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

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Abstract

The relative importance of biological and physical processes within the Southern Ocean for the storage of carbon and atmospheric pCO\(_2\) on glacial-interglacial timescales remains uncertain. Understanding the impact of surface biological production on carbon export in the past relies on the reconstruction of the nutrient supply from upwelling deep-waters. In particular, the upwelling of silicic acid (Si(OH)_4) is tightly coupled to carbon export in the Southern Ocean via diatom productivity. Here, we address how changes in deep-water Si(OH)_4 concentrations can be reconstructed using the silicon isotopic composition of deep-sea sponges. We report \(\delta^{30}\)Si of modern deep-sea sponge spicules and show that they reflect seawater Si(OH)_4 concentration. The fractionation factor of sponge \(\delta^{30}\)Si compared to seawater \(\delta^{30}\)Si shows a positive relationship with Si(OH)_4, which may be a growth rate effect. Application of this proxy in two down-core records from the Scotia Sea reveals that Si(OH)_4 concentrations in the deep Southern Ocean during the Last Glacial Maximum (LGM) were no different than today. Our result does not support a coupling of carbon and nutrient build up in an isolated deep-ocean reservoir during
the LGM. Our data, combined with records of stable isotopes from diatoms, are only consistent with enhanced LGM Southern Ocean nutrient utilization if there was also a concurrent reduction in diatom silicification or a shift from siliceous to organic-walled phytoplankton.

Keywords: Porifera, spicule, silicic acid, deep-water, silicon cycle, glacial
1. Introduction

Debate still surrounds the relative importance of physical and biological mechanisms behind glacial-interglacial variations in atmospheric carbon dioxide (pCO$_2$; reviewed by Sigman and Boyle, 2000). The Southern Ocean has been implicated in the regulation of greenhouse gases through both types of mechanism. Firstly, a physical reduction in the ventilation of deep waters due to greater glacial sea-ice cover and ocean stratification, enhanced in a cooler ocean, would result in less outgassing of CO$_2$ to the atmosphere (e.g. de Boer et al., 2007). Secondly, an increase in biological export, accompanied by enhanced burial of carbon, would also reduce atmospheric pCO$_2$ during glacial periods (e.g. Kohfeld et al., 2005). A “biogeochemical divide” has been proposed, whereby biological export in the Antarctic Zone of the Southern Ocean regulates CO$_2$ directly, whereas export in the Subantarctic Zone controls global preformed nutrient supply, such that different regions around Antarctica may drive or respond to climate change by different mechanisms (Marinov et al., 2006). An understanding of Southern Ocean nutrients is clearly required to distinguish the physical and biological mechanisms that impact pCO$_2$ over glacial-interglacial timescales.

The concentration of silicic acid, [Si(OH)$_4$], in deep-waters is governed by tectonics and silicate weathering on long timescales (>10$^4$ years) and by ocean productivity and ocean circulation on glacial-interglacial timescales (10$^3$-10$^4$ years; Ragueneau et al., 2000; Falkowski et al., 2004). As such the Si cycle is a synergistic driver of, and respondent to, the carbon (C) cycle and global climatic change. In the modern surface ocean, biological precipitation of amorphous silica (opal) by diatoms is the dominant process that removes
Si(OH)$_4$ from seawater, efficiently transporting silica and organic C to the seafloor. The partitioning of C and Si between the surface and deep-ocean is controlled by the export and remineralization of this biological material relative to vertical mixing rates (Toggweiler et al., 1999; Ragueneau et al., 2000).

Diatom blooms rely on upwelling sources of Si(OH)$_4$ because efficient utilization strips almost all of the Si from surface waters (Ragueneau et al., 2000). The nutrient composition of upwelling waters, in particular the ratio of Si to other major nutrients, plays a strong role in the population structure of phytoplankton growing in surface waters and the biological pumping of C to deep-water (Yool and Tyrell, 2003; Falkowski et al., 2004). Furthermore, reduced vertical mixing, or enhanced stratification, results in an increase in deep-water C, and a corresponding reduction in atmospheric pCO$_2$. (Toggweiler, 1999).

Quantifying changes in the Si(OH)$_4$ content of deep-water is an important step towards understanding the link between the sequestration of C, Si and other nutrients over glacial cycles (Brzezinski et al., 2002; Matsumoto et al., 2002). The Southern Ocean is a key location for studying paleo-Si(OH)$_4$ because of the regional and global importance of Si-based productivity and its potential sensitivity to well documented proximal climatic changes (Anderson et al., 2002).

The silicon isotopic composition ($\delta^{30}$Si) of biogenic opal provides a direct method for quantifying seawater Si(OH)$_4$ budgets (de la Rocha et al., 1997; de la Rocha, 2003; Beucher et al., 2007). Siliceous sponges (Phylum Porifera, Classes Demospongea and Hexactinellida) produce needle-like skeletal elements, spicules, composed of hydrated amorphous silica. Uptake of ambient Si(OH)$_4$ occurs via a sodium transporter, which
resembles active transporters isolated from other metazoans (Schroeder et al., 2004).

Biosilicification in sponges is controlled by two enzymes silicatein, which promotes condensation reactions, and silicase, which dissolves silica (Müller et al., 2007). A previously published study shows that the uptake of Si(OH)₄ results in fractionation of Si isotopes, such that spicules have some of the lightest δ³⁰Si signatures known in natural systems (de la Rocha, 2003). The δ³⁰Si of sponge spicules is a potential proxy to quantify whole ocean changes in Si cycling over timescales longer than the residence time of Si in the oceans (~15 ka), as well as changes in intermediate and deep-water Si(OH)₄ composition on shorter timescales (de la Rocha, 2003; de la Rocha and Bickle, 2005).

Here, we investigate the Si isotope composition of modern sponges and ambient waters from the Southern Ocean, and find a clear relationship between [Si(OH)₄] and sponge spicule δ³⁰Si and Si isotope fractionation. We have then applied this calibration to sponge spicules picked from two cores in the Scotia Sea (Figure 1) to determine if [Si(OH)₄] changed in response to the major climatic shifts since the Last Glacial Maximum (LGM).

2. Methods

2.1. Field setting and sample materials

The modern day Southern Ocean has large [Si(OH)₄] gradients (Pollard et al., 2002) and an abundance of living sponges. Therefore, we have used a transect across the Drake Passage and Scotia Sea to undertake a calibration of sponge δ³⁰Si fractionation as a function of ambient [Si(OH)₄]. We focus our reconstruction of past Si(OH)₄ on the Scotia
Sea, which plays a disproportionately important role in global oceanography. It contains both Antarctic and Subantarctic Zone waters, and acts as a bathymetric channel for the Antarctic Circumpolar Current (ACC) and major oceanographic fronts. This flow results in intense mixing and modification between the well ventilated and Si-rich Weddell Sea derived deep-waters and the rest of the global oceans (Naveira Garabato et al., 2002). For the calibration, we collected and analysed living specimens from a north-south transect across the Scotia Sea and Drake Passage, encompassing a range of $[\text{Si(OH)}_4]$ (12 to 120 $\mu$M) and depths (300 to 2500 m; Figure 1A, 1B, Table 1). The $[\text{Si(OH)}_4]$ increases polewards and with depth through a combination of water-mass mixing, remineralization and an isopycnal gradient (Figure 1B; Pollard et al., 2002). Sponges were collected aboard the R/V Nathaniel B. Palmer by either benthic trawl or dredge, and dried or frozen for transit (April-May 2008). Water samples for Si(OH)$_4$ analysis were collected in niskin bottles attached to deep-water CTD casts and a towed camera system (WHOI TowCam), filtered immediately through 0.4 $\mu$m polycarbonate membranes (Whatman) and stored in pre-cleaned HDPE bottles.

Additional samples were collected from coastal West Antarctic Peninsula (Figure 1) and the North Atlantic. Core material was obtained from two cores in the Scotia Sea, from south of the ACC (Piston core PC034, 1652m) and within the ACC (Kaston core KC081, 3662m; Figure 1; Table 2). All core material was sampled from the British Antarctic Survey.

2.2. Laboratory methods
The modern spicules were initially separated from organic matter by repeatedly heating and sonicating in concentrated HNO₃ and H₂O₂ (Analar). Sediment grains were removed by picking until visual inspection showed the spicules to be clear of detritus. The spicules were then cleaned of any remaining organic matter and surface contaminants in a class 100 laboratory by heating in 50% quartz-distilled HNO₃/10% quartz-distilled HCl. Sediment samples were deflocculated in sodium hexametaphosphate (5% w/v), sieved at 200 μm and rinsed thoroughly in 18 MΩ.cm Milli-Q water. Approximately 20-30 spicules were hand picked, rinsed with reagent grade methanol to remove clays, and heated with H₂O₂ to remove organic matter.

The sponge spicules were then dissolved by heating in 0.2 M NaOH (Analar) at 100 °C for 3 days (Cardinal et al., 2007). The solution was then acidified to pH~2 using 0.2 N thermally distilled HCl. Quantitative separation of Si from major ions was achieved using a cation exchange resin (BioRad AG50W-X12; Georg et al., 2006), and diluted to 300-600 ppb Si depending on machine sensitivity.

The Si isotope analyses were carried out for Si isotopes ²⁸Si, ²⁹Si and ³⁰Si using the NuPlasma HR MC-ICP-MS (University of Oxford) in medium resolution mode. The samples were bracketed with a concentration-matched NBS28 standard (Georg et al., 2006, 2009; Reynolds et al., 2007), and isotope ratios calculated according to Equation 1.

$$\delta^iSi = \left( \frac{R_{num}}{R_{nbs28}} - 1 \right) \times 1000$$ (1)
Each sample was measured 8 times on the mass spectrometer, and mean ratios calculated. Standards were checked before every batch run to ensure accuracy (either “diatomite” with $\delta^{30}\text{Si} = +1.26\%\text{oo} \ (0.08)$, $\delta^{29}\text{Si}= +0.65\%\text{oo} \ (0.03)$ or “Big Batch” with $\delta^{30}\text{Si} = -10.67\%\text{oo} \ (0.08)$, $\delta^{29}\text{Si} = -5.48\%\text{oo} \ (0.05)$, parentheses indicating $2\sigma_{\text{SE}} = 2\sigma_{\text{SD}}\sqrt{n}$; Reynolds et al., 2007). Repeat dissolutions, and repeat aliquots of the same dissolution, indicate an adequate level of reproducibility comparable to previous studies (repeat measurements agree within $\sim\pm0.15\%\text{oo}$). Subsamples from the same modern sponge specimens were also analysed using in-line gas fluorination followed by Isotope Ratio Mass Spectroscopy (IRMS; Finnigan MAT 253) by M. Leng at the NERC Isotope Geosciences Laboratory (NIGL, Nottingham, UK), yielding $\delta^{30}\text{Si}$ values within error of the measurements made at the University of Oxford by MC-ICP-MS.

The $[\text{Si(OH)}_{4}]$ of water samples from the site of sponge collection were analysed at the WHOI nutrient facility, and were consistent with Southern Ocean data from existing databases (Schlitzer, 2000; Garcia et al., 2006). If there were no water samples collected in the vicinity of the sponges, then $[\text{Si(OH)}_{4}]$ was estimated from existing data (Schlitzer, 2000; Garcia et al., 2006). For isotopic analysis, Si was quantitatively separated from seawater using a modified Mg co-precipitation technique (Cardinal et al., 2005; Reynolds et al., 2006). 2% by volume of 1M NaOH (Aristar) was added to 10-15 ml of seawater to precipitate Mg(OH)$_2$, shaken, left for 1 hour, centrifuged and the supernatant transferred to a new, clean tube. To ensure quantitative yields, the process was repeated twice adding 1% by volume NaOH to the supernatant each time. The precipitate was washed twice with $\sim$0.001M NaOH to remove anions, which can suppress intensity on the MC-ICP-MS.
chromatography was used to show the precipitate wash effectively removed excess Cl\(^{-}\) and F\(^{-}\) ions. The precipitate was then dissolved in 5% thermally distilled HNO\(_3\) or HCl. The Si was then purified using cation exchange as above; as before, matrix tests show the resin effectively removes Na and other cations. The \(\delta^{30}\)Si was measured using the same protocol as for the spicules.

3. Results and discussion

3.1. Modern calibration

Modern Southern Ocean sponge \(\delta^{30}\)Si ranges from -0.70\% to -4.13\% (Figure 2A; Table 3), in agreement with the limited published data from archived sponges (de la Rocha, 2003). A three isotope plot of all the silicon isotope data collected (\(\delta^{29}\)Si vs. \(\delta^{30}\)Si) has a slope of 0.51 (±0.01) calculated by model II regression (parentheses denotes the 95% confidence interval), which is consistent with that anticipated for kinetic equilibrium (0.509 or 0.511 depending on whether Si or SiO\(_2\) undergoes fractionation; Reynolds et al., 2007; Figure 2C). We find an inverse linear functional relationship between sponge \(\delta^{30}\)Si and [Si(OH)\(_4\)] \((r^2 = 0.75)\) according to Equation 2 (parentheses denotes the 95% confidence interval, such that a single measurement of \(\delta^{30}\)Si\(_{sponge}\) can give a Si(OH)\(_4\) concentration to approximately ±20 \(\mu\)M).

\[
[\text{Si(OH)}_4] = -30.3(\pm8.2)\delta^{30}\text{Si}_{\text{sponge}} - 13.79 \quad (2)
\]

The measured seawater \(\delta^{30}\)Si\(_{\text{Si(OH)}}\) in the collected waters agree well with modeled (Table 4; Wischmeyer et al., 2003; Reynolds, 2009) and published data from other sectors of the
Southern Ocean (de la Rocha et al., 2000). Our $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ values were used to calculate a fractionation factor, $\epsilon$ (Equation 3; de la Rocha, 2003), which ranges from -2.5 to -5.3‰ and increases with ambient Si(OH)$_4$ ($r^2=0.56$; Figure 3A).

$$\epsilon \approx \delta^{30}\text{Si}_{\text{sponge}} - \delta^{30}\text{Si}_{\text{Si(OH)}_4}$$ (3)

Subsamples from the same specimen, and of two co-existing specimens of the same species, show $\delta^{30}\text{Si}$ is homogeneous within and between individuals bathed in the same water mass (Figure 2B). We cannot rule out a -0.5‰ species-specific offset in fractionation, but it is small compared to the effect of environmental controls (~4‰; Figure 2A).

Other factors that are known to influence biomineralization co-vary with [Si(OH)$_4$] in the Southern Ocean (e.g. temperature and pH; Foo et al., 2004). However, the samples from coastal West Antarctic Peninsula and the deep North Atlantic show similar isotope fractionations for a given [Si(OH)$_4$] compared to sponges from the deep Southern Ocean despite being collected under very different temperature, salinity and pH conditions (Figure 3B-D). Consistent with growth under low Si(OH)$_4$ conditions, and in line with our data, shallow-water sponges from a low nutrient tropical shelf show relatively heavy isotopic compositions ($\delta^{30}\text{Si}_{\text{sponge}}$ from -2 to +0.5‰; Vroon et al., 2004). Our interpretation that [Si(OH)$_4$] is the dominant control over $\delta^{30}\text{Si}_{\text{sponge}}$ appears to hold in a variety of oceanographic settings, providing a robust proxy for paleo-[Si(OH)$_4$].

The environmental control over $\delta^{30}\text{Si}$ in sponges is likely to be a physiological growth rate response to varying ambient Si(OH)$_4$ concentrations because $\epsilon$ is variable, and
correlates with Si(OH)$_4$ (Figure 3A). This control is not unexpected because silicification is known to depend on Si(OH)$_4$ availability. Sponges produce different types of spicules under Si limiting and replete conditions (Maldonado et al., 1999). Further, sponge culture studies show there is a positive correlation between Si(OH)$_4$ availability and uptake rates, and no apparent relationship with temperature (Frølich & Barthel, 1997). If the fractionation process occurs at the site of Si uptake, greater uptake rates may lead to a greater fractionation. Alternatively, Si(OH)$_4$ availability may control the internal biochemical pathways involved during silicification, which may in turn determine isotopic fractionation. For example, ambient Si(OH)$_4$ is a known modulating factor that regulates the expression of silicatein and silicase, and induces expression of genes for other enzymes involved in biosilicification (Perovic-Ottstadt et al., 2005; Müller et al., 2007). Further work is required to understand the biosilicification process and, in particular, the reactions that result in isotopic fractionation.

The Si isotope fractionation observed during the formation of sponge spicules is greater than the fractionation observed during silicification of diatom opal ($\varepsilon = -0.8$ to $-2.1\%$; Cardinal et al., 2005, 2007). Although diatoms use uptake transporters and condensation/dissolution enzymes distinct to sponges, the mechanisms are somewhat similar and may be homologous (Foo et al., 2004). However, we suggest the two groups evolved Si acquisition mechanisms, which likely impact Si isotopes differentially, at distinct points in Earth history. Siliceous sponges originated in the Precambrian (Love et al., 2009), with a relatively low affinity for Si (Frølich & Barthel, 1997), at a time when weathering of silicate rocks resulted in high oceanic Si(OH)$_4$ (Siever, 1992). In contrast,
Diatoms evolved in the Jurassic (Sims et al., 2006) with a higher affinity for Si, probably because biological utilization by other siliceous organisms resulted in lower oceanic Si(OH)₄ (Maldonado et al., 1999).

3.2. Downcore data

We use the modern relationship between [Si(OH)₄] and δ³⁰Siₙₐ₃ponge, and analyses of spicules hand-picked from two Scotia Sea sediment cores, to investigate whether deep-water [Si(OH)₄] changed within the ACC on glacial-interglacial timescales, and to address the potential consequences for atmospheric pCO₂ levels in the past.

Our modern core-top sample from piston core PC034 (Figure 4A; δ³⁰Siₙₐ₃ponge = -3.86±0.17‰, ±2σSD) agrees well with the living sponges collected from the southern Scotia Sea, growing in [Si(OH)₄] of approximately 100 μM (Figure 2A, 4B). The youngest section of the northern site (KC081) has been dated at ~6 ka (Figure 4A), so we are unable to measure a core-top sample at the site. In both cores, the Last Glacial Maximum (LGM) value is similar to the modern, suggesting deep-water [Si(OH)₄] was not significantly different at the LGM compared to today at either site (within ~20 μM). The similarity between LGM and modern [Si(OH)₄] in Southern Ocean deep-waters provides insight into processes occurring in different regions of the water column on glacial-interglacial timescales.

The fractionation factor, ε, would be the most appropriate parameter to record because it would account for changes in seawater δ³⁰Si_{Si(OH)₄}. However, δ³⁰Si_{Si(OH)₄} of seawater cannot be constrained directly downcore, and so here we present δ³⁰Siₙₐ₃ponge and
assume that $\delta^{30}\text{Si}_{\text{Si(OH)4}}$ of deep waters is constant over glacial-interglacial cycles in accord
with recent box modeling (Georg et al., 2009).

There are two important caveats when interpreting our downcore data. Firstly, age
models for cores in the Southern Ocean are notoriously challenging due to poor
preservation of benthic foraminifera and other dateable carbonates. Here, we apply the
best dating constraints available, based on radiocarbon measurements and stratigraphic
markers, locating the LGM using the abundance of diatoms and the radiolarian
*Cycladophora davisiana* (Figure 4A). The limited number of tie-points results in an
inherent degree of uncertainty on the age model. Secondly, as is a common problem with
any sedimentary proxy, there is a possibility that core components, such as spicules,
undergo differential transport and are of different ages to surrounding grains. However,
sponges are benthic and, in life, comprise a large proportion of sticky organic matter,
making significant post-mortem transportation of spicules less likely than, for example,
planktonic diatoms or foraminifera. Opal-specific dating methods may resolve any issues
arising from particulate transportation (Ingalls et al., 2004).

3.2.1. Deep processes: the glacial carbon reservoir

A leading hypothesis for the reduced pCO$_2$ during the glacial is the presence of an
isolated reservoir of C-rich water in the Pacific and Southern Oceans (Marchitto and
Broecker 2006; Marchitto et al., 2007). Radiocarbon records from Baja California and the
Equatorial Pacific point towards a deglacial degassing of old C from a reservoir isolated
during the LGM (Marchitto et al., 2007; Stott et al., 2009). Deglacial age deep-sea corals
from the Drake Passage, dated to Heinrich Event 1 (~16.7 ka), also show radiocarbon depletion, but not to such a great extent as the Baja California record (Robinson & van de Flierdt, 2009). Benthic foraminiferal records from the Southern Ocean show very light $\delta^{13}C$ signatures, indicative of a high nutrient content or significant changes in air-sea exchange of inorganic C (Curry et al., 1998; Marchitto and Broecker, 2006; Marchitto et al., 2007). Specifically, there is evidence for a strong vertical $\delta^{13}C$ gradient at approximately 2.5km to the north of the polar front in the South Atlantic during the glacial (Hodell et al., 2003). However, records of benthic foraminiferal Cd/Ca, a proxy for dissolved phosphate (P), do not support a significant change between the nutrient content of the modern and LGM deep Southern Ocean (Boyle, 1992). This discrepancy has led to considerable debate in the paleoceanographic community surrounding the continued presence of nutrient-poor North Atlantic derived waters in the ACC. One possibility, consistent with a continued presence of NADW in the Glacial Southern Ocean, is that the light $\delta^{13}C$ was associated either with changes in air-sea exchange of C (Broecker, 1993; Lynch-Stieglitz & Fairbanks, 1994; Marchitto & Broecker, 2006) or organic matter with high C:P content (Arrigo, 1999; Elderfield & Rickaby, 2000). Alternatively, several studies have highlighted caveats and artifacts associated with both $\delta^{13}C$ in regions of high organic matter accumulation rate (Mackensen et al., 1993) and Cd/Ca where significant dissolution has occurred (McCorkle et al., 1995). When outliers in Southern Ocean datasets of individual foraminiferal shells of a single benthic species, potentially arising from changes in productivity in high organic accumulation rate regions, are removed the resulting “representative” $\delta^{13}C$ brings $\delta^{13}C$ more inline with Cd/Ca. These data, together
with $^{231}$Pa/$^{230}$Th records of water mass export (Yu et al., 1996), are consistent Glacial
NADW entering the ACC followed by transportation to the North Pacific in a similar
fashion to the modern ocean (Matsumoto & Lynch-Stieglitz, 1999).

Our $\delta^{30}$Si results from KC081, situated greater than 3km, below the glacial $\delta^{13}$C gradient,
(Hodell et al., 2003), do not show a change between the modern and the LGM, so we infer
that, any isotopically light C in the deep Southern Ocean was not associated with higher
levels of Si(OH)$_4$. Furthermore, our results are consistent with the benthic foraminiferal
Cd/Ca records, suggesting there were insignificant changes in both refractory and labile
nutrient concentrations in Southern Ocean deep-waters during the LGM. In this case, the
light $\delta^{13}$C signature of the LGM Southern Ocean could have been caused by a reduction in
air-sea exchange of inorganic C (CO$_2$) due to poor ventilation, or changes in the surface
temperature or residence time of subducting deep waters (e.g. Broecker, 1993; Lynch-
Stieglitz & Fairbanks, 1994; Mackensen, 2001). For example, the isolation of a deep-
water mass, due to stratification or sea-ice cover, could lead to a depletion in $\delta^{13}$C and a
decrease in atmospheric CO$_2$ without a concurrent change in nutrients (Toggweiler, 1999).

Alternatively, the light $\delta^{13}$C could originate from the remineralization of organic C
that is not associated with significant quantities of Si(OH)$_4$ or P. This decoupling could be
a result of physiological changes within the diatom populations, or shifts in the
phytoplankton population structure, during the LGM. Firstly, extensive field and
laboratory experiments have shown that diatoms have both lower cellular Si:N and P:N
when grown under Fe replete conditions than when Fe stressed or limited (Timmermans et
al., 2004; Brzezinski et al., 2005; Price, 2005). The higher Fe conditions existing in the
Southern Ocean during glacials, due to enhanced dust supply (e.g. Kohfeld et al., 2005), are thought to promote lower Si:N uptake ratios in diatoms compared to Fe-stressed diatoms growing during interglacials (Brzezinski et al., 2002). Secondly, the non-siliceous dinoflagellate *Phaeocystis* shows a high N:P uptake ratio during modern Southern Ocean blooms. If *Phaeocystis* blooms became more dominant in stratified waters during the LGM (Arrigo, 1999; Elderfield and Rickaby 2000), then export of the associated organic C, and subsequent remineralization in deep-waters, could result in a depletion in δ¹³C and an increase in NO₃ without a concurrent increase in either Si(OH)₄ or P. These two scenarios are not mutually exclusive, and both may have contributed to the nutrient conditions prevailing in the glacial Southern Ocean.

3.2.2. Surface processes: glacial nutrient utilization

In addition to the deep-water signal, our results provide further information about biological utilization in surface waters at the LGM. The Silicic Acid Leakage Hypothesis (SALH) proposes that reduced productivity, due the physiological response of phytoplankton to Fe fertilization, caused a reduction in the Si to N uptake ratio in the Southern Ocean during the LGM (Brzezinski et al., 2002; Matsumoto et al., 2002). According to the SALH, a pool of excess Si(OH)₄ in Antarctic surface waters was exported to lower latitudes, via intermediate water, promoting diatom production at the expense of carbonate-producing coccolithophores. In this scenario, there would be an increase in export of organic C with respect to inorganic C in the low latitudes associated with a rise in ocean alkalinity and lowered atmospheric pCO₂ (Brzezinski et al., 2002; Matsumoto et al., 2002). Diatom δ³⁰Si records show a 0.5‰ change across the deglaciation, which have
been interpreted as a reduction in the fraction of Si(OH)$_4$ utilized in the Antarctic (de la Rocha et al., 1997), subantarctic and subtropics during the LGM (Beucher et al., 2007). Since whole ocean $\delta^{30}$Si changes are unlikely over this timescale (Georg et al., 2009), our new record demonstrates that the decrease in Si(OH)$_4$ surface depletion in the subantarctic region (Beucher et al., 2007) was not caused by changes in the [Si(OH)$_4$] concentration of upwelling waters (Figure 4B). Instead it must have been a consequence of either an increase in upwelling intensity or reduced surface utilization. We argue above that the geochemical evidence points towards an increase in stratification in the ACC south of the polar front during the LGM, so the diatom $\delta^{30}$Si data is best explained by changes in the efficiency of surface utilization (Beucher et al., 2007). Records of nitrogen isotopes ($\delta^{15}$N) of diatom-bound organic matter indicate an increase in utilization of nitrate in surface waters (Sigman et al., 1999; Robinson et al., 2004). This can be reconciled with the diatom $\delta^{30}$Si data if there was a large-scale physiological change in diatoms reducing Si:N and P:N uptake ratios (e.g. Brzezinski et al., 2005), or an increase in productivity by non-siliceous phytoplankton, such as *Phaeocystis* (Arrigo, 1999; Elderfield and Rickaby, 2000).

**3.2.3. Implications for glacial pCO$_2$**

Our new sponge $\delta^{30}$Si data, when combined with other geochemical proxies, bring new insight into the mechanisms behind the lower glacial atmospheric pCO$_2$. Deep-water C and macronutrients are decoupled on glacial-interglacial timescales as a result of physical processes, such as ocean stratification or sea-ice cover, which lock-up C in the deep ocean and lower atmospheric pCO$_2$ (Toggweiler, 1999; Stephens and Keeling, 2000).
An increase in the biological export of C from the surface to the deep ocean is consistent with all of the currently available data if there was either a concurrent decrease in diatom silicification, or a shift away from siliceous to organic-walled phytoplankton production, in the Southern Ocean. Whilst this could increase the C:Si and C:P content of the deep ocean, without significant mineral ballast a lightly-silicified diatom or *Phaeocystis* dominated biological pump would not export as C efficiently as one dominated by heavily-silicified diatoms (Jin et al., 2006), limiting the impact on atmospheric pCO$_2$. However, the excess Si(OH)$_4$ resulting from a decrease in surface utilization in the Southern Ocean could have been exported away from the subantarctic via mode waters without impacting the deep-water Si inventory. This would have the potential to impact atmospheric pCO$_2$ by increasing the relative productivity of diatoms in the lower latitudes (Matsumoto et al., 2002; Bradtmiller et al., 2007).

3.2.4. The deglaciation

During the deglacial (after ~ 18 kyr), our records indicate a depletion in deep-water [Si(OH)$_4$] both within and south of the ACC (Figure 4B). In the late Holocene, deep-water [Si(OH)$_4$] recovers to modern values. Given the uncertainty on the age models, we cannot pin point the exact timing of these changes but the decline is a robust observation in both cores. Our best estimate for the maximum rate of change of deep-water [Si(OH)$_4$] is approximately 10 μM ky$^{-1}$

We hypothesize two possible mechanisms behind this decline in deep-water Si(OH)$_4$: large scale changes in nutrients arising from decomposition of biogenic particles
in the deep Southern Ocean ("remineralized nutrients") or localized changes in unutilized nutrients subducted during deep-water formation ("preformed nutrients"; Marinov et al., 2006). Firstly, our data are consistent with storage of Si(OH)_4 in the form of a large-scale opal deposition in the Southern Ocean during the deglacial (10-16 kyr), caused by wind-driven upwelling of water enriched in Si(OH)_4 relative to the surface. Enhanced opal fluxes during the deglaciation, coupled with ^231^Pa/^230^Th activity ratios, have been observed in Pacific and Atlantic Sectors of the Southern Ocean and equatorial regions (Anderson et al., 2009). Such a significant and widespread burial of opal could have resulted in a drop in deep ACC remineralized Si(OH)_4, whilst the enhanced upwelling drove a concurrent rise in pCO_2 (Anderson et al., 2009). The decline in deep-water [Si(OH)_4] would have led to a negative feedback, by limiting the amount of productivity that could be supported by upwelling water and an eventual restoration of export production rates, opal fluxes and [Si(OH)_4] gradients over time. Such changes in remineralized nutrients cannot change global deep-water [Si(OH)_4] over timescales of less than the residence time of Si in the whole ocean (~15 ky; Georg et al., 2009). However, we constructed a simple one-box model for the deep Southern Ocean alone (south of 50°S, > 400 m depth, area ~ 25 x 10^{12} m^2), using a mean modern [Si(OH)_4] of 100 µM and mean depth of 4000 m (Garcia et al., 2006), and modern opal accumulation fluxes of ~ 0.2 mol Si m^{-2} yr^{-1} (Pondaven et al., 2000). Using this model, we estimate changes in the opal burial rate relative to Si inputs of ~ 20% (less than observed in core TN057-13-4PC; Figure 4b, Anderson et al., 2009) could cause changes of the order of 10 µM in 1000 years, which are sufficient to explain our observations.
Alternatively, the rapid rates in change indicate the decline in deep-water [Si(OH)$_4$] during the deglaciation was at least in part a result of localized inputs of preformed nutrients. For example, the retreat of the Weddell Sea ice shelf during the deglacial and early Holocene “Hypothermal” may have changed deep-water formation processes and led to a decline in the input of highly Si-enriched Weddell Sea Deep Water (WSDW) into the ACC (Yoon et al., 2007). This could explain both the rapid decline in deep-water Si(OH)$_4$ and the apparent divergence in the records between ~6-10 ky (higher [Si(OH)$_4$] from the southern core compared to the northern core; Figure 4B). Resumption of WSDW input to the ACC could be in part responsible for the recovery in deep-water Si(OH)$_4$ in the later Holocene. Future research should focus on constraining this climatically important time, in order to understand the response of Southern Ocean deep-water circulation during periods of global warming.

4. Summary and conclusions

In summary, we show the potential for combined $\delta^{30}$Si records from diatoms and sponges to constrain the surface and deep components of the Si biological pump. We investigate fractionation by modern deep-sea sponges, and find the $\delta^{30}$Si of spicules and fractionation with respect to ambient seawater correlate with the ambient [Si(OH)$_4$]. We then apply this calibration to two downcore records from the Scotia Sea. Our results show that the deep-waters of the LGM Southern Ocean were not enriched in Si(OH)$_4$, suggesting that the isolated reservoir of old, isotopically depleted C was not associated with an increase in either Si(OH)$_4$ or P. Instead, the Southern Ocean resulted in lower atmospheric $pCO_2$ during the glacial largely due to reduction in air-sea exchange of C via a physical
process. If there was an enhanced glacial biological pump in the Southern Ocean, it was likely to have been dominated by lightly-silicified diatoms or organic-walled phytoplankton (e.g. *Phaeocystis*) resulting in a concurrent increase in surface nitrate utilization, and a change in deep-water nutrient ratios that may not have been associated with a considerable increase in pump efficiency. Utilization of Si-rich upwelling waters by diatoms was lower during the LGM, providing a surplus of Si(OH)$_4$ that could then be exported to lower latitudes via intermediate waters, where enhanced export production could lower atmospheric CO$_2$. During the deglaciation, there is a robust and significant decrease in deep-water Si(OH)$_4$, which could be associated with a pulse of opal burial linked with wind-driven upwelling and concurrent rise in pCO$_2$, or a change in water mass inputs.

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Figure 1: A) Location of sample sites in the Southern Ocean and coastal Antarctica. Grey stars indicate modern sponge sample sites; grey squares indicate deep-water samples; grey dotted circles show cores PC034 and KC081. Map production by K. Scanlon (USGS).

B) Dissolved silicic acid concentrations from across the Drake Passage. Drawn using Ocean Data View (Schlitzer, 2000).

Figure 2: A) The relationship between modern sponge silicon isotope composition and ambient seawater Si(OH)$_4$ concentration ($r^2=0.75$; Equation 2). Filled symbols show values for Hexactinellid sponges; open symbols show values for Demosponges. There is no consistent difference between the two classes of sponges, although there may be species-specific fractionation (~0.5%). Error bars show 2$\sigma_{SD}$.

B) Isotopic homogeneity between individuals of the same species from one locality, and within an individual. The black symbols show duplicate measurements of spicule silicon isotopes taken from three different specimens; the white triangles show the silicon isotopic composition of two specimens of Rosella collected from the same site; the white circles show the silicon isotopic composition of two different types of spicules from the same specimen (dermal and perenchymal). Error bars show 2$\sigma_{SD}$. 
C) A three-isotope plot for all sponge samples. The equation was calculated using model II regression, and numbers in parentheses indicate 95% confidence intervals of the slope and intercept respectively. The relationship between $\delta^{28}\text{Si}_{\text{sponge}}$ and $\delta^{30}\text{Si}_{\text{sponge}}$ is consistent with mass dependent fractionation under kinetic equilibrium. Error bars show $2\sigma_{SD}$.

Figure 3: Fractionation of silicon isotopes by sponges. The black circles show the fractionation by sponges from the deep Southern Ocean; the grey squares show the fractionation by sponges from the West Antarctic Peninsula; the white triangles show the fractionation by sponges from the deep North Atlantic (assuming Atlantic deep water $\delta^{30}\text{Si}_{\text{Si(OH)}_4} = 1.6\%$; Reynolds, 2009). Fractionation is plotted against ambient A) Si(OH)4 concentrations; B) salinity; C) temperature and D) pH (data from the British Antarctic Survey and Garcia et al., 2006). Error bars are propagated from $\pm 2\sigma_{SD}$ of $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ and $\delta^{30}\text{Si}_{\text{sponge}}$.

Figure 4: A) Age models for the two cores based on magnetic susceptibility (dashed lines) and diatom abundances (squares). Note for PC034, the shallower peak in magnetic susceptibility has been interpreted as showing the Antarctic Climate Reversal. For KC081, age constraints are also available from the occurrence of the radiolarian Cycladophora davisiana (triangles), which are abundant in glacial sediments, and corrected radiocarbon ages (indicated by black arrows) showing core top $\sim$ 6.3 ka, 0.23 mbsf $\sim$ 11.3 ka and 1.59 mbsf $\sim$ 23.5 ka (NERC Publication Code AA-28113-5). Data and interpretation from C. Allen (BAS). Also shown are locations of the cores with respect to major oceanographic fronts, although these can vary by several degrees in the modern setting (SAF = Sub-Antarctic Front; PF = Polar Front; SACCF = Southern Antarctic Circumpolar Front; SB = Southern Boundary of the ACC, adapted from Naveira Garabato et al., 2002). White symbols correspond to the northern core (KC081) and black symbols to the southern core (PC034).

B) Composition of sponges (error bars show $2\sigma_{SD}$) and reconstructed deep-water Si(OH)$_4$ concentrations (95% confidence intervals $\sim$ 20 $\mu$M; Equation 2). White symbols correspond to the northern core (KC081) and black symbols to the southern core (PC034). The white box shows $\delta^{30}\text{Si}$ of modern sponges found near KC081; the black box shows $\delta^{30}\text{Si}$ of modern sponges found near PC034. The age model is based on the information in A). Also shown: opal flux and $^{231}\text{Pa}/^{230}\text{Th}$ from core TN057-13-4PC from south of the Polar Front in the Atlantic Sector (Anderson et al., 2009); EPICA ice core records of pCO$_2$ and $\delta$D, a proxy for local temperature (Indermüle et al., 1999; Fluckiger et al., 1999; Monnin et al., 2001, 2004).
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Table 1: Samples used in the modern calibration collected from the Southern Ocean. CRS-956 was collected by R. Waller (University of Hawaii) from near Anvers Island; RB-Mycale was collected by J. Berman (BAS) from near Adelaide Island.

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Table 2: Locations of cores used in this study.

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Table 3: Silicon isotopic composition of modern sponge spicules. Temperature, salinity, pH and nutrient values courtesy of WHOI, BAS, Palmer LTER, WOCE (Schlitzer, 2000) and World Ocean Atlas 05 (WOA05; Garcia et al., 2006). Numbers in parentheses are 2(σ/n). *δ30Si is the expected δ29Si value calculated assuming mass dependent fractionation:

\[ *δ^{30}Si = 0.51 \times δ^{30}Si_{sponge} \]

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<td>62.14</td>
<td>300</td>
<td>11.8</td>
<td>1.76 (0.05)</td>
</tr>
<tr>
<td>CAM3-bottom</td>
<td>61.28</td>
<td>56.42</td>
<td>400</td>
<td>95.8</td>
<td>1.03 (0.05)</td>
</tr>
<tr>
<td>CAM7-1500</td>
<td>60.55</td>
<td>65.94</td>
<td>1500</td>
<td>100.6</td>
<td>1.10 (0.06)</td>
</tr>
<tr>
<td>repeat</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.04 (0.06)</td>
</tr>
<tr>
<td>CAM8-600</td>
<td>59.89</td>
<td>68.86</td>
<td>600</td>
<td>40.4</td>
<td>1.40 (0.06)</td>
</tr>
</tbody>
</table>

Table 4: Seawater Si(OH)4 and δ30Si values. Si(OH)4 measured by WHOI nutrient facility; δ30Si measured using a co-precipitation method. Numbers in parentheses are 2(σ/n).
Figure

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\[ \delta^{29}Si = \delta^{30}Si \times 0.51(\pm 0.01) - 0.02(\pm 0.04) \]

\[ r^2 = 0.999 \]