

# Kinetics of Dissolution of Antarctic Diatom Frustules and the Biogeochemical Cycle of Silicon in the Southern Ocean

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Summary. In order to simulate the fate of biogenic silica generated in the surface waters of the Southern Ocean, the dissolution of silica frustules was studied for seven natural assemblages of diatoms, collected during summer 1984 in the Indian sector, and two typical Antarctic diatoms (Nitzschia cylindrus and Chaetoceros deflandrei), following the procedure of Kamatani and Riley (1979). For mean summer conditions in the surface waters of the Southern Ocean  $(2 < T^{\circ}C < 12;$ 7.5 < pH < 8) rate coefficients of dissolution range from 2.2 to  $18.5 \times 10^{-3} d^{-1}$  for the natural assemblages. The silica frustules trapped by fecal pellets and by gelatinous aggregates, and rapidly transported through the cold waters of the Circumpolar Current, reach the sea bottom of either the continental shelves of the abysses without loosing much of the initial amount of silica (less than 10%). A model based on Stokes' law, modified to take in account of non ideal conditions and of the upwelling rate, is used in order to simulate the fate of silica of unaggregated particles settling down in the cold waters of the Antarctic Divergence. It supports the ideas that 1-the cycle of siliceous particles which radii are  $< 2 \,\mu m$  (i.e., of a part of the nanoplankton) is completely achieved in the surface layer, 2-although the biogenic silica of large unaggregated particles (radii over 25 µm) may reach the seabottom (within one month to a few years) without complete dissolution, the main explanation for the accumulation of biogenic silica on Antarctic abysses remains transport by fecal pellets and gelatinous aggregates.

## Introduction

In spite of low primary production in the photic layer of the Southern Ocean (Priddle et al. 1986a, b; von Bodungen et al. 1986; Tréguer and Jacques 1986), large amounts of biogenic silica have been observed on the abyssal sea bottom and continental shelves (Lisitzin 1972; Pichon 1985; Dunbar 1984; Dunbar et al. 1985a, b; Ledford-Hoffman et al. 1986). This silicon paradox may result from rapid transportation of silica debris incorporated in fecal pellets (Schrader 1971; Urrere and Knauer 1981; Suess and Ungerer 1981; Tsunogaï et al. 1986, among others), fecal material and marine snow (Smetacek 1985). It might also result from the slow dissolution of silica frustules (Nelson and Gordon 1982) settling down in low temperature and relatively low pH Antarctic waters. Although several works (review in Kamatani et al. 1988) have evidenced the effects of temperature and pH on the frustule dissolution of diatom assemblages, most of them dealed with the behaviour of silica particles at the water-sediment interface. Only few studies are concerned with the fate of Antarctic diatoms in the water column (e.g., Van Bennekom et al. 1988). The simple first-order reaction law for the dissolution of biogenic silica, proposed by Kamatani and Riley (1979) and used in the present study, offers the advantage of introducing a pseudo rate constant (herein called "rate coefficient") expressed in time $^{-1}$ , i.e., comparable to the specific dissolution rate V<sub>diss</sub> determined by the isotopic method of Nelson and Gordon (1982)

The objectives of this work are: 1) measuring the dissolution rates of biogenic silica for specific and natural assemblages of Antarctic diatoms, at conditions prevailing in Antarctic surface waters during summer; 2) simulating the fate of the biogenic silica particles settling down through the cold and turbulent waters of the Circumpolar Current.

## **Material and Methods**

#### 1 Samples of Biogenic Silica

a) Specific Populations. The two Antarctic diatoms Nitzschia cylindrus (Grunow) Hasle and Chaetoceros deflandrei (Manguin) were grown on a Müller medium (salinity: 34 PSU) at 4 °C under LD cycle (illumination: 113  $\mu$ E m<sup>-2</sup> s<sup>-1</sup>). After 12 days, the diatom cells were collected by filtration and stored in a refrigerator until used. Samples were not sterilized.

Table 1. Dates of experiments, location of sampling stations and dominant species composition of phytoplankton natural assemblages

| Dates of                            | Sam-<br>ple | Stati | ions              | Dominant species   |  |  |
|-------------------------------------|-------------|-------|-------------------|--|--|--|
| experiments                         |             | No.   | Location          |  |  |  |
| November<br>and Septem-<br>ber 1984 | (A)         | 7:    | 51°S-62°30'E      | Nitzschia heimii –<br>Nitzschia pro-<br>longatoides – Nitz-<br>schia turgidula |  |  |
|                                     | <b>(B)</b>  | 11:   | 65°30'S-69°10'E   | Nitzschia cylindrus –  |  |  |
|                                     |             | 13:   | 67°30′S – 72°30′E | Fragilariopsis rhom-<br>bica – Nitzschia<br>kerguelensis                       |  |  |
|                                     | (C)         | 39:   | 55°S-74°E         | N. cylindrus –<br>N. kerguelensis –<br>Fragilariopsis sp.                      |  |  |
| October                             | (D)         | 8:    | 54°30′S-64°E      | N. kerguelensis  |  |  |
| 1985                                | (E)         | 26:   | 60° S – 88°30' E  | Nitzschia barkleyi –<br>N. prolongatoides –<br>N. turgidula                    |  |  |
| February                            | (A)         | 7:    | 51° S – 62° 30' E | (see above)  |  |  |
| 1986                                | (E)         | 26:   | 60° S – 88° 30' E | (see above)  |  |  |

b) Natural Populations. Diatom assemblages were collected using a phytoplankton net, during the Antiprod 3-Apsara 2 cruise (January–February 1984, Indian sector of the Southern Ocean). The location of the sampling stations and dominant species are given in Table 1. Samples were kept frozen  $(-20^{\circ}C)$  until experimentation at the laboratory.

#### 2 In vitro Dissolution Experiments

Dissolution experiments were carried out on biogenic material according to Kamatani and Riley (1979). Five pH values were chosen: 7.5, 7.75, 8.0, 8.25, 8.5 for three different temperatures:  $2.5^{\circ}$ ,  $12^{\circ}$  and  $22^{\circ}$ C. The biogenic material was suspended in sea water collected either in the Southern Ocean (September and October 1984 sets) or in coastal water from the Bay of Brest (November 1984 and February 1986 sets). In each case, the sea water, filtered on Millipore filter (0.45 µm), was treated with 25 ml/l of 0.1 M Tris solution (Merck p.a.) and finally adjusted to the desired pH using HCl 0.1 N or NaOH 0.1 N. Predetermined weights of diatom samples were suspended in the seawater of desired pH. The

mixture was then transfered into 1-l polyethylene bottles placed in a constant temperature room  $(\pm 1 \,^{\circ}\text{C})$  and shaken at 100-120 strokes per minute. The initial concentrations of biogenic silica used for the experiments are shown in Tables 2 and 3.

Approximately 10 ml sample were removed at regular intervals; after centrifugation, orthosilicic acid concentration was determined by the automatic method of Tréguer and Le Corre (1975). The accuracy of the method is  $\pm 0.2 \,\mu$ g at-Si in the range  $0-15 \,\mu$ g at-Si and  $\pm 1.7 \,\mu$ g at-Si in the range  $0-200 \,\mu$ g at-Si.

#### 3 Calculation of the Rate Coefficient

The variation of the concentration C of biogenic silica versus time t follows equation (1): dC/dt = -KC; K is a pseudo kinetic constant (expressed in time<sup>-1</sup>) called herein "rate coefficient", C<sub>0</sub> being the initial concentration of C at time t = 0. The integration of (1) gives equation (2): ln ((C<sub>0</sub>-c)/C<sub>0</sub>) = -Kt. The decrease in C corresponds to the increase in orthosilicic acid c as measured in the solution.

## Results

Figure 1 shows typical plots of the variation of dissolved orthosilicic acid concentrations versus time (according to equation 2), during the dissolution of diatom assemblages collected at 3 stations of the Antiprod 3-Apsara 2 cruise. The rate coefficient is calculated from the slope of each curve. Firstly, this figure evidences the effect of temperature on the dissolution: the highest the temperature, the fastest the dissolution of biogenic silica. Secondly, it also illustrates significant variations of the rate coefficient depending on the composition of the diatom assemblages (Table 1): at  $2.5 \degree C$  and pH = 8, the rate constant was  $2.3 \cdot 10^{-3} d^{-1}$  for phytoplankton populations dominated by Nitzschia cylindrus and Nitzschia kerguelensis (55 °S),  $2.7 \cdot 10^{-3} d^{-1}$  for populations dominated by Nitzschia cylindrus and N. rhombica and  $3.9 \cdot 10^{-3} d^{-1}$ (64°−65°S), for populations dominated by Nitzschia sp. (51 °S). It must be noted that the whole samples contained debris of diatoms. Thirdly, Fig. 1 shows that during the first 20 days of the experiments no significant dissolution of untreated diatom ooze dominated by Rhizosolenia sp. (sample collected by

**Table 2.** Kinetics of dissolution of biogenic silica (diatom natural assemblages): mean rate coefficients  $(K_1 \times 10^{-3} d^{-1})$  for different conditions of temperature and pH

| Samples | Dates of       | Initial amount        | tt Temperature $pH$<br>(°C) $7.5$ 7.75 | pH   |      |      |      |      |
|---------|----------------|-----------------------|--|------|------|------|------|------|
|         | experiments    | $(\text{mg SiO}_2/1)$ |  | 8.0  | 8.25 | 8.5  |      |      |
| A/B/C   | September 1984 | 34/28/27              | 2.5                                    |      |      | 3.0  |      |      |
| A/B/C   | November 1984  | 31/36/45              | 2.5                                    | 1.9  |      |      |      |      |
| D/E     | October 1985   | 18/8                  | 2.5                                    | 2.2  | 4.2  |      | 3.3  | 4.0  |
| A/E     | February 1986  | 11/26.5               | 2.5                                    |      | 2.0  |      | 1.5  |      |
| A/B/C   | September 1984 | 34/28/27              | 11.5                                   |      |      | 13.0 |      |      |
| A/B/C   | November 1984  | 31/36/45              | 12.0                                   | 8.6  |      |      |      | 7.8  |
| D/E     | October 1985   | 18/8                  | 13.5                                   | 15.9 | 15.6 |      | 52.1 | 39.7 |
| A/E     | February 1986  | 11/26.5               | 12.0                                   |      | 13.0 |      | 11.3 |      |
| A/B/C   | September 1984 | 34/28/27              | 24.0                                   |      |      | 41.2 |      |      |
| A/B/C   | November 1984  | 31/36/45              | 22.0                                   | 17.0 |      |      |      | 22.3 |
| D/E     | October 1985   | 18/8                  | 22.0                                   | 44.0 | 65.0 |      | 91.0 | 62.0 |
| A/E     | February 1986  | 11/26.5               | 23.0                                   |      | 46.2 |      | 33.0 |      |

**Table 3.** Kinetics of dissolution of biogenic silica (monospecific populations of diatoms): rate coefficient ( $K_1 \times 10^{-3} d^{-1}$ ). F = Chaetoceros deflandrei; G = Nitzschia cylindrus

| Temperature<br>(°C) | Diatom species | Initial amount<br>(mg SiO <sub>2</sub> /l) | pН  | <b>K</b> <sub>1</sub> |  |
|---------------------|----------------|--|-----|-----------------------|--|
| 2                   | F              | 41.0                                       | 7.5 | 3.1                   |  |
| 2                   | F              | 38.5                                       | 8.5 | 0.5                   |  |
| 2                   | G              | 57.3                                       | 7.5 | 1.9                   |  |
| 2                   | G              | 42.2                                       | 8.5 | 0.9                   |  |
| 14                  | F              | 41.0                                       | 7.5 | 7.1                   |  |
| 14                  | F              | 38.5                                       | 8.5 | 3.2                   |  |
| 14                  | G              | 57.3                                       | 7.5 | 6.6                   |  |
| 14                  | G              | 42.2                                       | 8.5 | 5.8                   |  |
| 22                  | F              | 41.0                                       | 7.5 | 14.7                  |  |
| 22                  | F              | 38.5                                       | 8.5 | 12.5                  |  |
| 22                  | G              | 57.3                                       | 7.5 | 17.4                  |  |
| 22                  | G              | 42.2                                       | 8.5 | 15.6                  |  |

corer, in the Pacific sector,  $64^{\circ}16.3'$ S;  $136^{\circ}06.8'$ E, 3200 m depth, by courtesy of Dr. Nemoto) was measured: the dissolution of biogenic silica in Antarctic surface waters is much more rapid than that of diatoms at the sediment-water interface (for a review of the dissolution of ooze, see Kamatani et al. 1988). *Fourthly*, Fig. 1 evidences two stages in the dissolution of the silica frustules, the first one being slower than the second: the enhancement of the kinetic rate, observed after 10-15 days for samples B and C at  $11.5^{\circ}$ C, might correspond to the removal of the protective coating of organic matter which has remained in the samples and to different stages of hydration for biogenic silica (Lewin 1961; Kamatani et al. 1980). Herein



Fig. 1. Kinetics of dissolution of silica frustules of Antarctic diatoms at pH 8: plots of Y =  $-\ln (C_0 - C)/(C_0)$  versus time. Natural assemblages collected during summer in the Indian sector (Antiprod 3-Apsara 2 cruise, see Table 1):  $A \circ 2^{\circ}$ C, ● 11.5 °C;  $B \square 2^{\circ}$ C, ■ 11.5 °C;  $C \nabla 2^{\circ}$ C, ▼ 11.5 °C. Diatoms ooze (from the Pacific sector, see text):  $F \blacktriangle 11.5^{\circ}$ C

is only considered the first step of the kinetics of dissolution of biogenic silica (constant rate  $K_1$ , Table 2).

The mean rate coefficients for the different conditions of temperature and pH used during our experiments with natural assemblages are given in Table 2. According to Hurd (1973) and Hubbard and Riley (1984), the dissolution rate of frustules depends on pH. Table 2 shows that for natural assemblages A/B/C the rate coefficient goes through a maximum at pH 8 ( $K_1 = 13 \cdot 10^{-3}$ and  $41.2 \cdot 10^{-3} d^{-1}$ , respectively, at 12° and 22°C) compared with pH 7.5 ( $K_1 = 8.6$  and  $17.0 \cdot 10^{-3} d^{-1}$ , respectively, at  $12^{\circ}$  and  $22^{\circ}$ C); the maximum is reached at pH 8.25 for samples D/E. The effect of pH on the dissolution rate is usually explained by metals-silica interactions (Harvey 1937; Goldberg 1952; Iler 1955; Geissler 1958; Ives 1959: Lewin 1961: Martin and Knauer 1973: Van Bennekom and Van der Gaast 1976; Van Bennekom 1981).

The effect of temperature for the two specific Antarctic diatoms upon the rate coefficient is illustrated in Fig.2 as compared with previous measurements data on several diatoms collected in coastal waters (Kamatani 1982). At pH 7.5 a linear regression is achieved between  $\ln K_1$  and temperature ranging between 2° and 23°C, with a mean slope of -0.11, i.e., in good agreement with previous results by Kamatani (1982) for temperature varing between 8° and 28°C. The corresponding mean slopes for the Antarctic natural assemblages varied between -0.11and -0.19. This clearly demonstrates that the dissolution of biogenic silica at the northern limit of the Southern Ocean (12°C) is 4 to 14 times as large as that near the continent (-1.8°C).



**Fig. 2.** Effect of temperature variations on the dissolution of silica frustules: rate constant  $K_1$  versus temperature (°C); the continous lines, drawn according to Kamatani (1982), delimitate the domain of variations of the rate constant, for different species. Monospecific populations of Antarctic diatoms: *Chaetoceros deflandrei*  $\circ$  pH 7.5,  $\bullet$  pH 8.5; *Nitzschia cylindrus*  $\Box$  pH 7.5,  $\blacksquare$  pH 8.5. The *dashed line* shows the regression line at pH 7.5 (see text)

# Discussion

# 1 Comparison Between the Rates Measured by the Present Method and the Isotopic Method

Nelson and Gordon (1982) have measured the dissolution of biogenic silica during summer, in surface waters of the Pacific sector, by using an isotopic method. Between 51°30 to 64°15S, i.e., for temperature varying between about 12° to 2°C, the specific dissolution rate  $V_{diss}$ ranged between 9.2 and  $58 \cdot 10^{-8} \text{ s}^{-1}$ . Although the specific rates measured at the two stations located in cold surface waters are close together (mean rate =  $29 \cdot 10^{-8} \text{ s}^{-1}$  at  $62^{\circ} - 67^{\circ} \text{S}$ ), the mean rate measured at  $51^{\circ}30\text{S}$  was only  $17 \cdot 10^{-8} \text{ s}^{-1}$  (Fig. 7, p. 497 in Nelson and Gordon 1982), suggesting that other factors than the temperature may control the dissolution of the biogenic silica in the photic layer. In the same temperature range our method gave  $K_1$  between 2.2 and  $18.5 \cdot 10^{-8} \text{ s}^{-1}$ ; although our upper limit is compatible with Nelson and Gordon's results, our lower limit is about 4 times as small as that of these authors, suggesting a possible under-evaluation of the dissolution rate by the in vitro method we used for this study.

Although Kamatani and Riley's method on the one hand, Nelson and Gordon's method on the other hand, used natural assemblages (grazed or ungrazed diatoms) for the experiments, the main difference between both methods arises from the different size classes of the particles of biogenic silica. No filtration is required by the isotopic method which measures the silica dissolution of the whole frustules present in the seawater sample, while our method does not take into account the dissolution of the small components of natural assemblages as they are not collected by the net (50 µm mesh). This suggests that the silica frustules of small particles (i.e., a fraction of the nanoplankton) might dissolved more rapidly than those of the diatoms of microphytoplankton. In the model we built to simulate the fate of the biogenic silica in the Southern Ocean, the mean rate coefficients measured by the isotopic method are supposed to be more representative of the dissolution of the silica for small particles. and those measured by the Kamatani and Riley's method will be used for large particles (radius over 25 µm).

## 2 The Fate of Biogenic Silica in the Southern Ocean

If surface-water temperature is a major factor that controls the silica dissolution rates in the ocean, it would result in a higher fraction of the biogenic silica generated in the photic zone being transported to depth and sea bottom at polar and subpolar areas than in the tropical and subtropical areas. Previous works show that in coastal upwelling ecosystems and in warm-core rings (e.g., in Gulf Stream) the recycling of orthosilic acid can be very intense (80% - 100% of the pelagic biogenic silica production is dissolving in the upper 100 m layer, review in Nelson and Goering 1977; Richards 1981; Jacques and Tréguer 1986; Brzezinski 1987). On the contrary in the Southern Ocean between 18% and 58% of the biogenic silica production is dissolved in surface layers (Nelson and Gordon 1982): the other part escapes from this layer as the result of rapid transportation by fecal pellets and gelatinous aggregates, and/or settling of unaggregated diatom cells.

By comparing field observations and measured data about the dissolution rate of biogenic silica, the following questions are adressed in this discussion: 1) which size classes of siliceous particles are able to dissolved in the surface layer? 2) Which size classes of siliceous particles are able to reach the sea bottoms of the different Antarctic domains?

In the Bransfield Strait Dunbar (1984) noted that, the trapped material was predominantly composed 1) of fecal pellets (cylindrical and compact ellipsoïdal pellets being more abundant in the deeper trap samples) 2) of biogenic silica (fine diatoms fragments being predominant). For the Ross Sea, the importance of both low density gelatinous aggregates and diatom tests in the sediment traps was noticed, settling rates as high as 200 to 400 m per day being measured (Dunbar et al. 1985b) for zooplankton fecal pellets. Tsunogaï et al. (1986) demonstrated that one of the most striking features of the Southern Ocean ecosystem is the very rapid settling rate of biogenic silica particles (230 m/day). Moreover observations made by Pichon (1985) reveal good preservation of diatoms in marine sediments south of Polar Front. Sediment deposits deeper than 4000 m are composed of large species (Thalasiosira lentiginosa) and also of small species (Nitzschia curta, N. cylindrus).

2a The Fate of Biogenic Silica Trapped by Fecal Pellets and Gelatinous Aggregates in Coastal Areas and Open-Ocean Areas

Let us suppose that large particles of biogenic silica escape from the surface layer and are transported within the cold deep waters at a rate of 200-300 m/day.

In the coastal seas of the Antarctic domain, recent studies (Nelson and Smith 1986; Nelson et al. 1987) demonstrated that very productive diatom blooms, supporting intense food demand of krill and other herbivorous, are associated with the seasonal retreating of ice, especially over the Antarctic continental shelves of Ross Sea and Weddell Sea (which are about 500-600 m deep). Only two to three days are needed by the biogenic silica particles, produced in surface water, and then picked up by fecal pellets, to reach the water-sediment interface. During this period the particles settle down through cold waters ( $<2^{\circ}$ C) and the amount of biogenic silica dissolved during this transport is negligible (less than 2%, from with  $2.2 < K_1 \times 10^{-8} s^{-1} < 4.9$ equation (1) for 7.5<pH<8, see Table 2). In Antarctic open-ocean (depths over 4000 m) the silica particles collected by fecal pellets and gelatinous aggregates, escape from the mixed layer, settle down through the water column (temperature  $< 2^{\circ}$ C) reaching the sea bottom within 10 to

20 days; during this transport (using equation (1) and  $2.2 < K_1 \times 10^{-8} s^{-1} < 18.5$ ) we can calculated that more than 90% of the initial amount of biogenic silica are preserved from dissolution, ultimately accumulating on the Antarctic abysses (Ledford-Hoffman et al. 1986).

# 2b The Fate of Unaggregated Particles of Biogenic Silica Settling Down Through the Water Column

In order to simulate the fate of the biogenic silica particles generated in the surface layer and settling down at slow rate (compared with the gravitational settling rates of aggregates), through the cold waters (about  $2 \,^{\circ}$ C) of the Antarctic Divergence, a model based on Stokes' law is used. As compared with previous models (e.g., Wollast 1974) the improvement comes from taking into account of: 1) the upwelling rate of the Circumpolar Deep Water (t  $^{\circ}$ C about  $2 \,^{\circ}$ C) which rises to the surface, resulting in a decrease of the usual Stokes' settling rate, 2) the dissolution rate coefficient measured for different natural assemblages (expressed in time<sup>-1</sup>), 3) the shape factor occuring for various kinds of diatoms frustules, 4) the effect of turbulence on the sedimentation rate.

Let us first suppose that an idealized solid sphere (radius  $R_0$  at the surface and radius R at depth z, molar mass M, specific mass RO<sub>s</sub>) of biogenic silica is settling down through the water column (specific mass RO<sub>w</sub>). The total amount of silica skeletons per unit of volume C is given by equation (3)  $C = (4\pi R^3/3 M)RO_{cn}$ , n being the number of particles settling per unit volume of seawater. From equation (1) and (3), the variation of R versus time is given by equation (4)  $dR/dt = -(K_1/3)dR$ . Taking in account of (5) dR/dt = (dR/dz)/(dz/dt) and of the upwelling rate W (mean value  $50 \text{ m y}^{-1}$  or  $1.6 \cdot 10^{-4} \text{ cm s}^{-1}$  at the Antarctic Divergence, according to Gordon and Taylor 1975), the usual Stockes' law for a laminar conditions must be modified following equation (6)  $dz/dt = BR^2 - W$ , (B is given by (7):  $B = (2 g(RO_s - RO_w)/9 Nu)$ , g is the gravitational acceleration: 981 cm/s, and Nu is the viscosity of seawater:  $1.72 \cdot 10^{-2}$  poise for cold waters, according to Walton Smith 1974). The mean wet density of plankton particles may vary between 1.528 to  $1.057 \,\mathrm{g \, cm^{-3}}$  for particles which radius is between 0.7 µm and 181 µm, the largest the size of the particle, the smallest the wet density (McCave 1975); the mean specific mass of Antarctic seawater is about  $1.028 \text{ g cm}^{-3}$  consequently B ranges between 367 (large particles) and 6337  $\text{cm}^{-1} \text{s}^{-1}$  (small particles).

In equation (6), "BR<sup>2</sup>" represents the rate of particles settling in a motionless watermass; "BR<sup>2</sup>-W" being the net settling rate in waters of the Antarctic Divergence (Fig. 3). Following (6), the settling rate dz/dt = 0 when  $BR_c^2 = W$ , which means: when the radius of the particle decreases to R<sub>c</sub> (herein called "compensation radius"), at time t<sub>c</sub> ("compensation time"), the particle stops settling down at depth z<sub>c</sub> ("compensation depth"), and then this particle will rise towards the surface. This is a unique feature of the movement of particles in a divergence zone.

$$z_c = (-(3 \text{ B}/2K_1) \times (R_c^2 - R_0^2)) + (3 \text{ W/k}_1) \times \ln(R_c/R_0)$$
 (8)

$$t_c = -(3/K_1) \times \ln (R_c/R_0)$$
 (9)

$$R_{c} = (W/B)^{1/2}$$
(10)

To simulate the conditions prevailing in situ we must take in account of the effect of the different shapes of the particles upon the settling rate. This is done by modifying the parameters B as  $k \times B$ , with k = 1 for spheres, k is about 1.3 for lamelles, between 0.96 and 1.7 for ellipsoïdal particles (Brun-Cottan 1976a, b; MacNown et al. 1951), and may reach value as high as 10 for needles. So, the settling rate of the non spherical particles may be twice as fast as that of ideal spherical particles; this settling rate may be ten times as fast for silica needles. For non spherical particles, in the above equations "R" represents an "equivalent spherical radius" (McCave 1975).

Although the conditions prevailing in-situ are far from laminary flow, the effect of turbulence on the mean settling rate is usually considered to be negligible, and the Stokes law is often used to simulate the settling of particles in the ocean (review in McCave 1975). However, from experimental studies carried out with large spherical particles (radius ranging between 31.5 and 80 µm), Dietlin (1982) demonstrated that the turbulence increases the settling rate up to a factor of about 2 (the smallest the particle, the biggest the effect of turbulence). In case of non spherical particles we will consider herein that turbulence combines its effect to that of the shape factor: in the above equations " $4 \times B$ " is substituted to "B" and the corresponding maximum settling rate (for non ideal conditions) is 4 times as high as the Stokes settling rate (for ideal conditions).

2b1 The Fate of the Biogenic Silica of Unaggregated Small Particles. The upwelling of Circumpolar Deep Water (CDW) at the Antarctic Divergence results in slowing down the settlement of particles. From McCave (1975) and from the above considerations, for this size class of particle, "B" ranges between 4056 and 25348 cm<sup>-1</sup> s<sup>-1</sup>: from equation (10), any plankton particle, which radius is less than 2 µm ("compensation radius" for ideal conditions) to 0.79 µm (non ideal conditions), cannot escape the surface layer. Consequently the silica cycle of a part of the siliceous nanoplankton is completely achieved in the Antarctic surface mixed layer. By using a mean dissolution rate coefficient  $K_1 = V_{diss} = 29 \cdot 10^{-8} \text{ s}^{-1}$  (Nelson and Gordon 1982), for this size class of particle, about 5.9 months would be necessary to dissolved 99% of the initial amount of silica of small particles. Of course during such a period the probability to be grazed or picked up by gelatinous stuff and so to escape from the surface layer is not negligible. The above considerations support the idea that the siliceous which dissolved in Antarctic surface waters comes mainly from nanoplankton.

2b2 The Fate of the Large Particles in Coastal and Open-Ocean Areas. In order to illustrate the dissolution of silica from large size class particles, the fate of a particle which radius is 25  $\mu$ m is herein examined. From the above considerations "B" ranges between 1020 and 4080 cm<sup>-1</sup> s<sup>-1</sup> and values of the rate coefficient K<sub>1</sub> for natural assemblages are considered in the above equations.

In the Antarctic domain, the surface water summer temperature is about 2°C and K<sub>1</sub> ranges between 2.2 and  $4.9 \cdot 10^{-8}$  s<sup>-1</sup> for natural assemblages. Between 3 and 6.6 years are needed to dissolve 99% of the initial amount of biogenic silica; with mean settling rate between ranging between 1.6 and 6.7 m per day, a 25 µm radius particle is able to reach depths between 1710 m (for ideal conditions) and over 5000 m (non ideal conditions) (Fig. 3). This means that the large unaggregated particles are able to reach the bottom of the continental shelves (500-600 m) and even of the Antarctic abysses. In the former case a silica particle is able to reach the bottom within 1 to 3 months (between 67% to 94% of the initial amount of particles being preserved from dissolution). In the latter case the silica particle can reach the Antarctic abyss within one year (Fig. 3), about 20% of the initial amount of biogenic silica being preserved from dissolution. This means that a contribution from this process may be considered to explain the accumulation of biogenic silica on Antarctic abysses.



Fig. 3. The settling of an unaggregated 25 µm radius silica particle trough the waters of the Antarctic Divergence (2 °C) simulated by using a modified Stokes' law (see text),  $k_1 = 4.9 \cdot 10^{-8} s^{-1}$ ; ideal conditions:  $B = 1020 \text{ cm}^{-1} s^{-1}$  ( $\bigcirc \bullet$ ), non ideal conditions:  $B = 4080 \text{ cm}^{-1} s^{-1}$  ( $\bigcirc \bullet$ ), non ideal conditions:  $B = 4080 \text{ cm}^{-1} s^{-1}$  ( $\bigcirc \bullet$ ), no ideal conditions:  $B = 4080 \text{ cm}^{-1} s^{-1}$  ( $\bigcirc \bullet$ ), no ideal conditions:  $B = 4080 \text{ cm}^{-1} s^{-1}$  ( $\bigcirc \bullet$ ), no ideal conditions:  $B = 4080 \text{ cm}^{-1} s^{-1}$  ( $\bigcirc \bullet$ ), upwelling rate w = 0.00016 \text{ cm} s^{-1} (*continuous line*); w = 0 (*dashed line*). Depth (km) versus time (year)

In the subantarctic domain, out from the oceanic upwelling area (w = 0), the dissolution of biogenic silica is first performed in temperate surface waters  $(12^{\circ}-14^{\circ}C; K_1 \text{ ranges between 10 and } 18.5 \cdot 10^{-8} \text{ s}^{-1})$ . With mean settling rates varying between 5 to 20 m d<sup>-1</sup>, a 25 µm radius particle is able to reach the base of the surface layer (100 m) within a period of between about 5 days to 3 weeks. During this first step, between 3% and 27% of the initial amount of biogenic silica is dissolved. Then this reduced radius particle enters the cold deep water layer, i.e., it meets analogous conditions to those of the previous case, except that the settling rate is not slowed down (Fig. 3) as the upwelling rate is nul. Consequently, the probability that large particles reach the sea bottom of the subantarctic domain has also to be considered.

The above considerations based on the control of silica dissolution mainly by temperature, support the idea that if siliceous particles transported by aggregates do reach the Antarctic sea bottoms without any significant dissolution, deposits of unaggregated large particles of biogenic silica must be expected either at the water-sediment interface of the continental shelves or even of the abysses.

## Conclusion

The present data confirm that the dissolution of biogenic silica from Antarctic diatoms, within the water column are exceptionally slow, due to low temperatures which prevail in the whole water column of the Southern Ocean. The empirical model used in this study brings to ideas in agreement with field observations: upwelling conditions favours a part of the siliceous nanoplankton to be confined in the surface layer where its dissolution may be completely achieved; small particles are not able to reach the sea-bottom except when picked up by aggregates; intense accumulation of diatom skeletons and siliceous debris can reach the bottom of continental shelves and the Antarctic abysses without complete dissolution, resulting either from the transport of different size classes of particles trapped by fecal pellets and gelatinous aggregates, or from the settlement of ungrazed large particles.

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