

1 **Importance of particle formation to reconstructed water column**
2 **biogenic silica fluxes**

3
4 **by**

5 **Moriceau, Brivaëla, Gallinari, Morgane, Soetaert, Karline, Ragueneau, Olivier**

6 UMR CNRS 6539, Institut Universitaire Européen de la Mer, Place Copernic,
7 Technopôle Brest-Iroise, 29280 Plouzané, France

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For correspondence:

Brivaëla MORICEAU

UMR 6539, Institut Universitaire Européen de la Mer
Technopole Brest-Iroise, Place Nicolas Copernic
F – 29280 Plouzané, France

Tel: ++33 2.98.49.88.99 · Fax: ++33 2.98.49.86.45

E-mail: moriceau@univ-brest.fr

15 **Abstract**

16 The particles sinking out of the ocean's surface layer are made up of a mixture of living and dead
17 algal cells, fecal pellets and aggregates, while the parameters used to describe the behaviour of
18 biogenic silica (bSiO₂) in today's models are experimentally determined on freely suspended
19 diatoms (FC). In a simple advection-reaction model we combine sinking rates of FC,
20 zooplankton fecal pellets and aggregates with recent measurements of bSiO₂ dissolution to
21 reconstruct theoretical downward profiles of bSiO₂ fluxes at 8 sites in the world ocean. Statistical
22 analyses showed that sinking and dissolution parameters for two pools of bSiO₂ are required to
23 model particle fluxes accurately. The 2-pool model results confirm the importance of seasonality
24 for particle formation and its connection to the percentage of the bSiO₂ production that reaches
25 the seafloor. The depth of bSiO₂ recycling appears to be influenced more by particle formation
26 than by dissolution rates of bSiO₂ or the ballast effect of the dense diatom frustules.

27

28

28 1. Introduction

29 Diatoms form the basis of a short food chain that leads to carbon export to higher trophic
30 levels [*Cushing*, 1989; *Thornton*, 2002] and to deeper waters [*Buesseler*, 1998]. They are an
31 important player in the global carbon cycle because of their participation in an efficient food web
32 and their ability to aggregate [*Smetacek*, 1999]. Because diatoms require silica to build their
33 frustules, their share in total primary production (PP) depends on the availability of the nutrient
34 silicic acid (DSi) in many regions of the world ocean such as the equatorial Pacific [*Dugdale et*
35 *al.*, 1995; *Leynaert et al.*, 2001] or the Southern Ocean [*Brzezinski et al.*, 2001; *Pondaven et al.*,
36 1998]. The availability of DSi in surface waters, in particular relative to other nutrients, is linked
37 to the composition of the source waters in upwelling regions and/or the intensity of biogenic
38 silica (bSiO_2) recycling in surface waters in other oceanic regions. Depending on the depth of
39 bSiO_2 dissolution, diatom production is affected on different time scale. Shallow depth
40 mineralization immediately influences diatom production and phytoplankton dynamics [*Officer*
41 *and Ryther*, 1980]. Recycling in intermediate waters [*Sarmiento et al.*, 2004] and/or deep waters
42 [*Ragueneau et al.*, 2000] affects the meridional distribution of DSi or the redistribution of DSi
43 among oceanic basins, respectively, with implications for intermediate to long time scales.
44 A global average of 60% of the bSiO_2 produced in surface waters is recycled in the first 100 m
45 [*Nelson et al.*, 1995; *Tréguer et al.*, 1995]. This global mean hides large regional differences
46 [*Nelson et al.*, 1995; *Ragueneau et al.*, 2000, 2002], which can not be related to any simple trend
47 in production or diatom abundance, nor to any single mechanism known to influence dissolution,
48 such as temperature [*Lawson et al.*, 1978] or bacterial activity [*Bidle and Azam*, 1999]. The
49 dissolution to production ratio, integrated over the surface layer ($\text{J}^{\text{D}}:\text{J}^{\text{P}}$), has been related to the
50 formation of diatom blooms by *Brzezinski et al.* [2003]; this ratio is lower during blooms,
51 leaving more room for export and deeper recycling. However, the use of global biogeochemical
52 models to reproduce both DSi and bSiO_2 flux profiles in the global ocean is difficult and does

53 not always agree with in situ measurements [Aumont *et al.*, 2003]. We hypothesize that the
54 present difficulty in modeling both the bSiO₂ and DSi profiles of the global ocean are due to
55 underestimating the importance of particle formation. Whereas aggregates and fecal pellets of
56 large grazers are major vehicles for export [review in Turner, 2002 and Thornton, 2002], the
57 parameters used to represent the fate of PP in global ocean models are still measured on freely
58 suspended diatoms.

59 To test this hypothesis, we developed a simple advection-reaction model using one and then
60 two different pools of particles. The model combines a series of in vitro bSiO₂ dissolution
61 experiments undertaken on the different constituents of the flux: freely suspended diatoms
62 [compiled in Van Cappellen *et al.*, 2002], zooplankton fecal pellets [Gallinari *et al.*,
63 unpublished; Schultes *et al.*, 2004] and aggregates [Moriceau *et al.*, 2007] with data on bSiO₂
64 production, export and deep fluxes from 8 biogeochemical provinces of the world ocean
65 [described in Ragueneau *et al.*, 2002]. The bSiO₂ downward fluxes are modeled to fit the
66 downward flux data at the eight sites. This allows us to derive important information about
67 particle formation in the upper ocean. The composition of the bSiO₂ fluxes in terms of large or
68 small particles and, the sinking and specific bSiO₂ dissolution rates of each component help to
69 unravel mechanisms involved in the spatial variability of the intensity and depth of bSiO₂
70 dissolution.

71 2. Approach: from laboratory experiments to a virtual water column

72 2.1. Experimental measurements

73 The flux of matter sinking through the water column is mainly composed of freely
74 suspended phytoplankton cells, aggregates, and zooplankton fecal pellets [Turner, 2002;
75 Thornton, 2002]. Specific bSiO₂ dissolution rates are usually measured experimentally on freely
76 suspended diatoms [compiled by Van Cappellen *et al.*, 2002]. Recently, however, specific
77 dissolution rates of bSiO₂ incorporated into aggregates [Moriceau *et al.*, 2007] and fecal pellets

78 [Schultes, 2004; Gallinari, unpublished] have been measured in the laboratory and shown to be
79 about half the rates measured on freely suspended diatoms (Table 1). Including the dissolution
80 rates of all particle types in models should enable us to predict the bSiO₂ sedimentation flux
81 more precisely. Here we consider a model of bSiO₂ flux with depth that includes two types of
82 particles (free diatom cells: FC and large particles: LP). We can keep the model simple with
83 only two particle types by assuming that the sinking rates and specific bSiO₂ dissolution rate of
84 aggregates and fecal pellets are similar as is demonstrated in Table 1. The FC group has the
85 slow sinking rate and fast specific bSiO₂ dissolution rate characteristic of free diatom cells. The
86 LP group has faster sinking rates than the FC and half the specific bSiO₂ dissolution rate. For
87 comparison, the model was first run using only one type of particle with sinking properties and
88 bSiO₂ dissolution rates between those of FC and LP particles as described below.

89 The data used for this study were collected in eight biogeochemical provinces of the
90 world ocean, for which annual measurements of bSiO₂ production, export and deep fluxes (at 2
91 depths) are available [data in *Ragueneau et al.*, 2002]. In this dataset, export fluxes (at 200 m)
92 were derived from models or from sediment trap measurements while deeper water fluxes (1000
93 and 3000 m depth) were measured using sediment traps. Two sites are located in the Equatorial
94 (EqPac) and North Pacific (OSP), and two in the North Atlantic Ocean (PAP and BATS). Four
95 are located in the Southern Ocean: one north of the Polar Front in the Pacific sector (NACC),
96 two in the Polar Front Zone of the Atlantic (APFA) and Pacific (APFP) sectors, and one just
97 south of the Polar Front in the Indian sector (POOZ) (see positions in Table 2). Four data points
98 can be fitted for each site, providing a total of 32 data points.

99

100 **2.2. Model description**

101 The concentration profiles of bSiO₂ for each particle pool *i* (LP or FC) can be described
102 by a simple advection-reaction model (Eq. 1):

103

$$104 \quad \frac{\partial b\text{SiO}_{2i}}{\partial t} = -S_i \cdot \frac{\partial b\text{SiO}_{2i}}{\partial z} - k_i(T) \cdot b\text{SiO}_{2i} \quad (1)$$

105

106 where t is time (d), z depth (m), S_i is the sinking rate (m d^{-1}), and $k_i(T)$ is the (temperature-
 107 dependent) first-order specific $b\text{SiO}_2$ dissolution rate (d^{-1}). Such first-order dissolution of $b\text{SiO}_2$
 108 is often observed in batch experiments and leads to a simple exponential increase in the DSi
 109 concentration as a function of time [e.g. *Greenwood et al.*, 2001].

110 Assuming steady-state ($\frac{\partial b\text{SiO}_{2i}}{\partial t} = 0$), and constant sinking and dissolution rates, the
 111 concentration (mmol m^{-3}) and flux of $b\text{SiO}_2$ ($\text{mmol m}^{-2} \text{d}^{-1}$) at each water column depth (z) are
 112 given by equation 2:

113

$$114 \quad b\text{SiO}_{2i}(z) = b\text{SiO}_{2i}(0) \cdot e^{-\frac{k_i}{S_i} z} \quad (2)$$

115

116 which in terms of the total fluxes for the 1-particle model and the 2-particle model gives
 117 equation 3 and 3' respectively:

118

$$119 \quad F_{b\text{SiO}_2}(z) = PP_{b\text{SiO}_2} \cdot e^{-\frac{k}{s} z} \quad (3)$$

$$120 \quad F_{b\text{SiO}_2}(z) = PP_{b\text{SiO}_2} \cdot \left[\alpha \cdot e^{-\frac{k_{FC}}{S_{FC}} z} + (1 - \alpha) \cdot e^{-\frac{k_{LP}}{S_{LP}} z} \right] \quad (3')$$

121

122 where α and $(1 - \alpha)$ correspond to bSiO₂ production (PP_{bSiO_2} , in mmol m⁻² d⁻¹) in the FC and the
 123 LP groups in the upper layer, respectively.

124 As temperature is allowed to vary, we use a piecewise approximation to model equation
 125 3. The water column is subdivided into a number of layers (with thickness Δz) in which
 126 temperature is assumed constant. Then, for each fraction, the flux at the bottom ($z + \Delta z$) and top
 127 (z) of this layer are related by:

$$129 \quad \text{FbSiO}_{2i}(z + \Delta z) = \text{FbSiO}_{2i}(z) \cdot e^{-\frac{k_i(T) \cdot \Delta z}{S_i}} \quad (4)$$

130
 131 For the 1-particle model the flux at $z = 0$ equals the bSiO₂ production (PP_{bSiO_2}), and for the 2-
 132 particle model the bSiO₂ flux at each depth is the sum of the LP and FC fluxes.

$$133 \quad \begin{aligned} \text{FbSiO}_{2\text{FC}}(0) &= \alpha \cdot PP_{\text{bSiO}_2} \\ \text{FbSiO}_{2\text{LP}}(0) &= (1 - \alpha) \cdot PP_{\text{bSiO}_2} \\ \text{FbSiO}_{2\text{TOT}}(z) &= \text{FbSiO}_{2\text{FC}}(z) + \text{FbSiO}_{2\text{LP}}(z) \end{aligned} \quad (5)$$

134
 135 In these equations, $\text{FbSiO}_{2\text{TOT}}(z)$ is the flux of total bSiO₂ in mmol m⁻² d⁻¹ at depth z ;
 136 PP_{bSiO_2} is the production flux of bSiO₂ in mmol m⁻² d⁻¹; $\text{FbSiO}_{2\text{FC}}(z)$ and $\text{FbSiO}_{2\text{LP}}(z)$ are the
 137 fluxes of bSiO₂ in the FC and LP groups at depth z respectively. $k_{\text{FC}}(T)$ and $k_{\text{LP}}(T)$ are the
 138 specific bSiO₂ dissolution rates in d⁻¹ given in the literature for FC particles (Table 1) and
 139 corrected by the factor of 2 less that was measured experimentally for LP particles. Rates were
 140 also corrected for temperature, according to equation (6) from *Rickert et al.* [2002]; temperature
 141 profiles of the water column at each site were from the NODC (Levitus) World Ocean Atlas
 142 1998 (<http://www.cdc.noaa.gov/>).

143

144
$$\ln(k_z(T_2)) = \ln(k_1) + \frac{E_{app}}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

145
 146 where k_1 is the specific bSiO₂ dissolution rate in d⁻¹ measured in controlled conditions in the
 147 laboratory; T_1 is the experimental temperature in degrees Kelvin (286.15 K); $k_z(T_2)$ is the rate
 148 recalculated for the depth z at the in situ temperature T_2 ; and $E_{app}/R = 7211$ °K.

149 To facilitate comparison among sites, the total flux is normalized to the production flux
 150 to obtain a profile of bSiO₂ flux expressed in % of bSiO₂ production.

151 For both models we have:

152
 153
$$\%FbSiO_2(z) = \frac{FbSiO_{2tot}(z)}{PP_{bSiO_2}} \times 100 \quad (7)$$

154
 155 which for the 2-particle model becomes:

156
 157
$$\%FbSiO_2(z) = \frac{FbSiO_{2FC}(z) + FbSiO_{2LP}(z)}{PP_{bSiO_2}} \times 100 \quad (7')$$

158
 159 **2.3. Parameter determination**

160 As a first step, we applied the 1-pool model to fit the bSiO₂ flux profiles measured in the
 161 field. The specific dissolution rate was set to the value given in Table 1 for FC, and corrected for
 162 temperature at each site and depth using eq. 6. At each site, the model 1 calculated the bSiO₂
 163 sinking rate required to fit the in situ bSiO₂ flux data. Note that the fit is not improved when the
 164 model uses LP specific dissolution rates instead of k_{FC} nor an average of the two values.

165 In a second step, bSiO₂ specific dissolution rates and the sinking rates for two pools of
 166 particles were included in the model (model 2). Specific bSiO₂ dissolution rates of FC and LP
 167 were set to values presented in Table 1 and corrected for in situ temperature at each depth using
 168 equation 6. The model 2 calculated a global sinking rate for FC particles (S_{FC}) for all sites, one
 169 LP sinking rate per site and the percent of bSiO₂ from the production which is incorporated into
 170 large particles ($1-\alpha$) or stays freely suspended (α).

171 Finally in a third step (model 3), the parameter S_{FC} was allowed to vary at each site.
 172 In the three versions of the model, parameters were calculated by minimizing the sum of the
 173 square residuals using the Excel Solver and the GRG method (Generalized Reduced Gradient).
 174 These calculations were tested for many initial values because the algorithm used is non linear.
 175 Best fits to the data using the three model versions are shown for each of the eight sites in Fig. 1.

176

177 **2.4. Statistical comparison of the 1-particle and 2-particle models**

178 We used an F-test to compare the three versions of the model. The null hypothesis
 179 considers that adding complexity to the model does not significantly decrease the sum of the
 180 square residuals between model and observed data (SSR). The calculated F value is obtained
 181 using equation (8) and compared to the F test critical value.

$$182 \quad F = (SSR1-SSR2) (df1-df2) / (SSR2/df2) \quad (8)$$

183 SSR1 and SSR2 are the sum of the square residuals between the modeled and the experimental
 184 values; df1 and df2 are the degrees of freedom of the different versions of the model calculated
 185 as follow.

$$186 \quad dfi = E - P - 1 \quad (9)$$

187 With E, the number of observed values the models has to fit (4 data for each of the 8 sites), and P
 188 the number of variable parameters used to optimize the fit.

189 The F test was first applied to compare the 1-particle model (hereafter referred to as
190 model 1) to a 2-particle model using a global S_{FC} (model 2). Next, we compared two versions of
191 the 2-particle model, one using a global S_{FC} (model 2 again) and one using a variable S_{FC} at each
192 site (model 3). When the model considered only one type of particle, it had 23 degrees of
193 freedom. Model 2 used 17 parameters, providing 14 degrees of freedom. Finally, model 3 had 7
194 degrees of freedom.

195

196 **3. Results**

197 **3.1. Comparison of the model versions: Importance of particle formation**

198 Figure 1 shows the reconstructed $bSiO_2$ profiles at the eight sites for the three versions of
199 the model. Model 1 is clearly not able to fit the experimental data at any of the eight sites. When
200 the model uses two different pools of $bSiO_2$ but only one global S_{FC} , the $bSiO_2$ profiles are close
201 to the measured values except for APFP, NACC and PAP. The F-test determined, at a 99%
202 confidence level, that model 2 provides a better fit to the data than model 1. Thus the use of a
203 global S_{FC} of 2.76 m d^{-1} (Table 2) is a good approximation. Note that at the PAP site, the flux at
204 1000 m is low compared to the flux at 3000 m and can be explained by the presence of
205 swimmers in the trap [*Lampitt et al.*, 2001].

206 Model 2, which considered a global FC sinking rate (S_{FC}), gives more degrees of freedom
207 than model 1, but the use of a global S_{FC} is also an oversimplification. Indeed, for the PAP site in
208 the North East Atlantic Ocean, and for the NACC and APFP sites located in the Pacific sector of
209 the Southern Ocean (North of the Polar Front and on the Polar Front respectively), this approach
210 doesn't fit the data closely. To improve the reconstruction of these $bSiO_2$ fluxes, the model has
211 to use a S_{FC} higher than the global one. Reconstructions of the Southern Ocean profiles are
212 generally improved by using model 3 with a varying S_{FC} (Fig. 1). The F-test also favors model 3

213 over model 2 at the 95% confidence level. At the annual scale, FC sinking rates can be classified
214 into two groups: fast S_{FC} in the Southern Ocean and PAP site and slow S_{FC} in the rest of the
215 world. This trend may well reflect the production of large, fast sinking diatoms commonly
216 observed in the Southern Ocean [Kemp *et al.*, 2006].

217 Freely suspended diatoms and large particles have such different sinking rates and
218 specific $bSiO_2$ dissolution rates that parameters of the two groups of particles must be considered
219 to correctly reconstruct $bSiO_2$ flux profiles. The role and importance of each particle type is
220 confirmed by a sensitivity analysis performed on the profiles using model 3 for the sinking rates
221 of the two particles (shown for POOZ, Fig. 2). Profiles of $bSiO_2$ fluxes are quite sensitive to
222 variation in sinking rates: in the upper 1000 m the profile is mostly affected by the sinking rate
223 of FC whereas deeper, the profile is more sensitive to variation of the LP sinking rate. The
224 composition of the flux in the upper layer (parameter α) is well constrained, as when the
225 contribution of FC and LP changes by only 5-10 %, the resulting profile of $bSiO_2$ flux
226 significantly differs from the one measured (Fig. 2c).

227

228 **3.2. Model outputs**

229 For the eight sites, model 3 provides sinking rates ranging from 45 to 605 $m d^{-1}$ for the
230 LP and from 0.1 to 10.4 $m d^{-1}$ for the FC (Table 2; Fig. 1), consistent with ranges found in the
231 literature (Table 1). The sinking rates calculated by model 3 confirm the prevalence of
232 aggregates and fecal pellets in the LP group (see values and references in Table1) and the fact
233 that the FC group must be essentially composed of freely suspended diatoms, small and large.
234 Note that the 2- particles models (models 2 and 3) can not always strictly separate LP and FC
235 using $bSiO_2$ sinking and specific dissolution rates. For the two sites located in the Southern
236 Ocean (APFP and NACC) and for PAP, model 3 produces faster FC sinking rates and a faster LP
237 sinking rates than those calculated by model 2. The S_{FC} calculated by the model 2 is in these

238 cases lowered by the other sites' S_{FC} . The difference between the results of the two models for
239 APFP, NACC and PAP shows the importance of a third group of particles that is included in LP
240 in model 2 results and in FC in model 3 results. Large diatoms that have been observed in areas
241 like the Southern Ocean, Gulf of California, and North Pacific Gyre [*Kemp et al.*, 2000, 2006]
242 apparently dominate the production of APFP, NACC and PAP. Following the same argument,
243 the very low S_{LP} and S_{FC} calculated by model 3 for APFA and POOZ suggest simultaneous
244 production of small and large diatoms. Therefore, there are really three groups of particles (LP,
245 freely-suspended large cells, and freely-suspended small cells); however, the large, freely-
246 suspended diatoms have been included in the LP group here as the best compromise since the
247 model can only account for two groups of particles.

248 Also, even if not shown here, giant aggregates with small and even null sinking rates
249 such as those observed by *Rinaldi et al.* [1995] would certainly be integrated into the FC group
250 of particles.

251

252 4. DISCUSSION

253 4.1. Particle formation: a major factor determining $bSiO_2$ export and recycling

254 In their global analysis of $bSiO_2$ production and dissolution, *Brzezinski et al.* [2003]
255 demonstrated that the dissolution to production ratio integrated over the surface layer ($[D]:[P]$) is
256 low under bloom conditions, leaving ample room for net export. They underlined the importance
257 of considering dissolution when determining export of matter. Using the model results, we
258 compare the importance of the two processes, sinking and dissolution, by calculating particle
259 residence times in the mixed layer at each site with only sinking or only dissolution considered
260 (Table 3). The comparison of these $bSiO_2$ residence times in surface waters suggests that this
261 global data set of $bSiO_2$ production and dissolution cannot ignore particle formation. Sinking
262 rates of large particles act on much shorter time scales than dissolution rates, so, rather than

263 having the export determined by the intensity of the recycling, the intensity of export ($1-[D:]P$) is
 264 linked to the rate of large particle formation and drives the intensity of shallow-water recycling.
 265 The rate at which diatoms are incorporated into large particles will determine how rapidly
 266 exported they are as their fast sinking rates leave no time for dissolution to occur in surface
 267 waters. In such cases, the dissolution depth is translated downward. The recycling intensity in
 268 surface waters depends first on the ability of diatoms to remain as single cells and secondly on
 269 factors such as temperature [*Bidle et al.*, 2002; *Fujii and Chai*, 2005; *Lawson et al.*, 1978] and
 270 bacterial activity [*Bidle and Azam*, 1999] which control their fate in surface waters.

271 Thus, we suggest that low $[D:]P$ ratios under bloom conditions [*Brzezinski et al.*, 2003]
 272 are caused by a rapid export of bloom diatoms [*Buesseler*, 1998], which extracts $bSiO_2$ from the
 273 surface waters where intense recycling generally occurs under non-bloom conditions.
 274 Recognizing the importance of seasonality to the sinking of particles, we calculated the
 275 seasonality index of each site as defined by *Berger and Wefer* [1990] (Table 2) as six minus the
 276 number of months necessary to generate one half of the annual productivity when the data are
 277 ordered from the most productive to the least productive month (the ‘production half-time’).
 278 Considering productivity, the eight sites could be classified in three groups [*Berger and Wefer*,
 279 1990]: EqPac and BATS have constant productivity (seasonality index close to 0); OSP, APFA,
 280 NACC, POOZ, PAP have sinusoidal production (seasonality index between 2 and 3) and APFP
 281 has a strong seasonal peak in productivity (seasonality index > 3.5). As shown in Figure 3, sites
 282 exhibiting the lowest seasonality (EqPac, BATS) also exhibit the lowest export at 100 m (i.e. low
 283 $1-[D:]P$). Conversely, sites with higher seasonality (APFP, NACC and APFA) display a larger $1-[D:]P$
 284 $[D:]P$ at 100 m. Even if seasonality is not the only important factor, Figure 3 confirms its major
 285 role in particle formation. Indeed grazing and aggregation processes are more abundant at the
 286 end of a bloom [*Buesseler*, 1998] and consequently the export of matter out of the surface layer
 287 is also increased. To properly model diatom export versus recycling, further research efforts

288 must focus not only on dissolution properties, but perhaps more importantly, on representing
289 particle formation during bloom termination.

290 Another implication of our model results concerns the ballast theory. *Armstrong et al.*
291 [2002] established a correlation between organic carbon and ballast (bSiO₂, CaCO₃) fluxes
292 below the mixing layer. Based on this model, *Klaas and Archer* [2002] concluded that organic
293 carbon is carried into the deeper waters preferentially by calcium carbonate, which has a higher
294 density (2.71 g cm⁻³) than opal (2.1 g cm⁻³). *Passow* [2004] proposed the inverse of this
295 hypothesis, that carbon, in the form of TEP, could transport organic matter and ballast to the
296 deep sea by promoting aggregation. In APFP, OSP and NACC sites (Table 2), the fast S_{LP}
297 suggested the dominance of large diatoms. At these sites, freely suspended diatoms can be
298 exported from the mixed layer (Table 4) due to the low temperature at the surface layer and/or
299 high sinking rates. But at most other sites, even ballasted with a frustule whose density is twice
300 that of organic matter (1.06 g cm⁻³), a single diatom almost completely dissolves in the upper
301 WML. This observation calls for more caution when considering the ballast theory and
302 emphasizes once again the importance of bloom-ending processes to explain sedimentation
303 fluxes. The fact that POC and ballast fluxes are closely linked below the mixed layer [*Armstrong*
304 *et al.*, 2002] is not necessarily related only to the higher density of bSiO₂ and CaCO₃ compared
305 to that of organic matter. The efficiency of sedimentation depends primarily on the incorporation
306 of diatoms into large particles like aggregates or fecal pellets (Fig. 2c) in the mixed layer; the
307 ballasting of these large particles throughout the whole water column plays a secondary role
308 (Fig. 2b).

309

310 **4.2. Implications for the silicate pump**

311 The silicate pump is the process by which bSiO₂ is exported from surface waters with a
312 greater efficiency than PON, driving the system towards DSi limitation. According to *Dugdale et*

313 *al.*, [1995], grazers are the motor of this silicate pump; whereas nitrogen is largely assimilated or
314 recycled by grazers and therefore retained at the surface, bSiO₂ is packaged into fast-sinking
315 fecal pellets and exported from the mixed layer. The silicate pump model was developed initially
316 for the Equatorial Pacific [*Dugdale and Wilkerson*, 1998] and later applied to the Southern
317 Ocean [*Brzezinski et al.*, 2001]. It is based on several assumptions, including that bSiO₂
318 dissolution in surface waters is negligible [*Dugdale et al.*, 1995]. Our results clearly contradict
319 this assumption at the EqPac site [*Dugdale and Wilkerson*, 1998]. EqPac is the site with the
320 shallowest recycling in our model output (Fig. 1), as observed previously in the field [*Blain et*
321 *al.*, 1999]. The EqPac site is well-known for its low export efficiency [*Buesseler*, 1998], possibly
322 related to its small seasonal variability (Table 2, Fig. 3). Consequently, the fraction of bSiO₂
323 production incorporated into large particles by aggregation/ fecal pellet production is lowest at
324 the EqPac site on an annual basis (Table 2). Our results (Table 4) suggest that the vast majority
325 of the diatoms remain as single cells in surface waters, and 88% dissolve before reaching the
326 base of the mixed layer (on average, 50 m). This extensive dissolution is consistent with the high
327 temperatures (i.e., high dissolution rate) and bacterial activity (i.e., fast removal of protective
328 organic coatings) encountered in these equatorial waters [*Bidle et al.*, 2002]. It is important to
329 note that these are annual fluxes. Episodic events such as Tropical Instability Waves have been
330 shown to trigger intense diatom concentrations at fronts [*Yoder et al.*, 1994], leading to massive
331 sinking of algal material and the formation of large flocs of phytodetritus on the seafloor [*Smith*
332 *et al.*, 1996]. However, although these episodes may be very important for sustaining life in the
333 mesopelagic and at the sediment-water interface [*Smith et al.*, 2002; *Smith Jr et al.*, 2002], or for
334 formation of paleoceanographic records [*Ragueneau et al.*, 2000], our results suggest that they
335 do not contribute appreciably to annual POC and bSiO₂ fluxes in oligotrophic ecosystems.

336 *Brzezinski et al.* [2003] have suggested that a measure of the strength of the silicate pump
337 can be obtained by comparing $1 - [D]:[P]$ for Si with the f-ratio for N (representing export intensity
338 for Si and N respectively). When the $1 - [D]:[P]$ values obtained from our model are plotted versus

339 the f-ratio for each site (obtained from *Nelson et al.* [2002] for the Southern Ocean and from
340 *Falkowski et al.* [2003] for the other sites) (Fig. 4), the silica pump appears to be most
341 pronounced at APFP and NACC sites. At the EqPac site, $1-f_{D:P}$ is close to 0.12, whereas the f-
342 ratio is between 0.1 and 0.17 [*Dugdale et al.*, 1992; *Mc Carthy et al.*, 1996]. Since $1-f_{D:P}$ is less
343 than or equal to the f-ratio at this site, it would appear that the silicate pump is weak or
344 nonexistent.

345 The silicate pump will be most pronounced under the following two conditions: (1) when
346 particle formation is extensive enough to induce rapid export from the mixed layer, and (2) when
347 Si and N cycling are decoupled, so that more Si is exported relative to N. To simplify the model
348 as much as possible, we pooled aggregates and fecal pellets into a single group to reconstruct
349 $bSiO_2$ fluxes. This simplification may lead to some inaccuracies, as grazing (i.e., fecal pellet
350 production) and aggregation can have very different effects on the silicate pump [see *Ragueneau*
351 *et al.*, 2006]. While grazers assimilate C and N from diatom material, $bSiO_2$ passes through the
352 gut quasi-inertly, leading to a five-fold increase in the Si/C ratio as the material is egested
353 [*Cowie and Hedges*, 1996; *Tande and Slagstad*, 1985]. By contrast, diatoms that are incorporated
354 within aggregates rather than ingested by zooplankton would tend to remain alive for a longer
355 time, fixing their Si/C ratio at a relatively constant value [*Moriceau et al.*, 2007]. Despite this
356 caveat, with our simple model we can at least identify sites with a high flux of fast-sinking
357 particles, and see that $1-f_{D:P}$ (at 100 m) is highest at sites with the most seasonality (Fig. 3).
358 Clearly, particle formation at the end of blooms is a key factor controlling the silicate pump.
359 Further investigation of aggregation dynamics is crucial for understanding temporal and spatial
360 variations in the strength of the silicate pump, as well as the role of diatoms in the biological
361 carbon pump [e.g., *Ragueneau et al.*, 2006].

362

363 **4.3. Impact on the geochemistry of the seafloor**

364 Our results have important implications for the calibration of bSiO₂ mass accumulation
365 rates (MAR) as a proxy of paleoproductivity [Ragueneau *et al.*, 2000]. Larger opal MAR need
366 not necessarily be ascribed to higher surface productivity. At the POOZ site (Fig. 2), for
367 example, a doubling in the bSiO₂ rain rate can be achieved without any change in surface bSiO₂
368 production, through either (1) a doubling in the incorporation of bSiO₂ into large particles (i.e.,
369 from 20% to 40%), (2) a 3.33-fold increase in the LP sinking rate (from 30 to 100 m d⁻¹), or (3) a
370 2.67-fold decrease in the LP dissolution rate from 0.04 to 0.015 d⁻¹. These ranges in values are
371 all realistic, and a small variation in one of them can significantly increase the amount of bSiO₂
372 reaching the seafloor. Furthermore, these 3 factors are not necessarily independent and can
373 therefore have additive effects. For example, incorporation into large particles would most likely
374 increase both the particle sinking rate and decrease the bSiO₂ dissolution rate [Moriceau *et al.*,
375 2007]. Clearly, improving our understanding of how siliceous sediments accumulate requires
376 proper consideration of particle formation and biogeochemical cycling in sinking particles. This
377 is crucial not only for determining the depth of bSiO₂ dissolution in the water column, but also
378 the extent of silica burial in sediments [Gallinari *et al.*, 2002; Khalil *et al.*, 2007].

379

380 5. Conclusions and perspectives

381 In this paper, we have combined sinking and silica dissolution rates [Schultes, 2004;
382 Moriceau *et al.*, 2007] for three types of siliceous particles (diatoms as free cells, incorporated
383 into zooplankton fecal pellets, or into aggregates) to reconstruct theoretical downward profiles of
384 bSiO₂ fluxes. By applying a simple advection-reaction model to 8 sites of the world ocean where
385 annual estimates of bSiO₂ production are available [Ragueneau *et al.*, 2002], we were able to fit
386 these theoretical profiles to measured bSiO₂ fluxes derived from sediment trap data. Such an
387 approach allowed us to derive the sinking rates of particles and partitioning of bSiO₂ between
388 freely-suspended diatoms and large particles. When diatoms are incorporated into large particles

389 via aggregation or incorporation into fecal pellets, this can impact bSiO₂ recycling and possibly
390 other elements like C and N. Further experimentation would be needed, however, to assess this
391 last point.

392 The competition between recycling in surface waters and export to depth is controlled by
393 the intensity of particle formation rather than by the extent of dissolution in surface waters. For
394 bSiO₂ incorporated into sinking aggregates and fecal pellets, export is much faster than
395 dissolution. Therefore, the extent of dissolution in surface waters depends primarily on the
396 amount of diatom cells that remain freely suspended and can subsequently be degraded by
397 bacteria [*Bidle and Azam, 1999*]. Thus, even ballasted by its frustule, a diatom would be recycled
398 if not incorporated into fast-sinking aggregates or fecal pellets.

399 This finding also has implications for the use of opal MAR as a proxy of
400 paleoproductivity, which should account not only for the production signal, but also the extent of
401 incorporation into large particles. Furthermore, just as bSiO₂ preservation depends on the types
402 of particles transporting diatoms toward the seafloor, it likely affects C preservation as well.
403 Further investigation is needed of the extent of C recycling within aggregates and fecal pellets, as
404 this has major implications for C export and benthic food webs.

405 Our model demonstrated that dissolution in surface waters is extremely high at the EqPac
406 site, most likely due to the small percentage of bSiO₂ production being incorporated, on an
407 annual basis, into large sinking particles (Table 2). This result does not support the idea of a
408 strong silicate pump in the equatorial Pacific, as previously suggested by *Dugdale et al.* [1995].
409 Rather, it appears that such a mechanism would be most applicable at highly seasonal sites like
410 NACC or APFP where the fraction of bSiO₂ production that is exported from the surface layer is
411 highest (Fig. 3). At such locations, the efficiency of the silica pump will depend upon the relative
412 fates of Si and N in sinking particles. Since aggregation and incorporation into fecal pellets may
413 have very distinct influences on Si and N decoupling during sinking [*Ragueneau et al., 2006*],
414 differentiating between these two transport pathways is essential for improving our

415 understanding of the functioning of the silicate pump, the role of diatoms in the biological pump,
416 and the nutritional properties of particles supporting deep-sea food webs.

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Figure caption

Figure 1: Best fits (lines) of the three versions of the models and in situ (dots) bSiO₂ flux profiles, for eight sites in the global ocean described in *Ragueneau et al.* [2002] (positions given in Table 2). The dashed lines are the fits obtained from the 1-particle model, the dotted lines describe the bSiO₂ fluxes calculated with the 2-particle model that uses a global S_{FC} and the plain lines depict the bSiO₂ profiles obtained from the 2-particle model that uses a variable S_{FC} calculated at each site.

Figure 2: Sensitivity of the model, represented by successive variation of parameters. Fig. 2a sensitivity of the model to the sinking rate of the slow sinking/fast dissolving particle S_{FC}, with S_{LP} set at 51 m d⁻¹ and α at 68%, Fig. 2b, sensitivity of the model to the sinking rate of the fast sinking/slow dissolving particle S_{LP}, with S_{FC} set at 1.4 m d⁻¹ and α at 68%, Fig. 2c, sensitivity of the model to the repartition of the bSiO₂ between the FC group α, and the LP group (1- α), with S_{LP} set at 51 m d⁻¹ and S_{FC} at 1.4 m d⁻¹. The graphs represent the results of the test for the POOZ site, the full circles and the full lines in each graph represent the in situ measurements of the bSiO₂ fluxes and the results of the model 3.

Figure 3: Importance of the seasonality. 1-[D]:[P] at 100 m calculated from the model outputs as a function of the seasonality index [*Berger and Wefer* 1990]. The site names are given near each corresponding point.

Figure 4: 1-[D]:[P] calculated at 100 m with the model 3 versus the f-ratios. The f-ratios are from *Nelson et al.* [2002] for the Southern Ocean and *Falkowski et al.* [2003] for the other sites. The names of seven of the eight sites are indicated near the corresponding point. APFA site is not in the graph as no f-ratio is available at this site. The plain line delimits the zones where f-ratio is higher or lower than 1-[D]:[P] at 100 m which gives an indication of the strength of the silica pump.

	sinking rate $m\ d^{-1}$		dissolution rate d^{-1}		Used in this study
	range	References	range	References	
Cells	0.2-20	<i>Bienfang, 1981; Mann and Lazier, 1996; Smayda, 1970; Turner, 2002]</i>	0.005-1.3	[<i>Van Cappellen et al., 2002]</i>	0.044
Aggregates	1-370	[<i>Allredge and Gotschalk, 1988; Ridgwell et al., 2002]</i>	0.012-0.056	[<i>Moriceau et al., 2007]</i>	0.022
Copepod fecal pellets	5-220	[<i>Turner, 2002; Wassmann et al., 1999]</i>	0.003-0.027	[<i>Gallinari et al., unpubl.; Schultes, 2004]</i>	

Table 1: Range of sinking rates and specific dissolution rates cited in the literature for freely suspended cells, aggregates and copepods fecal pellets. The column “Used in this study”, gives the dissolution values actually used herein. For the slow sinking/fast dissolving group (FC), we used the mean value given by *Van Cappellen et al. [2002]* from a compilation of studies, whereas for the LP (aggregates + fecal pellets) the rates are calculated from the average value given by *Van Cappellen et al. [2002]* divided by the factor of two which is the average decrease in dissolution rates observed when cells are incorporated into fecal pellets and aggregates [*Gallinari et al., unpubl; Schultes, 2004; Moriceau et al., 2007]*].

	POOZ	APFP	NACC	APFA	OSP	EqPac	BATS	PAP	
Latitude	-52	-60	-56.9	-50.1	50	1	28	48.8	
Longitude	62	-170	-170.1	5.8	-145	-139	-67.5	-16.5	
MMLD (m)	259	235	390	180	100	48	100	576	
SI	2.80	3.75	2.80	2.70	2.50	0.33	1.30	3.00	
% PP_{bSiO₂} in FC stage α	80%	70%	40%	20%	69%	88%	83%	65%	
Model 2: 2-particle model global S_{FC}	S_{FC} (m d⁻¹)	2.76							
	% PP_{bSiO₂} into LP (1- α)	20%	30%	60%	80%	31%	12%	17%	35%
	S_{LP} (m d⁻¹)	470	53	27	47	90	812	92	55
Model 3: 2-particle model variable S_{FC}	% PP_{bSiO₂} in FC stage α	68%	81%	78%	17%	64%	88%	83%	85%
	S_{FC} (m d⁻¹)	1.4	4.5	10.3	0.1	2	0.1	0.1	6.7
	% PP_{bSiO₂} into LP (1- α)	32%	19%	22%	83%	36%	12%	17%	15%
	S_{LP} (m d⁻¹)	51	452	242	45	62	500	90	605

Table 2: Environmental characteristics and results of the two versions of the 2-particle model calculated to fit the bSiO₂ flux profiles at eight sites of the global ocean (Fig. 1). The depth of the maximum mixed layer (MMLD) and the location of the sites are from *Ragueneau et al.* [2002]. The seasonality indexes (SI) are calculated following the work of *Berger and Wefer* [1990]. The last rows depict combinations of sinking rates for FC (S_{FC}) and LP (S_{LP}) and percentage of bSiO₂ incorporated into the two groups of particles calculated with each version of the 2-particle model from the best fits.

		POOZ	APFP	NACC	APFA	OSP	EqPac	BATS	PAP
residence time of FC in surface layer	Considering only sinking	0.7	0.2	0.1	10	0.5	10	10	0.15
	Considering dissolution	56	56	43	60	36	8	8	21
residence time of LP in surface layer	Considering only sinking	0.020	0.002	0.004	0.022	0.016	0.002	0.011	0.002
	Considering dissolution	113	113	86	121	71	15	17	42

Table 3: Residence times of the particles in the mixing layer (ML) in days calculated considering only dissolution processes and considering only sedimentation rates at the eight sites. To calculate the residence time of the particles considering only sinking processes, the sinking rates are normalized by the depth of the mixed layer (MLD) as given Table 2. The residence times of the particles in the mixed layer considering only dissolution processes are equal to $1/k(T)$, with $k(T)$ the specific dissolution rates corrected for temperature at each site.

	POOZ	APFP	NACC	APFA	OSP	EqPac	BATS	PAP
% PP_{bSiO_2} reaching the MMLD	34%	53%	58%	80%	50%	12%	16%	18%
% PP_{bSiO_2} on FC stage at the MMLD	4%	34%	36%	0%	16%	0%	0%	3%
% PP_{bSiO_2} reaching the seafloor	17%	18%	18%	37%	19%	11%	7%	14%

Table 4: $bSiO_2$ fluxes of the eight sites at the maximum mixed layer depth (MMLD) (see also Table 2), in terms of % of total $bSiO_2$ production at the surface layer (PP_{bSiO_2}), contribution of the slow sinking/fast dissolving group (FC) to the % of PP_{bSiO_2} that reaches this depth, and % of PP_{bSiO_2} that sinks down to the seafloor.

● Experimental data bSiO₂ - - - - bSiO₂ modelled flux 1-particle model
 - - - - bSiO₂ modelled flux 2 particles global S_{FC} ——— bSiO₂ modelled flux 2 particles Variable S_{FC}









