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The annual silica cycle of the North Pacific subtropical gyre

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ABSTRACT

Silica cycling in the upper 175 m of the North Pacific Subtropical Gyre was examined over a two year period (January 2008–December 2009) at the Hawaii Ocean Time-series (HOT) station ALOHA. Silicic acid concentrations in surface waters ranged from 0.6 to 1.6 μM , exhibiting no clear seasonal trends. Biogenic silica concentrations and silica production rates increased by an order of magnitude each summer following stratification of the upper 50 m reaching values of 157 nmol Si L^{-1} and 81 $\text{nmol Si L}^{-1} \text{d}^{-1}$, in 2008 and 2009, respectively. Sea surface height anomalies together with analyses of variability in isothermal surfaces at 150–175 m indicated that the summer periods of elevated biogenic silica were associated with anticyclonic mesoscale features during both years. Lithogenic silica concentrations increased in the spring during the known period of maximum atmospheric dust concentrations with maximum values of 36 nmol Si L^{-1} in the upper 10 m. Dust deposition would enhance levels of dissolved iron in surface waters, but there was no response of diatom biomass or silica production to increases in near-surface ocean lithogenic silica concentrations suggesting iron sufficiency of diatom silica production rates.

Low ambient silicic acid concentrations restricted silica production rates to an average of 43% of maximum potential rates. Si sufficiency only occurred during the summer period when diatom biomass was elevated suggesting that bloom diatoms are adapted to exploit low silicic acid concentrations. Annual silica production at HOT is estimated to be 63 $\text{mmol Si m}^{-2} \text{a}^{-1}$ with summer blooms contributing 29% of the annual total. Diatoms are estimated to account for 3–7% of total phytoplankton primary productivity, but 9–20% of organic carbon export confirming past suggestions that diatoms are relatively minor contributors to primary productivity and autotrophic biomass, but important contributors to new and export production in oligotrophic open-ocean ecosystems.

Annual silica production at HOT is nearly 4-fold lower than estimates at the Bermuda Atlantic Time-series Study (BATS) site in the Sargasso Sea from the 1990s, but annual silica export at the base of the euphotic zone is similar between the two gyres indicating very different balances between silica production and its loss in surface waters. On a relative basis, BATS is a more productive system with respect to silica, where biogenic silica is recycled with high efficiency in surface waters; in contrast the NPSG is a lower productivity system with respect to silica, but where lower recycling efficiency leads to a much higher fraction of new silica production. The two gyres show contrasting long-term trends in diatom biomass as biogenic silica concentrations at HOT have been increasing since 1997, but they have been decreasing at BATS suggesting very different forcing of decadal trends in the contribution of diatoms in carbon cycling between these gyres. Combining the data from both gyres indicates that globally subtropical gyres produce 13 Tmol Si a^{-1} , which is only 51% of previous estimates reducing the contribution of subtropical gyres to 5–7% of global annual marine silica production.

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1. Introduction

Studies of silica cycling in open-ocean pelagic ecosystems have provided new insight into the importance of diatoms in upper-ocean carbon cycling and the contribution of these regions to the global marine silicon budget. Results to date suggest that the contribution of diatoms to new and export production in oligotrophic ecosystems

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is considerably higher than their contribution to autotrophic biomass and primary productivity (e.g. Nelson and Brzezinski, 1997; Karl, 2002; Goldman and McGillicuddy, 2003). Diatom biomass in oligotrophic ocean systems is typically < 10% of that associated with the more abundant picophytoplankton (Goericke, 1998; Steinberg et al., 2001). However, diatoms are estimated to account for 15–20% of new production in the equatorial Pacific (Krause et al., 2011b) and up to 30% of carbon export in the Sargasso Sea (Nelson and Brzezinski, 1997). In the oligotrophic North Pacific Subtropical Gyre (NPSG) diatoms have been implicated to be important to new and export production (Brzezinski et al., 1998; Scharek et al., 1999a, 1999b; Karl, 2002), but the annual cycle of diatom abundance and productivity in the NPSG has not been quantified.

The euphotic zone of the subtropical gyres is one of the largest oligotrophic biomes in the sea, but data to estimate the contribution of these systems to the global marine silicon budget is limited. Only five studies have examined silica cycling in subtropical gyres: a time-series study of silica cycling at the Bermuda Atlantic Time-series Study (BATS) site in the Sargasso Sea (Nelson and Brzezinski, 1997), a spring transect (Brzezinski and Kosman, 1996) and two late-winter cruises (Krause et al., 2009b) in the Sargasso Sea, a North and a South Atlantic meridional transect (Poulton et al., 2006) and a pair of summer cruises in the NPSG (Brzezinski et al., 1998). Nelson and Brzezinski (1997) estimated the annual silica production at the BATS site to be $239 \text{ mmol m}^{-2} \text{ a}^{-1}$ based on three years of data from 1991–1994. Extrapolation of that rate to all mid-ocean gyres implies that subtropical gyre systems account for 11% of global marine silica production (Nelson et al., 1995). Data from other gyres suggests that 11% may be a significant underestimate as silica production measured on two cruises to the NPSG revealed rates of silica production in surface waters that are significantly higher than in the Sargasso Sea (Brzezinski et al., 1998).

A major determinant of how diatom production translates into the export of both particulate carbon and biogenic silica is the fraction of the biogenic silica production that is lost to dissolution in the euphotic zone. The frustules of living diatoms are protected from physicochemical dissolution by the organic matter that surrounds the silica within the cell wall (Bidle and Azam, 1999). When diatoms die, bacteria remove this organic matrix, thereby accelerating both silica dissolution (Bidle and Azam, 1999, 2001; Bidle et al., 2003) and respiratory losses of organic carbon. In some cases, these losses can be substantial: eighty percent of the silica produced in the upper 150 m of the Sargasso Sea undergoes local dissolution (Nelson and Brzezinski, 1997), diminishing the efficiency of the export of diatom silica to < 20%. Whether such low export efficiency is typical of other subtropical gyres is unknown; however, sediment trap studies at the Hawaii Ocean Time-series (HOT) station ALOHA (e.g. Scharek et al., 1999a, 2001; Buesseler et al., 2007) reveal that diatoms account for a significant fraction of the organic carbon exported to the deep sea in the NPSG (Dore et al., 2008).

The HOT program offers a unique opportunity to examine the annual silica cycle of the NPSG. Diatom dynamics at HOT differ significantly from those in the Sargasso Sea. For instance, diatom blooms occur at both locations nearly every year, but at HOT blooms occur during summer when inorganic macro-nutrient concentrations in surface waters are at their annual minimum and stratification is strong (Dore et al., 2008), while at BATS in the Sargasso Sea diatom blooms occur in the spring, coincident with stratification of the upper water column following nutrient inputs from winter convective overturn (Brzezinski and Nelson, 1995). The unusual timing of diatom blooms at HOT may be related to the symbiosis between several major diatom bloom-forming genera and nitrogen-fixing heterocystous cyanobacteria. Diatoms belonging to the genera *Hemiaulus*, *Rhizosolenia*, and *Chaetoceros*

are known to bloom during summer months in the NPSG, and these diatoms have been reported to contain or to be associated with diazotrophic cyanobacteria belonging to the genera *Richelia* and *Calothrix* (Villareal, 1990, 1991, 1992; Foster and Zehr, 2006; Fong et al., 2008). The highly stratified summer period typified by low N:P and low N:Si nutrient ratios in the euphotic zone has been hypothesized to provide favorable conditions for diazotrophs (White et al., 2007) possibly favoring the proliferation of diatoms capable of harboring these organisms as symbionts. These same diatoms can dominate the annual summer pulse of organic carbon exported to the deep sea, and those pulses have been reported to contain significant numbers of intact diatom cells still harboring endosymbionts (Scharek et al., 1999b). Recently the abundance of genes associated with *Richelia* and *Calothrix* were shown to increase during periods of positive sea-surface height anomalies at HOT (Church et al., 2009), and mesoscale physical dynamics have been hypothesized to favor the proliferation of diatoms and their symbiotic nitrogen fixers.

The extent to which diatom silica production is regulated by $[\text{Si}(\text{OH})_4]$ in the NPSG is largely unconstrained. Assessing Si limitation is inherently easier than examining limitation by other macronutrients, such as nitrogen and phosphorus, which exist in a variety of organic and inorganic forms or compared to trace metals, which are largely bound to ligands altering their bioavailability. In contrast, at seawater pH 97% of dissolved silicon exists as undissociated monomeric silicic acid, $\text{Si}(\text{OH})_4$, which is readily taken up by diatoms (Del Amo and Brzezinski, 1999), with nearly all of the remainder being $\text{SiO}(\text{OH})_3^-$ (Stumm and Morgan, 1981). Silicic acid concentrations in surface waters generally exceed those of inorganic N and P by one to two orders of magnitude and show regional variation among subtropical gyres. Concentrations in the upper ocean of the Pacific are generally higher than in the Atlantic, with $[\text{Si}(\text{OH})_4]$ reported to be between 0.9 and $3.0 \mu\text{M}$ in the NPSG and between 0.6 and $0.9 \mu\text{M}$ in the Sargasso Sea (Brzezinski and Nelson, 1995). In both systems silicic acid concentrations in the euphotic zone are less than the average half saturation constant for Si uptake by diatoms in culture studies (Martin-Jézéquel et al., 2000) suggesting widespread and persistent Si uptake limitation in both gyres. The occurrence of strong Si limitation of silica production rates in the NPSG was confirmed by Brzezinski et al. (1998) during two cruises in the summers of 1995 and 1996 and in the Sargasso Sea by Brzezinski and Nelson (1996) and Krause et al. (2010b).

Motivated by these data we examined silica cycling in the upper 175 m at the HOT station ALOHA over a two-year period at approximately monthly temporal resolution. Major goals were to quantify annual rates of silica production, silica dissolution and silica export for comparison with rates measured in the Sargasso Sea and to re-evaluate the role of mid-ocean gyres in the global marine silica cycle. We also tested the hypothesis that Si limitation would regulate rates of silica production. Finally, we sought to evaluate the contribution of diatoms to primary and export production to access their role in regional carbon cycling.

2. Methods

2.1. Study area and sampling

Silica cycling in the upper 175 m at station ALOHA ($22^\circ 45' \text{N}$, $158^\circ 00' \text{W}$) was examined on 18 HOT cruises from January 2008 through December 2009. Water samples were collected using 12 L PVC sampling bottles on a rosette equipped with a Seabird 911 CTD. Seawater was drained directly from the water samplers into sample bottles through acid-washed silicone tubing.

2.2. Silicic acid and particulate silica analyses

Samples for silicic acid concentration analysis were dispensed into 50 mL polypropylene tubes and refrigerated at 4 °C until analysis ashore as described by Brzezinski and Nelson (1995). Seawater for particulate silica analysis was collected in 2.8 L polycarbonate bottles and immediately filtered through 0.6 µm polycarbonate filters. Each filter containing the particulate material was folded in quarters, placed in a polypropylene screw cap vial, loosely capped and dried at 60 °C. Once dried the vials were capped tightly and stored at room temperature until analysis for both biogenic (bSiO₂) and lithogenic silica (lSiO₂) concentrations via a serial NaOH/HF digestion procedure described in Brzezinski and Nelson (1995) and Nelson et al. (1991), but using Teflon instead of polypropylene tubes, which provide low and stable blank values (Krause et al., 2010b). This method has a detection limit of 0.2 nmol Si L⁻¹ for biogenic silica concentration when using 2.8 L samples and a 10 cm cuvette. The sodium hydroxide digestion dissolves 10–15% of the lithogenic silica present in the sample (e.g. Ragueneau and Tréguer, 1994), which at the lithogenic silica concentrations observed in this study results in an average bias of < 1 nmol Si L⁻¹ in the reported biogenic silica concentrations, but up to a 3 nmol Si L⁻¹ bias in the upper 10 m during three cruises with higher surface lithogenic silica concentrations. These biases are small compared to the changes in [bSiO₂] observed.

2.3. Silica production rates and limitation of Si uptake

Silica production rates were measured using the radioisotope ³²Si in the form of sodium silicate. Seawater for these measurements was obtained from two CTD/rosette casts separated in time by approximately one day on each cruise. On each cast samples were obtained before dawn from nominal depths of 5, 25, 50, 75, 100, 125, 150, 175 m. An acid-washed polycarbonate bottle (300 mL) was filled with seawater from each depth and 361 Bq of Chelex-cleaned high specific activity, 42–50 kBq (µg Si)⁻¹, ³²Si(OH)₄ was added. The tracer addition increased ambient [Si(OH)₄] by < 0.3 nM. The experimental bottles from each profile were deployed on free-drifting *in situ* arrays before dawn with each sample incubated at the depth corresponding to the origin of the seawater that it contained. One array was deployed from dawn to dusk and the other was deployed for 24 h. Upon retrieval of each array, the particulate matter in each incubation bottle was collected on a 25 mm, 0.6 µm polycarbonate filter and processed as described below. The background ³²Si activity due to sample processing was assessed by adding the same ³²Si(OH)₄ addition as used for incubations to replicate 300 mL volumes of 0.2 µm-filtered seawater followed by immediate filtration and processing of the filter as described below.

Limitation of silica production by [Si(OH)₄] was evaluated by comparing rates of silica production in samples with and without supplemental Si(OH)₄. A pair of 300 mL polycarbonate bottles were filled with water from 25 m depth. Aqueous sodium metasilicate was added to one bottle of the pair to increase the dissolved silicon concentration by 20 µM followed by the addition of ³²Si(OH)₄ to both bottles. In 2008 both bottles of each experimental pair received 361 Bq of ³²Si(OH)₄. In 2009 the isotope addition for the bottles receiving the 20 µM Si(OH)₄ addition was increased to 1084 Bq to improve sensitivity. The bottles were incubated at 25 m on the *in situ* array deployed for 24 h, retrieved and processed as described below. The 20 µM addition of non-radioactive Si(OH)₄ diluted the specific activity of the ³²Si tracer significantly resulting in low ³²Si activity in the particulate material from the +20 µM additions irrespective of the isotope addition. Uptake rate values were discarded whenever the difference in the ³²Si activity between a sample and the corresponding

blanks was less than twice the standard deviation of the activity in the blanks. Silica production rates (in units of nmol Si L⁻¹ d⁻¹) and specific rates of silica production (V_b in units of d⁻¹) were calculated as in Brzezinski and Phillips (1997).

The enhancement statistic, Enh, was calculated as the ratio of the silica production rate obtained with the 20 µM addition of Si(OH)₄ to that obtained at the ambient [Si(OH)₄] (Brzezinski et al., 2003). In principle values of Enh > 1.0 indicate that the ambient [Si(OH)₄] is insufficient to support maximum rates of silica production. In practice analytical uncertainties in production rate measurements require that Enh exceed 1.2 to reliably indicate that Si(OH)₄ addition increased uptake rates (Nelson et al., 2001). Thus values of Enh > 1.2 are indicative of stimulation of the rate of silica production by [Si(OH)₄] (Nelson et al., 2001). Assuming that the addition of 20 µM Si(OH)₄ saturated uptake rates, 1:Enh approximates the fraction of the maximum specific uptake rate, V_m , supported *in situ*.

The activity of ³²Si in particles collected on the filters from the silica production and enhancement experiments was determined by gas proportional counting (Krause et al., 2011a). Immediately following filtration the wet filter was placed on a nylon planchette, air dried and covered with Mylar film. ³²Si activity was determined using a Risø GM-25–5 A low-level beta counter (typical background of < 0.3 cpm, see also van der Loeff et al. (2006)) after secular equilibrium had been established between ³²Si and its daughter isotope ³²P (~120 days). Comparisons between the activity of ³²Si measured on filters using this method and that obtained using liquid scintillation counting (Brzezinski and Phillips, 1997) show agreement between methods to be better than 5% (Krause et al., 2011a). Silica production rates from the 24 h deployments represent daily rates of silica production with those from the dawn to dusk deployments representing production during daylight. Night time silica production was computed as the difference between the daily and the daytime rates.

2.4. Particulate silica export and silica dissolution rates

The export of biogenic and lithogenic silica at 150 m was measured using the HOT program's free drifting Multitrap sediment trap array (Knauer et al., 1979; Karl et al., 1996). For the silica measurements, two polycarbonate collector tubes fitted with entrance baffles were filled with brine (50 g L⁻¹ NaCl in 0.2 µm filtered surface seawater from ALOHA) without preservative and deployed at 150 m for approximately 3 days. A subsample of the brine used to fill each trap was taken for dissolved silicon analysis prior to deployment. Upon retrieval the seawater that had infiltrated the upper portion of each trap was siphoned off to the interface between the brine and ambient seawater as described by Karl et al. (1996). Then each trap was capped, the seawater mixed and subsampled for dissolved silicon (50 mL) and biogenic and lithogenic silica concentration analysis (250–500 mL). This trap array has been shown to undercollect particulate matter relative to rates of export determined from ²³⁴Th:²³⁸U disequilibria (Benitez-Nelson et al., 2001) suggesting that the rates reported here are conservatively low.

Silica dissolution within each trap was determined based on the increase in dissolved silicon concentration in the brine solution over the deployment period. That estimate was corrected for the Si(OH)₄ added with the dilution of the brine with ambient seawater (presumably at the surface during trap deployment), from the change in salinity of the brine measured with a refractometer and the [Si(OH)₄] profile following Brzezinski and Nelson (1995).

The dissolution rate for biogenic silica was calculated using two methods. First, the difference between integrated rates of silica production and the rate of bSiO₂ export at 150 m was assumed to reflect losses to dissolution yielding an average

integrated rate of silica dissolution for the upper 150 m ($\text{mmol Si m}^{-2} \text{d}^{-1}$). Second, the sediment trap data allow specific rates of dissolution (V_{diss} , in units of d^{-1}) to be calculated for sinking particles based on the partitioning of the captured silicon between the particulate and dissolved phases within the traps (Brzezinski and Nelson, 1995; Nelson and Brzezinski, 1997). The method involved simulating the trap deployment mathematically and estimating V_{diss} by iteration. For a given trap the total biogenic silica flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$) was set to be the sum of the moles of Si recovered as Si(OH)_4 from the dissolution of particulate silica and the moles of biogenic silica captured divided by the trap deployment interval. V_{diss} was assumed to be equal and constant for all particles of biogenic silica and the rain rate of particulate silica into the traps was assumed to be constant over the deployment period. Lithogenic silica was assumed to not dissolve as the specific rate of dissolution of mineral silica in seawater is orders of magnitude slower than that of biogenic silica (Hurd, 1972; Krausee et al., 1983). The trap deployment was simulated by allowing particles to enter the trap at the measured rate of biogenic silica flux with conversion of particulate to dissolved Si within the trap occurring at rate, V_{diss} , resulting in a simulated partitioning between dissolved and particulate silica at the end of the deployment period. The simulated partitioning between dissolved and particulate silica was compared to observation and the value of V_{diss} adjusted up or down to reduce the observed discrepancy. The process was repeated until the predicted concentration of particulate and dissolved silicon in the trap at the end of the simulated deployment period exactly matched the measured values.

3. Results

3.1. Physical setting

Fig. 1 shows time series of physical and Si cycle variables during 2008 and 2009. Data from the two CTD/rosette casts sampled on each cruise were used to construct the plots and thus the contours average the conditions encountered on each cruise.

Seawater temperature in the upper 175 m at ALOHA followed the know pattern of weaker thermal stratification during the winter months with maximum thermal stratification in the upper 50 m during July and August (Fig. 1A). Temperature between 150 and 175 m displayed alternating periods of relatively warm and relatively cold water with the periods of relative warmth coinciding with maximum thermal stratification in the upper 50 m (Fig. 1A). Salinity in the upper 175 m was generally higher in 2009 compared to 2008 (Fig. 1A). In both years relatively low salinity was observed in the upper 50 m as stratification in that depth zone intensified each spring. Salinity variations between 150 and 175 m mirrored the oscillations in temperature in this depth zone with relatively high salinity present in the warmer waters and with relatively low salinity associated with cooler temperatures.

3.2. Dissolved and particulate silicon distributions

Silicic acid concentrations in the upper 100 m were generally between 0.8 and 1.25 μM (mean $1.04 \pm 0.17 \mu\text{M}$; \pm SD) with no regular seasonal trend (Fig. 1B). The lowest concentrations observed in the upper 100 m occurred during the winter of 2008 and during

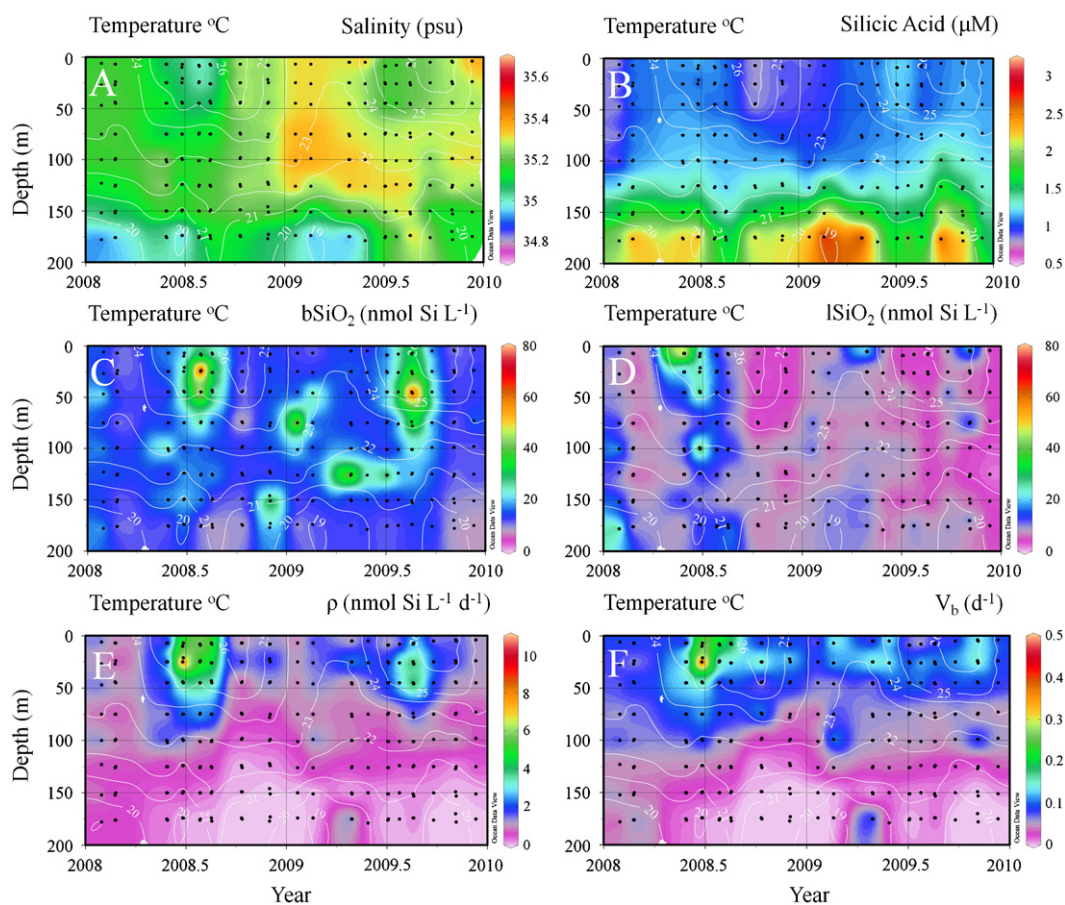


Fig. 1. Time series of physical, chemical and silica cycle parameters in the upper 175 m at station ALOHA. (A) salinity, (B) silicic acid concentration, (C) biogenic silica concentration, bSiO₂, (D) lithogenic silica concentration, lSiO₂, (E) silica production rates, ρ , (F) specific rates of silica production, V_b . Contours lines in each plot are isotherms ($^{\circ}\text{C}$).

the fall of 2009 when concentrations were $< 1 \mu\text{M}$. Concentrations did not decline during the winter of 2009 with concentrations in the upper 100 m remaining above $1 \mu\text{M}$.

Biogenic silica concentrations were low, averaging $17 \pm 14 \text{ nmol Si L}^{-1}$ equivalent to about 1% of the average silicic acid concentration (Fig. 1C). Two periods of elevated diatom biomass were apparent with peak concentrations up to $157 \text{ nmol Si L}^{-1}$, which in most other systems would not be considered a bloom, but at ALOHA increases of this magnitude represent a doubling in integrated biogenic silica concentrations in the upper 175 m and an order of magnitude increase in $[\text{bSiO}_2]$ in the upper 50 m. These periods (June 2008, July 2008, August 2009) will hereafter be referred to as blooms.

Diatom blooms occurred during the summer of each year after surface temperatures had increased to $> 25^\circ\text{C}$. Siliceous biomass was patchy during these periods; for example, biogenic silica concentrations at 25 m in July 2008 ranged between 31 and $157 \text{ nmol Si L}^{-1}$ (averaging $94 \pm 89 \text{ nmol Si L}^{-1}$) for the two casts made on that cruise. Average concentrations were lower and less variable during the summer of 2009 when maximum concentrations at $\sim 50 \text{ m}$ ranged between 73 and $81 \text{ nmol Si L}^{-1}$ (averaging $77 \pm 6 \text{ nmol Si L}^{-1}$) during the August cruise. Blooms were observed on single cruises during both years implying that the duration of these events was 1–2 months or less. The average integrated biogenic silica concentrations for all cruises was $3.0 \pm 1.1 \text{ mmol Si m}^{-2}$, but reached 5.8 ± 0.9 and $6.2 \pm 0.2 \text{ mmol Si m}^{-2}$ during blooms in 2008 and 2009, respectively (average of the two profiles acquired on each cruise, see Section 2, Fig. 2A). Blooms during both years (Fig. 1C) coincided with relative minima in salinity in surface waters and the downward displacement of isotherms in the lower euphotic zone (150–175 m; Fig. 1A). Individual samples with higher biomass (e.g. 20–40 nmol Si L^{-1}) were occasionally observed between 75 and 150 m (Fig. 1C).

Lithogenic silica concentrations at ALOHA are among the lowest reported for the surface ocean with concentrations generally $< 10 \text{ nmol Si L}^{-1}$ (Fig. 1D). Maxima in lithogenic silica concentrations occurred in the upper 10 m each spring. In 2008 the maximum in lithogenic silica concentration was observed during May and June with near-surface concentrations reaching $53 \text{ nmol Si L}^{-1}$. In 2009 maximum $[\text{lSiO}_2]$ was observed in April with average concentrations of $23 \pm 18 \text{ nmol Si L}^{-1}$. Another near-surface maximum was observed in November 2009, $19 \pm 22 \text{ nmol Si L}^{-1}$. As the observed maxima were confined to the upper 10 m they did not dramatically increase lithogenic silica concentrations integrated to 175 m (Fig. 2B). Lithogenic silica concentrations were a sizable fraction of the concentration of biogenic silica. Overall integrated $[\text{lSiO}_2]$ concentrations averaged $1.5 \pm 0.8 \text{ mmol Si m}^{-2}$ corresponding to three-quarters of the average integrated biogenic silica concentration.

3.3. Silica production and Si uptake limitation

Integrated silica production rates showed no consistent diurnal pattern. On average daytime and nighttime rates were nearly equal with an average day:night ratio of 1.2 ± 0.4 in 2008 and 1.0 ± 0.3 in 2009. Based on these results daytime rates obtained from the dawn to dusk incubations were extrapolated to 24 h to yield a second estimate of the daily rate of silica production for each cruise to compliment that obtained from the separate 24 h array. Daily rates for each cruise are reported as the average of these two estimates.

Silica production rates generally followed the same temporal pattern as did biogenic silica concentrations with an annual maximum in the upper 50 m each summer (Fig. 1E). The annual increase in silica production preceded that in biomass by one sampling period (approximately one month) in 2008, but not in 2009 when the increase in biomass and production were

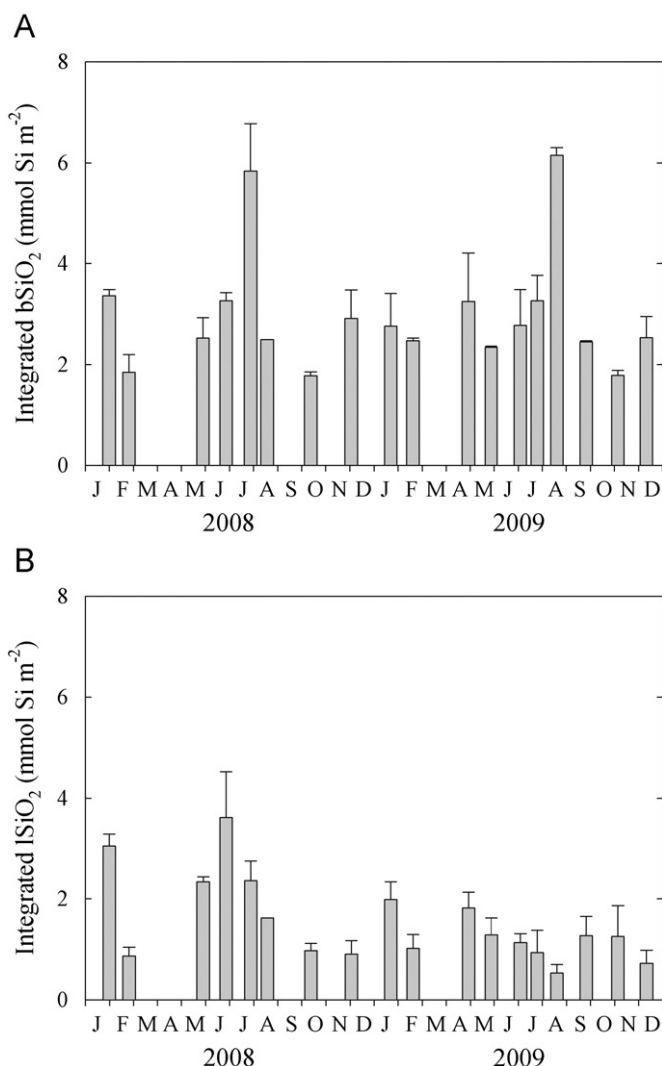


Fig. 2. Time series of: (A) integrated biogenic silica concentration and (B) integrated lithogenic silica concentration. Average and error (SD) are reported using the two profiles (12 and 24 h arrays) for each cruise.

coincident in time (Fig. 1C and E). Silica production in 2008 was highest in June with the highest rates occurring at 25 m depth (average rate at 25 m: $10.0 \pm 9.3 \text{ nmol Si L}^{-1} \text{ d}^{-1}$, $\pm \text{SD}$). Elevated rates were again observed in August 2009 with high rates at both 25 and 50 m that averaged $4.5 \pm 1.8 \text{ nmol Si L}^{-1} \text{ d}^{-1}$. These peaks are reflected in the integrated rates of silica production (175 m) that show a maximum in June 2008, $0.48 \pm 0.27 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, and in August of 2009, $0.33 \pm 0.10 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ (Fig. 3A).

Specific silica production rates increased the month prior to the increase in siliceous biomass in 2008, but specific rates did not increase appreciably either before or during the biomass increase in August 2009 (Fig. 1F). A subsurface maximum in V_b was present at 25 m in June 2008 (mean $V_b = 0.50 \pm 0.51 \text{ d}^{-1}$, range 0.13–0.86 d^{-1}). The highest specific rate observed in that depth range implies diatom doubling times of 19 h. In general V_b was between 0.2 and 0.3 d^{-1} in July 2008 and $< 0.1 \text{ d}^{-1}$ in August of 2009. Depth-normalized integrated specific rates, $V_{b\text{AVE}}$, were only elevated during July 2008 with an average across both years of $0.07 \pm 0.02 \text{ d}^{-1}$ (Fig. 4A).

Substrate limitation of silica production ($\text{Enh} > 1.2$) was detected on 10 of 12 cruises (Fig. 4B). Abatement of substrate limitation ($\text{Enh} = 1.0\text{--}1.2$) occurred during only two cruises that were each associated with summer increases in siliceous biomass

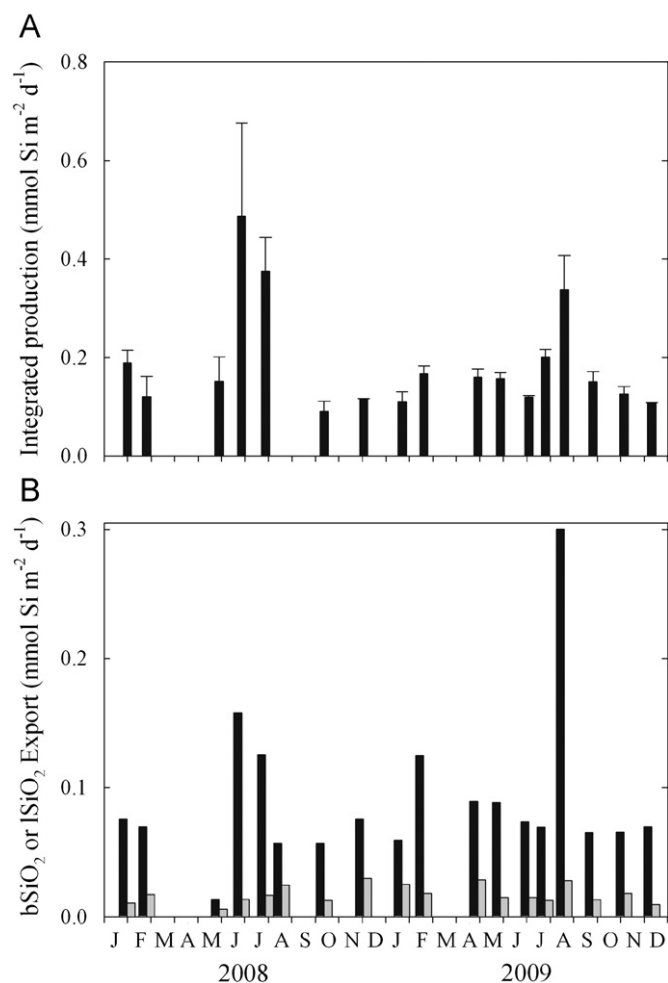


Fig. 3. Time series of: (A) integrated silica production and (B) the export rate of biogenic silica, black bars, and of lithogenic silica, gray bars. Averages and errors as in Fig. 2.

and silica production (Fig. 4B). For the other cruises Enh averaged 3.2 ± 1.2 indicating that on average the addition of $20 \mu\text{M}$ silicic acid nearly tripled the rate of silica production. Low Enh was observed during the July 2008 bloom coincident with the peak in production during that year. Enh was again low in July 2009 one month before biogenic silica concentrations increased in August 2009. To estimate the level of Si limitation ($V_b/V_m=1/\text{Enh}$; see methods) the inverse of the values of Enh for each cruise were averaged. That calculation reveals that under non-bloom conditions silica production rates were restricted to $0.35 \pm 0.11\%$ of potential maximum rates (Table 1). The annual average including blooms was $43 \pm 21\%$.

3.4. Silica export and dissolution

The rate of export of biogenic silica was relatively uniform over time during both years except for increases in export during summer associated with periods of elevated diatom biomass in surface waters (Fig. 3B). During June and July of 2008 biogenic silica export reached $0.16 \text{ mmol Si m}^{-2} \text{d}^{-1}$ and $0.13 \text{ mmol Si m}^{-2} \text{d}^{-1}$, respectively, with high rates, $0.30 \text{ mmol Si m}^{-2} \text{d}^{-1}$, also observed in August 2009. An export event of similar magnitude to that associated with the summer of 2008 was detected in February of 2009, but it was not associated with an increase in biogenic silica concentrations in surface waters. The overall average flux of biogenic silica was $0.091 \pm 0.061 \text{ mmol Si m}^{-2} \text{d}^{-1}$ (Table 1). On

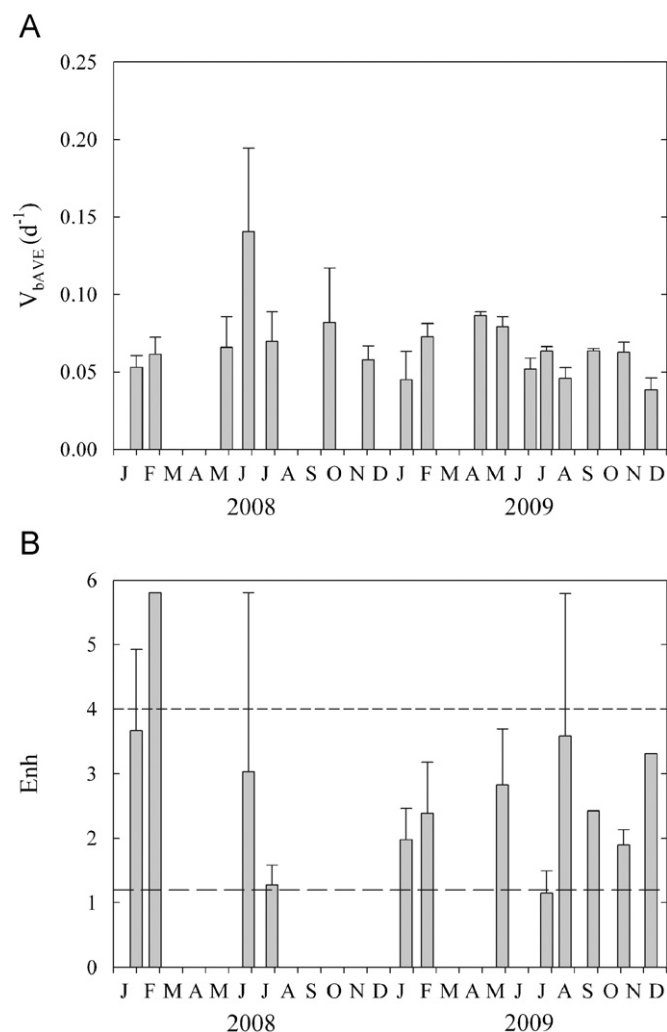


Fig. 4. Time series of: (A) the depth-normalized integrated specific rates of silica production, V_{BAVE} , and (B) the enhancement statistic, Enh. Long dashed line in B at an Enh value of 1.2 indicates the threshold for Enh above which the statistic indicates limitation of Si uptake at ambient $[\text{Si}(\text{OH})_4]$. Short dashed line at an Enh value of 4 is the threshold above which growth limitation by Si is implied (see text for details). Averages and errors are as in Fig. 2, where no error is reported only one Enh experiment was successfully obtained on a given cruise.

average the ratio of the rate of export of biogenic silica at 150 m to its rate of production in the upper 150 m was 0.54 ± 0.19 (Table 1). The ratio of export to production for biogenic silica during summer periods of elevated biogenic silica concentration (mean = 0.52 ± 0.16) was similar to the average for the rest of the year (mean = 0.54 ± 0.33). The average rate of lithogenic silica export was five-times less than that of biogenic silica with no apparent seasonality (Fig. 3B). Turnover time (ratio of integrated biomass to export flux) was more rapid for biogenic silica (43 days) than for lithogenic silica (112 days).

The observation that the flux of biogenic silica at 150 m averaged 54% of the overlying rate of silica production implies that the remaining 46% dissolved in the upper 150 m corresponding to an average dissolution rate of $0.087 \text{ mmol Si m}^{-2} \text{d}^{-1}$ ($\int_{0m}^{150m} \rho \times 0.46$; Table 1). Analysis of the brine solutions from sediment traps showed that an average of 21% of the mass of total Si (dissolved+particulate) captured was present as $\text{Si}(\text{OH})_4$. The calculated values of V_{diss} in traps were fairly uniform through time with the exception of a high value in May 2008 and a low value in Feb 2008 (Fig. 5). The average V_{diss} for the time series was $0.10 \pm 0.08 \text{ d}^{-1}$.

Table 1

A comparison of parameters at the BATS (Nelson et al., 1995) and HOT stations during multi-year studies of Si cycling at each location. Values are means (\pm SD), with ranges in parentheses if available.

	BATS	ALOHA
Dissolved Si		
[Si(OH) ₄] (μ M) (upper 50 m)	0.82 \pm 0.21 (0.4–2.6)	1.04 \pm 0.17 (0.6–1.6)
Particulate silica		
[bSiO ₂] (nmol Si L ⁻¹)	27 \pm 52 (2–584)	16 \pm 14 (3–163) ^a
<i>f</i> bSiO ₂ (mmol Si m ⁻²)	4.0 \pm 6.8 ^b	3.0 \pm 1.1 (1.8–6.2) ^{a,b}
[lSiO ₂] (nmol Si L ⁻¹)	5.9 \pm 5.9 (0.2–44)	9.0 \pm 9.1
<i>f</i> lSiO ₂ (mmol Si m ⁻²)	0.80 \pm 0.40 (0.13–1.9) ^b	1.5 \pm 0.8 (0.5–3.6) ^b
Silica production		
ρ (nmol Si L ⁻¹ h ⁻¹)	2.6 \pm 2.4 (0.0–19.6)	1.4 \pm 2.5 (0.0–29.7)
<i>f</i> ρ (mmol Si m ⁻² d ⁻¹)	0.42 \pm 0.22 (0.10–0.93) ^c	0.19 \pm 0.11 (0.090–0.49) ^a
		0.18 \pm 0.11 (0.090–0.48) ^c
<i>V_b</i> (d ⁻¹)	0.15 \pm 0.15 (0–1.11)	0.07 \pm 0.02 (0.04–0.14)
Annual production (mmol Si m ⁻² a ⁻¹)	239	63
Si limitation		
<i>V_b</i> / <i>V_m</i>	(< 0.12–0.16) ^d	0.43 \pm 0.21 ^e
		0.35 \pm 0.11 ^f
Enh		2.6 \pm 0.9 ^e
		3.2 \pm 1.2 ^f
Silica dissolution		
<i>f</i> ρ _{diss} (mmol Si m ⁻² d ⁻¹)	0.34	0.087 ^c
<i>f</i> D: <i>f</i> P	0.82	0.46 ^c
Silica export at 150 m		
bSiO ₂ export (mmol Si m ⁻² d ⁻¹)	0.098 \pm 0.13 (0.017–0.70)	0.091 \pm 0.061 (0.014–0.30)
lSiO ₂ export (mmol Si m ⁻² d ⁻¹)	0.024 \pm 0.013 (0.006–0.074)	0.018 \pm 0.007 (0.006–0.030)
1 – <i>f</i> D: <i>f</i> P (new Si production ratio)	0.18 \pm 0.13 (0.03–0.44)	0.54 \pm 0.19 (0.13–0.90)
Annual bSiO ₂ export (mmol Si m ⁻² a ⁻¹)	32	33
Diatom contribution to organic matter cycng		
% primary production by diatoms	15–25	3–7
% POC export by diatoms	~30	9–20

^a October 1996–December 2009.

^b Depth of integration 175 m.

^c Depth of integration 150 m.

^d From Brzezinski and Nelson (1996).

^e Annual average (includes bloom and non-bloom conditions).

^f Average for non-bloom condition.

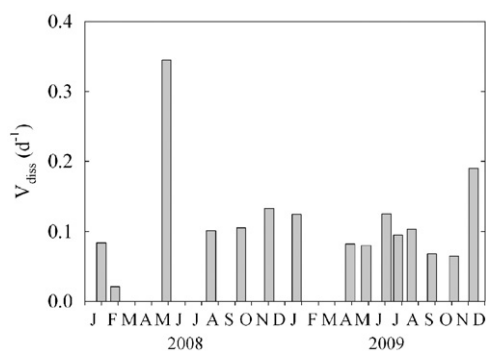


Fig. 5. Time series of the specific rate of silica dissolution, V_{diss} , of sinking particles at 150 m.

4. Discussion

4.1. Silicic acid and particulate silica concentrations

Silicic acid concentrations in the upper 100 m did not follow a regular seasonal cycle, but did vary by $\sim 1 \mu\text{M}$ each year equivalent to a relative variance of about 50%. Silicic acid concentrations were typically at least 10 times greater than biogenic silica concentrations, even during periods of peak biomass, such that local diatom production would not impact ambient [Si(OH)₄] significantly on short time scales. Ultimately vertical gradients

in [Si(OH)₄] are maintained through net biological consumption and export; however, the low rates of silica production observed in this study would require 50–100 days to make a $1 \mu\text{M}$ change in [Si(OH)₄] even when losses to dissolution, which would slow Si depletion, are ignored. Near surface [Si(OH)₄] are thus predominately related to the history of silicic acid supply and silica production in the water masses advecting past station ALOHA rather than being driven by local processes.

The concentrations of biogenic silica during non-bloom conditions at ALOHA are among the lowest ever reported in the ocean. They are orders of magnitude lower than the micromolar concentrations that are typically observed in coastal systems or in the Southern Ocean (e.g. Nelson et al., 1991; Brzezinski et al., 2003), 3–4 times lower than observed in the equatorial Pacific (Krause et al., 2011b), and 25–50% lower than in the Sargasso Sea (Nelson and Brzezinski, 1997; Krause et al., 2009a). Despite such low concentrations siliceous biomass showed a regular seasonal pattern with approximately order of magnitude increases each year following the intensification of stratification in the upper 50 m each summer.

The HOT program has measured profiles of biogenic silica concentrations in the upper 175 m at ALOHA since October 1996 providing historic context for the present study (Fig. 6A). Integrated biogenic silica concentrations measured in the present study and by the HOT program generally agree to within 30% despite samples being taken on separate casts and the sample analysis being done by different investigators using different

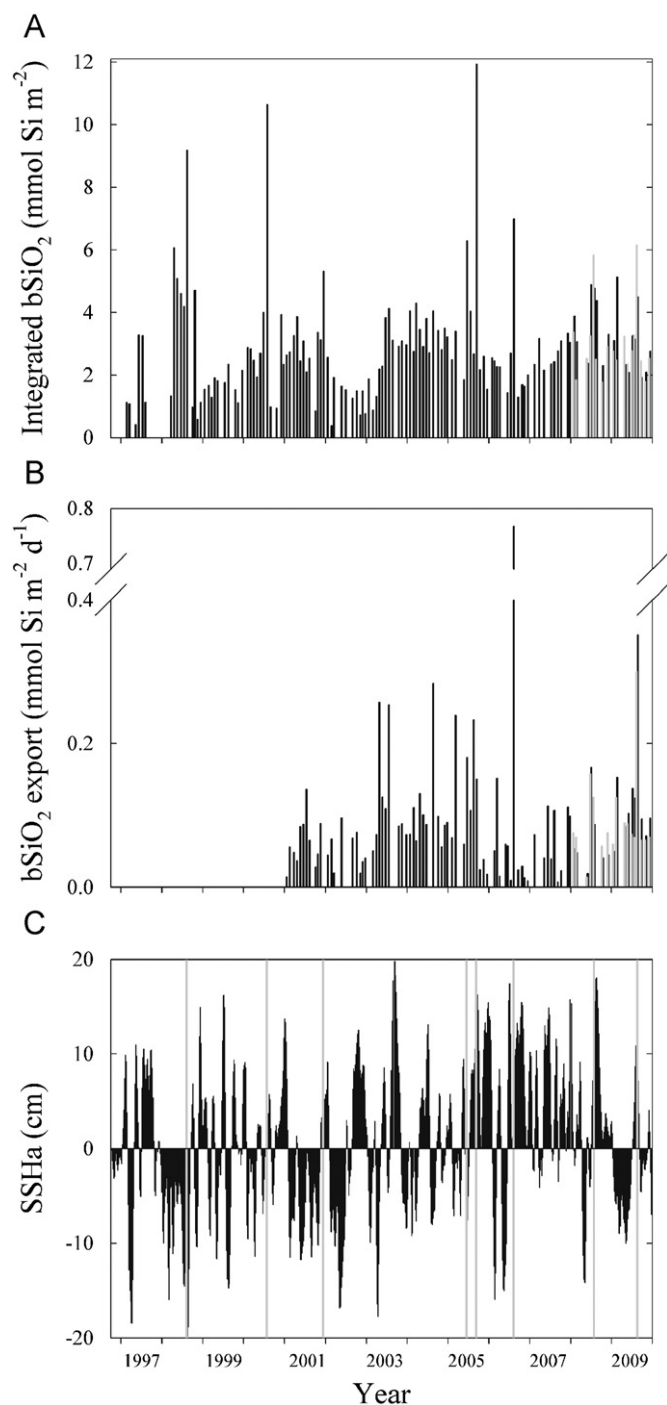


Fig. 6. Time series of: (A) integrated biogenic silica concentrations in the upper 175 m at station ALOHA. (B) the rate of export of biogenic silica at 150 m. Black bars are data from the HOT program with the gray bars representing data from the present study. Note that measurement of bSiO₂ export began in 2000. (C) Sea Surface height anomalies (SSHa) at station ALOHA. Gray bars mark the timing of blooms in A with integrated biogenic silica concentrations > 4 mmol Si m⁻². SSHa data products are from merged altimetry datasets obtained from the Archiving, Validation, and Interpretation of Satellite Oceanographic data server, <http://las.avisio.oceanobs.com>.

methods; HOT: sodium carbonate digestion (Demaster, 1981), this study: sodium hydroxide digestion (see methods). Integrated biogenic silica concentrations during 2008 and 2009 were generally between 1 and 3 mmol Si m⁻² similar to previous years. Since 1999 biogenic silica concentrations at ALOHA have oscillated with about a 4-year periodicity with minima observed in

1998, 2002, and 2006 (Fig. 6A). The mechanisms driving this oscillation are beyond the scope of the present study, but correlations with the Pacific Decadal Oscillation (PDO) and the North Pacific Gyre Oscillation (NPGO) are poor (data not shown). The magnitude of the summer blooms observed in 2008 and 2009 are similar to past blooms at ALOHA except for three exceptionally large events that occurred in August 1998, July 2000 and September 2005 when integrated concentrations approached or exceeded 10 mmol Si m⁻² (Fig. 6A). The majority of blooms since 1997 occurred during mid-summer similar to our observations in 2008 and 2009 supporting the idea that summer diatom blooms are a regular feature at ALOHA (Dore et al., 2008).

Lithogenic silica concentrations showed maxima in the upper 10 m in May 2008 and in April 2009 (Fig. 1D). That pattern matches the previously reported seasonal pattern in aerosol abundance measured at the Moana Loa Observatory, with lowest aerosol concentrations typically present from July through January and highest concentrations from March through June (Boyle et al., 2005). Thus, high near-surface maxima in [iSiO₂] likely reflect seasonal inputs of atmospheric dust. These dust events would be expected to enhance levels of dissolved iron favoring the growth of large diatoms and potentially favoring nitrogen fixation both of which have a high iron requirement (Timmermans et al., 2001, 2004; Mills et al., 2004; Berman-Frank et al., 2001; Moore et al., 2009). Increases in lithogenic silica concentrations were not accompanied by increases in diatom biomass or by increases in silica production rates and there was no stimulation of nitrogen fixation as these times (Church, unpublished). As several important bloom forming diatom species are known to harbor heterocystous nitrogen-fixing cyanobacteria (e.g. Villareal, 1990, 1991, 1992) this result suggests that neither diatoms nor the success of diatom-diazotroph symbiosis were limited by Fe during the period of our sampling.

4.2. Silica production and Si uptake limitation

Rates of silica production at ALOHA were considerably lower than rates observed previously in the northern regions of the NPSG. Silica production at ALOHA averaged 0.19 mmol Si m⁻² d⁻¹, which represents a composite of the higher rates observed during bloom periods (0.40 mmol Si m⁻² d⁻¹) and the lower rates during non-bloom periods (0.14 mmol Si m⁻² d⁻¹). In contrast, Brzezinski et al. (1998) measured silica production rates that were 4–5 times greater both within (maximum of 1.8 mmol Si m⁻² d⁻¹) and outside (average of 1.2 mmol Si m⁻² d⁻¹) diatom blooms near the subtropical front in the NPSG. Concentrations of biogenic silica were also elevated at the subtropical front compared to ALOHA with average integrated biogenic silica concentrations of 7.1 ± 3.0 mmol Si m⁻² (Brzezinski et al., 1998) compared to the average of 3.0 mmol Si m⁻² at ALOHA (Table 1). These trends are consistent with observations of enhanced primary production and chlorophyll biomass in this frontal zone (Wilson, 2003; Ayers and Lozier, 2010; Howard et al., 2010).

There are several approaches to constructing an estimate of annual silica production rates from the time series data collected in this study. However, all of these approaches suggest annual silica production is very low at ALOHA. Because HOT cruises are not evenly spaced in time, we chose to estimate average production rates during bloom and non-bloom periods and then to extrapolate those average rates over the fraction of the year represented by each condition (e.g. Nelson and Brzezinski, 1997). Our time series sampled blooms in each of two years with elevated production rates for two sampling periods in 2008 and for one sampling period in 2009. Based on these data we assume that the annual summer diatom bloom lasts 1.5 months each year with silica production during blooms occurring at a rate equal to the average for the 2008 and 2009 blooms or 0.40 mmol Si m⁻² d⁻¹. Silica production during the remaining 10.5 months of the year is

estimated as the average rate during this period across 2008 and 2009, $0.14 \text{ mmol Si m}^{-2} \text{ d}^{-1}$. Thus, our estimated annual silica production is $(45 \text{ days} \times 0.40 \text{ mmol m}^{-2} \text{ d}^{-1}) + (320 \text{ days} \times 0.14 \text{ mmol m}^{-2} \text{ d}^{-1}) = 18.0 + 44.8 = 62.8 \text{ mmol Si m}^{-2} \text{ a}^{-1}$, with blooms contributing 29% of the total.

Limitation of silica uptake by the ambient $[\text{Si}(\text{OH})_4]$ was pervasive during non-bloom periods with V_b averaging only 35% of V_m . That level of uptake limitation suggests that diatoms have thinned their frustules in response to low Si availability; however, it is not sufficiently strong to conclusively demonstrate Si limitation of diatom growth rates. Diatoms are known to be capable of changing the Si content of their frustules by 2–4 fold (Paasche, 1975; Thomas and Dodson, 1975; Brzezinski et al., 1990) such that V_b/V_m could drop to 0.25 before cells would theoretically not be able to thin their frustules further and thus be forced to reduce division rates.

Brzezinski et al. (1998) reported similar values of V_b/V_m (mean = 0.30 ± 0.24) to the north of ALOHA near the subtropical front. Krause and Brzezinski (unpublished) examined Si uptake limitation in 2008 and 2009 to the northwest of ALOHA again near the subtropical front where V_b/V_m averaged 0.59 ± 0.10 in 2008 and 0.53 ± 0.14 in 2009. However all of these other studies represent summer conditions. Here we show that significant limitation of silica production occurs over most of the year at station ALOHA. Values of the Enh parameter of 1.0–1.2 that would indicate Si sufficiency only occurred once each summer in association with the summer diatom blooms. Those data provide support for the hypothesis of Brzezinski et al. (1998) that the high Si uptake efficiency of bloom diatoms in the NPSG allows them to exploit the low concentrations of silicic acid in the NPSG to create new diatom biomass while avoiding growth limitation by Si. The sediment-trap observations by Scharek et al. (1999b) that diatoms exported from the surface waters during summer blooms in the NPSG have more robust frustules compared to species exported at other times of year is consistent with our data, as Si sufficiency observed during two summer cruises would result in diatom cells with frustules of maximum thickness.

The highest values of V_b observed imply rapid diatom doubling times. The highest value was observed during the summer of 2008, 0.86 d^{-1} . That value corresponds to a doubling time of 19 h for diatom biomass, which approaches the doubling times of nutrient-replete diatoms in culture, suggesting that limitation of diatoms by any resource during blooms may be mild to non-existent. Our estimated doubling times are also conservatively low as V_b underestimates the rate of uptake of living cells due to the presence of siliceous detritus (Goering et al., 1973). The presence of siliceous detritus could also account for the low specific production rates observed during the 2009 bloom as has been suggested in another open-ocean region (Krause et al., 2010a) rather than reflecting low rates by living diatoms.

4.3. Dissolution and export of particulate silica

Silica dissolution leads to significant recycling of biogenic silica in the upper 150 m at ALOHA. On average nearly half (46%) of silica production is lost to dissolution in this depth zone (Table 1). The average specific rate of silica dissolution of biogenic silica in the upper 150 m, V_{diss} can be estimated as $\int \rho_{\text{diss}} / \int \text{bSi} = 0.46 \int \rho / \int \text{bSi} = (0.46 * 0.18) / 2.7 = 0.031 \text{ d}^{-1}$ ($\int \text{bSi}$ and $\int \rho$ recalculated for 150 m rather than 175 m to match depth of sediment trap deployment, Table 1). That value of V_{diss} for suspended particulate matter is lower than that estimated in the sediment traps, $0.10 \pm 0.08 \text{ d}^{-1}$. A likely explanation is that sinking biogenic silica contains a higher fraction of detrital silica than does suspended biogenic silica. Silica in the frustules of living diatoms is protected by an organic coating and thus dissolves at very slow

rates if at all (Nelson et al., 1976). Bacteria remove the protective organic coating from the frustules of dead diatoms accelerating specific dissolution rates of detrital biogenic silica (Bidle and Azam, 1999, 2001; Bidle et al., 2003). We did not evaluate the fraction of intact diatom frustules in traps, but previous sediment trap studies at ALOHA have found that intact frustules typically comprised < 20% of frustules in traps (Scharek et al., 1999a).

The trends in the time series of biogenic silica export during 2008 and 2009 conform to trends measured by the HOT program since 2001 (Fig. 6B). The mean rate of export during 2008 and 2009, $0.091 \pm 0.061 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, is nearly identical to the mean from 2001–2007, $0.090 \pm 0.101 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, with the mean for the entire time series (2001–2009) being $0.092 \pm 0.096 \text{ mmol Si m}^{-2} \text{ d}^{-1}$. These average rates are punctuated by brief episodes of more rapid export generally between 0.1 and $0.2 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ with the largest event approaching $0.8 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ (Fig. 6B). Peaks in export are most often, but not always, associated with high integrated biogenic silica concentrations in the upper 175 m (Fig. 6A and B).

Comparison of biogenic silica export at ALOHA to past measurements in subtropical gyres reveals a high level of consistency in the magnitude of export among these systems. The observed average rate of export of biogenic silica at 150 m at ALOHA, $0.091 \pm 0.061 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ (Table 1) is similar to past observations at this same site by Scharek et al. (1999a) at 165 m (0.030 – $0.140 \text{ mmol Si m}^{-2} \text{ d}^{-1}$). Our daily export rate extrapolated to an annual export rate of $33 \text{ mmol Si m}^{-2} \text{ a}^{-1}$, which is also similar to that calculated by Scharek et al. (1999a), $23.7 \text{ mmol Si m}^{-2} \text{ a}^{-1}$ with both of these rates being similar to that observed in the Sargasso Sea, $36 \text{ mmol Si m}^{-2} \text{ a}^{-1}$ (Nelson and Brzezinski, 1997). When the ratio of biogenic silica export to silica production is averaged across all cruises in the 2008–2009 time series the resulting value, 54%, is quite high compared to other oligotrophic systems (Brzezinski et al., 2003). The seasonal pattern of export in both gyres consists of low levels of export for much of the year punctuated by relatively high flux events that are generally associated with diatom blooms (Brzezinski and Nelson, 1995; Nelson and Brzezinski, 1997).

The contribution of diatom blooms to annual silica export at ALOHA was estimated using the data from 2008 and 2009 to be consistent with the annual production rate estimate. Assuming that export from blooms occurred over the same 1.5 month time scale as the blooms themselves and that the average rate of export during the two summer blooms observed, $0.20 \text{ mmol m}^{-2} \text{ d}^{-1}$, is representative of the export from bloom events in general, the resulting export during blooms, $9.0 \text{ mmol Si m}^{-2} \text{ a}^{-1}$, is 27% of the total annual biogenic silica flux (Table 1). This result supports existing evidence that bloom diatoms are efficiently exported to depth at station ALOHA (Scharek et al., 1999a, 1999b; Buesseler et al., 2007). It was estimated above that the blooms account for 29% of annual silica production which is very similar to the estimate of the contribution of blooms to biogenic silica export, 27%. However, each of these contributions occurs over 1 to 1.5 months, or 8.3–12.5% of the year, making blooms at least twice as efficient in terms of both rates of silica production and silica export compared to the rates of these processes occurring during non-bloom periods.

4.4. Drivers of diatom bloom dynamics

The seasonal pattern of siliceous biomass and silica production in surface waters appears linked to changes in upper water column physical forcing. Silica production at station ALOHA follows the seasonal pattern in upper ocean stratification. Stratification intensifies in spring with diatom blooms occurring later in summer after the upper 50 m warms to between 25 and 26°C . This same pattern is observed for other phytoplankton groups

such as filamentous cyanobacteria that bloom during the summer and fall when mixed layers are shallow (White et al., 2007). Diatom blooms during 2008 and 2009 were also associated with a depression of the isotherms and of the silicicline at 140 m (Fig. 1B). Church et al. (2009) showed these changes in physical structure to be related to changes in sea surface height anomalies (SSHa), presumably associated with the presence of anticyclones at station ALOHA. Evaluation of SSHa during 2008 and 2009 confirmed that the summer blooms during both years were also associated with positive SSHa at station ALOHA (Fig. 7A and B). SSHa data reveal anticyclones propagating towards ALOHA from the southeast (data not shown) consistent with the salinity minima in the upper 50 m during both of these periods (Fig. 1A) as salinity decreases to the south of ALOHA during summer. The timing of those events is shown in the Hofmoeller plot of SSHa at 22.6°N latitude between 162 and 152°W longitude during the summers of 2008 and 2009 (Fig. 7C). During the July 2008 bloom, a positive SSHa with maximum values of +11.5 cm was advecting toward ALOHA with our sampling occurring at the leading edge of this feature (Fig. 7A). During August 2009, sampling occurred closer to the center of a mesoscale feature with a maximum SSHa of +9.2 cm (Fig. 7B).

Examination of the historical data set of biogenic silica stocks and SSHa at ALOHA reveals that the blooms in September 2005 and August 2006 (Fig. 6B) were also associated with periods of strong positive SSHa (+16 and +10 cm, respectively; Fig. 6C). Brzezinski et al. (1998) noted elevated biomass associated with isopycnal uplift in the upper 200 m suggesting a relationship between a diatom bloom and an eddy further to the north of ALOHA near the subtropical front. Results from the present study

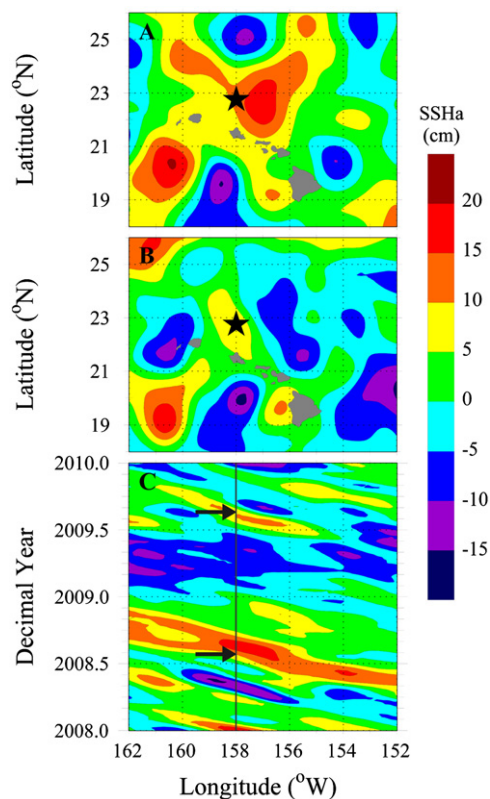


Fig. 7. Sea Surface Height anomalies (SSHa) at ALOHA during 2008 and 2009. (A) SSHa near station ALOHA (22°45'N 158°W, black star) during the July 2008 bloom. (B) as in A but for the August 2009 bloom. (C) Hofmoeller plot of SSHa at 22.6°N latitude between 162 and 152°W longitude from January 2008 through December 2009. Vertical black line indicates the longitude of station ALOHA. Arrows indicate the time of the July 2008 and August 2009 blooms, respectively.

support the idea that the passage of mesoscale features past ALOHA during the summer can enhance phytoplankton biomass and physiological rates (Sakamoto et al., 2004; Nicholson et al., 2008; Church et al., 2009). However, several of these previous studies emphasized mesoscale dynamics that inject nutrients into the base of the euphotic zone. This is not the mechanism driving the blooms observed in the present study as the response to the passage of the anticyclones was confined to the upper 50 m rather than the base of the euphotic zone. Moreover, the observed depression of isopycnals at depth would reduce, rather than enhance, vertical nutrient supply.

Although the repeated observation of diatom blooms associated with mesoscale features suggests that such dynamics are important drivers of diatom production at ALOHA other blooms are not associated with these features. For example the diatom blooms in April 1998, July 2000 and December 2001 (Fig. 6B) were not associated with significant SSHa (Fig. 6C). Summer phytoplankton blooms in the NPSG have also been observed to occur over much larger spatial scales than can be attributed solely to mesoscale features (Dore et al., 2008; Wilson, 2003). Recent sampling within these blooms suggests that at least some of these larger-scale events are dominated by diatoms (Krause and Brzezinski, unpublished) indicating that larger scale physical forcing, including possibly eddy–eddy interactions, could also be involved in controlling diatom dynamics in the NPSG.

The abundance of diazotrophs associated with bloom diatom species also responded to the changes in SSHa during 2008 and 2009. Analysis of diatom *rbcL* gene and diazotroph *nifH* gene abundances (Li, 2011) show an increase in *Hemiaulus* spp. and its associated N_2 fixing cyanobacteria symbiont in June 2008 coincident with the increase in silica production observed on the same cruise. In 2009, *Hemiaulus*, *Rhizosolenia*, and diazotroph *nifH* gene abundances rose in July coincident with the increase in biogenic silica concentrations that year. Such observations reinforce the importance of diatom/diazotroph symbioses to diatom population dynamics in the NPSG (Scharek et al., 1999a, 1999b; Karl, 2002; Karl et al., 2002) and support previous findings that diatom–diazotroph associations (DDAs) are quantitatively important to upper ocean silica cycling (Brzezinski et al., 1998).

4.5. Contribution of diatoms to primary productivity, nitrogen fixation and carbon export

Our data suggest that diatoms account for a very small fraction of primary production at ALOHA. To estimate carbon fixation rates by diatoms the annual rate of silica production, $63 \text{ mmol Si m}^{-2} \text{ a}^{-1}$, is multiplied by the C:Si ratio of living diatoms. Nutrient-replete diatoms have a C:Si mole ratio of 7.7 (Brzezinski, 1985). That ratio likely underestimates the C:Si ratio of diatoms at ALOHA where the estimates of $V_b:V_m$ imply considerable thinning of diatom frustules. Using the annual average $V_b:V_m$ that includes both bloom and non-bloom conditions, 0.43 (Table 1), to account for frustules thinning suggests a diatom C:Si of $7.7 \div 0.43 = 17.9$, which is within the range of values observed in Si-stressed diatom cultures (e.g. De La Rocha et al., 2010). Using these ratios the likely range of diatom primary productivity is $63 \text{ mmol Si m}^{-2} \text{ a}^{-1} \times (7.7 \text{ or } 17.9) \times 0.012 \text{ g C (mmol C)}^{-1} = 5.8\text{--}13.5 \text{ g C m}^{-2} \text{ a}^{-1}$. Those rates are only 3–7% of the average annual primary productivity determined from ^{14}C -bicarbonate uptake experiments for 2008 and 2009 at ALOHA, $188 \pm 19 \text{ g C m}^{-2} \text{ a}^{-1}$ (HOT program data, <http://hahana.soest.hawaii.edu/hot/>). This is likely an overestimate as rates of gross primary production determined using ^{18}O at ALOHA are 1.5–2.0 times that measured by the ^{14}C method (Juraneck and Quay, 2005) making our estimate of the contribution of diatoms to total primary production conservatively high.

Our data imply that nitrogen fixation supports a fairly small fraction of diatom silica production in the NPSG. Levels of nitrogen fixation in the $> 10 \mu\text{M}$ size fraction at ALOHA that would include the larger diatoms associated with DDAs have been measured to average $0.028 \text{ mmol N m}^{-2} \text{ d}^{-1}$ from 2004–2008 (Church et al., 2009). Assuming that all nitrogen fixation in the larger size fraction is by diatoms and assuming a Si:N mole ratio of 1:1 for nutrient-replete diatoms (Brzezinski, 1985) and 0.43 under the level of Si stress measured during this study, the range in the silica production rate necessary to support the observed rate of N_2 fixation is $0.012\text{--}0.028 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, which is only 6–15% of the mean integrated silica production rate observed in our study (Table 1). This is an overestimate as the calculation ignores the contribution of large diazotrophs that do not form DDAs to the measured rates of nitrogen fixation, especially *Trichodesmium*. Based on these data it appears that only a small fraction of diatom silica production is controlled by DDAs and supported by N_2 fixation.

There is growing evidence that diatoms contribute more to new and export production in oligotrophic systems than they do to primary production (e.g. Nelson and Brzezinski, 1997; Karl et al., 2002; Goldman and McGillicuddy, 2003; Krause et al., 2011b). This relationship also holds for the NPSG at station ALOHA. To estimate the contribution of diatoms to carbon export we compared rates of carbon export at 150 m measured by the HOT program using the same floating sediment trap array as employed in our study to estimate diatom carbon export from the measured opal flux and a C:Si mole ratio of diatom-based exported particulate matter. The appropriate ratio can be estimated by adjusting the C:Si ratio of living diatoms for the losses due to the recycling of organic carbon and biogenic silica within the euphotic zone. As detailed above the C:Si ratio of living diatoms likely lies between 7.7 and 17.9. Carbon recycling is taken from Buesseler et al. (2007) who show that 12% of the carbon production is exported from the euphotic zone at ALOHA. For the loss of biogenic silica we use our estimate that on average 46% of silica production is lost to dissolution in the upper 150 m (Table 1). Combining these parameters leads to a C:Si mole ratio of exported diatom-based particulate matter of $(7.7 \text{ or } 17.9) \times 0.12 \div 0.46 = 2.0\text{--}4.7$. Comparing the product of those ratios and the measured annual opal flux to the rates of carbon export for 2008 and 2009 (HOT program data, <http://hahana.soest.hawaii.edu/hot/>) indicates that diatoms were responsible for 9–20% of the carbon exported through 150 m, which supports the estimate of Dore et al. (2008) that diatoms account for 18% of new production at ALOHA. Both estimates are several times higher than our estimated contribution of diatoms to primary production, 3–7%.

4.6. Comparison of silica cycling among subtropical gyres

The Sargasso Sea is the only other subtropical gyre where the annual silica cycle of upper-ocean has been examined over multiple years. Silica cycling was examined over three years in the 1990s at the BATS site (Brzezinski and Nelson, 1995, 1996; Nelson and Brzezinski, 1997). Comparison of those data with the present data set from the NPSG reveals strong differences and some key similarities in upper-ocean Si cycling between these two subtropical gyres. For simplicity the terms HOT and BATS will be used when referring to data from times-series station ALOHA in the NPSG and from the BATS deployment area in the Sargasso Sea, respectively.

Near surface $[\text{Si}(\text{OH})_4]$ is generally higher at HOT compared to BATS (Table 1), reflecting the well known differences in silicic acid concentration between the Pacific and Atlantic basins. $[\text{Si}(\text{OH})_4]$ in the upper 100 m shows a regular seasonality at BATS where

relatively high concentrations ($1.0\text{--}1.5 \mu\text{M}$) are observed following convective overturn during winter. Silicic acid concentrations in the upper 50 m at BATS gradually decline during spring reaching a minimum during late summer and fall (Nelson and Brzezinski, 1997). The annual variability in near-surface $[\text{Si}(\text{OH})_4]$ at HOT is nearly equivalent to that at BATS, but because the NPSG does not undergo extensive seasonal convective mixing silicic acid concentrations do not follow a regular seasonal pattern.

The largest diatom blooms are of similar magnitude at HOT and BATS. Integrated biogenic silica concentrations during diatom blooms at BATS commonly reach $10 \text{ mmol Si m}^{-2}$. Blooms with integrated biogenic silica concentrations of $10 \text{ mmol Si m}^{-2}$ are also observed at HOT (Fig. 6A), but they are less common than at BATS. High diatom biomass is associated with mesoscale features at both HOT and BATS (McGillicuddy et al., 2007; Krause et al., 2010b; this study), but mesoscale circulation has been observed to result in higher concentrations of biogenic silica at BATS ($11.7\text{--}50.8 \text{ mmol Si m}^{-2}$, mean 25.7, Krause et al. 2009a) than at HOT ($\leq 10 \text{ mmol Si m}^{-2}$). The most significant difference in diatom bloom dynamics between HOT and BATS is the strong difference in the timing of blooms. Diatom blooms generally occur in late winter/early spring at BATS (Nelson and Brzezinski, 1997) and in mid-summer at HOT (Dore et al., 2002; this study). Blooms only occur during one or two approximately monthly samplings each year at both locations implying bloom durations of up to 1–1.5 months at both sites.

Biogenic silica concentrations during non-bloom periods are somewhat higher at BATS than at HOT averaging $27 \text{ nmol Si L}^{-1}$ at BATS and $16 \text{ nmol Si L}^{-1}$ at HOT in the upper 100 m. The difference in average biogenic silica concentrations at HOT and BATS may be changing due to opposing long-term trends in biogenic silica concentrations at the two sites. Krause et al. (2009a) showed that $[\text{bSiO}_2]$ at BATS declined by about 40% between 1989 and the end of 2003. When the historic data from HOT are filtered to remove the seasonal trends using the methods of Krause et al. (2009a), a trend of increasing integrated biogenic silica concentration from 1997–2009 is seen (Fig. 8). Remarkably the rate of decline at BATS is nearly identical to the rate of increase at HOT. The BATS data set presently ends in December 2003, but if the trend of declining $[\text{bSiO}_2]$ at BATS has continued to the present day then average biogenic silica concentrations at HOT would now exceed those at BATS (Fig. 8).

Both the concentration of ISiO_2 and its vertical distribution in the upper 200 m are similar between BATS and HOT with maxima in the near surface waters at both sites coincident with seasonal maxima in aerosol dust levels. Maximum surface concentrations of ISiO_2 occur earlier in the year at HOT than at BATS due to differences in the timing of seasonal dust inputs. Asian dust inputs are highest during spring at HOT (Boyle et al., 2005) with mid-summer being the period of maximum dust inputs from the Sahara at BATS (Arimoto et al., 1992; Ellis et al., 1993). HOT and BATS also differ in the timing of maximum lithogenic silica export. The rate of export of ISiO_2 is consistently low ($< 0.030 \text{ mmol Si m}^{-2} \text{ d}^{-1}$; Fig. 3B) at HOT with no clear seasonal trends while ISiO_2 export at BATS peaks during summer with the input of Saharan dust (Nelson and Brzezinski, 1997).

Integrated rates of silica production are much lower at HOT than at BATS. The average integrated rate of silica production at HOT, $0.19 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, which includes production during blooms, is less than half the average measured at BATS, which does not include production during blooms, $0.42 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ (Table 1). Substrate limitation of silicic acid uptake is common at both HOT and BATS but is more severe at BATS. Specific silica production rates are restricted to an average of 43% of V_m at HOT, but to 12–16% of V_m at BATS (Brzezinski and Nelson, 1996) with a value of 17% measured in a mode-water eddy near the BATS site (Krause et al. 2010b). The values

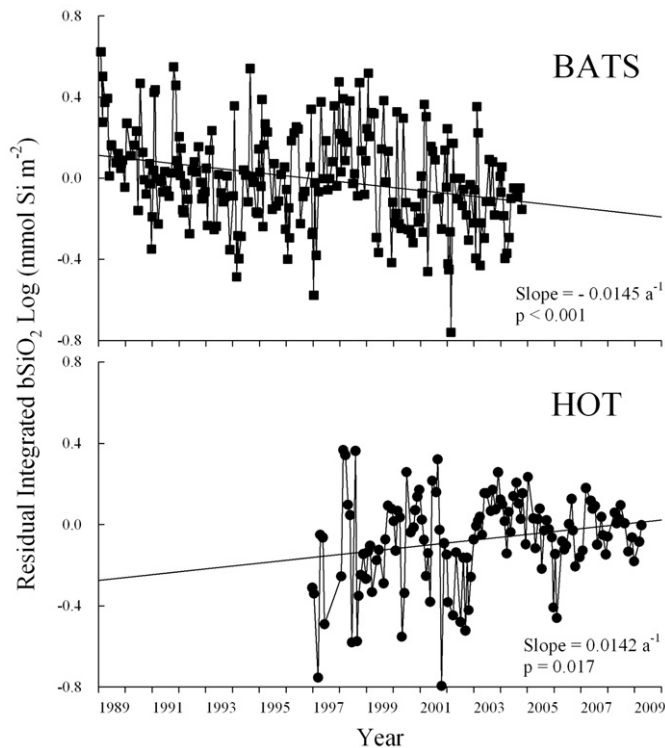


Fig. 8. Time course of the long term change in integrated biogenic silica concentration at BATS (1989 through 2003) and HOT (1997 through 2009). Biogenic silica concentrations were integrated to 175 m at both sites and filtered to remove seasonal trends as described by Krause et al. (2009a). The line in each plot is a least-squares regression along with the regression slope and the probability (p -value) that the regression slope is not positive or negative (i.e. equal to zero).

of V_b/V_m from the BATS area are all below the threshold of $0.25V_m$ for growth limitation by Si suggesting a high likelihood of diatom growth rate limitation by Si at BATS (Brzezinski and Nelson, 1996) whereas only one experiment at HOT meets this criteria (Fig. 4B) making growth limitation of diatoms by Si unlikely at HOT. Values of Enh near unity (i.e. $V_b/V_m=1$), which would imply silicic acid sufficiency were only observed during or just prior to diatom blooms at HOT (compare Figs. 1C and E, and 4B). Whether abatement of Si limitation is typical of blooms in both gyres cannot be determined as no measures of Si uptake kinetics have been made at BATS during the spring diatom bloom (Nelson and Brzezinski, 1997).

A significantly larger fraction of the biogenic silica produced in the Sargasso Sea is lost to dissolution in the upper 150–200 m compared to the NPSG. The dissolution: production ratio ($fD:fP$) at BATS has been estimated to be 0.82 (Table 1). The $fD:fP$ value at HOT is about half as large averaging 0.46 (Table 1). The mechanism leading to this large difference is unclear, but it may be related to the large size of some of the diatoms at HOT, which increases their export efficiency (Scharek et al., 1999a). In both regions the $fD:fP$ ratio was derived from a comparison of integrated silica production to biogenic silica export. Estimates of the average integrated rate of silica dissolution, $\int \rho_{diss}$, at each site were obtained as the product of $fD:fP$ and $\int \rho$ yielding values of $\int \rho_{diss}=0.087 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ at HOT and $0.34 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ at BATS (Table 1). The estimate at BATS applies to the non-bloom period as direct measures of silica production during diatom blooms are not available. However, even if dissolution rates were nearly zero during blooms the average rate of dissolution at BATS would still be considerably higher than that at HOT since blooms at BATS are only present for 1.5 months each year (i.e. $\sim 13\%$ of the year).

One of the most significant biogeochemical similarities between HOT and BATS is that the annual export of biogenic silica is nearly the

same at each location despite the large difference in annual silica production rates between sites (Table 1). This implies a far higher export efficiency for $bSiO_2$ at HOT compared to BATS. New silica production is defined as $(1 - fD:fP)$ which is equivalent to the f -ratio that is used as an index of the fraction of nitrogen production that is driven by nitrate (Eppley and Peterson, 1979). $1 - fD:fP$ is only 0.18 at BATS, but is 0.54 at HOT (Table 1) indicating a much higher fraction of new silica production at HOT. Multiplying gross rates of silica production by $1 - fD:fP$ approximates new silica production yielding values of $0.42 \times 0.18=0.075 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ at BATS if only the non-bloom period is considered and $0.65 \times 0.18=0.12 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ if the production during blooms estimated by Nelson and Brzezinski (1997) is included when calculating an average rate. The estimate for HOT, $0.19 \times 0.54=0.10 \text{ mmol Si m}^{-2} \text{ d}^{-1}$, falls between the two estimates for BATS. Thus despite large differences in silica production between the two gyres diatom Si export production is similar, but the balance of processes leading to that similarity are quite different: On a relative basis, the north Atlantic subtropical gyre appears to be a region of relatively high silica production that experiences greater silica loss due to dissolution in the upper ocean, whereas the NPSG has lower rates of silica production, but proportionally lower dissolution in the upper ocean, leading to similar rates of biogenic silica export out of the euphotic zone in both gyres.

The differences between the North Pacific and Atlantic subtropical gyres extend to estimates of the contribution of diatoms to organic matter cycling and export in each region. Our estimated diatom contribution to primary productivity at HOT, 3–7%, is substantially less than the estimate at BATS, 15–25% (Nelson and Brzezinski, 1997); however, in both cases the estimated contribution of diatoms to organic carbon export is near 30% (Table 1). Thus in both systems the contribution of diatoms to carbon export production is disproportionately large compared to their contribution to primary production. This likely results from primary production being dominated by small picophytoplankton at each site, which have negligible sinking rates and are efficiently recycled by upper-ocean food webs, whereas diatom are much larger and have significant sinking rates as either individual cells or when packed into large fast-sinking fecal pellets produced by mesozooplankton grazers.

4.7. Revised contribution of subtropical gyres to global marine Si budget

Our data lead to a significant change in the estimated contribution of subtropical gyres to global silica production. The ocean remains severely under sampled relative to measurements of silica production. Nelson et al. (1995) made an estimate of the contribution of all subtropical gyres to global silica production based solely on data from the Sargasso Sea, which was the only subtropical gyre where silica production rates had been measured at that time. The time-series data from the NPSG show strong differences between gyres that can be used to refine that estimate. Our annual silica production estimate for the NPSG is only 27% of that in the Sargasso Sea. When the rates obtained in each gyre are weighted by the relative area of the Pacific and Atlantic Oceans (surface area of the Pacific is ~ 2 -fold that of the Atlantic excluding adjacent seas in both basins, Kennish, 2000), the estimate of the contribution of subtropical gyres to global marine silica production becomes 51% of the estimate of Nelson et al. (1995) or $13 \text{ Tmol Si a}^{-1}$ reducing the contribution of subtropical gyres to 5–7% of global annual marine silica production.

5. Conclusions

Silica cycling data from the NPSG reveal a unique annual silica cycle marked by summer peaks in both silica production and

diatom biomass. Blooms can be associated with anticyclones, but it remains unclear how conditions within anticyclones promote diatom growth. Diatom bloom species such as *Hemiaulus* spp., *Chaetoceros* and *Rhizosolenia* spp. likely benefit from their symbiotic relationship with diazotrophs, but it is unclear which half of the symbiosis responds first to summertime conditions triggering proliferation of these diatoms.

Comparison of silica dynamics in the NPSG and the Sargasso Sea reveals both common features and strong qualitative and quantitative differences. One commonality between gyres is the near-chronic substrate limitation of Si uptake. At HOT Si sufficiency was only detected just prior to or during summer diatom blooms suggesting high kinetic efficiency for silicic acid promotes bloom development. Diatom blooms are regular features in both gyres and blooms significantly impact silica production and export at both locations, but their timing and magnitude differ indicating fundamental differences in the mechanisms driving diatom dynamics between gyres. Rates of biogenic silica export are similar between gyres, but the magnitude of export is arrived at by a fundamentally different balance between silica production and its loss to dissolution at each location. Differences in the drivers of diatom dynamics among subtropical gyres present a challenge for future biogeochemical models that are increasingly incorporating diatoms as a specific subcategory within the phytoplankton.

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