argue in the following that reservoir mixing is the best explanation for the observed silicon isotope partitioning between dSi and bSi.

To date, silicon isotope data for radiolaria are scarce and partly derived from radiolarian-rich siliceous rocks from the Palaeozoic and Mesozoic (Ding et al., 1996; Wu et al., 1997), ranging from -0.6‰ to 1.2‰. Egan et al. (2012) measured radiolaria-bearing sediments from the Antarctic Peninsula as well as the Pacific and Atlantic sectors of the Southern Ocean, and documented values as low as -1.84‰. Unpublished in-house results for radiolarian opal of grain sizes 63-80 µm and >125 µm from the Atlantic sector of the Southern Ocean (kindly provided by Andrea Abelmann, Alfred-Wegener Institute, Bremerhaven) yield δ30Si values between -2.12‰ and +0.68‰. Though the data are scarce, a wide spatial and temporal range is covered in the available data. According to this evidence, radiolarian opal appears to be on average isotopically lighter than diatom opal. This makes intuitive sense, since radiolaria are not directly dependent on sunlight, and are hence able to dwell deeper within the water column (Takahashi, 1991). Thus, as for sponges (De La Rocha, 2003; Hendry and Robinson, 2012), an isotopically lighter dSi pool from below the euphotic zone, inaccessible to diatoms, is available for radiolarian biosilification. If we consider sample 8044, a binary mixture consisting of radiolaria and diatoms, for an illustrative mass-balance calculation, using a diatom and bulk sample δ30Si of 1.55‰ and 0.81‰ (as for sample 8044), respectively, and a radiolaria abundance of 25% (Table 3.2, Figure 3.2), the required δ30Si of radiolaria is -1.4‰. This value falls well within the aforementioned range of observed radiolarian δ30Si values.

An additional argument for the importance of mixing of different silicon isotope pools comes from the paleoceanographic and stratigraphic context of the different samples. Figure 3.4 shows the dSi and bSi data for 8044 against depth in the sediment core (in metres of composite depth). Also shown are two samples (8043, 8047) of <20 µm grain size that consist of highly enriched diatom opal. Both data points fit well within the observed range of South Atlantic diatom δ30Si (Brzezinski et al., 2002; Cavagna et al., 2011; Horn et al., 2011; Fripiat et al., 2012; Egan et al., 2012). Previously published down-core diatom δ30Si records from the same region reveal an average difference of about 0.8‰ (Brzezinski et al., 2002; Horn et al., 2011) between the environmental extremes of full glacial conditions and full interglacial conditions. If 8044’s bulk δ30Si of 0.81‰ is not biased by light radiolarian opal, the offset to stratigraphically neighbouring samples 8043 and 8047 is about 0.7‰. Such a strong negative excursion is hard to reconcile with what we know of glacial nutrient dynamics during this time (Brzezinski et al., 2002; Crosta and Shemesh, 2002; Robinson and Sigman, 2008; Anderson et al., 2009; Horn et al., 2011).
Figure 3.4: Silicon isotope composition of dSi and bSi of sample 8044 (20-62 µm) against sediment core depth (in metres composite depth). Dark grey area indicates typical radiolaria isotope compositions, whereas the light grey area represents typical diatom isotope compositions. The two stars represent additional sediment core opal samples of grain size fraction <20 µm (data not shown in Table 3.2), which are considered as contamination-free diatom isotope fingerprints. In the text we argue that 8044 dSi represents a diatom-rich binary mixture with radiolaria of unknown isotope composition. Only later dissolution of isotopically lighter radiolarian opal decreases the dSi $\delta^{30}$Si towards the bulk sample’s $\delta^{30}$Si of 0.81‰.

In summary, there is evidence based on microscopic observations, literature data, and mass balance considerations that radiolarian opal-derived silicon interferes with the silicon isotope signal of dissolving diatoms. Whether this process is able to mimic the isotope evolution of dissolution experiments with isotope fractionation will be illustrated with a simple model in the next section.

### 3.4.2 Apparent isotope effects through mixing

Can dissolution of two isotopically different reservoirs and subsequent mixing create apparent isotope effects that mimic the effects created by isotope fractionation as illustrated in Figure 3.1? Such mixing effects would be dependent on the solubilities of the two particulate silicon pools, which we do not know. Therefore, a simple model should be used here to consider two different cases:

1. Dissolution of a 9:1 diatom: radiolaria mixture with higher diatom solubility,
(2) dissolution of a 9:1 diatom: radiolaria mixture with higher radiolaria solubility.

Starting with a given amount of opal, in case 1 we dissolve 3% of diatom opal per time step and only 1% of radiolarian opal. In case 2 the solubilities are exactly opposite. The result is that in case 1 the diatom: radiolaria ratio decreases during dissolution, while it increases in case 2. At each time step we can calculate the accumulated and residual fractions of diatom and radiolarian opal, since we know the molar $\text{Si}_{\text{diatom}}:\text{Si}_{\text{radiolaria}}$. By simple mass balance we obtain the $\delta^{30}\text{Si}$ value of the bulk solution and residual opal for each time step, assuming $\delta^{30}\text{Si}$ values for diatoms and radiolaria of 1.6‰ and -1.4‰ (bulk sample at diatom: radiolaria=9:1 is 1.3‰), respectively. Additionally, we calculate the apparent isotope effects for each time step based on eq. (3.3).

Figure 3.5: Evolution of residual and product $\delta^{30}\text{Si}$ (a, c) and the apparent isotope effect (b, d) during dissolution of a sample with a diatom: radiolaria mixture of 9:1 (molar) for two model scenarios: (a, b) Case 1, where diatoms are more soluble than radiolaria, and (c, d) Case 2, where radiolaria are more soluble than diatoms. In both cases diatom and radiolaria $\delta^{30}\text{Si}$ are set to +1.6‰ and -1.4‰, respectively. The samples’ bulk value is 1.3‰. Note the similarity to the evolution of isotope compositions in the case of true isotope fractionation in Figure 3.1.

In Figure 3.5 we illustrate the model results as the evolution of $\delta^{30}\text{Si}$ in the solution and the residual undissolved fraction with time (as fraction dissolved). In case 1 (Fig. 3.5a), the solution
starts out with an isotopic composition similar to the diatom isotope signal of 1.6‰, while the residual opal is still close to the sample’s bulk composition of 1.3‰. This is because diatoms were set to dissolve more readily and consequently control the isotopic composition of the solution. With time the opal’s diatom:radiolaria ratio decreases, as reflected by the constantly decreasing isotope composition of the residual opal. Towards the end of dissolution the remaining opal is very light due to a very low diatom:radiolaria ratio, which is visible in a marked final decrease in the isotope composition of the accumulated solution, ending up at 1.3‰ when dissolution is complete. Figure 3.5b shows how the apparent isotope fractionation evolves throughout dissolution in case 1. It is striking that the isotopic compositions of solution and residual opal in case 1 follow a similar trend as in a unidirectional isotope fractionation model as shown in Figure 3.1b. We can conclude that differential dissolution as in case 1 can create a pseudo-isotope fractionation signal that is very similar to a unidirectional reaction with isotope fractionation.

Figure 3.5c shows the model results for case 2. The higher solubility of radiolarian opal results in a low $\delta^{30}$Si at the start. With time, the diatom:radiolaria ratio increases, leading to an increase in $\delta^{30}$Si of both the accumulating dSi and the residual opal. After ~90% dissolution, no radiolaria remain and only diatoms dissolve, resulting in a constant residual opal $\delta^{30}$Si but an accumulating solution with a $\delta^{30}$Si value that continues to increase until it reaches the bulk sample $\delta^{30}$Si of 1.3‰ at 100% dissolution. In this model case, the influence of radiolarian opal is obvious from the beginning, but due its low abundance of 10% the solution evolves rather steadily in $\delta^{30}$Si. The evolution of isotope compositions of residual opal and product in this case is surprisingly similar to a reaction with isotope exchange, as shown in Figure 3.1a. As Figure 3.5d illustrates, the apparent isotope effect changes only slightly, from -0.45‰ to -0.3‰, which is hard to resolve analytically given a reproducibility of 0.14‰. We can therefore conclude that differential dissolution of isotopically distinct silicon sources, as in model case 2, can create a pseudo-isotope fractionation signal that is very similar to a bidirectional reaction with isotope fractionation.

These two simple models clearly demonstrate that sample heterogeneities can create isotope effects during dissolution that are very similar to the effects created by isotope fractionation. Demarest et al. (2009) stated that their samples contained no radiolarian opal and only minor amounts of silicoflagellates, which casts doubts on the suggestion that sample heterogeneities were causing the effects observed by Demarest et al. (2009). However, the model clearly illustrates that time series experiments are sensitive to the sample composition and could be biased by isotope effects other than isotope fractionation. For sample 8044, we consider dissolution and subsequent mixing of distinctly different silicon isotope reservoirs as the most likely explanation, since we have a good idea about the sample composition. The sensitivity of our results to sample impurities is striking and suggests that the sample composition must be well-known for such silicon isotope studies (Egan et al., 2012).
3.4.3 The potential for silicon isotope fractionation during dissolution

As demonstrated above, mixing of silicon from different sources is the most likely explanation of the isotope effects observed for sample 8044. What requires discussion, however, is, whether the isotope effects observed for our two pure diatom samples or the samples of Demarest et al. (2009) were affected by isotope effects due to sample heterogeneities. If not, then other experimental parameters, which are discussed below, must be considered as the sources of the different isotope partitioning behaviour observed here and by Demarest et al. (2009).

The two major differences in the experimental setups of Demarest et al. (2009) and this study are the dissolution medium and the type of biogenic silica used. Rate and mechanism of dissolution is ultimately linked to the surface properties of the dissolving phase. The silica surface consists of siloxane (−Si–O–Si−) bonds with variable amounts of silanol groups (−Si–OH) attached to it (Iler, 1979). With increasing pH, silanol groups become ionised. This negative surface charge gives rise to the basic properties of silica. Demarest et al. (2009) used natural seawater (pH around 8.2) and temperatures of 3, 15, and 20°C. Since from pH 9 to 10.7 the solubility of amorphous silica has been shown to increase 6-7 fold (Iler, 1979), our experimental setup using 5 mM NaOH (pH=11.7) and temperatures of 20 and 100°C should constitute a significantly more corrosive environment. This is mainly due to water being a much weaker nucleophile compared to hydroxyl ions. On the other hand, the presence of alkali salts has been shown to enhance diatom opal and quartz dissolution rates significantly (e.g. van Lier et al., 1960; Dove and Crerar, 1990; Barker et al., 1994; Dove, 1999). Loucaides et al. (2008) found bSi dissolution rates in seawater to be on average 5 times higher than in freshwater. Dove (1999) addresses the dependence of dissolution rates on the solute composition and suggests that the frequency of nucleophilic attacks is increased due to the local formation of hydroxyl ions and that the presence of hydrated cations may improve the accessibility of nucleophiles at the water-silica interface. If the breakage of siloxane bonds is the rate-limiting step and associated with silicon isotope fractionation, and salts have a catalytic effect on the activation energy to break the bonds, then silicon isotope fractionation could be sensitive to the composition of the dissolution medium.

Such matrix effects also have a large influence on back-reactions. At pH values of 8.2, silicic acid is entirely present as H₄SiO₄. At pH values of 11.7, however, silicic acid occurs mainly as H₂SiO₄⁻. Consequently, in our experiments the main product is electrostatically repelled from the negatively charged silanol groups. Taking the high degrees of undersaturation in our experiments into account, this drastically reduces the likelihood of an adsorption back-reaction compared to Demarest et al. (2009). On the other hand, adsorption of silicic acid has been observed to occur even in strongly alkaline media (Holt and King, 1955; Weres et al., 1981; Thornton and Radke, 1988). Stöber (1967) pointed out the influence of silicic acid adsorption during dissolution on the overall solubility of silica. Thornton and Radke (1988), and Weres et al. (1981) suggest that adsorbed silica is an integral intermediate part of dissolution/condensation reactions. To our knowledge, no study has examined silicon isotope fractionation during adsorption of silicic acid onto bSi. Ziegler et al. (2005) observed preferential sorption of isotopically light dissolved silicon
onto particles in soil. Similarly, Delstanche et al. (2009) and Opfergelt et al. (2009) report isotopically light silicic acid adsorption onto iron oxides, and enrichment of heavy silicon in the dissolved phase. These examples may not be readily comparable to sorption onto diatom surfaces, but they point towards a systematic kinetic effect of light isotopes being preferentially adsorbed. The overall influence of adsorption during dissolution on isotope partitioning, however, seems to be an integral part of the reaction and should be investigated.

The second major difference between our study and that of Demarest et al. (2009) is the sample’s species composition and age. Demarest et al. (2009) used fresh opal samples, while we used sedimentary diatoms from up ~16 m depth, corresponding to ages between 15 and 54 ka. In natural environments, both types of diatom opal differ substantially in their properties. Van Cappellen and Qiu (1997b) describe a substantial loss of reactivity of opal with age and depth in sediment. Their explanation is a decrease in surface reactive sites on the opal surface due to increasing occupation of these sites by contaminants and authigenic minerals. Aluminium has been shown to substantially impact opal solubility through sorption and (re-)precipitation of secondary aluminosilicates (Van Bennekom et al., 1991; Van Cappellen et al., 2002; Gehlen et al., 2002). In their literature data compilation, Van Cappellen et al. (2002) show that the specific dissolution rates of core-top siliceous sediments can be up to three orders of magnitude lower than fresh surface ocean diatoms. This observation suggests that the aluminium penetrates deeply into the opal structure, and that even strong chemical leaching in the course of sample preparation does not remove all contaminants. During dissolution, the Al$^{3+}$ might act as an adsorbant onto the strongly negatively charged opal surface (Iler, 1979), reducing the density of surface reactive sites suitable for nucleophilic attacks, but also with potential influences on the molecular sterics. If the breaking of siloxane bonds is the rate-limiting step during dissolution, therefore controlling silicon isotope fractionation, opal surface properties might influence the likelihood of nucleophilic attacks.

Lastly, our samples are from the Atlantic sector of the Southern Ocean and dominated by the diatoms *F. kerguelensis*, and *Thalassiothrix spp.*, and *Thalassiosira lentiginosa*). Samples from Demarest et al. (2009) are from the Pacific sector of the Southern Ocean and dominated by *Chaetoceros*. As recently shown by Sutton et al. (2013), silicon isotope fractionation during biosilicification is species-dependent. However, this dependency is likely due to the fact that diatom silicon uptake involves vital processes, whilst opal dissolution is unlikely to be affected by species-specific isotope fractionation. Dissolution rates, on the other hand, might be affected significantly by species-related differences in surface areas and their respective age-dependent reactivity (Van Cappellen et al., 2002 and references therein). Consequently, in corrosive environments, the forward reaction might gain or lose significance, impacting the net isotope effect. At low dissolution rates and pH values close to 8, reprecipitation or sorption could influence the magnitude and sign of silicon isotope fractionation. Samples 8036 and 8062 have different species compositions and specific-surface areas, such that we cannot rule out the possibility that those sample properties are responsible for the different dissolution results of these samples.
3.5 Conclusions

The main finding of this study is the strong influence of non-diatom biogenic silica with different silicon isotope compositions on silicon isotope partitioning during dissolution of diatom-rich opal samples. Conversely, the results from our diatom-only samples indicate that the dissolution of biogenic opal from marine sediments does not fractionate silicon isotope strongly, if at all. Using a simple model, we show that differential dissolution of isotopically distinct silicon sources can create apparent isotope effects that can be mistaken for isotope fractionation. In particular, time series experiments, such as the dissolution experiments presented here, are sensitive to sample heterogeneities. This finding stresses the importance of a robust sample preparation and cleaning procedure. Overall, our findings reinforce the suggestion of Demarest et al. (2009) that the observed dissolution effects are unlikely to change the original diatom silicon isotope fingerprint important for paleoceanographic studies.

The fact that different isotope effects during dissolution of diatom opal were observed here and by Demarest et al. (2009) may suggest that silicon isotope fractionation is sensitive to the experimental boundary conditions. Factors that might give rise to differential silicon isotope fractionation during dissolution might be sample age and the type of dissolution medium used. Isotope fractionation associated with adsorption, even during dissolution, might have an impact on the overall isotope effect of the dissolution reaction as long as it is not completed. Since back-reactions like adsorption are expected to occur in nature, we recommend future work on silicon isotope partitioning during sorption between biogenic silica and dissolved silicic acid.
References


Shemesh A., Burckle L. H. and Hays J. D. (1995) Late Pleistocene oxygen isotope records of


Chapter 4 – Silicon isotope exchange of diatom opal with the environment

Abstract

The isotopic fingerprint of diatoms that was acquired in the surface ocean, might be compromised by processes in the sedimentary environment. Increasing pressure and temperature during diagenesis ultimately determine the fate of the opal, transforming it from the amorphous phase opal-A via microcrystalline opal-CT to chert. This phase transformation sequence naturally limits the applicability of silicon isotopes in diatom opal as a nutrient utilisation proxy. No constraints, however, exist on the thermodynamic stability of the silicon isotope signal in diatom opal. Previous studies have focused on silicon exchange at magmatic temperatures, since diffusion rates are much faster and easier to measure experimentally. The thermodynamic conditions at which the silicon isotope signals of diatom, radiolarian, and sponge opal, authigenic silicate minerals, as well as circulating pore water fluids equilibrate are very diverse. If there is silicon isotopic disequilibrium between these, it could give rise to silicon isotope exchange when they are in contact with each other. The driving question of this thesis chapter is to assess the time scales at which silicon isotope re-equilibration occurs, in order to constrain the integrity of the diatom silicon isotope tracer as a function of sediment core depth, age, and composition. In addition, an analytical protocol has been established that allows the accurate and precise measurements of samples spiked with one silicon isotope.

The experimental setup consists of two solutions of seawater composition that are spiked with different proportions of the isotope $^{29}$Si. These solutions were designed to have total silicon concentrations of 161 and 800 µM, representative of a deep bottom water and a sedimentary pore fluid with silica saturation. Diatom opal has a natural silicon isotope composition, such that isotopic disequilibrium with the solution is established after addition to the solutions. The reactors were exposed to temperatures of 22°C and 5°C and sampled at different times up to 482 days, in order to trace silicon isotope exchange between solution and opal with time.
The analytical protocol developed in this study to measure spiked silicon solutions is shown to yield accurate and precise data that can be quickly acquired. The external reproducibility was found to be 0.18‰ and 0.15‰ (2SD) for δ^{30}Si and δ^{29}Si, respectively, which is comparable to the precision obtained for natural silicon isotope compositions in real environmental samples.

Under the experimental conditions silicon isotope exchange could not be confidently detected, as other processes dominated and camouflaged the potential exchange signal. Primarily, the silicon isotope composition of the solutions after the experiment can be explained by opal dissolution. An experimental limitation is that the silicon isotope composition of the opal can not be measured, as the opal surface strongly adsorbed silicic acid from the solution. The two silicon pools could not be separated without compromising the silicon isotope composition of the opal itself. As the amount and silicon isotope composition of the adsorbed silicon is unknown, the degree of diatom dissolution represents a minimum estimate, such that the mass balance of the system is not accurately enough determined to distinguish between isotope exchange and opal dissolution. This uncertainty is further enhanced by the measurement uncertainty of silicon concentrations, the precision of which is crucial in confidently constraining the influence of opal dissolution so that it can be distinguished from silicon isotope exchange.

The information that the results of the experiment provided, however, will help in designing a similar experimental setup that should be sensitive enough to measure silicon isotope exchange rates. Additionally, the strong tendency of silicic acid to adsorb onto opal may constitute an important process in natural environments, such as rivers, that has not yet been adequately characterised. Similar affinities likely exist for quartz and other silicate minerals, and may exert a significant influence on riverine silicon isotope compositions and budgets.
4.1 Rationale & expectations

It has been observed that marked steps in oxygen isotopic composition can be related to the phase transformations of opal-A to opal-CT to chert (Kolodny and Epstein, 1976; Murata et al., 1977). For silicon, systematic studies have not yet been done, even though cherts have recently been of increasing interest (Robert and Chaussidon, 2006; Marin-Carbonne et al., 2011; Chakrabarti et al., 2012). Temperatures at which the phase transformation from opal-A to opal-CT occurs are usually reported to be between 18 and 56°C, but temperatures as low as 0-4°C have been observed (Botz and Bohrmann, 1991, and references therein). Depending on the geothermal gradient, this temperature range corresponds to depths of roughly 0-1 km. Since the transformation of opal-A to opal-CT involves dissolution-reprecipitation processes (Williams and Crerar, 1985), diatom opal can be expected to lose its original silicon isotope fingerprint somewhere within 1 km depth, corresponding to several million years of sediment age in the Southern Ocean opal belt. Since dissolution and re-precipitation depend on the solubilities of the sediment components and their proportions in the sediment, as well as temperature, large spatial and consequently temporal uncertainty exists about the threshold integrity of diatom δ30Si and δ29Si.

In the upper few cm’s of the sediment dissolution of opal leads to an asymptotic build-up of H4SiO4 concentrations in the pore fluid until saturation is reached (Schink et al., 1975; McManus et al., 1995; Ragueneau et al., 2001). A dynamic equilibrium is established between dissolving opal and precipitation of less soluble phases such as aluminosilicates (Dixit et al., 2001). While the formation of secondary minerals is associated with silicon isotope fractionation (Ziegler et al., 2005; Basile-Doelsch, 2006, and references therein), opal, fluid, and secondary mineral are expected to be in isotopic equilibrium at the given thermodynamic boundary conditions. Though all of the phases might have different isotope compositions (see Figure 1.3), they are in thermodynamic equilibrium and no isotope exchange is expected. With subsequent burial of the opal, these conditions change as pressure and temperature increase. Newly formed secondary phases are expected to be in isotopic equilibrium with the fluid, but not necessarily with diatom opal. Pore waters may also percolate through the sediment such that opal and pore water develop isotopic disequilibrium.

Based on published diffusion coefficients for silicon, a rough estimate can be made of the time scales of silicon isotope exchange. Solid-state diffusion coefficients of silicon in forsterite, quartz, and amorphous silica have been shown to be in the order of 10^-8-10^-14 m²/ka at temperatures between 800 and 1530°C and pressures of 3 GPa to ambient (Giletti et al., 1976; Brebec et al., 1980; Fei et al., 2012). These experimental data cannot easily be extrapolated to <50°C. However, considering that diffusion is a strongly temperature-sensitive process, solid-state silicon diffusion within a 1 km thick sediment layer of siliceous ooze can be neglected. In the presence of fluids silicon transport can, however, be significantly enhanced. Diffusion coefficients for molecular diffusion of silicic acid between the sediment-seawater interface are in the order of 3-16 m²/ka (Fanning and Pilson, 1974; Rutgers van der Loeff and Van Bennekom, 1989; Wollast and Garrels...
1971). From their experiments Watson and Wark (1997) estimated that the diffusive transport of aqueous silicon in the crust can exceed 500 m in 1 Ma at temperatures >500°C.

In summary, the experimental data illustrate that diffusion of silicon in the upper 1000 m of sediment, at temperatures of about 50°C, is sluggish and likely has limited influence on the diatom opal $\delta^{30/29}$Si. However, experimental data are scarce and often limited to high-temperature systems, and cannot simply be extrapolated to low-temperature systems. For the first time, this work aims at measuring silicon isotope exchange rates between seawater and diatom opal at temperatures between 5 and 22°C. The exchange rates measured at different temperatures should provide a basis for estimating depth and temperature ranges beyond which the silicon isotope fingerprint of diatoms is disturbed by exchange with the environment.

4.2 Methods

4.2.1 Theoretical background

In order to evaluate silicon isotope exchange, a three-isotope method is employed (e.g. Li et al., 2011). By exposing diatoms to a $^{29}$Si-spiked solution it is expected that, in response to isotopic disequilibrium, $^{28}$Si diffuses into the opal. Fig. 4.1 schematically illustrates the process in a triple isotope diagram. With no isotope fractionation occurring during silicon isotope exchange, both opal and solution will compositionally evolve along a mixing line towards 100% exchange. If isotope fractionation occurs, the isotope compositions of opal and solution evolve towards a secondary fractionation line that parallels the terrestrial fractionation line and intersects the system’s average composition. The degree of isotope fractionation can then be inferred from the difference in $\delta^{30}$Si and $\delta^{28}$Si between opal and solution.

At a given time, the degree of isotope exchange can be inferred according to:

$$F = \frac{(\delta_t - \delta_i)}{(\delta_e - \delta_i)}$$  \hspace{1cm} eq. (4.1)

here $\delta_i$ is the isotope composition at time t, $\delta_i$ the initial isotope composition, and $\delta_e$ the isotope composition at equilibrium (Graham, 1981; Criss et al., 1987). The degree of isotope exchange, F, can then be used to calculate the rate constant $k$ of the reaction, where the reaction may be of first- or second-order (Criss et al., 1987):

$$\ln (1 - F) = -k_t t$$  \hspace{1cm} eq. (4.2)
\[ F / (1 - F) = k_2 t \]  

eq. (4.3)

The temperature dependence of the reaction can be assessed in an Arrhenius-plot, in which the natural logarithm of the rate constant is plotted against the inverse temperature. According to equation 4.4, the slope of the linear relationship gives the activation energy for the reaction:

\[ \ln (k_{1,2}) = \ln (A) + \left( \frac{E_a}{R T} \right) \]

where \( A \) is the pre-exponential factor (y-axis intercept), \( E_a \) the activation energy, \( R \) the universal gas constant, and \( T \) the temperature.

**Figure 4.1:** Schematic illustration of silicon isotope exchange between opal and spiked solution under saturated conditions, with and without silicon isotope fractionation during exchange (after Li et al., 2011). Initially, the opal has a natural silicon isotope composition and plots on the terrestrial fractionation line. The spiked solution has, in this example, the same \( \delta^{30}\text{Si} \) composition as the opal, but an unnatural (spiked) \( \delta^{29}\text{Si} \) composition. If no isotope fractionation is associated with the exchange, the isotopic compositions of opal and solution will evolve towards the system’s average. In case of isotope fractionation, opal and solution will evolve towards a secondary fractionation line with the same slope as the terrestrial fractionation line. According to mass balance, the silicon isotope compositions of opal and solution are connected with tie-lines that cross the system average throughout the reaction. The degree of isotope fractionation can be inferred from the difference in \( \delta^{30}\text{Si} \) and \( \delta^{29}\text{Si} \) between opal and solution.
4.2.2 Experimental setup

The experiment is designed such that silicon isotope exchange occurs in an environment close to natural conditions, i.e. in a deep sea or sedimentary environment. Two stock solutions were made up containing >97.5 volume-% of Pacific deep seawater. One stock solution was designed to mimic deep seawater with a silicon concentration (henceforth denoted as [Si]) of 161 µM, and two stock solutions were designed to reproduce interstitial sediment pore waters with a [Si] of 800 µM, which is close to opal saturation. $^{29}$Si-spike was added to all solutions such that natural-Si/spike-Si ratios were between 10 and 150. The idea of using different natural-Si/spike-Si ratios was to account for an uncertainty on the detection limit of silicon isotope exchange and as a monitor for consistency of the final dataset.

Figure 4.2 illustrates the experimental components and design. Both stock solutions mainly consist of Pacific deep seawater from 4500 m depth with [Si]=150 µM, collected during the 2002 Intergovernmental Oceanographic Commission (IOC) Contaminant Baseline Survey Expedition (Station 9; Measures et al., 2006), on-board filtered with a 0.45 µm Millipore cellulose filter, and afterwards acidified to pH 1-2 with HCl. $^{29}$Si-spike was introduced to both solutions, in the form of a solution in an artificial seawater matrix (see 4.2.5). Solution 1 and 2 were prepared to have an order of magnitude different natural-Si/spike-Si ratio. Stock solution 2 contains additional silicon added via a 1000 ppm standard (Alfa-Aesar) to reach a pore water concentration of 800 µM. The concentration was chosen based on observations from the Southern Ocean (Rabouille et al., 1997; Gallinari et al., 2002), with the intention of creating a silica saturated environment. Since the true solubility of the sedimentary opal sample was unknown, a literature value was preferred over the assumption of a theoretical opal solubility. Any uncertainty on this can be accounted for by mass balance considerations, since [Si] is measured before and after the experiment such that opal dissolution due to undersaturation can be quantified. The pH of the final solutions was adjusted to 8 using semi-conductor grade NaOH (e.g. Jourabchi et al., 2008). A bulk volume of 250 ml for each stock solution was prepared and stored in 500 ml acid-cleaned polypropylene bottles, which were sealed with parafilm to avoid evaporative loss of water.

The experiment started by mixing twelve 0.67-0.74 mg aliquots of opal with 6 x 20 ml of stock solution 1 and 6 x 20 ml of stock solution 2 in 30 ml acid-cleaned HD-PE bottles. The diatom opal chosen was from ODP Core 1093 (Leg 177, southeast Atlantic, S49°58’35, E5°51’55, 3624 m depth), with a grain size of <20 µm, and originating from 20.69 metres composite depth (corresponding to an age of ~78.5 ka). Separation and cleaning of the opal was done in the Weizman Institute of Science, Rehovot, Israel (courtesy of Aldo Shemesh), and followed the procedure described in chapter 2. The amount of opal added was deliberately chosen to exceed the amount of silicon in stock solutions resulting in strong (solution 1) and weak undersaturation (solution 2). Dissolution of diatom opal is relatively straightforward to monitor through [Si] measurements, and has been shown to result in minor or no isotope effects (Wetzel et al., submitted; chapter 3). Thus, the undersaturation approach was chosen in order to inhibit the formation of secondary phases of unknown chemistry, quantity and isotopic composition. To assess the temperature dependence of
silicon isotope exchange, stock solutions were split (2 x 3) into 5°C and 22°C experiments (Fig. 4.2). While the 5°C samples are close to deep seawater conditions, a temperature of 22°C would correspond to a crustal depth of about 300 m (assuming a geothermal gradient of 6°C/100 m) and was chosen for simplicity as this was the average room temperature of the laboratory (±0.5°C). For each temperature samples were left reacting for 364-482 days.

Figure 4.2: Experimental setup and components. The total sample batch consists of 12 samples.

After a given time interval, the sample was transferred into a 50 ml acid-cleaned polypropylene centrifuge tube and centrifuged for 20 min at 3200 rpm to gravitationally separate diatoms and solution. Afterwards, the solution was carefully pipetted off into an acid-cleaned polypropylene centrifuge tube and used for cation exchange chemistry (4.2.3) to purify the solutions for mass
spectrometric silicon isotope analyses. As described in 4.2.6, the opal was not further processed for mass-spectrometric analyses due to the methodological difficulty of removing adsorbed silicic acid from the opal surfaces.

4.2.3 Chromatographic purification of silicon

The chemical protocol for chromatographic purification of silicon from solutions is based on Karl and Tien (1992) and de Souza et al. (2012) and involves brucite (Mg(OH)$_2$) co-precipitation to concentrate silicon while reducing the amount of cations and anions, and subsequent cation exchange chemistry to purify the solutions. The protocol was applied to all solutions before and after reaction, the pure $^{29}$Si-spike, as well as the deep seawater, including replicates of all. Due to the high [Si] of 35.61 mM (1000 ppm) and low matrix element concentrations, the Si-standard was simply diluted by a factor of 100 and directly loaded onto the cation exchange column. Silicon yields of the co-precipitation method were usually >99% and always >97.5%. Before and after the experiment, total [Si] was measured photospectrometrically in all stock solutions and components, following the molybdate blue method (Strickland and Parsons, 1968). The uncertainty on [Si] associated with this method is usually within ±4%. All components as well as stock solutions were measured repeatedly on different sample replicates across analytical sessions (see 4.2.4).

Before the experiment, diatom opal was processed according to the protocol described by Wetzel et al. (submitted; chapter 3). $\delta^{30/29}$Si was measured repeatedly on different sample replicates across analytical sessions.

4.2.4 MC-ICP-MS analyses

All isotope ratio measurements have been done with the NuPlasma 1700 high-resolution MC-ICP-MS (Nu Instruments, UK) at ETH Zurich. The analytical protocol for analyses of samples with natural silicon isotope composition is based on Georg et al. (2006b) and involves standard-sample bracketing and the use of a desolvating unit (DSN-100, Nu Instruments). On-peak $\delta^{30/29}$Si measurements consisted of 5 bracketed measurements, each with 36 x 5 s integrations. All solutions have been measured on different sample replicates across analytical sessions. Analytical accuracy was constantly monitored with the secondary standard Diatomite (Brzezinski et al., 2006).

One aim of this study was to set up a robust analytical protocol for accurate and reproducible silicon isotope measurements of spiked solutions. The introduction of spike into the mass-spectrometer and desolvating unit requires an optimised washout protocol and background correction method to ensure that signal memory effects do not compromise measurements. Background correction methods in this study are based either on on-peak acquisition (on-peak zero, OPZ), or by deflection of the beam by the electrostatic analyser (ESA). In OPZ mode silicon
background levels derived from nebuliser, desolvater, torch, injector, cone, lens and wash solutions are recorded on peak. Due to low background intensities, commonly 25 mV ($10^{11}$ Ω resistance), counting times have been increased to reduce counting errors. In contrast, in ESA beam deflection mode the scatter of the electronic baseline is recorded, which is much less variable and intense, allowing comparatively quick background acquisition.

At ETH, measurement of samples with natural silicon isotope compositions has commonly been performed in ESA deflection mode. For natural samples, this method allows robust and comparatively quick silicon isotope ratio acquisition at reasonably high sample/background intensity ratios. For example, a sample/background intensity ratio of 100 results in a 1% error on the $\delta^{29}$Si values which can be translated into a maximum error of ±0.04‰, given a natural range in $\delta^{29}$Si values of -4‰ and +4‰, and a blank $\delta^{29}$Si of 0‰ (Fig. 1.3; chapter 1). This error is about three times smaller than the long-term external reproducibility of 0.14‰. Throughout this thesis, sample/background ratios were between 101 and 1182, with a median of 275. Furthermore, the measured $\delta^{29}$Si values of diatoms and seawater are commonly much closer to zero than 4, such that errors due to ignoring the silicon background are usually ≪0.04‰. In comparison, longer counting times in OPZ mode increases the time between each standard and sample measurement, which is generally undesirable, because plasma conditions may not be identical for samples and standards, such that drifts in instrumental mass bias occur. Therefore, background acquisition by ESA beam deflection is capable of yielding robust and reliable results, with the caveat that sample/background ratios have to be reasonably high, and blank and samples need to have similar (natural) silicon isotope compositions.

Non-natural silicon isotope compositions, such as the spiked solutions in the present experiment are, however, potentially affected by the overall background signal, i.e. the blank of the sample introduction system and mass spectrometer, since the relative difference in sample and background isotope compositions is much larger. For example, a spike signal of 7 V with $\delta^{29}$Si of 5900‰, and a background signal of 35 mV with $\delta^{29}$Si 0‰ (sample/background ratio 200) yield a bulk $\delta^{29}$Si of 5871‰. Thus, the measured $\delta^{29}$Si is by 29‰ lower than the true $\delta^{29}$Si, which is about a factor of 200 higher than the reproducibility for $\delta^{29}$Si of 0.15‰ in this study (see 4.3.1). To compare both background acquisition modes, all spiked samples and internal standards have been measured using both. Diatoms and seawater have natural isotope compositions and have been measured, with the exception of one seawater sample, in ESA deflection mode. In ESA beam deflection mode, backgrounds were collected for 30 s, preceded by 160 s washout (3 x 40 s wash and 40 s transfer). In OPZ mode, backgrounds were measured on peak for 60 s before each standard and sample measurement. Background collection was preceded by a total washout of 180 s with 50 mM HCl, consisting of 3x 45 s wash time plus 45 s transfer time. The time scales of washouts have been optimised to avoid memory effects of spiked silicon signals in preceding tests. Analytical accuracy was monitored with the secondary standard Diatomite (Reynolds et al., 2007).
4.2.5 Spike preparation

The $^{29}$Si-spike available for this study is a mixture of several components and was originally produced for internal other purposes (Ben Reynolds). It consists of a mixture of an original $^{29}$Si spike (95.6% $^{29}$Si) made by the Oak Ridge National Laboratory in SiO$_2$ form, an elemental silicon standard (Puratronic, Alfa-Aesar, 99.999% SiO$_2$) with natural silicon isotope composition, and a silicon-free artificial seawater medium. Both, spike and the Puratronic standard were dissolved by alkaline fusion (Georg, Reynolds, Frank and Halliday, 2006b). The resulting liquid was neutralised with HCl and an artificial seawater medium was added according to the procedure given by Goldman and McCarthy (1978) and McLachlan (1964) (Table 4.1).

Table 4.1: Composition of the artificial seawater medium that was mixed with the spike (McLachlan, 1964; Goldman and McCarthy, 1978).

<table>
<thead>
<tr>
<th>Mineral Salts</th>
<th>Concentration [mM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>400</td>
</tr>
<tr>
<td>MgSO$_4$ • 7H$_2$O</td>
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</tr>
<tr>
<td>CaCl$_2$ • 2H$_2$O</td>
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</tr>
<tr>
<td>KBr</td>
<td>1.7</td>
</tr>
<tr>
<td>KCl</td>
<td>10</td>
</tr>
<tr>
<td>MgCl$_2$ • 6H$_2$O</td>
<td>20</td>
</tr>
</tbody>
</table>

4.2.6 Physical limitations

During the course of the experimental runs, several attempts were made to set up a method capable of quantitative separation of diatom opal and dissolved silicic acid at the end of the experiment. A first test involved the mixing of spiked seawater with diatoms, followed after a few seconds by their rapid separation by filtering (PTFE filter, 0.2 µm pore size) and rinsing with MQe (>16.2 MΩ). Over such a short time scale no detectable isotope exchange could have occurred, while adsorption is likely. Subsequent mass-spectrometric analyses of the opal showed that substantial amounts of spike-derived silicon were adsorbed onto opal surfaces and not removed by rinsing. Alternatively, some spike solution was trapped within the frustule pore space and not removed by rinsing. Repeated tests involved rinsing with 3-6 M HCl, HNO$_3$, MQe, and/or ethanol, but the opal was found still to carry significant and un reproducible amounts of spike silicon. Leaching with 5 mM NaOH for 1 hour at room temperature eventually removed the spike signal. Leaching, however, also destroys the outermost part of the frustule, and with it any possible isotope exchange signal.
Some important considerations have to be taken into account, when the solutions instead of the opal are measured. Dissolution of diatom opal will increase [Si] in the solutions and contribute silicon with a natural silicon isotope composition. Due to the extreme isotopic disequilibrium in this experiment, the degree of opal dissolution needs to be accurately determined. Similarly, losses of silicon from the solution may occur through precipitation of silicate phases or adsorption. While the fact that the solutions were kept below opal saturation reduces the likelihood for precipitation of secondary minerals, the amount of silicon that was potentially adsorbed onto the opal is hard to quantify, since it is a function of the (unknown) surface area of the sample. The surface area is directly related to the number of reactive surface sites, i.e. the number of silanol groups (–Si–OH; –Si–O) at the surface to which silicic acid can adsorb. Using theoretical considerations, however, the impact of sorption can be estimated. Assuming a reactive surface site density of 2 nm$^{-2}$ (Dixit and Van Cappellen, 2002), and an opal surface area of 20 m$^2$/g (as measured for a sample with similar characteristics in chapter 3), the average number of reactive surface sites in the experiment (using 0.7 mg opal) is $2.8 \cdot 10^{16}$. If each site can be occupied by one silicic acid molecule of the solution, the corresponding loss of silicon from the solution will change [Si] by about 1.5% for solution 1 and <0.3% for solution 2. Though this change is rather small, and expected to be superimposed upon opal dissolution, it will be shown in chapter 4.4 that this small silicon pool cannot simply be excluded from the mass balance calculation of the system.

### 4.3 Results

#### 4.3.1 Overall analytical performance

The analytical and instrumental performance can be assessed with the secondary standard Diatomite. In OPZ mode Diatomite $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ were $1.25\pm0.18\%$ (2SD) and $0.66\pm0.15\%$ (2SD) (n=12), respectively, and in ESA deflection mode $1.26\pm0.13\%$ (2SD) and $0.64\pm0.06\%$ (2SD) (n=14), respectively, consistent with the consensus values of $1.26\pm0.02\%$ (2SEM) and $0.64\pm0.01\%$ (2SEM) (Reynolds et al., 2007; Table 4.2). The respective uncertainties of the mean values are very comparable to the external reproducibility of Diatomite during this PhD ($\pm0.14\%$ 2SD for $\delta^{30}\text{Si}$ and $\pm0.09\%$ 2SD for $\delta^{29}\text{Si}$, n=104; see chapter 2). The slightly larger uncertainties on $\delta^{30,29}\text{Si}$ values in OPZ mode reflect the larger variability of the background silicon signal compared to variability of the electronic baseline. In summary, the secondary standard Diatomite is accurately and precisely measured throughout the experiment, independent of the background acquisition technique. The long-term external reproducibility (2SD) of $\delta$-values in OPZ mode is $\pm0.18\%$ for $\delta^{30}\text{Si}$ and $\pm0.15\%$ $\delta^{29}\text{Si}$.

A further indicator of accurate analytical performance is the mass-dependency of isotope fractionation during mass spectrometric analyses. Figure 4.3 illustrates the fractionation line for all
natural samples analysed during the experiment for both background acquisition methods (Table 4.3). In ESA beam deflection mode the linear regression (least square fit) yields a slope of 0.512±0.008 (2SEM), and in OPZ mode the regression yields a value of 0.523±0.035 (2SEM). Both values are thus in good agreement with the theoretical range for mass-dependent silicon isotope fractionation, of 0.5092 for kinetic fractionation and 0.5178 for equilibrium fractionation (Reynolds et al., 2007).

Table 4.2: Internal standard measurements of Diatomite (Brzezinski et al., 2006) collected over the entire experiment in background acquisition modes of on-peak zero (OPZ) and electrostatic analyser beam deflection (ESA). Inter-calibrated δ^{30}Si and δ^{29}Si for Diatomite are 1.26±0.02‰ (2SEM) and 0.64±0.01‰ (2SEM).

<table>
<thead>
<tr>
<th>Mode</th>
<th>δ^{30}Si [%]</th>
<th>1 SD</th>
<th>δ^{29}Si [%]</th>
<th>1 SD</th>
<th>Δ^{29}Si [%]</th>
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</table>

\(^2\) All Δ^{29}Si values provided in this study are calculated using the relation: Δ^{29}Si = δ^{29}Si - 0.51 x δ^{30}Si (Reynolds et al., 2007).
### Table 4.3: Silicon isotope compositions of stock solutions 1 and 2 prior to reaction with diatoms, along with their components seawater, Si-Standard, and spike, and the diatoms used in the experiments. Also given is the measured sample-to-background beam intensity ratio of spiked samples for each on-peak zero (OPZ) measurement. Note, that δ/Δ²⁹Si values are always lower in electrostatic analyser beam deflection mode (ESA) compared to OPZ mode. Unless stated otherwise, only OPZ data will be considered for the rest of the discussion (see text for details).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mode</th>
<th>δ³⁰Si [‰]</th>
<th>1 SD</th>
<th>δ²⁹Si [‰]</th>
<th>1 SD</th>
<th>Δ²⁹Si [‰]</th>
<th>sample/</th>
<th>background</th>
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<td>seawater</td>
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<td>0.09</td>
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<td>41.87</td>
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<td>0.09</td>
<td>41.86</td>
<td>0.16</td>
<td>41.85</td>
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</table>
Figure 4.3: Triple isotope plot of all samples with natural silicon isotope compositions measured in ESA beam deflection (A) and on-peak zero mode (B). The defined slopes are in agreement with mass-dependent isotope fractionation for both analytical background acquisition schemes.

For all spiked samples $\delta^{30}\text{Si}$ values were systematically lower by 0.30% (median) in ESA deflection mode (Table 4.3, 4.4). As mentioned in 4.2.4, it is expected that $\delta$-values are higher in OPZ mode since they are corrected for background silicon that has a $\delta^{30}\text{Si}$ of 0.1‰ (Fig. 2.4). Observed sample/background intensity ratios for spiked samples were around 368 (median), which translates, according to mass balance, to 0.27% higher $\delta^{30}\text{Si}$ values than in ESA beam deflection mode. Hence, there is excellent agreement between observed and theoretical delta values based on beam intensities, indicating the internal consistency of both acquisition schemes. For example, the mean $\delta^{30}\text{Si}$ of solution 2 is 41.80‰ in ESA deflection mode and on average 0.26% lower compared to the OPZ mean of 41.91‰ (Tab. 4.5). From the observed mean sample/background intensity ratio of 389 for solution 2, and an assumed background $\delta^{30}\text{Si}$ of 0.1‰, the sample in ESA deflection mode should indeed yield 41.80‰. Such a perfect agreement of observation and theory, however, is not always the case. For example, the $\delta^{30}\text{Si}$ of solution 1 (20°C, 429 d) is 329.49‰ in ESA deflection and hence 0.42% lower compared to the OPZ value of 330.86‰ (Tab. 4.5). From an observed sample/background intensity ratio of 380 and assuming a background $\delta^{30}\text{Si}$ of 0.1‰, the sample in ESA deflection mode should yield 329.99‰. This apparent mismatch of nearly 1‰ can potentially be explained with poorly constrained background $\delta^{30}\text{Si}$, which can by chance have anomalous $\delta^{30}\text{Si}$ values of $\pm$20‰ (Fig. 2.4). However, the overall strong agreement of theoretical and observed $\delta^{30}\text{Si}$ offsets suggests that the backgrounds are usually well constrained in OPZ background acquisition mode.
Table 4.4: Silicon isotope compositions of all samples as measured after the experiment and separation of diatoms. The apparent opal dissolution was calculated assuming SiO$_2$ stoichiometry for the opal and has to be considered as a minimum estimate of opal dissolution, because any losses of silicon due to sorption or precipitation of silicate minerals. Also given is the measured sample-to-background beam intensity ratio for each run in on-peak zero mode (OPZ). Note, that $\delta$/$\Delta$Si values are always lower in OPZ mode compared to electrostatic analyser beam deflection mode (ESA). See text for details.

<table>
<thead>
<tr>
<th>Sample</th>
<th>days</th>
<th>mg opal</th>
<th>Si [µM] t=start</th>
<th>Si [µM] t=end</th>
<th>apparent opal dissol.</th>
<th>Mode</th>
<th>$\delta^{30}$Si [%]</th>
<th>1 SD</th>
<th>$\delta^{29}$Si [%]</th>
<th>1 SD</th>
<th>$\Delta^{29}$Si [%]</th>
<th>1 SD</th>
<th>sample/background</th>
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<td>0.74</td>
<td>161</td>
<td>182</td>
<td>3.4%</td>
<td>OPZ</td>
<td>1.64</td>
<td>0.10</td>
<td>334.81</td>
<td>0.24</td>
<td>333.76</td>
<td>0.15</td>
<td>345</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>ESA</td>
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<td>333.66</td>
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<td>4.2%</td>
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<tr>
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<td>164</td>
<td>0.6%</td>
<td>OPZ</td>
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<td>381.35</td>
<td>0.12</td>
<td>380.53</td>
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<td>0.06</td>
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<td>830</td>
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<td>0.07</td>
<td>39.93</td>
<td>0.05</td>
<td>39.87</td>
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<td>790</td>
<td>-1.6%</td>
<td>OPZ</td>
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<td>800</td>
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<td>800</td>
<td>790</td>
<td>-1.7%</td>
<td>OPZ</td>
<td>0.12</td>
<td>0.19</td>
<td>41.57</td>
<td>0.19</td>
<td>41.51</td>
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<td>41.38</td>
<td>0.10</td>
<td>41.33</td>
<td>0.03</td>
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In summary, the analytical protocol that has been developed in this study is able to yield precise, reproducible, and consistent results for both natural and non-natural silicon isotope compositions. Spiked samples need to be measured in OPZ mode, since the instrumental silicon background causes significant bias in the measurements that is most accurately visible in the spiked isotope. Samples with natural silicon isotope compositions can be accurately measured in ESA beam deflection mode. Both background acquisition methods give consistent results if the silicon background is accurately quantified. In the following, all isotope data of spiked solutions shown are corrected for background using OPZ measurements.

4.3.2 The accuracy of $^{29}$Si-spike measurements

In order to test whether spiked samples are accurately measured, seawater and $^{29}$Si-spike have been mixed in various proportions and analysed.

Figure 4.4: Silicon isotope compositions of mixtures of $^{29}$Si-spike and seawater. Linear regressions through the data yield $R^2$-values of 0.9962 (Fig. 4.4a) and 0.99991 (Fig. 4.4b), indicating that natural and spiked samples are accurately measured. Error bars associated with measured data are internal 2SD (note, that error bars in 4.4b are smaller than the symbol size). The end-member values are taken from Table 4.3 (error bars are 2SEM) but are not used in the regression.

Figure 4.4a shows a linear regression through the $\delta^{30}$Si values yielding a slope of 4.49±0.32 (2SE) and an $R^2$ of 0.996. The y-axis is intercepted at 1.27±0.18 (2SE), in good agreement with the value measured for seawater (Table 4.3). Based on the regression, at $f_{\text{spike}}=1$ the $\delta^{30}$Si value is
5.77‰, and hence also in good agreement with the measured $\delta^{30}\text{Si}$ for the spike of 5.80‰ (Table 4.3). Linear regression through $\delta^{30}\text{Si}$ values yields a slope of 5916±66 (2SE) and an $R^2$ of 0.99991 (Fig. 4.4b). Based on the regression, the seawater end-member has a $\delta^{30}\text{Si}$ value of -26±37‰ (2SE) and the spike a $\delta^{30}\text{Si}$ of 5890‰. Given the rather large absolute errors (but very small relative errors) of the regression, the results are in good agreement with the measured values (Table 4.3). Consequently, the regression provides a robust relationship between $\delta^{30/29}\text{Si}$ values and the amount of spike in the sample, such that it can be concluded that $\delta^{30/29}\text{Si}$ values are measured accurately over the range of $\delta$-values in this study.

4.3.3 $\delta^{30/29}\text{Si}$ before reaction with diatoms

The silicon isotope compositions of the stock solutions before addition of diatoms are listed in Table 4.3. Solution 1 has a $\delta^{30}\text{Si}$ of 1.59±0.12‰ (2SEM), which is close to the $\delta^{30}\text{Si}$ of the seawater that makes up 99 volume-% of the bulk solution. The $\delta^{29}\text{Si}$ value is 398.87±0.47‰ (2SEM), resulting in a $\Delta^{29}\text{Si}$ of 398.05‰. Based on the mixing proportions listed in Figure 4.2, $\Delta^{29}\text{Si}$ should be 397.802‰. Solution 2 was characterised with a $\delta^{30}\text{Si}$ of 0.12±0.09‰ (2SEM), and a $\delta^{29}\text{Si}$ of 41.91±0.05‰ (2SEM), resulting in a $\Delta^{29}\text{Si}$ of 41.84‰.

4.3.4 [Si] and $\delta^{30/29}\text{Si}$ after reaction with diatoms

The measured [Si] before and after the experiment, as well as $\delta^{30/29}\text{Si}$ values of the solutions after termination of the experiment, are summarised in Table 4.3. In all experimental solutions [Si] changed, but there is no systematic trend with time. In the 5ºC batch of solution 2 a decrease in [Si] was observed, indicating that some silicon from the solution was adsorbed onto the opal and/or precipitation of secondary silicate phases occurred. In all other solutions [Si] increased which, because any losses of silicon due to adsorption or precipitation are unknown and not quantified, has to be considered as a net increase and a minimum degree of diatom dissolution. Accordingly, the increase is referred to as ‘apparent opal dissolution’ (Table 4.4). In solution 1, the increase [Si] indicates net opal dissolution, and the increase was proportionally higher for the 22ºC batches than for the 5ºC batches. Surprisingly, apparent opal dissolution in the nearly saturated solution 2 was about 2% greater for the 22ºC batch than for the same temperature batch of the much more undersaturated solution 1. This observation is in conflict with the suggestion that undersaturation is the main thermodynamic driving force for dissolution. All [Si] analyses of the 22ºC batch were performed on the same day, such that systematic instrumental bias is unlikely. Given that the same sample material was used throughout the experiment, the higher dissolution rates cannot be explained by sample-related properties such as significantly different surface areas. Precipitation of
silicate minerals, and a concomitant decrease in [Si], would rather be expected in the nearly saturated solution 2, more than for solution 1, and is not able to explain the observed feature. Adsorption of dissolved silicon onto opal surfaces does indeed have a stronger impact on solution 1 [Si] compared to solution 2 [Si] due to its overall lower [Si], but this is only able to partially explain the lower apparent dissolution rates for solution 1. Even if the reactive surface site density for adsorption and surface area of the opal were much higher than assumed in 4.2.6, adsorption is not able to create higher opal dissolution rates for solution 1 than for solution 2. The only process that could create the apparent mismatch is evaporation of the solution, which would lead to a proportionally greater increase of [Si] in solution 2 compared to solution 1. This scenario will be discussed in 4.4.3.

Figure 4.5: Silicon isotope compositions of solution 1 (a) and solution 2 (b) after the experiment, plotted against reaction time with diatoms. The bands represent the starting $\delta^{29}\text{Si}$ (green) and $\delta^{30}\text{Si}$ (grey) of solution 1 with their associated 2SEM. Data point error bars are 1SD of the respective on-peak zero measurement. While $\delta^{30}\text{Si}$ values are indistinguishable from the starting composition, $\delta^{29}\text{Si}$ values decreased, with a stronger decrease for the 22°C samples.

Figure 4.5 illustrates the silicon isotope compositions of the solutions versus reaction time. For all solutions and temperatures, $\delta^{30}\text{Si}$ values are indistinguishable within 1 SD from the starting composition of the solution. This observation is partly due to the similarity in $\delta^{30}\text{Si}$ of solution and diatoms (for solution 1), and partly due to the overall low degrees of dissolution, and hence only minor addition of diatom-derived silicon to the solutions (solution 1 and 2). In comparison, $\delta^{29}\text{Si}$ values are significantly lower, by about 10-69‰ compared to the mean $\delta^{30}\text{Si}$ value of solution 1, and 0.3-1.9‰ lower compared to the mean $\delta^{30}\text{Si}$ value of solution 2, with the lower values observed for
the 22°C batches. No trend with time is observable, indicating that all reaction rates were low on the time scale of the experiment. For both solutions, $\delta^{29}\text{Si}$ values are lower in the 22°C batches compared to the 5°C batches. This observation could either be consistent with isotope exchange between solution or opal dissolution.

4.4 Discussion

4.4.1 Processes affecting the isotope composition of the solutions

The impact of opal dissolution, silicon isotope exchange between solution and opal, adsorption, and mineral precipitation can be studied in triple isotope space.

Figure 4.6: Schematic illustration of how the silicon isotope composition of a solution evolves in triple isotope space when different processes are involved. Precipitation and adsorption fractionate silicon isotopes mass-dependently, either enriching the solution in heavy isotopes (precipitation) or depleting it in the heavy isotopes (whether isotope fractionation during adsorption occurs is unknown but for illustrative purposes it is here shown to discriminate against the lighter isotopes), resulting in a rather horizontal fractionation line. Opal dissolution and isotope exchange are mixing processes, such that they will move the solution towards the composition of the bulk system (if no isotope fractionation is associated with these processes).

Figure 4.6 schematically illustrates how the silicon isotope composition of a solution would change if any of these processes occurred. The precipitation of silicate minerals is associated with preferential incorporation of the light isotopes into the mineral phase, enriching the residual solution in the heavy isotopes (e.g. Georg et al. 2006a). For silicon adsorption, no systematic studies yet
exist, such that isotope discrimination may be either against the heavy or light isotopes. Adsorption and mineral formation will fractionate the isotopes mass-dependently, which will have a proportionally stronger effect on the low $\delta^{30}$Si values of the solutions compared to $\delta^{29}$Si values, resulting in a rather horizontal fractionation line. In contrast, opal dissolution and isotope exchange between solution and opal will primarily move the solution vertically, towards the isotopic composition of the bulk system (compare with Fig. 4.1). In principle, both processes should be distinguishable, as with isotope exchange no net mass transfer occurs, while dissolution of opal results in increasing [Si] of the solution.

**Figure 4.7:** Silicon isotope composition of the solutions after reaction with diatoms in a triple isotope plot. The dotted line represents the hypothetical composition of the solutions starting from the initial composition (black square), with increasing percentage of opal-derived silicon (calculations assumed no silicon isotope fractionation during dissolution). Grey squares represent the isotope compositions of the solution calculated based on the observed increase in [Si] (Table 4.4). Any difference between the grey squares and measured samples (red circles) should be indicative of processes other than opal dissolution (see text for discussion). Error bars of the measured data are 2SD as measured in on-peak zero mode, while error bars of the initials are 2SEM. Vertical bars indicate the uncertainty on the compositions of the ‘dissolution only’ values based on the measurement error on [Si] of ±4% (see 4.4.2).
In Figure 4.5 it was demonstrated that the $\delta^{29}\text{Si}$ composition of the solutions decreased in all cases. In order to resolve whether dissolution or isotope exchange caused the decrease, the data are plotted in triple isotope space (Fig. 4.7). From the initial silicon isotope composition of the solution a mixing line indicating the degree of opal dissolution is shown. Based on the change in [Si] with time, the minimum amount of diatom-derived silicon is known, and therefore the hypothetical composition of the solution if only opal dissolution was responsible for the change in $\delta^{29}\text{Si}$.

For solution 1, 5°C and solution 2, 22°C the measured values are broadly consistent with diatom dissolution. The measured data are slightly lighter in $\delta^{29}\text{Si}$, which would be consistent with about 0.5-1.5% more dissolution than actually observed. However, the absolute amount of dissolution is unknown and represents a minimum estimate, as no information on the amount of precipitated or adsorbed silicon are available. In 4.2.6 the amount of silicon that can get adsorbed onto opal in solution 1 was estimated to be about 1.5%, which could explain the slight offset between the measured and hypothetical data. The rather large error bars on $\delta^{30}\text{Si}$, and the fact that the magnitude of isotope fractionation during adsorption is unknown, do not allow quantification of the amount of adsorbed silicon or a distinction between adsorption and precipitation. If both processes have similar degrees of isotope fractionation in opposite directions, then the measured samples would remain on the opal mixing line. Additionally, if significant amounts of silicon were removed from solution by adsorption and precipitation, then opal dissolution becomes even more underestimated, such that opal dissolution is most likely the reason for the observed silicon isotope compositions of these solutions.

The measured values for solution 1, 22°C have a $\delta^{29}\text{Si}$ composition that is about 20‰ lighter than expected if diatom dissolution was the only process changing the solution’s $\delta^{29}\text{Si}$ signature, possibly indicating silicon isotope exchange between solution and opal. On the other hand, this offset could also indicate ~2% more opal dissolution than suggested by the [Si] measurement. Based on the previous considerations of the possible influence of adsorption and precipitation on [Si], it could still be possible that opal dissolution was the most dominant process that lowered the solution’s $\delta^{29}\text{Si}$ values rather than isotope exchange. In any case, the amount of exchange that occurred was obviously very small and barely analytically resolvable.

In solution 2, 5°C, a decrease in [Si] was observed, indicating that adsorption and/or precipitation occurred. The measured isotopic values are slightly lower than the initial isotopic composition of the solution and partly indistinguishable from it. Again, this might indicate isotope exchange, but is similarly consistent with, for instance, a small addition of opal-derived silicon and an accompanying larger loss of silicon due to adsorption and precipitation.

In summary, a clear signal of isotope exchange cannot be resolved, as the effect of opal dissolution had the strongest influence on the silicon isotope composition of the solutions. In cases where dissolution does not appear to fully explain the silicon isotope composition of the solutions, adsorption and precipitation could have removed silicon from the solutions, such that the amount of opal dissolution is underestimated. The quantification of the influence of adsorption and precipitation, however, is impossible, as the surface area of the opal and its potential for adsorption,
as well as the mineral phases that may have precipitated from solution and the associated magnitude of isotope fractionation with precipitation and adsorption are unknown. Thus, the mass balance constraints remain incomplete. As will be shown in the following, another limitation that compromises the detection of isotope exchange in these experiments is the measurement uncertainty on [Si], which has substantial impact on the interpretation of the data.

### 4.4.2 Uncertainties on [Si] and their impact on $\delta^{30/29}$Si

As demonstrated in the previous section, the change in the silicon isotope composition of the solutions with time appears to be primarily the result of opal dissolution. From this observation two crucial inferences can be made. First, silicon isotope exchange rates between solution and opal were too low to be clearly resolved over the time scale and temperature range of the experiment. Secondly, the consequence of this observation is that the amount of opal that dissolved must be very precisely known in order to resolve any isotope exchange between opal and solution from dissolution, adsorption, and precipitation. Therefore, in the following the robustness of [Si] measurements and the sensitivity of the interpretation of the results to associated uncertainties on are discussed.

![Figure 4.8](image)

**Figure 4.8:** Normalised mixing lines of solution 1 (a) and 2 (b) with diatom opal, illustrating the sensitivity of $\delta^{30/29}$Si values of the solutions to uncertainties on the total amount of dissolved opal as estimated from the measured final [Si]. Examples for (a) solution 1, 22°C, 396 d, and (b) solution 2, 22°C, 471 d, are illustrated. The vertical grey bars represent the measured final [Si], intercepting the mixing lines at the theoretical isotope compositions of the solutions if the increase in [Si] was purely due to opal dissolution. In (a), a 1 µM uncertainty propagates into a $\pm 2\%$ change in $\delta^{29}$Si, which is about 10x the external reproducibility of samples measured in on-peak zero mode (see 4.3.1). The change in $\delta^{30}$Si is negligible, due to the similarity of $\delta^{30}$Si of solution 1 and opal. In (b) a 10 µM uncertainty on [Si] propagates into a $\pm 0.5\%$ change in $\delta^{29}$Si, and hence significant uncertainty on the theoretical $\delta^{29}$Si of the solution based on opal dissolution.
All sample [Si] in this study have been determined photospectrometrically using the molybdate-blue method (Strickland and Parsons, 1968). The spectrometer is calibrated to a concentration range of 0-36 µM, such that all solutions were diluted by factors of 10-30. Hence, the concentrations could be both over- or underestimated by dilution errors. A small relative error due to dilution translates into larger absolute errors for all solutions with [Si] of 800 µM compared to solutions with 160 µM. Dilution errors are impossible to reconstruct, but it could be expected that they are random and produce outliers, which is not supported by the measured [Si].

Evaporation of solutions can lead to an increase in [Si], with a larger effect on solution 2 with its high [Si] of 800 µM. As a result, the dissolution rates for the solutions could be overestimated. If the sample volume of 20 ml has been reduced due to evaporation by 2% (19.6 ml), then the apparent opal dissolution rates for all samples of solution 1 are slightly higher than those of solution 2, and for 2.5% (19.5 ml) of evaporation, twice as high. How realistic 2-2.5% of evaporation is at room temperature is hard to assess, as the amount of evaporation depends on temperature and humidity, but also on the type of plastic and on how well the lids seal the sample beakers. In the clean lab facilities, temperatures are constant within few a percent at 22°C, while humidity is less stable but fairly high, between 50 and 70%. A reconstruction of the amount of liquid that potentially evaporated off by, for instance, measuring the salinities of the solutions before and after the experiment is unfortunately impossible, as the solutions have been processed through cation-exchange chemistry after the experiment.

Prior to sample measurements, the photospectrometer was calibrated using a 467 ppb Si standard (HACH-LANGE, Germany). The error of the calibration is usually within ±4%. The effect of a 4% uncertainty on the [Si] after the experiment (and thus the apparent opal dissolution), is demonstrated in Figure 4.8. While the δ30Si values are barely affected by uncertainties on [Si] due to the similarity of diatom and solution δ30Si, the δ29Si values are significantly biased. For solution 1, 22°C, 396 d (Fig. 4.8a), the measured [Si] after the experiment was about 182 µM. An uncertainty of ±4% on [Si] would affect the expected δ30Si of the solution by about ±15‰. For solution 1, 22°C, the measured δ29Si values have been observed to be about 20‰ lower than the expected composition of the solution after the observed amounts of opal dissolution. Hence, an uncertainty of 4% on [Si] for that solution would explain a large part of the observed offset, leaving 5‰ unexplained. For solution 1, a 5‰ reduction in δ29Si could be explained with a reduction in [Si] of about 1.4‰, which corresponds to the estimated amount of silicon adsorption that could have occurred in the system (4.2.6). Consequently, the measured δ30Si values of the solutions can be interpreted as the result of diatom dissolution, silicon adsorption onto opal, and a 4% error on the [Si] measurement. Similarly, for solution 2, 22°C, 471 d, which had a final [Si] of 830 µM, a ±4% error on [Si] translates into a change of up to 1.5‰ in δ30Si values, which could explain 75% of the 2‰ lower sample δ30Si values.

The uncertainty on [Si] of ±4‰, and its effect on δ30Si values in all solutions, is illustrated as an uncertainty bar in Figure 4.7. From this it is obvious that the measured isotopic compositions of all measured samples from solution 2 and the 5°C batch of solution 1 can be explained by opal dissolution within an uncertainty on [Si] of 1-3‰, even without the need for consideration of
adsorption and precipitation.

4.5 Concluding remarks and outlook

In this study an analytical protocol was established for the precise and reproducible measurement of spiked solutions and opal. The initial aim of quantifying silicon exchange rates between spiked seawater/pore fluid solutions and diatom opal was not realised due to several difficulties that emerged. The solutions were strongly spiked with $^{29}$Si in order to create a large isotopic disequilibrium with the opal, such that small degrees of exchange should be easily detectable in the opal. However, while the analytical error for silicon isotope measurements was small, the precision of silicon concentration measurements was found to be too low, which gave rise to uncertainties on silicon partitioning during the experiment. Accurate and precise silicon concentrations before and after the experiment are required in order to have a well-quantified mass balance model of the system. Any uncertainties on mass transfer during the experiment translate into large uncertainties on the silicon isotope composition of the solutions that are expected from dissolution of diatom opal, a crucial parameter that needs to be well defined in order to distinguish between silicon isotope exchange between solution and opal versus opal dissolution. Unfortunately, these uncertainties were found to far exceed the analytical precision, such that silicon isotope exchange between solution and opal could not be confidently detected. It can, however, be concluded that over time scale and temperature range of the experiment silicon isotope exchange is slow and possibly barely analytically resolvable.

These limitations could be circumvented if it were possible to measure the silicon isotope composition of the opal. However, it was found that an adsorptively-bound silicon pool is associated with the opal that could not be safely separated without destroying the silicon isotope signature of the opal. Furthermore, little is known about the kinetics of, and isotope fractionation during, silicic acid sorption onto opal surfaces, such that this silicon pool cannot be confidently constrained by means of mass balance. The insights provided by the experiment now help to redesign an experiment that would be capable of measuring silicon isotope exchange rates:

(1) The silicon isotope composition of the opal is biased by adsorbed silicic acid that carries the spike-signature and camouflages any silicon isotope exchange signal. It has to be tested if there is a reagent that inhibits adsorption of silicic acid onto opal by occupying the sorption-reactive sites, such that the opal could be confidently separated and measured for its silicon isotope composition.

(2) The reaction rates of dissolution, sorption, and (potentially) precipitation of silicate phases are faster than silicon isotope exchange and must be well constrained. If adsorption can be suppressed as mentioned in (1) or precisely constrained in terms of mass balance, then the establishment of an opal-saturated solution, in which dissolution and precipitation are in dynamic equilibrium, should provide an environment that is sensitive to silicon isotope
exchange between solution and opal.

(3) The conventional method of photospectrometrical silicon concentration determination does not provide a high-enough precision for the presented experimental approach. More precise measurements of the silicon concentrations of solutions should be possible by isotope dilution and subsequent mass-spectrometric analysis.
References


Watson E. B. and Wark D. A. (1997) Diffusion of dissolved SiO₂ in H₂O at 1 GPa, with implications


Chapter 5 – Application of diatom $\delta^{30}$Si to sediment core samples: Insights into glacial-interglacial silicic acid utilisation

Abstract

Mounting evidence suggests that incomplete uptake by diatoms led to excess silicic acid in the surface Southern Ocean during glacial times. As the surface waters of the Southern Ocean are an important source of nutrients to the global low latitude thermocline, excess silicic acid could give rise to increased low-latitude diatom production at the expense of calcifying organisms. Such an ecological shift would reduce the CaCO$_3$/organic carbon rain ratio resulting in an increase in ocean alkalinity and atmospheric CO$_2$ uptake (silicic acid leakage hypothesis). The silicon isotope composition of diatom opal has been used as a proxy for the degree of surface ocean silicic acid consumption. Based on this, up to 75% excess silicic acid has been estimated in the Southern Ocean during the Last Glacial Maximum (LGM). The lack of evidence for increased supply of silicic acid in lower latitude settings, however, represents a challenge to the observations based on the silicon isotope composition of diatom opal.

Here, new sedimentary diatom $\delta^{30}$Si data from the Atlantic sector of the Southern Ocean are presented. These data are used in an uptake-fractionation model that accounts for species-dependent silicon isotope fractionation, in order to assess the amount of unutilised silicic acid in the Southern Ocean over the last 80,000 years. Furthermore, variation in the silicon isotope composition of the silicic acid taken up by diatoms is also considered in different model scenarios, to assess the sensitivity of the calculated amount of preformed silicic acid to the input composition. Such variation has previously been inadequately addressed, though changes likely occurred in conjunction with glacial-interglacial water mass reorganisations.

Taking variations of species composition in the samples into account, and assuming that the silicon isotope composition of the supplied silicic acid stays constant over time, the model yields 30-70% of preformed silicic acid during the glacial and deglaciation, which is up to 30% higher than

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*a version of this chapter is considered to be submitted to Paleoceanography.*
when species composition variations are not considered. This estimate is in good agreement with previous observations, and indicates that the species composition mainly influences the calculated amounts of preformed silicic acid, but is not the cause of down-core variations in diatom δ30Si. One end-member model scenario explores the possibility that all diatom δ30Si variability is due to changes in the upwelled silicic acid. The changes in δ30Si of the source that are required, however, are large and hard to reconcile with the paleoceanographic changes, such that it is concluded that the diatom opal δ30Si cannot be entirely explained by changes in δ30Si of the supplied silicic acid. Overall, and importantly, the data suggest that at least 20-40% excess silicic acid existed in the glacial Southern Ocean. Finally, a transient supply of isotopically light silicic acid (i.e. an increased supply from the deep ocean) associated with pulses of deep and silicic acid rich upwelling water during the deglaciation is considered. Such pulses reduce the calculated amount of preformed silicic acid in the surface Southern Ocean to levels of 0-40% during the deglaciation. The models presented here, therefore demonstrate that a large uncertainty is introduced into the interpretation of down-core diatom opal δ30Si data, as the δ30Si of the upwelled silicic acid is unknown for the past. At the limits of uncertainty, the results suggest between 0% and 70% of preformed silicic acid during the deglaciation, which is too large an uncertainty to unambiguously argue for or against the potential for significant silicic acid transport out of the Southern Ocean.
5.1 Introduction

Changes in the efficiency of the biological pump in the Southern Ocean have been invoked as a critical influence on atmosphere-ocean CO$_2$ partitioning over glacial-interglacial time scales (Sarmiento, 1984; Knox and McElroy, 1984; Siegenthaler and Wenk, 1984; Anderson et al., 2002; Sigman et al., 2010). Diatoms play a crucial role in this partitioning, as they dominate primary production in the Southern Ocean supported by upwelled nutrients, such as silicic acid and nitrate (Treguer et al., 1995; Raguenseau et al., 2000). Today, the utilisation of nitrate in the Antarctic region of Southern Ocean surface waters is incomplete due to limited availability of iron (e.g. Moore et al., 2013; Fig. 5.1), implying a low efficiency of the biological pump. As a result CO$_2$ is released to the atmosphere south of the Antarctic Polar Front (APF; Takahashi et al., 2009). In contrast, diatoms respond physiologically to low-iron conditions by utilising proportionally more silicic acid over nitrate (Hutchins and Bruland, 1998; Takeda, 1998; Franck et al., 2000; Brzezinski et al., 2003), which results in near complete silicic acid depletion as Antarctic surface waters reach the APF (Fig. 5.1). Consequently, large amounts of nitrate, but virtually no silicic acid, are transported out of the Southern Ocean via Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW), which are the main conduits of Southern Ocean surface waters to lower latitudes (Sarmiento et al., 2004). The existence of excess (also preformed) nitrate in SAMW has important consequences for nutrient distribution in the global low-latitude thermocline, where the exported nitrate feeds up to 75% of primary production (Sarmiento et al., 2004; Palter et al., 2010).

It has been hypothesised that the glacial surface Southern Ocean was more nitrate depleted and silicic acid rich (Brzezinski et al., 2002; Matsumoto et al., 2002), i.e. the reversed situation of today. If excess silicic acid was transported into lower latitudes through AAIW and SAMW, it could give rise to diatom blooms in regions that are otherwise dominated by calcifying organisms. Such an ecological shift would lead to a decrease in the CaCO$_3$/organic carbon rain ratio, an increase in ocean alkalinity (Broecker and Peng, 1987; Archer and Maier-Reimer, 1994), and consequently increased oceanic uptake of atmospheric CO$_2$. This feedback mechanism has been termed the silicic acid leakage hypothesis (SALH; Matsumoto et al., 2002). In support of these ideas, several studies have found evidence for excess silicic acid in the glacial Southern Ocean using the silicon isotope composition of diatom opal (De La Rocha et al., 1998; Brzezinski et al., 2002; Beucher et al., 2007; Horn et al., 2011). Diatoms preferentially utilise isotopically lighter silicic acid to form their opaline frustules (De La Rocha et al., 1997). As a consequence of the preferred utilisation of isotopically light silicic acid, residual silicic acid and subsequent opal both become isotopically heavier, whereas diatom opal will always be isotopically lighter than silicic acid. According to this concept, it was found that glacial diatom opal recovered from Southern Ocean sediments was isotopically lighter than Holocene opal, which would imply that glacial silicic acid utilisation was weaker than today (De La Rocha et al., 1998; Brzezinski et al., 2002; Beucher et al., 2007; Horn et al., 2011). De La Rocha et al. (1998), Beucher et al. (2007), and De La Rocha et al. (2011) estimated 60-75% excess silicic acid in the Southern Ocean surface waters during the LGM. While
the silicon isotope signatures of diatom opal provide a consistent view of excess silicic acid during the LGM, other attempts to validate the SALH have had limited success. For example, studies of increased opal productivity in the lower latitudes ocean during times of proposed excess silicic acid in the Southern Ocean, have been shown to yield ambiguous results (Higginson and Altabet, 2004; Crosta et al., 2005b; Kienast et al., 2006; Bradtmiller et al., 2006; Beucher et al., 2007; Crosta et al., 2007; Meckler et al., 2013). The lack of evidence for increased supply of silicic acid to low latitudes has been explained in terms of reduced formation rates of AAIW and SAMW during the LGM (Crosta et al., 2007; Came et al., 2008; Xie et al., 2012).

There are two problems with previous attempts to estimate the amount of preformed silicic acid in the glacial Southern Ocean based on the diatom silicon isotope composition that may have led to overestimation of the preformed silicic acid pool. The aim of the present study is to address the potential impact of both of these issues.

First, a recent study by Sutton et al. (2013) found that different diatom species fractionate silicon isotopes to different degrees, opening up the possibility that previously observed apparent differences in glacial-interglacial silicic acid utilisation are partly, or even entirely, due to shifts in species composition. Sutton et al. (2013) applied a species-correction to sedimentary diatom opal from the Southern Ocean and found that about one-third of the glacial-interglacial difference in the silicon isotope composition of the diatom opal is due to shifts in the species composition. Compared
to the earlier mentioned estimates, that would still leave 40-50% excess silicic acid in the glacial surface Southern Ocean. That the effect of species variability is rather small is supported by a Southern Ocean core-top study, which did not detect any impact of the species composition.

Second, the calculation of the amount of silicic acid not taken up by diatoms using the silicon isotope composition of diatoms requires knowledge on the silicon isotope composition of the source silicic acid. For instance, Antarctic Surface Water (AASW) has a comparatively heavy silicon isotope signature, which is the result of the uptake of isotopically light silicic acid by diatoms during the spring bloom (e.g. Fripiat et al., 2011a; de Souza et al., 2012b). Moreover, the signature is influenced by seasonal mixing with underlying water masses that have a lighter silicon isotope signature due to the dissolution of isotopically lighter diatom opal at depth (Cardinal et al., 2005; Fripiat et al., 2011a; de Souza et al., 2012b). Based on field-studies, the silicon isotope composition of silicic acid before uptake by diatoms is comparatively well known for the modern ocean. For the glacial Southern Ocean, however, it is to be expected that the silicon isotope composition of the source silicic acid was different from today. This expectation is mainly based on two lines of evidence. First, if silicic acid utilisation has been significantly reduced during the LGM, as suggested by the down-core silicon isotope composition of the opal, then it is expected that silicic acid would become isotopically lighter as well, as the waters are less fractionated. Second, the glacial Southern Ocean was likely more stratified, which would have decreased the supply of isotopically lighter silicic acid from the deep ocean (Sigman et al., 2010; Oppo and Curry, 2012, and references therein). Both processes thus act in opposing directions and may have compensated each other. However, changes in vertical mixing rates in the Southern Ocean, such as the deglacial increase in wind-driven upwelling (Anderson et al., 2009), could supply transient pulses of isotopically light silicic acid from the deep Southern Ocean, and may thus significantly change the interpretation of records of diatom opal silicon isotopes. Such changes have not yet been taken into account in calculations of excess silicic acid from the silicon isotope composition of diatom opal.

In this study, new data for the silicon isotope composition of diatom opal from a sediment core from the Atlantic sector of the Southern Ocean are presented in order to better constrain the amount of preformed silicic acid in the glacial surface Southern Ocean. An uptake-fractionation model is used to infer the amount of preformed silicic acid over the last 80 ka, while taking into account changes in species composition. Furthermore, changes in the source silicic acid isotope composition are considered in different model scenarios to assess the sensitivity of the calculated amount of preformed silicic acid to the input composition.
5.2 Methods

5.2.1 Age model

Site 1093 was drilled during ODP Leg 177 in the Atlantic sector of the Southern Ocean, at a depth of 3624 m, and is located at the present day position of the Polar Front (49°58’S, 5°51’E; Fig. 5.1). The age model of the core is based on the Epica Dome C time scale by graphical correlation of ice δD and dust records from Dome C with records of transfer function-derived SSST and δ¹⁸O of Neogloboquadrina pachyderma (Hodell et al., 2002), and magnetic susceptibility (Gersonde et al., 1999) from 1093. In order to compare the presented data with deglacial opal flux data from the nearby core TN057-13 (53.2°S, 5.1°E, 2850 m depth; Anderson et al., 2009), core 1093 was tied to the age model of TN057-13 for the last 17 ka, by graphical correlation of diatom-derived SSST (Nielsen, 2004; Schneider-Mor et al., 2008), and δ¹⁸O of Neogloboquadrina pachyderma (Kanfoush et al., 2002; Hodell et al., 2002; Fig. 5.2).

5.2.2 Sample preparation

The core was sampled in 5-15 cm steps and diatoms were micro-separated and cleaned (courtesy of A. Shemesh) following the procedures of Shemesh et al. (1988) and Singer and...
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Shemesh (1995). The procedure involves four principle steps: (1) oxidation of organic matter using H₂O₂ and removal of carbonates using HCl; (2) sieving, so that only the fraction <20 µm was used for isotope analyses, as this grain size fraction is highly enriched in diatom opal with only insignificant contributions of non-diatom material (Egan et al., 2012); (3) heavy-liquid separation to gravitationally separate diatom opal from mineral particles such as clays; (4) leaching and oxidation of the outermost opal surface containing adsorbed ions and metals, clays, and secondary precipitates using HNO₃ and HCl. Within and after this procedure, the samples were checked for purity using light and secondary electron microscopes.

5.2.3 Diatom species counts

The recent finding that silicon isotope fractionation by diatoms is species-dependent (Sutton et al., 2013), means that the species composition of the samples is required in order to interpret diatom silicon isotope records. Species counts do not take into account size and density variations of the different frustules, such that volumetric abundances of diatom taxa only serve as a first-order approximation for the amount of silicon that is associated with each species. Because of the short time between the publication of the study by Sutton et al. (2013) and the writing of this thesis, it was not possible to obtain species counts for all samples. Hence, emphasis was put on samples from the last 80 ka, as the sample density is reasonably high and similar literature data are more abundant for this time period than for the penultimate glacial-interglacial cycle (e.g. Horn et al., 2011).

The counts have been done at the School of Earth and Ocean Sciences, Cardiff University (courtesy of Jennifer Pike) following the random settling method of Scherer (1994). A small amount of sample was dispersed in warm water and Calgon and left settling onto a cover slip for 1 hour. Afterwards, the liquid was drained and covers slips were air-dried and mounted onto microscope slides using Norland Optical Adhesive (Norland Products, US). For all samples at least 200 valves were counted. Due to severe fragmentation of the samples it was impossible to obtain a representative species composition for most samples without including valve fragments. Some valves, such as the elongated pennate valves of Thalassiothrix are more prone to fragmentation than others, such as the less elongated pennate valves of F. kerguelensis, which may result in an overestimation of F. kerguelensis. Tests, in which the same sample was counted once excluding fragments and once including fragments >10 µm, however, showed consistent results, such that for every sample fragments >10 µm were counted.

5.2.4 Silicon isotope analyses

The silicon isotope composition of the opal is commonly reported as δ³⁰Si, which expresses the deviations of a sample’s ³⁰Si/²⁸Si ratio from that of a reference material (NBS28) in parts per thousand [%o]:
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$$\delta^{30}\text{Si} = \left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}} \times 1000$$

Silicon isotope measurements of the diatom opal were acquired following the methods of Georg et al. (2006) and (Wetzel et al., submitted; chapter 3). About 0.5 mg of opal was dissolved in 5 mM NaOH at 100°C for at least 24 hours to assure complete dissolution. Whether complete dissolution was achieved or not, could not be verified macroscopically due to the small sample grain size. However, it was recently shown that incomplete dissolution of diatom opal from the same sediment core samples does not affect the silicon isotope composition of the opal or the solution (Wetzel et al., submitted; chapter 3). After dissolution, the solutions were loaded directly onto a cation-exchange resin (AG50W-X8, BioRad Laboratories) that separates the negatively charged silicon species from the Na$^+$-matrix. Silicon isotope measurements have been acquired at ETH Zurich using the NuPlasma 1700 high-resolution multi-collector inductively coupled plasma mass spectrometer (Nu Instruments, UK). Samples were measured in standard-sample-standard bracketing mode against the international standard NBS28. Each reported $\delta^{30}\text{Si}$ value consists of the mean of 5 bracketed measurements of the sample (36 x 5 s integrations each). The long-term external reproducibility of $\delta^{30}\text{Si}$ values is given by repeated measurements of the inter-laboratory calibrated secondary standards Diatomite and LMG08 (Reynolds et al., 2006; Hendry et al., 2011) and is 0.14‰ (2SD) for both Diatomite (n=88, 2.5 years) and LMG08 (n=11, 2 years).

5.3 Results and discussion

5.3.1 Diatom species composition

Figure 5.3a shows the percentage of species for which a silicon isotope fractionation factor is known from culturing studies (Sutton et al., 2013). The species assemblage is dominated by *F. kerguelensis* throughout the record, with abundances of >43%, averaging 67%. During glacial times, *Chaetoceros* resting spores$^3$ were found to be proportionally more abundant than in the Holocene. The species *P. glacialis* has been detected in only one sample with an abundance of 0.5%. Species, for which no isotope fractionation factor is known, are here collectively called ‘other species’. This group is dominated by *T. lentiginosa* (3-22%), *T. gracilis* (0.4-14%), *E. antarctica* (0-

$^3$ Rather than intact valves, *Chaetoceros* spp. is often present as resting spores in the sediment. As no $\delta^{30}\text{Si}$ data are available for resting spores, it is assumed that the isotope fractionation factor available for vegetative cells of Chaetoceros brevis is the same.
13%), and Thalassiothix spp (0.5-7%). Overall, the taxonomic composition of the sediment core agrees very well with literature observations from the Polar Frontal region in the South Atlantic (e.g. Bianchi and Gersonde, 2004; Crosta et al., 2005a), indicating that the true species abundances were not substantially biased by fragment counting. The elevated abundances of 'other species' during the LGM (MIS 2, ~20 ka) and Marine Isotope Stage 4 (MIS 4, ~65 ka) are primarily due to increased occurrence of E. Antarctica (Fig. 5.3b). This species has been observed to proliferate under Fe-replete conditions (Hinz et al., 2012; Salter et al., 2012; Quéguiner, 2013), and the co-variation of its abundance with ice-core dust (Fig. 5.3b) further supports the accuracy of the counting method.

Figure 5.3: Diatom species abundances in the samples from ODP core 1093 (a). Species for which no isotope fractionation factor is known are collectively called ‘other species’. Also shown is the abundance of the species Eucampia Antarctica and the mass of dust as recorded in EPICA Dome C ice cores (b; EPICA Community Members, 2004).

5.3.2 Pattern of diatom opal $\delta^{30}$Si over the last 170 ka

Figure 5.4 shows the silicon isotope composition of diatom opal from ODP 1093 for the last 170 ka as measured. The main feature of the record is that during times of elevated atmospheric CO$_2$ concentrations $\delta^{30}$Si values are up to 0.6‰ higher than during glacial times and low atmospheric CO$_2$ concentrations. This offset is consistent with other published records from the Southern Ocean that did not account for species-dependent silicon isotope fractionation (De La Rocha et al., 1998; Brzezinski et al., 2002; Beucher et al., 2007; Horn et al., 2011). The lowest $\delta^{30}$Si values are associated with MIS 2, 4, and 6, which are times of increased Subantarctic productivity and atmospheric iron deposition (Wolff et al., 2006; Martinez-Garcia et al., 2009; Martinez-Garcia et al., 2011; Fig. 5.3b). It has been shown in several studies that the silicon demand of diatoms is significantly reduced when iron is not a limiting micronutrient (Hutchins and Bruland, 1998; Takeda,
suggesting that the lower diatom opal $\delta^{30}\text{Si}$ values may originate from increased iron fertilisation. On the other hand, increased iron availability has been observed to be associated with shifts in species diversity (e.g. Quéguiner, 2013). Therefore, it cannot be ruled out that the lowest $\delta^{30}\text{Si}$ values are the result of species-dependent silicon isotope effects during uptake.

Figure 5.4: Silicon isotope composition of diatom opal for the last 170 ka from ODP core 1093. EPICA Dome C ice core CO$_2$ concentrations are also shown (EPICA Community Members, 2004). Shading and numbers on top mark Marine Isotope Stages (MIS). During interglacials, $\delta^{30}\text{Si}$ values are consistently higher by about 0.6‰ than during glacial periods, suggesting that silicic acid utilisation by diatoms was weaker during glacial periods.

Three main factors may be responsible for the variations in diatom opal $\delta^{30}\text{Si}$. First, the observed glacial-interglacial $\delta^{30}\text{Si}$ differences may be the result of changes in the degree of silicic acid utilisation by diatoms. Second, the variability of $\delta^{30}\text{Si}$ may be due to changes in the taxonomic composition of the samples. Third, the $\delta^{30}\text{Si}$ record may reflect changes in the $\delta^{30}\text{Si}$ composition of the supplied silicic acid. A combination of all three factors is possible. In the following section, the sensitivity of the silicon isotope record to all three parameters is assessed using an uptake-fractionation model. These scenarios help to constrain the extent to which the degree of diatom opal $\delta^{30}\text{Si}$ variations presented here originate from changes in the degree of silicic acid utilisation.
5.3.2 An uptake-fractionation model for Si utilisation of the past 80 ka

In order to account for species-dependent silicon isotope fractionation, a simple model is introduced. First, an isotope enrichment factor that is weighted by the fractional abundances of species in each sample is calculated:

$$\varepsilon_w = \left( \frac{F}{100} \times -0.54‰ \right) + \left( \frac{C}{100} \times -2.09‰ \right) + \left( \frac{O}{100} \times -1.10‰ \right)$$

eq. (5.1)

where F, C, and O stand for the percentages of *F. kerguelensis*, Chaetoceros resting spores, and ‘other species’. The individual enrichment factors for *F. kerguelensis* and Chaetoceros resting spores are taken from Sutton et al. (2013). For ‘other species’ the enrichment factor is assumed to be -1.1‰, which has been observed during field studies (Varela et al., 2004; Cardinal et al., 2005; Fripiat et al., 2011b).

The weighted isotope enrichment factor $\varepsilon_w$ is then used in an open (eq. 5.2) and closed system (eq. 5.3) fractionation model to derive the amount of preformed (unutilised) silicic acid. Here, both open and closed systems are considered, as silicic acid uptake by diatoms in the ocean cannot be simply assigned to either one on its own (e.g. Fripiat et al., 2012).

$$\delta^{30}\text{Si}_{\text{bsi}} = \delta^{30}\text{Si}_{\text{dSi source}} + f_{\text{preformed}} \, \varepsilon_w$$

(eq. 5.2)

$$\delta^{30}\text{Si}_{\text{bsi}} = \delta^{30}\text{Si}_{\text{dSi source}} - \varepsilon_w \ln \left( \frac{f_{\text{preformed}}}{1-f_{\text{preformed}}} \right)$$

(eq. 5.3)

where $\delta^{30}\text{Si}_{\text{bsi}}$ is the silicon isotope composition of the diatom opal, $\delta^{30}\text{Si}_{\text{dSi source}}$ the composition of silicic acid before biological uptake, and $f_{\text{preformed}}$ the fraction of silicic acid that is unutilised. As eq. 5.3 cannot be solved for $f_{\text{preformed}}$, the values have to be derived iteratively. In order to solve the equations for $f_{\text{preformed}}$ a value for $\delta^{30}\text{Si}_{\text{dSi source}}$ has to be assumed. Here, it is assumed that $\delta^{30}\text{Si}_{\text{dSi source}}$ is 2‰. This reasoning for this value is: (1) today, diatom opal from both core-top (this study) and water column (Fripiat et al., 2012) have a $\delta^{30}\text{Si}$ of 1.8 to 1.9‰. As silicic acid is almost completely drawn down, the $\delta^{30}\text{Si}_{\text{dSi source}}$ must be close to these values. (2) For AAIW, which carries 97% of the silicon characteristics of AASW (Fripiat et al., 2011a), values of 1.8 to 2.0‰ have been observed in the winter mixed layer (Fripiat et al., 2011a; de Souza et al., 2012a).

To test the impact of uncertainties on the value chosen for $\delta^{30}\text{Si}_{\text{dSi source}}$ three scenarios are developed. First, a conservative approach is chosen, in which it is assumed that $\delta^{30}\text{Si}_{\text{dSi source}}$ has been constant at 2.0‰ throughout the last 80 ka (scenario 1). Second, $f_{\text{preformed}}$ is kept constant with time at the value observed today in the Southern Ocean, such that all changes in the opal $\delta^{30}\text{Si}$
record reflect changes in $\delta^{30}\text{Si}_{\text{dSi source}}$. This scenario demonstrates the degree to which $\delta^{30}\text{Si}_{\text{dSi source}}$ has to vary in order to create the observed variability in diatom $\delta^{30}\text{Si}$ (scenario 2). Third, $\delta^{30}\text{Si}_{\text{dSi source}}$ is assumed to vary with upwelling intensity in the Southern Ocean, and thus nutrient supply (scenario 3). This scenario allows assessment of the sensitivity of the deglacial features of the record to changes in $\delta^{30}\text{Si}_{\text{dSi source}}$ for the last 20 ka.

**Scenario 1: constant source $\delta^{30}\text{Si}$**

Figure 5.5 shows how the preformed silicic acid content in the Southern Ocean surface waters is calculated to change with time according to equations 5.2 and 5.3, when $\delta^{30}\text{Si}_{\text{dSi source}}$ is constant at 2‰, and when observed variations in species abundances are taken into account (eq. 5.1). Also illustrated are reference curves calculated assuming a constant $\varepsilon$ of -1.1‰, thus showing the preformed silicic acid content if species changes were not accounted for (in shape, simply the inverse of the diatom opal $\delta^{30}\text{Si}$ record, Fig. 5.4).

First, the effect of variations in species abundances is considered. The species-corrected model results (for both open and closed system) yield preformed silicic acid abundances that are up to 30% elevated compared to the uncorrected records (Fig 5.5a). This observation is mainly the result of the weighted $\varepsilon$-values being significantly lower than -1.1‰, mainly due to the high abundances of *F. kerguelensis* and the low $\varepsilon$-value of that species, at -0.58‰ (Sutton et al., 2013). As a result, the overall glacial-interglacial difference in preformed silicic acid is enhanced in the species-corrected model by about 10%.

Furthermore, the species-correction does not significantly change the trends observed in the records (Fig. 5.5a, b; Fig. 5.4). Specifically, diatom $\delta^{30}\text{Si}$ data from Figure 5.4 suggest low degrees of silicic acid utilisation during the LGM (~20 ka) and MIS 4 (~60-70 ka). After consideration of species variations, the model yields high preformed silicic acid abundances during these times (Fig. 5.5a, b). Similarly, the increased diatom $\delta^{30}\text{Si}$ data suggest more complete silicic acid utilisation during the Holocene, which is well reflected in low preformed silicic acid abundances as obtained by the model. Even detailed features of the record, such as the W-shaped pattern between 15 and 10 ka (Fig. 5.5b), are well preserved in the species-corrected model.

In summary, the results demonstrate that the species composition of the samples has no significant impact on the large- and small-scale patterns of the amount of preformed silicic acid calculated from diatom silicon isotope data for the last 80 ka. However, the absolute values of preformed silicic acid are impacted significantly. In the model scenario presented here, taking the isotope enrichments for different species into account results in calculated amounts of preformed silicic acid that are up to 30% higher than when species differences are not accounted for.

The open and closed system records suggest about 30-70% preformed silicic acid in the glacial ocean. In comparison, preformed surface nitrate abundances in the modern Southern Ocean at the APF are about 90% (e.g. Robinson and Sigman, 2008; Fig. 5.1). The amount of preformed silicic acid provided by the model is a relative number and not easily convertible to concentrations, as
water masses during glacial might have had significantly different properties. A reconstruction of 
depth water silicic acid concentrations suggests that the concentration was not different during the 
LGM (Hendry et al., 2010). If that applied to thermocline waters as well, 30-70% preformed silicic 
acid could correspond to about 20-40 µM of unutilised silicic acid in the glacial ocean (Fripiat et al., 
2011a).

Figure 5.5: Preformed silicic acid contents calculated for open (green) and closed system (red) isotope 
fractionation according to equations 5.1-5.3 and based on measured diatom opal δ³⁰Si. Thick lines are 
corrected for variations in species abundances. Thin lines serve as reference lines for 
a model without species-
dependent silicon isotope fractionation (ε = const. = -1.1‰), to illustrate the effect of the correction. For all 
cases a constant δ³⁰Si of 2‰ is used. (a) shows the modelled preformed silicic acid abundances for the 
last 80 ka. (b) shows a 
expanded view of 
the last 20 ka. Opal flux data in (b) were 
obtained from a nearby 
core and taken from Anderson et al. (2009). See text for discussion.

In Figure 5.5b the modelled preformed silicic acid content is shown in more detail over the last 
20 ka, alongside opal flux data from a nearby core that has been interpreted as reflecting increased 
upwelling in the Southern Ocean and, thus, increased nutrient supply (Anderson et al., 2009). 
According to the data and model, the increased supply of silicic acid between 16 and 15 ka had no 
significant impact on the amount of preformed silicic acid, suggesting that the increased supply 
was largely balanced by increased opal production. However, as the supply decreased at around 
14 ka, the preformed silicic acid content decreased radically towards modern-like preformed values 
of 10-20%. Such a large drop to preformed values seen at the present day is rather surprising, 
since the opal flux at 14 ka is still comparatively high. One explanation may be the availability of iron 
which, if in abundance, reduces the diatom’s demand for silicon over organic tissue (Takeda, 1998).
Atmospheric dust deposition has been shown to have been increased during the LGM, and until about 15 ka (Wolff et al., 2006). The strongly reduced atmospheric deposition of dust after 15 ka may thus explain the strong reduction in preformed silicic acid between 14 and 15 ka. Similarly, as the supply of silicic acid increased around 13 ka, the preformed silicic acid content increased as well, but did not reach previous values of up to 70%, but rather 20-40%. A small reduction in upwelling intensity around 11-12 ka is then associated with complete utilisation of silicic acid in both the open and closed system model. Afterwards, the record exhibits more or less stable preformed silicic acid content of about 10-20%. One exception is the very high value at around 8.5 ka, which suggests high preformed silicic acid contents, even though the supply of silicic acid is rather reduced. It may be, however, possible that this increase is not well dated, as the age control after 10 ka is weak (Fig. 5.2).

In summary, the diatom taxonomic composition of the sediments had no substantial impact on the overall features of the record observed in Fig. 5.4, though the absolute amounts of preformed silicic acid are enhanced. The amount of preformed silicic acid over the last 80 ka varies strongly, from 0 to 70%. This variability is, however, dependent on the $\delta^{30}$Si composition of the supplied silicic acid assumed for the model. Therefore, the next two scenarios will consider variations in $\delta^{30}$Si$_{\text{dSi source}}$.

**Scenario 2: constant degree of utilisation**

Figure 5.6 shows the evolution of $\delta^{30}$Si$_{\text{dSi source}}$ throughout the last 80 ka calculated assuming $f_{\text{preformed}}$ was constant at 7% (modern closed system value for $f_{\text{preformed}}$ in scenario 1). Both open and closed system $\delta^{30}$Si$_{\text{dSi source}}$ values are 0.4 to 0.5‰ lighter during the glacial than the interglacial, suggesting that the low diatom $\delta^{30}$Si during the glacial could, in principle, be the result of the $\delta^{30}$Si$_{\text{dSi source}}$ having a value of about 1.5‰ rather than 2‰. A reduction in $\delta^{30}$Si$_{\text{dSi source}}$ by 0.5‰ would require an enhanced supply rate of isotopically light silicic acid to the glacial surface ocean. The deep South Atlantic has $\delta^{30}$Si$_{\text{dSi}}$ of 1.2‰ (de Souza et al., 2012b), resulting from the dissolution of isotopically light opal. Stronger vertical mixing would therefore supply proportionally more isotopically light silicic acid to the surface Southern Ocean. Stronger glacial upwelling is at odds, however, with suggestions that nutrient supply to the surface ocean during the glacial was reduced, as the ocean was more stratified (Francois et al., 1997; Sigman et al., 2004). If during glacial times the supply rate of regenerated isotopically light silicic acid from the deep ocean was reduced, then one would expect $\delta^{30}$Si$_{\text{dSi source}}$ to increase rather than decrease. Similarly, during the deglaciation $\delta^{30}$Si$_{\text{dSi source}}$ increases in the model, while the deglacial increase in deep ocean ventilation in the Southern Ocean would supply isotopically lighter silicic acid to the surface (Anderson et al., 2009; de Souza et al., 2012b). It can therefore be concluded that the observed variations in diatom opal $\delta^{30}$Si over the last 80 ka are unlikely to be entirely due to changes in the silicon isotope composition of the supplied silicic acid. In the third scenario, the degree to which a transient change in $\delta^{30}$Si$_{\text{dSi source}}$ would affect the preformed silicic acid content is assessed.
Scenario 3: change in source δ³⁰Si with degree of silicic acid supply

In this scenario it is assumed that δ³⁰Si_{source} is generally 2‰, but that the deglacial peaks in opal production, and thus nutrient supply, were associated with enhanced supply of deep ocean-sourced and isotopically lighter silicic acid of 1.8‰. This value has been chosen based on the findings of scenario 2, which showed that values as low as 1.5-1.6‰ are rather unlikely. It is acknowledged that uncertainty exists about the exact value of δ³⁰Si_{source}, but it does serve to demonstrate the sensitivity of the preformed silicic acid abundances to an isotopically lighter source composition.

Figure 5.7 illustrates that such a reduction in δ³⁰Si_{source} leads to a decrease in the calculated preformed silicic acid content in the surface ocean during times of enhanced supply of silicic acid, relative to the scenario with constant δ³⁰Si_{source}. Compared to scenario 1, where 30-70% of preformed silicic acid were observed for the upwelling event between 14 and 16 ka, in scenario 3 it is only as high as 60% at the beginning (for the open system case), but then decreases to virtually no preformed silicic acid. As the supply of silicic acid stalled around 14 ka, the amount of preformed silicic acid stays low, which may again be the result of the increased demand for silicon by diatoms due to reduced atmospheric iron deposition. Also in contrast to scenario 1, the amount of preformed silicic acid during the second upwelling event from 13 ka on does not result in increased preformed silicic acid.
Figure 5.7: Preformed silicic acid contents calculated for open (green) and closed system (red) isotope fractionation according to equations 5.1-5.3 and based on measured diatom opal $\delta^{30}$Si, species-corrected isotope enrichment factor, and assuming a $\delta^{30}$Si$_{\text{dSi}}$ source of 2‰ for times of low opal flux (open symbols) and a $\delta^{30}$Si$_{\text{dSi}}$ source of 1.8‰ for times of high opal flux (solid symbols). Opal flux data are from Anderson et al. (2009). See text for discussion.

5.3.3 Synthesis of model results and implications for glacial-interglacial silicic acid utilisation

New down-core data for diatom opal $\delta^{30}$Si are presented here, and show substantial variations over the last 170 ka. Whether these variations record changes in the degree of silicic acid utilisation by diatoms, rather than changes in the species composition, or $\delta^{30}$Si of the supplied silicic acid, has been assessed by using an uptake-fractionation model. The model converts diatom $\delta^{30}$Si values into fraction of preformed, i.e. unutilised, silicic acid and accounts for species-dependent silicon isotope fractionation (Sutton et al., 2013). For the first time, it is shown that over the last 80 ka changes in species composition do not change the observed trends in diatom opal $\delta^{30}$Si, even though they do influence the magnitude of inferred silicic acid consumption. This result supports the use of diatom $\delta^{30}$Si as a proxy for past silicic acid utilisation. Though it is acknowledged that not all species are included into the model, as no isotope fractionation factor is known, it appears unlikely that their inclusion will significantly change the observations, given the small sensitivity to the overall trends observed in scenario 1. The modelled preformed silicic acid contents are, however, sensitive to the
species composition, as well as the assumed composition of the supplied silicic acid. Thus, while the diatom opal $\delta^{30}Si$ composition can be used as a first-order guide for silicic acid consumption, the species composition needs to be known in order to infer accurate degrees of utilisation.

Variations in the silicon isotope composition of the supplied silicic acid and their impact on the interpretation of the diatom $\delta^{30}Si$ record have been considered. In scenario 2 it was shown that changes in the $\delta^{30}Si$ of the supplied silicic acid are unlikely to be the main factor controlling diatom $\delta^{30}Si$, since the sign of the implied change of $\delta^{30}Si$ of the source is inconsistent with what is known about paleoceanographic changes. Nonetheless, ocean circulation during the last glacial and deglaciation was certainly different than today (Oppo and Curry, 2012, and references therein), such that changes in the supply rate of silicic acid to the surface Southern Ocean were likely accompanied by changes in its isotope composition. Two different types of changes should be distinguished: (1) a *steady-state* change in the silicon isotope composition of the ocean can be expected on time scales exceeding the residence of silicon in the ocean (10,000-17,000; Laruelle et al., 2009; Tréguer and De La Rocha, 2013). The steady-state change can therefore not explain features of the diatom $\delta^{30}Si$ record such as the glacial-interglacial difference of about 0.6‰, which occurred in <10,000 ka. (2) *Transient* changes, however, are associated with reorganisation of ocean circulation and water mass mixing (such as the bipolar seesaw mechanism; Broecker, 1998), and thus occur on much shorter time scales. On a yearly basis, the silicon isotope composition of the surface ocean is largely determined by the properties of the winter-mixed layer, which bears the characteristics of the strongly fractionated surface mixed layer and the deeper water column, with its light silicon isotope composition from regenerated opal (Cardinal et al., 2005; Fripiat et al., 2011a; de Souza et al., 2012a). If this system gets disturbed by, for instance, a permanent stratification of the water column, the supply of isotopically light silicic acid from the deep ocean will be reduced.

The two model scenarios 1 and 3 demonstrated the significantly different impact of a changing silicic acid source on the interpretation of diatom opal $\delta^{30}Si$. In both scenarios a glacial $\delta^{30}Si_{\text{source}}$ of 2‰ resulted in preformed silicic acid contents of 30-70% (depending on open or closed system conditions). The modelled amount of preformed silicic acid is critically dependent on the value assumed for $\delta^{30}Si_{\text{source}}$. If it were 1.9‰ or 1.8‰ rather than 2‰ during the glacial, the preformed silicic acid content would decrease to 20-40% respectively. In return, that would still leave at least 20-40% preformed silicic acid in the glacial surface Southern Ocean and, hence, significantly more than today.

This finding is important, as it would strongly support that excess silicic acid existed in the glacial Southern Ocean. If it were exported to lower latitudes, it could give rise to oceanic CO$_2$ uptake via the feedback mechanism suggested by SALH. For instance, Griffiths et al. (2013) found elevated silicic acid concentrations in AAIW during MIS 4 (60-70 ka), along with increased opal productivity in the tropical Atlantic, and interpreted the finding as evidence for silicic acid leakage. The record presented here shows elevated preformed silicic acid contents in the Southern Ocean during this time, suggesting that there is a link between the two findings.
For the deglaciation, the interpretation of the diatom δ³⁰Si record depends more critically on the assumption of δ³⁰Si\textsubscript{dSi} source. While in scenario 1 large amounts of preformed silicic acid are still modelled during the deglaciation, in scenario 3, silicic acid is virtually depleted in the surface from the beginning of the deglaciation on. Which of the two scenarios pertained is crucial for the understanding of marine nutrient distributions during the deglaciation. Recently, Meckler et al. (2013) found distinct opal production peaks in subtropical sediments from the North Atlantic during the last six deglaciations. They interpreted the increased opal production to be the result of increased silicon supply from the deep Atlantic rather than supply through AAIW and SAMW, an interpretation that thus potentially conforms to model scenario 3. This interpretation is, for instance, based on studies that found reduced formation rates of AAIW and SAMW during the glacial and early deglaciation (Crosta et al., 2007; Came et al., 2008; Xie et al., 2012). On the other hand, if model scenario 1 was the most likely, then the Southern Ocean might have been the ultimate source of silicic acid for the subtropical opal production. One way to resolve this issue would be to follow the approach of Griffiths et al. (2013), who looked for increased silicic acid concentrations in Southern Ocean-derived intermediate waters.

All in all, the new diatom opal δ³⁰Si data presented here provide further evidence that, even after consideration of species-dependent silicon isotope fractionation and potential changes in the silicon isotope composition of the supplied silicic acid, the amount of preformed silicic acid during the last glacial was higher than today. The origin of this excess appears to be at least partly linked to a reduced silicon demand by diatoms due to relief from iron limitation (Hutchins and Bruland, 1998; Takeda, 1998; Franck et al., 2000; Brzezinski et al., 2003). Similar models as presented here, applied to other sediment core diatom δ³⁰Si data, will help to further constrain the amount of preformed silicic acid in the glacial Southern Ocean. Whether the excess silicic acid supported low-latitude productivity that may have resulted in a positive feedback in which additional atmospheric CO\textsubscript{2} was taken up by the ocean, remains to be further investigated (Griffiths et al., 2013).
References


Egan K. E., Rickaby R. E. M., Leng M. J., Hendry K. R., Hermoso M., Sloane H. J., Bostock H. and


nutrients during the Last Glacial Maximum deduced from sponge silicon isotopic compositions. 


Paleoceanography 27, PA3221.
6. Concluding remarks

6.1 Synthesis

The objective of this thesis was to test the integrity of the silicon isotope composition of sedimentary diatom opal against post-mortem modification. Furthermore, the impact of the variability in paleoceanographic boundary conditions on the interpretation of diatom opal $\delta^{30}\text{Si}$ has been assessed.

Over the past ten years, the growing interest in diatom $\delta^{30}\text{Si}$ as a tracer of past surface ocean silicic acid utilisation has been somewhat qualified by an insufficient understanding of the reliability of the proxy due to the lack of substantial ground-truthing studies. Most recently, this situation has begun to change, with core-top calibrations and improved microseparation techniques developed that avoid sample contamination with non-diatom silicon (Ehlert et al., 2012; Egan et al., 2012). These studies all conclude that sedimentary diatom opal $\delta^{30}\text{Si}$ records the degree of silicic acid utilisation in the surface ocean when certain conditions are met (for instance the successful removal of radiolarian opal from the samples). The observation that diatom opal $\delta^{30}\text{Si}$ is preserved during settling through the water column and early diagenesis is important as it is not intuitive, considering the physical (e.g. decreasing surface area) and chemical changes in the properties (e.g. structural incorporation of aluminium) of the opal after death (Van Cappellen et al., 2002). Driven by the potential consequences of changes that the diatom opal undergoes after death, this thesis has assessed the potential for silicon isotope fractionation during dissolution of post-mortem opal. In previous work, it was found that dissolution of fresh diatom opal collected from the water column involves a measurable fractionation of silicon isotopes but, given the excellent preservation of sedimentary opal, and thus low degrees of dissolution, the fractionation has no significant effect on diatom $\delta^{30}\text{Si}$ (Demarest et al., 2009). An outstanding question is therefore whether this effect is also insignificant in the sedimentary environment. The results presented in chapter 3 demonstrated that silicon isotopes are not measurably fractionated during dissolution of mature sediment core diatom opal, which is in agreement with the results of core-top studies.
The results of chapter 3 may be of importance for studies using seawater \( \delta^{30}\text{Si} \) as a tracer for the marine silicon cycle. After the discovery that the lighter silicon isotopes are preferentially released during dissolution of fresh diatom opal (Demarest et al., 2009), subsequent studies incorporated the isotope effect into mass balance models on silicon cycling in the ocean (e.g. Fripiat et al., 2011; Fripiat et al., 2012). The results obtained in this thesis suggest, however, that the isotope effect associated with dissolution is not a constant, but is prone to variability caused by processes in the water column and the sedimentary environment. About 40% of the globally produced diatom opal dissolves in the deep ocean (Tréguer and De La Rocha, 2013), and thus in regions where the isotope effect during dissolution of diatom opal may be different than previously assumed.

Though there is compelling evidence that core-top diatom opal \( \delta^{30}\text{Si} \) records surface ocean silicic acid utilisation, the burial depth at which the isotope composition becomes compromised by diagenetic processes is unknown. Since diagenetic processes, such as recrystallisation, diffusion, and reprecipitation, physically and chemically degrade the opal, there is a natural threshold integrity of diatom \( \delta^{30}\text{Si} \). In chapter 4, an experiment was presented, which aimed at measuring silicon isotope exchange rates between diatom opal and pore fluid at temperatures of 5 and 22ºC, corresponding to a sediment depth of about 0-300 m in the opal belt of the Atlantic Southern Ocean. It was demonstrated that silicon isotope exchange was, within analytical uncertainties, not detectable for reaction times up to 482 days. This result shows for the first time that silicon isotope exchange between opal and fluid at these temperatures is not significant. However, the fact that silicon isotope exchange was not detectable means that the temperature and sediment depth at which silicon isotope exchange disturbs the integrity of diatom opal \( \delta^{30}\text{Si} \) remains an open question. The experiment presented here, however, provided a plethora of information that would help to guide a future experiment that is more sensitive to silicon isotope exchange (see 6.2).

A further important contribution to our understanding of diatom opal \( \delta^{30}\text{Si} \) was provided by Sutton et al. (2013). Based on culturing studies, they demonstrated that different diatom species fractionate silicon isotopes differently. This finding affects both the interpretation of diatom opal \( \delta^{30}\text{Si} \) in terms of paleoceanography, and of \( \delta^{30}\text{Si} \) of dissolved silicic acid in the modern ocean, as either tracer is sensitive to the diatom species assemblage. For the interpretation of sediment core diatom \( \delta^{30}\text{Si} \), the species assemblage must be known in order to obtain accurate estimates of the degree of past silicic acid utilisation. In chapter 5 of this thesis it was demonstrated for a sediment core from the Atlantic sector of the Southern Ocean that patterns of down-core variations of diatom opal \( \delta^{30}\text{Si} \) are not caused by variations in the diatom species composition, but that species variations affect the absolute estimates of preformed silicic acid (i.e. the amount of excess silicic acid in the surface Southern Ocean that is available for export to the low latitude ocean via Intermediate and Mode waters). A similar impact on such estimates is introduced by the \( \delta^{30}\text{Si} \) of the upwelled silicic acid, which is unknown for the past. The models presented in chapter 5 represent the first in-depth quantification of past silicic acid utilisation, and the impact of uncertainties on \( \delta^{30}\text{Si} \) of upwelled silicic acid in the past on the calculations. While it was argued that at least 20-40% of preformed
silicic acid likely existed during the LGM in the surface Southern Ocean, uncertainties are larger for the preformed silicic acid content during the deglaciation. As the deglaciation was associated with a significant reorganisation of ocean circulation (Oppo and Curry, 2012), it may be expected that the $\delta^{30}$Si of the source silicic acid also changed significantly, and thus the estimated amount of preformed silicic acid. Taking into account variations in the $\delta^{30}$Si of source silicic acid during the deglaciation results in calculated preformed silicic acid amounts of 0-70%. This large uncertainty results in ambiguous interpretations of the potential for silicic acid to be exported out of the Southern Ocean into the low-latitude ocean. It is important to stress, however, that variations in past $\delta^{30}$Si of silicic acid cannot explain the full variability of diatom opal $\delta^{30}$Si, but they do need to be considered.

6.2 Outlook

The information provided by diatom opal dissolution experiments demonstrate that silicon isotope fractionation has no significant influence on diatom opal $\delta^{30}$Si. However, the observation that during dissolution of fresh and mature diatom opal, silicon isotopes fractionate differently remains to be explained. Optimised experimental setups are required in order to understand the exact mechanisms and controlling factors of silicon isotope fractionation during opal dissolution.

As pointed out in the discussion in chapter 3, it cannot entirely be ruled out that the different isotope effects observed here and in previous work are the result of the experimental boundary conditions rather than an inherent feature of opal dissolution. For instance, it has been observed that diatom opal dissolution appears to deviate from simple first-order kinetics, and in their review of such observations Loucaides et al. (2012) argue that this deviation is more likely to be inherent to batch reactor dissolution experiments. The disadvantage of batch reactor systems, as used here or by Demarest et al. (2009), is that the concentration of dissolved silicic acid continuously changes (i.e. increases) during the reaction. It has been suggested that a decreasing degree of undersaturation may lead to a change in the dissolution mechanism (Van Cappellen et al., 2002), which could potentially explain the deviation from first-order kinetics. A change in dissolution mechanism is, however, undesirable, as the degree of silicon isotope fractionation would very likely change as well. One way to circumvent this experimental problem is to use flow-through reactors, in which dissolution takes place under steady-state conditions (e.g. Van Cappellen, 1996; Khalil et al., 2007). Steady-state conditions would also eliminate interferences from adsorption-desorption processes (Khalil et al., 2007), which could play a critical role in batch reactor dissolution experiments (chapter 3; Demarest et al., 2009). Alternatively, batch reactor dissolution experiments could be done using diatom opal samples that have reached different stages of maturity (thus having different chemical and physical properties), to trace changes in silicon isotope fractionation.

In order to measure silicon isotope exchange rates between diatom opal and pore fluid, only limited changes to the experimental setup presented in chapter 4 are required. The most important
aim is to eliminate, or reduce the significance of, processes, such as opal dissolution and sorption, that interfere with silicon isotope exchange and introduce uncertainties in the mass balance of the system. First, the experiments should be conducted at diatom opal saturation to eliminate the influence of opal dissolution. Moreover, high silicon concentrations in saturated solutions would also reduce the impact on the mass balance of the system of adsorption of silicic acid onto opal surfaces. Ideally, adsorption of silicic acid onto opal and potential silicon isotope effects should be well characterised in a separate experiment (see below). Second, the experiment could be conducted at higher temperatures in order to facilitate silicon isotope exchange. Third, silicon concentration measurements could be done using isotope dilution, which is more accurate than photospectrometric methods. The analytical protocol that was developed in chapter 4 for silicon isotope measurements of spiked solutions has been shown to provide precise and accurate data and can be applied to future studies.

One inference that can be drawn from the experimental work presented in this thesis is that sorption processes are not well understood and characterised. Sorption of silicic acid onto mineral surfaces has been demonstrated to be associated with silicon isotope fractionation and has been suggested to impact the silicon isotope composition of riverine waters (Ziegler et al., 2005; Delstanche et al., 2009; Opfergelt et al., 2009). Similar studies for biogenic silica, however, do not yet exist. The fact that adsorption of silicic acid onto diatom opal is not well-characterised results in uncertainties on mass balance calculations in the silicon isotope exchange experiment in chapter 4. Considering that fresh-water opal plays a significant part in the terrestrial silicon cycle (Tréguer and De La Rocha, 2013), the characterisation of sorption processes involving silicic acid and biogenic silica may thus not only be of importance for experiments as presented in this thesis.

The diatom opal $\delta^{30}$Si composition is an excellent qualitative indicator of past silicic acid utilisation, but uncertainties are associated with its quantitative application (chapter 5). In addition, even if diatom $\delta^{30}$Si data confidently showed that large amounts of preformed silicic acid existed in the glacial Southern Ocean, the degree to which such excess silicic acid was exported into the lower latitude thermocline via Intermediate and Mode waters (cf. Crosta et al., 2007; Came et al., 2008; Xie et al., 2012) needs to be assessed, as this is the pre-requisite for the climate feedback mechanism, proposed in the silicic acid leakage hypothesis (Brzeziński et al., 2002; Matsumoto and Sarmiento, 2008). The recent work of Griffiths et al. (2013) represents an important milestone in the field. They used the $\delta^{30}$Si composition of siliceous sponges to trace past silicic acid concentrations in Antarctic Intermediate Water. During Marine Isotope Stage 4, a time during which elevated preformed silicic acid concentrations in the Southern Ocean are suggested (chapter 5), they found elevated silicic acid concentrations in this water mass, thus providing the first direct evidence of silicic acid leakage. The synergies between records of Antarctic diatom opal $\delta^{30}$Si, Subantarctic/Subtropical sponge $\delta^{30}$Si, and low-latitude opal productivity (e.g. $^{231}$Pa/$^{230}$Th; Bradtmiller et al., 2006) can thus substantially contribute to a holistic picture of the marine silicon cycle of the past.

The silicon isotope composition of radiolarian opal and the potential information their silicon
isotope composition may provide, is a relatively unexplored field. Since radiolarians are not directly dependent on sunlight, they are able to dwell deeper in the water column than diatoms (Takahashi, 1991). Thus, there is potential for the $\delta^{30}\text{Si}$ of radiolarian opal to provide information on the silicon cycle beyond the surface mixed layer. For instance, as the interpretation of diatom $\delta^{30}\text{Si}$ depends on $\delta^{30}\text{Si}$ of the source silicic acid (chapter 5), radiolarian opal $\delta^{30}\text{Si}$ may be sensitive to changes in water column stratification and hence supply rates of silicic acid to the surface mixed layer. Based on such theoretical considerations, radiolarian $\delta^{30}\text{Si}$ shows good prospects for being an informative tracer of past changes in the marine silicon cycle.

Down-core variations of diatom opal $\delta^{30}\text{Si}$ and diatom-bound $\delta^{15}\text{N}$ from the Antarctic sector of the Southern Ocean show coherent but opposing trends for at least the last 30 ka (De La Rocha et al., 1998; Sigman et al., 1999; Shemesh et al., 2002; Brzezinski et al., 2002; Crosta and Shemesh, 2002; Jacot Des Combes et al., 2008; Robinson and Sigman, 2008; Schneider-Mor et al., 2008; Horn et al., 2011; chapter 5). It has been suggested that in the glacial Southern Ocean nitrogen was more limiting than silicon (Brzezinski et al., 2002), which has been ascribed to a reduced demand of diatoms for silicon in response to the limited availability of iron (e.g. Horn et al., 2011). A reduced demand for silicon over nitrogen under iron-replete conditions has been observed in laboratory culturing experiments (e.g. Takeda, 1998; Marchetti and Harrison, 2007; Bucciarelli et al., 2010), but also in situ iron fertilisation experiments (e.g. Takeda, 1998; Brzezinski et al., 2003; Baines et al., 2010). While these studies focused on variations of the elemental Redfield proportions of silicon and nitrogen in diatoms, there is no study yet that has directly linked such variations to changes in the silicon and nitrogen isotopic composition of the opal. For instance, laboratory culturing experiments under variable iron conditions would allow quantification of the amount of iron that is needed to cause a certain shift in the silicon and nitrogen isotopic composition of the opal. These results might then allow an estimate of the amount of iron that is required to explain the observed down-core variations in glacial diatom $\delta^{30}\text{Si}$ and $\delta^{15}\text{N}$ in the Southern Ocean, and whether the required amounts are coherent with the increased deposition of atmospheric dust during the glacial (e.g. Wolff et al., 2006). If not, then other sources of iron, such as meltwater-derived iron (Bhatia et al., 2013), may have been more important than previously thought. It is also conceivable that processes other than increased iron fertilisation, that have not been considered yet, may have played an important role in the decoupling of silicon and nitrogen, and ultimately the efficiency of the biological pump.
References


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