Seafloor Sediments

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Interaction with the Ocean and Early Diagenesis

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Plan

- Sediments in the present-day ocean
- Interest of sediments in Earth sciences
- Role of seafloor sediments in biogeochemical cycles
- Processes: transport and reaction
- Advection-diffusion-reaction model(s)

The Seafloor and its Sediments: a First Exploration
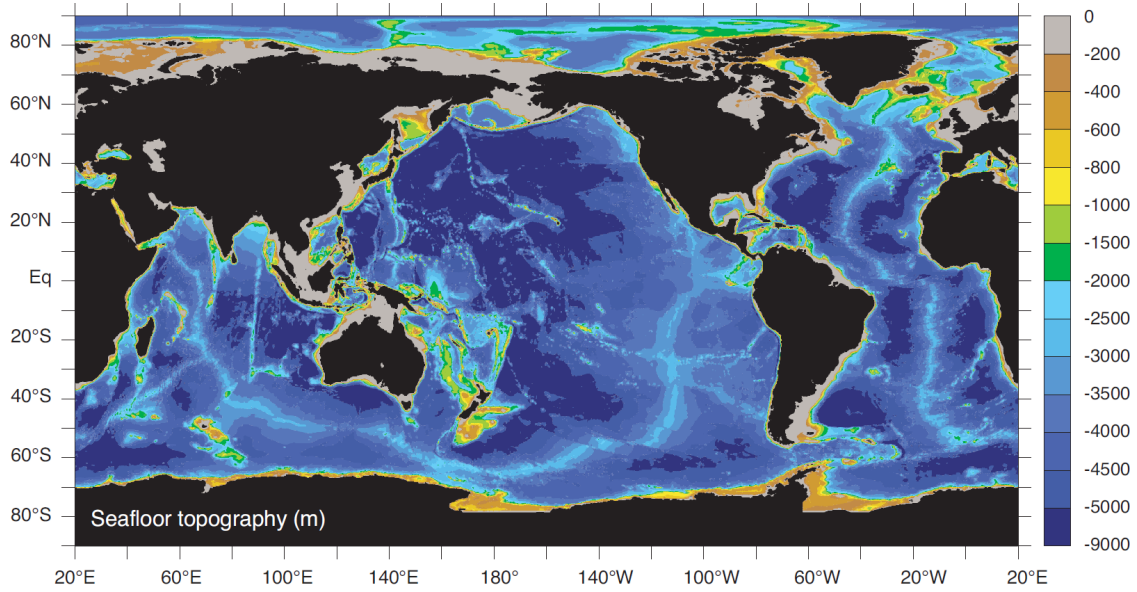
Seafloor topography (m)

Source: Sarmiento and Gruber (2006)

The Seafloor and its Sediments: a First Exploration

Sediment $CaCO_3$ (weight %)
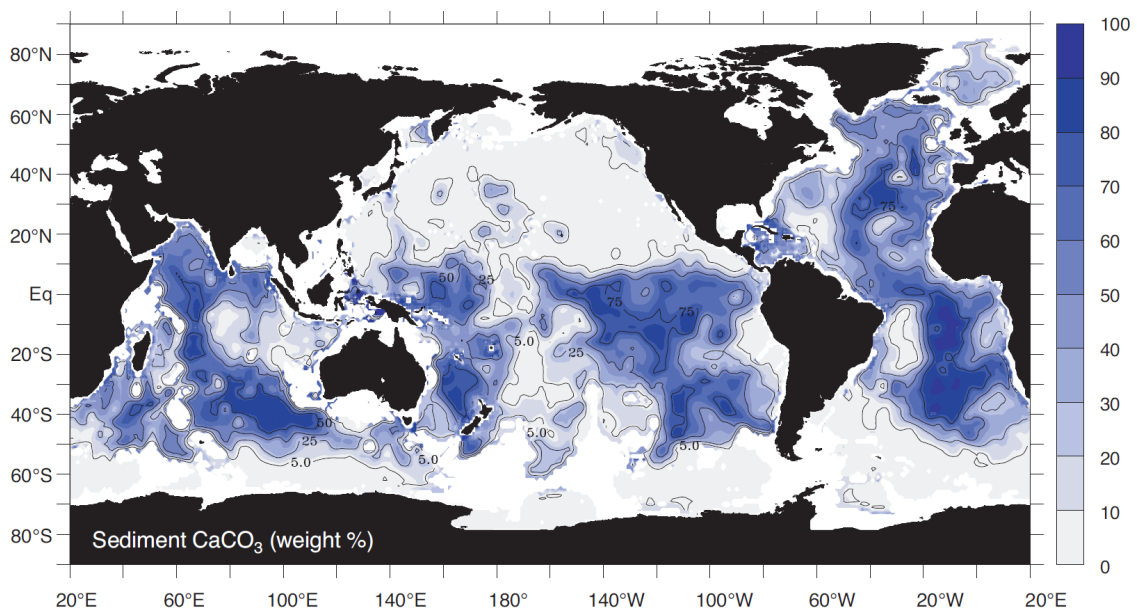
Source: Sarmiento and Gruber (2006)

The Seafloor and its Sediments: a First Exploration

Source: Broecker and Peng (1982)
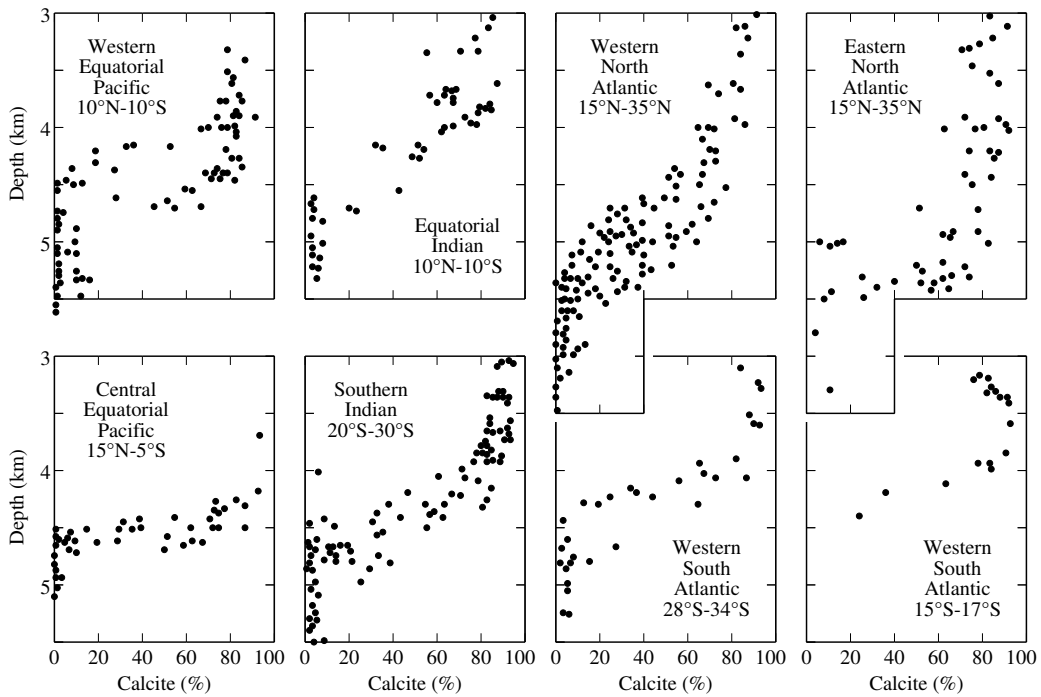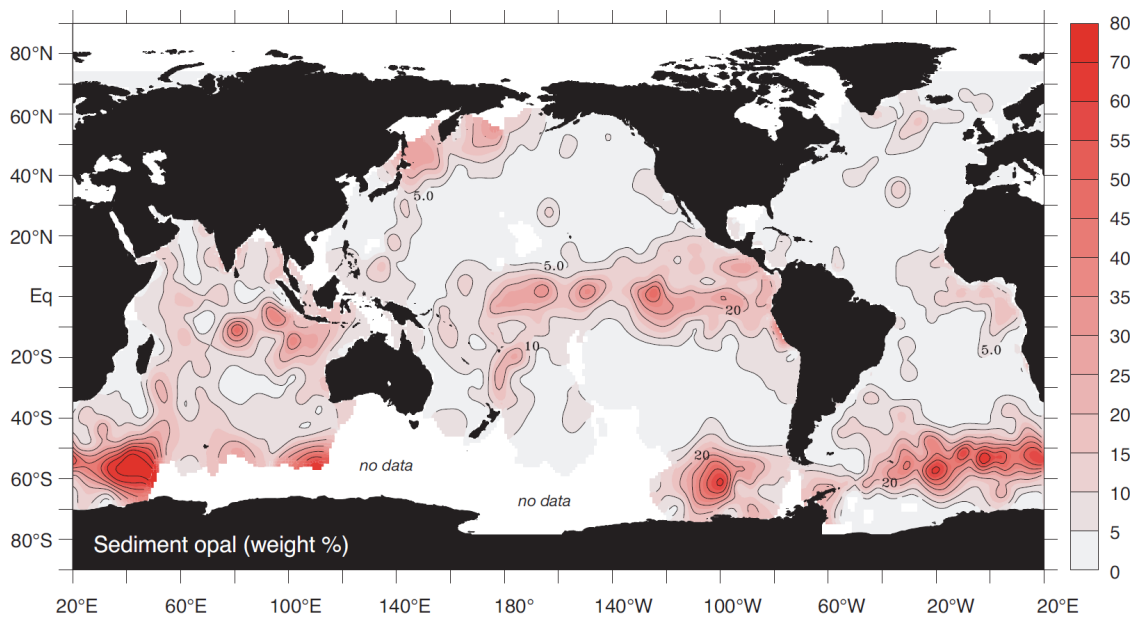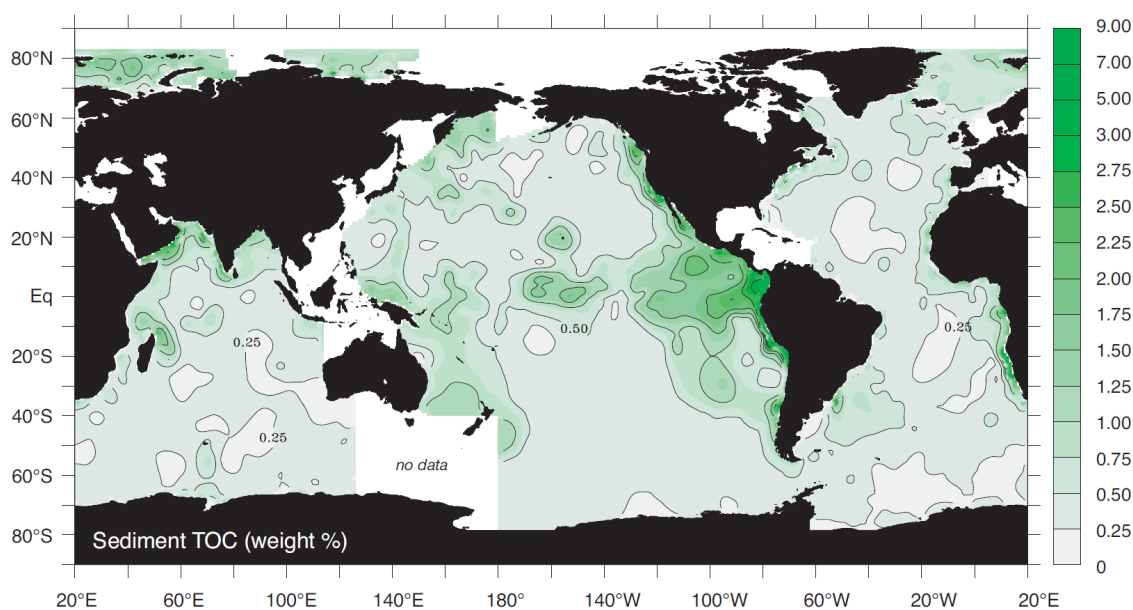
The Seafloor and its Sediments: a First Exploration

Source: Sarmiento and Gruber (2006)

The Seafloor and its Sediments: a First Exploration

Source: Sarmiento and Gruber (2006)

Seafloor Sediments: Biogenic Components

- Carbonates
  - distribution related to seafloor depth:
    deepest sediments devoid of carbonate
  - up to 90% on mid-ocean ridges
- Opal
  - abundant in the Southern Ocean (*Opal Belt*)
  - abundant in the Eastern Equatorial Pacific
    — nutrient-rich upwelling zone
- Organic Carbon
  - generally 1–2%, but locally up to 10%
  - oxidation of organic carbon plays important
    role for carbonate dissolution
   (CO_2 source, porewater acidification)

Seafloor Sediments: Non Biogenic Components

- Clay minerals
- Chlorite → product of continental weathering
  in temperate and arctic regions
- Kaolinite and gibbsite → product of continental weathering
  in tropical regions
- Quartz → detrital material, of aeolian or glacial origin
  (sedimentation in coastal areas due to the activity of
  glaciers and ice-sheets)
- *Authigenic* minerals, formed *in situ*,
  by alteration of volcanic materiel (e. g., basaltic glasses)
  or by precipitation of biogenic material during early diagenesis
  (e. g., phosphate minerals)

Seafloor Sediments: Archives of the Earth's History

- 1920s: different plankton assemblages
  depending on the climate regimes

- 1947–1948: *Swedish Deep-Sea
  Expedition* on R.V. Albatross,
  visiting 403 sites and retrieving
  of 223 undisturbed cores
  ($\simeq 15\,\text{m}$) from different
  equatorial oceans

- Chemical analyses for $\%CaCO_3$
  by Gustaf Arrhenius (1952)
  reveal glacial-interglacial cycles

Core #45
Lat: N 7° 40'
Long: W 106° 21'

Core #60
Lat: N 1° 35'
Long: W 134° 57'
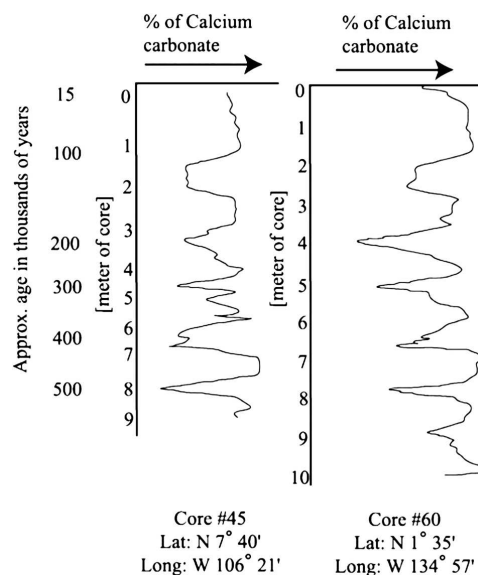
Source: http://earthguide.ucsd.edu/
virtualmuseum/climatechange2/02_4.shtml

Sedimentary Archives: C. Emiliani's δ^{18}O

- Cesare Emiliani. Pleistocene Temperatures.
  Journal of Geology 63:538-578, 1955.
- Measurements of the evolution of the isotopic ratio ^{18}O/^{16}O on microfossils preserved in different cores, carried out in Harold Urey's lab (University of Chicago)
  $\rightarrow$ glacial-interglacial cycles
- Establishes the relationship between oxygen isotopes and climatic variables
- Observed variations attributed for
  - 60% to temperature changes
  - 40% to ice-volume changes

Sedimentary Archives: C. Emiliani's δ^{18}O

- Dating beyond 50 000 years difficult and unreliable
- Correlation with terrestrial chronologies, witnessing of only four glaciations during the Pleistocene
- Tentative correlation with insolation cycles (Milankovitch)
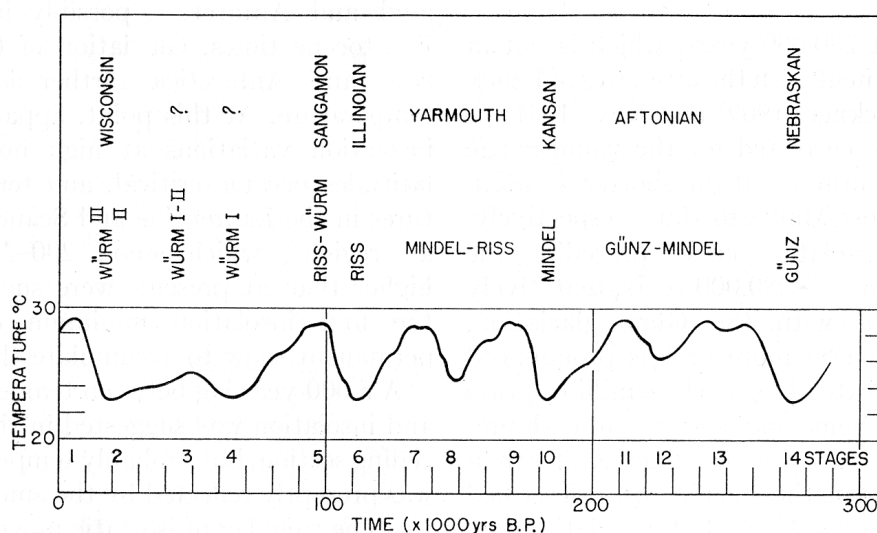
Source: Emiliani (1955)

Sedimentary Archives: N. Shackleton's δ^{18}O's

- Shackleton (1967)
  - joint ^{18}O/^{16}O measurements on planktonic (surface dwelling) and benthic (deep-sea dwelling) shells
  - co-variation $\rightarrow$ ice-volume changes dominate ^{18}O/^{16}O variations
- Shackleton and Opdyke (1973)
  - measurement of ^{18}O/^{16}O and location of the last reversal of the Earth's magnetic field (Brunhes-Matuyama) on the same core (V28-238, Ontong-Java Plateau)
  - about eight cycles for 700 kyr $\rightarrow \simeq 90$ kyr per cycle
  - Brunhes-Matuyama revised to 780–790 kyr in the 1990s
- Hays, Imbrie and Shackleton (1976)
  - Validation of the Milankovich theory

Sedimentary Archives: Dating of Brunhes-Matuyama
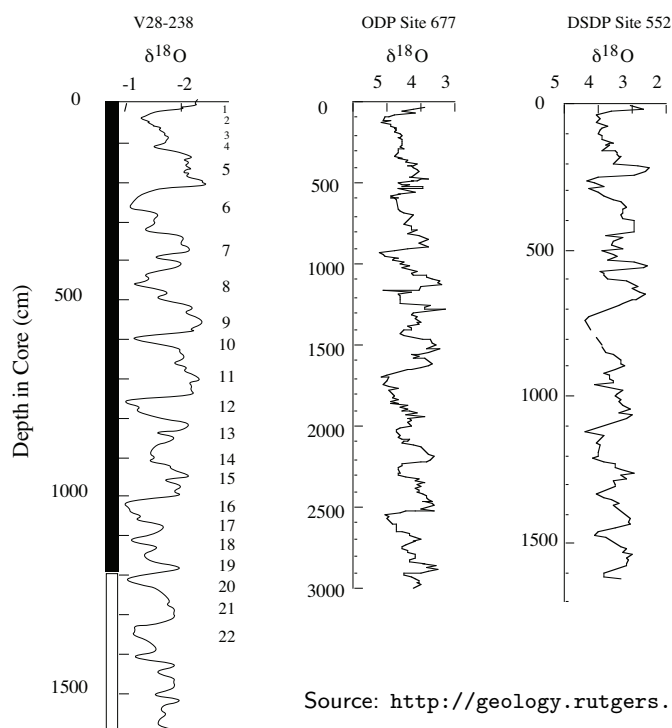
- V28-238: Western Equatorial Pacific (planktonic forams)
- ODP677: Eastern Equatorial Pacific (benthic forams)
- DSDP552: North Atlantic (benthic forams)

Source: http://geology.rutgers.edu/~jdwright/JDWWeb/1999/JDWright_NUREG.pdf

Role of Sediments in Biogeochemical Cycling

- Active role in ocean biogeochemical cycling
- Locus of preservation and remineralization of biogenic material (carbonates, opal, organic matter, etc.)
- Concentration gradients of similar amplitude in water column and in surface sediment

Concentration Gradients: Ocean vs. Surface Sediment

Dissolved Oxygen in the Water Column
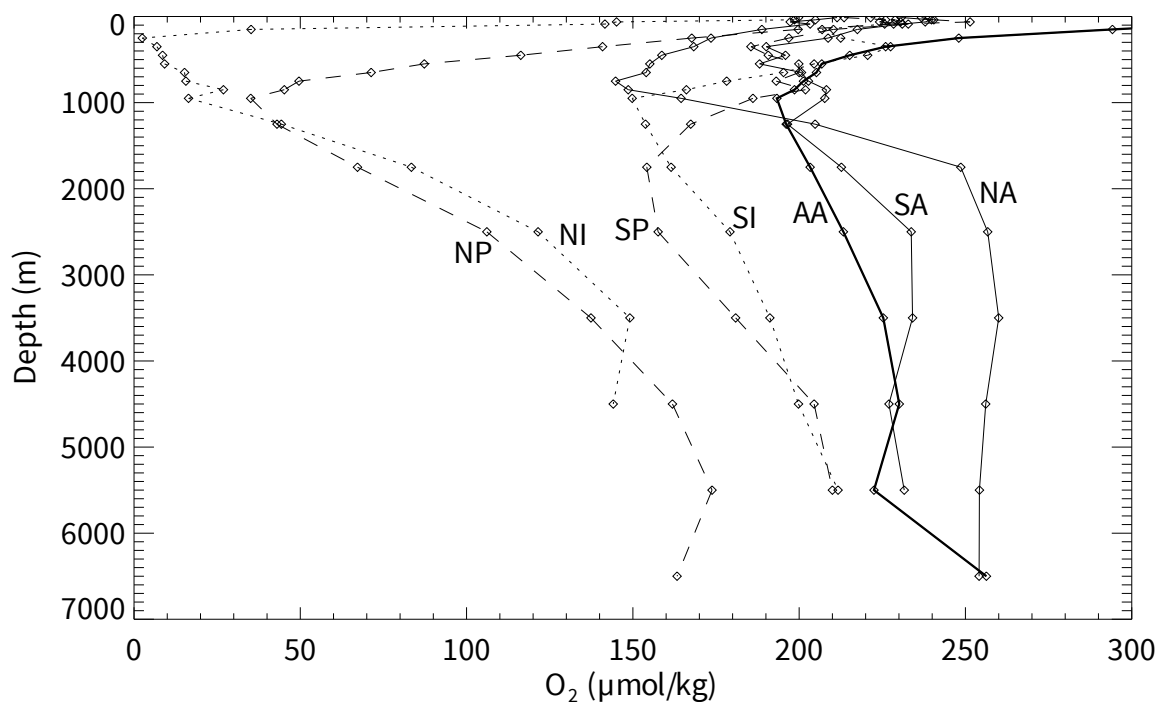
Concentration Gradients: Ocean vs. Surface Sediment

Dissolved Oxygen in the Surface Sediment Porewater

Gulf of Guinea
(2.68°N, 6.73°E)

2185 m

DBSWI (cm)

O_2 (µmol/L)
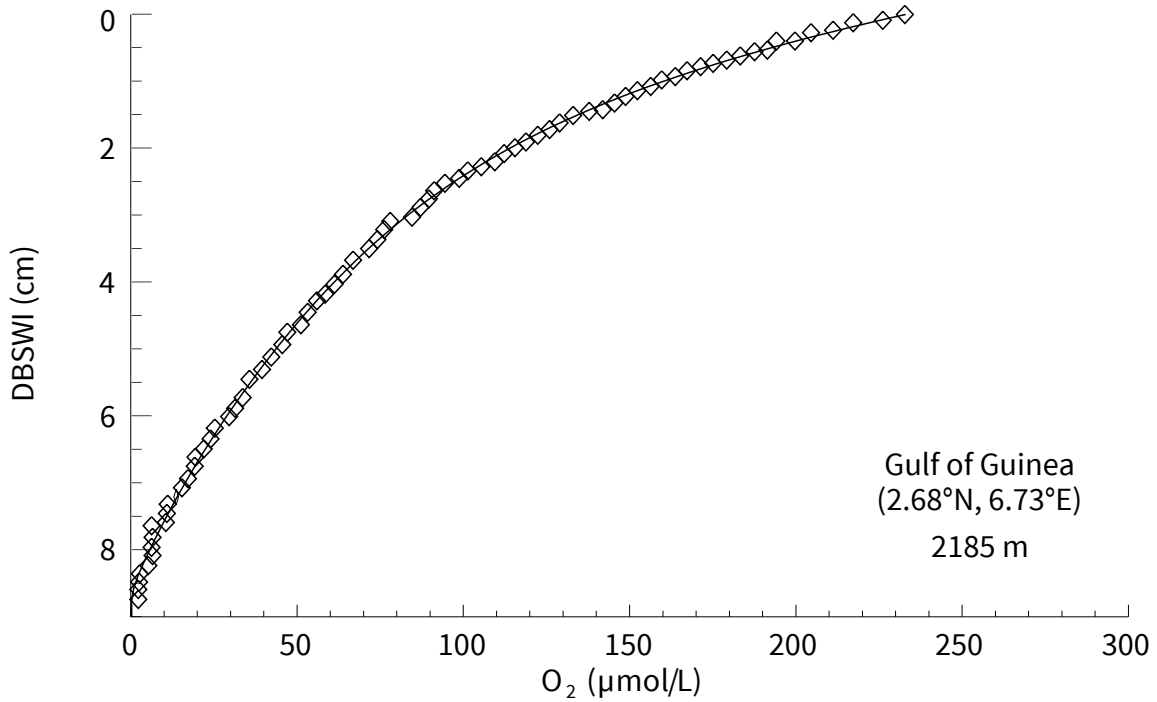
Acidification: Perturbation of the Ocean-Sediment Exchange

Marine carbonates: ocean-sediment exchange

$[CO_3^=]$

$[CO_3^=]_{in\ situ}$

CSH

$[CO_3^=]_{sat}$

CCD

depth
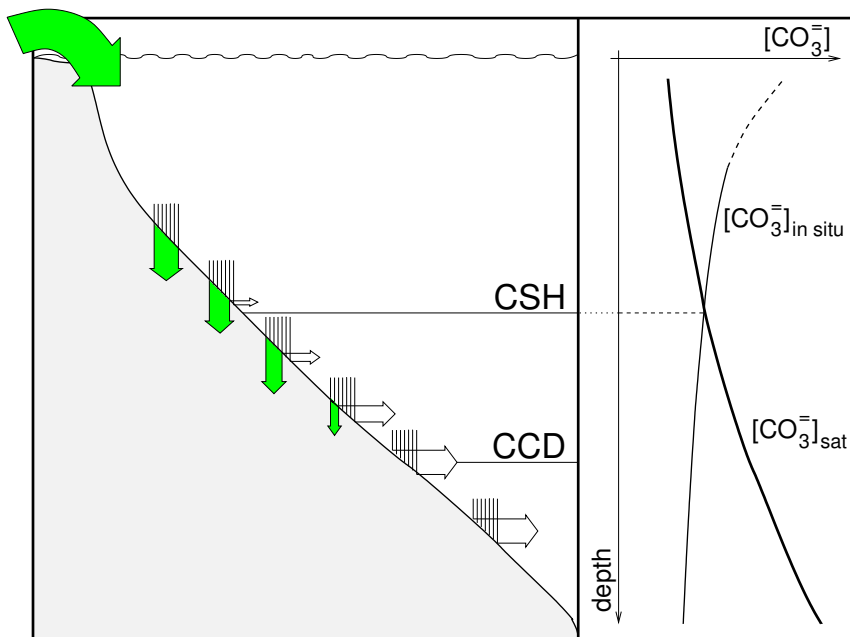
Preludes: geometric setting
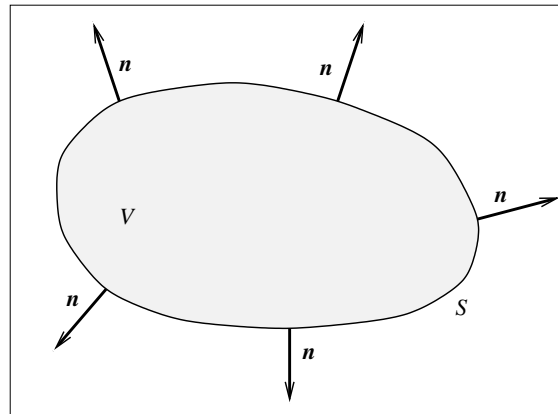
- V – arbitrary volume (fixed w/r to the coordinate system)
- S – surface delimiting V
- $\boldsymbol{n}$ – unitary normal vector at each point of S, external to V

General Continuity Equation

$$\frac{\partial}{\partial t} \iiint_V \hat{C}_i \, dV = -\iint_S \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n} \, dS + \iiint_V \hat{R}_i^V \, dV.$$

- $\hat{C}_i$ is the concentration of constituent i in units of mass per unit volume of total sediment (solid fraction + porewater);
- $\hat{\boldsymbol{J}}_i$ is the total flux of i in units of mass per unit surface of total sediment per unit time;
- $\hat{R}_i^V = \hat{P}_i^V - \hat{D}_i^V$ is the *net* rate of production of i, obtained as the difference between sources (rate of *production*, $\hat{P}_i^V \geq 0$) and sinks (i.e., rate of consumption and *destruction*, $\hat{D}_i^V \geq 0$) within V, in units of mass per unit volume of total sediment per unit time.

General Continuity Equation

- V fixed: integral and derivative may commute
- Divergence theorem

$$\iint_S \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}\, dS = \iiint_V \nabla \hat{\boldsymbol{J}}_i\, dV$$

- General equation may be rewritten as

$$\iiint_V \left\{ \frac{\partial \hat{C}_i}{\partial t} + \nabla \hat{\boldsymbol{J}}_i - \hat{R}_i^V \right\} dV = 0$$

- V is arbitrary, and thus

$$\frac{\partial \hat{C}_i}{\partial t} + \nabla \hat{\boldsymbol{J}}_i - \hat{R}_i^V = 0.$$

General Continuity Equation for Interfaces
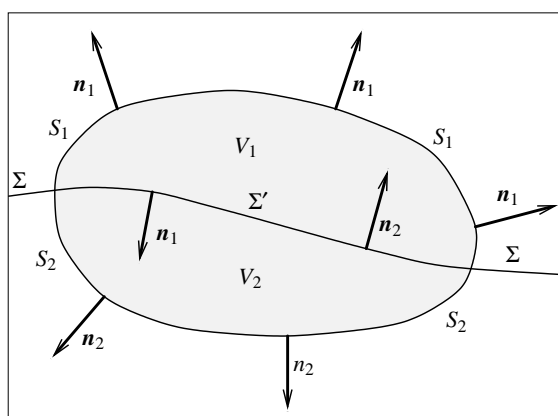
- V arbitrary volume, delimited by the surface S
- Σ arbitrary surface dividing V into V_1, V_2 and S into S_1, S_2
- Σ' the part of Σ contained in V
- $\boldsymbol{n}_1$, $\boldsymbol{n}_2$ unitary normal vectors in each point of S_1, S_2 et Σ', pointing to the outside of V_1 and V_2, resp.

General Continuity Equation for Interfaces

- Continuity equation in V, completed by possible reactions on Σ'

$$\frac{\partial}{\partial t} \iiint_V \hat{C}_i \, dV = - \iint_S \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n} \, dS + \iint_{\Sigma'} \hat{R}_i^{\Sigma} \, dS + \iiint_V \hat{R}_i^V \, dV,$$

with $\boldsymbol{n} = \boldsymbol{n}_1$ on S_1, and $\boldsymbol{n} = \boldsymbol{n}_2$ on S_2

- Conservation equations in V_1 and V_2

$$\frac{\partial}{\partial t} \iiint_{V_1} \hat{C}_i \, dV = - \iint_{S_1} \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}_1 \, dS - \iint_{\Sigma'} \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}_1 \, dS + \iiint_{V_1} \hat{R}_i^V \, dV$$

$$\frac{\partial}{\partial t} \iiint_{V_2} \hat{C}_i \, dV = - \iint_{S_2} \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}_2 \, dS - \iint_{\Sigma'} \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}_2 \, dS + \iiint_{V_2} \hat{R}_i^V \, dV.$$

General Continuity Equation for Interfaces

Since

$$\iiint_V \hat{C}_i \, dV = \iiint_{V_1} \hat{C}_i \, dV + \iiint_{V_2} \hat{C}_i \, dV,$$

$$\iiint_V \hat{R}_i^V \, dV = \iiint_{V_1} \hat{R}_i^V \, dV + \iiint_{V_2} \hat{R}_i^V \, dV,$$

and

$$\iint_S \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n} \, dS = \iint_{S_1} \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}_1 \, dS + \iint_{S_2} \hat{\boldsymbol{J}}_i \cdot \boldsymbol{n}_2 \, dS,$$

we get

$$\iint_{\Sigma'} \left\{ \hat{R}_i^{\Sigma} + \left(\hat{\boldsymbol{J}}_i|_1 \cdot \boldsymbol{n}_1 + \hat{\boldsymbol{J}}_i|_2 \cdot \boldsymbol{n}_2 \right) \right\} dS = 0$$

General Continuity Equation for Interfaces

Σ' being arbitary since Σ is arbitrary, we have the following continuity equation for any interface:

$$\hat{R}_i^{\Sigma} + \left(\hat{\boldsymbol{J}}_i\big|_1 \cdot \boldsymbol{n}_1 + \hat{\boldsymbol{J}}_i\big|_2 \cdot \boldsymbol{n}_2\right) = 0.$$

Noting that

$$\boldsymbol{n}_2 = -\boldsymbol{n}_1 \quad \text{on} \quad \Sigma',$$

we can rewrite this equation as

$$\hat{R}_i^{\Sigma} + \left(\hat{\boldsymbol{J}}_i\big|_1 - \hat{\boldsymbol{J}}_i\big|_2\right) \cdot \boldsymbol{n}_1 = 0.$$

Sediments: Two Phases and Multiples Constituents

- Two phases
  - solids $\rightarrow$ properties denoted by exponent 's'
  - porewater $\rightarrow$ properties denoted by exponent 'f'
- Surface sediment: typically 70–90% water
- Porosity $\varphi = \varphi(t, \boldsymbol{x})$ defined by

$$\varphi = \frac{\text{volume of connected porewater space}}{\text{total volume of sediment}}$$

- φ^{f} *water fraction* (fluid) and φ^{s} *solid fraction*
- Neglecting volumes of unconnected pores

$$\varphi^{\text{f}} = \varphi \quad \text{and} \quad \varphi^{\text{s}} = 1 - \varphi$$

## Total Concentrations and Phase Concentrations

- Continuity equations expressed in terms of $\hat{C}_i$, concentration of i per unit volume of total sediment
- More directly measurable
  - i solid: C_i^{s} concentration of i in units of mass per unit volume of solid sediment

$$\hat{C}_i = \varphi^{\mathsf{s}} C_i^{\mathsf{s}}$$

  - i solute: C_i^{f} concentration of i in units of mass (or moles) per unit volume of porewater

$$\hat{C}_i = \varphi^{\mathsf{f}} C_i^{\mathsf{f}}$$

One-Dimensional Model
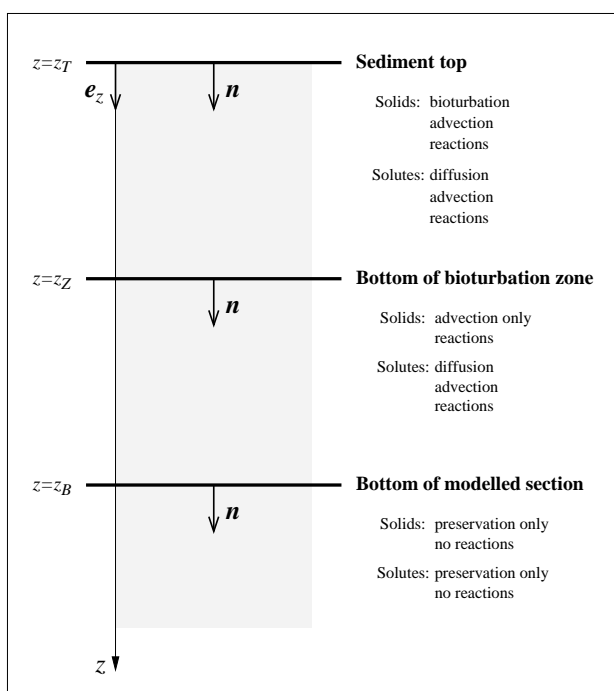
With $\hat{\boldsymbol{J}}_i = \hat{J}_i \boldsymbol{e}_z$, the continuity equation becomes

$$\frac{\partial \hat{C}_i}{\partial t} + \frac{\partial \hat{J}_i}{\partial z} - \hat{R}_i^V = 0.$$

At any interface Σ, with upper side '1' and lower side '2':

- $\hat{\boldsymbol{J}}_i^1 \boldsymbol{n}^1 = -\hat{J}_i^1$
- $\hat{\boldsymbol{J}}_i^2 \boldsymbol{n}^2 = \hat{J}_i^2$

Hence,

$$\hat{R}_i^{\Sigma} + \left(\hat{J}_i^2 - \hat{J}_i^1\right) = 0.$$

Flux Types

- Advection

    transport by the general movement of one or more phases

- Diffusion

    mixing processes

- Non-local transport

    representation (parametrization) of transport phenomena that cannot be taken explicitly into account in a one-dimensional framework
    $\rightarrow$ to include as sources or sinks, similarly to reactions

Transport in Porewater: Advection

- Solute i, of concentration C_i^{f} in porewater

$$\hat{J}_{\mathrm{adv}\,i} = u\hat{C}_i = \varphi^{\mathrm{f}} u C_i^{\mathrm{f}},$$

    where $u = u(z, t)$, such that $\boldsymbol{u} = u\boldsymbol{e}_z$ is the velocity of the porewater flux relative to the sediment-water interface
- Generally oriented upwards, as a result of compaction of the sedimentary column (φ decreases with z)
- u can possibly include a contribution from an externally impressed flow
- u is most often negligible compared to diffusion

Transport in Porewater: Diffusion

- Molecular and ionic diffusion
- Diffusive flux per unit area of porewater

$$J_{\text{diff } i}^{\text{f}} = -D_i^{\text{sed}} \frac{\partial C_i^{\text{f}}}{\partial z}$$

   where D_i^{sed} is the *effective diffusion coefficient* in the sediment and $\frac{\partial C_i^{\text{f}}}{\partial z}$ the concentration gradient of i in porewater along the vertical

- $J_{\text{diff } i}^{\text{f}}$, per unit area of porewater, must be related to $\hat{J}_{\text{diff } i}$, per unit area of total sediment

- Diffusion does not operate directly along the vertical, but along tortuous pathways: follows local concentration gradients, lower than the vertical gradient

Transport in Porewater: Diffusion

- Empirical relationship between D_i^{sed} and D_i^{sw}, the diffusion coefficient in seawater

$$D_i^{\text{sed}} = D_i^{\text{sw}}/\theta^2$$

   where $\theta = \frac{dL}{dz}$ is the *tortuosity*, dL being the total distance that a molecule has to travel to cover the distance dz along the vertical

- Empirical relationships between θ^2 and porosity

Archie's Law	$\theta^2 = \varphi^{1-m}$	$m = 2.14 \pm 0.03$	$r^2 = 0.53$
Burger-Frieke eqn.	$\theta^2 = \varphi + a(1-\varphi)$	$a = 3.79 \pm 0.11$	$r^2 = 0.64$
Weissberg rel.	$\theta^2 = 1 - b\ln\varphi$	$b = 2.02 \pm 0.08$	$r^2 = 0.65$

Transport in Porewater: Diffusion

- Relationship between $J^{\mathrm{f}}_{\mathrm{diff}\,i}$ and $\hat{J}_{\mathrm{diff}\,i}$: it is possible to show that

$$\hat{J}_{\mathrm{diff}\,i} = \varphi^{\mathrm{f}}\,J^{\mathrm{f}}_{\mathrm{diff}\,i}$$

- Finally:

$$\hat{J}_{\mathrm{diff}\,i} = -\varphi^{\mathrm{f}}\frac{D^{\mathrm{sw}}_i}{\theta^2}\frac{\partial C^{\mathrm{f}}_i}{\partial z}$$

- In summary: *total transport of a solute i*

$$\hat{J}_i = \varphi^{\mathrm{f}}uC^{\mathrm{f}}_i - \varphi^{\mathrm{f}}\frac{D^{\mathrm{sw}}_i}{\theta^2}\frac{\partial C^{\mathrm{f}}_i}{\partial z}$$

Transport in the Solid Phase: Advection

- Solid i, with concentration C^{s}_i in the solid sediment fraction

$$\hat{J}_{\mathrm{adv}\,i} = w\,\hat{C}_i = \varphi^{\mathrm{s}}wC^{\mathrm{s}}_i,$$

where $w = w(z,t)$, such that $\boldsymbol{w} = w\,\boldsymbol{e}_z$, is the velocity of the bulk solids relative to the water-sediment interface
- w may be positive (oriented downwards) or negative (oriented upwards), and may even change sign within the sediment column
  - $w \geq 0$: net accumulation
  - $w \leq 0$: erosion

Transport in the Solid Phase: Mixing Processes
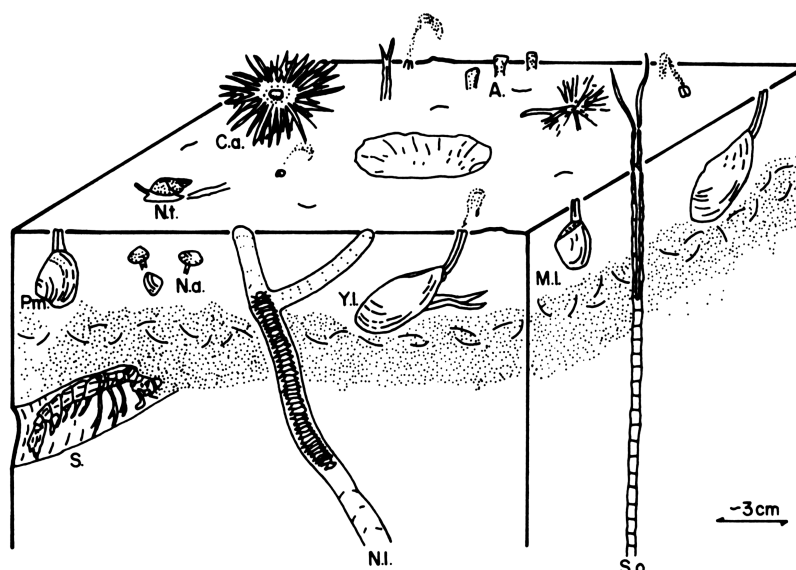
Macrofaunal activity (Berner, 1980)

Transport in the Solid Phase: Mixing Processes

- Bioturbation: mixing of the surface layer of the seafloor sediment by macro-organisms in their quest for food (organic matter)
- Assimilable to a diffusive process → *biodiffusion*
- Characterization of a biodiffusive process
  - biodiffusion coefficient D_{bio}
    (typical values: 0.1–10 cm^2/yr)
  - mixed-layer depth L — average depth of activity
    (global average observation: 9,8 cm $\pm$ 4,5 cm)
- Positive correlation between bioturbation and deposition rate of fresh organic matter
- Absence of bioturbation in anoxic sediments

Transport in the Solid Phase: Mixing Processes

- Two types of biodiffusion
  - *interphase*: the bulk sediment (solids and porewater) is mixed

$$\hat{J}_{\text{inter } i} = -D^{\text{inter}} \frac{\partial \varphi^s C_i^s}{\partial z}$$

  - *intraphase*: mixing operates separately on the fluid and the solid phases (possibly. even separately on different solids)

$$\hat{J}_{\text{intra } i} = -\varphi^s D_i^{\text{intra}} \frac{\partial C_i^s}{\partial z}$$

- Biodiffusion also affects solutes, but in general, $D_{\text{bio},i} \ll D_i^{\text{sw}}$

Advection, Diffusion, ... Reaction

- Dissolution rate of *calcite* $\hat{T}_{\text{Calc diss}}^V$, in units of mass per unit volume of total sediment

$$\hat{T}_{\text{Calc diss}}^V = k_{\text{Calc}} \times \varphi^s \times [\text{Calcite}]^s$$

with

$$k_{\text{Calc}} = \begin{cases} k_c \times (1 - \Omega_{\text{Calc}})^{n_c} & \text{si} \quad \Omega_{\text{Calc}} < 1 \\ 0 & \text{si} \quad \Omega_{\text{Calc}} \geq 1 \end{cases}$$

where

  - $\Omega_{\text{Calc}} = \frac{[\text{Ca}^{2+}]^f [\text{CO}_3^{2-}]^f}{K_{\text{Calc}}}$ is the degree of saturation of calcite, K_{Calc} being its (stoichiometric) solubility product
  - k_c is the dissolution rate constant
  - n_c is the apparent rate order

*Boundary Conditions: Ocean-Sediment Interface

- Apply the continuity equation to an interface

$$\hat{R}_i^{\Sigma} + \left(\hat{J}_i^- - \hat{J}_i^+ \right) = 0$$

- Let us define $\hat{J}_i^- = \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}}$ where $\hat{I}_i^{\text{top}} \geq 0$ is the gross input flux of i across the sediment-water interface and $\hat{O}_i^{\text{top}} \geq 0$ is the gross output flux.
  In the absence of surface reactions

$$\hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}} - \hat{J}_i^{z_T^+} = 0.$$

- *Solutes*: set concentrations (Dirichlet boundary conditions)
- *Solids*: continuity of the input flux (set $\hat{I}_i^{\text{top}}$)

*Boundary Conditions: Mixed-Layer Bottom

- Apply the continuity equation to an interface

$$\hat{R}_i^{\Sigma} + \left(\hat{J}_i^- - \hat{J}_i^+ \right) = 0$$

- *Solids*:
  - no boundary condition required for solids if $w_B \geq 0$;
  - boundary condition similar to that at the sediment-water interface if $w_B \leq 0$ (chemical erosion, input of materiel into the mixed-layer across the bottom)
- *Solutes*: continuity equation requires the porewater concentration gradients to vanish for each solute (C_i^f)

Boundary Conditions

Ocean-sediment interface

- *Solutes*: set concentrations (Dirichlet boundary conditions)
- *Solids*: continuity of the input flux ($\hat{J}_i^{z_T^+} = \hat{I}_i^{\text{top}}$)

Mixed-layer bottom

- *Solutes*: continuity equation requires porewater concentration gradients of each solute (C_i^f) to vanish
- *Solids*:
  - net accumulation ($w_B \geq 0$): no boundary condition
  - chemical erosion ($w_B \leq 0$): boundary condition similar to that at the sediment-water interface (input of materiel into the mixed-layer across the bottom)

A First Simple Carbonate Diagenesis Model

- Mixed layer 10 cm thick, with constant porosity
- Homogeneous ("well-mixed") solid phase
- Solids: calcite, inert material (clay, quartz)
- Solute: CO_3^{2-}
- Steady-state $[CO_3^{2-}]$ profile, advection neglected
- Equations
  - one global mass conservation equation for calcite and inert material in the mixed-layer
  - one diffusion-reaction equation for $[CO_3^{2-}]$
  - reaction term: $\hat{R}_{CO3}^V = \hat{T}_{\text{Calc diss}}^V$
- Exact analytical solution for $n_c = 1$, approximate analytical or numerical for $n_c \neq 1$

Insufficiency of the Simple Model

- Transport of DIC underestimated: CO_3^{2-} ions released during $CaCO_3$ dissolution react with porewater CO_2 to form HCO_3^- and DIC can thus also be transported under that form

- Significant $CaCO_3$ dissolution above the saturation horizon $\rightarrow$ dissolution promoted by the release of CO_2 during organic matter degradation in the mixed-layer

- Phenomenon impossible to represent with the simple model: no dissolution if $\Omega_{Calc}(z_{top}) > 1$

Organic Matter Remineralization

Organic matter remineralization reactions
$(OM = (CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$, following Redfield)

|		
(1)	Oxic Respiration	$OM + 138\,O_2$
		$\rightarrow 106\,CO_2 + 16\,HNO_3 + H_3PO_4 + 122\,H_2O$
(2a)	Complete	$OM + 94,4\,HNO_3$
	denitrification	$\rightarrow 106\,CO_2 + 55,2\,N_2 + H_3PO_4 + 177,2\,H_2O$
(2b)	Partial	$OM + 84,8\,HNO_3$
	denitrification	$\rightarrow 106\,CO_2 + 42,4\,N_2 + 16\,NH_3 + H_3PO_4 + 148,4\,H_2O$
(3)	Mn(IV) reduction	$OM + 236\,MnO_2 + 472\,H^+$
		$\rightarrow 106\,CO_2 + 8\,N_2 + H_3PO_4 + 236\,Mn^{2+} + 366\,H_2O$
(4)	Fe(III) reduction	$OM + 212\,Fe_2O_3 + 848\,H_2O$
		$\rightarrow 106\,CO_2 + 16\,NH_3 + H_3PO_4 + 472\,Fe^{2+}$
(5)	Sulfate reduction	$OM + 53\,SO_4^{2-}$
		$\rightarrow 106\,CO_2 + 16\,NH_3 + H_3PO_4 + 53\,S^{2-} + 106\,H_2O$
(6)	Methanogenesis	$OM \rightarrow 53\,CO_2 + 53\,CH_4 + 16\,NH_3 + H_3PO_4$

Porewater Solute Zonation
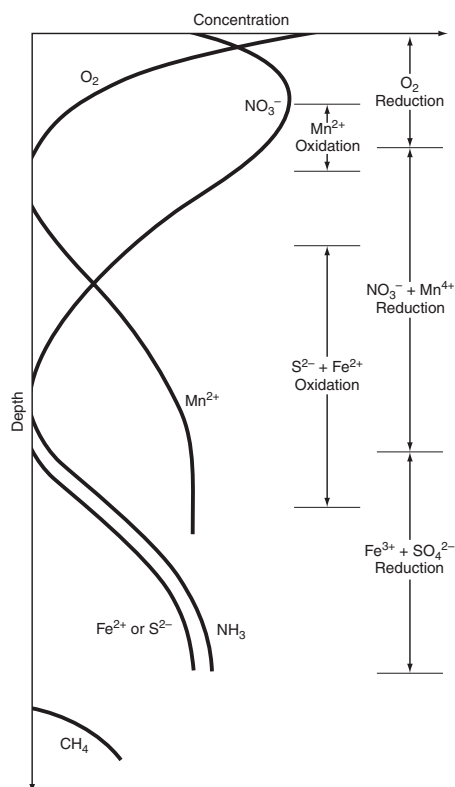
Source: Sarmiento et Gruber (2006)

Improved Carbonate Diagenesis Model

- Mixed-layer 10 cm thick
- Solids: calcite, inert material (clay, quartz) and organic matter, transported by advection and biodiffusion
- Solutes: CO_2, HCO_3^-, CO_3^{2-} et O_2, transported by molecular and ionic diffusion only
- Organic matter remineralization by oxic respiration:

$$OM + 138\,O_2 \rightarrow 106\,CO_2 + 16\,HNO_3 + H_3PO_4 + 122\,H_2O$$
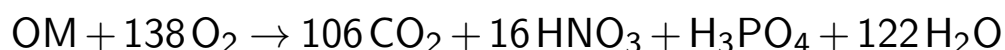
- Equations
  - one diffusion-reaction equation per solute
  - one advection-diffusion-reaction equation per solid

Improved Carbonate Diagenesis Model

Reaction terms: organic matter and oxygen

- Organic matter (OM) remineralization rate

$$\hat{T}^V_{\text{OM remin}} = k_{\text{OM}} \times \varphi^{\text{s}} \times [\text{OM}]^{\text{s}} \times \frac{[O_2]^{\text{f}}}{M_{O_2} + [O_2]^{\text{f}}}$$

  where M_{O_2} is a half-saturation constant
  and k_{OM} is a degradation rate constant

- Hence

$$\hat{R}^V_{\text{OM}} = -\hat{T}^V_{\text{OM remin}}$$
$$\hat{R}^V_{O_2} = -138 \times \hat{T}^V_{\text{OM remin}}$$

Improved Carbonate Diagenesis Model

Reaction terms: calcite

- Dissolution rate if calcite

$$\hat{T}^V_{\text{Calc diss}} = k_{\text{Calc}} \times \varphi^{\text{s}} \times [\text{Calcite}]^{\text{s}}$$

  with

$$k_{\text{Calc}} = \begin{cases} k_c \times (1 - \Omega_{\text{Calc}})^{n_c} & \text{si} \quad \Omega_{\text{Calc}} < 1 \\ 0 & \text{si} \quad \Omega_{\text{Calc}} \geq 1 \end{cases}$$
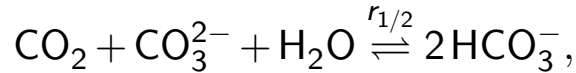
- Hence,

$$\hat{R}^V_{\text{Calc}} = -\hat{T}^V_{\text{Calc diss}}$$

Improved Carbonate Diagenesis Model

Reaction terms: dissolved inorganic carbon

- Chemical reaction

$$CO_2 + CO_3^{2-} + H_2O \overset{r_{1/2}}{\rightleftharpoons} 2\,HCO_3^-,$$

  where $r_{1/2}$ denotes the net reaction rate, from left to right

- Reaction terms for CO_2, HCO_3^- and CO_3^{2-}

$$
\begin{aligned}
\hat{R}_{CO2}^V &= -r_{1/2} + 106 \times \hat{T}_{OM\ remin}^V \\
\hat{R}_{HCO3}^V &= 2 \times r_{1/2} \\
\hat{R}_{CO3}^V &= -r_{1/2} + \hat{T}_{Calc\ diss}^V
\end{aligned}
$$

Improved Carbonate Diagenesis Model

Elimination of the fast reactions

- $r_{1/2} \gg \hat{T}_{Calc\ diss}^V, \hat{T}_{MO\ remin}^V$
  (characteristic time $\simeq 10^2 - 10^3$ s)
- Equilibrium hypothesis for interconversion reactions
- Elimination of $r_{1/2}$ from the eqns. for CO_2, HCO_3^- and CO_3^{2-}
  - replace the equation for CO_2 by the sum of the equations for CO_2, HCO_3^- and CO_3^{2-} ($\to$DIC)
  - replace the equation for HCO_3^- by the sum of the equation for HCO_3^- plus twice the equation for CO_3^{2-} ($\to$ALK)
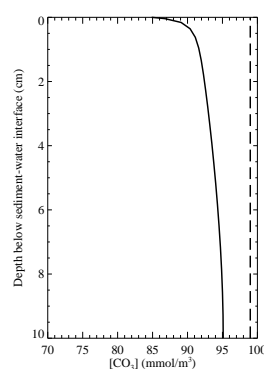 - replace the equation for CO_3^{2-} by the equilibrium condition

$$K_2([HCO_3^-]^f)^2 - K_1[CO_2]^f[CO_3^{2-}]^f = 0$$

- Transformation of the partial differential equation (PDE) system into a differential algebraic equation (DAE) system

Improved Carbonate Diagenesis Model
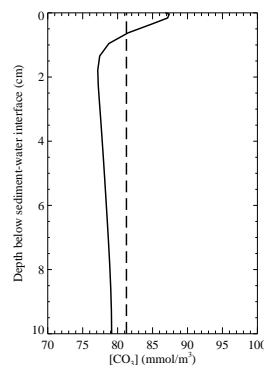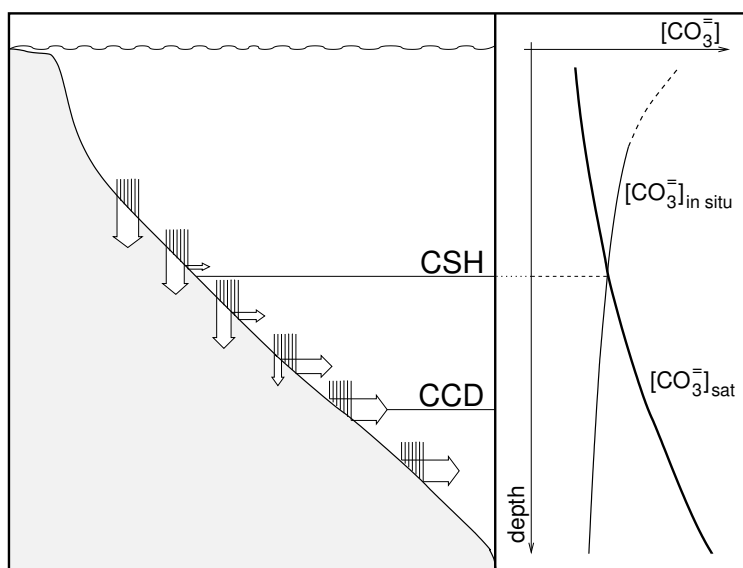
above
the CSH

below
the CSH

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