Effects of biogenic silica dissolution on silicon cycling and export production

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[1] Biogenic silica ($bSiO_2$) dissolution plays an important role in the marine silicon cycle, diatom production and vertical export production. An ocean ecosystem model that incorporates dependency of $bSiO_2$ dissolution on water temperature was used to examine the effects of $bSiO_2$ dissolution on diatom production and $bSiO_2$ export. Diatoms dominate with higher $bSiO_2$ dissolution rates because of enhanced silicic acid supply for diatom production. Annual $bSiO_2$ export does not change with $bSiO_2$ dissolution rate, because of less $bSiO_2$ production with lower rates and greater $bSiO_2$ dissolution with higher rates. The ratio of $bSiO_2$ export to production changes seasonally, with maximum in late spring. The contribution of spring diatom bloom to the annual $bSiO_2$ export is 21–30%, smaller than observation-based estimates. This suggests necessity for incorporating other factors controlling $bSiO_2$ dissolution besides water temperature, such as difference in organic coating protections against $bSiO_2$ dissolution between live and dead diatoms, in the model. **Citation:** Fujii, M., and F. Chai (2005), Effects of biogenic silica dissolution on silicon cycling and export production, *Geophys. Res. Lett.*, *32*, L05617, doi:10.1029/2004GL022054.

1. Introduction

[2] Marine biogenic silica ($bSiO_2$) is mainly produced by diatoms, a large phytoplankton species which deposit silica within their cell walls. Dissolution of $bSiO_2$ is the source of regenerated silicic acid ($Si(OH)_4$) in the ocean. However, because of the scarcity of in situ observations, understanding the linkages between $bSiO_2$ production and dissolution remains uncertain [e.g., *Nelson et al.*, 1995; *Ragueneau et al.*, 2000; *Brzezinski et al.*, 2001, 2003].

[3] Recently, several modeling studies have incorporated silicon cycling in marine ecosystem models [e.g., *Dugdale et al.*, 1995; *Pondaven et al.*, 1998; *Chai et al.*, 2002; *Fujii et al.*, 2002; *Moore et al.*, 2002; *Aumont et al.*, 2003]. Most of these models have focused on $Si(OH)_4$ regulation of diatom production, and none of them have paid attention to $bSiO_2$ dissolution process and its effect on silicon cycling and vertical export production. *Gnanadesikan* [1999] has embedded silicon cycling in an ocean general circulation model although the marine ecosystem is not considered. He found that the global $Si(OH)_4$ distribution was quite sensitive to the type of dissolution parameterization.

[4] We use a marine ecosystem model, incorporating both silicon and nitrogen cycles, to examine the effects of $bSiO_2$ dissolution on diatom production as well as relationships among production, dissolution and downward export of $bSiO_2$. This study focuses on the role of water temperature in controlling $bSiO_2$ dissolution, by conducting a series of model sensitivity experiments related to dependency of $bSiO_2$ dissolution rate on temperature.

2. Model Description and Experimental Design

[5] We use a fifteen-compartment marine ecosystem model developed originally for the subarctic Northwest Pacific [*Fujii et al.*, 2002; *Yamanaka et al.*, 2004]. The surface water is defined as the model domain above 100 m depth. In the model, the phytoplankton is divided into two categories: PL (large phytoplankton, all diatoms) and PS (non-diatom small phytoplankton). Diatom production is regulated by $Si(OH)_4$, nitrate (NO_3) and ammonium concentration, while small phytoplankton production is controlled only by NO_3 and ammonium concentration. The $bSiO_2$ is exposed to dissolution after being separated from live diatoms by the mortality of diatoms and the egestion of diatom-grazing zooplankton.

[6] This model has been applied to a time-series Station KNOT (*Kyodo* North Pacific Ocean Time series; 44°N, 155°E) located in the subarctic Northwest Pacific, which displays strong seasonality in diatom production. The model structure and forcing are the same as in work by *Fujii et al.* [2002]. The transition-domain water with high temperature, high salinity and low nutrients is sometimes advected horizontally from the subtropical gyre to Station KNOT. However the majority of the annual nutrient supply occurs through local vertical mixing in winter and is consumed by biological production in the surface water in spring and summer. Therefore, we have ignored the sporadic influence on horizontal charge/discharge of nutrients by the transition-domain water. Values of the model parameters are the same as those of *Fujii et al.* [2002], except the temperature coefficient for the $bSiO_2$ dissolution (k_{bSiO2}) is modified for this study. In the model, the specific $bSiO_2$ dissolution rate (V_{dis}) is calculated as $V_{dis} = V_{dis0} \times \exp(k_{bSiO2} \times T)$, where V_{dis0} is the specific $bSiO_2$ dissolution rate at temperature equals to 0°C and T is water temperature [°C]. Recent data show that bacterial protease activity accelerates the dissolution of $bSiO_2$ [*Bidle and Azam*, 1999], and that such process is strongly dependent on water temperature [*Bidle et al.*, 2002, 2003]. We set k_{bSiO2} to 0.097 [1/°C] to represent the dependency of $bSiO_2$ dissolution on water temperature by a factor of 2.63 for each 10°C ($Q_{10} = 2.63$ [*Bidle et al.*, 2003]), while the temperature coefficient for remineralization of organic nitrogen is set to 0.069 [1/°C] ($Q_{10} = 2.0$ [*Fujii et al.*, 2002]).

[7] We carry out a series of sensitivity studies by varying the dissolution rate of $bSiO_2$ at $0°C$ (V_{dis0}) to 0.000 (Case 1; no dissolution), 0.010 (Case 2), 0.025 (Case 3), 0.050 (Case 4), 0.100 (Case 5) and 0.200 (Case 6) [1/d] to reflect the range of measured values at this temperature, 0.00 and 0.20 [1/d] [e.g., *Beucher et al.*, 2004].

3. Results and Discussion

[8] The model results successfully reproduce the observed seasonal pattern of physical environments and biogeochemistry at Station KNOT [*Fujii et al.*, 2002]. The large seasonal amplitude of sea surface temperature (SST), from less than $2°C$ in March to $15°C$ in August, has impact on the calculation of $bSiO_2$ dissolution rate in the model (Figure 1). The low SST along with strong wind in winter enhances vertical mixing, which injects nutrient-rich deep water to the surface. The relatively high SST as well as weak wind from late spring to autumn result in vertical stratification of water column. This stratification and the following spring diatom bloom cause depletion of surface nutrients. Therefore, the surface nutrient concentration is the highest in late winter and the lowest in late summer. The modeled annual surface maximum and minimum $Si(OH)_4$ is 35 and 5 [$mmolSi/m^3$], consistent with the observed ones of 40 and 4 [$mmolSi/m^3$], respectively [*Fujii et al.*, 2002]. Due to higher temperature between late spring and autumn, the modeled $bSiO_2$ dissolution rate increases significantly, which causes dissolution to be the dominant source of $Si(OH)_4$ supporting $bSiO_2$ production during summer and autumn.

[9] The modeled annual-mean primary production by diatoms (PP_{PL}) increases with the $bSiO_2$ dissolution rate at $0°C$ (V_{dis0}), from 1.3 in Case 1 to 2.4 [$mmolN/m^2/d$] in Case 6 (Figure 2). Higher surface $Si(OH)_4$ concentration in response to higher V_{dis0} (Figure 3) enhances diatom production. For example, the modeled surface minimum $Si(OH)_4$ concentration in Case 6 is close to the half saturation constant for $Si(OH)_4$ uptake by diatoms (6.0 [$mmolSi/m^3$]). On the other hand, surface NO_3 concentration decreases with higher $bSiO_2$ dissolution rate. It is due to higher diatom production, which removes NO_3 as well. Therefore, this result shows that the $Si(OH)_4$ limitation becomes stronger with lower V_{dis0} while the NO_3 limitation takes over with higher V_{dis0}. Changing in the $bSiO_2$
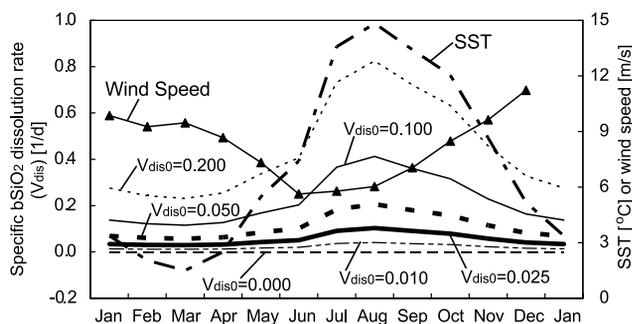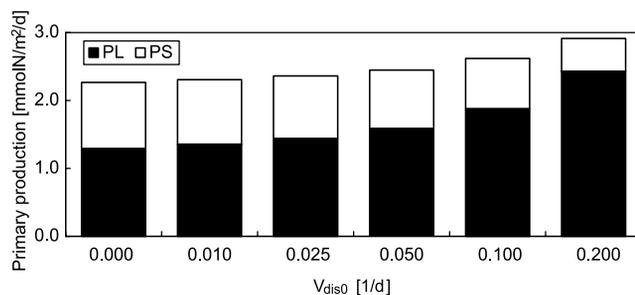
Figure 2. Modeled annual-mean primary production by diatoms (PL) and small phytoplankton (PS) [$mmolN/m^2/d$] in Case 1 through 6.

dissolution rate also alters competition between diatoms and small phytoplankton for NO_3, with diatoms taking more NO_3 results in decreasing available NO_3 for small phytoplankton. Therefore, the annual-mean primary production by small phytoplankton (PP_{PS}) in Case 6 decreases to 50% of that in Case 1, and diatoms dominate primary production as V_{dis0} increases (Figure 2). The diatom production (PP_{PL}) accounts for 57% and 83% of total primary production (PP_{total}) in Case 1 and Case 6, respectively. The PP_{total} increases as V_{dis0} increases, but only by 1.3 times because of compensation between increasing PP_{PL} and decreasing PP_{PS}.

[10] There are two pathways for the fate of $bSiO_2$, i.e., to be dissolved in the surface water or to sink to the deep water. In this study, we define the ratio of the $bSiO_2$ export across 100m to the $bSiO_2$ production in the surface water as a $bSiO_2$ export ratio. The variation in the $bSiO_2$ dissolution rate at $0°C$ (V_{dis0}) changes the annual $bSiO_2$ export ratio, with lower $bSiO_2$ export ratios corresponding to higher $bSiO_2$ dissolution rates (Figure 4a). For example, the annual $bSiO_2$ export ratio decreases from 1.0 in Case 1 to 0.57 in Case 6. The modeled $bSiO_2$ export ratio changes significantly in response to the variation of $bSiO_2$ dissolution rate, but the absolute value of the modeled annual $bSiO_2$ export change by <10% among all the six cases (Figure 4b). This result occurs because the $bSiO_2$ production is relatively low with lower dissolution rates due to less $Si(OH)_4$ supply for diatom production. With higher dissolution rates the $bSiO_2$ production is higher and a relatively large portion is
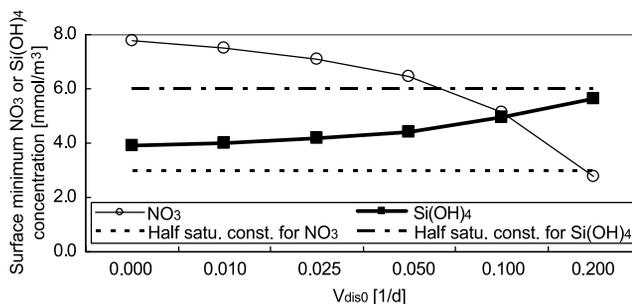

Figure 1. Seasonal changes of SST [$°C$] [*Fujii et al.*, 2002], wind speed [m/s] [*Tsurushima et al.*, 2002] and specific $bSiO_2$ dissolution rate (V_{dis}) [1/d] in Case 1 through 6.

Figure 3. Modeled annual surface minimum NO_3 and $Si(OH)_4$ concentration [$mmol/m^3$] in Case 1 through 6. The half saturation constant for NO_3 and $Si(OH)_4$ uptake by diatoms in the model is also shown (3.0 [$mmolN/m^3$] and 6.0 [$mmolSi/m^3$] [*Fujii et al.*, 2002], respectively).
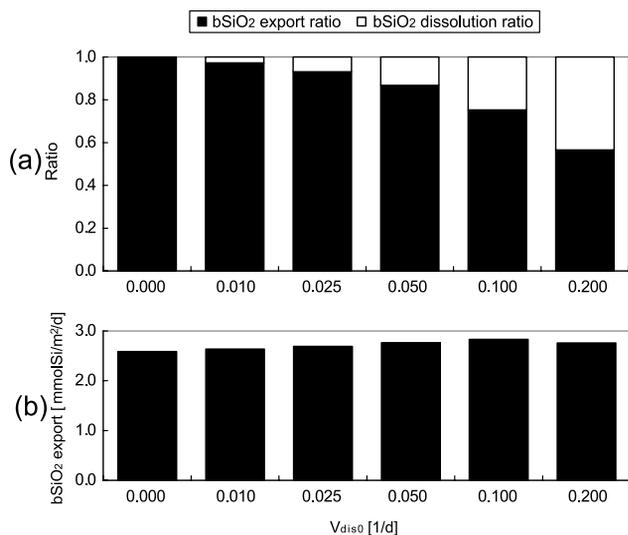
Figure 4. Modeled annual-mean (a) $bSiO_2$ export and dissolution ratio, and (b) $bSiO_2$ export across 100m depth [mmolSi/m^2/d], in Case 1 through 6.

dissolved in the surface water, therefore less $bSiO_2$ is exported to the deep water.

[11] Strong seasonal variation in the modeled $bSiO_2$ dissolution rate, corresponding to variability of water temperature, changes $Si(OH)_4$ concentration in the surface water, altering the magnitude, timing and duration of peaks of spring diatom bloom, primary and export production. Seasonal variation of the modeled $bSiO_2$ production and export, and the $bSiO_2$ export ratio in Cases 1, 5 and 6 are shown in Figure 5. From late spring to early autumn, approximately May to October, increasing $Si(OH)_4$ limitation from Case 6 to Case 1 (e.g., no $bSiO_2$ dissolution) terminates the spring diatom bloom progressively earlier and reduces annual diatom production, which leads to large differences in the $bSiO_2$ production among these three cases (Figure 5a). The difference in the $bSiO_2$ production among the cases is smaller during other times of the year, because diatom production is enhanced during the period when $Si(OH)_4$ is plentiful in the surface water due to stronger physical transport. On the other hand, difference in the $bSiO_2$ export among all cases is small on an annual basis (Figure 5b). The $bSiO_2$ export during the spring diatom bloom period, defined as from mid-April to mid-May, is lowest in Case 6 due to high $bSiO_2$ dissolution rate. The $bSiO_2$ export ratio changes seasonally and has its maximum during the post-bloom period (Figure 5c). The ratio can exceed 1.0 because the $bSiO_2$ export by the mortality of diatoms and the egestion of diatom-grazing zooplankton occurs several days later than the $bSiO_2$ production.

[12] Of the total modeled annual $bSiO_2$ export in Case 1 and 6, 60 and 54% occur in spring (30 and 21% during the bloom period, and 30 and 33% during the non-bloom period), 19 and 27% in summer, 10 and 9% in autumn, and 11 and 10% in winter, respectively. This means that the spring diatom bloom, which occurs for less than 10% of the entire year, plays a disproportionately large role in transporting the $bSiO_2$ to the deep water, resulting from the enhanced $bSiO_2$ production. The vertical export of $bSiO_2$ is

also largest during the bloom period because of relatively low temperature and subsequent less $bSiO_2$ dissolution in the surface water.

[13] All the model results shown above are applicable not only to the subarctic Northwest Pacific but to the global ocean where silicic acid is a potentially limiting factor on diatom production. Therefore, the model results can be compared with the global observation-based data. The modeled significant vertical export of $bSiO_2$ during the bloom period is consistent with evidences from observations in some oceanic areas [e.g., *Truesdale and Kellogg*, 1979; *DeMaster et al.*, 1992; *Brzezinski and Nelson*, 1995; *Nelson et al.*, 1995]. However, contribution of the diatom bloom to the annual export of $bSiO_2$ seems smaller in this modeling study, with a value of 21 to 30%, and some other observation-based estimates are 40 to 60% [e.g., *Nelson et al.*, 1995; *Nelson and Brzezinski*, 1997; *Brzezinski et al.*, 2001; *Shipe and Brzezinski*, 2001], higher than the modeled results.

[14] By examining global data sets, *Brzezinski et al.* [2003] have demonstrated that the larger contribution of diatom bloom on the observed $bSiO_2$ export is associated with systematically higher fraction of $bSiO_2$ production supported by new $Si(OH)_4$ $(1-\int D:\int P)$ during the bloom period. We can change the minimum and maximum values of $bSiO_2$ export ratio (Figure 5c) by changing values of the $bSiO_2$ dissolution rate at 0°C (V_{dis0}) and the temperature coefficient for the $bSiO_2$ dissolution ($kbSiO_2$). However, the model cannot reproduce the observed shift of $bSiO_2$ export ratio, between low ratio during the non-bloom period and higher ratio during the bloom period. In the current model,
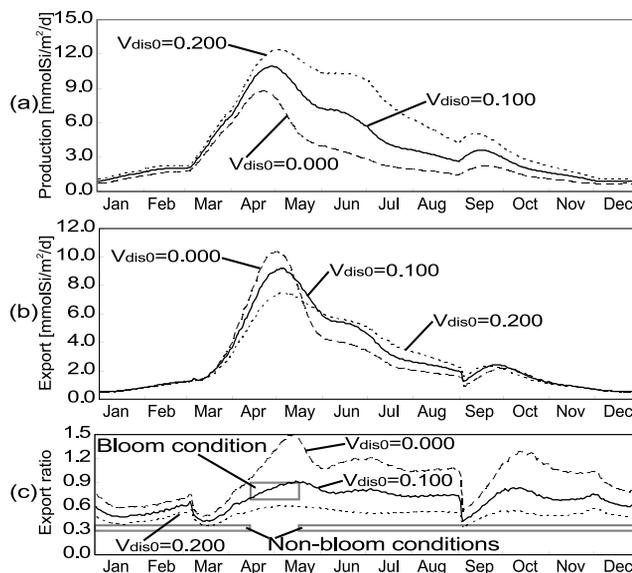
Figure 5. Modeled (a) $bSiO_2$ production [mmolSi/m^2/d], (b) $bSiO_2$ export [mmolSi/m^2/d], and (c) $bSiO_2$ export ratio, in Cases 1, 5 and 6 from January to December. Observation-based fraction of $bSiO_2$ production supported by new $Si(OH)_4$ $(1-\int D:\int P)$ during bloom and non-bloom conditions [*Brzezinski et al.*, 2003] is also shown in Figure 5c. Note that $bSiO_2$ export ratio is not always equal to $1-\int D:\int P$ in a short temporal scale of several days because of the time lag between $bSiO_2$ production and export.

we only include $bSiO_2$ dissolution from silicon detritus pool that does not include live diatoms. *Beucher et al.* [2004] showed that V_{dis0} was correlated to the percentage of dead diatoms. To reproduce the systematically higher $bSiO_2$ export ratio during the bloom period, other factors controlling $bSiO_2$ dissolution rate besides water temperature, such as difference in organic coating protections against $bSiO_2$ dissolution between live and dead diatoms, are probably required to be incorporated in the model.

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