<table>
<thead>
<tr>
<th>Title</th>
<th>Modeling carbon and silicon cycling in the equatorial Pacific</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Fujii, Masahiko; Chai, Fei</td>
</tr>
<tr>
<td>Citation</td>
<td>Deep Sea Research Part II : Topical Studies in Oceanography, 54(5-7): 496-520</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2007-03</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/28236">http://hdl.handle.net/2115/28236</a></td>
</tr>
<tr>
<td>Type</td>
<td>article (author version)</td>
</tr>
<tr>
<td>File Information</td>
<td>DSRT54-5-7.pdf</td>
</tr>
</tbody>
</table>

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP
Modeling carbon and silicon cycling in the equatorial Pacific

Masahiko Fujii\textsuperscript{1,2,*} and Fei Chai\textsuperscript{1}

\textsuperscript{1}School of Marine Sciences, 5706 Aubert Hall, University of Maine, Orono, ME 04469-5706, USA
\textsuperscript{2}Now at Sustainability Governance Project, Hokkaido University, Sapporo, Hokkaido 060-0809, Japan

*Corresponding author. Tel: +81-11-706-4536; Fax: +81-11-706-4534
E-mail: mfujii@sgp.hokudai.ac.jp (M. Fujii)
Abstract

The equatorial Pacific is a region of significant particulate inorganic carbon (PIC) and biogenic silica sedimentation, the majority of which is carried out by coccolithophorids and diatoms. We developed an ecosystem model that explicitly includes three phytoplankton functional groups (picoplankton, coccolithophorids, and diatoms), two zooplankton functional groups (microzooplankton and mesozooplankton), nutrients (nitrate NO$_3$, ammonium NH$_4$, and silicate Si(OH)$_4$), detritus (particulate organic matter, biogenic silica, and PIC), total alkalinity, total CO$_2$, and partial pressure of CO$_2$ at the surface water (pCO$_{2\text{sea}}$). The model is capable of reproducing many biogeochemical features for the region, such as high-nutrient low-chlorophyll condition, significant exposure of phytoplankton under grazing controls by zooplankton, and large CO$_2$ release to the atmosphere. The export ratio of PIC to particulate organic carbon (rain ratio) to the deep water was 0.16, higher than the global-mean values, implying predominant PIC sedimentation in the equatorial Pacific upwelling region. Comparison between calcification and no-calcification model results indicates that when coccolithophorids were present, the community interactions actually induced more diatom biomass, export fluxes of detritus, and CO$_2$ release to the atmosphere. The model results show remarkable calcification in the subsurface layers, which suggests more field data on calcification processes are needed. Increase of source (120m depth) Si(OH)$_4$ concentration associated with the tropical instability waves lead to a linear increase in biogenic silica export. Higher Si(OH)$_4$ concentration stimulated diatom growth, which caused a decrease in picoplankton because feeding pressure by mesozooplankton switched from picoplankton’s grazer, microzooplankton, to the abundant diatoms. Surface coccolithophorid biomass had its maximum at intermediate source Si(OH)$_4$ concentrations as a result of higher grazing pressure on coccolithophorids and higher NO$_3$ regulation on coccolithophorid growth, with lower and higher source Si(OH)$_4$ concentrations, respectively. Surface total alkalinity had its minimum and TCO$_2$ had its
maximum at intermediate source Si(OH)$_4$ concentrations. The two effects on pCO$_{2\text{sea}}$ resulted in maximum CO$_2$ release to the atmosphere and PIC export to the deep water, with nearby standard source Si(OH)$_4$ concentration of 7.5 [mmolSi m$^{-3}$]. The enhanced changes in biogenic silica export flux than in surface diatom biomass, confirmed by the model sensitivity study, suggests sedimented detritus under the equatorial Pacific upwelling region acts as an amplifier of changes in surface properties. The model results suggest that physical forcings, such as tropical instability waves, Kelvin waves, and La Niña, which are capable of changing Si(OH)$_4$ and iron concentrations in the euphotic zone, significantly affect both carbon and silicon fluxes in the region.
1. Introduction

1.1 Calcification in the equatorial Pacific

Calcifying plankton have a great role in oceanic carbon cycling and global climate change because of particulate inorganic carbon (PIC) shell production resulting in reduced alkalinity and CO₂ release to the atmosphere, the ballasting effect of carbonate minerals, and the packaging effect of promoting the transfer of organic carbon to the deep sea (e.g. Armstrong et al., 2002; Francois et al., 2002).

Previous studies have indicated that the majority (80%) of global marine biogenic carbonate precipitation is carried out by coccolithophorids (Deuser and Ross, 1989; Fabry, 1989; Westbroek et al., 1989) through their production of PIC coccoliths. Coccolithophorids acts as a significant biotic source of dimethyl sulfide (DMS) for the atmosphere and may influence regional albedo via increased cloud formation (e.g. Bates et al., 1987; Charlson et al., 1987; Brown and Yoder, 1994). The coccolithophorid bloom affects physical environments through changing albedo due to their unique light scattering properties, and biogeochemical processes from lower to higher trophic levels. The progressive increase in atmospheric CO₂ concentrations predicted for the next few decades will decrease the production of PIC in the surface ocean (Riebesell et al., 2000; Orr et al., 2005), and thus this response could potentially act as a negative feedback on atmospheric CO₂ levels (Iglesias-Rodríguez et al., 2002).

Although satellite-based estimates of coccolithophore blooms appear in high-latitude oceans, and the relative paucity of such blooms in the tropics (e.g., Holligan et al., 1983; Brown and Yoder, 1994; Brown, 1999; Iglesias-Rodríguez et al., 2002), the equatorial Pacific is known as a region of significant PIC sedimentation (van Andel, 1975), which represents 12-19% of global PIC production, and is on the same order of magnitude as new production in this region (Chavez and Barber, 1987; Balch and Kilpatrick, 1996). The equatorial Pacific is a largest natural CO₂ source to the atmosphere,
and therefore, change in calcification in the region can significantly impact on the global carbon cycling.

Calcification in the equatorial Pacific is poorly understood from ecological and biogeochemical perspectives because direct field estimates of calcification are few (Balch and Kilpatrick, 1996). Ecosystem modeling can help us to fill the gaps in observations and interpret observed results. Several ecosystem models have incorporated calcifying plankton as well as carbonate system (e.g. Fujii et al., 2002; Moore et al., 2002; Pätsch et al., 2002; Yamanaka et al., 2004). However, they all assumed a constant composition ratio of coccolithophorids to total phytoplankton or a constant ratio of calcification to net community production. Only very few previous studies have incorporated calcifying plankton in their models as an independent state variable (Pasquer et al., 2005; Buitenhuis et al., 2006).

1.2 Silicification in the equatorial Pacific

The equatorial Pacific upwelling region is known as one of the major high-nutrient, low-chlorophyll (HNLC) regions. This oceanic region is also characterized by permanently lower Si(OH)₄ than NO₃ concentration. For example, typical source (120m depth) concentration is 7.5 [mmolSi m⁻³] for Si(OH)₄ and 12.5 [mmolSi m⁻³] for NO₃, which leads to lower surface Si(OH)₄ than NO₃ concentration and potential Si(OH)₄ limitation on the diatom growth (e.g., Ku et al., 1995; Dugdale et al., 1995; Dugdale and Wilkerson, 1998). However, field data in this region have shown that the source Si(OH)₄ concentration ranges substantially from 3 to 13 [mmolSi m⁻³] (e.g., Dugdale et al., 2002). This means that the Si(OH)₄ limitation on the diatom growth and, therefore, phytoplankton community composition, could change widely in response to the source Si(OH)₄ concentration. Recent iron enrichment experiments in the equatorial Pacific have shown that iron as well as Si(OH)₄
concentration are crucial factors determining diatom growth and its biomass accumulation (e.g., Martin et al., 1994; Coale et al., 1996; Price et al., 1994; Sanderson et al., 1995).

Both Si(OH)₄ and iron in the surface water are primarily supplied by upwelling from the deep water (e.g., Chavez et al., 1991; Dugdale et al., 2002), although less is known of the distribution of iron, its form, and cycling. The nutrient concentrations change with physical forcing that varies on different time scales from days to years. Several previous studies have investigated biogeochemical responses in the equatorial Pacific to the non steady-state event associated with the passage of the tropical instability waves (TIWs), La Niña and Kelvin waves (e.g., Barber et al., 1996; Foley et al., 1996; Dunne et al., 1999; Dugdale et al., 2002). The passage of the TIWs lifts isopycnals, presumably elevating Si(OH)₄ and iron concentrations, as well as diatom production in the euphotic zone for a short period (e.g., Flament et al., 1996; Archer et al., 1997). The passage of Kelvin waves, by contrast, depresses the thermocline (e.g., Kessler and McPhaden, 1995), decreasing inputs of iron to the euphotic zone.

Although the concept of non steady-state is important in understanding equatorial biogeochemical cycles (e.g., Dunne et al., 1999), the total impact of the TIWs and Kelvin waves and their frequency still remains uncertain mainly due to a paucity of field data. In parallel, several modeling studies have examined the biological responses to enhanced nutrients by the TIWs. Using a ten-compartment ecosystem model that fully incorporates silicon cycling, and representing iron enrichment by changing two photosynthetic parameters of the diatoms, Chai et al. (2002) reproduced several ecological behaviors similar to those observed during the second mesoscale iron enrichment experiment (IronExII; at 3.5°S, 104°W). These behaviors included a rapid increase in diatom growth and biomass, termination of the iron-induced diatom bloom due to exhaustion of available iron and Si(OH)₄, and increased mesozooplankton population as a grazer on diatoms. Using the same ecosystem model, Dugdale et al. (2002) suggested that the stability of the equatorial system with its narrow range
of biological and chemical variables is conferred by the action of diatoms providing food for mesozooplankton, whose grazing also depletes picoplankton. They also suggested that diatoms increase while picoplankton population and NO$_3$ consumption decrease with source Si(OH)$_4$ increases. As a result, a maximum surface total carbon dioxide (TCO$_2$) and increased CO$_2$ flux to the atmosphere appear at intermediate source Si(OH)$_4$ concentrations.

1.3. Objective of this study

To elucidate factors that affect calcification and PIC sedimentation in the equatorial Pacific, we propose to address the roles of coccolithophorids and other phytoplankton and zooplankton groups that affect coccolithophorids. We develop and use an ecosystem model incorporating coccolithophorids, PIC, and total alkalinity. The model performance is tested by applying the model to the equatorial Pacific upwelling region. Model sensitivity analysis to biogeochemical parameters (Experiment 1) is conducted to understand dominant biological processes in the newly-developed ecosystem model.

To examine responses of the biogeochemistry in the equatorial Pacific to changes in Si(OH)$_4$ and iron concentrations in the euphotic zone induced by the TIWs, we conduct a model sensitivity study (Experiment 2). In Experiment 2, we investigate model sensitivity to the source (120m depth) Si(OH)$_4$ concentrations under the steady-state conditions. We compare all the model results to those with no-calcification model simulation, as well as the JGOFS EqPac field data.
2. Experimental design

2.1. Model description

We added three prognostic variables, namely calcifying phytoplankton (coccolithophorids, or P3), total alkalinity (TAlk), and particulate inorganic carbon (PIC) (Fig. 1), as well as the other phytoplankton functional groups (picoplankton (P1) and diatoms (P2)), zooplankton (microzooplankton (Z1) and mesozooplankton (Z2)), nutrients (NO₃, NH₄ and Si(OH)₄), detritus (particulate organic nitrogen and carbon (PON and POC) and biogenic silica (bSiO₂)), total CO₂ (TCO₂), and partial pressure of CO₂ in the surface water (pCO₂sea) which were embedded in a 1-D marine ecosystem model (Chai et al., 2002). The phytoplankton and zooplankton were separated by their functional groups, not only by their size but also according to their growth and vulnerability to grazing. All the phytoplankton take up NO₃, NH₄, and TCO₂ by the photosynthesis. The diatoms also utilize Si(OH)₄ for their silification process and the coccolithophorids take up TAlk as well as TCO₂ for its calcification process. The microzooplankton graze on picoplankton. The mesozooplankton feed on diatoms, coccolithophorids, microzooplankton and PON. The explicit representation of TAlk and TCO₂ in the model allows us to calculate pCO₂sea and the air-sea CO₂ flux. The phytoplankton carbon-chlorophyll-a ratio by weight was fixed to 50. The governing equations and formulations of biogeochemical processes were denoted in Appendix.

The model was applied to 5°S-5°N, 90-180°W (the “Wyrtki Box”, Wyrtki, 1981; Chai et al., 2002). The physical forcing is the same, and most of the biogeochemical parameter values are the same as Chai et al. (2002) (Table 1). The parameter values were obtained to reproduce the temporally-averaged observed constituents such as nutrient concentrations and new production in the euphotic layer (Chai et al., 1996), which varied between El Niño and non-El Niño periods (e.g. McCarthy et al., 1996). Steady-state results obtained by running the model up to 1000 days with the
constant vertical velocity and diffusivity were used.

2.2. Data description

Datasets were used to tune the biological parameters and to compare with model outputs. Datasets used in this study are as follows: the U.S. JGOFS EqPac observations in February-March (Survey I; TT007), March-April (Time series I; TT008), August-September (Survey II; TT011) and October (Time series II; TT012) of 1992 (e.g. Murray et al., 1995, 1996 and 1997; Balch and Kilpatrick, 1996; Barber et al., 1996); the France JGOFS fluxes in the Pacific transect (FLUPAC) in October of 1994 (Le Borgne et al., 1995; Rodier and Le Borgne, 1997); the Oligotrophie en Pacifique (OLIPAC) in November 1994 (Rainbault et al., 1999); the U.S. Zonal Flux transect (Zonal Flux) in April-May of 1996 (Dunne et al., 1999); the Etude du Broutage en Zone Equatoriale (EBENE) cruise in October-November of 1996 (Le Borgne et al., 1998; Leynaert et al., 2001); the World Ocean Database 2001 (WOD01; Conkright et al., 2002); the IronExII field data (Coale et al., 1996; Landry et al., 2000).

2.3. Comparison between calcification and no-calcification model simulations

To elucidate effects of newly-introduced coccolithophorids and its calcification processes on the entire biogeochemistry in the equatorial Pacific upwelling region, we compared model results with and without components and processes that were relevant to the calcification. In the no-calcification model simulation, we have excluded state variables of coccolithophorids and PIC. The no-calcification model structure was identical to that in Chai et al. (2002) and Dugdale et al. (2002). Small differences in the model results from the previous studies were attributed to different values in several biogeochemical parameters between the studies (Table 1; Chai et al. 2002).
3. Results

3.1. Calcification model

The modeling results reasonably reproduced the measured vertical features in the biogeochemistry in the equatorial Pacific, such as consistently higher NO$_3$ than Si(OH)$_4$ concentration (solid line in Fig. 2 (d), (f)). The modeled picoplankton (P1) was more abundant than diatoms (P2) and coccolithophorids (P3) (solid lines in Fig. 2 (a)), which has been suggested from the observations (Bidigare and Ondrusek, 1996). The modeled vertically-averaged phytoplankton abundance was 0.15 [mmolN m$^{-3}$] for picoplankton, 0.06 [mmolN m$^{-3}$] for diatoms, and 0.03 [mmolN m$^{-3}$] for coccolithophorids (Table 2). The percentage of diatoms in the total modeled phytoplankton biomass was 24%, which was slightly higher but was consistent with the observed range of 5-20% (Bidigare and Ondrusek, 1996).

The modeled vertically-averaged biomass was 0.13 [mmolN m$^{-3}$] for microzooplankton (Z1) and 0.28 [mmolN m$^{-3}$] for mesozooplankton (Z2) (Table 2), indicating that mesozooplankton was more plentiful than the other plankton, and therefore, possibly high grazing or predation pressure by mesozooplankton in the equatorial Pacific upwelling region. The abundance in the modeled zooplankton rapidly decreased with depth (solid lines in Fig. 2 (c)), as a result of their grazing and predation being dependent on biomass of their prey (Appendix A.2).

The modeled NO$_3$ and Si(OH)$_4$ increased with depth (solid line in Fig. 2 (d), (f)), resulting from nutrient uptake by phytoplankton near the surface and remineralization of PON and bSiO$_2$ below the depth. At 120m, Si(OH)$_4$ concentration was 7.5 [mmolSi m$^{-3}$], whereas NO$_3$ concentration was 12.0 [mmolN m$^{-3}$], and these values are close to the observed climatological data, respectively (e.g. Levitus et al., 1993; Murray et al., 1995; Chai et al., 2002; Dugdale et al., 2002). The surface concentration was 6.1 [mmolN m$^{-3}$] in NO$_3$ and 3.1 [mmolSi m$^{-3}$] in Si(OH)$_4$. The model captured the observed
subsurface maximum of NH$_4$ concentration (solid line in Fig. 2 (e); Murray et al., 1995). The subsurface NH$_4$ maximum is due to higher uptake rate of NH$_4$ near the surface mainly by picoplankton which has relatively smaller half-saturation constant for NH$_4$ uptake (0.1 [mmolN m$^{-3}$]) than the other phytoplankton has (1.0 [mmolN m$^{-3}$]) (Table 1).

The modeled TCO$_2$ had similar vertical profile as of nutrients, increasing with depth (solid line in Fig. 2 (h)), as a result of TCO$_2$ uptake by phytoplankton growth and calcification by coccolithophorids in the upper layer and decomposition of POC and PIC in the lower layer. The TAlk was only changed by the calcification process, i.e. shell formation by coccolithophorids in the upper layer and dissolution of PIC in the lower layer, so the vertical change was smaller in TAlk than in TCO$_2$ (solid lines in Fig. 2 (g), (h)). The pCO$_{2\text{sea}}$ depends on TAlk as well as the temperature, salinity and TCO$_2$ in the surface water, so it could be estimated more precisely than with previous models which did not explicitly incorporate change of TAlk (e.g. Chai et al., 2002). The pCO$_{2\text{sea}}$ was 401 [µatm] (Table 3), close to the observed values (e.g. Feely et al., 1997). The pCO$_{2\text{sea}}$ was much higher than the partial pressure of CO$_2$ in the atmosphere of 357 [µatm] (Appendix A.1; Chai et al., 2002), suggesting the equatorial Pacific upwelling region as a large CO$_2$ source to the atmosphere, as the observed.

The modeled net community production was obtained by multiplying the nitrogen changes in the water column by the Redfield stoichiometric ratio of 6.625 (Table 1). The modeled vertical profile of net community production reproduced well the observations (Fig. 3 (a)), implying that fixing a phytoplankton carbon:nitrogen ratio is a good assumption in this region. The modeled calcification in the euphotic zone (Fig. 3 (b)) was lower than the field data during EqPac Survey II (TT011; in August 1992) in which the measured calcification was considered to be higher than the normal conditions (Balch and Kilpatrick, 1996). The modeled column-integrated ratio of calcification to net community production was 0.06, lies on a lower end of the observed range from 0.03 to 0.12 during EqPac Survey
II (Balch and Kilpatrick, 1996). A higher ratio of the calcification to the net community production could be reproduced by changing a few model parameter values which are relevant to coccolithophorids, such as the maximum specific growth rate of coccolithophorids ($\mu_{3\text{max}}$) and the half-saturation constant for NH$_4$ uptake by coccolithophorids ($K_{P3\_NH4}$), as described in the next subsection.

The modeled bSiO$_2$ production with depth showed a pattern similar to that of the net community production although the modeled bSiO$_2$ production decreased more rapidly with depth (Fig. 3 (a), (c)). The modeled vertical profile reproduced the field data (Leynaert et al., 2001), but the model overestimated the field results in the lower layer. Unlike the calcification data, the bSiO$_2$ data were collected during the EBENE cruise in October-November 1996, which took place during a “neutral scenario” between El Niño and La Niña (Leynaert et al., 2001). Therefore, the bSiO$_2$ data can be considered to be normal, and the model-data misfit was probably caused by other biological factors such as a vertical change in the diatom Si:N uptake ratio that was not considered in the present model.

The modeled bSiO$_2$:POC production ratio remarkably decreased with depth, from 0.03 at the surface to nearly zero at 120m depth, following the rapid decrease in diatom biomass with depth (solid line in Fig. 2 (a)) as observed (e.g. Barber et al., 1996). The modeled PIC:POC production ratio, by contrast, was relatively similar with depth but had its maximum of 0.07 around 50m depth (Fig. 3 (d)). The increased dominancy of coccolithophorids in the subsurface layers resulted from its strategy to seek for NH$_4$ which was rapidly consumed by picoplankton in the surface water (solid line in Fig. 2 (e)). This implies that the calcification in the subsurface layers, which cannot be detected by satellite observations, plays a considerable role in significant PIC sedimentation in the equatorial Pacific.

The modeled export flux of PON, POC, bSiO$_2$, and PIC at 120m depth was 0.58 [mmolN m$^{-2}$ day$^{-1}$], 3.84 [mmolC m$^{-2}$ day$^{-1}$], 1.46 [mmolSi m$^{-2}$ day$^{-1}$], and 0.60 [mmolC m$^{-2}$ day$^{-1}$], respectively.
(Table 4). All the export fluxes of PON, POC and bSiO$_2$ lie within the observed wide ranges of 0.38-4.65 [mmolN m$^{-2}$ day$^{-1}$], 0.6-20 [mmolC m$^{-2}$ day$^{-1}$] and 0.05-3.9 [mmolSi m$^{-2}$ day$^{-1}$], respectively. The PIC:POC export ratio (rain ratio) in the equatorial Pacific upwelling region was 0.16 in this study (Table 4). This is relatively higher than recent estimates of 0.05-0.08 for the global-mean rain ratio (e.g. Yamanaka and Tajika, 1996; Najjar and Orr, 1998; Milliman et al., 1999; Sarmiento et al., 2002; Fujii et al., 2005a), implying notable PIC export in the equatorial Pacific compared to the global ocean, as reported by Balch and Kilpatrick (1996).

The modeled bSiO$_2$:PON export ratio was 2.52 (Table 4), which lies between the maximum ratio of nearly 4 obtained by Dugdale et al. (2002) and other sediment trap data of 0.10-1.25 (Dunne et al., 1999). Recent data show that bacterial protease activity accelerates the dissolution of bSiO$_2$ in the euphotic zone (Bidle and Azam, 1999), and that such process is strongly dependent on water temperature (Bidle et al., 2002, 2003). Other previous studies suggested that the dissolution of bSiO$_2$ is correlated to the percentage of dead diatoms, and that other factors controlling bSiO$_2$ dissolution rate besides water temperature, such as differences in organic coatings that protect against bSiO$_2$ dissolution between live and dead diatoms, are probably required (Beucher et al., 2004; Fujii and Chai, 2005). These factors, which were not taken into account in the present model, probably contributed to the large spatial and temporal variation among the observed bSiO$_2$:PON export ratios and to regard sedimented biogenic silica under the equatorial upwelling area as an amplifier of changes in surface properties (Dugdale et al., 2002).

### 3.2. Comparison with no-calcification model results

We compared the standard model experimental results with and without coccolithophorids and its calcification processes (hereafter calcification and no-calcification model simulation, respectively).
The no-calcification model results were obtained by eliminating all the parameters that are associated with coccolithophorids and its calcification processes and by modifying the grazing preference by mesozooplankton properly (Table 1).

The model results showed that surface diatom biomass was less than half in the no-calcification model simulation, although the diatom specific growth rate (diatom growth rate divided by its biomass) was 23% higher due to higher Si(OH)$_4$ concentration (Table 3; Fig. 2 (a), (f)). This results from absence of grazing pathway by mesozooplankton on coccolithophorids and subsequently higher grazing pressure on diatoms by mesozooplankton (by a factor of 1.3 in terms of the specific grazing rate, grazing rate divided by prey’s biomass) in the no-calcification model simulation (Table 3). The absence of coccolithophorids in the no-calcification model simulation yielded enhancement of the other feeding pathways by mesozooplankton, namely predation on microzooplankton and grazing on PON as well, by a factor of 1.6 and 1.8, respectively (Table 3). As a result, mesozooplankton biomass was 26% higher in the no-calcification model simulation (Table 3; Fig. 2 (c)). The substantially enhanced predation on microzooplankton by mesozooplankton in the no-calcification model simulation slightly lowered grazing pressure on picoplankton by microzooplankton, which lead to 33% higher picoplankton biomass regardless of its lower specific growth rate due to lower NH$_4$ and NO$_3$ concentrations than in the calcification model simulation (Table 3; Fig. 2 (a), (d), (e)).

Compared to the change in each phytoplankton biomass between the calcification and no-calcification model simulations, the total phytoplankton biomass in the surface water was similar between the two models, because the absence of coccolithophorids and the lower diatom biomass in the no-calcification model simulation were partly compensated by the higher picoplankton biomass (Table 3; Fig. 2 (a), (b)). The export flux of PON or POC, which is generated from phytoplankton mortality
and fecal pullet, was similar as well (changing only by 12%; Table 4). On the other hand, the bSiO$_2$ export was lower in the no-calcification model simulation by 49% (Table 4). Same as the relationship between the surface NO$_3$ and Si(OH)$_4$, the change was relatively smaller in surface TCO$_2$ than in TAlk between the two models (Table 3; Fig. 2 (g), (h)). The higher TAlk and lower TCO$_2$ causes lower pCO$_2$sea in the no-calcification model simulation by 47µatm (Table 3), which was primarily affected by the increase in TAlk.
4. Discussion

4.1. Sensitivity to biogeochemical parameters (Experiment 1)

We tested model sensitivity to each biogeochemical parameter by changing the parameter value from 0.5 to 1.5 times the standard value (Table 1). We found the model results, i.e., surface plankton abundance, concentrations of nutrients, TAlk and TCO$_2$, pCO$_{2\text{sea}}$, and export fluxes of PON, bSiO$_2$ and PIC, were especially sensitive to changes in six model parameters relevant to grazing or predation by zooplankton, namely the maximum grazing and/or predation rates by zooplankton ($G_{1\text{max}}$ and $G_{2\text{max}}$), the half-saturation constants for zooplankton ingestion ($K_{1gr}$ and $K_{2gr}$), the mesozooplankton excretion rate to NH$_4$ ($r_{eg2}$), and the mesozooplankton specific mortality rate ($\gamma_2$) (Table 5). This suggests that the phytoplankton in the equatorial Pacific upwelling area is universally and severely exposed under the top-down (grazing) control by zooplankton. This is consistent with the observed results that grazing has been invoked as the control on loss rates (e.g. Walsh, 1976; Landry et al., 1997; Dugdale et al., 2002).

The maximum grazing or predation rate by mesozooplankton ($G_{2\text{max}}$) was the most significant parameter to determine surface diatoms, coccolithophorids, Si(OH)$_4$, TAlk, TCO$_2$, and export fluxes of PON and PIC (Table 5; Fig. 4). The lower $G_{2\text{max}}$ caused lower grazing pressure on diatoms and coccolithophorids and subsequently higher diatom and coccolithophorid biomass, which lead to higher export fluxes of POC, bSiO$_2$ and PIC, and lower TAlk and TCO$_2$ (Fig. 4 (a), (b), (c), (d), (f)). The simultaneous decrease in TAlk and TCO$_2$ (238 [mmol m$^{-3}$] and 149 [mmolC m$^{-3}$], respectively) with $G_{2\text{max}}$ decrease compensated each other in terms of pCO$_{2\text{sea}}$ change, which yielded pCO$_{2\text{sea}}$ decrease of 137 [$\mu$atm] (Fig. 4 (e)), significant but relatively small compared to the individual changes in TAlk and TCO$_2$.

The maximum grazing rate on picoplankton by microzooplankton ($G_{1\text{max}}$) was the most
effective parameter in determining surface picoplankton biomass and NO$_3$ (Table 5). Two phytoplankton-related parameters (the initial slope of P-I curve ($\alpha$) and the maximum specific growth rate of picoplankton ($\mu_{1\text{max}}$)) also controlled the model results, but less broadly than the zooplankton-related parameters above did (Table 5). The surface TAlk and TCO$_2$ varied by 21-45 [mmol m$^{-3}$] and 53-81 [mmolC m$^{-3}$], respectively, by changing one of the three parameter values (Table 5; Fig. 5 (a), (b)). These changes were relatively small compared those brought by $G_{2\text{max}}$ change of 238 [mmol m$^{-3}$] and 149 [mmolC m$^{-3}$], respectively. However, surface TAlk and TCO$_2$ changed in a different way with parameter values, i.e., surface TAlk increased and TCO$_2$ decreased with parameter values of $\alpha$ and $\mu_{1\text{max}}$, and vice versa for $G_{1\text{max}}$. This is the reason why the pCO$_{2\text{sea}}$ change by changing these parameter values was relatively large (184, 147 and 160 [$\mu$atm] for $\alpha$, $\mu_{1\text{max}}$ and $G_{1\text{max}}$, respectively; Table 5; Fig. 5 (c)).

The surface coccolithophorid biomass and the export PIC flux at 120m depth were sensitive to many parameters (Table 5). For example, a few parameters like the maximum specific growth rates of coccolithophorids ($\mu_{3\text{max}}$) and the half-saturation constant for NH$_4$ uptake by coccolithophorids ($K_{P3\text{,NH4}}$) specialized to control the two model state variables. This means that the modeled coccolithophorids and PIC could change in a sensitive and complicated way with a narrow range of the parameter values. For more realistic simulation of carbon cycling in this region, we need further field data, especially for vertical profiles of POC, PIC, coccolithophorid biomass and its composition ratio for the phytoplankton community.

The model sensitivity study to the five parameters of $\alpha$, $\mu_{1\text{max}}$, $\mu_{3\text{max}}$, $G_{1\text{max}}$ and $G_{2\text{max}}$ revealed that the bSiO$_2$:PON export ratio and the PIC:POC export ratio (rain ratio) at 120m depth could vary by 0.40-2.83 and 0.00-0.56, respectively (Fig. 6). Considering that the observation-based estimates of the global rain ratio vary from 0.05 to 0.25 (e.g. Fujii et al., 2005a) and excluding the model results in
which the rain ratio was out of the range (Fig. 6 (b)), we obtained a range of 1.51-2.75 for the 
bSiO₂:PON export ratio (Fig. 6 (a)).

4.2. Sensitivity to source Si(OH)₄ concentration (Experiment 2)

Experiment 2 is similar to the experiment conducted by Dugdale et al. (2002), i.e., the source 
(120m depth) Si(OH)₄ concentration was varied from 3.0-15.0 [mmolSi m⁻³], corresponding to the full 
range of JGOFS equatorial values of 3-13 [mmolSi m⁻³] (Dugdale et al., 2002). The NO₃ concentration 
at 120m depth was held constant at 12.0 [mmolN m⁻³].

4.2.1. Calcification model simulation

With source (120m depth) Si(OH)₄ concentration increases, surface Si(OH)₄ concentration 
increased linearly from 1.8 to 6.6 [mmolSi m⁻³] (solid line in Fig. 7 (f)). The surface Si(OH)₄ increase 
enhanced surface diatom growth (Fig. 8 (b)) and increased surface diatom biomass by a factor of 4.3 
(solid green line in Fig. 7 (a)). The surface diatom increase resulted in a remarkable switch in feeding 
by mesozooplankton from microzooplankton to diatoms as the source Si(OH)₄ increased (Fig. 8 (b), 
(d)). The declined predation on microzooplankton by mesozooplankton enhanced grazing pressure on 
picoplankton by microzooplankton (Fig. 8 (a)), causing a decrease in surface picoplankton biomass 
with source Si(OH)₄ increase (solid line in Fig. 7 (a)). The decrease in surface picoplankton biomass 
was more rapid with lower source Si(OH)₄ concentrations.

The surface diatom increase with source Si(OH)₄ concentration also yielded a slight switch in 
grazing by mesozooplankton from coccolithophorids to diatoms (Fig. 8 (b), (c)), which increased 
surface coccolithophorid biomass (Fig. 7 (b)). The surface coccolithophorid biomass had its maximum 
at source Si(OH)₄=8-9 [mmolSi m⁻³] and then decreased with higher source Si(OH)₄ concentrations due
to slight NO\textsubscript{3} regulation on the coccolithophorid growth as the result of higher diatom growth (solid lines in Fig. 7 (b), (e), and Fig. 8 (b), (c)). The total phytoplankton biomass in the surface water had its minimum at source Si(OH)\textsubscript{4}=5 [mmolSi m\textsuperscript{-3}] (solid line in Fig. 7 (c)). The phytoplankton composition ratio in the surface water was 80, 11, and 9% at source Si(OH)\textsubscript{4}=3 [mmolSi m\textsuperscript{-3}]; 52, 33, and 15% at source Si(OH)\textsubscript{4}=7.5 [mmolSi m\textsuperscript{-3}]; and 46, 42, and 12% at source Si(OH)\textsubscript{4}=15 [mmolSi m\textsuperscript{-3}] (solid lines in Fig. 7 (d)), indicating substantial increase in diatoms and decrease in picoplankton and relatively similar coccolithophorid biomass with source Si(OH)\textsubscript{4} increase.

Surface T\textsubscript{Alk} is taken up by the coccolithophorids’ calcification process. Hence, T\textsubscript{Alk} had its minimum with source Si(OH)\textsubscript{4}=7-8 [mmolSi m\textsuperscript{-3}] at which surface coccolithophorids biomass had its maximum (solid lines in Fig. 7 (b), (g)). The surface TCO\textsubscript{2}, which is taken up by both phytoplankton growth and calcification, had its maximum with source Si(OH)\textsubscript{4}=7 [mmolSi m\textsuperscript{-3}], mainly as the result of the lowest total phytoplankton biomass in the surface water (solid line in Fig. 7 (c) and (h)). The pCO\textsubscript{2sea} decreases with T\textsubscript{Alk} increase and increases with TCO\textsubscript{2} increase. The two opposite changes in the pCO\textsubscript{2sea} by T\textsubscript{Alk} and TCO\textsubscript{2} varies formed a maximum pCO\textsubscript{2sea} with source Si(OH)\textsubscript{4}=7 [mmolSi m\textsuperscript{-3}] (solid line in Fig. 7 (i)). The pCO\textsubscript{2sea} changed from 357 to 401 [µatm], in a similar range as observed (e.g., Feely \textit{et al.}, 1997).

With source Si(OH)\textsubscript{4} increase, or with surface diatom biomass increase, the modeled bSiO\textsubscript{2} export at 120m depth dramatically increased by a factor of 6.6 from 0.38 to 2.52 [mmolSi m\textsuperscript{-2} day\textsuperscript{-1}] (solid line in Fig. 9 (a)). The modeled PON or POC export at 120m depth also increased with source Si(OH)\textsubscript{4} concentrations, but only slightly by a factor of 1.2. The modeled PIC export at 120m depth changed by a factor of 1.6 from 0.38 to 0.60 [mmolC m\textsuperscript{-2} day\textsuperscript{-1}] and had its maximum around the standard source Si(OH)\textsubscript{4} concentration of 7.5 [mmolSi m\textsuperscript{-3}] (Fig. 9 (b)). The difference in the curve among PON or POC, bSiO\textsubscript{2}, and PIC appeared because PON or POC was produced by fecal pellet and
phytoplankton mortality, while bSiO$_2$ and PIC were only produced by diatoms and coccolithophorids, respectively. The modeled bSiO$_2$:PON export ratio at 120m depth changed by a factor of 5.6, from 0.7 to 3.9 with source Si(OH)$_4$ concentrations (solid line in Fig. 9 (c)). The larger extent of change in bSiO$_2$ export with source Si(OH)$_4$ concentrations (solid line in Fig. 9 (a)) than of surface diatom biomass (by a factor of 4.3; solid line in Figs. 7 (a)) suggests sedimented detritus under the equatorial Pacific upwelling region act as an amplifier of changes in surface properties (Dugdale et al., 2002). The modeled PIC:POC export ratio (rain ratio) at 120m depth changed by a factor of 1.5 from 0.11 to 0.16, and its maximum appeared at source Si(OH)$_4$=7, close to the standard concentration of 7.5 [mmolSi m$^{-3}$] (Fig. 9 (d)).

The model results showed that pCO$_{2\text{sea}}$ and export PIC:POC and bSiO$_2$:PON ratios, all of which are excellent indices for assessing abilities of CO$_2$ release to the atmosphere and detritus sedimentations in the equatorial Pacific, were sensitive to source Si(OH)$_4$ concentrations. In particular, the carbonate system in the surface water, PIC export, and the rain ratio at 120m depth had their peaks near the standard source Si(OH)$_4$ concentration of 7.5 [mmolSi m$^{-3}$], suggesting sensitive change in the CO$_2$ release to the atmosphere within a narrow range of the source Si(OH)$_4$ concentrations presumably caused by the physical forcing in the equatorial Pacific upwelling region.

4.2.2. Comparison with no-calcification model results

By eliminating coccolithophorids in the no-calcification model simulation, grazing on diatoms by mesozooplankton was elevated in order to compensate the missing grazing pathway from coccolithophorids to mesozooplankton (Fig. 10 (b)). Therefore, the diatom biomass was lower and the Si(OH)$_4$ concentration was higher in the no-calcification model simulation (Fig. 7 (a), (f)). For the same reason, the predation on microzooplankton by mesozooplankton was also elevated in the
no-calcification model simulation (Fig. 10 (c)). The greater predation on microzooplankton by mesozooplankton alleviated grazing pressure on picoplankton by microzooplankton (Fig. 10 (a)), which yielded higher surface picoplankton biomass with lower source Si(OH)$_4$ concentrations in the no-calcification model simulation (Fig. 7 (a)). As the source Si(OH)$_4$ concentration increased, the surface diatom biomass increased, which lead to dominant mesozooplankton’s grazing on diatoms over predation on microzooplankton, in both models (Figs. 7 (a) and 10 (b), (c)). But the amplitude of decrease in predation on microzooplankton with source Si(OH)$_4$ concentrations was greater in the no-calcification model simulation (Fig. 10 (c)), which yielded greater amplitude of increase in grazing on picoplankton by microzooplankton and decrease in the surface picoplankton biomass (Figs. 7 (a) and 10 (a)) than in the calcification model simulation. The surface diatom biomass was constantly lower in the no-calcification model simulation because of substantially higher grazing pressure by mesozooplankton than seen in the calcification model simulation (Figs. 7 (a) and 10 (b)).

The total phytoplankton biomass in the surface water decreased with source Si(OH)$_4$ increase in the no-calcification model simulation (dotted line in Fig. 7 (c)), which was followed by increases in surface NO$_3$ and TCO$_2$ concentrations (dotted line in Fig. 7 (e), (h)). The surface TAlk was higher and was kept constant in the no-calcification model simulation (dotted line in Fig. 7 (g)). Therefore, the pCO$_{2\text{sea}}$ change in the no-calcification model simulation, increasing linearly with source Si(OH)$_4$, from 326 to 380 [µatm], was primarily controlled by the surface TCO$_2$ change (dotted line in Fig. 7 (h), (i)). The lower surface total phytoplankton and diatom biomass in the no-calcification model simulation resulted in lower export fluxes of PON or POC and bSiO$_2$, and a lower bSiO$_2$:PON export ratio than in the calcification model simulation (Figs. 7 (a), (c) and 9 (a), (c)).
4.3. Comparison with field data

The passage of the TIWs during the JGOFS TT012 cruise gave a natural experiment of how the surface nutrients and ecosystem might respond to changes in source nutrients for comparison with the model sensitivity experiments carried out in this study (Dugdale et al., 2002). The source Si(OH)$_4$ increased dramatically from a minimum of 6 [mmolSi m$^{-3}$] in early October to a maximum of 13 [mmolSi m$^{-3}$] by October 16, 1992, while the source NO$_3$ concentration varied from a low of 10 [mmolN m$^{-3}$] to a maximum of 14 [mmolN m$^{-3}$] (Fig. 11 (c), (d)). Large increases in chlorophyll concentration and net community production, particularly for diatoms, were observed during this event (Fig. 11 (a) and (b); Iriarte and Fryxell, 1995; Barber et al., 1996).

We compared the model results in Experiment 2 with the JGOFS TT012 cruise data during the passage of the TIWs (Fig. 12). Because the source Si(OH)$_4$ concentration was enhanced by the TIWs (Fig. 12 (d)), the x-axes in Fig. 12 clearly correspond to the time series. The profiles of state variables in the surface water vs. source Si(OH)$_4$ concentrations showed that the model results well captured the observed features during the passage of the TIWs, such as a linear surface Si(OH)$_4$ increase with source Si(OH)$_4$ increase (Fig. 12 (b)), and maxima of surface NO$_3$, TCO$_2$, and pCO$_2$sea at intermediate source Si(OH)$_4$ concentrations (Fig. 12 (a), (c), (d)). The maxima of surface NO$_3$, TCO$_2$, and pCO$_2$sea were regarded as results of increases and decreases in these state variables during and after the passage of the TIWs, respectively.

The model results with each source Si(OH)$_4$ concentration in Experiment 2 were obtained by establishing steady states, running the model for 1000 days. Therefore, the model results in Experiment 2 may not reproduce the observed rapid increases in phytoplankton growth and chlorophyll concentration in response to the TIWs (Fig. 11 (a), (b)). We hypothesize that this is because the dramatic changes in phytoplankton growth and biomass would be caused by non steady-state biological
responses to the passage of the TIWs, which may not be reproduced by Experiment 2.
5. Concluding remarks

To understand factors and mechanisms controlling carbon and silicon cycling in the equatorial Pacific upwelling region, an ecosystem model with coccolithophorids and its calcification processes has been constructed. We examined biogeochemical responses to the tropical instability waves with increases of source (120m depth) Si(OH)$_4$ concentration. The model results revealed the top-down control (grazing by zooplankton) on phytoplankton biomass and bottom-up control (nutrient limitations, especially Si(OH)$_4$ limitation on diatom growth) on phytoplankton growth.

The model sensitivity study to the increase of source (120m depth) Si(OH)$_4$ concentration showed linear increase in surface diatoms and biogenic silica export, decrease in surface picoplankton, and a maximum surface coccolithophorids at intermediate source Si(OH)$_4$ concentrations. Surface total alkalinity and total CO$_2$ had the minimum and maximum, respectively, at intermediate source Si(OH)$_4$ concentrations, which produced highest CO$_2$ release to the atmosphere with the source Si(OH)$_4$ concentration of 7.5 [mmolSi m$^{-3}$]. The export ratio of PIC to particulate organic carbon (rain ratio) at 120m depth had its maximum of 0.16 with the source Si(OH)$_4$ concentration of 7.5 [mmolSi m$^{-3}$], suggesting a significant PIC sedimentation in the equatorial Pacific upwelling region. Enhanced change in biogenic silica export flux than in surface diatom biomass suggests that sedimented detritus under the region acts as an amplifier of changes in surface properties.

Comparison between calcification and no-calcification model results revealed that the presence of coccolithophorids persistently elevated diatom biomass and export fluxes of detritus while it decreased total alkalinity and enhanced CO$_2$ release to the atmosphere. Large changes in the carbonate system in responses to source Si(OH)$_4$ concentrations suggest that physical forcing, such as the tropical instability waves, Kelvin waves, and La Niña, significantly affect the carbon and silicon fluxes in the region.
To better understand the carbon and silicon cycling in the equatorial Pacific upwelling region, we need more information on the processes regulating calcifiers and PIC, not only in the surface but also in the subsurface layer where the calcification is considered significant.

Acknowledgements. The authors thank two anonymous reviewers for improving the manuscript, and Drs. Richard Dugdale, Richard Barber, and Tsung-Hung Peng for the discussion on comparison with observations in the equatorial Pacific. Funding for this work was provided to F. Chai by a NSF grant (OCE-0137272) and a NASA grant (NAG5-9348) and to M. Fujii by MEXT through Special Coordination Funds for Promoting Science and Technology.
Appendix

A.1 Governing equations

The model equations describing each compartment all take the form:

\[
\frac{\partial C_i}{\partial t} \text{[mmol m}^{-3} \text{ day}^{-1}] = \text{PHYSICS}(C_i) + \text{BIOLOGY}(C_i),
\]

(A1)

\[i = 1, \ldots, 13.\]

The term PHYSICS(C_i) represents the contribution to the concentration change due to physical processes, including vertical advection and eddy diffusion:

\[
\text{PHYSICS}(C_i) \text{[mmol m}^{-3} \text{ day}^{-1} ] = -W \frac{\partial C_i}{\partial z} + \frac{\partial}{\partial z} \left( A_{Tv} \frac{\partial C_i}{\partial z} \right),
\]

(A2)

where W is vertical velocity, and A_{Tv} is vertical coefficient. The term BIOLOGY (C_i) represents biological sources and sinks of that compartment. In the euphotic zone (the upper 120m), the biological terms, BIOLOGY(C_i) are:

\[
\text{BIOLOGY} (P1) \text{[mmol m}^{-3} \text{ day}^{-1} ] = NP1 + RPI - \frac{G_4}{\text{grazing by } Z1},
\]

(A3)

\[
\text{BIOLOGY} (P2) \text{[mmol m}^{-3} \text{ day}^{-1} ] = NP2 + RPS - \frac{G_5}{\text{grazing by } Z2} - \frac{\gamma_{SP2}}{\text{mortality}} - \frac{\partial}{\partial z} (W_z P2),
\]

(A4)

\[
\text{BIOLOGY} (P3) \text{[mmol m}^{-3} \text{ day}^{-1} ] = NP3 + RPS - \frac{G_5}{\text{grazing by } Z2} - \frac{\gamma_{SP3}}{\text{mortality}} - \frac{\partial}{\partial z} (W_z P3),
\]

(A5)

\[
\text{BIOLOGY} (Z1) \text{[mmol m}^{-3} \text{ day}^{-1} ] = \frac{G_1}{\text{grazing on } P1} - \frac{G_3}{\text{predation by } Z2} - \frac{\text{reg}, Z1}{\text{excretion}}.
\]

(A6)
Each biological process is described in next subsection. See Table 1 for abbreviations.

PIC production reduces TAlk, and PIC dissolution increases TAlk (e.g. Broecker and Peng, 1982). Brewer and Goldman (1976) demonstrated that the phytoplankton growth could affect TAlk through nutrient uptake of nutrients as well. Uptake of NO$_3^-$ caused an increase in TAlk, whereas uptake of NH$_4^+$ produced a decrease. This is because one mole of NO$_3^-$ assimilation by phytoplankton generates one equivalent of strong base (OH$^-$), and for NH$_4^+$, one equivalent of strong acid (H$^+$). Therefore, the biological term for TAlk is written as follows:
\[
BIOLOGY(Talk) [\text{mmol m}^{-3} \text{ day}^{-1}] = 2.0 \times \left\{ \frac{\gamma_s \text{ PIC}}{\text{ PIC dissolution}} - R_{CN} \epsilon(NP3 + RP3) \right\} \\
- BIOLOGY(NO_3) + BIOLOGY(NH_4).
\]

The photosynthesis and calcification are associated with a decrease in TCO$_2$. The distribution of TCO$_2$ in the water column can be given as

\[
\frac{\partial (TCO_2)}{\partial t} [\text{mmol C m}^{-3} \text{ day}^{-1}] = PHYSICS(TCO_2) + BIOLOGY(TCO_2) + EVASION(TCO_2),
\]

\[BIOLOGY(TCO_2) [\text{mmol C m}^{-3} \text{ day}^{-1}] = \frac{\gamma_s \text{ PIC}}{\text{ PIC dissolution}} - R_{CN} \epsilon(NP3 + RP3) \]

\[+ R_{CN} BIOLOGY(NO_3) + R_{CN} BIOLOGY(NH_4),
\]

\[EVASION(TCO_2) [\text{mmol C m}^{-3} \text{ day}^{-1}] = E \Delta pCO_2,
\]

where \(E\) is the mean CO$_2$ exchange coefficient of 0.0391 [mmolC m$^{-3}$ day$^{-1}$ ppm$^{-1}$] at partial pressure of CO$_2$ (pCO$_2$) of 280ppm, and \(\Delta pCO_2\) is the difference in pCO$_2$ between surface water and atmosphere. The atmospheric pCO$_2$ is assumed to be constant at 357ppm (Chai et al., 2002). The EVASION (TCO$_2$) term is only applied to the surface level, and is equal to zero in the water column below surface level.
A.2 Formulation of biological processes

(Irradiance)

\[ I \left[ \text{W m}^{-2} \right] = I_0 \exp \left\{ -k_1z - k_2 \int_z^0 (P_1 + P_2 + P_3) \, dz \right\} \]  
(A18)

\[ I_0 \left[ \text{W m}^{-2} \right] = \begin{cases} I_0^{\text{Noon}} \sin \left( \frac{t-6}{12} \pi \right) & \text{(from 6 am to 6 pm),} \\ 0 & \text{(from 6 pm to 6 am),} \end{cases} \]  
(A19)

where \( I_0^{\text{Noon}} \) is the averaged surface noontime irradiance (410 [W m\(^{-2}\); Chai et al., 2002).

(NO\(_3\) uptake by picoplankton)

\[ \text{NPI} \left[ \text{mmolN m}^{-3} \, \text{day}^{-1} \right] = \mu_l \max \frac{\text{NO}_3}{K_{\text{NO}_3} + \text{NO}_3} \, e^{-\text{\text{NH}_3} \text{inhibition}} \left(1 - e^{-\frac{\alpha}{\mu_l \max}}\right) \, \text{Pl.} \]  
(A20)

(NH\(_4\) uptake by picoplankton)

\[ \text{RPI} \left[ \text{mmolN m}^{-3} \, \text{day}^{-1} \right] = \mu_l \max \frac{\text{NH}_4}{K_{\text{NH}_4} + \text{NH}_4} \left(1 - e^{-\frac{\alpha}{\mu_l \max}}\right) \, \text{Pl.} \]  
(A21)

(NO\(_3\) and NH\(_4\) uptake by diatoms)

If \[
\frac{1}{R_{\text{SN}}} \frac{\text{Si(OH)}_4}{K_{\text{Si(OH)}_4} + \text{Si(OH)}_4} > \frac{\text{NH}_4}{K_{\text{NH}_4} + \text{NH}_4},
\]
\[ NP2 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = \mu_{\text{max}}^2 \left\{ \frac{1}{R_{SN} \left( K_{Si(OH)} + Si(OH) \right)} + K_{P_{2-NH}} + NH_4 \right\} \times \left(1 - e^{-\frac{\mu_{\text{max}}}{\mu_{\text{max}}^2}} \right) P2, \] (A22)

\[ RP2 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = \mu_{\text{max}}^2 \frac{NH_4}{K_{P_{2-NH}} + NH_4} \left(1 - e^{-\frac{\mu_{\text{max}}}{\mu_{\text{max}}^2}} \right) P2. \] (A23)

If \( \frac{1}{R_{SN} \left( K_{Si(OH)} + Si(OH) \right)} \leq \frac{NH_4}{K_{P_{2-NH}} + NH_4} \),

\[ NP2 = 0, \] (A24)

\[ RP2 = \mu_{\text{max}}^2 \frac{1}{R_{SN} \left( K_{Si(OH)} + Si(OH) \right)} \left(1 - e^{-\frac{\mu_{\text{max}}}{\mu_{\text{max}}^2}} \right) P2. \] (A25)

\( (\text{NO}_3 \ \text{uptake by coccolithophorids}) \)

\[ NP3 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = \mu_{\text{max}}^3 \frac{NO_3}{K_{P_{3-NO}} + NO_3} e^{-\frac{NO_3}{NH_4}} \left(1 - e^{-\frac{\mu_{\text{max}}}{\mu_{\text{max}}^3}} \right) P3. \] (A26)

\( (\text{NH}_4 \ \text{uptake by coccolithophorids}) \)

\[ RP3 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = \mu_{\text{max}}^3 \frac{NH_4}{K_{P_{3-NH}} + NH_4} \left(1 - e^{-\frac{\mu_{\text{max}}}{\mu_{\text{max}}^3}} \right) P3. \] (A27)

\( (\text{Grazing on picoplankton by microzooplankton}) \)
\[ G_1 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = G_1^{\text{max}} \frac{P_1}{K_{gr} + P_1} \frac{P_1}{P_{1}^{\text{ave}}} \ Z_1, \]  
\text{(A28)}

\[ P_{1 \text{ave}} \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = \frac{1}{Z'} \int_0^Z P_1 \text{d}z, \]  
\text{(A29)}

where \( Z' \) is the depth of the euphotic zone (120m).

(Grazing or predation on diatoms, coccolithophorids, microzooplankton, and PON by mesozooplankton)

\[ G_2 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = G_2^{\text{max}} \frac{\zeta_1 P_2}{K_{gr} + \zeta_1 P_2 + \zeta_2 Z_1 + \zeta_3 \text{PON} + \zeta_4 P_3} Z_2, \]  
\text{(A30)}

\[ G_3 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = G_2^{\text{max}} \frac{\zeta_2 Z_1}{K_{gr} + \zeta_1 P_2 + \zeta_2 Z_1 + \zeta_3 \text{PON} + \zeta_4 P_3} Z_2, \]  
\text{(A31)}

\[ G_4 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = G_2^{\text{max}} \frac{\zeta_3 \text{PON}}{K_{gr} + \zeta_1 P_2 + \zeta_2 Z_1 + \zeta_3 \text{PON} + \zeta_4 P_3} Z_2, \]  
\text{(A32)}

\[ G_5 \ [\text{mmolN m}^{-3} \ \text{day}^{-1}] = G_2^{\text{max}} \frac{\zeta_4 P_3}{K_{gr} + \zeta_1 P_2 + \zeta_2 Z_1 + \zeta_3 \text{PON} + \zeta_4 P_3} Z_2, \]  
\text{(A33)}

where

\[ \zeta_1 = \frac{\rho_1 P_2}{\rho_1 P_2 + \rho_2 Z_1 + \rho_3 \text{PON} + \rho_4 P_3}, \]  
\text{(A34)}

\[ \zeta_2 = \frac{\rho_2 Z_1}{\rho_1 P_2 + \rho_2 Z_1 + \rho_3 \text{PON} + \rho_4 P_3}, \]  
\text{(A35)}

\[ \zeta_3 = \frac{\rho_3 \text{PON}}{\rho_1 P_2 + \rho_2 Z_1 + \rho_3 \text{PON} + \rho_4 P_3}, \]  
\text{(A36)}
\[ \zeta_4 = \frac{\rho_4 P^3}{\rho_1 P^2 + \rho_2 Z \Gamma + \rho_3 PON + \rho_4 P^3}. \] (A37)
References


Fujii, M., Chai, F., 2007. Influences of initial plankton conditions and mixed layer depth on the outcome of iron-fertilization experiments. submitted to J. Geophys. Res.


Fujii, M., Yoshie, N., Yamanaka, Y., Chai, F., 2005b. Simulated biogeochemical responses to iron enrichments in three high nutrient, low chlorophyll (HNLC) regions, Prog. Oceanogr. 64, 307-324.


Yoshie, N., Fujii, M., Yamanaka, Y, 2005. Ecosystem changes after the SEEDS iron fertilization in the western North Pacific simulated by a one-dimensional ecosystem model. Prog. Oceanogr. 64, 283-306.
Table 1. The model parameters. Columns (I) and (II) denotes the standard values of parameters in calcification model simulation and no-calcification model simulation, respectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>(I)</th>
<th>(II)</th>
<th>Unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light attenuation due to water</td>
<td>$k_1$</td>
<td>0.046</td>
<td>0.046</td>
<td>m$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Light attenuation by phytoplankton</td>
<td>$k_2$</td>
<td>0.03</td>
<td>0.03</td>
<td>m$^{-1}$ (mmolNm$^{-3}$)$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Initial slope of the P-I curve</td>
<td>$\alpha$</td>
<td>0.025</td>
<td>0.025</td>
<td>day$^{-1}$ (W m$^{-2}$)$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Maximum specific growth rate of picoplankton</td>
<td>$\mu_{1\text{max}}$</td>
<td>2.0</td>
<td>2.0</td>
<td>day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>NH$_4$ inhibition parameter</td>
<td>$\Psi$</td>
<td>5.59</td>
<td>5.59</td>
<td>(mmolN m$^{-3}$)$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Half-saturation for NO$_3$ uptake by picoplankton</td>
<td>$K_{\text{NO}_3}$</td>
<td>1.0</td>
<td>1.0</td>
<td>mmolN m$^{-3}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Half-saturation for NH$_4$ uptake by picoplankton</td>
<td>$K_{\text{NH}_4}$</td>
<td>0.1</td>
<td>0.1</td>
<td>mmolN m$^{-3}$</td>
<td>This study</td>
</tr>
<tr>
<td>Maximum specific growth rate of diatoms</td>
<td>$\mu_{2\text{max}}$</td>
<td>3.0</td>
<td>3.0</td>
<td>day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Half-saturation for Si(OH)$_4$ uptake</td>
<td>$K_{\text{Si(OH)}_4}$</td>
<td>3.0</td>
<td>3.0</td>
<td>mmolSi m$^{-3}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Half-saturation for NH$_4$ uptake by diatoms</td>
<td>$K_{\text{P}_2\text{NH}_4}$</td>
<td>1.0</td>
<td>1.0</td>
<td>mmolN m$^{-3}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Diatom sinking speed</td>
<td>$W_1$</td>
<td>1.0</td>
<td>1.0</td>
<td>m day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Maximum specific growth rate of coccolithophorids</td>
<td>$\mu_{3\text{max}}$</td>
<td>1.0</td>
<td>N/A</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>Half-saturation for NO$_3$ uptake by coccolithophorids</td>
<td>$K_{\text{P}_3\text{NO}_3}$</td>
<td>1.0</td>
<td>N/A</td>
<td>mmolN m$^{-3}$</td>
<td>This study</td>
</tr>
<tr>
<td>Half-saturation for NH$_4$ uptake by coccolithophorids</td>
<td>$K_{\text{P}_3\text{NH}_4}$</td>
<td>1.0</td>
<td>N/A</td>
<td>mmolN m$^{-3}$</td>
<td>This study</td>
</tr>
<tr>
<td>Coccolithophorid sinking speed</td>
<td>$W_3$</td>
<td>1.0</td>
<td>N/A</td>
<td>m day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>Microzooplankton maximum specific grazing rate</td>
<td>$G_{1\text{max}}$</td>
<td>1.25</td>
<td>1.25</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>Half-saturation for microzooplankton ingestion</td>
<td>$K_{\text{gr}}$</td>
<td>0.5</td>
<td>0.5</td>
<td>mmolN m$^{-3}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Microzooplankton excretion rate to NH$_4$</td>
<td>$\text{reg}_1$</td>
<td>0.2</td>
<td>0.2</td>
<td>day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Mesozooplankton maximum specific grazing rate</td>
<td>$G_{2\text{max}}$</td>
<td>0.48</td>
<td>0.48</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>Mesozooplankton assimilation efficiency</td>
<td>$\gamma_1$</td>
<td>0.75</td>
<td>0.75</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>Half-saturation for mesozooplankton ingestion for diatoms, coccolithophorids, microzooplankton and PON</td>
<td>$K_{2\text{gr}}$</td>
<td>0.25</td>
<td>0.25</td>
<td>mmolN m$^{-3}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Diatom specific mortality rate</td>
<td>$\gamma_3$</td>
<td>0.05</td>
<td>0.05</td>
<td>day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Coccolithophorid specific mortality rate</td>
<td>$\gamma_6$</td>
<td>0.05</td>
<td>N/A</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>Mesozooplankton specific mortality rate</td>
<td>$\gamma_2$</td>
<td>0.05</td>
<td>0.05</td>
<td>day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Mesozooplankton excretion rate to NH$_4$</td>
<td>$\text{reg}_2$</td>
<td>0.1</td>
<td>0.1</td>
<td>day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>Grazing preference for diatoms</td>
<td>$\rho_1$</td>
<td>0.35</td>
<td>0.7</td>
<td>dimensionless</td>
<td>This study</td>
</tr>
<tr>
<td>Grazing preference for microzooplankton</td>
<td>$\rho_2$</td>
<td>0.2</td>
<td>0.2</td>
<td>dimensionless</td>
<td>(1)</td>
</tr>
<tr>
<td>Grazing preference for PON</td>
<td>$\rho_3$</td>
<td>0.1</td>
<td>0.1</td>
<td>dimensionless</td>
<td>(1)</td>
</tr>
<tr>
<td>Grazing preference for coccolithophorids</td>
<td>$\rho_4$</td>
<td>0.35</td>
<td>N/A</td>
<td>dimensionless</td>
<td>This study</td>
</tr>
<tr>
<td>PON remineralization rate</td>
<td>$\gamma_7$</td>
<td>0.01</td>
<td>0.01</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>bSiO$_2$ dissolution rate</td>
<td>$\gamma_4$</td>
<td>0.01</td>
<td>0.01</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>PIC dissolution rate</td>
<td>$\gamma_8$</td>
<td>0.005</td>
<td>N/A</td>
<td>day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>PON sinking speed</td>
<td>$W_5$</td>
<td>10.0</td>
<td>10.0</td>
<td>m day$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>bSiO$_2$ sinking speed</td>
<td>$W_4$</td>
<td>20.0</td>
<td>20.0</td>
<td>m day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>PIC sinking speed</td>
<td>$W_5$</td>
<td>20.0</td>
<td>N/A</td>
<td>m day$^{-1}$</td>
<td>This study</td>
</tr>
<tr>
<td>Diatom Si:N uptake ratio</td>
<td>$R_{\text{SiN}}$</td>
<td>1.5</td>
<td>1.5</td>
<td>molSi (molN)$^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>Nitrification rate</td>
<td>$\gamma_5$</td>
<td>0.025</td>
<td>0.025</td>
<td>day$^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>Ratio of PIC to organic carbon in coccolithophorids</td>
<td>$\varepsilon$</td>
<td>1.0</td>
<td>N/A</td>
<td>molC (molC)$^{-1}$</td>
<td>(3)</td>
</tr>
<tr>
<td>Ratio of carbon to nitrogen in phytoplankton</td>
<td>$R_{\text{CN}}$</td>
<td>6.625</td>
<td>6.625</td>
<td>molC (molN)$^{-1}$</td>
<td>(1)</td>
</tr>
</tbody>
</table>

*Sources noted here are: (1) Chai et al. (2002); (2) Jiang et al. (2003); (3) Fujii et al. (2002).*
Table 2. Vertically-averaged plankton biomass in the euphotic zone (up to 120m) in (1) calcification model and (2) no-calcification model simulations. Composition ratio of each phytoplankton species to total phytoplankton is shown in percentage term in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Picoplankton (P1) [mmolN m$^{-3}$]</th>
<th>Diatoms (P2) [mmolN m$^{-3}$]</th>
<th>Coccolithophorids (P3) [mmolN m$^{-3}$]</th>
<th>Microzooplankton (Z1) [mmolN m$^{-3}$]</th>
<th>Mesozooplankton (Z2) [mmolN m$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.15 (63%)</td>
<td>0.06 (24%)</td>
<td>0.03 (13%)</td>
<td>0.13</td>
<td>0.28</td>
</tr>
<tr>
<td>(2)</td>
<td>0.17 (77%)</td>
<td>0.05 (23%)</td>
<td>N/A</td>
<td>0.14</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Table 3. Model results in the surface water in (I) calcification model simulation and (II) no-calcification model simulations.

<table>
<thead>
<tr>
<th>State variable</th>
<th>(I)</th>
<th>(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picoplankton [mmolN m(^{-3})]</td>
<td>0.23</td>
<td>0.36</td>
</tr>
<tr>
<td>Diatoms [mmolN m(^{-3})]</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>Coccolithophorids [mmolN m(^{-3})]</td>
<td>0.06</td>
<td>N/A</td>
</tr>
<tr>
<td>Total phytoplankton [mmolN m(^{-3})]</td>
<td>0.43</td>
<td>0.42</td>
</tr>
<tr>
<td>Microzooplankton [mmolN m(^{-3})]</td>
<td>0.35</td>
<td>0.38</td>
</tr>
<tr>
<td>Mesozooplankton [mmolN m(^{-3})]</td>
<td>0.65</td>
<td>0.89</td>
</tr>
<tr>
<td>Total zooplankton [mmolN m(^{-3})]</td>
<td>0.99</td>
<td>1.27</td>
</tr>
<tr>
<td>NO(_3) [mmolN m(^{-3})]</td>
<td>6.08</td>
<td>3.56</td>
</tr>
<tr>
<td>NH(_4) [mmolN m(^{-3})]</td>
<td>0.14</td>
<td>0.10</td>
</tr>
<tr>
<td>Si(OH)(_4) [mmolSi m(^{-3})]</td>
<td>3.08</td>
<td>5.30</td>
</tr>
<tr>
<td>TA(_{Alk}) [mmol m(^{-3})]</td>
<td>2360.9</td>
<td>2383.7</td>
</tr>
<tr>
<td>TCO(_2) [mmolC m(^{-3})]</td>
<td>2045.9</td>
<td>2034.5</td>
</tr>
<tr>
<td>pCO(_{2,sea}) [µatm]</td>
<td>401.0</td>
<td>353.5</td>
</tr>
<tr>
<td>Picoplankton specific growth rate [day(^{-1})]</td>
<td>1.01</td>
<td>0.97</td>
</tr>
<tr>
<td>Diatom specific growth rate [day(^{-1})]</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>Coccolithophorid specific growth rate [day(^{-1})]</td>
<td>0.24</td>
<td>N/A</td>
</tr>
<tr>
<td>Specific grazing rate on picoplankton by microzooplankton [day(^{-1})]</td>
<td>0.95</td>
<td>0.92</td>
</tr>
<tr>
<td>Specific grazing rate on diatoms by mesozooplankton [day(^{-1})]</td>
<td>0.23</td>
<td>0.30</td>
</tr>
<tr>
<td>Specific grazing rate on coccolithophorids by mesozooplankton [day(^{-1})]</td>
<td>0.10</td>
<td>N/A</td>
</tr>
<tr>
<td>Specific predation rate on microzooplankton by mesozooplankton [day(^{-1})]</td>
<td>0.32</td>
<td>0.51</td>
</tr>
<tr>
<td>Specific grazing rate on PON by mesozooplankton [day(^{-1})]</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Table 4. Comparison of export fluxes and ratios at the bottom of euphotic zone (120m depth).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PON [mmolN m(^{-2}) day(^{-1})]</th>
<th>POC [mmolC m(^{-2}) day(^{-1})]</th>
<th>hSiO(_2) [mmolSi m(^{-2}) day(^{-1})]</th>
<th>PIC [mmolC m(^{-2}) day(^{-1})]</th>
<th>bSiO(_2):PON ratio</th>
<th>PIC:POC ratio</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Survey I (TT007)</td>
<td>0.38-0.95</td>
<td>0.6-6.3</td>
<td>0.05-0.1</td>
<td>0.29-0.34</td>
<td>(1),(2),</td>
<td></td>
<td>(3),(4)</td>
</tr>
<tr>
<td>Time series I (TT008)</td>
<td>1.9-5</td>
<td></td>
<td></td>
<td></td>
<td>(5),(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Survey II (TT011)</td>
<td>0.6-4.65</td>
<td>1.5-19.5</td>
<td>0.4-3.9</td>
<td>0.79-1.25</td>
<td>(1),(2),</td>
<td></td>
<td>(3),(4)</td>
</tr>
<tr>
<td>Time series II (TT012)</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td>(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FLUPAC</td>
<td>2.90±0.65</td>
<td>17.0±2.5</td>
<td>2.3±0.3</td>
<td>0.10-0.23</td>
<td>(7),(8),</td>
<td></td>
<td>(3),(4)</td>
</tr>
<tr>
<td>OLIPAC</td>
<td>0.68</td>
<td>7.1</td>
<td></td>
<td></td>
<td>(9),(3),</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zonal Flux</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EBENE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>1.36-1.39</td>
<td>9-20</td>
<td>2.6</td>
<td>0.14-0.45</td>
<td>(10),(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model</td>
<td>0.76</td>
<td>5.01</td>
<td>2.36</td>
<td>N/A</td>
<td>3.11</td>
<td>N/A</td>
<td>(12),(4)</td>
</tr>
<tr>
<td>Model</td>
<td>0.69-0.98</td>
<td>5.04-7.15</td>
<td>0.35-3.20</td>
<td>N/A</td>
<td>0.36-4.64</td>
<td>N/A</td>
<td>(13)</td>
</tr>
<tr>
<td>(calcification model simulation) Model</td>
<td><strong>0.58</strong></td>
<td><strong>3.84</strong></td>
<td><strong>1.46</strong></td>
<td><strong>0.60</strong></td>
<td><strong>2.52</strong></td>
<td><strong>0.16</strong></td>
<td>This study</td>
</tr>
<tr>
<td>(no-calcification model simulation) Model</td>
<td><strong>0.51</strong></td>
<td><strong>3.38</strong></td>
<td><strong>0.74</strong></td>
<td>N/A</td>
<td><strong>1.45</strong></td>
<td>N/A</td>
<td>This study</td>
</tr>
</tbody>
</table>

Sources noted here are: (1) Luo et al. (1995); (2) Murray et al. (1996); (3) Dunne et al. (1999); (4) Dugdale et al. (2002); (5) Buesseler et al. (1995); (6) Bacon et al. (1996); (7) Le Borgne et al. (1995); (8) Rodier and Le Borgne (1997); (9) Rainbault et al. (1999); (10) Le Borgne et al. (1998); (11) Leynaert et al. (2001); (12) Loukos et al. (1997); (13) Dugdale and Wilkerson (1998).
Table 5. Sensitivity of surface phytoplankton (P1, P2 and P3 [mmolN m\(^{-3}\)], zooplankton (Z1 and Z2 [mmolN m\(^{-3}\)], nutrients (NO\(_3\) [mmolN m\(^{-3}\)], NH\(_4\) [mmolN m\(^{-3}\)] and Si(OH)\(_4\) [mmolSi m\(^{-3}\)], TAlk [mmol m\(^{-3}\)], TCO\(_2\) [mmolC m\(^{-3}\)] and pCO\(_{2\text{sea}}\) [µatm] and of export PON [mmolN m\(^{-2}\) day\(^{-1}\)], bSiO\(_2\) [mmolSi m\(^{-2}\) day\(^{-1}\)] and PIC [mmolC m\(^{-2}\) day\(^{-1}\)] fluxes, to biogeochemical parameters in calcification model. Values in parentheses denote model results in the standard experiment. The other values mean difference by changing each parameter value from 0.5 to 1.5 times the standard parameter value. The values in bold letters are those that exceed 100% of each model compartment concentration (10% of those for Talk, TCO\(_2\), and pCO\(_{2\text{sea}}\)). The parameters in bold letters strongly affect the model results and are described in Section 4.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P1 (0.23)</th>
<th>P2 (0.13)</th>
<th>P3 (0.06)</th>
<th>Z1 (0.35)</th>
<th>Z2 (0.65)</th>
<th>NO(_3) (6.08)</th>
<th>NH(_4) (1.14)</th>
<th>Si(OH)(_4) (3.08)</th>
<th>TAlk (2360.9)</th>
<th>TCO(_2) (2045.9)</th>
<th>pCO(_{2\text{sea}}) (401.02)</th>
<th>PON (0.58)</th>
<th>bSiO(_2) (1.36)</th>
<th>PIC (0.60)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>0.24</td>
<td>0.08</td>
<td>0.08</td>
<td>0.17</td>
<td>0.75</td>
<td>7.84</td>
<td>0.08</td>
<td>0.53</td>
<td>21.39</td>
<td>80.91</td>
<td>183.84</td>
<td>0.19</td>
<td>0.16</td>
<td>0.46</td>
</tr>
<tr>
<td>(\mu)</td>
<td>0.20</td>
<td>0.08</td>
<td>0.08</td>
<td>0.21</td>
<td>0.66</td>
<td>6.49</td>
<td>0.08</td>
<td>1.90</td>
<td>33.12</td>
<td>52.64</td>
<td>147.05</td>
<td>0.03</td>
<td>0.59</td>
<td>0.84</td>
</tr>
<tr>
<td>(K_{\text{NO3}})</td>
<td>0.17</td>
<td>0.05</td>
<td>0.04</td>
<td>0.10</td>
<td>0.50</td>
<td>5.53</td>
<td>0.10</td>
<td>1.50</td>
<td>18.69</td>
<td>47.19</td>
<td>108.01</td>
<td>0.05</td>
<td>0.48</td>
<td>0.42</td>
</tr>
<tr>
<td>(K_{\text{NH4}})</td>
<td>0.09</td>
<td>0.09</td>
<td>0.02</td>
<td>0.15</td>
<td>1.31</td>
<td>3.03</td>
<td>0.32</td>
<td>3.22</td>
<td>6.92</td>
<td>10.22</td>
<td>26.92</td>
<td>0.04</td>
<td>0.97</td>
<td>0.19</td>
</tr>
<tr>
<td>(\mu)</td>
<td>0.02</td>
<td>0.04</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.16</td>
<td>0.04</td>
<td>0.38</td>
<td>5.20</td>
<td>1.53</td>
<td>5.00</td>
<td>0.02</td>
<td>0.12</td>
<td>0.16</td>
</tr>
<tr>
<td>(K_{\text{SO4}})</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.15</td>
<td>0.13</td>
<td>0.24</td>
<td>0.65</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>(K_{\text{Z2-NH4}})</td>
<td>0.15</td>
<td>0.11</td>
<td>0.02</td>
<td>0.32</td>
<td>3.18</td>
<td>0.44</td>
<td>46.51</td>
<td>14.33</td>
<td>12.70</td>
<td>0.09</td>
<td>0.45</td>
<td>1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\mu)</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.03</td>
<td>0.22</td>
<td>0.15</td>
<td>5.52</td>
<td>0.92</td>
<td>6.62</td>
<td>0.01</td>
<td>0.05</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(K_{\text{Z3-NH4}})</td>
<td>0.06</td>
<td>0.02</td>
<td>0.07</td>
<td>0.03</td>
<td>0.11</td>
<td>0.71</td>
<td>0.01</td>
<td>0.57</td>
<td>15.24</td>
<td>15.30</td>
<td>26.28</td>
<td>0.09</td>
<td>0.18</td>
<td>1.08</td>
</tr>
<tr>
<td>(W_3)</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.29</td>
<td>0.17</td>
<td>4.55</td>
<td>0.25</td>
<td>7.00</td>
<td>0.01</td>
<td>0.06</td>
<td>0.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(G_{1\text{max}})</td>
<td>2.04</td>
<td>0.15</td>
<td>0.11</td>
<td>0.16</td>
<td>0.70</td>
<td>8.20</td>
<td>0.16</td>
<td>3.84</td>
<td>45.39</td>
<td>55.90</td>
<td>160.23</td>
<td>0.34</td>
<td>1.37</td>
<td>1.14</td>
</tr>
<tr>
<td>(K_{1})</td>
<td>0.43</td>
<td>0.09</td>
<td>0.11</td>
<td>0.22</td>
<td>0.72</td>
<td>7.62</td>
<td>0.09</td>
<td>2.54</td>
<td>43.93</td>
<td>58.95</td>
<td>174.41</td>
<td>0.04</td>
<td>0.81</td>
<td>1.13</td>
</tr>
<tr>
<td>(reg_1)</td>
<td>0.21</td>
<td>0.03</td>
<td>0.04</td>
<td>0.08</td>
<td>1.01</td>
<td>2.79</td>
<td>0.01</td>
<td>2.17</td>
<td>40.41</td>
<td>46.01</td>
<td>112.43</td>
<td>0.02</td>
<td>0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>(G_{2\text{max}})</td>
<td>1.02</td>
<td>0.45</td>
<td>1.12</td>
<td>0.21</td>
<td>0.71</td>
<td>7.23</td>
<td>0.15</td>
<td>5.95</td>
<td>237.68</td>
<td>148.84</td>
<td>137.18</td>
<td>1.74</td>
<td>1.75</td>
<td>7.25</td>
</tr>
<tr>
<td>(K_{2\text{gr}})</td>
<td>1.19</td>
<td>0.23</td>
<td>0.22</td>
<td>0.31</td>
<td>0.92</td>
<td>7.15</td>
<td>0.85</td>
<td>5.75</td>
<td>72.74</td>
<td>36.60</td>
<td>138.33</td>
<td>0.76</td>
<td>1.82</td>
<td>2.04</td>
</tr>
<tr>
<td>(\gamma_3)</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
<td>0.02</td>
<td>0.12</td>
<td>0.93</td>
<td>0.01</td>
<td>0.53</td>
<td>15.21</td>
<td>2.43</td>
<td>25.48</td>
<td>0.01</td>
<td>0.17</td>
<td>0.42</td>
</tr>
<tr>
<td>(\gamma_5)</td>
<td>0.48</td>
<td>0.12</td>
<td>0.09</td>
<td>0.06</td>
<td>1.01</td>
<td>6.13</td>
<td>0.09</td>
<td>3.57</td>
<td>36.12</td>
<td>55.47</td>
<td>135.07</td>
<td>0.15</td>
<td>1.10</td>
<td>0.92</td>
</tr>
<tr>
<td>(reg_2)</td>
<td>0.51</td>
<td>0.23</td>
<td>0.26</td>
<td>0.18</td>
<td>0.77</td>
<td>7.51</td>
<td>0.15</td>
<td>5.08</td>
<td>85.02</td>
<td>33.55</td>
<td>114.90</td>
<td>0.59</td>
<td>1.56</td>
<td>2.42</td>
</tr>
<tr>
<td>(\gamma_7)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.59</td>
<td>0.68</td>
<td>0.30</td>
<td>0.57</td>
<td>1.32</td>
<td>0.78</td>
<td>0.58</td>
<td>0.46</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>(\gamma_4)</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.15</td>
<td>0.15</td>
<td>0.06</td>
<td>0.57</td>
<td>1.32</td>
<td>0.78</td>
<td>0.58</td>
<td>0.46</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>(\gamma_6)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(\gamma_2)</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(\gamma_4)</td>
<td>0.02</td>
<td>0.04</td>
<td>0.00</td>
<td>0.01</td>
<td>0.38</td>
<td>0.11</td>
<td>0.94</td>
<td>1.88</td>
<td>4.76</td>
<td>0.03</td>
<td>1.22</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\gamma_5)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>(RSi)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Fig. 1 The inter-compartmental flow chart of the ecosystem and linkage to physical processes. The flows of nitrogen or carbon are indicated by solid lines, the flows of silicon are indicated by dashed lines, and the flows of calcium are indicated by line-dashed lines. P1: picoplankton, P2: diatoms, P3: coccolithophorids, Z1: microzooplankton, and Z2: mesozooplankton.
Fig. 2. Modeled vertical profiles of (a) phytoplankton biomass [mmolN m\(^{-3}\)], (b) chlorophyll [mgChl m\(^{-3}\)], (c) zooplankton biomass [mmolN m\(^{-3}\)], (d) NO\(_3\) [mmolN m\(^{-3}\)], (e) NH\(_4\) [mmolN m\(^{-3}\)], (f) Si(OH)\(_4\) [mmolSi m\(^{-3}\)], (g) TAlk [mmol m\(^{-3}\)], and (h) TCO\(_2\) [mmolC m\(^{-3}\)]. Solid lines: calcification model results. Dotted lines: no-calcification model results. Dots denote the JGOFS EqPac data for TT008 (red dots), TT011 (green dots) and TT012 (blue dots).
Fig. 3. Modeled (a) vertical profile of net community production [mmolC m⁻³ day⁻¹], (b) vertical profile of calcification [mmolC m⁻³ day⁻¹], (c) vertical profile of bSiO₂ production [mmolSi m⁻³ day⁻¹], (d) calcification [mmolC m⁻³ day⁻¹] vs. net community production [mmolC m⁻³ day⁻¹], and (e) bSiO₂ production [mmolSi m⁻³ day⁻¹] vs. net community production [mmolC m⁻³ day⁻¹] in the euphotic zone. Dots denote the field observation data from EBENE (Leynaert et al., 2001) for bSiO₂ production and EqPac Survey II (TT011) (Balch and Kilpatrick, 1996) for the others.
Fig. 4. Modeled (a) surface TAlk [mmol kg\(^{-3}\)], (b) export POC flux [mmolC m\(^{-2}\) day\(^{-1}\)] at 120m depth, (c) surface TCO\(_2\) [mmolC m\(^{-3}\)], (d) export bSiO\(_2\) flux [mmolSi m\(^{-2}\) day\(^{-1}\)] at 120m depth, (e) pCO\(_2\)\(_{sea}\) [µatm], and (f) export PIC flux at 120m depth [mmolC m\(^{-2}\) day\(^{-1}\)], obtained by changing the maximum grazing or predation rate by mesozooplankton (\(G_{2max}\)) from 0.5 to 1.5 times the standard value.
Fig. 5. Modeled (a) surface TAlk [mmol m\(^{-3}\)], (b) surface TCO\(_2\) [mmolC \(m^{-3}\)], and (c) pCO\(_{2sea}\) [\(\mu\text{atm}\)], obtained by changing the initial slope of P-I curve (\(\alpha\)), the maximum specific growth rates of picoplankton (\(\mu_{1max}\)), and the maximum specific grazing rate on picoplankton by mesozooplankton (\(G_{1max}\)) from 0.5 to 1.5 times the standard value.
Fig. 6. Modeled (a) bSiO$_2$:PON export ratio and (b) PIC:POC export ratio (rain ratio) at 120m depth, obtained by changing the initial slope of P-I curve ($\alpha$), the maximum specific growth rates of picoplankton ($\mu_{1\text{max}}$) and coccolithophorids ($\mu_{3\text{max}}$), the maximum specific grazing or predation rates by mesozooplankton ($G_{1\text{max}}$) and mesozooplankton ($G_{2\text{max}}$) from 0.5 to 1.5 times the standard values.
Fig. 7 Modeled surface (a) picoplankton (P1; in blue) and diatom (P2; in green) [mmolN m\(^{-3}\)], (b) coccolithophorids (P3) [mmolN m\(^{-3}\)], (c) total phytoplankton (P1+P2+P3 for calcification model simulation and P1+P2 for no-calcification model simulation) [mmolN m\(^{-3}\)], (d) phytoplankton composition ratio of picoplankton (in blue), diatoms (in green), and coccolithophorids (in red) to total phytoplankton, (e) NO\(_3\) [mmolN m\(^{-3}\)], (f) Si(OH)\(_4\) [mmolSi m\(^{-3}\)], (g) TAlk [mmol m\(^{-3}\)], (h) TCO\(_2\) [mmolC m\(^{-3}\)], and (i) pCO\(_{2\text{sea}}\) [µatm], vs. source Si(OH)\(_4\) concentration [mmolSi m\(^{-3}\)] in Experiment 2. Solid lines: calcification model results. Dotted lines: no-calcification model results.
(a) Picoplankton (P1)
(b) Diatoms (P2)
(c) Coccolithophorids (P3)
(d) Microzooplankton (Z1)

Fig. 8. Modeled specific (divided by each biomass) (a) grazing rate on picoplankton (P1) by microzooplankton (Z1) [day⁻¹], (b) diatom (P2) growth rate and grazing rate by mesozooplankton (Z2) [day⁻¹], (c) coccolithophorid (P3) growth rate and grazing rate by mesozooplankton [day⁻¹], and (d) predation rate on microzooplankton by mesozooplankton [day⁻¹] in the surface water, vs. source Si(OH)₄ concentration [mmolSi m⁻³] in Experiment 2.
Fig. 9. Modeled (a) export flux of POC [mmolC m\(^{-2}\) day\(^{-1}\)] and bSiO\(_2\) [mmolSi m\(^{-2}\) day\(^{-1}\)], (b) export PIC flux [mmolC m\(^{-2}\) day\(^{-1}\)], (c) export bSiO\(_2\):PON ratio, and (d) export PIC:POC ratio (rain ratio) at 120m depth vs. source Si(OH)\(_4\) concentration [mmolSi m\(^{-3}\)] in Experiment 2. Solid lines: calcification model results. Dotted lines: no-calcification model results.
Fig. 10. Modeled specific (divided by each biomass) (a) grazing rate on picoplankton (P1) by microzooplankton (Z1) [day$^{-1}$], (b) grazing rate on diatom (P2) by mesozooplankton (Z2) [day$^{-1}$], and (c) predation rate on microzooplankton (Z1) by mesozooplankton (Z2) [day$^{-1}$] in the surface water vs. source Si(OH)$_4$ concentration [mmolSi m$^{-3}$] in Experiment 2. Solid lines: calcification model results. Dotted lines: no-calcification model results.
Fig. 11. (a) chlorophyll [mgChl m\(^{-3}\)], (b) net community production [mgC m\(^{-3}\) day\(^{-1}\)], (c) NO\(_3\) [mmolN m\(^{-3}\)], and (d) Si(OH)\(_4\) [mmolSi m\(^{-3}\)] at the surface (open dots) or bottom (crosses) of the euphotic zone (120m depth) during the JGOFS EqPac Time series II (TT012) from Oct. 2 to Oct. 21, 1992.
Fig. 12. Surface (a) NO$_3$ [mmolN m$^{-3}$], (b) Si(OH)$_4$ [mmolSi m$^{-3}$], (c) TCO$_2$ [mmolC m$^{-3}$] and (d) pCO$_2$$_{sea}$ [µatm] vs. source Si(OH)$_4$ concentration [mmolSi m$^{-3}$]. Open dots: the JGOFS EqPac Time series II (TT012) data from Oct. 2 to Oct. 21, 1992; Solid lines: calcification model results in Experiment 2.