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1 **Putting the silicon cycle in a bag: Field observations of silicon isotope fractionation in**  
2 **subtropical waters east of New Zealand**

3

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24

## 25 **Abstract**

26 A mesocosm experiment was used to investigate the fractionation of silicon (Si) isotopes in  
27 subtropical surface waters east of New Zealand. This region surface waters were characterised  
28 by relatively low concentrations of silicic acid ( $\text{Si}(\text{OH})_4$ ) ( $\sim 2 \mu\text{mol L}^{-1}$ ) and higher nitrate ( $\sim 5$   
29  $\mu\text{mol L}^{-1}$ ) and dissolved iron (Fe) concentrations ( $\sim 0.4 \text{ nmol L}^{-1}$ ) prior to development of the  
30 annual springtime phytoplankton bloom. To simulate initiation of the bloom, a large ( $\sim 700 \text{ L}$ )  
31 mesocosm experiment was undertaken whereby surface seawater containing the natural  
32 plankton community was incubated for a 168-hr period. During the mesocosm experiment the  
33 concentrations of  $\text{Si}(\text{OH})_4$ , nitrate, phosphate and dissolved iron all decreased while the  
34 concentration of biogenic silica (BSi) increased 12-fold. Coupled with the increase in BSi was  
35 a change in the Si-isotope composition of BSi ( $\delta^{30}\text{Si}_{\text{BSi}}$ ) which increased from 1.49 ‰ to 2.64  
36 ‰ after 168 hr. Complementary observations to those made for the mesocosm experiment were  
37 made for corresponding surface waters. For these waters we observed a small decline in the  
38 concentrations of nitrate, phosphate and dissolved Fe, but little change in the concentrations of  
39  $\text{Si}(\text{OH})_4$  and BSi. In contrast to the mesocosm experiment, surface water  $\delta^{30}\text{Si}_{\text{BSi}}$  values became  
40 lighter during bloom initiation, suggestive of  $\text{Si}(\text{OH})_4$  being replenished into surface waters.  
41 These differences in the drawdown and utilisation of nutrients and dissolved Fe between the  
42 mesocosm and surface waters during bloom initiation likely result from favourable Fe and light  
43 supply conditions within the mesocosm. In contrast, water column stability (i.e. vertical  
44 mixing), and the supply of dissolved Fe are likely to influence bloom initiation and its  
45 longevity. The fractionation of Si-isotopes in the mesocosm experiment followed closed-  
46 system Rayleigh fractionation kinetics, and an enrichment factor ( $\epsilon$ ) of -1.13 ‰ was calculated  
47 for the exponential phase of growth for the diatom community, which was marked by the  
48 presence of the diatoms *Asterionelopsis glacilis* and *Mellosira moniliformis*. The isotope  
49 enrichment factor agreed well with previous observations of Si isotope fraction in diatoms from  
50 field communities, and appeared to be independent of variations in the ambient  $\text{Si}(\text{OH})_4$   
51 concentration, and phytoplankton species composition.

## 52        1. Introduction

53        The biological fractionation of silicon (Si) isotopes by diatoms in the surface ocean makes the  
54        stable isotope composition of biogenic silica ( $\delta^{30}\text{Si}_{\text{BSi}}$ ) an extremely sensitive tracer of the  
55        marine biogeochemical Si-cycle (de Souza et al., 2012b; Sutton et al., 2018). Understanding  
56        the processes governing Si-isotope fractionation is particularly important in the Southern  
57        Ocean, a region where silicic acid ( $\text{Si}(\text{OH})_4$ ) is retained as a result of diatoms in sub-polar  
58        waters preferentially removing  $\text{Si}(\text{OH})_4$  relative to nitrate ( $\text{NO}_3^-$ ) from the water column. These  
59        Si-poor waters extend northward as Sub-Antarctic Mode Water (SAMW) and play a significant  
60        role in setting the nutrient status of the global ocean (Sarmiento et al., 2004). The strong de-  
61        coupling of  $\text{Si}(\text{OH})_4$  and  $\text{NO}_3^-$  in Antarctic polar waters has a particularly important bearing on  
62        marine productivity at lower latitudes, and is due to a complex interplay between, (1) different  
63        diatom species and morphological types displaying varying degrees of bio-silicification  
64        (Baines and Pace, 1991), (2) Fe and light limitation inducing heavier rates of bio-silicification  
65        and reduced uptake of  $\text{NO}_3^-$  in diatoms (Brzezinski et al., 2002; Franck et al., 2003; Marchetti  
66        et al., 2010), (3) the export and deep remineralisation of  $\text{Si}(\text{OH})_4$  relative to  $\text{NO}_3^-$  (Pichevin et  
67        al., 2014; Sarmiento et al., 2007), and (4) grazer induced variations in cell wall bio-silicification  
68        and cell morphology (Smetacek et al., 2004). Deciphering the relative importance of these  
69        processes is key to understanding the nutrient distribution in and outside of the Southern Ocean  
70        (Sarmiento et al., 2004).

71        The distribution of  $\delta^{30}\text{Si}_{\text{BSi}}$  is extremely sensitive to these processes and acts as a useful tracer  
72        for examining the cycling of Si in resident diatom communities (De La Rocha et al., 1997;  
73        Fripiat et al., 2012; Milligan et al., 2004). The uptake of  $\text{Si}(\text{OH})_4$  by diatoms in the ocean  
74        influences the isotopic compositions of both  $\text{Si}(\text{OH})_4$  and biogenic silica (BSi) in surface  
75        waters. During  $\text{Si}(\text{OH})_4$  uptake, the lighter Si isotope ( $^{28}\text{Si}$ ) is preferentially taken up, and is  
76        defined by a fractionation factor ( $\epsilon$ ). For laboratory cultures and field populations of diatoms  $\epsilon$   
77        generally ranges between -0.53 and -1.9 ‰, with the odd individual species having more  
78        extreme values e.g. *Chaetoceros brevis* (Cardinal et al., 2007; De La Rocha et al., 1997; Fripiat  
79        et al., 2011; Meyerink et al., 2017; Sutton et al., 2013; Varela et al., 2004). In general, the  
80        factors that influence Si silicon isotope fractionation during a phytoplankton bloom formation  
81        are not well characterised. The aim of this study was to simulate the formation of the annual  
82        spring bloom using mesocosm approach and complement mesocosm observations with water  
83        column measurements.

84 This study took place within a warm-core eddy (39°20S 180°00'W) east of New Zealand where  
85 an annual spring phytoplankton bloom has been observed to occur based on satellite and field  
86 measurements (Boyd et al., 2012; Ellwood et al., 2015; Murphy et al., 2001). The region is a  
87 site of considerable eddy activity, which arises from the convergence of SubAntarctic Water  
88 (SAW) and Sub-Tropical Water (STW) (Bostock et al., 2013; Butler et al., 1992; Fernandez et  
89 al., 2014). The convergence zone is locked topographically to the Chatham Rise, a shallow  
90 (<300 m deep) submarine ridge, and is a region of high temperature, salinity and nutrient  
91 gradients as a result of the confluence of two significantly different water masses (SAW and  
92 STW) (Chiswell et al., 2015; Nodder et al., 2005). A warm core eddy immediately north of the  
93 Chatham Rise is a persistent feature in the region, which extends to 2000 m depth; and has  
94 been observed to have a spring bloom at its centre, which induces oligotrophic conditions in  
95 summer, and is followed by deep winter mixing and low productivity in winter (Murphy et al.,  
96 2001; Nodder et al., 2005). Phytoplankton community structure in the bloom is generally  
97 characterised by chlorophyll (Chl) concentrations  $>1 \text{ mg m}^{-3}$ , and large phytoplankton ( $>20$   
98  $\mu\text{m}$ ) (Boyd et al., 2012). Consequently, the area is marked by high seasonal fluxes of biogenic  
99 material to deeper waters (Nodder et al., 2005; Nodder and Northcote, 2001).

100 The relatively low concentrations of  $\text{Si(OH)}_4$  ( $\sim 2 \mu\text{mol L}^{-1}$ ) compared to  $\text{NO}_3^-$  ( $\sim 4 \mu\text{mol L}^{-1}$ ) in  
101 surface-ocean waters testify to the influence of SAW in the region (Boyd et al., 1999). A  
102 number of Fe-process studies have been undertaken in the region (e.g. (Boyd et al., 2012; Boyd  
103 et al., 2015; Ellwood et al., 2015)). These studies found that during the 2008 annual spring  
104 bloom dissolved Fe and nutrients are sufficient to support bloom initiation, however its  
105 duration and magnitude is primarily set by competition for dissolved Fe between various  
106 microbe and phytoplankton groups, which ultimately limits overall production in these waters.  
107 In contrast, relatively little is known on the biological fractionation of Si-isotopes by diatoms  
108 in New Zealand surface waters. Instead, a majority of the processes relating to variations in  
109  $\delta^{30}\text{Si}$  in  $\text{Si(OH)}_4$  and diatom derived BSi in the region are inferred from previous studies in the  
110 Southern Ocean and Equatorial Pacific e.g. (Beucher et al., 2008; de Souza et al., 2012a; Fripiat  
111 et al., 2012). At present, the only studies investigating Si-isotopes in New Zealand waters are  
112 for diatoms and sponges collected in the mesopelagic zone south of New Zealand, an area that  
113 is more strongly influenced by SAW (Egan et al., 2012; Rousseau et al., 2016; Wille et al.,  
114 2010).

115 The aims of the voyage were to (1) investigate the physicochemical factors driving the  
116 longevity, magnitude and termination of the spring phytoplankton bloom, (2) to investigate

117 trace metal cycling within the bloom, and (3) to relate this mechanistic understanding of  
118 environmental controls on bloom dynamics to remotely sensed-trends in phytoplankton blooms  
119 across the mesoscale eddy field east of New Zealand (See Ellwood *et al.* 2015 and references  
120 therein). The survey drew on the findings from an earlier voyage in September 2008 (FeCycle  
121 II), and utilised a mesocosm experiment to investigate pelagic Fe-cycling within the resident  
122 phytoplankton community (Boyd *et al.*, 2012; Ellwood *et al.*, 2015; Ellwood *et al.*, 2014). The  
123 work presented here is a supporting study that investigated factors driving BSi formation and  
124 Si-isotope fractionation within the spring bloom in the convergence zone east of New Zealand.  
125 The aim of this work was to investigate whether the fractionation of Si isotopes in subtropical  
126 surface waters east of New Zealand are influence by changes in Fe bioavailability as the annual  
127 spring bloom develops. To elucidate whether Fe bioavailability and phytoplankton bloom  
128 development influence  $\delta^{30}\text{Si}$ , we complemented water column sampling with a large mesocosm  
129 (700 L) experiment and smaller (20 L) incubation experiments. Here, we present comparisons  
130 of BSi production and Si-isotope ( $\delta^{30}\text{Si}_{\text{BSi}}$ ) fractionation in the mesocosm with new  $\delta^{30}\text{Si}_{\text{BSi}}$   
131 data from the subtropical-convergence zone.

132

## 133 **2. Methods**

### 134 *2.1 Sampling Site and Experimental Design*

135 The present survey (TAN1212) was part of a GEOTRACES process study and took place in a  
136 zone of confluence east of New Zealand (approximately 179°W, 39°S). The voyage took place  
137 between 15 September 2012 (year day 259) and 7 October 2012 (year day 281). Survey  
138 methods were similar to those for a previous voyage in September of 2008 (Boyd *et al.*, 2012);  
139 where after an initial survey of the eddy, a drogued drifter was deployed at the centre of the  
140 eddy to provide the quasi-Lagrangian sampling platform needed to interpret biogeochemical  
141 observations of the feature (for further details on eddy formation, see Boyd *et al.* (2012) and  
142 Ellwood *et al.* (2014)).

143 Sea surface (0 – 10m depth) samples for BSi and Si-isotopes were collected between days 263  
144 and 279 using the ships underway seawater supply. Sea surface Chl *a* fluorescence,  
145 photosystem II (PSII) photochemical efficiency ( $F_v/F_m$ ), and the effective absorption cross  
146 section of PSII ( $\sigma_{\text{PSII}}$ ) were monitored in real-time using a Chelsea Instruments Fast Repetition  
147 Rate (FRR) fluorometer that was plumbed into the ships underway water supply. Periodically,

148 size-fractionated Chl *a* samples were collected for analysis. Daily sea-surface samples (10m  
149 depth) were collected for dissolved macro-nutrients ( $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{Si}(\text{OH})_4$  and  $\text{PO}_4^{3-}$ ),  
150 particulate nitrogen (PON), particulate carbon (POC), and particulate phosphorus (POP) were  
151 collected off pre-dawn sampling casts utilising Niskin bottles deployed on a 24 bottle CTD  
152 rosette system (SBE 911plus CTD rosette). Samples for bacteria, *Synechococcus*,  
153 *Prochlorococcus*, and pico-eukaryote cell enumeration were collected using the procedures  
154 described by Hall et al. (2004)

155 Daily sea-surface samples (10 m depth) for dissolved Fe (DFe) were obtained using a trace  
156 metal clean (TM) rosette. Macro-nutrient concentrations were measured in real-time using a  
157 micro-segmented flow analyzer (Astoria Pacific International [API300]) with digital detection  
158 (Ellwood et al., 2014). Dissolved Fe (DFe) concentrations were determined onboard by flow-  
159 injection analysis with chemiluminescence detection of Fe using luminol after Fe pre-  
160 concentration on to Toyopearl AF-Chelate-650 M resin (de Jong et al., 1998) and spiking with  
161 hydrogen peroxide (Lohan et al., 2006). Samples for DOC were analysed at the National  
162 Institute of Water and Atmospheric Research (NIWA) according to APHA method 5310B  
163 using a TOC analyser.

164 A mesocosm experiment was conducted on day 266 using an acid cleaned 1000 L LDPE bag  
165 filled with 350 L of surface seawater that was pre-filtered using an acid cleaned 0.2  $\mu\text{m}$  capsule  
166 filter (Supor Acropak 200; Pall). Surface seawater was collected in a trace metal clean manner  
167 using a tow fish (Ellwood et al., 2014). The main aim of the mesocosm experiment was to  
168 mimic Fe cycling of pelagic Fe in the water column (see Ellwood et al. (2015) for more details).  
169 Two bags were used, one spiked with 0.2  $\text{nmol L}^{-1}$  of the radionuclide  $^{55}\text{Fe}$  and a control, spiked  
170 with 0.2  $\text{nmol L}^{-1}$  of non-radioactive Fe. Both bags were allowed to equilibrate with natural  
171 ligands present in the filtered seawater for 12 hours before being inoculated with another 350  
172 L of unfiltered seawater collected using the TM tow fish containing the natural plankton  
173 community (Ellwood et al., 2015). The total volume in each bag was 700 L. The bags were  
174 incubated on deck for 168 hours at 50% of the ambient light intensity (attenuated with neutral  
175 density screening), and kept at ambient seawater temperature by continual surface seawater  
176 circulation around the bags. All analyses and observations for the work presented in this study  
177 were made on the bag spiked with non-radioactive Fe. The Fe cycling results for the radioactive  
178 Fe experiments are were presented by Ellwood et al. (2015).

179 To determine the influence the addition of Fe in the mesocosm might have on the resident  
180 diatom community, and hence BSi production and the fractionation of  $\delta^{30}\text{Si}_{\text{BSi}}$ , a smaller  
181 microcosm experiment was run in conjunction on day 272. The experiment was run for 96  
182 hours and acted as an Fe-free control. For this experiment, four 20 L low density polyethene  
183 cubic containers were filled using unfiltered seawater from the tow fish, with two of the  
184 containers spiked with  $0.5 \text{ nmol L}^{-1}$  of dissolved Fe, and incubated as described for the  
185 mesocosm experiment. For the mesocosm and microcosm experiments pre-incubation samples  
186 were collected for macro-nutrient concentrations, BSi and Si-isotopes, photosynthetic  
187 parameters (fluorescence,  $F_v/F_m$  and  $\sigma_{\text{PSII}}$ ) and POC, PON and POP. The 700 L mesocosm  
188 experiment was sampled every 12-24 hours while the 20 L microcosm experiment was only  
189 sampled at the end of the 96-hour incubation in order to avoid possible Fe contamination.

190

## 191 *2.2 POC, PON, POP and BSi Analysis*

192 Samples for POC and PON analysis were collected by filtering between 500 and 750 mL of  
193 seawater through a pre-combusted 25 mm GFF filter (Merck-Millipore), before rinsing with  
194 50 ml of filtered seawater. Filters were stored at  $-80^\circ\text{C}$  before analysis. Samples for BSi and  
195 silicon isotope analysis were collected onto 25 mm  $0.4 \mu\text{m}$  polycarbonate filters (Pall). Surface  
196 seawater samples and samples from the mesocosm experiment were collected by filtering 30 –  
197 60 L (for surface seawater) and 10 – 20 L (for mesocosm and microcosm samples) of sample,  
198 respectively, through a 142 mm  $0.4 \mu\text{m}$  polycarbonate filter. The filter was immediately placed  
199 in a 50 ml polypropylene tube and capped. All filters were stored at  $-20^\circ\text{C}$  prior to analysis.  
200 Hydrolysis of the samples for BSi content was carried out by adding 18 ml of 0.5% (w/w)  
201  $\text{Na}_2\text{CO}_3$  solution to the tubes and heating them to  $85^\circ\text{C}$  for 2 hr (Paasche, 1980). When cool,  
202 each tube was neutralized with 0.5 M HCl to the turning point of methyl orange (pH 3–4),  
203 before being made up to 25 mL with deionised water. Silicate concentrations were determined  
204 using the molybdenum blue method (Strickland and Parsons, 1972).

205

## 206 *2.3 Preparation of samples for determination of $\delta^{30}\text{Si}$ of BSi*

207 Samples for  $\delta^{30}\text{Si}_{\text{BSi}}$  determination were rinsed from their filters into 2.5 ml Teflon bombs using  
208 deionised water. They were then evaporated to dryness at  $50^\circ\text{C}$  in a drying oven overnight. To  
209 remove any organics that may interfere with the analysis; the samples were treated with 1 mL  
210 of 30% (v/v)  $\text{H}_2\text{O}_2$  solution and refluxed for 24 hours at  $70^\circ\text{C}$  on a hotplate. Following the



211 oxidation of organics, the lids of the Teflon bombs were removed, and the samples were left to  
212 evaporate to dryness before adding 2 mL of 0.5 M NaOH to dissolve the sample. Samples were  
213 then left to reflux for 24 hours at 50 °C. A portion of the sample was removed, neutralised and  
214 the silicate concentration determined using the molybdenum blue method (Strickland and  
215 Parsons, 1965). Prior to silicon isotope analysis, sodium was removed from the samples using  
216 cation exchange chromatography. Twelve cation exchange columns were prepared using  
217 modified polypropylene 2.5 mL Pasteur Pipettes loaded with approximately 1 ml Dowex 50W-  
218 X8 cation exchange resin (200-400 mesh). Columns were cleaned by passing 0.5 ml of 8%  
219 (v/v) hydrofluoric acid (HF) and 3x 0.75 mL of deionised water over the resin. The resin was  
220 then protonated with 3x 0.75 mL 4M HCl followed by 3x 0.75 mL deionised water rinses. Each  
221 column was loaded with 0.5 mL of sample and then rinsed with 4x 0.75 mL of deionised water  
222 to ensure the entire sample was eluted. To minimize contamination, samples were collected in  
223 vials that were cleaned using 8% (v/v) HF, before being rinsed with deionised water.  
224

#### 225 *2.4 Determination of $\delta^{30}\text{Si}$ in particulate BSi*

226 The  $\delta^{30}\text{Si}$  of diatom BSi was determined according to methods developed by (Wille et al., 2010)  
227 using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS)  
228 (Finnigan Neptune, Germany) in medium-resolution mode. An ESI-Apex nebulizer fitted with  
229 a Teflon inlet system and a demountable torch fitted with an alumina injector was used for  
230 sample introduction. We used a standard-sample-standard bracketing technique for data  
231 acquisition and reduction (Wille et al., 2010). The  $\delta^{30}\text{Si}$  signal (based on the relative abundance  
232 of  $^{30}\text{Si}$  to  $^{28}\text{Si}$  ( $^{30}\text{Si}/^{28}\text{Si}$ )) was calculated using the following formula:  
233

$$234 \quad \delta^{30}\text{Si} = \left[ \left( \frac{R_{\text{Sample}}}{R_{\text{Std}}} \right) - 1 \right] \times 1000 \quad (1)$$

235  
236 Where  $R_{\text{sample}}$  is the  $^{30}\text{Si}/^{28}\text{Si}$  ratio of the sample and  $R_{\text{Std}}$  is the  $^{30}\text{Si}/^{28}\text{Si}$  ratio of the in-house  
237 RC11 diatomaceous standard. Measured  $\delta^{30}\text{Si}$  and the  $\delta^{29}\text{Si}$  values were then converted to be  
238 relative to the NBS28 reference standard based on the daily offset between the in-house RC11  
239 diatomaceous standard and NBS28. The overall offset between the in-house standard and the  
240 NBS28 standard was  $-2.28 \pm 0.14$  ( $n = 11$ ; mean  $\pm 2x$  standard deviation). Measurements of

241 sample blanks were made prior to each run to ensure that the combined blank and background  
 242 was <1% of the total sample signal. NBS28 and the “Diatomite” standard detailed in Reynolds  
 243 et al. (2007) were also prepared with each daily run, and were measured with every three  
 244 samples ( $\leq 8$  diatomite/NBS28 standards per daily run). The  $\delta^{30}\text{Si}$  composition of the  
 245 “Diatomite” standard (again relative to NBS28) produced average values for  $\delta^{29}\text{Si}$  of  $0.73 \pm$   
 246  $0.11 \text{ ‰}$  and  $\delta^{30}\text{Si}$  of  $1.42 \pm 0.17 \text{ ‰}$  (2 SD,  $n = 11$ ), and are within the upper 90% confidence  
 247 range ( $\delta^{29}\text{Si} = 0.79 \text{ ‰}$ ,  $\delta^{30}\text{Si} = 1.54 \text{ ‰}$ ) of the modal values ( $\delta^{29}\text{Si} = 0.66 \text{ ‰}$ ,  $\delta^{30}\text{Si} = 1.27 \text{ ‰}$ )  
 248 from inter-laboratory comparisons performed by Reynolds et al. (2007).

249  
 250 Sample  $\delta^{30}\text{Si}$  and the  $\delta^{29}\text{Si}$  values were plotted against each other to ascertain the best-fit mass-  
 251 dependent fractionation line (MDF, Figure 1). Our calculated slope for the best-fit MDF line  
 252 was 0.55 with a regression error of 0.13 (2SE,  $n = 11$ ) and is consistent with the consensus  
 253 slope of 0.511 obtained from inter-laboratory silicon standard measurements (Figure 1). This  
 254 value agrees with the slope of the theoretical fractionation line for Si of 0.5092 (Reynolds et  
 255 al., 2007).

256 Silicon isotope fractionation in diatoms has been modelled using both closed and open  
 257 steady-state models (Cardinal et al., 2007; De La Rocha et al., 1997; Varela et al., 2004). The  
 258 closed system model is employed when there is no net import or export of  $\text{Si}(\text{OH})_4$  or BSi out  
 259 of surface waters during the period of biological incorporation of Si (Varela et al., 2004); for  
 260 example, during periods of intense water column stratification where mixing across the  
 261 density interface separating the surface mixed layer from deeper waters is minimal  
 262 (Brzezinski et al., 2001). Because the mesocosm experiment has no inputs or outputs, a  
 263 closed system model can be used to define the evolution of  $\delta^{30}\text{Si}$  through the following  
 264 relationships:

$$265 \quad \delta^{30}\text{Si}(\text{OH})_4 = \delta^{30}\text{Si}(\text{OH})_{4 \text{ initial}} + \varepsilon \ln f \quad (2)$$

$$266 \quad \delta^{30}\text{Si}_{\text{BSi.inst}} = \delta^{30}\text{Si}(\text{OH})_4 + \varepsilon \quad (3)$$

$$267 \quad \delta^{30}\text{Si}_{\text{BSi.acc}} = \delta^{30}\text{Si}(\text{OH})_{4 \text{ initial}} - \varepsilon (f \ln f / (1 - f)) \quad (4)$$

268 Where  $\delta^{30}\text{Si}(\text{OH})_4$  is the isotopic composition of  $\text{Si}(\text{OH})_4$  in seawater,  $\delta^{30}\text{Si}(\text{OH})_{4 \text{ initial}}$  is the  
 269 initial isotopic composition of  $\text{Si}(\text{OH})_4$  in seawater prior to biological incorporation of  $\text{Si}(\text{OH})_4$ ,  
 270  $\delta^{30}\text{BSi}_{\text{inst}}$  and  $\delta^{30}\text{BSi}_{\text{acc}}$  are the instantaneous BSi product and accumulated BSi product

271 (respectively), and  $f$  is the fraction of  $\text{Si(OH)}_4$  remaining in the system after BSi formation  
272 ( $[\text{Si(OH)}_4]/[\text{Si(OH)}_{4\text{initial}}]$ ) (Varela et al., 2004). The Rayleigh isotope fractionation model  
273 assumes a constant value for  $\alpha$  (the fractionation factor), also known as the enrichment factor  
274 ( $\epsilon$ ), where  $\epsilon$  (‰)  $\approx (1 - \alpha) \times 1000$ .

275

## 276 3. Results

### 277 3.1 Surface water data

278 Phytoplankton bloom initiation commenced with a shoaling of the mixed layer on day 272 and  
279 continued until the end of the voyage on day 279, with surface fluorescence (Arbitrary units,  
280 AU) ranging from  $< 0.5$  prior to bloom formation, to 1.0 after the bloom (Figure 2A). Nitrate  
281 and DFe concentrations exhibit 1.5 – 3 fold decreases in surface concentrations during bloom  
282 initiation (Figures 2B, 3 and 4A), with  $\text{NO}_3^-$  concentrations decreasing from  $>4.8 \mu\text{mol L}^{-1}$  on  
283 day 267 to  $< 2.3 \mu\text{mol L}^{-1}$  on day 278, and DFe concentrations decreasing from  $> 0.3 \text{ nmol L}^{-1}$   
284  $^1$  on day 267 to  $< 0.2 \text{ nmol L}^{-1}$  on days 278 and 279. Silicic acid concentrations were relatively  
285 low ( $< 2 \mu\text{mol L}^{-1}$ ) in comparison to  $\text{NO}_3^-$  ( $\leq 5 \mu\text{mol L}^{-1}$ ) during the voyage and exhibited little  
286 variation during bloom initiation (Figure 4A).

287 From the start of the voyage, the phytoplankton community composition in surface waters was  
288 dominated by eukaryotic pico-phytoplankton ( $0.2 - 2 \mu\text{m}$  in size) and prokaryote pico-  
289 phytoplankton (*Synechococcus* and *Prochlorococcus*) (Figure 4B). Pico-eukaryotic plankton  
290 cell numbers increased relative to the other plankton groups, exhibiting a 2-fold increase on  
291 day 270 and a 3-fold increase by day 279. In comparison, both *Synechococcus* and  
292 *Prochlorococcus* populations exhibit little variation between days 263 and 273. *Synechococcus*  
293 and *Prochlorococcus* populations change rapidly, however, following day 273, where they  
294 exhibit 5-fold and 8-fold increases in their respective populations between days 273 and 279.  
295 The pico-phytoplankton also dominated the Chl *a* estimates of phytoplankton biomass (Figure  
296 4D). Night-time measurements of  $F_v/F_m$  average around 0.4 between days 263 and 272 before  
297 dropping to around 0.3 by day 274 (Figure 4B), following the decline in dissolved Fe  
298 concentration (Figure 4A). Between days 274 and 278,  $F_v/F_m$  remained around 0.3.

299 Surface elemental ratios and POC, PON and BSi concentrations are presented in Figure 4,  
300 while surface values for  $\delta^{30}\text{Si}$  from BSi are presented in Table 1. BSi concentrations  
301 remained consistent at  $0.07 \pm 0.02 \mu\text{mol L}^{-1}$  for the duration of the voyage and displayed little  
302 variation despite a relative increase in concentration at the onset of the bloom, from  $0.049$   
303  $\mu\text{mol L}^{-1}$  on day 273 to  $0.103 \mu\text{mol L}^{-1}$  on day 276 (Table 1, Figure 4C). The lack of variation  
304 in surface BSi is reflected in the relatively small change in surface  $\text{Si}(\text{OH})_4$  concentrations  
305 over the duration of the voyage (Figure 4A). Particulate organic nitrogen exhibits a 2-fold  
306 increase on day 273 (Figure 4C), which is concomitant with a relative decrease in the surface  
307  $\text{NO}_3^-$  concentration of  $\sim 1.3 \mu\text{mol L}^{-1}$  (Figure 4A). Samples for  $\delta^{30}\text{Si}_{\text{BSi}}$  from BSi were taken

308 prior to bloom initiation on days 268 and 270 and exhibited  $\delta^{30}\text{Si}_{\text{BSi}}$  values of  $1.61 \pm 0.2 \text{ ‰}$   
309 and  $1.83 \pm 0.2 \text{ ‰}$ , respectively (Figure 2B, Table 1), whereas  $\delta^{30}\text{Si}_{\text{BSi}}$  values were relatively  
310 lighter with respect to  $^{30}\text{Si}$  following bloom initiation, with  $\delta^{30}\text{Si}_{\text{BSi}}$  values of  $1.35 \pm 0.2 \text{ ‰}$  on  
311 day 275, and  $1.22 \pm 0.2 \text{ ‰}$  on day 279, respectively.

### 312 3.2. Mesocosm (700 L bag) experiment

313 There was a significantly different response in the mesocosm experiment compared to the  
314 response in surface waters over the duration of the voyage. Fluorescence and  $F_v/F_m$  increased  
315 with peak fluorescence at around 160 hr (Table 2 Figure 5A). BSi,  $\text{NO}_3^-$  and  $\text{Si}(\text{OH})_4$   
316 concentrations in the bag at the start of the experiment were comparable to sea-surface  
317 concentrations of BSi,  $\text{NO}_3^-$  and  $\text{Si}(\text{OH})_4$  on day 266, when the experiment was initiated. Both  
318  $\text{NO}_3^-$  and  $\text{Si}(\text{OH})_4$  concentrations exhibited an 11-fold and 9-fold decrease (respectively) by the  
319 end of the mesocosm experiment, while BSi concentrations increased from  $0.1 \mu\text{mol L}^{-1}$  to  $1.3$   
320  $\mu\text{mol L}^{-1}$  by the end of the mesocosm experiment (Figure 5B). There was almost complete  
321 utilisation of the  $\text{Si}(\text{OH})_4$  pool in the mesocosm by siliceous organisms, with BSi production  
322 reaching  $18 \pm 1 \text{ nmol L}^{-1} \text{ hr}^{-1}$  during the exponential phase of growth. This value closely  
323 resembles the rate of  $\text{Si}(\text{OH})_4$  depletion in the mesocosm, which reached  $20 \pm 1 \text{ nmol L}^{-1} \text{ hr}^{-1}$   
324 during the exponential phase of growth.

325 The starting value  $\delta^{30}\text{Si}_{\text{BSi}}$  for BSi in the mesocosm experiment was  $1.49 \pm 0.2 \text{ ‰}$  ( $t = 0 \text{ hr}$ )  
326 and comparable to the sea-surface  $\delta^{30}\text{Si}_{\text{BSi}}$  value of  $1.61 \pm 0.2 \text{ ‰}$  collected on day 268 (Figure  
327 5B). Over the course of the mesocosm experiment,  $\delta^{30}\text{Si}_{\text{BSi}}$  values became heavier with respect  
328 to  $^{30}\text{Si}$ , with  $\delta^{30}\text{Si}_{\text{BSi}}$  values increasing to  $2.64 \pm 0.2 \text{ ‰}$  by the end of the experiment (Figure  
329 5B). Silicon isotope fractionation within the experiment closely resembled Rayleigh  
330 fractionation kinetics, and a fractionation factor ( $\alpha$ ) of 0.9989, and an initial  $\delta^{30}\text{Si}_{\text{DSi}}$  value of  
331  $2.92 \pm 0.1 \text{ ‰}$  was calculated by fitting a model to the  $\delta^{30}\text{Si}_{\text{BSi}}$  for BSi (Figure 5C) (De La Rocha  
332 et al., 1997). While no phytoplankton community data were available for the mesocosm  
333 experiment, examination of late exponential populations confirmed the presence of the diatoms  
334 *Asterionelopsis glacilis*, *Mellosira moniliformis* and *Ceratium arcticum* (Figure 6).

### 335 3.3. Microcosm (20 L) experiment

336 Derived photosynthetic parameters from the microcosm experiment are presented in Figure 7.  
337 Despite the increase in Chl *a* fluorescence at the end of the experimental period in both control  
338 and Fe-addition experiments, both  $F_v/F_m$  and Chl *a* concentration decreased in the control  
339 experiment, whilst Chl *a* concentration and  $F_v/F_m$  increased ( $p < 0.05$ ) in response to Fe-

340 addition (Figure 7A, Table 3). The PSII effective absorption cross-section ( $\sigma_{PSII}$ ) decreased in  
341 both treatments by the end of the experimental period, however, this decrease was more  
342 pronounced in the Fe-addition experiment. BSi concentration increased from  $0.1 \mu\text{mol L}^{-1}$  at  
343  $T=0$  to  $0.9 \pm 0.2 \mu\text{mol L}^{-1}$  and  $1.1 \pm 0.1 \mu\text{mol L}^{-1}$  at  $T=96$  in the control and Fe-addition  
344 experiments, respectively. The increase in BSi concentration is consistent with the mesocosm  
345 (700 L bag experiment, Figure 7) which exhibited a 12-fold increase in BSi concentration at  
346 the end of the experimental period. In addition, both POC and PON concentrations exhibited a  
347 2 – 3 fold increase at the end of the experimental period (Figure 7B), with POC responding  
348 more strongly to Fe-addition in comparison to the control experiment. As a result, both  
349 treatments exhibited significant increases in elemental ratios at the end of the experimental  
350 period (Figure 7C). The increase in the C:N ratio, however, was more pronounced in the Fe-  
351 addition treatment, where POC concentration increased 3-fold compared to a 2.4-fold increase  
352 in the control. Increases in Si:N and Si:C ratios were due to a more pronounced increase in BSi  
353 concentrations compared to increases in PON and POC concentrations. The addition of  
354 dissolved Fe appeared had little effect ( $p > 0.1$ ) on the Si:N and Si:C ratios at the end of the  
355 experimental period (Figure 7C).

356

#### 357 4. Discussion

358 Here we first discuss the silicic acid, BSi and silicon isotope results from the mesocosm and  
359 microcosm experiments. We then place the experiments into context by comparing the  
360 findings with water column measurements. We then detail the processes that might regulate  
361 silicic acid utilisation in the waters east of New Zealand.

362 The fractionation of Si isotopes in the mesocosm bag experiment closely resembled Rayleigh  
363 fractionation closed-system kinetics as  $\text{Si}(\text{OH})_4$  was drawdown (Figure 5B). BSi concentration  
364 increased 12-fold in the mesocosm over 8 days resultant from increased in diatoms production  
365 thus leading to an increase in  $\delta^{30}\text{Si}_{\text{BSi}}$ . The value for  $\delta^{30}\text{Si}_{\text{BSi}}$  at the beginning of the mesocosm  
366 experiment was  $1.49 \pm 0.2 \text{ ‰}$ , which closely resembled surface values for  $\delta^{30}\text{Si}_{\text{BSi}}$  measured  
367 prior to bloom initiation on days 268 and 270 (Figure 5, Table 1). As the experiment progressed  
368  $\delta^{30}\text{Si}_{\text{BSi}}$  increased to  $2.64 \pm 0.2 \text{ ‰}$  by the end of the experiment. Based on the increase in  
369  $\delta^{30}\text{Si}_{\text{BSi}}$  and the drawdown in silicic acid as the mesocosm bag experiment progressed, we were  
370 able to calculate a fractionation factor ( $\alpha$ ) of 0.9989 ( $\epsilon = -1.1 \text{ ‰}$ ) and a starting seawater value  
371 for  $\delta^{30}\text{Si}_{\text{DSi}}$  of  $2.92 \pm 0.1 \text{ ‰}$ . The fractionation factor reported from the mesocosm experiment  
372 closely resembles fractionation factors previously published for laboratory and field  
373 communities. De La Rocha et al. (1997) obtained a value for  $\epsilon$  of  $-1.1 \pm 0.4 \text{ ‰}$  for the diatoms  
374 *Thalassiosira weissflogii*, *Thalassiosira sp.* and *Skeletonema costatum* cultured in the  
375 laboratory and found that fractionation was independent of species or temperature. More  
376 recently Sutton et al. (2013), however, found significant variations in  $\epsilon$  between the Southern  
377 Ocean species *Chaetoceros brevis* ( $-2.09 \pm 0.09 \text{ ‰}$ ) and *Fragilariopsis kergulensis* ( $-0.56 \pm$   
378  $0.07 \text{ ‰}$ )., The fractionation factor reported here ( $-1.13 \pm 0.1 \text{ ‰}$ ) from the mesocosm  
379 experiment also closely resembles fractionation factors reported for field communities, e.g.  
380 Varela et al. (2004)( $-1.2 \pm 0.2 \text{ ‰}$ ), Fripiat et al. (2011)( $-1.0 \pm 0.3 \text{ ‰}$ ) suggesting that species  
381 composition of the overall diatom community in the open ocean plays an important role in  
382 governing the Si isotope composition in surface waters.

383 The high  $\delta^{30}\text{Si}_{\text{DSi}}$  value calculated from the mesocosm experiment reflects the relatively high  
384  $\delta^{30}\text{Si}_{\text{BSi}}$  values observed at the start of the experiment and also reflects the surface water  
385 composition prior to bloom initiation on days 268 and 270 (Figure 5, Table 1). The calculated  
386  $\delta^{30}\text{Si}_{\text{DSi}}$  of  $2.92 \pm 0.1 \text{ ‰}$  from the experiment is within the range expected for sub-tropical and  
387 tropical water (Beucher et al., 2008) and matches those reported from the Polar Frontal Zone  
388 of the Pacific Sector of the Southern Ocean ( $\sim 3.2 \text{ ‰}$ ) (de Souza et al., 2012b).

389 In contrast to the mesocosm experiment, changes to  $\text{Si}(\text{OH})_4$  and BSi concentrations for surface  
390 waters within the eddy were relatively subtle (Figure 2B). In contrast to mesocosm experiment,  
391 sea-surface values for  $\delta^{30}\text{Si}_{\text{BSi}}$  were relatively constant between days 268 and 270 and then  
392 decline by about  $\sim 0.5$  ‰ through to day 279, following bloom initiation (Table 1). The surface  
393 water values presented here on days 275 and 279 for  $\delta^{30}\text{Si}_{\text{BSi}}$  resemble values reported for  
394 waters north of the Sub-tropical front in the Atlantic sector of the Southern Ocean ( $1.30 \pm 0.1$   
395 ‰)(Fripiat et al., 2012). It is likely that the observed shift in the  $\delta^{30}\text{Si}_{\text{BSi}}$  composition in surface  
396 waters towards lighter Si isotopes could be attributable to a change in the supply of  $\text{Si}(\text{OH})_4$  to  
397 surface waters, possibly from SAW (Figure 2B). It also reflects the open system nature of the  
398 area.

399 In contrast to the mesocosm experiment the BSi concentration in surface waters varied little  
400 during the  $\sim 17$  day voyage, only increasing from  $0.05 \mu\text{mol L}^{-1}$  on Day 264 to  $0.11 \mu\text{mol L}^{-1}$   
401 on day 278 (Figure 4C). The relatively rapid uptake of  $\text{Si}(\text{OH})_4$  in the mesocosm experiment  
402 as well as the 12-fold increase in BSi concentrations, in contrast to lack of *in situ* BSi  
403 production, suggest that changes in water-column stability may have encouraged more rapid  
404 bloom initiation compared to surface waters. It is possible that Fe had a small stimulatory effect  
405 within the mesocosm experiment, although it was only increased by  $0.2 \text{ nmol L}^{-1}$  relative to  
406 surface waters, which were  $0.3\text{-}0.4 \text{ nmol L}^{-1}$ . This was tested in smaller microcosm (20 L)  
407 experiments, where the rate of BSi production show little variation between control and Fe-  
408 addition replicates ( $p > 0.05$ ). In these smaller experiments, Fe addition did seem to affect  
409 photosynthetic parameters ( $F_v/F_m$ ,  $\sigma_{\text{PSII}}$  and Chl *a* fluorescence) as well as POC concentration  
410 in comparison to the control experiment such that some community dynamics may have  
411 differed in the mesocosm experiment compared to the community in surface waters. It is  
412 possible that the small addition of Fe may have removed resource competition between diatoms  
413 and other phytoplankton in the mesocosm experiment, however, it is more likely that the larger  
414 phytoplankton were initially dominating before being run into nitrate and possibly Fe-  
415 limitation (Boyd et al., 2012; Ellwood et al., 2015; Ellwood et al., 2014).

416 The surface water plankton community was dominated by the presence of eukaryotic  
417 picoplankton ( $0.2 - 2 \mu\text{m}$ ), and a background population of photosynthetic prokaryotes  
418 (*Synechococcus* and *Prochlorococcus*). Size-fractionated Chl *a* distribution suggests that the  
419 picoplankton community dominated photosynthetic biomass. Previous studies in the area also  
420 suggest that at its peak, the phytoplankton bloom is dominated by photosynthetic prokaryotes  
421 and large diatoms such as *Asterionellopsis glacialis* (cell volume  $\sim 60 \mu\text{m}^3$ ) and



422 *Leptocylindrus* sp. ( $\sim 600 \mu\text{m}^3$ ) (Boyd et al., 2012). Similarly, we observed an increased  
423 abundance of *A. glacialis*, *M. moniliformis* and *C. arcticum* in the exponential stage population  
424 in the mesocosm experiment, but not for our water column measurements.

425 At this stage it is difficult to determine why  $\text{Si(OH)}_4$  was depleted in the mesocosm, whilst the  
426 sea-surface inventory was maintained. The consumption of  $\text{Si(OH)}_4$  and the formation of BSi  
427 in the mesocosm experiment suggests that  $\text{Si(OH)}_4$  is not the ultimate factor limiting diatom  
428 productivity as the water column stratifies and the spring bloom progresses (Boyd et al., 2012).  
429 Ultimately the lack of bloom formation in the present study is likely due to water column  
430 instability and unfavourable Fe and light supply conditions for bloom initiation (Chiswell et al.  
431 submitted), as well as a dominant diatom phytoplankton assemblage compared to picoplankton.  
432 Zooplankton grazing may also be suppressed in the mesocosm experiment, which may allow  
433 full nutrient and Fe consumption, although during spring bloom development primary  
434 producers tend to outcompete grazers (Boyd et al., 2012). For the current study, a fully  
435 developed spring bloom did not occur at this site, even after the voyage was completed  
436 (Chiswell et al. submitted); there is a hint of a potential iron limitation of the plankton  
437 community whereby  $F_v/F_m$  declined from 0.4 to 0.3 following a decline in dissolved Fe  
438 concentration (Figure 4), so perhaps this was contributing factor to the lack of bloom  
439 development.

440 One of the more important findings of the study was that despite the large species-level  
441 variability in Si isotope fractionation factors observed by Sutton et al. (2013), the community  
442 level fractionation factor of  $-1.1 \text{‰}$  determined in in this study agrees well with previous  
443 estimates of  $-1.2 \text{‰}$  (observed by Fripiat et al. 2012), and  $-1.1 \text{‰}$  (observed by De la Rocha et  
444 al. 1997). Furthermore, the fractionation factor that was obtained from the mesocosm  
445 experiment appears to exhibit little variation despite the relatively low ambient  $\text{Si(OH)}_4$   
446 concentrations of  $2 \mu\text{mol L}^{-1}$  (compared to the Southern Ocean waters, where Si concentrations  
447 can be  $>20 \mu\text{mol L}^{-1}$ ) (de Souza et al., 2012b; Frank et al., 2003). This highlights the utility of  
448 the diatom  $\delta^{30}\text{Si}$  as a proxy for diatom  $\text{Si(OH)}_4$  utilisation in paleo-reconstructions (e.g.  
449 Beucher et al., 2007; De La Rocha et al., 1998) and that species level variation in Si isotope  
450 fractionation may not be important when considering past trends in diatom  $\text{Si(OH)}_4$  utilisation.

451

452

453 **4.3. Conclusions**

454 Contrasting results between the mesocosm (700 L) bag experiment and sea-surface  
455 measurements suggest that  $\delta^{30}\text{Si}_{\text{BSi}}$  in surface waters rarely exceeds  $\sim 2 \text{ ‰}$  as a result of Fe-  
456 limitation of the diatom population at the end of a phytoplankton bloom (Boyd et al., 2012);  
457 and the continuous re-supply of  $\text{Si}(\text{OH})_4$  to surface waters. Despite this,  $\delta^{30}\text{Si}_{\text{DSi}}$  values in  
458 subtropical surface waters east of New Zealand are relatively high, and it is likely that silicic  
459 acid resupply by waters enriched in  $^{30}\text{Si}$  likely plays a larger role in governing the  $\delta^{30}\text{Si}$   
460 composition of surface waters, in addition to biological fractionation by diatoms. We also  
461 observed that the community level Si isotope fractionation factor is independent of species  
462 composition and  $\text{Si}(\text{OH})_4$  concentration. Our observed value of  $-1.1 \text{ ‰}$  is also consistent with  
463 previous field studies (Fripiat et al. 2012 and Varela et al. 1997) and similar to mono-specific  
464 lab culture studies (De la Rocha et al. 1997 and Milligan et al. 2004).

465

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472

473 **Table 1.** Surface BSi concentrations and  $\delta^{30}\text{BSi}$  values over the duration of the voyage. Duplicate  
 474 samples for BSi were taken on days 266, 268 and 270 (mean  $\pm$  1 SD).  $\delta^{29}\text{Si}_{\text{BSi}}$  and  $\delta^{30}\text{Si}_{\text{BSi}}$  values are  
 475 per mil (‰) with errors based on 2 standard deviation calculated from multiple measurements.

Longitude/Latitude	Day	Date	$\delta^{29}\text{Si}_{\text{BSi}}$	$\delta^{30}\text{Si}_{\text{BSi}}$	Surface BSi concentration ( $\mu\text{mol L}^{-1}$ )
179.14 W 39.09 S	263	19/09/2012			0.092
179.15 W 39.07 S	264	20/09/2012			0.084
179.15 W 39.07 S	265	21/09/2012			0.074
179.17 W 39.02 S	266	22/09/2012			0.091 $\pm$ 0.050
179.24 W 38.58 S	267	23/09/2012			0.055
179.29 W 38.58 S	268	24/09/2012	0.82 $\pm$ 0.17	1.61 $\pm$ 0.25	0.073 $\pm$ 0.010
179.30 W 38.58 S	269	25/09/2012			0.040
179.27 W 39.10 S	270	26/09/2012	0.96 $\pm$ 0.17	1.83 $\pm$ 0.25	0.071 $\pm$ 0.010
179.34 W 38.50 S	271	27/09/2012			0.056
179.40 W 38.52 S	272	28/09/2012			0.049
179.40 W 39.04 S	273	29/09/2012			0.049
179.38 W 38.52 S	274	30/09/2012			0.046
179.56 W 38.28 S	275	01/10/2012	0.66 $\pm$ 0.17	1.35 $\pm$ 0.25	0.045
179.53 W 38.28 S	276	02/10/2012			0.102
179.58 W 38.59 S	277	03/10/2012			0.088
179.45 W 39.04 S	278	04/10/2012			0.110
179.49 W 38.60 S	279	05/10/2012	0.60 $\pm$ 0.17	1.22 $\pm$ 0.25	0.092

476

477

478 **Table 2.** Results from the mesocosm (700 L bag) experiment for BSi, NO<sub>3</sub><sup>-</sup> and Si(OH)<sub>4</sub>, the isotope  
 479 composition ( $\delta^{30}\text{Si}_{\text{BSi}}$ ) of BSi, fluorescence, and F<sub>v</sub>/F<sub>m</sub>.

Time (hr)	BSi ( $\mu\text{mol L}^{-1}$ )	$\delta^{30}\text{Si}_{\text{BSi}}$ (‰)	Si(OH) <sub>4</sub> ( $\mu\text{mol L}^{-1}$ )	NO <sub>3</sub> ( $\mu\text{mol L}^{-1}$ )	F <sub>o</sub>	F <sub>v</sub> /F <sub>m</sub>
0	0.091	1.49			2.40	0.06
22					1.90	0.19
24	0.042	1.62	1.88	4.78		
36	0.049	1.94				
38			1.94	4.77		
46					1.80	0.23
48	0.087					
51			1.95	4.70		
58					2.00	0.23
61			1.87	4.58		
72	0.157				2.30	0.23
75			1.81	4.44		
94					3.20	0.35
96	0.332	2.04				
98			1.74	3.53		
118					7.10	0.36
120	0.542	2.19				
122			1.16	2.50		
144	0.750	2.54			12.8	0.26
146			0.82	1.55		
166					13.2	0.27
168	1.29	2.64				
170			0.47	0.42		
190					12.8	0.24
194			0.28			

480

481 **Table 3.** Values from microcosm (20 L) experiment at T = 0 hours and at T = 96 hours (n ≥ 3, 1 S.D).  
 482 BSi, Si:N and Si:C values with no error (\*) reflect the single BSi measurement taken at T= 0 hours  
 483 prior to the start of the experiment.

Parameter	T = 0 hr	Control (T = 96 hr)	Fe-addition (T = 96 hr)
Chl <i>a</i> fluorescence	3.95 ±0.1	9.12 ±0.4	8.62 ±0.5
F <sub>v</sub> /F <sub>m</sub>	0.38 ±0.02	0.35 ±0.01	0.41 ±0.01*
σPSII	762 ±61	717 ±35	595 ±41*
Chl <i>a</i> (mg L <sup>-1</sup> )	1.34 ±0.1	1.26 ±0.1	1.75 ±0.1 <sup>†</sup>
POC (μmol L <sup>-1</sup> )	10.2 ±0.5	24.7 ±1.1	31.6 ±2.5 <sup>†</sup>
PON (μmol L <sup>-1</sup> )	1.6 ±0.01	3.24 ±0.2	3.22 ±0.2
BSi (μmol L <sup>-1</sup> )	0.1*	0.92 ±0.2	1.09 ±0.1
Si:N (mol/mol)	0.06*	0.28 ±0.05	0.34 ±0.03
Si:C (mol/mol)	0.01*	0.04 ±0.001	0.03 ±0.004
C:N (mol/mol)	6.38 ±0.23	7.64 ±0.09	9.8 ±0.18 <sup>‡</sup>

484 \*Variation from control at the 90-95 % confidence interval

485 <sup>†</sup>Variation from control at the 95-99% confidence interval

486 <sup>‡</sup>Variation from control at >99% confidence interval

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621 **Figures**

622 **Figure 1.** Mass dependent fractionation (MDF) of  $\delta^{29}\text{Si}$  vs  $\delta^{30}\text{Si}$  line for all diatom samples relative to  
623 NBS28. MDF line represented by  $\delta^{29}\text{Si} = 0.55 \pm 0.02[\delta^{30}\text{Si}] - 0.08 \pm 0.04$ ,  $r^2 = 0$ .

624 **Figure 2. A.** Underway surface Chlorophyll fluorescence data, measured in arbitrary units (AU)  
625 obtained from the FRR (Fast Repetition Rate) Fluorometer for year days 268, 270, 275 and 279 of the  
626 voyage. Black dots represent drogue drifter tracks. **B.** Surface (0 - 10m) values for BSi,  $\text{Si}(\text{OH})_4$ ,  $\delta^{30}\text{Si}$   
627 and DFe for year days 268, 270, 275 and 279.

628 **Figure 3.** Profiles of DFe,  $\text{Si}(\text{OH})_4$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  concentration versus depth for year days 267,  
629 270, 275 and 278.

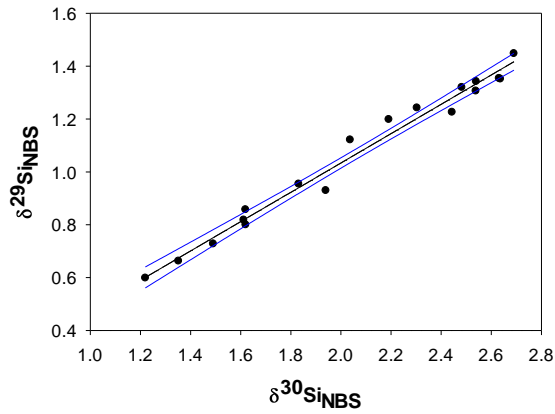
630 **Figure 4. A** Mean surface (0 – 10 m) nutrients ( $\text{Si}(\text{OH})_4$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and DFe) over the duration  
631 survey. **B.** cell counts for cyanobacteria and size fractionated eukaryotic phytoplankton along with  
632 night-time  $F_v/F_m$  measurements. **C.** Concentrations of POC, PON and BSi. **D.** Size fractionated  
633 Chlorophyll *a* concentrations and the Chl:C ratio. For surface macro-nutrients ( $\text{Si}(\text{OH})_4$ ,  $\text{NO}_3^-$  and  
634  $\text{PO}_4^{3-}$ ), values are in  $\mu\text{mol L}^{-1} \pm 1\text{SD}$  ( $n = 2$ ). For mean DFe concentrations, values are in  $\text{nmol L}^{-1}$ ,  
635  $\pm 1\text{SD}$  ( $n \geq 4$ ).

636 **Figure 5.** Results from the mesocosm (700 L bag) experiment; **A.** Photosynthetic parameters  
637 **B** Concentrations of BSi,  $\text{NO}_3^-$  and  $\text{Si}(\text{OH})_4$  and the isotope composition ( $\delta^{30}\text{Si}_{\text{BSi}}$ ) of BSi  
638 over the experimental period; **C.** Variation in  $\delta^{30}\text{Si}_{\text{BSi}}$  during the experimental period, where *f*  
639 is the fraction of dissolved silicon remaining ( $\text{Si}/\text{Si}_0$ , where  $\text{Si}_0$  is the starting concentration of  
640  $\text{Si}(\text{OH})_4$  in the bag). Instrumental errors for  $\delta^{30}\text{Si}$  values are 0.2 ‰ (2SE). A fractionation  
641 factor ( $\alpha$ ) of 0.9989 was calculated using a SOLVER based algorithms to fit a model  
642 (equation 4) to the data and closely resembles the reported fractionation factor ( $\epsilon$ ) of  $-1.2 \pm$   
643  $0.02$  ‰ for diatoms in the field (Fripiat et al., 2011). Also present is the model (equation 2)  
644 for evolution of  $\delta^{30}\text{Si}(\text{OH})_4$  during the experiment.

645 **Figure 6.** Microscope images of *Asterionelopsis glacilis* and *Mellosira moniliformis*. **A.**  
646 *glacilis* is a pennate diatom (general length, 30 – 150  $\mu\text{m}$ ), while *M. moniliformis* is a centric  
647 diatom (Length, 11-30  $\mu\text{m}$ , diameter, 17 – 70  $\mu\text{m}$ ).

648 **Figure 7.** Change in **A.** photosynthetic parameters **B.** POC, PON and BSi concentration **C.**  
649 and elemental ratios for microcosm (20 L) experiment harvested after 96 hours incubation  
650 time. Experiments represents T0, control and Fe-addition experiments.

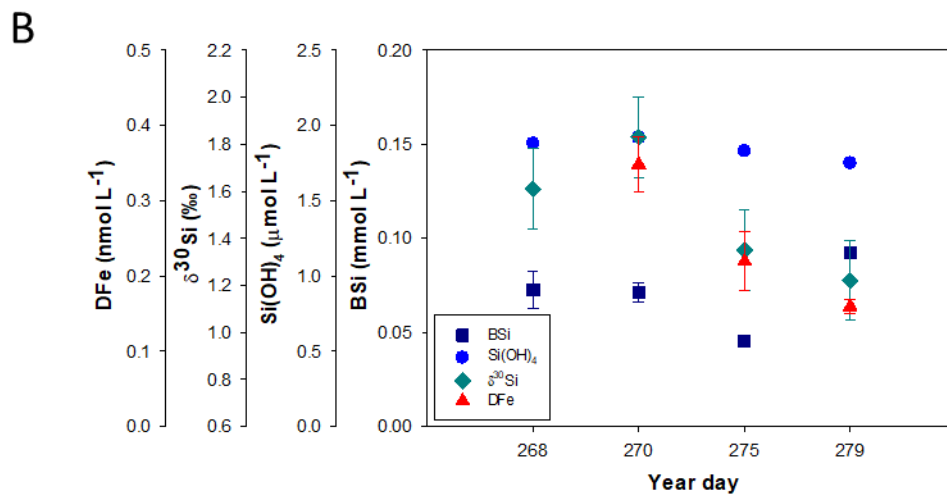
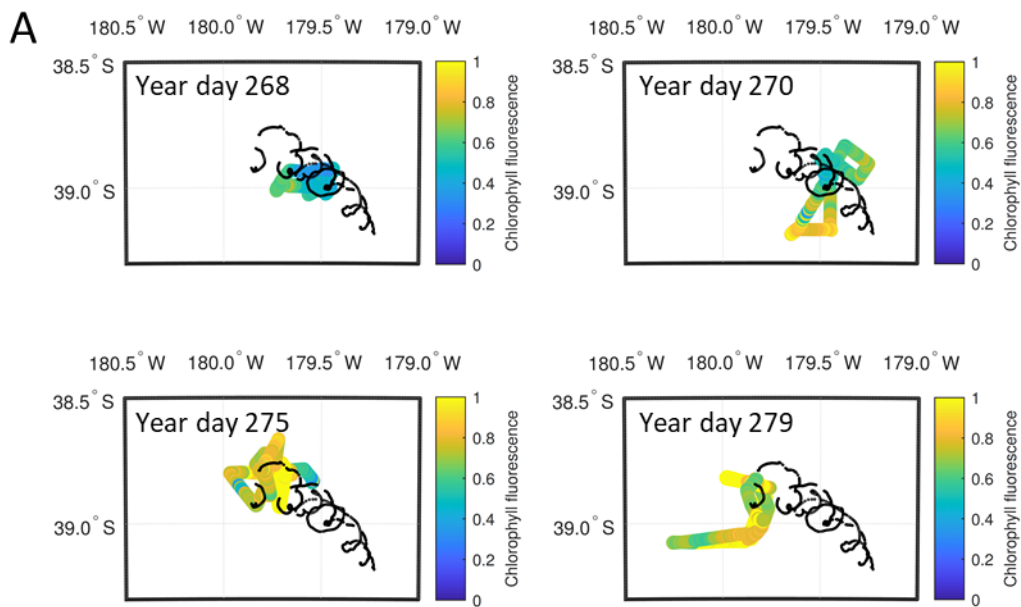
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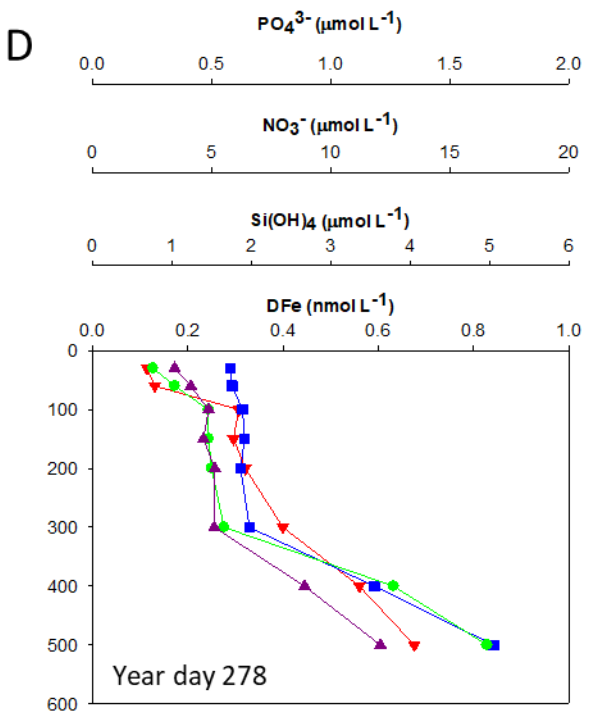
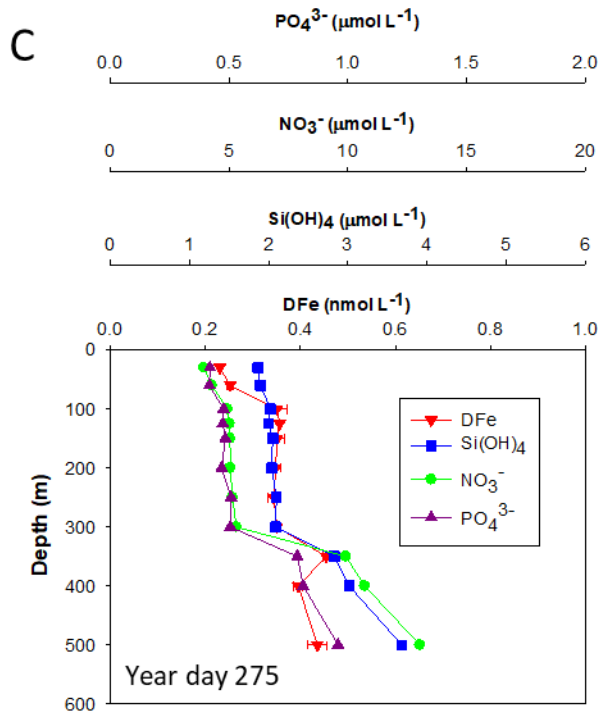
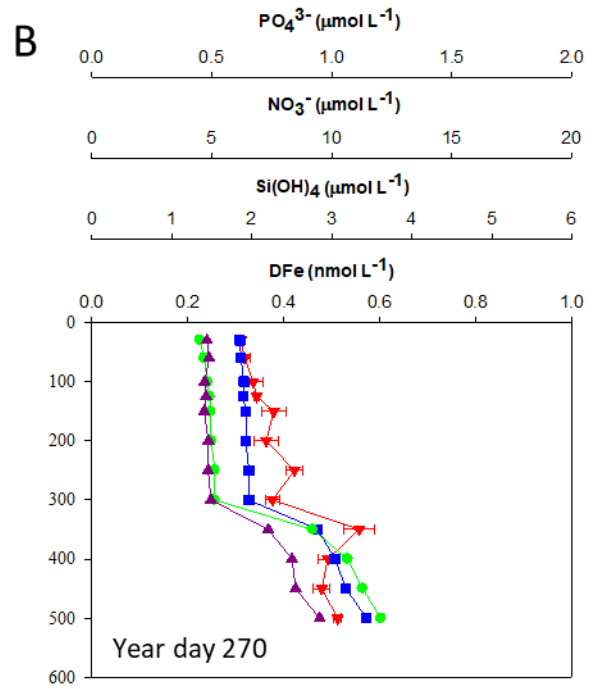
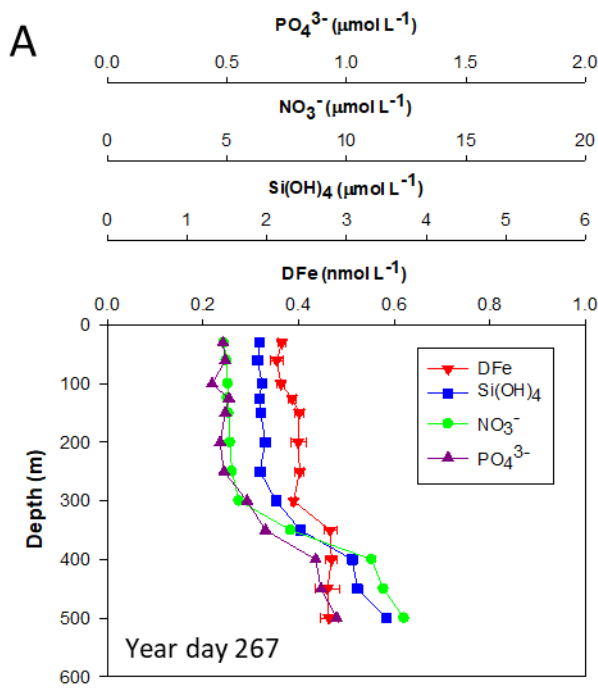
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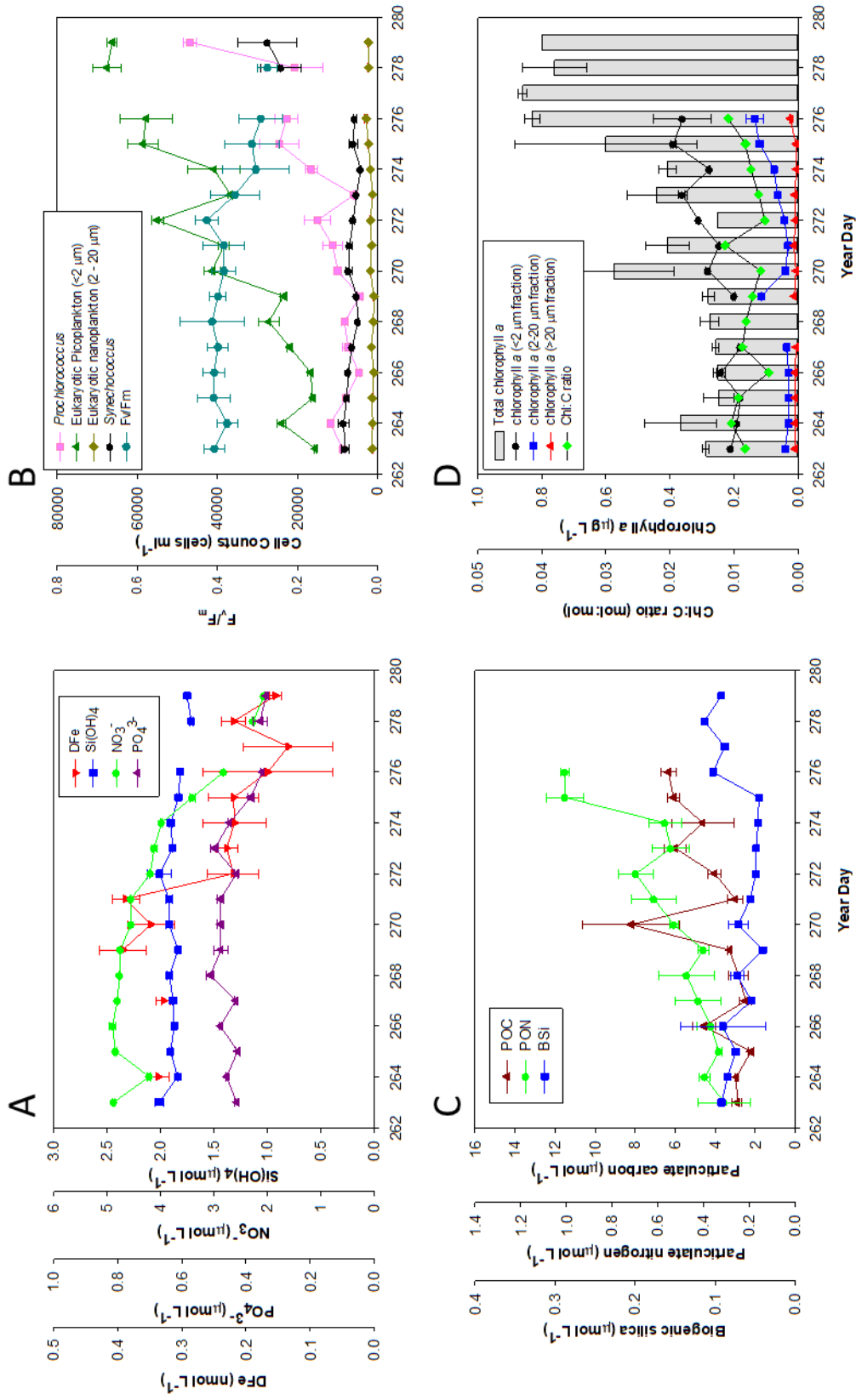


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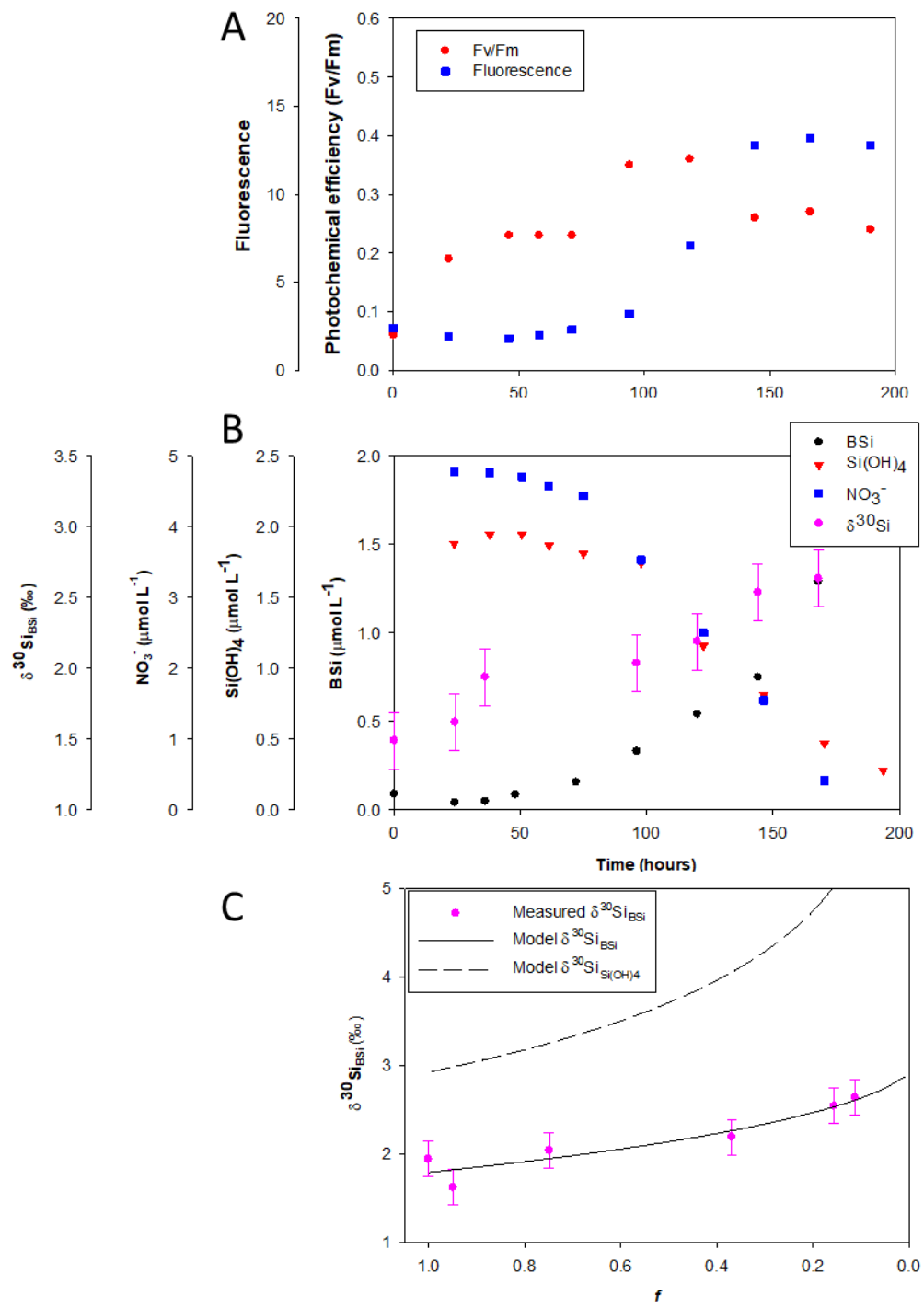
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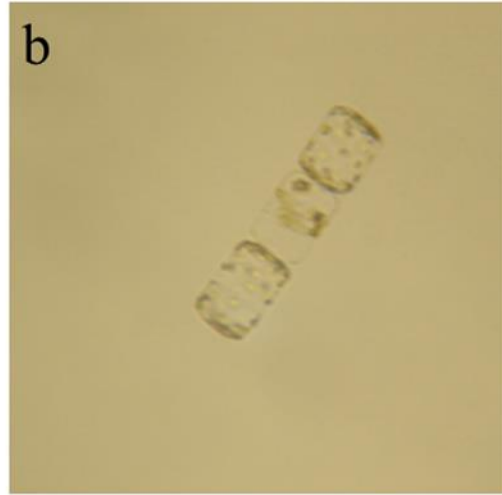
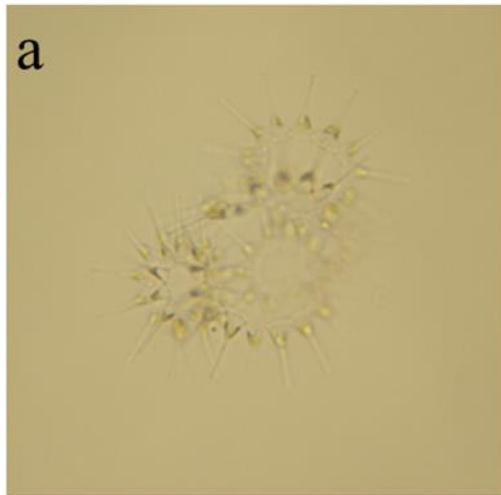


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