Diagenesis - overview (with color code)

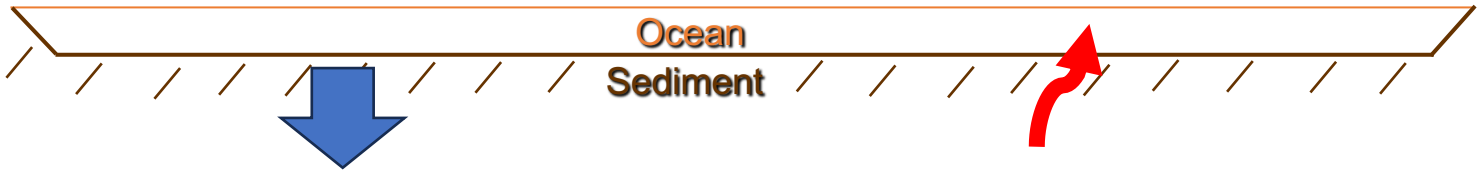
- Introduction to sediments & (early) diagenesis
- Organic matter degradation:
  - Redox control / zones
  - Sediment solute profiles: biogeochemical reactions & diffusive fluxes
  - Factors impacting sediment solute profiles / redox zones
  - Why do we care about diagenesis? Sediments as sources & sinks of nutrients and carbon

Diagenesis – learning objectives

- Why are sediments important, how do they differ from the water column?
- What is early diagenesis, what processes does it include, what is its impact on dissolved and solid species?
- What redox reactions (can) occur in marine sediments during organic matter degradation (in what sequence); what determines which reactions occur?
- What can sediment solute profiles tell us about reactions and fluxes in a sediment?

Why Study Sediments?

- Very large surface area of sediments with respect to the volume of seawater:



Vertical distance = 4 - 6 km

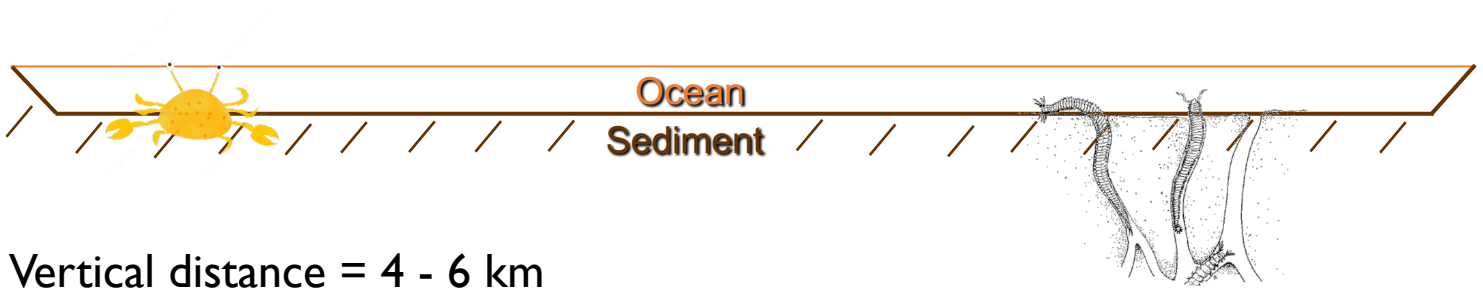
Horizontal distance = 1000's km

+ topographic features

- Large area of contact between seawater and sediment
- Strong potential for the two reservoirs to interact
- Geochemical balances of many elements depend on balance between burial and remobilization

Why Study Sediments?

- Very large surface area of sediments with respect to the volume of seawater:



Vertical distance = 4 - 6 km

Horizontal distance = 1000's km

+ topographic features

- Large area of contact between seawater and sediment
- Strong potential for the two reservoirs to interact
- Geochemical balances of many elements depend on balance between burial and remobilization
- Surface sediments are habitat for a wide range of organisms

What is Diagenesis?

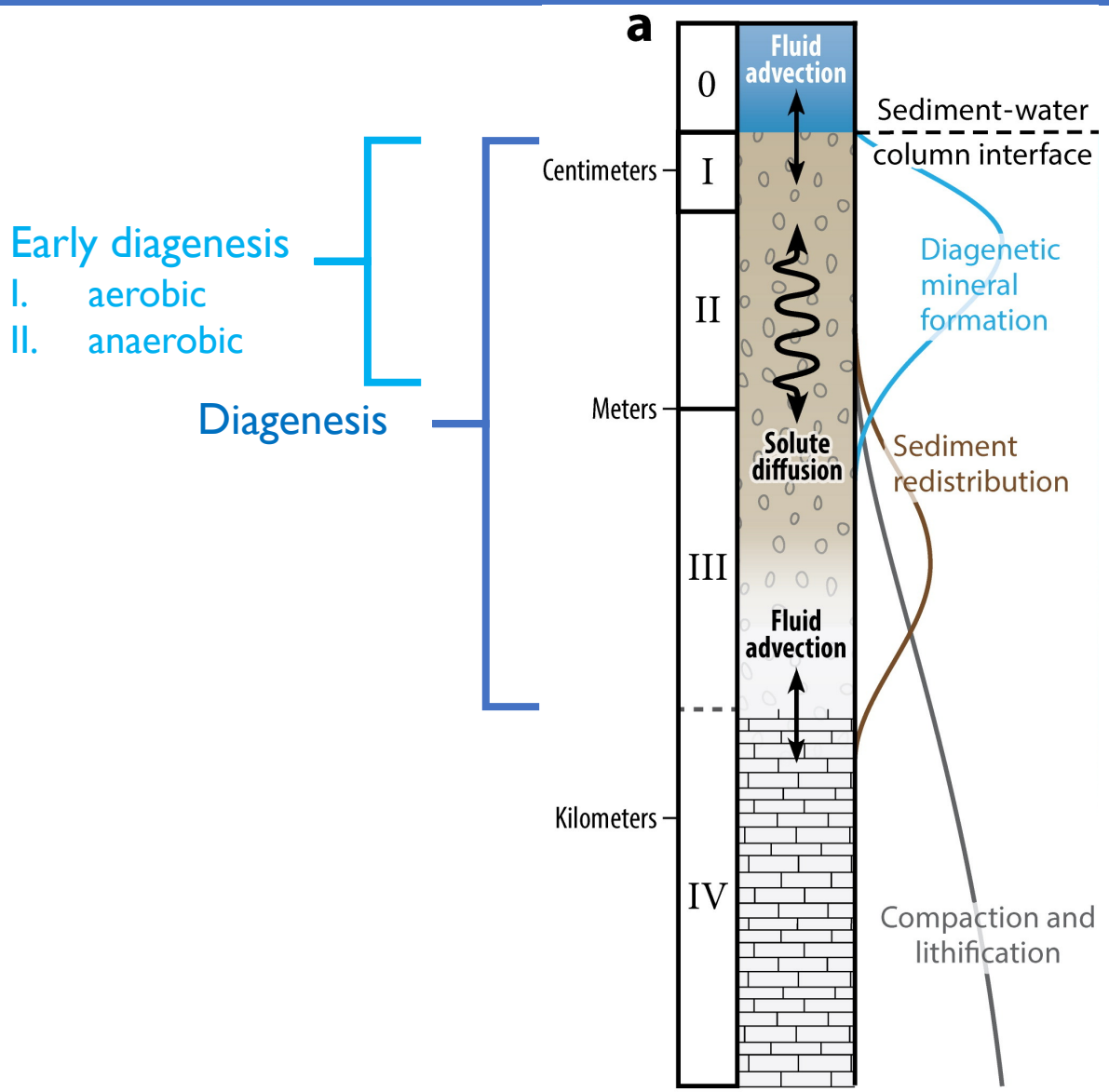
- Greek etymology:

  dia -- "passing through"

  genesis -- "origin, birth"

- Diagenesis is the "sum of all processes that change a sediment or sedimentary rock subsequent to its deposition from water, but excluding metamorphism and weathering" (Berner, 1980)
- Simply: "Reactions in Modern sediments…"

Reactions that occur at sediment depths shallower than a few 100 m (and < 50° C)



Fantle MS, et al. 2020. *Annu. Rev. Earth Planet. Sci.* 48:549–83

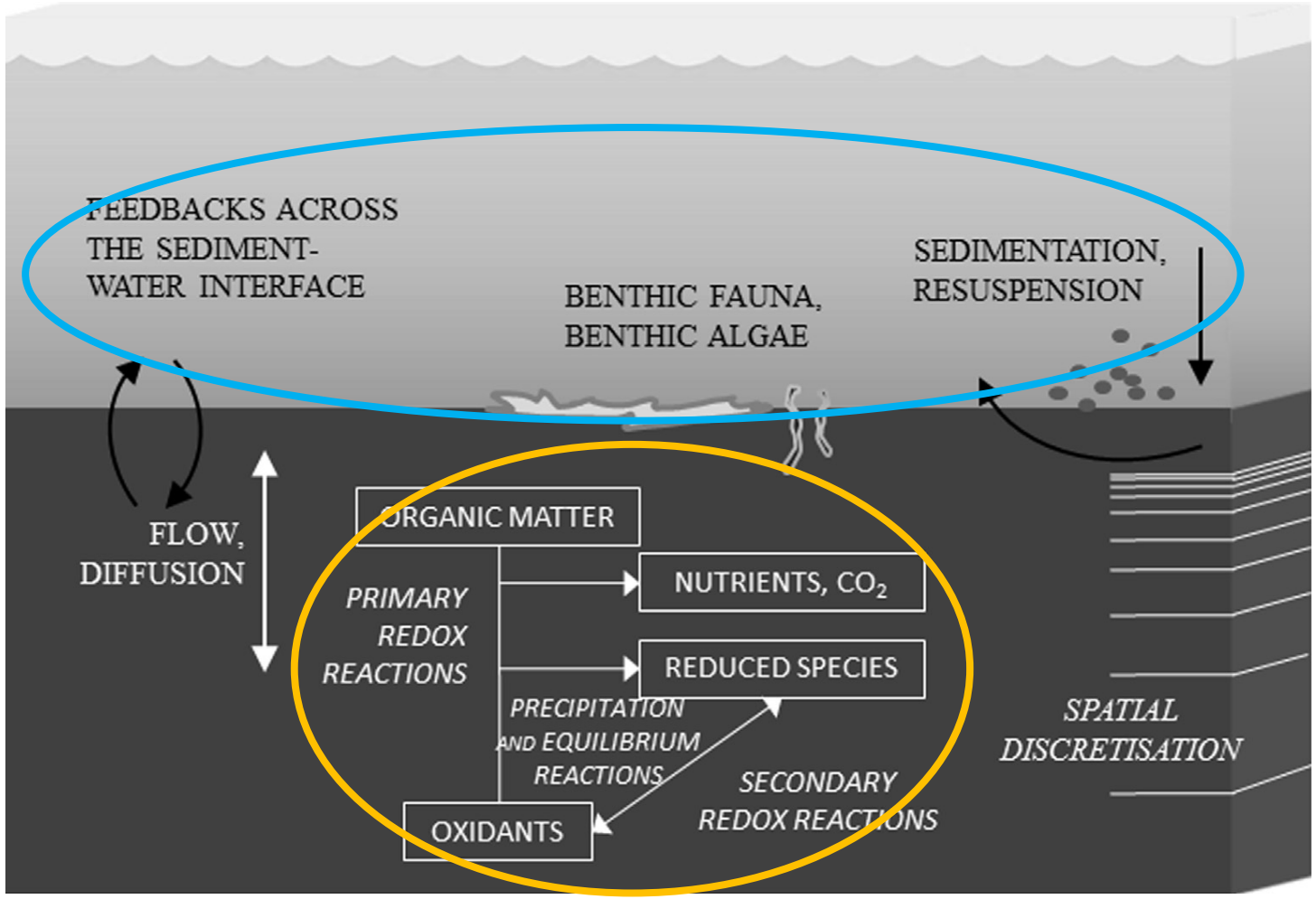
(Early) Diagenesis - Processes

(Biogeo-)Chemical reactions:

- Redox reactions
- Dissolution of solids
- Diffusion of dissolved species
- Precipitation of dissolved species

Biological / physical processes:

- Microbial activity
- Compaction
- Dewatering
- Bioturbation of solids
- Bioirrigation
- …



Paraska et al. 2014, *Environ. Model Softw.*

Overall Result of (early) Diagenesis

Terrestrial debris (inorganic, organic)
+
Reactive marine organic matter / biogenic debris

Diagenetic Reactions



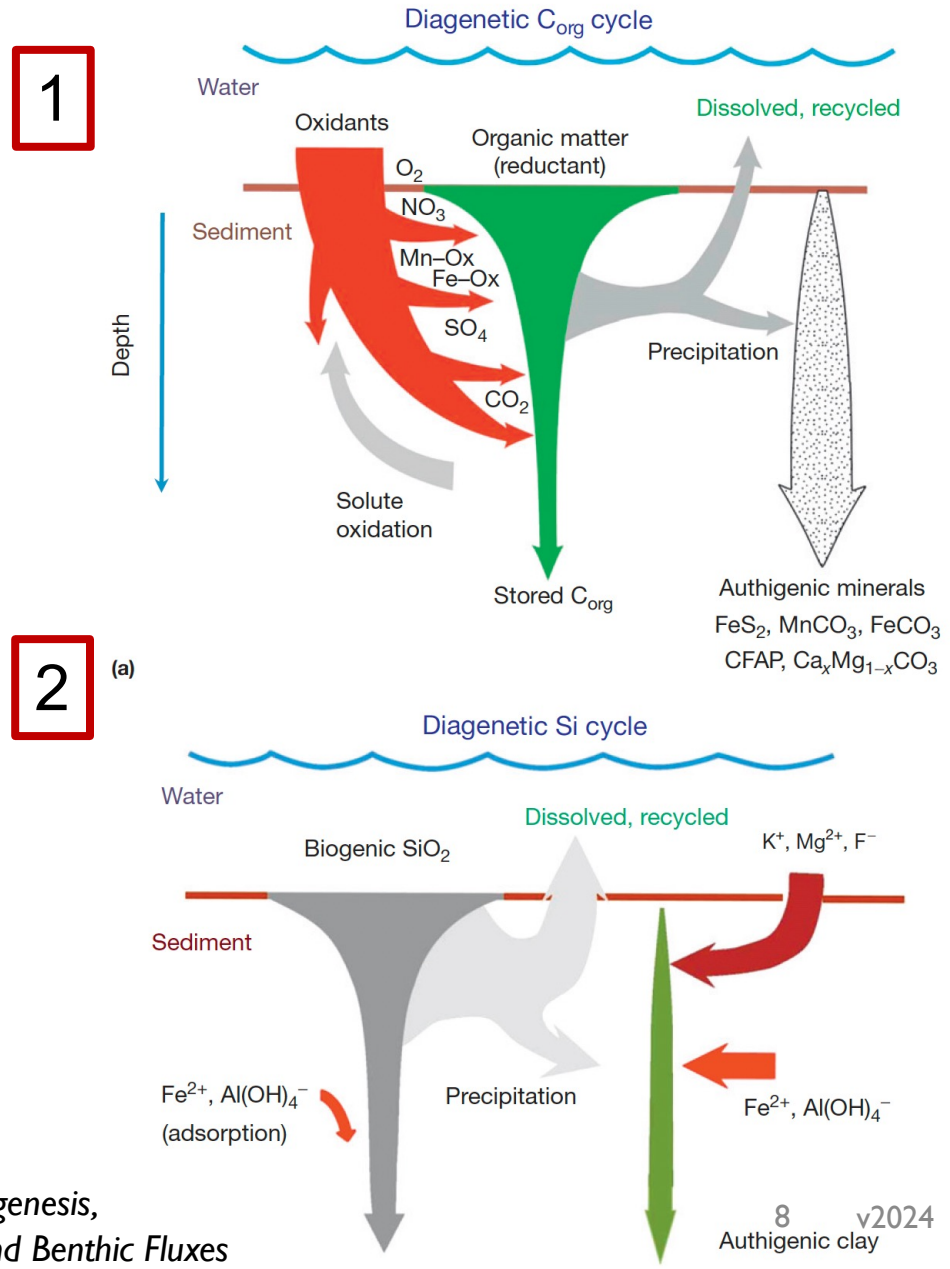
Product	***Fate***
Remineralized (inorganic) dissolved species (C, N, P, metals…)	Released, buried
Authigenic minerals (C, P, S, Si, Mn-Fe) (grow in place, not transported)	Buried
Residual OM	Buried

Early diagenesis: Biogeochemical reactions

Biogeochemical reactions during early diagenesis can be sorted into three groups* based on substrate:

1. Related to organic matter degradation
2. Related to degradation of biogenic silica
   - 'reverse weathering'
3. Related to degradation (dissolution) of biogenic carbonate minerals

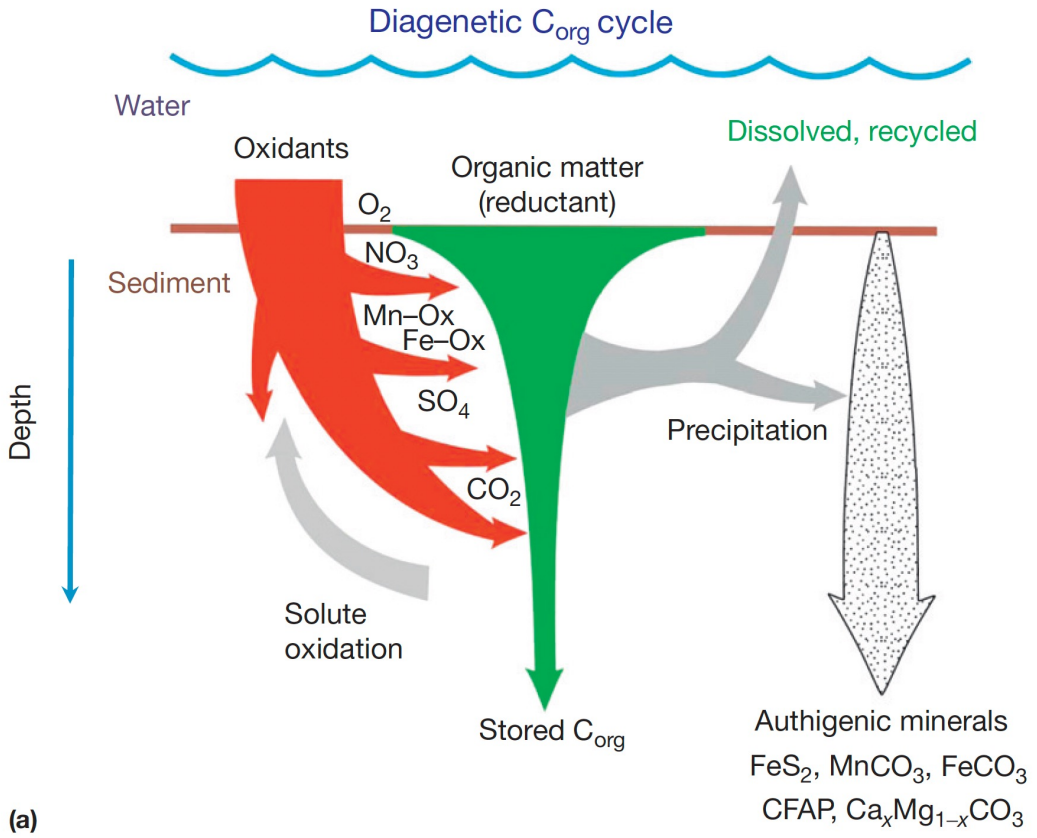
*that interact with each other



Aller 2014: *Sedimentary Diagenesis, Depositional Environments, and Benthic Fluxes*

Organic matter degradation – redox controlled

- OM in sediments is thermodynamically unstable
- Decomposition occurs by various processes, each of which leads to formation of specific species in solution and precipitation of authigenic minerals
  - Involves series of reactions using electron acceptors that are consumed sequentially
  - Each successive reaction is energetically less favorable, and does not occur until the electron acceptor from the (previous) more favorable reaction has been mostly consumed

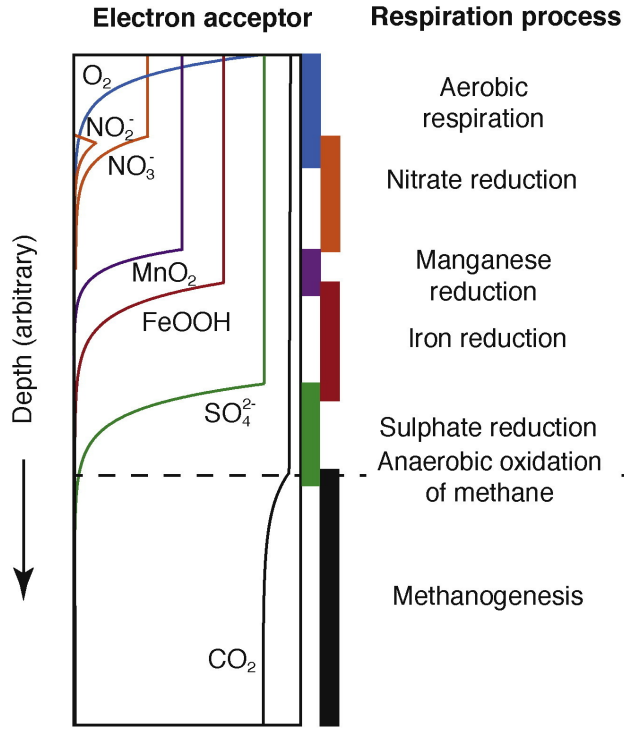


Organic matter degradation – redox zones

Table 1 The standard free energy of reaction, ΔG_r^0, for the dominant environmental redox reactions

Reaction	*ΔG_r^0 (kJ mol^{-1}) (half reaction)*		*ΔG_r^0 (kJ mol^{-1})*
Oxidation			
$CH_2O^a_{(aq)} + H_2O \rightarrow CO_{2(g)} + 4H^+ + 4e^-$	−27.4		
$^2/_3CH_3OH_{(aq)} + {}^2/_3H_2O \rightarrow {}^2/_3CO_{2(g)} + 4H^+ + 4e^-$	12.1		
$½\ CH_{4(aq)} + H_2O \rightarrow ½CO_2 + 4H^+ + 4e^-$	57.2		
Reduction			
$4e^- + 4H^+ + O_{2(aq)} \rightarrow 2H_2O$	−491.0		−518.4
$4e^- + 4.8H^+ + 0.8NO_3^-{}_{(aq)} \rightarrow 0.4N_{2(g)} + 2.4H_2O$	−480.2		−507.6
$4e^- + 8H^+ + 2MnO_{2(s)} \rightarrow 2Mn^{2+}{}_{(aq)} + 4H_2O$	−474.5		−501.9
$4e^- + 12H^+ + 2FeOOH_{(s)} \rightarrow 4Fe^{2+}{}_{(aq)} + 8H_2O$	−258.5		−285.9
$4e^- + 5H^+ + ½SO_4^{2-}{}_{(aq)} \rightarrow ½H_2S_{(aq)} + 2H_2O$	−116.0		−143.4
$4e^- + 4H^+ + ½CO_{2(g)} \rightarrow ½CH_{4(aq)} + H_2O$	−57.2		−84.6

Sequence, i.e., one used up after the other (more or less)



Things to note:

- The amount of oxidant required to oxidise 1 mol of CH_2O differs
  - e.g., only 1 mol O_3^- but 2 moles of FeOOH → FeOOH is used up twice as fast
- Redox reactions are generally catalysed by different bacteria or archaea that use this for energy

Organic matter degradation – redox zones

Overall reaction:

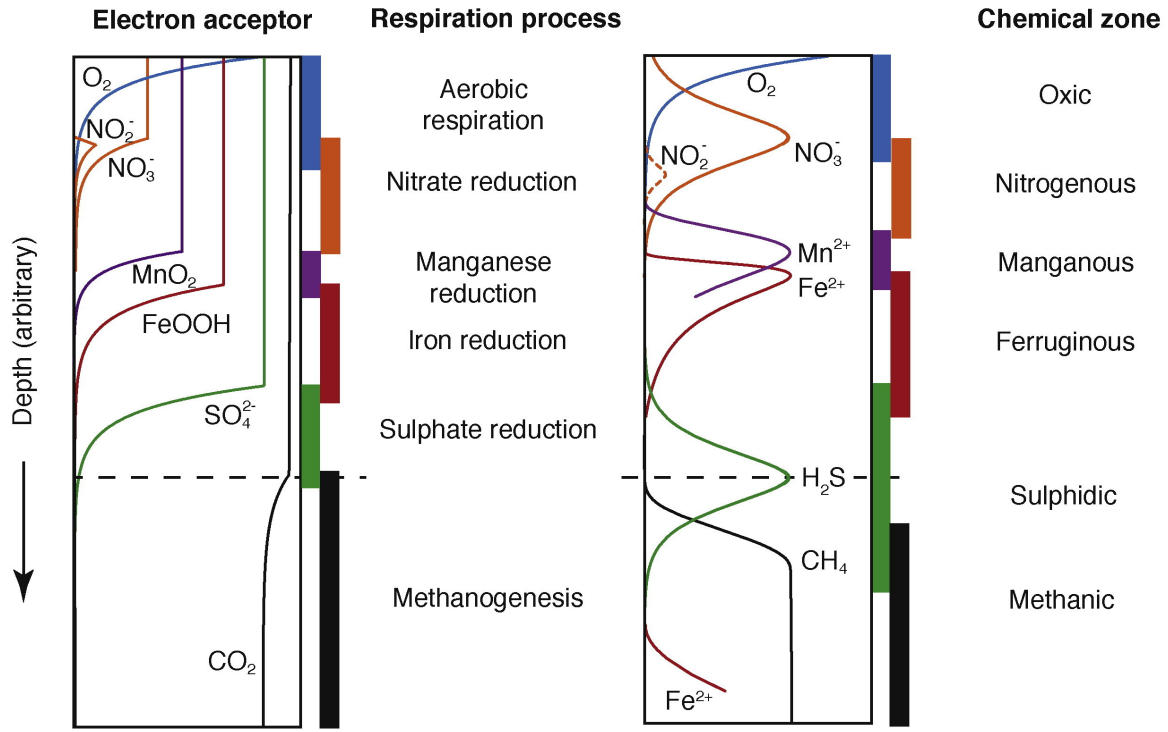
- Combining oxidation half-reaction (i.e., oxidation of CH_2O to CO_2) with reduction half-reaction
- Account for nutrients in organic material (i.e., NH_3, H_3PO_4) that are released as OM is oxidised

Table 3 Overall stoichiometric (C/N/P) organic matter oxidation reactions. Model Redfield ratios for *x*, *y*, and *z* are typically taken as 106, 16, and 1

Metabolic redox process	*Overall reaction*
Aerobic respiration	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (x+2y)O_2 \rightarrow xCO_2 + (x+y)H_2O + yHNO_3 + zH_3PO_4$
Nitrate reduction	$5(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 4xNO_3^- \rightarrow xCO_2 + 3xH_2O + 4xHCO_3^- + 2xN_2 + 5yNH_3 + 5zH_3PO_4$
Manganese reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 2xMnO_2(s) + 3xCO_2 + xH_2O \rightarrow 2xMn^{2+} + 4xHCO_3^- + yNH_3 + zH_3PO_4$
Iron reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 4xFe(OH)_3 + 7xCO_2 \rightarrow 4xFe^{2+} + 8xHCO_3^- + 3xH_2O + yNH_3 + zH_3PO_4$
Sulfate reduction	$2(CH_2O)_x(NH_3)_y(H_3PO_4)_z + xSO_4^{2-} \rightarrow xH_2S + 2xHCO_3^- + 2yNH_3 + 2zH_3PO_4$
Methane production	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z \rightarrow {}^x/_2CH_4 + {}^x/_2CO_2 + yNH_3 + zH_3PO_4$

All organic matter degradation (aerobic or anaerobic) release nutrients (NH_3, HPO_4^{2-})!

OM degradation – solute profiles

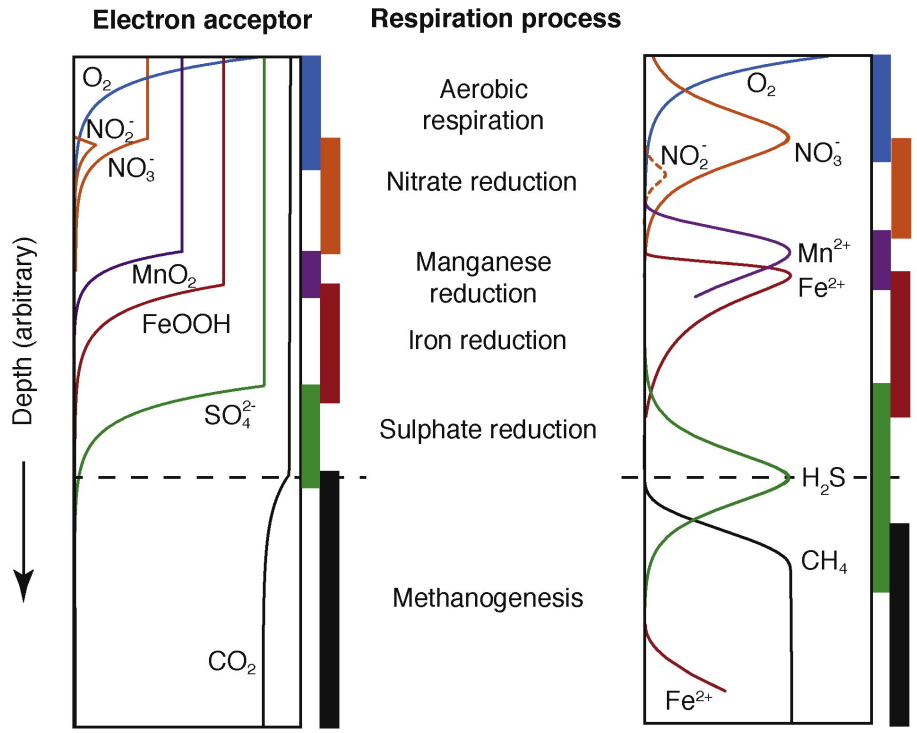


Roberts 2015, *Earth-Science Reviews*

Redox zones can be identified by the dissolved species their dominant reactions release to (Mn^{2+}, Fe^{2+}, H_2S, CH_4) or taken up from (O_2, NO_3, SO_4^{2-}) sediment porewaters.

Need to also account for removal via precipitation & diffusion.

OM degradation – solute profiles



Roberts 2015, *Earth-Science Reviews*

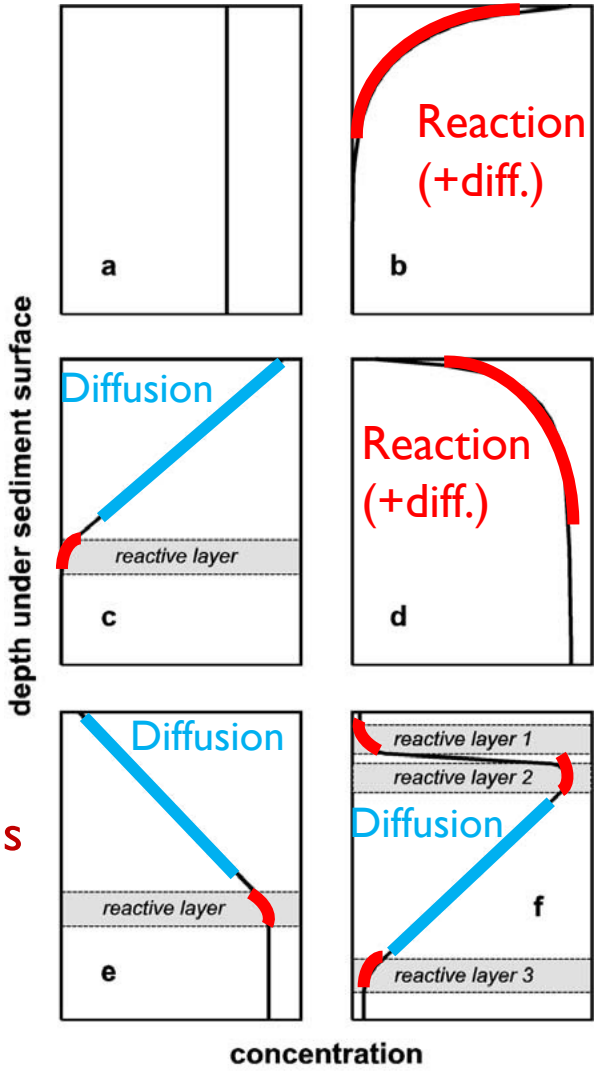
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Need to also account for removal via precipitation & diffusion.

Interpreting sediment solute profiles:

a) No reaction (e.g., Cl^-)
b) Removal in upper sediment (e.g., O_2)
c) Removal in specific layer (e.g., SO_4^{2-})
d) Production in upper sediment (e.g., silica)
e) Production in specific layer
f) Production in one layer (2), removal in two other (1,3; e.g., NO_3, Fe^{2+}, Mn^{2+})

Shape of solute profile depends on the reaction(s) a solute is involved in and diffusion*



*technically only applicable to fine grain sediments (no advection) without any disturbance by bioturbation or physical processes

Calculating fluxes from steady state solute profiles

Diffusive flux of solute i:

$$J_{sed,i} = -D_{sed,i}\ \varphi\ \frac{\partial C_i}{\partial z}$$

$D_{sed,i}$ diffusion coefficient of i within sediment

φ porosity

$\frac{\partial C_i}{\partial z}$ concentration gradient of i in sediment

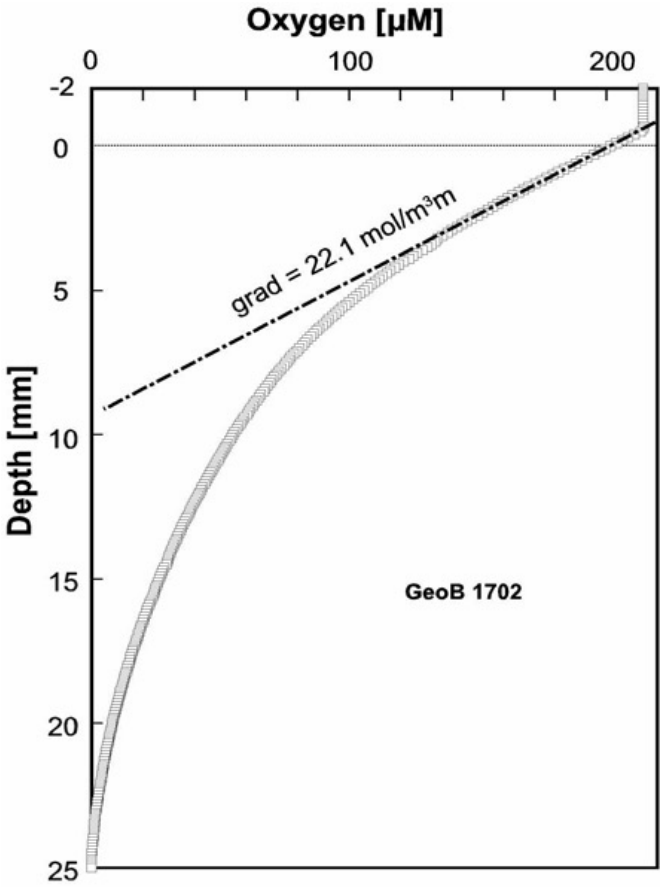
Diffusivity of solute i within in sediment*:

$$D_{sed,i} = D_{sw,i}\ \varphi^2$$

$D_{sw,i}$ diffusion coefficient of solute i in seawater

**this is just one way to calculate D_{sed}; there are other parametrisations*

Example: O_2 flux into sediment:



J_{sed} = ???

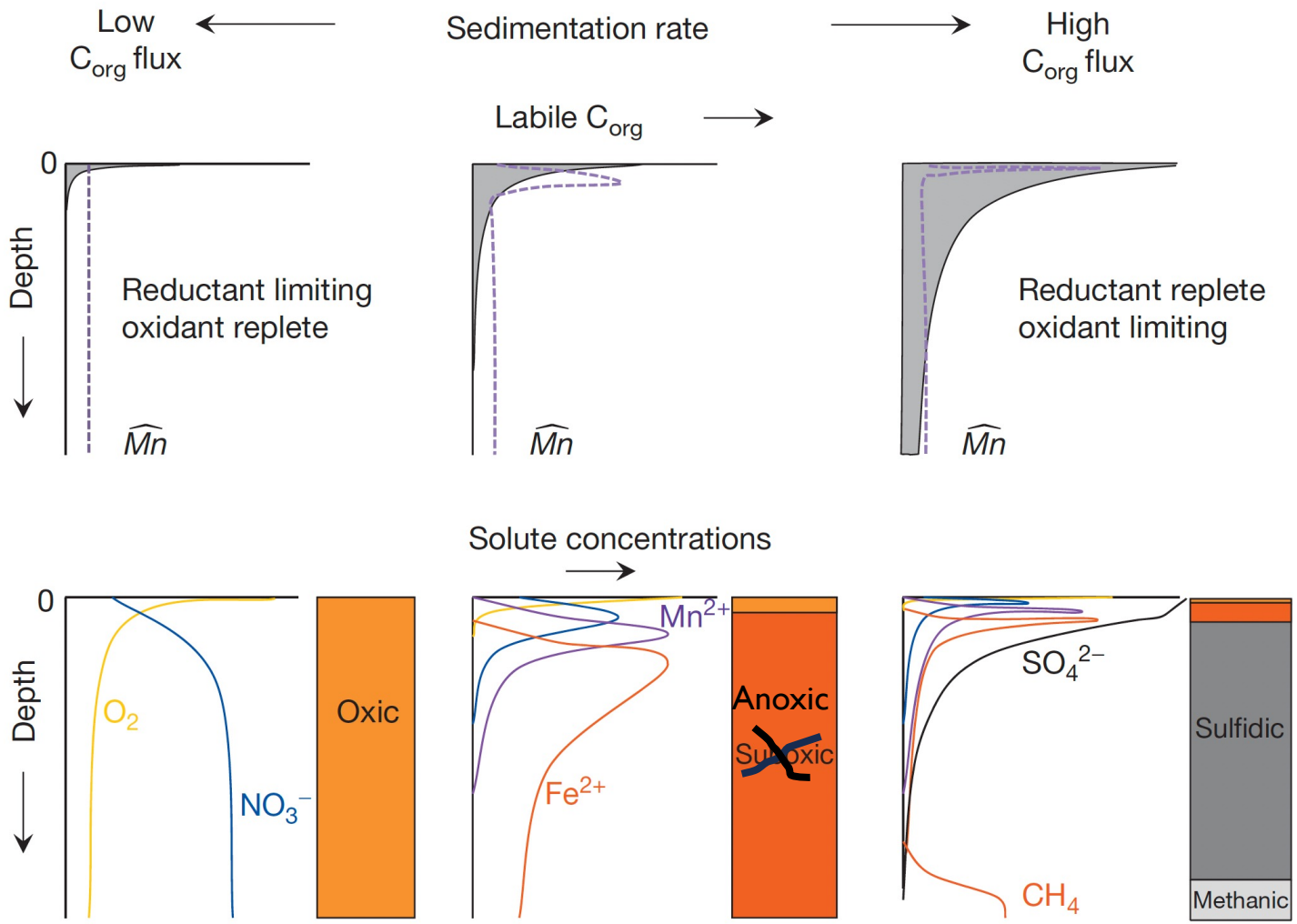
φ = 0.8

D_{sw} (at 5°C)= 1.23 ·10^{-9} m^{2}s^{-1}

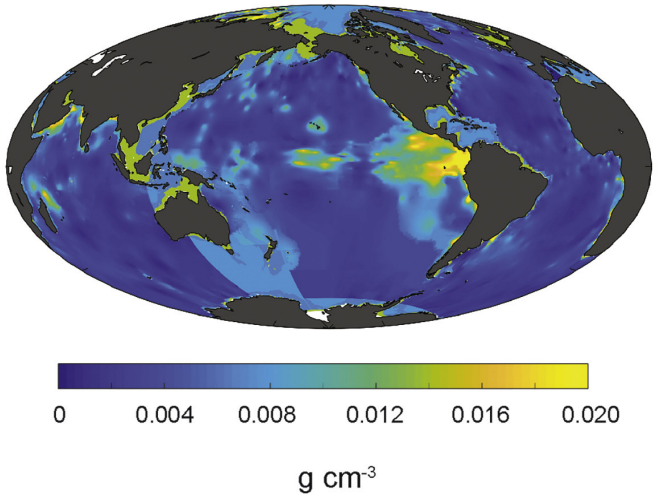
What determines redox zones/solute profiles?

- Availability (and quality?) of reductant (organic matter)
  - organic matter supply / sedimentation rate
- Availability of oxidant(s)
  - Sediment type (biogenic, lithogenic…)
  - Bottom water oxygen
- Physical characteristics & processes
  - porosity, permeability, …
  - sediment resuspension, …
- Presence of macrofauna
  - Bioturbation & irrigation

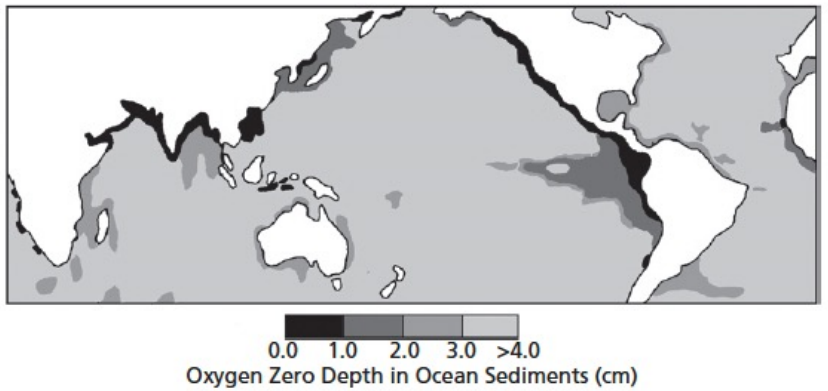
Reductant (organic carbon) supply



Concentration of particular organic carbon (POC) at the sea floor:



LaRowe et al. 2020, *Earth Sci. Rev.*

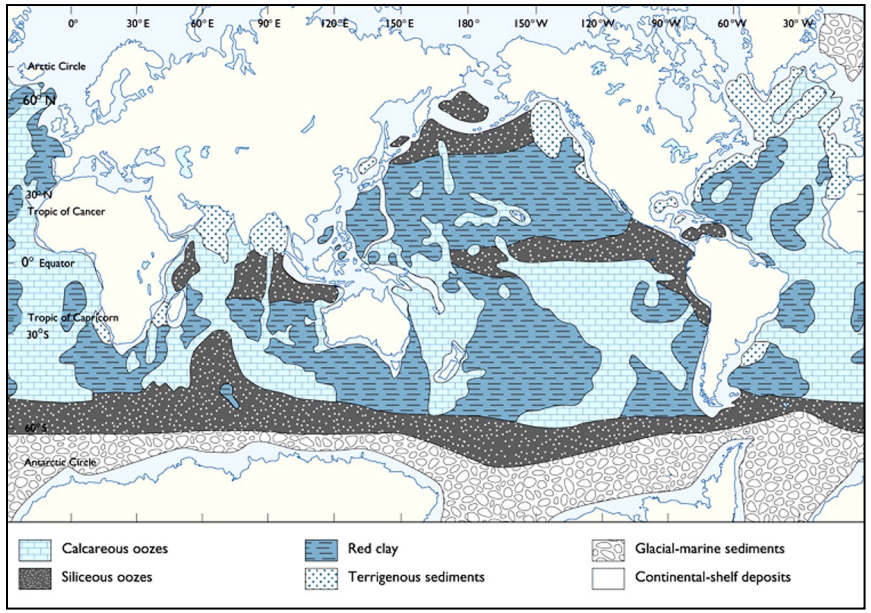


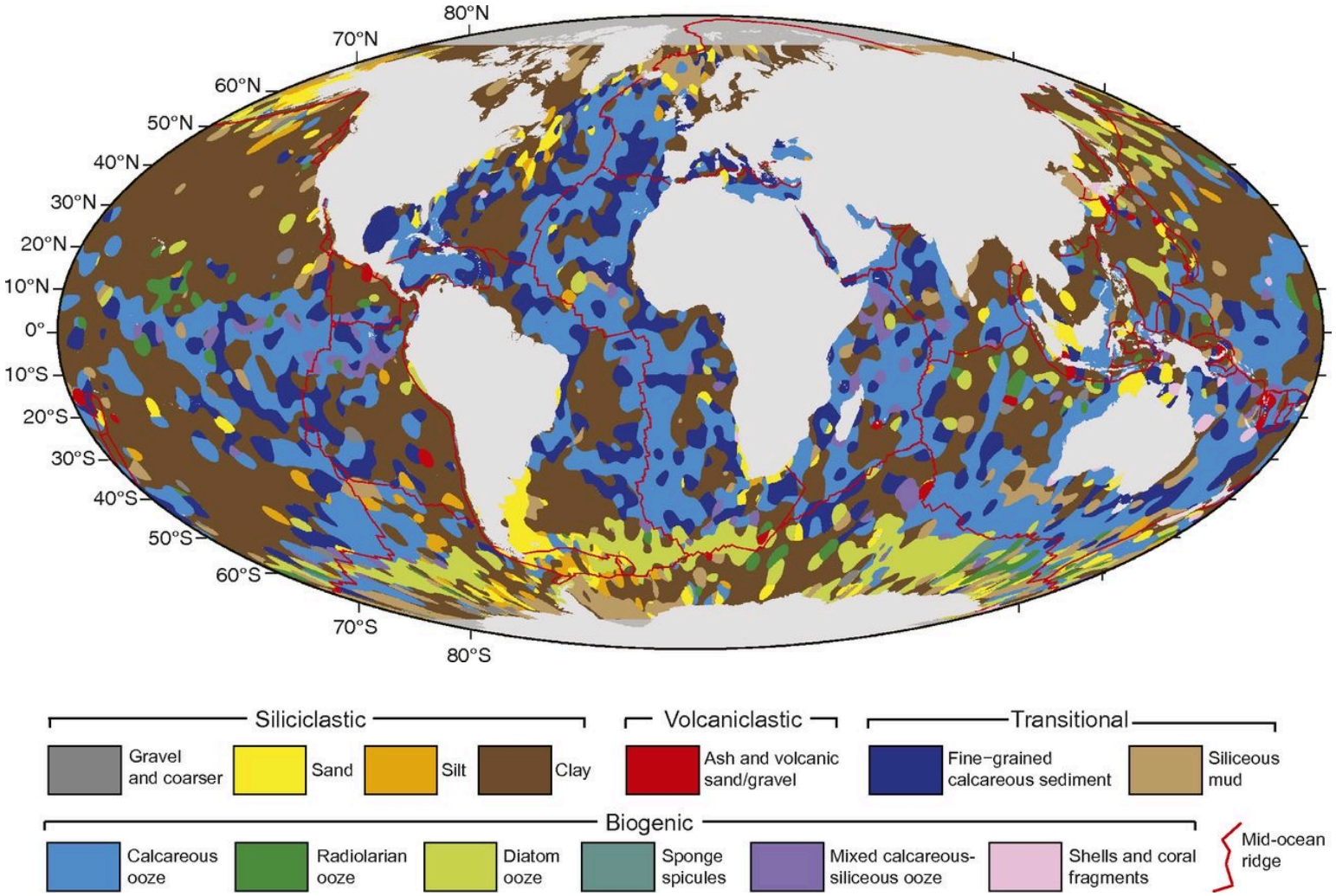
Aller, 2014

Sediment type – classifications (review)

- Origin of particles (i.e., how/where they were formed)
  - **biogenous (biogenic):** produced by living organisms
  - **lithogenous (lithogenic):** produced from weathering
    - also: **terrigenous**: produced on land, **detrital**
  - **hydrogenous:** formed by reactions in water
    - similar: **authigenic:** produced in situ (i.e., in sediments)
  - **cosmogenous:** produced from extraterrestrial sources
  - …
- Grain size
  - gravel, sand, silt, clay
- Location/depth relative to land
  - Shelf, slope, deep ocean (pelagic) sediments, …
- …

Sediment types – where are they found?

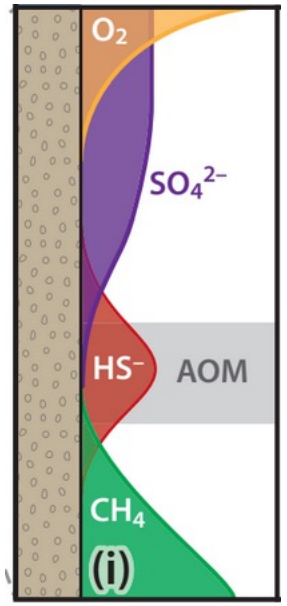




Dutkiewicz et al. 2015, *Geology* – based on >14000 seafloor samples

Sediment types – impact on OM degradation?

- Geochemistry
  - e.g., biogenic (carbonates, opal) vs. lithogenic sediments
  - mineralogy (e.g., type of aluminosilicates)
  - …



Organic matter degradation in carbonate sediments

Fantle et al 2020, *Ann. Rev. Earth. Plan. Sci.*

- Grain size (clay < silt < sand) impacts:
  - Porosity
    - clay (~0.8) > silt (~0.6) > sand (~0.5)
  - Permeability:
    - sand > silt > clay
  - Surface area
    - clay > silt > sand

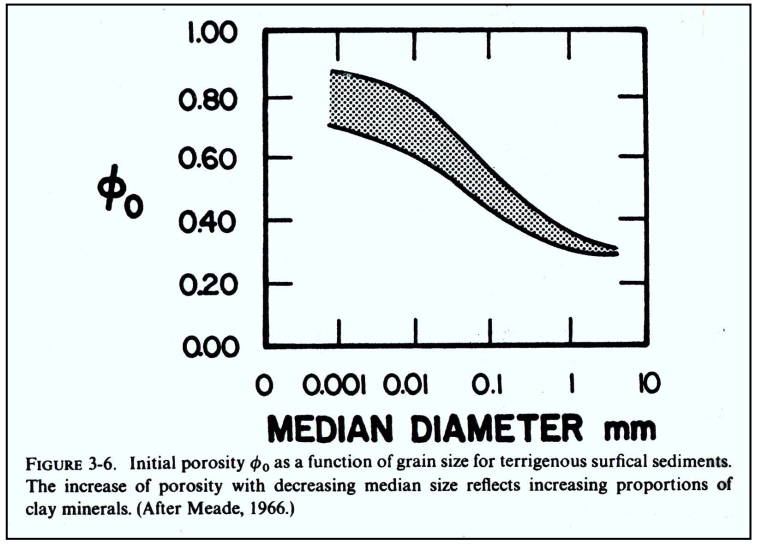


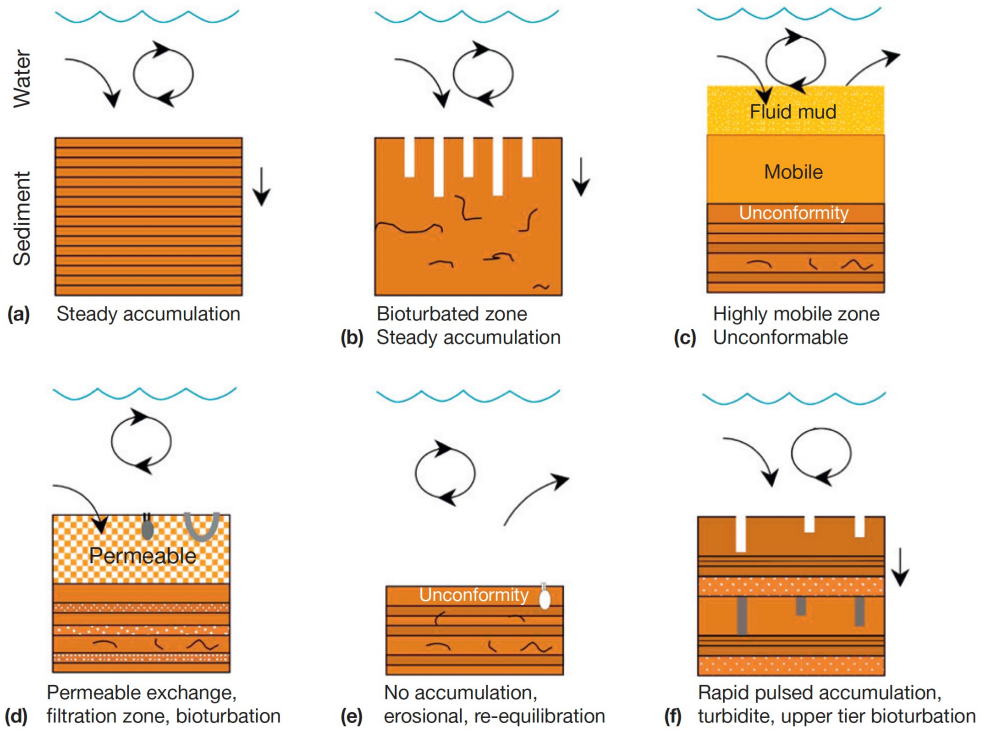
FIGURE 3-6. Initial porosity ϕ_0 as a function of grain size for terrigenous surfical sediments. The increase of porosity with decreasing median size reflects increasing proportions of clay minerals. (After Meade, 1966.)

(Bio-)physical processes

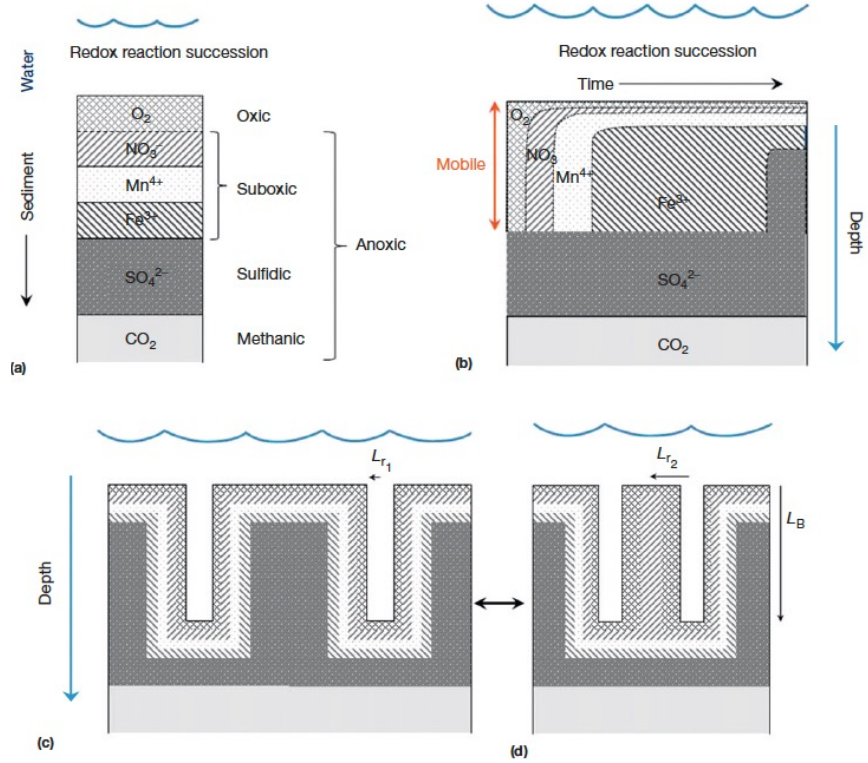
Reoxygenation and/or sediment mixing thanks to:

- Bioturbation/-irrigation by macrofauna
  - left: b, f, g
  - right: c,d
- Sediment resuspension in mobile layer (via waves, etc.)
  - left: c,
  - right: b
- Advection through permeable (sandy) layers
  - left: d

Processes:



Effect on redox zonation:



Aller 2014

Bioturbation / Bioirrigation







aRPD = apparent redox potential discontinuity

Why do we care about diagenesis?

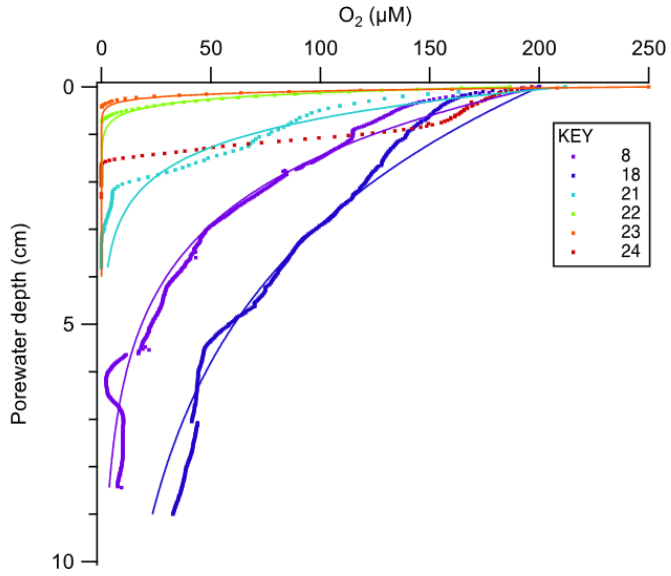
From a marine chemistry perspective:

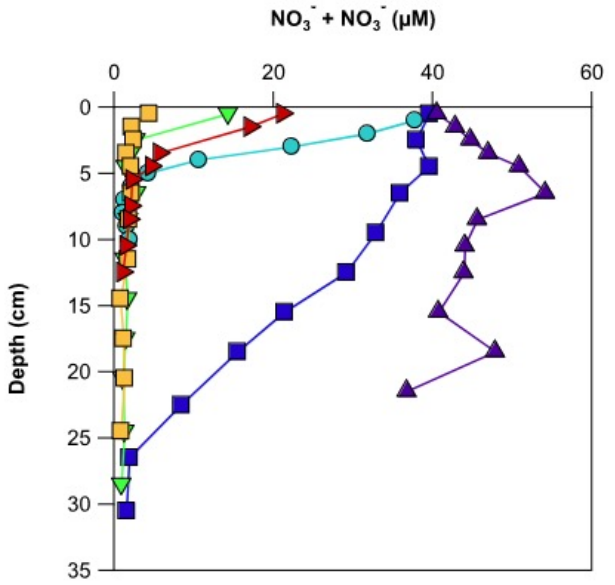
- Solute exchange:
  - source or sink of nutrients (NO_3, NH_3, PO_4, Fe, other micronutrients)
  - source or sink of pollutants (e.g., heavy metals, As)
  - source of greenhouse gases (CO_2, N_2O, CH_4)
- Burial vs. remineralization of organic matter
  - sequestration of carbon
- …

Sediment sources & sinks – macronutrients O_2 & Fe

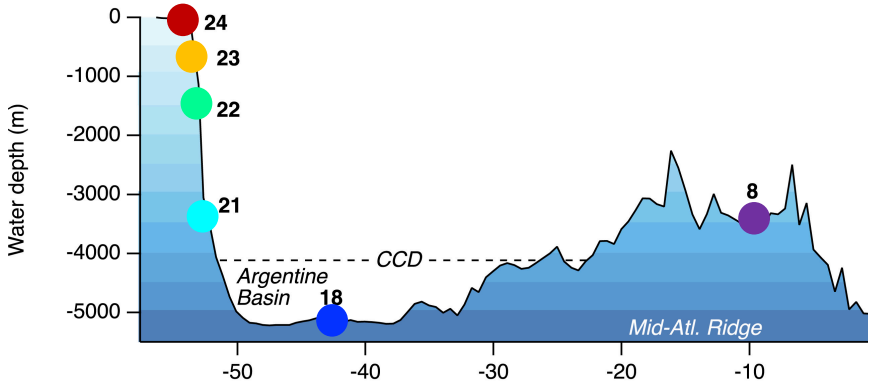
Are sediments a source or sink of:

- Oxygen?
- Nitrogen?
- Fe, Mn?
- Phosporus?

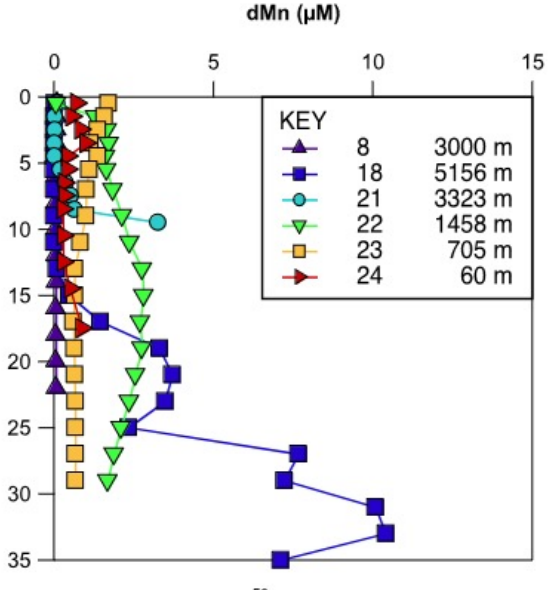


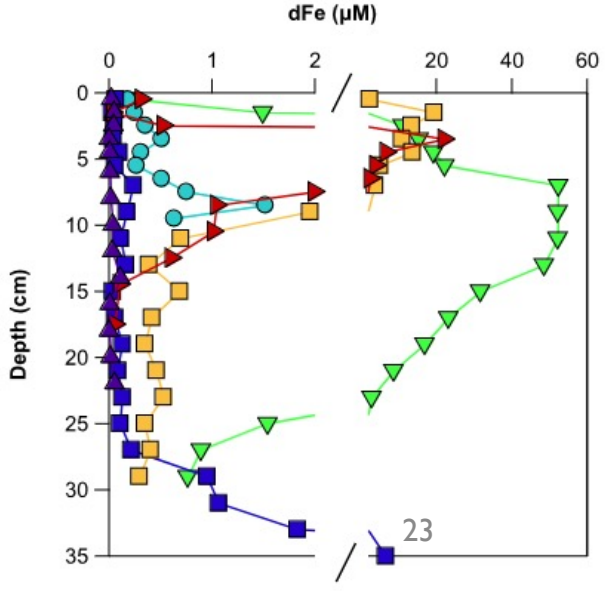


Examples profiles (southwest Atlantic; east of Uruguay)



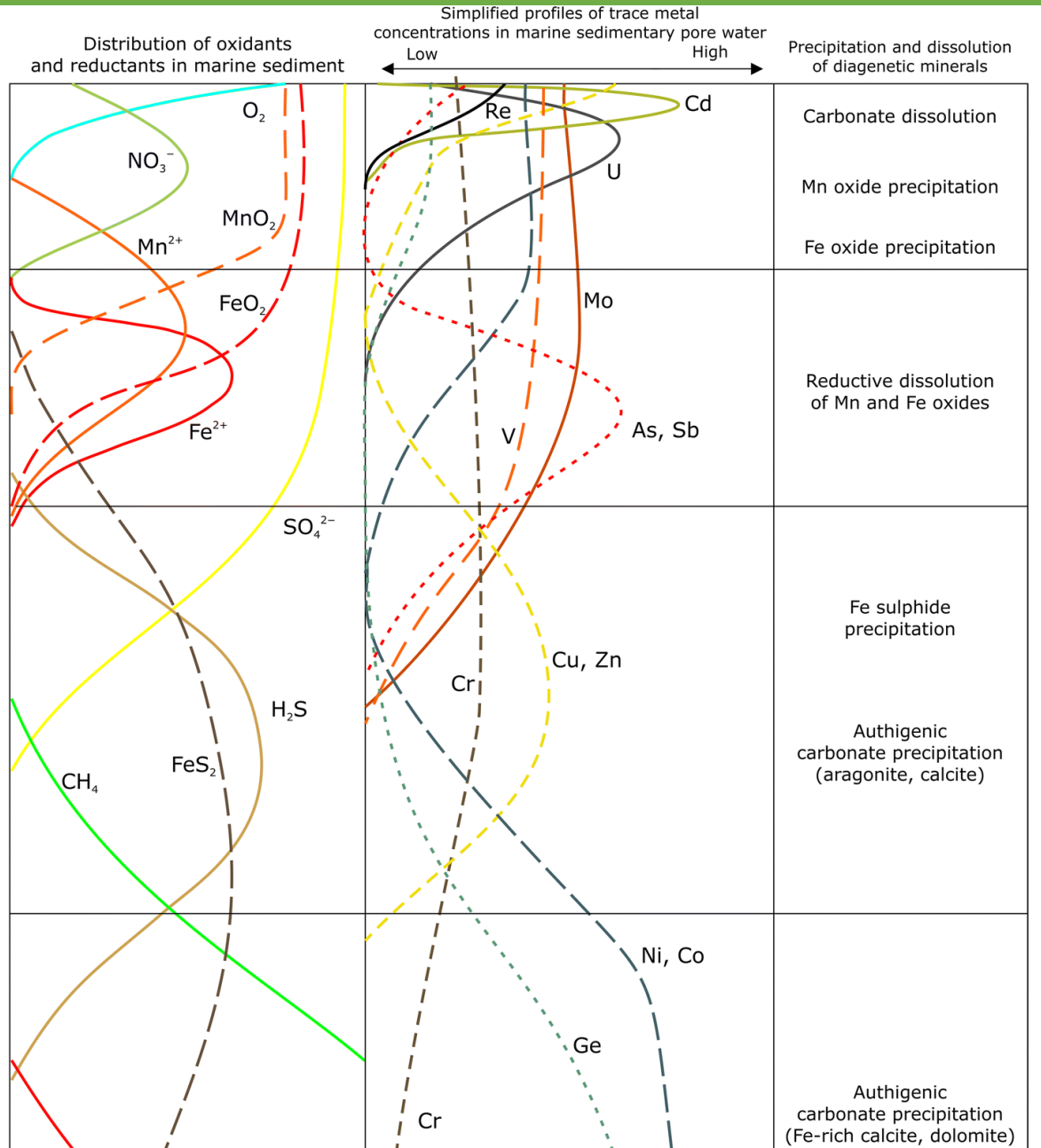
Homoky et al. 2021, *PNAS*





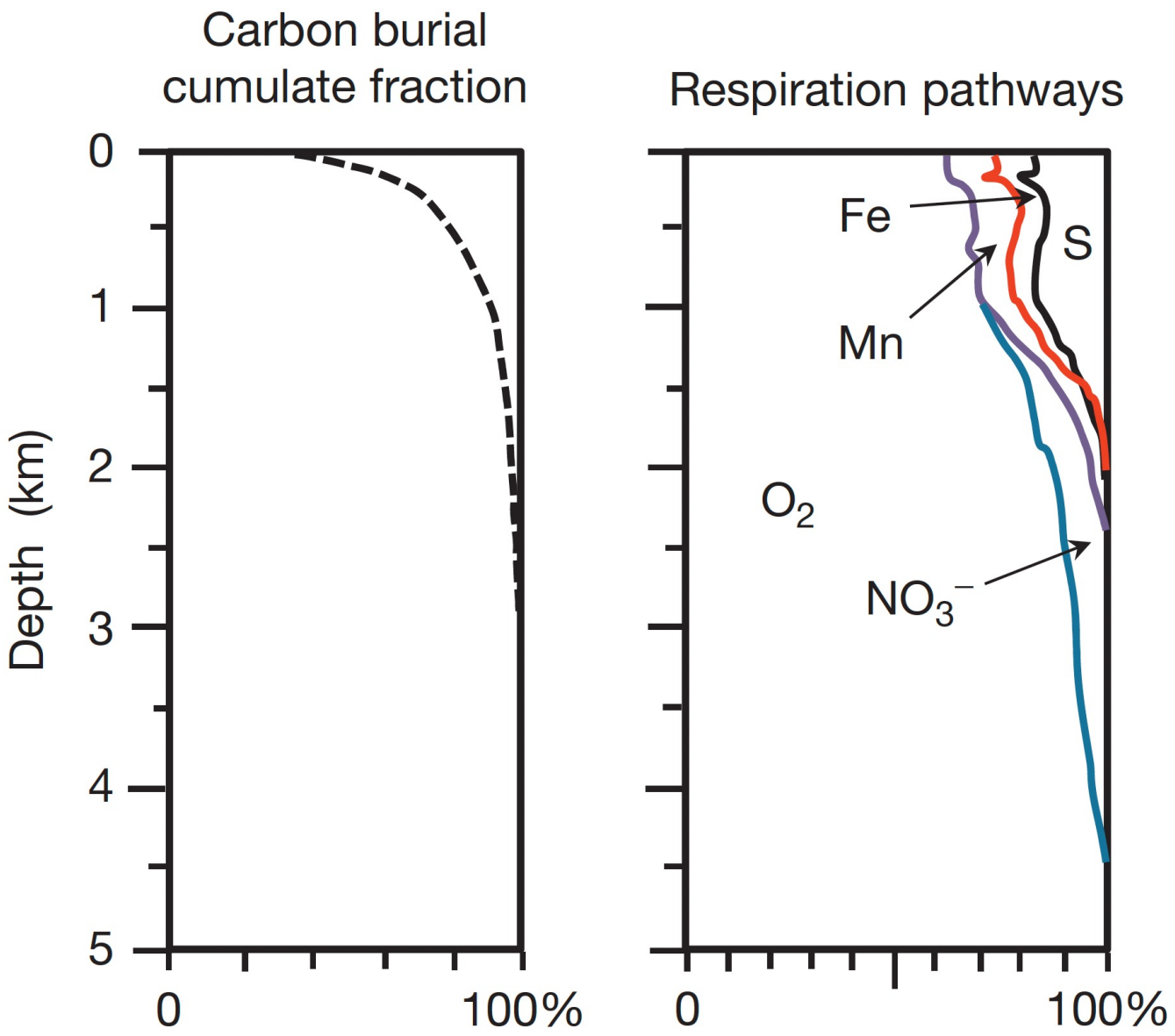
Sediment sources & sinks – micronutrients / pollutants

- Trace elements can be nutrients (e.g., Co, Zn) or pollutants (e.g., Cd, As) or both (e.g., Cu)
- Some trace metals are associated with certain solid phases (e.g., Mn, Fe oxides) and are removed or released when those precipitate / dissolve
- Some trace metals get reduced themselves in more reductive layers and may become more/less soluble (or toxic)



Smrzka et al. 2019, *Facies*

Carbon respiration & burial – where and why?



- 90% of organic carbon is respired in the water column and only ~1% or less ends up buried in sediments (i.e. not respired in sediments)
- Majority of organic carbon is buried (but also respired) in relatively shallow regions (near coasts)
- Oxic respiration most important pathway

Table 14.1 Ocean Organic Carbon Burial 10^{12} g organic C yr^{-1}. Based on Burdige (2007).

Depth Range (km)	% ocean area	Organic Carbon Burial (% of total in brackets)
0–0.2	7	152 (50%)
0.2–2	9	96 (31%)
>2	84	61 (20%)

Carbon preservation – factors

- Recalcitrance of OM (i.e., undegradable substrate)?
  - Protection by mineral surfaces?
    - positive correlation of OM preservation & surface area
  - Association with Fe, Mn
- Oxidant availability?
- Oxygen exposure time?
  - Sedimentation rate
  - Bottom water oxygen
  - (Bio-)physical reworking
- …

Middelburg 1989

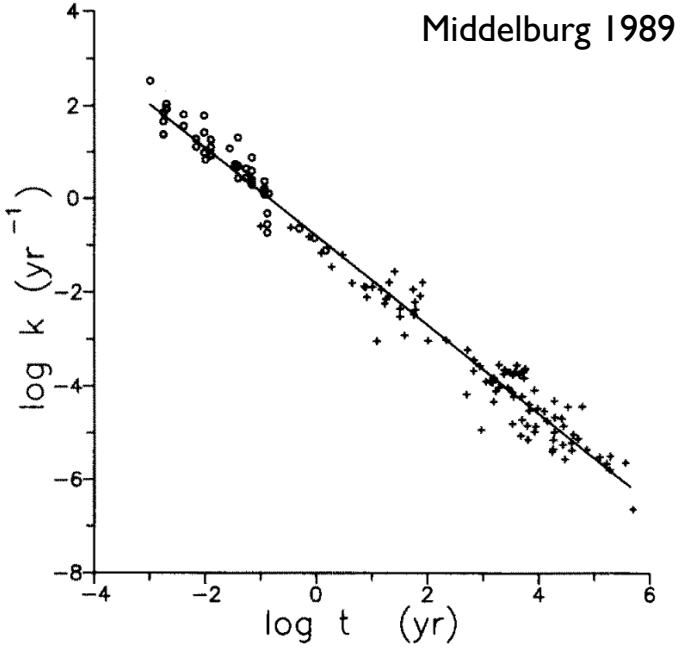


FIG. 2. The reactivity of organic carbon (k) *versus* time (t). First-

Article

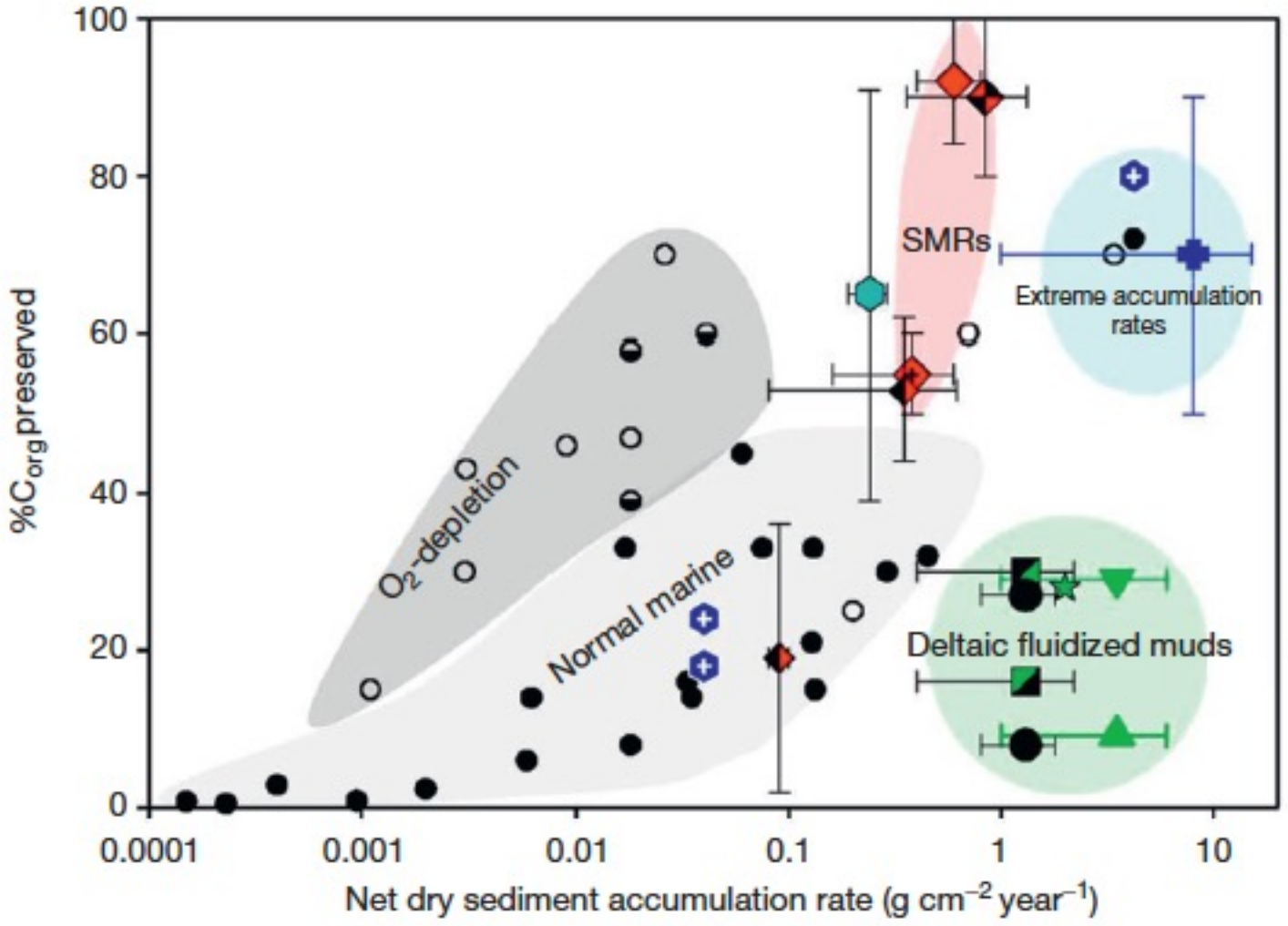
Long-term organic carbon preservation enhanced by iron and manganese

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The balance between degradation and preservation of sedimentary organic carbon (OC) is important for global carbon and oxygen cycles[1]. The relative importance of different mechanisms and environmental conditions contributing to marine sedimentary OC preservation, however, remains unclear[2–8]. Simple organic molecules can be geopolymerized into recalcitrant forms by means of the Maillard reaction[5], although reaction kinetics at marine sedimentary temperatures are thought to be

Carbon preservation – factors



"reactivity of organic matter is determined by the interaction between the compound and its ecosystem, not just the chemical nature of the organic compounds" – LaRowe et al. 2020, *Earth Sci. Rev.*

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