Seafloor Sediments — Interaction with the Ocean and Early Diagenesis

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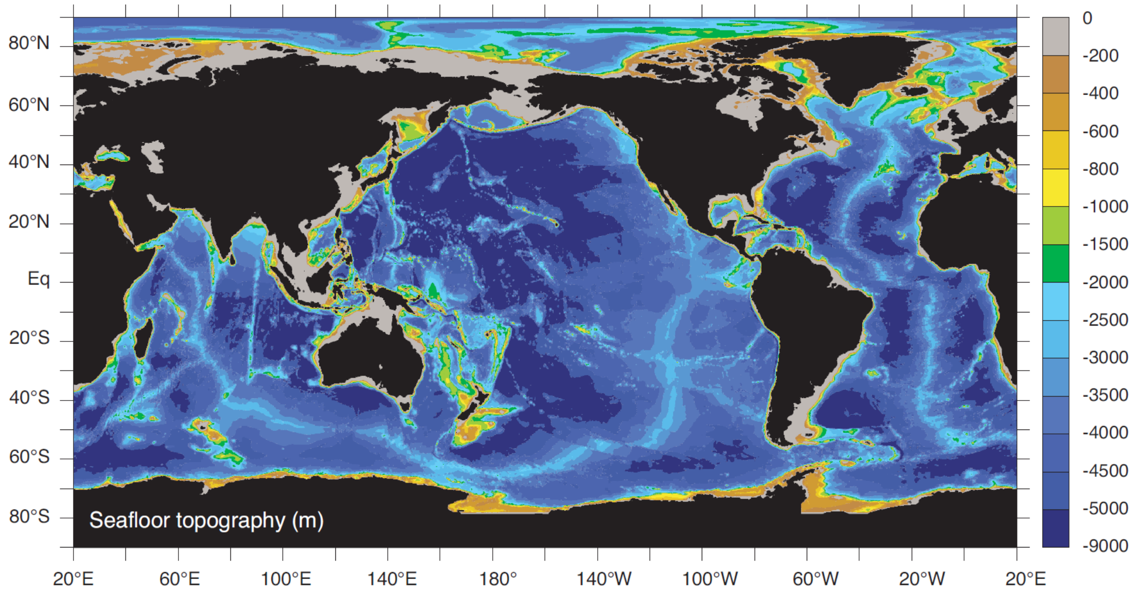
Plan

- 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



Source: Sarmiento and Gruber (2006)

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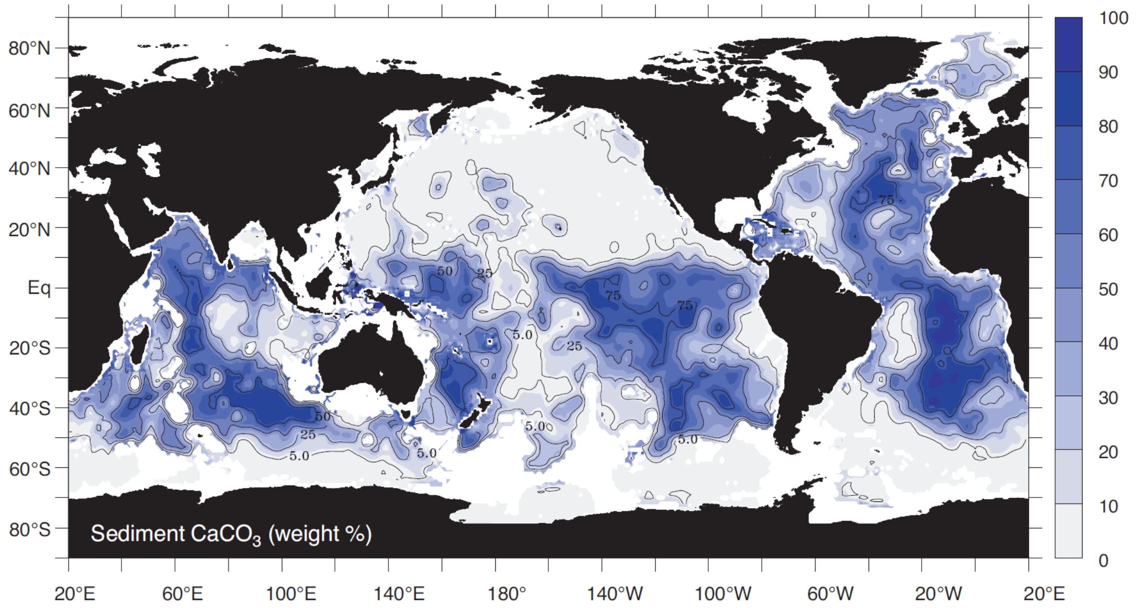

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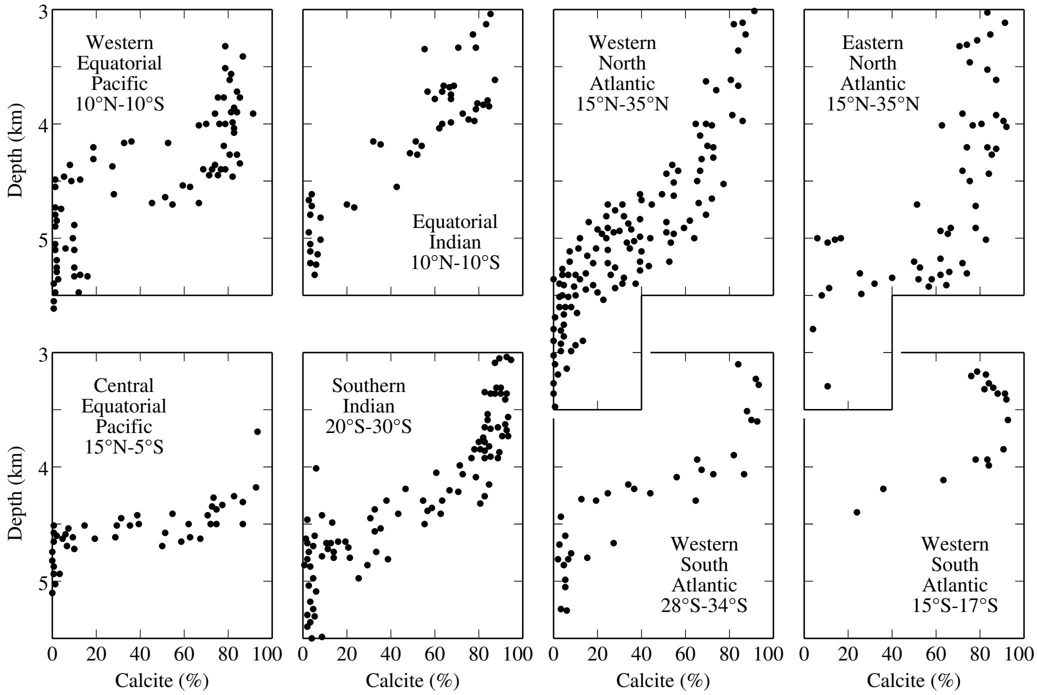

Source: Broecker and Peng (1982)

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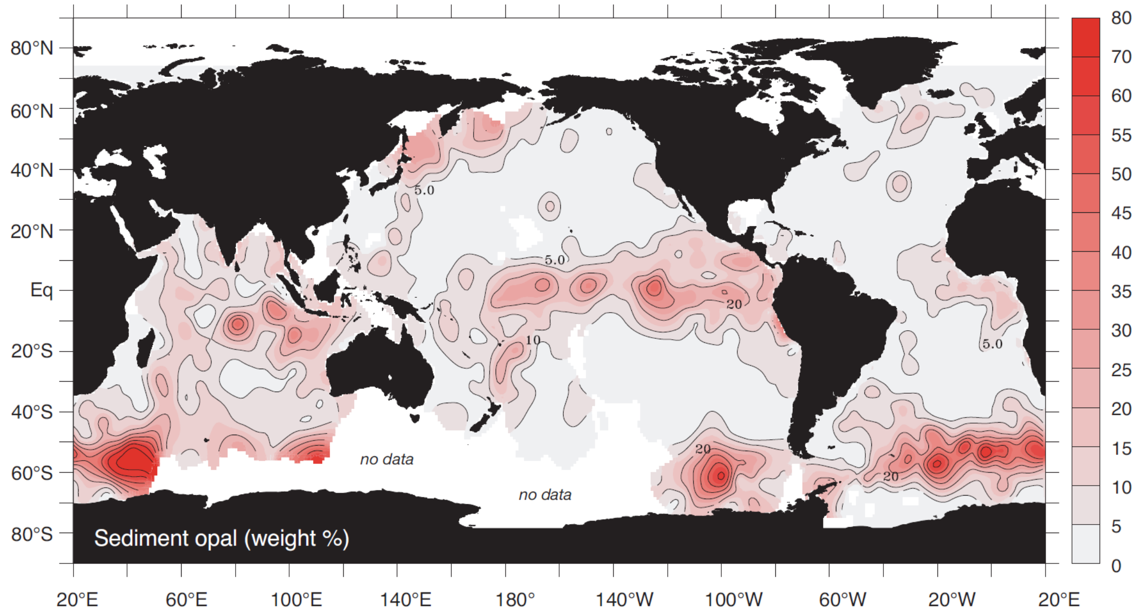

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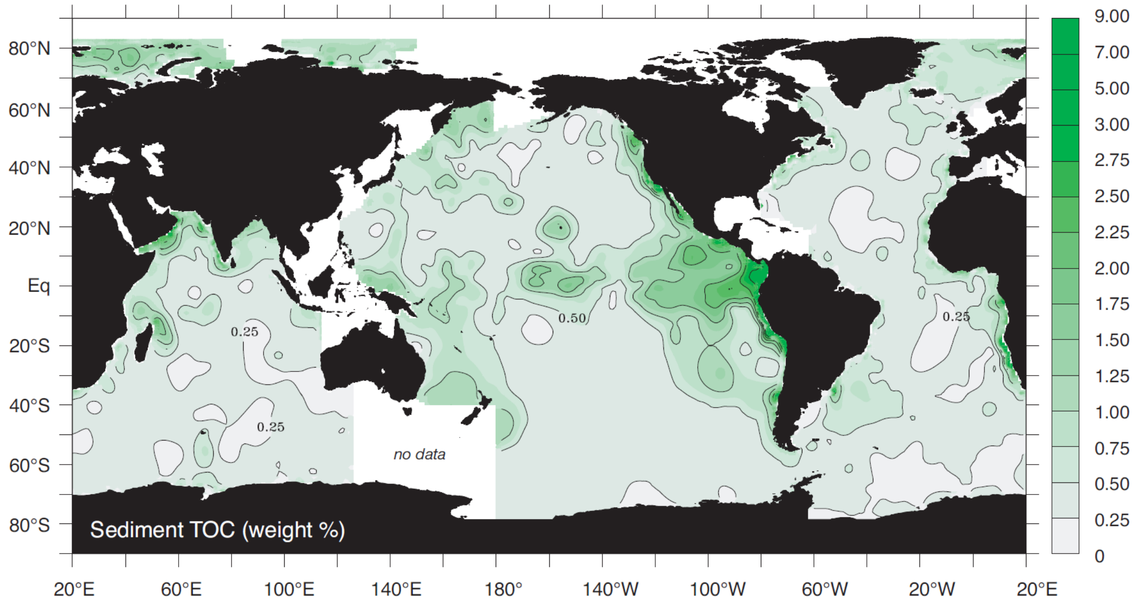

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Seafloor Sediments: Biogenic Components

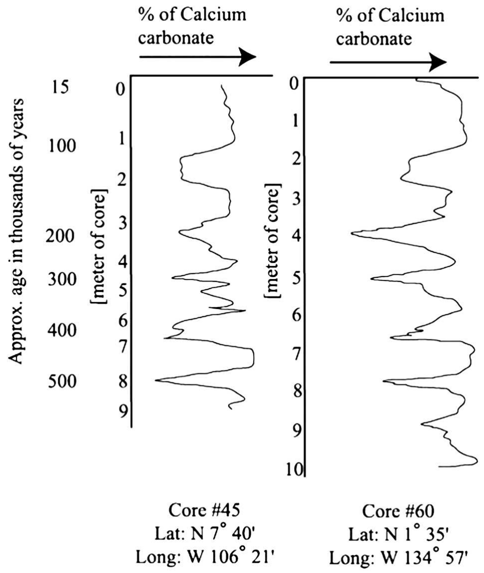
- Carbonates
  - distribution related to seafloor depth: deepest sediments devoid of carbonate
  - up to 90% on mid-ocean ridges
- Opal
  - abundant in the Southern Ocean (*Opal Belt*)
  - abundant in the Eastern Equatorial Pacific — nutrient-rich upwelling zone
- Organic Carbon
  - generally 1–2%, but 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 ($\simeq 15\,\mathrm{m}$) from different equatorial oceans
- Chemical analyses for %$CaCO_3$ by Gustaf Arrhenius (1952) reveal glacial-interglacial cycles



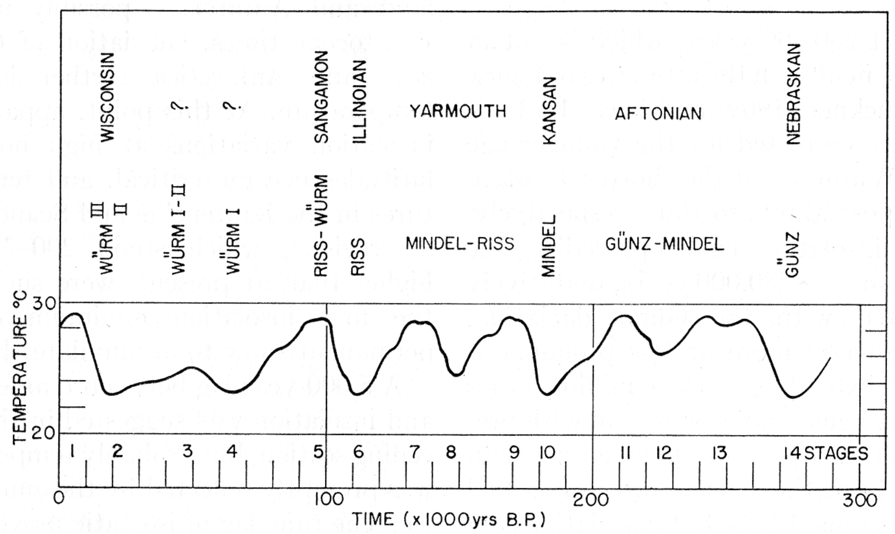
Source: `http://earthguide.ucsd.edu/virtualmuseum/climatechange2/02_4.shtml`

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

- 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)
  → 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 $\delta^{18}O$

- 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)

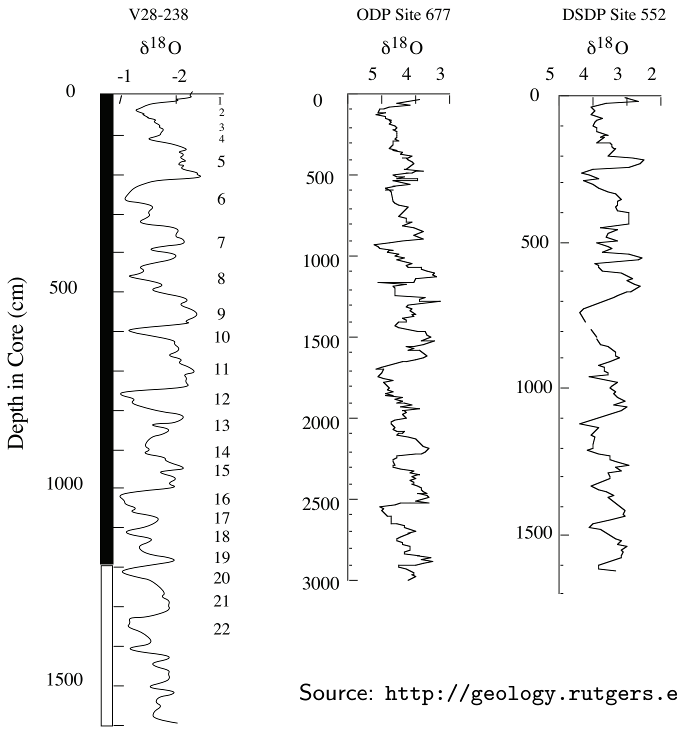


Source: Emiliani (1955)

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 → 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 → $\simeq$ 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

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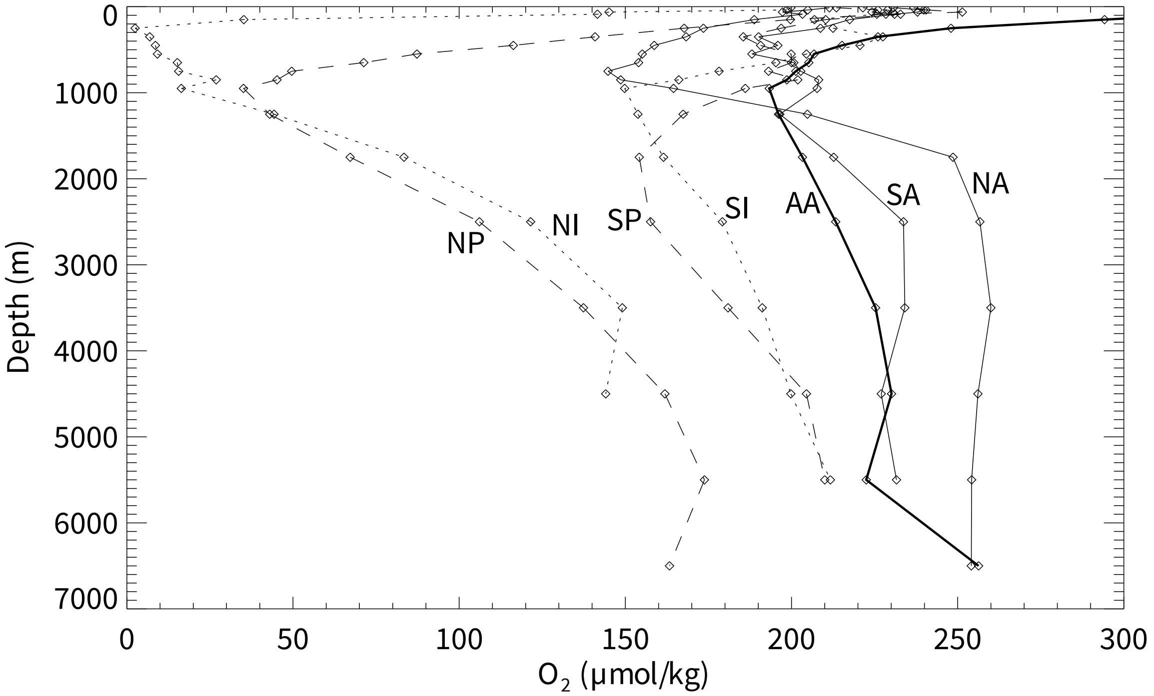
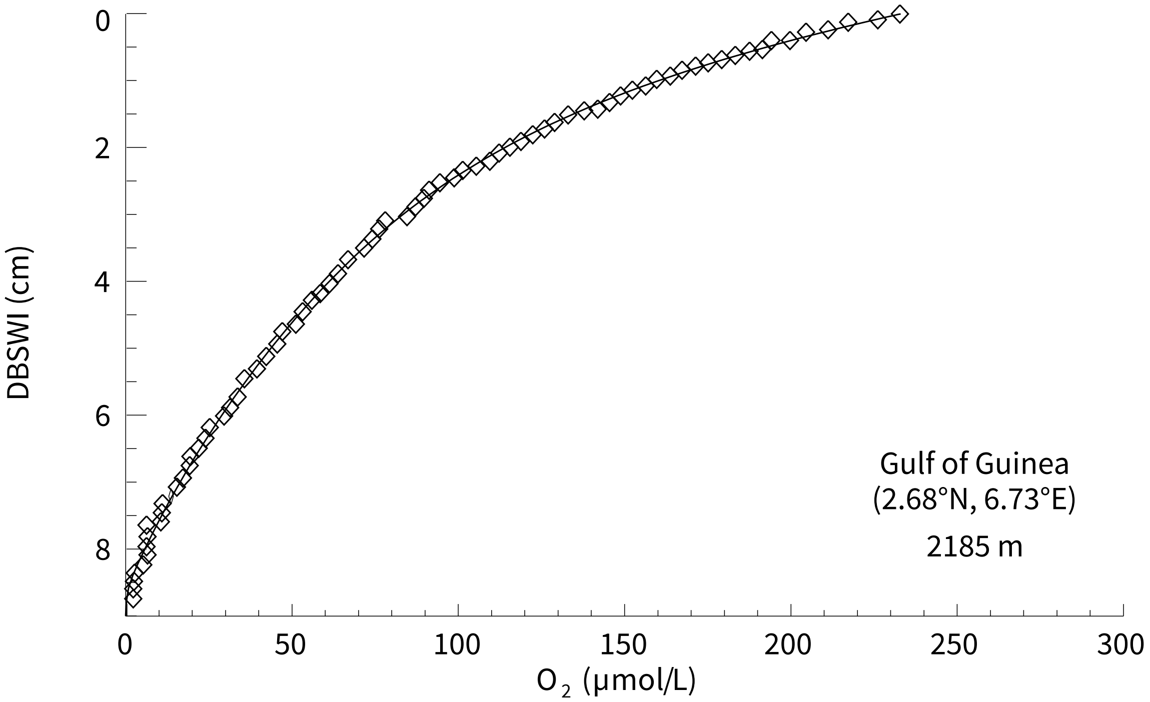
Concentration Gradients: Ocean vs. Surface Sediment



Dissolved Oxygen in the Water Column

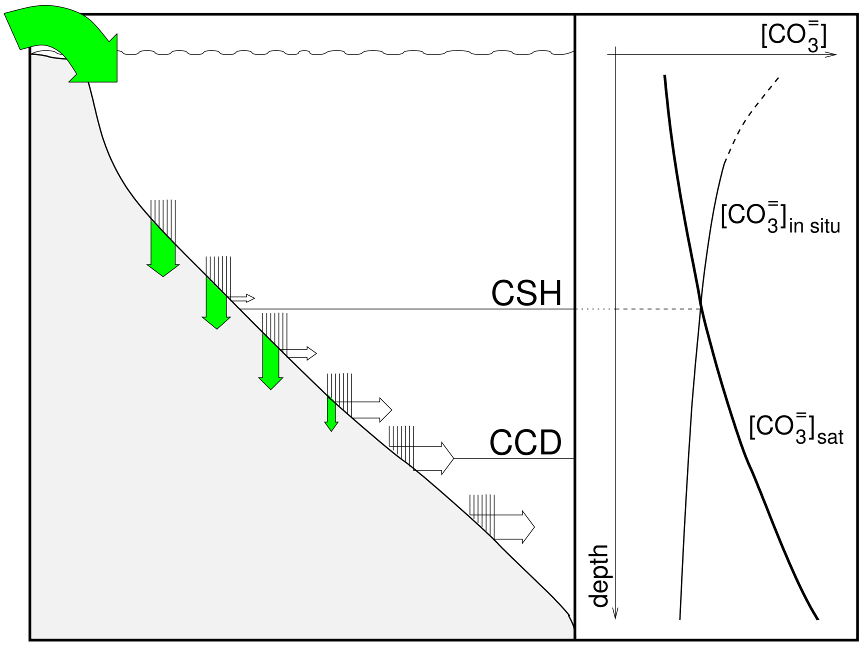
Concentration Gradients: Ocean vs. Surface Sediment

Dissolved Oxygen in the Surface Sediment Porewater



Acidification: Perturbation of the Ocean-Sediment Exchange

Marine carbonates: ocean-sediment exchange



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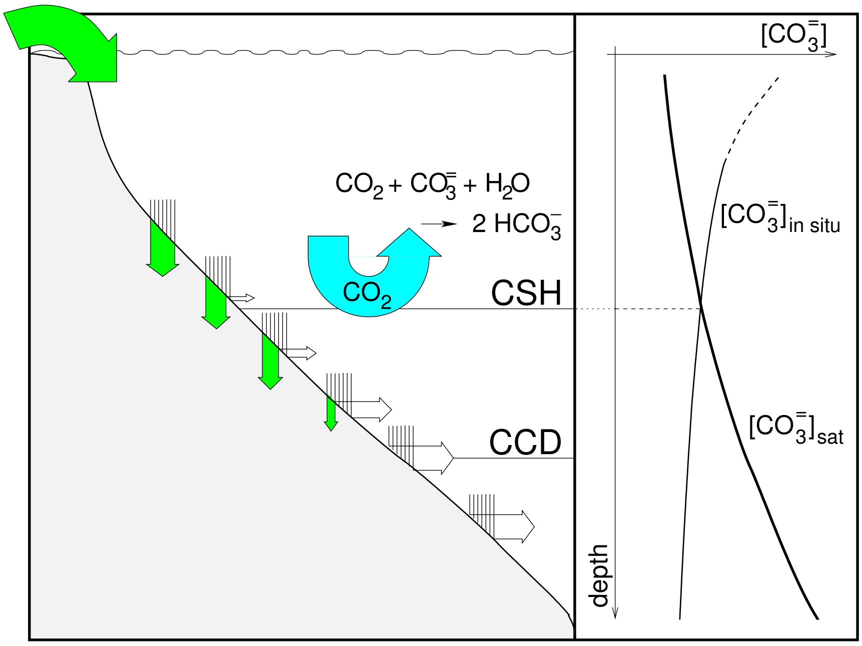

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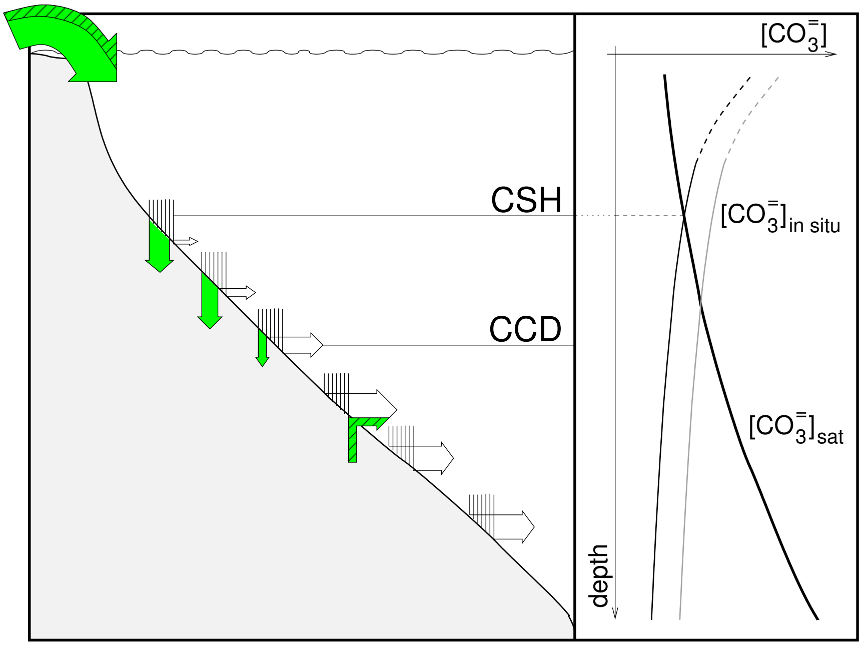
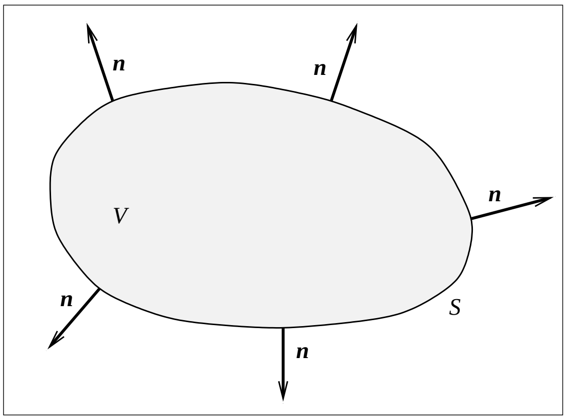


Preludes: geometric setting



- 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

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

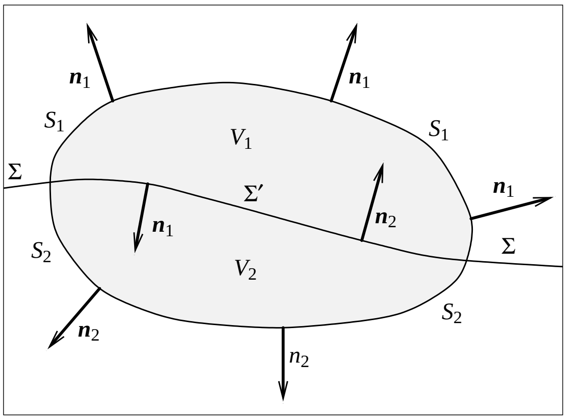
- General equation may be rewritten as

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

- 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:

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

Noting that

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

we can rewrite this equation as

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

Sediments: Two Phases and Multiples Constituents

- Two phases
  - solids → properties denoted by exponent ‘s’
  - porewater → 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

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

Total Concentrations and Phase Concentrations

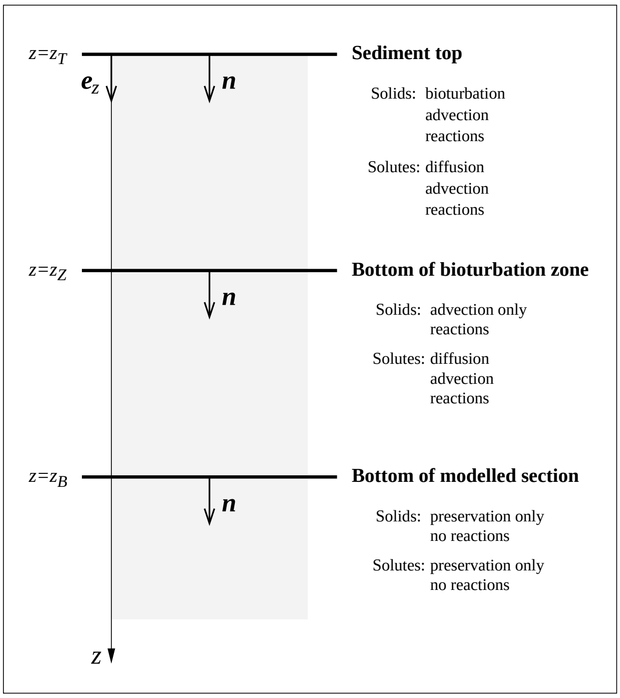
- Continuity equations expressed in terms of $\hat{C}_i$, concentration of i per unit volume of total sediment
- More directly measurable
  - i solid: C_i^s concentration of i in units of mass per unit volume of solid sediment

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

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

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

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
  → 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

$$J^{\mathrm{f}}_{\mathrm{diff}\,i} = -D^{\mathrm{sed}}_i \frac{\partial C^{\mathrm{f}}_i}{\partial z}$$

  where D^{sed}_i is the *effective diffusion coefficient* in the sediment and $\frac{\partial C^{\mathrm{f}}_i}{\partial z}$ the concentration gradient of i in porewater along the vertical

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

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Transport in Porewater: Diffusion

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

$$D^{\mathrm{sed}}_i = D^{\mathrm{sw}}_i / \theta^2$$

  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.	$\theta^2 = 1 - b \ln \varphi$	$b = 2.02 \pm 0.08$	$r^2 = 0.65$

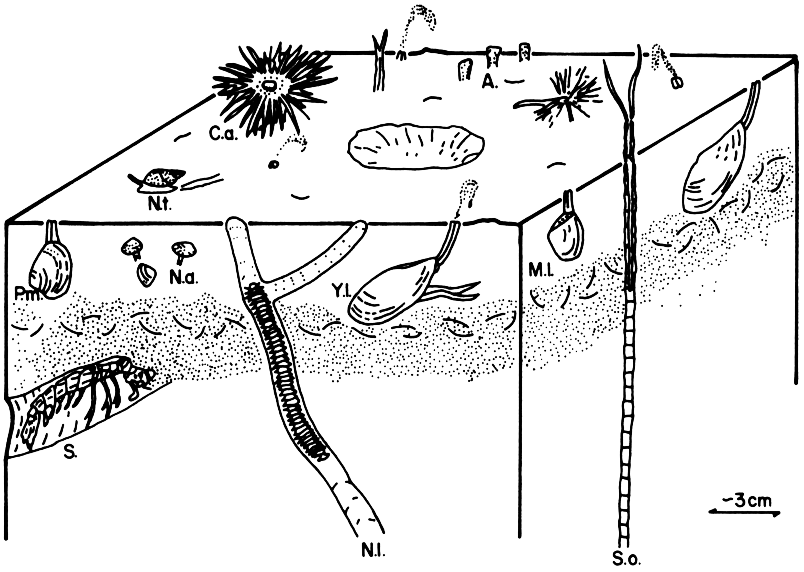
Transport in Porewater: Diffusion

- 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:
$$\hat{J}_{\mathrm{diff}\,i} = -\varphi^{\mathrm{f}}\frac{D_i^{\mathrm{sw}}}{\theta^2}\frac{\partial C_i^{\mathrm{f}}}{\partial z}$$
- In summary: *total transport of a solute i*
$$\hat{J}_i = \varphi^{\mathrm{f}} u C_i^{\mathrm{f}} - \varphi^{\mathrm{f}}\frac{D_i^{\mathrm{sw}}}{\theta^2}\frac{\partial C_i^{\mathrm{f}}}{\partial z}$$

Transport in the Solid Phase: Advection

- Solid i, with concentration C_i^{s} in the solid sediment fraction
$$\hat{J}_{\mathrm{adv}\,i} = w\hat{C}_i = \varphi^{\mathrm{s}} w C_i^{\mathrm{s}},$$
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: $9{,}8\,\text{cm} \pm 4{,}5\,\text{cm}$)
- 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

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

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

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

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

Advection, Diffusion, . . . Reaction

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

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

with

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

where

- $\Omega_{\text{Calc}} = \frac{[\text{Ca}^{2+}]^{\text{f}}[\text{CO}_3^{2-}]^{\text{f}}}{K_{\text{Calc}}}$ 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 $\hat{I}_i^{\text{top}}$)

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*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 $w_\mathrm{B} \geq 0$;
  - boundary condition similar to that at the sediment-water interface if $w_\mathrm{B} \leq 0$ (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 ($\hat{J}_i^{z_T^+} = \hat{I}_i^{\mathrm{top}}$)

Mixed-layer bottom

- *Solutes*: continuity equation requires porewater concentration gradients of each solute (C_i^{f}) to vanish
- *Solids*:
  - net accumulation ($w_{\mathrm{B}} \geq 0$): no boundary condition
  - chemical erosion ($w_{\mathrm{B}} \leq 0$): 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: $\hat{R}_{\mathrm{CO3}}^V = \hat{T}_{\mathrm{Calc\ diss}}^V$
- Exact analytical solution for $n_c = 1$, approximate analytical or numerical for $n_c \neq 1$

Insufficiency of the Simple Model

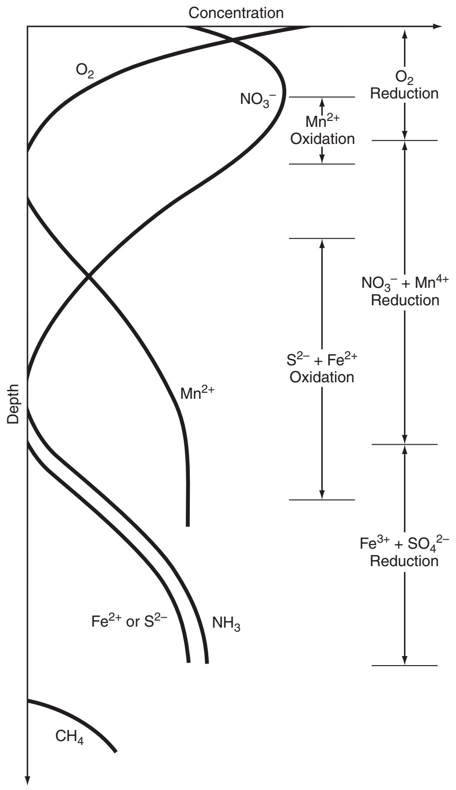
- Transport of DIC underestimated: CO_3^{2-} ions released during $CaCO_3$ dissolution react with porewater CO_2 to form HCO_3^- and DIC can thus also be transported under that form
- Significant $CaCO_3$ dissolution above the saturation horizon → dissolution promoted by the release of CO_2 during organic matter degradation in the mixed-layer
- Phenomenon impossible to represent with the simple model: no dissolution if $\Omega_{\text{Calc}}(z_{\text{top}}) > 1$

Organic Matter Remineralization

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

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

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:

$$\mathrm{OM} + 138\,\mathrm{O_2} \rightarrow 106\,\mathrm{CO_2} + 16\,\mathrm{HNO_3} + \mathrm{H_3PO_4} + 122\,\mathrm{H_2O}$$

- 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

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

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

- Hence

$$\begin{aligned} \hat{R}^V_{\mathrm{OM}} &= -\hat{T}^V_{\mathrm{OM\ remin}} \\ \hat{R}^V_{\mathrm{O_2}} &= -138 \times \hat{T}^V_{\mathrm{OM\ remin}} \end{aligned}$$

Improved Carbonate Diagenesis Model

Reaction terms: calcite

- Dissolution rate if calcite

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

  with

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

- Hence,

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

Improved Carbonate Diagenesis Model

Reaction terms: dissolved inorganic carbon

- Chemical reaction

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

  where $r_{1/2}$ denotes the net reaction rate, from left to right
- Reaction terms for $\mathrm{CO_2}$, $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$

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

Improved Carbonate Diagenesis Model

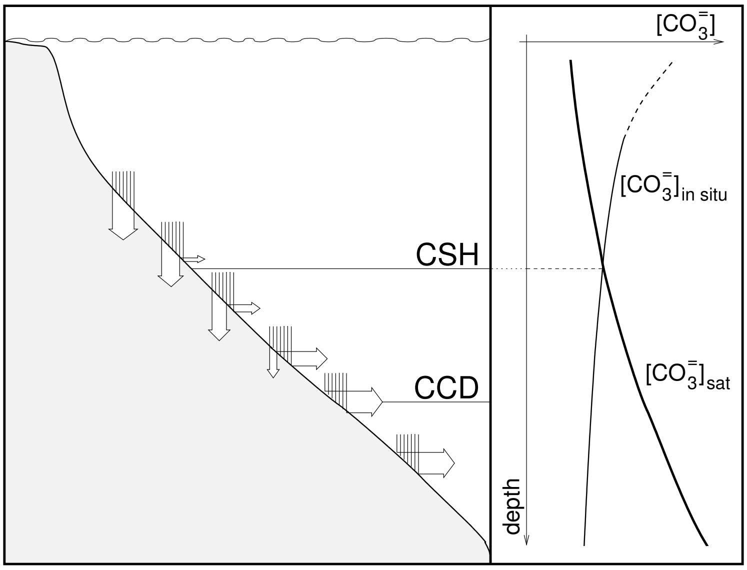
Elimination of the fast reactions

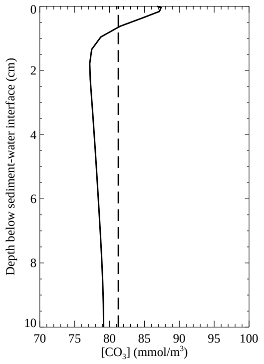
- $r_{1/2} \gg \hat{T}^V_{\mathrm{Calc\ diss}}, \hat{T}^V_{\mathrm{MO\ remin}}$
  (characteristic time $\simeq 10^2 - 10^3$ s)
- Equilibrium hypothesis for interconversion reactions
- Elimination of $r_{1/2}$ from the eqns. for $\mathrm{CO_2}$, $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$
  - replace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

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

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

Improved Carbonate Diagenesis Model





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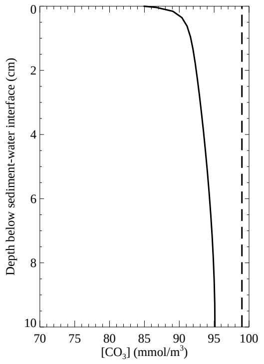

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the CSH

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