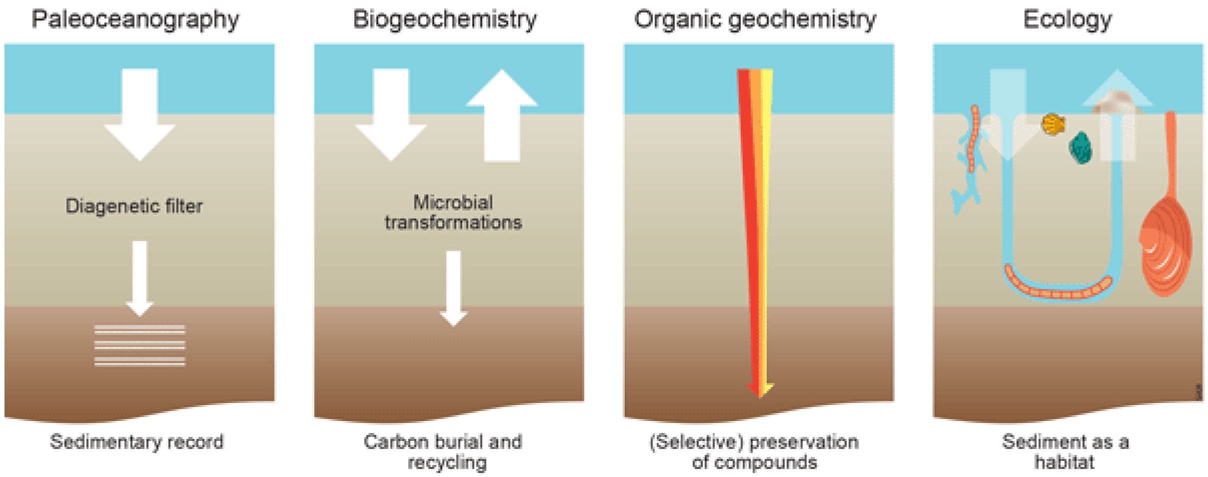
Diagenetic processes and modeling in PISCES

Brief introduction



Some preliminary comments

- This presentation is not a detailed course on diagenetic processes
- This presentation is also not a detailed course on diagenetic modeling
    - ➔ It just gives some elements to have a basic understanding of the training session

Two parts :

1) A rapid description of the biogeochemical processes in the marine sediments
2) Some elements on the sediment module of PISCES

Transport in the sediments

- Transport in the sediments tends to be mainly 1D (vertical)

- Vertical advection w is given by the sedimentation rate : from ~ 0.1 cm/kyr in low productive open ocean areas to > 1m/kyr in some coastal areas

- If no compaction and benthic reactions, w = deposition rate at the sediment water interface

- Diffusion processes are related to two distinct processes :

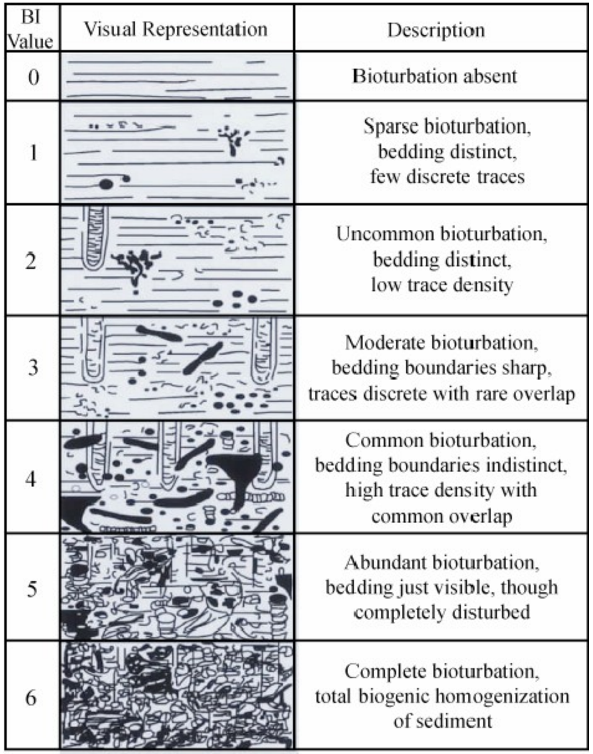
    1) Solute diffusion in a porous medium, i.e. diffusion of dissolved species in interstitial water

    2) Mixing resulting from the activities of benthic organisms, i.e. mixing of solid species

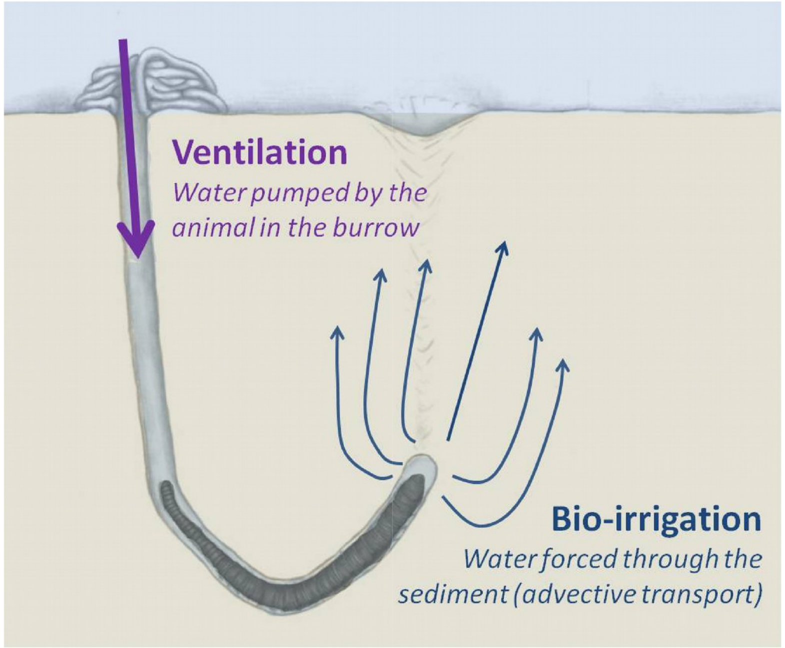
- Irrigation which is pumped flow through animal burrows

Bioturbation, bio-irrigation

Both processes are associated to the activities of organisms living in the sediments

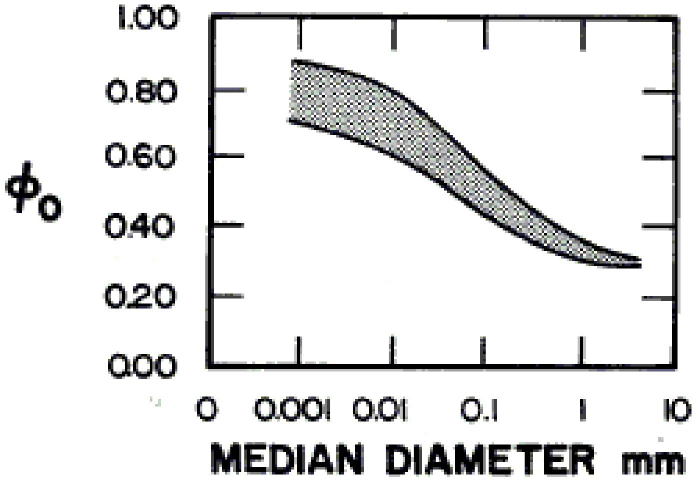


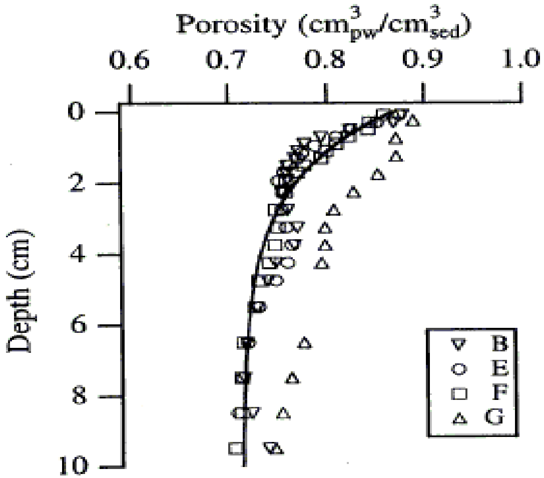
BI Value	Visual Representation	Description
0		Bioturbation absent
1		Sparse bioturbation, bedding distinct, few discrete traces
2		Uncommon bioturbation, bedding distinct, low trace density
3		Moderate bioturbation, bedding boundaries sharp, traces discrete with rare overlap
4		Common bioturbation, bedding boundaries indistinct, high trace density with common overlap
5		Abundant bioturbation, bedding just visible, though completely disturbed
6		Complete bioturbation, total biogenic homogenization of sediment



Physical structure of the sediments

Porosity defines the relative volume of seawater in the sediment : φ





Initial (uncompacted) porosity increases as grain size decreases and as sorting decreases

Porosity decreases with depth as a consequence of compaction

Some thoughts on the time scales

Time : *Particles fall through the water column:*

$$\tau \leq \frac{3500m}{50\,{}^{m}/_{day}} \approx 70\ days$$

Sea Water Interface

Mixed layer ~
"reaction layer"

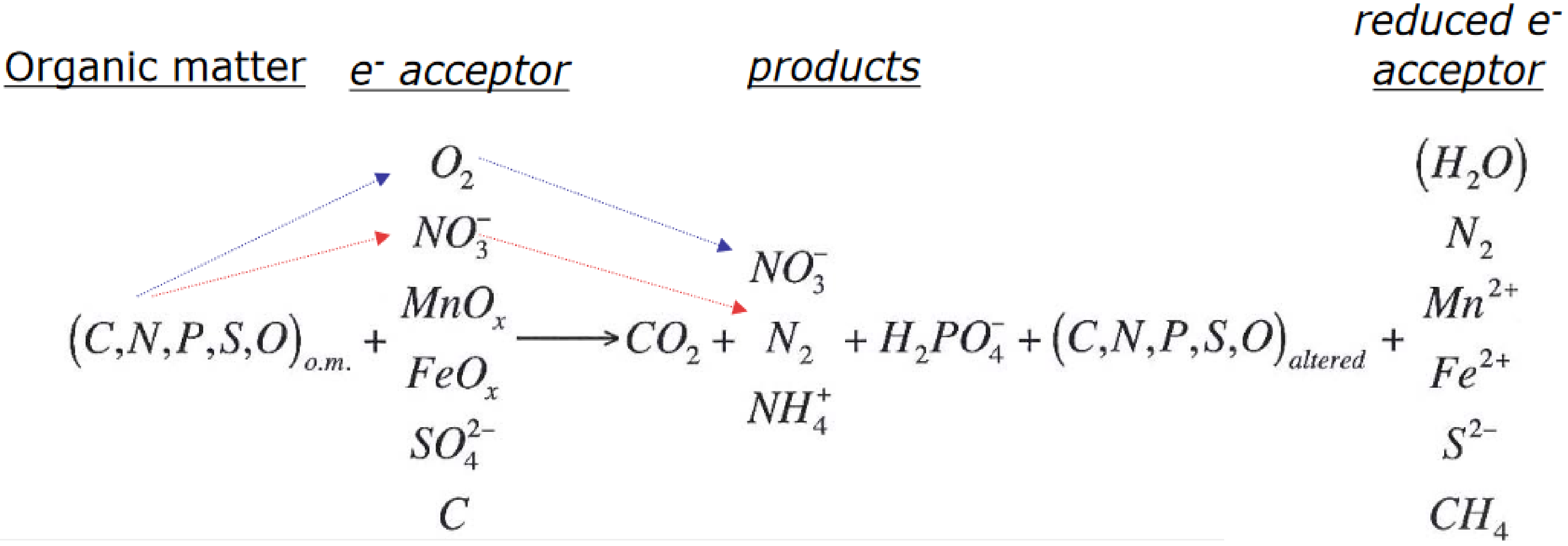
$$\tau \sim \frac{8cm}{0.001\,{}^{cm}/_{y}} \sim 8000yr \rightarrow \frac{20cm}{0.1\,{}^{cm}/_{y}} \sim 200yr$$

(pelagic) *(coastal)*

Reactions that are too slow to occur in the water column can happen in surface sediments

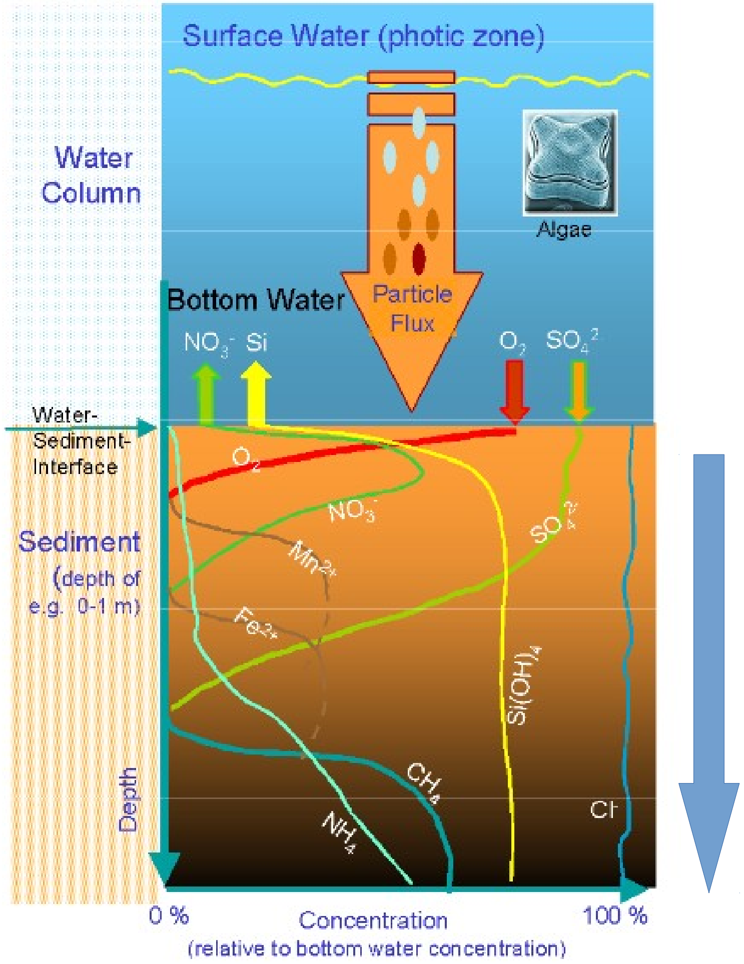
Mechanisms for organic matter oxidation

Typical reactions but many of them never occur in the open ocean



Order : decreasing -ΔG (Gibbs free energy)

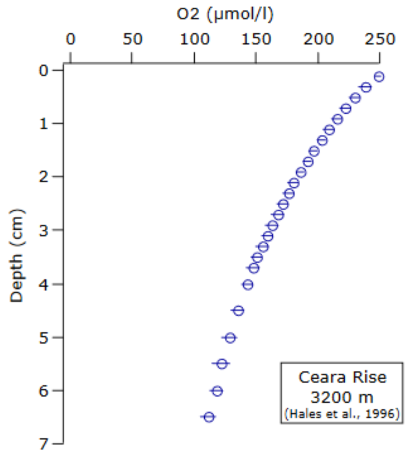
Vertical ordering of the reactions

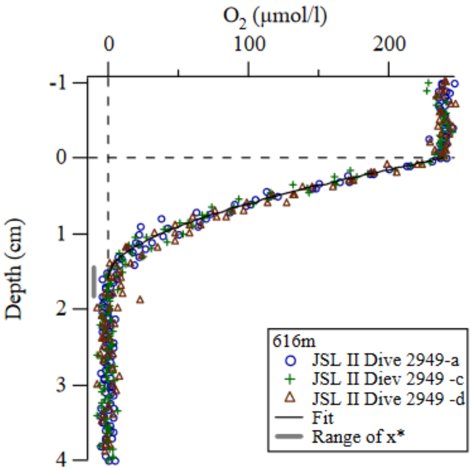


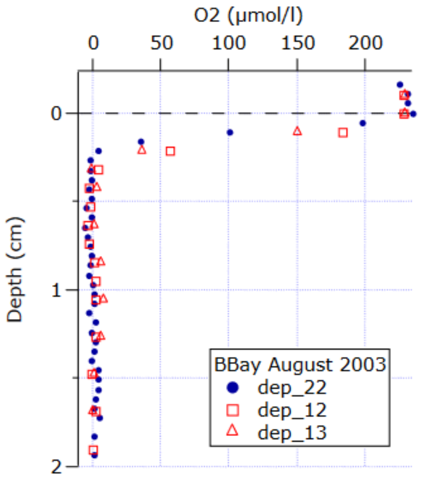
ΔG↗

Aerobic respiration	$CH_3COO^- + 2O_2 \rightarrow H_2O + 2CO_2 + OH^-$ $\Delta G^{0\prime} = -854$ kJ/reaction
Denitrification	$CH_3COO^- + 1.6NO_3^- \rightarrow 2CO_2 + 0.8N_2 + 2.6OH^- + 0.2H_2O$ $\Delta G^{0\prime} = -801$ kJ/reaction
Mn(IV) reduction	$CH_3COO^- + 4MnO_2 + 3H_2O \rightarrow 4Mn^{2+} + 2HCO_3^- + 7OH^-$ $\Delta G^{0\prime} = -558$ kJ/reaction
Fe(III) reduction	$CH_3COO^- + 8Fe(OH)_3 \rightarrow 8Fe^{2+} + 2HCO_3^- + 15OH^- + 5H_2O$ $\Delta G^{0\prime} = -337$ kJ/reaction
Sulfate reduction	$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2HCO_3^-$ $\Delta G^{0\prime} = -48$ kJ/reaction
Methanogenesis	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$ $\Delta G^{0\prime} = -31$ kJ/reaction

Oxygen penetration depth, some examples







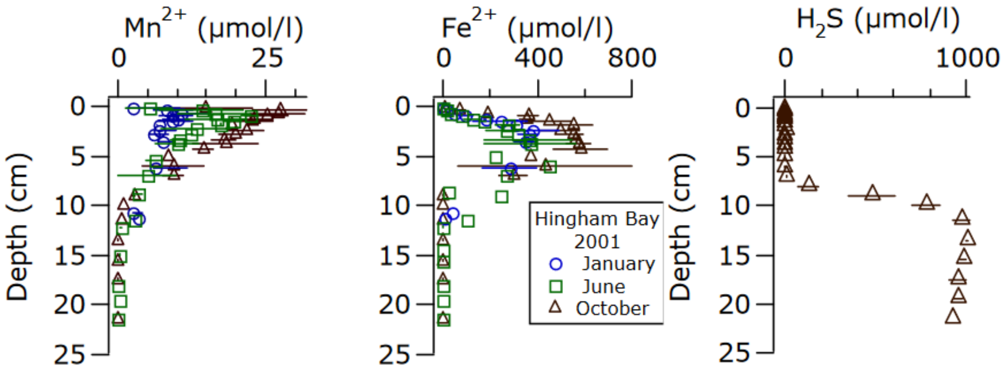
Total Corg ox. Rate (µmol/cm2/y)	14	45	350

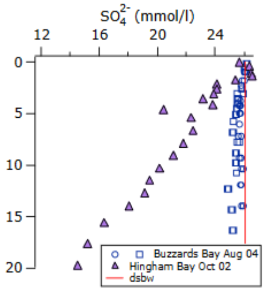
It highly depends on the POC sedimentation rate but not only !

- overlying water properties, temperature, biological activity, organic matter reactivity, ...

Higher order reactions : generally in coastal areas

High POC sedimentation rates and/or low oxygen overlying waters





Coastal site

POC sed. Rate: 850 µmol C/cm^2/yr

Secondary redox reactions

- Secondary redox reactions make the system much more complex
- Adsorption/desorption processes : NH4, PO4, Fe, …
- Precipitation/dissolution reactions link solid and dissolved species

Other reactions†

$$2O_2 + NH_4^+ + 2HCO_3^- \rightarrow NO_3^- + 2CO_2 + 3H_2O‡$$

$$O_2 + 2Mn^{2+} + 4HCO_3^- \rightarrow 2MnO_2^{\alpha} + 4CO_2 + 2H_2O‡$$

$$O_2 + 4Fe^{2+} + 8HCO_3^- + H_2O + 4\chi H_2PO_4^- \rightarrow 4Fe(OH)_3^{\alpha} + 4\chi Fe - P^{\alpha} + 8CO_2‡$$

$$2O_2 + FeS \rightarrow SO_4^= + Fe^{2+}$$

$$7O_2 + 2FeS_2 + 2H_2O \rightarrow 4SO_4^= + 2Fe^{2+} + 4H^+$$

$$2O_2 + H_2S + 2HCO_3^- \rightarrow SO_4^= + 2CO_2 + 2H_2O‡$$

$$O_2 + CH_4 \rightarrow CO_2 + H_2O‡$$

$$MnO_2^{\alpha,\beta} + 2Fe^{2+} + 2\chi H_2PO_4^- + 2H_2O + 2HCO_3^- \rightarrow 2Fe(OH)_3^{\alpha} + 2\chi Fe - P^{\alpha} + Mn^{2+} + 2CO_2$$

$$MnO_2^{\alpha,\beta} + H_2S + 2CO_2 \rightarrow Mn^{2+} + S_0 + 2HCO_3^-$$

$$2Fe(OH)_3^{\alpha,\beta} + 2\chi Fe - P^{\alpha,\beta} + H_2S + 4CO_2 \rightarrow 2Fe^{2+} + 2\chi H_2PO_4^- + S_0 + 4HCO_3^- + 2H_2O$$

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+‡$$

$$SO_4^= + CH_4 + CO_2 \rightarrow 2HCO_3^- + H_2S‡$$

$$4S_0 + 4H_2O \rightarrow 3H_2S + SO_4^= + 2H^+$$

$$FeS + S_0 \rightarrow FeS_2$$

$$Fe(OH)_3^{\alpha} + \chi Fe - P^{\alpha} \rightarrow Fe(OH)_3^{\beta} + \chi Fe - P^{\beta}$$

$$MnO_2^{\alpha} \rightarrow MnO_2^{\beta}$$

Diagenetic module in PISCES

Basic description

Continuity equations

Continuity equation of the dissolved species

$$\varphi \frac{\partial C_i}{\partial t} = \frac{\partial}{\partial z}\left(\varphi D_i \frac{\partial C_i}{\partial z} - \varphi v C_i\right) + \varphi \alpha(z)(C_{i,ow} - C_i(z)) + \sum_k v_{i,k} R_k$$

Solute diffusion (tortuosity)

Advection

Bioirrigation

Biogeochemical reactions

Continuity equation of the solid species

$$(1-\varphi)\frac{\partial S_i}{\partial t} = \frac{\partial}{\partial z}\left((1-\varphi) D_B(z) \frac{\partial S_i}{\partial z} - (1-\varphi) w S_i\right) + \sum_k v_{i,k} R_k$$

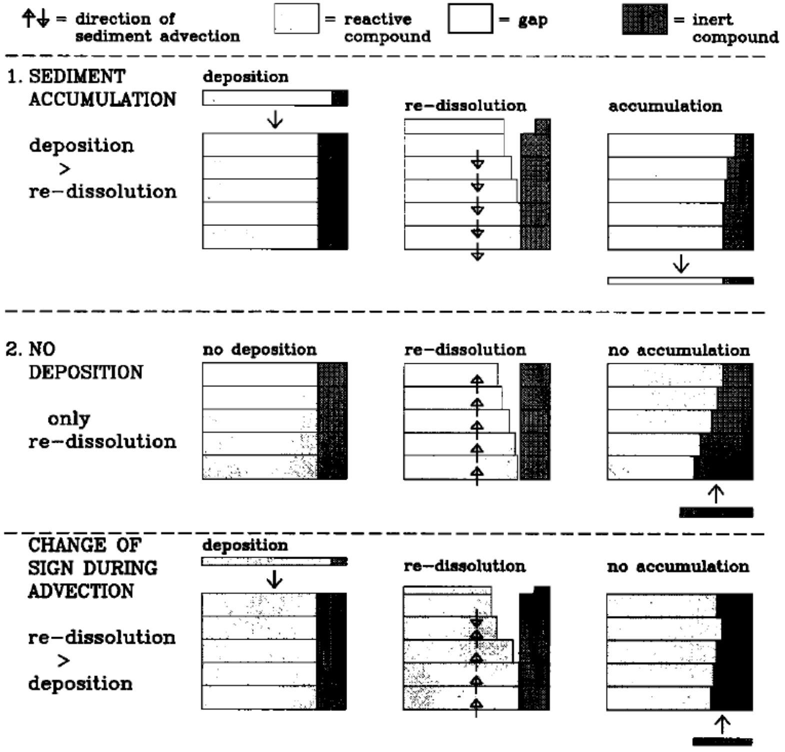
bioturbation

Advection

Biogeochemical reactions

Discretization, advection, diffusion

- Typical vertical discretization with varying layer thickness (increasing with depth, defined in the namelist)
- Horizontal grid is identical to that of the ocean model and is made 1D. Land points are removed



  - Advection scheme Heinze et al. (1999)
  - Diffusion is solved using an implicit temporal scheme
  - **Important notice : the first sediment layer = the bottom of the water column**

Primary and secondary redox reactions

Primary reactions

Aerobic respiration	$CH_3COO^- + 2O_2 \rightarrow H_2O + 2CO_2 + OH^-$ $\Delta G^{0'} = -854$ kJ/reaction
Denitrification	$CH_3COO^- + 1.6NO_3^- \rightarrow 2CO_2 + 0.8N_2 + 2.6OH^- + 0.2H_2O$ $\Delta G^{0'} = -801$ kJ/reaction
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Secondary reactions

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$$4S_0 + 4H_2O \rightarrow 3H_2S + SO_4^{=} + 2H^+$$
$$FeS + S_0 \rightarrow FeS_2$$
$$Fe(OH)_3^{\alpha} + \chi Fe - P^{\alpha} \rightarrow Fe(OH)_3^{\beta} + \chi Fe - P^{\beta}$$
$$MnO_2^{\alpha} \rightarrow MnO_2^{\beta}$$

Numerical schemes for redox reactions

- Necessary to keep the possibility to use long time steps due to the slow characteristic time scales
- Primary reactions are relatively slow (~ weeks to years).
- An implicit scheme is used to allow large time steps
- Secondary reactions can be extremely fast (~minutes)

  ➔ **Necessary to use a solver suitable for stiff systems**

Temporal schemes for secondary redox

- Use of a second order Strand splitting scheme which is based on operator splitting (Wang et al., 2018; Nguyen et al., 2013)

- Each reaction (starting from the fastest) is successively solved assuming equilibrium at t+1/2 and then the same is done in the reverse order at t+1

$$R_{2nd}^{(\Delta t)} = R_1^{(\frac{\Delta t}{2})} \circ R_2^{(\frac{\Delta t}{2})} \circ \cdots \circ R_{N_r-1}^{(\frac{\Delta t}{2})} \circ R_{N_r}^{(\frac{\Delta t}{2})} \circ R_{N_r}^{(\frac{\Delta t}{2})} \circ R_{N_r-1}^{(\frac{\Delta t}{2})} \circ \cdots \circ R_2^{(\frac{\Delta t}{2})} \circ R_1^{(\frac{\Delta t}{2})}$$

- This scheme is unconditionally stable

- A similar scheme is used for diffusion/bioturbation and redox reactions

$$U^{n+1} = S_c^{(\frac{\Delta t}{2})} \circ S_r^{(\Delta t)} \circ S_c^{(\frac{\Delta t}{2})} U^n$$

A brief overview of the sediment module code (1)

- The module can be run offline (without PISCES running) and online either in 1-way or 2-way modes.

- There are 8 solid phases : Biogenic silica (SedBSi), clay (SedClay), calcite (SedCaCO3), Fe hydroxides (SedFeO), Fe sulfide (SedFeS) and three lability classes of POC : labile (SedPOC), semi-refractory (SedPOS) and refractory (SedPOR)

- There are 10 dissolved species : O2 (SedO2), DIC (SedDIC), Alkalinity (SedAlkalini), PO4 (SedPO4), NO3 (SedNO3), NH4 (SedNH4), Fe (SedFe2), SO4 (SedSO4), H2S (SedH2S),

- pH and organic ligands are diagnosed

A brief overview of the sediment module code (2)

- sedstp.F90 : main sediment module, temporal loop
  - seddta.F90: Fluxes, boundary conditions for the sediments
  - sedchem.F90: computes the chemical constants
  - sedbtb.F90: 1st pass of bioturbation (t+1/2)
  - sedorg.F90: organic carbon related reactions
    - seddiff.F90: 1st pass of solute diffusion (t+1/2)
    - seddsr.F90: primary redox reactions (t+1)
      - sed_dsr_redoxb: secondary redox reactions
    - seddiff.F90: 2nd pass of solute diffusion (t+1)
  - sedinorg.F90: inorganic reactions (Bsi, CaCO3, Clay) (t+1)

To continue on next slide

A brief overview of the sediment module code (3)

sedstp.F90 : main sediment module, temporal loop

- sedbtb.F90: 2nd pass of bioturbation (t+1)
- sedadv.F90: vertical advection, burial
- sedco3.F90: DIC chemistry, pH computation
- sedmbc.F90: mass balance computation
- sedsfc.F90: updated bottom water concentrations (2-way)

Some important aspects of diagenetic modeling

- In the open ocean, sediment exchanges at the interface are not first order for timescales from < 1 yr to ~100 years for the carbon cycle/nutrient cycles

- It is 1^{st} order for trace metals such as Fe and Mn

- In coastal areas, it plays a critical role and should ideally be considered (using a full model or a metamodel)

- **Very slow to adjust (> 100 years to 100000 years) which is problematic for most cases**

    - Equilibrate the diagnetic model in an offline mode using output from a simulation with no sediments (not ideal when sediments play a critical role)

    - Use an initial state coming from another simulation, potentially run at global scale and at a potentially lower resolution (also not ideal)

Some reading to go beyond

Boudreau, Diagenetic Models and Their Implementation: Modelling Transport and Reactions in Aquatic Sediments, 1997: **the bible**

Burdige, Geochemistry of marine sediments, 2020

Kristensen, Organic matter diagenesis at the oxic/anoxic interface in coastal marine sediments, with emphasis on the role of burrowing animals, hydrobiologia, 2000

Boudreau, the mathematics of early diagnesis: From worms to waves, Reviews of Geophysics, 2000

Archer et al., A model of suboxic sedimentary diagenesis suitable for automatic tuning and gridded global domains, Global Biogeochemical Cycles, 2002

Paraska et al., Sediment diagenesis models: Review of approaches, challenges and opportunities, Environmental Modelling & Software, 2014