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The upper ocean silicon cycle of the subarctic Pacific during the EXPORTS field **campaign**--Manuscript Draft--

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Abstract:	The contribution of diatoms to the production and export of organic carbon is highly modified in high-nutrient low-chlorophyll (HNLC) regions due to the decoupling of upper-ocean silicon and carbon cycling caused by low iron. The Si cycle and the role of diatoms in the biological carbon pump was examined at Ocean Station Papa (OSP) in the HNLC region of the northeastern subarctic Pacific during the NASA EX port P rocesses in the O cean from R emo T e Sensing (EXPORTS) field study. Sampling occurred during the annual minimum in surface silicic acid concentration, [Si(OH) 4]. Biogenic silica (bSi) concentrations were low being in the tens of nanomolar range despite high [Si(OH) 4], ~15 μ M. On average the > 5.0 μ m particle size fraction dominated Si dynamics accounting for 65% of bSi stocks and 81% of Si uptake compared to the small fraction (0.6 - 5.0 μ m). Limitation of Si uptake was detected in the small, but not the large, size fraction. Small diatoms were co-limited with growth rate restricted by Fe and Si uptake restricted by [Si(OH) 4], whereas larger diatoms were only growth limited by Fe. About a third of silica production was exported out of the upper 100 m. The contribution of diatoms to carbon export (9 - 13%) was about twice their contribution to primary productivity (3 - 7%). The combination of low silica production, low diatom primary productivity and high bSi export efficiency at OSP was more similar to the dynamics in the subtropical gyres than to other HNLC regions.
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Please find the research article entitled "The upper ocean silicon cycle of the subarctic Pacific during the EXPORTS field campaign" by Brzezinski and co-authors. This article fits well into the Ocean Science knowledge domain at ELEMENTA and is a new submission to the Special Feature "Accomplishments from the EXport Processes in the Ocean from RemoTe Sensing (EXPORTS) Field Campaign to the Northeast Pacific Ocean".

The article describes work at Ocean station Papa (OSP) in the northeast Pacific that is one of the most prominent high-nutrient low-chlorophyll (HNLC) regions in the global ocean characterized by intense iron limitation of phytoplankton growth and productivity. Iron limitation strongly modifies upper ocean silicon cycling by diatoms and their contribution to carbon cycling. In most HNLC regions these effects lead to enhanced silicic acid depletion and secondary Si limitation. OSP is uniquely different in that silicic acid depletion is rare indicating unique effect of Fe on Si cycling and export. Very few measures of silica production rates have been made at OSP and none have been made in association with evaluations of the export of opal and organic carbon. In this paper, we evaluate silica cycling in the euphotic zone at OSP relative to direct measures of opal export as part of the EXPORTS program specifically evaluating effects of iron and silicon limitation on silica production by large and small phytoplankton and the contribution of diatoms to the biological carbon pump.

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The upper ocean silicon cycle of the subarctic Pacific during the EXPORTS field campaign

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ABSTRACT

The contribution of diatoms to the production and export of organic carbon is highly modified in high-nutrient low-chlorophyll (HNLC) regions due to the decoupling of upper-ocean silicon and carbon cycling caused by low iron. The Si cycle and the role of diatoms in the biological carbon pump was examined at Ocean Station Papa (OSP) in the HNLC region of the northeastern subarctic Pacific during the NASA EXport Processes in the Ocean from RemoTe Sensing (EXPORTS) field study. Sampling occurred during the annual minimum in surface silicic acid concentration, [Si(OH)4]. Biogenic silica (bSi) concentrations were low being in the tens of nanomolar range despite high $[Si(OH)_4]$, ~15 μ M. On average the > 5.0 μ m particle size fraction dominated Si dynamics accounting for 65 % of bSi stocks and 81 % of Si uptake compared to the small fraction (0.6 - 5.0 µm). Limitation of Si uptake was detected in the small, but not the large, size fraction. Small diatoms were co-limited with growth rate restricted by Fe and Si uptake restricted by [Si(OH)4], whereas larger diatoms were only growth limited by Fe. About a third of silica production was exported out of the upper 100 m. The contribution of diatoms to carbon export (9 - 13 %) was about twice their contribution to primary productivity (3 - 7 %). The combination of low silica production, low diatom primary productivity and high bSi export efficiency at OSP was more similar to the dynamics in the subtropical gyres than to other HNLC regions.

INTRODUCTION

Silicon cycling in the High-Nutrient Low-Chlorophyll (HNLC) region of the northeastern subarctic Pacific region was examined as part of the NASA <u>EXport Processes</u> in the <u>Ocean from RemoTe Sensing (EXPORTS)</u> program. The northeast subarctic Pacific was the first ocean region to be designated as High-Nutrient Low-Chlorophyll (HNLC) characterized by persistent high macronutrient concentrations and low phytoplankton biomass caused by iron limitation of phytoplankton growth (Martin and Fitzwater, 1988; Martin et al., 1994; Boyd et al., 1996). Iron (Fe) limitation severely restricts the abundance of large diatoms in the northeast subarctic Pacific (Marchetti et al., 2006b) and in all other major HNLC regions including parts of coastal California (Hutchins et al., 1998), the eastern equatorial Pacific (Coale et al., 1996) and the Southern Ocean (Boyd and Law, 2001).

Fe limitation strongly modifies silicon cycling in HNLC waters through two opposing effects. By reducing diatom growth and biomass, Fe limitation acts to diminish the consumption of silicic acid. In contrast, diatom physiology can respond to low Fe by increasing cellular demand for silicic acid relative to other macronutrients. In most HNLC regions outside of the northeastern subarctic Pacific, diatom growth is still sufficient for the increased Si demand to overwhelm the potential for growth limitation, causing the preferential depletion of silicic acid compared to nitrate and orthophosphate (Dugdale et al., 1995; Hutchins and Bruland, 1998; Bruland et al., 2001; Sarmiento et al., 2004; Bruland et al., 2005; Marchetti et al., 2006a) and resulting in secondary Si limitation of diatom Si uptake rates and in some cases Si-limited diatom growth (Franck et al., 2000; Nelson et al., 2001; Brzezinski et al., 2008). This phenomenon has led to the suggestion that the description of these systems should be revised to High-Nitrate Low-Silicate Low-Chlorophyll (HNLSLC) (Wilkerson and Dugdale, 1996).

The northeastern subarctic Pacific differs from other HNLC regions in that a low silicic acid condition is rare, occurring only every few years (Wong and Matear, 1999) with concentrations typically remaining above $\sim\!15~\mu M$. Persistent silicic acid concentrations $\geq 15~\mu M$

would be considered to be a Si-replete condition for most diatoms (Martin-Jézéquel et al., 2000) implying that Si limitation is also rare. The lack of frequent silicic acid depletion in the northeastern subarctic Pacific is likely the result of the lower Fe supply in the northeast subarctic Pacific compared to other HNLC regions. The ferricline in the subarctic Pacific is deeper than the nutricline for macronutrients (Nishioka and Obata, 2017) and corresponds to the depth of winter mixing. Thus, modest vertical mixing injects relatively little Fe into the euphotic zone compared to macronutrients creating a near chronic low Fe condition in surface waters of the northeast subarctic Pacific that may exclude large diatoms to a greater extent than in other HNLC regions. The contrasting silicic acid dynamics between the northeastern subarctic Pacific and other HNLC regions suggest that the effects of Fe on Si cycling in the subarctic Pacific may be unique.

Iron stress affects both diatom physiology and diatom community structure. At the cellular level, low Fe increases diatom Si content relative to that of organic matter either by elevating diatom Si content directly through frustule thickening (Hutchins and Bruland, 1998; Takeda, 1998), by reducing organic matter content (Hoffman et al., 2006; Marchetti and Harrison, 2007), or through both of these responses (Takeda, 1998). Low Fe can also shift diatom community structure towards more robust diatom species with inherently higher Si:N and Si:C ratios (Marchetti et al., 2010; Durkin et al., 2012; Assmy et al., 2013). There is also evidence that smaller diatoms may not experience the same degree of Fe limitation as do larger diatom taxa in HNLC waters. In the equatorial Pacific relatively small diatoms of the genus *Pseudo-nitzschia* were the dominant diatoms under ambient conditions and experiments showed that they were not significantly stressed by either Fe or Si (Brzezinski et al., 2011a). In the Southern Ocean, even modest-sized diatoms like *Fragillariopsis kerguelensis* persist under low Fe conditions (Assmy et al., 2013). Thus, diatom responses at the community and physiological levels appear system-specific.

Diatoms in some HNLC regions appear to have two distinct growth strategies that affect their contribution to carbon export. In the Southern Ocean, thin-shelled forms respond rapidly to changes in Fe with a boom-and-bust growth strategy resulting in relatively efficient diatom carbon export during Fe-stimulated blooms (Assmy et al., 2013). In contrast to these 'carbon sinkers', thick-shelled forms persist in relatively low abundance under low Fe relying on their heavy silicification for protection from grazing to facilitate persistence despite slow growth. Taxa employing the latter strategy have been dubbed 'silica sinkers' as they are inefficient at exporting organic matter relative to biogenic silica (ibid). Thus, from both evolutionary and biogeochemical perspectives, low Fe in HNLC regions can impede the export and sequestration of organic carbon by diatoms through species and/or physiological effects on diatom Si:C ratios. It is unclear how applicable these concepts are outside of the Southern Ocean. For example, in HNLC regions such as the equatorial Pacific small thin-shelled forms dominate under low Fe (Brzezinski et al., 2011a), but their contribution to export is unknown.

The lack of strong depletion of silicic acid and other macronutrients in the northeast subarctic Pacific makes this area a true HNLC region with respect to low Fe being the predominate limiting nutrient, distinct from all other major HNLC areas. Data indicate that biogenic silica concentrations in the euphotic zone at Ocean Station Papa (OSP, 145°W, 50°N) are <100 nmol Si L⁻¹ and generally < 50 nmol Si L⁻¹ (Lipsen, 2008). Net silica production rates implied by seasonal net silicic acid depletion are also low. The annual cycle of silicic acid concentration shows a maximum concentration of about 23 μ M in late winter (Whitney and

Freeland, 1999; Harrison, 2002) that begins to decrease in June ultimately declining by about 7.5 μM through the summer reaching a seasonal minimum of about 15 μM in mid-August (Peña and Varela, 2007). The magnitude of net depletion of silicic acid implies a relatively low average net silica production rate (production minus dissolution in surface waters) over the three-month productive period of 7.5 μ M ÷ 90 days = 83 nmol Si L⁻¹ d⁻¹. That is a conservatively low estimate of silica production as it does not account for the consumption of silicic acid introduced to surface waters through vertical eddy diffusion across the nutricline. Applying Fick's law, assuming a diapycnal diffusion coefficient of 2 x 10⁻⁵ m⁻² s⁻¹ and a silicic acid gradient across the nutricline of ~0.3 µmol m⁻⁴ at OSP (Whitney and Freeland, 1999), yields an approximate additional Si supply of 0.5 mmol Si m⁻² d⁻¹ or ~7 nmol Si L⁻¹ d⁻¹. Averaging that supply over the upper 70 m leads to a revised average net silica production rate of 90 nmol Si L⁻¹ d⁻¹ or 6.3 mmol Si m⁻² d⁻¹ which is still conservative as it does not account for other forms of vertical nutrient injection. Integrated gross silica production rates measured using silicon-32 tracer in deck-board incubations during June and August/September were lower at 1.2 ± 0.9 mmol Si m⁻² d⁻¹ (n = 3) and 1.5 ± 1.6 mmol Si m⁻² d⁻¹ (n = 3; these and all subsequent uncertainty terms are standard deviations), respectively (Lipsen, 2008). Sediment trap studies have shown that the export of biogenic silica is highest in spring (Wong et al., 1999; Timothy et al., 2013) when diatom productivity based on the rate of silicic acid depletion is also at its annual maximum. Biogenic silica export out of the euphotic zone follows the same seasonal dynamics as silicic acid concentration reaching an annual minimum in late August to early September (Whitney and Freeland, 1999; Wong et al., 1999).

Another salient feature of OSP is that while cyanobacteria of the genus *Synechococcus* are abundant, *Prochlorococcus* are not present (Tortell et al., 1999). Significant Si quotas have been measured for *Synechococcus* in the equatorial Pacific (Baines et al., 2012), in the Sargasso Sea (Ohnemus et al., 2016) and in laboratory cultures (Brzezinski et al., 2017). Their rates of Si uptake in situ have been inferred from studies of Si use by different particle size fractions in the Sargasso Sea (Krause et al., 2017) and in the South Pacific (Leblanc et al., 2018). In the ocean regions that have been examined, *Synechococcus* and *Prochlorococcus* co-occur. As Si use by *Prochlorococcus* is currently unknown, their absence from OSP reduces uncertainty in interpreting Si uptake by the cyanobacteria in this area.

In the present study, the Si cycle near OSP was examined as part of the EXPORTS program during August and September 2018 near the time of the annual minimum in both surface silicic acid concentration and net silicic acid depletion. Dissolved and particulate silica concentrations along with rates of silica production and assessments of Si and Fe limitation are compared to rates of biogenic silica and organic carbon export to evaluate the upper ocean Si cycle and the role of diatoms in the region's biological carbon pump.

METHODS

General approach:

The logistics and general findings of the EXPORTS program's deployment to the subarctic Pacific have been described in detail by Siegel et al. (2021). Briefly, the study was conducted at Ocean Station Papa, OSP (nominally 50°N latitude, 145°W longitude) and involved three ships: The R/V Sally Ride and the R/V Roger Revelle from the United States (US) that both sampled near OSP from 16 August through 7 September 2018 and the CCGS John P. Tully from Canada that sampled the EXPORTS study site on 20 - 22 September 2018 twelve days after the

US ships departed. The R/V Revelle sampled following a Lagrangian float that was drogued at ~ 100 m for the entire time, while R/V Ride sampled a wider geographic area in survey mode. Sampling aboard R/V Revelle and R/V Ride occurred in three 8 - day cycles, referred to as epochs (Siegel et al., 2021), organized around three sets of sediment trap deployments from R/V Revelle. Particle export was also assessed on R/V Ride using the 234 Th method tied to elemental ratios obtained from particles collected using in situ pumps (Buesseler et al., 2020; Estapa et al., 2021; Roca-Martí et al., 2021). Particle export was not measured aboard CCGS Tully.

Sampling and Analyses:

Seawater samples for silicic acid and biogenic silica concentration analysis were taken on all three ships using mostly common procedures. On the *R/V* Revelle nutrient samples were taken on casts of a conventional CTD/rosette equipped with 12 L Niskin samplers and on casts of a trace-metal-clean CTD/rosette system using 10 L Go-Flo bottles. Samples for biogenic silica concentration on the *R/V* Revelle were collected from the trace-metal-clean CTD/rosette system only. Aboard the *R/V* Ride both nutrient and biogenic silica samples were taken from Niskin samplers using a conventional CTD/rosette system. Both rosette systems were equipped with SeaBird 911 CTDs. Aboard the *CCGS* Tully, all samples were taken from 12 L Niskin samplers on a conventional CTD/rosette system equipped with a SeaBird SBE 911 CTD with samples for silicic acid, biogenic silica, and silica production always collected from the same Niskin samplers at each one of the 6 light depths (100, 50, 30, 15, 1 and 0.1%).

On each US ship seawater nutrient samples were filtered through 0.2 μ m polycarbonate filters into acid-cleaned plastic vials and immediately frozen at -20°C. On the *CCGS* Tully, samples for dissolved Si were filtered through 0.6 μ m polycarbonate filters into 15 - mL plastic centrifuge tubes and kept at 4°C until analysis ashore. On all ships, seawater samples for biogenic silica concentration were processed by filtering 600 to 1000 mL of seawater through polycarbonate filters. On the *R/V* Ride, seawater was filtered through 47 mm diameter, 0.6 μ m pore size filters. On the *R/V* Revelle and on the *CCGS* Tully size fractionation of seawater samples for biogenic silica analysis was performed by sequential filtration of each sample through 5.0 μ m and then 0.6 μ m pore-size 47 mm polycarbonate filters. On the *CCGS* Tully a separate sample for total biogenic silica concentration was filtered through a separate 0.6 μ m filter. For all biogenic silica samples, filters containing the particulate matter were folded, stored in individual plastic containers and immediately frozen at -20°C to prevent opal dissolution.

At the end of the US expedition, silicic acid and biogenic silica samples from both the R/Vs Ride and Revelle were transported frozen on dry ice to the University of California Santa Barbara. Seawater silicic acid concentrations were determined on a Lachet 8500 series 2 flow injection system with a detection limit of $0.2 \,\mu\text{M}$ [Si(OH)₄] or 3%, whichever is larger. The concentration of silicic acid for samples from CCGS Tully was measured with a Beckman DU 530 ultraviolet-visible (UV/Vis) spectrophotometer following (Strickland and Parsons, 1972) modified to use a reverse-order reagent blank (Brzezinski, 1986) with a detection limit of < 0.05 μ M. Biogenic silica samples from the US ships were analyzed using the NaOH digestion method described by (Krause et al., 2009) using manual colorimetry with a detection limit of 0.05 μ mol Si L-1. Upon completion of the Canadian leg, the frozen biogenic silica samples from the CCGS Tully were kept on ice during the short transfer to the University of Victoria, and stored at -20°C until analysis following the same NaOH digestion method used for US samples.

Profiles of size fractionated silica production rates were obtained on the R/V Revelle using the radiotracer silicon-32 (Brzezinski and Phillips, 1997). Nine profiles, each sampling five depths spanning the 55% to the 1% light depth were obtained across the three epochs using the trace-metal-clean rosette system. All subsampling of Go-Flo samplers was conducted in a tracemetal clean van and the subsamples were transferred within clear plastic bags to a radioisotope van for tracer addition. Seawater for rate measurements was subsampled into trace-metal cleaned 300 mL polycarbonate bottles and then spiked with 230 Bq of Chelex-cleaned high-specific activity silicon-32 (15,567 Bq µg⁻¹ Si). Each sample bottle was capped and the closure sealed with parafilm before being transferred to deck incubators simulating the light levels at each sample collection depth using a combination of neutral density screening and blue plastic film. Incubators were cooled with flowing surface seawater except for those at the two deepest light depths that were held at near in situ temperature using recirculating chillers. Following 24 h of incubation, water samples were size fractionated through 25 mm diameter 5.0 µm pore size, and then 0.6 µm pore size, polycarbonate filters paralleling the size fractionation of biogenic silica samples. ³²Si activity on the filters was measured using low-level beta detection as in Krause et al. (2011a).

The degree to which iron and/or silicic acid limited rates of silica production and rates of primary production was quantified at all eight stations sampled using water collected with the trace-metal rosette at the 40% and 10% light depths. +Si treatments increased silicic acid concentration by 20 µM using a solution of sodium metasilicate, +Fe additions targeted an increase of 1 nM Fe using ferric chloride with a +Si & +Fe treatment combining both additions (+20 uM silicate, +1 nM Fe). Samples of unamended seawater served as controls. Incubations were conducted for 24 h. The experiment was replicated eight times during the cruise, but treatments were not replicated within single experiments. The silicate stock for the +Si addition was analyzed for dissolved Fe. The iron concentration in the Si stock caused the 20 µM Si(OH)₄ addition to raise ambient [dFe] by 0.05 nM. Immediately after amendments, Si production samples were spiked with silicon-32, incubated and processed as described for silicon-32 rate profiles. The effect of the same +Si, +Fe and combined +Si & +Fe additions on primary productivity was determined in a parallel set of incubations using ¹⁴C-bicarbonate tracer following the light/dark bottle method described by Brzezinski and Washburn (2011). Samples for carbon fixation were size fractionated through the same diameter and pore sizes filters as used for silicon-32 tracer experiments and sample activity evaluated at sea using liquid scintillation counting in Ultima Gold XR cocktail.

RESULTS

Environmental Setting -

The environmental conditions encountered during EXPORTS have been published elsewhere (Siegel et al., 2021). Briefly, salinity in the mixed layer averaged 32.3 with little variation, increasing by ~ 0.2 at the base of the euphotic zone (1% light depth). Mixed layer temperatures were 14.0 – 14.2 °C decreasing to 6.3 -7.0 °C at the 1% light depth. Analysis of these physical properties showed the presence of three distinct water types in the mixed layer during EXPORTS (Siegel et al., 2021) and during sampling by the *CCGS* Tully. Water types 1 and 3 were salty and fresh compared to type 2 and were mainly sampled at the beginning and end of the US cruise, respectively. Water type 3 was still present at the site of the Lagrangian float during sampling by CCGS Tully. Sampling by *R/V* Revelle occurred predominantly in water mass type 2 with *R/V* Ride sampling all three water types during spatial surveys. The euphotic

zone (defined at the depth where photosynthetic active radiation reached 1% of incident sunlight) at the stations where rate measurements were performed aboard R/V Revelle was between 63 -70 m with shallower depths occurring later in the cruise.

Intercalibration between R/V Ride and R/V Revelle -

There were four occasions when the R/V Ride and R/V Revelle both sampled the upper water column nearly simultaneously when the two ships were within 18 km of each other. In three cases the ships were in the same surface water type based on T/S characteristics (Siegel et al., 2021) while they were in different water types on the fourth (Table 1). To compare silicic acid concentrations, the values from the upper 20 m (all within the mixed later) were averaged for each ship on each occasion. For biogenic silica concentrations, the values obtained from each ship were integrated to a common depth of 70 m using linear interpolation between sampling depths when necessary. Integrated concentrations were divided by the integration depth to calculate a depth-weighted average biogenic silica concentration in the euphotic zone.

INSERT TABLE 1 HERE. PROVIDED AS SEPARATE FILE

At three of the four stations average mixed-layer silicic acid concentrations on the two ships agreed to within 7 - 12 % (Table 1). On the fourth, which sampled a different water type, dissolved Si values were still within 39 % of each other. The level of agreement for biogenic silica concentrations, on the other hand, did not relate to water type. For biogenic silica concentration, in the one case when the ships were in different water types the integrated, depthnormalized biogenic silica concentration measured on samples from the R/V Ride was 6.7 times higher than measured on R/V Revelle. For the other three comparisons, the ships were in same water type. In one instance, the normalized concentrations obtained on each ship are within 1% of each other. For the other two, values are 2.0 and 2.2 times higher for the R/V Ride compared to those from R/V Revelle (Table 1).

Silicic acid concentrations -

Profiles of silicic acid concentration measured on R/V Revelle revealed concentrations consistently >12 μ M in euphotic zone with an average integrated depth-normalized average concentration in the upper 70 m of 15.7 \pm 1.2 μ M (n = 33) with a median concentration of 16.0 μ M (Figures 1, 2). Profiles of silicic acid concentration from R/V Ride displayed similar vertical patterns as those from R/V Revelle (Figure 1A), but on average depth-normalized integrated concentrations sampled by R/V Ride in the upper 70 m were lower, mean 13.4 \pm 2.1 μ M (n = 63), median 13.6 μ M. On both ships, the nutricline for silicic acid was between 90 and 100 m (Figure 1A), significantly deeper than the euphotic zone as defined by the 1% light depth (63 - 70 m). No systematic spatial pattern in average concentrations was apparent in data from either ship (Figure 2). When the CCGS Tully sampled the EXPORTS site, the average silicic acid concentration in the euphotic zone, 16.2 μ M, was similar to that observed by R/V Revelle.

Silicic acid concentrations from R/V Revelle associated with profiles of rate process measurements are listed in Table 2 with the relevant profiles depicted in Figure 3. Euphotic zone integrated depth-normalized values averaged $15.4 \pm 1.8 \, \mu M$ (n = 9) with a median value of $16.1 \, \mu M$. Concentrations at the deepest depth sampled shift from initially relatively low values to higher values on year day 242 and remain high for rest of cruise. Density, σ_{θ} , at the deepest depth sampled across all of these profiles was 25.42 ± 0.05 (n = 9) indicating that the change in silicic acid concentrations at the 1% light depth was not due to a change in water type.

INSERT TABLE 2 HERE. PROVIDED AS SEPARATE FILE

Biogenic silica concentrations -

Biogenic silica concentrations were generally low during the entire EXPORTS cruise. Concentrations measured on samples from R/V Revelle were ≤ 210 nmol Si L⁻¹ (Figure 1B, 2), with integrated concentrations in the euphotic zone averaging 6.4 ± 2.2 mmol Si m⁻² (n = 9, Table 2). The shape of the profiles was variable with surface or mid-depth maxima observed on occasion with otherwise relatively uniform values with depth (Figure 4). Significant biogenic silica was present at the 1% light level (Figure 1B, 4) making euphotic zone integrals conservatively low relative to total upper water column inventories.

Although the R/V Ride sampled waters that had lower average silicic acid concentration compared to R/V Revelle, the average depth-normalized integrated biogenic silica concentration sampled on R/V Ride was higher (R/V Ride: 132 ± 112 nmol Si L⁻¹, n = 42, R/V Revelle: 83 ± 46 nmol Si L⁻¹, n = 9; t-test, p = 0.005, Figure 1). The maximum biogenic silica concentration measured on R/V Ride reached 500 nmol Si L⁻¹, but was 210 nM on Revelle (Figure 1B). The average of the normalized biogenic silica concentrations for all samples from both ships was 120 \pm 102 nmol Si L⁻¹ (n = 51). Integrated values for the euphotic zone on R/V Ride averaged 8.3 ± 4.6 mmol Si m⁻² (n = 42) range 1.8 - 21.8 mmol Si m⁻². On R/V Revelle mean integrated concentrations were 6.4 ± 2.2 mmol Si m⁻² (n = 9), range 3.2 - 9.4 mmol Si m⁻² (Table 2). Averaged across all samples from both ships the mean integrated biogenic silica concentration was 8.0 ± 4.3 mmol Si m⁻² (n = 51). The integrated biogenic silica concentration measured by CCGS Tully was 18.4 mmol Si m⁻² (Table 2) which is two to three times higher than the average for either US ship, but not out of the range of values for individual stations sampled by R/V Ride.

The nine profiles of size-fractionated biogenic silica concentrations from R/V Revelle were fairly uniform with depth for both size fractions with occasional surface or mid - depth (~25 m) maxima (Figure 4). Integrated depth - normalized concentrations in the $0.6-5.0~\mu m$ fraction averaged 2.1 ± 0.7 mmol Si m⁻² (range 1.2-3.1 mmol Si m⁻²) with the corresponding data for the >5.0 μm fraction being 4.4 ± 2.0 mmol Si m⁻² (range 0.5-7.2 mmol Si m⁻²). The proportion of biogenic silica in the larger fraction was fairly consistent except at the first station where it was only 17% of total biogenic silica. On average 6.5 ± 1.9 % of the biogenic silica was > 5.0 μm with the median being 71% (Table 2, Figure 4). Average biogenic silica concentration in the > 5.0 μm fraction was twice that in the small fraction with significant biomass present in both fractions at deepest depth sampled (1% light, Figure 4). By the time of the Canadian occupation of the study site the distribution of biomass between the two size fractions reversed compared to that during most of the US occupation. The small fraction comprised 64% of the total integrated biogenic silica stock with the > 5.0 μm fraction dropping to 36% similar to the very first station occupied by R/V Revelle (Table 2).

Silica production rates -

Total silica production rates calculated as the sum of the rates in the two size fractions across all nine profiles sampled by R/V Revelle were low with a mean of 10.1 ± 9.2 nmol Si L⁻¹ d⁻¹. Rates ranged from a low of 0.12 nmol Si L⁻¹ d⁻¹ at the base of the euphotic zone (1 % light) to a high of 49.9 nmol Si L⁻¹ d⁻¹ in shallower waters. Total production rates integrated to the 1 % light level averaged 0.62 ± 0.26 mmol Si m⁻² d⁻¹ with a range of 0.25 - 1.19 mmol Si m⁻² d⁻¹ (Table 2).

Profiles of silica production rates (ρ) in both size fractions were relatively uniform declining slightly with depth with occasional surface or mid depth maxima (Figure 4). The large size fraction that dominated siliceous biomass also dominated silica production (Table 2). Integrated production rates for the > 5.0 μ m fraction average 0.50 \pm 0.2 mmol Si m⁻² d⁻¹ compared to 0.12 \pm 0.07 mmol Si m⁻² d⁻¹ for the small fraction. Rates in both size fractions were still significant at 1 % light (Figure 4) so integrals are conservatively low estimates of total upper water column silica production.

Like profiles of ρ , profiles of the specific rate of silica production, V_b , showed little vertical structure (Figure 4). V_b was generally low implying doubling times of about 2 weeks for both size fractions: 18 and 15 days for the small and large size fractions, respectively. Much higher specific rates were measured at the beginning of the cruise (year day 228, epoch 1, day 2) in the large size fraction implying a doubling time of 0.9 days. Specific rates at the 1% light depth were often similar to near surface indicating continued silica production in deeper waters.

In the upper euphotic zone, specific production rates were generally higher in the large size fraction than in the small (Figure 4, Table 2), but specific rates switched to becoming higher in the small fraction at the base of the euphotic zone (Figure 5). The contribution of the small size fraction to silica production averaged across the 9 profiles was fairly constant throughout the upper euphotic zone. There the small fraction accounted for 15 - 20 % of total silica production with specific production rates that were about half those in the larger size fraction. The contribution of the small size fraction to total silica production rose to 40 % near the base of the euphotic zone where specific rates in the small fraction were over twice those in the larger size class. (Figure 5).

Apparent Temporal trends -

Temporal trends observed in Lagrangian mode aboard R/V Revelle show significant transitions (Figure 6). The depth normalized silicic acid concentration in the mixed layer sampled by the conventional CTD/rosette (mixed layer depth defined as first depth where the change in potential temperature from 5 m, or first recorded depth exceeded 0.2 °C) were low when R/V Revelle began sampling in water type 1 and remained low during the transition to water type 2 on year day 230. Then, while remaining in water type 2, depth-normalized integrated values increased beginning on year day 231 from ~16 μ M to ~18 μ M by year day 233. Concentrations remained at 18 μ M until year day 238 when concentrations declined to near 16 μ M again and remained there until the end of the cruise.

Changes in siliceous biomass occurred during the same transition periods that were observed for silicic acid concentration (Figure 6). The biogenic silica concentration in the small size fraction exceeded that of the large size fraction at the beginning of the cruise. The depthnormalized concentration in the > 5.0 µm fraction then increased and that in the small size fraction declined during the transition in water type and from low to higher silicic acid concentration on year day 230 although the biomass data have limited temporal resolution during this period. Biomass in both size fractions increase during the transition to lower silicic acid concentrations from year day 231 - 233 and then declined over the last week of the cruise. Sampling during the Canadian occupation on year day 264 revealed that a bloom had occurred with biogenic silica tripling in the large size fraction and increasing 6 - fold in the in small size fraction (Table 2).

Silica production was dominated by the large size fraction throughout the US expedition (Figure 6). Production in the large size fraction initially declined, but then rose between year day 234 and 242 somewhat independent of the changes in silicic acid and biogenic silica concentrations (Figure 6). Silica production in the large size fraction abruptly peaked on year day 244 three days after the observed decline in silicic acid concentration. Temporal dynamics in silica production were more muted in the small size fraction where rates were essentially constant through time with a small peak in production that coincided with the increase in the production by the large size fraction on year day 244 (Figure 6).

Si and Fe limitation -

An analysis of variance (ANOVA) was used to investigate the responses of silica production to the +Si, +Fe and +Si & +Fe additions in the nutrient limitation experiments at the 40 % and 10 % light levels. Light depth, nutrient addition and size fraction were assigned as main effects with all pairwise and three way interactions included. All interaction terms were not significant at p = 0.05. The analysis showed no significant effect of light depth (F= 1.75, d.f. = 1, p = 0.19) but a significant effect of nutrient addition (F = 5.8, df = 2, p = 0.004) and a significant effect of size fraction (F = 17.5, d.f. = 1, p < 0.001). A similar ANOVA for the response of primary productivity showed a single significant effect related to light level reflecting a slightly more muted response to treatments at the 10 % light level compared to the 40% (F = 9.4, d.f. = 1, p = 0.003).

The results of the ANOVA analyses were further investigated using t-tests (Table 3). V_b in the > 5.0 µm fraction did not show a consistent response to added Si, added Fe or to the addition of both nutrients together (Figure 7). There were individual experiments where treatment effects were observed, but the mean response of the large size fraction across all experiments was not significant at either the 40% or 10% light depth (Table 3). In contrast, there was a statistically significant mean response of Si uptake to added Si and to added Si & Fe by the small size fraction at both the 40% and 10% light depths (the response at 40% light was only marginally significant) with V_b in treatments increasing by an average of 2.5 \pm 1.3 times relative to controls (Table 3, Figure 7). Like the large size fraction, the small size fraction did not respond to added Fe, indicating a Si-driven response in the combined +Si & +Fe treatment. The +Si, +Fe and the +Si & +Fe additions did not elicit a significant response of carbon fixation rates for either size fraction (Table 3).

Table 3. Significance tests of the response to experimental treatments. Shown are p values for t tests evaluating the ratio of the response to treatments relative to controls was different than unity.

Light depth	Treatment	$\begin{array}{c} V_b \\ (0.6-5.0~\mu m) \end{array}$	V _b (>5 μm)	Primary Productivity (0.6 – 5.0 μm)	Primary Productivity (>5.0 µm)
40%	+Si	0.054	0.416	0.677	0.473
	+Fe	0.742	0.780	0.408	0.170
	+Si & +Fe	0.037	0.510	0.361	0.308
10%	+Si	0.002	0.233	0.240	0.634
	+Fe	0.223	0.088	0.208	0.517
	+Si & +Fe	0.005	0.702	0.121	0.336

DISCUSSION

The EXPORTS program sampled the northeast subarctic Pacific during the seasonal minimum in surface silicic acid concentration. Both biogenic silica and silica production rates in the euphotic zone were found to be low during the sampling by the US ships, but an apparent bloom had occurred by the time the site was sampled by the Canadian ship. Here we interpret these results in the context of data from the larger EXPORTS program and previous published results to evaluate controls on upper-ocean Si cycling and the role of diatoms in the local biological pump.

Dissolved and particulate silica stocks-

Care was taken to compare observations on the R/V Ride and R/V Revelle by conducting simultaneous CTD casts when the two ships were in relative close proximity to one another. Differences in both silicic acid and biogenic silica concentrations between ships during the four intercalibration casts were observed. This was likely not the result of analytical differences. The same sampling, preservation and sample shipping methods were used for both sample sets and the samples from both ships were all analyzed in same laboratory using the same procedures. Both the intercalibration casts and data from regular sampling casts indicate that silicic acid concentrations were lower, but biogenic silica concentrations higher, on the R/V Ride compared to R/V Revelle. These differences suggest a fair level of patchiness in biological activity and nutrient consumption, even within the same water type, implying that different portions of the same physical water type experienced variable biological histories.

Silicic acid concentrations in the euphotic zone were in the range expected from climatology for the late summer. During EXPORTS biogenic silica concentrations were two orders of magnitude lower compared to silicic acid concentrations, likely reflecting strong Fe limitation of diatoms. Seasonal profiles of biogenic silica concentrations at OSP in 1999 and 2000 found integrated concentrations of 18.1 ± 0.3 mmol Si m⁻² (n = 2) in February, 41.8 ± 10.6

mmol Si m⁻² (n = 3) in June and 17.7 ± 9.9 mmol Si m⁻² (n = 3) in August/September (Peña and Varela, 2007; Lipsen, 2008) which are all higher than the overall average from EXPORTS of 8.0 \pm 4.3 mmol Si m⁻². The integrated total biogenic silica concentration of 18.4 mmol Si m⁻² observed on the *CCGS Tully* is much higher than the cruise averages for the two US ships, but not that different from the historic observations during the same time period and it is also similar to the highest values observed from *R/V* Ride (Figure 2).

During the US sampling, most of the biogenic silica was $> 5.0 \, \mu m$ with about 35 % present in the small $0.6-5.0 \, \mu m$ fraction. This differs from other size fractionated biomass measurements during EXPORTS, such as chl a concentration and primary productivity, that show dominance by small cells for the phytoplankton overall (Marchetti pers. comm.). The dramatic increase in biogenic silica concentrations during the Canadian sampling coupled with the shift in dominance to the small fraction suggests a fundamental change in dynamics, but we lack the temporal resolution to diagnose the mechanism. A similar dominance by the small size fraction, but at a lower overall biomass, was observed just once at the very first station sampled by R/V Revelle, suggesting considerable patchiness.

Size fractionated measurements of biogenic silica concentration are uncommon, so limited data are available for comparison with the present data set. Krause et al. (2017) observed that only 4 % of biogenic silica in the Sargasso Sea was between 0.2 and 3 um. In the Pacific Ocean Leblanc et al. (2018) observed that between 11 and 26 % of biogenic silica in the South Pacific was between 0.2 and 2 µm, while Wei et al. (2021) found 66% of the biogenic silica in the oligotrophic western tropical North Pacific was $0.2 - 2.0 \mu m$ in size. Those values bracket the average of 35 % in the $0.6 - 5.0 \mu m$ fraction during EXPORTS with the value for the western tropical North Pacific being similar to the 64 % observed in the small size fraction on the CCGS Tully. Rigorous comparison of the data among these studies is difficult given the differences in the filter pore sizes used among studies. The 0.6 µm lower cut-off filter used during EXPORTS may have missed some small Si containing cyanobacteria (Baines et al., 2012) that would be captured on the 0.2 µm filters used for the Krause et al. (2017), Leblanc et al. (2018) and Wei et al. (2021) studies, while the 5.0 µm upper limit used during EXPORTS would have included more larger particles than the $2 - 3 \mu m$ pore sizes used to define the upper limit of the small size fraction in the other studies. The importance of the small size class at OSP appears to be at the high end of what has been observed, at least during the Canadian sampling and at the first station sampled by R/V Revelle when the small size class was highly dominant. The identity of the organisms responsible will be discussed below.

Silica production rates -

The measured rates of silica production were low being only a few tens of nanomoles of biogenic silica produced per liter each day. Specific rates were extremely low with implied doubling times for biogenic silica in both size fractions of about two weeks. Such low rates are consistent with the timing of the cruise during the annual minimum in net silicic acid drawdown. The main seasonal drawdown of silicic acid from climatology occurs between May and August (90 days) when silicic acid concentrations decline by 7.5 μ M (Peña and Varela, 2007) corresponding to an integrated net silica production rate of 5.8 mmol Si m⁻² d⁻¹ assuming a 70 m productive layer. Adding in an estimate of silica production supported through vertical eddy diffusion across the nutricline increases the integrated net daily rate to 6.3 mmol Si m⁻² d⁻¹ (see Introduction). The net silica production rate is the difference between gross silica production and losses due to silica dissolution in surface waters. To compare that rate to the gross silica

production rates measured during EXPORTS using silicon-32 tracer, we calculate gross silica production during the spring/summer period as follows: integrated rates of silica production compared with the export of biogenic silica (see below) yields an estimated dissolution:production ratio in the productive surface layer during EXPORTS of 0.44; net silica production, ρ_{net} , is the difference between gross silica production, ρ_{gross} , and losses to dissolution. Thus, ρ_{diss} :

$$\rho_{\text{net}} = \rho_{\text{gross}} - \rho_{\text{diss}} \tag{1}$$

and given the $\rho_{diss} \div \rho_{gross}$ of 0.44 rearranging equation (1) yields:

$$\rho_{\rm diss} = 0.44 \; \rho_{\rm gross} \tag{2}$$

Substituting into equation (1):

$$\rho_{\text{net}} = \rho_{\text{gross}} - 0.44 \ \rho_{\text{gross}} = 0.56 \ \rho_{\text{gross}}$$
 (3)

and solving for ρ_{gross} :

$$\rho_{gross} = \rho_{net} \div 0.56 \tag{4}$$

For the spring-summer productive period, the average gross silica production rate is then estimated to be $6.3 \div 0.56 = 11$ mmol Si m⁻² d⁻¹ which is nearly 18 times higher than the average gross silica production rate of 0.62 ± 0.26 mmol Si m⁻² d⁻¹ measured during EXPORTS.

While the estimate of silica production for spring/summer implies a strong seasonal cycle in silica production, actual measured rates of silica production do not. Lipsen (2008) measured integrated silica production rates of 1.2 ± 0.9 mmol Si m⁻² d⁻¹ (n = 3 profiles) and 1.5 ± 1.6 mmol Si m⁻² d⁻¹ (n = 3 profiles) at OSP in June and August/September in 1999 and 2000, respectively. Those rates are lower than the seasonal estimate based on silicic acid drawdown, but higher than observed during EXPORTS. While it is difficult to discern a clear seasonal pattern in production from the available data, these comparisons confirm that EXPORTS sampled during a period low diatom activity with the potential for significantly different Si cycling dynamics during spring and summer.

The temporal transitions in silicic acid concentrations and biogenic silica concentrations in the mixed layer (Figure 6) were much faster than can be supported by the measured biological rates. During the transitions, the rate of change in silicic acid concentration is approximately 1 µmol Si L⁻¹ d⁻¹ which is 100 times faster than the average silica production rate of 10.1 ± 9.2 nmol Si L⁻¹ d⁻¹ (n = 9). Integrated biogenic silica concentrations in both size fractions changed by 2 - 4 nmol Si m⁻² d⁻¹ which exceeds measured integrated production rates by 4 - 8 times for the large size fraction and 16 - 33 times for the small. This would imply that the observed changes in the concentration of silicic acid and biogenic silica over time were the result of spatial variation among and within water types established over relatively long intervals of time compared to the temporal resolution of our measurements.

The two-week doubling times implied by the specific rates of silica production underestimate the doubling times of diatoms. V_b underestimates the specific rate of living cells as it is normalized to total biogenic silica that includes both living siliceous organisms, mainly diatoms, and detrital silica. Values of V_b can be made congruent with the biomass changes if the detrital silica comprised ~ 80 % of the biogenic silica present. Such a high detrital fraction is consistent with the findings of Krause et al. (2010) who found that 80-90 % of the biogenic silica in the equatorial Pacific HNLC region was detrital. Such high percentages may be

characteristic of severely Fe-limited regions where both diatom growth rates and biomass are low.

Si and Fe limitation -

The lack of evidence for Fe limitation of silica production and primary production in both size fractions in the nutrient limitation experiments may be related to the relatively short 24 h incubations employed. Longer-term grow out experiments lasting several days on the same cruise show strong growth responses and biogenic silica increases in response to the same level of added Fe in the same two size fractions that were used in the present study (Jenkins, pers com.). Interestingly, Si addition alone did not increase the growth or biomass of either size fraction in the longer-term experiments (ibid) whereas Si uptake in the small size fraction was clearly stimulated by added Si over 24 h in the experiments reported here. Taken together, results suggest that Fe limited the growth rate of diatoms in the small size fraction, while their Si uptake was substrate-limited as has been observed to the diatom community as a whole in the equatorial Pacific (Brzezinski et al., 2008). This hypothesis is consistent with both the short-term and long-term experimental results, as without Fe to permit the growth that would support a persistent demand for Si, cell division and hence frustule deposition, would be severely truncated eliminating any response to added Si on longer time scales.

The lack of experimental evidence for Si limitation of silica production in the large fraction is not surprising. The average half saturation constant (Ks) for silicic acid uptake in diatoms is about 2 μM (Martin-Jézéquel et al., 2000). Assuming Michaelis-Menten uptake kinetics, diatoms with a Ks of 2 μM growing in waters with 12 μM to 15 μM silicic acid would be taking up silicic acid at 86 - 88 % of their maximum rate (Vm). The response of Si uptake of the small size fraction to added Si is surprising, both because it occurred in the small 'non-diatom' fraction and it occurred in a system where silicic acid was >12 μM at all depths in the euphotic zone implying inefficient uptake kinetics by the organisms responsible for the response.

Organisms responsible for dynamics in the small size fraction -

A fair fraction of the biogenic silica (35 %) and Si uptake (19 %) was by organisms between 0.6 and 5 μ m in size and the small size fraction dominated siliceous biomass at the very first station sampled by R/V Revelle (83%) and during the sampling aboard CCGS Tully (65 %) (Table 1). At roughly half the stations sampled by R/V Revelle the average V_b in the small size fraction was nearly the same as that in large fraction and the small fraction exhibited much higher specific rates deeper in the euphotic zone compared to the larger size class (Table 1). Notwithstanding the issues with detritus, those specific rates imply active growth and Si use by both small and large cells. The small size fraction also displayed unique Si uptake physiology not shared by the larger fraction with a statistically significant increase in Si uptake in response to added silicic acid. Explanations for activity in the small size fraction include the passage of larger cells through the 5.0 μ m filter that were then captured on the 0.6 μ m filter during sample processing, Si uptake by cyanobacteria in the picoplankton size class, and presence of small diatoms or other small silicifiers that were < 5.0 μ m.

Pseudo-nitzschia were the most abundant large diatom taxa present during the EXPORTS cruise forming visible chains in micrographs from imaging flow cytometers (https://ifcb-data.whoi.edu/timeline?dataset=EXPORTS). There is some potential for these taxa to contribute to the small size fraction. Marchetti et al. (2008) measured the physical dimensions of the frustules of five *Pseudo-nitzschia* taxa isolated from OSP and all had transapical widths < 5 μm

so all isolates could pass through a 5.0 µm filter pore if aligned end on. However, if the passage of *Pseudo-nitzschia* was responsible for the observed activity in the small size fraction then the increase in Si uptake in response to added Si should have been evident in both size fractions as *Pseudo-nitzschia* dominated the large size fraction. That pattern was not observed making this possibility unlikely.

Small cyanobacteria of the genus *Synechococcus* are known to contain significant amounts of Si relative to their size (Baines et al., 2011; Ohnemus et al., 2016) and culture studies have shown that Si uptake by *Synechococcus* increases with added Si up to at least 500 μ M (Brzezinski et al., 2017) consistent with observed increase in Si uptake in this size class at the high (~30 μ M) silicic acid concentration in experimental treatments with added Si. During EXPORTS *Synechococcus* integrated abundances in the euphotic zone (1% light) averaged 1.1 x $10^{12} \pm 0.4 \times 10^{12}$ (1 σ_{SD}) cells m⁻² (Jason Graff, pers. com.). Estimating their contribution to standing stock of biogenic silica requires knowledge of their cellular Si content. We use the measured values by Ohnemus et al. (2016) in the Sargasso Sea of 46 amol Si cell⁻¹ to convert *Synechococcus* abundance during EXPORTS to a biogenic silica concentration. The resulting integrated biogenic silica concentration of 0.05 mmol Si m⁻² is only 2 % of the average integrated biogenic silica concentration in the 0.6 - 5.0 μ m fraction similar to estimates from the Sargasso Sea by Krause et al. (2017). The estimated fraction is so low that *Synechococcus* is not likely to be responsible for observed Si uptake and response to added Si in the small size fraction.

It is also possible that small relatively under-studied eukaryotes, such as the silicified *Bolidophycae* could be contributing to Si uptake in the small size fraction. These sister taxa to diatoms are 10 times more prevalent in the small size fraction (0.8-5µm) than in larger size fractions in the Tara Oceans global ocean sampling datasets (Ichinomiya et al., 2016) and common throughout the global ocean, however they typically comprise a minor component of the photosynthetic community. Thus it is unlikely that a novel group of eukaryotes are contributing to the Si uptake signature in the small size fraction at OSP.

Extremely small diatoms, such as *Minidiscus* sp., are known from OSP (Clemons and Miller, 1984) and small pennate diatoms in the < 5 um size class have been reported at abundances of 10^4 cells L⁻¹ (Boyd and Harrison, 1999). Size fractionated HPLC pigment data from the underway sampling system aboard R/V Ride (3 - 5 m depth) during EXPORTS show that the fucoxanthin:chlorophyll a ratio and the chlorophyll c: chlorophyll a ratios in the 0.7 - 5.0 um size fraction were 80 - 100 % of the same ratios in the > 5 μ m fraction indicating the presence of < 5.0 μ m diatoms (https://oceandata.sci.gsfc. nasa.gov/ob/getfile/da771c20f8ed_EXPORTS_EXPORTSNP_HPLC-inline_survey_R1.sb). Therefore, small diatoms most likely account for the silica production in the small size fraction and the uptake response of that fraction to added Si.

Substrate limitation of Si uptake for small diatoms at ambient silicic acid concentration as high as $\sim 15~\mu M$ is surprising given the Si uptake kinetics of most diatoms. However, that expectation is based on Si uptake kinetics for diatoms from culture studies that have generally examined relatively large taxa. Also potentially notable is the fact that the Si additions made during EXPORTS raised ambient silicic acid concentrations to above 30 μM . In laboratory culture, this is near the threshold concentration where diatoms switch from transporter-mediated Si uptake to reliance on diffusive transport (Shrestha and Hildebrand, 2015). The factors that control diffusive flux differ for large and small cells in ways that are consistent with a stronger

uptake response to high silicic acid concentration in smaller cells. The rate of diffusion of a nutrient to the cell surface is a function of cell radius, R, whereas the Si requirement for the frustule is a function of cell surface area that varies as R^2 diminishing the effectiveness of diffusion as a means to support silica production in larger cells. For example, for a small (4 μm diameter) and large (20 μm diameter) diatom, each with the same frustule thickness, the 2.5-fold increase in cell radius increases the diffusive flux of silicic acid by a factor of 4, but the Si required to construct the frustule increases by a factor of 25. This is a conservative estimate of the discrepancy between small and large cells as larger cells tend to have thicker frustules, which would amplify the contrast. Even with the same thickness, the 2.5 fold increase in the biogenic silica normalized specific uptake rate, V_b , observed in response to added silicic acid in the small cells would truncate to a 2.5 x (5 \div 25) = 50 % increase in V_b for the larger cell. Given that V_b in the larger size fraction was about twice that in the small fraction on average at ambient silicic acid concentration (Table 2), the effective increase in uptake in the larger cells would drop to 25% which is close to the experimental uncertainty for these types of field experiments (Nelson et al., 2001).

Efficiency of biogenic silica export -

Data from the overall EXPORTS program allows euphotic-zone silica cycling to be linked to the export of diatom silica and to diatom organic carbon export out of the surface ocean. One conceptual metric for the efficiency of export is the Ez ratio (Buesseler and Boyd, 2009). For organic carbon, the Ez ratio is defined as the rate of export of organic carbon out of the base of the productive surface layer expressed as a fraction of the rate of net primary production in that layer. There is no fixed convention to define the depth of the productive layer. For EXPORTS the reference depth for calculating Ez ratios for organic carbon was defined as the depth where in situ chlorophyll fluorescence as measured by the fluorometers on the CTD/rosette declined to 10 % of the maximum signal measured in overlying waters (Buesseler et al., 2020; Estapa et al., 2021), which is approximately the 0.1% light level and very close to the depth of the nutricline for silicic acid (Figure 1A). An Ez ratio for silicon would be defined similarly to be the ratio of the rate of opal export at the base of the productive layer expressed as a fraction of net silica production in that layer.

Silicon-32 rate measurements are often referred to as gross silica production rates (e.g. equations 1 - 4) as tracer methods measure Si uptake independent of losses due to silica dissolution (Nelson, 1975). This is an older convention that does not take into consideration the efflux of the Si taken up by diatoms out of the cell which is now known to occur (Milligan et al., 2004) possibly mediated by specific Si efflux transporters (Shrestha et al., 2012). Thus silicon-32 production rate measurements actually reflect the net rate of Si incorporation into particles and are thus conceptually equivalent to net primary productivity (NPP) for organic carbon in that the measurement does not include Si that is lost from cells due to Si efflux, analogous to phytoplankton respiratory C losses for NPP. By contrast, rates of silica production determined using silicon-32 after accounting for losses due to the dissolution of diatom frustules in the euphotic zone would be analogous to net community production (NCP) for organic carbon that accounts for respiratory losses of C within the entire upper ocean food web and at steady state, those rates would be equivalent to the rate of export of biogenic silica out of the productive layer.

The Ez ratio for Si was variable in time and space and differed significantly depending on the method used to measure biogenic silica export. The export of biogenic silica was measured using both neutrally buoyant sediment traps (NBSTs) and surface tethered sediment traps (SSTs)

at 95 -105 m once per epoch during EXPORTS (Estapa et al., 2021). Ez ratios calculated using those data and total integrated silica production in the euphotic zone, denoted as Ez_{100} ratios, varied by a factor of two across epochs averaging 56 ± 15 % (n = 3, Table 4). Those ratios are biased high as the sampling to the 1% light depth for silica production rate measurements did not reach the depth limit of silica production (Figure 4). The average implies the silica dissolution:production ratio in the euphotic zone (D:P = $1 - Ez_{100}$ ratio) of 0.44 is somewhat lower than the global average of 0.5 - 0.6 (Tréguer and De La Rocha, 2013).

Table 4. Average flux of biogenic silica during each epoch measured in sediment traps at ~95 m^a.

ЕРОСН	bSi Flux (mmol m ⁻² d ⁻¹)	Ez ₁₀₀ ratio Traps (%)	Ez _{1%} ratio 70 m ²³⁴ Th (%)	Ez ₁₀₀ ratio 100 m ^{234Th} (%)
1	0.20 ± 0.01 (2)	$52 \pm 24 (2)$		
2	0.21 ± 0.09 (2)	$37 \pm 17 (2)$		
3	0.68 ± 0.18 (2)	78 ± 33 (2)		
Mean	0.34 ± 0.26 (6)	$56 \pm 15 (6)$	133 ± 64	118 ± 62

a Ez_{100} ratios were calculated as the ratio of the flux at ~100m measured by traps or using 234 Th to integrated silica production (to 1% light). The $Ez_{1\%}$ ratio was calculated similarly using the 234 Th flux of biogenic silica interpolated to 70 m (average 1% light depth). Uncertainty terms are standard deviations. Values in parentheses are the number of observations

Biogenic silica export rates during EXPORTS based on ²³⁴Th are available as cruise averages for multiple depths in the upper 100 m (Roca-Martí et al., 2021). Those data were used to estimate of the Ez ratio referenced to the base of the euphotic zone, Ez_{1%} ratio, to align with the depth range for silica production measurements and also to estimate an Ez₁₀₀ ratio to parallel the analysis above using data from sediment traps. The silica export rate at the average euphotic zone depth of 70 m was estimated to be 0.83 ± 0.24 mmol Si m⁻² d⁻¹ by interpolating the average silica export rates at 65 and 80 m to 70 m. The flux of biogenic silica at 100 m was lower, $0.73 \pm$ 0.23 mmol Si m⁻² d⁻¹. The ²³⁴Th-based estimates of the Ez₁% ratio, 1.33 ± 0.64 at 70 m and the Ez_{100} ratio, 1.18 ± 0.62 both exceed unity (Table 4). Considering the Lagrangian sampling strategy employed on R/V Revelle, this implies that the standing stock of biogenic silica should have diminished substantially during the three weeks of the cruise, which was not observed. The discrepancy between the rate of biogenic silica export measured in traps compared to ²³⁴Th is unresolved. Estapa et al. (2021) point out that the traps failed to collect the flux of ²³⁴Th predicted by water column thorium deficits, implying under sampling of sinking particles by traps, significant zooplankton active migrant fluxes or a spatial-temporal mismatch in the processes sampled by the two approaches.

Given that the EXPORTS cruise occurred during the seasonal low in net silicic acid drawdown in the upper water column, we estimate the Ez₁₀₀ ratio for biogenic silica during the more productive spring and summer period for comparison. Timothy et al. (2013) measured the flux of biogenic silica from May through August at OSP to be 1.0 mmol Si m⁻² d⁻¹ at 200 m. To compare these rates to those measured during EXPORTS at 100 m, the 200 m rates must be corrected for the attenuation of the flux of biogenic silica between 100 and 200 m. Estapa et al. (2021) measured the ratio of the flux of biogenic silica at 200 m to that at 100 m to be 0.56 during EXPORTS. Applying that ratio to the 200 m flux measured by Timothy et al. (2013)

yields a rate of biogenic silica export during spring and summer at 100 m of 1.8 mmol Si m⁻² d⁻¹. That value is considerably higher than the average of 0.36 ± 0.28 mmol Si m⁻² d⁻¹ measured using traps during EXPORTS despite potential undercollection of particles by the relatively shallow moored conical traps employed by Timothy et al. (2013).

The Ez_{100} ratio for biogenic silica during the spring/summer period is then estimated using the gross silica production rates determined above for the spring through summer period of 11 mmol Si m⁻² d⁻¹. The resulting Ez_{100} ratio of $1.8 \div 11 = 0.16$ is three times lower than measured during EXPORTS. While only approximate, the lower value of the Ez_{100} ratio and the much higher rates of both Si production and biogenic silica export in the spring and summer imply a greater potential for both diatom biomass accumulation in surface waters and for higher opal export earlier in the year as has been documented in part during time-series trap studies (Wong et al., 1999; Timothy et al., 2013). We note that the lower silica production rates obtained by Lipsen (2008) using silicon-32 incubations in June of 1999 and 2000 (average 1.2 ± 0.9 mmol Si m⁻² d⁻¹) yield a correspondingly higher Ez_{100} ratio of 1.5. The estimate from climatological nutrient depletion is likely more representative given the potential for significant variability in daily silica production.

Diatom contribution to carbon fixation and export-

Wong and Matear (1999) estimate that in spring diatoms account for 35-51 % of phytoplankton carbon fixation at OSP. That estimate was obtained by converting net silicic acid depletion to diatom primary production using a Si:C of 0.27 citing Hutchins et al. (1998) as the source of the appropriate ratio in low Fe waters. Applying that same Si:C ratio to the net silica production measured on EXPORTS yields an average diatom carbon fixation across all profiles that is 4.6 ± 2.0 % (n = 9) of measured total carbon fixation reported by Stephens et al. (2021). A low percent contribution of diatoms to primary productivity is to be expected as bSi:POC mole ratios of particles in the euphotic zone averaged ~0.02 (Roca-Martí et al., 2021).

The measured flux of biogenic silica in traps at ~100 m averaged 0.36 mmol Si m⁻² d⁻¹ (Table 4) implying a maximum carbon export by diatoms of $0.36 \div 0.27 = 1.33$ mmol C m⁻² d⁻¹. That value nearly equals the average total organic carbon flux measured in traps, 1.38 ± 0.77 mmol C m⁻² d⁻¹ at 100 m (Estapa et al., 2021). A similar calculation using the silica export at 100 m measured by the 234 Th method, $0.73 \div 0.27 = 2.7$ mmol C m⁻² d⁻¹ (Roca-Martí et al., 2021), yields a diatom carbon export that exceeds the measured total carbon flux estimate from the 234 Th method of 2.01 \pm 0.56 mmol C m⁻² d⁻¹. The use of a Si:C ratio of 0.27 to make these estimates assumes that all diatom carbon export occurred as intact diatom cells; however, intact diatoms were only a minor fraction of exported cells (Durkin et al., 2021). A better average may be obtained from an examination of Si:C ratios in exported particles. The bSi:POC mole ratio in material sinking into traps at ~ 100 m, 0.29 ± 0.02 (Estapa et al., 2021), was ten-fold higher than the ratio in the euphotic zone, 0.02 (Roca-Martí et al., 2021), reflecting the more rapid remineralization of organic matter compared to opal. Assuming that diatom carbon decreased by ten-fold relative to diatom silica by 100 m lowers the estimated diatom carbon export from 1.33 mmol C m⁻² d⁻¹ to 0.13 mmol C m⁻² d⁻¹ for the estimate from traps, and from 2.7 mmol C m⁻² d⁻¹ to 0.27 mmol C m⁻² d⁻¹ for the estimate from ²³⁴Th which would make diatoms responsible for 9 - 13 % of total organic C export. That estimate of the contribution of diatoms to carbon export is two to three times greater than their estimated contribution to primary production (3-7% see above) and is consistent with prior observations that diatoms contribute more to C export than to

primary productivity in oligotrophic systems (Nelson and Brzezinski, 1997; Brzezinski et al., 2011b).

Regional comparisons -

As this is the first detailed study of the Si cycle in the subarctic Pacific it is valuable to compare the observations obtained to those in other HNLC and open-ocean systems. Table 5 compares the major elements of the silicon cycle at OSP to the HNLC regions of the Southern Ocean and Equatorial Pacific, and to Si cycling at other open ocean sites off Hawaii at station ALOHA and off Bermuda at the Bermuda Atlantic Time Series (BATS) site. A caveat of this exercise is that the parameter estimates for the Southern Ocean, BATS and ALOHA are based on seasonal to annual data, while much of the data for the equatorial Pacific and the subarctic Pacific are from fewer sampling events.

INSERT TABLE 5 HERE. PROVIDED AS SEPARATE FILE

The Southern Ocean dominates all other systems in terms of siliceous biomass, silica production and silica export (Table 5) and is thus largely excluded from further comparison. For the remaining regions, integrated biogenic silica concentrations at OSP exceed those in the subtropical gyres (ALOHA, BATS), but are less than in the upwelling zone of the eastern equatorial Pacific. Integrated silica production rates are intermediate with rates at OSP being most similar to those at BATS, but less that measured in the equatorial Pacific and greater than at ALOHA.

Si limitation at OSP occurred in only the small size fraction and affected the rate of Si uptake, but likely not growth rate. In contrast, substrate limitation of Si uptake is pervasive in the other three systems (Table 5), and occurs in both the Antarctic and Subantarctic sectors of the Southern Ocean (Franck et al., 2000; Nelson et al., 2001). Limitation of Si uptake is sufficiently severe at BATS that Si limitation of growth rate may occur (Brzezinski and Nelson, 1996). Size fractionated Si uptake rates are not available for the other systems, but experiments in the equatorial Pacific showed that the small Pseudo-nitzchia species that dominated the ambient diatom community were Si replete (Brzezinski et al., 2008; Brzezinski et al., 2011a) rather than being uptake limited as observed at OSP. Co-limitation of growth rate by Fe and Si uptake by Si occurs both at OSP (this study) and in the equatorial Pacific (Brzezinski et al., 2008; Brzezinski et al., 2011a), but the effect is observed for large diatoms in the equatorial Pacific while it was confined to small diatoms at OSP with the larger diatoms being solely limited by iron (Jenkins, pers. com.). Given that severe silicic acid depletion is rare at OSP (Wong and Matear, 1999) the unmet demand for Si by small diatoms appears held in check by iron limitation of their growth rates, which combined with the direct evidence for strong Fe, but not Si, limitation of larger diatoms (this study, Jenkins pers. com.; Martin and Fitzwater, 1988; Martin et al., 1994; Boyd et al., 1996) indicates that the northeastern subarctic Pacific is unique in that it is a true Fe-limited HNLC region while dynamics in all other low Fe regions are better described as High-Nitrate Low-Silicate Low-Chlorophyll (HNLSLC) (Wilkerson and Dugdale, 1996).

Of the four systems outside the Southern Ocean, the export of biogenic silica at OSP measured by both traps and 234 Th is the highest, with a high Ez ratio during EXPORTS that is similar to that at ALOHA (Table 5). Our indirect estimate of the Ez ratio during spring and summer, 0.16, falls to levels observed at BATS. Lower water temperatures may be a significant factor controlling the Ez ratio for opal at OSP. Water temperatures at OSP are more than $10\,^{\circ}$ C colder than at ALOHA or at BATS. Silica dissolution is highly temperature dependent with a Q_{10}

of between 2.2 and 2.6 (Kamatani and Riley, 1979; Kamatani, 1982; Natori et al., 2006) which would lead to dissolution rates in OSP surface waters that are less than half those in the two warmer systems. No direct measure of silica dissolution rates are available from OSP, but the average dissolution: production ratio (D:P) estimated from traps as (1 - Ez₁₀₀) of 0.44 implies that D:P at OSP is relatively low and similar to ALOHA which has been described as low productivity high export system (Brzezinski et al., 2011b). While slower rates of silica dissolution at lower temperatures may enhance opal preservation at OSP it clearly cannot explain the similarity in Ez between ALOHA and OSP. Overall, in comparison to the equatorial Pacific and the north Pacific and north Atlantic subtropical gyres, OSP is intermediate in biogenic silica concentration, intermediate in rates of silica production, but high relative to the magnitude and efficiency of biogenic silica export.

CONCLUSIONS

The upper ocean silica cycle in the subarctic Pacific near OSP was examined as part of the EXPORTS program. The conditions encountered were consistent with climatology and indicated that sampling occurred during the annual minimum in net silicic acid depletion in surface waters. Biogenic silica concentration was low being in the tens of nanomolar range. Rates of silica production were also low and more similar to those found in the subtropical gyres of the North Pacific and the North Atlantic than to other open-ocean HNLC regions. However, it is estimated that silica production rates may be ten times higher during the more productive spring and summer period.

A fair fraction of biogenic silica and Si uptake occurred in the $0.6-5.0~\mu m$ fraction, though on average the $>5.0~\mu m$ fraction dominated at 65% of biomass and 81% of Si uptake during EXPORTS. A bloom event appeared to occur after the EXPORTS cruise as revealed by sampling 12 days later aboard the *CCGS* Tully that showed strong increases in biogenic silica concentrations especially in the smaller size fraction, which became dominant.

Iron limitation of silica production and primary productivity was not detected in short-term experiments lasting 24 h, in contrast to longer-term grow outs during EXPORTS that reveled strong Fe limitation of both the large and small size fractions (Jenkins, per. com.). Si limitation of Si uptake was detected in the small, but not the large size fraction, potentially due to diatom reliance on diffusive transport under the experimental conditions. Indirect evidence points to the response in the small size fraction as being due to < 5.0 µm diatoms rather than to cyanobacteria or to larger diatoms that passed through the 5.0 µm filter. Those small diatom taxa appear to be co-limited with growth rate limited by Fe and Si uptake rate restricted by ambient silicic acid concentration as observed for large diatoms in the HNLC region of the equatorial Pacific. Exceptionally strong Fe-limitation of all diatoms in the subarctic Pacific may explain the lack of preferential draw down of silicic acid relative to nitrate at OSP (Wong and Matear, 1999) compared to other Fe-limited regions where it is common. The northeastern subarctic Pacific is thus unique, in that it is a true HNLC region with high concentrations of all macronutrients, including silicic acid.

About a third of the biogenic silica produced in the euphotic zone was exported through 100 m depth as estimated from sediment traps. Conditions at OSP most resembled those at station ALOHA off Hawaii in that OSP appeared as a low productivity, high export system relative to biogenic silica. However, the drivers of this pattern differ between the two regions with strong Fe limitation reducing production and colder temperatures lowering silica dissolution

at OSP and low silicic acid concentration and near permanent stratification lowering silica production at ALOHA with greater relative losses to dissolution in the warmer subtropical waters. The estimated contribution of diatoms to organic carbon export during EXPORTS (9 - 13 %) was disproportionately high compared to their estimated contribution to primary productivity (3 - 7 %) as has been observed in other oligotrophic systems (Nelson and Brzezinski, 1997).

References

- Assmy P, Smetacek V, Montresor M, Klaas C, Henjes J, et al. 2013. Thick-shelled, grazer-protected diatoms decouple ocean carbon and silicon cycles in the iron-limited Antarctic Circumpolar Current. *Proceedings of the National Academy of Sciences* **110**(51): 20633-20638. doi:10.1073/pnas.1309345110.
- Baines SB, Twining BS, Brzeinski MA, Krause JW, Vogt S, et al. 2011. Significant silicon accumulation by marine picocyanobacteria. *Natire Geoscience* **5**(12): 886-891.
- Baines SB, Twining BS, Brzeinski MA, Krause JW, Vogt S, et al. 2012. Significant silicon accumulation by marine picocyanobacteria *Nature Geosciences* **5**: 886-891.
- Boyd P, Harrison PJ. 1999. Phytoplankton dynamics in the NE subarctic Pacific. *Deep Sea Research Part II: Topical Studies in Oceanography* **46**(11): 2405-2432. doi:https://doi.org/10.1016/S0967-0645(99)00069-7.
- Boyd PW, Law CS. 2001. The Southern Ocean Iron RElease Experiment (SOIREE)-introduction and summary. *Deep Sea Research II* **48**: 2425-2438.
- Boyd PW, Muggli DL, Varela DE, Goldblatt RH, Chretien R, et al. 1996. In vitro iron enrichment experiments in the NE subarctic Pacific. *Mar Ecol Prog Ser* **136**: 179-193.
- Bruland KW, Rue EL, Smith GJ. 2001. Iron and macronutrients in California coastal upwelling regions: Implications for diatom blooms. *Limnol Oceanogr* **46**(7): 1661-1674.
- Bruland KW, Rue EL, Smith GJ, DiTullio GR. 2005. Iron, macronutrients and diatom blooms in the Peru upwelling regime: brown and blue waters of Peru. *Mar Chem* **93**(2–4): 81-103. doi:http://dx.doi.org/10.1016/j.marchem.2004.06.011.
- Brzezinski MA. 1986. Colorimetric determination of nanomolar concentrations of ammonium in seawater using solvent extraction. *Mar Chem* **20**: 277-288.
- Brzezinski MA, Baines SB, Balch WM, Beucher CP, Chai F, et al. 2011a. Co-limitation of diatoms by iron and silicic acid in the equatorial Pacific. *Deep Sea Research Part II: Topical Studies in Oceanography* **58**(3-4): 493-511.
- Brzezinski MA, Dummousseaud C, Krause JW, Mesasures CI, Nelson DM. 2008. Iron and silicic acid concentrations together regulate Si uptake in the equatorial Pacific Ocean. *Limnol Oceanogr* **53**(3): 875-889.
- Brzezinski MA, Krause JW, Baines SB, Collier JL, Ohnemus DC, et al. 2017. Patterns and regulation of silicon accumulation in Synechococcus spp. *J Phycol*: n/a-n/a. doi:10.1111/jpy.12545.
- Brzezinski MA, Krause JW, Church MJ, Karl DM, Li B, et al. 2011b. The annual silica cycle of the North Pacific subtropical gyre. *Deep Sea Research I* **58**: 988-1001.
- Brzezinski MA, Nelson DM. 1995. The annual silica cycle in the Sargasso Sea near Bermuda. *Deep-Sea Res I* **42**(7): 1215-1237.
- Brzezinski MA, Nelson DM. 1996. Chronic substrate limitation of silicic acid uptake rates in the western Sargasso Sea. *Deep-Sea Res II* **43**: 437-453.
- Brzezinski MA, Nelson DM, Franck VM, Sigmon DE. 2001. Silicon dynamics within an intense open-ocean diatom bloom in the Pacific sector of the Southern Ocean. *Deep-Sea Res II* **48**: 3997-4018.

- Brzezinski MA, Phillips DR. 1997. Evaluation of ³²Si as a tracer for measuring silica production rates in marine waters. *Limnol Oceanogr* **42**(5): 856-865.
- Brzezinski MA, Villareal TA, Lipschultz F. 1998. Silica production and the contribution of diatoms to new and primary production in the central North Pacific. *Mar Ecol Prog Ser* **167**: 89-104.
- Brzezinski MA, Washburn L. 2011. Phytoplankton primary productivity in the Santa Barbara Channel: Effects of wind-driven upwelling and mesoscale eddies. *Journal of Geophysical Research* **116**: C12013. doi:10.1029/2011JC007397.
- Buesseler KO, Ball L, Andrews J, Cochran JK, Hirschberg DJ, et al. 2001. Upper ocean export of particulate organic carbon and biogenic silica in the Southern Ocean along 170W. *Deep-Sea Res II* **48**(19-20): 4275-4297.
- Buesseler KO, Benitez-Nelson CR, Roca-Martí M, Wyatt A, Resplandy L, et al. 2020. High-resolution spatial and temporal measurements of particulate organic carbon flux using thorium-234 in the northeast Pacific Ocean during the EXport Processes in the Ocean from RemoTe Sensing field campaign. . *Elementa: Science of he Anthropocene* 8(1). doi:doi: 10.1525/elementa.030.
- Buesseler KO, Boyd PW. 2009. Shedding light on processes that control particle export and flux attenuation in the twilight zone of the open ocean. *Limnol Oceanogr* **54**(4): 1210-1232. doi:https://doi.org/10.4319/lo.2009.54.4.1210.
- Clemons MJ, Miller CB. 1984. Blooms of large diatoms in the oceanic, subarctic Pacific. *Deep Sea Research Part A Oceanographic Research Papers* **31**(1): 85-95. doi:https://doi.org/10.1016/0198-0149(84)90076-1.
- Coale KH, Fitzwarter. SE, Gordon RM, Johnson KS, Barber RT. 1996. Control of community growth and export production by upwelled iron in the equatorial Pacific Ocean. *Nature* **379**: 621-624.
- Dugdale RC, Wilkerson FP, Minas HJ. 1995. The role of a silicate pump in driving new production. *Deep Sea Research* **42**(5): 697-719.
- Dunne JP, Murray JW, Aufdenkampe AK, Blain S, Rodier M. 1999. Silicon-nitrogen coupling in the equatorial Pacific upwelling zone. *Global Biogeochem Cycles* **13**(3): 715-726. doi:https://doi.org/10.1029/1999GB900031.
- Durkin CA, Bender SJ, Chan KYK, Gasessner K, Gunbaum D, et al. 2012. Silicic acid supplied to coastal diatom communities influences cellular silicification and the potential export of carbon. *Limnol Oceanogr* **58**(2): 1707-1726. doi:10.4319/lo.2013.58.5.1707.
- Durkin CA, Buesseler KO, Cetinić I, Estapa ML, Kelly RP, et al. 2021. A visual tour of carbon export by sinking particles. *bioRxiv*: 2021.02.16.431317. doi:10.1101/2021.02.16.431317.
- Estapa M, Buesseler K, Durkin CA, Omand M, Benitez-Nelson CR, et al. 2021. Biogenic sinking particle fluxes and sediment trap collection efficiency at Ocean Station Papa. *Elementa: Science of the Anthropocene* **9**(1). doi:10.1525/elementa.2020.00122.
- Franck VM, Brzezinski MA, Coale KH, Nelson DM. 2000. Iron and silicic acid concentrations regulate Si uptake north and south of the Polar Frontal Zone in the Pacific Sector of the Southern Ocean. *Deep-Sea Res II* 47(15-16): 3315-3338.
- Harrison PJ. 2002. Station Papa Time Series: Insights into Ecosystem Dynamics. *Journal of Oceanography* **58**(2): 259-264. doi:10.1023/a:1015857624562.
- Hoffman LJ, Peeken I, Lochte K, Assmy P, Veldhuis M. 2006. Different reactions of Southern Ocean phytoplankton size clases to iron fertilization. *Limnol Oceanogr* **51**(3): 1217-1229.

- Honjo S, Manganini SJ, Krishfield RA, Francois R. 2008. Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global sediment trap programs since 1983. *Progress in Oceanography* **76**(3): 217-285. doi:https://doi.org/10.1016/j.pocean.2007.11.003.
- Hutchins DA, Bruland KW. 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. *Nature* **393**: 561-564.
- Hutchins DA, DiTullio GR, Zhang Y, Bruland KW. 1998. An iron limitation mosaic in the California upwelling regime. *Limnol Oceanogr* **43**(6): 1037-1054.
- Ichinomiya M, dos Santos AL, Gourvil P, Yoshikawa S, Kamiya M, et al. 2016. Diversity and oceanic distribution of the Parmales (Bolidophyceae), a picoplanktonic group closely related to diatoms. *The ISME Journal* **10**(10): 2419-2434. doi:10.1038/ismej.2016.38.
- Kamatani A. 1982. Dissolution rates of silica from diatoms decomposing at various temperatures. *Mar Biol* **68**: 91-96.
- Kamatani A, Riley JP. 1979. Rate of dissolution of diatom silica walls in seawater. *Mar Biol* **55**: 29-35.
- Krause JW, Brzezinski MA, Baines SB, Collier JL, Twining BS, et al. 2017. Picoplankton contribution to biogenic silica stocks and production rates in the Sargasso Sea. *Global Biogeochem Cycles* **31**(5): 762-774. doi:10.1002/2017gb005619.
- Krause JW, Brzezinski MA, Jones JL. 2011a. Application of low-level beta counting of ³²Si for the measurement of silica production rates in aquatic environments. *Mar Chem* **127**: 40-47.
- Krause JW, Brzezinski MA, Landry MR, Baines SB, Nelson DM, et al. 2010. The effects of biogenic silica detritus, zooplankton grazing, and diatom size structure on silicon cycling in the euphotic zone of the eastern equatorial Pacific. *Limnol Oceanogr* **55**(6): 2608-2622.
- Krause JW, Nelson DM, Brzezinski MA. 2011b. Biogenic silica production and the diatom contribution to primary production and nitrate uptake in the eastern equatorial Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* **58**(3-4): 434-448.
- Krause JW, Nelson DM, Lomas MW. 2009. Biogeochemical responses to late-winter storms in the Sargasso Sea, II: Increased rates of biogenic silica production and export. *Deep Sea Research Part I: Oceanographic Research Papers* **56**(6): 861-874.
- Leblanc K, Cornet V, Rimmelin-Maury P, Grosso O, Hélias-Nunige S, et al. 2018. Silicon cycle in the tropical South Pacific: contribution to the global Si cycle and evidence for an active pico-sized siliceous plankton. *Biogeosciences* **15**(18): 5595-5620. doi:10.5194/bg-15-5595-2018.
- Lipsen MS. 2008. Phytoplankton dynamics in the northeast subarctic Pacific during the 1998 El Niño, the 1999 La Niña and 2000 with special consideration to the role of coccolithophores and diatoms [Text]. University of British Columbia, Botany. Available at https://open.library.ubc.ca/collections/24/items/1.0066372.
- Marchetti A, Harrison PJ. 2007. Coupled changes in the cell morphology and the elemental (C, N and Si) composition of the pennate diatom *Pseudo-nitzschia* due to iron deficiency. *Limnol Oceanogr* **52**(5): 2270-2284.
- Marchetti A, Juneau P, Whitney FA, Wong C-S, Harrison PJ. 2006a. Phytoplankton processes during a mesoscale iron enrichment in the NE subarctic Pacific: Part II—Nutrient utilization. *Deep Sea Research Part II: Topical Studies in Oceanography* **53**(20): 2114-2130. doi:https://doi.org/10.1016/j.dsr2.2006.05.031.

- Marchetti A, Lundholm N, Kotaki Y, Hubbard K, Harrison PJ, et al. 2008. Identification and assessment of domoic acid production in oceanic *Pseudonitzschia* (Bacillariophycaea) form iron-limited wayers in the northeast subarctic Pacific 1. *J Phycol* 44(3): 650-661. doi:https://doi.org/10.1111/j.1529-8817.2008.00526.x.
- Marchetti A, Sherry ND, Kiyosawa H, Tsuda A, Harrison PJ. 2006b. Phytoplankton processes during a mesoscale iron enrichment in the NE subarctic Pacific: Part I—Biomass and assemblage. *Deep Sea Research Part II: Topical Studies in Oceanography* **53**(20): 2095-2113. doi:https://doi.org/10.1016/j.dsr2.2006.05.038.
- Marchetti A, Varela DE, Lance VP, Johnson Z, Palmucci M, et al. 2010. Iron and silicic acid effects on phytoplankton productivity, diversity, and chemical composition in the equatorial Pacific Ocean. *Limnology and Oceanography Methods* **55**(1): 11-29.
- Martin-Jézéquel V, Hildebrand M, Brzezinski MA. 2000. Silicon metabolism in diatoms: Implications for growth. *J Phycol* **36**(5): 821-840.
- Martin JH, Coale KH, Johnson KS, Fitzwater SE, Gordon RM, et al. 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* **371**: 123-129.
- Martin JH, Fitzwater SE. 1988. Iron deficiency limits phytoplankton growth in the north-east Subarctic Pacific. *Nature* **331**: 341-343.
- Milligan AJ, Varela DE, Brzezinski MA, Morel FMM. 2004. Dynamics of silicon metabolism and silicon isotopic discrimination in a marine diatom as a function of pCO₂. *Limnol Oceanogr* **49**(2): 322-329.
- Natori Y, Haneda A, Suzuki Y. 2006. Vertical and seasonal differences in biogenic silica dissolution in natural seawater in Suruga Bay, Japan: Effects of temperature and organic matter. *Mar Chem* **102**(3): 230-241. doi:https://doi.org/10.1016/j.marchem.2006.04.007.
- Nelson DM. 1975. Uptake and regeneration of silicic acid by marine phytoplankton [Ph.D. Dissertation]. Fairbanks: University of Alaska.
- Nelson DM, Brzezinski MA. 1997. Diatom growth and productivity in an oligotrophic midocean gyre: A 3-yr record from the Sargasso Sea near Bermuda. *Limnol Oceanogr* **42**(3): 473-486.
- Nelson DM, Brzezinski MA, Sigmon DE, Franck VM. 2001. A seasonal progression of Si limitation in the Pacific sector of the Southern Ocean. *Deep-Sea Res II* **48**: 3973-3995.
- Nishioka J, Obata H. 2017. Dissolved iron distribution in the western and central subarctic Pacific: HNLC water formation and biogeochemical processes. *Limnol Oceanogr* **62**(5): 2004-2022. doi:https://doi.org/10.1002/lno.10548.
- Ohnemus DC, Rauschenberg S, Krause JW, Brzezinski MA, Collier JL, et al. 2016. Silicon content of individual cells of Synechococcus from the North Atlantic Ocean. *Mar Chem* **187**: 16-24. doi:10.1016/j.marchem.2016.10.003.
- Peña MA, Varela DE. 2007. Seasonal and interannual variability in phytoplankton and nutrient dynamics along Line P in the NE subarctic Pacific. *Progress in Oceanography* **75**(2): 200-222. doi:https://doi.org/10.1016/j.pocean.2007.08.009.
- Roca-Martí M, Benitez-Nelson CR, Umhau BP, Wyatt AM, Clevenger SJ, et al. 2021. Concentrations, ratios, and sinking fluxes of major bioelements at Ocean Station Papa. *Elementa: Science of the Anthropocene* **9**(1). doi:10.1525/elementa.2020.00166.
- Sarmiento JL, Brzezinski MA, Gruber N, Dunne JP. 2004. High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature* **427**: 56-60.
- Shrestha RP, Hildebrand M. 2015. Evidence for a regulatory role of diatom silicon transporters in cellular silicon responses *Eukaryotic Cell* **14**(1): 29-40. doi:doi:10.1128/EC.00209-14.

- Shrestha RP, Tesson B, Norden-Krichmar T, Federowicz S, Hildebrand M, et al. 2012. Whole transcriptome analysis of the silicon response of the diatom Thalassiosira pseudonana. *BMC Genomics* **13**(1): 499. doi:10.1186/1471-2164-13-499.
- Siegel DA, Cetinić I, Graff JR, Lee CM, Nelson N, et al. 2021. An operational overview of the EXport Processes in the Ocean from RemoTe Sensing (EXPORTS) Northeast Pacific field deployment. *Elementa: Science of the Anthropocene* **9**(1). doi:10.1525/elementa.2020.00107.
- Stephens BM, Fox J., Liu S, Halsey KH, Carlson CA. 2021. Bacterial production, biomass and community composition influenced by amino acids at the subarctic Pacific's Ocean Station Papa. *Elementa: Science of the Anthropocene*. Submitted.
- Strickland JDH, Parsons TR. 1972. <u>A Practical Handbook of Seawater Analysis</u> 2 nd. Ottowa, Canada: <u>Fish</u>. <u>Res</u>. <u>Bd</u>. <u>Can</u>. bull.
- Takeda S. 1998. Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. *Nature* **393**(6687): 774-777.
- Timothy DA, Wong CS, Barwell-Clarke JE, Page JS, White LA, et al. 2013. Climatology of sediment flux and composition in the subarctic Northeast Pacific Ocean with biogeochemical implications. *Progress in Oceanography* **116**: 95-129. doi:https://doi.org/10.1016/j.pocean.2013.06.017.
- Tortell PD, Maldonado MT, Granger J, Price NM. 1999. Marine bacteria and biogeochemical cycling of iron in the oceans. *FEMS Microbiol Ecol* **29**(1): 1-11. doi:10.1111/j.1574-6941.1999.tb00593.x.
- Tréguer PJ, De La Rocha CL. 2013. The World Ocean Silica Cycle. *Annual Review of Marine Science* **5**: 477-501. doi:10.1146/annurev-marine-121211-172346.
- Wei Y, Zhang Z, Cui Z, Sun J. 2021. Size-Fractionated Biogenic Silica Standing Stocks and Carbon Biomass in the Western Tropical North Pacific: Evidence for the Ecological Importance of Pico-Sized Plankton in Oligotrophic Gyres. *Frontiers in Marine Science* 8: 1058.
- Whitney FA, Freeland HJ. 1999. Variability in upper-ocean water properties in the NE Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography* **46**(11): 2351-2370. doi:https://doi.org/10.1016/S0967-0645(99)00067-3.
- Wilkerson FP, Dugdale RC. 1996. Silicate versus nitrate limitation in the equatorial Pacific estimated from satellite-derived sea-surface temperatures. *Advances in Space Research* **18**(7): 81-89. doi:https://doi.org/10.1016/0273-1177(95)00951-5.
- Wong CS, Matear RJ. 1999. Sporadic silicate limitation of phytoplankton productivity in the subarctic NE Pacific. *Deep-Sea Res* **46**(11 / 12): 2539.
- Wong CS, Whitney FA, Crawford DW, Iseki K, Matear RJ, et al. 1999. Seasonal and interannual variability in particle fluxes of carbon, nitrogen and silicon from time series of sediment traps at Ocean Station P, 1982–1993: relationship to changes in subarctic primary productivity. *Deep Sea Research Part II: Topical Studies in Oceanography* **46**(11): 2735–2760. doi:https://doi.org/10.1016/S0967-0645(99)00082-X.

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Contributed to acquisition of data: SMK, JLJ, MAB, BDJ, KNB, DEV.

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Competing interests

The authors declare that they have no conflict of interest.

Data accessibility statement

Data sets used in this paper can be found at: EXPORTS, 2018, SeaBASS, DOI:http://dx.doi.org/10.5067/SeaBASS/EXPORTS/DATA001. EXPORTS, 2018., BCO-DMO, https://www.bco-dmo.org/program/757397. DataVerse, https://dataverse.scholarsportal.info/ privateurl.xhtml?token=f93ba246-9955-48cc-8bf9-21e7312db9a8.

Figure Legends:

Figure 1. Depth profiles of dissolved and particulate silicon. Depth profiles of the concentrations of: A. Silicic acid from R/V Revelle sampled using the trace - metal clean rosette (brown squares) or the conventional rosette (brown circles), form R/V Ride (blue circles) and CCGS Tully (green triangles); B. Biogenic silica from R/V Revelle (brown squares), R/V Ride (blue circles), and CCGS Tully (green triangles).

Figure 2. Spatial distribution of dissolved and particulate silicon. Spatial maps of: A) The average silicic acid concentration in the upper 20 m from R/V Ride (red circles) and R/V Revelle (black circles) and B) The integrated biogenic silica concentration in the upper 70 m from R/V Ride (red circles) and R/V Revelle (black circles). Parameter values are proportional to circle diameter with a reference circle illustrated in each panel. Panels C and D show frequency histograms of the data from R/V Revelle (black bars) and R/V Ride (open bars), respectively that is depicted spatially in A and B, respectively.

Figure 3. Profiles of silicic acid concentration from casts where silica production was measured. Profiles of silicic acid concentration obtained in parallel with profiles of silica production rate from R/V Revelle. Legend indicates the epoch (E) day with the 8-day epoch (D) for each cast listed in Table 2.

Figure 4. Profiles of size fractionated siliceous biomass and silica production rates. Profiles of biogenic silica concentrations, silica production rates, and the specific rate of silica production in the $0.6-5.0~\mu m$ size class (left hand panels) and in the $>5.0~\mu m$ size fraction (right hand panels). Legend indicates the epoch (E) and epoch sequence day with the 8-day epoch (D) for each cast listed in Table 2.

Figure 5. Comparison of the specific rate of silica production in the small and large size classes. The ratio of the specific rate of silica production, V_b , in the small to that in the large size fraction (black circles) and the percent of total silica production occurring in the small size fraction (orange circles), both as a function of light level in the upper water column. Uncertainty bars are ± 1 standard deviation.

Figure 6. Temporal changes. Time course of A) Upper 70 m average silicic acid concentration and average biogenic silica concentration in the small size fraction, in the large size fraction and in the sum of the two fractions; and B) Integrated rates of silica production in the small size fraction, in the large size fraction and in the sum of the two fractions. Vertical lines denote the boundaries between the three epochs. Sampling on year day 227 and 228 was in water type 1 with all other sampling within water type 2.

Figure 7. Assessment of silicon and iron limitation. The ratio of the response in the specific rate of silica production (V_b) and of primary production (PP) in the large and small size fractions in experimental treatments versus the controls for additions of silicic acid (+Si), iron (+Fe) and both silicic acid and iron (+Si) and +Fe) at the 40% and 15% light depths. Uncertainty bars are standard errors. Asterisks indicate a significant response in treatments relative to controls. Horizontal line indicates a ratio of 1 denoting the expectation with no effect of treatments.

Table 1. Intercalibration of depth-integrated biogenic silica concentration (bSi) and silicic acid concentration (DSi) between the R/V Sally Ride and R/V Roger Revelle

				R/V Ride			<i>R/V</i> Revelle	Ratio Ride:Revelle		
Epoch/Day	Year Day	Distance (km)	Water Type	bSi (nmol L ⁻¹)	DSi (μM)	Water Type	bSi (nmol L ⁻¹)	DSi (μM)	bSi	DSi
E1/D2	228	17.4	1	311	13.7	2	46	12.3	6.72	1.12
E2/D6	240	12.4	2	123	14.8	2	124	16.1	0.99	0.91
E3/D2	244	14.4	2	187	15.2	2	96	16.4	1.95	0.93
E3/D4	246	5.7	2	179	12.1	2	81	17.5	2.22	0.69

Table 2. Silicic acid concentration (DSi), biogenic silica concentration (bSi) and silica production rates from the trace metal rosette casts aboard R/V Revelle and comparison of mean values among ships. Uncertainty terms are standard deviation.

Epoch/Day	Year Day	Water Type	DSi (μM)	Integrate	ed bSi (mm	ol Si m ⁻²)		ted Silica Prod (mmol Si m ⁻² d		Dept	h Normalized \mathbf{V}_{b}	(d ⁻¹)		% > 5 μι	m	V _b ratio Large:Small
				Total	0.6-5.0 μm	>5.0 μm	Total	0.6-5.0 μm	>5.0 μm	>0.6 μm	0.6-5.0 μm	>5.0 µm	bSi	ρ	Vb	
R/V Revelle																
E1/D2	228	2	12.3	3.2	2.7	0.5	0.50	0.07	0.43	0.160	0.039	0.759	17	85	475	19.5
E1/D8	234	2	12.6	5.0	1.6	3.4	0.25	0.05	0.20	0.051	0.030	0.033	69	81	65	1.1
E2/D2	236	2	15.1	5.5	1.2	4.4	0.49	0.06	0.42	0.026	0.038	0.048	79	87	183	1.3
E2/D4	238	2	16.0	4.4	1.3	3.1	0.51	0.12	0.39	0.051	0.060	0.054	71	76	105	0.9
E2/D6	240	2	16.1	8.7	3.1	5.6	0.62	0.09	0.53	0.032	0.029	0.040	64	86	124	1.4
E2/D8	242	2	16.3	9.4	2.2	7.2	0.58	0.10	0.48	0.021	0.045	0.016	77	83	76	0.4
E3/D2	244	2	16.4	6.7	2.5	4.2	1.19	0.23	0.96	0.082	0.038	0.109	63	80	132	2.9
E3/D4	246	2	17.5	5.6	1.5	4.2	0.76	0.10	0.66	0.100	0.075	0.109	74	86	109	1.5
E3/D8	250	3	16.2	9.1	2.5	6.6	0.66	0.21	0.45	0.046	0.101	0.026	72	68	57	0.3
Means:																
R/V Revelle			15.4 ± 1.8	6.4 ± 2.2	2.1 ± 0.7	4.4 ± 2.0	618 ± 257	0.12 ± 0.06	0.50 ± 0.21	0.063 ± 0.044	0.050 ± 0.024	0.133 ± 0.237	65 ± 19	81 ± 6	147 ± 129	3.2 ± 6.1
R/V Ride			13.4 ± 2.1	8.3 ± 4.6												
CCGS Tully			16.2	18.4	11.7	6.7										

Table 5. A comparison of silicon cycling in the North Atlantic Subtropical gyre at the BATS station, in the North Pacific Subtropical Gyre at station ALOHA, in the equatorial Pacific, at OSP, and in the Southern Ocean. Values are means $(\pm SD)$, with ranges in parentheses when available

	BATS	ALOHA	OSP	Eq. Pacific	Southern Ocean
Dissolved Si					
[Si(OH) ₄] (µM) (upper 50 m)	$0.82 \pm 0.21 \ (0.4 - 2.6)$	$1.04 \pm 0.17 \ (0.6 - 1.6)$	$14.4 \pm 2.5 \ (8.4 - 18.9)$	4.38 ± 1.38	1 - 60
Particulate Silica					
[bSiO ₂] (nmol Si L ⁻¹)	$27 \pm 52 (2 - 584)$	$16 \pm 14 (3 - 163)^d$	$121 \pm 102 (14 - 532)$	96 (18-268)	100 – 16,000
∫bSiO ₂ (mmol Si m ⁻²)	4.0 ± 6.8^{a}	$3.0 \pm 1.1 \ (1.8 - 6.2)^{a, d}$	$8.0 \pm 4.3 \ (1.8 - 21.8)$	10.08 ± 2.85	100 - 418
Silica Production					
ρ (nmol Si L ⁻¹ h ⁻¹)	$2.6 \pm 2.4 \ (0.0 - 19.6)$	$1.4 \pm 2.5 \; (\; 0.0 \; -29.7)$	$3.2 \pm 3.7 (0.1 - 47)$		250 - 1500
∫ρ (mmol Si m ⁻² d ⁻¹)	$0.42 \pm 0.22 \ (0.10 - 0.93)^{b}$	$0.19 \pm 0.11 \ (0.090 - 0.49)^a$	$0.62 \pm 0.26 \ (0.25 - 1.19)$	1.44 ± 0.06	5.5 - 27.5
		$0.18 \pm 0.11 \ (0.090 \text{-} 0.48)^{\text{b}}$			
V_b (d-1)	$0.15 \pm 0.15 (0 - 1.11)$	$0.07 \pm 0.02 \ (0.04 \text{-} 0.14)$	$0.06 \pm 0.04 \ (0.02 - 0.16)$	0.14 ± 0.05	0.05 - 0.2
Annual production (mmol Si m ⁻² a ⁻¹)	239	63			2426 ± 689
Si Limitation					
V_b/V_m	(<0.12 – 0.16)°	0.43 ± 0.21^{e}		0.63 ± 0.13	
		0.35± 0.11 ^f			
Enh (=Vm/V)		$2.6\pm0.9^{\rm e}$	1.77- 2.88 (0.6-5μm)		1.0 - ~4
			1.1 - 1.89 (>5 μm)		
		$3.2 \pm 1.2^{\rm f}$			
Silica Dissolution					
$\int \rho_{diss}$ (mmol Si m ⁻² d ⁻¹)	0.34	0.087 ^b			
∫D:∫P	0.82	0.46 ^b	0.44 to -0.33	0.84 blain	0.23 -0.67
Silica Export					
bSiO ₂ export (mmol Si m ⁻² d ⁻¹)	$0.098 \pm 0.13 \ (0.017 \ 0.70)$	$0.091 \pm 0.061 \ (0.014 - 0.30)$	0.34 ± 0.26 (sediment traps)	0.1 – 1.9	1.5 - 11
			$0.83 \pm 0.24 (^{234}\text{Th})$		
1 - ∫D:∫P (new Si production ratio)	$0.18 \pm 0.13 \; (0.03 \text{-} 0.44)$	$0.54 \pm 0.19 \ (0.13 - 0.90)$			
Annual bSiO ₂ export (mmol Si m ⁻² a ⁻¹)	32	33		214 ± 117	
Ez ratio	0.18	0.54	56 ± 15 (EXPORTS)	0.16	0.27 -1.89
			0.16 ^g		
Diatom contribution					
% primary production by diatoms	15-25	3-7	3 - 7		
% POC export by diatoms	~30	9-20	9 - 13		

a depth of integration 175 m

b depth of integration 150m

c from Brzezinski and Nelson (1996)

d October 1996 – December 2009

e annual average (includes bloom and non-bloom conditions)

f average for non-bloom condition

g Estimated from Timothy et al (2013)

Data Sources: North Atlantic Subtropical gyre at the BATS station (Brzezinski and Nelson, 1995; 1996; Nelson and Brzezinski, 1997), the North Pacific Subtropical Gyre at station ALOHA (Brzezinski et al., 1998), the equatorial Pacific (Dunne et al., 1999; Brzezinski et al., 2008; Honjo et al., 2008; Brzezinski et al., 2011a; Krause et al., 2011b), at OSP (Lipsen, 2008; this study) and in the Southern Ocean (Brzezinski et al., 2001; Buesseler et al., 2001; Nelson et al., 2001).















