

Seafloor Sediments

Interaction with the Ocean and Early Diagenesis

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Ocean Sediment-Interaction and Early Diagenesis

Seafloor Sediments
Modelling

Interest for our knowledge of the Earth System
Role of Sediments in Biogeochemical Cycling

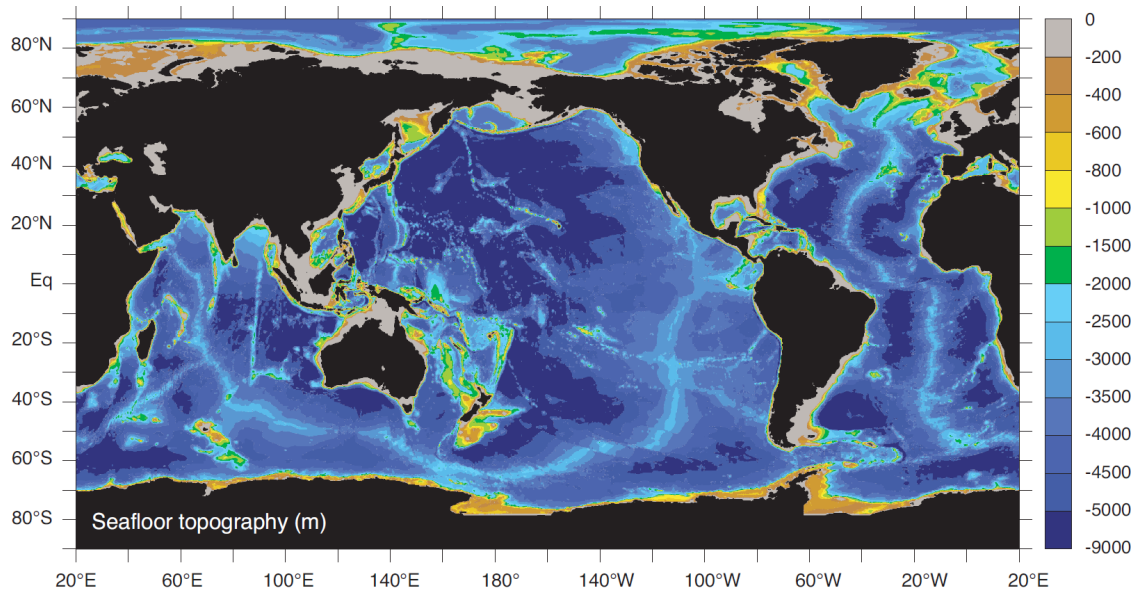
Plan

- 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)

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Ocean Sediment-Interaction and Early Diagenesis

The Seafloor and its Sediments: a First Exploration

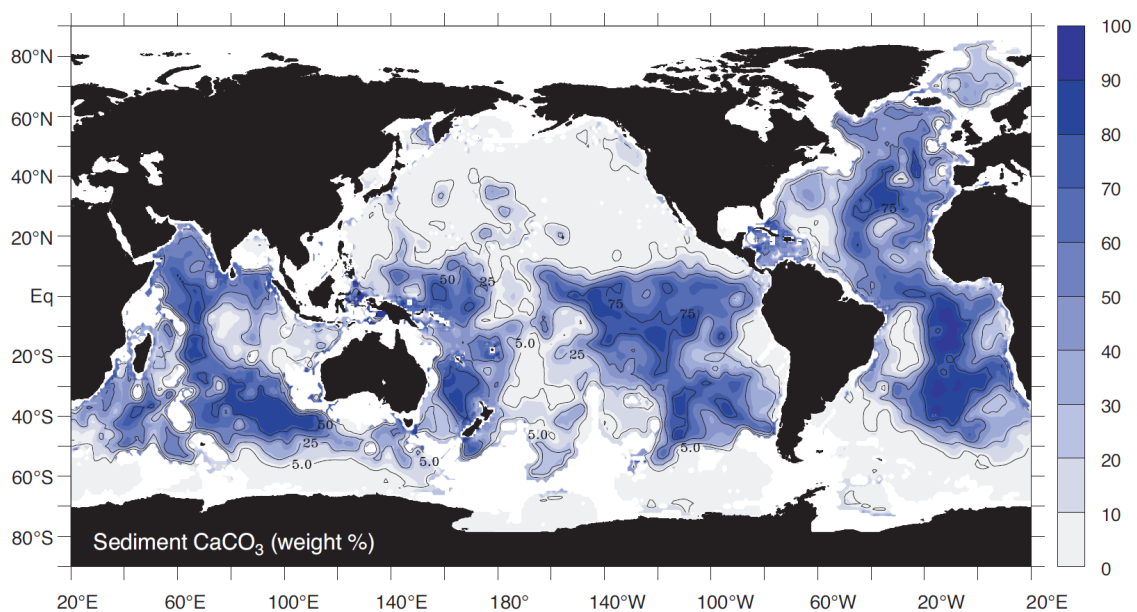


Source: Sarmiento and Gruber (2006)

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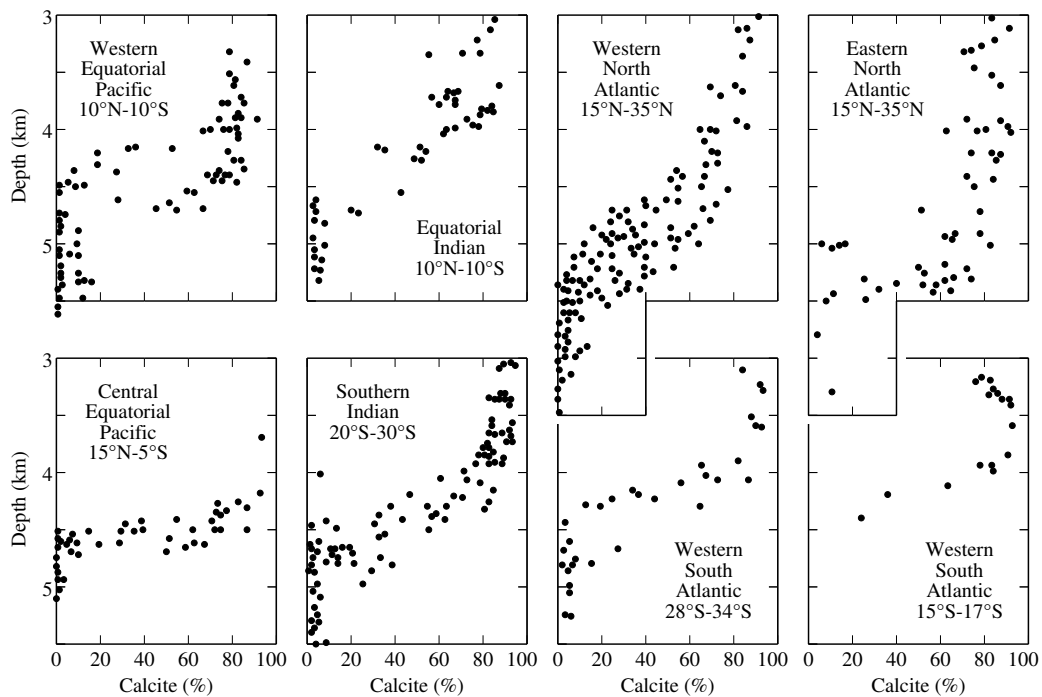


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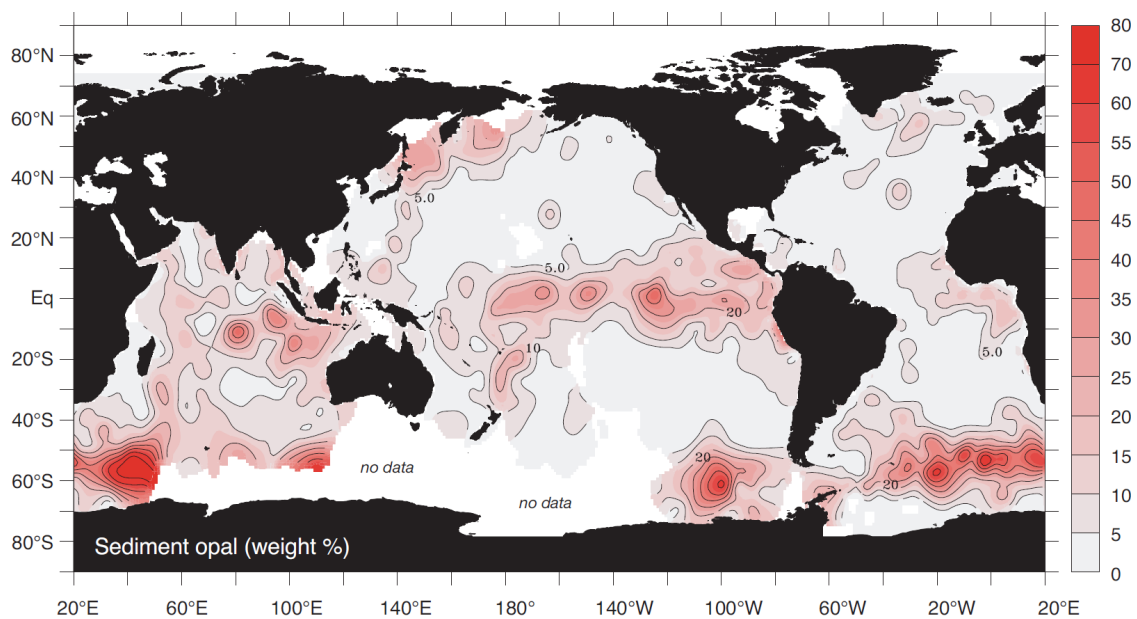
Ocean Sediment-Interaction and Early Diagenesis

The Seafloor and its Sediments: a First Exploration



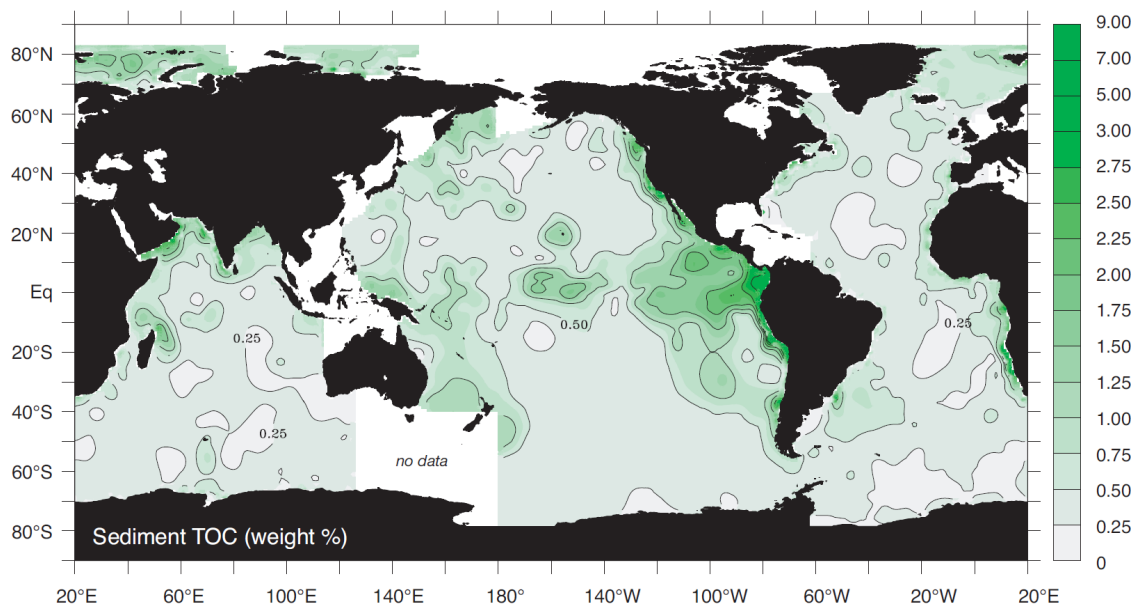
Source: Broecker and Peng (1982)

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 (CO₂ source, porewater acidification)

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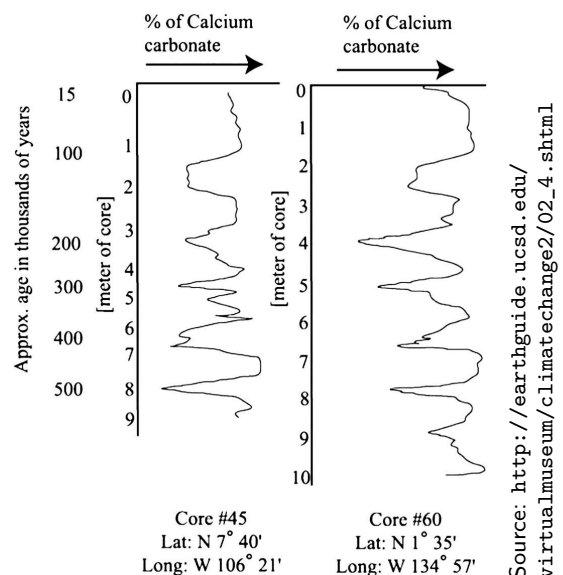
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Seafloor Sediments: Non Biogenic Components

- 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 ($\simeq 15$ m) from different equatorial oceans
- Chemical analyses for %CaCO₃ by Gustaf Arrhenius (1952) reveal glacial-interglacial cycles

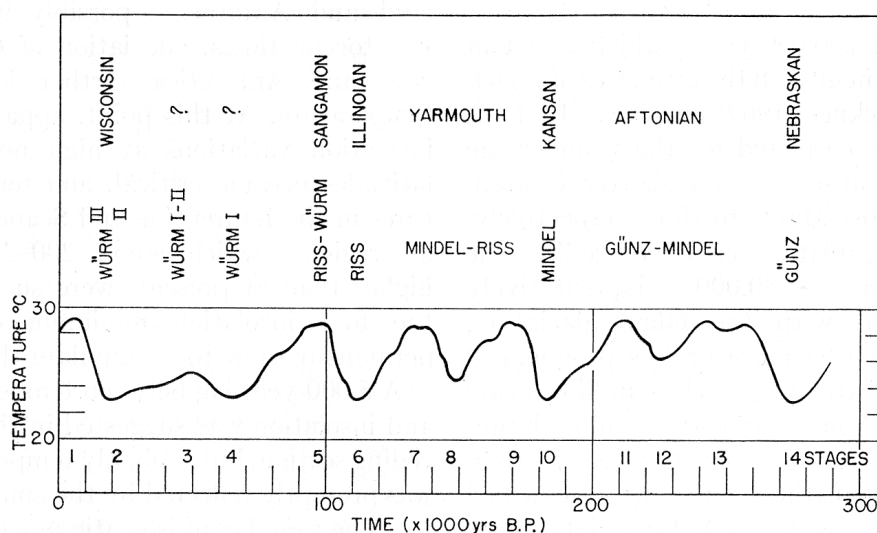


Sedimentary Archives: C. Emiliani's $\delta^{18}\text{O}$

- 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)



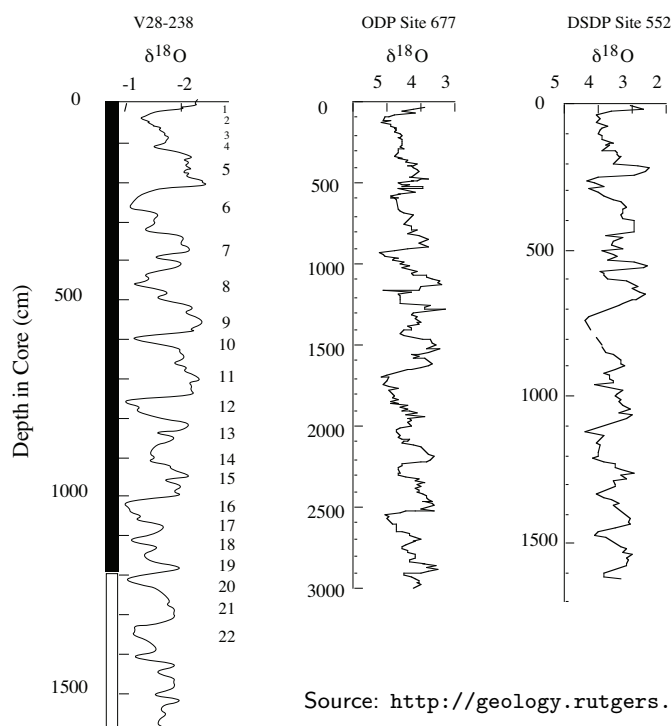
Sedimentary Archives: N. Shackleton's $\delta^{18}\text{O}$'s

- 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

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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

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Role of Sediments in Biogeochemical Cycling

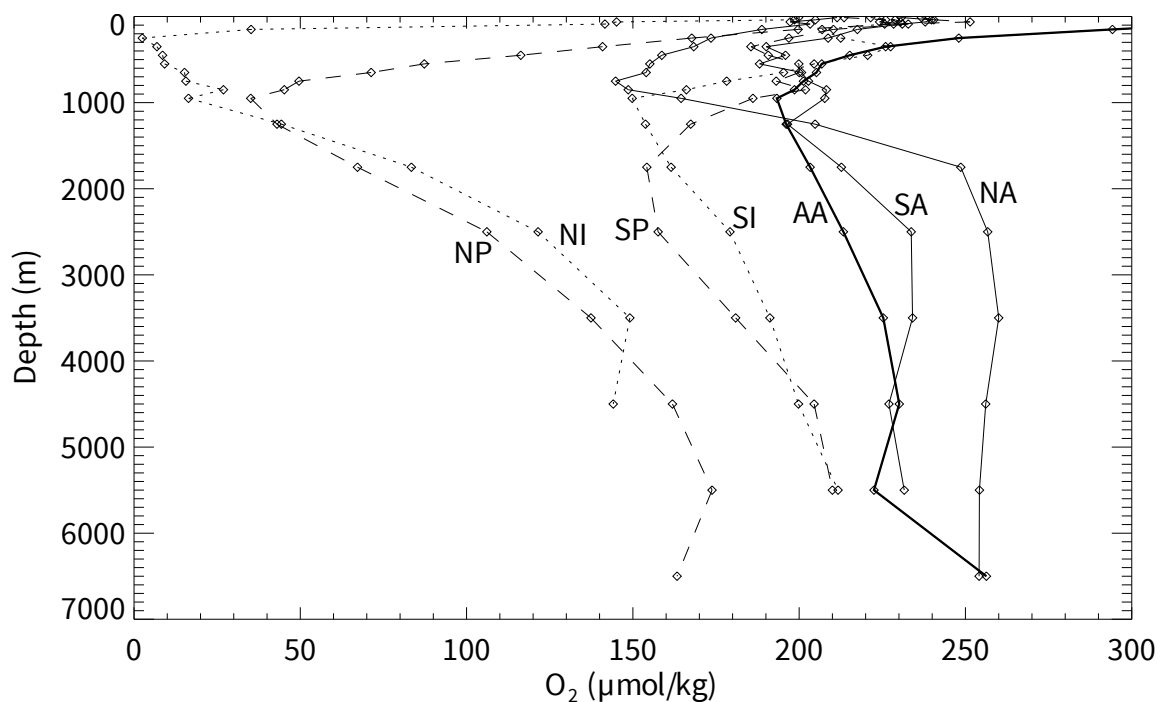
- Active role in ocean biogeochemical cycling
- Locus of preservation and remineralization of biogenic material (carbonates, opal, organic matter, etc.)
- Concentration gradients of similar amplitude in water column and in surface sediment

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Concentration Gradients: Ocean vs. Surface Sediment

Dissolved Oxygen in the Water Column

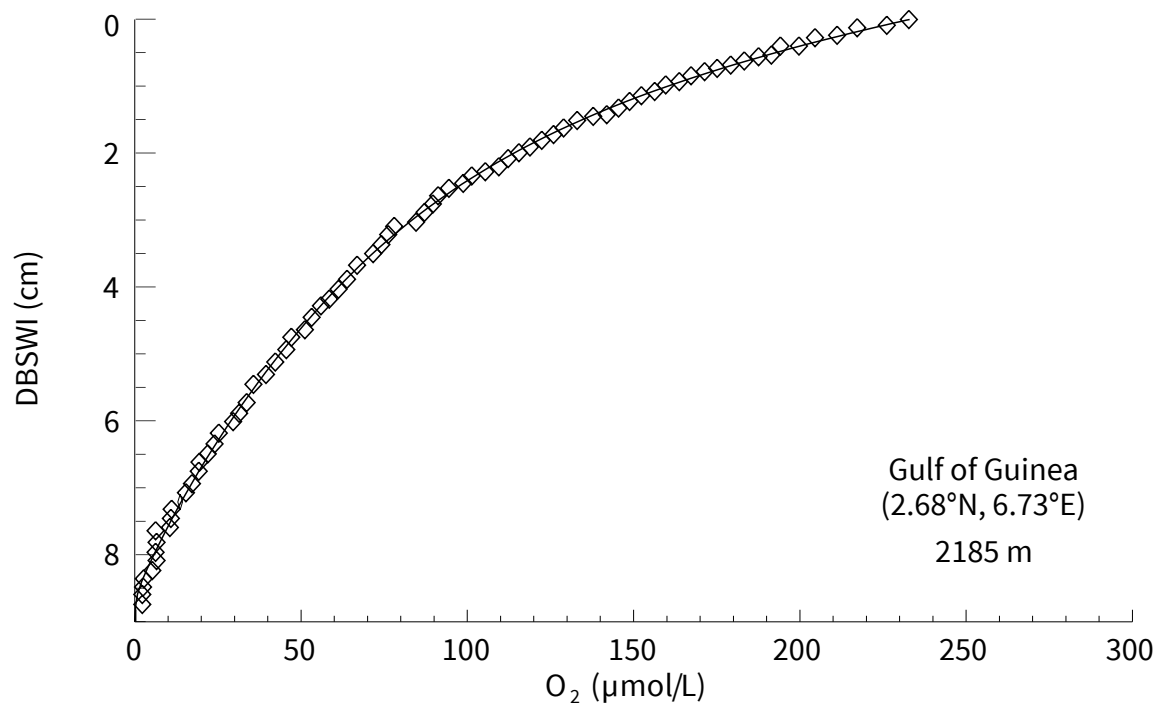


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Concentration Gradients: Ocean vs. Surface Sediment

Dissolved Oxygen in the Surface Sediment Porewater

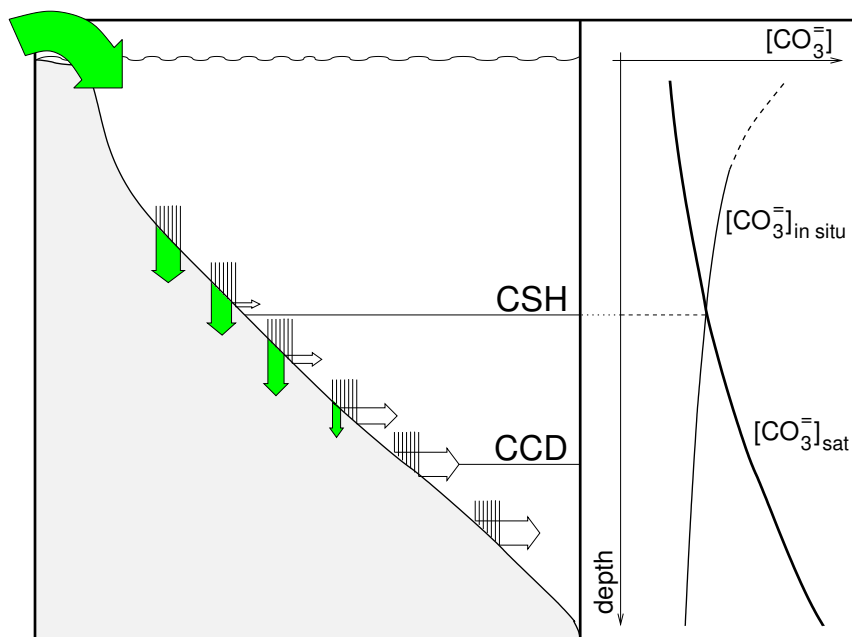


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Acidification: Perturbation of the Ocean-Sediment Exchange

Marine carbonates: ocean-sediment exchange

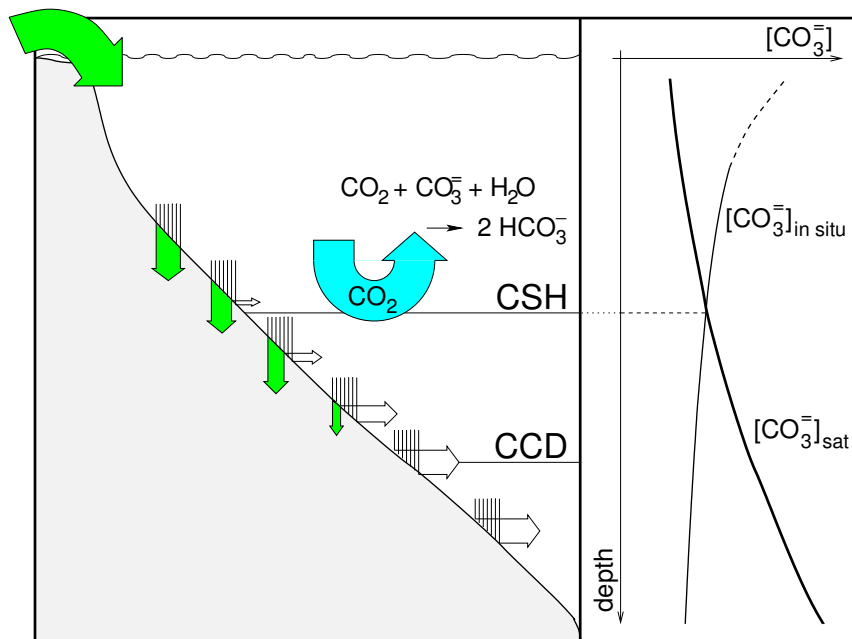


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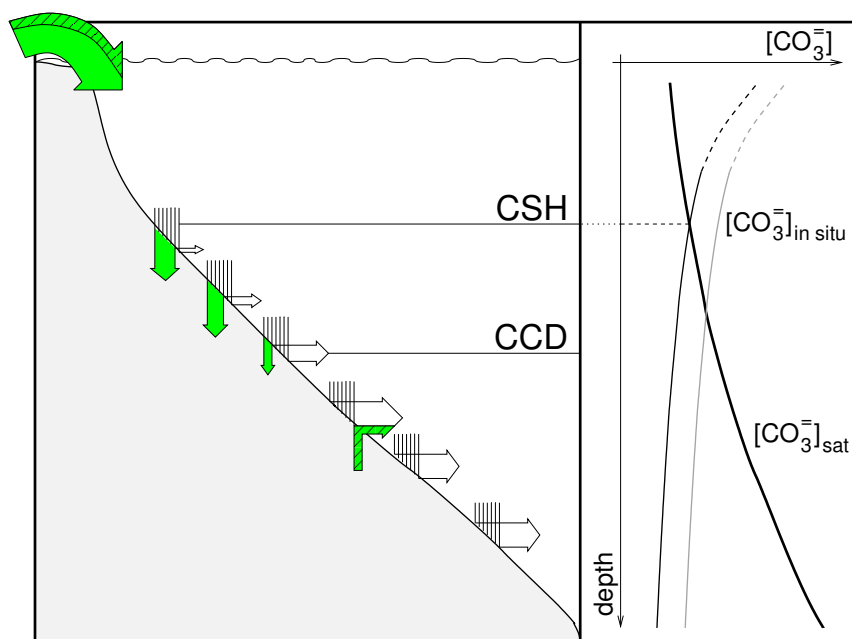


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Acidification: Perturbation of the Ocean-Sediment Exchange

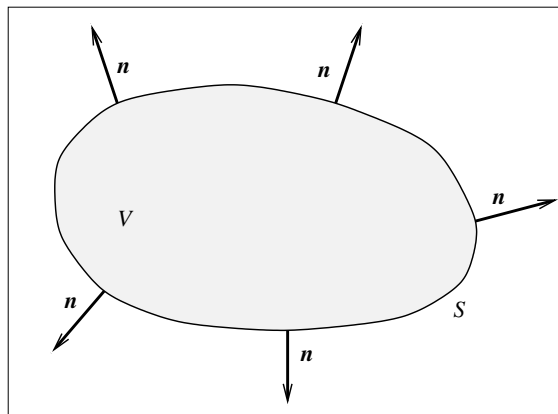
Marine carbonates: ocean-sediment exchange



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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

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

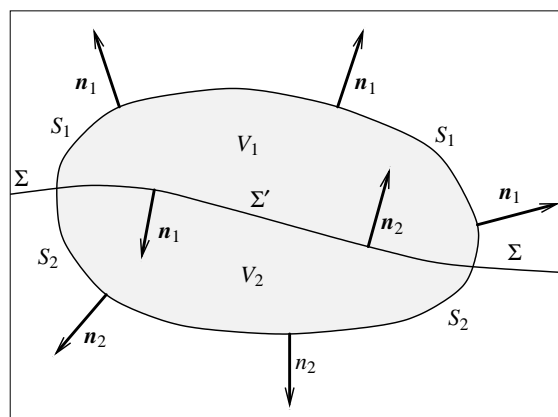
- General equation may be rewritten as

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

- 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
- 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
- \mathbf{n}_1 , \mathbf{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'

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

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

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

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

Noting that

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

we can rewrite this equation as

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

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

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

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

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

Total Concentrations and Phase Concentrations

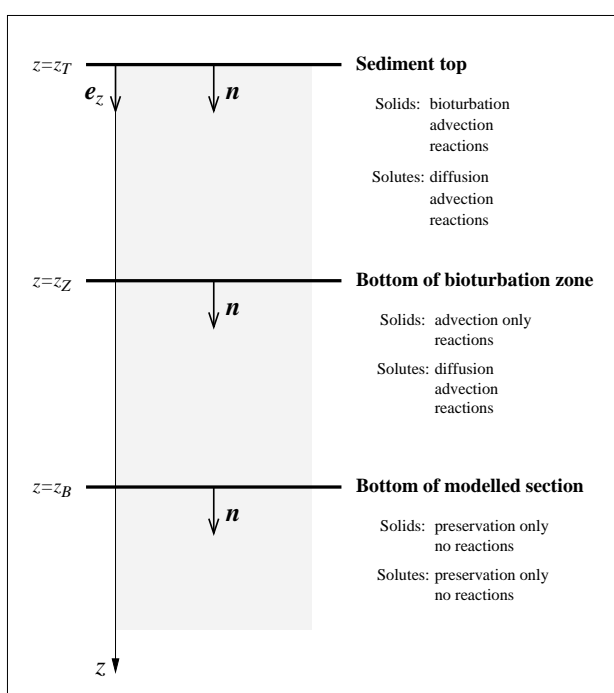
- Continuity equations expressed in terms of \hat{C}_i , concentration of i per unit volume of total sediment
- More directly measurable
 - i solid: C_i^s concentration of i in units of mass per unit volume of solid sediment

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

- 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 Σ , with upper side '1' and lower side '2':

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

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

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

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 (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

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

where D_i^{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^{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	$\theta^2 = \phi^{1-m}$	$m = 2.14 \pm 0.03$	$r^2 = 0.53$
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

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

- Finally:

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

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

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

Transport in the Solid Phase: Advection

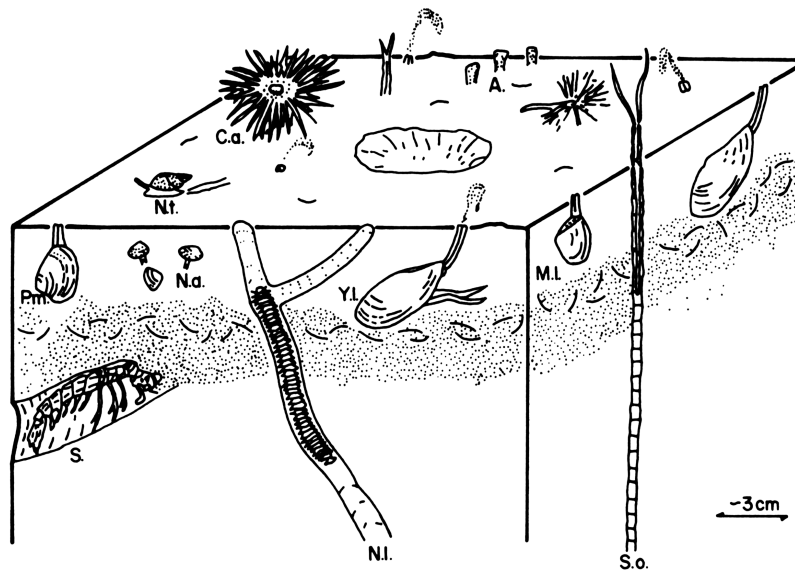
- Solid i , with concentration C_i^s in the solid sediment fraction

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

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_{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_{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 $\hat{J}_i^{-} = \hat{I}_i^{\text{top}} - \hat{O}_i^{\text{top}}$ 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^{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 ($\hat{J}_i^{z_T^+} = \hat{J}_i^{\text{top}}$)

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: 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: 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 $\Omega_{\text{Calc}}(z_{\text{top}}) > 1$

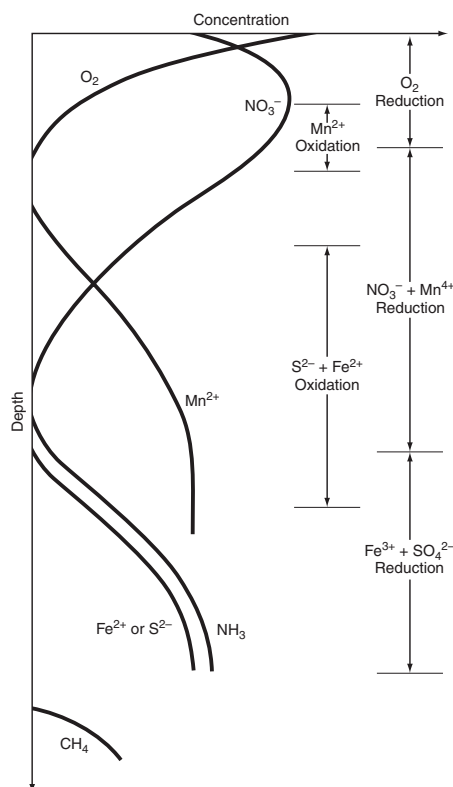
Organic Matter Remineralization

Organic matter remineralization reactions

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

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

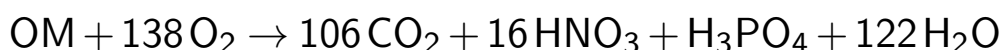
Porewater Solute Zonation



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_2 , HCO_3^- , CO_3^{2-} et O_2 , 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_{O_2} is a half-saturation constant
and k_{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 if calcite

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

with

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

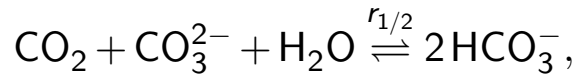
- Hence,

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

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 CO_2 , HCO_3^- and 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

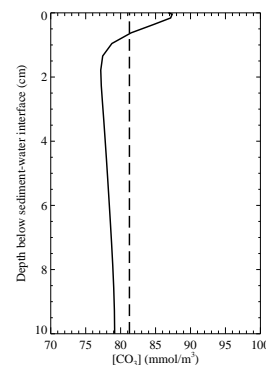
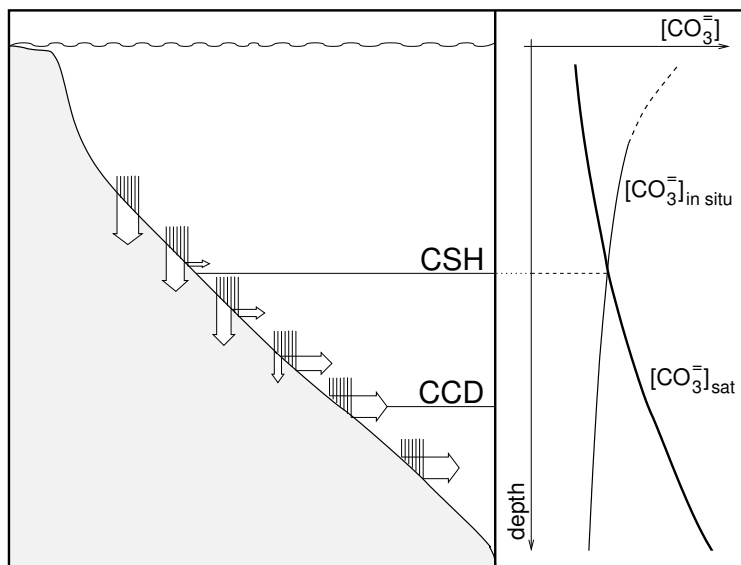
Elimination of the fast reactions

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

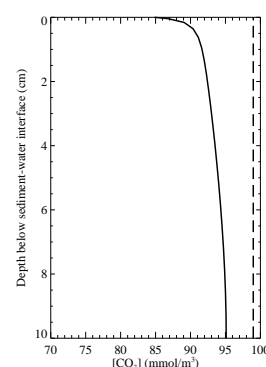
$$K_2([\text{HCO}_3^-]^f)^2 - K_1[\text{CO}_2]^f[\text{CO}_3^{2-}]^f = 0$$

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

Improved Carbonate Diagenesis Model



above
the CSH



below
the CSH

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References Cited and Recommended

- Berner R. (1980) *Early Diagenesis. A Theoretical Approach*. Princeton University Press, Princeton, NJ. 256 pp.
- Broecker W. S. and Peng T.-H. (1982) *Tracers in the Sea*, Eldigio Press, Palisades, NY. 690 pp. (https://www.ldeo.columbia.edu/~broecker/Home_files/TracersInTheSea_searchable.pdf)
- C. Emiliani (1955) Pleistocene Temperatures. *J. Geology* 63:538–578.
- G. Munhoven (1997) *Modelling Glacial-Interglacial Atmospheric CO₂ Variations: The Role of Continental Weathering*. University of Liège. 273 pp. (<http://hdl.handle.net/2268/161314>).
- G. Munhoven (2021) Model of Early Diagenesis in the Upper Sediment with Adaptable complexity – MEDUSA (v. 2): a time-dependent biogeochemical sediment module for Earth system models, process analysis and teaching. *Geosci. Model. Dev.* 14:3603–3631. (<https://doi.org/10.5194/gmd-14-3603-2021>).
- J. Sarmiento and Gruber N. (2006) *Ocean Biogeochemical Dynamics*. Princeton University Press, Princeton, NJ. 503 pp.
- N. J. Shackleton and N. D. Opdyke (1973) Oxygen isotope and palaeomagnetic stratigraphy of Equatorial Pacific core V28-238: Oxygen isotope temperatures and ice volumes on a 10⁵ year and 10⁶ year scale. *Quat. Res.* 3:39–55.

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