Predictions of carbon fixation during a bloom of *Emiliania huxleyi* is highly sensitive to assumed response to shift in pCO2

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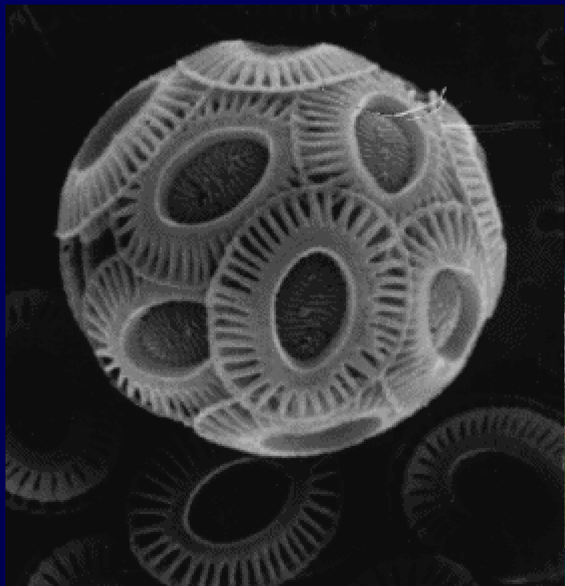
Coccolithophorids play an important role in CO2 trapping



1/3 of the total marine $CaCO_3$ production

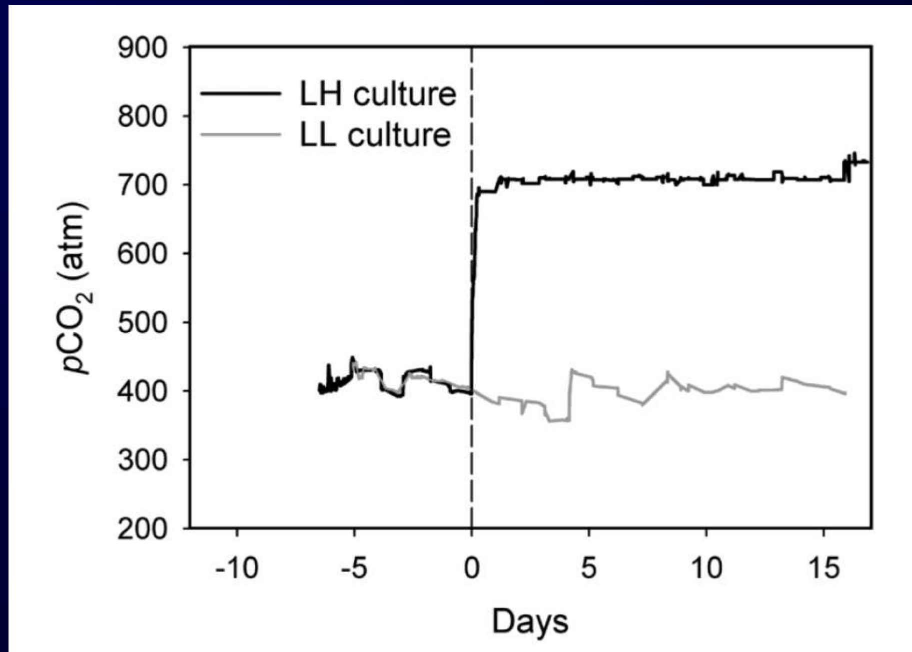
Effect of pCO2 increase

- Underlying mechanisms still to be clarified
- Effect of pCO_2 subject of intense debates

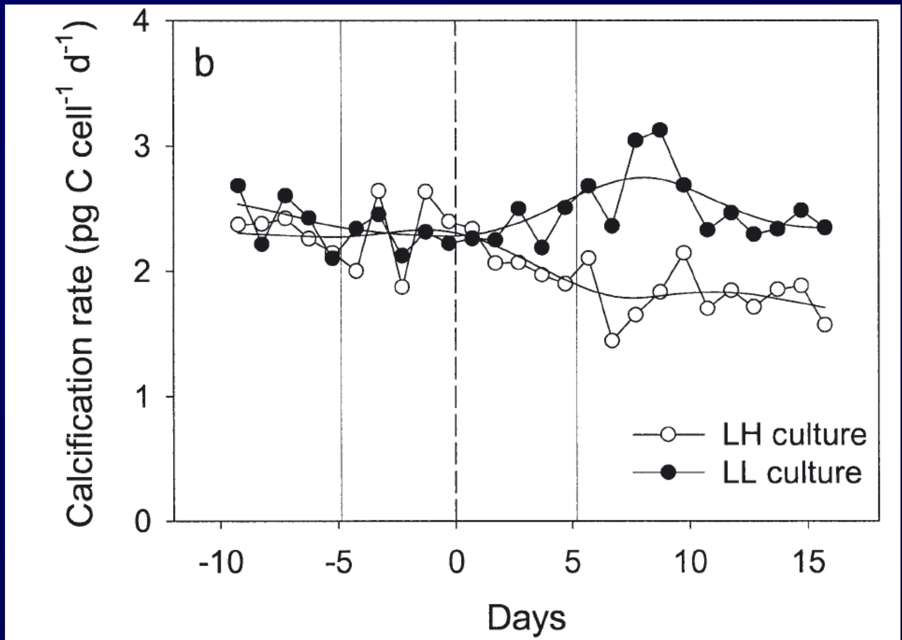
  - Decrease of calcification in *Emiliania huxleyi* (Riebesell et al., 2000), batch experiments
  - Increase in calcification in *E.huxleyi* (Iglesias-Rodriguez et al. 2008), batch experiments
  - Decrease in calcification and photosynthesis *E.huxleyi* (Sciandra et al., 2003) Chemostat experiments

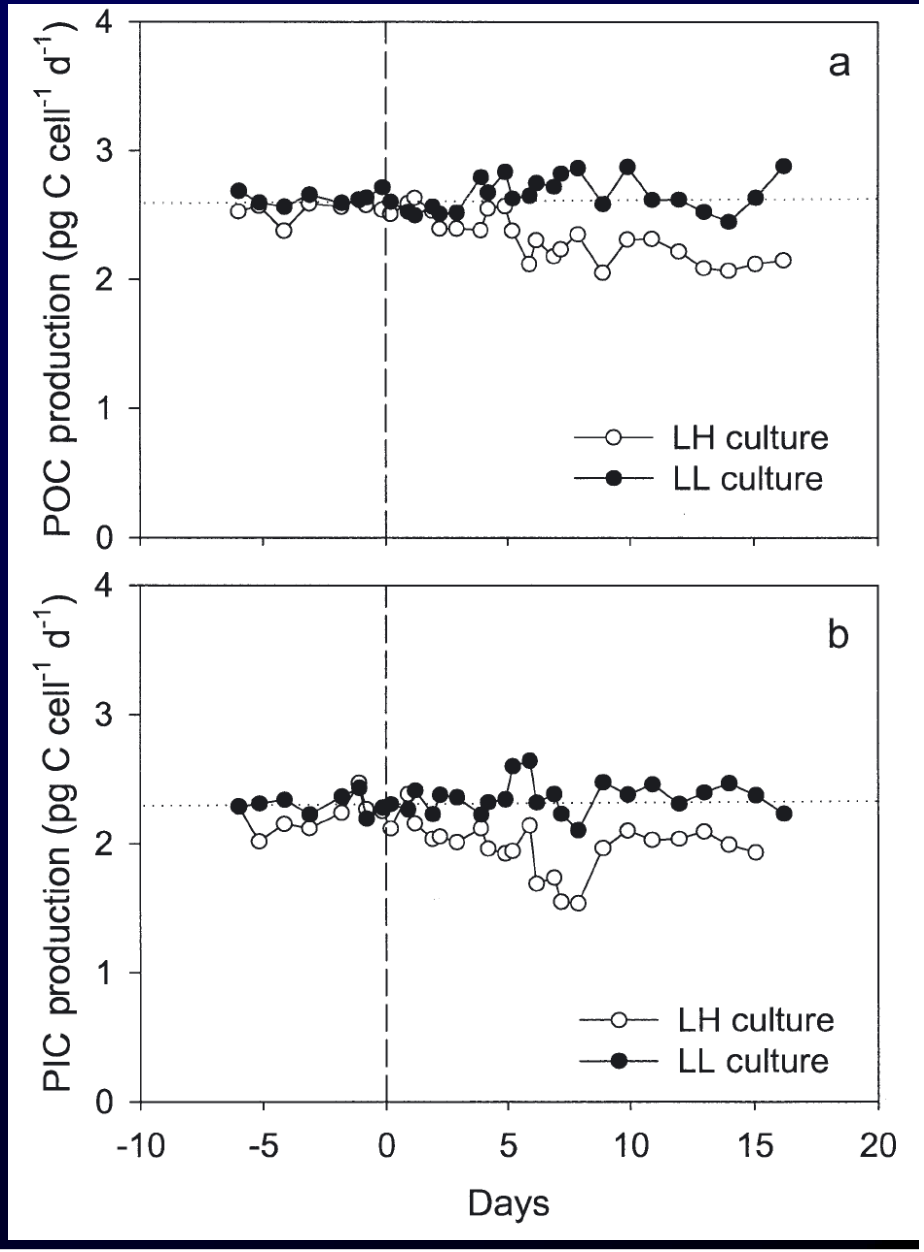
Performed experiments

• pH regulation to achieve a dissolved CO2 concentration corresponding to pCO2 415 ppm → 710 ppm



Experimental results





Sciandra et al. 2003

MODEL DESIGN

Model principles

- Integrate both biology and carbonate system dynamics
- Test several possible coupling and regulation mechanisms
- Based on a quota model (Droop like)
- Keep a general (and generic) structure

Simplified point of view

Photosynthesis

$$6CO_2 + 12H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 + 6H_20$$

Coupling ?

Calcification

$$Ca_2^+ + 2HCO_3^- \longrightarrow CaCO_3 + CO_2 + H_2O$$

Simplified carbonate system modelling

- The carbonate system

$$D = [HCO_3^-] + [CO_3^{2-}] + [CO_2]$$

$$CA = [HCO_3^-] + 2[CO_3^{2-}]$$

- Alkalinity

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

- Electroneutrality

$$[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [Cl^-] + [Br^-] + [F^-] + 2[SO_4^{2-}] + \\ = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Sr^{2+}] + 2[Ca^{2+}] + [H^+] + \ldots$$

Simplified carbonate system modelling

- **Electroneutrality**

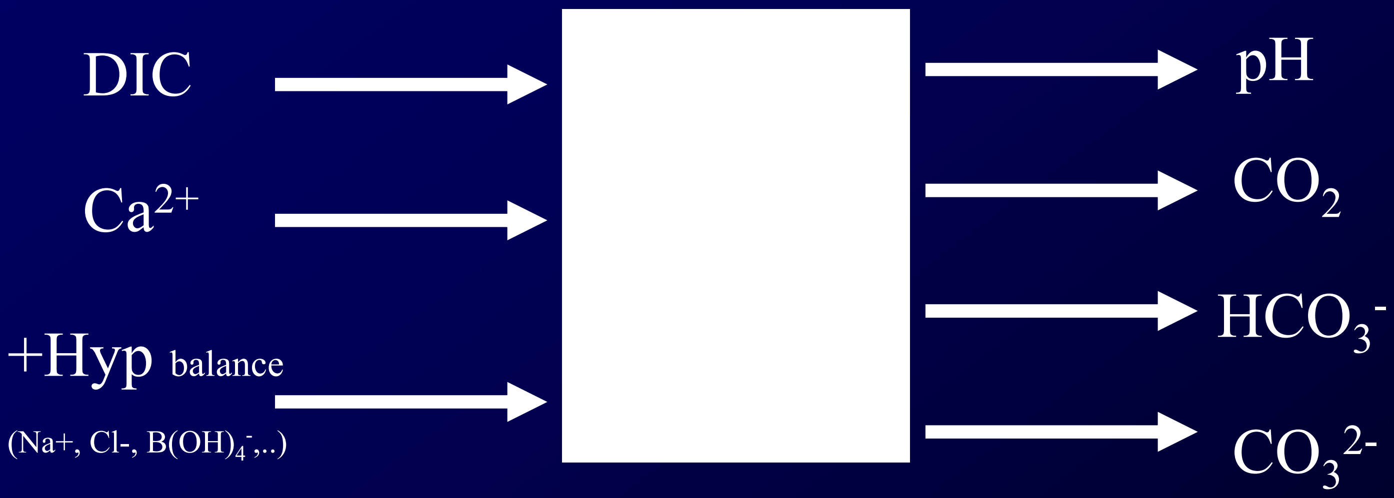
$$CA = \underbrace{\lambda - \lambda_0}_{\approx \text{ constant}} + 2[Ca^{2+}] = [HCO_3^-] + 2[CO_3^{2-}]$$

- **Affinity constants**

$$h = [H^+]$$

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

Carbonate system modelling



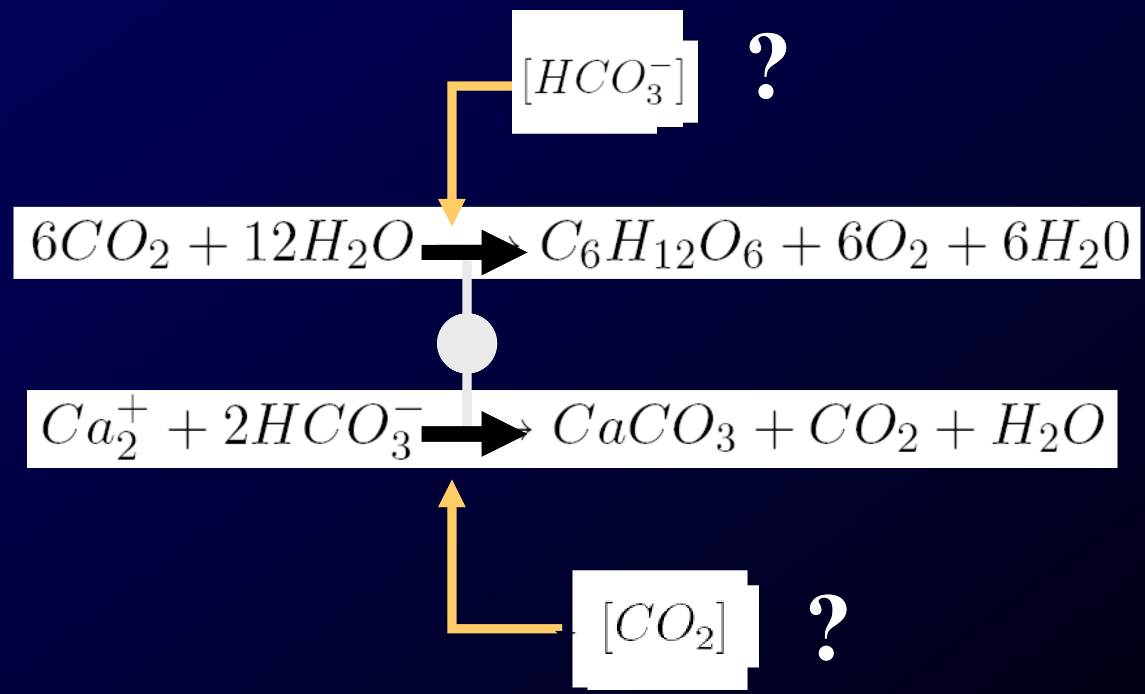
12 possible models

1. Which species regulate photosynthesis & calcification ?

2. Are photosynthesis and calcification coupled ?

Photosynthesis

Calcification



Coupled carbon uptake model

- Mass flows

  Nitrogen uptake

  $$NO_3 \xrightarrow{\rho(.)X} \text{PON}$$

  Carbon uptake

  $$\frac{1-\alpha}{\alpha} Ca^{2+} + \frac{1}{\alpha}\text{DIC} \xrightarrow{\mu(.)X} \frac{1-\alpha}{\alpha} C + X$$

- **Model equations**

$$\begin{aligned}
\dot{NO}_3 &= d(NO_{3in} - NO_3) - \rho(NO_3)X \\
\dot{Q} &= \rho(NO_3) - \mu(Q, Dp)Q \\
\dot{X} &= -dX + \mu(Q, Dp)X \\
\dot{C} &= -dC + \tfrac{1-\alpha}{\alpha}\mu(Q, Dp)X \\
\dot{\text{DIC}} &= d(\text{DIC}_{\text{in}} - \text{DIC}) - \tfrac{1}{\alpha}\mu(\text{Q}, \text{Dp})\text{X} - \text{K}_\text{L}\text{a}(\psi(\text{Ca}^{2+}, \text{DIC}) - \text{K}_\text{H}\text{pCO}_2) \\
\dot{C}a^{2+} &= d(Ca_{in}^{2+} - Ca^{2+}) - \tfrac{1-\alpha}{\alpha}\mu(Q, Dp)X
\end{aligned}$$

$$Dp = [HCO_3^-] \quad [CO_3^{2-}] \quad [CO_2]$$

Carbon fixation specific rate

<u>Hypothesis</u>: μ(Q,Dp) is an increasing function of Q and Dp

Example: Droop with regulation by Dp

$$\mu(Q, Dp) = \bar{\mu}(1 - \frac{k_Q}{Q})\frac{Dp}{Dp + k_D p} - R$$

In the analysis μ(Q,Dp) is left generic !

CI models:
Coupled Inorganic carbon uptake

•3 models

CI-HCO_3^- , CI-CO_2 , CI-CO_3^{2-}

$$\dot{S}_1 = d(S_{1in} - S_1) - \rho(S_1)X$$
$$\dot{Q} = \rho(S_1) - \mu(Q, Dp)Q$$
$$\dot{X} = -dX + \mu(Q, Dp)X$$
$$\dot{C} = -dC + \frac{1-\alpha}{\alpha}\mu(Q, Dp)X$$
$$\dot{D} = d(D_{in} - D) - \frac{1}{\alpha}\mu(Q, Dp)X - K_L a(\psi(S_2, D) - K_H pCO_2)$$
$$\dot{S}_2 = d(S_{2in} - S_2) - \frac{1-\alpha}{\alpha}\mu(Q, Dp)X$$

Uncoupled carbon uptake model

- Mass flows
  - Nitrogen uptake
  - Photosynthesis
  - Calcification

$$NO_3 \xrightarrow{\rho(.)X} \mathrm{PON}$$
$$\mathrm{DIC} \xrightarrow{\mu(.)X} X$$
$$Ca^{2+} + \mathrm{DIC} \xrightarrow{\sigma(.)X} C$$

- Model equations

$$\begin{aligned}
\dot{NO_3} &= d(NO_{3in} - NO_3) - \rho(NO_3)X \\
\dot{Q} &= \rho(NO_3) - \mu(Q, Dp)Q \\
\dot{X} &= -dX + \mu(Q, Dp)X \\
\dot{C} &= -dC + \sigma(Dc)X \\
\dot{\mathrm{DIC}} &= d(\mathrm{DIC_{in}} - \mathrm{DIC}) - \mu(\mathrm{Q}, \mathrm{Dp})\mathrm{X} - \sigma(\mathrm{Dc})\mathrm{X} - \mathrm{K_La}(\psi(\mathrm{Ca}^{2+}, \mathrm{DIC}) - \mathrm{K_HpCO_2}) \\
\dot{Ca}^{2+} &= d(Ca_{in}^{2+} - Ca^{2+}) - \sigma(Dc)X
\end{aligned}$$

$$Dc = \quad [HCO_3^-] \quad [CO_3^{2-}]$$
$$Dp = \quad [CO_2]$$

MATHEMATICAL MODEL STUDY

Results analysis

	CI			UI								
Photosynthesis	HCO_3^-	CO_2	CO_3^{2-}	HCO_3^-	HCO_3^-	HCO_3^-	CO_2	CO_2	CO_2	CO_3^{2-}	CO_3^{2-}	CO_3^{2-}
Calcification				HCO_3^-	CO_2	CO_3^{2-}	HCO_3^-	CO_2	CO_3^{2-}	HCO_3^-	CO_2	CO_3^{2-}
DIC	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗
Dp^*	↗	↗	↘	↗	↗	↗	↗	↗	↗	↘	↘	↘
Dc^*	↗	↗	↘	↗	↗	↘	↗	↗	↘	↗	↗	↘
X^*	↗	↗	↘	↗	↗	↗	↗	↗	↗	↘	↘	↘
Q^*	↘	↘	↗	↘	↘	↘	↘	↘	↘	↗	↗	↗
S_1^*	↘	↘	↗	↘	↘	↘	↘	↘	↘	↗	↗	↗
C^*	↗	↗	↘	↗	↗	↘	↗	↗	↘	↘	↗	↘
Ca_2^+	↘	↘	↗	↘	↘	↗	↘	↘	↗	↗	↘	↗
$\frac{C^*}{X^*}$	→	→	→	↗	↗	↘	↗	↗	↘	↗	↗	↘
pH^*	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘
CA	↘	↘	↗	↘	↘	↗	↘	↘	↗	↗	↘	↗
TA	↘	↘	↗	↘	↘	↗	↘	↘	↗	↗	↘	↗
Φ^*	↗	↗	↘	↗	↗	↘*	↗	↗	↘*	↘	↘	↘
Φ_p^*	↗	↗	↘	↗	↗	↗	↗	↗	↗	↘	↘	↘
Φ_c^*	↗	↗	↘	↗	↗	↘	↗	↗	↘	↘	↘	↘
$\frac{\Phi_p^*}{\Phi_c^*}$	→	→	→	↘	↘	↗	↘	↘	↗	↘	↘	↗

variables

Experimental Observations Sciandra et al. 2003

Bernard et al. 2008

Consequences

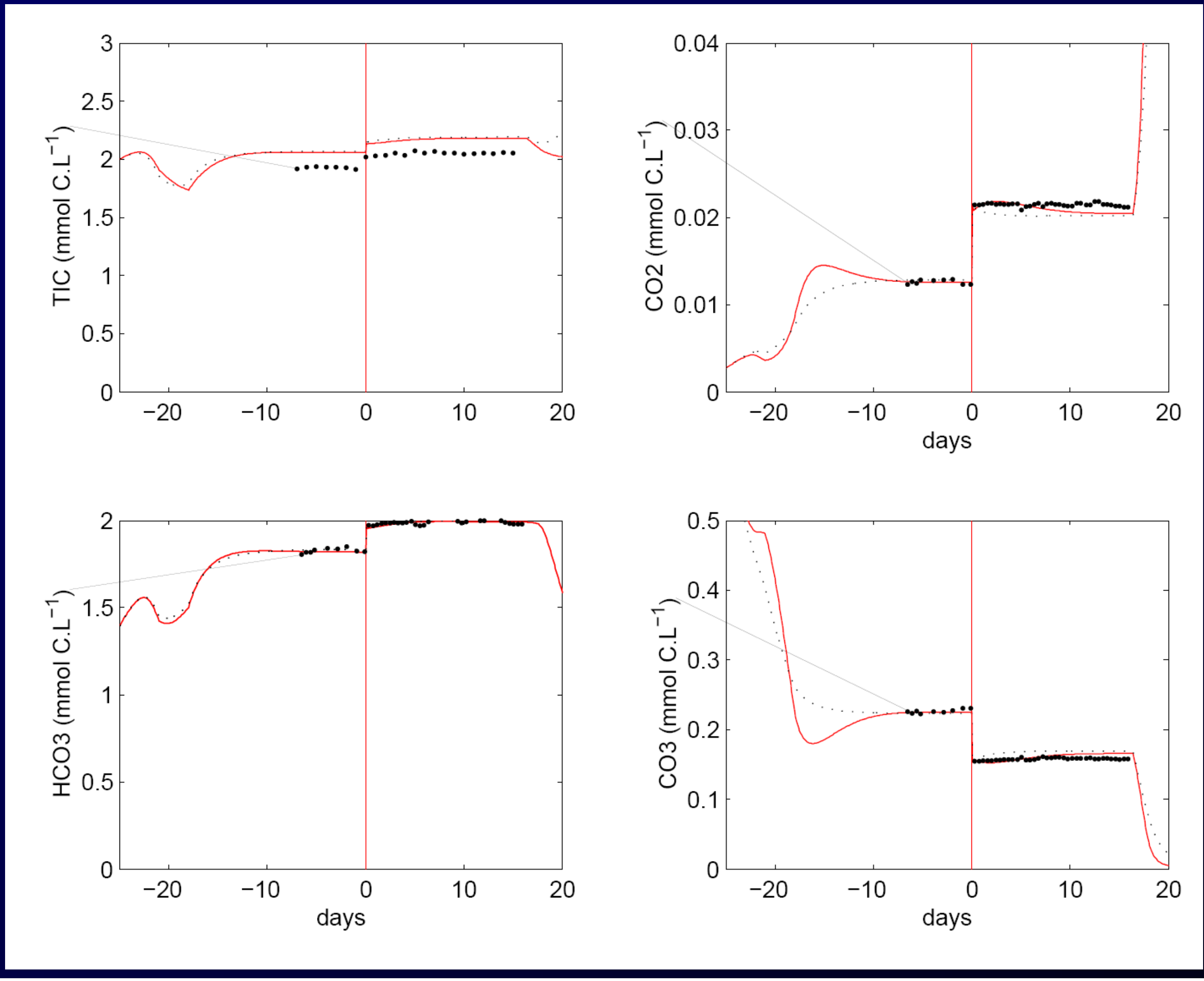
• From this analysis 4 models can explain data from Sciandra et al. 2003:

Photosynthesis regulated by CO_3^{2-} !!!!

⇒ This is not the classical hypothesis for N-replete experiments

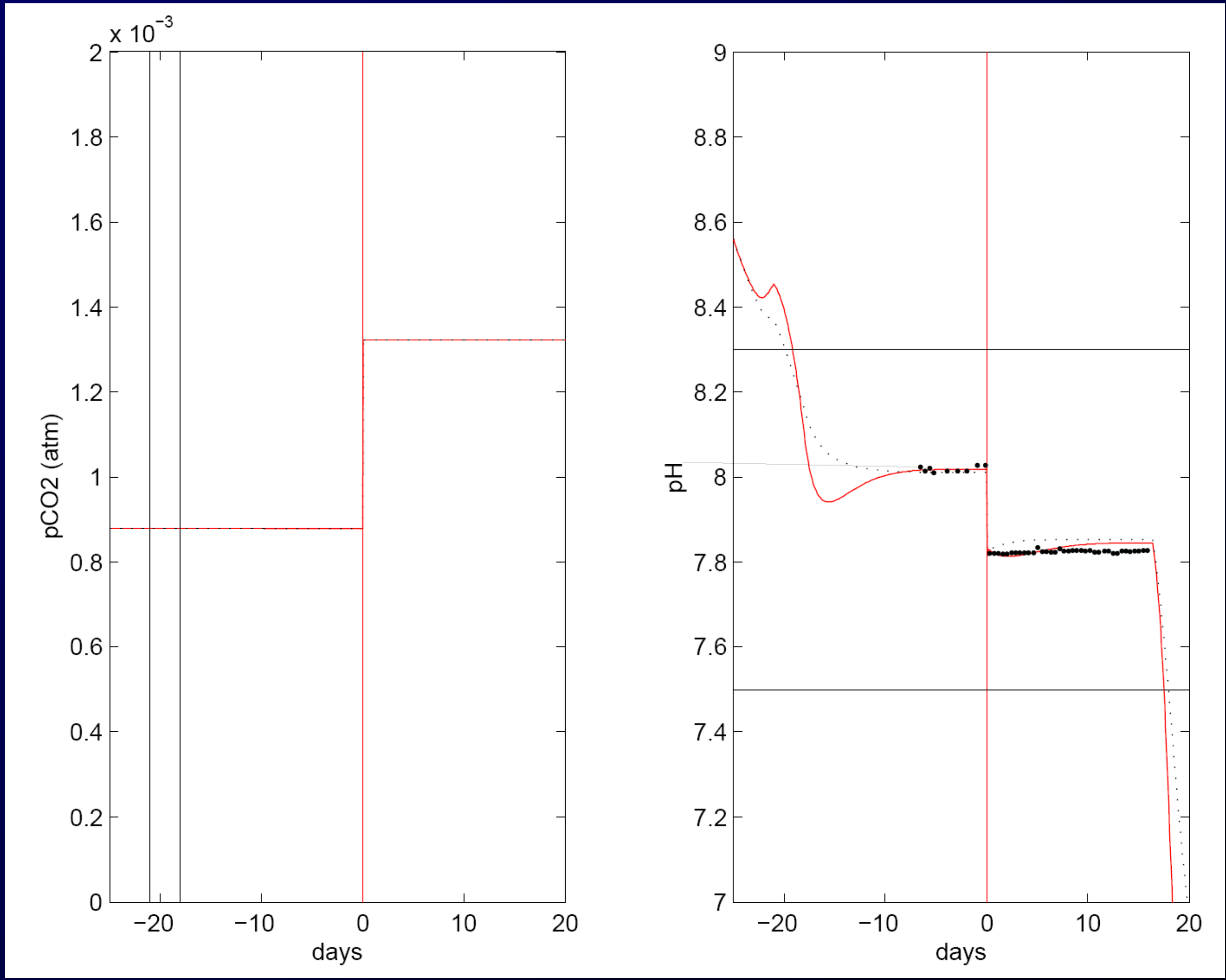
Remark: pH can play the same role in the model than CO_3^{2-}

Model simulations

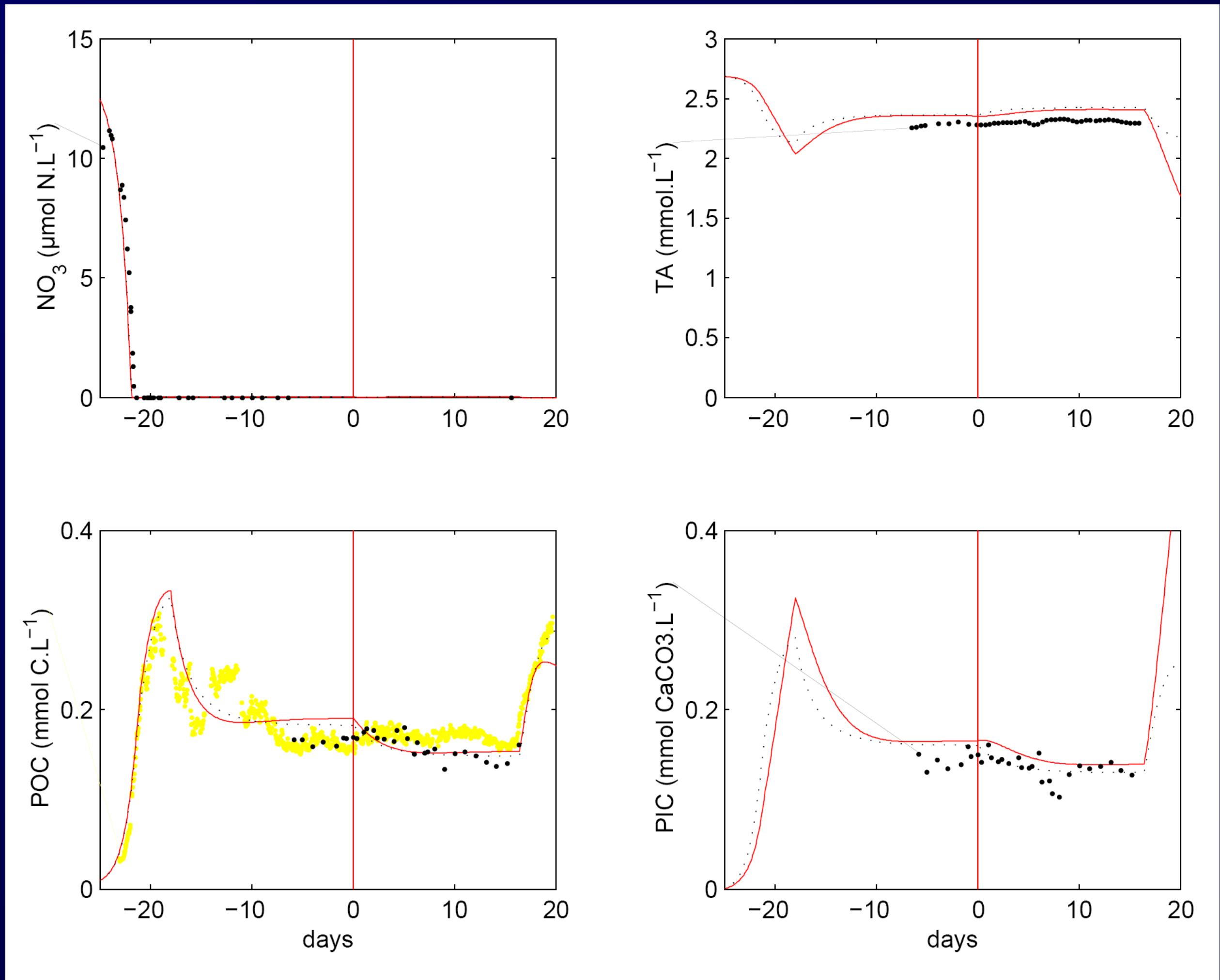


model CI-CO_3^{2-} (–), UI-CO_3^{2-} -HCO_3^- (…) and data

Model simulations



Model simulations



model CI-CO_3^{2-} (–), UI-CO_3^{2-} -HCO_3^- (. . .) and data

SIMULATION OF A BLOOM OF *E.HUXLEYI*

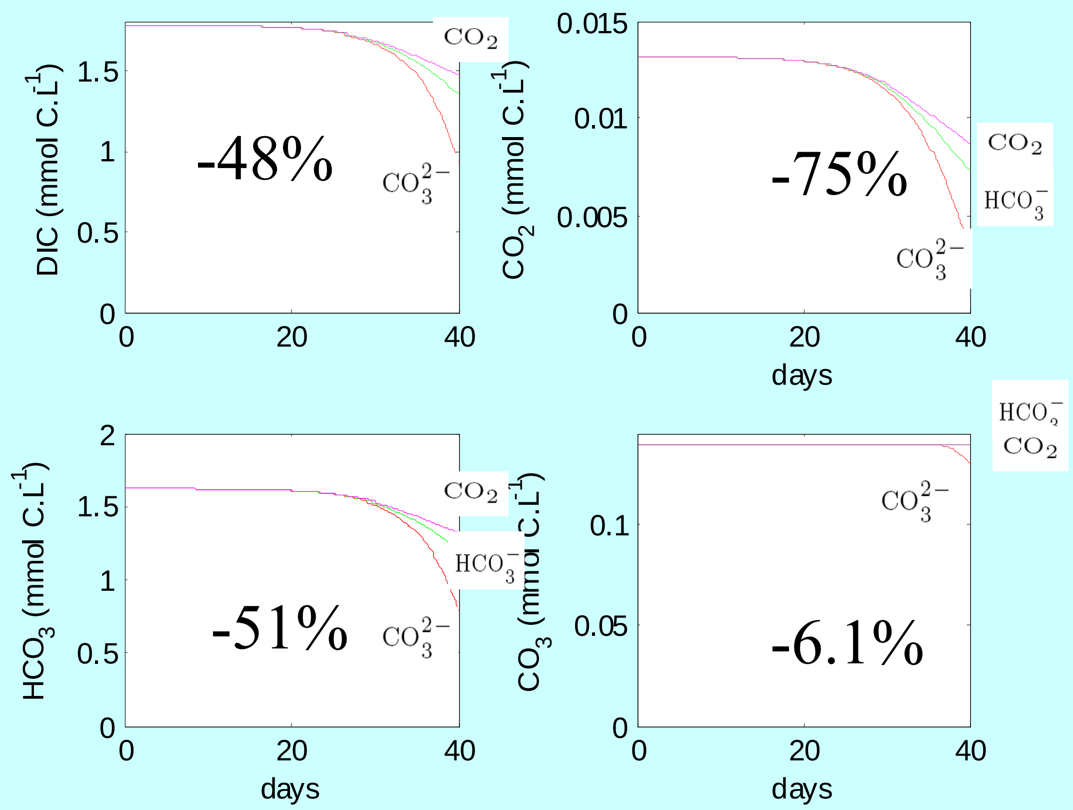
Hypotheses

- Caricature and academic
- Homogeneous mixed layer (10 m), strong stratification
- Simulation of a very intense bloom (pCO_2 drops to 100 ppm)
- 3 possible *scenarii*

Calcification and photosynthesis are regulated by:

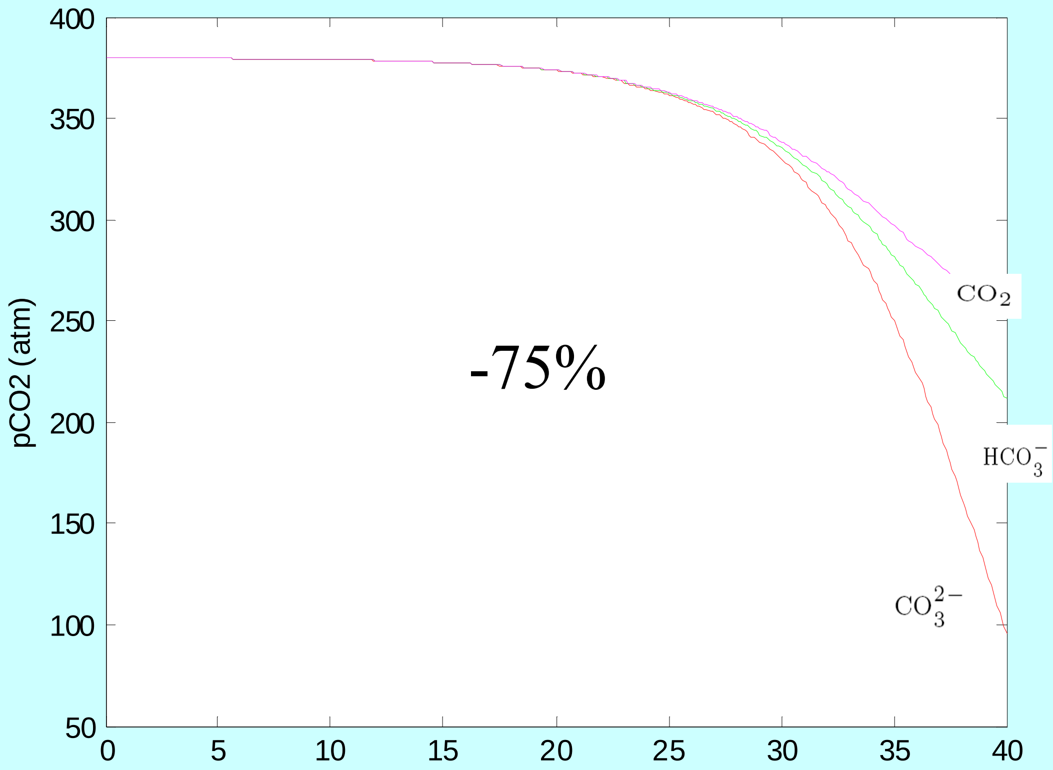
i. CO_2 | *ii*. HCO_3^- | *iii*. CO_3^{2-}

Simulations of the 3 models



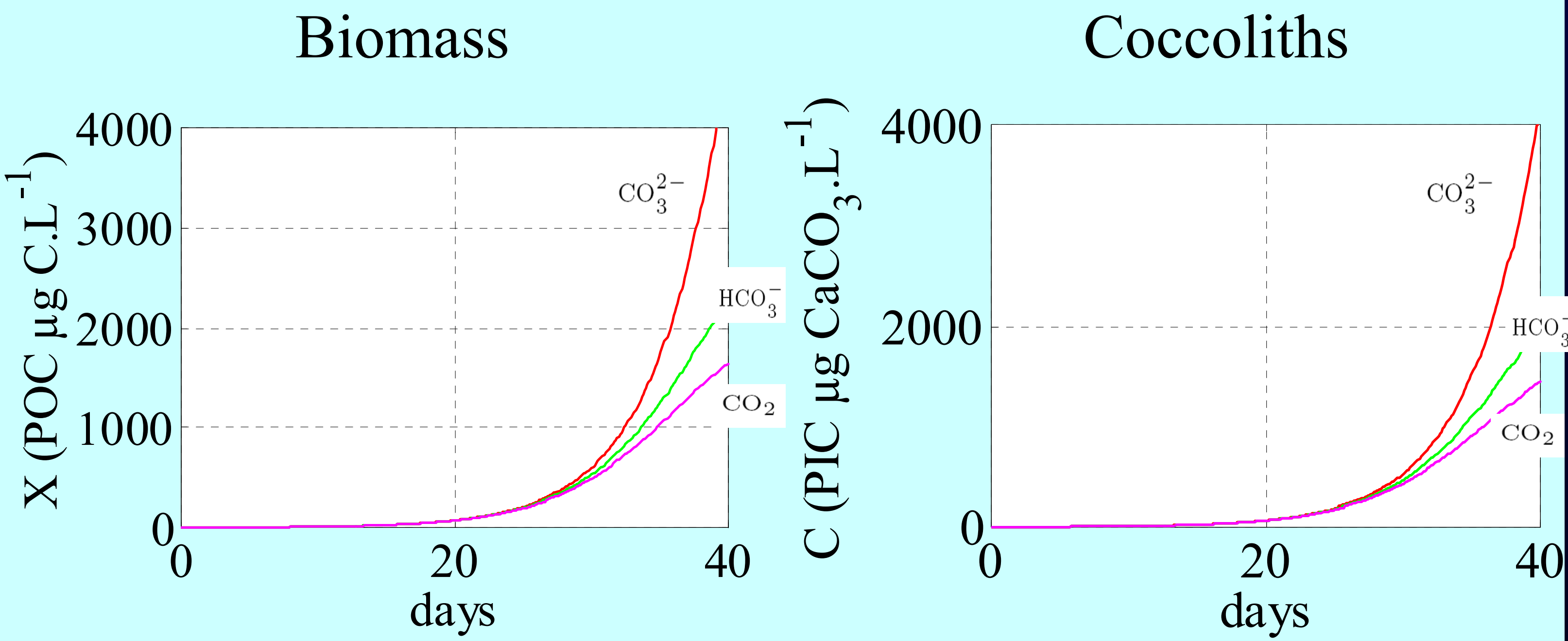
Decrease of DIC and Alkalinity (but CO_3^{2-} less affected)

Simulations of the 3 models



Decrease of pCO_2 during the bloom

Simulations of the 3 models



Total fixed carbon (compared to CO_3^{2-})

CI-HCO_3^- : -35%, CI-CO_2: -47%

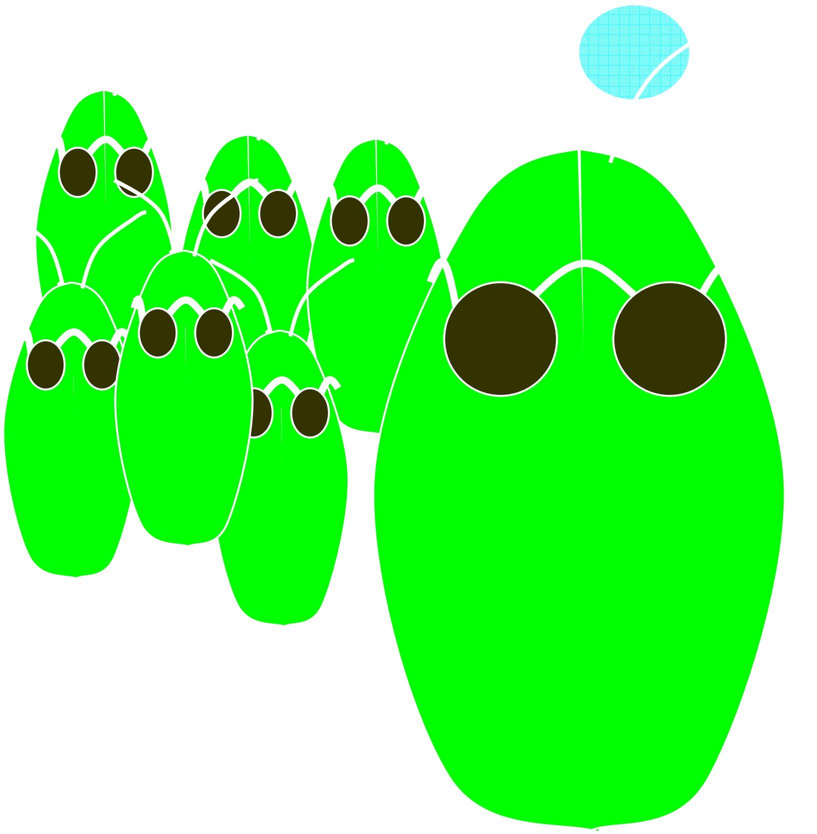
Models where growth and calcification are related to CO_3^{2-} or HCO_3^- show a strong slow down of the bloom.

CONCLUSION

- Transient and local phenomenon: cells may experience a broad range of pCO_2 values.

- Quantitative simulations can differ by up to 50% on carbon fluxes predictions

- For intense blooms, the right modelling of the regulating factor is capital



$$\begin{cases} \dot{x}_1 = u(s_i - x_1) - \rho(x_1)x_2 \\ \dot{x}_2 = (\mu(x_3) - u)x_2 \\ \dot{x}_3 = \rho(x_1) - \mu(x_3)x_3 \end{cases}$$