Predictions of Carbon Fixation during a Bloom of *Emiliania huxleyi* as a Function of the Regulating Inorganic Species

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Abstract. Large scale precipitation of calcium carbonate in the oceans by coccolithophorids is a phenomenon that plays an important role in carbon sequestration. However, there is a controversy on the effect of an increase in atmospheric CO2 concentration on both calcification and photosynthesis of coccolithophorids. Indeed recent experiments, performed in conditions of nitrogen limitation, revealed that the associated fluxes may be slowed down, while other authors claim the reverse response. We have designed models to account for various scenarii of calcification and photosynthesis regulation in chemostat cultures of Emiliania huxleyi, based on different hypotheses of regulation mechanism. These models, which are kept at a general and generic level, consider that either carbon dioxide, bicarbonate, carbonate or pH is the regulating factor.

These models are calibrated to predict the same carbon fluxes in nowadays pCO2, but they turn out to respond differently to an increase of CO2 concentration. Thus, we simulated a bloom of Emiliania huxleyi using the four considered regulation scenarii. For high biomass concentration, the coccolithophorids can significantly affect the inorganic carbon and the pH in their environment, thus leading to a feedback in their growth rate which is, depending on the model, positive or negative. It results that the prediction of the carbon fixed during the bloom varies by a factor 2, depending on the assumed regulating mechanism hypothesized for growth and calcification.

Introduction

Phytoplankton uses light energy to build up organic cell components from inorganic carbon, and thus participates in the so-called 'biologic pump' that traps CO_2 from the atmosphere. In the world oceans, the activity of phytoplankton accounts for about 40 % of the total, primary production on Earth.

As pCO_2 levels in the atmosphere rise, phytoplankton growth might be positively stimulated by an increased availability of dissolved CO_2 in the upper oceans. However, a trade-off appears between CO_2 being more available for growth, and a lowered pH due to the chemical equilibrium of the carbonate system and the consequent ocean acidification.

Coccolithophorids are particularly abundant in the oceans and thus play an important role in CO_2 trapping [6]. These organisms are remarkable by the presence of solid, calcite structures called coccoliths that surround their cell. Coccolithophorids hence account for up to a third of the total, marine $CaCO_3$ production. Such structures are relatively sensitive to pH and tend to dissolve when the water becomes too acidic. It is expected that increases in pCO_2 will have direct consequences on the ability of these organisms to maintain their growth rate. As a corollary, acidification of the oceans due to atmospheric pCO_2 increases could jeopardize their role as a CO_2 pump.

Hence, how Coccolithophorids may respond to shifts in global pCO_2 is a critical question to be answered. However, if the photosynthesis mechanisms are well known, the effects of pCO_2 changes, whether on photosynthesis or on calcification, are still subject to intense debates. In batch experiments, contradictory observations have been made, where increases in p CO_2 either led to a decrease [8] or an increase [7] in calcification in *Emiliana huxleyi* , while photosynthesis was enhanced. Continuous cultures experiments in chemostats supported the hypothesis that both photosynthesis and calcification decrease [9].

In this paper, we investigate the relations between photosynthesis and calcification. We present a set of models, extended from [1], that integrate both phytoplankton growth and the carbonates system dynamics in the water.

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They were specifically designed to test several possible couplings and regulation mechanisms, assuming that calcification is regulated by one of the chemical species among CO_2, HCO_3^- and CO_3^{2-}. The model, based on the representation of a cell quota, is a Droop-like model [3, 2, 4] that we kept as general and generic as possible. Then, we add a fourth model where the calcite dissolution state acts as a regulating factor.

To complete these biological models, a simplified representation of the carbonate system is proposed with three equations. Hence, knowing the concentration of dissolved inorganic carbon (DIC), the concentration in Ca^{2+} and considering the hypothesis of a constant concentration of the other ions in the water, the seawater model can predict the pH value and concentrations of CO_2, HCO_3^- and CO_3^{2-}. This leads to four possible simplified models that can each represent a bloom of E.hux. These models bring two noteworthy results. We show that the predicted biomass can vary two-fold depending on the model, and that pCO_2 has little influence on the bloom, due to the slow transfer of inorganic carbon at the atmosphere – seawater interface.

1 Modelling Growth and Calcification

1.1 Biological Aspects

Here we present the mass flows in the model corresponding to nitrogen and carbon uptake. Uptake of inorganic nitrogen (nitrate, denoted S_1) into the phytoplanktonic biomass (whose particulate nitrogen concentration is denoted N), can be represented by the following mass flow, where ρ (.) is the nitrate absorption rate:

$$S_1 \xrightarrow{\rho(.)} N \qquad (1)$$

The flux of inorganic carbon into organic biomass X and coccoliths C is associated to a flux of calcium (Ca^{2+}, denoted S_2):

$$\frac{1-\alpha}{\alpha} S^2 + \frac{1}{\alpha} D \xrightarrow{\mu(.)X} \frac{1-\alpha}{\alpha} C + X \qquad (2)$$

There μ (.) is the photosynthesis rate.

The next question is the modelling of both the nitrate absorption rate ρ (.) and the photosynthesis rate μ(.).

Generally, the nitrate uptake rate is assumed to depend on external nitrate concentration $NO3$, following a Michaelis-Menten type equation [5].

The expression of the rate of inorganic carbon acquisition is trickier, as shown by [3, 4], it must depend on the internal nitrogen quota Q. However, coccolithophorids photosynthesis and calcification are also sensitive to the DIC concentration, and there is a consensus to admit that CO_2 is the substrate for photosynthesis while HCO_3^- is the substrate of calcification. Therefore the regulation of growth and calcification can theoretically be triggered by CO_2 or HCO_3^-. We also examine the possibility that CO_3^{2-} is involved in the regulation process of inorganic carbon acquisition [1]. Finally, we also propose in this paper to consider the availability of calcium as a possible regulating factor of photosynthesis and calcification. In this last hypothesis, we examine the possibility that μ(.) is regulated by Ω, the saturation state of calcite ($CaCO_3$); there solubility constant yields K_{sp}=5.1510^{-7}mol^2.L^{-2}:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \qquad (3)$$

As a consequence, in the sequel we examine four possible models that only differ by the regulation mechanisms of inorganic carbon acquisition.

- CO_2 is the regulating species, and thus $\mu(Q, CO_2)$ is an increasing function of both Q and CO_2.
- HCO_3^- iss the regulating species, and thus $\mu(Q, HCO_3^-)$ is an increasing function of both Q and HCO_3^-.
- CO_3^{2-} is the regulating species, and thus $\mu(Q, CO_3^{2-})$ is an increasing function of both Q and CO_3^{2-}.
- Ω is the regulating species, and thus $\mu(Q,\Omega)$ is an increasing function of both Q and Ω.

To keep a general denomination, we denote μ_p (Q, D_p) the growth rate, where, depending on the model M_p, D_p has to be chosen CO_2, HCO_3^-, CO_3^{2-} and Ω.

For simulation purposes, we represent the NO_3 uptake rate [5], $\rho(S_1)= \rho_m S_1 /(S_1 + k_N)$, where ρ_m and k_N are the maximum uptake rate and the half-saturation constant, respectively. Based on the Droop model [3, 4], the net growth rate may be written as:

$$\mu(Q, D_p) = \bar{\mu}\left(1 - \frac{k_Q}{Q}\right)\frac{D_p}{D_p + k_{D_p}} - R \qquad (4)$$

where k_Q, μ and k_{Dp} are respectively the subsistence internal quota, the maximum hypothetical growth rate and the half-saturation constant for the chosen regulating species. R is the respiration rate (supposed to be constant).

1.1 Seawater Modelling

In order to compute CO_2, HCO_3^-, CO_3^{2-} and Ω from D and S_2 , classical equations of the seawater carbonate system must be considered [10]. The carbonate alkalinity (CA) represents the electric charges carried in the carbonate system:

The total alkalinity (TA) is defined by (see [10] for more details):

$$CA = [HCO_3^-] + 2[CO_3^{2-}] \qquad (5)$$

The total alkalinity (*CA*) is defined by (see [10] for more details) :

$$TA = CA + [B(OH)_4^-] + [OH^-] - [H^+] \qquad (6)$$

We denote $\lambda = TA - 2[Ca^{2+}] = TA - 2S_2$. In a first approximation, the ions that most contribute to λ depend on the salinity and remain constant.

Following the previous considerations, carbonate alkalinity thus only depends on calcium: $CA = \lambda - \lambda_0 + 2S_2$ (where, in a first approximation, $\lambda_0 = [B(OH)_4^-] + [OH^-] - [H^+]$ remains constant compared to *CA*). In order to compute the $[HCO_3^-]$ and $[CO_3^{2-}]$ concentrations, we use the dissociation constants of the carbon dioxide (K_1) and bicarbonate (K_2) (the proton concentration, $[H^+]$, will be denoted h):

$$K_1 = \frac{h[HCO_3^-]}{[CO_2]}, \qquad K_2 = \frac{h[CO_3^{2-}]}{[HCO_3^-]} \qquad (7)$$

The total dissolved inorganic carbon (D) is defined as:

$$D = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \qquad (8)$$

Note that, in the considered pH range, we have $[HCO_3^-] >> [CO_3^{2-}] >> [CO_2]$ (see for example [10]). It follows that bicarbonate is the main carbon species in the bicarbonate system:

$$[HCO_3^-] \cong D \qquad (9)$$

We deduced from equations (5) and (8), in the considered pH range:

$$[CO_3^{2-}] \cong CA - D \qquad (10)$$

With this approximation, we can now compute the following ratio: $r = \frac{D}{CA}$ using equations (5), (8) and (7), we get:

$$r = \frac{h + K_2 + h^2/K_1}{h + 2K_2} \qquad (11)$$

It follows that h can be computed as a function of r:

$$h = u(r) = \\ = \left(-1 + r + \sqrt{(1-2r)\left(1 - \frac{4K_2}{K_1}\right) + r^2}\right)\frac{K_1}{2} \qquad (12)$$

Now using equations (7) and (5) we can compute the exact CO_2 concentration:

$$[CO_2] = \frac{CA}{K_1}\frac{h^2}{h + 2K_2} = CAv(r) = \psi(S_2, D) \qquad (13)$$

This simplified seawater modelling allowed a mathematical analysis of coccolithophorids models [1]. However, in the simulation, we used a more accurate model that does not make any approximation. The used Matlab code is a supplement to [10].

2 Modelling of a *E. Huxleyi B*loom in a Mixed Layer

In summer, increasing temperatures lead to a density gradient that stabilizes the water column, which then stratifies. The surface layer remains mixed over a generally shallow depth (in the order of 20m) and to keep the model as simple as possible, we assume a homogeneous distribution. We simulated the growth of coccolithophorids in this mixed layer, as represented in Figure 1. CO_2 concentration in the water equilibrates with that in the atmosphere, following the difference in concentration between the two compartments and according to the diffusion coefficient K_La.

Diffusion at the ocean surface is generated by wind stress, and so much lower K_La values must be considered here compared to *e.g.* bioreactors. That is, the low value (0.06 day^{-1}) used in the model is representative of the natural environment.

As a corollary, it is expected that high biomasses may draw down the DIC pool faster than it is renewed. In the water, CO_2 equilibrates with HCO_3^- and CO_3^{2-}. The CO_2 pool in the water is also affected by the coccolithophorids activity, being fuelled by respiration and consumed through the growth process (see (2)).

The model simulates a nitrate uptake limited by the availability of NO_3 , as illustrated by (1), while growth and coccoliths formation depend on the availability of both Ca^{2+} and CO_3^{2-} (see (2)). NO_3 and Ca^{2+} are provided by upwelling of deeper waters underlying the mixed layer (with an exchange rate K_d).

The water acidity affects the coccoliths persistence; we accounted for a possible dissolution of coccoliths, whose rate is dependent upon pH and represented by $\frac{K_{diss}}{\Omega} C$.

Settlement of calcite (detached coccoliths) is represented through $CaCO_3$ sinking below the mixed layer.

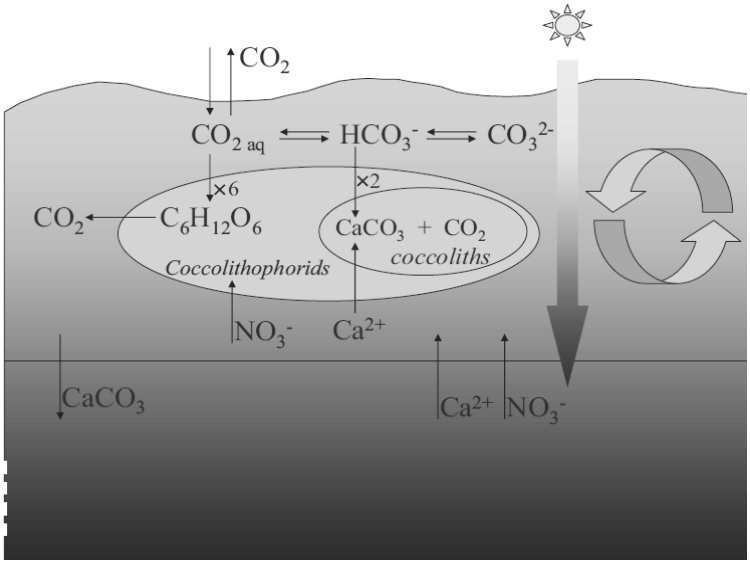

Figure 1. Schematic diagram of the well mixed upper ocean represented by the model.

Parameters	Values	Units
S_{10}	50	μ *molN.L*$^{-1}$
S_{20}	10.4	*mmolCa.L*
D_0	1.77	*mmolC. L*$^{-1}$
$K_L a$	0.06	*d*$^{-1}$
ρ_m	100.19	μ *molN.mmolC*$^{-1}$*.d*$^{-1}$
k_Q	32.29	μ *molN.mmolC*$^{-1}$
k_{S_1}	0.038	μ *molN.L*$^{-1}$
K_1	1.392 10^{-6}	*mmol.L*$^{-1}$
K_2	1.189 10^{-9}	*mmol.L*$^{-1}$
K_H	36.7	*mmolCO2 .L*$^{-1}$ *.*μ atm
α	0.53	—
λ	-17.31[3]	*mmol.L*$^{-1}$
λ_0	0.086[3]	*mmol.L*$^{-1}$
K_{diss}	0.15	*d*$^{-1}$
K_d	0.8	*d*$^{-1}$
K_{sed}	0.15	*d*$^{-1}$
R	0.01	*d*$^{-1}$

Table 1. Values of the model parameters.

Model equations can then be directly deduced from the mass flows (1) and (2). D_p is the regulating factor (among CO_2, HCO_3^{-}, CO_3^{2-} and Ω) assumed to regulate both photosynthesis and calcification. The system of equations reads:

$$\dot{S}_1 = K_d(S_{10} - S_1) - \rho(S_1)X \quad (14)$$

$$\dot{Q} = \rho(S_1) - \mu(Q, D_p)\, Q \quad (15)$$

$$\dot{X} = -K_d X + \mu(Q, D_p)X - RX - K_{sed}X \quad (16)$$

$$\dot{C} = -K_d C + \frac{1-\alpha}{\alpha}\mu(Q, D_p)X - K_{sed}C - \frac{K_{diss}}{\Omega} C \quad (17)$$

$$\dot{D} = K_d(D_0 - D) - \frac{1}{\alpha}\mu(Q, D_p)X - R\,X - \\ - \; K_L\alpha(\psi(S_2, D) - K_H pCO_2) + \frac{K_{diss}}{\Omega} C \quad (18)$$

$$\dot{S}_2 = K_d(S_{20} - S_2) - \frac{1-\alpha}{\alpha}\mu(S_1)X \quad (19)$$

There the exchange rate at the thermocline level is K_d , the sedimentation rate is K_{sed} , and the coccoliths dissolution rate is $\frac{K_{diss}}{\Omega}$.

The specific rate of carbon fixation is described as an increasing function of Q and D_p , which allows a generic analysis of the model [1]. Depending on the choice for D_p, four different models are obtained, based on three different hypotheses on the mechanisms driving both photosynthesis and calcification.

Parameters	CO_3^{2-}	HCO_3^-	CO_2	Ω	Units
k_{D_p}	0.076	1.65	0.01	1.53*	$\mu molC.L^{-1}$
$\bar{\mu}$	2.83	3.76	3.24	2.88	d^{-1}

Table 2. Kinetics parameters depending on the chosen model.(* unitless for k_Ω).

The models have been calibrated in order to predict the same carbon fluxes in nowadays pCO_2, on the basis on available experimental results [1]. Parameter values are presented in Table 1 and Table 2.

The model analysis proposed in [1] demonstrates that M_p models where D_p is either CO_2 or HCO_3^- support the results of [7], while models where CO_3^{2-} or Ω is the regulating factor support the results obtained by [9]. Last, none of these models allowed a qualitative prediction of the experimental results reported by [8]. Different model hypotheses were then required to reproduce these observations: photosynthesis had to be regulated by either CO_2 or HCO_3^- while calcification was driven by CO_3^{2-} or Ω [1].

3 Model Simulation

We used each of these models to simulate a large development (bloom) of *Emiliania huxleyi*. Phytoplankton cells are assumed to grow in a homogeneous layer, where aqueous CO_2 is in equilibrium with the atmosphere. The considered, realistic K_La being rather low, the time necessary to supply inorganic carbon to the cells can be long. This can explain the significantly different behaviour between the 4 scenarii (Figure 2).

Indeed, it turns out that, for high biomass concentrations, the coccolithophorids can significantly draw down the inorganic carbon and thus affect the pH in their environment. Depending on the model, the simulated mechanisms induce a positive (in the models with CO_3^{2-} or Ω as regulating factor) or negative (in models with CO_2 or HCO_3^-) feedback on the growth rate.

It results that the prediction of carbon fixed during the bloom formation can vary by a factor up to 2, depending on the assumed regulating mechanism hypothesized for growth and calcification (Figure 3).

The simulations with Ω as regulating factor make little difference to that with CO_3^{2-}. Such result can be explained by the fact that changes in Ca^{2+} concentrations being small, Ω fluctuations are similar to that of CO_3^{2-}.

When introducing a coccoliths dissolution term, model results remain close to that obtained without dissolution rate. Hence, the rate of coccoliths dissolution stayed low.

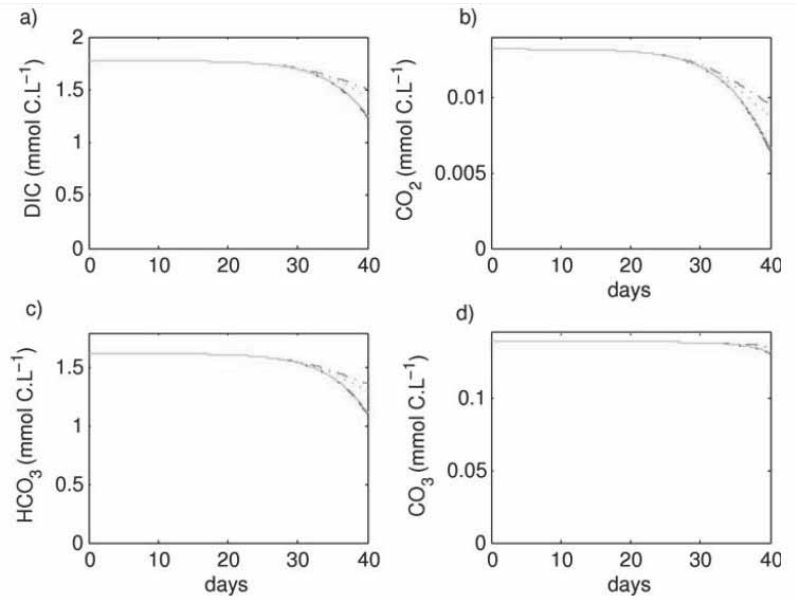

Figure 2. Depending on the considered choice of D_p (CO_2: ._._ , HCO_3^-: ..... , CO_3^{2-}: ____ , Ω: _ _ _), evolution of the various compartment of inorganic carbon. The model where HCO_3^- is the regulating factor shows the strongest impact on the inorganic carbon.

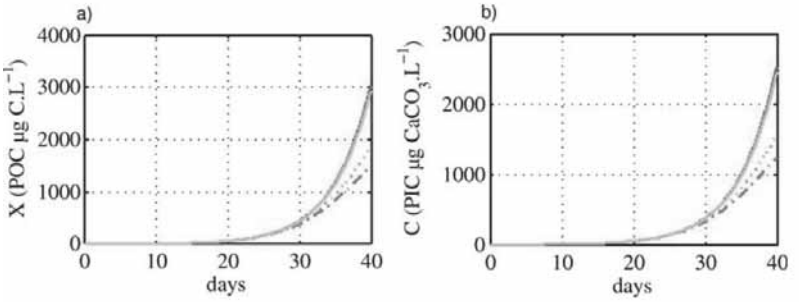

Figure 3. Amount of inorganic carbon which is fixed through photosynthesis (a) and calcification (b), depending on the considered (CO_2: ._._ , HCO_3^-: ..... , CO_3^{2-}: ____ , Ω: _ _ _), The models where D_p= CO_3^{2-}or D_p =Ω predict much higher carbon fluxes.

This can be explained by the remarkable stability of CO_3^{2-} whose concentration variation did not exceed 10%. Indeed the decrease of CO_3^{2-} due to exhaustion of total inorganic carbon is compensated by the pH increase that favors the form CO_3^{2-} to the detriment of HCO_3^-.

Last, investigating the influence of different surface pCO_2 revealed very little impact on growth. An increase from 380 ppm to 600 ppm only modified the total production by about 2%. At the air/sea interface, low K_La values limit the increase in dissolved CO_2 concentrations and, as a corrolary, short time scales (month) changes in pCO_2 in the water do not reflect that in the atmosphere. Consequently, model results suggest that biomass production remains relatively insensitive to changes in atmospheric pCO_2.

4 Conclusion

This study stresses how a correct identification of the chemical species that drive(s) calcification and photosynthesis processes is critical to accurately predict a bloom of coccolithophorids and the consequent amount of carbon withdrawn from the atmosphere and trapped into the deep ocean. The model results reveal a striking difference in the predicted biomass increase when the saturation state Ω (or equivalently CO_3^{2-}) is the regulating factor.

In the configuration of a low air/sea exchange, model results suggest that increased pCO_2 in the air show very little impact on growth. Due to the exhaustion of the DIC pool by the high biomasses formed during the bloom and low transfer coefficient, changes in surface pCO_2 hardly affect the bloom intensity. Such paradoxical transient behaviour only apply to off shore marine systems. Coastal, shallow ecosystems may present higher diffusion rates and model results then suggest a higher impact of surface pCO_2 on growth: under conditions of higher K_La values, the CO_2 resupply to the water participates in enhancing bloom formations for models regulated by CO_2 or HCO_3^- and shows a positive effect on growth, while the opposite behaviour is observed for models regulated by CO_3^{2-} or Ω.

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