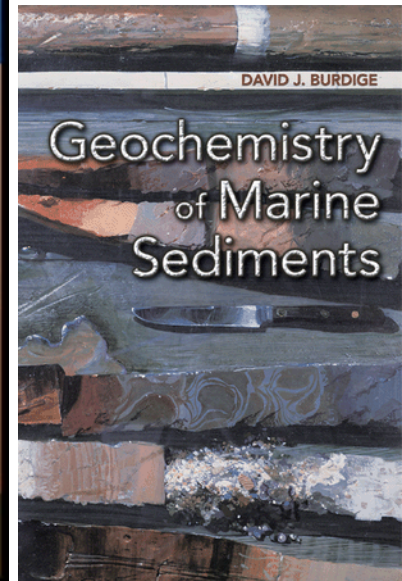
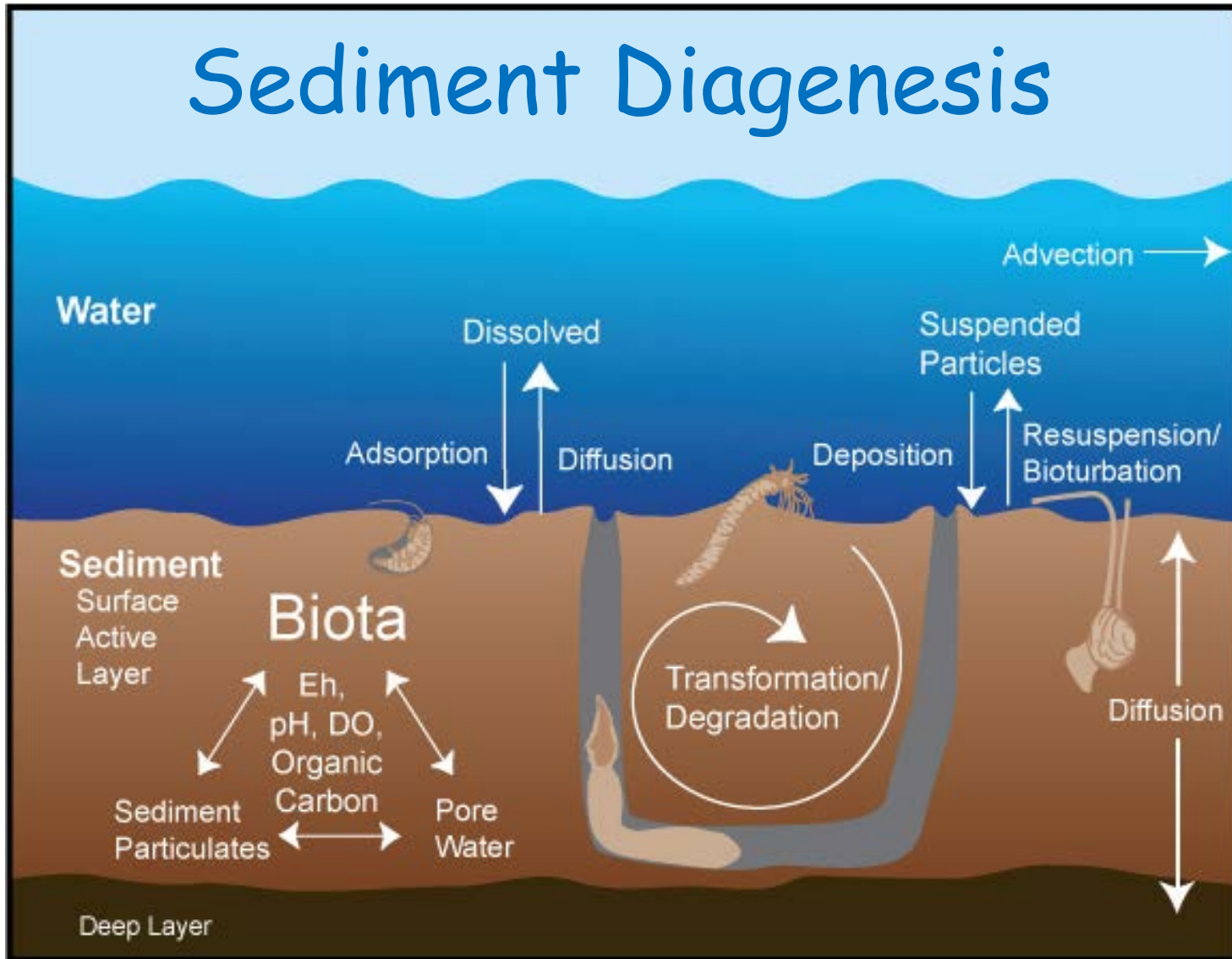


Sediment Diagenesis



Sediment Diagenesis

Diagenesis refers to the sum of all the processes that bring about changes (e.g., composition and texture) in a sediment or sedimentary rock subsequent to deposition in water. The processes may be physical, chemical, and/or biological in nature and may occur at any time subsequent to the arrival of a particle at the sediment-water interface.

The range of physical and chemical conditions included in diagenesis is 0 to 200°C, 1 to 2000 bars and water salinities from fresh water to concentrated brines. In fact, the range of diagenetic environments is potentially large and diagenesis can occur in any depositional or post-depositional setting in which a sediment or rock may be placed by sedimentary or tectonic processes. This includes deep burial processes but excludes more extensive high temperature or pressure metamorphic processes.

Early diagenesis refers to changes occurring during burial up to a few hundred meters where elevated temperatures are not encountered (< 140°C) and where uplift above sea level does not occur, so that pore spaces of the sediment are continually filled with water.

Early Diagenesis

1. **Physical effects: compaction.**
2. Biological/physical/chemical influence of burrowing organisms: bioturbation and bioirrigation.
3. Formation of new minerals and modification of pre-existing minerals.
4. Complete or partial dissolution of minerals.
5. Post-depositional mobilization and migration of elements.
6. Bacterial degradation of organic matter.

Compaction of sediments

(most significant as a lithification process in fine-grained sediments - shale, since sands and coarser sediments are only slightly compressible)

As sediments accumulate through time, the weight of the overlying material compresses the deeper sediments. As the mineral grains are pressed closer and closer together, there is a reduction in pore space and expulsion of water. The porosity decreases progressively with depth.

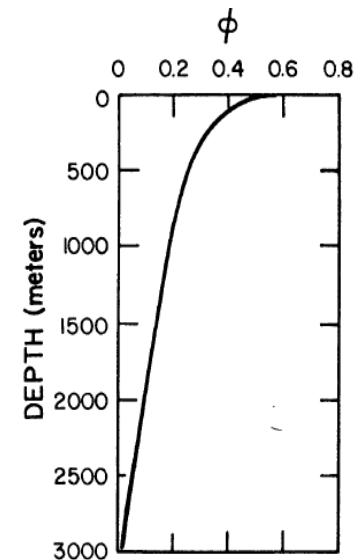
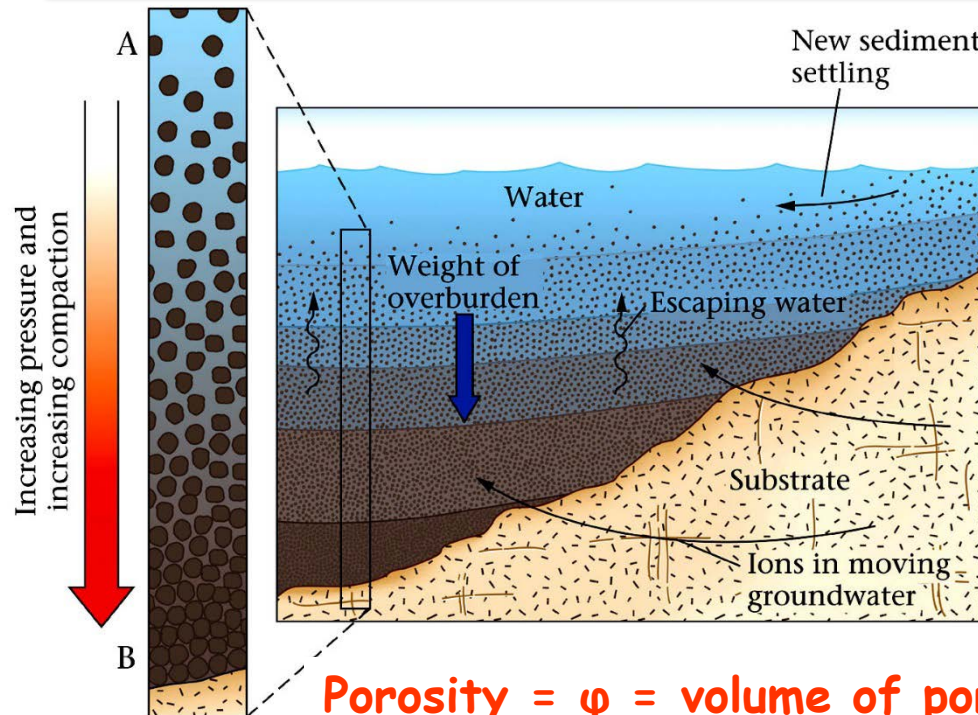
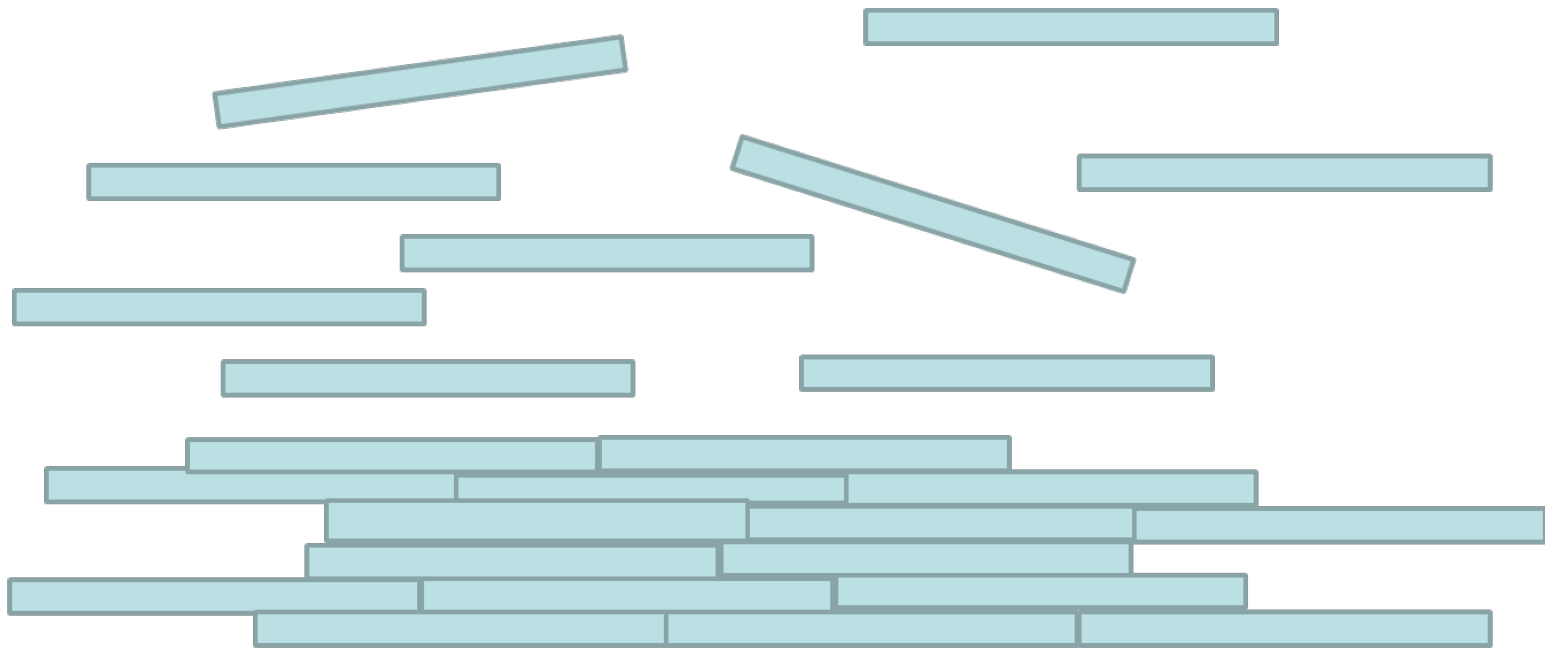


FIGURE 3-9. Porosity of clay sediments. Composite based on data for Recent, Tertiary, and Lias sediments. (After Engelhardt, 1977.)

Porosity = ϕ = volume of pore water/volume of total sediment



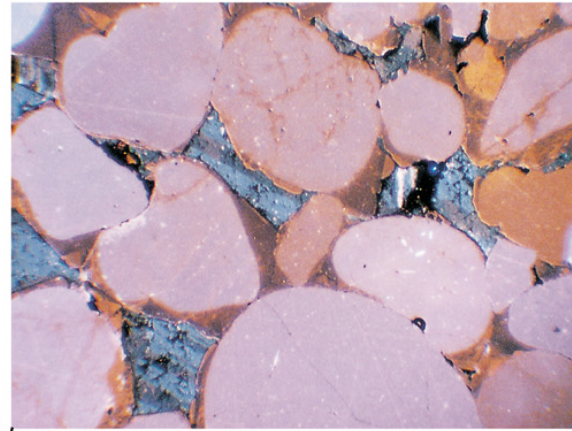
Compaction/stacking of tabular clay particles leading to
lithification

Cementation

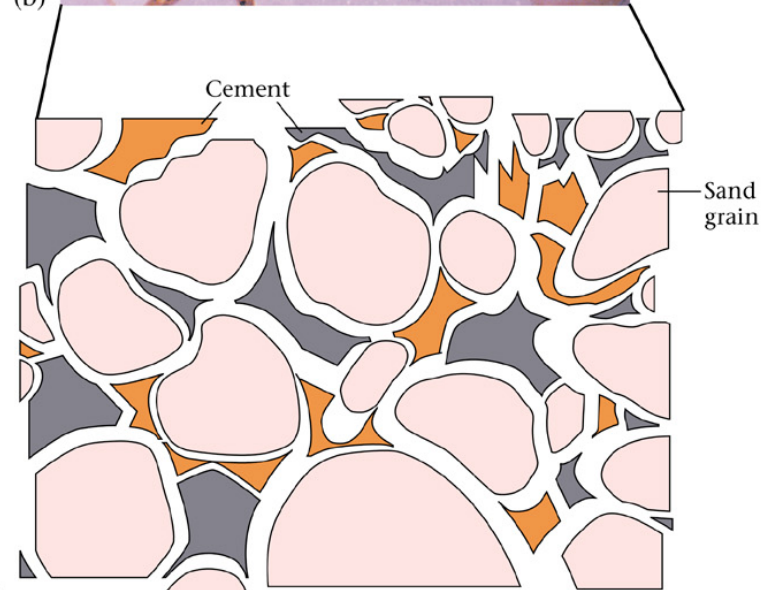
(Precipitation of dissolved substances by water circulating through pore spaces)



(a)



(b)



(c)

Common cements include:
calcite (CaCO_3), silica (SiO_2) and
iron oxides (FeO_x).

Early Diagenesis

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Bioturbation/bioirrigation

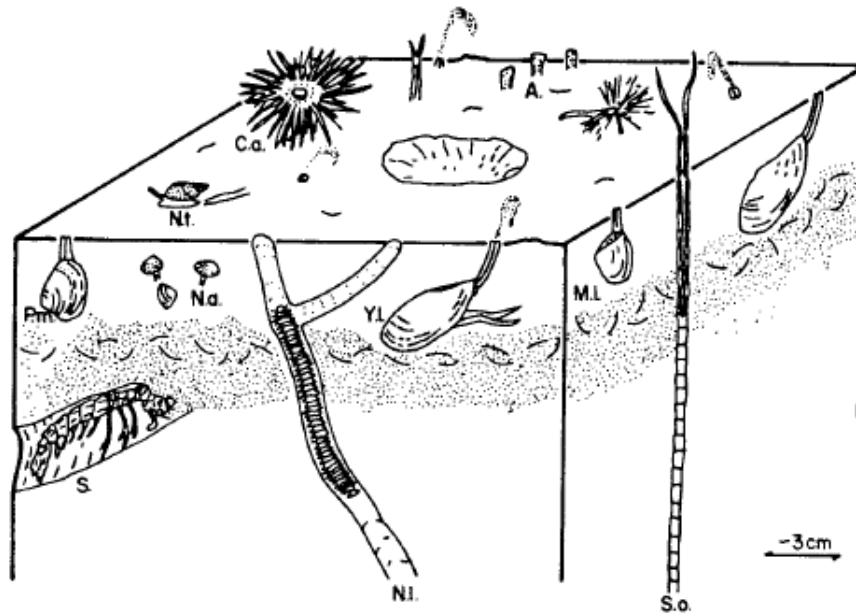
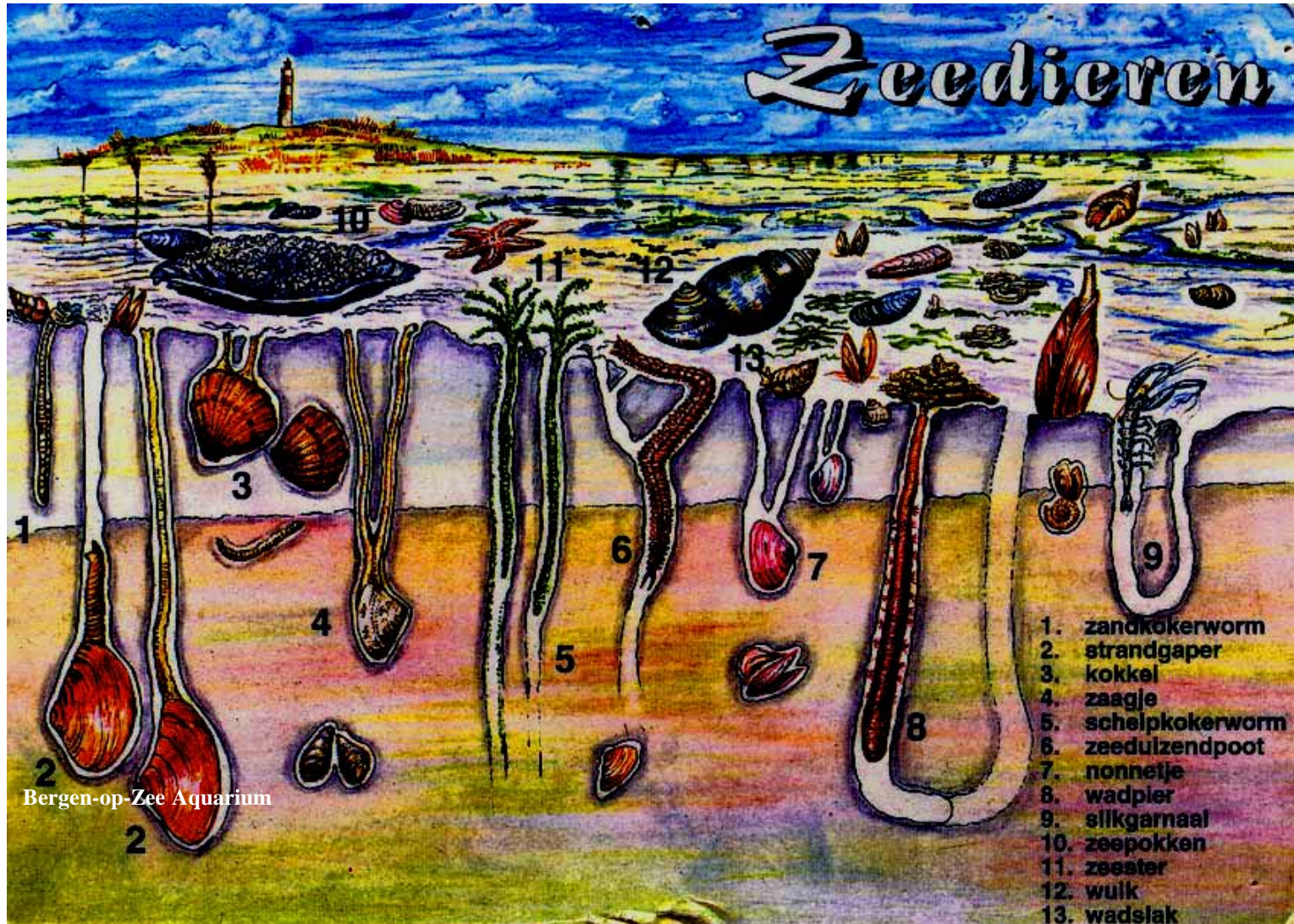


FIGURE 3-12. Schematic representation of major burrowing fauna from a sediment locality (NWC) in Long Island Sound. (From Aller, 1977; 1980.)

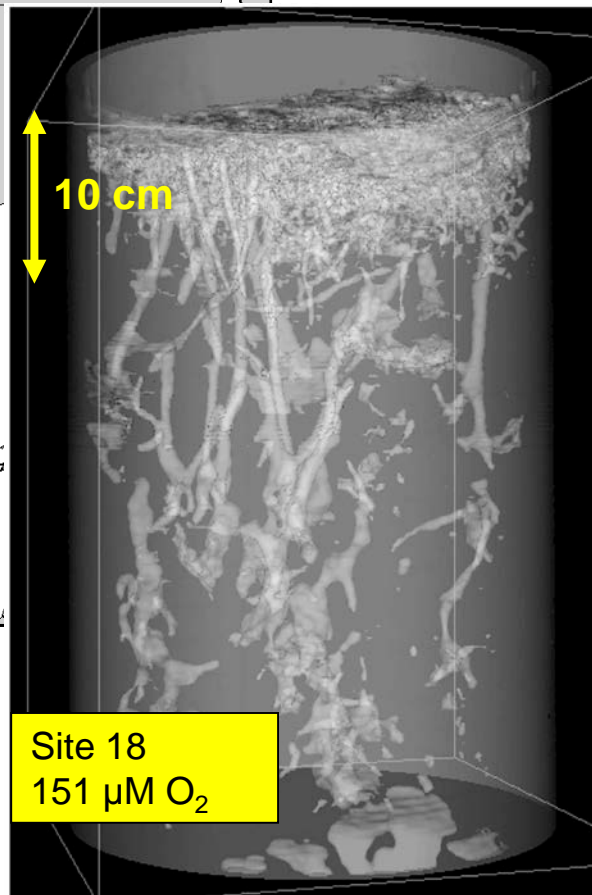
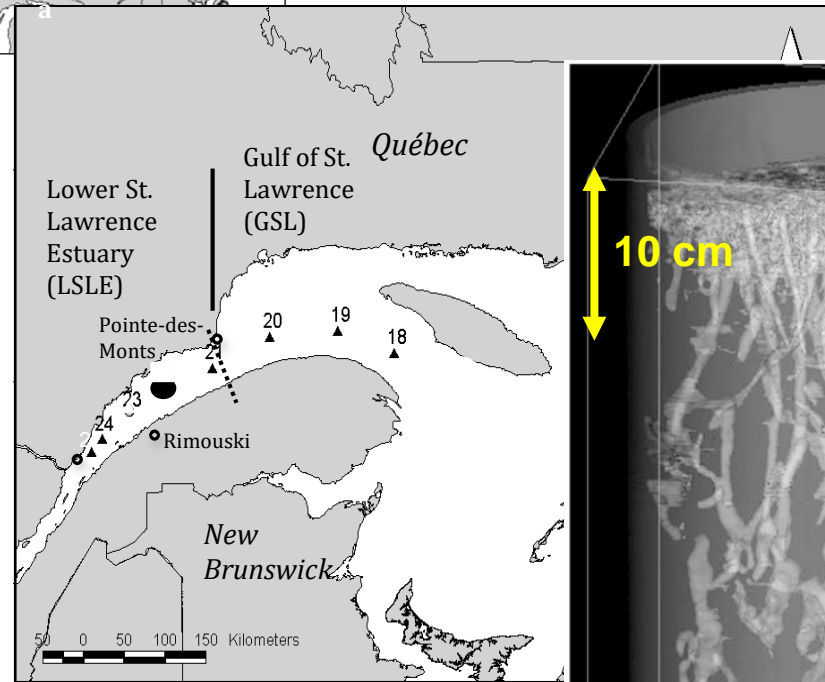


Some organisms, such as crabs and snails, mix surface sediments simply by crawling and plowing through it. More importantly, others, especially polychaete worms and bivalves, burrow into the sediment and ingest the sediment particles to extract organic matter as food. Such burrowing activity can extend to several tens of centimetres. Once their burrows are constructed, some organisms remain in them and flush the burrows with overlying seawater, bringing about enhanced exchange between pore waters and overlying seawater. This process is referred to as **bioirrigation**.

Life in mud



Bioturbation/bioirrigation



^{14}C dating of a sediment core

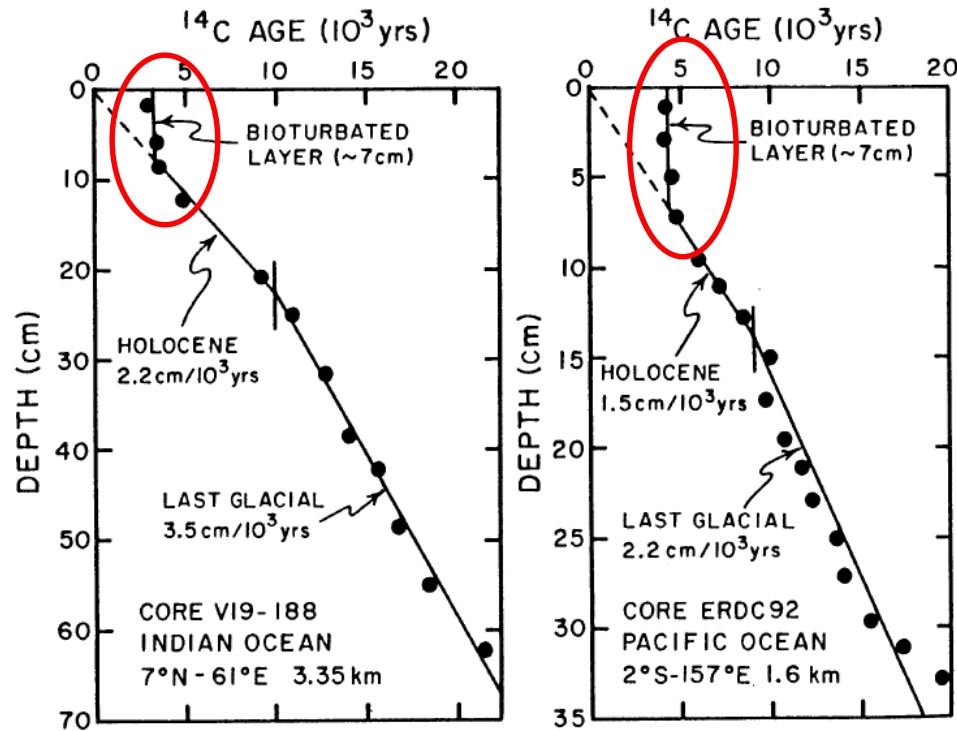
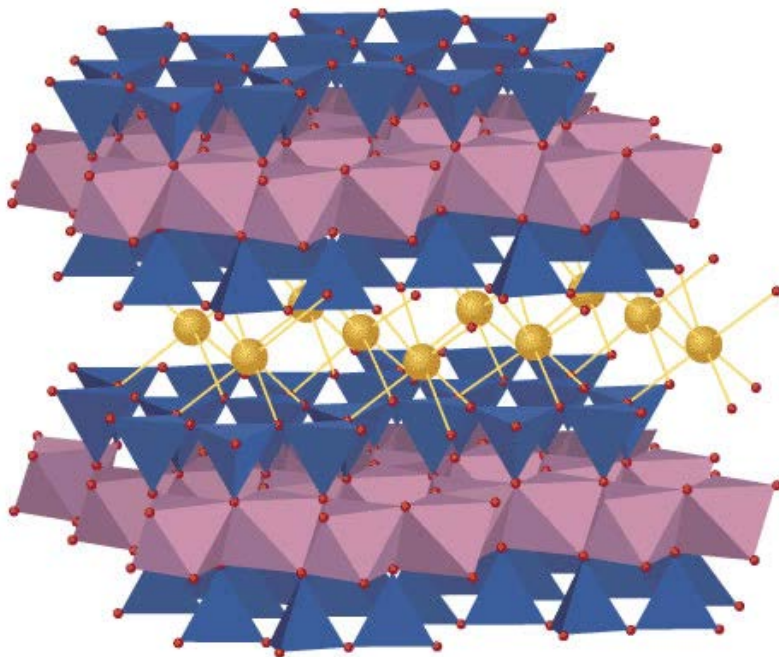


Figure 5-13. Radiocarbon ages as a function of depth in two deep sea cores. The near constancy of these ages down to a depth of about 7 cm bears witness to the action of organisms which "burrow" into the sediment. Below this zone of bioturbation the ages show the expected regular increase. The changes in the slope of the age versus depth line at the time close to the end of the last glacial period (i.e., ~10,000 years ago) reflects the influence of climate on the rate at which the various materials making up the sediment rain onto the sea floor. These results were obtained by Peng of the Lamont-Doherty Geological Observatory (197, 199).

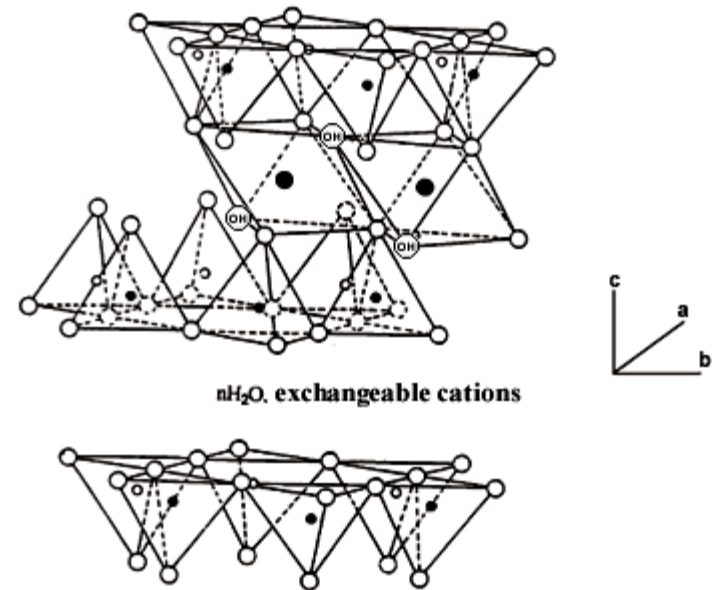
Early Diagenesis

1. Physical effects: compaction.
2. Biological/physical/chemical influence of burrowing organisms: bioturbation and bioirrigation.
3. Formation of new minerals and modification of pre-existing minerals.
4. Complete or partial dissolution of minerals.
5. Post-depositional mobilization and migration of elements
6. Bacterial degradation of organic matter.

Ion exchange on the surface and intra-sheet layers of clay minerals



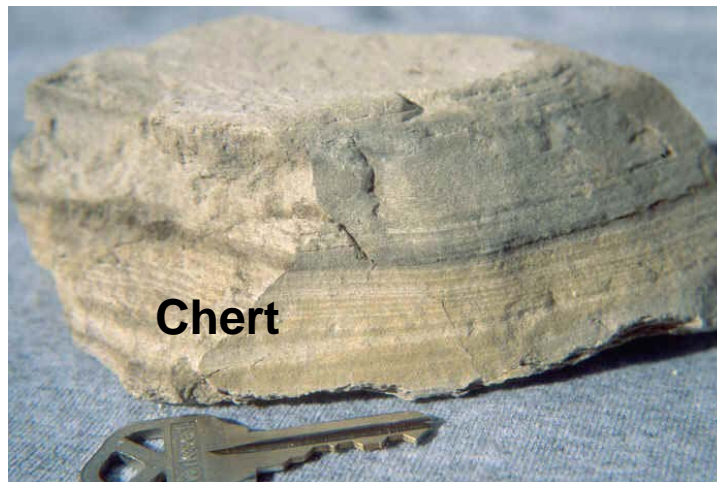
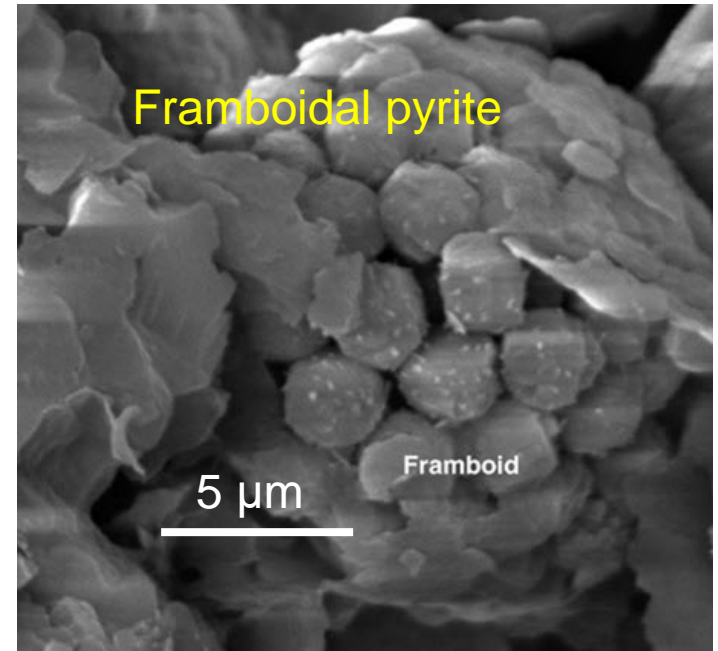
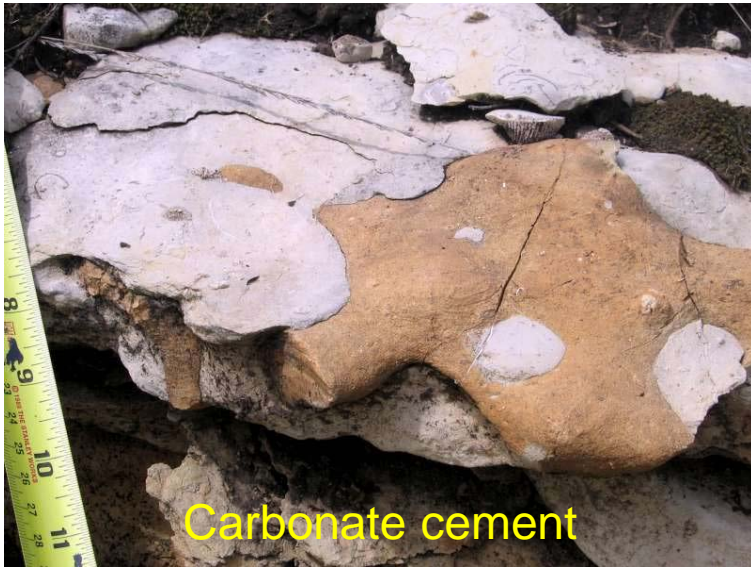
The molecular structure of smectite clays consists of 2 silicon-centered tetrahedral layers (blue) and one aluminum octahedral layer (purple) form crystalline sheets.



- Oxygens (OH) Hydroxyls ● Aluminum, iron, magnesium
- and ○ Silicon, occasionally aluminum

Figure 2. Schematic diagram of the structure of smectites (adapted from Grim¹⁰)

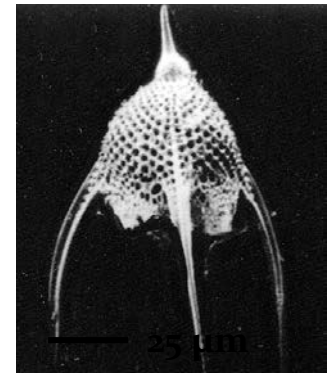
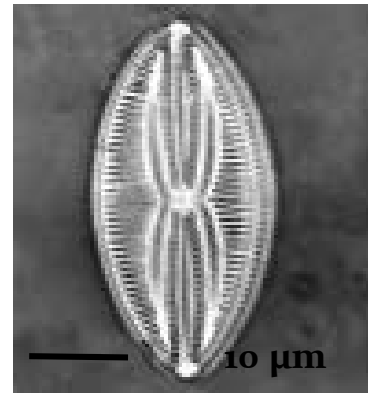
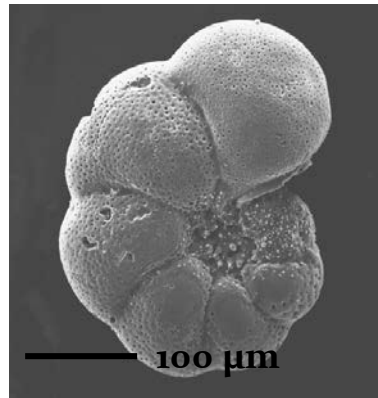
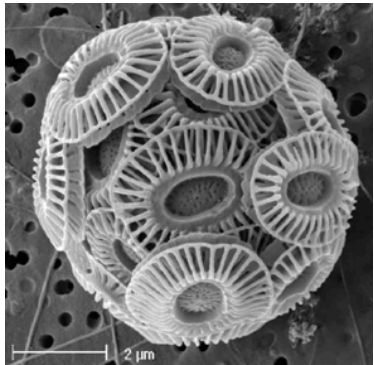
Authigenic minerals



Early Diagenesis

1. Physical effects: compaction.
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3. Formation of new minerals and modification of pre-existing minerals.
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5. Post-depositional mobilization and migration of elements.
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Biogenic sediments

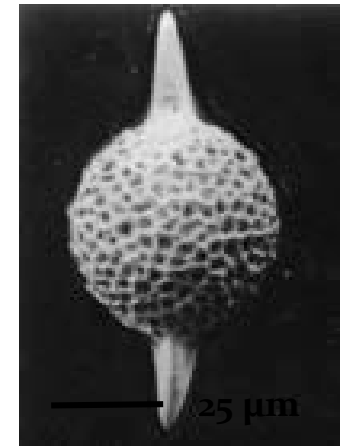
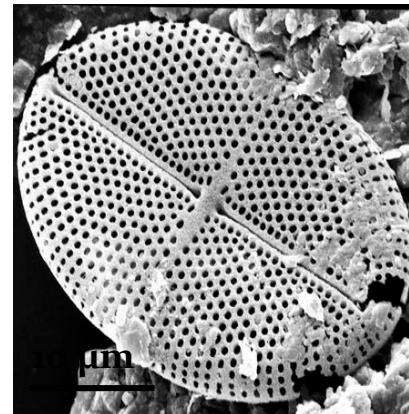
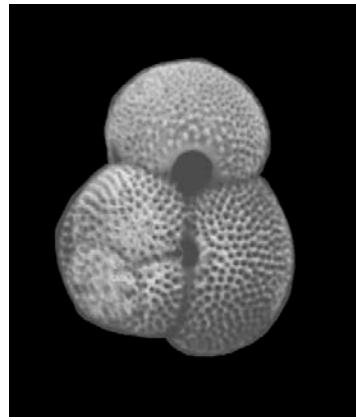
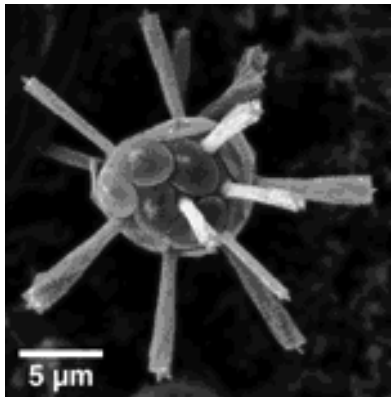


Coccolithophores

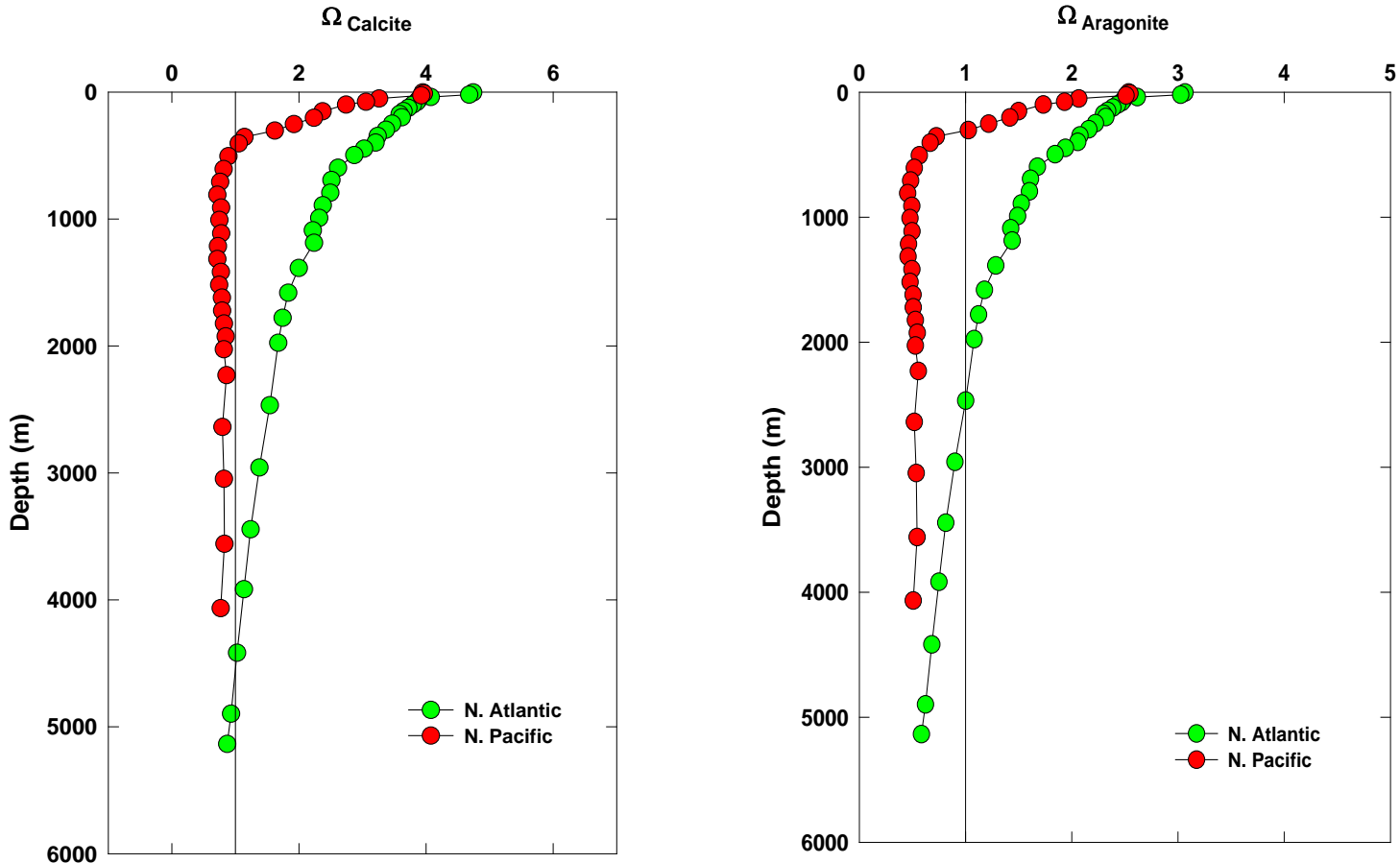
Foraminifera

Diatoms

Radiolaria

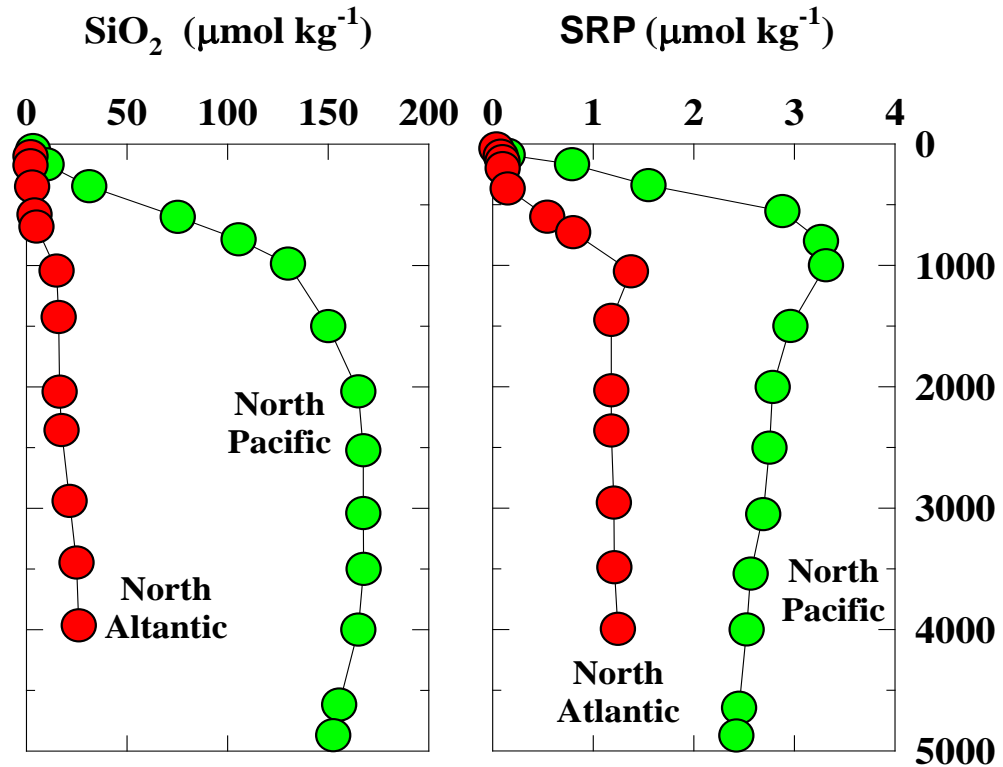
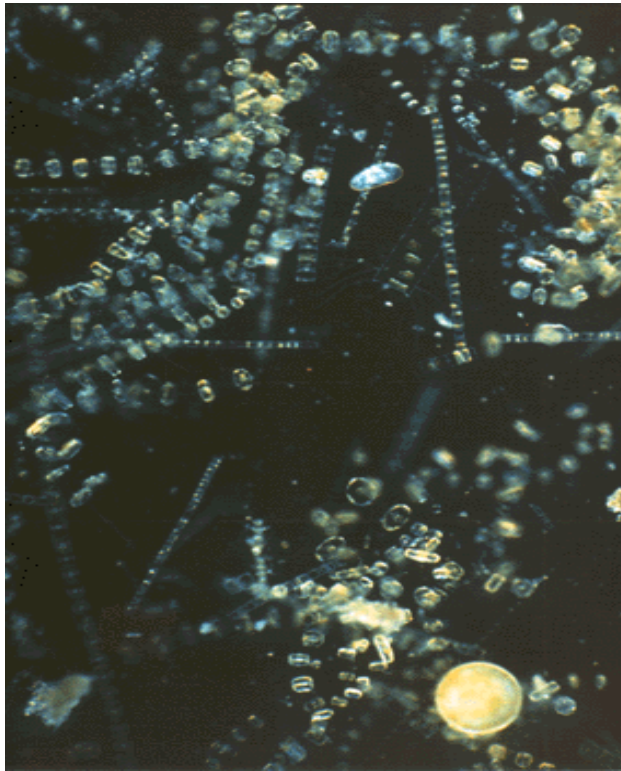


Saturation state of the oceanic water column



We will also see how carbonate mineral dissolution is closely linked to the oxidative degradation of organic matter.

Opaline silica



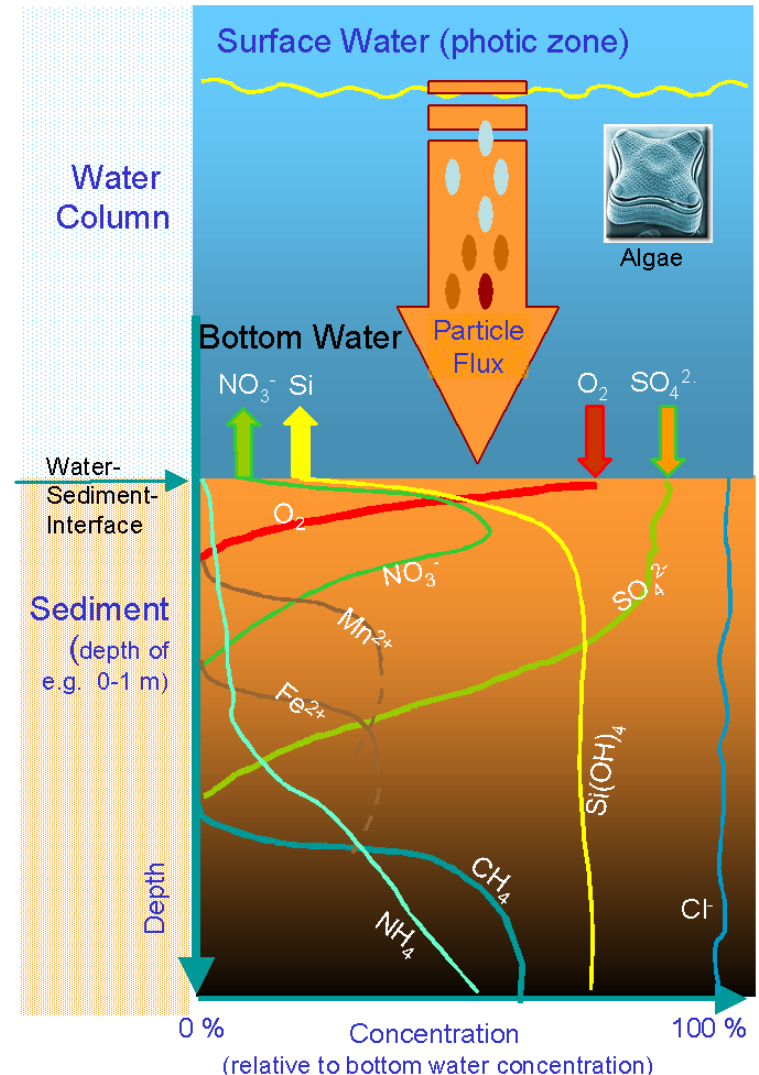
Unlike CaCO₃, all the oceanic water column is undersaturated with respect to amorphous silica but only a fraction (<50%) of this material dissolves in the water column as it falls through it after the death of the organisms. Most of the opal dissolution occurs at the seafloor.

Early Diagenesis

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6. Bacterial degradation of organic matter.

Post-depositional remobilization

While some elements escape the sediment through advection of pore waters as a result of compaction, many others migrate in and out of the sediment by diffusion, driven by concentration gradients established as a result of diagenetic processes such as mineral dissolution, ion-exchange, and bacterial degradation of organic matter.



Early Diagenesis

1. Physical effects: compaction.
2. Biological/physical/chemical influence of burrowing organisms: bioturbation and bioirrigation.
3. Formation of new minerals and modification of pre-existing minerals.
4. Complete or partial dissolution of minerals.
5. Post-depositional mobilization and migration of elements.
6. Bacterial degradation of organic matter.
(main driving force for most diagenetic processes)

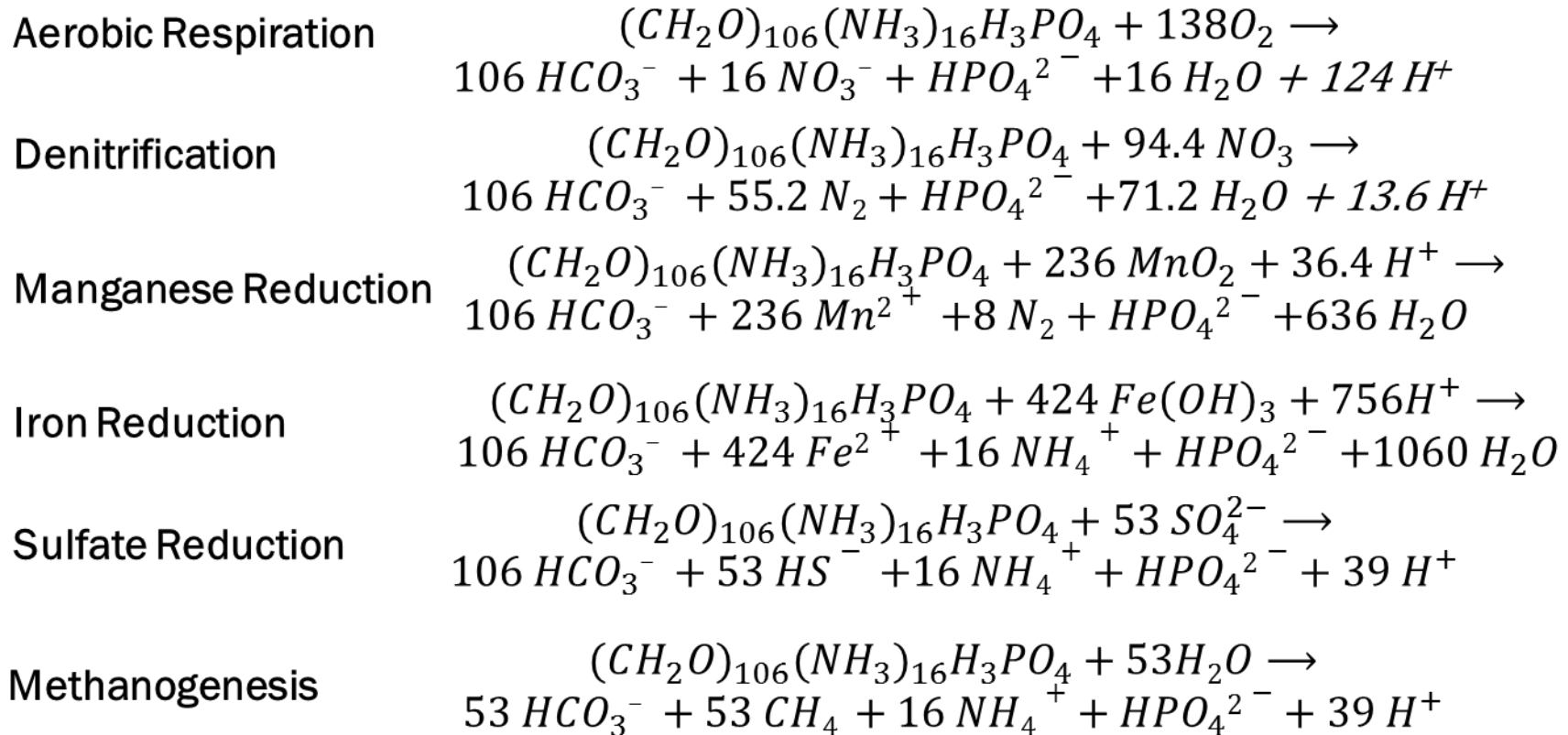
Anabolic processes



Sequence of catabolic reactions

<i>In the presence of free O₂:</i>	ΔG (kJ/mol)
(1) Aerobic respiration: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 138\text{O}_2 \rightarrow \text{H}_3\text{PO}_4 + 16\text{HNO}_3 + 106\text{CO}_2 + 122\text{H}_2\text{O}$	-475
<i>In the absence of free O₂:</i>	
(1) Denitrification: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 94.4\text{HNO}_3 \rightarrow \text{H}_3\text{PO}_4 + 55.2\text{N}_2 + 106\text{CO}_2 + 177.2\text{H}_2\text{O}$	-448
(1) Manganese reduction: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 236\text{MnO}_2 + 472\text{H}^+ \rightarrow \text{H}_3\text{PO}_4 + 236\text{Mn}^{2+} + 16\text{NH}_3 + 106\text{CO}_2 + 366\text{H}_2\text{O}$	-349
(1) Iron reduction: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 212\text{Fe}_2\text{O}_3 + 848\text{H}^+ \rightarrow \text{H}_3\text{PO}_4 + 424\text{Fe}^{2+} + 16\text{NH}_3 + 106\text{CO}_2 + 530\text{H}_2\text{O}$	-114
(1) Sulfate reduction: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 53\text{SO}_4^{2-} \rightarrow \text{H}_3\text{PO}_4 + 53\text{S}^{2-} + 16\text{NH}_3 + 106\text{CO}_2 + 106\text{H}_2\text{O}$	-77
<i>In the absence of free and linked oxygen:</i>	
(1) Fermentation/Disproportionation: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 \rightarrow \text{H}_3\text{PO}_4 + 16\text{NH}_3 + 53\text{CO}_2 + 53\text{CH}_4$	-58

Sequence of catabolic reactions



Sequence of catabolic reactions

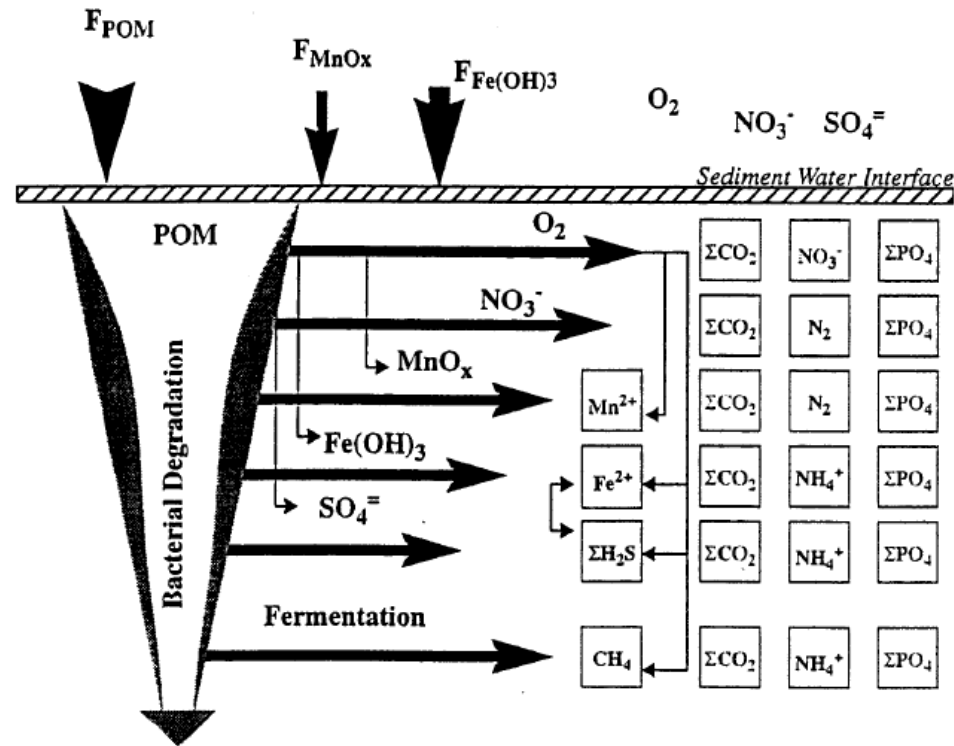


Fig 1: Schematic Diagram of the sequence of early diagenetic reactions occurring in surficial sediments. F_x represents the fluxes of the chemical species x reaching the water interface under particulate form, and POM the Particulate Organic Matter. The arrows indicate that the soluble by-products can diffuse in the porous medium and be re-oxidized in presence of electron acceptors (e.g. O_2).

Oxygen penetration depth

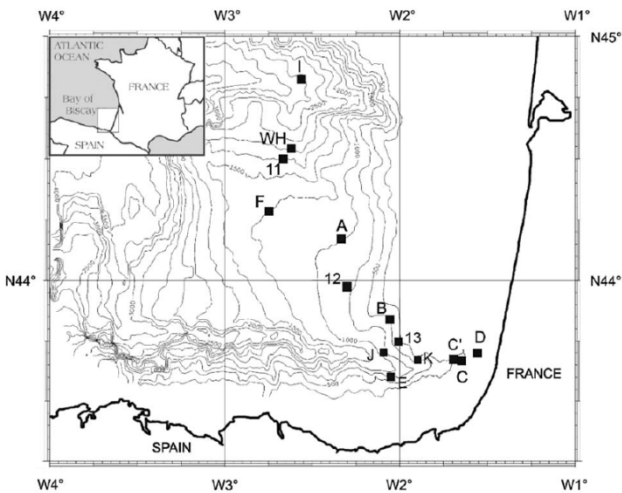


Fig. 1. Map of the southeastern part of the Bay of Biscay showing the location of the stations.

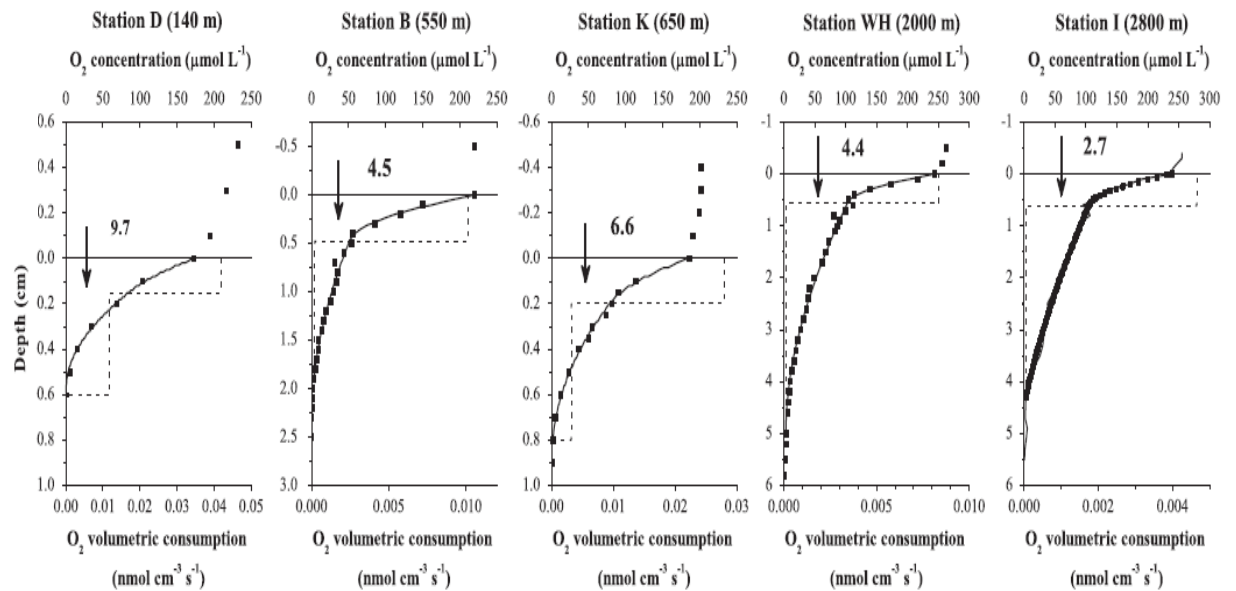


Fig. 2. Selected O_2 microprofiles at six different stations. Output of the PROFILE model (Berg et al., 1998) show the curve fitting and the volumetric O_2 uptake. The numbers and black arrows indicate the diffusive flux of O_2 ($mmol\ m^{-2}\ d^{-1}$) across the sediment-water interface. A example of temporal variation of O_2 profiles is shown for station A sediments. The 0-value at the ordinate indicates the relative position of the estimated sediment surface.

Oxygen penetration depth

1. Oxygen content of the overlying waters
2. Porosity
3. Rate of organic matter catabolism
 - Organic matter content
 - Reactivity of the organic matter
 - Temperature

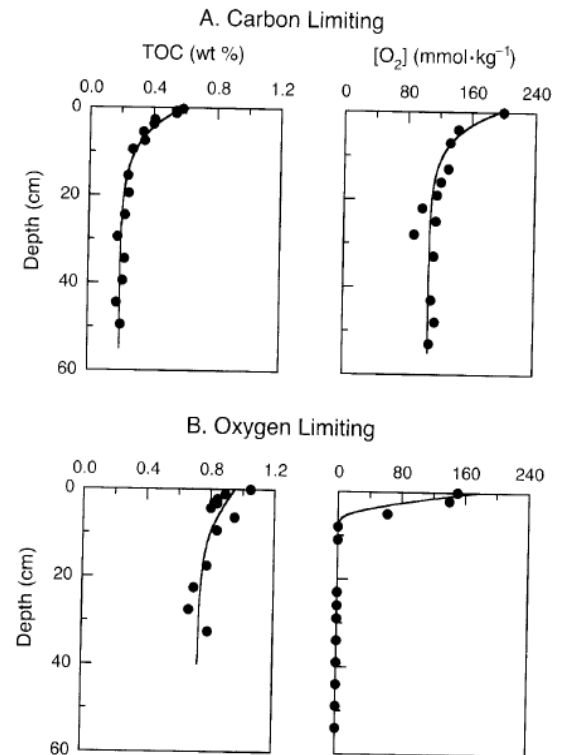
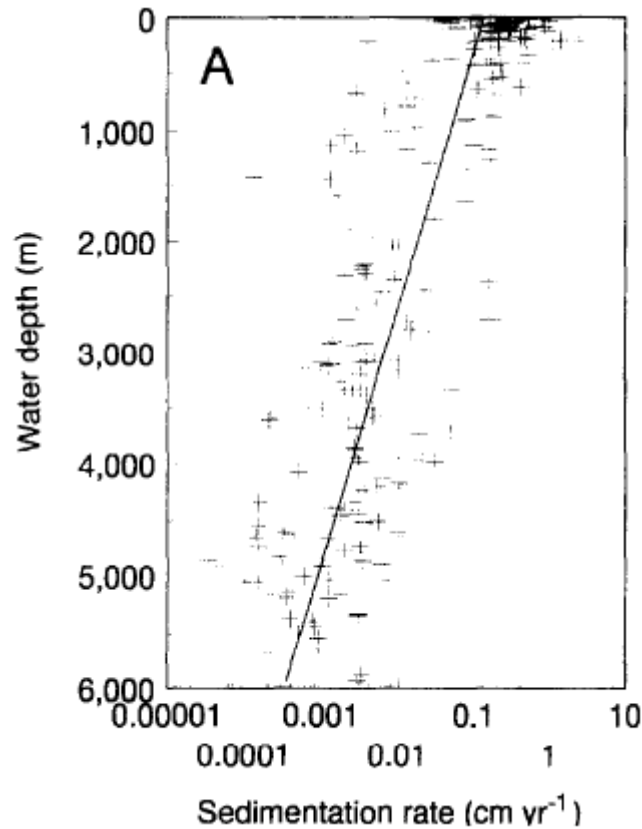


Figure 7.8 Sediment data from carbon limiting (A) and oxygen limiting (B) pelagic sediments (modified after Emerson and Hedges, 2003). Carbon limiting data are for a site in the central equatorial Pacific (Grundmanis and Murray, 1982) while oxygen limiting data are for a site in the northeast Pacific (Murray and Kuivala, 1990).

Oxygen penetration depth



From: Middelburg et al. (1997)
Deep-Sea Res. I 44: 327-344

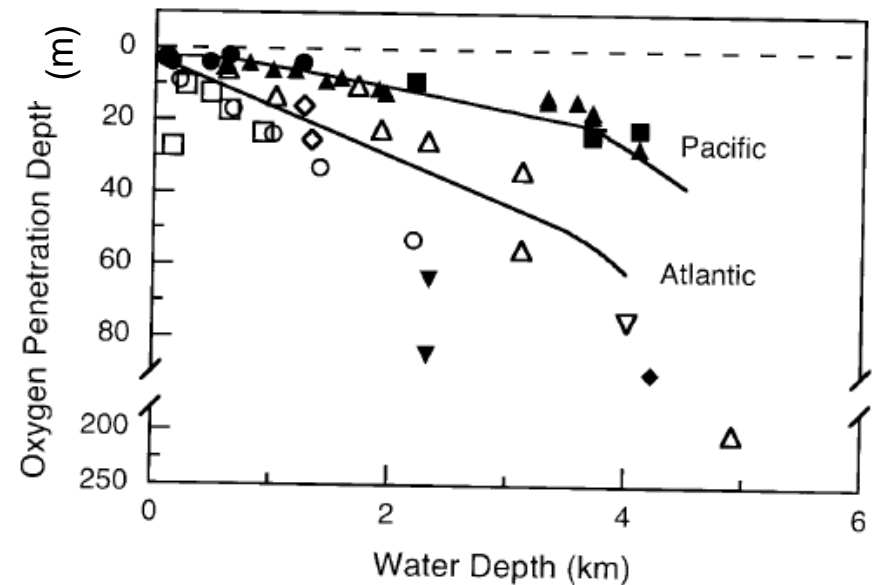


Figure 7.9 The sediment oxygen penetration depth as a function of water column depth in the Atlantic Ocean (open symbols) and Pacific Ocean (closed symbols). Data are from several sources (Murray and Kuivala, 1990; Archer and Devol, 1992; Reimers et al., 1992; Glud et al., 1994; Cai et al., 1995; Hales and Emerson, 1996, 1997a; Lohse et al., 1998; Martin and Sayles, 2003; Adler et al., 2001; Nealson and Berelson, 2003). Martin and Sayles (2003) suggest that these interocean differences are related to the presence of the intense oxygen minimum in the northeast Pacific. However, differences in the reactivity of sediment organic matter at equivalent depths in the two oceans may also play a role here (see discussions in section 14.3).

From: Burdige (2006) Geochemistry of Marine Sediments

Sequence of catabolic reactions

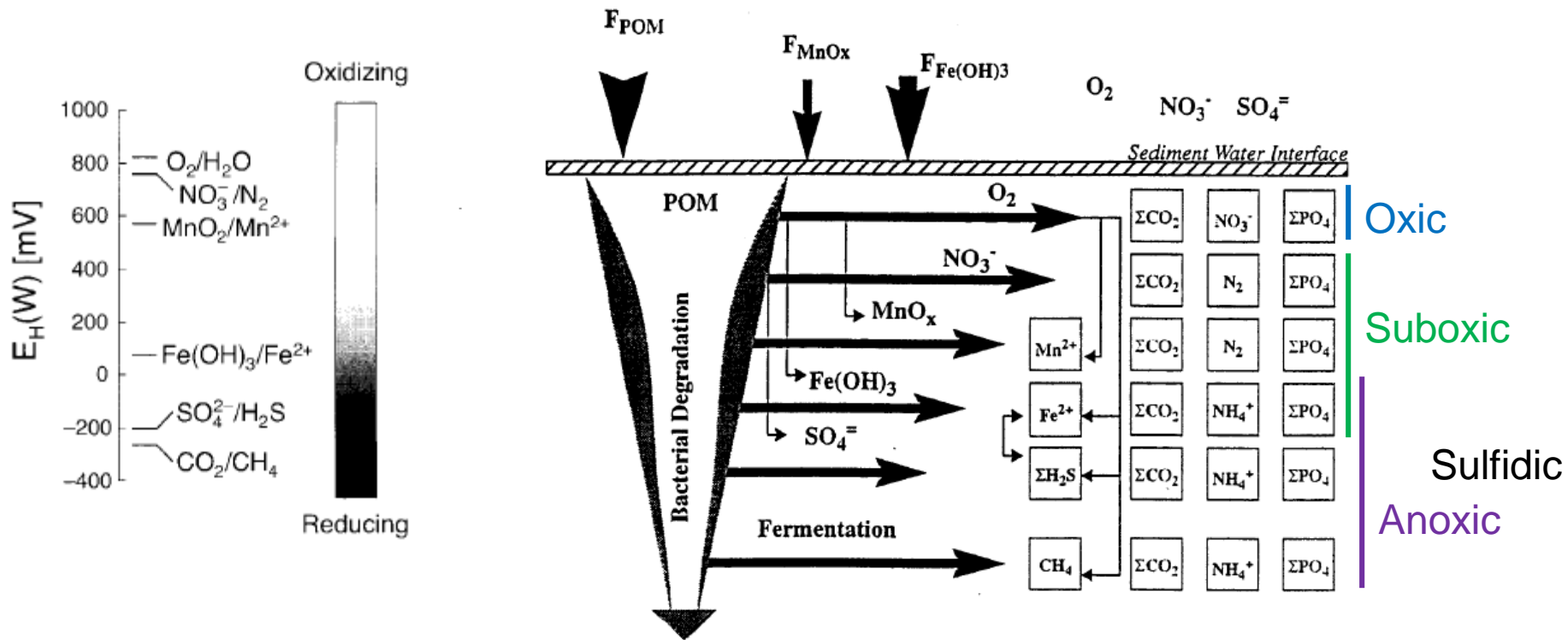


Fig 1: Schematic Diagram of the sequence of early diagenetic reactions occurring in surficial sediments. F_x represents the fluxes of the chemical species x reaching the water interface under particulate form, and POM the Particulate Organic Matter. The arrows indicate that the soluble by-products can diffuse in the porous medium and be re-oxidized in presence of electron acceptors (e.g. O_2).

Redox zonation

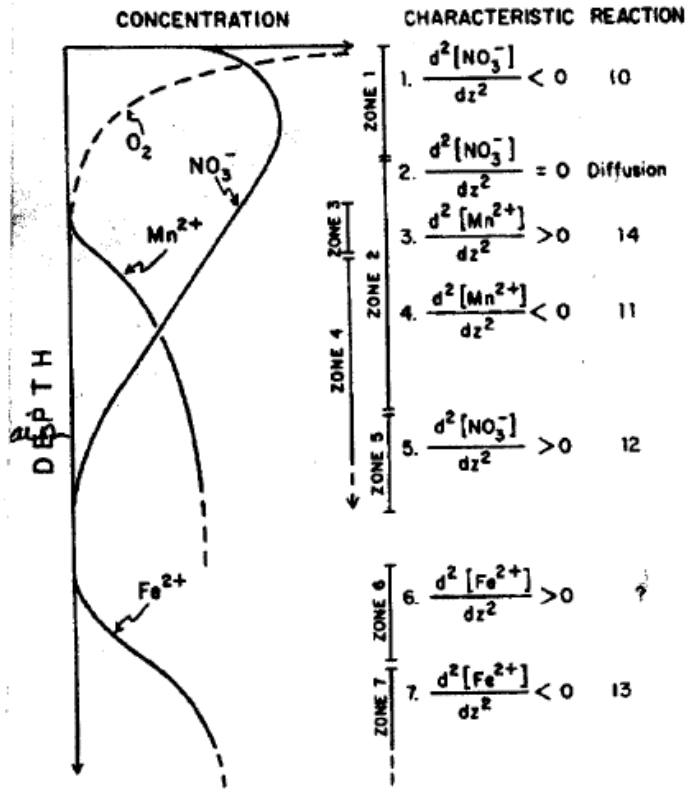


Fig. 17. Schematic representation of trends in pore water profiles. Depth and concentration axes are in arbitrary units. The zones, characteristic curvature of the gradients, and reaction numbers are discussed in the text.

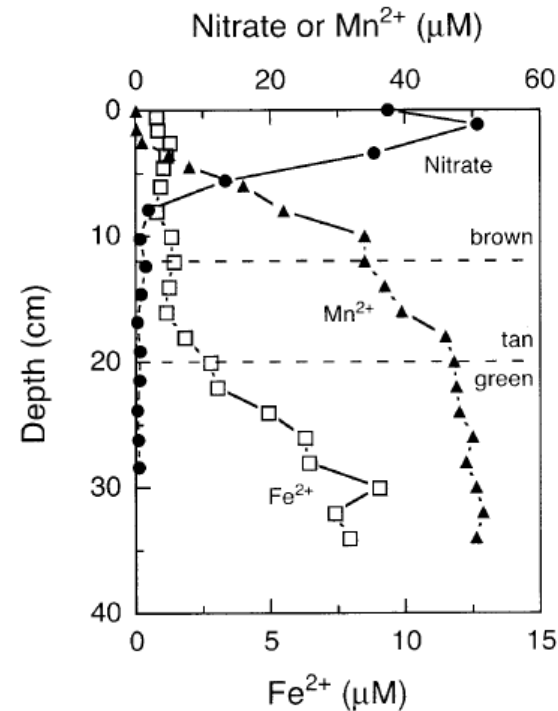


Figure 7.4 Pore-water profiles of nitrate (\bullet), Mn^{2+} (\blacktriangle) and Fe^{2+} (\square) at MANOP site M. As discussed in the text, there is some degree of overlap between the zones of denitrification and manganese reduction above ~ 15 cm. Also note that the zone of iron reduction (as inferred from the accumulation of Fe^{2+} in the pore waters) does not appear to occur until nitrate is depleted, in association with the tan-green color change in the sediments. Data sources: Lyle, 1983 (Mn^{2+} , Fe^{2+} , sediment color); Klinkhammer, 1980 (nitrate). These data (along with other data from MANOP site M) are also shown in fig. 8.4.