

# Seafloor Sediments

## Interaction with the Ocean and Early Diagenesis

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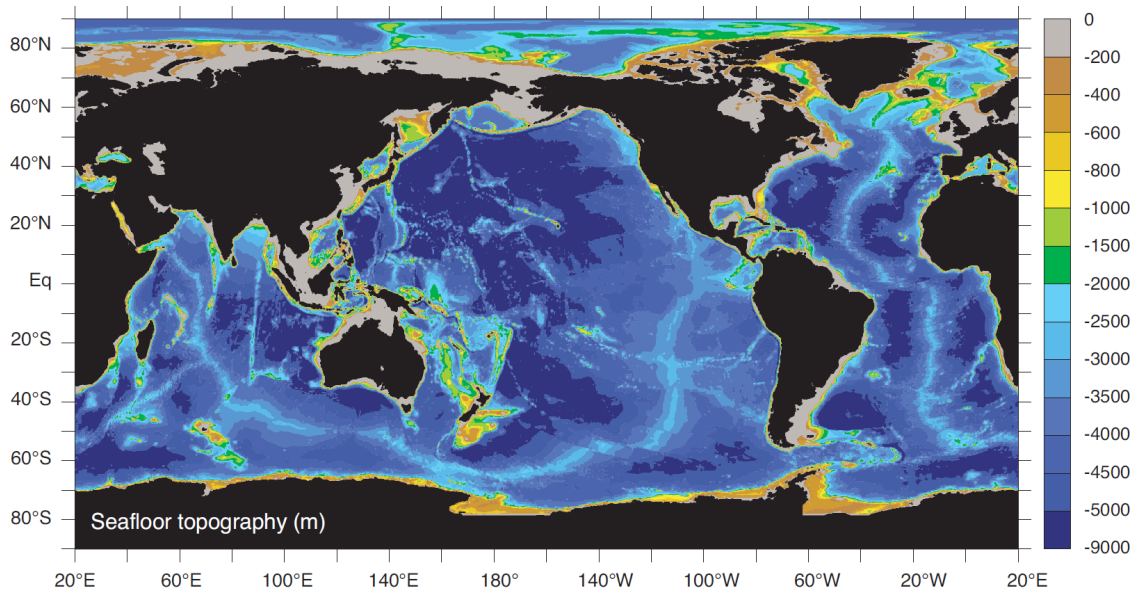
28th February 2024

6th March 2024

## Plan

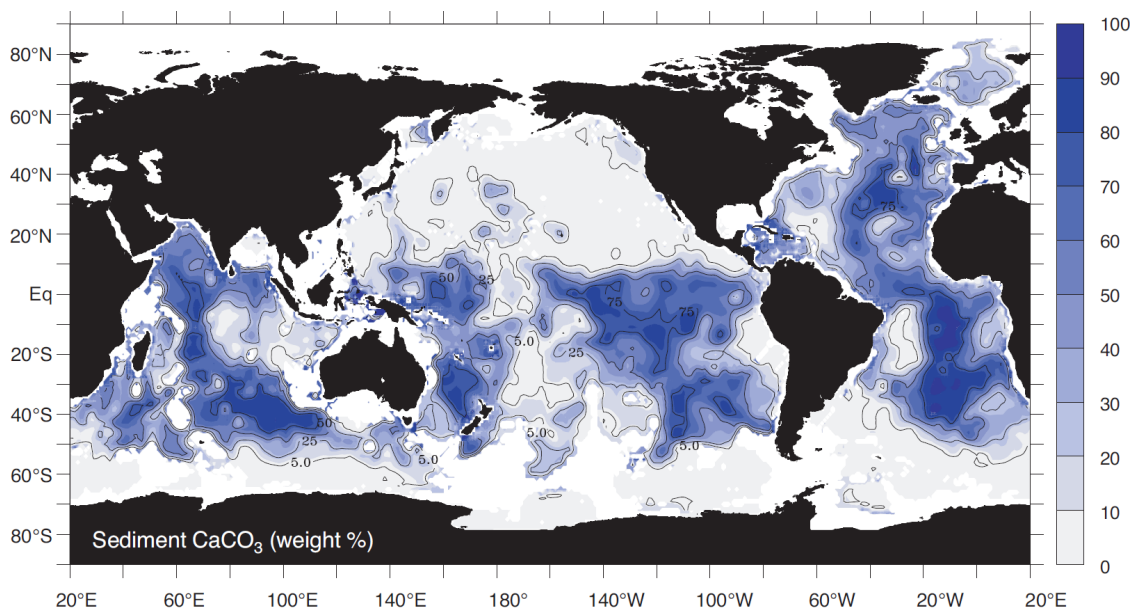
- Sediments in the present-day ocean
- Interest of sediments in Earth sciences
- Role of seafloor sediments in biogeochemical cycles
- Processes: transport and reaction
- Advection-diffusion-reaction model(s)

# The Seafloor and its Sediments: a First Exploration



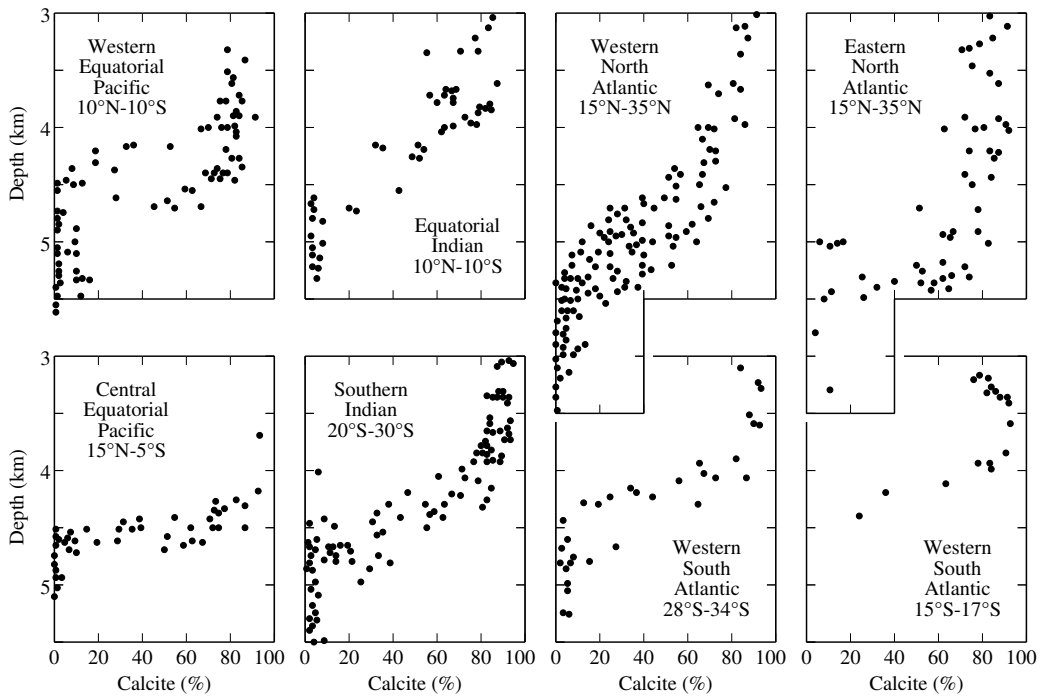
Source: Sarmiento and Gruber (2006)

# The Seafloor and its Sediments: a First Exploration



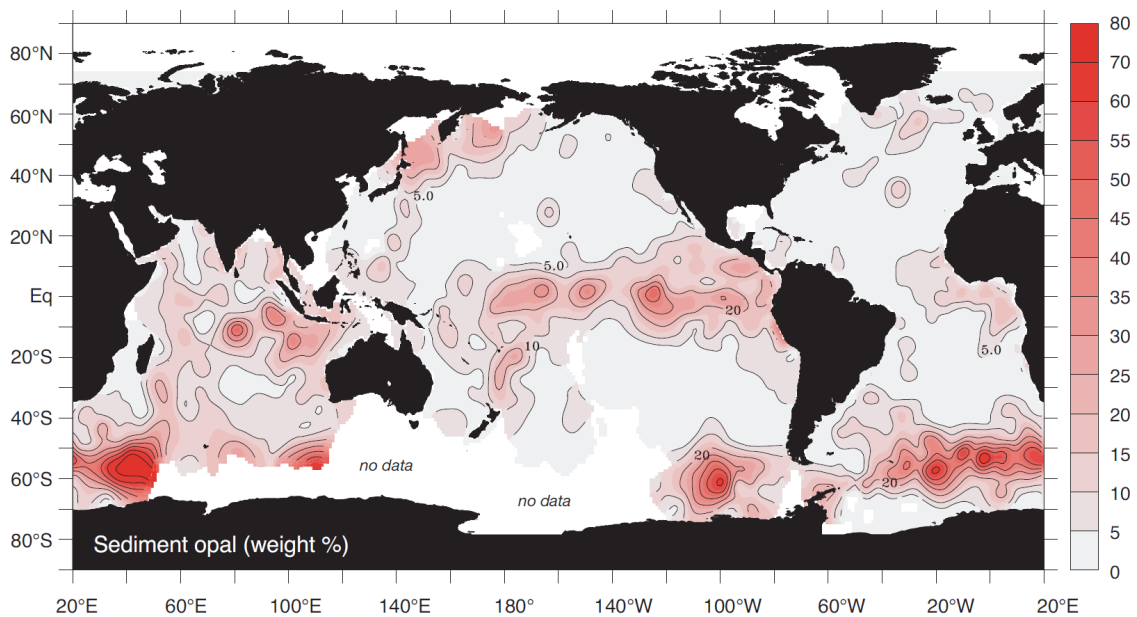
Source: Sarmiento and Gruber (2006)

# The Seafloor and its Sediments: a First Exploration



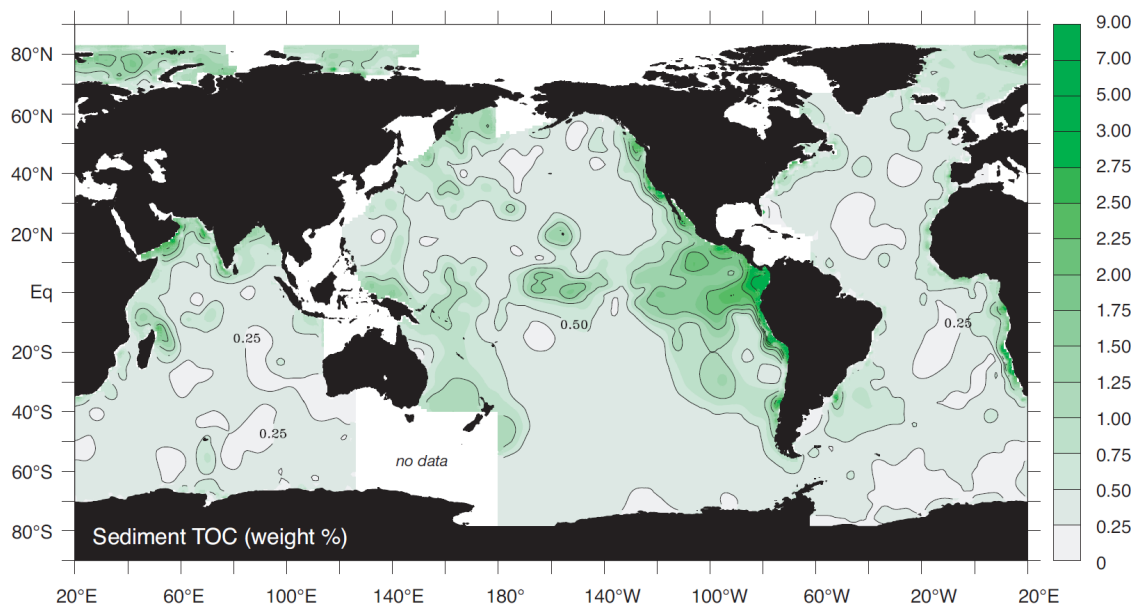
Source: Broecker and Peng (1982)

# The Seafloor and its Sediments: a First Exploration



Source: Sarmiento and Gruber (2006)

# The Seafloor and its Sediments: a First Exploration



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Ocean Sediment-Interaction and Early Diagenesis

## 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<sub>2</sub> source, porewater acidification)

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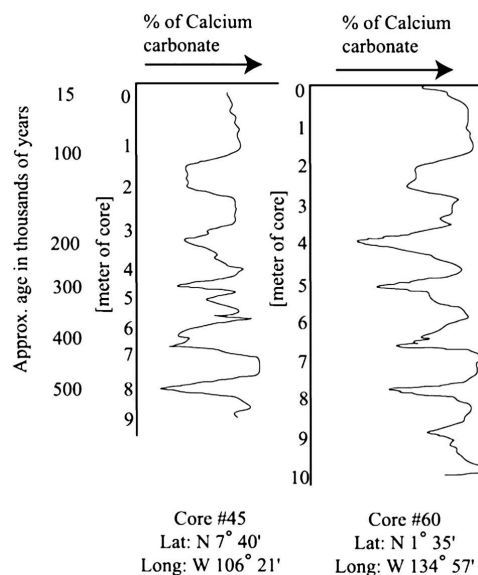
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## Seafloor Sediments: Non Biogenic Components

- 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 material (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 ( $\approx 15$  m) from different equatorial oceans
- Chemical analyses for  $\%CaCO_3$  by Gustaf Arrhenius (1952) reveal glacial-interglacial cycles



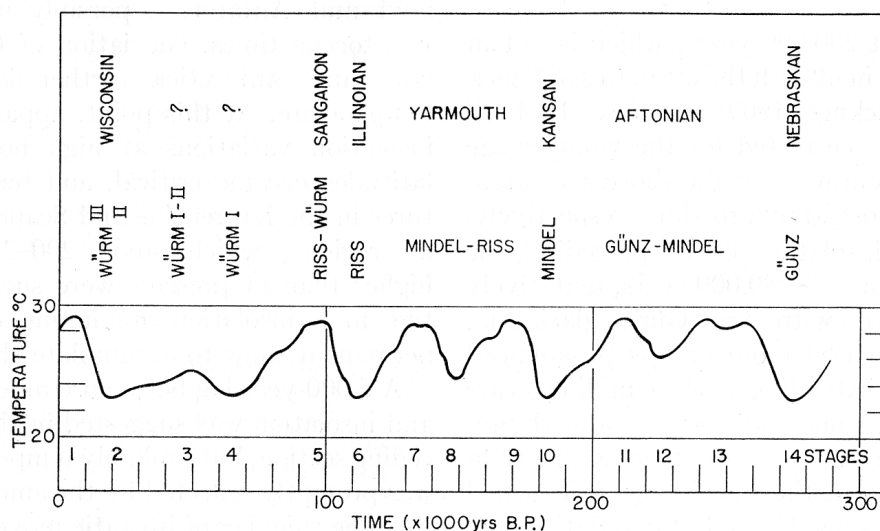
Source: [http://earthguide.ucsd.edu/virtualmuseum/climatechange/02\\_4.shtml](http://earthguide.ucsd.edu/virtualmuseum/climatechange/02_4.shtml)

Sedimentary Archives: C. Emiliani's  $\delta^{18}\text{O}$ 

- Cesare Emiliani. Pleistocene Temperatures. *Journal of Geology* 63:538-578, 1955.
- Measurements of the evolution of the isotopic ratio  $^{18}\text{O}/^{16}\text{O}$  on microfossils preserved in different cores, carried out in Harold Urey's lab (University of Chicago)  
→ 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  $\delta^{18}\text{O}$ 

- 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)



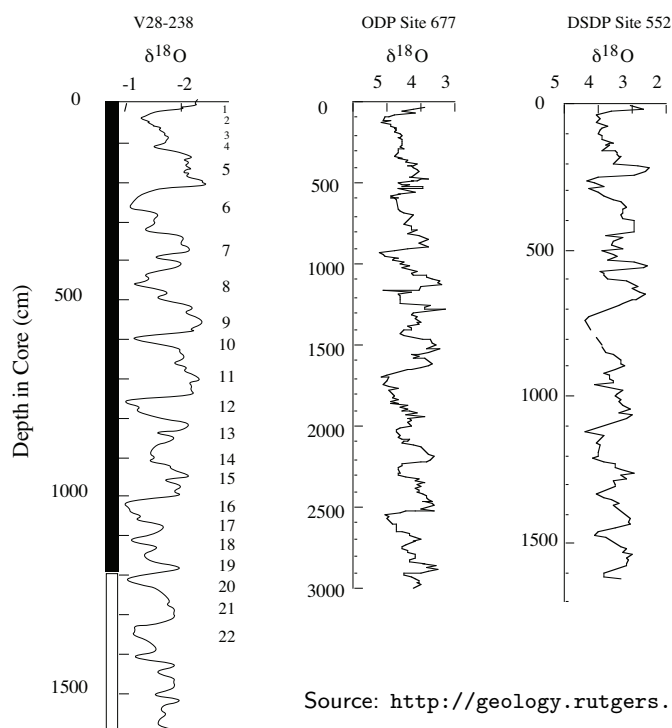
Source: Emiliani (1955)



Sedimentary Archives: N. Shackleton's  $\delta^{18}\text{O}$ 's

- Shackleton (1967)
  - joint  $^{18}\text{O}/^{16}\text{O}$  measurements on planktonic (surface dwelling) and benthic (deep-sea dwelling) shells
  - co-variation  $\rightarrow$  ice-volume changes dominate  $^{18}\text{O}/^{16}\text{O}$  variations
- Shackleton and Opdyke (1973)
  - measurement of  $^{18}\text{O}/^{16}\text{O}$  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](http://geology.rutgers.edu/~jdwright/JDWWeb/1999/JDWright_NUREG.pdf)

# Role of Sediments in Biogeochemical Cycling

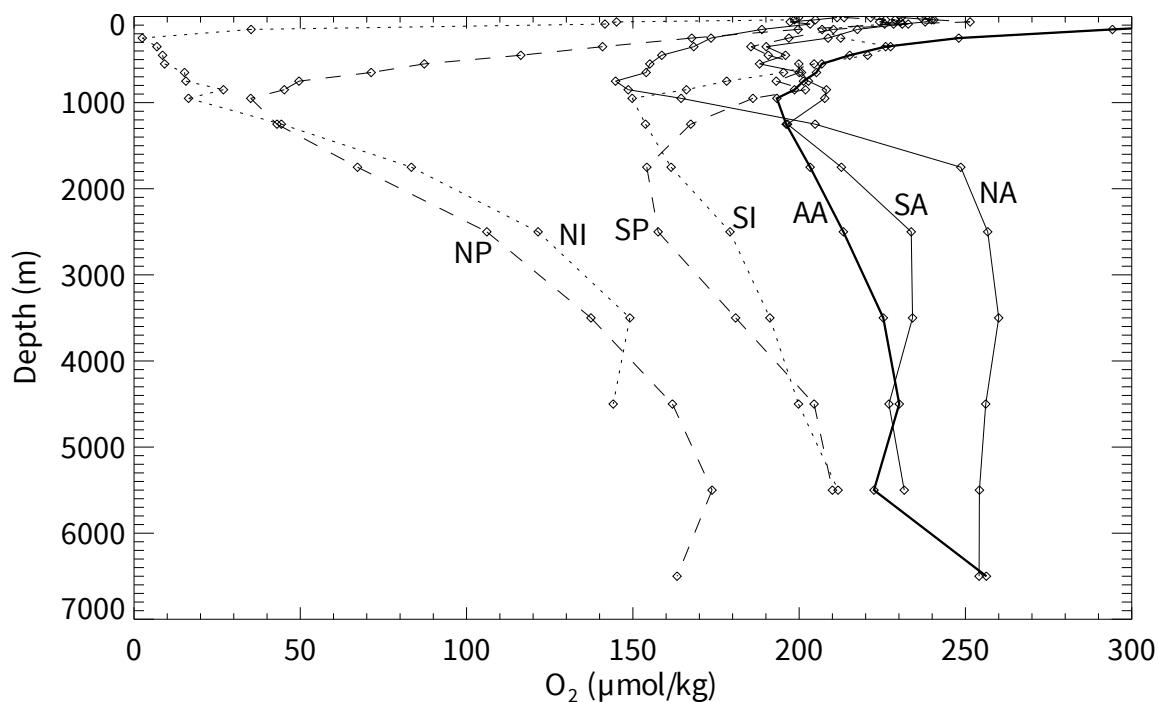
- Active role in ocean biogeochemical cycling
- Locus of preservation and remineralization of biogenic material (carbonates, opal, organic matter, etc.)
- Concentration gradients of similar amplitude in water column and in surface sediment

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## Concentration Gradients: Ocean vs. Surface Sediment

### Dissolved Oxygen in the Water Column



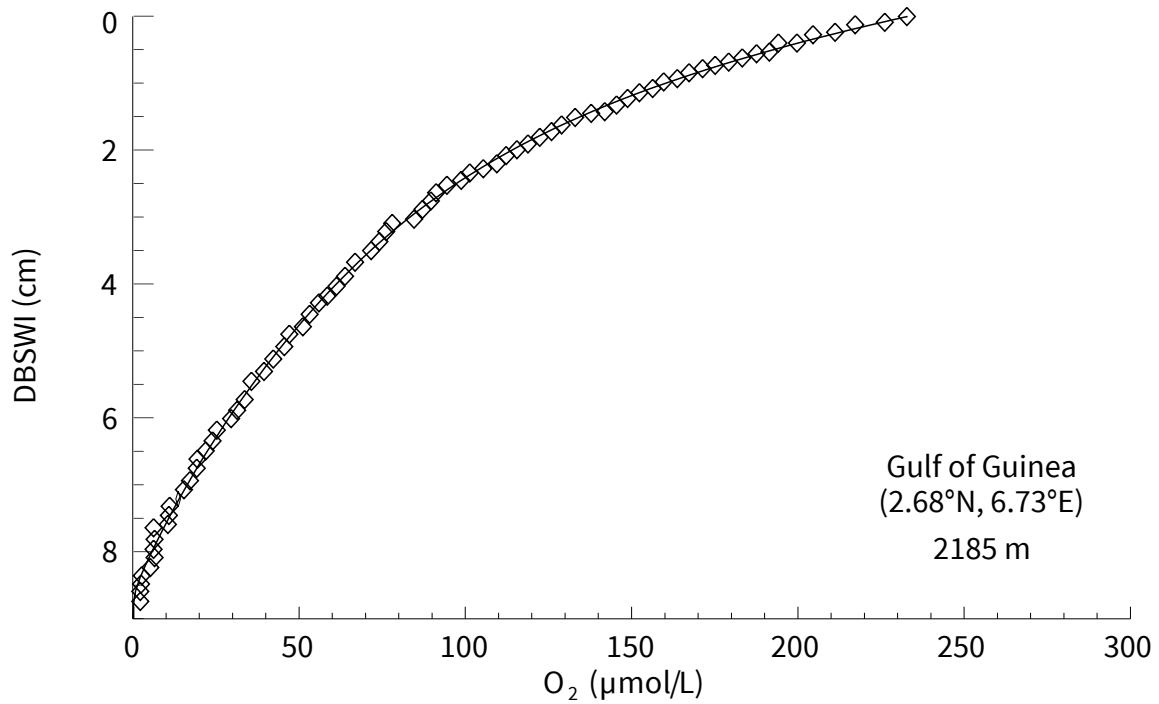
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# Concentration Gradients: Ocean vs. Surface Sediment

## Dissolved Oxygen in the Surface Sediment Porewater

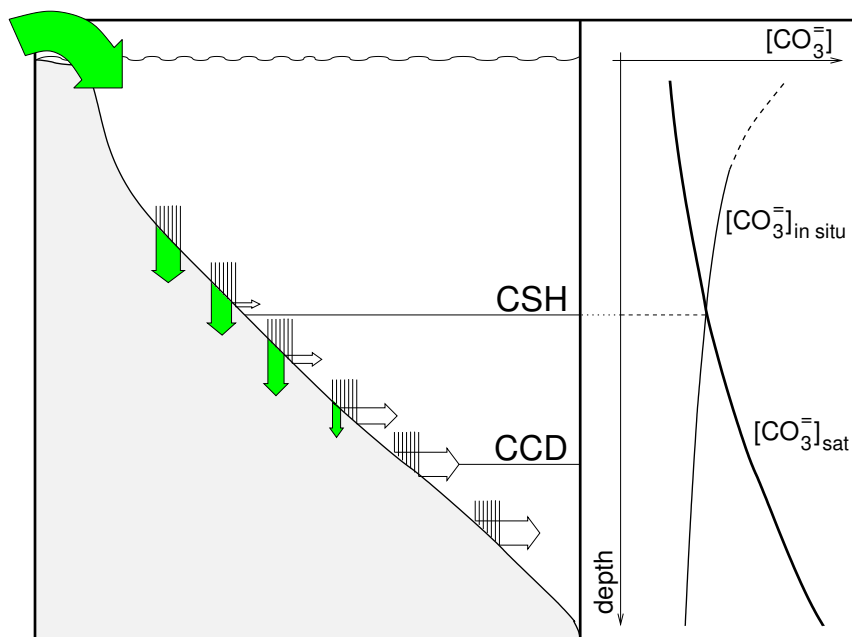


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# Acidification: Perturbation of the Ocean-Sediment Exchange

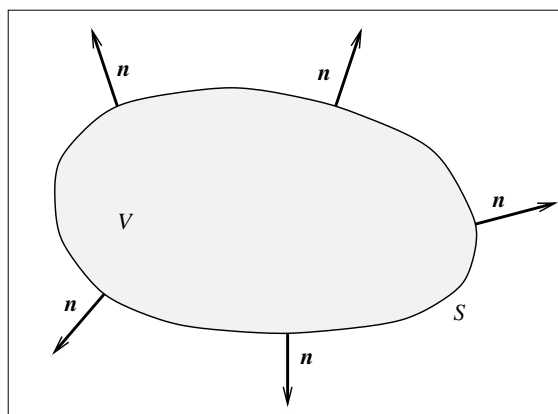
## Marine carbonates: ocean-sediment exchange



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## Preludes: geometric setting



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

## General Continuity Equation

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

- $\hat{C}_i$  is the concentration of constituent  $i$  in units of mass per unit volume of total sediment (solid fraction + porewater);
- $\hat{\mathbf{J}}_i$  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

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

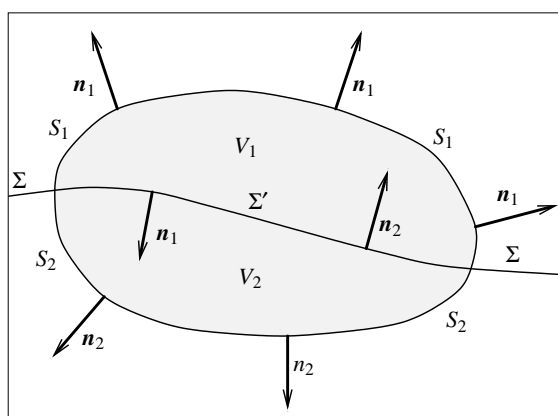
- General equation may be rewritten as

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

- $V$  is arbitrary, and thus

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

## General Continuity Equation for Interfaces



- $V$  arbitrary volume, delimited by the surface  $S$
- $\Sigma$  arbitrary surface dividing  $V$  into  $V_1$ ,  $V_2$  and  $S$  into  $S_1$ ,  $S_2$
- $\Sigma'$  the part of  $\Sigma$  contained in  $V$
- $\mathbf{n}_1$ ,  $\mathbf{n}_2$  unitary normal vectors in each point of  $S_1$ ,  $S_2$  et  $\Sigma'$ , 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  $\Sigma'$

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

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

- Conservation equations in  $V_1$  and  $V_2$

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

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

## 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

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

we get

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

## General Continuity Equation for Interfaces

$\Sigma'$  being arbitrary since  $\Sigma$  is arbitrary, we have the following continuity equation for any interface:

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

Noting that

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

we can rewrite this equation as

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

## 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  $\varphi = \varphi(t, \mathbf{x})$  defined by

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

- $\varphi^f$  *water fraction* (fluid) and  $\varphi^s$  *solid fraction*
- Neglecting volumes of unconnected pores

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

# Total Concentrations and Phase Concentrations

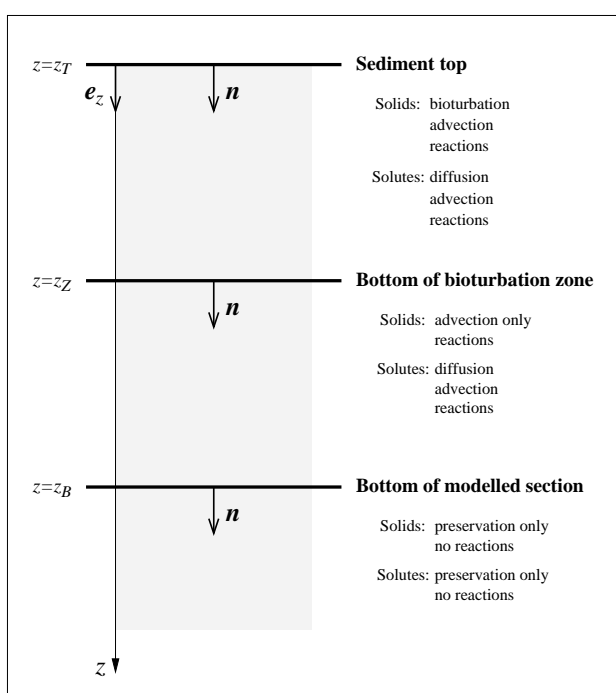
- Continuity equations expressed in terms of  $\hat{C}_i$ , concentration of  $i$  per unit volume of total sediment
- More directly measurable
  - $i$  solid:  $C_i^s$  concentration of  $i$  in units of mass per unit volume of solid sediment

$$\hat{C}_i = \phi^s C_i^s$$

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

$$\hat{C}_i = \phi^f C_i^f$$

# One-Dimensional Model



With  $\hat{J}_i = \hat{J}_i e_z$ , 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  $\Sigma$ , with upper side '1' and lower side '2':

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

Hence,

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

## 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  
→ to include as sources or sinks, similarly to reactions

## Transport in Porewater: Advection

- Solute  $i$ , of concentration  $C_i^f$  in porewater

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

where  $u = u(z, t)$ , such that  $\mathbf{u} = u\mathbf{e}_z$  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 ( $\varphi$  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

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

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

- $J_{\text{diff } i}^f$ , 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  $D_i^{\text{sed}}$  and  $D_i^{\text{sw}}$ , 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  $\theta^2$  and porosity

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

## Transport in Porewater: Diffusion

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

$$\hat{J}_{\text{diff } i} = \varphi^f J_{\text{diff } i}^f$$

- Finally:

$$\hat{J}_{\text{diff } i} = -\varphi^f \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^f}{\partial z}$$

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

$$\hat{J}_i = \varphi^f u C_i^f - \varphi^f \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^f}{\partial z}$$

## Transport in the Solid Phase: Advection

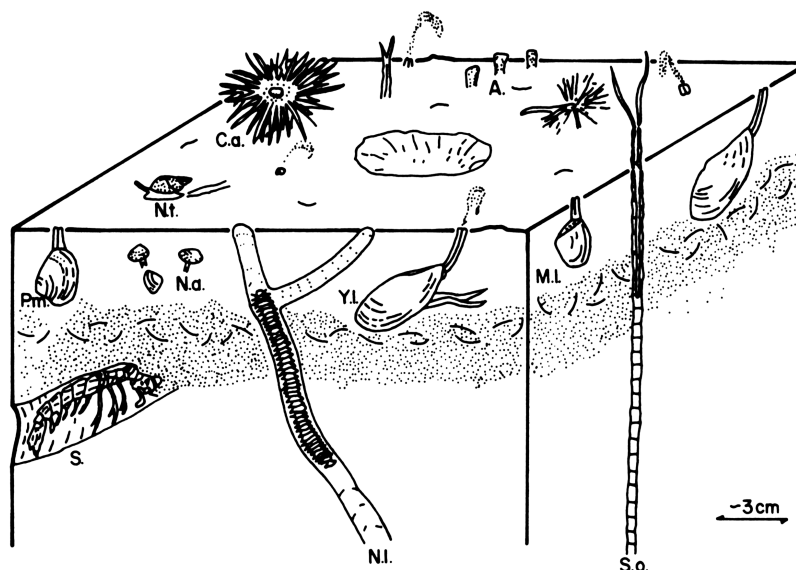
- Solid  $i$ , with concentration  $C_i^s$  in the solid sediment fraction

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

where  $w = w(z, t)$ , such that  $\mathbf{w} = w \mathbf{e}_z$ , 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  $D_{\text{bio}}$   
(typical values:  $0.1\text{--}10\text{ cm}^2/\text{yr}$ )
  - mixed-layer depth  $L$  — average depth of activity  
(global average observation:  $9,8\text{ cm} \pm 4,5\text{ cm}$ )
- 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

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

- *intrapphase*: 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

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

where

- $\Omega_{\text{Calc}} = \frac{[\text{Ca}^{2+}]^f [\text{CO}_3^{2-}]^f}{K_{\text{Calc}}}$  is the degree of saturation of calcite,  $K_{\text{Calc}}$  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

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

- Let us define  $\hat{J}_i^- = \hat{l}_i^{\text{top}} - \hat{O}_i^{\text{top}}$  where  $\hat{l}_i^{\text{top}} \geq 0$  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

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

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

## \*Boundary Conditions: Mixed-Layer Bottom

- Apply the continuity equation to an interface

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

- *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 material 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 material 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:  $\text{CO}_3^{2-}$
- Steady-state  $[\text{CO}_3^{2-}]$  profile, advection neglected
- Equations
  - one global mass conservation equation for calcite and inert material in the mixed-layer
  - one diffusion-reaction equation for  $[\text{CO}_3^{2-}]$
  - reaction term:  $\hat{R}_{\text{CO}_3}^V = \hat{T}_{\text{Calc diss}}^V$
- 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:  $\text{CO}_3^{2-}$  ions released during  $\text{CaCO}_3$  dissolution react with porewater  $\text{CO}_2$  to form  $\text{HCO}_3^-$  and DIC can thus also be transported under that form
- Significant  $\text{CaCO}_3$  dissolution above the saturation horizon  
→ dissolution promoted by the release of  $\text{CO}_2$  during organic matter degradation in the mixed-layer
- Phenomenon impossible to represent with the simple model:  
no dissolution if  $\Omega_{\text{Calc}}(z_{\text{top}}) > 1$

## Organic Matter Remineralization

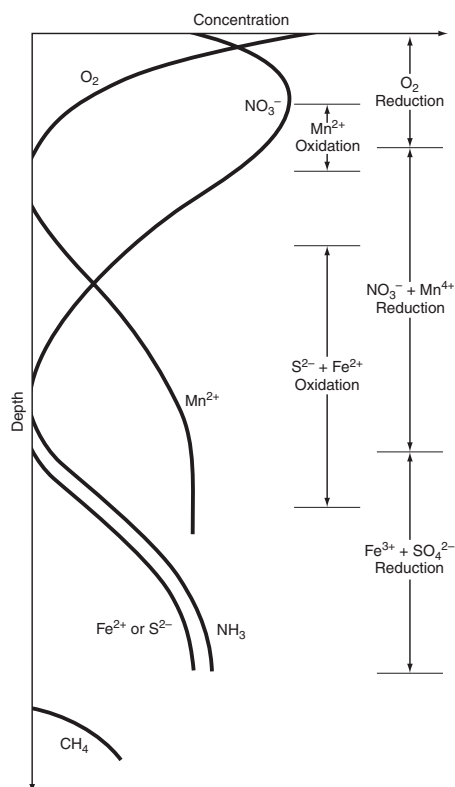
Organic matter remineralization reactions

(OM =  $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ , following Redfield)

- |                               |   |
|-------------------------------|---|
| (1) Oxidic Respiration        | $\text{OM} + 138 \text{O}_2$<br>→ $106 \text{CO}_2 + 16 \text{HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O}$                                      |
| (2a) Complete denitrification | $\text{OM} + 94, 4 \text{HNO}_3$<br>→ $106 \text{CO}_2 + 55, 2 \text{N}_2 + \text{H}_3\text{PO}_4 + 177, 2 \text{H}_2\text{O}$                              |
| (2b) Partial denitrification  | $\text{OM} + 84, 8 \text{HNO}_3$<br>→ $106 \text{CO}_2 + 42, 4 \text{N}_2 + 16 \text{NH}_3 + \text{H}_3\text{PO}_4 + 148, 4 \text{H}_2\text{O}$             |
| (3) Mn(IV) reduction          | $\text{OM} + 236 \text{MnO}_2 + 472 \text{H}^+$<br>→ $106 \text{CO}_2 + 8 \text{N}_2 + \text{H}_3\text{PO}_4 + 236 \text{Mn}^{2+} + 366 \text{H}_2\text{O}$ |
| (4) Fe(III) reduction         | $\text{OM} + 212 \text{Fe}_2\text{O}_3 + 848 \text{H}_2\text{O}$<br>→ $106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_3\text{PO}_4 + 472 \text{Fe}^{2+}$       |
| (5) Sulfate reduction         | $\text{OM} + 53 \text{SO}_4^{2-}$<br>→ $106 \text{CO}_2 + 16 \text{NH}_3 + \text{H}_3\text{PO}_4 + 53 \text{S}^{2-} + 106 \text{H}_2\text{O}$               |
| (6) Methanogenesis            | $\text{OM} \rightarrow 53 \text{CO}_2 + 53 \text{CH}_4 + 16 \text{NH}_3 + \text{H}_3\text{PO}_4$  |



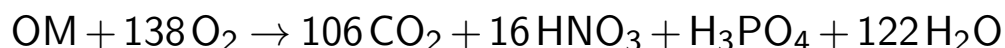
# Porewater Solute Zonation



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<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> et O<sub>2</sub>, transported by molecular and ionic diffusion only
- Organic matter remineralization by oxic respiration:



- 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

$$\hat{T}_{\text{OM remin}}^V = k_{\text{OM}} \times \varphi^s \times [\text{OM}]^s \times \frac{[\text{O}_2]^f}{M_{\text{O}_2} + [\text{O}_2]^f}$$

where  $M_{\text{O}_2}$  is a half-saturation constant  
and  $k_{\text{OM}}$  is a degradation rate constant

- Hence

$$\begin{aligned}\hat{R}_{\text{OM}}^V &= -\hat{T}_{\text{OM remin}}^V \\ \hat{R}_{\text{O}_2}^V &= -138 \times \hat{T}_{\text{OM remin}}^V\end{aligned}$$

# Improved Carbonate Diagenesis Model

## Reaction terms: calcite

- Dissolution rate of calcite

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

with

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

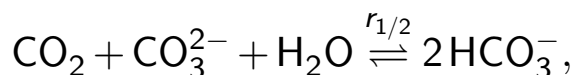
- Hence,

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

# Improved Carbonate Diagenesis Model

## Reaction terms: dissolved inorganic carbon

- Chemical reaction



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

- Reaction terms for  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$

$$\begin{aligned}\hat{R}_{\text{CO}_2}^V &= -r_{1/2} + 106 \times \hat{T}_{\text{OM remin}}^V \\ \hat{R}_{\text{HCO}_3}^V &= 2 \times r_{1/2} \\ \hat{R}_{\text{CO}_3}^V &= -r_{1/2} + \hat{T}_{\text{Calc diss}}^V\end{aligned}$$

# Improved Carbonate Diagenesis Model

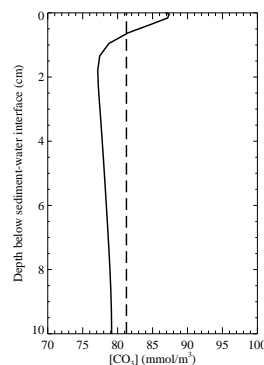
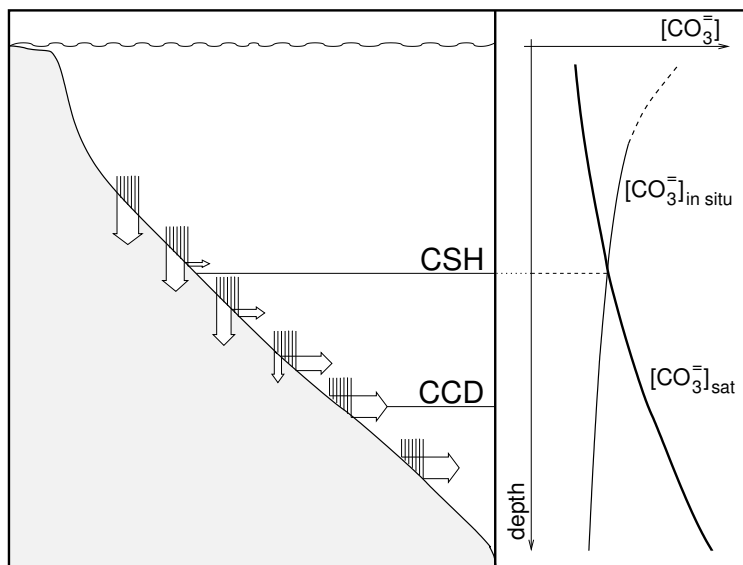
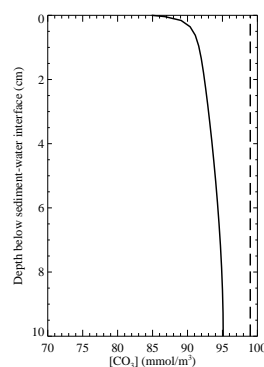
## Elimination of the fast reactions

- $r_{1/2} \gg \hat{T}_{\text{Calc diss}}^V, \hat{T}_{\text{MO remin}}^V$   
(characteristic time  $\simeq 10^2 - 10^3$  s)
- Equilibrium hypothesis for interconversion reactions
- Elimination of  $r_{1/2}$  from the eqns. for  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ 
  - replace the equation for  $\text{CO}_2$  by the sum of the equations for  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ( $\rightarrow$ DIC)
  - replace the equation for  $\text{HCO}_3^-$  by the sum of the equation for  $\text{HCO}_3^-$  plus twice the equation for  $\text{CO}_3^{2-}$  ( $\rightarrow$ ALK)
  - replace the equation for  $\text{CO}_3^{2-}$  by the equilibrium condition

$$K_2([\text{HCO}_3^-]^f)^2 - K_1[\text{CO}_2]^f[\text{CO}_3^{2-}]^f = 0$$

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

## Improved Carbonate Diagenesis Model

above  
the CSHbelow  
the CSH

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