



PERGAMON

Deep-Sea Research II 49 (2002) 3155–3167

DEEP-SEA RESEARCH
PART II

www.elsevier.com/locate/dsr2

The accumulation and cycling of biogenic silica in the Southern Ocean: revisiting the marine silica budget

David J. DeMaster

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, USA

Received 10 December 2000; received in revised form 5 July 2001; accepted 10 September 2001

Abstract

In many of the recent marine silica budgets (e.g., Science 268 (1995) 375), a majority of the world's biogenic silica accumulation is attributed to the siliceous-ooze deposits in the Antarctic deep sea. Based on ^{230}Th -normalized sediment accumulation rates as well as comparative studies of silica preservation (seabed accumulation compared to surface biogenic production), the rate of biogenic silica accumulation in Antarctic siliceous-ooze deposits has been over-estimated by as much as 35%. The current estimate for silica accumulation in these high-latitude deposits is $3.1 \times 10^{12} \text{ mol yr}^{-1}$ (as compared to previous values of $4.1\text{--}4.8 \times 10^{12} \text{ mol yr}^{-1}$). To maintain balance between silicate supply and biogenic silica removal in the oceans, an additional repository is needed. Evidence from continental shelf and upper slope sediments suggests that biogenic silica accumulation in continental margin deposits may account for a much larger fraction of the marine silica burial than previously thought, compensating for the diminished accumulation in the Antarctic deep sea. If biogenic silica accumulation in continental margin sediments replaces nearly a third of the silica accumulation in the Antarctic deep sea, the marine cycles of organic matter and biogenic silica are coupled to a greater extent than reported in previous budgets. © 2002 Elsevier Science Ltd. All rights reserved.

Résumé

Plusieurs travaux récents (e.g. The silica balance in the world ocean: A re-estimate. Science, 268, 375-379) montrent que la majorité des dépôts sédimentaires de silice biogène (= opale) de l'océan mondial intervient dans l'Océan Antarctique abyssal. En normalisant les vitesses d'accumulation des sédiments par la technique au ^{230}Th nous montrons que le flux d'accumulation de l'opale dans l'Antarctique est de $3,1 \text{ E12 moles par an}$, soit de 35% inférieur aux estimations antérieures ($4,1 \text{ à } 4,8 \text{ E12 mol par an}$). Si les apports nets de silicium dans l'océan sont compensés par les dépôts nets d'opale biogène (hypothèse du cycle du silicium à l'état stationnaire) un autre puits d'opale doit exister dans l'océan. Nos données tendent à montrer que ce puits pourrait se trouver dans les marges continentales de l'océan mondial, contrairement à ce que l'on pensait jusqu'à présent. Si l'accumulation d'opale dans ces marges remplace environ $1/3$ du dépôt sédimentaire abyssal en Antarctique, ceci signifie que les cycles océanique de la matière organique et de la silice biogène sont plus couplés qu'il n'était généralement admis.

1. Introduction

Silicate, or silicic acid (H_4SiO_4), is a very important nutrient in the ocean. Unlike the other major nutrients such as phosphate, nitrate, or

E-mail address: dave_demaster@ncsu.edu (D.J. DeMaster).

ammonium, which are needed by almost all marine plankton, silicate is an essential chemical requirement only for certain biota such as diatoms, radiolaria, silicoflagellates, and siliceous sponges. The dissolved silicate in the ocean is converted by these various plants and animals into particulate silica (SiO_2), which serves primarily as structural material (i.e. the biota's hard parts). The reason that silicate cycling has received significant scientific attention in the past 5 yr is that some researchers believe that diatoms are one of the dominant phytoplankton responsible for export production from the surface ocean (Dugdale et al., 1995), which contributes to the transport of particulate matter (including carbon) to the deep ocean via a process known as the biological pump. Consequently, silicate and silica may play an important role in the global carbon cycle, which affects the world's climate through greenhouse feedback mechanisms (Broecker and Peng, 1993). In addition, the accumulation of biogenic silica on the ocean floor can tell us where in the ocean export production has occurred on time scales ranging from hundreds to millions of years, which in turn reveals important information concerning ocean circulation and paleoproductivity (Ragueneau et al., 2000). The mean oceanic residence time for silicate is approximately 10,000–15,000 yr (Martin and Whitfield, 1983; Treguer et al., 1995), which is short enough so that concentrations and fluxes can respond to glacial/interglacial perturbations.

Numerous budgets for the marine silica cycle have appeared in the literature over the past three decades (e.g., Calvert, 1968; Heath, 1973; Wollast, 1974; DeMaster, 1981; and Treguer et al., 1995). An essential question to address, however, is whether or not the oceans should attain a steady-state balance between Si supply and Si removal. The marine sedimentary record exhibits siliceous microfossils of various biota for millions of years and does not reveal geochemical distributions consistent with wide-spread inorganic precipitation of silica (Drever et al., 1988). Consequently, conditions of extreme undersaturation or extreme supersaturation probably can be ruled out. However, it is possible that the dissolved silicate concentration in the oceans has varied with

time (as may have the inputs and the removal terms). There is not a good paleochemical indicator of deep-water silicate (such as there is for atmospheric carbon dioxide in the ice core record), which makes it difficult to assess the steady-state nature of the marine silica budget over time. Probably the best argument for treating the oceanic Si budget as a steady-state system comes from the feedback mechanisms described in Broecker (1971). In this article, Broecker hypothesizes that oceanic deep water attains a silicate concentration in which upwelling and eddy diffusion transports enough silicate to the surface such that biogenic silica production can generate sufficient material in surface waters to account for water-column and seabed dissolution as well as long-term burial of biogenic silica in the seabed (at a rate comparable to the oceanic dissolved input terms). Supporting this claim is the observation that nearly 100% of the silicate reaching surface waters via vertical transport processes is converted into particulate biogenic silica. Therefore, there may not be an exact balance between supply and removal of Si in the marine environment, but a large imbalance in these fluxes is not expected either. For this paper the presumption is made that the supply of silicate and the removal of silica in the oceans are essentially balanced over the past 10,000 yr (approximately the residence time of the nutrient). Biogenic silica production rates measured during the past few decades are assumed to be representative of Holocene time.

Treguer et al. (1995) estimate that the external flux of dissolved silicate supplied to the oceans (Table 1) is on the order of $6.7 \times 10^{12} \text{ mol yr}^{-1}$, coming not only primarily from rivers (84%), but also from basalt weathering (6%), eolian inputs (7%), and hydrothermal emanations (3%). Based on silicate fluxes from the seafloor (see Treguer et al., 1995), dissolution of biogenic silica in surficial sediments may supply as much as $23 \times 10^{12} \text{ mol yr}^{-1}$ of Si to bottom waters. Consequently, it is useful to consider the upper 10–20 cm of the seabed, where most of the biogenic silica dissolution takes place, as part of the water column and focus on the accumulation of biogenic silica below this zone as the ultimate burial term. In this way dissolution of biogenic silica in surface

Table 1
The marine silica budget

	DeMaster (1981); Treguer et al. (1995) ^a	Revised budget ^a
<i>Sources of silicate</i>		
Rivers	5.6	5.6
Hydrothermal emanations + weathering of marine basalt	0.6	0.6
Eolian	0.5	0.5
Total supply rate	6.7	6.7
<i>Sedimentary repositories for biogenic silica</i>		
Deep sea total	5.1–6.0	4.1–4.3
Antarctic	4.1–4.8	3.1
Polar Front	2.7–3.4	0.3
Non-Polar Front	1.4	2.8
Bering Sea	0.5	0.5
North Pacific	0.3	0.3
Sea of Okhotsk	0.2	0.2
Low Si Sediments	<0.2	<0.2
Eq. Pacific	0.02	0.02
Continental margins total	0.4–1.5	2.4–3.1
Estuaries	0.2–0.6	<0.6
Gulf of California	0.2	0.2
Walvis Bay	<0.2	0.2
Peru/Chile	<0.1	<0.1
Antarctic margin	0.2	0.2
Other margins	<0.2	1.8
Total removal rates	5.5–7.5	6.5–7.4

^a All fluxes are expressed in units of $\times 10^{12} \text{ mol yr}^{-1}$.

sediments is treated as an internal cycle and the uncertainty in its value does not overwhelm the overall marine silica budget. Conley (1997) estimates that amorphous silica transported from terrestrial environments to the ocean via rivers may be an additional source of silicate to the marine environment (as much as 16% of the global riverine silicate flux), but the fate of this material in the coastal environment is uncertain. If the terrigenous silica is buried or transformed into clay minerals (Michalopoulos and Aller, 1995) within the continental margin, there would be no contribution to the marine silica budget. However, if this material dissolves, it could be a small but significant contribution to the overall silicate

supply to the ocean. Until the fate of this material is better understood, the contribution of terrestrially produced amorphous silica remains uncertain. Most scientists agree that the removal of Si from the water column occurs primarily via the burial of biogenic silica, although minor amounts of abiogenic precipitation of amorphous silica probably occur near hydrothermal vents and some silicate may be removed via authigenic mineral formation in certain estuarine environments (Michalopoulos and Aller, 1995). In most of the recent marine silica budgets (e.g., DeMaster, 1981; Treguer et al., 1995), the dominant site of biogenic silica burial is in the Antarctic, primarily in a region just south of the Polar Front. Accumulation rates for many of these deposits have been determined by biostratigraphy, using the radiolarian, *Cycladophora davisiana* (e.g., Cooke and Hays, 1981) as well as oxygen-isotopic stratigraphies (e.g., Charles et al., 1991). The absolute rates of accumulation for individual cores are not in question, but there may be problems extrapolating the accumulation rates from individual cores collected near the Polar Front (the regions defined as the Polar Front Zone and the northern portion of the Permanently Open Ocean Zone by Treguer and Van Bennekom, 1991) to the entire Polar Front region. Evidence for potential errors in this extrapolation come from two sources: (1) disagreement between silica preservation rates in the Antarctic Polar Front Region and preservation rates already established for the Ross Sea; and (2) excess inventories of the naturally occurring radioisotope, ^{230}Th , in numerous Polar Front cores. This paper examines the evidence for overestimating Polar Front biogenic silica accumulation in the past and establishes a revised budget for the Antarctic and the world oceans. Previous authors have discussed the importance of lateral focusing in Southern Ocean sediments (e.g., Francois et al., 1993; Frank, 1996; Frank et al., 1996, 1999), and recently, Pondaven et al. (2000) constructed a Si budget for a five-core transect in the Indian Ocean sector of the Southern Ocean. This paper brings together these processes for the entire Southern Ocean siliceous belt and discusses the associated ramifications for the global marine silica budget. There are numerous papers

discussing Southern Ocean biogenic silica accumulation rates and silica preservation (e.g., van Bennekom et al., 1988; Bareille et al., 1991; Rabouille et al., 1997; Ragueneau et al., 2000), but this paper focuses solely on cores where sediment focusing has been assessed through ^{230}Th -normalization techniques. Initial evidence is presented that continental margin silica accumulation may have been underestimated previously and may compensate for the diminished biogenic silica accumulation in the Antarctic. Burial of biogenic silica in the Antarctic deep sea occurs with very little coexisting organic matter (Si/C molar ratios as high as 20–60 (DeMaster et al., 1991; Ragueneau et al., 2002), whereas continental margin systems preserve a much greater extent of their organic matter as the biogenic silica is buried (Si/C ratios on the order of 0.4–1). If continental margins are an important sink for biogenic silica and the biogenic silica accumulation in the Antarctic deep sea is reduced by as much as 35%, the coupling between the biogenic silica and organic carbon cycles occurs to a greater extent than previously thought.

2. Results and discussion

2.1. Silica preservation in the Southern Ocean

According to Treguer et al. (1995) and DeMaster (1981), the rate of biogenic silica accumulation in Antarctic deep-sea sediments varies between 4.1 and $4.8 \times 10^{12} \text{ mol yr}^{-1}$. If these estimates are divided by the production rate for biogenic silica in Southern Ocean surface waters, the silica preservation efficiency (seabed accumulation/surface production) can be determined (see DeMaster et al., 1996; Nelson et al., 1996; for more details concerning calculation of preservation efficiencies). Some of the initial estimates for silica production in the Southern Ocean came from direct production measurements based on Si isotopic data (see Nelson et al., 1995 for a review; $17\text{--}37 \times 10^{12} \text{ mol yr}^{-1}$). Combining these production estimates with the accumulation rate data yields preservation efficiencies ranging from 11% to 28%. If the production rate of biogenic silica

over the Antarctic siliceous-ooze belt is used (instead of the rate for the entire Southern Ocean), these estimates of biogenic silica preservation double (to 22% and 56%) because the siliceous-ooze deposits occupy approximately half of the Southern Ocean. In either case the preservation efficiencies are distinctly higher (by at least a factor of 2) than the biogenic silica preservation efficiencies measured in the Ross Sea (5.8%; Nelson et al., 1996; DeMaster et al., 1996).

There are several reasons why the silica preservation efficiency in the Antarctic deep sea would be expected to be lower than in the Ross Sea. First, the Antarctic siliceous-ooze belt is considerably farther north ($\sim 50\text{--}65^\circ\text{S}$) than the Ross Sea ($70\text{--}80^\circ\text{S}$), which causes temperatures in surface waters to be warmer on average ($3\text{--}6^\circ\text{C}$ versus -2°C to 2°C), enhancing the rate of dissolution (Lawson et al., 1978). Secondly, the average water depth is greater in the waters associated with the siliceous-ooze belt (typically 3000–4500 m) than in the Ross Sea (water depths typically 500–1000 m). The increased water depths in the Antarctic deep sea enhance the extent of dissolution because of greater settling times. The mode of vertical transport of biogenic silica through the water column (e.g., discrete particles versus fecal pellets) also can affect silica preservation efficiency, but there is no convincing evidence that vertical transport over the Antarctic siliceous-ooze belt is more rapid and efficient than that occurring in the Ross Sea (Smith and Dunbar, 1998). Similarly, if the biogenic silica produced beneath the Polar Front were more robust in morphology (i.e. fewer delicate and high-surface-area structures) or dissolved less readily than the siliceous material in the Ross Sea, the higher preservation efficiencies for the Southern Ocean siliceous belt (relative to the Ross Sea) could be explained at least in part. The literature reveals no obvious trend in morphology nor in biogenic silica dissolution rate (e.g., Van Cappellen and Qiu, 1997), leaving the apparent discrepancy unexplained. With no obvious reason for enhanced preservation in this deeper and warmer environment (11–28% vs. 5.8% in the Ross Sea), it is not unreasonable to examine the Southern Ocean deep-sea data for potential errors in the estimates.

If the rate of biogenic silica accumulation in the Antarctic deep sea were lower or the biogenic silica production rate greater than previously reported in the literature, the preservation efficiency would be diminished, which would bring the Ross Sea and Antarctic deep-sea data into better agreement. Although the majority of silica preservation efficiency data for the Antarctic continental margin come from the Ross Sea (DeMaster et al., 1996; Nelson et al., 1996), flux measurements from the Weddell Sea also reveal low preservation efficiencies for silica (Schluter, 1990; Queguiner et al., 1991).

Recently two papers have described biogenic silica preservation efficiencies in the Antarctic deep sea, confirming that the initial Southern ocean silica data may be suspect. Pondaven et al. (2000) reported a preservation efficiency (seabed accumulation/surface silica production) of 3% for the Polar Front Zone (based on two cores) and 6% for the Permanently Open Ocean Zone (based on three cores) in the Indian sector of the Southern Ocean. Similarly, Nelson et al. (2002) reported silica preservation efficiencies of 1–7% for a suite of six deep-sea stations along a 170°W transect in the Pacific sector of the Southern Ocean. All of these data support the hypothesis that the earlier preservation efficiency data may not be representative of the Southern Ocean as a whole.

2.2. *Lateral focusing of sediment in the Antarctic deep sea*

One reason that the burial rate of biogenic silica could be overestimated in Antarctic deep-sea deposits is lateral focusing of bottom sediment. Much of the sediment beneath the Antarctic Polar Front (where most of the biogenic silica is believed to be buried) accumulates in areas of very rugged topography. In areas of high relief, sediments may accumulate more rapidly in deeper areas and more slowly along flanks and ridges because of the effects of resuspension and downslope mass transport. If the flanks of the basins are sufficiently steep, little or no sediment may accumulate in some locations. Consequently, if a random coring grid is used for site selection, high accumulation sites in the deep basins would provide a thick

sediment cover (creating a high retrieval rate for coring), whereas slowly accumulating areas on the flanks and ridges would have a thinner sediment cover (making core retrieval less likely). In this way the higher accumulation sites could be sampled more readily, causing an overestimation of regional sediment accumulation because the area would be over-represented with cores from the basins (as a result of the lower success rate in core retrieval from flank and ridge sites). Multiplying the mean accumulation rate for a given region (biased by the disproportionate number of high-accumulation sites) by the overall area, therefore, could lead to an erroneously high estimate of sediment accumulation rate.

There is qualitative evidence of lateral sediment transport in Polar Front cores. Several diatoms that only grow in waters considerably further south have been documented in many siliceous cores beneath the Polar Front and extending up into the Argentine Basin (Burckle and Stanton, 1975). In addition, quantitative evidence of lateral transport can be obtained by examining the radiochemical inventory of the naturally occurring radioisotope, ^{230}Th (Bacon and Rosholt, 1982; Francois et al., 1993, 1997; Frank, 1996; Frank et al., 1999). ^{230}Th is produced from the decay of ^{234}U in seawater. Thorium is a particle-reactive element, so most of it is scavenged from the water column by settling particles (unlike its much more soluble U parent). The U content as well as the isotopic ratios are well known and constant in seawater (Ku et al., 1977), which enables the determination of ^{230}Th production in the water column (as a function of water depth). For nearly all of the ocean the inventory of excess ^{230}Th in the seabed (total ^{230}Th activity minus that supported by ^{234}U) is within 10–20% of that predicted from production in the overlying water (Lao et al., 1993). However, siliceous sediments beneath the Antarctic Polar Front often show enhanced excess ^{230}Th inventories, with values as much as 12 times greater for the Holocene relative to that predicted from ^{234}U production (e.g., DeMaster, 1979; Francois et al., 1993; Frank, 1996; Frank et al., 1999). These high radiochemical inventories could be the result of enhanced particle scavenging in the water column as described by Rutgers van der

Loeff and Berger (1991, 1993) and Walter et al. (1997) or lateral transport of sediment. Direct measurements of dissolved ^{230}Th in Polar Front waters reveal that scavenging of this radionuclide is not unusually high relative to other areas (Rutgers van der Loeff and Berger, 1993). In addition, recent data from the US Southern Ocean JGOFS Project suggest that the ^{230}Th flux in Polar Front particle traps is in reasonable agreement with water-column production from ^{234}U (R. Anderson, personal communication). Consequently, the high ^{230}Th inventories in Polar Front siliceous cores can be explained best by lateral transport in near-bottom waters (Frank et al., 1999; Walter et al., 1999).

The ^{230}Th normalization technique uses age-corrected excess ^{230}Th activities from a given site and then, based on the production from ^{234}U in the overlying water column ($0.00256 \text{ dpm cm}^{-2} \text{ yr}^{-1} \text{ km}^{-1}$ of water depth), ascribes a sedimentary mass flux such that the water-column production of the radioisotope is matched by the seabed accumulation rate (Bacon and Rosholt, 1982). The distribution of ^{230}Th -normalized biogenic silica accumulation rates in the Southern Ocean siliceous belt is shown in Fig. 1. This tabulation consists of data from: Francois et al. (1997)—16 cores; Sayles et al. (2001)—seven cores; Pondaven et al. (2000)—five cores; and Frank (1996)—three cores. If the accumulation rates from all 31 cores are averaged and extrapolated over the entire region ($2.3 \times 10^{17} \text{ cm}^2$) accumulating siliceous ooze in the Southern Ocean (excluding erosional areas), the overall biogenic silica accumulation rate is $3.1 \times 10^{12} \text{ mol Si yr}^{-1}$. If the Southern Ocean accumulation rates are grouped by oceanic basin, the corresponding silica fluxes are: $0.86 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Atlantic Ocean basin ($n = 9$; area = $0.51 \times 10^{17} \text{ cm}^2$); $1.7 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Indian Ocean basin ($n = 15$; area = $1.2 \times 10^{17} \text{ cm}^2$); and $0.50 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Pacific Ocean basin ($n = 7$; area = $0.59 \times 10^{17} \text{ cm}^2$). The sum of the individual oceanic basin fluxes is $3.1 \times 10^{12} \text{ mol Si yr}^{-1}$, which is identical to the flux determined from the overall average value for the Southern Ocean siliceous-ooze belt. Lastly, if the accumulation rates are grouped according to the Treguer and van Bennekom (1991) regional

designations, the biogenic silica accumulation rates are: $0.29 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Polar Front Zone ($n = 19$; area = $0.3 \times 10^{17} \text{ cm}^2$); $2.2 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Permanently Open Ocean Zone ($n = 8$; area = $1.2 \times 10^{17} \text{ cm}^2$); and $0.64 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Seasonal Ice Zone ($n = 4$; area = $0.8 \times 10^{17} \text{ cm}^2$), which totals to $3.2 \times 10^{12} \text{ mol Si yr}^{-1}$. Therefore, the biogenic silica accumulation rate for the Southern Ocean siliceous belt is believed to be $\sim 3.1 \times 10^{12} \text{ mol}$, which is as much as 35% lower than previously thought (Table 1).

Several important conclusions regarding Southern Ocean biogenic silica accumulation come out of these calculations. First, the ^{230}Th -normalization removed the Polar Front Zone as the dominant site of Antarctic silica accumulation. In the DeMaster (1981) data set the mean Atlantic Polar Front Zone biogenic silica accumulation rate was 5 times greater than the mean accumulation rate from the non-Polar Front areas. The mean silica accumulation rates for the three Antarctic zones examined in this paper are: $9.6 \pm 10.2 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ for the Polar Front Zone; $18.6 \pm 10.0 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ for the Permanently Open Ocean Zone; and $8.0 \pm 4.8 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$ for the Seasonal Ice Zone. None of these values are statistically different from one another at the 90% confidence level. In addition, there is no statistical difference between the Southern Ocean accumulation rates in the Atlantic basin ($16.7 \pm 14.6 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$), the Indian basin ($14.2 \pm 7.5 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$), and the Pacific basin ($8.4 \pm 9.4 \mu\text{mol cm}^{-2} \text{ yr}^{-1}$) at the 90% confidence limit. In DeMaster (1981) Southern Ocean data, biogenic silica accumulation rates in the Atlantic Polar Front stations were 3–4 times greater than those in the southeast Pacific Polar Front region. These apparent differences probably resulted from variations in lateral sediment focusing intensity (rather than real differences in regional flux patterns). As more data become available regional trends may develop, but at present there is high variability in Southern Ocean biogenic silica accumulation rates and no consistent spatial pattern.

As described earlier, the biogenic silica preservation efficiencies for the Southern Ocean can be brought into closer agreement with values from

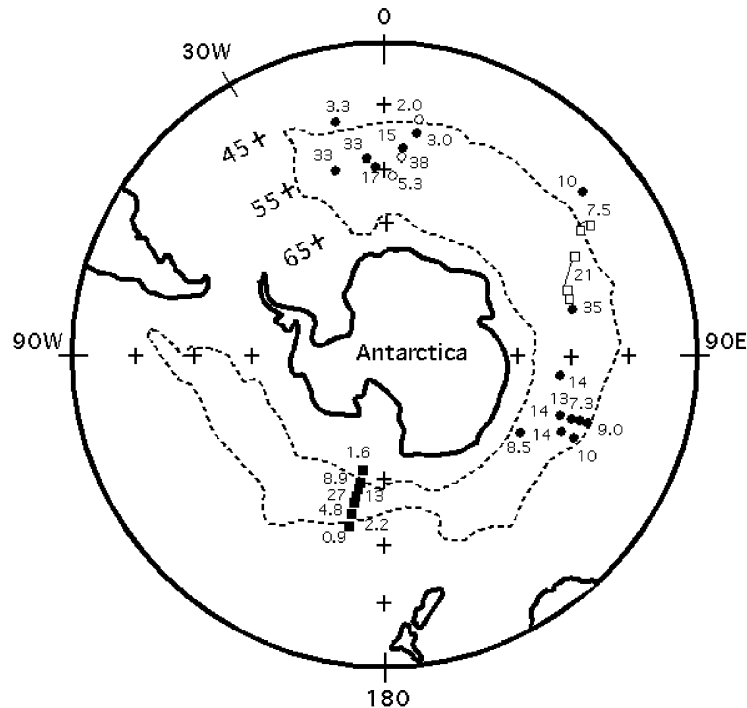


Fig. 1. The distribution of ^{230}Th -normalized biogenic silica accumulation rates (in $\mu\text{mol cm}^{-2}\text{yr}^{-1}$) for Southern Ocean siliceous-ooze deposits. The data from Francois et al. (1997) are represented by filled circles; the data of Frank (1996) and Frank et al. (1999) are represented by open circles; the data of Pondaven et al. (2000) are represented by open squares; and the data of Sayles et al. (2001) are represented by filled squares. The dashed line indicates the limits of the Southern Ocean siliceous-ooze deposits.

the Ross Sea and other Antarctic locations if the rate of biogenic silica accumulation in this area is reduced (see calculations above). Another way to reduce the silica preservation efficiencies in the Southern Ocean is to have higher production rates for biogenic silica in Southern Ocean surface waters. When the last marine silica budget was developed (Treguer et al., 1995), the best estimates of biogenic silica production in the Southern Ocean came from Nelson et al. (1995), whose data yielded values between 17 and $37 \times 10^{12} \text{ mol Si yr}^{-1}$ (Table 2). Earlier estimates of surface silica production in the Southern Ocean were as high as $50 \times 10^{12} \text{ mol Si yr}^{-1}$ (Treguer and van Bennekom, 1991). More recently, new silica production data have been published in two papers: (1) Pondaven et al. (2000) for the Indian sector of the Southern Ocean and (2) Nelson et al. (2002) for the Pacific sector of the Southern Ocean. Biogenic silica

production rates are reported in these two papers from the Polar Front Zone ($95\text{--}240 \mu\text{mol cm}^{-2}\text{yr}^{-1}$), the Permanently Open Ocean Zone ($240\text{--}330 \mu\text{mol cm}^{-2}\text{yr}^{-1}$), and the Seasonal Ice Zone ($70\text{--}160 \mu\text{mol cm}^{-2}\text{yr}^{-1}$), which when coupled to their respective areas (0.3 , 1.4 , and $1.6 \times 10^{17} \text{ cm}^2$, respectively) yield silica production rates ranging from 50 to $80 \times 10^{12} \text{ mol Si yr}^{-1}$. The modeling efforts of Gnanadesikan (1999) support the higher silica production rates in the recent tabulations as he determined a silica export production rate of $38 \times 10^{12} \text{ mol Si yr}^{-1}$ for the Southern Ocean euphotic zone, which probably corresponds to a total silica production rate on the order of $70 \times 10^{12} \text{ mol Si yr}^{-1}$. Most of these silica production rates are more than twice the previous literature values, and when combined with the Southern Ocean biogenic silica accumulation rate calculated earlier in this paper ($3.1 \times 10^{12} \text{ mol}$

Table 2
Silica cycling in various marine environments

Location	Seabed silica accumulation ($\times 10^{12}$ mol Si yr ⁻¹)	Surface silica production ($\times 10^{12}$ mol Si yr ⁻¹)	Accumulation/ Production (%)
Southern Ocean (prev. literature)	4.1–4.8 ^a	27 ^b	15–18
Ross Sea ^c	0.038 ^d	0.67 ^e	6
Revised Southern Ocean	3.1 ^f	50–80 ^g	4–6
Global Ocean	6.7 ^a	230 ^g	3

^aFrom DeMaster (1981) and Treguer et al. (1995).

^bFrom Nelson et al. (1995).

^cFrom Nelson et al. (1995).

^dFrom DeMaster et al. (1996).

^eFrom Nelson et al. (1996).

^fFrom this study.

^gFrom Pondaven et al. (2000) and Nelson et al. (2001).

Si yr⁻¹) yield preservation efficiencies (4–6%) consistent with the Ross Sea preservation efficiency data (6%) of Nelson et al. (1996) as well as the Pondaven et al. (2000) preservation efficiency data (3–6%) from the Indian sector of the Southern Ocean and the Nelson et al. (2002) preservation efficiency data (3–7%) from the Pacific sector of the Southern Ocean (Table 2). The Southern Ocean and Ross Sea preservation efficiency data were determined from independent data bases, whereas the preservation efficiencies in the Southern Ocean, from the Pondaven et al. (2000) transect, and from the Nelson et al. (2002) transect share some common silica accumulation rate data and silica production data. Although there is overlap in some of these data sets, the internal consistency of all of these Antarctic preservation efficiencies suggest common processes and mechanisms.

2.3. Biogenic silica accumulation in continental margin environments

Estuarine environments are potential locations for biogenic silica burial because they are regions of high nutrient flux and high primary productivity (commonly supporting abundant diatom blooms). Milliman and Boyle (1975) reported extensive diatom growth (accounting for nearly 50% of the riverine silicate flux) in the surface waters of the

Amazon river/ocean mixing zone. This dispersal system alone supplies approximately 20% of all the riverine flow to the marine environment. Based on nutrient distributions in the water column, Edmond et al. (1981) and later Shiller (1996) suggested that burial of biogenic silica on the Amazon shelf may account for as much as 20–40% of the riverine silicate flux. However, the biogenic silica content of Amazon shelf sediments is very low (~ 0.2 – 0.4 wt% SiO₂, DeMaster et al., 1983), and consequently, burial of biogenic silica can account for only a few percent of the riverine silicate flux. Michalopoulos and Aller (1995) report that authigenic aluminosilicates are forming in Amazon shelf sediments as diatom silica dissolves, but quantifying the silica buried in these authigenic phases is difficult because of the high terrigenous particulate flux in this region. Based on silicate and biogenic silica budgets for the Amazon shelf (Daley, 1998; DeMaster and Aller, 2001), nearly all of the silicate supplied to this river/ocean mixing zone is transported offshore as either silicate or as biogenic silica. A substantial flux of biogenic silica is exported from the shelf by lateral advection (corresponding to approximately a third of the riverine silicate supply), which may explain the chemical distributions reported by Edmond et al. (1981) and Shiller (1996). Most of this exported biogenic silica probably dissolves in open-ocean waters (Froelich et al., 1978), and

consequently, the exported biogenic silica does not represent a net repository for riverine silicate. Therefore, despite the high primary production rates in estuaries, many of them may not be very efficient traps for riverine silicate. Clearly, some estuarine environments do have significant biogenic silica removal occurring within them (e.g., Long Island Sound, DeMaster, 1981, or Chesapeake Bay, Conley and Malone, 1992). However, until biogenic silica accumulation rates can be measured in the sedimentary deposits of many more dispersal systems, the extent of estuarine biogenic silica removal will remain uncertain. Based on the estuarine data compilation in DeMaster (1981) and the Amazon shelf Si budget presented in DeMaster and Aller (2001), the maximum biogenic silica removal rate in estuarine environments was chosen to be 10% of the dissolved riverine flux (or 0.6×10^{12} mol Si yr^{-1}).

The continental margins as a whole are areas of relatively high biological production (Berger et al., 1989). Because of the high terrigenous particulate flux, the biogenic silica contents of these deposits are not very high (typically <10 wt% silica). However, a substantial amount of biogenic silica can be buried in these deposits because of the rapid sediment accumulation rates. In fact, burial of 2–3 wt% biogenic silica along with the riverine terrigenous flux of particulate material ($\sim 200 \times 10^{14}$ gm of sediment yr^{-1} ; Milliman and Meade, 1983) on the continental shelf and upper slope potentially could account for all of the silicate supplied to the marine environment (DeMaster, 1981).

Heath et al. (1976) noted that biogenic silica burial in continental margin environments could be of significant importance, based on biogenic silica data from off the coast of Oregon. Carrying this approach further, the biogenic silica accumulation rate in continental shelf and upper slope deposits can be estimated by normalizing the silica accumulation to the burial of organic matter. Fig. 2a shows the biogenic silica content of four stations collected on the North Carolina continental slope [water depth = 800 m; see DeMaster et al. (1994) for core locations]. The biogenic silica content of these deposits is low (1–5 wt% silica),

but the silica values are highly correlated with the organic carbon contents of these sediments. The slope of this graph yields a biogenic silica/organic C ratio (by weight) of 3.1 gm SiO_2 /gm of organic C (or a molar ratio of ~ 0.6). Fig. 2b shows how this relationship for biogenic silica and organic C on the North Carolina slope matches other continental margin environments (excluding deltaic areas dominated by terrigenous sedimentation). With the exception of the Ross Sea, most continental margin sites have reasonably comparable biogenic silica to organic C ratios.

If it is assumed that approximately 0.5–1 wt% of terrestrial organic carbon is buried with the detrital sediment on the continental margins (Bernier, 1982), then most of the increase in the organic C contents above this threshold (equal to the x-axis intercept on Fig. 2a) can be attributed to material of marine origin. Hedges and Keil (1995) estimate that a total of 5.7×10^{12} mol of organic C are buried annually in continental shelf and upper slope sediments. Correcting this total carbon burial rate for the terrigenous contribution (assume 0.7 wt% C from terrigenous organic matter relative to a total organic C content of 1.5 wt%) yields a burial rate of 3.0×10^{12} mol of marine organic C yr^{-1} on the shelf and upper slope. Multiplying this burial rate by the biogenic silica to organic C ratio (a molar value of 0.6) results in a biogenic silica accumulation rate of 1.8×10^{12} mol of silica yr^{-1} for the continental margin environment. Berger et al. (1989) also estimated the marine organic burial rate in continental margin sediments and their value (4.6×10^{12} mol of organic C yr^{-1}) was $\sim 50\%$ higher than the value derived from the Hedges and Keil (1995) data. Therefore, the 1.8×10^{12} mol yr^{-1} value is a conservative estimate for the continental margin biogenic silica burial rate. Clearly, there is a lot of uncertainty in this calculation. However, the data do indicate that continental margin sediments have the potential to compensate for the diminished amount of biogenic silica accumulating in the Southern Ocean, thus keeping the marine silica budget in near balance (Table 1).

An important ramification of changing the location of a major portion of the world's silica

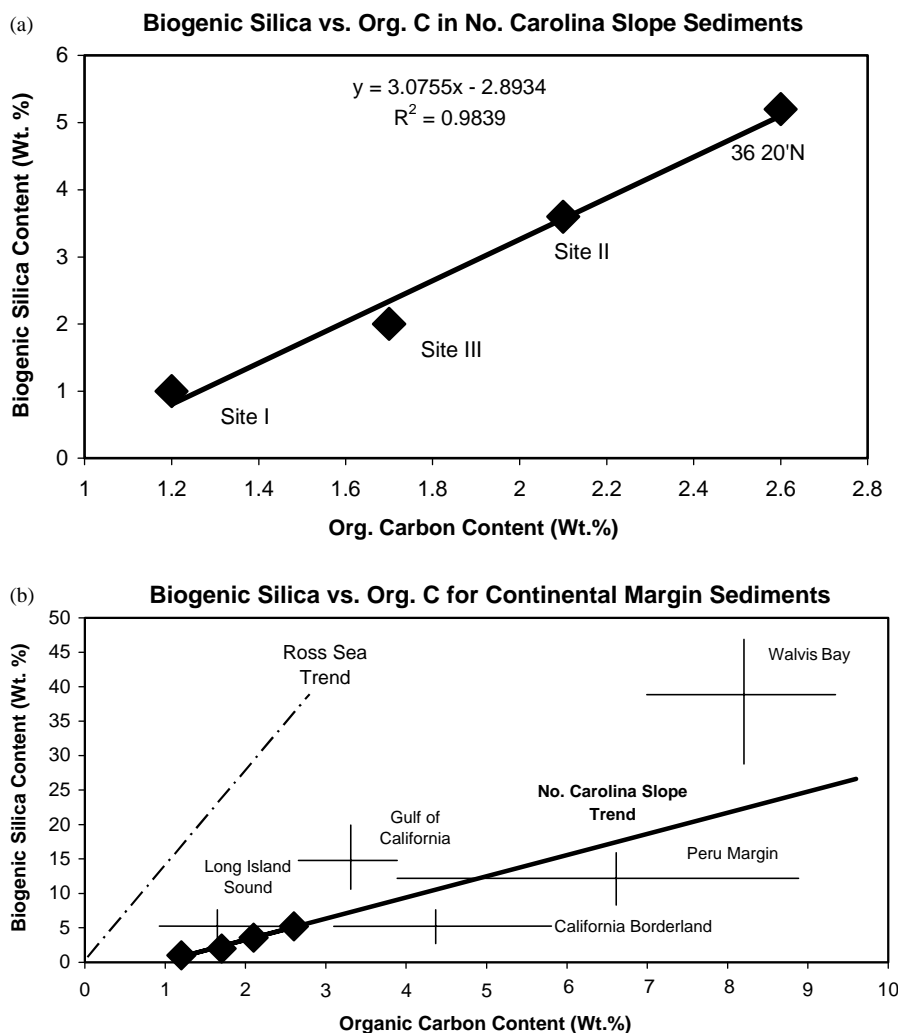


Fig. 2. (a) Biogenic silica content plotted as a function of organic carbon content from four sites on the North Carolina continental slope (see DeMaster et al., 1994 for core locations). (b) Biogenic silica content plotted as a function of organic carbon content from North Carolina slope sites as well as other continental margin environments. The lines representing data from the various continental margin locations reveal the ranges in the biogenic silica and organic carbon data. The continental margin biogenic silica and organic carbon data come from DeMaster (1979) and DeMaster et al. (1994, 1996).

burial from siliceous-ooze deposits in the Antarctic deep sea to continental margin deposits is that the coupling of the biogeochemical cycles of organic carbon and biogenic silica is distinctly altered. Antarctic siliceous-ooze deposits have very high biogenic silica/organic C ratios (20–60 on a molar basis; e.g., DeMaster et al., 1991), providing evidence that the accumulation of these biogenic

phases has been decoupled (the Si/C molar ratio for most living marine diatoms is on the order of 0.1–0.2; Brzezinski, 1985). In contrast, continental margin sediments have a biogenic silica/organic C ratio as much as 100 times less (~ 0.6) because of the enhanced preservation of both biogenic phases (primarily as a result of a shallower water column). Therefore, by having 20–25% of the global

biogenic silica buried in continental margin locations instead of in the Antarctic deep sea, the biogeochemical cycles of organic C and biogenic silica are more tightly coupled than previously thought.

3. Summary

Based on ^{230}Th data from the siliceous-ooze deposits of the Antarctic deep sea, the effects of lateral sediment transport on regional biogenic silica accumulation rates have been assessed. The rate of biogenic silica accumulation for the Southern Ocean siliceous belt ($3.1 \times 10^{12} \text{ mol Si yr}^{-1}$) is as much as 35% lower than previously reported in the literature. The ^{230}Th normalized biogenic silica accumulation rates in the Antarctic siliceous belt do not show any pattern among basins (Atlantic, Indian, Pacific) nor any pattern in latitudinal zonations (i.e. Polar Front Zone, Permanently Open Ocean Zone, and the Seasonal Ice Zone). Despite the lower silica accumulation rates in the Southern Ocean siliceous belt, an approximate balance between silicate supply and biogenic silica removal can be achieved for the marine environment by invoking increased biogenic silica burial in continental margin environments. Evidence supporting high rates of biogenic silica burial in continental margin sediments comes from biogenic silica to organic C ratios in these deposits and estimates of marine organic carbon burial rates in continental shelf and upper slope environments. With these changes in the world silica budget, the marine biogeochemical cycles of organic C and biogenic silica are much more tightly coupled than previously believed.

Acknowledgements

This paper benefited greatly from the efforts of three reviewers: M. Schluter, A. Shiller, and one anonymous reviewer. The patience of Paul Treguer, the guest editor for this special volume, is also appreciated by the author. Thanks are also due to F. Sayles, W. Martin, Z. Chase, and R. Anderson as well as D. Nelson and the rest of

the US JGOFS group for allowing use of data from their articles prior to final publication. R. Francois kindly provided tabulated data from his previous *Nature* and *Paleoceanography* articles.

References

- Bacon, M.P., Rosholt, J.N., 1982. Accumulation rates of ^{230}Th and ^{231}Pa and some transition metals on the Bermuda Rise. *Geochimica et Cosmochimica Acta* 46, 651–666.
- Bareille, G., Labracherie, M., Pichon, J.J., Turon, J.L., 1991. Biogenic silica accumulation rate during the Holocene in the southeastern Indian Ocean. *Marine Chemistry* 35, 537–552.
- Berger, W.H., Smetacek, V.S., Wefer, G., 1989. Ocean productivity and paleoproductivity: an overview. In: Berger, W.H., Smetacek, V.S., Wefer, G., (Eds.), *Productivity of the Ocean: Present and Past*. Wiley, New York, pp. 1–34.
- Berner, R.A., 1982. Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *American Journal of Science* 282, 451–473.
- Broecker, W.S., 1971. A kinetic model for the chemical composition of seawater. *Quaternary Research* 1, 188–207.
- Broecker, W.S., Peng, T.H., 1993. *Greenhouse Puzzles*. Columbia Press, New York, 85pp.
- Brzezinski, M.A., 1985. The Si: C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. *Journal of Phycology* 21, 347–357.
- Burckle, L.H., Stanton, D., 1975. Distribution of displaced Antarctic diatoms in the Argentine Basin. *Diatom Symposium Volume, Diatom Conference*, Kiel, Germany, pp. 283–291.
- Calvert, S.E., 1968. Silica balance in the ocean and diagenesis. *Nature* 219, 919–920.
- Charles, C.D., Froelich, P.N., Zibello, M.A., Mortlock, R.A., Morley, J.J., 1991. Biogenic opal in Southern Ocean sediments over the past 450,000 years: implications for surface chemistry and circulation. *Paleoceanography* 6, 697–728.
- Conley, D.J., 1997. Riverine contribution of biogenic silica to the oceanic silica budget. *Limnology and Oceanography* 42, 774–777.
- Conley, D.J., Malone, T.C., 1992. Annual cycle of dissolved silicate in Chesapeake Bay—implications for the production and fate of phytoplankton biomass. *Marine Ecology-Progress Series* 81, 121–128.
- Cooke, D.W., Hays, J.D., 1981. Glacial–interglacial sedimentation changes in the Antarctic Ocean. In: Craddock, C. (Ed.), *Third International Symposium on Antarctic Geology and Geophysics*. University of Wisconsin Press, Madison, pp. 1017–1026.
- Daley, D.E., 1998. Amazon shelf nutrient dynamics: a modeling and field study. M.S. Thesis, North Carolina State University, Raleigh, NC, 73pp.
- DeMaster, D.J., 1979. The marine budgets of silica and ^{32}Si . Ph.D. Dissertation, Yale University, 308pp.

- DeMaster, D.J., 1981. The supply and removal of silica from the marine environment. *Geochimica et Cosmochimica Acta* 45, 1715–1732.
- DeMaster, D.J., Aller, R.C., 2001. Biogeochemical processes on the Amazon shelf: changes in dissolved and particulate fluxes during river/ocean mixing. In: McClain, M.E., Victoria, R.L., Richey, J.E. (Eds.), *The Biogeochemistry of the Amazon Basin*. Oxford University Press, New York, pp. 328–357.
- DeMaster, D.J., Knapp, G.B., Nittrouer, C.A., 1983. Biological uptake and accumulation of silica on the Amazon continental shelf. *Geochimica et Cosmochimica Acta* 47, 1713–1723.
- DeMaster, D.J., Nelson, T.M., Harden, S.L., 1991. The cycling and accumulation of biogenic silica and organic carbon in Antarctic deep-sea and continental margin environments. *Marine Chemistry* 35, 489–502.
- DeMaster, D.J., Pope, R.H., Levin, L.A., Blair, N.E., 1994. Biological mixing intensity and rates of organic carbon accumulation in North Carolina slope sediments. *Deep-Sea Research II* 41, 735–753.
- DeMaster, D.J., Ragueneau, O., Nittrouer, C.A., 1996. Preservation efficiencies and accumulation rates for biogenic silica and organic C, N, and P in high-latitude sediments: the Ross Sea. *Journal of Geophysical Research* 101, 18501–18518.
- Drever, J.I., Li, Y.H., Maynard, J.B., 1988. Geochemical cycles: the continental crust and the oceans. In: Gregor, C.B., Garrels, R.M., Mackenzie, F.T., Maynard, J.B. (Eds.), *Chemical Cycles in the Evolution of the Earth*. Wiley, New York, pp. 17–53.
- Dugdale, R.C., Wilkerson, F.P., Minas, H.J., 1995. The role of a silicate pump in driving new production. *Deep-Sea Research I* 42, 697–719.
- Edmond, J.M., Boyle, E.A., Grant, B., Stallard, R.F., 1981. The chemical mass balance in the Amazon plume-I. The nutrients. *Deep-Sea Research* 28, 1339–1374.
- Francois, R., Bacon, M.P., Altabet, M.A., 1993. Glacial/interglacial changes in sediment rain rate in the SW Indian sector of subantarctic waters as recorded by ^{230}Th , ^{231}Pa , U and delta ^{15}N . *Paleoceanography* 8, 611–629.
- Francois, R., Altabet, M.A., Yu, E.F., Sigman, D., Bacon, M.P., Frank, M., Bohrmann, G., Bareille, G., Labeyrie, L., 1997. Dominance of upper water column stratification in the Southern Ocean's contribution to low glacial atmospheric CO_2 . *Nature* 389, 929–935.
- Frank, M., 1996. Reconstruction of late Quaternary environmental conditions applying the natural radionuclides ^{230}Th , ^{10}Be , ^{231}Pa , and ^{238}U : a study of deep-sea sediments from the Eastern Atlantic sector of the Antarctic circumpolar current system. *Ber Polarforsch Bremerhaven* 186, 1–136.
- Frank, M., Gersonde, R., Rutgers van der Loeff, M., Kuhn, G., Mangini, A., 1996. Late Quaternary sediment dating and quantification of lateral sediment redistribution applying $^{230}\text{Th}_{\text{ex}}$: a study from the Eastern Atlantic sector of the Southern Ocean. *Geologische Rundschau* 85, 554–566.
- Frank, M., Gersonde, R., Mangini, A., 1999. Sediment redistribution, $^{230}\text{Th}_{\text{ex}}$ -normalization and implications for the reconstruction of particle flux and export paleoproductivity. In: Fischer, G., Wefer, G. (Eds.), *Use of Proxies in Paleooceanography: Examples from the South Atlantic*. Springer, Berlin, pp. 409–426.
- Froelich, P.N., Atwood Jr., D.K., Giese, G.S., 1978. Influence of Amazon River discharge on surface salinity and dissolved silicate concentration in the Caribbean Sea. *Deep-Sea Research* 25, 735–744.
- Gnanadesikan, A., 1999. A global model of silicon cycling: sensitivity to eddy parameterization and dissolution. *Global Biogeochemical Cycles* 13, 199–220.
- Heath, G.R., 1974. Dissolved silica in deep-sea sediments. In: Hay, W.W. (Ed.), *Studies in Paleo-Oceanography*, Vol. 20. Soc. Econ. Pet. Min, Tulsa, pp. 77–93.
- Heath, G.R., Moore Jr., T.C., Dauphin, J.P., 1976. Late Quaternary accumulation rates of opal, quartz, organic carbon, and calcium carbonate in the Cascadia Basin area Northeast Pacific. In: Cline, R.M., Hays, J.D. (Eds.), *Investigations of Late Quaternary Paleooceanography and Paleoclimatology*, 145. Geological Society of America, Mem, pp. 393–409.
- Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry* 49, 81–115.
- Ku, T.L., Knauss, K.G., Mathieu, G.G., 1977. Uranium in the open ocean: concentration and isotopic composition. *Deep-Sea Research* 24, 1005–1017.
- Lao, Y., Anderson, R.F., Broecker, W.S., Hofmann, H.J., Wolfli, W., 1993. Particulate fluxes of ^{230}Th , ^{231}Pa , and ^{10}Be in the Northeastern Pacific Ocean. *Geochimica et Cosmochimica Acta* 57, 205–217.
- Lawson, D.S., Hurd, D.C., Pankratz, H.S., 1978. Silica dissolution rates of decomposing assemblages at various temperatures. *American Journal of Science* 278, 1373–1393.
- Martin, J.M., Whitfield, M., 1983. The significance of the river input of chemical elements to the ocean. In: Wong, C.S., Boyle, E., Bruland, K.W., Burton, J.D., Goldberg, E.D. (Eds.), *Trace Metals in Sea Water*. Plenum Press, New York, pp. 265–296.
- Michalopoulos, P., Aller, R.C., 1995. Rapid clay mineral formation in Amazon delta sediments: reverse weathering and oceanic elemental fluxes. *Science* 270, 614–617.
- Milliman, J.D., Boyle, E., 1975. Biological uptake of dissolved silica in the Amazon river estuary. *Science* 189, 995–997.
- Milliman, J.D., Meade, R.H., 1983. Worldwide delivery of river sediments to the oceans. *Journal of Geology* 91, 1–21.
- Nelson, D.M., Treguer, P., Brzezinski, M.A., Leynaert, A., Queguiner, B., 1995. Production and dissolution of biogenic silica in the ocean: revised global estimates, comparison with regional data and relationship to biogenic sedimentation. *Global Biogeochemical Cycles* 9, 359–372.
- Nelson, D.M., DeMaster, D.J., Dunbar, R.B., Smith Jr., W.O., 1996. Cycling of organic carbon and biogenic silica in the Southern Ocean: estimates of water-column and sedimen-

- tary fluxes on the Ross Sea continental shelf. *Journal of Geophysical Research* 101, 18519–18532.
- Nelson, D.M., Anderson, R.F., Barber, R.T., Brzezinski, M.A., Buesseler, K.O., Chase, Z., Collier, R.W., Dickson, M.L., Francois, R., Hiscock, M.R., Honjo, S., Mara, J., Martin, W.R., Sambrotto, R.N., Sayles, F.L., Sigmon, D.E., 2002. Vertical budgets for organic carbon and biogenic silica in the Pacific sector of the Southern Ocean, 1996–1998. *Deep-Sea Research II* 49 (9–10), 1645–1674.
- Pondaven, P., Ragueneau, O., Treguer, P., Hauvespre, A., Dezileau, L., Reyss, J.L., 2000. Resolving the “opal paradox” in the Southern Ocean. *Nature* 405, 168–172.
- Queguiner, B., Treguer, P., Nelson, D.M., 1991. The production of biogenic silica in the Weddell and Scotia Seas. *Marine Chemistry* 35, 449–460.
- Rabouille, C., Gaillard, J.F., Treguer, P., Vincendeau, M.A., 1997. Biogenic silica recycling in surficial sediments across the Polar Front of the Southern Ocean (Indian Sector). *Deep-Sea Research II* 44, 1151–1176.
- Ragueneau, O., Treguer, P., Leynaert, A., Anderson, R.F., Brzezinski, M.A., DeMaster, D.J., Dugdale, R.C., Dymond, J., Fischer, G., Francois, R., Heinze, C., Maier-Reimer, E., Martin-Jezequel, V., Nelson, D.M., Queguiner, B., 2000. A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy. *Global and Planetary Change* 26, 317–365.
- Ragueneau, O., Dittert, N., Treguer, P., Pondaven, P., Corrin, L., 2002. Si/C decoupling in the world ocean: is the southern ocean really different? *Deep-Sea Research II* 49, 3127–3154.
- Rutgers van der Loeff, M.M., Berger, G.W., 1991. Scavenging and particle flux: seasonal and regional variations in the southern ocean (Atlantic sector). *Marine Chemistry* 35, 553–567.
- Rutgers van der Loeff, M.M., Berger, G.W., 1993. Scavenging of ^{230}Th and ^{231}Pa near the Antarctic Polar Front in the South Atlantic. *Deep-Sea Research I* 40, 339–357.
- Sayles, F.L., Martin, W.R., Chase, Z., Anderson, R.F., 2001. Benthic remineralization and burial of biogenic SiO_2 CaCO_3 organic carbon, and detrital material in the southern ocean along a transect at 170 degrees west. *Deep-Sea Research II* 48, 4323–4383.
- Schluter, M., 1990. Early diagenesis of organic carbon and opal in sediments of the southern and eastern Weddell Sea. Geochemical analysis and modeling. Rep. Polar Res. Ber. Polarforsch 73, 156.
- Shiller, A.M., 1996. The effect of recycling traps and upwelling on estuarine chemical flux estimates. *Geochimica et Cosmochimica Acta* 60, 3177–3185.
- Smith Jr., W.O., Dunbar, R.B., 1998. The relationship between new production and vertical flux on the Ross Sea continental shelf. *Journal of Marine Systems* 17, 445–457.
- Treguer, P., van Bennekom, A.J., 1991. The annual production of biogenic silica in the Antarctic Ocean. *Marine Chemistry* 35, 477–488.
- Treguer, P., Nelson, D.A., van Bennekom, A.J., DeMaster, D.J., Leynaert, A., Queguiner, B., 1995. The silica balance in the world ocean: a re-estimate. *Science* 268, 375–379.
- van Bennekom, A.J., Berger, G.W., Van der Gaast, S.J., De Vries, R.T., 1988. Primary productivity and the silica cycle in the Southern Ocean (Atlantic Sector). *Palaeogeography, Palaeoclimatology, Palaeoecology* 67, 19–30.
- Van Cappellen, P., Qiu, L., 1997. Biogenic silica dissolution in sediment of the Southern Ocean. II. Kinetics. *Deep-Sea Research II* 44, 1129–1149.
- Walter, H.J., Rutgers van der Loeff, M.M., Hoeltzen, H., 1997. Enhanced scavenging of ^{231}Pa relative to ^{230}Th in the South Atlantic south of the Polar Front: implications for the use of the $^{231}\text{Pa}/^{230}\text{Th}$ ratio as a paleoproductivity proxy. *Earth and Planetary Science Letters* 149, 85–100.
- Walter, H.J., Rutgers van der Loeff, M.M., Francois, R., 1999. Reliability of the $^{231}\text{Pa}/^{230}\text{Th}$ activity ratio as a tracer for bioproductivity of the ocean. In: Fischer, G., Wefer, G. (Eds.), *Use of Proxies in Paleoclimatology: Examples from the South Atlantic*. Springer, Berlin, pp. 393–408.
- Wollast, R., 1974. The silica problem. In: Goldberg, E.D. (Ed.), *The Sea*, Vol. 5. Wiley, New York, pp. 359–392.