Modelling of the Marine Carbon Cycle

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### Outline

#### Part I – The Art of Modelling

Carbon cycle

- processes
- time scales
- modelling: why?
- Oeveloping a model: main principles
- Illustration: simple carbon cycle model
- Onclusions and perspectives

#### Part II – Marine Carbon Cycle Modelling

1 ...

### Global Carbon Cycle: Processes and Time Scales



- $\rightarrow$  Natural Processes with *long* time scales  $\rightarrow$  Natural Processes with *short* time scales
- $\rightarrow$  Human Perturbations

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### Model Development: General Principles

- Four stages
  - Problem Identification
  - 2 Model Formulation
  - Model Solution
  - Interpretation of the results
- Equal importance for each stage
- Not a uni-directional procedure

(following Boudreau, 1997)



- Formulation
  - processes to include / exclude
  - mathematical representation of the processes
  - approximations adopted
  - hypotheses made
- Solution
  - depends on the situation
- Interpretation
  - secondary results: consequences
  - model to be refined or to simplified

(following Boudreau, 1997)

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### Illustration: Application to an Actual Question

#### Question

How much CO<sub>2</sub> is released by volcanic and hydrothermal activity (metamorphic fluxes included)?

How does this compare to the amount of  $CO_2$  released by human activity?



- Time Scale: 1,000 10,000 years and more
  - little variability of volcanic and hydrothermal fluxes
  - biosphere at steady state : fluxes have no influence
  - burial of organic matter counter-balanced by kerogen carbon weathering: fluxes cancel out
  - sea-floor weathering poorly known and small: neglected
- Steady state

# Carbon Cycle Model: Processes Considered



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#### The Art of Modelling Marine Carbon Cycle Modelling Carbonate Chemistry in Seawater

• Carbonate system equilibria

$$\begin{array}{rcl} \mathsf{CO}_{2(\mathsf{aq})} + 2 \ \mathsf{H}_2\mathsf{O} & \rightleftharpoons & \mathsf{HCO}_3^- + \mathsf{H}_3\mathsf{O}^+ \\ & \mathsf{HCO}_3^- + \mathsf{H}_2\mathsf{O} & \rightleftharpoons & \mathsf{CO}_3^{2-} + \mathsf{H}_3\mathsf{O}^+ \end{array}$$

- Special roles played by particular species
  - atmospheric  $p_{CO_2} \longleftrightarrow [CO_{2(aq)}]_{surface}$
  - $CaCO_3$  burial  $\longleftrightarrow [CO_3^{2-}]_{deep-sea}$
- Speciation calculated from combinations
  - Dissolved Inorganic Carbon

$$C_{\rm T} = [{\rm CO}_{2({\rm aq})}] + [{\rm HCO}_3^-] + [{\rm CO}_3^{2-}]$$

• Total Alkalinity  $A_{\rm T} \simeq [{\rm HCO}_3^-] + 2[{\rm CO}_3^{2-}] + [{\rm B}({\rm OH})_4^-] + [{\rm OH}^-] - [{\rm H}_3{\rm O}^+]$ 

## Carbon Cycle Model: Fluxes Considered



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# Carbon Cycle Model: Conservation Equations

- $C_{\text{atm}}$  : total amount of C in the atmosphere
- $C_{\text{oce}}$  : total amount of C in the ocean
- $C_{atm} + C_{oce} = C$
- A : total amount of alkalinity in the ocean

$$\frac{d\mathbf{C}_{atm}}{dt} = C_{vol} - C_{sil-a} - C_{car-a} + C_{o\rightarrow a} - C_{a\rightarrow o}$$

$$\frac{d\mathbf{C}_{oce}}{dt} = C_{hyd} + C_{sil-a} + C_{car-a} + C_{car-r} - C_{o\rightarrow a} + C_{a\rightarrow o} - C_{sed}$$

$$\frac{d\mathbf{C}_{atm}}{dt} + \frac{d\mathbf{C}_{oce}}{dt} = \frac{d\mathbf{C}}{dt} = C_{hyd} + C_{vol} + C_{car-r} - C_{sed}$$

$$\frac{d\mathbf{A}}{dt} = A_{sil} + A_{car} - A_{sed}$$

# Typical Weathering Reactions for Silicate Minerals

• Dissolution of albite with precipitation of kaolinite

$$2 \operatorname{NaAlSi}_{3}O_{8} + 2 \operatorname{CO}_{2} + 11 \operatorname{H}_{2}O \longrightarrow$$
  
Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> + 2 Na<sup>+</sup> + 2 HCO<sub>3</sub><sup>-</sup> + 4 H<sub>4</sub>SiO<sub>4</sub>

• Dissolution of anorthite with precipitation of kaolinite

$$CaAl_{2}Si_{2}O_{8} + 2CO_{2} + 3H_{2}O \longrightarrow$$
$$Al_{2}Si_{2}O_{5}(OH)_{4} + Ca^{2+} + 2HCO_{3}^{-}$$

### • Dissolution of microcline with precipitation of pyrophillite

$$2 \text{KAlSi}_{3}\text{O}_{8} + 2 \text{CO}_{2} + 6 \text{H}_{2}\text{O} \longrightarrow$$
$$\text{Al}_{2}\text{Si}_{4}\text{O}_{10}(\text{OH})_{2} + 2 \text{K}^{+} + 2 \text{HCO}_{3}^{-} + 2 \text{H}_{4}\text{SiO}_{4}$$

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Typical Weathering Reactions for Silicate Minerals

• Dissolution of chlorite with precipitation of kaolinite

$$Mg_5Al_2Si_3O_{10} + 10CO_2 + 5H_2O \longrightarrow$$
$$Al_2Si_2O_5(OH)_4 + 5Mg^{2+} + 10HCO_3^- + H_4SiO_4$$

• Dissolution of microcline with precipitation of gibbsite

$$\begin{array}{l} \mathsf{KAISi}_3\mathsf{O}_8 + \mathbb{C}\mathsf{O}_2 + 4\,\mathsf{H}_2\mathsf{O} \longrightarrow \\ \mathsf{AI}(\mathsf{OH})_3 + \mathsf{K}^+ + \mathsf{H}\mathbb{C}\mathsf{O}_3^- + \mathsf{H}_4\mathsf{SiO}_4 \end{array}$$

## Sources and Sinks of DIC and TA in the Ocean

• Sources : continental weathering

• carbonate rocks: congruent dissolution

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^{-}$$

• silicate rocks: incongruent dissolution

silicate mineral +  $b CO_2$  + water  $\longrightarrow$ secondary minerals + cations +  $b HCO_3^- + s H_4SiO_4$ 

• Sinks : burial of biogenic carbonates

$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3 + CO_2 + H_2O$$

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Global Balance of the Ocean-Atmosphere System

• Relationships between carbon and alkalinity fluxes

$$C_{car-r} = C_{car-a}$$

$$A_{sil} = C_{sil-a}$$

$$A_{car} = C_{car-a} + C_{car-r} = 2 C_{car-r}$$

$$A_{sed} = 2 C_{sed}$$

• Upon introduction into the C et A balance equations:

$$\frac{d\mathbf{C}}{dt} = C_{\text{hyd}} + C_{\text{vol}} + C_{\text{car}-r} - C_{\text{sed}}$$
$$\frac{d\mathbf{A}}{dt} = A_{\text{sil}} + A_{\text{car}} - A_{\text{sed}}$$

# Carbon Cycle Model: Resolution

$$\frac{d\mathbf{C}}{dt} = C_{\text{hyd}} + C_{\text{vol}} + C_{\text{car}-r} - C_{\text{sed}}$$
$$\frac{d\mathbf{A}}{dt} = C_{\text{sil}-a} + 2C_{\text{car}-r} - 2C_{\text{sed}}$$

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• Steady state conditions:  $\Delta t > 10^6 \, {
m yr}$ 

$$\frac{d\mathbf{C}}{dt} = 0$$
 et  $\frac{d\mathbf{A}}{dt} = 0$ 

#### • Accordingly, the balance equations for C et A become

$$C_{\rm hyd} + C_{\rm vol} + C_{\rm car-r} - C_{\rm sed} = 0 \qquad (1)$$

$$C_{\rm sil-a} + 2 C_{\rm car-r} - 2 C_{\rm sed} = 0 \qquad (2)$$

• Finally, equation  $(1) - \frac{1}{2} \times$  equation (2) yields

$$C_{\text{hyd}} + C_{\text{vol}} = \frac{1}{2} C_{\text{sil}-\text{a}}$$

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# Carbon Cycle Model: Resolution

• Initial problem reduced to:  $C_{sil-a} = ?$ 

$$C_{\rm riv} = \underbrace{\underbrace{C_{\rm sil-a} + C_{\rm car-a}}_{32\%} + \underbrace{C_{\rm car-r}}_{34\%}$$

- Riverine  $HCO_3^-$  data analysis total amount: 31,6 37,7  $\times$  10<sup>12</sup> mol $HCO_3^-$  per year
  - 66% stem from the atmosphere
- Hence:

$$C_{\rm sil-a} = 0.32 \times C_{\rm riv}$$

and thus

$$C_{\text{hyd}} + C_{\text{vol}} = 0.16 \times C_{\text{riv}}.$$

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Solution and Interpretation

#### Result

Since

$$C_{\rm riv} = (31.6 - 37.7) \times 10^{12} \, {\rm mol} \, {\rm C/yr},$$

we find that

$$C_{\rm hyd} + C_{\rm vol} = (5.1 - 6.0) \times 10^{12} \, {\rm mol} \, {\rm C/yr}$$

# Solution and Interpretation

#### Interpretation

- Comparison with anthropogenic CO<sub>2</sub> emissions
- Secondary result: sedimentary flux C<sub>sed</sub>

$$C_{sed} = C_{hyd} + C_{vol} + C_{car-r} \quad (equation (1))$$
  
=  $\frac{1}{2}C_{sil-a} + C_{car-r}$   
=  $\frac{1}{2}C_{sil-a} + \frac{1}{2}C_{car-a} + \frac{1}{2}C_{car-r}$   
=  $\frac{1}{2}C_{riv}$ 

• Hence:

$$C_{
m sed} ~=~ (15.8 - 18.9) imes 10^{12} \, 
m mol \, C/
m an$$

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## Solution and Interpretation



	Coal	Oil	Gas	Cement	Flaring	Total
1850	4.5	0.0	0.0	0.0	0.0	4.5
1900	42.9	1.3	0.3	0.0	0.0	44.5
1950	89.9	35.3	8.1	1.5	1.9	135.8
2000	197.5	234.8	107.3	18.8	4.0	562.5
2010	317.3	259.9	141.0	37.3	6.1	761.6

Units: Tmol C/yr (original data in Tg C/yr). Data sources: Boden et al. (2011), for years before 2008; Boden and Blasing (2012) for 2009–2010 (preliminary).

# Carbon Cycle: Present-day and Pre-industrial



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### Summary of Part I

- Geochemical Carbon Cycle: complex system
  - $\Rightarrow$  quantitative study requires models
- Four stages for development of a model
  - Identification of the problem
  - Pormulation of the model
  - 8 Resolution of the model
  - Interpretation of the results
- Illustration on an concrete example



#### Part I – The Art of Modelling

#### Part II – Marine Carbon Cycle Modelling

- Marine Carbon Cycle Modelling: why?
- Marine Carbon Cycle: Global Features
- **③** Types of Models
- Outline of a Typical Plankton Model
- Sesults

# Marine Carbon Cycle Modelling: Why?

- CO\_2 uptake:  $\simeq$  25–35% of human-released atmospheric CO\_2 absorbed by the oceans
- biological activity responsible for 80% of the vertical DIC gradient (Six and Maier-Reimer, 1996)
- seasonal pCO<sub>2</sub> times series strongly influenced by biological processes
- paleoclimatic records derived from biogenic sediments: interpreting them requires understanding of how they form
- understanding carbon cycle variations in the deep past

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Marine Carbon Cycling: Global Features

#### Looking at the oceans from above

• surface ocean  $\Delta p CO_2$  (Takahashi et al., 2009)

#### Looking underneath

• sediment types and their distributions

#### Opening it up

- vertical profiles
- thermohaline circulation
- geochemical separation Atlantic vs. Indian and Pacific



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# Sea-floor and Surface Sediments: Bathymetry





### Sea-floor and Surface Sediments: Carbonate



Source: Sarmiento and Gruber (2006)

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Source: Sarmiento and Gruber (2006)

# Sea-floor and Surface Sediments: Opal



Source: Sarmiento and Gruber (2006)

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# Surface Sediment Composition in Summary

- Carbonate
  - distribution linked to depth of the sea-floor below sea-level: sediments at great depth are devoid of carbonate
  - up to 90% on mid-ocean ridges
- Organic Carbon
  - generally 1-2%, locally up to 10%
  - organic carbon oxidation plays important role for carbonate dissolution (source of CO<sub>2</sub>, pore water acidification)
- Opal
  - abundant in the Southern Ocean (Opal Belt)
  - abundant in the Eastern Equatorial Pacific
- Non biogenic
  - clay minerals (*Red Clay* deep-sea sediments)
  - quartz (aeolian input, detrital)
  - volcanic ash and authigenic minerals

## Carbon Cycle: Present-day and Pre-industrial



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# **DIC** Gradients



## Origin of DIC Gradients in the Ocean





- $Pump \longrightarrow$  transport against a concentration gradient
- DIC low in euphotic zone, high at depth
- Organic production in euphotic zone fuelled by upwelled macronutrients (phosphate, nitrate)
- Effects on atmospheric CO<sub>2</sub> (Broecker and Peng, 1993)
  - shut-down of organic production in the euphotic zone (*Strangelove Ocean*):  $pCO_2 = 470 ppm$
  - complete consumption of all upwelled nutrients:  $\ensuremath{\mathsf{pCO}_2}=150\,\ensuremath{\mathsf{ppm}}$

## Gradients of Dissolved Oxygen



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# Gradients of Phosphate



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# The Carbonate (Counter)Pump

- For every 10 moles of carbon that get exported as organic carbon about 1 mol gets exported as carbonate carbon
- Rain Ratio: carbonate-C/organic-C
  - about 0.1 on average
  - close to 0 at high latitudes: little carbonate production, but rather opal (siliceous) production instead
  - typically 0.3 at low latitudes
- Increasing carbonate export to the deep ocean makes CO<sub>2</sub> increase as well
- May be counter-intuitive at first, but ...

 $\mathsf{Ca}^{2+} + 2 \,\mathsf{HCO}_3^- \to \mathsf{CaCO}_3 + \mathsf{CO}_2 + \mathsf{H}_2\mathsf{O}$ 

• Acts mainly through alkalinity changes

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Gradients of Alkalinity



N• and S• – Northern and Southern part of  $\bullet$ 

- Box models: 1 15 boxes typically, 1 4 vertical layers, simple productivity flux expressions
- **Box-diffusion models**: similar horizontal resolution than box models, fine vertical resolution (generally > 50 levels)
- 3D models: horizontal resolution of the order of 2° to 3°, 30 unevenly spaced vertical levels and more, complex biogeochemical/ecosystem models with 2 5 nutrients, 2 4 plankton classes, etc.
- Earth system Models of Intermediate Complexity (EMICs): compromise on spatial resolution (coarser resolution, reduced dimensions), improve on feedback network

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## Box Model of the Ocean Carbon Cycle: MBM-MEDUSA



Munhoven (2007)

# Box Model of the Ocean Carbon Cycle: MBM-MEDUSA

- One-box atmosphere and ten-box ocean with prescribed hydrodynamics
- Tracers: pCO<sub>2</sub>, DIC, alkalinity, PO<sub>4</sub>, O<sub>2</sub>, <sup>13</sup>C, <sup>14</sup>C
- Biogeochemical fluxes
  - POM: proportional to PO<sub>4</sub> influx into surface boxes
  - carbonate: proportional to POC
  - calcite/aragonite: prescribed partitioning of carbonate
- Coupled to the sediment model MEDUSA for calcite, aragonite, POM, clay

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Box Model of the Ocean Carbon Cycle: MBM-MEDUSA



Munhoven (2007)

### **Box Models**

- Long-term simulation experiments are possible (up to millions of years)
- Prescribed hydrodynamics limit applicability
- Representation of complete feedback loop difficult or necessarily highly parametrised (e.g., no interactive climate modules in general, ...)
- Detailed analysis of response is possible
- More comprehensive exploration of the model parameter space than with other model types



- Attractive alternative to both box and 3D models
- Large variety
- Focus on atmospheric, oceanic and marine biogeochemical components

### Atmosphere (Ritz et al., 2011)

 2D single-layer Energy and Moisture Balance Model (36 × 36 grid cells)

#### Ocean

- $36 \times 36$  grid cells, 32 vertical levels
- frictional geostrophic balance model (Müller et al., 2006)

Ocean Biogeochemistry (Parekh et al., 2008)

- tracers: DIC, alkalinity, DOM, <sup>13</sup>C, <sup>14</sup>C, PO<sub>4</sub>, O<sub>2</sub>, iron and silicic acid
- Biogeochemical model with POM, opaline and carbonate shells (calcite, aragonite)

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#### Atmosphere

• 2D energy and moisture balance model (EMBM) after Weaver et al. (2001)

#### Ocean

- $36 \times 36$  grid with equal-area elements, 8 vertical levels
- reduced physics (frictional geostrophic) 3D-model, coupled to a dynamic-thermodynamic sea-ice model (Edwards and Marsh, 2005)

### **Ocean Biogeochemistry**

- tracers: DIC, alkalinity, PO<sub>4</sub>, O<sub>2</sub>,  $^{13}$ C and  $^{14}$ C, Si, ...
- reference: Ridgwell et al. (2007), Ridgwell and Hargreaves (2007)

### Atmosphere (Weaver et al., 2001)

 3.6° (zonal) by 1.8° (meridional) Energy and Moisture Balance Model

### Ocean

- GFDL Modular Ocean Model (MOM) version 2.2
- 3.6° (zonal) by 1.8° (meridional), 19 unequally spaced levels, from 50 m at the surface to 518 m at the deepest level (bottom at 5396 m).

### Ocean Biogeochemistry (Schmittner et al., 2008)

- tracers: DIC, alkalinity, NO<sub>3</sub>, PO<sub>4</sub>, O<sub>2</sub>
- NPZD model with two phytoplankton classes, carbonate



### Atmosphere

• quasi-geostrophic model ECBilt (T21L3 resolution, i.e.,  $64 \times 32$  Gaussian grid) by Opsteegh et al. (1998)

### Ocean

- CLIO3, a primitive-equation, free-surface Oceanic General Circulation Model coupled to a thermodynamic-dynamic sea-ice model (Goosse and Fichefet, 1999)
- $3^{\circ} \times 3^{\circ}$ , 20 vertical levels

### Ocean Biogeochemistry

- LOCH ocean carbon cycle model (Mouchet, 2011)
- tracers: DIC, alkalinity, PO<sub>4</sub>, O<sub>2</sub>, Si, DOM (DOP), <sup>13</sup>C, <sup>14</sup>C,
- biogeochemical model with POM, calcite, aragonite,

#### Atmosphere

 2.5-dimensional statistical-dynamical model (Petoukhov et al., 2000; Ganopolski et al., 2001)

#### Ocean

- multi-basin zonally averaged model (after Stocker et al., 1992)
- $2.5^{\circ}$  latitudinal resolution, 11 uneven vertical levels with an upper mixed layer of 50 m thickness

#### Ocean Biogeochemistry (Brovkin et al., 2002)

- representation of biological processes based upon the model of Six and Maier-Reimer (1996), extended to two DOM types
- tracers: PO<sub>4</sub>, O<sub>2</sub>, alkalinity, DIC, fast DOM, slow DOM, <sup>13</sup>C and <sup>14</sup>C for DIC and DOM



- Variety of EMIC configurations: 2D multi-basin ocean models, various horizontal and vertical resolutions
- Similarity of carbon cycle models: biogeochemical export flux models (*export* out of the euphotic layer)
- Illustration of principles and ideas: the plankton model of Six and Maier-Reimer (1996)

### **Basic Plankton Model**

- Following developments of Six and Maier-Reimer (1996)
- Export production model
- In conjunction with a transport model providing the distribution of advective, diffusive and convective velocities
- Five compartments: extended NPZD model
  - **N**utrients
  - Phytoplankton
  - Zooplankton (grazers, herbivores and carnivores)
  - Detritus (dead phytoplankton and zooplankton, faecal pellets) also called Particulate Organic Matter (POM)
  - Dissolved Organic Matter



$$\frac{dP}{dt} = \text{transport}_P$$

 $+\operatorname{growth}_{P}-\operatorname{grazing}_{P\operatorname{by}Z}-\operatorname{death}_{P}-\operatorname{DOM}_{-\operatorname{exudation}_{P}}$ 

 growth<sub>P</sub> (photosynthesis) depends on P itself and is limited by nutrient (N) availability

$$\mathsf{growth}_P = \mu_P(T, L) \times P \times \frac{N}{N_0 + N}$$

- μ<sub>P</sub>(T,L) maximum growth rate, depends on temperature (T) and limited by incoming light (L)
- growth<sub>P</sub> vanishes below the euphotic zone (top 100 m)

## Phytoplankton (P)

$$\frac{dP}{dt} = \text{transport}_P$$

 $+\operatorname{growth}_{P}-\operatorname{grazing}_{P\operatorname{by}Z}-\operatorname{death}_{P}-\operatorname{DOM}_{-\operatorname{exudation}_{P}}$ 

 grazing<sub>PbyZ</sub> (the grazing loss from herbivores, i.e., zooplankton) depends on the zooplankton concentration (Z, incl. herbivores and carnivores), and is limited by P

$$\operatorname{grazing}_{P\operatorname{by} Z} = g(T) \times Z \times \frac{P - P_{\min}}{P_0 + P}$$

- $P_{\min}$  needed to avoid that phytoplankton goes extinct
- g(T) grazing rate, (weakly) depends on temperature

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Phytoplankton (P)	

$$\frac{dP}{dt} = \text{transport}_P$$

 $+\operatorname{growth}_{P}-\operatorname{grazing}_{P\operatorname{by}Z}-\operatorname{death}_{P}-\operatorname{DOM}_{-\operatorname{exudation}_{P}}$ 

• death<sub>P</sub> — death rate of phytoplankton (by senescence), set to

$$\mathsf{death}_P = d_P(P - P_{\mathsf{min}})$$

assumed to be exported as POM out of the euphotic layer

DOM\_exudation<sub>P</sub> — exudation rate of DOM by phytoplankton

$$DOM_{exudation_P} = x_P(P - P_{min})$$

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### Monod Rate Law



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$$\frac{dZ}{dt} = \text{transport}_Z$$

 $+ \operatorname{growth}_{Z} - \operatorname{death}_{Z} - \operatorname{DOM}_{-}\operatorname{exudation}_{Z}$ 

- growth<sub>Z</sub> results from phytoplankton ingestion
  - only a fraction  $\varepsilon_{her}$  of "grazing<sub>PbyZ</sub>" is ingested, the rest  $(1 - \varepsilon_{her})$  is egested as faecal pellets (to POM)
  - only a fraction  $\gamma_Z$  of the ingested phytoplankton contributes to growth, the rest  $(1 \gamma_Z)$  of the ingested phytoplankton is lost by metabolism (to N and DIC)



 $DOM_{exudation_Z} = x_Z(Z - Z_{min})$ 

# Dissolved Organic Matter (DOM)

 $\frac{d\text{DOM}}{dt}$ 

$$=$$
 transport<sub>DOM</sub>

 $+ DOM_{exupt} + DOM_{exupt} - remin_{DOM}$ 

- sources: exudation of DOM by phyto- and zooplankton
- remin<sub>DOM</sub> remineralization rate of DOM by bacterial activity, set to

$$\mathsf{remin}_{\mathsf{DOM}} = \mathsf{r}_{\mathsf{DOM}}(\mathsf{N}) imes \mathsf{DOM}$$

where

$$r_{\text{DOM}}(N) = r_{\text{DOM0}} imes rac{N}{N_{\text{remin}} + N}$$

reflecting the fact that bacteria require nutrients

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Detritus (D or POM)

$$\frac{dD}{dt} = \frac{d}{dz} \operatorname{sinking}_{D} - \operatorname{remin}_{D}(O_{2})$$

- *D* fed by the *Total Particle Production* (TPP) in the euphotic zone, i.e., the faecal pellets and *P*-detritus produced there
- in the euphotic zone (above 100 m):  $D \equiv 0$
- below the euphotic zone (below 100 m):

sinking<sub>D</sub> = TPP × 
$$\left(\frac{z}{100 \text{ m}}\right)^{-0.8}$$

following the particle flux profile of Suess (1980), where

$$\mathsf{TPP} = \int_0^{100\,\mathsf{m}} (\mathsf{death}_P + \mathsf{egest}_{P\,\mathsf{by}\,Z} + \mathsf{export}_Z) dz$$

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# Detritus (D or POM)

$$\frac{dD}{dt} = \frac{d}{dz} \operatorname{sinking}_{D} - \operatorname{remin}_{D}(O_{2})$$

• remin<sub>D</sub>(O<sub>2</sub>) — oxic remineralization rate, limited by a maximum rate  $r_{D0} \times D$  and by the available dissolved O<sub>2</sub>.

$$\frac{dN}{dt} = \text{transport}_{N}$$
  
- growth<sub>P</sub> + metabol<sub>P by Z</sub> + metabol<sub>Z by Z</sub>  
+ remin<sub>DOM</sub> + remin<sub>D</sub>

 nutrients linked to carbon content of different compartments and fluxes by constant Redfield-type ratios

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### **Redfield** Ratios

- Redfield (1934): mean biomass N:P ratio of plankton  $\simeq 16$
- Redfield, Ketchum, and Richards (1963): mean biomass C:P ratio of plankton  $\simeq 106$
- Suggests idealized composition

 $OM = (CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ 

and idealized "chemical reaction" for the formation of plankton biomass

 $106\,\text{CO}_2 + 16\,\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\,\text{H}_2\text{O} \rightarrow \text{OM} + 138\,\text{O}_2$ 

- Redfield ratio C:N:P:O<sub>2</sub> = 106:16:1:-138
- Planktonic N:P ratio close to seawater  $NO_3^-:PO_4^{3-}$  ratio

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**Redfield** Ratios



### **Redfield** Ratios

Several possible pathways of OM remineralization

• oxic respiration

 $\mathsf{OM} + 138\,\mathsf{O}_2 \to 106\,\mathsf{CO}_2 + 16\,\mathsf{HNO}_3 + \mathsf{H}_3\mathsf{PO}_4 + 122\,\mathsf{H}_2\mathsf{O}$ 

• partial denitrification

 $\mathsf{OM} + 84.8\mathsf{HNO}_3 \rightarrow 106\,\mathsf{CO}_2 + 42.4\,\mathsf{N}_2 + 16\,\mathsf{NH}_3 + \mathsf{H}_3\mathsf{PO}_4 + 148.4\,\mathsf{H}_2\mathsf{O}$ 

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• and others: complete denitrification,  $Mn^{2+}$  reduction, Fe reduction,  $SO_4^{2-}$  reduction, methanogenesis

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## Shells in the Export Production

- Export flux (TPP) must be completed to include hard parts (carbonate and opaline shells)
- Competitive advantage of silicate-builders over carbonate-builders (Maier-Reimer, 1993)
- Silicate shell (opal) production (Maier-Reimer et al., 2005)

$$\mathsf{export}_{\mathsf{sil}} = \mu_{\mathsf{sil}} \times \mathsf{TPP} \times \frac{[\mathsf{Si}]}{[\mathsf{Si}]_0 + [\mathsf{Si}]}$$

• Carbonate shell export production (Maier-Reimer et al., 2005)

$$\mathsf{export}_{\mathsf{carb}} = \mu_{\mathsf{carb}} imes \mathsf{TPP} imes rac{[\mathsf{Si}]_0}{[\mathsf{Si}]_0 + [\mathsf{Si}]}$$

## Further Details For the Hungry

- Limiting nutrient: phosphate
- Only processes outlined: actual implementation needs consideration of units linking the different compartments and allowing conversion between them
- Light limitation depends on latitude, season, ice-cover, possibly on auto-shading, ...
- Phytoplankton growth in the Six and Maier-Reimer model also dependent on mixed-layer depth

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New Developments

- Additional limiting nutrients: NO<sub>3</sub>, Fe, Si
- Opaline and carbonate shells
- Calcite and aragonite
- Suboxic remineralization of detritus (e.g., by nitrate reduction)
- PISCES (*Pelagic Interaction Scheme for Carbon and Ecosystem Studies*, Aumont and Bopp, 2006):
  - Twenty-four compartments: two living phytoplankton size classes, two living zooplankton size types, three non-living compartments, ...
  - Five modelled limiting nutrients for phytoplankton growth: Nitrate and Ammonium, Phosphate, Silicate and Iron
- PlankTOM (Dynamic Green Ocean Project): marine ecosystem dynamics based on *Plankton Functional Types* (see Le Quéré et al., 2005)

# CLIMBER-2: Present-Day Phosphate



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# CLIMBER-2: Present-Day Oxygen



#### Observation

Model

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# CLIMBER-2: Present-Day Dissolved Inorganic Carbon



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# CLIMBER-2: Present-Day Total Alkalinity



Observation

Model

## Bern3D: Opal and Carbonate Export Fluxes, DIC



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