

Silicon isotopes in spring Southern Ocean diatoms: Large zonal changes despite homogeneity among size fractions [☆]

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Abstract

We determine Southern Ocean diatom silicon isotopic signatures and compare them with the previously published data for dissolved silicic acid from the same locations. Five stations distributed along the WOCE SR-3 transect (Australian Sector of the Southern Ocean) in different biogeochemical provinces are presented: Polar Front and Inter-Polar Front Zones (PFZ–IPFZ), Southern Antarctic Zone (AZ-S), Seasonal Ice Zone (SIZ). Total (>0.4 μm), medium-sized (20–70 μm), and large diatoms (>70 μm) were sampled at 2–4 depths in the upper 150 m. Silicon isotopic compositions of biogenic silica (diatoms) and seawater were then measured by MC-ICP-MS, in dry plasma mode using external Mg doping. Results are expressed as δ²⁹Si relative to the NBS28 standard. The isotopic composition of diatoms (δ²⁹Si_{BSi}) is generally homogeneous in the mixed layer and does not exhibit a systematic isotopic fractionation linked to a size effect. δ²⁹Si_{BSi} are always lighter than the ambient dissolved silicic acid signatures (δ²⁹Si_{DSi}), reflecting the preferential uptake of light isotopes by diatoms. A trend of lighter isotopic signatures southward is observed both in diatoms and seawater samples but the δ²⁹Si_{BSi} latitudinal gradient is much steeper. A diatom signature as low as –0.26‰ in the southernmost SIZ station strongly contrasts with the +0.65‰ signature measured on PFZ diatoms. The difference between the ambient dissolved silicic acid and diatom isotopic signatures, Δ²⁹Si, strongly increases southward: from 0.4 in the PFZ up to 1.08‰ in the SIZ. This points toward occurrence of mixing events in the PFZ–IPFZ with diatoms not being under equilibrium with their surrounding water and/or, possible variation of the diatom–seawater equilibrium fractionation factor, ²⁹ε. Apart from mixing, we found that the other parameters likely responsible of such variation are temperature, dissolved Si contents and, Si specific uptake and dissolution rates although at this stage none of these could be clearly recognized as the leading cause. Thorough examination of these parameters through *in vitro* experiments reflecting the extreme Southern Ocean conditions is needed to determine whether the observed latitudinal variation of Δ²⁹Si reflects real variable fractionation or results from non-equilibrium or different time-scales recorded between dissolved and biogenic Si isotopic signatures. Our results also call for the development of more realistic models for describing short-term isotopic composition changes due to e.g. Si consumption, export

[☆] This work is gratefully dedicated to the memory of Roland Wollast as a special recognition of the excellence of his pioneer work on the silicon cycle. His brilliance, intuitive insights, kindness and zest for life are sadly missed.

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and resupply via mixing. Finally, by comparing $\delta^{29}\text{Si}_{\text{BSi}}$ within and below the mixed layer, we could identify a two-step history of the PFZ–IPFZ bloom in contrast to the recently started diatom bloom in the SIZ.

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1. Introduction

The Southern Ocean is a major carbon sink owing to its large physical and biological C uptake capacity (Takahashi et al., 2002; Sabine et al., 2004). Diatoms have a key role in this biological carbon pump because they often dominate the phytoplankton biomass from the Polar Front Zone southward (Kopczynska et al., 2001, submitted for publication) and are prone to be easily exported from the mixed layer because of their opal frustules. Indeed due to the near absence of coccolithophorids south of the Polar Front, they are the leading Antarctic phytoplankton group accountable for this so-called ballast effect (François et al., 2002; Klaas and Archer, 2002). Therefore the silicon cycle in the Southern Ocean and its close link to that of carbon is being increasingly scrutinised (e.g. Ragueneau et al., 2002).

The strong South–North dissolved silicon (also referred to as silicates or silicic acid, H_4SiO_4) gradient from replete conditions in the Seasonal Ice Zone to depleted conditions in the Subantarctic Zone is a prominent feature of the Southern Ocean. It can be explained by the progressive diatom-controlled Si drawdown and export to the intermediate ocean in the course of northward transport of surface waters by Ekman drift (e.g., Trull et al., 2001; Brzezinski et al., 2002; Sarmiento et al., 2004) along with diapycnic mixing (Pollard et al., 2002). While the high-nutrient low chlorophyll (HNLC) modern Southern Ocean, appears to be non-limited in macro-nutrients such as phosphate and nitrate, this is not the case for the micro-nutrient iron (Martin et al., 1990; Boyd et al., 2000). Some uncertainty remains about the relative importance of other limiting factors such as grazing pressure (Becquevort, 1997; Smetacek et al., 2004), light (Lancelot et al., 2000), and Si availability (Nelson et al., 2001; Trull et al., 2001), in comparison to Fe-limitation. Nonetheless, it is clear that Fe stress not only limits phytoplankton growth, but also affects the diatom Si:NO₃ uptake ratio, leading to increased Si-uptake relative to NO₃-uptake (Takeda, 1998; Hutchins and Bruland, 1998). For that reason considerable attention has been paid to the understanding of processes influencing Si:N ratios in solution and diatoms, both

in the natural environment and in laboratory experiments (e.g., Claquin et al., 2002; Brzezinski et al., 2003; Wang et al., 2003; Sarmiento et al., 2004).

Variations of the diatom Si:N ratio through time have been proposed as a possible contributor to changes in global ocean production and ocean–atmosphere partitioning of carbon dioxide. In this “silica leakage hypothesis” iron control of the Si:N ratio supports higher silicate:nitrate ratio of subducting Antarctic Intermediate Waters (AAIW) and Subantarctic Mode Waters (SAMW) during glacial stages (Brzezinski et al., 2002; Matsumoto et al., 2002; Sarmiento et al., 2004). Such changed nutrient ratios would then change the carbonate rain ratio at lower latitude by favouring diatom over coccolithophorid predominance. The N and Si isotopic signatures of diatoms in the Southern Ocean sediments, which are proxies of relative N and Si utilisation, have provided major support to this view (e.g. François et al., 1997; De La Rocha et al., 1998; Sigman et al., 1999a; Brzezinski et al., 2002; Crosta et al., 2005), despite the fact that processes acting on the isotopic signatures of Si and N are far from being constrained, especially as concerns the fractionation factor.

Several studies on seawater and, suspended and sinking particles have addressed controls on N isotope variations in a very thorough way recently, gradually building a more constrained but also a more complex picture of N isotopic fractionation in the ocean, in particular in the Southern Ocean (Sigman et al., 1999b; Altabet and François, 2001; Lourey et al., 2003; Karsh et al., 2003; Needoba and Harrison, 2004; Needoba et al., 2004). The marine isotopic system for Si should be simpler compared to N, because silicon is taken up only as silicic acid (mainly the H_4SiO_4 form; Del Amo and Brzezinski, 1999; Wischmeyer et al., 2003) and mostly by one phytoplankton group (diatoms), while N occurs as different chemical species and is utilised by all phytoplankton groups. Yet, the marine studies on Si isotopes are particularly scarce and the results are sometimes conflicting. This is especially the case for the fractionation factor between diatoms and seawater as well as the assessment of parameters and accurate models to describe the Si isotopic system at the local to ocean basin scale (De La Rocha et al., 1997, 2000; Varela et al., 2004; Milligan et al., 2004; Cardinal et al., 2005a).

This study presents the first dataset of natural Si isotopic composition for size-fractionated diatoms, from the Polar Front to the Seasonal Ice Zones during spring in the Southern Ocean south of Australia (WOCE SR-3 transect). The isotopic compositions of biogenic silica are compared with those for dissolved silicate, obtained for the same cruise and published previously (Cardinal et al., 2005a). We also compare our results with other Southern Ocean data reported by Varela et al. (2004). The results are discussed with reference to the significant findings concerning Southern Ocean physics, diatom silicification and Si isotopes (De La Rocha et al., 1997; Martin-Jézéquel et al., 2000; Claquin et al., 2002; Claquin and Martin-Jézéquel, 2005; Milligan et al., 2004).

2. Sampling and methods

2.1. Sampling

A total of five stations (seven samplings) were sampled along the WOCE SR-3 transect at 139–140°E for Si isotope studies. During the southbound transect we sampled one station each in the Polar Front Zone (PFZ at 53.7°S), the Inter-Polar Front Zone (IPFZ at 56.9°S), the Southern Antarctic Zone (AZ-S at 60.9°S) and two stations in the Seasonal Ice Zone (SIZ at 63.9 and 64.9°S, called SIZ-1 and SIZ-2, respectively). At the time of SIZ-1 sampling (24 Nov. 2001) sea ice coverage was ~40%, whereas for SIZ-2, located 1° latitude further south but

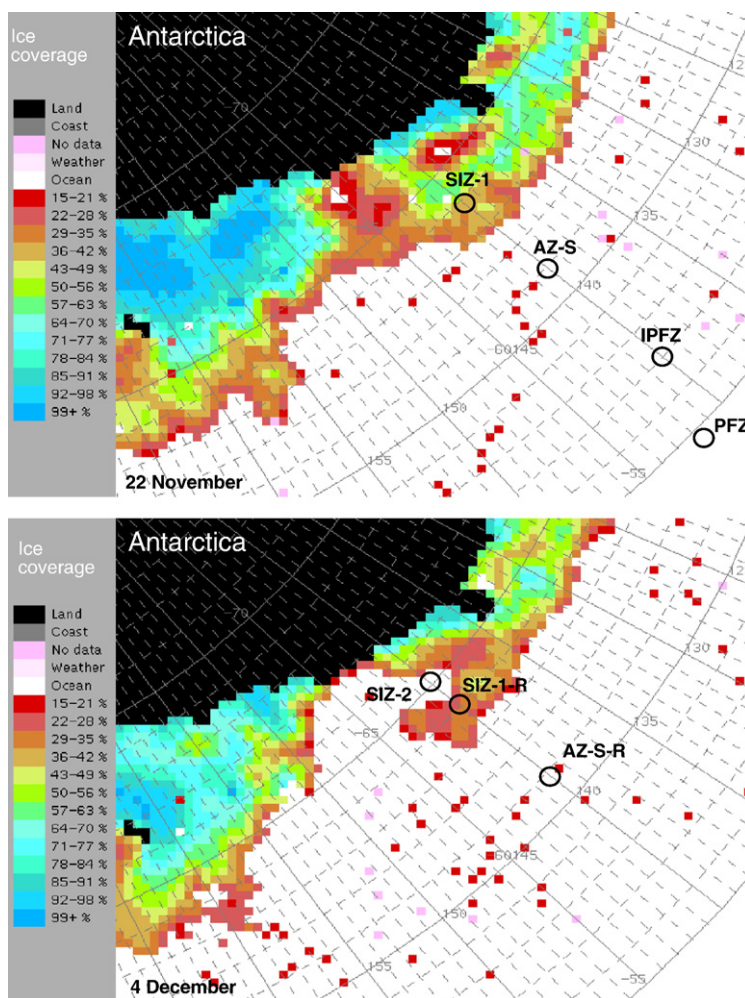


Fig. 1. Sea ice coverage on two sampling dates. 22 November 2001 (upper panel) was 2 days after AZ-S sampling and 2 days before SIZ-1 sampling. On 4th December 2001 (lower panel) SIZ-2 was sampled (one day before SIZ-1-R on the way back). Locations of stations are also indicated on the panel closest to their sampling dates. Actual date for each station is given in Table 2. See text for the definitions of acronyms. Sea ice concentrations from the NASA Earth Observing System SSM/I passive microwave remote sensing 25 × 25 km gridded product from the Distributed Active Archive Center (DAAC) at the U.S. National Snow and Ice Center, University of Colorado, Boulder, USA (data and documentation available on-line at <http://nsidc.org/data/seaiice/pm.html>).

sampled 9 days later, large melting had taken place leaving the area ice-free (Fig. 1). Two repeat stations were sampled on the northbound transect: AZ-S on 8 Dec., and SIZ-1 on 6 Dec., i.e. 17 and 11 days after the first visits, respectively. These latter stations are referred to further as AZ-S-R and SIZ-1-R. Surface ocean physics of the study area are described in detail in Chaigneau et al. (2004).

Particulate silica samples (largely dominated by diatoms) were obtained from both Niskin bottles mounted in a CTD rosette and a submersible electrical pump which returns water to the ship via a hose (Trull and Armand, 2001) hereafter referred to as the “bow pump”.

Seawater from the Niskin bottles was filtered through 0.4 μm polycarbonate membranes in Perspex filtration units under pressure. The air supplying the filtration unit was also filtered with the same type of membranes. The detailed sampling procedure is given in Cardinal et al. (2005b).

In general for the bow pumps, there were two sampling depths within the mixed layer, varying from 5–20 m for the upper part of the mixed layer and between 40 m (64.9°S) and 75 m (53.7 and 60.9°S) for the deeper part of the mixed layer. A third depth was sampled just below the mixed layer (100–120 m) for collecting diatoms and particles recently exported from the mixed layer. Two fractions of phytoplankton (20–70 μm and >70 μm) were sampled by filtering 30 to 1100 l of water in series through 142 mm diameter nylon mesh sieves. These particles were then resuspended and filtered onto 0.4 μm pore size polycarbonate membranes filters. All the filters were then dried at 50 °C before storage for analysis in the laboratory.

2.2. Methods

Biogenic silica (BSi) was extracted by a single leaching step in order to minimise potential lithogenic contamination (40 min at 100 °C with 0.2 M NaOH; Ragueneau et al., 2005). Such alkaline leaching has been shown to extract quantitatively 10–15 μmol BSi for every 4 ml NaOH 0.2 M. To optimise the single leaching step for Si isotopes analyses we first measured precisely BSi contents in a 2 to 3-step alkaline leaching performed on other filters (i.e., different CTD for the >0.4 μm Niskin samples) or different filter aliquots (for the bow pumps). The 1-step leaching for Si-isotopic analyses was then adapted from the previous BSi measurements, i.e. NaOH was added in small excess. Due to natural BSi variation between samples this leaching might not have been 100% quantitative. Our concern for natural Si-isotopic composition was actually to avoid as much as possible lithogenic Si contamination (see below) rather than a strict 100% BSi

recovery. This approach is also supported by the current consensus that chemical dissolution does not fractionate Si isotopes as reported by De La Rocha et al. (1998). Therefore it is unlikely that incomplete BSi dissolution could have led to Si isotopic bias. Al was analysed in this leachate and found to be below ICP-AES detection limit (0.05 ppm) confirming only a negligible contribution, if any, of lithogenic Si. The Si isotopic composition of clays varies within the –1 to 0‰ range (Douthitt, 1982; Ding et al., 1996; De La Rocha et al., 2000; Basile-Doelsch, 2006) which is relatively close to the one we expect for Antarctic diatoms (–0.2 to +1.5; Varela et al., 2004). Maximising the lithogenic Si isotopic contamination for the heaviest diatom $\delta^{29}\text{Si}$ composition (+1.5‰) by taking Al content at the ICP-AES detection limit, an upper crust Si:Al mass ratio at 3.74 (Taylor and McLennan, 1985) with a $\delta^{29}\text{Si}$ signature at –1‰ (lightest end member for clays) induces a shift of less than 0.1‰. This maximal potential bias is less than the $\pm 0.07\text{‰}$ obtained from full replication at the $\pm 2\sigma_{\text{D}}$ level (see below). Therefore lithogenic Si contamination should not significantly alter our measured BSi isotopic signature after this 1-step NaOH leaching, even if the Si:Al ratio is significantly lower than 3.74. Si was subsequently purified through its quantitative reaction with triethylamine–molybdate (De La Rocha et al., 1996). After final dissolution in dilute HF/HCl, silicon isotopic compositions were then measured on a Nu Plasma MC-ICP-MS in dry plasma mode following Cardinal et al. (2003). The results are presented as $\delta^{29}\text{Si}$ relative to NBS28 quartz standard because ^{30}Si cannot be measured on the Nu Plasma due to an irresolvable $^{14}\text{N}^{16}\text{O}$ interference. This method has been intercalibrated (Cardinal et al., 2003; Carignan et al., 2004) and sample replicates (including the triethylamine–molybdate step) are within $\pm 0.07\text{‰}$ ($\pm 2\sigma_{\text{D}}$, Cardinal et al., 2005a). Assuming a mass dependent Si isotope fractionation under thermodynamic equilibrium (Young et al., 2002), $\delta^{29}\text{Si}$ can be converted to $\delta^{30}\text{Si}$ by applying a multiplying factor of 1.93.

3. Results

All BSi isotopic signatures ($\delta^{29}\text{Si}_{\text{BSi}}$) are presented in Table 1. Due to time and sample limitations it was not possible to replicate every single isotopic composition. Among the 39 BSi samples, eight were fully replicated starting from the NaOH step, and four were duplicated from the same HF/HCl final digestion solution. The average difference between the replicated $\delta^{29}\text{Si}_{\text{BSi}}$ is 0.07‰ (0.05‰ when removing an outlier, Table 1), well in accordance with previous results as obtained for the dissolved silicon phase (Cardinal et al., 2005a) and for in-house standards (Cardinal et al., 2003).

Table 1
Complete $\delta^{29}\text{Si}_{\text{BSi}}$ analyses from CLIVAR-SR3

Depth (m)	Size fraction (μm)	$\delta^{29}\text{Si}_{\text{BSi}}$ ($\% \pm 1$ st. error)
<i>53.7°S — PFZ — CTD51</i>		
10	>70	0.55±0.04
"	"	0.59±0.05
17.5	>0.4	0.57±0.04
50	>0.4	0.55±0.03
75	>70	0.66±0.04
" "	" "	0.57±0.04
120	20–70	0.49±0.04
120	>70	0.49±0.04
<i>56.9°S — IPFZ — CTD63</i>		
5	>0.4	0.48±0.03
10	20–70	0.45±0.04
10	>70	0.60±0.03
"	"	0.62±0.04
50	>0.4	0.45±0.04
75	>70	0.59±0.04
"	"	0.51±0.03
120	20–70	0.41±0.03
120	>70	0.37±0.04
<i>60.8°S — AZ-S — CTD73</i>		
5	>0.4	0.47±0.04
10	20–70	0.20±0.03
10	>70	0.21±0.04
50	>0.4	0.38±0.05
" "	" "	0.33±0.04
75	>70	0.24±0.04
120	20–70	0.34±0.04
<i>60.8°S — AZ-S-R — CTD130</i>		
5	>0.4	0.55±0.04
10	20–70	0.38±0.04
10	>70	0.36±0.04
50	>0.4	0.33±0.06
100	>0.4	0.47±0.05
"	"	0.41±0.03
120	20–70	0.36±0.03
" "	" "	0.38±0.05
120	>70	0.25±0.04
" "	" "	0.57±0.04
<i>63.9°S — SIZ-1 — CTD85</i>		
5	>0.4	0.27±0.04
10	20–70	0.21±0.04
10	>70	0.17±0.04
" "	" "	0.28±0.04
55	20–70	0.28±0.04
55	>70	0.23±0.03
120	20–70	0.18±0.03
" "	" "	0.15±0.05
120	>70	0.16±0.04
"	"	0.14±0.04
<i>63.9°S — SIZ-1-R — CTD127</i>		
5	>0.4	-0.05±0.04
50	>0.4	0.11±0.04

Table 1 (continued)

Depth (m)	Size fraction (μm)	$\delta^{29}\text{Si}_{\text{BSi}}$ ($\% \pm 1$ st. error)
<i>64.9°S — SIZ-2</i>		
10	20–70	-0.06±0.04
10	>70	-0.23±0.04
40	20–70	-0.09±0.04
40	>70	-0.26±0.04
120	20–70	-0.05±0.04
" "	" "	-0.07±0.04
120	>70	-0.18±0.04

st. error refers to the analytical error of the isotopic ratios measured on the standard and samples runs and propagated to $\delta^{29}\text{Si}$ (Cardinal et al., 2003). See section Sampling for the definition of acronyms. CTD numbers refer for Niskin samplings only (i.e. >0.4 μm size fraction).

" " indicate full replicates.

" indicate analytical replicate.

Profiles of dissolved Si isotopic compositions ($\delta^{29}\text{Si}_{\text{DSi}}$) have been acquired from close CTD casts and discussed in a previous paper (Cardinal et al., 2005a). In Table 2 average mixed layer isotopic data are presented along with main characteristics relevant to silicon. Fig. 2 displays the latitudinal trend of the BSi and DSi isotopic compositions. Note that large size fraction may contain some radiolarians even if the diatom valves to radiolarian cells ratio is 10^4 – 10^5 in Antarctic waters (Abelmann and Gersonde, 1991). $\delta^{29}\text{Si}_{\text{BSi}}$ are systematically lighter than the ones of silicic acid in agreement with the preferential uptake of light isotopes by diatoms (De La Rocha et al., 1997; Milligan et al., 2004; Varela et al., 2004; Alleman et al., 2005). We observe a southward trend of $\delta^{29}\text{Si}_{\text{BSi}}$ becoming lighter, whatever the size fraction. A much smoother southward trend is also observed for $\delta^{29}\text{Si}_{\text{DSi}}$.

Over the whole north to south SR-3 transect, there is no systematic size or depth related variation of the $\delta^{29}\text{Si}_{\text{BSi}}$ signature. Mixed layer $\delta^{29}\text{Si}_{\text{BSi}}$ values appear homogeneous for all size fractions at PFZ and SIZ-1, and to a lesser extent at AZ-S-R. However, significant differences are recorded for the other stations: large diatoms are isotopically heavier in the IPFZ, whereas they are lighter for AZ-S (mixed layer) and SIZ-2 (both depths). SIZ-2 is the only station exhibiting size related differences in the isotopic composition of mixed layer and exported diatoms (i.e. within the deeper layer). Comparing isotopic signatures for mixed layer diatoms with those for sub-mixed layer samples ('exported' diatoms) reveals significantly lighter isotopic compositions below the mixed layer at the two northern stations (PFZ–IPFZ). Signatures of these 'exported' diatoms are heavier in the AZ-S, while they are homogeneous for the two SIZ stations and in AZ-S-R.

Table 2

Summary of Si contents and isotopic measurements averaged per depth layer: mixed layer and just below

		PFZ	IPFZ	AZ-S	AZ-S- R	SIZ-1	SIZ-1 R	SIZ-2
Latitude	(°S)	53.7	56.9	60.8	60.8	63.9	63.9	64.9
Sampling date (2001)		13 Nov.	16 Nov.	20 Nov.	7 Dec.	24 Nov.	5 Dec.	4 Dec.
Mixed layer depth ^a	(m)	76	92	97	97	41	38	104
Mixed layer temperature	(°C)	2.94	1.58	-0.08	0.08	-1.68	-1.5	-1.42
[DSi] _{initial} ^a	($\mu\text{mol l}^{-1}$)	19.8	31.5	55.1	55.1	77.4	77.4	72.1
[DSi] _{ML} ^a	($\mu\text{mol l}^{-1}$)	11.0	15.8	28.1	27.3	40.8	43.4	60.7
[BSi] _{ML} >0.4 μm	($\mu\text{mol l}^{-1}$)	0.39±0.15	0.86±0.61	1.66±0.21	3.92±1.30	0.83±0.01	1.41±0.59	0.40±0.09
[BSi] _{ML} 20–70 μm	($\mu\text{mol l}^{-1}$)	nd	0.08±0.01	1.26±0.36	1.44	0.61	0.00	0.07±0.02
[BSi] _{ML} >70 μm	($\mu\text{mol l}^{-1}$)	0.28±0.05	0.25±0.05	0.85±0.13	1.45	0.56	na	0.04±0.01
$\delta^{29}\text{Si}_{\text{DSi-ML}}$ ^a	(‰)	1.02	0.99±0.01	0.97±0.04	1.09±0.08	0.97	0.97	0.84±0.03
$\delta^{29}\text{Si}_{\text{BSi-ML}}>0.4 \mu\text{m}$	(‰)	0.56±0.01	0.46±0.03	0.40±0.07	0.44±0.15	0.27	-0.05	
$\delta^{29}\text{Si}_{\text{BSi-ML}} 20-70 \mu\text{m}$	(‰)	na	0.45	0.20	0.38	0.21	na	-0.08±0.02
$\delta^{29}\text{Si}_{\text{BSi-ML}}>70 \mu\text{m}$	(‰)	0.59±0.05	0.58±0.05	0.22±0.02	0.36	0.22±0.07	na	-0.24±0.03
$\delta^{29}\text{Si}_{\text{BSi-deep}}>0.4 \mu\text{m}$	(‰)	na	na	na	0.44±0.04	na	0.11	na
$\delta^{29}\text{Si}_{\text{BSi-deep}} 20-70 \mu\text{m}$	(‰)	0.49	0.41	0.34	0.37±0.02	0.20±0.07	na	-0.06±0.02
$\delta^{29}\text{Si}_{\text{BSi-deep}}>70 \mu\text{m}$	(‰)	0.49	0.37	na	0.41±0.23	0.18±0.05	na	-0.18

DSi: dissolved Si. BSi: Biogenic Si. R: repeat stations. ML: Mixed Layer. Deep: from bow pumps sampling below ML.

1 standard deviation calculated on all analyses available per depth layer (i.e. ML or deep) is given (see Table 1 for the complete dataset).

No standard deviation indicates single measurement at this depth layer.

na: no data available; nd: not detectable.

See section Sampling for the definition of acronyms.

^a Data from Cardinal et al. (2005a). Initial: refers to the conditions before start of Si consumption as discussed in Cardinal et al. (2005a).

Fig. 3 displays the latitudinal trend of BSi concentration ([BSi]) and diatom cell concentration (the latter data from Savoye et al., 2004a; Kopczynska et al., submitted for

publication). There is a good correlation ($r^2=0.87$, not shown) between diatom cell numbers and [BSi] (>20 μm). The maximum [BSi] was observed in the AZ-S, and the

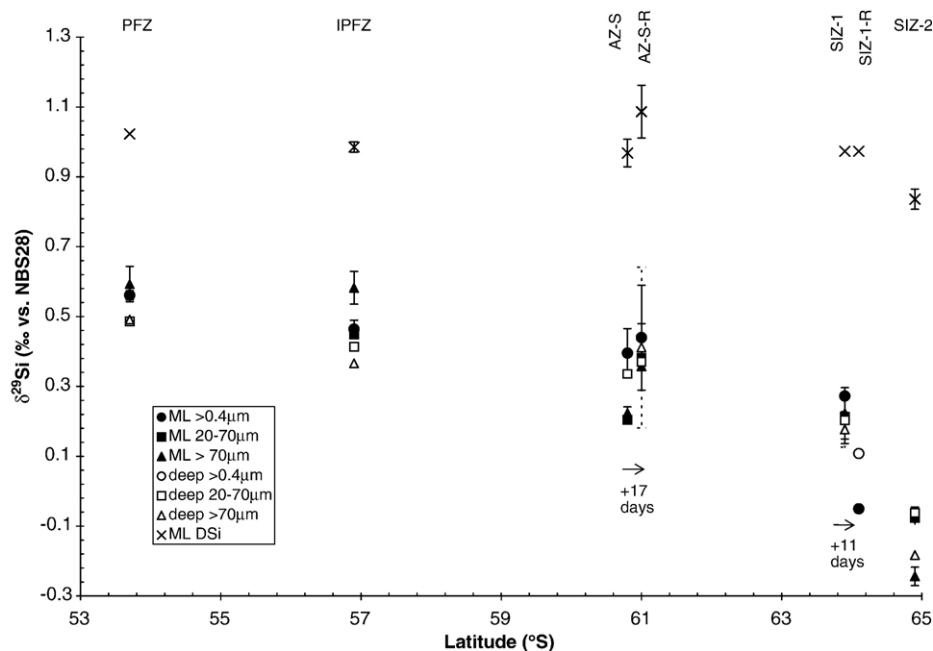


Fig. 2. Zonal variation of the isotopic composition of silicic acid (also referred to as silicate) (crosses: mixed layer data from Cardinal et al., 2005a) and biogenic silica: circles: >0.4 μm fraction; squares: 20–70 μm ; triangles: >70 μm ; filled symbols: mixed layer average; empty symbols: below mixed layer depth. Arrows link two repeat samplings at the same location (delay is given). Latitudes displayed for repeat stations have been slightly shifted in the figure to avoid overlap with first sampling (AZ-S-R has been put at 61.2°S instead of 60.8°S and SIZ-1-R at 65.1°S instead of 64.9°S). Error bars are the standard deviation calculated when several analyses have been acquired (see Tables 1 and 2). See section sampling for the definition of acronyms.

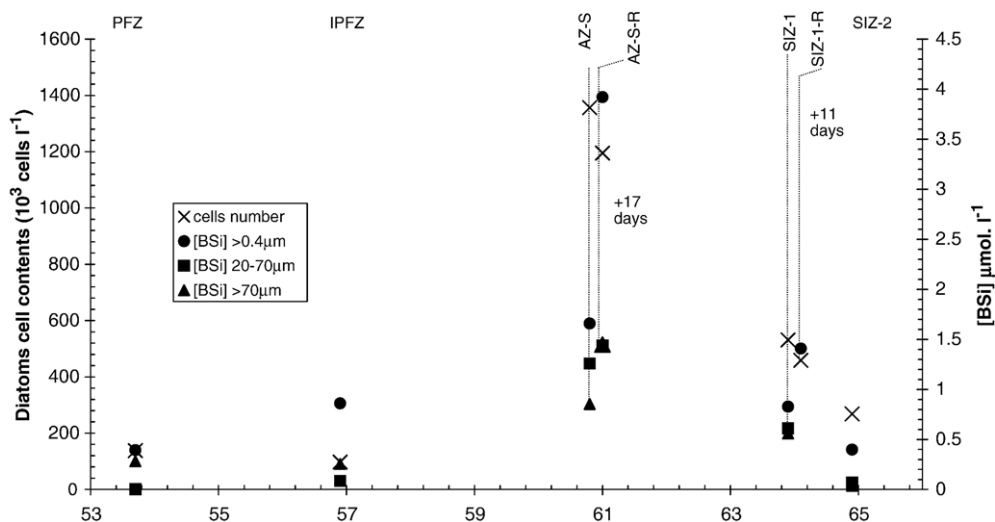


Fig. 3. Mixed layer average BSi contents (filled symbols) and upper 70-m diatom cell contents (crosses) vs. latitude °S. Vertical lines indicate two repeat samplings at the same location (delay is given). Latitudes displayed for repeat stations have been slightly shifted in the figure to avoid overlap with first sampling (AZ-S-R has been put at 61.2°S instead of 60.8°S and SIZ-1-R at 65.1°S instead of 64.9°S). See section sampling for the definition of acronyms.

lowest at the northern (PFZ–IPFZ) and southern (SIZ-2) edges of the transect. Diatom cell numbers follow the same pattern. The medium (20–70 μm) and large (> 70 μm) size fractions have similar [BSi] contents in the SIZ (and AZ-S-R), whereas in the PFZ–IPFZ [BSi] of the > 70 μm size fraction exceeds that of the 20–70 μm size fraction.

Overall, micro-sized diatoms (> 20 μm) are dominant and account for $80 \pm 45\%$ of the BSi concentration of the > 0.4 μm size fraction (assuming this fraction reflects total [BSi] even if under sampling with Niskin can occur). A similar size distribution has been reported by Quéguiner and Brzezinski (2002) in the spring Southern Ocean. A significant increase of BSi was observed at the repeat stations; at AZ-S-R diatom biomass increased more than twofold in between successive visits, but this increase was mainly carried by the smaller sized diatoms. Indeed, [BSi] in the > 0.4 μm size fraction increased by $2.2 \mu\text{mol l}^{-1}$, while [BSi] in the > 20 μm fraction increased only by $0.8 \mu\text{mol l}^{-1}$. Diatom cell counts, on the contrary, decreased by 12–14% between repeat visits of the AZ-S and SIZ-1 sites (Fig. 3) indicating that diatoms were more silicified at the repeat visits. In both cases, the increase of [BSi] over time was not counterbalanced by a decrease in [DSi] (Table 2).

4. Discussion

4.1. Apparent fractionation factor

In vitro experiments of De La Rocha et al. (1997) have established the basic understanding of Si isotopes as a

proxy of relative Si utilisation by showing that the equilibrium fractionation factor, expressed as $^{29}\epsilon$ or $^{30}\epsilon$ (with $^{30}\epsilon = 1.93 \times ^{29}\epsilon$), between diatoms and dissolved silicon ($^{29}\epsilon = -0.56 \pm 0.2\text{‰}$) appeared to be independent of temperature (12–22 °C range), species (three tropical species) and cell growth rate. It is worth noting that such incubations have however never been performed on conditions close to the ones found in the Southern Ocean. Milligan et al. (2004) have recently made important progress on physiological aspects and provide strong support for the idea that isotopic fractionation takes place only during membrane transport and not during the polymerisation–precipitation process. Therefore, the step involved in Si-isotopic fractionation differs from the main process involved for N isotopic fractionation which is the intra-cellular reduction of NO_3^- by nitrate reductase (Needoba and Harrison, 2004; Granger et al., 2004). Actually the difference in the mechanisms involved for the Si vs. N isotopic fractionation processes is not surprising as the Si cycle in a diatom's cell is decoupled from C and N cycles (e.g. Claquin et al., 2002; Claquin and Martin-Jézéquel, 2005).

Going a step beyond laboratory experiments, data on silicon isotopic signatures in the modern ocean are limited to the studies by De La Rocha et al. (2000), Varela et al. (2004), and Cardinal et al. (2005a), with the most two recent providing detailed datasets exclusively for the Southern Ocean. Our $\delta^{29}\text{Si}_{\text{BSi}}$ data are actually very similar to the ones of Varela et al. (2004) acquired for several repeat samplings (mostly in summer) along a North–South transect in the S.O. eastward to the SR-3 line (SOFEX and AESOPS programs at 170°W). Based

on their summer BSi and DSi data Varela et al. (2004) deduced a fractionation factor ($^{29}\epsilon$) ranging between -0.55 and -0.98% and showing no latitudinal gradient. In their approach Varela et al. considered the section between the Polar Front and the Southern Antarctic Circumpolar Current Front as one single system (i.e. with same Si contents and isotopic signature of the source). Furthermore, they applied the open steady-state (Sigman et al., 1999b) or closed system Rayleigh type (Mariotti et al., 1981) models to their data in which biological activity appears to have had a larger impact than physical mixing (spring or samples taken after strong mixing events were excluded from this calculation). The description of these models is given in Fig. 4. In contrast, Cardinal et al. (2005a), studying $\delta^{29}\text{Si}_{\text{DSi}}$ in spring, applied an open system, multi-box approach and deduced a fractionation factor very close ($-0.54 \pm 0.2\%$) to the value reported by De La Rocha et al. (1997). The equations of these open steady-state and closed systems assume a constant equilibrium fractionation factor between diatoms and dissolved silicon and describe the evolution of $\delta^{29}\text{Si}_{\text{DSi}}$ and $\delta^{29}\text{Si}_{\text{BSi}}$ as function of ϵ , relative Si utilisation ($f = [\text{DSi}]/[\text{DSi}]_{\text{initial}}$, ratio of actual silicic acid content over initial content) and $\delta^{29}\text{Si}_{\text{DSi}}$ isotopic signature of the substrate before any consumption had started (Fig. 4). While providing new ϵ estimates, Varela et al. (2004) and Cardinal et al. (2005a) reported that none of these models is likely to adequately describe the Southern Ocean system at the seasonal and regional scales. In particular we have shown that during the CLIVAR-SR3 spring cruise the system could hardly be considered to operate as a single closed one, but rather that each site rather functioned as an independent open system (Cardinal et al., 2005a). Therefore, applying the same closed system approach Varela et al. (2004) used for summer data to this spring $\delta^{29}\text{Si}_{\text{BSi}}$ CLIVAR-SR3 dataset is likely to lead to a flawed interpretation. Indeed, comparing $\delta^{29}\text{Si}_{\text{BSi}}$ with relative Si utilisation for a closed system makes sense only if (i) it is assumed that source silicon at all sites has the same isotopic composition and (ii) initial Si contents are well constrained. Furthermore, combining results from multiple sites can introduce sampling biases — for example in our case the observations at 64.9°S , where relative Si utilisation appears to be much lower than at the other sites would bias the overall interpretation by controlling one extremity of the regression line drawn (see Fig. 5 in Cardinal et al., 2005a).

$^{29}\epsilon$ could be independently assessed from the chosen theoretical model using the “apparent” fractionation factor, $\Delta^{29}\text{Si}$, which is the difference between the isotopic composition of the product, biogenic silica ($\delta^{29}\text{Si}_{\text{BSi}}$) and the ambient dissolved silicon ($\delta^{29}\text{Si}_{\text{DSi}}$). For both steady-

state open system (Fig. 4b) and closed system assuming that $\delta^{29}\text{Si}_{\text{BSi}}$ represents the instantaneous (i.e., non-accumulated) product signature (Fig. 4a), $\Delta^{29}\text{Si}$, should be an estimate of the fractionation factor, $^{29}\epsilon$. This condition only holds if the isotopic compositions of both phases represent instantaneous equilibrium conditions (Fig. 4). For instance if a closed system applies, $\Delta^{29}\text{Si}$ should increase along with DSi consumption as $\delta^{29}\text{Si}_{\text{BSi}}$ reflects the accumulated rather than the instantaneous product. As such, $\Delta^{29}\text{Si}$ is no longer representative of $^{29}\epsilon$ (Fig. 4a). Assuming $\Delta^{29}\text{Si} \sim ^{29}\epsilon$, Varela et al. (2004) obtained an average of -0.83% , giving additional support for a significantly larger ϵ value than deduced from laboratory experiments (De La Rocha et al., 1997), whereas recent $\Delta^{29}\text{Si}$ values reported by Alleman et al. (2005) for tropical freshwater lake diatoms are in the range of De La Rocha et al. (1997).

In the present study, the latitudinal trend for $\delta^{29}\text{Si}_{\text{BSi}}$ is much steeper than for $\delta^{29}\text{Si}_{\text{DSi}}$ inducing latitudinal varying $\Delta^{29}\text{Si}$ values. A similar trend could also be seen in Fig. 5 for the data from Varela et al. (2004). This suggests a possible latitudinal change in the water-diatom silicon fractionation factor and/or a bias induced by sporadic physical mixing events on our spring data. In Varela et al. (2004) the slope of $\delta^{29}\text{Si}_{\text{BSi}}$ vs. f , was significantly more negative (slope = $^{30}\epsilon = -2.1 \pm 0.2$) than the one for $\delta^{29}\text{Si}_{\text{DSi}}$ vs. f (slope = $^{30}\epsilon = -1.7 \pm 0.1$). In our previous study on $\delta^{29}\text{Si}_{\text{DSi}}$, we also observed a latitudinal trend in the fractionation factor, with values being more negative (larger fractionation) in the southern waters compared to those in the north (Cardinal et al., 2005a). Although those differences for $^{29}\epsilon$ were not statistically significant, the fact that they were present in Varela et al. (2004) and are observed in the present BSi dataset calls for a closer look at this aspect. For the PFZ–IPFZ zone, $\Delta^{29}\text{Si}$ falls well in the range of our previous $^{29}\epsilon$ estimates (De La Rocha et al., 1997; Cardinal et al., 2005a) but becomes progressively more negative southward (i.e. larger isotopic difference between BSi and DSi phases). SIZ-2 and SIZ-1-R are particularly off the expected range. In the following sections we discuss this latitude-related variation of $\Delta^{29}\text{Si}$ with respect to the likely factors that might have some control over it: 1) Sea ice diatoms, 2) Iron, 3) Temperature, 4) Si uptake and dissolution rates, 5) Sporadic physical mixing events in the frontal zones. Before entering into these discussions, we note that variations in the extent of product accumulation do not offer a simpler explanation of the latitudinal variations in $\Delta^{29}\text{Si}$ — because biogenic silica accumulations do not increase southward from the PFZ to the SIZ (Fig. 3). This issue is addressed in more detail in Section 4.1.5.

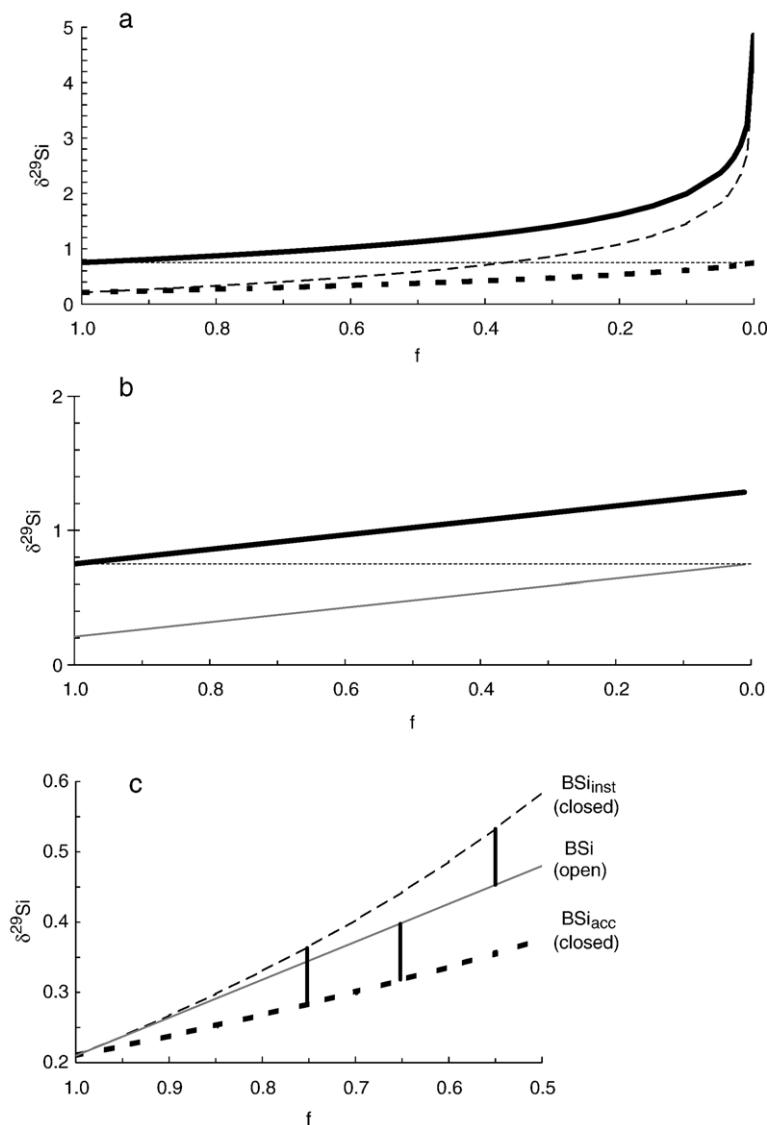


Fig. 4. Steady-state models describing the theoretical evolution of Si isotope signatures as a function of f ($f = [\text{DSi}]/[\text{DSi}]_{\text{initial}}$). Conditions set were expected in the SIZ as based on results from a previous study, i.e. $^{29}\epsilon = -0.54\text{‰}$ and $\delta^{29}\text{Si}_{\text{DSi-initial}} = 0.75\text{‰}$ (Cardinal et al., 2005a). Plain thick line: $\delta^{29}\text{Si}_{\text{DSi}}$; horizontal light dotted line indicates $\delta^{29}\text{Si}_{\text{DSi-initial}}$ (a): Closed Rayleigh system (Mariotti et al., 1981): $\delta^{29}\text{Si}_{\text{DSi}} = \delta^{29}\text{Si}_{\text{DSi-initial}} + ^{29}\epsilon \times \ln f$; $\delta^{29}\text{Si}_{\text{BSi-inst}} = \delta^{29}\text{Si}_{\text{DSi}} + ^{29}\epsilon$; $\delta^{29}\text{Si}_{\text{BSi-acc}} = \delta^{29}\text{Si}_{\text{DSi-initial}} - ^{29}\epsilon \times f \times (\ln f / (1 - f))$. $\delta^{29}\text{Si}_{\text{BSi-inst}}$ (light dashed curve) is the isotopic composition of diatom produced for a specific f_i (referred to as the instantaneous product), and $\delta^{29}\text{Si}_{\text{BSi-acc}}$ (thick dashed curve) is the resulting isotopic composition of the total diatoms population grown from $f=1$ up to f_i without export (referred to as the accumulated product). (b) Open system (Sigman et al., 1999b). $\delta^{29}\text{Si}_{\text{DSi}} = \delta^{29}\text{Si}_{\text{DSi-initial}} - ^{29}\epsilon \times (1 - f)$; $\delta^{29}\text{Si}_{\text{BSi}} = \delta^{29}\text{Si}_{\text{DSi-initial}} + ^{29}\epsilon \times f$. Note that in the open steady-state system diatoms all have the same isotopic signature (light plain line); i.e. the isotopic difference between $\delta^{29}\text{Si}_{\text{BSi-inst}}$ and $\delta^{29}\text{Si}_{\text{BSi-acc}}$ does not apply. (c) Comparison of $\delta^{29}\text{Si}_{\text{BSi}}$ signatures for the two systems. Vertical lines indicate where the difference between $\delta^{29}\text{Si}_{\text{BSi}}$ curves starts to become analytically significant (i.e., 0.08‰). Note that there is no significant difference for the three lines between $f=1$ and $f=0.75$ (i.e. 0–25% DSi utilisation). Significant differences between open and closed systems are for $f < 0.65$ (i.e., >35% DSi utilisation) and $f < 0.55$ (i.e. >45% DSi utilisation) considering accumulated or instantaneous $\delta^{29}\text{Si}_{\text{BSi}}$ respectively. Based on estimated winter mixed layer depth and DSi profiles, we calculate for the SIZ DSi that silicic acid utilisation during CLIVAR-SR3 ranged between 15 and 45% (Cardinal et al., 2005a), indicating non-significant model dependence for our SIZ $\delta^{29}\text{Si}_{\text{BSi}}$.

4.1.1. Sea ice diatoms

SIZ stations were still under sea ice influence at the time of sampling, with reduced ice coverage (SIZ-2-R)

or recent ice-free conditions (SIZ-1) (Fig. 1). Antarctic sea ice contains a significant amount of diatoms and their release during melting has been identified as an

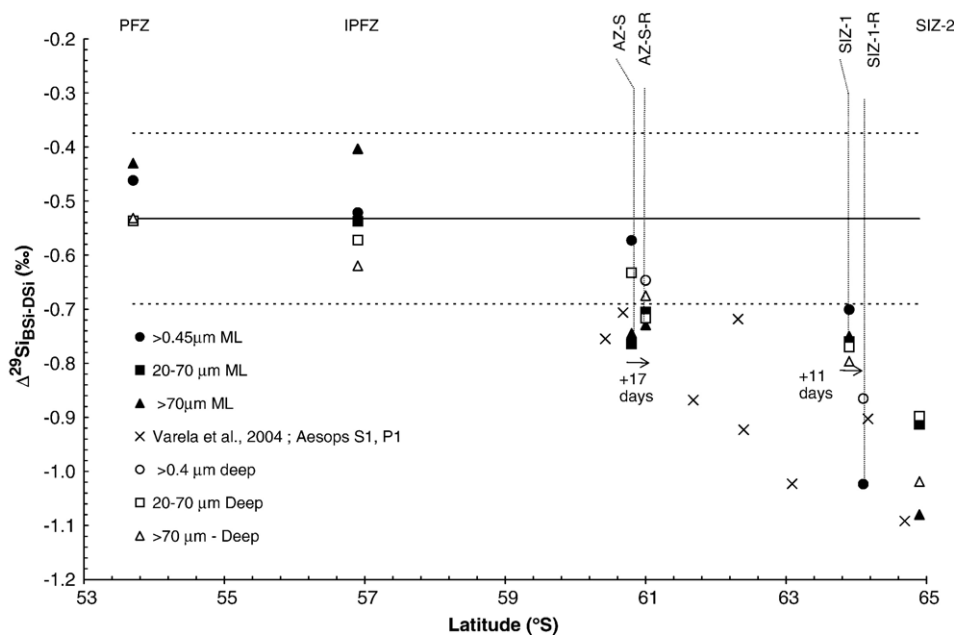


Fig. 5. Latitudinal variation of $\Delta^{29}\text{Si}$ ($\Delta^{29}\text{Si} = \delta^{29}\text{Si}_{\text{BSi}} - \delta^{29}\text{Si}_{\text{DSi}}$). Latitudes displayed for repeat stations have been slightly shifted in the figure to avoid overlap with first sampling (AZ-S-R has been put at 61.2°S instead of 60.8°S and SIZ-1-R at 65.1°S instead of 64.9°S). Filled symbols: average values for mixed layer (ML). Open symbols (deep): difference between $\delta^{29}\text{Si}_{\text{BSi}}$ below the ML and $\delta^{29}\text{Si}_{\text{DSi}}$ within the ML. Circles: $>0.4 \mu\text{m}$ fraction; squares: $20\text{--}70 \mu\text{m}$; triangles: $>70 \mu\text{m}$; crosses: spring data from Varela et al. (2004), i.e. AESOPS Survey 1 and Process 1. The straight horizontal line reflects the average fractionation factor estimate, $^{29}\epsilon$, based on $\delta^{29}\text{Si}_{\text{DSi}}$ data only for the zone PFZ to SIZ, (Cardinal et al., 2005a). This value is similar to the one of De La Rocha et al. (1997). Dashed lines indicate ± 1 standard deviation from this average estimate. See section sampling for the definition of acronyms.

important factor to initiate blooms in the SIZ (Lancelot et al., 1993; Goffart et al., 2000; Moore and Abbott, 2000; Riaux-Gobin et al., 2005). Diatom assemblages at SIZ-2 and SIZ-1-R (Kopczynska et al., submitted for publication) reveal the presence of characteristic sea ice related species such as *F. cylindrus* and *F. curta* (e.g. Armand et al., 2005) and these were not present in such abundance at SIZ-1 or at northern stations. A preliminary investigation does not support specific light isotopic signatures for sea ice diatoms. Indeed $\delta^{29}\text{Si}_{\text{BSi}}$ of diatoms sampled directly within sea ice cores during the ARISE spring 2003 cruise are much heavier ($+0.63 \pm 0.12\text{‰}$, $n=13$; Fripiat, 2005 and Fripiat et al., submitted for publication) than the ones we obtained for BSi in the SIZ mixed layer during CLIVAR-SR3 ($0.06 \pm 0.18\text{‰}$ Fig. 2 and Table 1) whereas silicate in brines has either a similar isotopic composition as in the surface mixed layer or is slightly heavier (Fripiat et al., submitted for publication). It is therefore unlikely that light $\delta^{29}\text{Si}_{\text{BSi}}$ values encountered at SIZ-2 and SIZ-1-R reflect the signature of sea ice diatoms. Indeed, diatoms in ice have a heavier Si isotopic composition, and there is no reason why they should become that light once released and in the course of blooming, given the $\delta^{29}\text{Si}_{\text{DSi}}$ signature of their Si source in the mixed layer ($\sim 0.92\text{‰}$). The fact that Varela et al.

(2004) reported similar negative BSi isotopic compositions at such southern latitudes for situations without evidence of recent sea ice influence corroborates this view.

4.1.2. Iron

Iron is a key factor for diatom's cell silicification and nitrate assimilation and its limitation increases the diatom Si:N ratios 2–8 fold (e.g. Hutchins and Bruland, 1998; Franck et al., 2000). Dissolved Fe concentrations during CLIVAR-SR3 were low and quite homogeneous ($\sim 0.1 \text{ nM}$) in the PFZ–IPFZ, AZ-S and SIZ and no Fe enrichment linked to sea ice melting was observed (Sedwick et al., submitted for publication). Timmermans et al. (2001) report that the extent of Fe limitation differs between small (nano) and large (micro) diatom species. Because Fe concentrations were homogenous and bulk $\delta^{29}\text{Si}_{\text{BSi}}$ signal was supported mostly by micro-sized diatoms ($>20 \mu\text{m}$; Table 2), we suspect that Fe stress was limiting diatom growth to a similar degree all along the transect studied here as reported by Sedwick et al. (submitted for publication). This argues against Fe availability as a leading factor of Si-isotopic fractionation during CLIVAR-SR3.

4.1.3. Temperature

A role of temperature on the fractionation factor can be invoked since it is well known that both equilibrium and kinetic isotopic fractionations are temperature dependent. No temperature effect has been detected in incubation experiments (De La Rocha et al., 1997) but this could have been because of the higher temperature (12–22 °C) and/or masked by the relative high standard deviation of $^{29}\epsilon$ estimates ($\pm 0.2\%$). Plotting $\Delta^{29}\text{Si}$ vs. mixed layer temperature (Fig. 6a) reveals a significant correlation on CLIVAR-SR3 data with larger fractionation for lower temperatures although sea ice $\Delta^{29}\text{Si}$ from Fripiat et al. (submitted for publication) are completely off-trend. In the Southern Ocean many parameters vary latitudinally which renders it difficult to decipher which factor is leading. In this regard, we note that a correlation also exists between [DSi] and $\Delta^{29}\text{Si}$ (Fig. 6b). The correlation is even better and is not in complete opposition with the sea ice results, in contrast

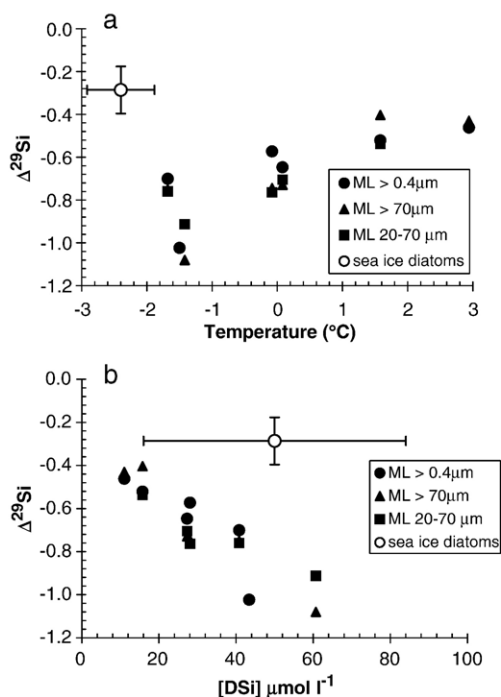


Fig. 6. Mixed layer $\Delta^{29}\text{Si}$ vs. temperature (a) and [DSi] (b). Filled circles: >0.4 μm ; filled squares: 20–70 μm ; filled triangles: >70 μm ; empty circles: sea ice diatoms. Temperatures and isotopic composition of sea ice diatoms ($n=10$) are from Fripiat et al. (in prep.) in cores sampled during the ARISE 2003 cruise (R/V *Aurora Australis*, October–November 2003, at $\sim 64.5^\circ\text{S}$, 117°E). Only data for temperatures $> -5^\circ\text{C}$ are presented because above this temperature the brine channels are open (Golden, 2001) and therefore $\delta^{29}\text{Si}_{\text{BSi}}$ is not likely to be biased by $\delta^{29}\text{Si}_{\text{BSiacc}}$ (Fig. 4a). As no [DSi] contents were measured directly in the brine pockets during this cruise we have taken the range obtained by Gleitz et al. (1995).

to the temperature relationship (this is briefly discussed in the next section). Moreover, low temperatures mostly affect the biomineralisation process (Sullivan, 1980) and, according to Milligan et al. (2004), this step is not thought to induce a measurable Si-isotopic fractionation. For these reasons, although temperature cannot be ruled out yet, it does not explain our variations satisfactorily. The possibility of a temperature effect remains to be addressed carefully by experimental growth experiments to verify if the non-dependency of ϵ on temperature (De La Rocha et al., 1997) can be extended to the very low temperatures (-1.0 to 3°C). A better understanding of diatom growth and associated silicon isotope fractionation in sea ice must also be tackled.

4.1.4. Si uptake and dissolution rates

Si is incorporated actively within a diatom cell by different types of silicon transporters, SIT (Hildebrand et al., 1997). Silicification in diatoms takes place during the G2 and M phases of cell division when no photosynthetic energy is involved and the necessary energy is supplied via respiration (cf. the review by Martin-Jézéquel et al., 2000). Consequently, silicification (Si content per cell) is enhanced at reduced light levels or when the ratio of dark over light period is high, i.e. when cell growth rate is lower (Claquin et al., 2002). This implies a decoupling between cell growth rate (cell division rate) and specific Si uptake rate (V_b in time^{-1}), which actually reflects the Si turn-over in the diatoms. Reaction kinetics usually have a strong impact on isotopic fractionation processes (Young et al., 2002). However, the current level of analytical precision for Si isotope ratio measurement precludes deciphering whether the biogenic isotopic fractionation is a kinetic or an equilibrium process (De La Rocha et al., 1997). In vitro measurements support the view that variable cell growth rate does not generate a variable fractionation factor (De La Rocha et al., 1997), but as Si specific uptake rate is decoupled from cell division rate (Martin-Jézéquel et al., 2000) this conclusion cannot be extended to V_b . Actually little is known about the influence of Si uptake and dissolution rates on the fractionation factor but we observed that there is a significant positive relationship between the $\Delta^{29}\text{Si}$ data from Varela et al. (2004) and the balance of Si uptake and Si release ($V_b - V_d$). Brzezinski et al. (2001) report for the same AESOPS stations. Si release from a diatom cell can occur according to two processes (Milligan et al., 2004): dissolution (depolymerisation of opal to silicic acid) and efflux (outward Si transport across the membrane). This efflux can take place via Si transporters or simple diffusion. Milligan et al. (2004) show that “Si dissolution

rates” assessed from ^{29}Si isotope enrichment experiments actually result from both Si efflux and dissolution. Since SIT are the loci of the Si isotopic fractionation during uptake (Milligan et al., 2004), it is likely that their involvement during efflux also fractionates Si isotopes. It would be worth looking at the relation between $\delta^{29}\text{Si}$ and the specific Si uptake and dissolution rates but such data are not available for CLIVAR-SR3. Further experimental evidence for the observed relationship between ε and (Vb–Vd) is needed since we cannot exclude that the balance between specific uptake and release rate (Vb–Vd) impacts on fractionation. Other likely explanations for the significant relationship between (Vb–Vd) and $\Delta^{30}\text{Si}$ during AESOPS are: (i) physical mixing that could have driven the Vb–Vd vs. $\Delta^{30}\text{Si}$ relationship by biasing the assumption $\Delta^{30}\text{Si} \sim {}^{30}\varepsilon$ (a process inducing such artefact is discussed in more detail in Section 4.1.5); (ii) indirect control of diatom silicification by the light:dark cycle (Claquin et al., 2002); (iii) the specific Si uptake rate is partly depending on the external DSi contents (e.g., Brzezinski et al., 2005) and therefore, in general, exhibits a latitudinal trend in the Southern Ocean (Nelson and Gordon, 1982; Brzezinski et al., 2001; Beucher et al., 2004). The stronger relationship between $\Delta^{29}\text{Si}$ and [DSi] compared to $\Delta^{29}\text{Si}$ and temperature seems to corroborate this (Fig. 6b). In this regard, hydroponic experiments on higher plants also support a larger $\Delta^{29}\text{Si}$ when DSi content of the continuous nutrient supply is higher (Opfergelt et al., in press).

4.1.5. Mixing and export as possible biases between $\Delta^{29}\text{Si}$ and ${}^{29}\varepsilon$

4.1.5.1. Mixing. Mixing events are frequent in the spring Southern Ocean especially in frontal zones such as PFZ and IPFZ. Indeed during CLIVAR-SR3, PFZ and IPFZ upper water layers were less stratified than SIZ upper waters as seen for instance in density profiles (Cardinal et al., 2005b). Mixing would entrain isotopically light silicic acid into the euphotic zone from depth, diminishing the difference between the isotopic signature of the diatoms previously formed and dissolved Si recently supplied. It also would reduce the latitudinal gradient of $\delta^{29}\text{Si}_{\text{DSi}}$ in the mixed layer, since mixed layer $\delta^{29}\text{Si}$ isotopic signatures would then result from the combined effects of vertical mixing (inducing changes of the source isotopic signature) and biological uptake (Cardinal et al., 2005a). Such processes are qualitatively (but not straightforwardly) similar to the ones setting latitudinal changes of silicic acid contents (Pollard et al., 2002). A steady-state open system model (Fig. 4b) takes into account mixing provided that nutrient is continuously supplied (with invariable source

isotopic composition) and partially consumed, with residual nutrient being exported at a steady-state rate, such that gross nutrient supply is balanced by biomass produced and the residual nutrient exported. When these conditions are fulfilled, mixing of surface and deeper waters tends to recombine waters which have experienced fractionation along the same isotopic path. This situation would not strongly influence ε estimates (Sigman et al., 1999b). However $\delta^{29}\text{Si}_{\text{BSi}}$ is the result of time-scale processes which may not be synchronous with those setting $\delta^{29}\text{Si}_{\text{DSi}}$, thus precluding the steady-state assumption needed for $\Delta^{29}\text{Si} \sim {}^{29}\varepsilon$ as discussed below.

In particular if recent and intense mixing events occurred at the PFZ–IPFZ locations just before sampling, they could have shifted $\delta^{29}\text{Si}_{\text{DSi}}$ towards lighter values before the $\delta^{29}\text{Si}$ of the diatoms population actually sampled had been affected by the recent isotopic change of the silicic acid source. We cannot rule out such a possibility, but some evidences go against this explanation. First it would imply that the true PFZ–IPFZ fractionation factor lies within the range of values found for $\Delta^{29}\text{Si}$ in the SIZ (i.e. around -0.9 to -1.1‰). Though Varela et al. (2004) provide some indication that the ${}^{29}\varepsilon$ might be larger than the 0.56‰ as expected from in vitro incubations on tropical marine diatoms (De La Rocha et al., 1997), this was not confirmed by our previous work (Cardinal et al., 2005a) and has not yet been quantified by others. Clearly this underlines the urgent need for reducing uncertainties on ε by means of in vitro incubations reproducing Southern Ocean conditions (temperature, species, DSi). Such studies are underway. Second, models predict that increasing vertical mixing enhances downwelling of Chl-a beneath the mixed layer (Larsson, 2004). Therefore, it is expected that high vertical mixing would diminish the (isotopic) heterogeneity between mixed layer and deep diatoms. However, the reverse is observed, i.e. BSi isotopic composition is more homogenous with depth in the SIZ than in PFZ–IPFZ (see discussion in Section 4.2).

4.1.5.2. Export. In case a significant amount of BSi is subject to export the open steady-state or closed system conditions are violated. Grazing pressure was high all along the SR3 section (Safi et al., submitted for publication; Kocczynska et al., submitted for publication) and other studies indicate that export was occurring (Savoie et al., 2004b; Cardinal et al., 2005b). SIZ stations were somewhat different in that grazing pressure was highest for the nanophytoplankton ($<20\ \mu\text{m}$) and lowest for the micro-phytoplankton cells, which dominated (Safi et al., submitted for publication). Indeed an export of most recently formed

diatoms (supposed to be isotopically heavier than the older ones, Fig. 4) could bias $\Delta^{29}\text{Si}$ toward larger values.

In a closed system with accumulation of BSi, $\Delta^{29}\text{Si}$ will also increase during the DSi drawdown as illustrated in Fig. 4a. By taking a constant equilibrium fractionation factor $^{29}\epsilon$ of -0.54‰ and an initial $\delta^{29}\text{Si}_{\text{DSi}}$ ranging from 0.77‰ and 0.92‰ (Cardinal et al., 2005a), it is impossible to reconcile a $\Delta^{29}\text{Si}$ value of -1.0‰ with the $\delta^{29}\text{Si}_{\text{DSi}}$ and $\delta^{29}\text{Si}_{\text{BSi}}$ measured in the SIZ-2 and SIZ-1-R. In the SIZ during CLIVAR-SR3 we assessed Si utilisation to be less than 40% (Cardinal et al., 2005a) and it is worth underlining that whatever model is chosen, there is no significant (i.e. measurable) difference among $\delta^{29}\text{Si}_{\text{BSi}}$ values for a Si utilisation less than 35–45% (see Fig. 4c).

Therefore the most likely bias on the $\Delta^{29}\text{Si} \sim ^{29}\epsilon$ assumption would rest on processes moving away $\delta^{29}\text{Si}_{\text{DSi}}$ and $\delta^{29}\text{Si}_{\text{BSi}}$ from models described in Fig. 4 such as different time-scales for the dissolved and particulate phases, i.e. mixing and/or export. Our data are snapshots and are very sensitive to short-term environmental changes, yielding to large variability. It is possible that at the annual or multi-annual time-scales, this short-term seasonal variation is smoothed out. Looking at seasonal or inter-annual variability from sediment trap isotopic signatures may provide key information on this aspect, as initiated by Varela et al. (2004).

4.2. BSi dynamics within zones

Even if the fractionation factor would be more variable than previously expected, it is likely that this variability during CLIVAR-SR3 was – directly or indirectly – related to latitude, as supported by the discussion above. Therefore we discuss the Si isotopic signatures in relation to spring diatoms and Si cycles within zones.

4.2.1. PFZ–IPFZ vs. SIZ

In the PFZ–IPFZ, deep $\delta^{29}\text{Si}_{\text{BSi}}$ are lighter than the surface signatures, giving support to the occurrence of two different populations of diatoms: below the mixed layer, we have diatoms that were rapidly exported at the beginning of the bloom (with lighter isotopic signature at the onset of Si consumption, as expected), whereas in the mixed layer the diatom population (getting progressively isotopically heavier) has not yet experienced export. Such decoupling would have been possible if stratification had occurred recently. The exported diatoms originally grew in an unstratified, open system before being exported and sealed off from the surface after stratification occurred. On the other hand, diatoms sampled from the mixed layer grew in a partly closed system and/or accumulated in the mixed layer for a while due to

stronger stratification. Since, on the contrary there is no depth-related Si-isotopic difference at stations SIZ-1, SIZ-2 and AZ-S, located further south, the deeper diatoms there must have been exported recently and should therefore have the same history as the ones still in the mixed layer. Likewise, for the PFZ in spring (Atlantic sector) Quéguiner and Brzezinski (2002) also report important peaks of BSi down to 200 m contrasting with more southern zones. Their BSi production rates provided additional support for significant BSi export while the bloom was still expanding. This overall picture is also consistent with the temporal dynamics of the diatom bloom in the Southern Ocean, which starts in the PFZ and then propagates southward when environmental conditions evolve favourably (Nelson et al., 2001; Brzezinski et al., 2001).

4.2.2. Repeat stations

4.2.2.1. AZ-S. At 60.8°S many parameters converge to indicate that a bloom was going on during the first visit (AZ-S) but that its intensity had decreased during the second visit (AZ-S-R). New production at AZ-S was the second highest of the whole transect but had decreased by one third at AZ-S-R (Savoie et al., 2004a). Diatom cell numbers were the highest at the first visit but had decreased by 20% (Fig. 3) while diatoms biomass increased by 45% (Cardinal et al., 2005b) along with a 2.3-fold increase of BSi contents (Table 2). This bloom clearly induced some particle export (Savoie et al., 2004b) and mesopelagic carbon remineralisation (Cardinal et al., 2005b) in accordance with the highest grazing pressure found at AZ-S for the $<20\ \mu\text{m}$ size fraction (Safi et al., submitted for publication). Whereas between successive visits Si isotopic signatures for both, dissolved and biogenic phases increased, with the most significant enrichment being measured for the larger ($>20\ \mu\text{m}$) micro-sized diatoms (Fig. 2), only a very small DSi depletion had occurred in the mixed layer ($0.8\ \mu\text{M}$ Si; Table 2). Note that the signature of deep diatoms did not significantly change between the two samplings. Such variation in isotopic signature would result from silicate consumption, but cannot easily be reconciled with the open steady-state or closed systems since any significant isotopic shift should be accompanied by a significant Si depletion (Fig. 4). Varela et al. (2004) and Cardinal et al. (2005a) have shown that none of these models are likely to describe adequately the Southern Ocean at the seasonal time-scale. In particular, if the open model is preferred for the CLIVAR-SR3 spring conditions as discussed in Cardinal et al. (2005a), it cannot describe non-steady-state conditions which are likely to occur when sporadic mixing and/or export events

take place (Varela et al., 2004). The fact that the isotopic change for large diatoms is larger than the change for $\delta^{29}\text{Si}_{\text{DSi}}$ could be due to a recent mixing event having resupplied the mixed layer in DSi, and thereby dampening $\delta^{29}\text{Si}_{\text{DSi}}$ without having affected $\delta^{29}\text{Si}_{\text{BSi}}$.

4.2.2.2. SIZ-1 vs. SIZ-1-R. As observed for the AZ-S situation, [BSi] (from 0.9 to 1.4 μM), diatom biomass (10 to 13 $\mu\text{g C l}^{-1}$; Cardinal et al., 2005b), Chl-a and ^{234}Th deficit (Savoie et al., 2004a,b) all increased in between the two visits, while diatom cell numbers decreased (–12–14%; Fig. 3). The $\delta^{29}\text{Si}_{\text{BSi}}$ of the $>0.4 \mu\text{m}$ fraction shifted from +0.32 to –0.08‰ in the mixed layer within 11 days. This shift was also present (though to a lesser extent) below the mixed layer (Fig. 2 and Table 2) while DSi slightly increased (from 40.8 to 43.8 μM). Decreasing $\delta^{29}\text{Si}_{\text{BSi}}$ and increasing silicate concentrations are a priori inconsistent with increasing diatom biomass and Chl-a characteristic of a bloom situation unless a sporadic mixing event occurred in between both visits at the SIZ-1 site, a kind of process described and discussed in Section 4.1.5.

5. Conclusions and perspectives

By reporting on Si-isotopic composition of Southern Ocean diatoms during spring this study complements our previous work on dissolved silicate from the same CLIVAR-SR3 cruise (Cardinal et al., 2005a). The Si-isotopic signatures of diatoms appear generally to be unrelated to particle size. The latitudinal trend toward lighter particulate isotopic composition ($\delta^{29}\text{Si}_{\text{BSi}}$) in the South is much steeper than the one for dissolved silicon in surface waters ($\delta^{29}\text{Si}_{\text{DSi}}$). Such discrepancy between dissolved and particulate phases might indicate a variable equilibrium fractionation factor between diatoms and seawater and/or non-equilibrium conditions. Taking into account the large amount of information available from the CLIVAR-SR3 cruise, we found that the factors most likely to produce such change are temperature, DSi contents, and, the specific Si uptake and dissolution rates. These factors are different from the ones controlling N isotopic fractionation which strengthens the picture of a decoupling between the Si and N cycles in diatoms as underlined by recent studies (Martin-Jézéquel et al., 2000; Claquin et al., 2002). Yet, these results are far from proving that Si-isotopic fractionation by diatoms is variable. As discussed, many parameters vary with latitude in the Southern Ocean and finding a significant relationship among the two, as in Fig. 6, does not necessarily mean that one causes the other. Moreover a decoupling between $\delta^{29}\text{Si}_{\text{BSi}}$ and $\delta^{29}\text{Si}_{\text{DSi}}$ resulting from different and/or too small time windows is also possible.

In particular, the latitudinal $\Delta^{29}\text{Si}$ trend could result from more intense and sporadic vertical mixing events in the PFZ–IPFZ which would result in undermining the assumption that apparent fractionation factor ($\Delta^{29}\text{Si}$) approximates equilibrium fractionation factor ($^{29}\epsilon$) as based on the simple models currently available. Such biases from model rationales recorded by snapshot sampling could be dampened at the annual or multi-annual time-scales and hence do not yet invalidate the potential of Si isotopes as a useful paleo-proxy.

Comparison of $\delta^{29}\text{Si}_{\text{BSi}}$ in the mixed layer with $\delta^{29}\text{Si}_{\text{BSi}}$ just below the mixed layer supports the view of dynamic changes in the Southern Ocean during spring, involving spatial differentiation due to progressive (latitudinal) delay of the season's onset as controlled by light, temperature and stratification. Although sampled in early October, the PFZ–IPFZ had already exported diatoms which were isotopically lighter than the ones found in the mixed layer. Farther south no depth-related isotopic change was observed in agreement with an ongoing recently started bloom.

Overall even if these results highlight important gaps in the understanding of the oceanic Si isotope system, the differences with previous estimates are significant only in the seasonal ice zone given the standard deviation of the fractionation factor estimates and the uncertainties linked to the choice of the model. Therefore further steps must be especially undertaken in order to (i) improve modelling of the Si isotope cycle in the upper water column at the seasonal scale and quantify the isotopic effect of mixing events, (ii) constrain the effect of low temperature, DSi contents, Si specific uptake and dissolution rates and species by in vitro experiments, (iii) measure the isotopic signature of exported diatoms on time series (sediment traps) to verify if the same variability is obtained on a larger time window, (iv) examine the special environment of sea ice hosted diatoms, and (v) investigate efflux and dissolution rates by detailed physiological studies: it should be of particular importance to know whether efflux is mostly controlled by silicon transporters (SIT) and/or diffusion, and identify the implications for the Si isotopic system.

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