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## Intense summer Si-recycling in the surface Southern Ocean

Charlotte Beucher, Paul Tréguer, Ana-Maria Hapette, and Rudolph Corvaisier

LEMAR, UMR 6539, European Institute for Marine Studies, Plouzané France

Nicolas Metzl

LBCM, IPSL UMR 7094, University P. and M. Curie, Paris, France

Jean-Jacques Pichon

EPOC, UMR 5805, University of Bordeaux, Talence, France

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[1] Si-cycle in surface waters was investigated in summer 2003 during a transect conducted from south-Australia to Antarctica. Diatoms dominated the microphytoplankton. Silicic acid was depleted up to 60°S; a subsurface maximum of biogenic silica (= biosilica) was observed in the Permanent Open Ocean Zone. In the 100–0.01% light zone, the ratio of depth-integrated biosilica dissolution rate (D) to depth-integrated biosilica production rate (P) ranged between 0 to 3.1, being >1 for 5 of our 6 stations. The biosilica dissolution was related to the percentage of dead diatoms but not to the temperature and might be, at least partially, under bacteria mediation. This study shows that during summer the Southern Ocean silicate pump can be much less efficient than usually expected. Existence of scenarios with intense surface Si-recycling in the Southern Ocean has major consequences both for modelers and paleoceanographers. *INDEX TERMS:* 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 1615 Global Change: Biogeochemical processes (4805); 4855 Oceanography: Biological and Chemical: Plankton; 4207 Oceanography: General: Arctic and Antarctic oceanography; 4870 Oceanography: Biological and Chemical: Stable isotopes. **Citation:** Beucher, C., P. Tréguer, A.-M. Hapette, R. Corvaisier, N. Metzl, and J.-J. Pichon (2004), Intense summer Si-recycling in the surface Southern Ocean, *Geophys. Res. Lett.*, 31, L09305, doi:10.1029/2003GL018998.

### 1. Introduction

[2] The Southern Ocean plays a key role in the global marine biological pump of carbon [e.g., Tréguer and Pondaven, 2002]. Diatoms are major players of the biological pump of the Southern Ocean, that is why the biogeochemical cycle of Si in the Southern Ocean is receiving much attention [e.g., Pondaven *et al.*, 2000]. This cycle is not well constrained, especially because only few measurements of Si-recycling are available. In the euphotic zone, the ratios of the depth-integrated biosilica dissolution rate to the depth-integrated biosilica production rate can double from a bloom period to a post-bloom period [Brzezinski *et al.*, 2003]. Currently, mostly because of abundant opal abyssal deposits, the Southern Ocean is viewed as a strong exporter of biosilica. We herein show that during austral summer, the integrated dissolution rate can exceed the integrated produc-

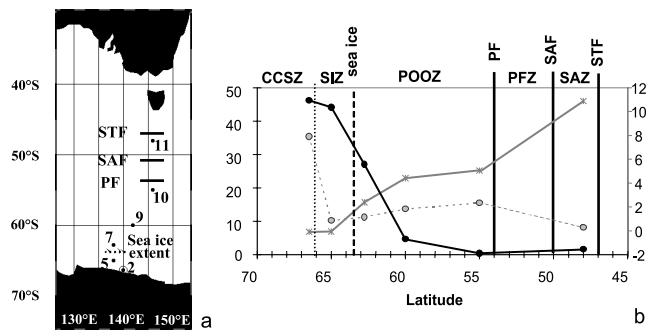
tion rate in the euphotic layer for various Antarctic subsystems, suggesting almost no export of opal to the deep ocean.

### 2. Methods

[3] The CADO/OISO cruise was conducted during austral summer 2003 (23 January–17 February 2003), south of Australia (Figure 1a). Hydrological fronts were located according to Chaigneau and Morrow [2002]. The latitude of maximal winter extent of sea ice was 63°30 S (<http://www.natice.noaa.gov/>). Our stations were distributed in different subsystems: the SAZ, the POOZ, the SIZ and the CCSZ. At each station, water sampling was performed at 6 depths (corresponding to 100, 50, 25, 10, 1 and 0.01 % of surface PAR).

[4] The concentrations of Si(OH)<sub>4</sub>, (NO<sub>3</sub> + NO<sub>2</sub>) and biosilica (bSiO<sub>2</sub>), and the microphytoplankton (2 per station) counting, determination (species) and characterization (full = alive, empty or broken = dead) were determined as described in Beucher *et al.* [2004]. Total bacteria (i.e., free-living and attached bacteria) protease activity (PA) was measured using commercially available substrate that employs amino-4-methylcoumarine (AMC) as the fluorophore [Hoppe, 1983]. Fluorogenic analog substrate (Leucine-AMC) was added at 20 μM final concentration.

[5] Biosilica production and dissolution rates were measured as described in Beucher *et al.* [2004]. Incubations were carried out 24 hours in a deck incubator cooled by running sea-surface water. Incubation flasks were fitted out with neutral photographic screens to simulate in situ light conditions. The method used is quite similar to that developed by Nelson and Goering [1977a, 1977b]; the sample was spiked by <sup>29</sup>Si(OH)<sub>4</sub> so that the increase of the in situ concentration did not exceed 10 %. The improvement of our method stands in the direct measurement of SiO<sub>2</sub><sup>-</sup> (not of SiF<sub>3</sub><sup>+</sup> avoiding using the hazardous HF). Dissolved Si was recovered by precipitation with a TEA/molybdate reagent [De La Rocha *et al.*, 1996] and purified by combustion up to 1100°C. For detailed chemical and analytical procedures, see R. Corvaisier *et al.* (Determination of the rate of production and dissolution of biosilica in marine waters by thermal ionisation mass spectrometry, submitted to *Analytica Chimica Acta*, 2004). Isotopic abundances were measured on a THQ Finnigan mass spectrometer with precision = 1 part in 10000 for the atom % of <sup>29</sup>Si and average blank = 9 nmol. The biosilica production (ρ<sub>P</sub>) and dissolution (ρ<sub>D</sub>) rates were constrained by the requirement

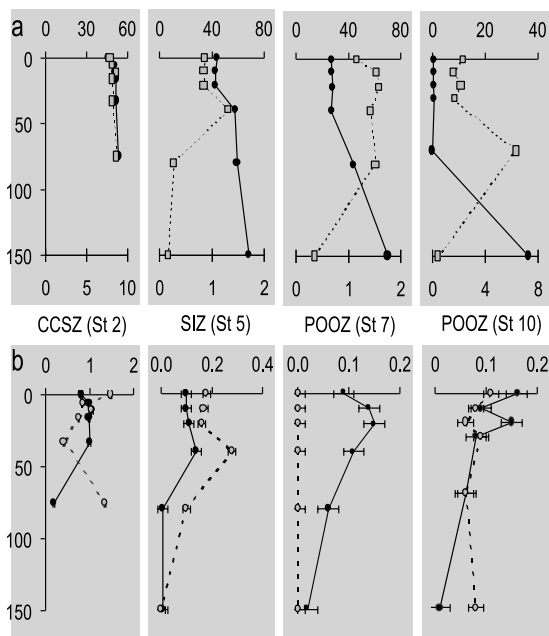


**Figure 1.** (a) Localization of stations sampled. Sub-Tropical Front (STF), Sub-Antarctic Front (SAF), Polar Front (PF), Sub-Antarctic Zone (SAZ), Permanent Open Ocean Zone (POOZ), Seasonal Ice Zone (SIZ) and Coastal and Continental Shelf Zone (CCSZ). (b) Distribution of temperature ( $^{\circ}\text{C}$ , stars, right scale),  $\text{Si}(\text{OH})_4$  ( $\mu\text{M}$ , black circles, left scale) and  $\text{bSiO}_2$  ( $\mu\text{mol l}^{-1}$ , grey circles, right scale) in surface waters versus latitude.

to fit mass and isotopic balances of the dissolved and the particulate phases (i.e., 4 equations for 2 unknowns); the best solution being found iteratively by minimizing the cost function [Elskens et al., 2002; Beucher et al., 2004]. Average specific production ( $\nabla_P$ ) and dissolution ( $\nabla_D$ ) rates were calculated for each profile (specific rate = absolute rate divided by biosilica concentration).

### 3. Results

[6]  $\text{NO}_3 + \text{NO}_2$  concentrations in surface waters ranged from 7.5 to 53  $\mu\text{M}$ , i.e. were everywhere sufficient to



**Figure 2.** (a) Profiles of  $\text{Si}(\text{OH})_4$  concentrations ( $\mu\text{M}$ , black, high scale) and  $\text{bSiO}_2$  concentrations ( $\mu\text{mol l}^{-1}$ , grey, low scale). (b) Profiles of biosilica production (black,  $\pm 0.02 \mu\text{mol l}^{-1} \text{d}^{-1}$ ) and dissolution (grey,  $\pm 0.015 \mu\text{mol l}^{-1} \text{d}^{-1}$ ) rates (error on replicates).

**Table 1.** Sampling Date (2003) of Stations, 0.01% Light Depth (m), Biosilica Parameters and Protease Activity of Total Bacteria

St.	date	0.01%	$\int \text{bSiO}_2$	$\int \rho_P$	$\int \rho_D$	$\int D:P$	$\nabla_P$	$\nabla_D$	$\int PA$
2	02-05	75	622	57.6	63.1	1.1	0.10	0.12	19.0
5	02-08	150	85	7.9	18.8	2.4	0.09	0.20	2.4
7	02-11	150	184	11.4	0.0	0.07	0.00	0.00	3.9
9	02-03	150	370	10.0	12.6	1.3	0.04	0.04	4.5
10	02-01	150	488	9.2	11.0	1.2	0.05	0.06	13.0
11	01-30	80	31	1.7	5.2	3.1	0.06	0.13	4.9

$\int \text{bSiO}_2$ : depth-integrated biosilica concentration ( $\text{mmol m}^{-2}$ ),  $\int \rho_P$  and  $\int \rho_D$ : depth-integrated biosilica production and dissolution rates ( $\text{mmol m}^{-2} \text{d}^{-1}$ ).  $\int D:P$ : ratio of  $\int \rho_D$  to  $\int \rho_P$ .  $\nabla_P$  and  $\nabla_D$ : average specific biosilica production and dissolution rates ( $\text{d}^{-1}$ ).  $\int PA$ : depth-integrated protease activity of total bacteria ( $\mu\text{mol m}^{-2} \text{h}^{-1}$ ).

prevent from N-limitation. Microphytoplankton was everywhere diatom-dominated.

[7] Station N<sup>o</sup>2, situated in the CCSZ, presented high concentrations of nutrients and biosilica (Figure 2, Table 1). The total percentage of dead diatoms was lower than in others stations (14%) (Table 2) and differed also by a large range among species. The small *Fragilariopsis curta* were dominant and mostly living (14% dead) whereas the big *Corethron criophilum* (220–300  $\mu\text{m}$ ) were mostly dead (60%). This suggests that the dominant small living diatoms ensured the production of biosilica whereas the dissolution was mostly due to the large dead cells. Very high biosilica production and dissolution rates were measured in this coastal station (Figure 2), in accordance with Nelson et al.'s study in the Ross Sea [1991]. The ratio of the depth-integrated dissolution to the depth-integrated production of biosilica ( $\int D:P$ ) was 1.1. This station presented the highest integrated bacterial protease activity ( $\int PA$ , Table 1).

[8] Station N<sup>o</sup>5, situated in the SIZ, was characterized by low biosilica concentration (Figure 2) and low biosilica production rate compared to POOZ stations. 31% of diatoms were dead (Table 2). This station was also characterized by the presence (5%) of *Corethron criophilum* mostly dead (60%). The specific dissolution rate reached a maximal value of 0.38  $\text{d}^{-1}$ . A net dissolution (dissolution overwhelming production) occurred at the 6 depths sampled:  $\int D:P$  was 2.4.  $\int PA$  was the lowest of this study (almost 10 times less than in the CCSZ, Table 1).

[9] The POOZ presented a  $\text{Si}(\text{OH})_4$  gradient (Figure 1), with surface concentrations decreasing from south to north.

**Table 2.** Percentage of Dead Diatoms and of Major Diatom Species

St	% dead	3 major species
2	14	<i>F. curta</i> (39%), <i>Nitzschia sp.</i> (19%), <i>Corethron criophilum</i> (12%)
5	31	<i>F. curta</i> (51%), <i>F. cylindrus</i> (20%), <i>Pseudonitzschia heimii</i> (11%)
7	28	<i>Fragilariopsis sp.</i> (27%), <i>F. curta</i> (19%), <i>F. kerguelensis</i> (18%)
9	29	<i>F. kerguelensis</i> (64%), <i>Fragilariopsis sp.</i> (9%), <i>Pseudonitzschia heimii</i> (6%)
10	19	<i>Fragilariopsis sp.</i> (27%), <i>F. kerguelensis</i> (24%), <i>Pseudonitzschia heimii</i> (18%)
11	35 <sup>a</sup>	<i>Pseudonitzschia heimii</i> (36%), <i>Thalassiosira</i> (21%), <i>Fragilariopsis sp.</i> (18%)

*F.*: *Fragilariopsis*,

<sup>a</sup>: calculated excluding *Pseudonitzschia lineola* (see text).





**Table 3.**  $\int D:\int P$  Ratios in the Southern Ocean 100–0.1% Light Layer From Which Vertically Integrated Data are Available (N = Number of Stations)

Season		N	low	mean	high
Austral spring					
O-N 1978	Pacific <sup>a</sup>	6	0.18	0.34	0.58
O-N 1997	Pacific survey I <sup>b</sup>	3	0.61	0.64	0.69
D 1997	Pacific Process I <sup>b</sup>	7	0.01	0.27	0.72
	total	16		0.37	
Austral summer					
J-F, 1990	Ross Sea <sup>c</sup>	9	0.41	0.65	1.1
F-M, 1998	Pacific Process II <sup>b</sup>	6	0.04	0.83	2.71
J-F, 2003	East Indian <sup>d</sup>	6	0.0	1.4	3.2
	total	21		0.9	

Data from:

<sup>a</sup>Nelson and Gordon [1982].

<sup>b</sup>Brzezinski et al. [2001].

<sup>c</sup>Nelson et al. [1991].

<sup>d</sup>This study (using 0.1% data estimated).

in order to compare previous studies to our, we have estimated, from our results,  $\rho_P$  and  $\rho_D$  at the 0.1% depth and calculated  $\int D:\int P$  in the 100–0.1% layer. These estimated ratios are 0.8, 2.3, 0, 1.3, 0.9 and 3.2 for stations 2, 5, 7, 9, 10 and 11, respectively (Table 3). Now, Table 3 offers a new vision of the Si-cycle in the surface waters of the Southern Ocean, and delivers a clear message: a higher Si-recycling occurs during summer ( $\int D:\int P$  average = 0.9) as opposed to spring ( $\int D:\int P$  average = 0.37). Although the Si-recycling varies within a large range during a given season, it is remarkable that during spring  $\int D:\int P$  never exceeds unity whereas in summer ratios  $>1$  are found for different systems of the Southern Ocean. In other words, this suggests that the silicate pump (a concept described by Dugdale et al. [1995]) is more efficient in the Southern Ocean during spring than during summer.

## 5. Conclusion

[17] This study clearly confirms that temperature alone does not control the biosilica dissolution in surface waters of the Southern Ocean, and supports Bidle and Azam's view on bacteria-mediated biosilica dissolution. This has strong implications for modelers who should take into account the role of the microbial loop on biosilica dissolution. Our results also show that a complete recycling of biosilica produced in the euphotic layer can occur during summer. This has strong implications for paleo-reconstructions, as diatom oozes apparently may mostly represent the spring production.

[18] **Acknowledgments.** This work is dedicated to the memory of J. J. Pichon. It was supported by INSU/CNRS/IPEV, France. We thank the captain and crew of the *R.V. Marion-Dufresne*, the chief scientists: X. Crosta and E. Michel and E. Follenfant for ( $\text{NO}_3 + \text{NO}_2$ ) analyses. Contribution No 908 of European Institute for Marine Studies, Brest, France.

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C. Beucher, R. Corvaisier, A.-M. Hapette, and P. Tréguer, LEMAR, UMR 6539, European Institute for Marine Studies, 29280 Plouzané, France. (charlotte.beucher@lifesci.ucsb.edu)

N. Metzl, LBCM, UMR 7094, University P. and M. Curie, 75252 Paris, France.

J.-J. Pichon, EPOC, UMR 5805, University of Bordeaux, 33405 Talence, France.