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Si cycle in the Cariaco Basin, Venezuela: Seasonal variability in silicate availability and the Si:C:N composition of sinking particles

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[1] A 9-year time series of water column and sediment trap measurements was used to examine silicon cycling within the anoxic Cariaco Basin. The dynamic hydrographic regime within Cariaco Basin results in strong seasonal changes in nutrient availability and the Si:C:N of sinking particles. Upwelling in early winter injects silicic acid ($\text{Si}(\text{OH})_4^-$) and nitrate (NO_3^-) rich waters into the photic zone which stimulates primary production and results in opal fluxes in excess of $4 \text{ mmol Si m}^{-2} \text{ d}^{-1}$. However, even during upwelling, surface waters tend to be depleted ($<1 \mu\text{M}$) in both $\text{Si}(\text{OH})_4^-$ and NO_3^- as a result of rapid utilization. In most years, the upper water column during winter and spring is marked by $\text{Si}(\text{OH})_4^-:\text{NO}_3^-$ and Si^* values of less than 1. This indicates that silicate limitation in Cariaco Basin is most severe during upwelling and may restrict diatom production. Conversely, during the summer and fall when upwelling is reduced, $\text{Si}(\text{OH})_4^-:\text{NO}_3^-$ ratios in the upper 50 m of the water column exceed 10, implying that nitrate rather than silicate is acting to limit production during this time of year. On average, sinking particles collected at 150-m depth in the Cariaco Basin have Si:C and Si:N values of 0.17 ± 0.01 and 1.14 ± 0.10 , respectively. These ratios increase with depth to 400 m and then remain relatively constant, suggesting minimal selective removal of elements with remineralization in the anoxic portion of the water column. Similar depth-dependent changes in these ratios are seen in surface sediments from the basin. Seasonally, particulate Si:C and Si:N are highest during the early part of the year when upwelling is most intense, while both ratios decrease to their lowest values during summer and fall. The observed seasonal variability in these ratios is due to changes in both nutrient utilization by diatoms and the contribution of diatoms to the total phytoplankton. The high ratios during upwelling suggest enhanced export of Si relative to C and N during this time of year.

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1. Introduction

[2] Diatoms are one of the most important primary producers in the oceans, possibly accounting for as much as 30–40% of total primary production [Nelson *et al.*, 1995; Treguer *et al.*, 1995]. As such, diatoms are a major vehicle for carbon export from surface waters, particularly in high latitudes and upwelling regions [Buesseler, 1998]. Thus, the

production and cycling of biogenic opal (bSiO_2) is an important component of the ocean's biological pump [Sarmiento and Gruber, 2006; Ragueneau *et al.*, 2006] and may play a major role in regulating the exchange of CO_2 between the ocean and atmosphere on a variety of timescales [Brzezinski *et al.*, 2002; Sarmiento *et al.*, 2004]. Despite this direct linkage between diatoms, primary production, and carbon export from the upper ocean, some workers have argued that there is a decoupling between the silicon (Si) and carbon (C) cycles based on geographic variations in Si and C uptake during opal production [Ragueneau *et al.*, 2002], changes in Si:C ratios of sinking particles with depth in the ocean, and regional variations in the accumulation of Si and C on the seafloor [DeMaster, 1981; Treguer *et al.*, 1995]. This concept has been reinforced by the hypothesis that, on a global basis, particulate organic carbon (POC) delivery to depth in the ocean is more effectively mediated by biogenic carbonate rather than opal

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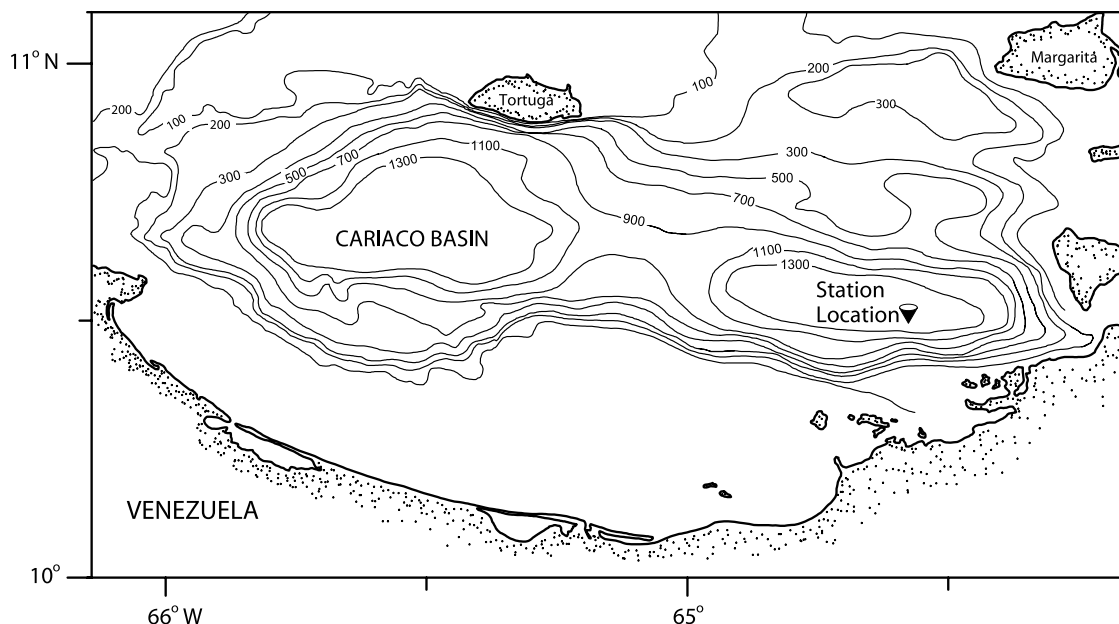


Figure 1. Bathymetric map of the Cariaco Basin showing the location of the time series study.

[Francois *et al.*, 2002; Klaas and Archer, 2002]. However, Ragueneau *et al.* [2006] have argued that this POC:mineral association varies regionally, with opal actually having a higher carrying coefficient than carbonate in both the Atlantic and Indian Oceans. Similarly, Thunell *et al.* [2007] examined POC fluxes in several highly productive, coastal upwelling regions and found opal to be the most important “ballast” mineral in the Cariaco Basin.

[3] While nitrate (NO_3^-) may be the “proximate” limiting nutrient for phytoplankton in most areas of the global ocean [Tyrrell, 1999], diatoms require Si to build their frustules. Thus, silicic acid ($\text{Si}(\text{OH})_4^-$) can be considered a limiting nutrient for this group of plankton [Brzezinski *et al.*, 1990]. In regions of the ocean where nitrate is high, but chlorophyll concentrations and productivity are low (the so-called “high-nitrate, low-chlorophyll” regions), it is thought that iron availability may be a critical factor in limiting production [Martin, 1994; Coale *et al.*, 1996; Behrenfeld *et al.* 2006]. However, there is evidence to suggest that silicate may also act as a limiting nutrient in some equatorial Pacific and Southern Ocean HNLC regions, with the silicate supply ultimately determining how much nitrate is utilized and the level of new production [Dugdale *et al.*, 1995; Dugdale and Wilkerson, 1998]. The low silicate concentrations in these regions relative to nitrate may be due to a “silicate pump,” with silicate being removed from the surface and delivered to depth before regeneration can occur, while nitrogen is recycled within the euphotic zone [Dugdale *et al.*, 1995; Wilkerson and Dugdale, 1996].

[4] On the basis of culture studies, Brzezinski [1985] has shown that diatoms typically have mean Si:C and Si:N ratios of ~ 0.13 and ~ 1.13 , respectively, when grown under nutrient-replete conditions. In regions where $\text{Si}(\text{OH})_4^-:\text{NO}_3^-$ ratios are less than 1, silicic acid is limiting and these uptake ratios will deviate from those that are typical of nutrient-rich conditions. Furthermore, on the basis of field observations

in the equatorial Pacific Ocean [Price *et al.*, 1994], the Southern Ocean [Takeda, 1998; Franck *et al.*, 2000; Brzezinski *et al.*, 2002], and coastal upwelling regimes [Hutchins and Bruland, 1998], as well as culturing studies [Timmermans *et al.*, 2004], it has been demonstrated that Fe limitation causes diatoms to increase their uptake of $\text{Si}(\text{OH})_4^-$ and decrease their consumption of NO_3^- , resulting in depletion of $\text{Si}(\text{OH})_4^-$ in surface waters. Thus, there may be a close association or coupling between Fe limitation and Si limitation [Nelson *et al.*, 2001; Franck *et al.*, 2000].

[5] In this paper we examine various aspects of the Si cycle in the Cariaco Basin, offshore Venezuela. We report on seasonal changes in upper water column $\text{Si}(\text{OH})_4^-$ and NO_3^- concentrations, as well as temporal and depth-dependent changes in the Si:C and Si:N ratios of sinking particles collected from multiple depths in the basin over a 9-year period. Specifically, we examine (1) how nitrate and silicic acid availability varies in response to seasonal changes in hydrography, particularly the occurrence of upwelling, (2) whether $\text{Si}(\text{OH})_4^-$ is a limiting nutrient in this environment, (3) how the Si:C and Si:N ratios of sinking materials reflect seasonal changes in nutrient availability and phytoplankton composition, and (4) how these ratios vary with depth both in the water column and on the seafloor due to remineralization under both oxic and anoxic conditions. The Cariaco Basin is an ideal location for such a study because Si fluxes in this tropical setting are comparable to those seen at high latitudes.

2. Materials and Methods

2.1. Study Area

[6] The Cariaco Basin (Figure 1) is a 1400-m deep depression on the Venezuelan continental margin. Surface waters are freely exchanged between the basin and the open Caribbean above a sill depth of ~ 100 m. Two channels

Table 1. Cariaco Basin Surface Sediment Core Data

Core	Latitude	Longitude	Water Depth (m)	Si:C	Si:N
HG-MC 12–101	10°49.26'N	64°42.86'W	250	0.16	1.67
HG-MC 4-A	10°39.01'N	64°36.64'W	432	0.22	2.23
PL07–103BC	10°45.40'N	65°20.20'W	1133	0.22	2.15
PL07–105BC	10°43.47'N	65°25.33'W	1296	0.23	2.02
PL07–64BC	10°33.55'N	64°47.31'W	1375	0.24	2.10

breach this sill, one in the northeast with a depth of ~ 135 m (La Tortuga) and a narrower one in the northwest with a depth of ~ 145 m (Centinela) [Lidz *et al.*, 1969; Richards, 1975]. Because of restricted turnover of subsurface waters and high surface productivity, the decomposition of sinking organic matter leads to anoxic conditions in the basin below ~ 250 – 300 m [Richards, 1975; Astor *et al.*, 2003].

[7] The annual migration of the Inter-Tropical Convergence Zone (ITCZ) about the equator results in strong seasonal changes in upper ocean conditions in Cariaco Basin [Muller-Karger and Aparicio Castro, 1994]. The ITCZ is in its most southerly position during boreal winter and spring, at which time rainfall is minimized and strong easterly winds cause intense upwelling (3 – 5 m d^{-1} ; Walsh *et al.* [1999]) and high primary productivity along the Venezuelan coast [Muller-Karger and Aparicio Castro, 1994]. Northward migration of the ITCZ occurs during the summer and early fall. This leads to an increase in rainfall and a decrease in trade wind strength in the Cariaco Basin region, with the latter causing upwelling and productivity to decrease. The relationship between seasonal changes in climatology and the production and flux of organic matter in the Cariaco Basin has been described by Thunell *et al.* [2000, 2007], Muller-Karger *et al.* [2001, 2004], and Goñi *et al.* [2003].

2.2. Field Program and Sample Collection

[8] An ongoing United States-Venezuelan time series study was initiated in Cariaco Basin in November 1995 [Muller-Karger *et al.*, 2000, 2001]. The study includes monthly sampling cruises to a site in the eastern basin (10.5°N , 64.67°W ; ~ 1400 -m water depth; Figure 1) and the continuous measurement of particle fluxes at multiple depths at this location. The monthly cruises include routine hydrographic measurements (temperature, salinity, dissolved oxygen, and light transmission) of the entire water column. Additionally, primary production is measured at eight depths over the upper 100 m, and water samples are collected for nutrient concentrations at discrete depths down to ~ 1300 m. A detailed description of the sampling program is provided by Muller-Karger *et al.* [2001].

[9] A single mooring containing five automated sediment traps is used to measure the vertical flux of particles at various depths in the Cariaco Basin water column. The two shallowest traps (Trap Z, ~ 150 m and Trap A, ~ 225 m) are positioned above the oxic/anoxic interface (~ 275 m), with the remaining traps at 410 m (Trap B), 810 m (Trap C), and 1200 m (Trap D). Each sediment trap contains 13 collecting cups, and samples are collected continuously for 2-week intervals. The mooring is recovered and redeployed every 6 months. For this study, we utilize samples collected from the four deepest sediment traps (A–D) for the 9-year period

from November 1996 through May 2005. Trap Z was added to the mooring in November 2003, and thus we have only a limited number of samples from this depth. In addition to the sediment trap samples, we analyzed surface sediment samples collected from multiple depths in the basin (Table 1).

2.3. Analytical Methods

[10] Water samples collected from 13 depths between the surface and 300-m water depth were used to determine the concentrations of NO_3^- and $\text{Si}(\text{OH})_4^-$. For each of these nutrients, 1 L of water from each depth was filtered through a $0.8\text{-}\mu\text{m}$ Nuclepore filter. The nitrate samples were frozen, while the water samples for $\text{Si}(\text{OH})_4^-$ were refrigerated. The nutrient analyses were carried on a Technicon Analyzer II using the protocols recommended by Gordon *et al.* [1993]. The detection limits were $0.01\text{ }\mu\text{M}$ for nitrate and $0.4\text{ }\mu\text{M}$ for silicic acid.

[11] Primary production ($\text{mg C m}^{-3} \text{ h}^{-1}$) was measured monthly on samples collected at eight depths (1, 7, 15, 25, 35, 55, 75, and 100 m) using a modified Steeman Nielsen [1952] $\text{NaH}^{14}\text{CO}_3$ uptake assay. Data were integrated for the upper 100 m to produce daily primary productivity estimates ($\text{g C m}^{-2} \text{ d}^{-1}$). The specifics of this sampling and procedure are provided by Muller-Karger *et al.* [2001].

[12] For the sediment trap samples, a buffered formalin solution was placed in each sample cup prior to deployment and served as a preservative for the particulate organic matter accumulating in the cups. Samples were stored in sealed containers and kept refrigerated after collection. Whole trap samples were split using a precision rotary splitter. A quarter of each sample was freeze-dried, ground, and used for a variety of geochemical analyses. Prior to freezing, these subsamples were examined under a microscope, and all obvious swimming organisms, not considered to be part of the particle flux, were removed before analysis.

[13] Particulate organic carbon (POC) and particulate nitrogen (PN) concentrations were determined for both the sediment trap and surface sediment samples following the procedures outlined by Froelich [1980]. Samples were acidified ($1\text{ M H}_3\text{PO}_4$) to remove the particulate inorganic carbon (i.e., carbonates) and then combusted at 930°C in a Perkin Elmer 2400 elemental analyzer. POC and PN concentrations and molar ratios were calculated for all samples.

[14] Biogenic silicon (bSi) was determined on the sediment trap and surface sediment samples using the wet chemical leaching technique described by Mortlock and Froelich [1989]. Samples were initially treated with hydrochloric acid and hydrogen peroxide to remove carbonates and organics, respectively. Sodium carbonate was then used to dissolve the biogenic silica (bSiO_2), and the concentration of dissolved bSi was determined using a spectrophotometer. Si:C and Si:N molar ratios were then calculated for all samples.

3. Results

3.1. Silicic Acid and Nitrate Concentrations in Cariaco Waters

[15] Silicic acid concentrations in the upper 300 m of Cariaco Basin range from $50\text{ }\mu\text{M}$ to less than $1.0\text{ }\mu\text{M}$ and

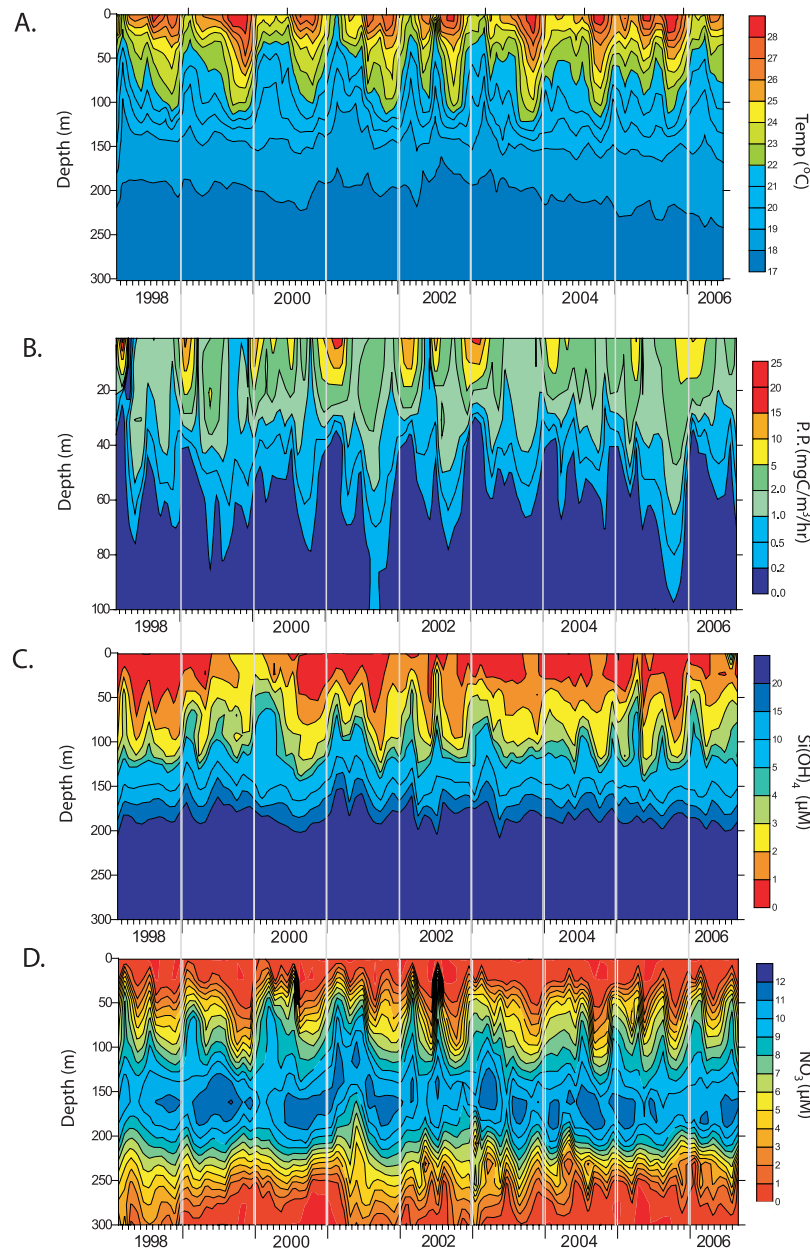


Figure 2. Seasonal variations in (a) temperature, (b) primary production, (c) silicic acid, and (d) nitrate in the upper 300 m of the water column at the Cariaco Basin time series study site for the period from 1998 to 2006, with the exception of primary production which is to 100-m depth.

are strongly depth-dependent (Figure 2). Surface waters are typically low in Si(OH)_4^- , with values in the upper 50 m frequently less than $1.0 \mu\text{M}$. At 100 m, Si(OH)_4^- concentrations usually reach $3\text{--}5 \mu\text{M}$ and increase systematically with depth at a rate of $\sim 0.2 \mu\text{M m}^{-1}$ due to opal remineralization.

[16] Superimposed on these depth trends are seasonal changes in Si(OH)_4^- that are most apparent in the upper 100–150 m (Figures 2 and 3). During winter-spring, deeper waters enriched in Si(OH)_4^- upwell to shallower depths; silicic acid concentrations of $2\text{--}4 \mu\text{M}$ are found to depths of 25–50 m during this period. However, even during upwell-

ing, surface waters commonly have Si(OH)_4^- concentrations of $<1.0 \mu\text{M}$. Conversely, during the summer and fall when surface waters are thermally stratified, Si(OH)_4^- concentrations in the upper 300 m of the water column tend to be lower than during upwelling. For example, the $2.0 \mu\text{M}$ Si(OH)_4^- isopleth generally deepens to $\sim 75\text{--}100$ m in the fall. These seasonal changes in silicic acid concentrations are also illustrated using mean vertical profiles for February and September (Figure 3). Figure 3 shows that Si(OH)_4^- is higher at all depths during the winter relative to the late summer, except for the upper 25 m that are equally depleted in silicic acid.

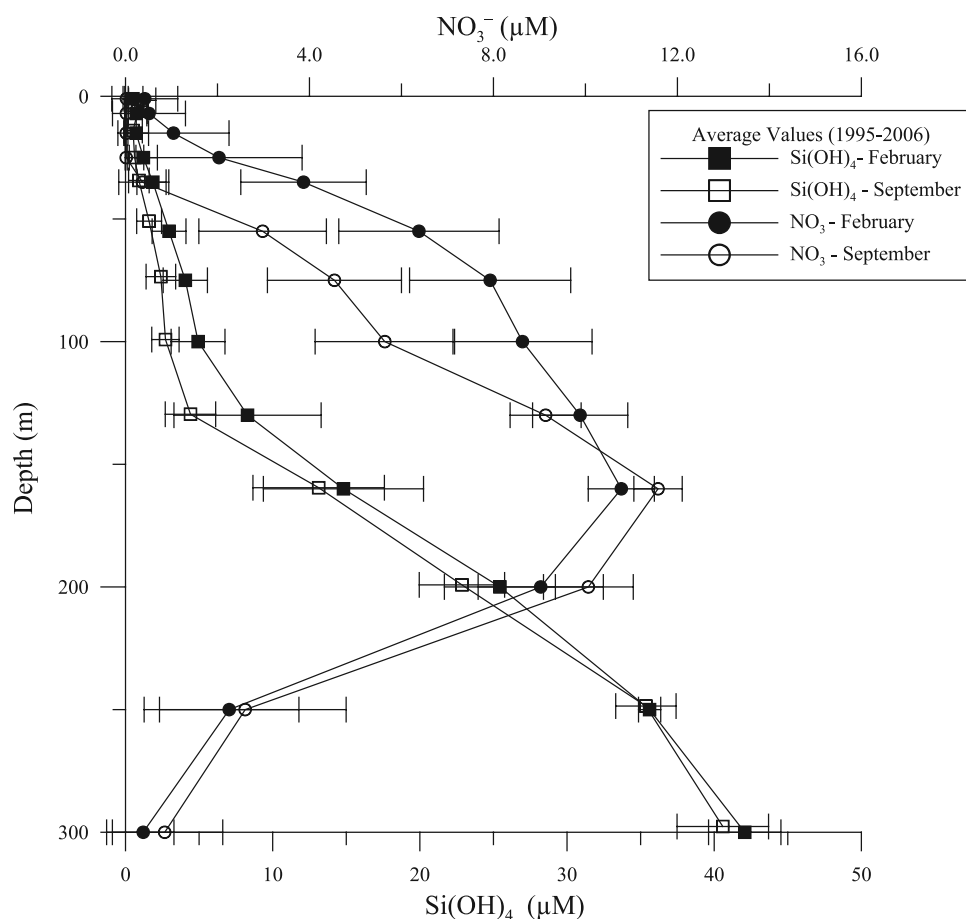


Figure 3. Mean depth profiles of nitrate (circles) and silicic acid (boxes) for February and September determined for the entire time series.

[17] Nitrate concentrations are low in the upper 50 m (generally $<2.0 \mu\text{M}$), increase steadily with depth to maximum values ($>10 \mu\text{M}$) between 100 and 200 m, and then decrease below 200 m (Figure 2). This subsurface decrease in NO_3^- is due to the nearly complete consumption of nitrate by denitrification at the oxic/anoxic interface [Thunell *et al.*, 2004]. Like silicic acid, there are distinctive seasonal trends in nitrate concentrations in the upper 100 m of the water column. In the early part of each year, it is common to find nitrate values as high as $8.0\text{--}9.0 \mu\text{M}$ between 50- and 100-m depth, with values as high as $5 \mu\text{M}$ extending upward to 25-m depth (Figure 3). By the latter part of the year, the $5\text{-}\mu\text{M}$ isopleth usually deepens to 75–100-m depth. The mean vertical profiles for February and September show that nitrate concentrations in the upper 25 m are $1.00 \pm 1.33 \mu\text{M}$ during winter upwelling and are depleted ($0.02 \pm 0.03 \mu\text{M}$) in summer (Figure 3).

[18] $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios and Si^* (defined as $\text{Si(OH)}_4^- - \text{NO}_3^-$ by Brzezinski *et al.* [2002]) were also calculated (Figure 4). Significant seasonal variability in $\text{Si(OH)}_4^-:\text{NO}_3^-$ exists in the upper 100 m of the water column. During the winter, surface $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios typically range from 2 to 4 and decrease to <1 by 25–50-m depth. In some years (i.e., 2001), $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios of less than 1 extend to the surface. Between approximately 75–150-m depth, this ratio

tends to be <1 throughout the year. Similarly, negative Si^* values indicate that waters between ~ 50 and 150 m are consistently depleted in Si(OH)_4^- relative to NO_3^- , with this depletion usually extending closer to the surface during winter and spring. During summer and fall, $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios in the upper 50 m increase significantly, with Si^* values becoming positive. The uniformly high ratios below 200 m are a consequence of denitrification.

3.2. Si:C and Si:N Ratios of Sinking Particles and Surface Sediments

[19] POC, PN, and Si fluxes were calculated for each sediment trap sample collected between November 1996 and May 2005 (except for trap Z where samples are only available for November 2003 to May 2005), and linear regression was used to determine the best fit values for the molar ratios of Si:C and Si:N at each of the five sediment trap depths (Figures 5 and 6). Significant correlations ($r > 0.8$, $p = 0.001$) exist for both Si versus C and Si versus N at each sediment trap depth. For both Si:C and Si:N, there is an increase in the ratios between 150 m and 410 m (Figures 5 and 6); Si:C increases from 0.17 ± 0.01 to 0.24 ± 0.01 , and Si:N increases from 1.14 ± 0.10 to 2.17 ± 0.10 over this depth range. Below 410 m, Si:C and Si:N values are fairly uniform. Similar depth-dependent changes are seen in the

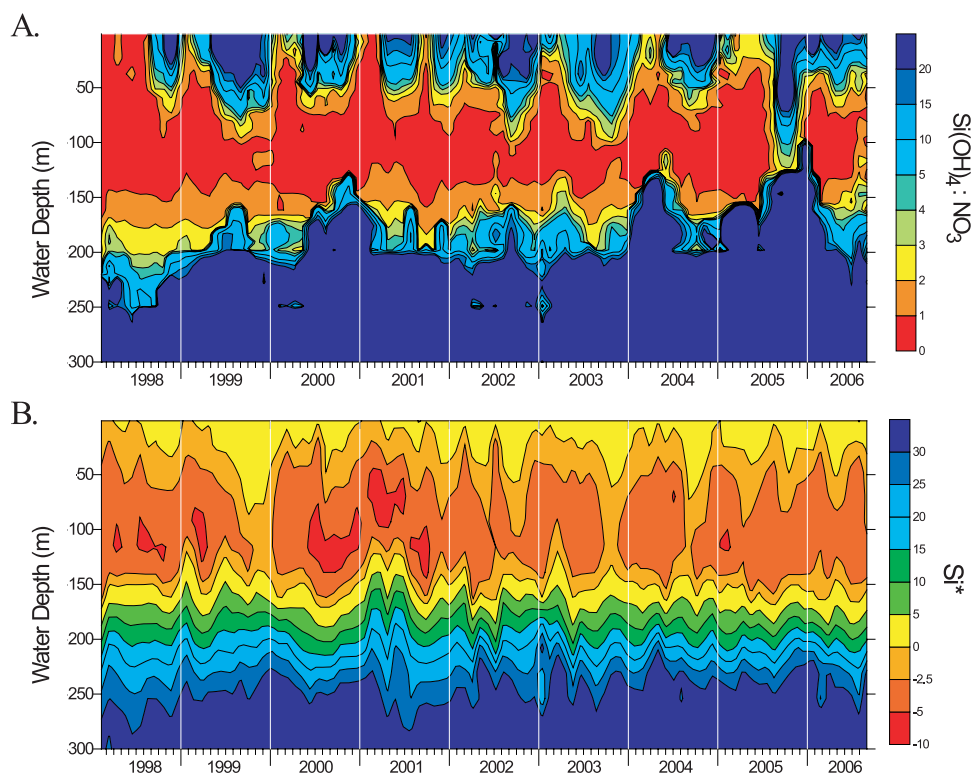


Figure 4. Seasonal variations in (a) the $\text{Si(OH)}_4:\text{NO}_3$ ratio and (b) Si^* in the upper 300 m of the water column at the Cariaco Basin time series study site for the period from 1998 to 2006.

Si:C and Si:N ratios of surface sediments from the basin (Figures 5 and 6). Between 250 and 430-m depth, surface sediment Si:C and Si:N ratios increase from 0.16 to 0.22 and from 1.67 to 2.23, respectively. Below 430 m, there is little change in the surface sediment ratios. The Si:C and Si:N ratios of 0.17 and 1.14, respectively, determined for the shallowest trap are very similar to the Si:C ratio of 1.1 and Si:N ratio of 0.13 found in diatom cultures grown under nutrient-replete conditions [Brzezinski, 1985].

[20] Temporal changes in the Si:C and Si:N ratios for each trap depth for the 9-year time series are plotted in order to evaluate seasonal to interannual variability in the composition of sinking particulates in Cariaco Basin (Figure 7). The time-dependent changes in Si:C and Si:N are strongly covariant and marked by distinctive seasonal cycles that are consistent with depth (Figures 7). Si:C values range from ~ 0.1 to 0.4, while most Si:N values fall between 1.0 and 3.0. For both ratios, the highest values occur during the winter and then decline during the early spring. In some years, this is followed by a secondary increase in both ratios in late spring to early summer, with minimum values of Si:C and Si:N occurring during the remainder of the summer and fall. There does not appear to be any systematic long-term change in either Si:C or Si:N during the last decade.

4. Discussion

4.1. Seasonal Changes in Si(OH)_4 and NO_3^- Availability

[21] Regional climate exerts a strong influence over hydrographic conditions and, in turn, the upper water

column nutrient chemistry in Cariaco Basin [Scranton *et al.*, 2006]. Increased trade wind velocities during winter-spring result in upwelling of nutrient-rich waters and high levels of primary production along this region of the Venezuelan margin [Muller-Karger and Aparicio Castro, 1994; Muller-Karger *et al.*, 2001]. This upwelling is visible in the rapid shoaling of isotherms that begins in December to January of each year and higher rates of primary production (Figures 2a and 2b). Conversely, relaxation of the winds during the summer and fall diminishes upwelling and results in lower primary production. The observed changes in Si(OH)_4 and NO_3^- concentrations in the upper 150 m of the water column (Figures 2c and 2d) are a manifestation of these seasonal hydrographic changes, along with nutrient utilization during photosynthesis.

[22] Upwelling in early winter brings silicate and nitrate-rich waters into the photic zone (Figures 2c and 2d). At 100-m depth, both silicic acid and nitrate increase to $10 \mu\text{M}$ at the onset of upwelling. At the same time, it is common to have Si(OH)_4 and NO_3^- values as high as $\sim 4 \mu\text{M}$ and $\sim 7 \mu\text{M}$, respectively, at depths as shallow as 25 m. During upwelling, the silicate and nitrate gradients in the upper 100 m of the water column reach their maximum. This injection of nutrients immediately stimulates primary production, with virtually all of this production occurring in the upper 50 m of the water column (Figure 2b). However, even during upwelling, surface waters tend to be depleted ($< 1 \mu\text{M}$) in both Si(OH)_4 and NO_3^- as a result of rapid utilization. Only in late 1999 to early 2000 do we observe silicate values as high as 2–3 μM at the surface. These values are

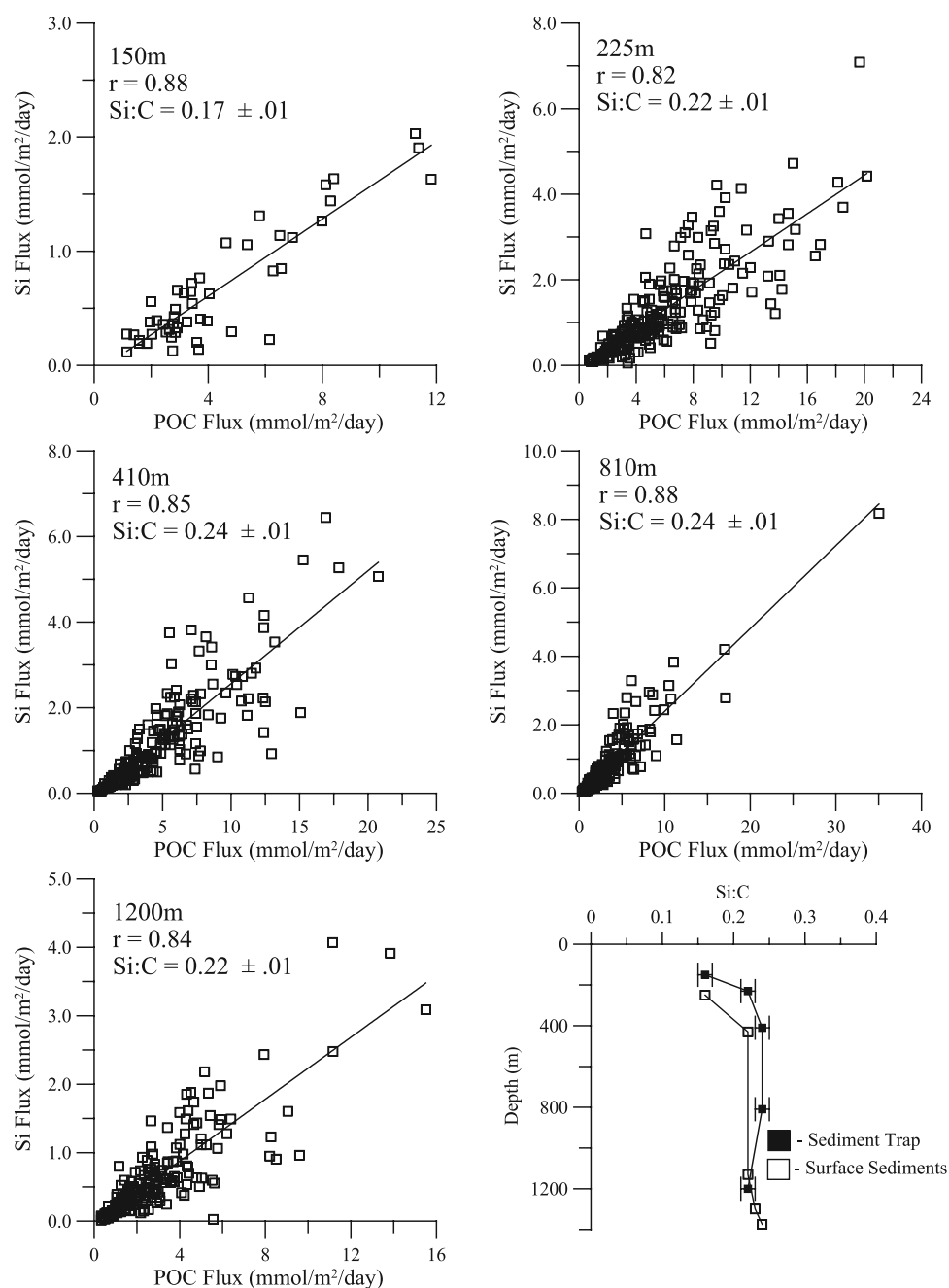


Figure 5. Si flux versus POC flux for the five Cariaco Basin sediment trap depths. All fluxes are in $\text{mmol m}^{-2} \text{d}^{-1}$. The best fit linear regression line, correlation coefficient (r), and average Si:C ratio are shown for each depth. Changes in the average sediment trap Si:C (solid boxes) and surface sediment Si:C (open boxes) as a function of depth are shown in the bottom right portion of the figure.

most likely due to the anomalously high precipitation and runoff that occurred in coastal Venezuela at this time [Wieczorek *et al.*, 2001]. As will be discussed in section 4.4, the generally low silicate values in surface waters during upwelling is an indication that silicate may act as a limiting nutrient for diatom growth in Cariaco Basin.

[23] With the relaxation of upwelling in the summer, the surface layer becomes thermally stratified and temperatures as warm as 22°C extend to 100-m depth during the fall

(Figure 2a). The silicic acid and nitrate gradients over this depth interval are at a minimum during the nonupwelling period. Surface water (upper 25 m) concentrations of both silicic acid ($0.78 \pm 0.71 \mu\text{M}$) and nitrate ($0.02 \pm 0.03 \mu\text{M}$) are very depleted during the nonupwelling season (Figures 2c, 2d, and 3).

[24] $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios and Si^* were calculated for the upper 300 m of the water column in order to determine if silicate availability may limit diatom growth in Cariaco

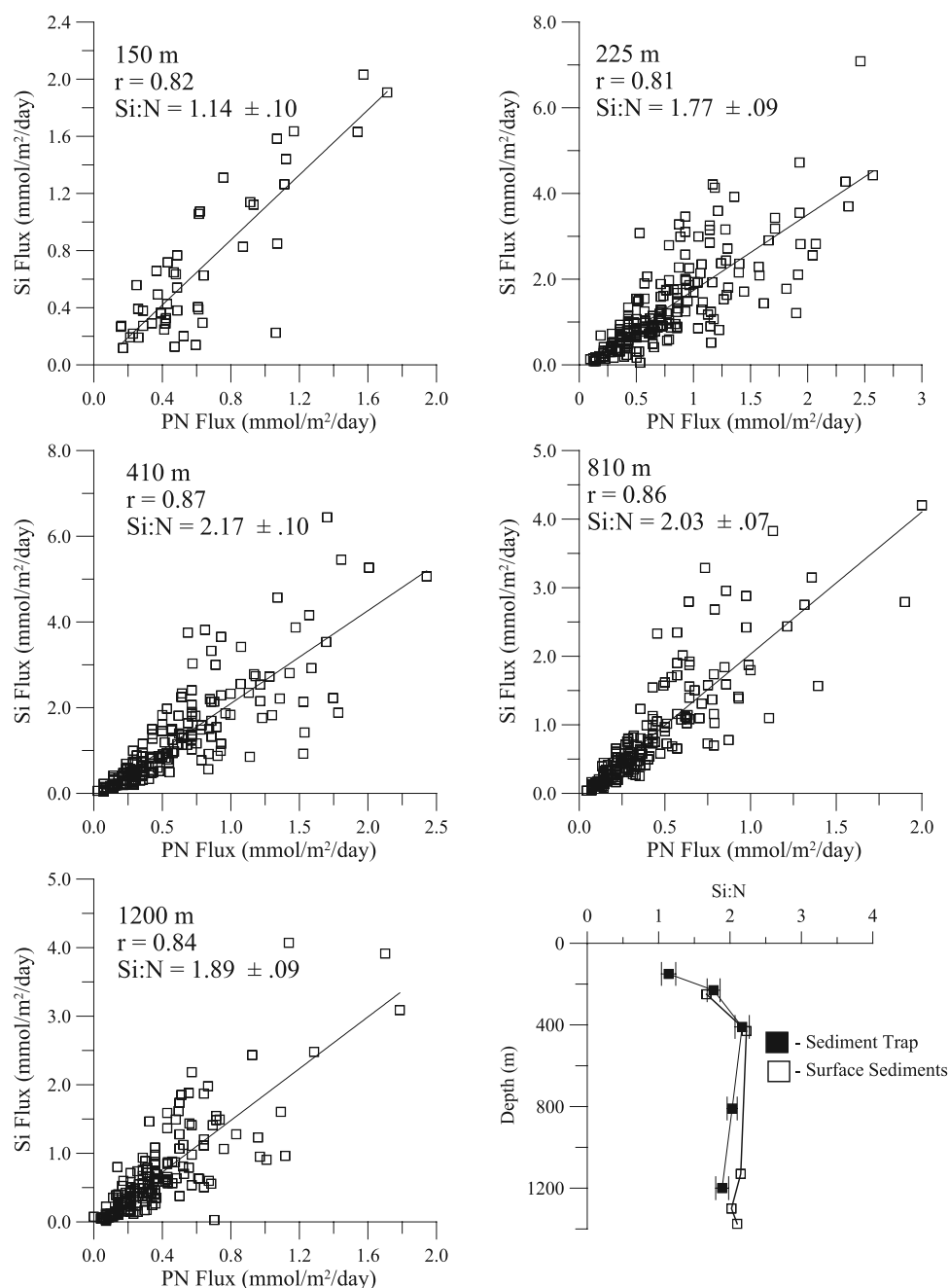


Figure 6. Si flux versus PN flux for the five Cariaco Basin sediment trap depths. All fluxes are in $\text{mmol m}^{-2} \text{d}^{-1}$. The best fit linear regression line, correlation coefficient (r), and average Si:N ratio are shown for each depth. Changes in the average sediment trap Si:N (solid boxes) and surface sediment Si:N (open boxes) as a function of depth are shown in the bottom right portion of the figure.

Basin (Figure 4). For example, if we assume that diatoms normally have a $\text{Si(OH)}_4^-:\text{NO}_3^-$ utilization ratio of roughly 1 [Brzezinski, 1985], then a ratio of less than 1 would indicate that diatoms are silicate limited. Negative values of Si^* further reflect silicate limiting conditions. We are particularly interested in the values for these two parameters in the upper 50–100 m of the water column since this is where most of the nutrient utilization and primary production occurs in Cariaco Basin (Figure 2b). Both $\text{Si(OH)}_4^-:\text{NO}_3^-$

ratios and Si^* clearly indicate that silicate concentrations may restrict the production of Si-dependent plankton, at least seasonally, in Cariaco Basin. In most years, the winter, and often the spring, are marked by $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios of less than 1 extending upward to depths shallower than 50 m (Figure 4a). Furthermore, Si^* values of less than 1 often extend to the surface during the first half of the year (Figure 4b). Thus, silicate limitation in Cariaco Basin is most severe during upwelling, when nutrient utilization and

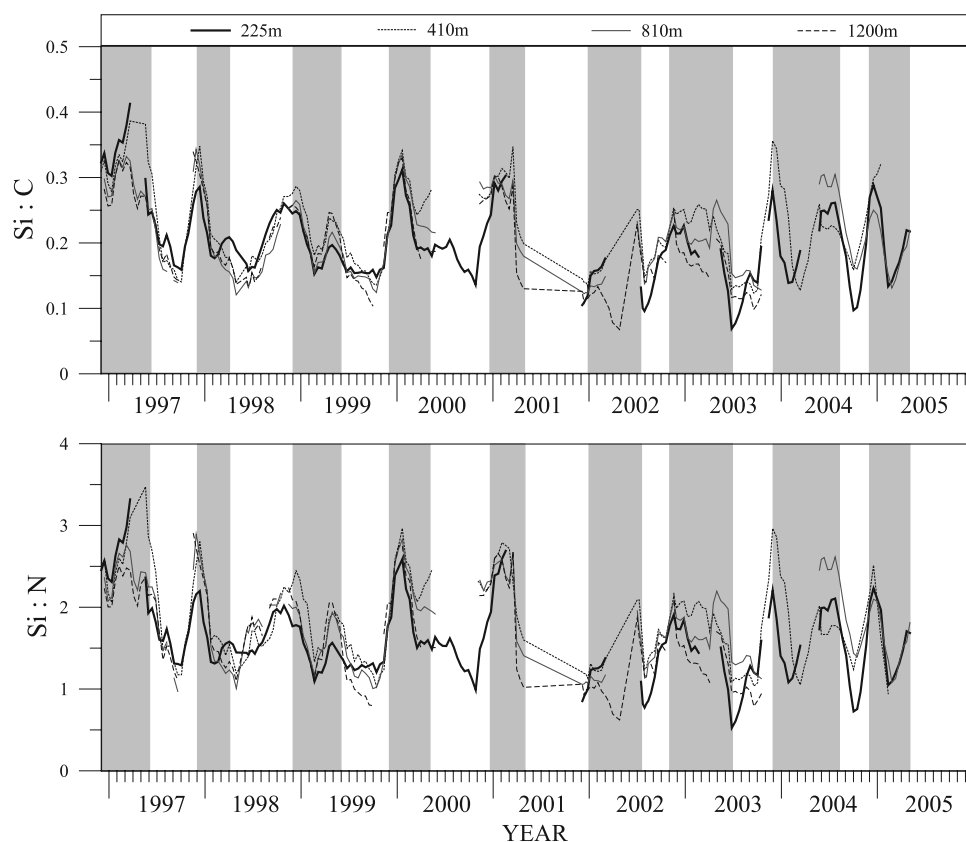


Figure 7. Seasonal changes in the (top) Si:C and (bottom) Si:N ratios of sinking particles collected in sediment traps A, B, C, and D for the period 1997 to 2005.

primary production are greatest. On the basis of an examination of the sediment trap samples, we know that diatom fluxes are highest during the upwelling season and that they dominate the total siliceous plankton production (O. Romero and R. Thunell, unpublished data, 2008). Thus, high utilization during the winter upwelling causes silicate concentrations in surface waters to be low. Conversely, during the summer and fall when upwelling is reduced and primary production decreases, we find that $\text{Si}(\text{OH})_4:\text{NO}_3^-$ ratios in the upper 50 m of the water column are frequently greater than 5 (Figure 4a), implying that nitrate rather than silicate is acting to limit production during this time of year. These

higher ratios reflect reduced utilization of silicate and virtually complete consumption of nitrate during this half of the year.

4.2. Biogenic Si Fluxes in Cariaco Basin

[25] On the basis of a compilation of available data, Nelson *et al.* [1995] estimated that the mean daily opal production rate in the global ocean is on the order $1.6\text{--}2.2 \text{ mmol Si m}^{-2} \text{ d}^{-1}$. Regionally, silica production rates vary significantly; oligotrophic midocean gyre regions commonly have production rates as low as $0.1\text{--}0.2 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, while it is not uncommon for coastal upwelling

Table 2. Sediment Trap Mean Daily Si Flux Estimates

Location	Trap Depth (m)	Si Flux ($\text{mmol m}^{-2} \text{ d}^{-1}$)	Reference
Cariaco Basin	225	1.30 ± 1.03	This study
Cariaco Basin	410	1.05 ± 0.88	This study
Cariaco Basin	810	0.74 ± 0.59	This study
Cariaco Basin	1200	0.61 ± 0.55	This study
Bransfield Strait Southern Ocean	494	2.49	Wefer <i>et al.</i> [1988]
Maud Rise Southern Ocean	360	1.09	Wefer and Fischer [1991]
Polar Front Southern Ocean	614	1.09	Ragueneau <i>et al.</i> [2000]
Equatorial Pacific Upwelling	1883	0.90	Dymond and Collier [1988]
California Current	1500	0.57	Dymond and Lyle [1994]
Arabian Sea Upwelling	914	1.01	Ragueneau <i>et al.</i> [2000]
Panama Basin	890	0.54	Honjo [1982]

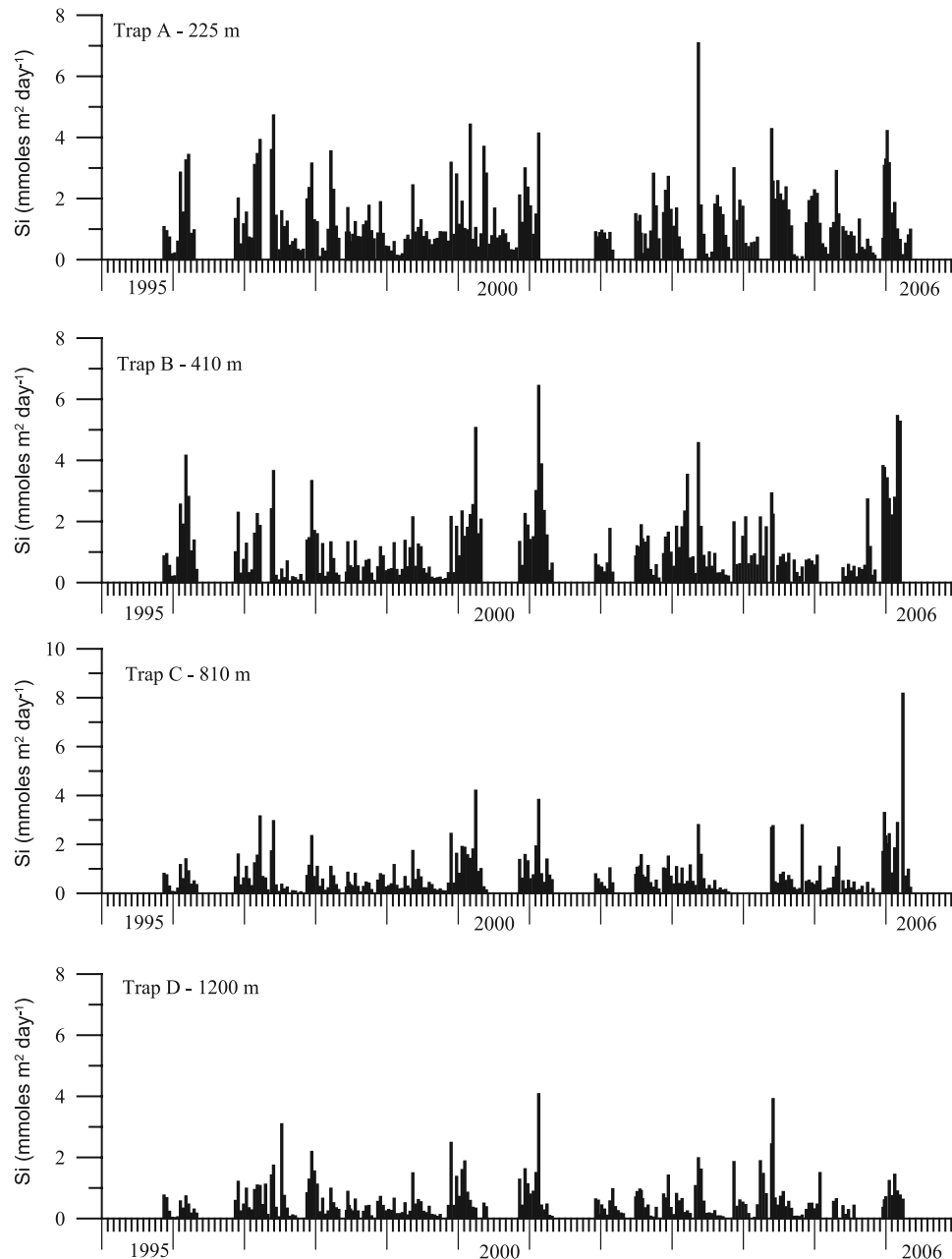


Figure 8. Time series of Si fluxes for sediment traps A, B, C, and D for the period 1996 to 2005. All fluxes are in $\text{mmol m}^{-2} \text{d}^{-1}$.

regions to have production rates exceeding $100 \text{ mmol Si m}^{-2} \text{d}^{-1}$ [Nelson *et al.*, 1995; Ragueneau *et al.*, 2000]. Unfortunately, no direct measurements of opal production are available for Cariaco Basin. However, biogenic Si fluxes should serve as an indirect measure of opal production even though remineralization has occurred. Since we have very limited data for the 150-m sediment trap, we use the data at 230 m as a proxy for surface opal production in Cariaco Basin (Table 2). At this depth, Si fluxes vary by nearly 2 orders of magnitude from less than $0.1 \text{ mmol m}^{-2} \text{d}^{-1}$ to almost $7.0 \text{ mmol m}^{-2} \text{d}^{-1}$ (Figure 8). Most years, the maximum Si fluxes are in the range of $3\text{--}4 \text{ mmol m}^{-2} \text{d}^{-1}$,

with the average 230-m flux for the entire 9-year time series being $1.30 \pm 1.03 \text{ mmol m}^{-2} \text{d}^{-1}$ (or an average annual Si flux of $0.47 \text{ moles m}^{-2} \text{a}^{-1}$) (Table 2 and Figure 8). These flux values are comparable to those previously reported for highly productive locations (Table 2) in the Southern Ocean [Wefer *et al.*, 1988; Pondaven *et al.*, 2000; Ragueneau *et al.*, 2000; Wefer and Fischer, 1991], as well upwelling zones in the equatorial Pacific [Dymond and Collier, 1988], the California Margin [Dymond and Lyle, 1982], the Arabian Sea [Ragueneau *et al.*, 2000], and the Panama Basin [Honjo, 1982]. On the basis of this similarity with Si fluxes from regions known to have very high opal

production rates, we infer that Cariaco Basin is also a region of high opal production.

4.3. Depth-Dependent Changes in the Si:C and Si:N Composition of Sinking Particles and Surface Sediments

[26] The elemental composition of both sinking and suspended particles is likely to change with depth because of differential remineralization rates for biogenic elements (*Honjo and Manganini* [1993], *Nelson et al.* [1996], *Schneider et al.* [2004], *Ragueneau et al.* [2002], among others). For example, *Honjo and Manganini* [1993] found PON to be the least resistant to degradation, followed by POC and bSi. Because of this differential preservation, more bSi is exported from surface waters relative to PON and POC, a phenomenon referred to as the “silicate pump” [*Dugdale et al.* 1995]. On the basis of a compilation of available elemental data, *Ragueneau et al.* [2002] determined that there is a systematic increase in Si:C with depth in the ocean and that this is controlled not only by different remineralization rates but also by a variety of other processes including herbivore grazing on diatoms within the mesopelagic zone.

[27] *Thunell et al.* [2000, 2007] previously demonstrated that there is significant loss of particles to remineralization and dissolution within both the oxic and anoxic zones of the Cariaco water column. They found that on average the POC flux decreased by ~55% between the 225- and 1200-m sediment traps. In this study, the mean Si flux decreases from 1.30 ± 1.03 mmol m⁻² d⁻¹ at 225 m to 0.61 ± 0.55 mmol m⁻² d⁻¹ at 1200 m, representing an average loss of over 50% (Table 2 and Figure 8). This loss may significantly affect the Si:C and Si:N ratios of the sinking particles in Cariaco Basin and thus their relative distributions in the dissolved phase.

[28] The Si:C and Si:N ratios of the sediment trap samples increase with depth, with most of this change occurring between trap Z (150 m) and trap B (410 m) (Figures 5 and 6). Si:C increases by 30% between 150 and 225 m (0.17 to 0.22) and by an additional 18% between 225- and 410-m depth (0.26). Below 410 m, there is no further increase in Si:C and, in fact, the ratio decreases slightly to 0.23 at 1200 m. The Si:N ratios follow a very similar depth similar pattern (Figure 6). There is a 55% increase in the ratio between 150 and 225 m, and a further increase of just over 20% by 410 m. Like Si:C, the Si:N ratio exhibits a small decrease from 2.17 at 410 m to 1.89 at 1200 m. The increases in both ratios within the upper several hundred meters of the water column can be attributed to the fact that organic matter is remineralized more rapidly than biogenic silica under aerobic conditions [*Ragueneau et al.*, 2002], with N being most rapidly regenerated. The lack of a further increase in either ratio below 410 m suggests that there is no selective removal of elements via remineralization in the anoxic portion of the water column, despite the fact that there is significant loss of sinking particles within this zone. A decrease in the rate of regeneration of organic matter within the anoxic portion would cause the Si:C and Si:N ratios to stabilize or even decrease. Thus, the impact of

remineralization processes on Si:C ratios in the upper several hundred meters of the water column in Cariaco Basin is similar to those in most regions of the open ocean [*Ragueneau et al.*, 2002]. However, this trend does not hold within the anoxic portion of the basin where C and N are no longer preferentially removed relative to Si because of changes in remineralization processes (i.e., sulfate reduction is the primary pathway for organic matter degradation in the anoxic portion of the basin [*Thunell et al.*, 2000]).

[29] The depth-dependent changes we observe in the Si:C and Si:N ratios of sinking particles are mirrored in the elemental ratios preserved in surface sediments (Table 1 and Figures 5 and 6). The Si:C and Si:N ratios of surface sediment samples increase by ~25% between 252 and 432 m, and then remain fairly uniform below this depth. This pattern, as well as the absolute values, is quite similar to sinking particles from comparable depths. For example, the mean Si:N ratio for the 225-m trap is 1.77 ± 0.9 , while surface sediment from 252 m has a Si:N ratio of 1.67. This ratio increases to 2.17 ± 0.10 for the 410-m trap and to 2.23 for the 432-m sediment sample. This strong similarity suggests that the surface sediments were recently deposited and have not undergone significant postdepositional remineralization.

4.4. Seasonal Changes in the Si:C and Si:N Composition of Sinking Particles

[30] The depth-dependent change in Si:C and Si:N ratios cannot explain the distinctive and consistent seasonal variations in these ratios seen at all trap depths (Figure 7). Rather, the observed temporal changes in Si:C and Si:N ratios of sinking particles produced in surface waters primarily are a function of two other factors: (1) nutrient availability and utilization by diatoms and (2) the relative contribution of diatoms to the total plankton community. As previously mentioned, diatoms grown in culture under nutrient-replete conditions have mean Si:C and Si:N ratios of 0.13 ± 0.04 and 1.12 ± 0.33 , respectively [*Brzezinski*, 1985], although in the ocean there is significant regional variability in these ratios due to these two factors [*Ragueneau et al.*, 2006]. For example, in the oligotrophic waters near Bermuda, low surface silicic acid concentrations result in a low contribution of diatoms to primary production and consequently Si:C ratios of only 0.02 [*Nelson and Brzezinski*, 1997]. Conversely, in the Southern Ocean, the Si:C ratio of newly produced particles averages ~0.25 because of significantly higher production rates of opal relative to organic carbon in this region [*Ragueneau et al.*, 2002]. Similarly, under Fe-limited conditions Si:N ratios may be several times higher than the expected ratio of ~1 [*Takeda*, 1998; *Hutchins and Bruland*, 1998].

[31] Clearly, not all of the primary production in Cariaco Basin is from diatoms. Although diatoms overwhelmingly dominate the siliceous plankton in the basin (*O. Romero and R. Thunell*, unpublished data, 2008), there are nonsiliceous plankton groups which contribute to the total particle flux. Since our elemental ratios are based on the analysis of bulk sediment samples, the inclusion of these nonsiliceous groups will cause the Si:N and Si:C ratios to be lower than

that of a sample composed predominantly of diatoms [Brzezinski *et al.*, 2003]. Also, the magnitude of this effect will vary seasonally as the proportion of diatoms to non-diatom phytoplankton changes. On the basis of the preliminary work of O. Romero and R. Thunell (unpublished data, 2008), diatoms contribute most significantly to the total plankton during the winter-spring upwelling period and then decrease in relative importance during the summer and fall. Furthermore, the trap ratios will be shifted higher than the original uptake values because of water column regeneration. Thus, we cannot use these ratios as absolute indicators of Si:N and Si:C uptake by diatoms in Cariaco Basin. Rather, the ratios provide an integrated measure of both changes in diatom nutrient utilization and the contribution of diatoms to the total plankton.

[32] For the four traps (A, B, C, and D) where we have multiple years of data, a repeatable seasonal pattern is present in the Si:C and Si:N ratios that is consistent at all depths (Figure 7). Both ratios are highest during the early part of the year when upwelling is most intense and diatoms are most abundant. During summer and fall, both Si:C and Si:N decrease to their lowest values. At least initially, the high values of these ratios during upwelling periods seem counterintuitive. Given that upwelling injects NO_3^- and Si(OH)_4^- -rich waters into the euphotic zone (Figure 2), it is reasonable to expect that the ratios during this time of year would be more in line with those associated with abundant nutrients [Brzezinski, 1985]. Specifically, we would expect Si:N and Si:C ratios to be closer to 1 and 0.1 during upwelling periods, rather than the observed values of 2–3 and 0.3, respectively (Figure 7). Such high values for these ratios can be attributed to the operation of a “silicate pump” in which particulate silica is more efficiently exported from surface waters relative to N and C [Dugdale *et al.*, 1995; Brzezinski *et al.*, 2003]. As a result of this preferential removal of silica, silicic acid concentrations become limiting and produce the low surface water values of $\text{Si(OH)}_4^-:\text{NO}_3^-$ and Si^* we observe during upwelling (Figure 4).

[33] During the nonupwelling period (summer and fall) we observe Si:N and Si:C ratios that are more typical of nutrient replete conditions. However, the diatom contribution to the total particle flux during this time of year is significantly reduced (O. Romero and R. Thunell, unpublished data, 2008), and thus the lower ratios may be largely attributed to a greater contribution of nonsiliceous plankton, rather than to a change in nutrient availability.

[34] Numerous studies have shown that under Fe limitation, NO_3^- utilization is suppressed and the resultant Si:N ratio of diatoms increases [Hutchins and Bruland, 1998; Takeda, 1998; Franck *et al.*, 2000; Brzezinski *et al.*, 2003]. Of particular relevance to our study is the work of Hutchins and Bruland [1998] carried out along the central California margin, a coastal upwelling regime very similar to that of Cariaco Basin. Despite its proximity to land, surface waters in this region have very low dissolved Fe concentrations. Hutchins and Bruland [1998] found that diatom Si:N uptake ratios were high (2–3) despite high nutrient concentrations associated with upwelling and attributed this to Fe limitation. The enhanced utilization of silicic acid associated with

Fe-deficiency causes surface waters to become more depleted in Si(OH)_4^- compared to NO_3^- , driving the system toward silica limitation. While we observe low $\text{Si(OH)}_4^-:\text{NO}_3^-$ ratios and negative Si^* values in the upper 50 m of Cariaco Basin each year during upwelling (Figure 4), we do not have any dissolved Fe data to determine directly if Fe limitation is occurring. At this point, we can only speculate that Fe limitation may be contributing to the high Si:N ratios that occur during the upwelling season in Cariaco Basin.

5. Conclusions

[35] The Cariaco Basin is a site of high opal production, and the cycling of Si in the basin is controlled largely by the pronounced seasonal changes in upper ocean conditions. Although upwelling during the winter and spring injects nutrients into the photic zone that stimulate production, surface waters are depleted in silicic acid relative to nitrate. Sinking particles produced during the winter/spring upwelling season tend to have high Si:C and Si:N ratios, indicating a more efficient export of Si relative to organic matter during this time of year. While high Si:N ratios are a sign of Fe limitation, we have no direct evidence to indicate that this is occurring in Cariaco Basin. The Si:C and Si:N ratios of sinking particles are considerably lower during the non-upwelling period. This most likely represents a significant increase in the production of nonsiliceous plankton during this time of year.

[36] Si:C and Si:N ratios of both sinking particles and surface sediments increase with depth within the upper several hundred meters because of selective remineralization, but then remain constant below 400 m within the anoxic portion of the basin. This depth-dependent pattern reflects the fact that organic matter (C and N) is degraded more rapidly than opal in the oxic portion of the water column and that this difference is minimized within the deeper, anoxic waters and sediments.

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