Continent-Ocean Interaction: Role of Weathering

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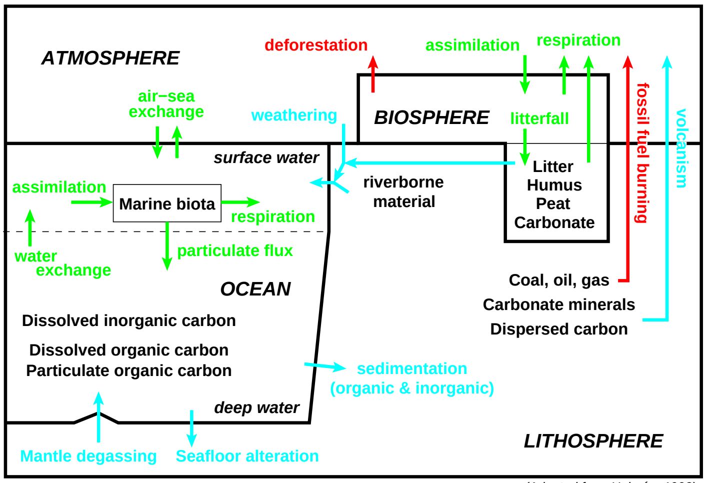
Organisation of the Lecture

1. Carbon cycle
   - processes
   - time scales
   - modelling: why?
2. Model development: general principles
3. Illustration: simple carbon cycle model
4. Conclusions and outlook

Carbon Cycle: Processes and Time Scales



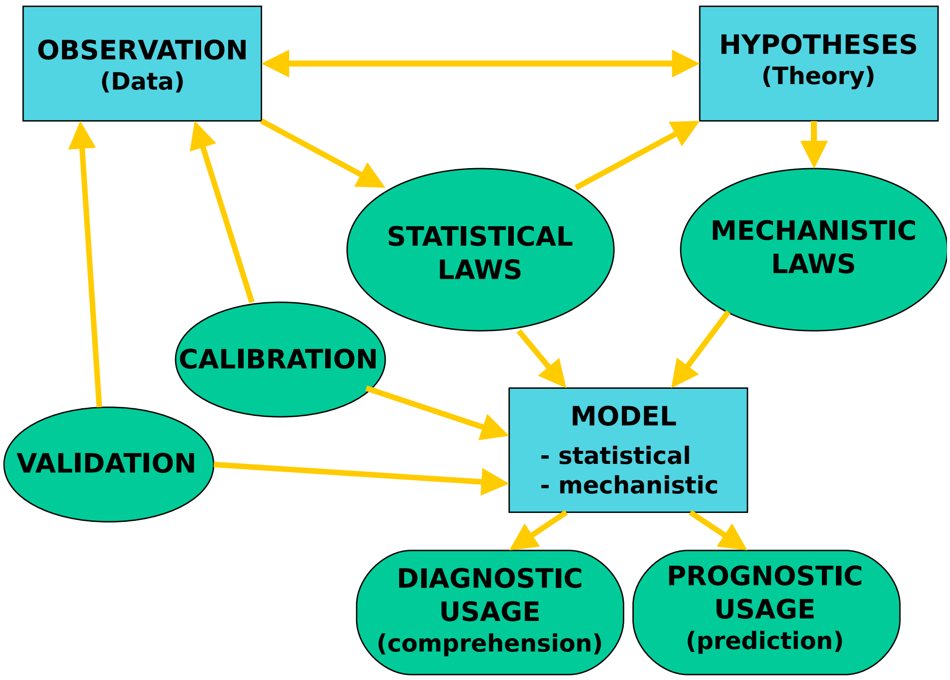
(Adapted from Holmén, 1992)

→ Natural Processes with *long* time scales

→ Natural Processes with *short* time scales

→ Human Perturbations

Modelling



Model Development: General Principles

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

(following Boudreau, 1997)

Development of a Model

- 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)

Illustration: Application to an Actual Question

Question

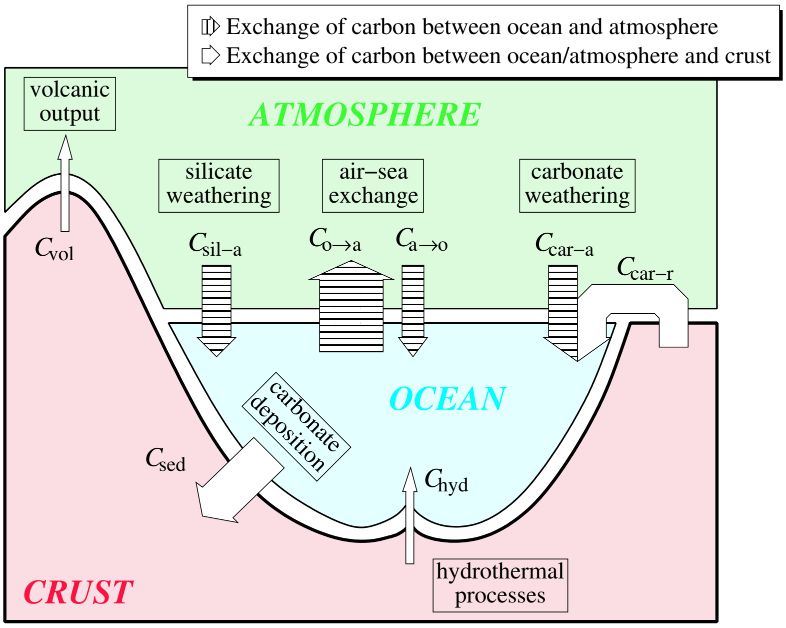
How much CO_2 is released by volcanic and hydrothermal activity (metamorphic fluxes included)?

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

Model Formulation: Hypotheses and Simplifications

- 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



Carbonate Chemistry in Seawater

- Carbonate system equilibria

$$CO_{2(aq)} + 2\ H_2O \rightleftharpoons HCO_3^- + H_3O^+$$
$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

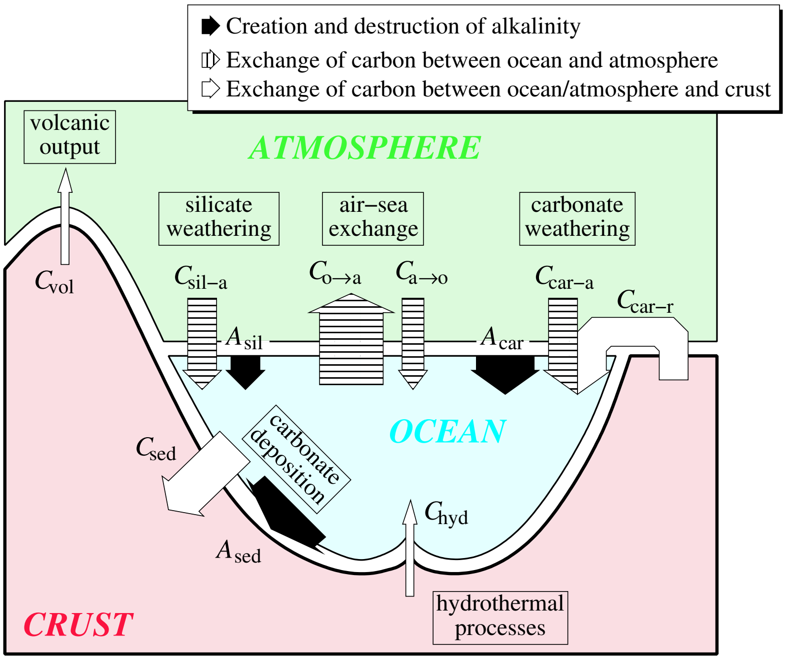
- Special roles played by particular species
  - atmospheric $p_{CO_2} \longleftrightarrow [CO_{2(aq)}]_{surface}$
  - $CaCO_3$ burial $\longleftrightarrow [CO_3^{2-}]_{deep-sea}$
- Speciation calculated from combinations
  - Dissolved Inorganic Carbon

$$C_T = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}]$$

  - Total Alkalinity

$$A_T \simeq [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H_3O^+]$$

Carbon Cycle Model: Fluxes Considered



Carbon Cycle Model: Conservation Equations

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

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

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

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

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

Typical Weathering Reactions for Silicate Minerals

- Dissolution of albite with precipitation of kaolinite

$$2\,NaAlSi_3O_8 + 2\,CO_2 + 11\,H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + 2\,Na^+ + 2\,HCO_3^- + 4\,H_4SiO_4$$

- Dissolution of anorthite with precipitation of kaolinite

$$CaAl_2Si_2O_8 + 2\,CO_2 + 3\,H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2\,HCO_3^-$$

- Dissolution of microcline with precipitation of pyrophillite

$$2\,KAlSi_3O_8 + 2\,CO_2 + 6\,H_2O \longrightarrow Al_2Si_4O_{10}(OH)_2 + 2\,K^+ + 2\,HCO_3^- + 2\,H_4SiO_4$$

Typical Weathering Reactions for Silicate Minerals

- Dissolution of chlorite with precipitation of kaolinite

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

- Dissolution of microcline with precipitation of gibbsite

$$KAlSi_3O_8 + CO_2 + 4\,H_2O \longrightarrow Al(OH)_3 + K^+ + HCO_3^- + H_4SiO_4$$

Sources and Sinks of DIC and TA in the Ocean

- Sources : continental weathering
  - carbonate rocks: *congruent* dissolution

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

  - silicate rocks: *incongruent* dissolution

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

- Sinks : burial of biogenic carbonates

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

Cycles to the Carbon Cycle: Ca, K, Mg, Na, Si

Residence times of coupled cycles' elements in the oceans

Element	τ_{oc} (10^6 yr)	Note
Ca	1	
Mg	13	
K	12	
Na	83	
Si	0.02	
DIC	0.07	*org. and inorg. sinks*
	0.10	*inorg. sinks only*
Alk	0.05	

Simplification: neglect K and Na contributions

- No significant K- or Na-carbonate depositions
- Only 5% of the total riverine HCO_3^- flux provided by Na- and K-silicate dissolution (Berner, 2004, based upon Berner and Berner, 1996)

  According to Gaillardet et al. (1999), this fraction is 19%, to be compared with 21% from Ca- and Mg-silicates
- This oceanic HCO_3^- source is counterbalanced by the HCO_3^- sink represented by authigenic Na- and K-mineral precipitation in marine sediments (*reverse weathering*, very slow process):

$$2\,K^+ + 3\,Al_2Si_2O_5(OH)_4 + 2\,HCO_3^- \longrightarrow 2\,KAl_3Si_3O_{10}(OH)_2 + 5\,H_2O + CO_2$$

Carbon Cycle – Silicate Cycle Coupling
Geochemical carbonate and silicate cycles

- Weathering of Ca- (or Mg-) carbonate

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

- Precipitation and sediment burial of carbonates

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

- Net balance:

$$—$$

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Carbon Cycle – Silicate Cycle Coupling

Geochemical carbonate and silicate cycles

- Weathering of Ca- (or Mg-) silicate

$$CaSiO_3 + 2\,CO_2 + 3\,H_2O \longrightarrow Ca^{2+} + H_4SiO_4 + 2\,HCO_3^-$$

- Precipitation and sediment burial of carbonate and opal

$$\begin{aligned} Ca^{2+} + 2\,HCO_3^- &\longrightarrow CaCO_3 + CO_2 + H_2O \\ H_4SiO_4 &\longrightarrow SiO_2 + 2\,H_2O \end{aligned}$$

- Net balance

$$CaSiO_3 + CO_2 \longrightarrow CaCO_3 + SiO_2$$

- Combined with reverse reaction (metamorphism)

$$CaSiO_3 + CO_2 \leftrightarrows CaCO_3 + SiO_2 \quad \textit{Urey's Reaction}$$

Global Balance of the Ocean-Atmosphere System

- Relationships between carbon and alkalinity fluxes

$$\begin{aligned} C_{car-r} &= C_{car-a} \\ A_{sil} &= C_{sil-a} \\ A_{car} &= C_{car-a} + C_{car-r} = 2\,C_{car-r} \\ A_{sed} &= 2\,C_{sed} \end{aligned}$$

- Upon introduction into the **C** et **A** balance equations:

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

Carbon Cycle Model: Resolution

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

Carbon Cycle Model: Resolution

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

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

- Accordingly, the balance equations for **C** et **A** become

$$C_{\mathrm{hyd}} + C_{\mathrm{vol}} + C_{\mathrm{car-r}} - C_{\mathrm{sed}} = 0 \qquad (1)$$
$$C_{\mathrm{sil-a}} + 2\,C_{\mathrm{car-r}} - 2\,C_{\mathrm{sed}} = 0 \qquad (2)$$

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

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

Carbon Cycle Model: Resolution

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

$$C_{\text{riv}} = \overbrace{\underbrace{C_{\text{sil}-\text{a}}}_{32\%}\ \Leftarrow\ + \underbrace{C_{\text{car}-\text{a}}}_{34\%}}^{66\%} + \overbrace{\underbrace{C_{\text{car}-\text{r}}}_{34\%}}^{\Rightarrow\ 34\%}$$

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

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

and thus

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

Solution and Interpretation

Result

Since

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

we find that

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

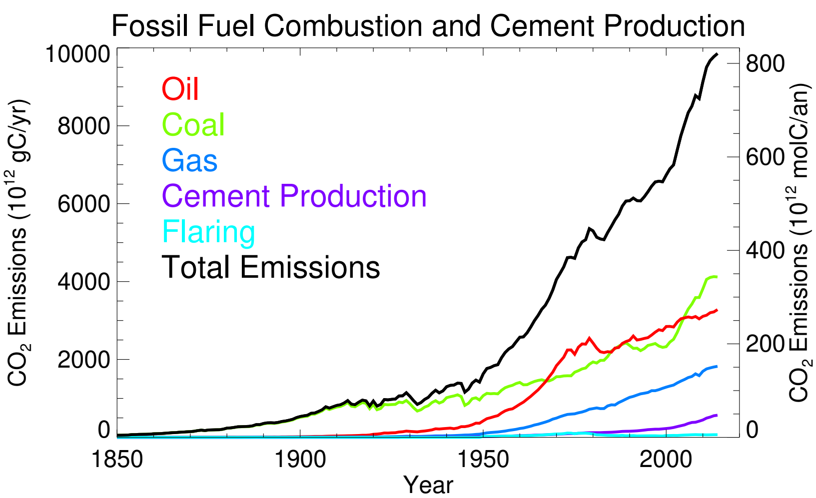
Interpretation

- Comparison with anthropogenic CO_2 emissions
- Secondary result: sedimentary flux C_{sed}

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

- Hence:

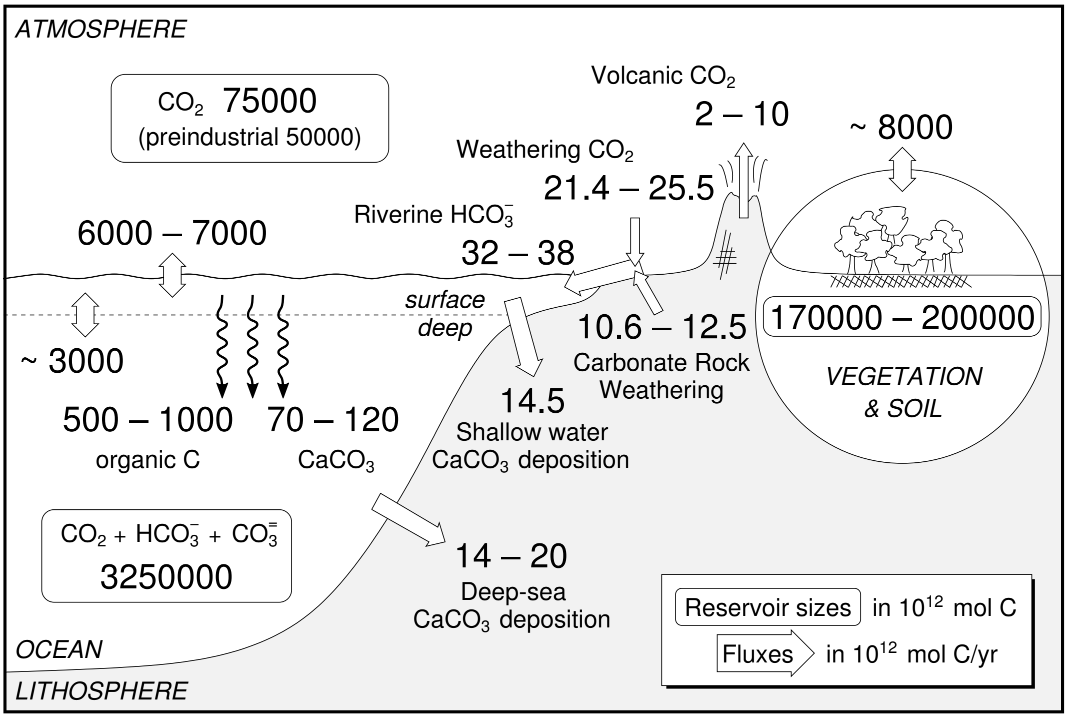
$$C_{sed} = (15.8 – 18.9) \times 10^{12}\,\text{mol C/an}$$



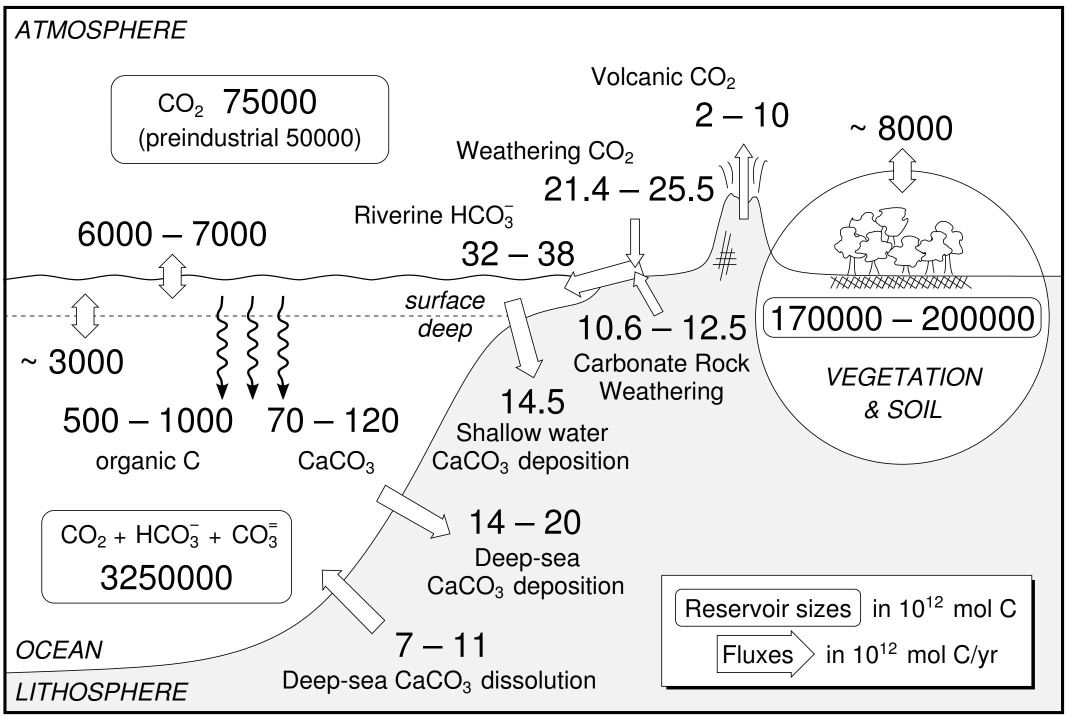
	Coal	Oil	Gas	Cement	Flaring	Total
1850	4.5	0.0	0.0	0.0	0.0	4.5
1900	42.9	1.3	0.3	0.0	0.0	44.5
1950	89.9	35.3	8.1	1.5	1.9	135.8
2000	197.5	234.8	107.3	18.8	4.0	562.5
2014	343.1	273.3	151.9	47.3	5.7	821.3

Units: Tmol C/yr (original data in Tg C/yr). Data sources: Boden et al. (2011).

Carbon Cycle: Present-day and Pre-industrial



Carbon Cycle: Present-day and Pre-industrial



Connecting the Carbon and Alkalinity Budgets

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

$$\frac{d\mathbf{A}}{dt} = C_{\mathrm{sil-a}} + 2\,C_{\mathrm{car-r}} - 2\,C_{\mathrm{sed}}$$

$$\frac{d\mathbf{A}}{dt} - 2 \times \frac{d\mathbf{C}}{dt} = C_{\mathrm{sil-a}} - 2 \times (C_{\mathrm{hyd}} + C_{\mathrm{vol}})$$

Basic Constraints of the System: Time Scales > 1 Myr

- $\tau_{\mathrm{carbon}} \simeq 100$ kyr
- $\tau_{\mathrm{alkalinity}} \simeq 50$ kyr
- Long time-scales (typically > 1 Myr):

  Global budgets of **C** and of **A** balanced

$$\left\{ \begin{array}{rcl} \overline{\frac{d\mathbf{A}}{dt}} & = & 0 \\ \overline{\frac{d\mathbf{C}}{dt}} & = & 0 \end{array} \right. \implies \overline{C_{\mathrm{sil-a}}} = 2 \times (\overline{C_{\mathrm{vol}} + C_{\mathrm{hyd}}})$$

Basic Constraints of the System: Time Scales < 1 Myr

On time scales of 10 – 100 kyr

- constraint fulfilled on average only ⇒ fluctuations possible
- classically, it has been assumed that hydrothermal and volcanic activity exhibit only small variability on these time scales

$$C_{hyd} + C_{vol} \cong \overline{C_{hyd} + C_{vol}} = \frac{1}{2}\,\overline{C_{sil-a}}$$

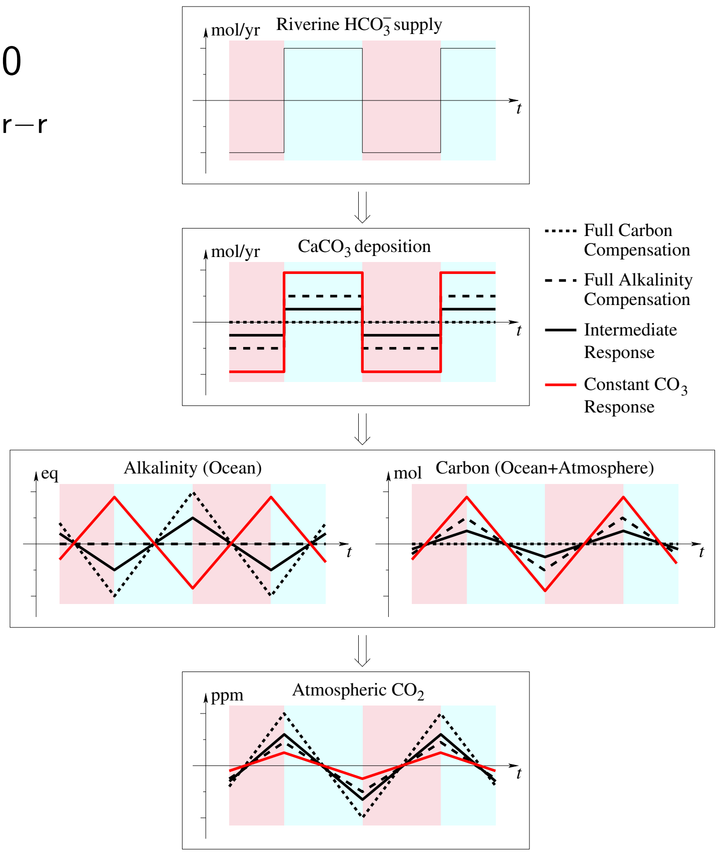
- Hence

$$\frac{d\mathbf{A}}{dt} - 2 \times \frac{d\mathbf{C}}{dt} = (C_{sil-a} - \overline{C_{sil-a}})$$

$$\frac{d\mathbf{A}}{dt} - 2 \times \frac{d\mathbf{C}}{dt} = \Delta C_{sil-a}$$

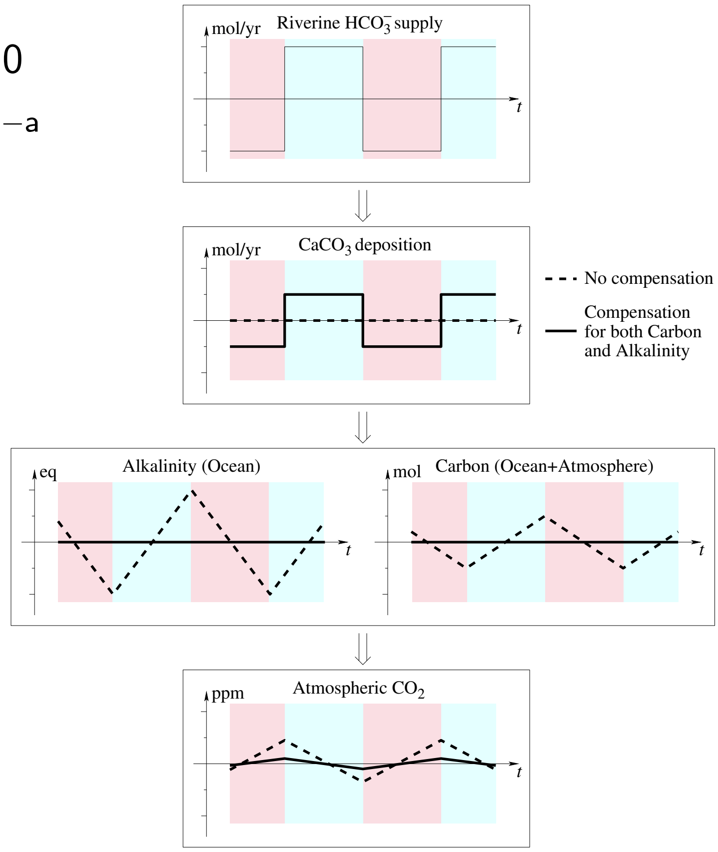
Sensitivity Analysis: Variable Silicate Weathering

$\Delta C_{hyd+vol} \equiv 0$
Constant C_{car-r}



Sensitivity Analysis: Variable Carbonate Weathering

$\Delta C_{hyd+vol} \equiv 0$
Constant C_{sil-a}



Sensitivity Analysis: How Does it Work in a Model?

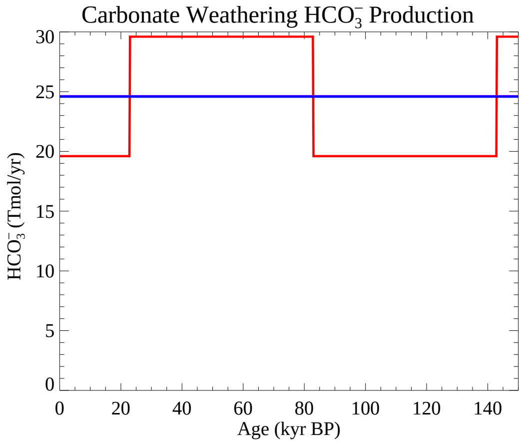
MBM – *Multi-Box Model* of ocean-atmosphere carbon cycle

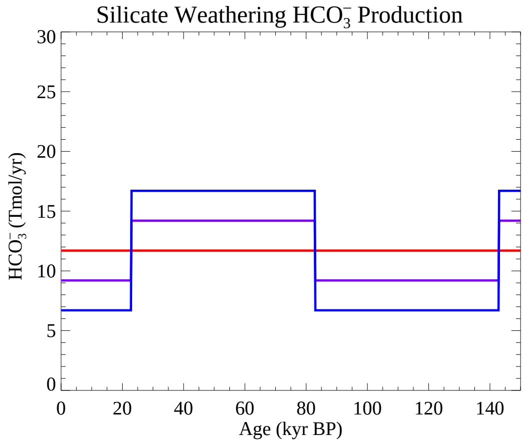
- ten oceanic and one atmospheric reservoirs
- realistic hypsometry
- fully coupled to . . . 304 copies of

MEDUSA *Model of Early Diagenesis in the Upper Sediment (A)*

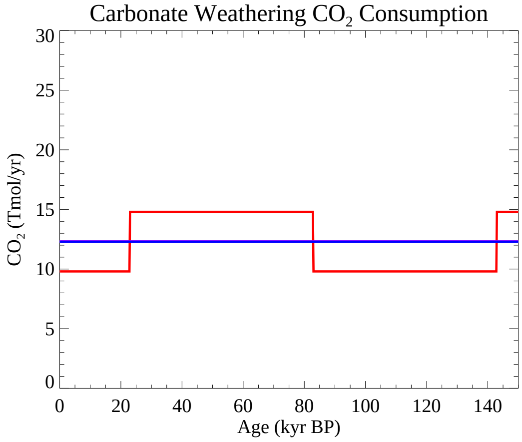
- bioturbated mixed-layer with 21 grid-points
  on top of a stack of thin layers (sediment core)
- solves time-dependent transport-reaction equations
- solids: calcite, aragonite, POM, clay
- solutes: CO_2, HCO_3^-, CO_3^{2-}, O_2
- fully bi-directional exchange between the two zones

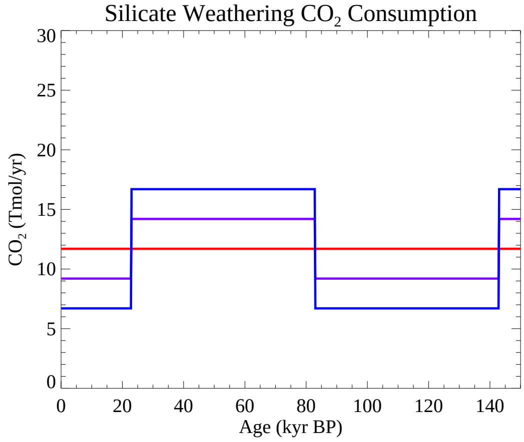
Bicarbonate Production Rate Scenarios



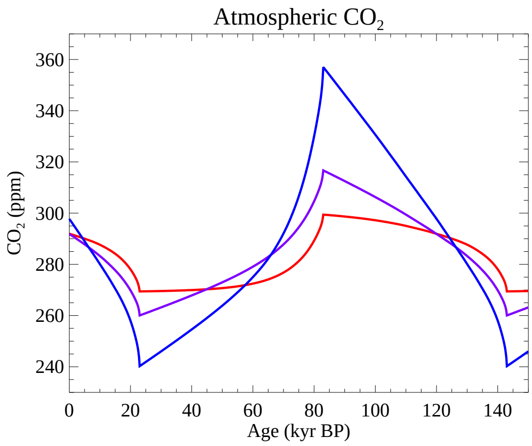


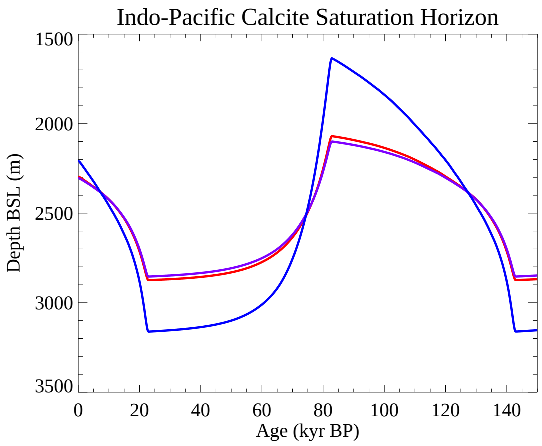
CO_2 Consumption Rate Scenarios





pCO_2 and Calcite Saturation Horizon Variations





Summary

- Geochemical Carbon Cycle: complex system
  - ⇒ quantitative study requires models
- Four stages for development of a model
  1. Identification of the problem
  2. Formulation of the model
  3. Resolution of the model
  4. Interpretation of the results
- Illustration on an actual example

References cited

T. A. Boden, G. Marland, and R. J. Andres. Global, regional, and national fossil-fuel CO_2 emissions (1751–2014) (v. 2017). Data base, Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge, TN, 2011. URL https://doi.org/10.3334/CDIAC/00001_V2017.

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