

Below, we address comments from Reviewer 1 (RC1), and Reviewer 2 (RC2). We cluster each comment and separate them as “1” Reviewer comments, “2,3” are responses and revisions.

REVIEWER 1

1) The manuscript of Krause *et al.* presents interesting results concerning biogenic silica production and export levels as well as estimates of kinetic constants from an opportunistic sampling near the Svalbard Archipelago in the Arctic Ocean by late spring. The data presented are the first direct (silicon-32 method) measurements of biogenic silica production in the Arctic Ocean, which in themselves deserve publication. From these data, the authors then attempt to establish the potential control of diatom production by the availability of silicic acid as well as the contribution of diatoms to total primary production. However, I think the authors are pushing their limited data set much too far and that the manuscript should be shortened by getting more concise.

2,3) We thank the reviewer for the constructive criticism, these have strengthened the manuscript. Below, we address the concerns. The revisions are aimed to both address these issues and make the manuscript more concise.

1) Firstly, I find it difficult to understand why the authors focus on the so-called Egge & Aksnes 2 μM H_4SiO_4 threshold value, as it is clear that the data from this publication have been wrongly interpreted in several past publications (which is recognized by the authors besides).

2,3) We agree with the reviewer and the focus on this apparent threshold value is due to its wide use in the field. As of August 2018, the Egge & Aksnes (1992) manuscript has been cited over 700 times, and many explicitly regard this 2 μM threshold for diatom microplankton dominance among many systems. This type of prose has been reduced (now just in the discussion (line 480)); however, given this is the threshold embraced by the community it must be acknowledged.

1) I suggest just using their kinetic values to discuss the potential limitation of diatom uptake by H_4SiO_4 availability, and then shortly discuss hypotheses for growth limitation, which is another point not directly assessed in this study. ON the other hand, authors might consider that the actual limitation starts under 2 times K_S .

2,3) The original version discusses kinetic limitation between lines 434 to 455, followed by a section discussing the possibility that silicic acid may be low enough to limit diatom growth (line 459 – 462). If we interpret the reviewer correctly, then “under 2 times K_S ” (i.e. half of the half-saturation constant) is the silicic acid concentration when uptake (i.e. V_b) is 25% of maximum uptake (i.e. V_{max}) which is the same metric we use to diagnose potential growth limitation (line 461). We have made this clearer (e.g. denote the equivalence of “under 2 times K_S ” and $V_b/V_{max} < 0.25$) in the revision (line 473-474).

1) The comparison between nitrate and silicic acid concentrations is not very clear. First, they mention a 2.5 slope (Figure 5) between nitrate and silicic acid, which means that nitrate is taken up 2.5 times faster than silicic acid, and then authors take a 1:1 ratio to discuss the potential for silicic acid limitation. I can imagine that they are trying to decipher the relative contribution of siliceous vs. non-siliceous (e.g. *Phaeocystis*) components of the phytoplankton community but this should be clearly indicated. On top of that, the use of a 1:1 Si:N ratio is questionable (large species-specific variations, see below for Si:C).

2,3) The approach silicic acid versus nitrate drawdown has been used elsewhere (Monterey

Bay, Brzezinski et al. 1997; Barents Sea, Rey et al. 1987; Southern Ocean diatom cultures, Takeda 1998). We agree with the reviewer that this nutrient data includes drawdown of nitrate from other organisms, likely *Phaeocystis*, hence the slope exceeds 1 (i.e. nitrate drawn down faster than silicic acid). Most polar culture work focuses on Fe-limitation (e.g. Takeda 1988, Nature) and Southern Ocean clones; however, under Fe-replete conditions Takeda (1998) reported Si:N between 0.73 (*Chaetoceros dichaeta*) and 1.2 (*Nitzschia* sp.), the average among these clones is 0.97, not unlike the 1:1 ratio from Brzezinski 1985. In the revision, we make this point with more clarity and provide the Takeda (1998) study as a literature basis for the 1:1 ratio (beyond the canonical Brzezinski stoichiometry) and also include new culture data in review (Lomas et al., which Krause is co-author on this manuscript) which examined 11 polar diatom clones (lines 416-424).

1) The contribution of diatoms to primary production is also another weak point of the ms. The calculation is based on a transformation of rSi to rC by using the average Brzezinski' ratio of 0.13. This is a very simplistic way of addressing this important question as this ratio is known to be subject to large species-specific variations (e.g. Brzezinski gives a Si:C biomass range of 0.15 ± 0.04 for large diatoms, which could result in a ~2 times range for rC estimates). This is somehow risky business and should, at least, be acknowledged and discussed.

2,3) As with the previous point, we agree that there is variability within the stoichiometry. While admittedly simplistic, we also have coarse resolution ($n = 6$ coupled measurements), which (in our opinion) do not merit as sophisticated approach given it would not be robust; this data coupling was serendipitous (hence the low n value) but does provide a first-order estimate. We have used the Lomas et al. (in review) diatom Si:C ratios (see methods, lines 218-223), which changed the magnitude of the estimates but not the general interpretations: 1) diatoms quantitative contribution to primary production is “boom and bust” and 2) even when diatom biomass is relatively low, their contribution to production can still be quantitatively important (e.g. 25%). Additionally, the new analysis is potentially conservative (line 510) given any movement of the Si:C ratio used toward the canonical Brzezinski ration increases the proportion of production attributed to diatoms.

1) Finally, the authors present data for direct diatom cell export but the underlying issue is not clearly stated: Do they want to compare direct diatom sedimentation by mass sinking to other export vectors such as repackaging? If yes this should be clearly stressed.

2,3) The reviewer's interpretation of our intent is correct, we suggest that the reason why cellular export is similar to previous studies, despite biogenic silica export being higher than other studies, is consistent with repackaging which we termed “food web effect.” We have revised this for clarification (paragraph starting on line 577).

1) line 28 : "diatom cellular export" – the wording is misleading (could be export from a diatom cell). I'd rather use "export of diatom cells".

2,3) Changed as suggested, here and in other places.

1) line 65 : " A more recent analysis demonstrated a decline in pre-bloom $[\text{Si}(\text{OH})_4]$ concentrations by 1–2 μM across the north Atlantic subpolar and polar regions over the last 25 years (Hátún *et al.*, 2017); this is consistent with the general Arctic region being a net exporter of silicic acid (Torres-Valdés *et al.*, 2013)." – I don't see the consistence between the decrease of H_4SiO_4 concentrations and the net exportation of this nutrient; please rephrase.

2,3) This is rephrased, e.g. removing “this is consistent with the general Arctic region being a

net exporter of silicic acid (Torres-Valdés *et al.*, 2013)” (now line 67).

1) line 68: " This is in stark contrast to the 10–60 μM $[\text{Si}(\text{OH})_4]$ observed in the surface waters of the Southern Ocean and the marginal ice zone around Antarctica (Nelson and Gordon, 1982; Brzezinski *et al.*, 2001), where $[\text{Si}(\text{OH})_4]$ is unlikely to limit the rate of diatom production or biomass yield." – I disagree; There are ample references to state that actually the reverse is true, due to sometimes unusual high KS (e.g. Nelson & Tréguer MEPS 1992, Nelson *et al.* DSR II 2001, Mosseri *et al.* DSR II 2008).

2,3) The reviewer is correct as kinetic limitation (i.e. ambient silicic acid limits the rate of diatom silica production) is clearly observed in the Southern Ocean. Our intent (which was not clearly conveyed) was to contrast the effects of the high silicic acid in the Southern Ocean vs. the Arctic. This is rephrased "... where $[\text{Si}(\text{OH})_4]$ is unlikely to limit diatom growth unless iron is replete, and stimulates exceptional blooms which consume Si, or assemblages are highly inefficient for Si uptake." (line 69-71).

1) line 76: " ... and a 2 μM threshold $[\text{Si}(\text{OH})_4]$ defines where diatoms are outcompeted by flagellates (Egge and Aksnes, 1992)." – I strongly disagree with that sentence. The work of Egge and Aksnes did not evidence any real threshold (no kinetic values measured) and just merely indicated areas of realized niches for diatom vs. flagellates with regards to Si vs. P availability. Please do not cite this reference in such a way that was even not addressed by the authors of this paper. + as indicated above.

2,3) We agree with the reviewer, especially in the lack of physiological data used in the original study to assess a threshold silicic acid; please see reply to general comment. We have revised by using more specific language “Egge and Aksnes (1992) data set shows diatoms may be outcompeted by flagellates when $[\text{Si}(\text{OH})_4] < 2 \mu\text{M}$, a value which is more reflective of an ecological niche opposed to a physiological threshold as has been purported in numerous citations of these data.” (line 480-483).

1) line 137: "... suggesting that N was likely more important than P for primary production." – As authors refer to absolute concentrations, the correct phrasing should be: "... suggesting that N was likely more important than P for potentially limiting primary production."

2,3) Changed as suggested.

1) line 138: "These phosphate data are not discussed." – Even though a range would be welcome.

2,3) Revised line 145 (e.g. “These phosphate data (0.1 – 0.6 μM in the upper 50 m) are not discussed.”)

1) line 153: "... fixed with an aldehyde mixture of hexamethylenetetramine-buffered formaldehyde and glutaraldehyde at 0.1 and 1% final concentration, respectively, as suggested by Tsuji and Yanagita (1981) ..." – although this should be OK this is not the usual fixative for diatoms (acidic Lugol preferred), partly due to its toxicity for the microscopical examiner.

2,3) Agreed. Given the interdisciplinary nature of the cruise and the lack of excess operation time, this fixative was used by the Norwegian Bølar Institute group to examine a wide range of protist groups from one sample; these other protist groups are beyond the scope of this communication.

1) line 164: "... neutral density screened bags ..." – please mention the photometric levels used.

2,3) Added "... neutral density screened bags simulating 50%, 20% and 1% of irradiance just below the surface." (line 171)

1) line 207: "Export rates were calculated using the standing stock measurements, length of deployment, and trap opening area." – Please give the model/type of sediment trap.

2,3) Added "KC Denmark design (outer diameter 72 mm, length 450 mm)." (line 127)

1) line 260: "... except for the Hinlopen ice algae, where the melt water ..." – Is that naturally-melted ice or meltwater produced by ice melting in the lab? Please clarify.

2,3) Thank you for the question, this has been clarified, e.g. "... water, which was melted at ambient air temperature on the vessel ..." (line 277).

1) Line 331: "Brown *et al.*, 2003" – Comment: For some strange reason L. Brown's incubations lasted for only 6 hours, which renders her production results questionable.

2,3) We agree with the reviewer; however, given the limited data from the Northeast Atlantic, we prefer to be thorough and include the Brown *et al.* publication here.

1) line 339: "... Varela *et al.* (2013) recently reported that [Si(OH)₄] in surface waters (>5 μM) are unlikely to be significantly limiting to diatoms in any sector of the Bering, Chukchi or Beaufort Sea regions." – Although for Subarctic waters Brown *et al.* (2003, mentioned just above) kinetic experiments show a strong limitation (non-saturating kinetics) up to 30 μM.

2,3) We agree with the reviewer; however, the goal of this sentence is to isolate the Canadian- & United-States Arctic waters with the European Arctic waters. We add the Brown *et al.* (2003) kinetic data in a section below (e.g. with Allen *et al.* 2005, Kristiansen *et al.* 2001 discussion in the paragraph starting at line 445).

1) line 387: "Suboptimal silicon availability affects the rate of diatom bSiO₂ production and can limit their growth. A widely cited [Si(OH)₄] threshold, below which diatoms will be outcompeted by other phytoplankton, is ~2.0 μM; this metric was derived from a comparison of diatom abundance (relative to total microplankton) versus [Si(OH)₄] during mesocosm experiments in a Norwegian fjord system (Egge and Aksnes, 1992)." – should be removed: No need to discuss this threshold as it is mentioned that it is strongly criticized (and see my comment above).

2,3) Thank you for the perspective; this section will be removed (please see response to earlier comments on this topic).

1) line 410: "This indeed indicates that phytoplankton can deplete nitrogen to levels below detection while they appear unable to deplete Si(OH)₄ pools below 0.5 μM, which would indicate 0.5 μM is the ultimate Si(OH)₄ concentration required to support diatom growth." – I disagree with this interpretation. The 0.5 μM Si level just reflects the residual H₄SiO₄ stock after complete removal of nitrate.

line 422: "... if diatoms are limited by an absolute [Si(OH)₄] (e.g. 2 μM), ..." – This is speculative: By what evidence is this proposition supported?

2,3) Given the reviewer's comments for the paragraphs starting in line 405 (i.e. line 410 comment) and line 41 (line 422 comment), these paragraphs have been revised (now line 441 – line 444).

1) line 436: "... the relationship between V_b and [Si(OH)₄] also supports that Si regulates diatom productivity to some degree." – The large dispersion of data points on Figure 5

results in a very weak relationship, so that there is certainly something else explaining the low realized V_b at the 4.5 μM H_4SiO_4 level.

2,3) The reviewer is correct, there is variability. But please note these data are from all diatom assemblages sampled among all stations and depths; thus, the linearity of the relationship would not be expected to be high, in fact, we were surprised to see 71% of the variability explained (when Hornsunddjupet excluded) given so many assemblages. However, we feel the Fig. 5B data, which integrates all samples, is the most conservative way to estimate the aggregate K_s value for euphotic diatoms among all stations at the time of this cruise. We also note that the incorrect slope and R^2 were plotted in the original version of Fig 5B (now corrected).

1) line 443: "... Allen *et al.* (2005) observed a linear response in V_b between ambient and 5 μM $[\text{Si}(\text{OH})_4]$, which suggests uptake did not show any degree of saturation at this concentration." – Also in Brown *et al.* (2003); as mentioned above.

2,3) The Brown *et al.* (2003) reference has been added here, as indeed, it is the original source of the Allen *et al.* 2005 Si-uptake data (e.g. line 454).

1) line 517: "At van Mijenfjorden, the rate of export in the upper 40 m represented 39% of the $\int b\text{SiO}_2$ standing stock (23.3 mmol Si m^{-2}) in the same vertical layer." – I don't understand as from Table 1 it seems that the standing stock is 10.8 and the export 9.03?

2,3) Thank you for the observation, this is clarified. We now reference Fig. 2C as the source of the van Mijenfjorden integral data (line 542). Table 1 integrates biogenic silica stock and production to 20 m (i.e. deepest depth among all profiles) whereas the shallowest depth for sediment traps among all deployments was from 40 m. For van Mijenfjorden, we have biogenic silica measurements down to 50 m (Fig. 2C), which allows for the comparison.

1) line 524: "The rate of $b\text{SiO}_2$ export was also at least a factor of four higher than $\int \rho$ in the upper 20 m." – I was not able to find where did this come from.

2,3) Thank you for the observation, this is a general trend among stations in Table 1 (i.e. biogenic silica export was much higher than integrated biogenic silica production). This has been revised "The rate of $b\text{SiO}_2$ export among all export- and production stations was also at least a factor of four higher than $\int \rho$ in the upper 20 m (Table 1)." (line 549, 550).

Below, we address comments from RC2. We cluster each comment and separate them as "1" Reviewer comments, "2,3" are responses and revisions. A pdf version (bg-2018-226-RC2-supplement_Krause_etal_response) of this response has been uploaded in the supplement.

REVIEWER 2

1) Krause *et al.* investigated phytoplankton, especially diatoms, and nutrients at 9 stations in the Atlantic sector north of 76°N . They measured silicate, nitrate plus nitrite, chlorophyll *a*, biogenic silica, determined diatom assemblage, estimate productivity and export (based on sediment traps). The silicic acid concentration in the upper 50 m was always below 5 $\mu\text{mol L}^{-1}$ and at most stations below the nitrate plus nitrite

concentration. At several stations $[\text{Si}(\text{OH})_4]$ was below 1 or even $0.5 \mu\text{mol L}^{-1}$ in the upper 20 m. In order to investigate Si uptake limitation, the authors performed on board growth experiments over a range of $[\text{Si}(\text{OH})_4]$ at 4 stations. Michaelis-Menten functions for silicic acid uptake (Eq.1) were fit to the data yielding estimates for maximum uptake rates (V_{max}) and half- saturation constants (K_S). Let me suggest listing these estimates in a table. The estimates for K_S are much higher than some estimates (for different diatom species) reported in the literature (for example, Paasche, 1973a,b), however, lower than the higher values given by Kristiansen et al. (2000). What might explain this large range and these differences? Could it be influenced by factors (other nutrients, grazing) differing between the various investigations/experiments?

2,3) We speculate that diversity and diatom origin (e.g. more Atlantic influenced waters, perhaps residual ice diatoms) may be some of the underlying factors. However, these are (unfortunately) beyond the scope of our data. What is important, at least from a modeling perspective, is that these kinetic parameters are published and available to ground truth regional simulations.

1) The manuscript contains valuable new data, is well written, and will be of interest to many readers of Biogeosciences. I recommend publication after minor revisions.

2,3) We thank the reviewer for this assessment and reply to the revisions below.

Further remarks/suggestions:

1) L123-129 Description of trap deployment was not very detailed ('at 3-7 depths between 20 and 150-200 m, based on bathymetry'). It would be good to add a list with depths and bottom depths (or a reference where to find this information).

2,3) This has been added to the prose (paragraph starting at line 122).

1) L132-134 Freezing sample for nutrient analysis: Procedures (thawing, measurements how long after thawing) and quality control (freeze certified reference material in parallel with samples) have been discussed in the literature (for example, Macdonald et al., 1986, Clementson & Wayte, 1992, Dore et al., 1996). Could you please give more details on the procedures and quality control?

2,3) Co-Author Kristiansen's laboratory has extensive experience in these analyses. Pertinent details have been added (lines 132-145) beyond the reference seawater from Ocean Scientific International Ltd. (UK) and detection limits are available in the initial submission. Standard practices (slow thawing of silicic acid samples to allow depolymerization, three parallels measured, etc.), have been added (and suggested references) along with prose regarding the analytical reproducibility (median coefficient of variation was 5% for NO_3+NO_2 and PO_4 , 2% for silicic acid and 9% for $\text{NO}_2 \rightarrow$ higher coefficient of variation was observed when the absolute concentrations were low, e.g. $<0.1 \mu\text{M}$, hence using the median value). Because of the cruise duration and transfers, and the well-known issues of getting reliable measurements from frozen samples, no ammonium was measured (also clarified in revision).

1) L136-138 "Phosphate was analyzed, but N:P ratios for nutrients were, on average, 8 among all stations, suggesting that N was likely more important than P for primary production." N:P is below Redfield thus N might be limiting primary production before P. However, 'N was likely more important than P for primary production' sounds strange. Please rewrite.

2,3) This has been modified. "Phosphate was analyzed, but N:P ratios for nutrients

were, on average, 8 among all stations; suggesting that N was likely more important than P for potentially limiting primary production. These phosphate data (0.1–0.6 μM in the upper 50 m) are not discussed.” (line 143-145)

1) L145,148,225 $60^{\circ}\text{C} \rightarrow 60^{\circ}\text{C}, -20^{\circ}\text{C} \rightarrow -20^{\circ}\text{C}, -2-1^{\circ}\text{C} \rightarrow -2\text{ to }+1^{\circ}\text{C}$ (no gaps; please check whole manuscript)

2,3) Gaps have been removed through the whole manuscript.

1) L175 please rewrite ”dividing by the depth integration” \rightarrow dividing by depth-integrated values

2,3) This has been modified as suggested.

1) L199 ml \rightarrow mL

2,3) This has been modified.

1) L205-206 using C:Si (instead of Si:C) would avoid the exponent -1 in Eq.(2) and give values more in Redfield-style, i.e. molar Si:C = 0.13 \rightarrow 7.7 C:Si (only slightly higher than the Redfield C:N). What’s the uncertainty of the Si:C estimate?

2,3) While C:Si and Si:C can both be used, we chose the Si:C based on convention established by other publications when making these types of estimates (e.g. Nelson et al. 1995, Nelson and Brzezinski 1997, Leynaert et al. 2001, Brzezinski et al. 2011, Krause et al. 2011, Krause et al. 2015). Regarding uncertainty, please see response to RC1.

1) L295-296 ”The rate of diatom biogenic silica production was reduced by ambient [Si(OH)₄] in 95% of the samples examined.” sounds strange. I guess you mean ’was kinetically limited by ambient [Si(OH)₄]’ based on comparison with estimated *K_S* values or based on enhancement factors.

2,3) This has been modified.

1) L317,548 Spearman’s Rho Test: add number of data n = ...

2,3) This has been added (n = 15).

1) L380-384 What about grazing?

2,3) Grazing would affect the standing stock of diatom biomass (and thus the absolute rate of production, Rho), but not the specific rates (e.g. *V_{AVE}*) which are more likely driven by growth/bottom up factors. However, in this region, grazing is likely the primary mechanism which transforms living diatom silica into detrital silica. Because the latter is a minor and speculative point given the data, we feel adding a complicated explanation about grazing here would stymie the narrative flow without adding enough clarity.

1) Clementson, Lesley A. and Wayte, Sally E. The effect of frozen storage of open-ocean seawater samples on the concentration of dissolved phosphate and nitrate. *Water Research*, 26(9):1171–1176, 1992.

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Macdonald, RW and McLaughlin, FA and Wong, CS. The storage of reactive silicate samples by freezing. *Limnology and Oceanography*, 31(5):1139–1142, 1986.

2,3) These two references were added (line 137-138); we thank the reviewer for the suggestion.

END OF RESPONSE

1 **Biogenic silica production and diatom dynamics in the Svalbard region during spring**

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21 **Abstract.**

22 Diatoms are generally the dominant contributors to the Arctic Ocean spring bloom, which is a key
23 event in regional food webs in terms of capacity for secondary production and organic matter
24 export.- Dissolved silicic acid is an obligate nutrient for diatoms and has been declining in the
25 European Arctic [since the early 1990s](#).- The lack of regional silicon cycling information precludes
26 understanding the consequences of such changes for diatom productivity during the Arctic spring
27 bloom.- This study communicates the results from a cruise in the European Arctic around Svalbard
28 reporting the first concurrent data on biogenic silica production and export, [export of](#) diatom
29 cell ~~sular export~~, the degree of kinetic limitation by ambient silicic acid, and diatom contribution
30 to primary production. Regional biogenic silica production rates were significantly lower than
31 those achievable in the Southern Ocean and silicic acid concentration limited the biogenic silica
32 production rate in 95% of samples. Compared to diatoms in the Atlantic subtropical gyre, regional
33 diatoms are less adapted for silicic acid uptake at low [substrate concentration](#), and at some stations
34 during the present study, silicon [kinetic](#) limitation may have been intense enough to limit diatom
35 growth.- Thus, silicic acid can play a critical role in diatom spring bloom dynamics.- [The d](#) diatom
36 contribution to primary production was variable, ranging from <10% to ~100% depending on the
37 bloom stage and phytoplankton composition. While there was agreement with previous studies
38 regarding the [export](#) rate of diatom cell ~~sular export~~, we observed significantly elevated biogenic
39 silica export.- Such a discrepancy can be resolved if a higher fraction of the diatom material
40 exported during our study was modified by zooplankton grazers ~~or originated from melting ice~~.
41 This study provides the most-direct evidence to date suggesting the important coupling of the
42 silicon and carbon cycles during the spring bloom in the European Arctic.

1 Introduction

Diatoms and the ~~flagellate-haptophyte~~ *Phaeocystis* are the dominant contributors to the Arctic Ocean spring bloom, a cornerstone event supplying much of the annual net community production (Vaquer-Sunyer et al., 2013; Rat'kova and Wassmann, 2002; Vaquer-Sunyer et al., 2013; Wassmann et al., 1999) that fuels Arctic food webs (Degerlund and Eilertsen (2010) and references therein).- Hydrographic and chemical changes in the Arctic water column are expected in the future, but whether these will alter diatoms' contribution to spring primary production and organic matter export remains uncertain.- Some studies predict ~~lack of reduction in~~ ice cover will enhance the spring bloom due to increased light availability (Arrigo et al., 2008), while others predict lower productivity driven by increased stratification and reduced nutrient supply (Schourup-Kristensen et al. 2018; Tremblay and Gagnon, 2009).- Additionally, models predict that warming will lead to a shift from a diatom-dominated bloom to one increasingly dominated by flagellates and picoautotrophs, which has been observed in certain sectors of the Arctic (Li et al., 2009; Lasternas and Agustí, 2010).- Because the spring diatom bloom is arguably the single most important productivity event for the Arctic Ocean ecosystem (Degerlund and Eilertsen, 2010; Holding et al., 2015; Vaquer-Sunyer et al., 2013), understanding how diatoms' ecological and biogeochemical importance changes in response to system-wide physical/chemical shifts is important to predict future food web alterations.- Diatoms have an obligate requirement for silicon, therefore understanding of regional ~~Si-silicon~~ cycling can provide insights into ~~the diatoms'~~ activity.- However, there is a current knowledge gap of regional silicon cycling, which precludes robust assessments of the spring bloom in future scenarios, e.g. Tréguer et al. (2018).

Diatom production is dependent on the availability of dissolved silicic acid ($\text{Si}(\text{OH})_4$), which they use to build their shells of biogenic silica (bSiO_2). $[\text{Si}(\text{OH})_4]$ has been observed to be low ($<5 \mu\text{M}$) in the Norwegian Seas and declining over time (Rey, 2012). A more recent analysis demonstrated a decline in pre-bloom $[\text{Si}(\text{OH})_4]$ concentrations by 1–2 μM across the north Atlantic subpolar and polar regions over the last 25 years (Hátún et al., 2017); ~~this is consistent with the general Arctic region being a net exporter of silicic acid (Torres Valdés et al., 2013).~~ This is in stark contrast to the 10–60 μM $[\text{Si}(\text{OH})_4]$ observed in the surface waters of the Southern Ocean and the marginal ice zone around Antarctica (Nelson and Gordon, 1982; Brzezinski et al., 2001), ~~where $[\text{Si}(\text{OH})_4]$ is unlikely to limit diatom growth unless iron is replete, and stimulates exceptional blooms which consume Si, or assemblages are highly inefficient for Si uptake (citation?) where $[\text{Si}(\text{OH})_4]$ is unlikely to limit the rate of diatom production or biomass yield.~~ Additionally, the stoichiometry of $\text{Si}(\text{OH})_4$ availability relative to nitrate ($\text{Si:N} < 1$) in the source waters, which fuel the spring bloom in most of the north Atlantic and European polar seas, suggests that during a bloom cycle diatoms may experience Si limitation prior to N limitation, especially if diatoms consumed Si and N in near equal quantities as in other diatom bloom regions (Brzezinski et al., 1997; Brzezinski, 1985; Dugdale et al., 1995) ~~and a 2 μM threshold $[\text{Si}(\text{OH})_4]$ defines where diatoms are outcompeted by flagellates (Egge and Aksnes, 1992).~~

Compared to the Southern Ocean, there is a paucity of field Si-cycling studies in the European Arctic.- Reports of diatom silica production are only available from the subarctic northeast Atlantic near $\sim 60^\circ\text{N}$, e.g. between Iceland and Scotland (Allen et al., 2005; Brown et al., 2003), Oslofjorden (Kristiansen et al., 2000), and limited data from Baffin Bay (Hoppe et al., 2018; Tremblay et al., 2002); these previous studies are in zones with higher $\text{Si}(\text{OH})_4$ availability than in the European Arctic.- Other studies have reported standing stocks of bSiO_2 and export in Oslofjorden or the European Arctic, e.g. Svalbard vicinity, Laptev Sea (Hodal et al., 2012; Heiskanen and Keck, 1996; Paasche and Ostergren, 1980; Lalande et al., 2016; Lalande et al.,

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89 2013), but none have concurrent measurements of bSiO₂ production.- Indeed, in the last major
90 review of the global marine silicon cycle, Tréguer and De La Rocha (2013) reported no studies
91 with published bSiO₂ production data derived from field measurements from the Arctic.

92 Currently, we lack a baseline understanding about diatom Si-cycling in the European Arctic
93 and broader high-latitude north Atlantic region.- And while models in the Barents Sea use Si as a
94 possible limiting nutrient (Wassmann et al., 2006; Slagstad and Støle-Hansen, 1991), there are no
95 field data to ground truth the modeled parameters governing diatom Si uptake.- Thus, there is no
96 contextual understanding to determine the consequences of the observed changes in regional
97 [Si(OH)₄] since the 1990s and if these affect spring bloom dynamics.- This study communicates
98 the results from a cruise in the European Arctic around Svalbard reporting the first concurrent
99 datasets on regional bSiO₂ production and export, [the export of diatom cells](#)~~sular export~~, and the
100 degree of kinetic limitation by ambient [Si(OH)₄].- Additionally, coupling bSiO₂ production rates
101 with contemporaneous primary production measurements provides an independent assessment for
102 the diatom contribution to system primary production.

104 2 Methods

105 2.1 Region and Sampling

106 This study was conducted aboard the RV *Helmer Hanssen* between May 17–29, 2016 as
107 part of the broader project, ARCEX–The Research Centre for ARctic Petroleum Exploration
108 (<http://www.arcex.no/>).- The main goal of this cruise was to study the pelagic and benthic
109 ecosystem during the Arctic spring bloom around Svalbard and in the northern Barents Sea at
110 stations influenced by various water masses.- The cruise started in the southwestern fjords
111 influenced by relatively warm Atlantic water, then transited east of Svalbard toward more Arctic-
112 influenced water (Fig. 1 blue arrow) before turning south towards stations near the Polar Front and
113 [south of the Polar Front in more Atlantic water-influenced waterstation](#) (Fig. 1 red arrows)~~located~~
114 [to the south of the Polar Front](#).

115 Vertical profiles with a CTD were conducted at all stations.- Hydrocasts were conducted
116 using a Seabird Electronics 911 plus CTD with an oxygen sensor, fluorometer, turbidity meter and
117 PAR sensor (Biospherical/LI-CORR, SN 1060).- The CTD was surrounded by a rosette with 12
118 five-liter Niskin bottles. At two stations, Edgeøya, and Hinlopen, only surface samples were
119 collected (no vertical profiles with ancillary measurements, Fig. 1). Water was sampled from the
120 rosette at depths within the upper 40 m (i.e. the extent of the photic layer); for any incubation
121 described below, the approximate irradiance at the sample depth during collection was mimicked
122 by placing incubation bottles into a bag made of neutral density screen. Incubation bags were
123 placed in a deck board acrylic incubator cooled with continuously flowing surface seawater. At
124 Hinlopen, a block of ice was collected by hand within ~10 m of the vessel and allowed to thaw in
125 a shaded container for 24 hours at ambient air temperature. After thawing, the melted solution
126 was homogenized and treated like a water sample for measurement of biomass and rates.

127 Four sediment trap arrays were deployed between 19 and 23 hours. Arrays in van
128 Mijenfjorden and Hornsund were anchored to the bottom ([60 and 130 m, respectively](#)), whereas
129 the other two arrays (~~Erik Erikssenstretet~~[Erik Erikssenstretet, 260 m bottom depth](#); Polar Front,
130 [290 m bottom depth](#)) were quasi-Lagrangian and drifted between 14–16 km during the
131 deployment. During the ~~Erik Erikssenstretet~~[Erik Erikssenstretet](#) deployment, the array was
132 anchored to an ice floe. Arrays included sediment trap cylinders (72 mm internal ~~diameter~~[diameter](#)
133 [x 450 mm length](#) ~1.8 L volume; ~~KC Denmark~~[KC Denmark](#)) at 3 ([van Mijenfjorden](#)) ~~to 7~~

134 ([Atlantic Station](#)) depths between 20 and 150–200 m, based on bathymetry. After recovery, trap
135 contents were pooled and subsampled for bSiO₂ and phytoplankton taxonomy.

136 2.2 Standing stock measurements

137 A suite of macronutrients were analyzed at all stations except Hinlopen (just Si(OH)₄).
138 Water was sampled directly from the rosette, filtered (0.7 μm pore size) and immediately frozen.
139 In the laboratory, nutrients were analyzed using a Flow Solution IV analyzer (O.I. Analytical,
140 USA) and calibrated with reference seawater (Ocean Scientific International Ltd. UK). Detection
141 limits for [NO₃ + NO₂] and [Si(OH)₄] were 0.02 and 0.07 (μM), respectively. [No ammonium was](#)
142 [measured. To avoid artefacts with prolonged freezing \(Clementson and Wayte, 1992; Macdonald](#)
143 [et al. 1986\), samples were analyzed within 4 months of collection and standard practices were used](#)
144 [\(e.g. prolonged thawing of Si\(OH\)₄ samples to allow depolymerization, three parallels measured\).](#)
145 [The median coefficient of variation among parallels was 5% for \[NO₃ + NO₂\] and \[PO₄\], 2% for](#)
146 [\[Si\(OH\)₄\] and 9% for \[NO₂\] —higher coefficient of variation was observed when the absolute](#)
147 [concentrations were low, e.g. <0.1 μM. Reproducibility was sufficient, and no parallels were](#)
148 [excluded.](#) Phosphate was analyzed, but N:P ratios for nutrients were, on average, 8 among all
149 stations, ~~suggesting thating that~~ N was [likely more important likely more important](#) than P [for](#)
150 [potentially limitingfor](#) primary production. These phosphate data [\(0.1–0.6 μM in the upper 50 m\)](#)
151 are not discussed.

152 Samples for biogenic particulates and phytoplankton community composition were taken
153 directly from the rosette and sediment traps. For bSiO₂ samples, 600 mL of seawater was collected
154 from the rosette, filtered through a 1.2 μm polycarbonate filter (Millipore); for sediment trap
155 material, less volume was necessary (e.g. 50–100 mL). Most bSiO₂ protocols use a 0.6 μm filter
156 cutoff, e.g. Lalande et al. (2016), however, given the magnitude bSiO₂ quantified and the size
157 range for regional diatoms we are confident that there was no meaningful systematic
158 underestimate. After filtration, all samples were dried at 60°C and stored until laboratory analysis
159 using an alkaline digestion in Teflon tubes (Krause et al., 2009). For Chl *a*, water-column and
160 sediment samples were collected similarly, filtered on Whatman GF/F (0.7 μm pore size) and
161 immediately frozen (-20°C). In the laboratory, Chl *a* was extracted in 5 mL methanol in the dark
162 at room temperature for 12 h. The solution was quantified using a Turner Design 10-AU
163 fluorometer, calibrated with Chl *a* standard (Sigma C6144), before and after adding two drops of
164 5% HCl (Holm-Hansen and Riemann, 1978). Phytoplankton taxonomy and abundance samples
165 were collected in 200 mL brown glass bottles from both the water column and sediment traps,
166 immediately fixed with an aldehyde mixture of hexamethylenetetramine-buffered formaldehyde
167 and glutaraldehyde at 0.1 and 1% final concentration, respectively, as suggested by Tsuji and
168 Yanagita (1981) and stored cool (5°C) and dark. Samples were analyzed with an inverted
169 epifluorescence microscope (Nikon TE300 and Ti-S, Japan), using the Utermöhl (1958) method,
170 in a service laboratory for diatom taxonomy (>90 individual genera/species categories were
171 identified) and abundance at the Institute of Oceanology Polish Academy of Science.

172 2.3 Rate measurements

173 Biogenic silica production was measured using the radioisotope tracer ³²Si. Approximately
174 150 or 300 mL samples, depending on the station biomass, were incubated with 260 Bq of high
175 specific activity ³²Si(OH)₄ (>20 kBq μmol Si⁻¹). After addition, samples were transported to the
176 deck-board incubator and placed in [neutral density screened bags, simulating 50%, 20% and 1%](#)
177 [of irradiance just below the surface, neutral density screened bags](#) for 24 hours. After incubation,
178

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180 samples were processed immediately by filtering bottle contents through a 25 mm, 1.2 μm
 181 polycarbonate filter (Millipore) —matching bSiO₂ filtrations. Each filter was then placed on a
 182 nylon planchette, covered with Mylar when completely dry, and secured using a nylon ring.
 183 Samples were aged into secular equilibrium between ³²Si and its daughter isotope, ³²P (~120 days).
 184 ³²Si activity was quantified on a GM Multicounter (Risø National Laboratory, Technical
 185 University of Denmark) as described in Krause et al. (2011). A biomass-specific rate (i.e. V_b) was
 186 determined by normalizing the gross rate (ρ) to the corresponding [bSiO₂] at the same depth of
 187 collection using a logistic-growth approach (Kristiansen et al., 2000; Krause et al., 2011). For
 188 bSiO₂ and ρ, values within a profile were integrated throughout the euphotic zone (i.e. surface to
 189 1% I₀) using a trapezoidal scheme. A depth-weighted V_b was calculated within the euphotic zone
 190 by integrating V_b and dividing by ~~the depth-integration values~~ (Krause et al., 2013).

191 Two methods were used to assess whether ambient silicic acid (Si(OH)₄) limited diatom Si
 192 uptake. The ³²Si activity additions, incubation conditions, and sample processing are as described
 193 above. At four stations (Edgeøya, Polar Front, Hinlopen and Atlantic), eight 300-mL samples
 194 collected at a single depth within the euphotic zone and were manipulated to make an eight-point
 195 concentration gradient between ambient and +18.0 μM [Si(OH)₄]; the maximum concentration
 196 was assumed to saturate Si uptake. Si uptake has been shown to conform to a rectangular
 197 hyperbola described by the Michaelis-Menten equation:

$$198 \quad V_b = \frac{V_{\max}[\text{Si(OH)}_4]}{K_S + [\text{Si(OH)}_4]} \quad (1)$$

199 where V_{max} is the maximum specific uptake rate and K_S is half-saturation constant, i.e.
 200 concentration where V_b = ½ V_{max}. Data were fit to the Eq. 1 using a non-linear curve fit algorithm
 201 (SigmaPlot 12.3). The second type of experiment used only two points: ambient and +18.0 μM
 202 [Si(OH)₄]; four-depth profiles were done at three stations (Bellsund Hula, Hornsunddjupet, ~~Erik~~
 203 ~~Eriksenstretet~~~~Erik Eriksenstretet~~). The ratio of Si uptake at +18.0 μM [Si(OH)₄] to Si uptake at
 204 ambient [Si(OH)₄] defines an enhancement (i.e. Enh) statistic. This two-point approach was
 205 conducted at all depths in the euphotic zone; Enh ratios >1.08 imply kinetic limitation beyond
 206 analytical error given the methodology (Krause et al., 2012).

207 Net primary productivity (PP) was quantified concurrently with biogenic silica production
 208 at six stations at the depth of approximately 50% of surface irradiance (Table 1). Carbon uptake
 209 rates were measured using a modification of the ¹⁴C uptake method (Steemann Nielsen, 1952).
 210 Water samples were spiked with 0.2 μCi mL⁻¹ of ¹⁴C labelled sodium bicarbonate (Perkin Elmer,
 211 USA) and distributed in three clear ~~and one dark~~ plastic bottles ~~and one dark~~ (40 mL each).
 212 Subsequently, they were incubated for 24 h in the deck incubator with a 50% light reduction mesh.
 213 After incubation, samples were filtered onto 0.2 μm nitrocellulose filters. The filters were stored
 214 frozen (-20-°C) in scintillation vials with 10 mL EcoLume scintillation liquid (MP Biomedicals
 215 LLC, USA) until further processing. Once on land, the particulate ¹⁴C was determined using a
 216 scintillation counter (TriCarb 2900 TR, Perkin Elmer, USA). The carbon uptake values in the dark
 217 were subtracted from the mean of the triplicate carbon uptake values measured in the light
 218 incubations. Using contemporaneous ρ measurements and PP measurements, the diatom
 219 contribution to PP is estimated as:

$$220 \quad \text{Diatom \%PP} = 100 \times \frac{\rho \times (\text{Si:C})^{-1}}{\text{PP}} \quad (2)$$

221 where the Si:C ratio for diatoms can be used from culture values. The most widely-used Si:C ratio
 222 is, e.g. 0.13 (Brzezinski, 1985); however, this study lacked polar diatom strains. Takeda (1998)
 223 grew two polar diatoms at 2°C, and in iron-replete media and reported Si:C from 0.10–0.18;
 224 however, this was extrapolated based on direct measurement of cellular N and converting using

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225 [the Redfield-Ketchum-Richards C:N ratio of 6.6. A more recent study, Lomas et al. \(in review\),](#)
226 [reported data on 11 polar diatom species grown at 2°C with direct measurement of biogenic silica](#)
227 [and particulate -organic- carbon and nitrogen. For larger diatom species \(>1000 μm³ biovolume\)](#)
228 [these authors observed the average Si:C was 0.25 ±0.04 \(SE\), with a higher ratio for smaller](#)
229 [species \(<1000 μm³\) 0.32 ±0.04 \(SE\). Most of the diatom assemblage during ARCEX was](#)
230 [composed of larger cells, thus, we use Si:C of 0.25.](#)

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232 Export rates were calculated using the standing stock measurements, length of deployment,
233 and trap opening area (0.004 m²). These approaches are common and detailed elsewhere
234 (Wiedmann et al., 2014; Krause et al., 2009).

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236 3 Results

237 3.1 Hydrography and Spatial patterns

238 The regional ecosystem around Svalbard is driven by ice dynamics (Sakshaug, 2004). One
239 week prior to the cruise, a majority of the southern Svalbard archipelago had open water, which
240 was anomalous compared to similar dates in previous years (e.g. 2014, 2015, ice data archived at
241 <http://polarview.met.no/>). By the end of the cruise, Svalbard could have been entirely circled by
242 the vessel, with only open drift ice in the northeastern region. While 2016 was among the lowest
243 years for total Arctic sea ice, the ice extent in Svalbard and the Barents Sea is highly dynamic. Ice
244 edges may be pushed southward into the Barents Sea proper by wind while areas to the north
245 remain ice free, e.g. Wassmann et al. (1999) and references therein.

246 Spatial patterns in hydrography and nutrients were highly variable. In the southwestern
247 stations (e.g. fjords and Atlantic-influenced water), the surface temperature ranged between 1–4
248 °C; similar temperature was observed in the Atlantic station south of the Polar Front (Fig. 1E).
249 Northeastern domain stations were more influenced by Arctic water and the surface temperatures
250 ranged between -2 and -1°C (Fig. 1E). Surface nutrient concentrations, particularly [NO₃+NO₂]
251 and [Si(OH)₄], showed a broad range. The highest surface [NO₃+NO₂] was observed in the
252 southwestern fjords, between 2 and >8 μM, and the Atlantic station (~3 μM, Fig. 1A). The
253 surface concentrations at the remaining stations were <0.5 μM or near detection limits (Fig. 1A).
254 [Si(OH)₄] was lower than [NO₃+NO₂] (i.e. Si:N <1) among stations where [NO₃+NO₂] was > 0.1
255 μM. At high [NO₃+NO₂] stations, the [Si(OH)₄] ranged from 1.1–4.5 μM (Fig. 1B) but the range
256 was lower among other stations (0.4–1.1 μM, Fig. 1B). bSiO₂ (proxy for diatom biomass, Fig.
257 1C) was typically similar to, or lower than, surface [Si(OH)₄]. The highest surface [bSiO₂] was
258 observed in the southern stations (Atlantic-influenced waters), ~ 2–3 μmol Si L⁻¹ (Fig. 1C). At
259 most other stations the [bSiO₂] was <1 μmol Si L⁻¹. Among all stations/depths bSiO₂ varied by a
260 factor of ~40 (does not include Hinlopen ice algae).

261 Primary productivity, measured at six stations at 5 m (approximately 50% of surface
262 irradiance), varied over two orders of magnitude. The lowest rates were observed at the four
263 stations having lowest surface [NO₃+NO₂] and ranged from 2–13 μg C L⁻¹ d⁻¹; at these stations
264 [Chl *a*] ranged from 2.0–4.8 μg L⁻¹ (Table 1, Fig. 1D). The highest rates were measured at van
265 Mijenfjorden and Bredjupet, 100 ±65 μg C L⁻¹ d⁻¹ and 27 ±1 μg C L⁻¹ d⁻¹, respectively, and
266 corresponded to high [NO₃+NO₂] and low [Chl *a*] 1.8 and 0.7 μg L⁻¹, respectively (Table 1, Fig.
267 1D).

270 3.2 Vertical profiles

271 As expected, most stations showed strong vertical gradients in nutrient concentrations.
272 Profiles in the southwestern region of Svalbard (van Mijenfjorden, Bredjupet) had elevated
273 $[\text{Si}(\text{OH})_4]$, with little vertical structure. Vertical $[\text{Si}(\text{OH})_4]$ profiles among other stations showed
274 typical nutrient drawdown between the surface and ~20 m. At these stations, surface $[\text{Si}(\text{OH})_4]$
275 concentrations were typically $<1.5 \mu\text{M}$ and subsurface values (to 20 m) ranged from $0.5\text{--}3.0 \mu\text{M}$
276 (Fig. 2A). $[\text{NO}_3+\text{NO}_2]$ exceeded $[\text{Si}(\text{OH})_4]$ among all depths at five stations (~~van Mijenfjorden,~~
277 ~~Bredjupet, Hornsund, Atlantic;~~ Fig. 2B), whereas in the remaining stations $[\text{NO}_3+\text{NO}_2]$ exceeded
278 $[\text{Si}(\text{OH})_4]$ (i.e. Si:N <1) at depths >5 m (Bellsund Hula), >20 m (~~Erik-Eriksenstretet~~~~Erik~~
279 ~~Eriksenstretet~~) and >27 m (Polar Front). For these latter three stations, $[\text{NO}_3+\text{NO}_2]$ had a
280 significant drawdown in surface waters, but then increased with depth without a similar degree of
281 vertical enhancement in $[\text{Si}(\text{OH})_4]$ (Fig. 2).

282 $[\text{bSiO}_2]$ was typically highest at or near the surface, with a maximum of $\sim 2 \mu\text{mol Si L}^{-1}$
283 (Fig. 2C). At the Bellsund Hula and ~~Erik-Eriksenstretet~~~~Erik Eriksenstretet~~ stations, subsurface
284 $[\text{bSiO}_2]$ maxima were present (Fig. 2C; note—no surface data are available for van Mijenfjorden).
285 Among non-profile stations, $[\text{bSiO}_2]$ was within the range observed among vertical profiles except
286 for the Hinlopen ice algae: where ~~ice, which was melted at ambient air temperature on the vessel,~~
287 ~~the melt water~~ had exceptionally high $[\text{bSiO}_2]$ (Fig. 2C). The surface-to-20-m integrated bSiO_2
288 ($\int \text{bSiO}_2$) spanned over an order of magnitude, with a low at Bredjupet ($1.9 \text{ mmol Si m}^{-2}$) and a
289 high at Hornsunddjupet ($42.4 \text{ mmol Si m}^{-2}$, Table 1) despite their proximity (~ 50 km).

290 Diatom abundance and taxonomy data were sampled at fewer stations, but the vertical and
291 spatial variability generally mirrored trends in $[\text{bSiO}_2]$. In the surface waters of van Mijenfjorden
292 and Hornsund, diatom abundances ranged between $5 \times 10^4\text{--}5 \times 10^5$ cells L^{-1} in the upper 50 m (Fig.
293 3A). However, within the same vertical layer at the ~~Erik-Eriksenstretet~~~~Erik Eriksenstretet~~ and
294 Polar Front (duplicate profiles) stations, diatom abundances were enhanced by up to two orders of
295 magnitude ($4 \times 10^4\text{--}4 \times 10^7$ cells L^{-1} , Fig. 3A). When integrated to 40-m depth ($\int \text{Diatom}$), matching
296 the shallowest sediment-trap depth among the three stations reported (Fig. 3E–H), diatom
297 inventories also showed a two-order of magnitude variability as observed in $\int \text{bSiO}_2$. $\int \text{Diatom}$ was
298 lowest at van Mijenfjorden (7.67×10^9 cells m^{-2}) and highest at Polar Front station (527×10^9 cells
299 m^{-2} , Table 1).

300 Among the stations which had corresponding sediment trap deployments (van
301 Mijenfjorden, Hornsund, ~~Erik-Eriksenstretet~~~~Erik Eriksenstretet~~), the diatom-assemblage
302 composition was similar despite differences in abundance. The van Mijenfjorden station was
303 dominated by *Thalassiosira* (e.g. *T. antarctica antarctica var. borealis*², *T. gravida*, *T. hyalina*, *T.*
304 *nordenskiöldii*), *Fragilariopsis cylindrus*, and *Chaetoceros furcellatus* (Fig. 3B). *Chaetoceros*
305 spp. was nearly absent from ~~Erik-Eriksenstretet~~~~Erik Eriksenstretet~~ (Fig. 3D) and of little
306 importance at Hornsund (Fig. 3C). *Thalassiosira* species (same as van Mijenfjorden) cells also
307 dominated Hornsund and ~~Erik-Eriksenstretet~~~~Erik Eriksenstretet~~ among most depths (Fig. 3C, D).
308 However, at Hornsund, deeper depths were dominated by diatom groups less frequently observed
309 (“Other diatom” category, Fig. 3), and with small contributions from *Fragilariopsis cylindrus* and
310 *Navicula vanhoefenii*.

311 Diatom bSiO_2 productivity, ρ , mirrored trends in biomass. Among the profiles, rates
312 generally varied from $\rho < 0.01$ to $0.11 \mu\text{mol Si L}^{-1} \text{ d}^{-1}$ (Fig. 2D). ρ was highest in the Atlantic
313 station (Fig. 2D), which was expected given the higher bSiO_2 (Fig. 2C). However, the rates in the
314 Hinlopen ice algae were like those quantified at Hornsunddjupet, $\sim 0.1 \mu\text{mol Si L}^{-1} \text{ d}^{-1}$, despite the
315 ice algae station having an order of magnitude more biomass. This suggests the Hinlopen ice algae
316 were senescent or stressed and a sizable portion of the measured bSiO_2 was non-active or detrital.

317 When integrated in the upper 20-m, $\int \rho$ ranged from 0.27—1.46 mmol Si m⁻² d⁻¹ (Table 1), which
318 is a smaller proportional range than observed in \int Diatoms and \int bSiO₂. Overall, bSiO₂-normalized
319 rates (V_b) were low among all stations and depths (<0.01 to 0.13 d⁻¹). The depth-weighted V_b , i.e.
320 V_{AVE} , had a narrower range between 0.03–0.13 d⁻¹. Thus, doubling times for bSiO₂ in the upper
321 20 m ranged between 5–23 days.

322 The rate of diatom biogenic silica production was kinetically limited ~~reduced~~ by ambient
323 [Si(OH)₄] in 95% of the samples examined. Full kinetic experiments verified that Si uptake
324 conformed to Michaelis-Menten kinetics (Fig. 4A; adjusted R² ranged 0.64–0.92 among
325 experiments). The highest V_{max} was observed in the Atlantic station (0.36 ± 0.02 d⁻¹), which also
326 had the highest ambient [Si(OH)₄] among the full kinetic experiments (1.4 μM). V_{max} observed at
327 Edgeøya and the Polar Front were nearly identical (0.05 ± <0.01 d⁻¹ for both) and lowest in the
328 Hinlopen ice diatoms (0.02 ± <0.01 d⁻¹). K_S constants had a narrower range, with a low of 0.8 ± 0.3
329 μM at the Polar Front and between 2.1–2.5 μM among the other three stations. Among these full-
330 kinetic experiments, the Enh ratio ranged from 1.8–7.7 with the most intense [Si(OH)₄] limitation
331 of uptake observed in the Hinlopen ice diatoms. For profiles where two-point kinetic experiments
332 were conducted, the same trends were observed (Fig. 4B). The Enh ratio was similar among depths
333 at Bellsund Hula (1.5–2.2), Hornsundjupet and Bredjupet (3.4–5.4 for latter two stations, Fig.
334 4B). At ~~Erik Erikssenstretet~~Erik Erikssenstretet, Enh ratios were more variable, ranging from 2.8–
335 7.3 in the upper 10 m with no Enh effect (i.e. <1.08) observed at 20 m —this was the only sample
336 and depth which showed no resolvable degree of kinetic limitation for Si uptake.

337 Rates of bSiO₂- and diatom export were variable. Among the three sediment trap regions,
338 bSiO₂ export rates ranged from ~4–10 mmol Si m⁻² d⁻¹ (Fig. 2E). These rates are significant and
339 represent up to 50% of the \int bSiO₂ in upper 20 m at van Mijenfjorden (Table 1). For diatom cells,
340 a similar degree of variability was observed. Export at van Mijenfjorden ranged from 390–1500
341 x10⁶ cells m⁻² d⁻¹, similar ranges to Hornsund (520–2800 x10⁶ cells m⁻² d⁻¹) and ~~Erik~~
342 ~~Erikssenstretet~~Erik Erikssenstretet (510–860 x10⁶ cells m⁻² d⁻¹, Fig. 3E). The Atlantic station had
343 significantly higher diatom export (800–2300 x10⁶ cells m⁻² d⁻¹) among all depths in the upper 120
344 m (Fig. 3E). The bSiO₂ and the export of diatom cells~~solar export~~ were highly correlated (r = 0.67,
345 p < 0.01, n = 15; Spearman's Rho Test). Among all stations, *Fragilariopsis cylindrus* had the
346 highest contribution to diatom export, and *Thalassiosira* species (e.g. *T. antarctica*, *T. gravida*, *T.*
347 *hyalina*, *T. nordenskiöldii*) were also important (Fig. 3F–H). In Hornsund, *Navicula* (*N.*
348 *vanhoefenii*, *N. sp.*) was an important group-genus for export (Fig. 3G) but this was not observed
349 elsewhere. Similarly, “Other diatom” groups were proportionally important at ~~Erik~~
350 ~~Erikssenstretet~~Erik Erikssenstretet (Fig. 3H), as were *Thalassiosira* resting spores at the Atlantic
351 station (data not shown). Among all diatoms, the only groups which were numerically important
352 in both the water column and the sediment traps were *Fragilariopsis cylindrus* and *Thalassiosira*
353 species (Fig. 3B–D, F–H).

355 4 Discussion

356 4.1 Diatom Si cycling relative to other systems

357 To our knowledge, this is the first report of bSiO₂ production data of the natural diatom
358 community in this sector of the Arctic. Other studies have reported ρ data in the subarctic Atlantic
359 Ocean (Brown et al., 2003; Kristiansen et al., 2000; Allen et al., 2005) ~10–20° latitude south of
360 our study region or in Baffin Bay (Hoppe et al., 2018; Tremblay et al., 2002). However, the Hoppe
361 et al. (2018) study only includes ρ measured after a 24-hour manipulation experiment and only at
362 one site and depth near the Clyde River just east of Nunavat (Canada), no data are reported for the

363 ambient conditions, and the measurements from Tremblay et al. (2002) are based on net changes
364 in standing stocks instead of gross bSiO₂ production. Banahan and Goering (1986) report the only
365 ρ to date in the southeastern Bering Sea; however, Varela et al. (2013) recently reported that
366 [Si(OH)₄] in surface waters (>5 μ M) are unlikely to be significantly limiting to diatoms in any
367 sector of the Bering, Chukchi or Beaufort Sea regions. Around Svalbard, some previous studies
368 have examined other Si-cycling components including variability in bSiO₂ in the water column
369 (Hodal et al., 2012) and sediments (Hulth et al., 1996), bSiO₂ and diatom export (Lalande et al.,
370 2016; Lalande et al., 2013), or trends in [Si(OH)₄] (Anderson and Dryssen, 1981). The ρ
371 measurements presented here have no straight forward study for comparison; therefore, we
372 compare these to the previous high-latitude Atlantic data and to well-studied sectors of the
373 Southern Ocean.

374 During our study, $\int\rho$ in the Svalbard vicinity was low. ~~Working in~~ In the NE Atlantic
375 between Iceland and Scotland, ~~Brown et al. (2003) the reported~~ $\int\rho$ ranged between 6–166 mmol Si
376 m⁻² d⁻¹ (Brown et al. 2003; Allen et al. 2005). ~~In the same region, under post-bloom conditions,~~
377 ~~Allen et al. (2005) reported 7 mmol Si m⁻² d⁻¹ for one profile.~~ These rates are significantly higher
378 than at our four profile stations (Table 1), and the degree of difference does not appear to be driven
379 by differences in integration depth (compared to our study, Table 1). Given the higher [Si(OH)₄]
380 in the southern region of the Atlantic subpolar gyre (Hátún et al., 2017), the maximum achievable
381 $\int\rho$ may vary with latitude. While our profile sampling was opportunistic, it appears we sampled
382 some stations with significant diatom biomass (high \int bSiO₂), but the corresponding production
383 rates ($\int\rho$) were low, with estimated doubling times on the order of 11–23 days. This suggests these
384 high-biomass stations may have been near, or past, peak bloom conditions (Fig. 2A, B) and the
385 seasonal timing is consistent with regional field and modeling studies inferring diatom bloom
386 dynamics from Chl *a* trends, e.g. (Wassmann et al., 2010; Oziel et al., 2017). Kristiansen et al.
387 (2000) reported ρ in Oslofjorden during the late winter (February–March), rates ranged from
388 0.03–2.0 μ mol Si L⁻¹ over nine sampling periods with corresponding V_b between <0.01–0.28 d⁻¹;
389 however, this system has a higher Si(OH)₄ supply and surface concentrations at the start of the
390 bloom period (~~were~~ >6 μ M), approximately 50% higher than the highest surface concentrations
391 observed during our study (Fig. 2A). ~~Nearly all the initial Si(OH)₄ was eventually converted to~~
392 ~~bSiO₂ during the bloom (Kristiansen et al., 2001; Kristiansen et al., 2000).~~ The specific rates
393 observed in our study fall within the lower values reported by Kristiansen et al. (2000), which may
394 be explained by the reduced uptake from lower [Si(OH)₄] (e.g. Fig. 4).

395 The Southern Ocean is one of the most globally significant regions for production of bSiO₂.
396 The surface [Si(OH)₄] and [NO₃+NO₂] are among the highest in the ocean and the source waters
397 usually have >50% excess Si(OH)₄ relative to nitrate (Brzezinski et al., 2002). Thus, exceptional
398 Si(OH)₄ drawdown relative to nitrate is required for diatom biomass yield to be limited by Si in
399 this region. The mean $\int\rho$ in sectors of the Southern Ocean are variable. In the Weddell Sea, winter
400 rates range between 2.0–3.2 mmol Si m⁻² d⁻¹ in the seasonal ice zone (Leynaert et al., 1993).
401 Within the sub-Antarctic zone, rates averaged 1.1 and 4.8 mmol Si m⁻² d⁻¹ in the summer and
402 spring, respectively (Fripiat et al., 2011). At the terminus of diatom blooms in the sub-Antarctic
403 and polar frontal zone, rates can be lower, e.g. 0.1–0.3 mmol Si m⁻² d⁻¹ (Fripiat et al., 2011); such
404 values are similar to the range observed during our study, especially since these Southern Ocean
405 studies integrated $\int\rho$ deeper than 40 m (e.g. 50–100 m). Brzezinski et al. (2001) reported average
406 $\int\rho$ ~25 mmol Si m⁻² d⁻¹ (integrated from surface to 80–120 m) during intense blooms in the seasonal
407 ice zone which propagated south of the Antarctic polar front. But despite the massive diatom bSiO₂
408 accumulating in these blooms, V_{AVE} generally ranged between 0.05–0.15 d⁻¹ (Brzezinski et al.,

409 2001). Given the order-of-magnitude difference in $[\text{Si}(\text{OH})_4]$ and $[\rho]$ between the Arctic and
410 Southern Ocean, the similar V_{AVE} in both regions may be more reflective of thermal effects on
411 diatom growth rate, since Si uptake and diatom growth rates are tightly coupled, or a significant
412 accumulation of detrital bSiO_2 (i.e. diatom fragments) in the Southern Ocean, where low
413 temperatures reduce bSiO_2 remineralization rates (Bidle et al., 2002).

414

415 4.2 Potential for Silicon limitation of diatom productivity

416 Suboptimal silicon availability affects the rate of diatom bSiO_2 production and can limit
417 their growth. A widely cited $[\text{Si}(\text{OH})_4]$ threshold, below which diatoms will be outcompeted by
418 other phytoplankton, is $2.0 \mu\text{M}$; this metric was derived from a comparison of diatom abundance
419 (relative to total microplankton) versus $[\text{Si}(\text{OH})_4]$ during mesocosm experiments in a Norwegian
420 fjord system (Egge and Aksnes, 1992). Applying this metric globally has been criticized due to
421 observation of diatom dominance among microplankton when $[\text{Si}(\text{OH})_4] < 1 \mu\text{M}$ in systems
422 ranging from fjords to the open ocean (Krause et al., 2013; Hodal et al., 2012; Kristiansen et al.,
423 2001) and also culture studies showing some diatom species can maintain high growth rates when
424 $[\text{Si}(\text{OH})_4] < 0.5 \mu\text{M}$ (reviewed by Kristiansen and Hoell (2002)). Stoichiometry of silicon
425 availability relative to nitrate also help diagnose Si limitation; the most widely accepted diatom
426 Si:N ratio is ~ 1 based on temperate and low latitude clones (Brzezinski, 1985). There is a paucity
427 of diatom culture studies examining stoichiometry in polar diatoms, but Si:N during spring blooms
428 in Oslofjorden are close to Brzezinski's Si:N ratio (Kristiansen et al., 2001). For diatoms in
429 Svalbard and the broader region of the subpolar and polar European Atlantic, both $[\text{Si}(\text{OH})_4]$ and
430 its availability relative to N appear to be suboptimal for creating intense diatom blooms, such as
431 those occurring in the Southern Ocean. Yet, the Arctic spring bloom is consistently dominated by
432 diatoms or *Phaeocystis* (Degerlund and Eilertsen, 2010), which suggests some level of adaptation
433 for diatoms to the low $[\text{Si}(\text{OH})_4]$ environment of the region. Stoichiometry of silicon availability
434 relative to nitrate can help diagnose Si limitation; the most widely accepted diatom Si:N ratio is
435 ~ 1 based on temperate and low-latitude clones (Brzezinski, 1985). The average Si:N ratio for two
436 polar diatom clones (silicic acid and iron replete) reported in Takeda (1998) was 0.96 ± 0.24 (SE).
437 A more recent culture study by Lomas et al. (in review), reported Si:N for 11 polar diatom clones
438 grown at 2°C among exponential/stationary growth phases, and replete/N-limiting nutrient
439 conditions; these authors observed Si:N among all clones, treatments, and nutrient conditions
440 (>150 data points) was 1.7 ± 0.10 (SE).

441 Nutrient relationships support the potential for silicon to be a controlling factor of
442 regional diatom productivity. When plotting $[\text{NO}_3 + \text{NO}_2]$ as a function of $[\text{Si}(\text{OH})_4]$ (Fig. 5A) a
443 few trends emerge: 1) The slope of the linear regression relationship ($2.5 \pm 0.1 \text{ mol N} (\text{mol Si})^{-1}$)
444 denotes that $\text{NO}_3 + \text{NO}_2$ is consumed at over twice the rate per unit $\text{Si}(\text{OH})_4$. 2) Given that the
445 source water $[\text{NO}_3 + \text{NO}_2]$ concentration is only \sim twice that of $[\text{Si}(\text{OH})_4]$, a 2.5 drawdown ratio
446 would predict $\text{NO}_3 + \text{NO}_2$ to be depleted before $\text{Si}(\text{OH})_4$. This indeed indicates that phytoplankton
447 can deplete nitrogen to levels below detection while they appear unable to deplete $\text{Si}(\text{OH})_4$ pools
448 below $0.5 \mu\text{M}$, which would indicate $0.5 \mu\text{M}$ is the ultimate $\text{Si}(\text{OH})_4$ concentration required to
449 support diatom growth. Nitrate and silicic acid drawdown within the upper 50 m during the spring
450 season (1980–1984) was discussed by Rey et al. (1987) who suggested apparent nitrate limitation
451 (1980, 1981) and silicic acid limitation (1983, 1984) are annually variable. The Reigstad et al.
452 (2002) analysis of nitrate and silicic acid drawdown in the central Barents Sea shows similarities
453 in that the diatom assemblage could only drawdown $[\text{Si}(\text{OH})_4]$ to $1 \mu\text{M}$ (May 1998) and $0.5 \mu\text{M}$
454 (July 1999). These authors suggest that physical effects on phytoplankton explain the interannual

455 variability in the maximum $[\text{Si}(\text{OH})_4]$ drawdown, where diatoms dominate in shallow mixed
456 waters opposed to *Phaeocystis pouchetii* dominating in deeper mixed waters. Clearly, interannual
457 and local differences in mixing, which may favor *Phaeocystis pouchetii* over diatoms (Reigstad et
458 al., 2002), can affect the assemblage and nutrient drawdown trajectory (e.g. see points with high
459 $[\text{Si}(\text{OH})_4]$ and little measurable $[\text{NO}_3+\text{NO}_2]$, Fig. 5A); therefore, diagnosing whether Si could limit
460 diatom growth requires additional analyses.

461 The silicon kinetic data provide clarity for interpreting Si and N nutrient drawdown.

462 None of these nitrate and silicic acid relationships capture the progressive dynamics of an
463 active diatom bloom. Using the ARCEX data (Fig. 5A), if diatoms are limited by an absolute
464 $[\text{Si}(\text{OH})_4]$ (e.g. $2\ \mu\text{M}$), then at this concentration there is still ample residual $[\text{NO}_3+\text{NO}_2]$ ($3.8\ \mu\text{M}$)
465 which could be used by other phytoplankton that do not consume Si (Fig. 5A). Even if the diatom
466 $[\text{Si}(\text{OH})_4]$ threshold is closer to $1\ \mu\text{M}$, this observation of excess $[\text{NO}_3+\text{NO}_2]$ ($1.4\ \mu\text{M}$) still holds.
467 Diatoms have an *r*-selected ecological strategy and are typically the first phytoplankton group to
468 bloom in this region under stratified shallow mixed conditions (Reigstad et al., 2002). The 1.7
469 Si:N from Lomas et al. (in review) for nutrient-replete polar diatoms suggests they consume 70%
470 more Si relative to N. However, under kinetic limitation diatoms have long been inferred to reduce
471 Si per cell in culture to avoid growth limitation (Paasche 1973) —this was recently observed
472 directly in the field for the first time (McNair et al. in press). Given the clear kinetic limitation
473 observed during ARCEX (Fig. 4), this likely reduced the diatom Si:N ratio closer to the canonical
474 1:1 ratio. Thus, the kinetic limitation in this region may result if they in consumed N and Si being
475 consumed in near equal amounts (i.e. Si:N ~ 1) without significant competition for N by other
476 major phytoplankton groups, it is highly probable that Si would limit them first during a bloom
477 and previous inferences of diatom processes based on 1:1 Si:N drawdown appear valid. Clearly,
478 interannual and local differences in mixing, which may favor *Phaeocystis pouchetii* over diatoms
479 (Reigstad et al., 2002), can affect the assemblage and nutrient drawdown trajectory (e.g. see points
480 with high $[\text{Si}(\text{OH})_4]$ and little measurable $[\text{NO}_3+\text{NO}_2]$, Fig. 5A); therefore, diagnosing whether Si
481 could limit diatom growth requires additional analyses.

482 Nutrient relationships support the potential for silicon to be a controlling factor of regional
483 diatom productivity. When plotting $[\text{NO}_3+\text{NO}_2]$ as a function of $[\text{Si}(\text{OH})_4]$ (Fig. 5A) a few trends
484 emerge: 1) The slope of the linear regression relationship ($2.5 \pm 0.1\ \text{mol N} (\text{mol Si})^{-1}$) denotes that
485 NO_3+NO_2 is consumed at over twice the rate per unit $\text{Si}(\text{OH})_4$. 2) Given that the source water
486 $[\text{NO}_3+\text{NO}_2]$ concentration is only \sim twice that of $[\text{Si}(\text{OH})_4]$, a 2.5 drawdown ratio would predict
487 NO_3+NO_2 to be depleted before $\text{Si}(\text{OH})_4$. The latter observation suggests that $\text{Si}(\text{OH})_4$ could be
488 the yield limiting nutrient for diatoms during a spring bloom period only if they dominate the
489 phytoplankton assemblage and consume Si:N in ratios >1 , e.g. 1.7 as reported by Lomas et al. (in
490 review). Field data demonstrate interannual variability. Nitrate and silicic acid drawdown within
491 the upper 50 m during the spring season (1980–1984) was discussed by Rev et al. (1987) who
492 suggested apparent nitrate limitation (1980, 1981) and silicic acid limitation (1983, 1984). The
493 Reigstad et al. (2002) analysis of nitrate and silicic acid drawdown in the central Barents Sea shows
494 similarities to ARCEX in that the diatom assemblage could only drawdown $[\text{Si}(\text{OH})_4]$ to $\sim 1\ \mu\text{M}$
495 (May 1998) and $\sim 0.5\ \mu\text{M}$ (July 1999). These authors suggest that physical effects on
496 phytoplankton explain the variability, where diatoms dominate in shallow mixed waters opposed
497 to *Phaeocystis pouchetii* dominating in deeper mixed waters. Clearly, interannual and local
498 differences in mixing, which may favor *Phaeocystis pouchetii* over diatoms (Reigstad et al., 2002),
499 can affect the assemblage and nutrient drawdown trajectory (e.g. see points with high $[\text{Si}(\text{OH})_4]$

500 ~~and little measurable~~ $[\text{NO}_3 + \text{NO}_2]$ ~~close to detection limit~~, Fig. 5A); therefore, diagnosing whether
501 ~~Si could limit diatom production should be accompanied by additional analyses.~~

502
503 When considering the European sector of the Arctic/sub-Arctic between 60°–80°N, there
504 is compelling evidence that ambient $[\text{Si}(\text{OH})_4]$ ~~limits~~ the rate of diatom bSiO_2 production. During
505 ARCEX, the relationship between V_b and $[\text{Si}(\text{OH})_4]$ also supports that Si regulates diatom
506 productivity to some degree (Fig. 4). Our kinetic data demonstrate that in three of four experiments
507 K_S was $\sim 2.0 \mu\text{M}$, but in the Polar Front the K_S was lower $\sim 0.8 \mu\text{M}$. These data are consistent with
508 community kinetic experiments reported in Oslofjorden where K_S and V_{max} were between 1.7–
509 11.5 μM and 0.16–0.64 d^{-1} , respectively, with the lowest V_{max} observed during the declining
510 diatom bloom (Kristiansen et al., 2000). These authors concluded that silicon ultimately controlled
511 diatom productivity during this bloom (Kristiansen et al., 2001). In the only other kinetic
512 experiments reported in the northeast Atlantic, ~~Allen et al. (2005) Brown et al. (2003) and Allen~~
513 ~~et al. (2005)~~ observed ~~a~~ linear responses in V_b between ambient and 5 μM $[\text{Si}(\text{OH})_4]$, which
514 suggests uptake did not show any degree of saturation at this concentration (Note: the single
515 ~~experiment reported in Allen et al. (2005) is one of four experiments originally reported in Brown~~
516 ~~et al. (2003)~~). These field-based K_S values are considerably higher than parameters used in Barents
517 Sea models, e.g. 0.5 μM (Slagstad and Støle-Hansen, 1991), 0.05 μM (Wassmann et al., 2006)
518 which reflect the high ~~efficiency~~ Si uptake ~~reported seen for~~ cultures (Paasche, 1975). Fitting a
519 regression to the $V_b V_{\text{max}}^{-1}$ as a function of $[\text{Si}(\text{OH})_4]$ (line shown in Fig. 5B) suggests that 2.3–
520 μM is the best constrained half-saturation concentration (i.e. concentration where $V_b V_{\text{max}}^{-1} = 0.5$)
521 for the regional assemblage. ~~This empirical value, however, this excludes is biased from the~~
522 ~~Hornsunddjupet assemblage (white symbols, Fig. 5B), their inclusion decreases and this~~
523 ~~aggregated half-saturation would increase to 2.38 μM if those data were not considered.~~ Unlike
524 diatoms in the north Atlantic Subtropical Gyre, e.g. Sargasso Sea (Krause et al., 2012), regional
525 diatoms do not appear well-adapted for maintaining $V_b V_{\text{max}}^{-1} > 0.5$ at low $[\text{Si}(\text{OH})_4]$. Instead,
526 diatoms during the spring season appear to be best adapted for concentrations exceeding 2.3 μM .
527 ~~I, which suggests it is plausible~~ that as $[\text{Si}(\text{OH})_4]$ is depleted, diatoms may slow growth ~~both from~~
528 ~~severe limitation of Si uptake (Fig. 5B) and/or biomass yield (i.e. stock of diatom bSiO_2 far exceeds~~
529 ~~$\text{Si}(\text{OH})_4$).~~

530 To avoid growth limitation ~~under conditions of kinetic limitation (i.e. suboptimal~~
531 ~~$[\text{Si}(\text{OH})_4]$), diatoms can reduce their silicon per cell when $[\text{Si}(\text{OH})_4]$ is suboptimal. A guideline~~
532 ~~accepted principal~~ from culture work is that diatoms can alter their silicon per cell by a factor of
533 four (Martin-Jézéquel et al., 2000). Thus, when uptake is reduced to $< 25\%$ of V_{max} (i.e.
534 ~~concentration which promotes uptake at half the half-saturation level), diatoms must slow growth~~
535 to take up enough Si to produce a new cell. Using the empirical half-saturation constant range
536 (2.3–2.8 μM) calculated from Fig. 5B and using Eq. 1 to solve for the concentrations where V_b
537 $V_{\text{max}}^{-1} \leq 0.25$ (V_{max} is a constant), suggests that when $[\text{Si}(\text{OH})_4]$ is below 0.3–0.8 μM , the degree
538 of kinetic limitation could force diatoms to slow growth in ~~response~~ response. This type of
539 ~~limitation could occur even if diatom bSiO_2 stock was not sufficiently high to induce yield~~
540 ~~limitation, e.g. it could not deplete all $\text{Si}(\text{OH})_4$ from the assemblage undergoing one division.~~
541 Such a range ~~could be biased low given the influence of the highly efficient Hornsunddjupet~~
542 ~~assemblage (which was associated with warmer Atlantic waters). But at these $[\text{Si}(\text{OH})_4]$ there~~
543 ~~would also be up to 0.8 μM $[\text{NO}_3 + \text{NO}_2]$ remaining (Fig. 5A). is lower than the common~~
544 ~~interpretation of the Egge and Aksnes (1992) data set showing diatoms may be outcompeted by~~
545 ~~flagellates when $[\text{Si}(\text{OH})_4] < 2 \mu\text{M}$, a value which is more reflective of an ecological niche opposed~~

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546 [to a physiological threshold as has been purported in numerous citations of these data. At these](#)
547 [inferred limiting \[Si\(OH\)₄\] there would be up to 0.8 μM \[NO₃ + NO₂\] remaining \(Fig. 5A\), which](#)
548 [would allow a secondary group\(s\) non-siliceous phytoplankton to draw down the remaining N.](#)
549 Therefore, under shallow stratified conditions which favor diatoms over *Phaeocystis* (*sensu*
550 Reigstad et al. (2002)), [Si(OH)₄] may regulate regional diatom productivity [during spring](#)
551 [consistent with similar results from southern Norway fjords \(Kristiansen et al., 2001\) through](#)
552 [either yield- or severe-kinetic limitation.](#) This provides the most direct assessment to date
553 supporting the general ideas [proposed for that Si regulation of may limit regional regional](#) diatom
554 productivity (Rey, 2012; Rey et al., 1987; Reigstad et al., 2002).

556 4.3 Diatom contribution to primary production

557 Among the six sites with paired PP and p measurements, the bloom phase can be inferred
558 from the magnitude of nutrient drawdown, [Chl *a*], PP, and pCO₂ (data not shown). Bredjupet
559 appeared to be a pre-bloom station given the [high surface nutrient concentrations](#), while the van
560 Mijenfjorden station ~~also~~ appeared to be in an early bloom phase [based on relative high nutrients](#)
561 [and moderate \[Chl *a*\].](#) The ~~Erik Erikssenstretet~~[Erik Erikssenstretet](#) station represented a peak
562 bloom condition, whereas assemblages at Hornsunddjupet and Edgeøya appeared to be post bloom
563 and in a stage of decline. The Polar Front station represented the end or late-phase bloom
564 condition; however, at this station *Phaeocystis* was abundant (data not shown), suggesting it may
565 have dominated the bloom dynamics instead of diatoms.

566 The diatom contribution to PP was highly variable. Among the stations with high [NO₃ +
567 NO₂] (van Mijenfjorden, Bredjupet) the diatom contribution to PP (e.g. Eq. 2) was low, ~~52–63%~~.
568 At two stations, Hornsunddjupet and the Polar Front, the diatom contribution to PP increased to
569 ~~4825–5730%~~. In the Edgeøya, and ~~Erik Erikssenstretet~~[Erik Erikssenstretet](#) stations, diatoms
570 accounted for ~~all a majority or all of PP, 70430% and 180340%, respectively.~~ [Such unrealistic](#)
571 [value at Erik Erikssenstretet could imply a potential issue with the Si:C ratio \(Eq. 2\), specifically](#)
572 [an increase in Si per cell and/or lower C per cell due to reduced growth rate associated with the](#)
573 [peak/end of the bloom. Given that diatoms can reduce their cellular Si in response to kinetic](#)
574 [limitation \(Paasche 1973, McNair et al. in press\), the Si:C ratio of 0.25 based on nutrient-replete](#)
575 [polar diatoms in culture may systematically underestimate diatom contribution to PP using our](#)
576 [approach. For example, if kinetic limitation reduced Si per cell by 50% \(i.e. \$V_b/V_{max}^{-1} \approx 0.50\$, Fig.](#)
577 [5B\) but did not affect cellular C, then the Si:C ratio would be 0.13 \(i.e., temperate Si:C diatom](#)
578 [value\), and nearly all the calculated diatom contributions would double. Considering the degree](#)
579 [of kinetic limitation at most stations \(Fig. 5B\), this suggests our estimates are conservative except](#)
580 [at ~~Erik Erikssenstretet~~~~Erik Erikssenstretet~~.](#) ~~Such an~~[The unrealistic value at ~~Erik Erikssenstretet~~~~Erik~~](#)
581 [Erikssenstretet could imply underscores a the potential issue with the Si:C ratio \(Eq. 2\), however,](#)
582 [adjusting Si:C downward would increase the diatom contribution. Thus, there](#)
583 [specifically an](#)
584 [increase in Si per cell and/or may have been lower C per cell for diatoms at this station due to other](#)
585 [factors reduced growth rate associated with the peak/end phase of the bloom and/or the different](#)
586 [assemblage, e.g. *Porosira glacialis* dominant at this station and has a large vacuole which could](#)
587 [lower C content thereby increasing Si:C \(data not shown\).](#)

588 Clearly, diatoms can play a significant role in local productivity, but these data demonstrate
589 a “bloom and bust” nature. At stations at or near peak bloom levels (e.g. Edgeøya, ~~Erik~~
590 ~~Erikssenstretet~~[Erik Erikssenstretet](#)), diatoms could account for nearly all primary production.
591 However, they may also ~~conduct contribute~~ an insignificant percentage of primary production prior
592 to the onset of the bloom (e.g. van Mijenfjorden, Bredjupet). But even when physical conditions

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592 may favor *Phaeocystis* blooms, diatoms appear to be significant contributors to primary production
593 (Polar Front station). In such a situation, N would be predicted to be the limiting nutrient as it will
594 be consumed by both *Phaeocystis* and diatoms whereas Si will only be consumed by the latter.

595 In the European Arctic, shifts in summer-period phytoplankton communities away from
596 diatom-dominated conditions have been observed in numerous studies. One of the dominant
597 features has been the increasing abundances of *Phaeocystis* in ice-edge (Lasternas and Agustí,
598 2010) or under-ice blooms (Assmy et al., 2017). These changes have corresponded with larger-
599 scale shifts in the export of diatoms to depth in the Fram Strait (Nöthig et al., 2015; Lalande et
600 al., 2013; Bauerfeind et al., 2009). The timing of these shifts, e.g. mid-2000s, correspond with the
601 broader regional reduction in winter mixed-layer $[\text{Si}(\text{OH})_4]$ concurrent with the shift to negative
602 gyre-index state in the latter half of the decade (Hátún et al., 2017). With a reduction in pre-bloom
603 $\text{Si}(\text{OH})_4$ supply, diatoms may run into limitation sooner during the bloom cycle and thus leave
604 more residual nitrate for non-diatom phytoplankton. Degerlund and Eilertsen (2010) also
605 demonstrate a dynamic temperature niche for individual diatom groups/species. Coello-Camba et
606 al. (2015) showed that temperature induced a shift in the Arctic phytoplankton community, with
607 diatoms declining as temperature increased and thereby favoring dominance of flagellates. Given
608 the highly variable contribution of diatoms to primary productivity in this system in spring and the
609 effects which carry over into summer, should climate change or natural physical oscillations affect
610 diatoms in this system, resolving a climate change or natural physical oscillation such a signal will
611 be challenging. A similar conclusion about detecting a climate-change signal was made in the
612 eastern Bering Sea by Lomas et al. (2012) given the natural variability in primary production.

613 4.4 Diatoms and export

614 The bSiO_2 export rates observed during ARCEX were significant relative to the standing
615 stocks. At van Mijenfjorden, the rate of export in the upper 40 m represented 39% of the $\int \text{bSiO}_2$
616 standing stock ($23.3 \text{ mmol Si m}^{-2}$, integral of data in Fig. 2C) in the same vertical layer. This
617 quantity was much higher than at ~~Erik Erikssenstretet~~Erik Erikssenstretet, where the 40-m export
618 rate was <11% of the $\int \text{bSiO}_2$ in the upper water column (note: no samples were taken deeper than
619 20 m, thus, additional bSiO_2 between 20–40 m would lower the 11% estimate). Given that the van
620 Mijenfjorden site was located within shallow fjord waters (bottom depth approximately 60 m),
621 such a high proportion export relative to standing stock may suggest either lateral focusing
622 processes (e.g. discussed by DeMaster (2002)) and/or resuspension of sediment bSiO_2 into the
623 water and resettlement. The rate of bSiO_2 export among all export- and production stations was
624 also at least a factor of four higher than $\int \rho$ in the upper 20 m (Table 1). The rate of bSiO_2 export
625 was also at least a factor of four higher than $\int \rho$ in the upper 20 m. It is likely that some fraction of
626 $\int \rho$ was missed due to lack of sampling between 20–40 m, but with a ~~lack of less~~ light at these depths,
627 it is unlikely systematic underestimates of ρ caused the disparity. Given the deeper water at the
628 ~~Erik Erikssenstretet~~Erik Erikssenstretet and Atlantic stations, such high bSiO_2 export may be driven
629 by previously high ρ and bSiO_2 standing stock which accumulated in the overlying waters or, given
630 the dynamic circulation in the region, this signal may have been laterally advected to these station
631 locations.

632 Relative to previous studies, the bSiO_2 export rates were also high. During May 2012 in
633 Kongsfjorden, Lalande et al. (2016) reported bSiO_2 export rates between $0.2\text{--}1.3 \text{ mmol Si m}^{-2} \text{ d}^{-1}$
634 in the upper 100 m, a similar range was observed by Lalande et al. (2013) in the eastern Fram
635 Strait using moored sediment traps (2002–2008) collecting at depths between 180–280 m. Lalande
636 et al. (2013) concluded that, despite warm anomaly conditions, pulses of bSiO_2 export were

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638 positively correlated to the presence of ice in the overlying waters which stratifies the water and
639 helps initiate a diatom bloom. However, if the light was insufficient to stimulate a bloom, Lalande
640 et al. (2013) suggested much of the pulse of bSiO₂ exported to depth may have originated in the
641 ice and sank during melting. Indeed, the low V_b (<0.01 d⁻¹) observed at the Hinlopen station (ice
642 algae), despite the moderate ρ measured (0.12 μmol Si L⁻¹ d⁻¹), suggests that most of the ice-
643 associated bSiO₂ was detrital and not associated with living diatoms. Thus, the recent ice retreat
644 observed prior to the ARCEX cruise was a potential source of such high bSiO₂ export to depth
645 despite the considerably lower |ρ in the upper 20 m.

646 Among the groups examined, the most important diatom genera for standing stock and
647 export were *Thalassiosira* and *Fragilariopsis*, suggesting these groups are important drivers of
648 bulk bSiO₂ fluxes. Given the large-size and chain-forming life histories for the dominant species
649 within each genus, it is likely that their dominance in the trap abundances helps explain the high
650 correlation (r = 0.67, p < 0.01; Spearman's Rho Test) between bSiO₂ and diatom export. Given this
651 degree of correlation, it would be expected that both bSiO₂ and diatom export would be similarly
652 enhanced relative to previous studies; however, this was not observed.

653 Comparing the magnitude of bulk bSiO₂ export and the export of diatom cells suggests
654 significant food web repackaging occurred. The export of diatom cellular export in
655 Kongsfjorden (Lalande et al., 2016) were similar-to or a factor of three lower than rates quantified
656 during ARCEX (Table 1, Fig. 3E), whereas bSiO₂ export during ARCEX was over an order of
657 magnitude higher than bSiO₂ export in Kongsfjorden. One possible explanation for the higher
658 degree of bSiO₂ export enhancement, relative to diatom-cellular export, between studies is that
659 more exported material during ARCEX was repackaged and modified in the food web. For
660 instance, in ~~Erik Erikssenstretet~~Erik Erikssenstretet gel traps confirm the presence of aggregates
661 and mesozooplankton fecal pellets (Wiedmann et al. in prep), and in van Mijenfjorden detrital
662 particles and sediment material were most prominent on the gel traps opposed to clearly
663 recognizable material (e.g. diatom valves). ~~These observations suggest the potential for~~
664 ~~considerable modification of diatom organic matter prior to export (diatoms in fecal pellets,~~
665 ~~fragments associated with aggregates, etc.).~~—This repackaging is consistent with previous
666 observation in the Barents Sea showing high potential for copepod fecal pellets to be exported in
667 the Polar Front and Arctic-influenced regions during spring (Wexels Riser et al., 2002). And
668 supports the general ideas for the importance of diatom organic matter in fueling secondary
669 production regionally during this season (Degerlund and Eilertsen (2010) and references therein).

670

671 4.5 Conclusion

672 This is the first regional data set with contemporaneous measurements of diatom bSiO₂
673 standing stock, production, export and assessment of kinetic limitation by [Si(OH)₄] in the
674 European Arctic. Among stations and depths there was widespread limitation of diatom bSiO₂
675 production rates by ambient [Si(OH)₄] during spring-bloom conditions. The kinetic parameters
676 for diatom Si uptake (e.g. K_S) quantified in our study are significantly higher than rates used in
677 regional models and quantified in polar diatom cultures; therefore, these data will help future
678 modeling efforts better simulate diatom/Si dynamics. Given the trajectories of Si and N
679 consumption, diatom-dominated blooms (vs. *Phaeocystis*-dominated) could deplete Si(OH)₄ prior
680 to nitrate (yield limitation); and at some stations, the degree of kinetic limitation by ambient
681 [Si(OH)₄] could have resulted in diatom growth being slowed. Diatom contribution to PP was
682 highly variable, ranging from <10% to ~100% depending on the bloom stage; but even when
683 *Phaeocystis* appeared to be favored, diatoms still had a significant (~~~50~~25%) contribution to PP.

684 While there was agreement with previous regional studies regarding the [export](#) rate of diatom
685 cell~~sular export~~, we observed significantly elevated bSiO₂ export. Such a discrepancy can be
686 resolved if a higher fraction of the diatom material exported during our study was modified by
687 zooplankton grazers, relative to previous studies, or if much of this bSiO₂ was derived from
688 melting ice and/or advection.

689
690 *Data availability.* All data are available upon request to the authors or are available through the
691 UiT research data bank (<https://dataverse.no/dataverse/uit>).

692
693 *Author contributions.* JK, CMD, SA conceived/designed the study and conducted analysis. JK,
694 CMD, IM, PA, MFM, IW, SA conducted the fieldwork. PW and SK conducted analysis. All co-
695 authors contributed to the writing of the paper, led by JK.

696
697 *Competing interests.* The authors declare that they have no conflict of interest.

698
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891 Table 1 – Station properties including surface temperature, nutrients and chlorophyll a (\pm standard deviation), 20-m biogenic silica stock (\int bSiO₂),
 892 production (\int ρ) and depth-weighted specific production (V_{AVE}), 40-m integrated diatom abundance (\int Diatom) and export of bSiO₂ and diatoms at
 893 40 m. The disparity between the integration depths for bSiO₂ standing stock and diatom abundance reflects the lack of bSiO₂ samples to 40 m
 894 depth and that the latter are used to compare with diatom export (Discussion). Note: Hinlopen (ice) station not included. The Polar Front \int Diatom
 895 is the mean of two profiles.

Station Name	T (°C)	[NO ₃ + NO ₂] (μM)	[Si(OH) ₄] (μM)	[Chl a] (μg L ⁻¹)	20-m \int bSiO ₂ (mmol Si m ⁻²)	20-m \int ρ (mmol Si m ⁻² d ⁻¹)	20-m V_{AVE} (d ⁻¹)	40-m \int Diatom abundance (10 ⁹ cells m ⁻²)	40-m bSiO ₂ export (mmol Si m ⁻² d ⁻¹)	40-m \int Diatom export (10 ⁶ cells m ⁻² d ⁻¹)
‡van Mijenfjorden	-0.43	8.1	3.8	1.84 ±0.19	10.8	-	-	7.67	9.03	769
‡Bredjupet	4.72	9.4	4.5	0.72 ±0.03	1.9	0.27	0.13	-	-	-
Bellsund Hula	0.69	<0.1	0.5	2.66 ±0.05	15.3	0.49	0.06	-	-	-
Hornsund	-0.28	1.6	1.1	2.50 ±0.20	-	-	-	8.97	-	1180
‡Hornsunddjupet	-0.20	<0.1	0.4	2.43 ±0.17	42.2	1.46	0.03	-	-	-
‡Edgeøya	-0.70	0	0.7	1.99 ±0.03	-	-	-	-	-	-
‡Erik Erikssenstretet	-1.58	0.4	0.4	4.77 ±0.31	34.9	1.03	0.04	252	4.00	436
‡*Polar Front Station	2.19	<0.1	1.1	3.00 ±0.03	-	-	-	527	-	-
Atlantic	4.10	3.3	1.4	6.66 ±0.33	-	-	-	-	9.20	2380

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896 †Surface value

897 *25 m depth

898 ‡Denotes concurrent primary production and biogenic silica production measurements at one depth

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903 Figure Captions:

904

905 Figure 1: Surface properties during 2016 ARCEX cruise including A) $\text{N}_{\text{nitrate}} + \text{N}_{\text{nitrite}}$ (μM), B)
906 dissolved silicic acid (μM), C) biogenic silica ($\mu\text{mol Si L}^{-1}$), D) Chlorophyll *a* ($\mu\text{g L}^{-1}$) and E)
907 Temperature ($^{\circ}\text{C}$) overlaid on station map. Station names are denoted on the map and colored arrows
908 generalize the flow of Atlantic-influenced (red) and Arctic-influenced (blue) waters.
909

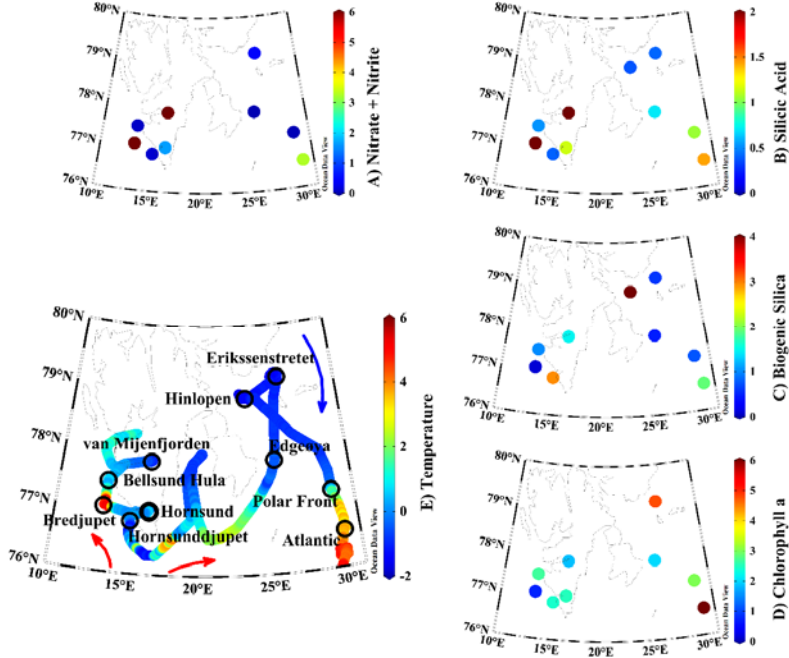
910 Figure 2: Vertical profiles for A) dissolved silicic acid, B) $\text{N}_{\text{nitrate}} - \text{nitrate} + \text{N}_{\text{nitrite}} - \text{nitrite}$, C) biogenic
911 silica standing stock, D) biogenic silica production rate, and E) biogenic silica export. Symbols are
912 associated by station, and line connectors are used to denote profile data opposed to individual symbols
913 noting samples at one depth.

914 Figure 3: Diatom abundance (A) and assemblage composition (B–D) in the water column, and diatom
915 export (E) and assemblage composition (F–H) within sediment traps. Note – taxonomy information only
916 shown for stations where both water-column and sediment-trap data were available (see text for species).
917 Resting spores (e.g. *Chaetoceros*, *Thalassiosira*) were absent from the 40-m sediment traps; thus,
918 proportional abundances for spore-producing taxa are entirely for vegetative cells. For panel A, there are
919 replicate diatom abundance measurements (from separate hydrocasts) for the Polar Front station.
920

921 Figure 4: Assessment of Si uptake limitation by available silicic acid during ARCEX. A) 8-point kinetic
922 experiments taken at four stations (legend next to panel B). Data were fit to a Michaelis-Menten
923 hyperbola using SigmaPlot 12.3 software. B) Enh. ratio profiles (i.e. V_b in $+18.0 \mu\text{M} [\text{Si}(\text{OH})_4]$ treatment
924 relative to V_b in the ambient $[\text{Si}(\text{OH})_4]$ treatment) at four stations.

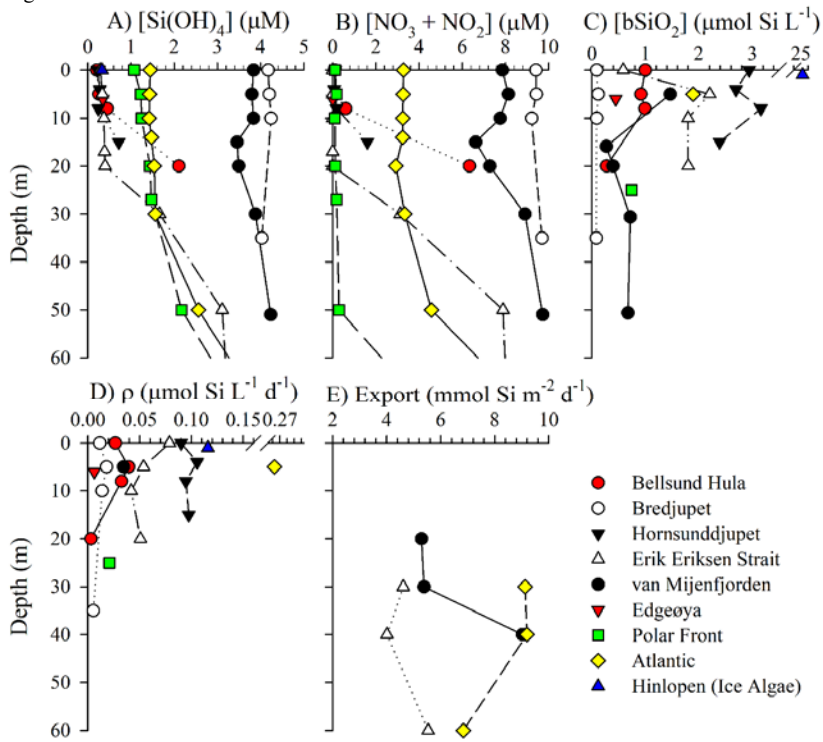
925 Figure 5: Diagnosis of potential silicon limitation for diatom production during ARCEX. A) Nitrate +
926 Nitrite drawdown as a function of dissolved silicic acid. B) The ratio of V_b at ambient $[\text{Si}(\text{OH})_4]$ to V_{max}
927 versus dissolved silicic acid. In both panels, linear regressions were done using a Model II reduced major
928 axis method; for panel B the regression line does not include the Hornsundjupet station (open circles).
929 For comparison, the same relationship for the Sargasso Sea in the North Atlantic subtropical gyre, as
930 synthesized in Krause et al. (2012).
931

932 Figure 1:



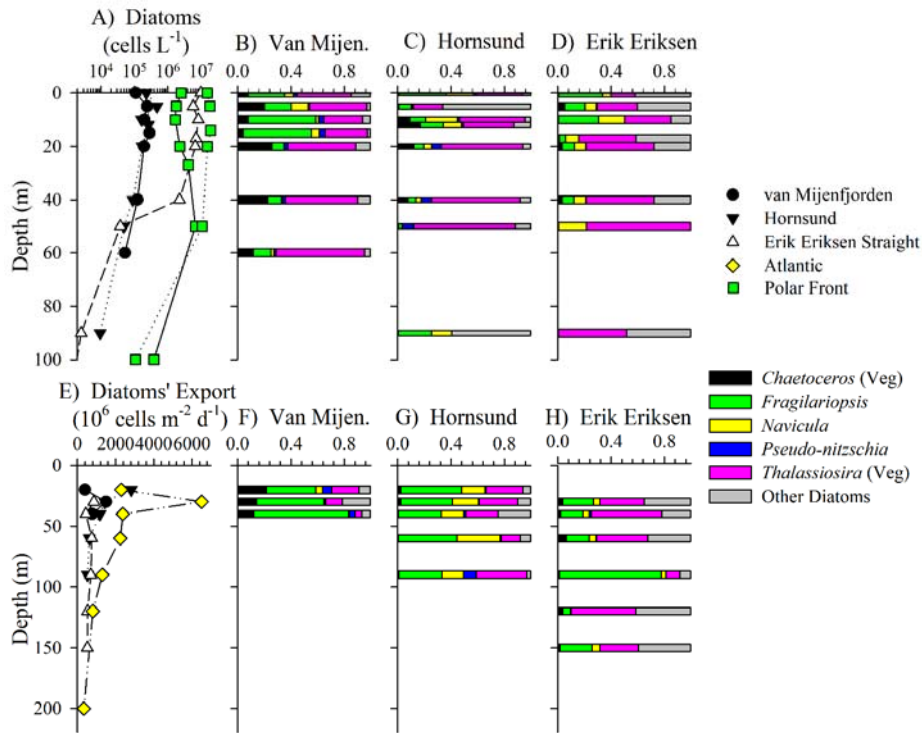
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935 Figure 2:



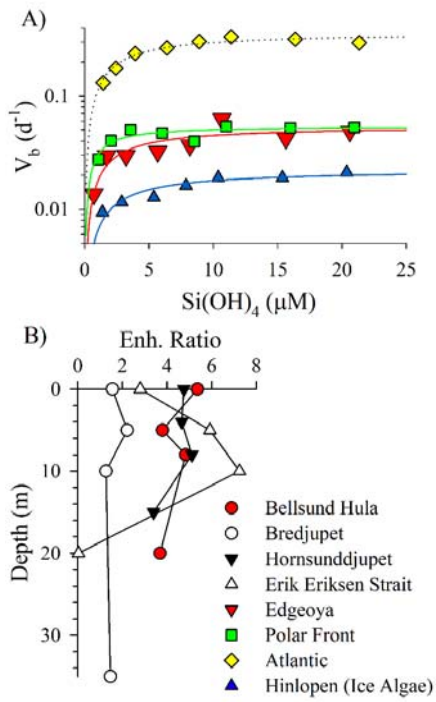
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938 Figure 3:



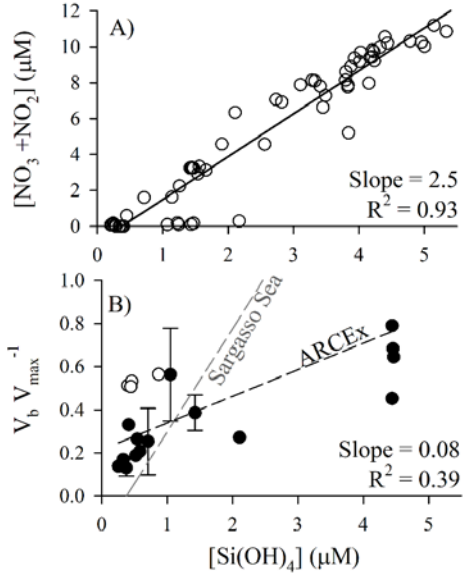
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941 Figure 4:

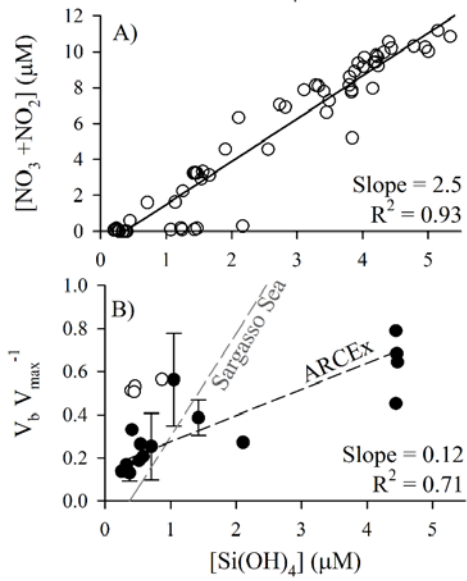


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944 Figure 5:



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