Importance of particle formation to reconstructed water column biogenic silica fluxes

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Running title: Reconstruction of bSiO$_2$ fluxes from dissolution experiments

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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 ($bSiO_2$) 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 $bSiO_2$ dissolution to

21 reconstruct theoretical downward profiles of $bSiO_2$ fluxes at 8 sites in the world ocean. Statistical

22 analyses showed that sinking and dissolution parameters for two pools of $bSiO_2$ 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 $bSiO_2$ production that reaches

25 the seafloor. The depth of $bSiO_2$ recycling appears to be influenced more by particle formation

26 than by dissolution rates of $bSiO_2$ or the ballast effect of the dense diatom frustules.

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1. Introduction

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

64   production, export and deep fluxes from 8 biogeochemical provinces of the world ocean

65   [described in *Ragueneau et al.,* 2002]. The $bSiO_2$ 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 $bSiO_2$ fluxes in terms of large or

68   small particles and, the sinking and specific $bSiO_2$ dissolution rates of each component help to

69   unravel mechanisms involved in the spatial variability of the intensity and depth of $bSiO_2$

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 $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ sedimentation flux

81   more precisely. Here we consider a model of $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ dissolution rate characteristic of free diatom cells. The

86   LP group has faster sinking rates than the FC and half the specific $bSiO_2$ dissolution rate. For

87   comparison, the model was first run using only one type of particle with sinking properties and

88   $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ for each particle pool i (LP or FC) can be described

102 by a simple advection-reaction model (Eq. 1):

103

$$\frac{\partial \mathrm{bSiO}_{2i}}{\partial t} = -S_i \cdot \frac{\partial \mathrm{bSiO}_{2i}}{\partial z} - k_i(T) \cdot \mathrm{bSiO}_{2i} \qquad (1)$$

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 bSiO$_2$ dissolution rate (d^{-1}). Such first-order dissolution of bSiO$_2$

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 ($\frac{\partial \mathrm{bSiO}_{2i}}{\partial t}=0$), and constant sinking and dissolution rates, the

111 concentration (mmol m^{-3}) and flux of bSiO$_2$ (mmol m^{-2} d^{-1}) at each water column depth (z) are

112 given by equation 2:

113

$$\mathrm{bSiO}_{2i}(z) = \mathrm{bSiO}_{2i}(0) \cdot e^{-\frac{k_i}{S_i} \cdot z} \qquad (2)$$

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

$$\mathrm{FbSiO}_2(z) = \mathrm{PP}_{\mathrm{bSiO}2} \cdot e^{-\frac{k}{s} \cdot z} \qquad (3)$$

$$\mathrm{FbSiO}_2(z) = \mathrm{PP}_{\mathrm{bSiO}2} \cdot [\alpha \cdot e^{-\frac{k_{FC}}{S_{FC}} \cdot z} + (1-\alpha) \cdot e^{-\frac{k_{LP}}{S_{LP}} \cdot z}] \qquad (3')$$

121

122   where α and (1- α) correspond to bSiO$_2$ production (PP$_{bSiO2}$, 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 + Δz) and top

127   (z) of this layer are related by:

128

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

130

131   For the 1-particle model the flux at z = 0 equals the bSiO$_2$ production (PP$_{bSiO2}$), and for the 2-

132   particle model the bSiO$_2$ flux at each depth is the sum of the LP and FC fluxes.

133
$$\mathrm{FbSiO}_{2FC}(0) = \alpha \cdot \mathrm{PP}_{bSiO2}$$
$$\mathrm{FbSiO}_{2LP}(0) = (1 - \alpha) \cdot \mathrm{PP}_{bSiO2}$$ (5)
$$\mathrm{FbSiO}_{2TOT}(z) = \mathrm{FbSiO}_{2FC}(z) + \mathrm{FbSiO}_{2LP}(z)$$

134

135   In these equations, FbSiO$_{2TOT}$(z) is the flux of total bSiO$_2$ in mmol m^{-2} d^{-1} at depth z;

136   PP$_{bSiO2}$ is the production flux of bSiO$_2$ in mmol m^{-2} d^{-1}; FbSiO$_2$ $_{FC}$(z) and FbSiO$_2$ $_{LP}$(z) are the

137   fluxes of bSiO$_2$ in the FC and LP groups at depth z respectively. k$_{FC}$(T) and k$_{LP}$(T) are the

138   specific bSiO$_2$ 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
$$\ln\left(k_z(T_2)\right) = \ln\left(k_1\right) + \frac{E_{app}}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
(6)

145

146   where k_1 is the specific $bSiO_2$ 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 Eapp/R = 7211 °K.

149   To facilitate comparison among sites, the total flux is normalized to the production flux

150   to obtain a profile of $bSiO_2$ flux expressed in % of $bSiO_2$ production.

151   For both models we have:

152

153
$$\%FbSiO_2(z) = \frac{FbSiO_{2tot}(z)}{PP_{bSiO2}} \times 100$$
(7)

154

155   which for the 2-particle model becomes:

156

157
$$\%FbSiO_2(z) = \frac{FbSiO_{2FC}(z) + FbSiO_{2LP}(z)}{PP_{bSiO2}} \times 100$$
(7')

158

159   **2.3. Parameter determination**

160   As a first step, we applied the 1-pool model to fit the $bSiO_2$ 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 $bSiO_2$

163   sinking rate required to fit the in situ $bSiO_2$ 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, $bSiO_2$ specific dissolution rates and the sinking rates for two pools of

166   particles were included in the model (model 2). Specific $bSiO_2$ 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 $bSiO_2$ from the production which is incorporated into

170   large particles (1-α) 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    $$F = (SSR1-SSR2) (df1-df2) / (SSR2/df2) \tag{8}$$

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    $$dfi = E - P - 1 \tag{9}$$

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, providing14 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 ($\int$D:$\int$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-

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 ($bSiO_2$, $CaCO_3$) 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 $bSiO_2$ and $CaCO_3$ 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 $bSiO_2$ 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, $bSiO_2$ 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 $bSiO_2$

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 $bSiO_2$

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 $bSiO_2$ 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-∫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-∫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-∫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 $bSiO_2$ 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 $bSiO_2$ rain rate can be achieved without any change in surface $bSiO_2$

368   production, through either (1) a doubling in the incorporation of $bSiO_2$ 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 $bSiO_2$

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 $bSiO_2$ 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 $bSiO_2$ 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    $bSiO_2$ fluxes. By applying a simple advection-reaction model to 8 sites of the world ocean where

385   annual estimates of $bSiO_2$ production are available [*Ragueneau et al.,* 2002], we were able to fit

386   these theoretical profiles to measured $bSiO_2$ fluxes derived from sediment trap data. Such an

387   approach allowed us to derive the sinking rates of particles and partitioning of $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ 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 $bSiO_2$ 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) bSiO$_2$ 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 bSiO$_2$ fluxes calculated with the 2-particle model that uses a global S$_{FC}$ and the plain lines depict the bSiO$_2$ 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 bSiO$_2$ 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 bSiO$_2$ fluxes and the results of the model 3.

Figure 3: Importance of the seasonality. 1-$\int$D:$\int$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-$\int$D:$\int$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-$\int$D:$\int$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	*Bienfang*, 1981; *Mann and Lazier*, 1996; *Smayda*, 1970; *Turner*, 2002]	0.005-1.3	[*Van Cappellen et al.*, 2002]	0.044
Aggregates	1-370	[*Alldredge and Gotschalk*, 1988; *Ridgwell et al.*, 2002]	0.012-0.056	[*Moriceau et al.*, 2007]	0.022
Copepod fecal pellets	5-220	[*Turner*, 2002; *Wassmann et al.*, 1999]	0.003-0.027	[*Gallinari et al.*, unpubl.; *Schultes*, 2004]	

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
Model 2: 2-particle model global S_{FC} — % PP_{bSiO2} in FC stage α	80%	70%	40%	20%	69%	88%	83%	65%
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 bSiO$_2$ 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 bSiO$_2$ 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$_{bSiO2}$ reaching the MMLD	34%	53%	58%	80%	50%	12%	16%	18%
% PP$_{bSiO2}$ on FC stage at the MMLD	4%	34%	36%	0%	16%	0%	0%	3%
% PP$_{bSiO2}$ 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$_{bSiO2}$), contribution of the slow sinking/fast dissolving group (FC) to the % of PP$_{bSiO2}$ that reaches this depth, and % of PP$_{bSiO2}$ that sinks down to the seafloor.

$$1\text{-}D\text{:}P(100\text{ m}) = 0.0949\ e^{0.6413\ SI}$$
$$R^2 = 0.8554$$

$BSiO_2$ (seafloor) = 36.75 $(1-\alpha)$ + 6.74
R^2 = 0.8767

%$BSiO_2$ at the seafloor

% of the $BSiO_2$ production integrated to LP $(1-\alpha)$