Continent-Ocean Interaction: Role of Weathering

Guy Munhoven

Institute of Astrophysics and Geophysics (Build. B5c)
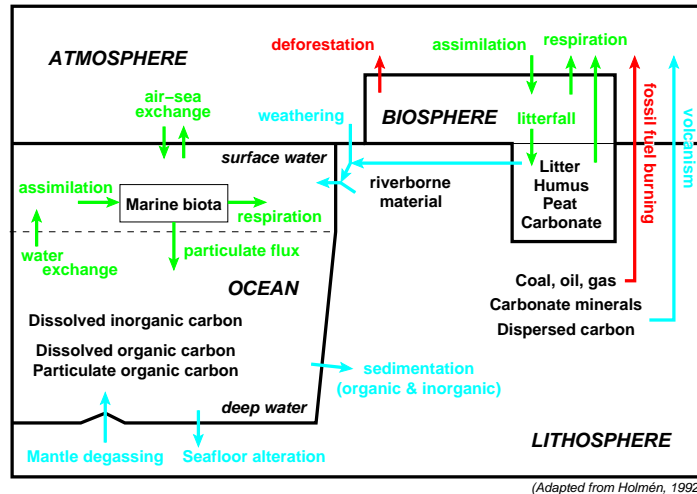Room 0/13
eMail: Guy.Munhoven@ulg.ac.be
Phone: 04-3669771

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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)

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

Modelling

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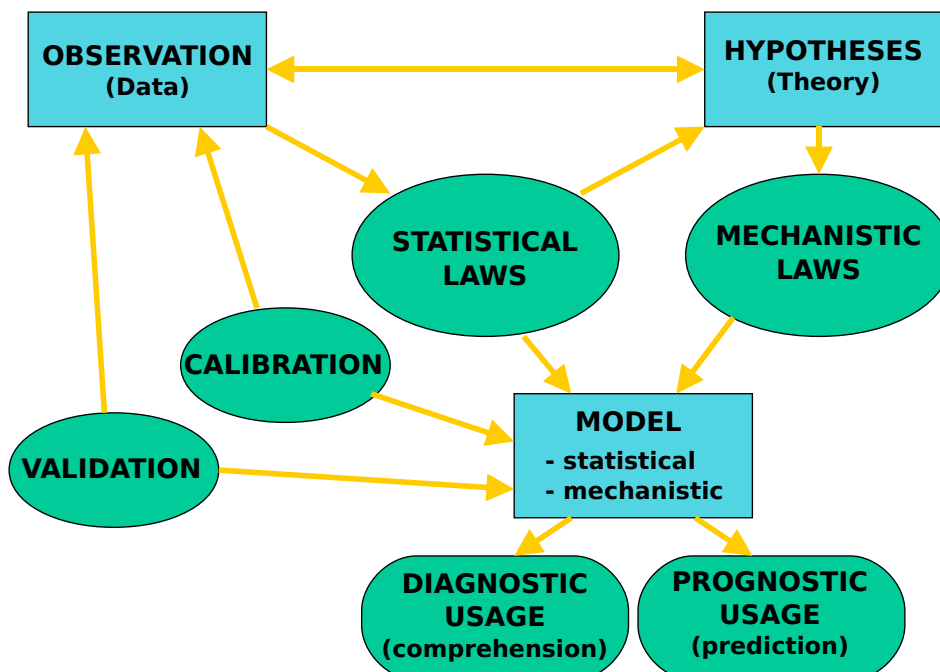
- Four stages
  1. Problem Identification
  2. Model Formulation
  3. Model Solution
  4. Interpretation of the results
- Equal importance for each stage
- Not a uni-directional procedure

(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
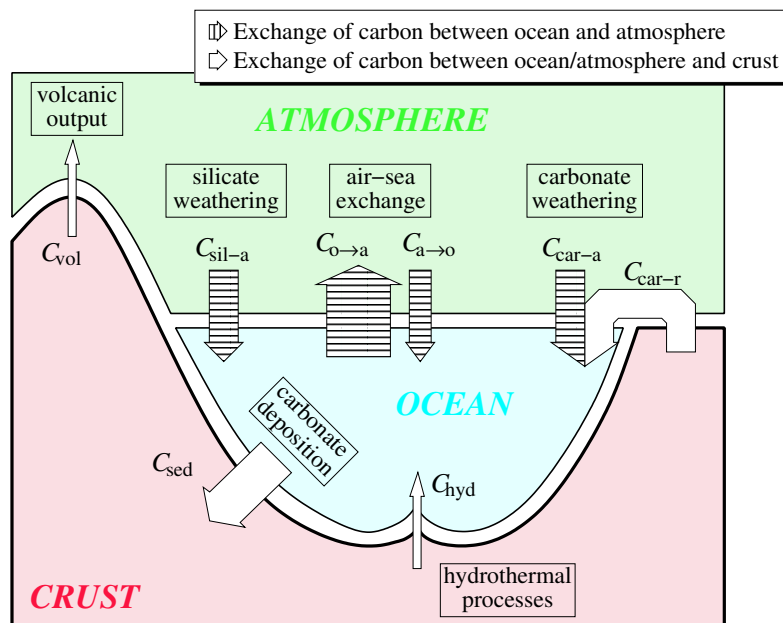 - model to be refined or to simplified

(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
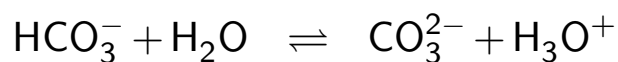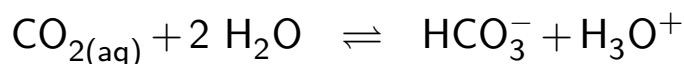- Steady state
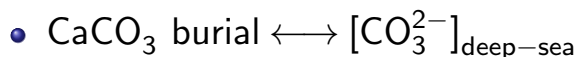
Carbon Cycle Model: Processes Considered

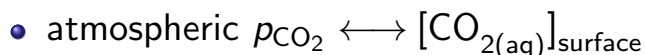> ⇨ Exchange of carbon between ocean and atmosphere
> ⇨ Exchange of carbon between ocean/atmosphere and crust

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 $p_{CO_2} \longleftrightarrow [CO_{2(aq)}]_{\text{surface}}$
  - $CaCO_3$ burial $\longleftrightarrow [CO_3^{2-}]_{\text{deep}-\text{sea}}$

- Speciation calculated from combinations
  - Dissolved Inorganic Carbon
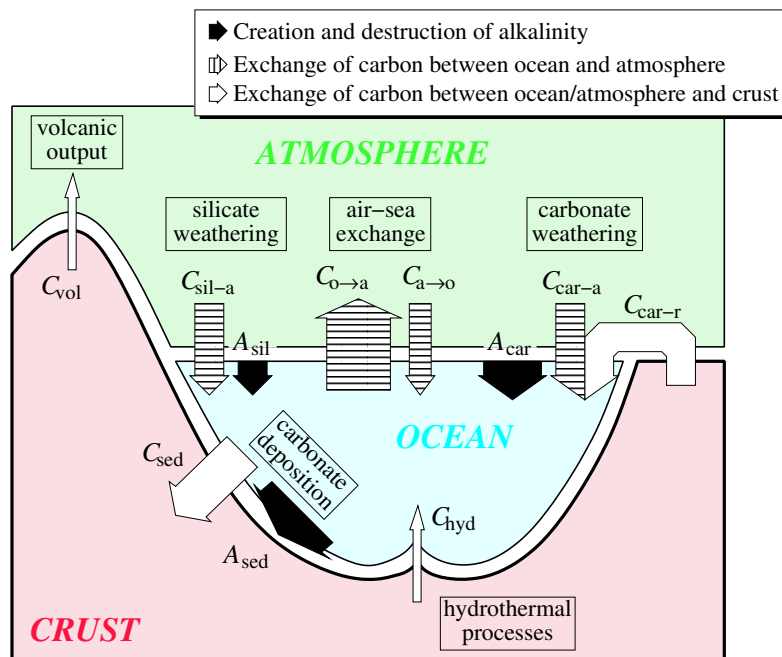 $$C_T = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}]$$
  - Total Alkalinity
    $$A_T \simeq [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H_3O^+]$$

Carbon Cycle Model: Fluxes Considered

- ▶ Creation and destruction of alkalinity
- ⇨ Exchange of carbon between ocean and atmosphere
- ⇨ Exchange of carbon between ocean/atmosphere and crust

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

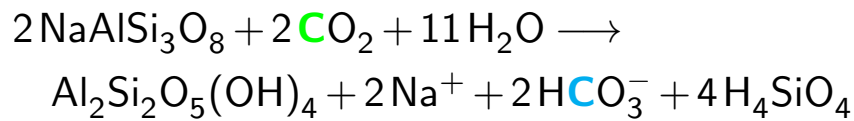$$\frac{d\mathbf{C}_{atm}}{dt} = C_{vol} - C_{sil-a} - C_{car-a} + C_{o\to a} - C_{a\to o}$$

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

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

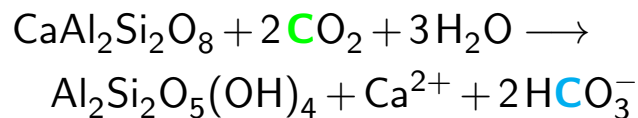$$\frac{d\mathbf{A}}{dt} = A_{sil} + A_{car} - A_{sed}$$
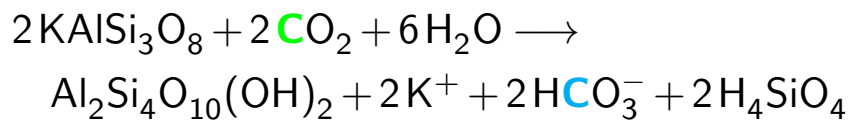
Typical Weathering Reactions for Silicate Minerals

- Dissolution of albite with precipitation of kaolinite

$$2\,NaAlSi_3O_8 + 2\,\mathbf{C}O_2 + 11\,H_2O \longrightarrow$$
$$Al_2Si_2O_5(OH)_4 + 2\,Na^+ + 2\,H\mathbf{C}O_3^- + 4\,H_4SiO_4$$

- Dissolution of anorthite with precipitation of kaolinite

$$CaAl_2Si_2O_8 + 2\,\mathbf{C}O_2 + 3\,H_2O \longrightarrow$$
$$Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2\,H\mathbf{C}O_3^-$$

- Dissolution of microcline with precipitation of pyrophillite

$$2\,KAlSi_3O_8 + 2\,\mathbf{C}O_2 + 6\,H_2O \longrightarrow$$
$$Al_2Si_4O_{10}(OH)_2 + 2\,K^+ + 2\,H\mathbf{C}O_3^- + 2\,H_4SiO_4$$

Typical Weathering Reactions for Silicate Minerals
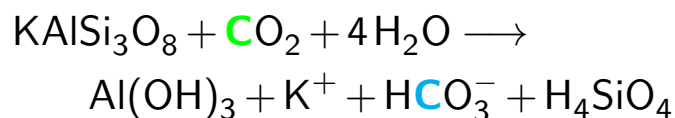
- Dissolution of chlorite with precipitation of kaolinite

$$Mg_5Al_2Si_3O_{10} + 10\,\mathbf{C}O_2 + 5\,H_2O \longrightarrow$$
$$Al_2Si_2O_5(OH)_4 + 5\,Mg^{2+} + 10\,H\mathbf{C}O_3^- + H_4SiO_4$$
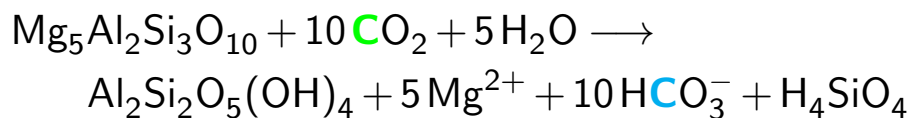
- Dissolution of microcline with precipitation of gibbsite

$$KAlSi_3O_8 + \mathbf{C}O_2 + 4\,H_2O \longrightarrow$$
$$Al(OH)_3 + K^+ + H\mathbf{C}O_3^- + H_4SiO_4$$

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

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^-$$
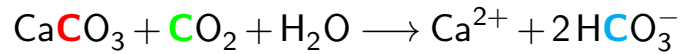
  - silicate rocks: *incongruent* dissolution

$$\text{silicate mineral} + b\,CO_2 + \text{water} \longrightarrow$$
$$\text{secondary minerals} + \text{cations} + b\,HCO_3^- + s\,H_4SiO_4$$
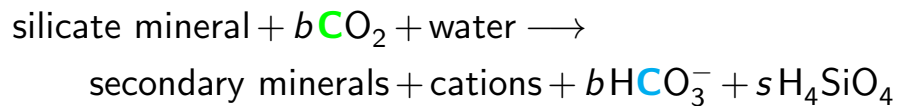
- Sinks : burial of biogenic carbonates

$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3 + CO_2 + H_2O$$
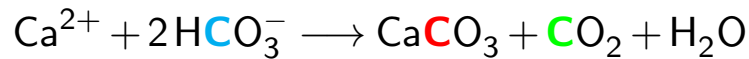
Cycles to the Carbon Cycle: Ca, K, Mg, Na, Si

Residence times of coupled cycles' elements in the oceans

| Element	τ_{oc} $(10^6\,\text{yr})$	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	

Carbon Cycle – Silicate Cycle Coupling
Geochemical carbonate and silicate cycles

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
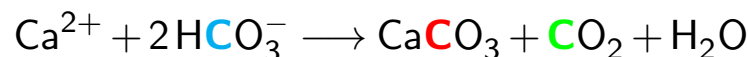 in marine sediments (*reverse weathering*, very slow process):
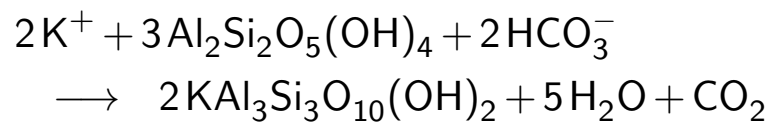
$$2\,K^+ + 3\,Al_2Si_2O_5(OH)_4 + 2\,HCO_3^-$$
$$\longrightarrow \quad 2\,KAl_3Si_3O_{10}(OH)_2 + 5\,H_2O + CO_2$$

Carbon Cycle – Silicate Cycle Coupling
Geochemical carbonate and silicate cycles

- Weathering of Ca- (or Mg-) carbonate

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2\,HCO_3^-$$
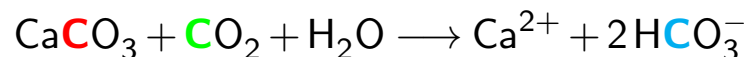
- Precipitation and sediment burial of carbonates

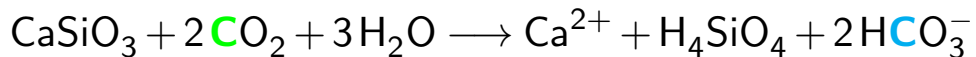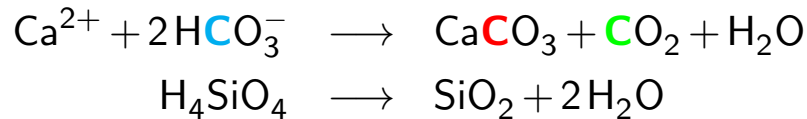$$Ca^{2+} + 2\,HCO_3^- \longrightarrow CaCO_3 + CO_2 + H_2O$$

- Net balance:

—

Carbon Cycle – Silicate Cycle Coupling
Geochemical carbonate and silicate cycles

- Weathering of Ca- (or Mg-) silicate

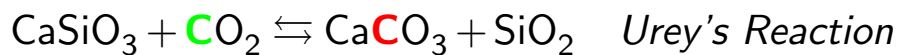$$CaSiO_3 + 2\,CO_2 + 3\,H_2O \longrightarrow Ca^{2+} + H_4SiO_4 + 2\,HCO_3^-$$

- Precipitation and sediment burial of carbonate and opal

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

- Net balance

$$CaSiO_3 + CO_2 \longrightarrow CaCO_3 + SiO_2$$
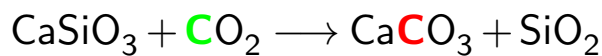
- Combined with reverse reaction (metamorphism)

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

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:

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

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

Carbon Cycle Model: Resolution

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

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

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

$$
\begin{aligned}
C_{\text{hyd}} + C_{\text{vol}} + C_{\text{car}-\text{r}} - C_{\text{sed}} &= 0 \qquad (1) \\
C_{\text{sil}-\text{a}} + 2\,C_{\text{car}-\text{r}} - 2\,C_{\text{sed}} &= 0 \qquad (2)
\end{aligned}
$$

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

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

Carbon Cycle Model: Resolution

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

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

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

and thus

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

Solution and Interpretation

Result

Since

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

we find that

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

Solution and Interpretation

<div align="center">
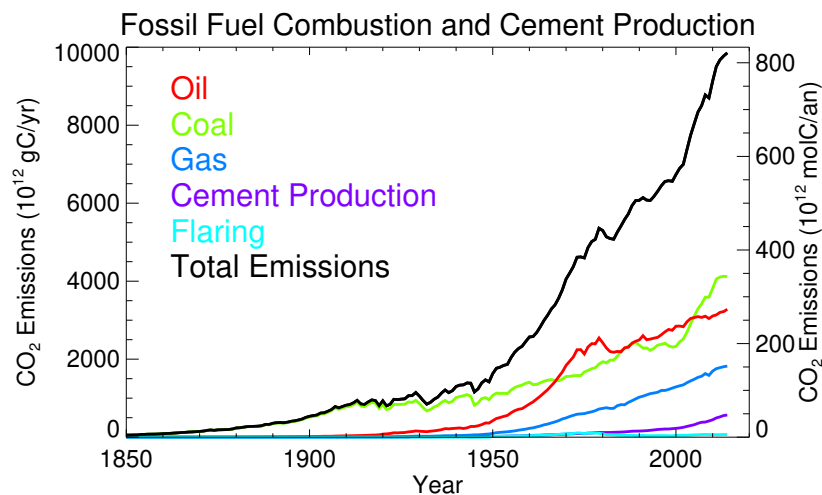
Interpretation

</div>

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

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

- Hence:

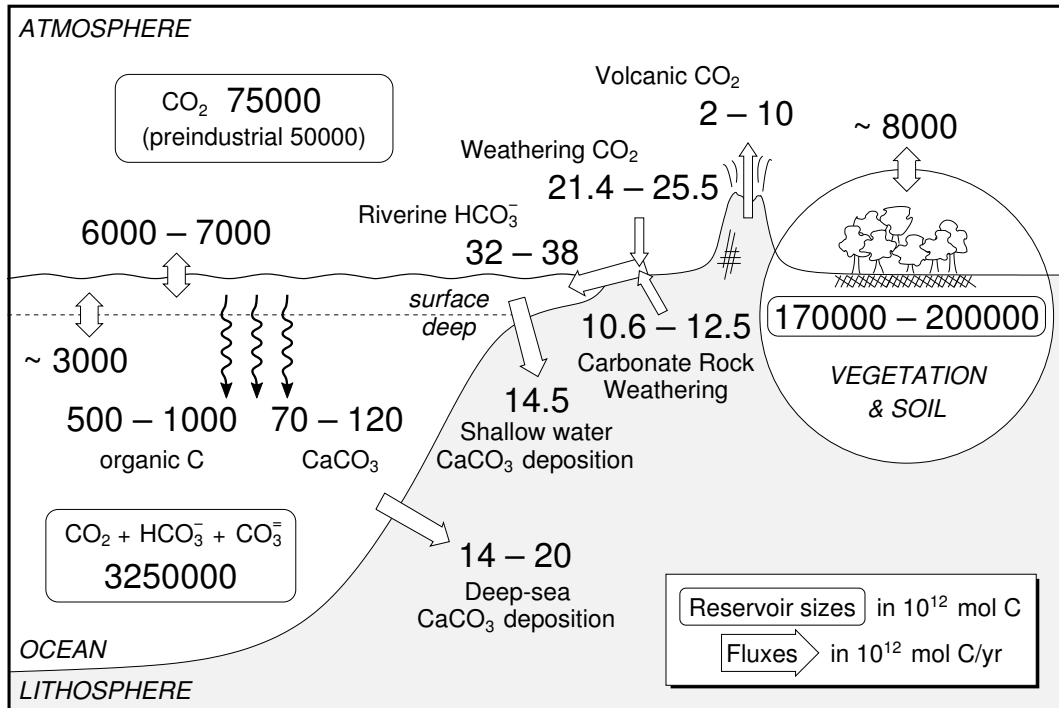$$
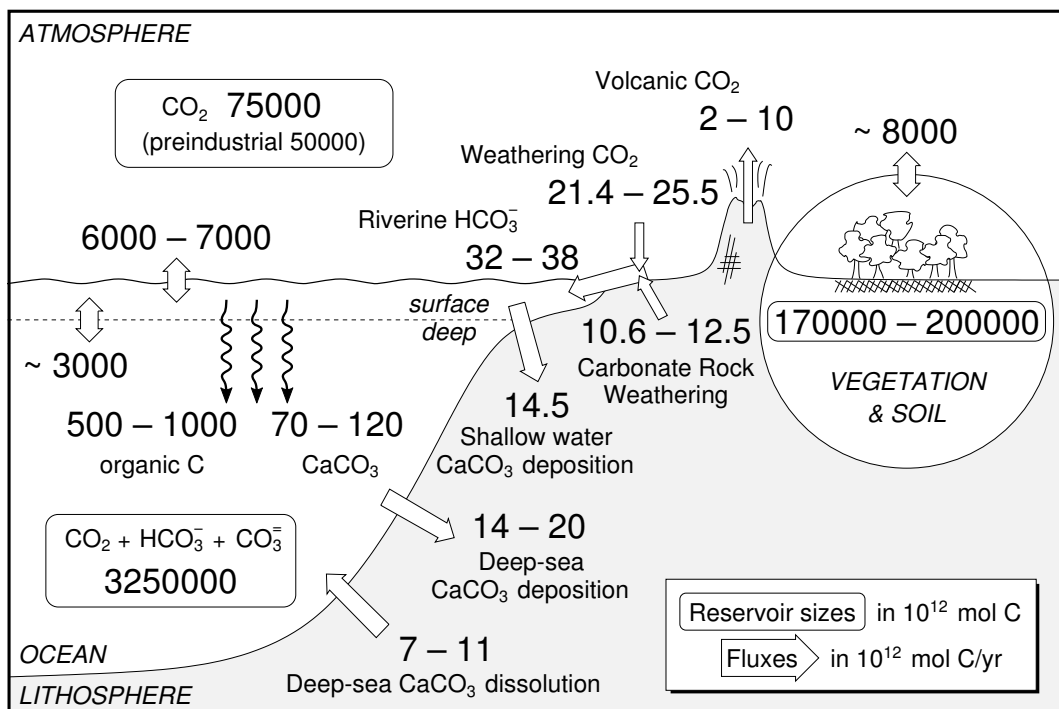C_{sed} = (15.8 - 18.9) \times 10^{12} \, \text{mol C/an}
$$

Solution and Interpretation

Fossil Fuel Combustion and Cement Production

	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

ATMOSPHERE

CO$_2$ 75000
(preindustrial 50000)

Volcanic CO$_2$
2 − 10

~ 8000

Weathering CO$_2$
21.4 − 25.5

Riverine HCO$_3^-$
32 − 38

6000 − 7000

surface
deep

~ 3000

500 − 1000   70 − 120
organic C   CaCO$_3$

10.6 − 12.5
Carbonate Rock
Weathering

170000 − 200000

VEGETATION
& SOIL

14.5
Shallow water
CaCO$_3$ deposition

CO$_2$ + HCO$_3^-$ + CO$_3^=$
3250000

14 − 20
Deep-sea
CaCO$_3$ deposition

7 − 11
Deep-sea CaCO$_3$ dissolution

Reservoir sizes in 10^{12} mol C
Fluxes in 10^{12} mol C/yr

OCEAN

LITHOSPHERE

Connecting the Carbon and Alkalinity Budgets

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

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

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

Basic Constraints of the System: Time Scales > 1 Myr

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

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

$$\begin{cases} \overline{\dfrac{d\mathbf{A}}{dt}} = 0 \\[2ex] \overline{\dfrac{d\mathbf{C}}{dt}} = 0 \end{cases} \implies \overline{C_{\text{sil}-\text{a}}} = 2 \times \left(\overline{C_{\text{vol}} + C_{\text{hyd}}}\right)$$

Basic Constraints of the System: Time Scales < 1 Myr

On time scales of $10 - 100$ kyr

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

$$C_{\text{hyd}} + C_{\text{vol}} \cong \overline{C_{\text{hyd}} + C_{\text{vol}}} = \tfrac{1}{2}\ \overline{C_{\text{sil}-a}}$$
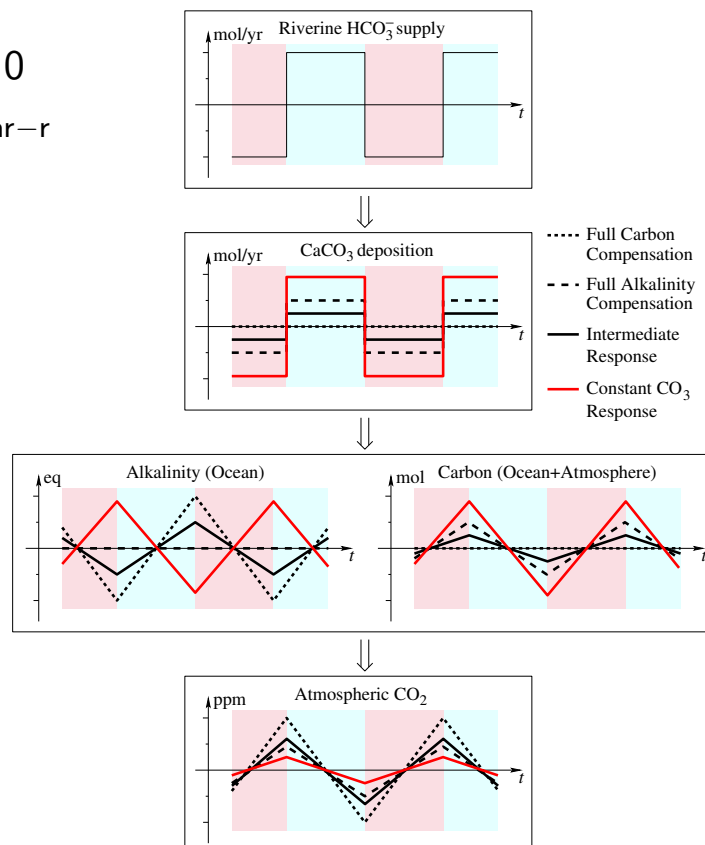
- Hence

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

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

Sensitivity Analysis: Variable Silicate Weathering

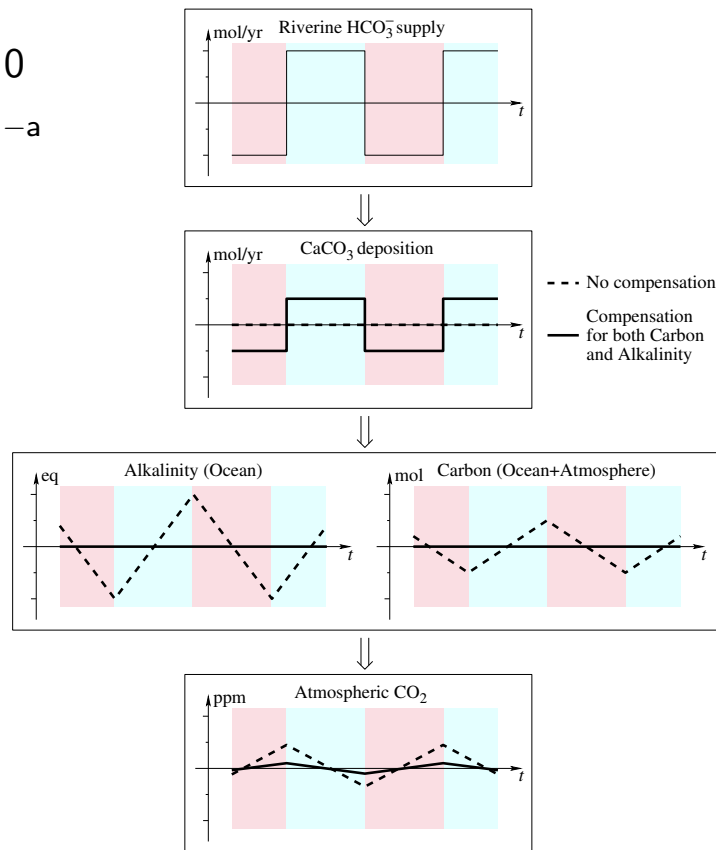$\Delta C_{\text{hyd}+\text{vol}} \equiv 0$
Constant $C_{\text{car}-r}$

Sensitivity Analysis: Variable Carbonate Weathering

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

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
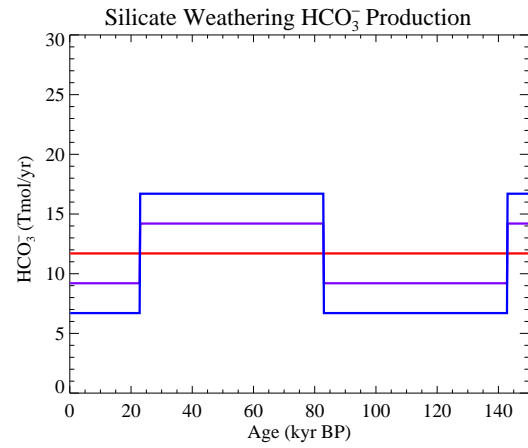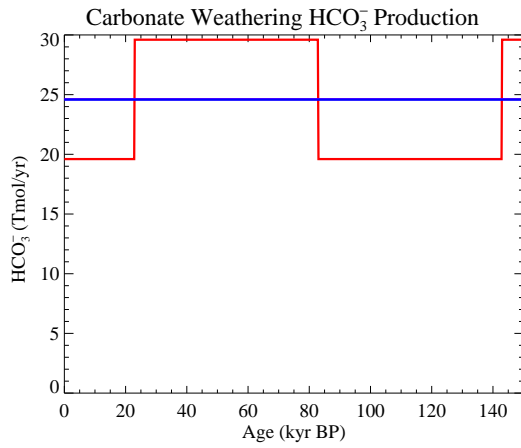- fully coupled to . . . 304 copies of

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
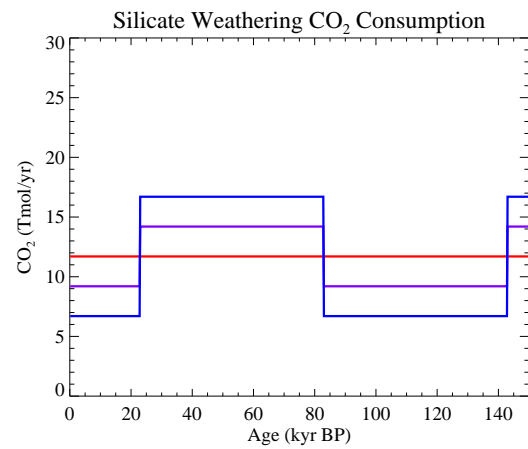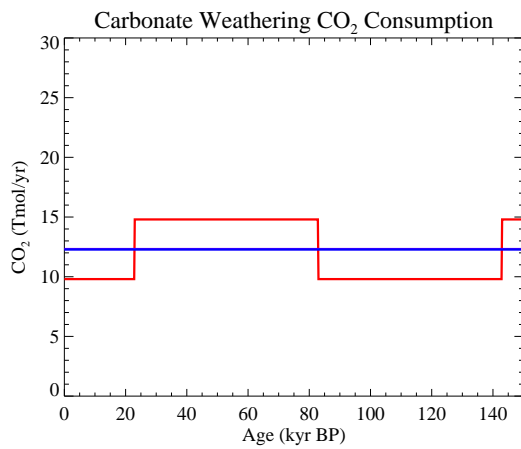- fully bi-directional exchange between the two zones

Bicarbonate Production Rate Scenarios

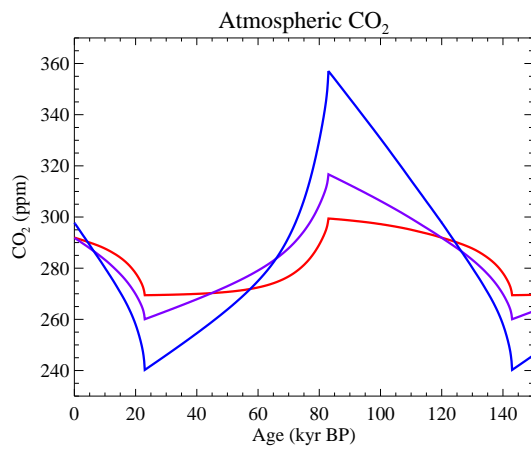Carbonate Weathering HCO_3^- Production

Silicate Weathering HCO_3^- Production

CO_2 Consumption Rate Scenarios

Carbonate Weathering CO_2 Consumption

Silicate Weathering CO_2 Consumption

pCO₂ and Calcite Saturation Horizon Variations

Atmospheric CO$_2$ — CO$_2$ (ppm) vs Age (kyr BP)

Indo-Pacific Calcite Saturation Horizon — Depth BSL (m) vs Age (kyr BP)
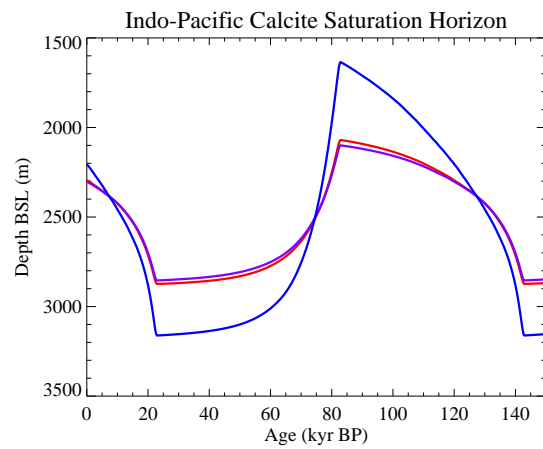
Summary

- 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`.

B. P. Boudreau. *Diagenetic Models and Their Implementation*. Springer-Verlag, Berlin (DE), 1997. ISBN 3-540-61125-8.