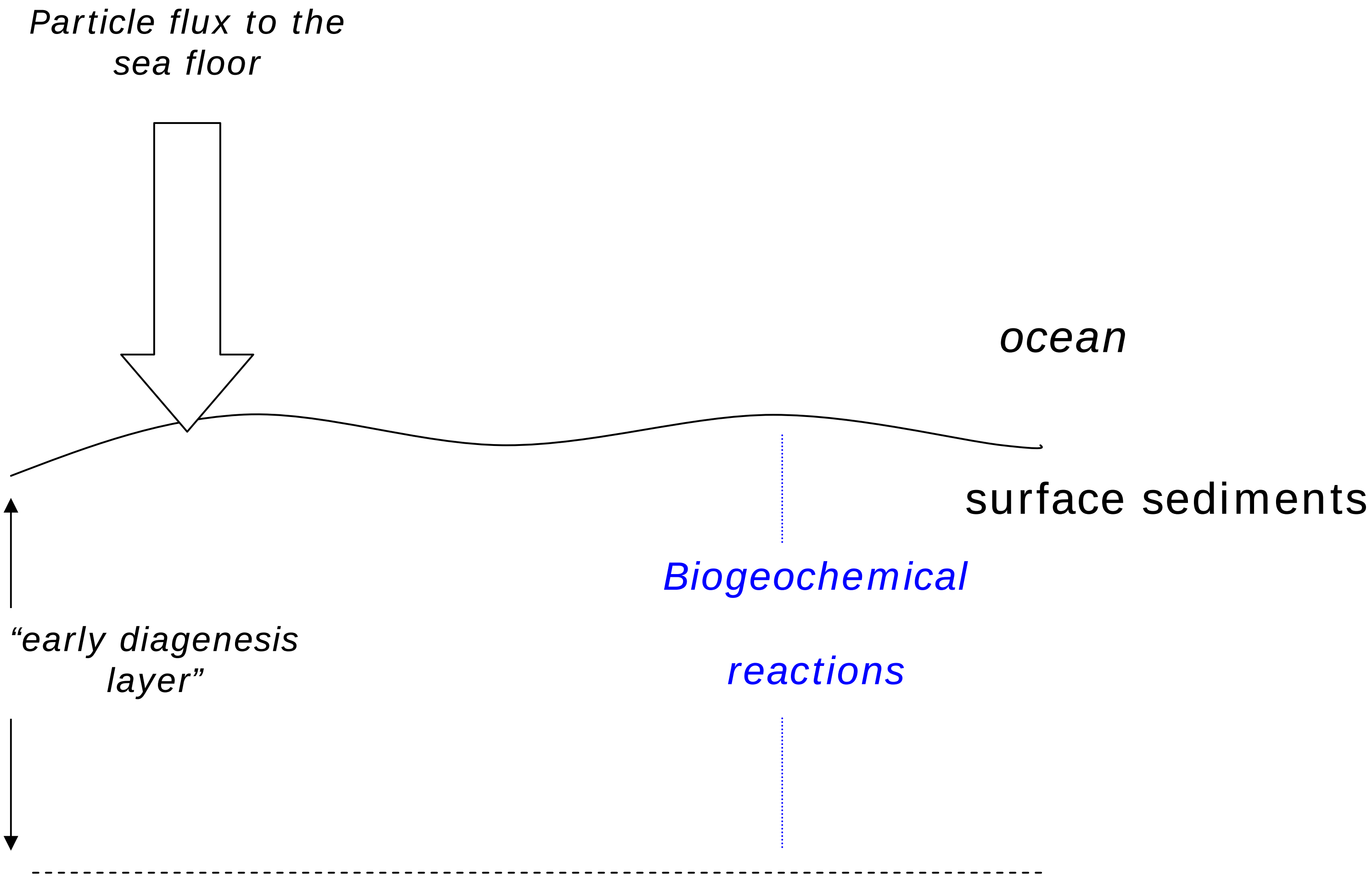
Early diagenesis in marine sediments

Why study this part of the ocean?



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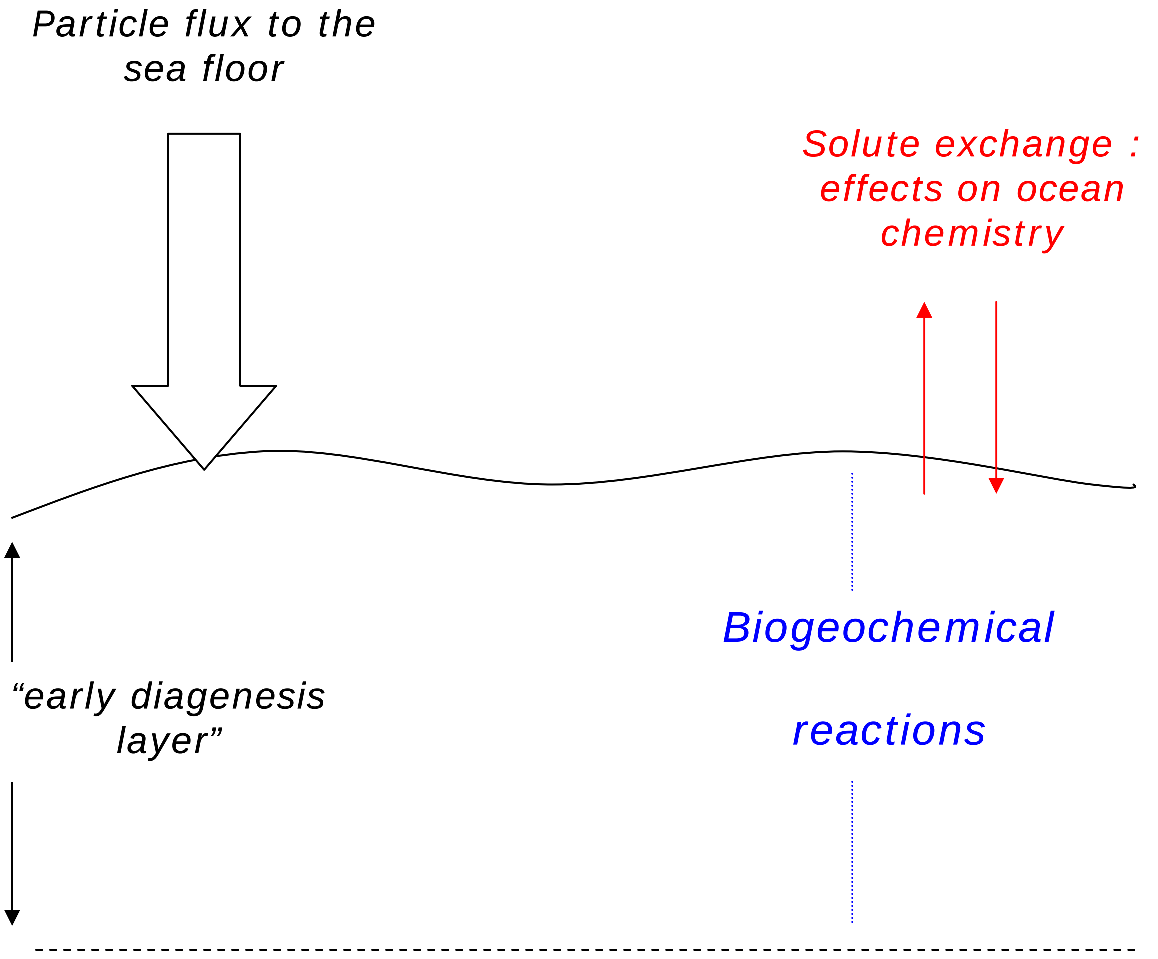
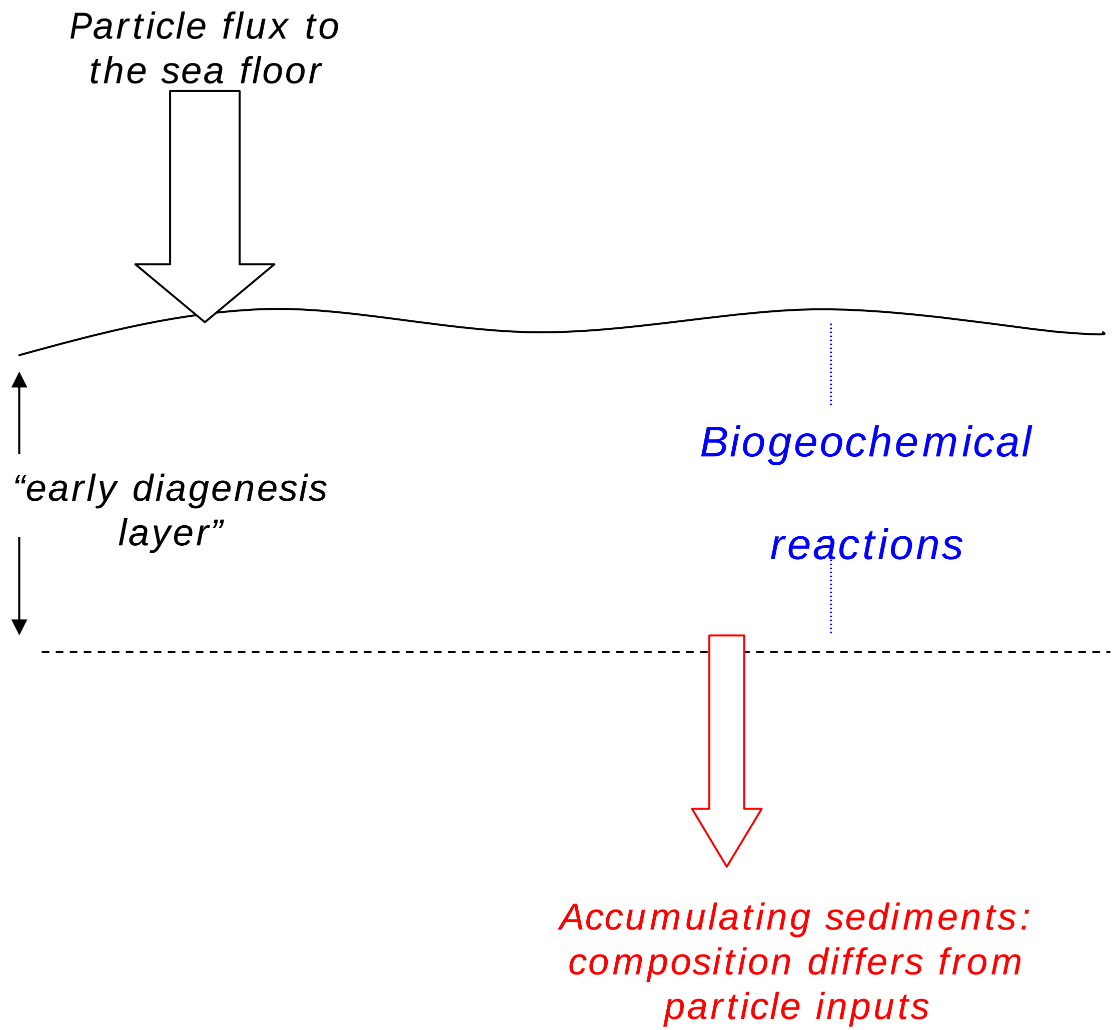


Why study this part of the ocean?



Marine Sediments

1) *The flux of particles to the sea floor*

2) *Preservation rates of biogenic components of the flux*

3) *Consequences of early diagenesis*

4) *Specifics:*
   For each of : Organic matter, $CaCO_3$, Biogenic SiO_2 :
   a) *mechanism for decomposition / dissolution*
   b) *how do we know?*

The composition of the particulate rain to the sea floor -- Examples

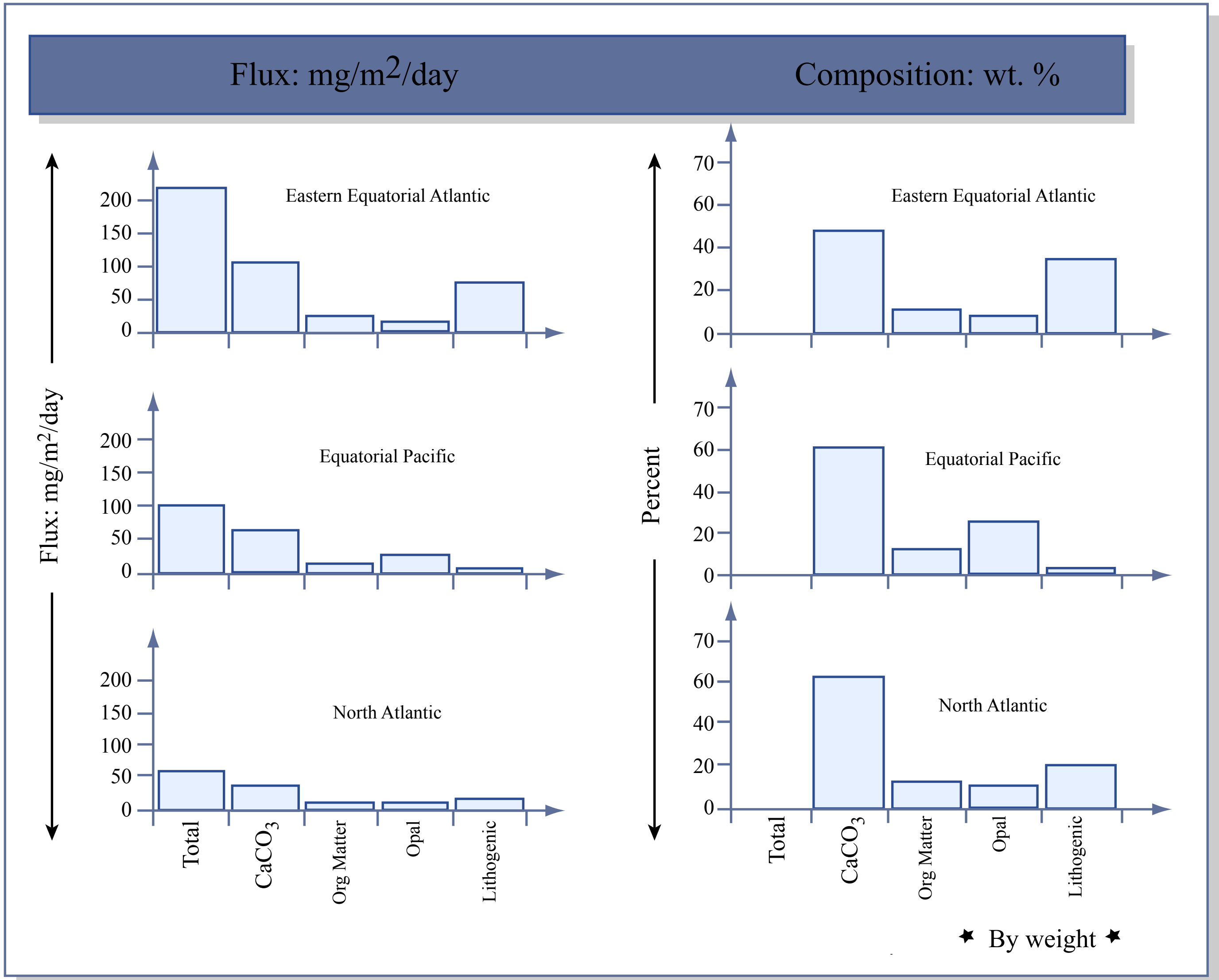


Figure by MIT OCW.

Composition of the particulate rain to the sea floor -- the Southern Ocean

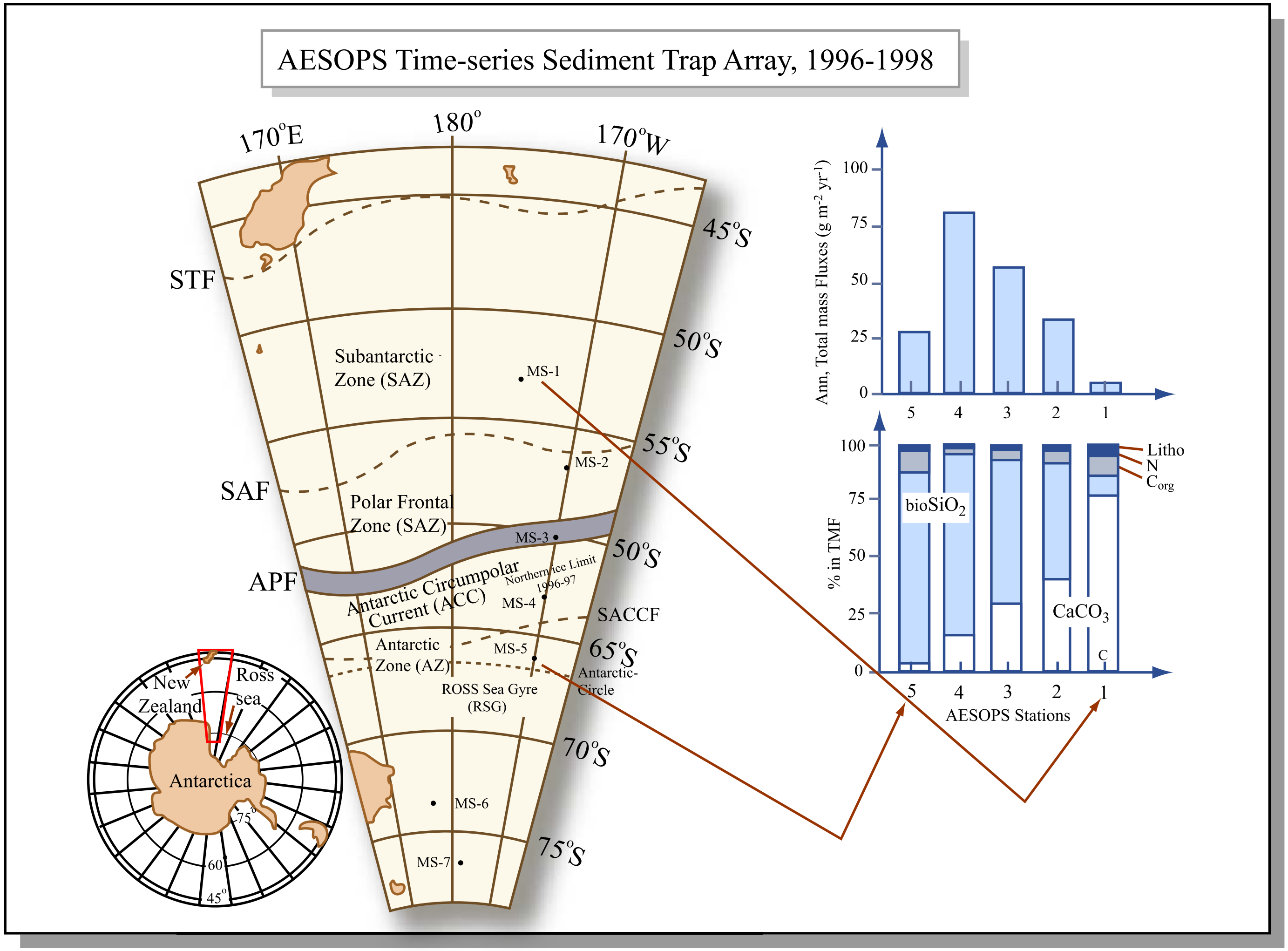


Figure by MIT OCW.

Preservation Rates of Biogenic Components: Generalizations

Organic Matter:

At depths > 1000m: Preservation Rates ~ always < 3%; range <1% to ~ 5%

Continental margins: more variable; sometimes (rarely) > 50%

$CaCO_3$

Above calcite saturation horizon: Preservation rate ~30 – 90%

Below: Drops to 0%

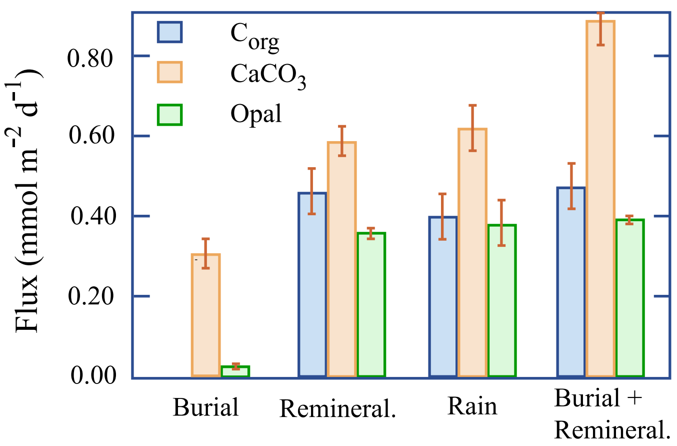
Biogenic Silica (opal)

Median, throughout oceans: ~ 10%

In 80% of areas studied, preservation rate < 15%

A specific example: Balance of fluxes in the central equatorial Pacific

Berelson et al., 1997, DSR II 2251-2282



Budgets of the biogenic constituents in the EqPac region, corrected and adjusted as describeded in the text.

Figure by MIT OCW.

Burial : measured accumulation rates

Remineralization : in situ benthic flux chamber determinations

Rain : sediment traps

Benthic Fluxes >> Burial Rates: Does it matter?

Goal : To learn about changes in rain rates to the sea floor over time from measurements of sediment accumulation rates

*Assume steady state. For a given component of particle flux:

Rain rate to sea floor = *Accumulation rate (preserved)* + *Diagenetic reaction rate (lost to reaction)*

In symbols

$$R = A + D$$

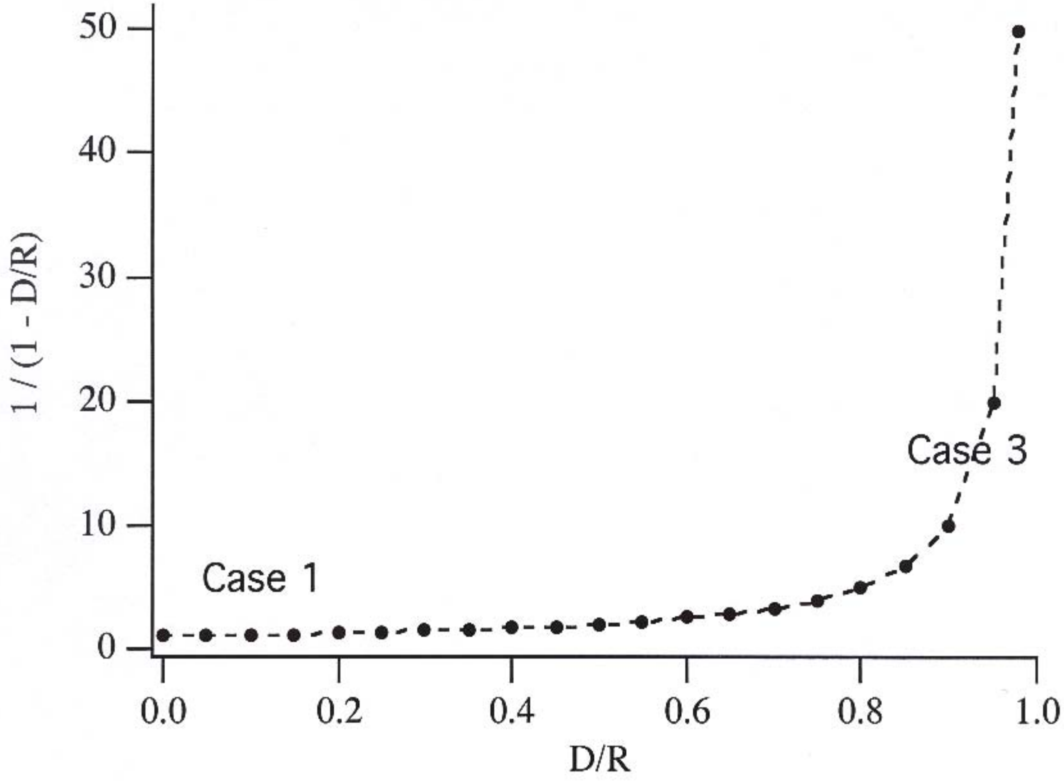
$$R = \left[\frac{1}{1 - D/R} \right] * A$$

===>

- *Case 1: D << R : R ~A*
- *Case 2: D/R constant : R α A*
- *Case 3: D~R, D/R variable:*
  small Δ(D/R) --> large ΔR

In picture form:

$$R = \left\lfloor \frac{1}{1 - D/R} \right\rfloor * A$$



Some consequences of early diagenesis

A. Low and variable preservation rates of biogenic components and the interpretation of the sedimentary record

B. Early diagenesis and atmospheric oxygen... (long time scales)

C. In the contemporary ocean...

1. Deep-water oxygen consumption
~ 50% of O_2 consumption below 1000m occurs in sediments

2. Denitrification...
>~ 50% of dentrification in the modern ocean occurs in sediments...

Continental margin sediments: O2 --> 0 near the sediment-water interface !

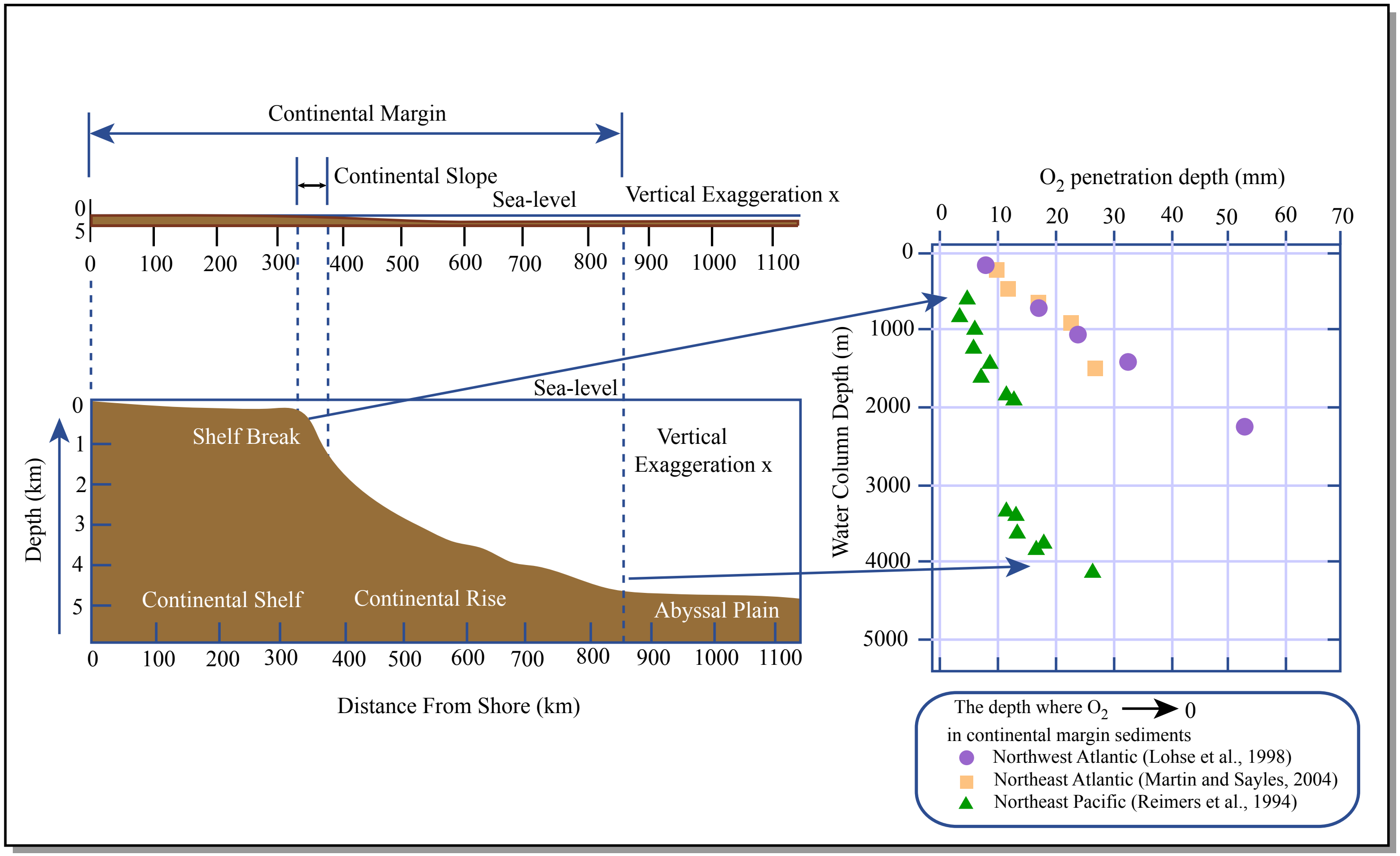


Figure by MIT OCW.

How sedimentary processes differ from water column processes

<u>Particles!</u> Surface sediments ~ 40-70% particles by weight

<u>Time</u> : *Particles fall through the water column:*

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

swi

Mixed layer ~

"reaction layer"

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

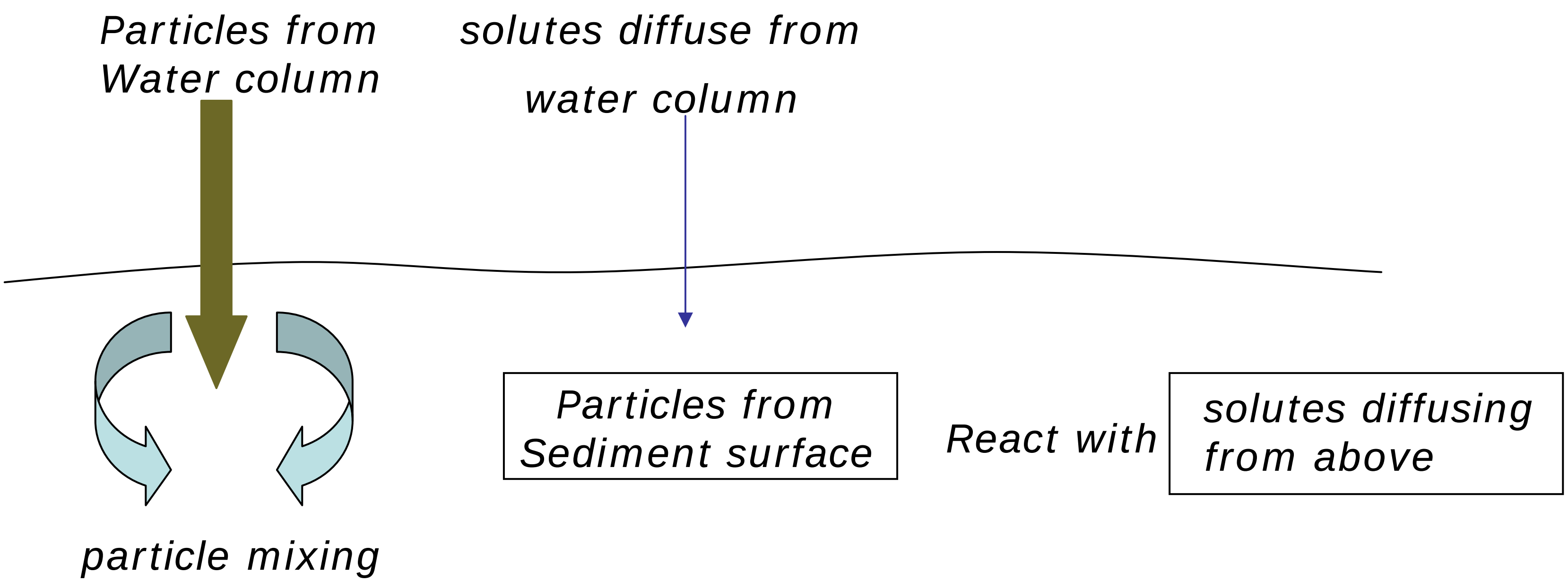
(pelagic) *(coastal)*

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

How sedimentary processes differ from water column processes

In sediments,

reactants are supplied from above:



First order approximation:*
sediments have a ***layered structure***

Mechanism for organic matter oxidation

Familiar Processes:

Organic matter	e^- acceptor	products	reduced e^- acceptor

$$(C,N,P,S,O)_{o.m.} + \begin{matrix} O_2 \\ NO_3^- \\ MnO_x \\ FeO_x \\ SO_4^{2-} \\ C \end{matrix} \longrightarrow CO_2 + \begin{matrix} NO_3^- \\ N_2 \\ NH_4^+ \end{matrix} + H_2PO_4^- + (C,N,P,S,O)_{altered} + \begin{matrix} (H_2O) \\ N_2 \\ Mn^{2+} \\ Fe^{2+} \\ S^{2-} \\ CH_4 \end{matrix}$$

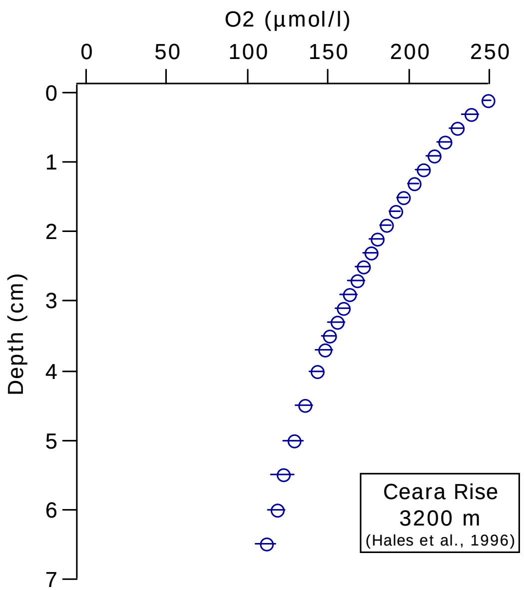
Mechanism: more complex than overall rxn written!

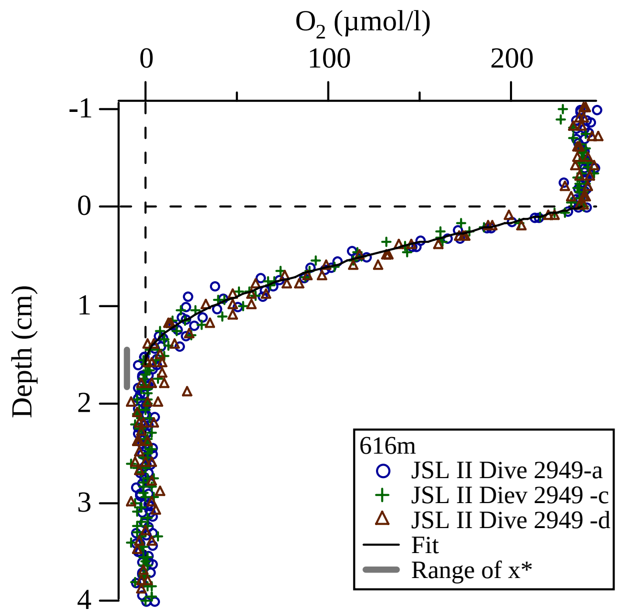
Order : decreasing ΔG

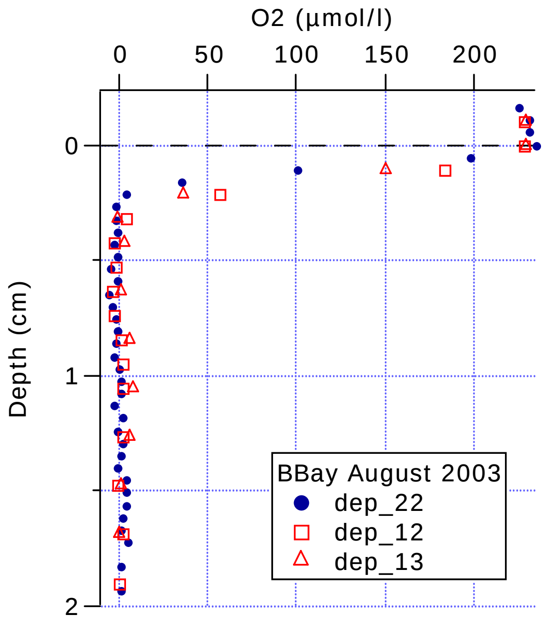
Evidence : Benthic fluxes and pore water profiles of reactants and / or products

Pore water profiles :O_2

all done by in situ microelectrode profiling



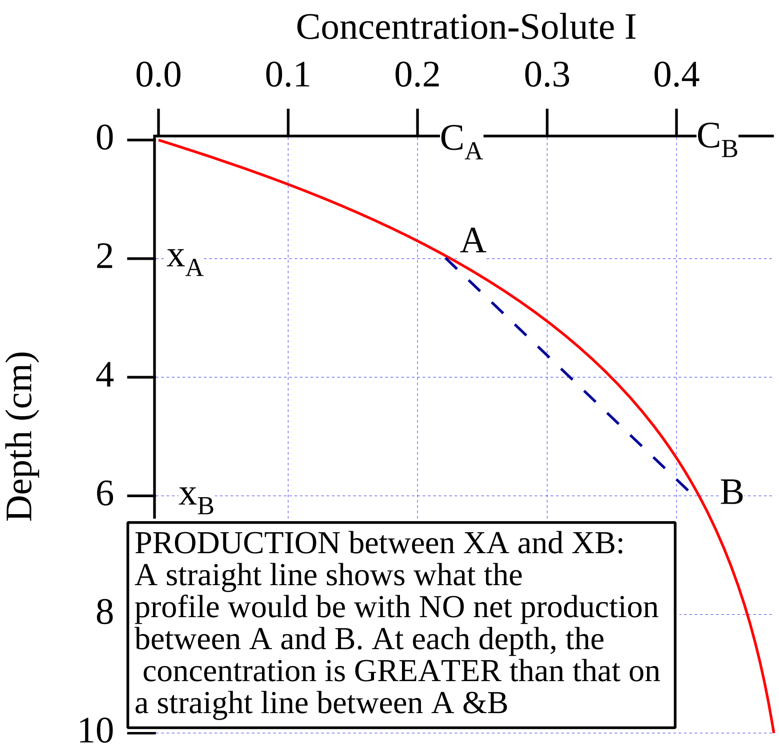


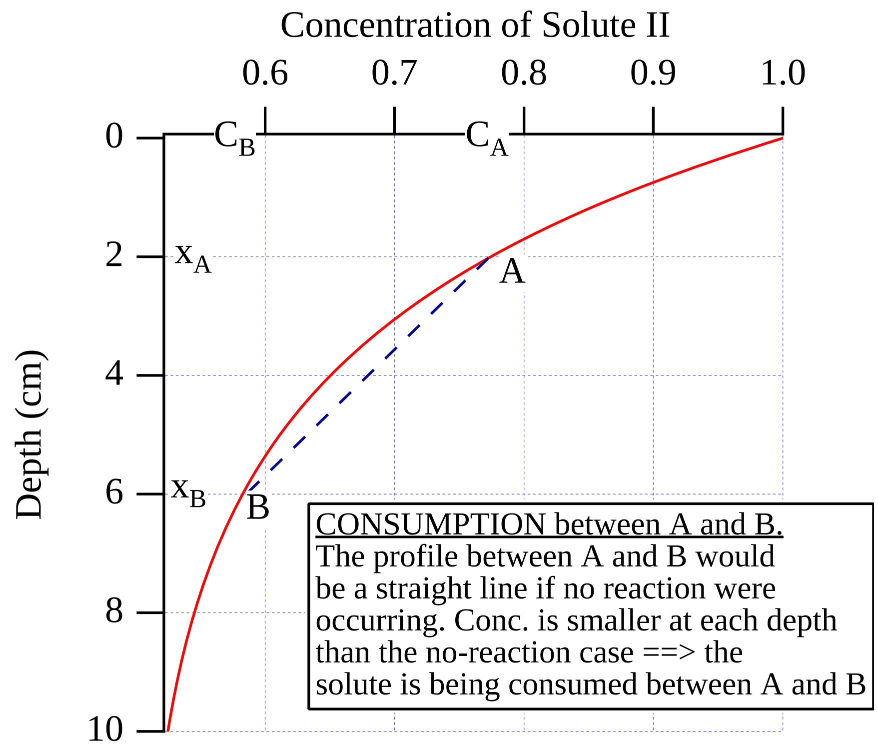


Total Corg ox. Rate (µmol/cm2/y)	14	45	350

Interpretation of pore water profiles : 1. Qualitative interpretation

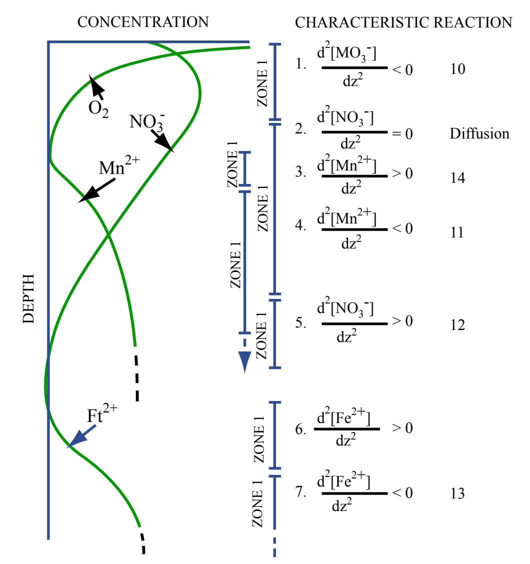
Assume: ** steady state ** + ~ constant porosity & diffusivity, negligible advection





APPLICATION I: IDENTIFICATION OF "REACTION ZONES" IN SEDIMENTS.

PORE WATER SOLUTES: SIGNS OF O.M. OX.



Schematic representation of trend in pore water profiles. Depth and concentration axes in arbitrary units. The zones, characteristic curvature OF the gradients and reaction numbers are discussed in the text.

Figure by MIT OCW.

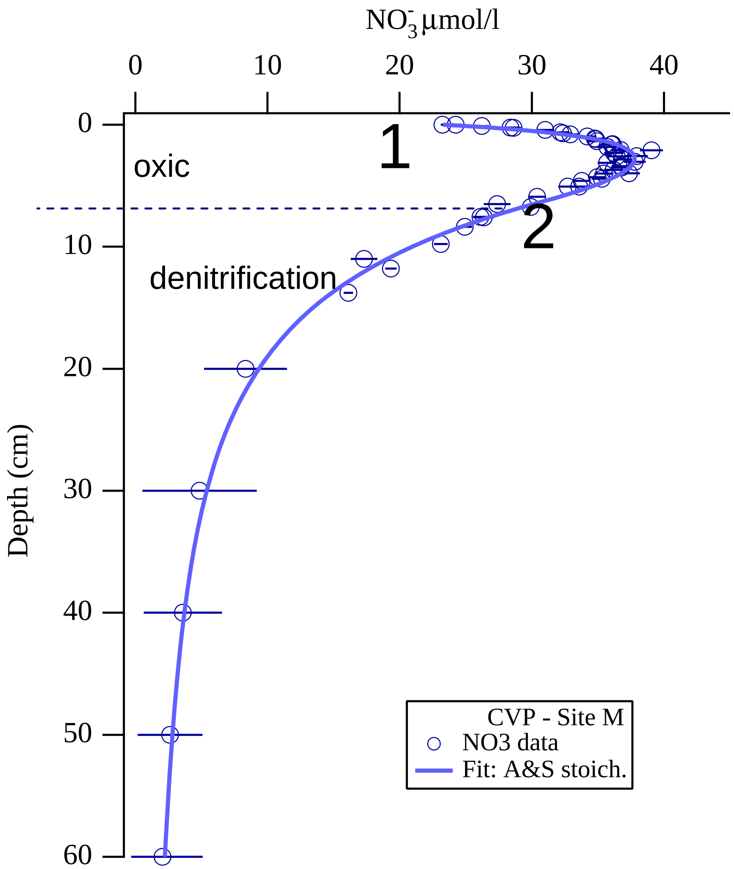
Interpretation of profile shapes : quantitative

Steady-state mass balance in a sediment layer: Rate of reaction within the layer = net flux out of the layer

$$R = F_{out} - F_{in}$$

Diffusive flux :

$$F = -\phi D_{sed} \frac{dC}{dx}$$



Flux at pt. 1 (x=0) : gives total, net NO3 Production in sediment column

Flux at pt. 2 : gives rate of NO3 consump. By denitrification

Sum of absolute values of Flux at 1 + Flux at 2: Gives rate of NO3 production by oxic Decomposition of organic matter

Example: pore water data
450m water depth, NW Atlantic

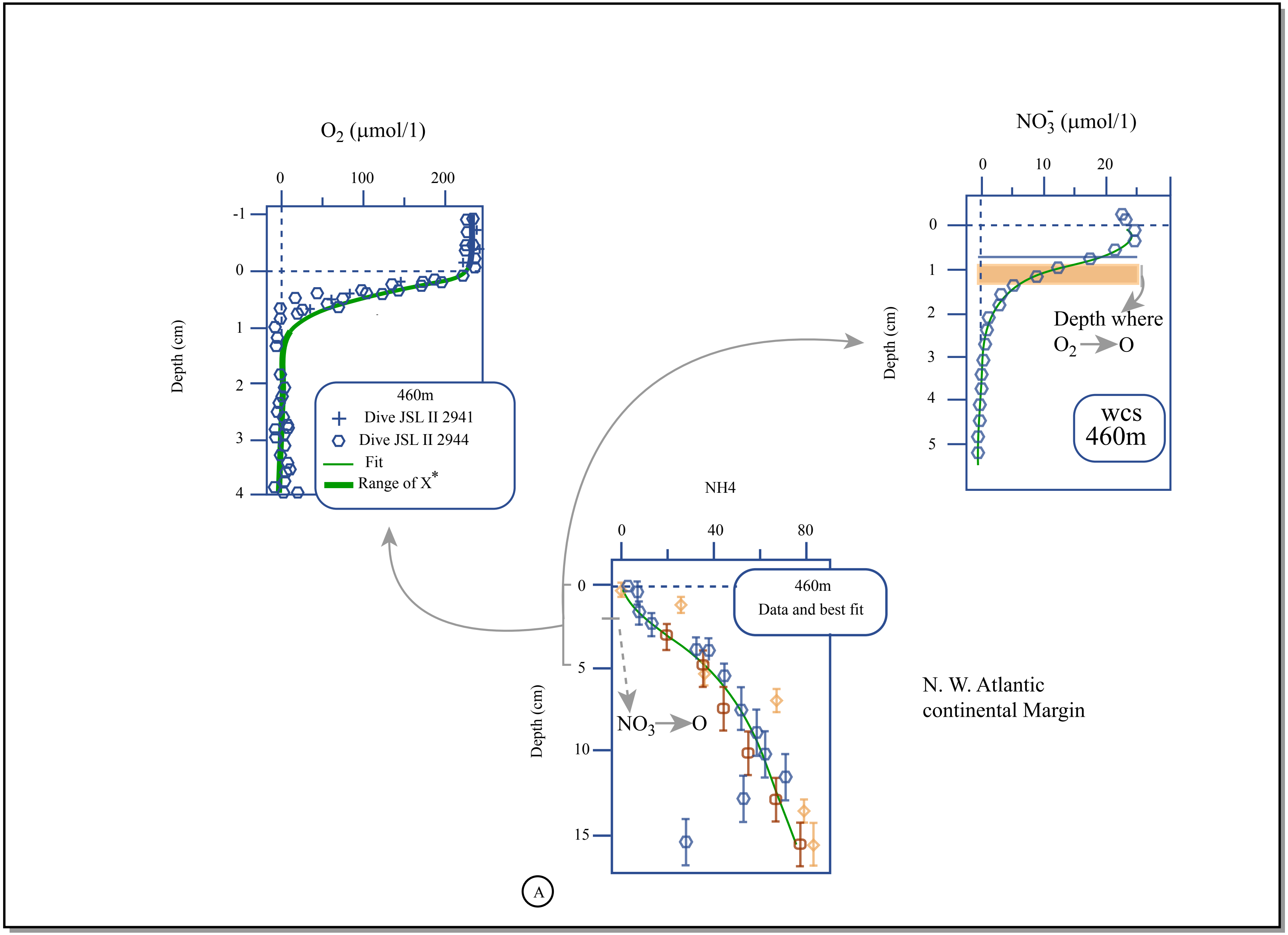
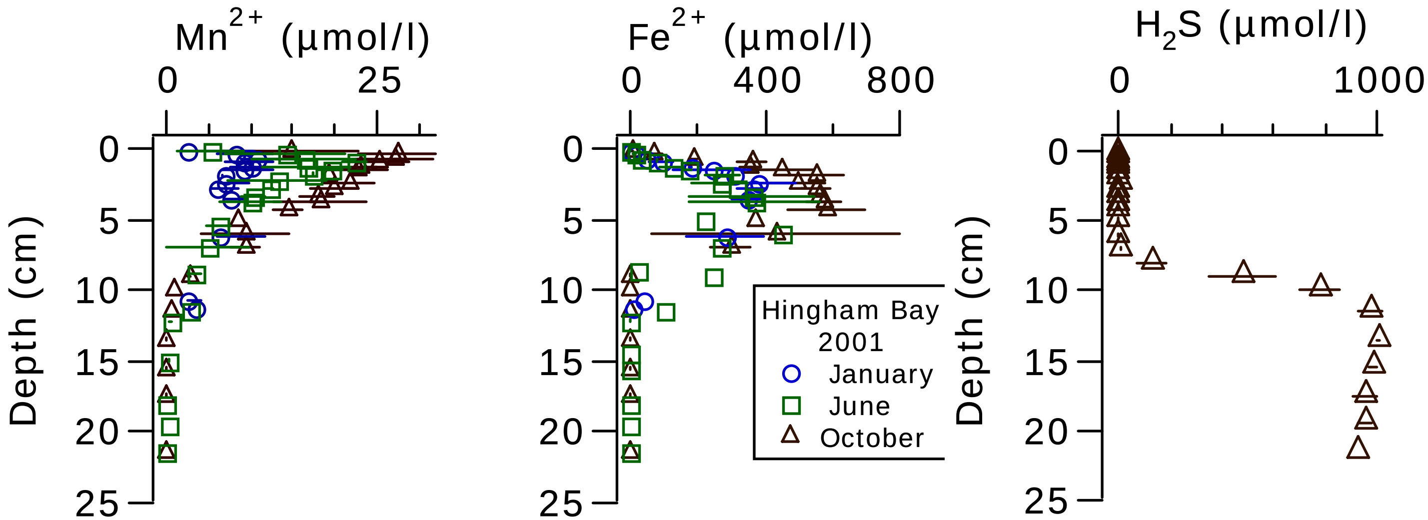
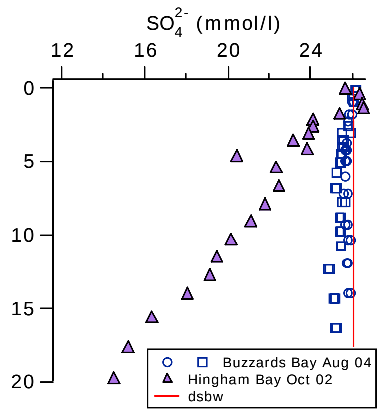


Figure by MIT OCW.

Example : pore water data
Coastal site
C_{org} ox. Rate ~ 850 µmol C / cm^2/y





Which electron acceptors are used the most in sediments for organic matter oxidation?

Electron Acceptors in Pelagic Sediment[1]

Site	Region	C_{org} ox. rate (µmol/cm²/y)	O_2	NO_3^-	Mn(IV)	FE(III)	SO_4^{2-}
MANOP H	E. Eq. Pacific	12.0	99.2	0.8	0.4		
MANOP C	Central Eq. Pac	20.4	98.1	1.6	0.4		
E. Eq. Atlantic	0-3°N, 6-16°W	12.4	93.8	4.4	0.1		1.8

Electron Acceptors in Continental Margin Sediments

			% of organic C oxidation by different election acceptors				
Location	Water depths	Total Corg ox (µmol/cm²/y)	O_2	NO_3^-	Mn	Fe	SO_4
N.E. Atlantic[1]	208-4500	36-158	67-97	1-8.5	0-2.1	0-1.7	1-20
N.W. Atlantic[2]	260-2510	36-52	74-90	1.8-6.0	← 8-20 →		
N.E. Pac: O2<50 µM[3]	780-1440	66-75	5.0-46	41-69	0.1	0.7-1.3	5.7-25
N.E. Pac: O2 = 73-145[3]	1900-4070	36-74	69-75	11-18	0.1-6.9	0.3-0.7	5.6-18

(1) Lohse et al., 1998; (2) Martin and Sayles, 2004; (3) Reimers et al., 1992

Figure by MIT OCW.

Which electron acceptors are used the most in sediments for organic matter oxidation?

Table 3: Electron Acceptors in Pelagic Sediments[1]

site	region	C_{org} ox. rate ($\mu mol/cm^2/y$)	% of organic C oxidation by different electron acceptors				
			O_2	NO_3^-	Mn(IV)	FE(III)	SO_4^{2-}
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(1) Summarized from Bender and Heggie, 1984

Table 4: Electron Acceptors in Continental Margin Sediments

Location	Water depths	Total Corg ox (μmol/cm2/y)	% of organic C oxidation by different electron acceptors				
			O2	NO3-	Mn	Fe	SO4
N.E. Atlantic[1]	208-4500	36-158	67-97	1-8.5	0-2.1	0-1.7	1-20
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(1) Lohse et al., 1998; (2) Martin and Sayles, 2004; (3) Reimers et al., 1992

ORGANIC CARBON BURIAL IN MARINE SEDIMENTS

Organic Carbon Burial Rates (and percentages)In Different Ocean Regimes

Sediment type	Deltaic	Shelf	Slope	Pelagic	Total
Data from Gershanovich et at. (1974)					
All sediment types	0 (0)	23 (10)	195 (88)	5 (2)	223 $\Sigma = 223$
Data from Berner(1989)					
→ Terrigenous deltaic-shelf sediments	104 (82)	0	0	0	104 ←
Biogenous sediments (high-productivity zones)	0	0	7 (6)	3 (2)	10
Shallow-water carbonates	0	6 (5)	0	0	6
Pelagic sediments (low-productivity zones)	0	0	0	5 (4)	5
Anoxic basins (e.g. Black sea)	0	1 (1)	0	0	1 $\Sigma = 126$
Recalculation of data from Berner (1989)[a]					
→ Deltaic sediments	70 (44)	0	0	0	70 ←
Shelves and upper slopes	0	68 (42)			68
Biogenous sediments (high-productivity zones)	0	0	7 (4)	3 (2)	10
Shallow-water carbonates	0	6 (4)	0	0	6
Pelagic sediments (low-productivity zones)	0	0	0	5 (3)	5
Anoxic basins (e.g. Black Sea)	0	1 (0.5)	0	0	1 $\Sigma = 160$

Units are 10^{12} g C yr^{-1} (parenthetical units = % of total burial)

a Deltaic-shelf sediments were reapportioned assuming that 33% of the sediment discharge from rivers is deposited either along non-delatic shelves or upper slopes, and assuming that those deposits have total loadings of 1.5% organic carbon rather then 0.7% as in delatic regions. Estimates for all other regions remain the same.

Figure by MIT OCW.

The distribution of organic matter in marine sediments :

What determines the observed pattern?

….local productivity?
….variable preservation?

Image removed due to copyright restrictions.

Organic carbon preservation

So:

A correspondence between regions of high 1° productivity and high % C_{org} in sediments,

And:

These regions of high %C_{org} are ALSO regions of low bottom water O_2 in many cases,

And:

It has been shown that some naturally occurring organic molecules REQUIRE O_2 for decomposition

... Does sedimentary %C_{org} (C_{org} accumulation rate, really) depend on:

productivity?
preservation? (bw O_2)
both?

"Oxygen Exposure Time"

Hartnett et al. (1998) Nature 391, 572-574

Studied 2 areas:

1) *squares: Washington margin: higher productivity, less intense O_2 min*
2) *Circles: Mexico margin: lower productivity, intense O_2 min.*

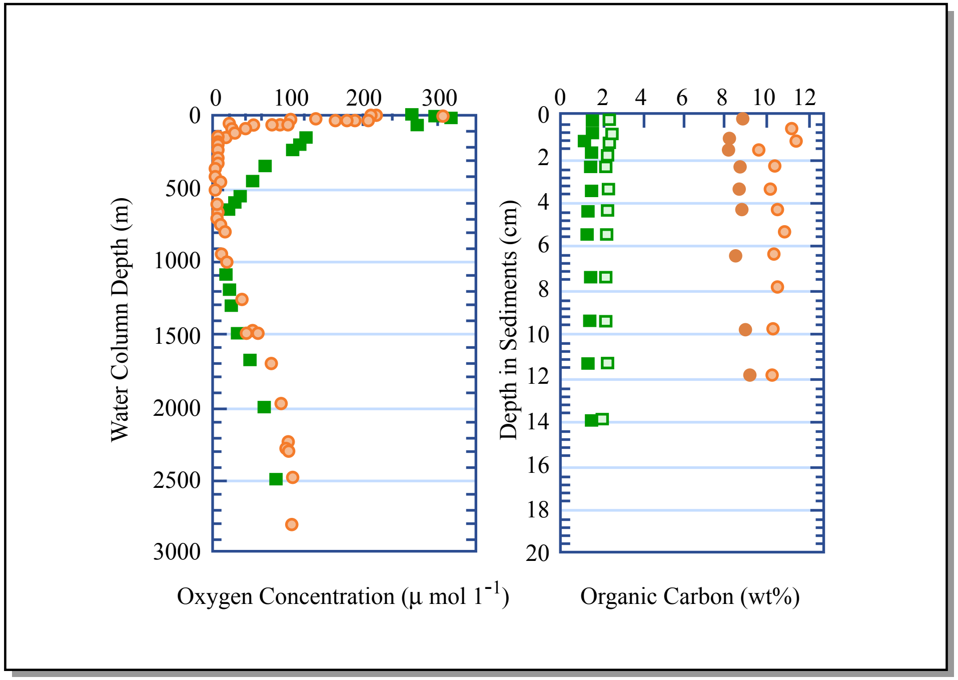
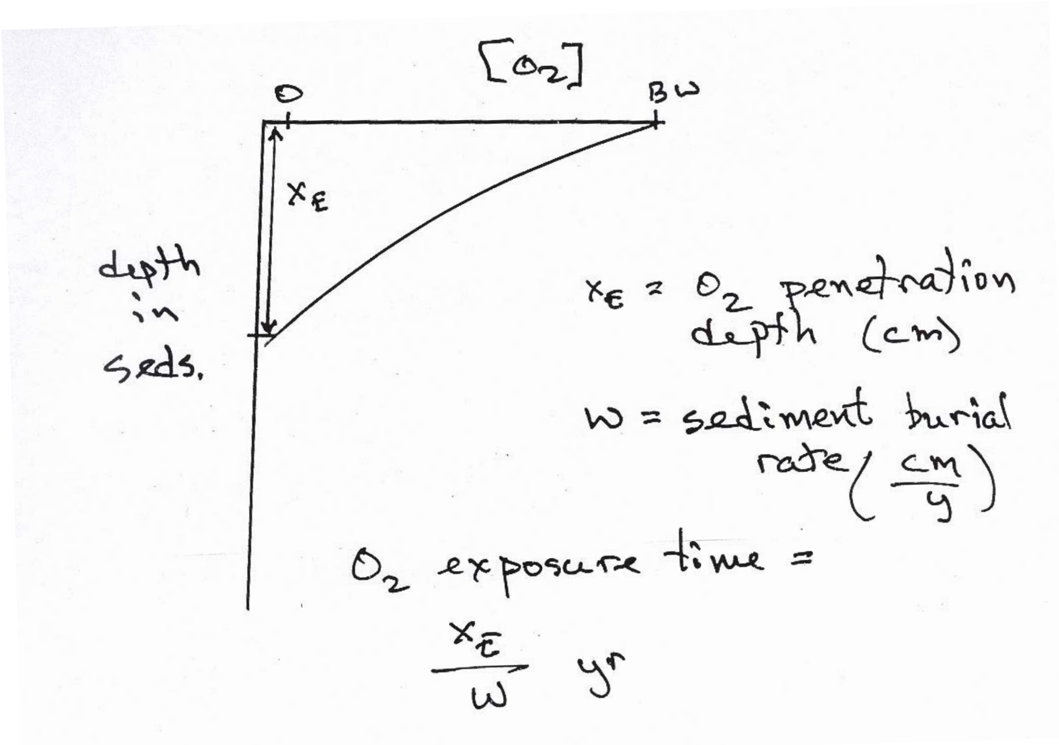


Figure by MIT OCW.

“Oxygen Exposure Time”

Hartnett et al. (1998) Nature 391, 572-574

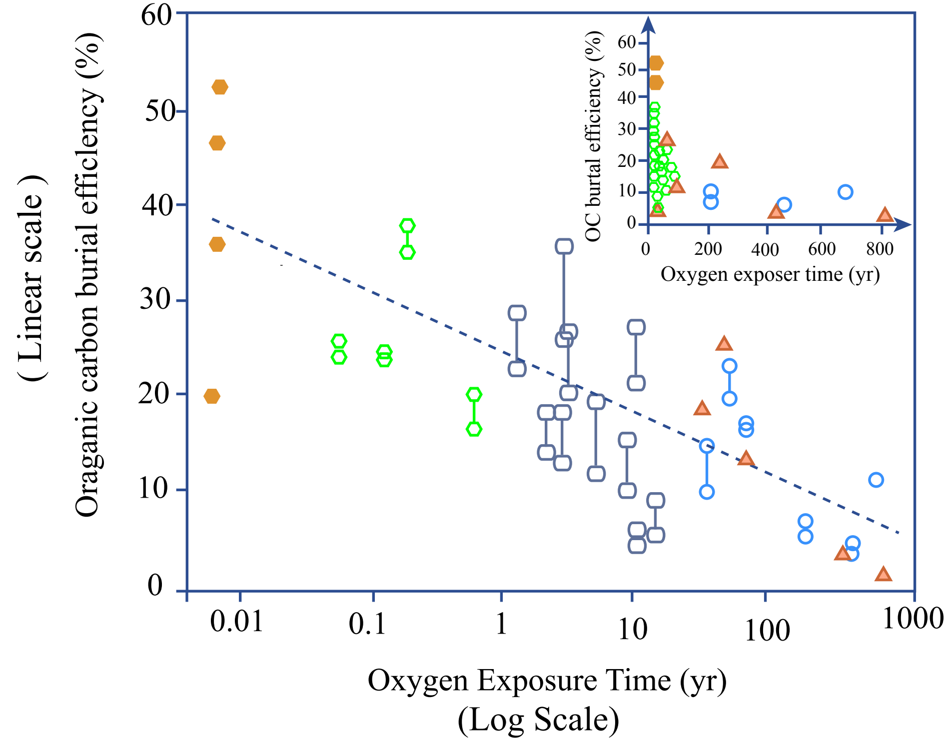
They defined “oxygen exposure time”:



And examined its effect on C_{org} “burial efficiency” (= burial rate / rain rate)

"Oxygen Exposure Time"

Hartnett et al. (1998) Nature 391, 572-574



Organic carbon burial efficiency as a function of oxygen exposure time

- Promising idea, Limited data
- Note: Provides feedback between atmospheric O_2 + Corg burial rate

Figure by MIT OCW.