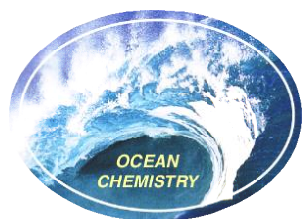




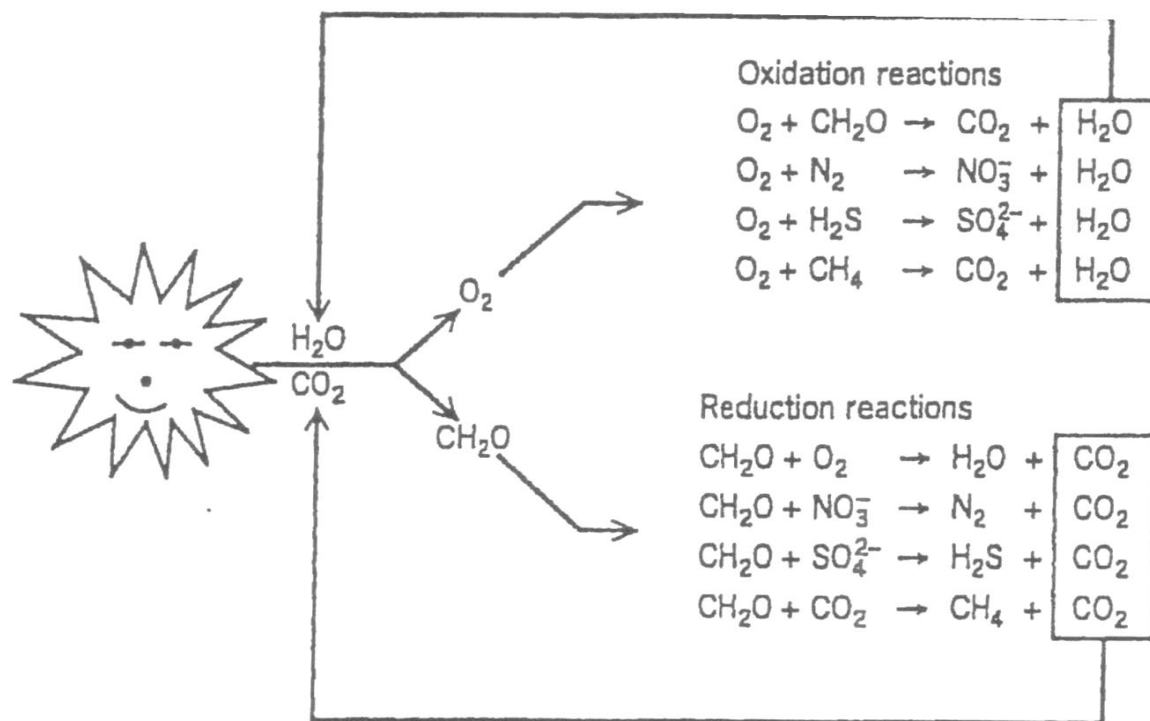
# ***Anoxic (Anaerobic) Environments and Removal of Sulphate ions***

# Redox concepts

- Seawater is thermodynamically unstable;
- Water column contains  $2 \times 10^{16}$  moles of reduced organic carbon;
- Water column contains  $3 \times 10^{17}$  moles of molecular  $O_2$ ;
- These two reactants are physically segregated by life processes and gravity;



# Global geochemical cycle of redox energy



Global geochemical cycle of redox energy.



*Kinetics of these reactions are slow and enzymatic catalysis by microbes drives these reactions under normal oceanic conditions*



# ***Anoxic (Anaerobic) Environments and Removal of Sulphate ion***

## **REDOX Reactions**

Many reactions can be considered to be REDOX reactions involving transfer of electrons from one chemical species to another.

**OXIDATION:** loss of electrons

**REDUCTION:** gain of electrons

Its often difficult to decide (for polyatomic species) whether an element has gained or lost electrons during a REDOX reaction:  
So: there is a set of simple rules to calculate ,oxidation states' for atoms contained in a molecule



Increasing oxidation number = OXIDATION (FeI to FeIII)

Decreasing oxidation number = REDUCTION (MnIV to MnII)

OXIDANT: a species that causes something else to be oxidised (lose electrons) during a reaction.

The oxidant is **REDUCED**: it is therefore an electron acceptor.

REDUCTANT: a species that causes something else to be reduced.

The reductant is **OXIDISED**: it is therefore an electron donor.

*Background Reading:*

*Chapter 7 of Libes ,An Introduction to Marine Biogeochemistry‘*

*and/or Millero Chemical Oceanography Fourth edition. Section 6.6.*

*Millero Chemical Oceanography Fourth edition. Section 10.3 and 10.3.1.*



## In the oceanic water column:

- $O_2 / H_2O$  is (usually) the dominant oxidant (electron acceptor).  
Surface waters oxygen levels are over  $200 \mu\text{mol/kg}$ , but even at very low levels at depth it is still the dominant oxidant.
- Organic material is (usually) the dominant reductant (electron donor)
- But in *anoxic environments* all of the oxygen is used up before all organic material is destroyed and other electron acceptors are used to oxidise organic material



## 1. The Water Column

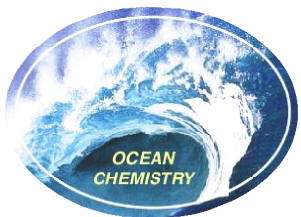
Anoxic conditions occur when:

- Rate of  $O_2$  removal  $>$  rate of  $O_2$  supply
- Respiration (oxidation of organic material) removes oxygen
- Photosynthesis and Gas-Exchange with atmosphere supply oxygen; this is in surface waters (only)
- Mixing and ocean circulation transport oxygen to the sub-surface ocean

# Apparent Oxygen Utilisation

$$AOU = O_{2_{saturation}} - O_{2_{measured}}$$

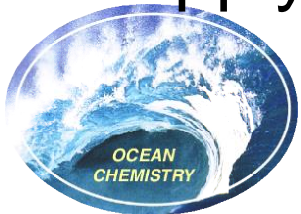
- In situ consumption ~ true utilisation;
- Supersaturation and non-ideal behaviour of  $O_2$  during mixing lead to small discrepancies;



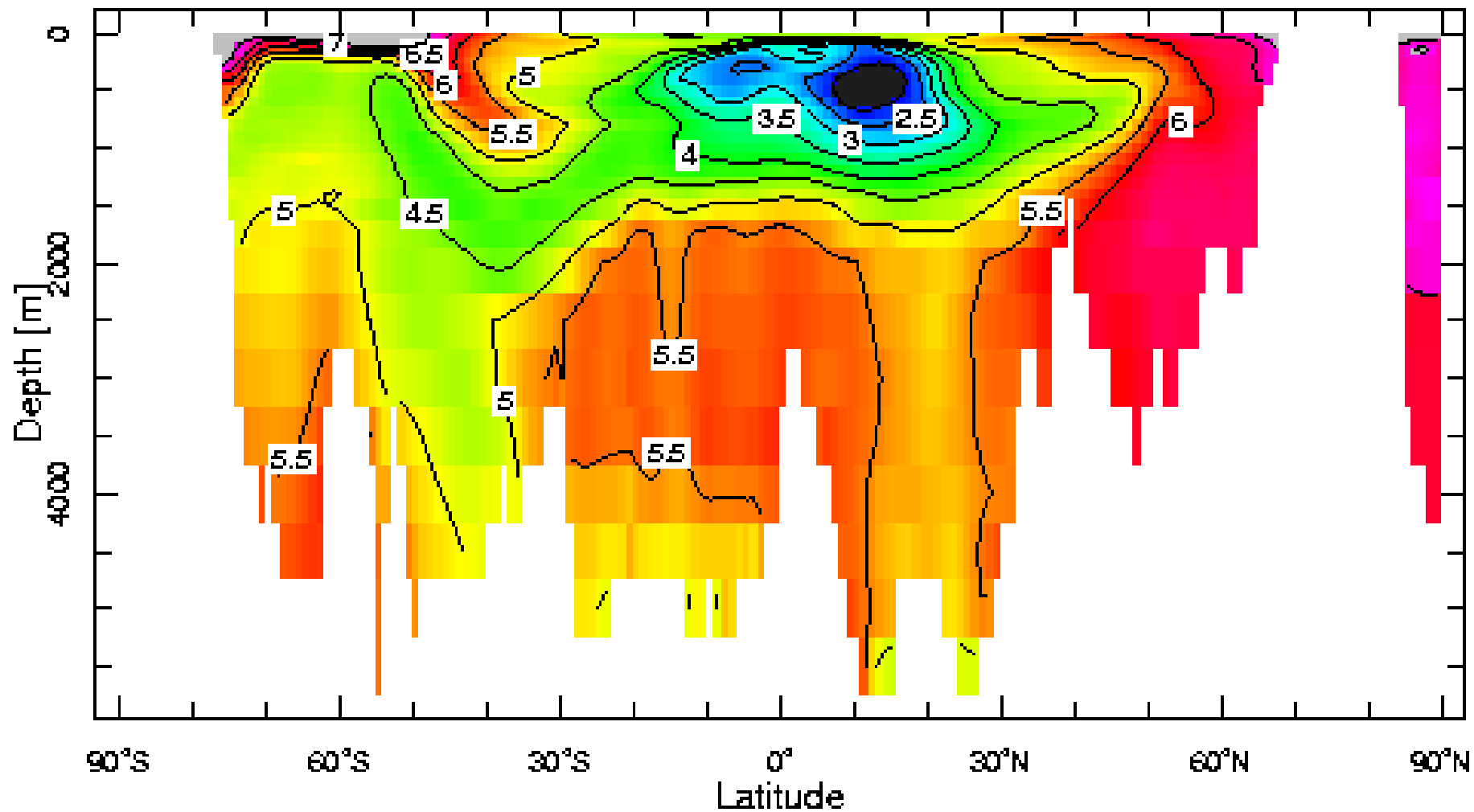


# Segregation of oxidants and reductants

- Gravitational settling of particulate organic carbon (POC); advective transport of dissolved organic carbon (DOC) and suspended POC, and active transfer of POC by zooplankton
- Apparent oxygen utilisation (AOU) reflects the carbon flux;
- This is offset by ventilation of oceans via thermohaline circulation and thereby oxygen supply;

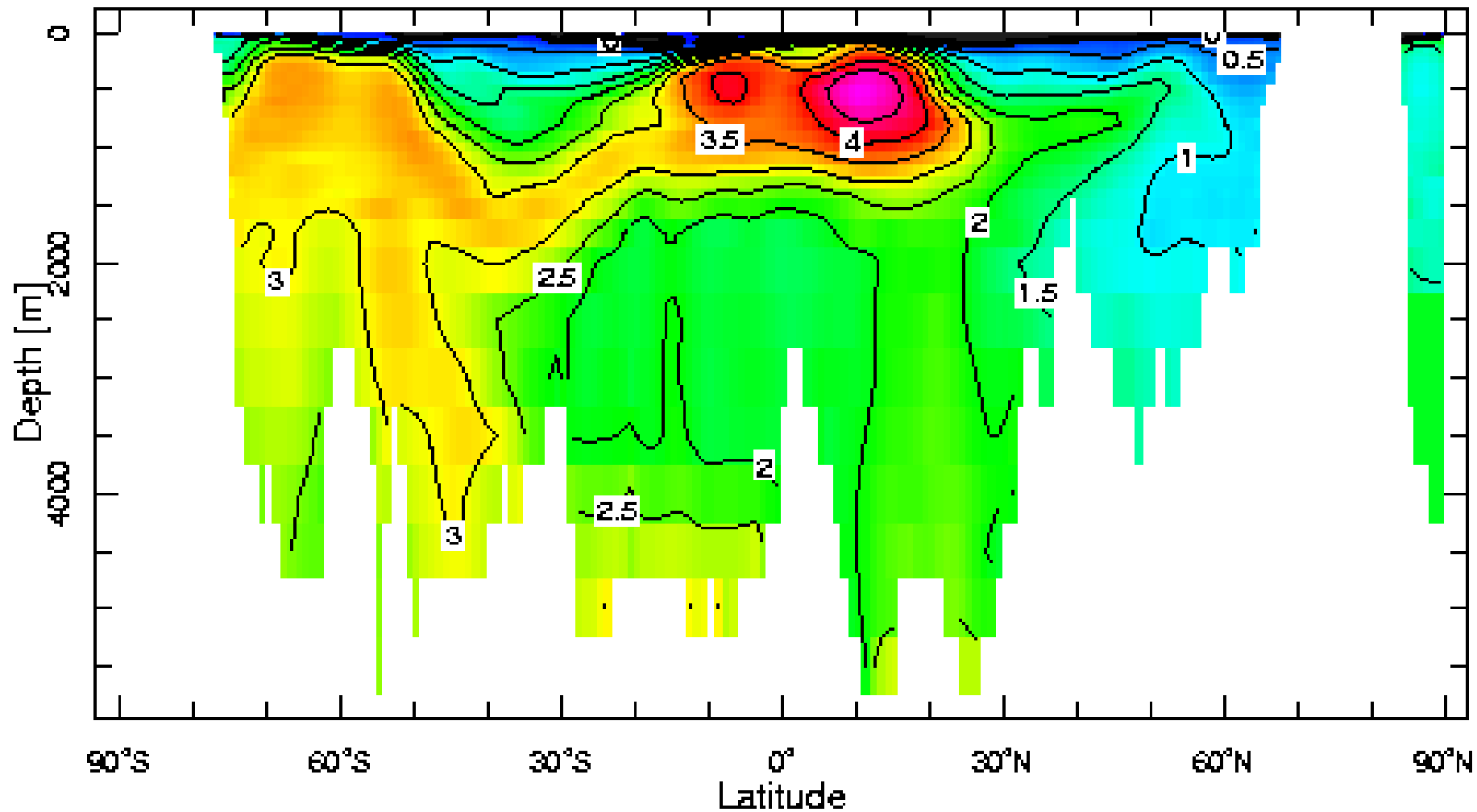


# N-S Dissolved Oxygen Section through Atlantic

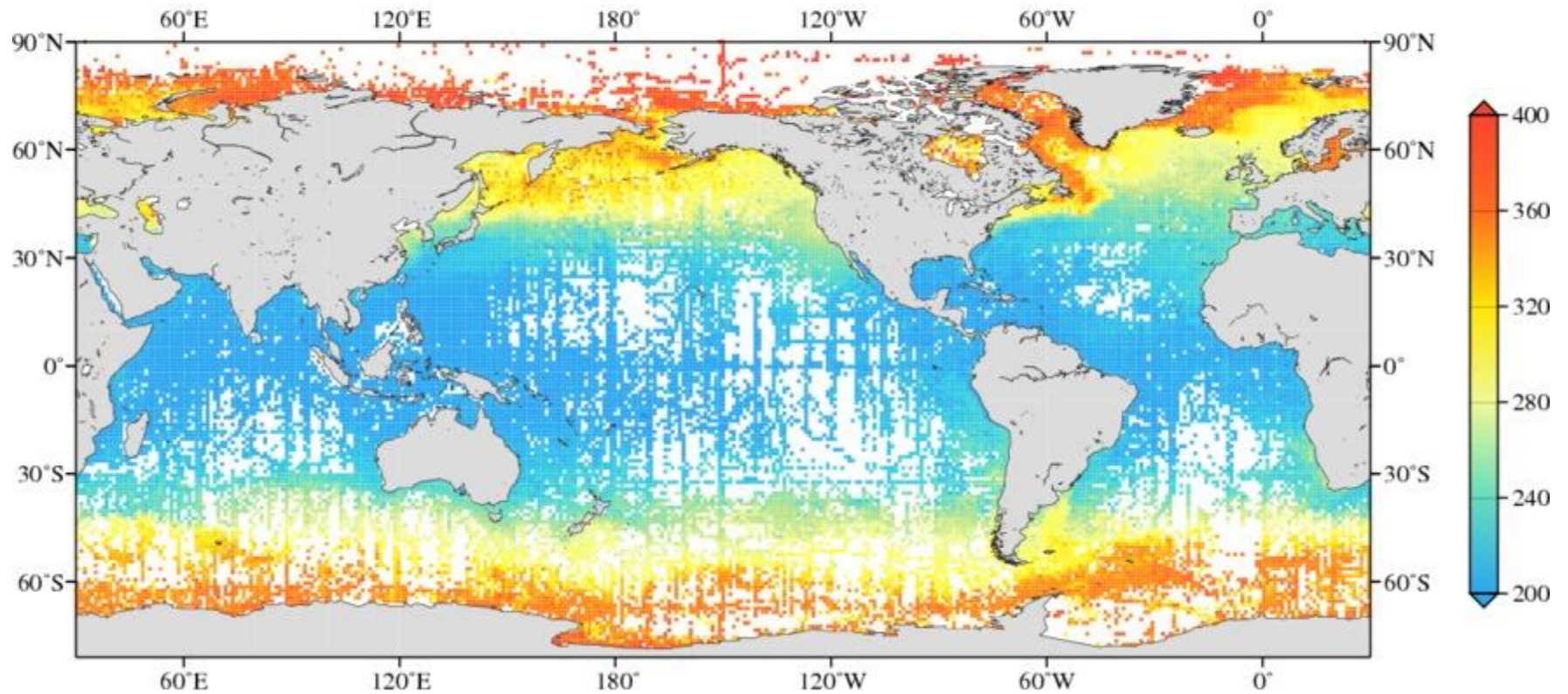


30.5W 0-8 ml/l

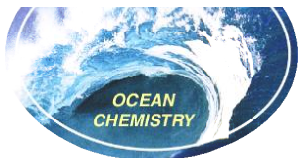
# N-S AOU section through the Atlantic



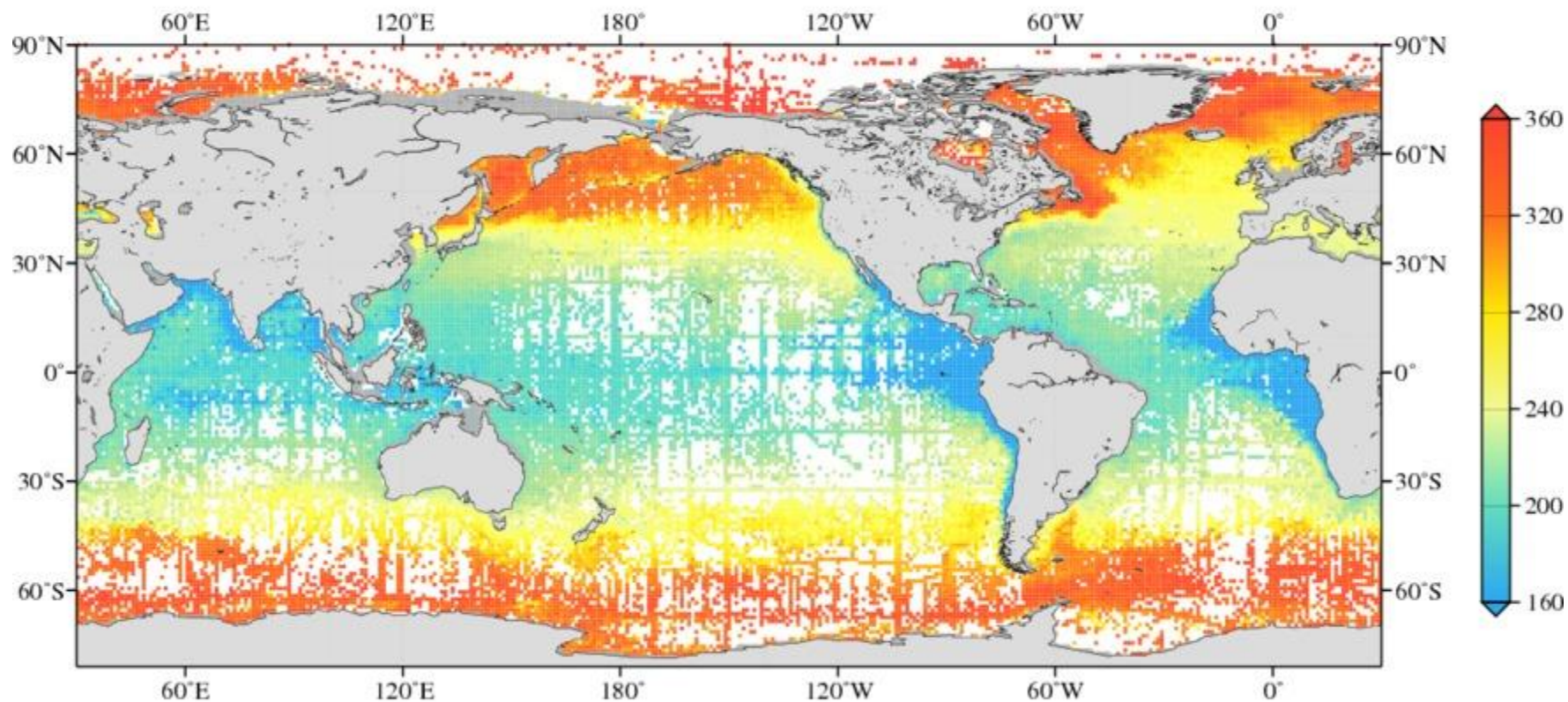
## World Ocean Atlas Climatology



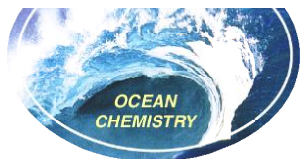
Annual oxygen [ $\mu\text{mol/kg}$ ] at the surface (one-degree grid)



## World Ocean Atlas Climatology

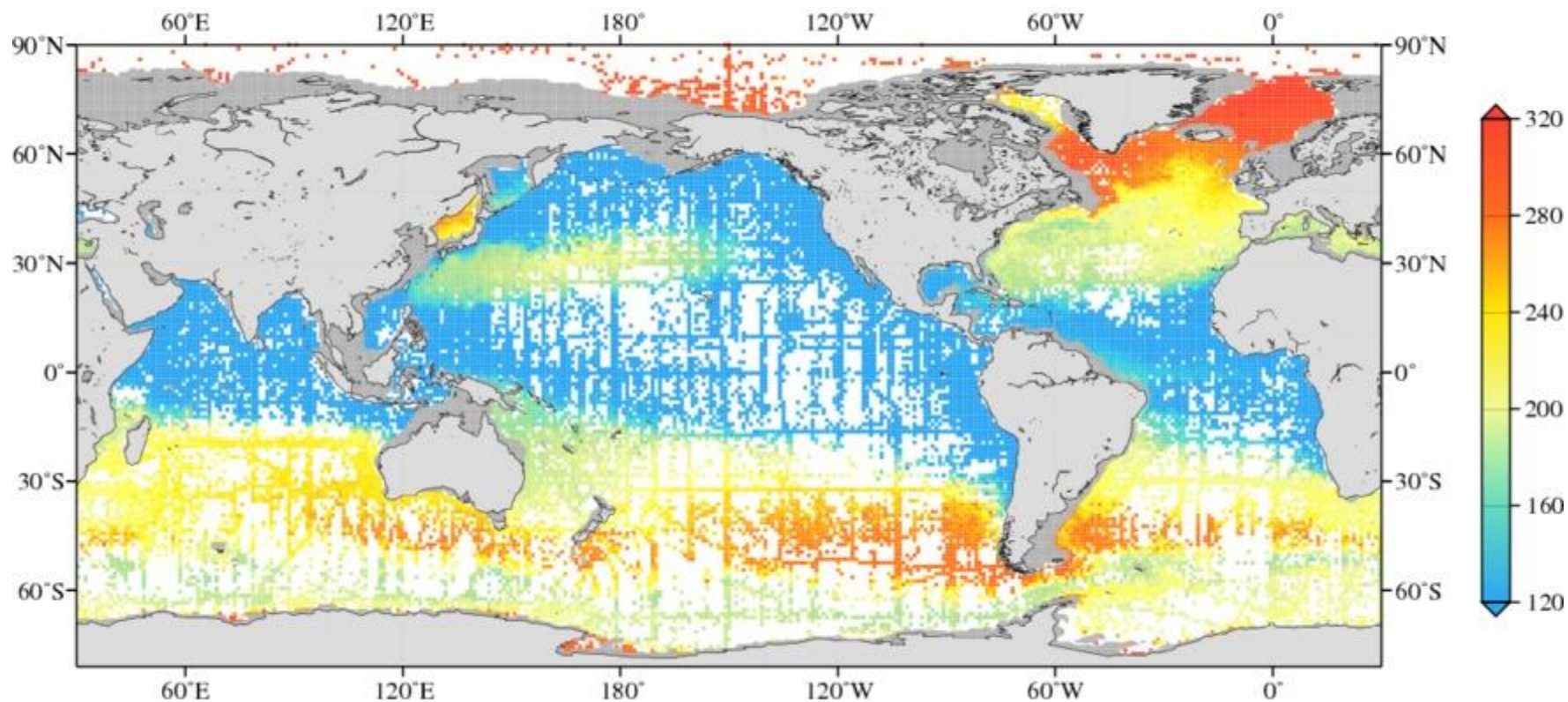


Annual oxygen [ $\mu\text{mol/kg}$ ] at 50 m. depth (one-degree grid)

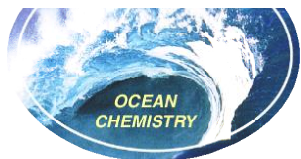




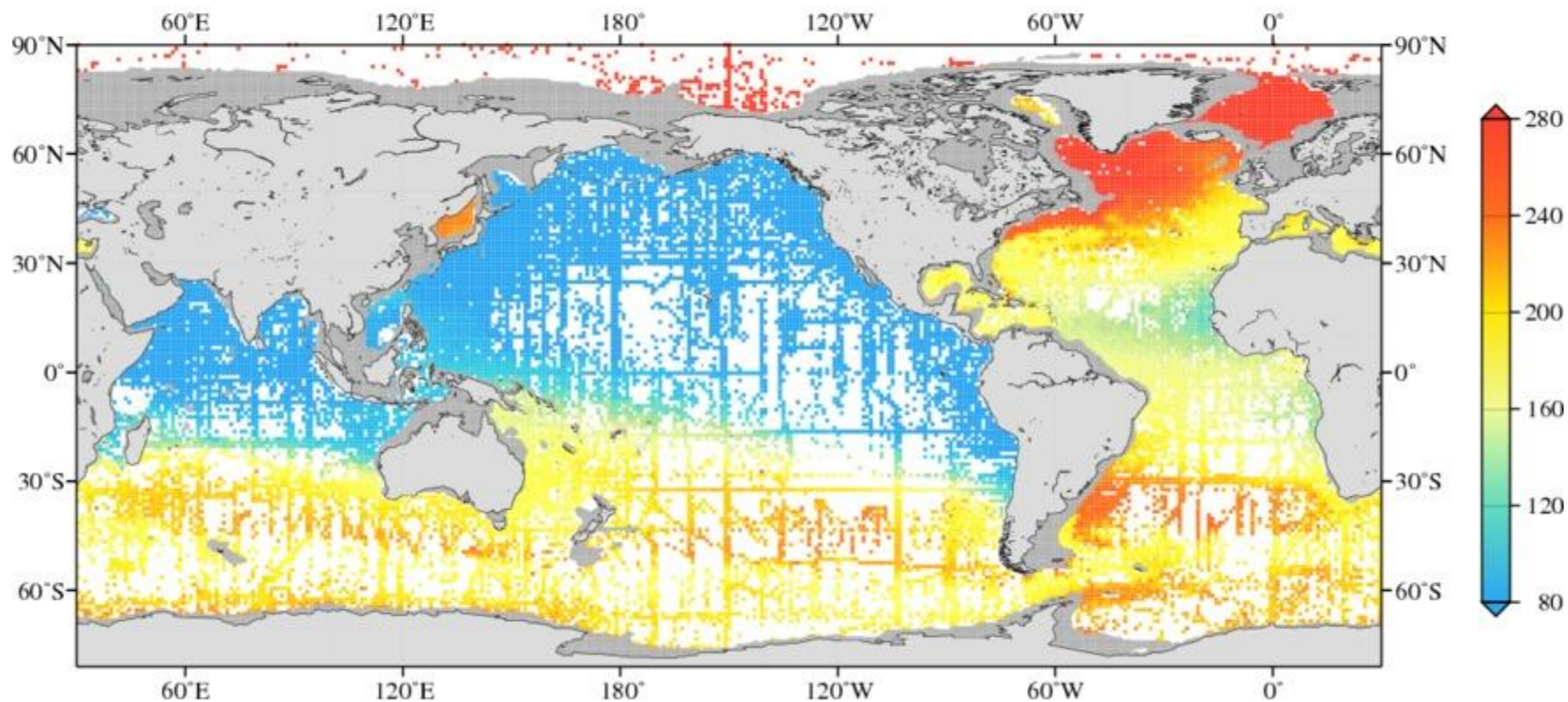
## World Ocean Atlas Climatology



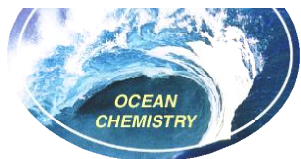
Annual oxygen [ $\mu\text{mol/kg}$ ] at 500 m. depth (one-degree grid)



## World Ocean Atlas Climatology

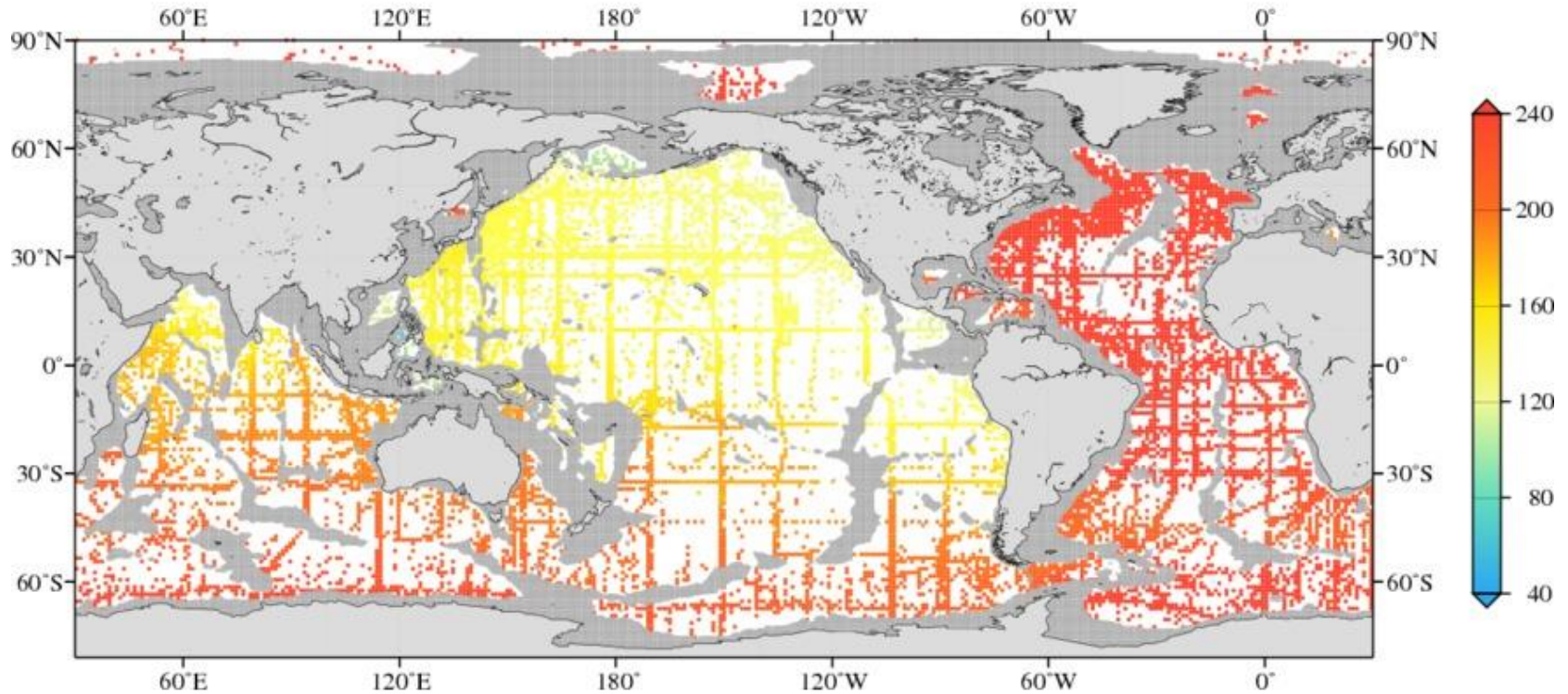


Annual oxygen [ $\mu\text{mol/kg}$ ] at 1000 m. depth (one-degree grid)





## World Ocean Atlas Climatology



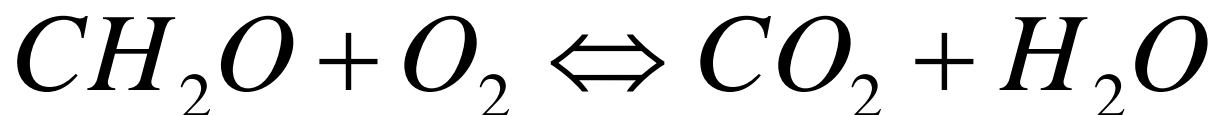
Annual oxygen [ $\mu\text{mol/kg}$ ] at 3500 m. depth (one-degree grid)



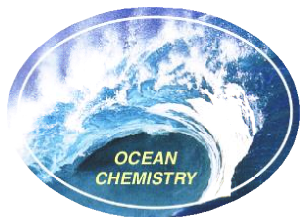


# Energetics of redox reactions

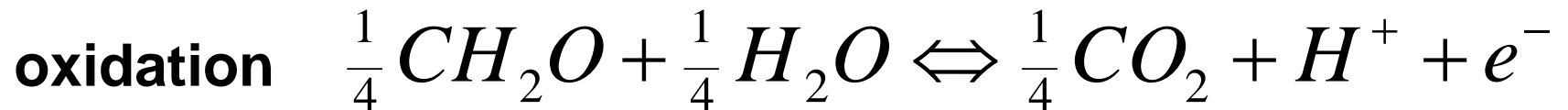
- We can calculate how far any chemical species is from equilibrium using thermodynamic considerations;
- Any reaction will have an equilibrium state which is predictable;



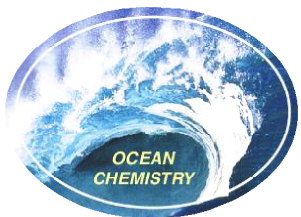
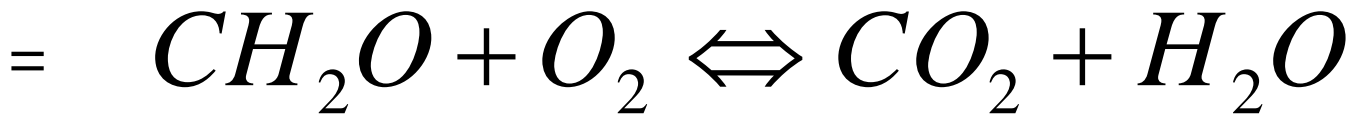
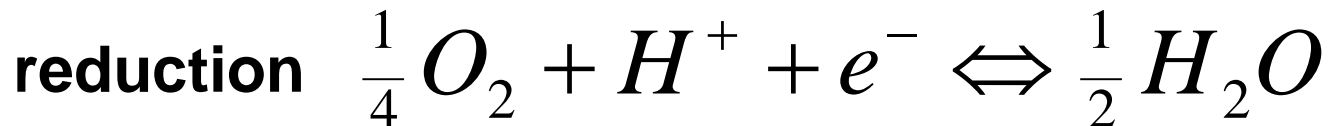
- Reactions with large equilibrium constants are most likely to proceed spontaneously giving off energy



# Redox reactions with organic matter



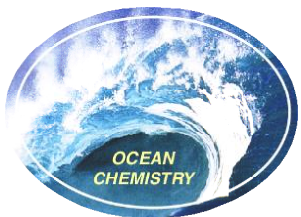
+



**Redox reactions involve electron transfer**

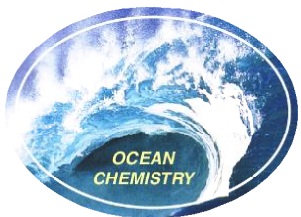
# Oxygen as an oxidant

- Oxygen is the most important oxidant in seawater because of relatively high concentration and enzyme catalysis;
- Using oxygen to oxidise organic matter gives off a lot of free energy;
- In fact  $\sim 30$  kcal of energy per mol;
- We can calculate the energy yield of any reaction from thermodynamics – this tells us the strength of the reaction but not the speed (kinetics)

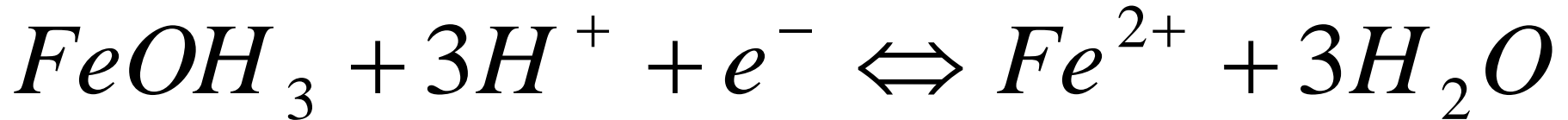


# Sequence of oxidising agents

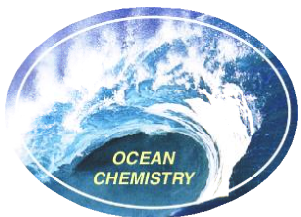
- $O_2$  – aerobic respiration;
- $NO_3^-$  - denitrification;
- $Fe^{3+}$  as Fe oxide - reduction of Fe oxides
- $SO_4^{2-}$  - sulphate reduction;
- $CH_2O$  – methane fermentation;

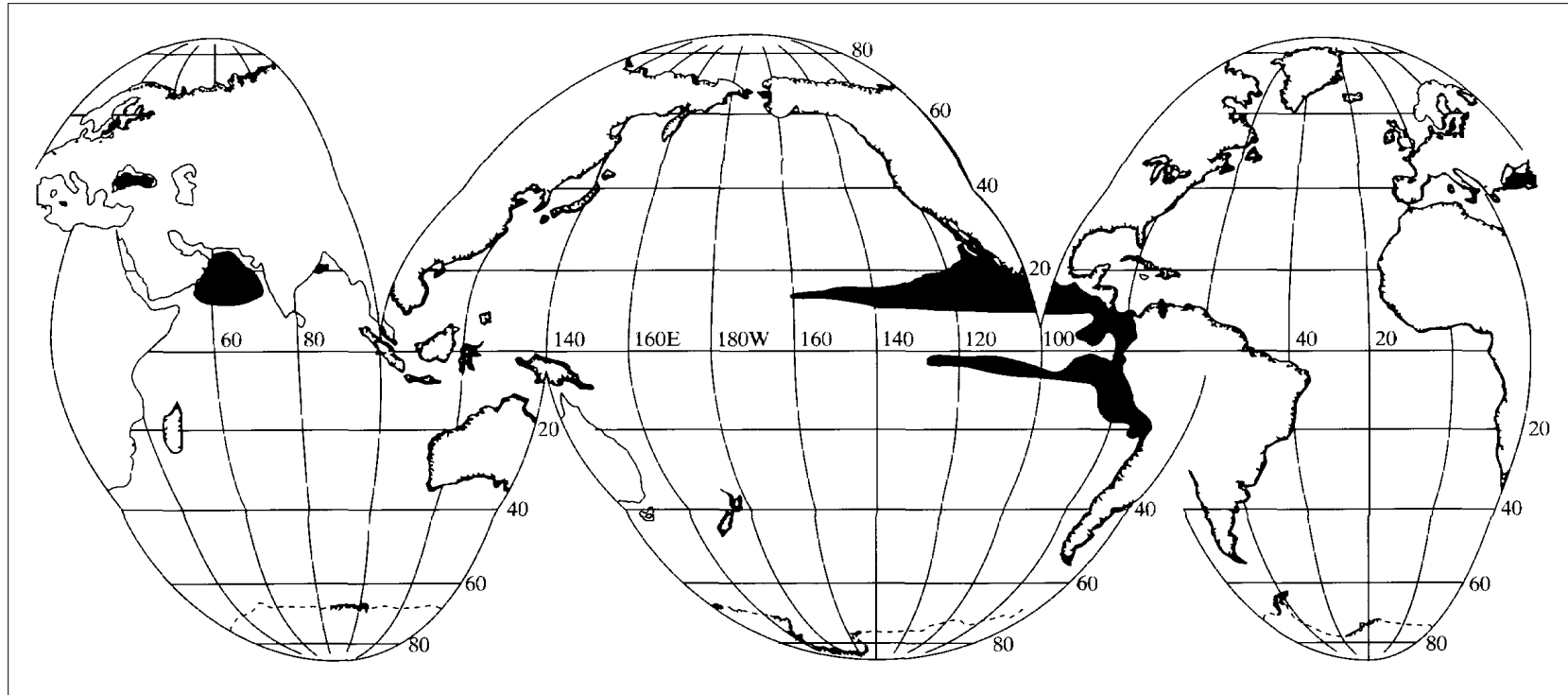


# Fe redox processes



- Equilibrium in oxygenated seawater is very far to left;
- Reaction is dependent on electron activity and pH;
- Organic matter provides the electrons and in the absence of oxygen this reaction proceeds to the right;

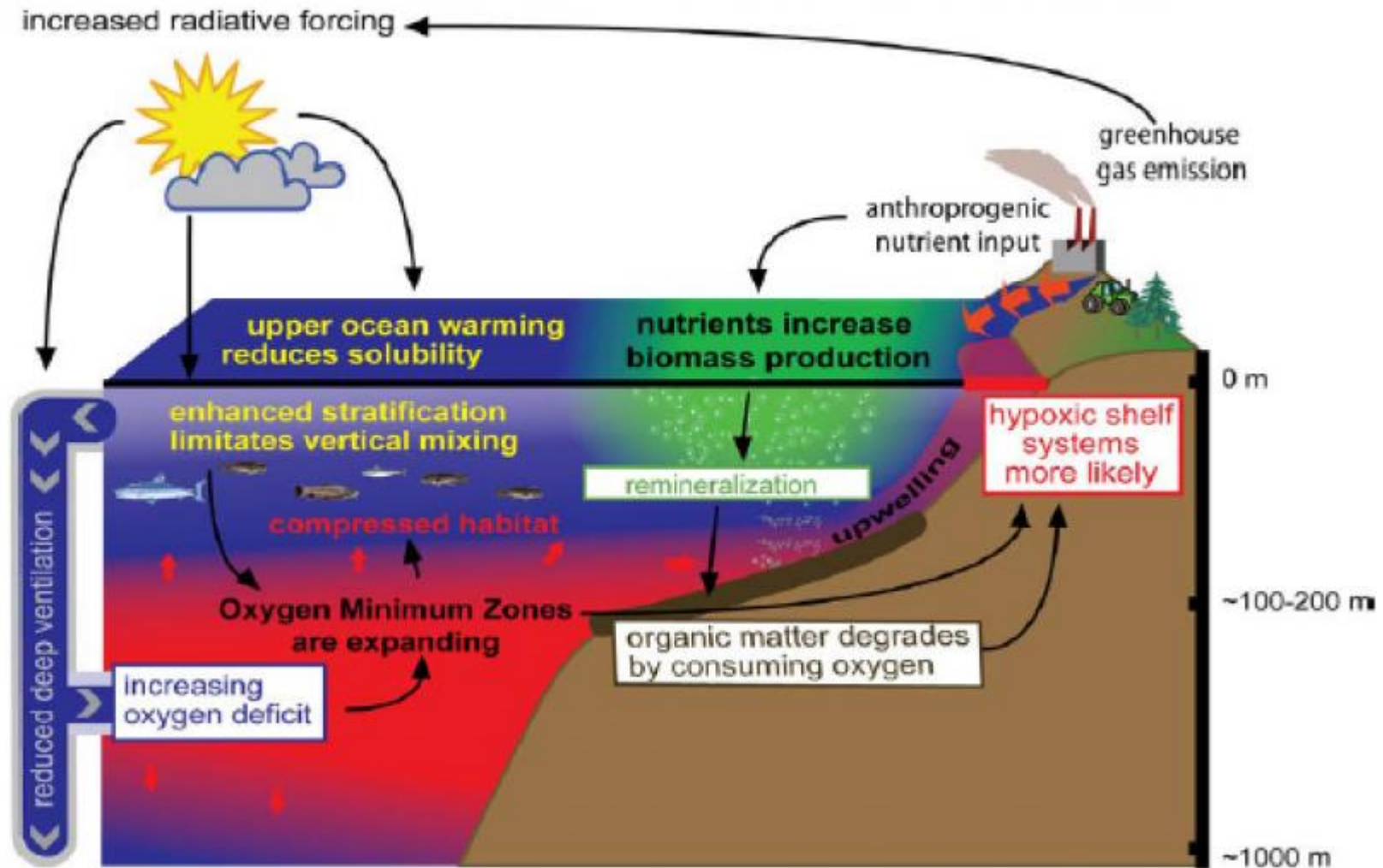


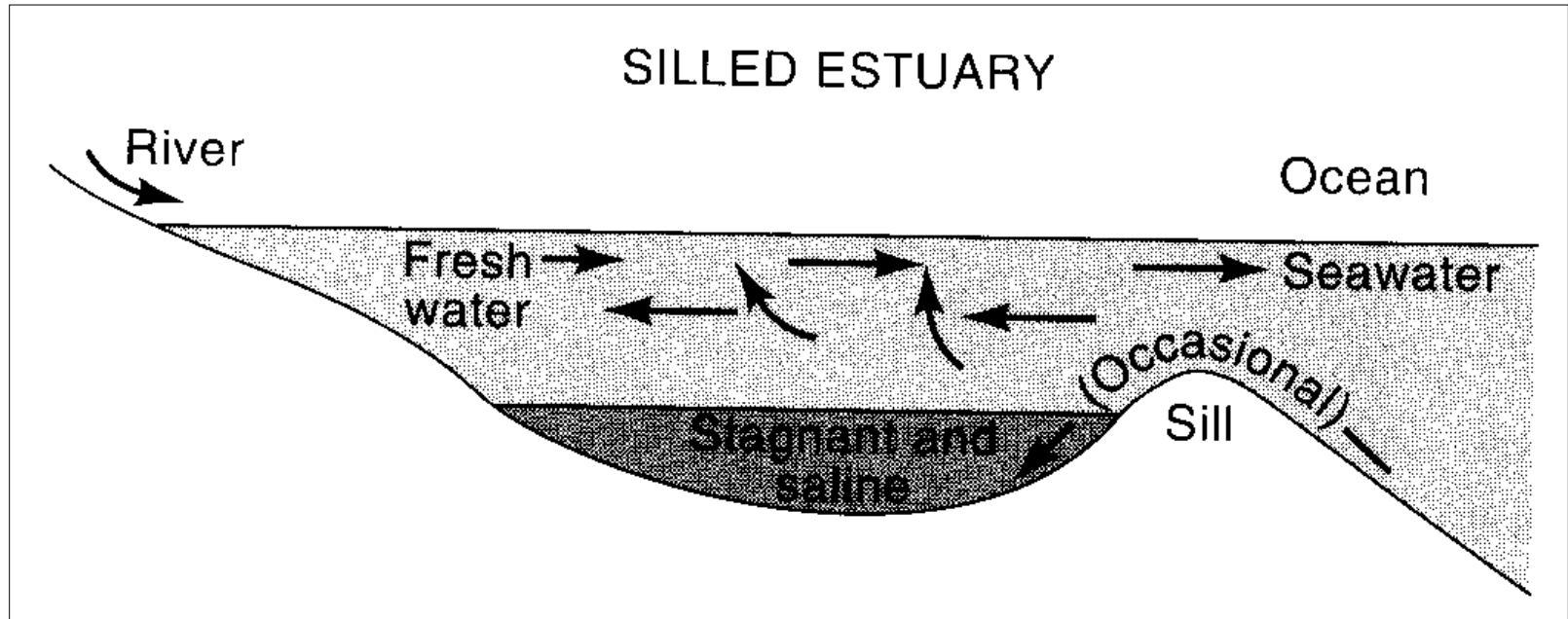


Low or zero oxygen regions are usually areas of restricted exchange with the upper ocean and/or areas of high biological productivity.

Anoxic waters currently confined to regions with strongly restricted vertical and horizontal exchanges of water: due to TOPOGRAPHY (horizontal exchanges) and (for vertical exchanges) strong salinity gradient (Baltic, Black Sea) or strong temperature gradient (Cariaco Trench).  
(Density-gradient : stability: reduces vertical mixing)

# Increasing size and intensity of oxygen minimum zones

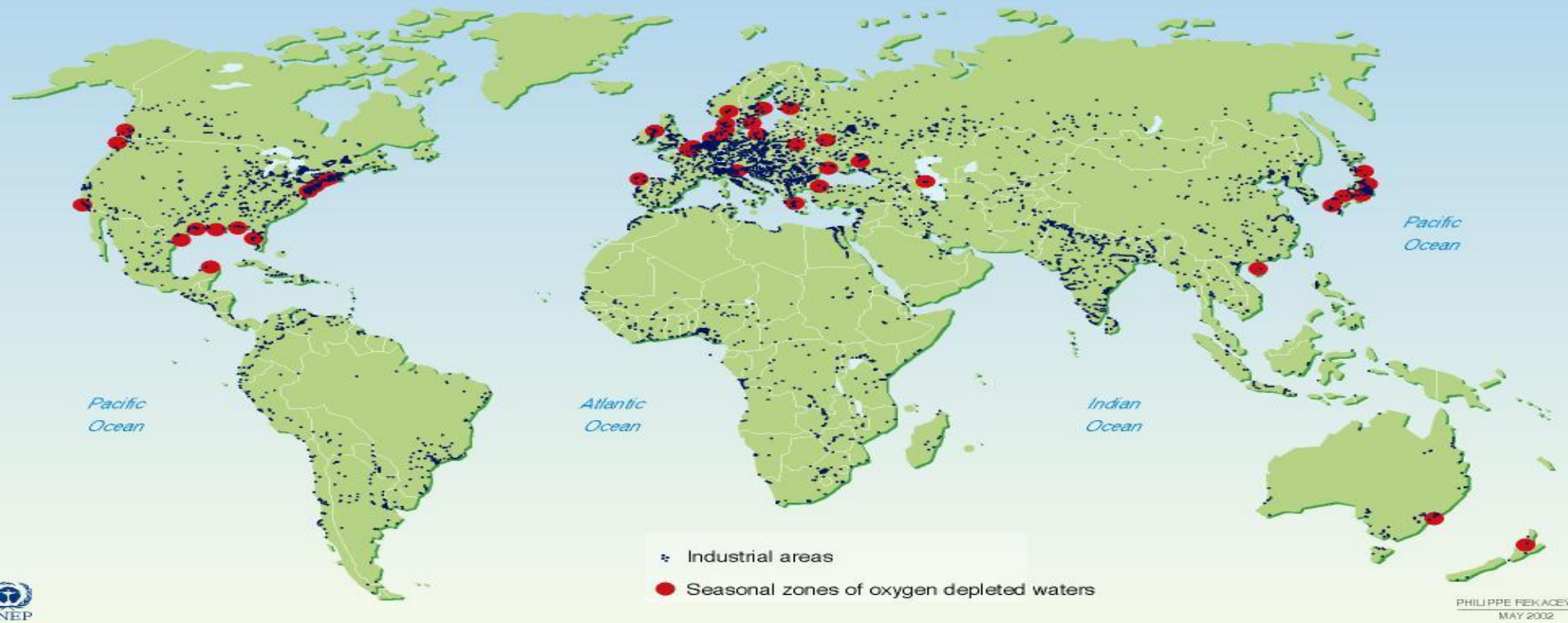




- Black Sea: became anoxic about 1500-2000 years ago
- Bottom water now 300-800 years 'old' on average
- Baltic: periodic inflows of oxygenated saline North Sea water
- Fjords: often anoxic below sill depth



## Industrial Areas and Seasonal Zones of Oxygen Depleted Waters



Source: D. Malakoff, 1998, after R.J. Diaz and R. Rosenberg, 1995; ESRI, 1990.

There is a strong link between areas with high densities of industrial activity and zones of seasonally oxygen depleted waters. It has been estimated that about 80% of all marine pollution originates from land-based activities. It reaches the ocean directly, via rivers, or through atmospheric depositions.

# Anthropogenically Induced De-Oxygenation

## Degradable Wastes

### **Wastes include:**

- ❑ Large part of urban sewage
- ❑ Agricultural wastes
- ❑ Food processing wastes
- ❑ Brewing and distillery wastes
- ❑ Paper pulp mill wastes
- ❑ Chemical industry wastes
- ❑ Oil spillages

# Degradable Wastes

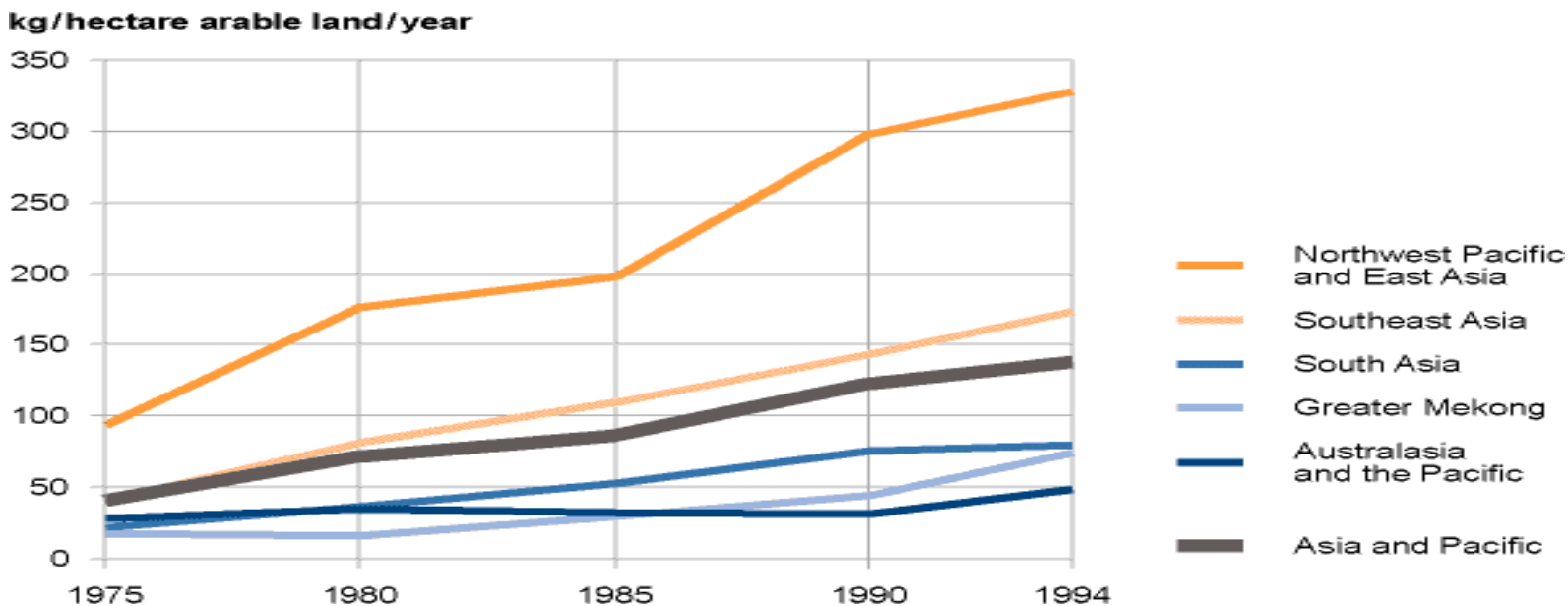
## **Degradable wastes – subject to bacterial decay**

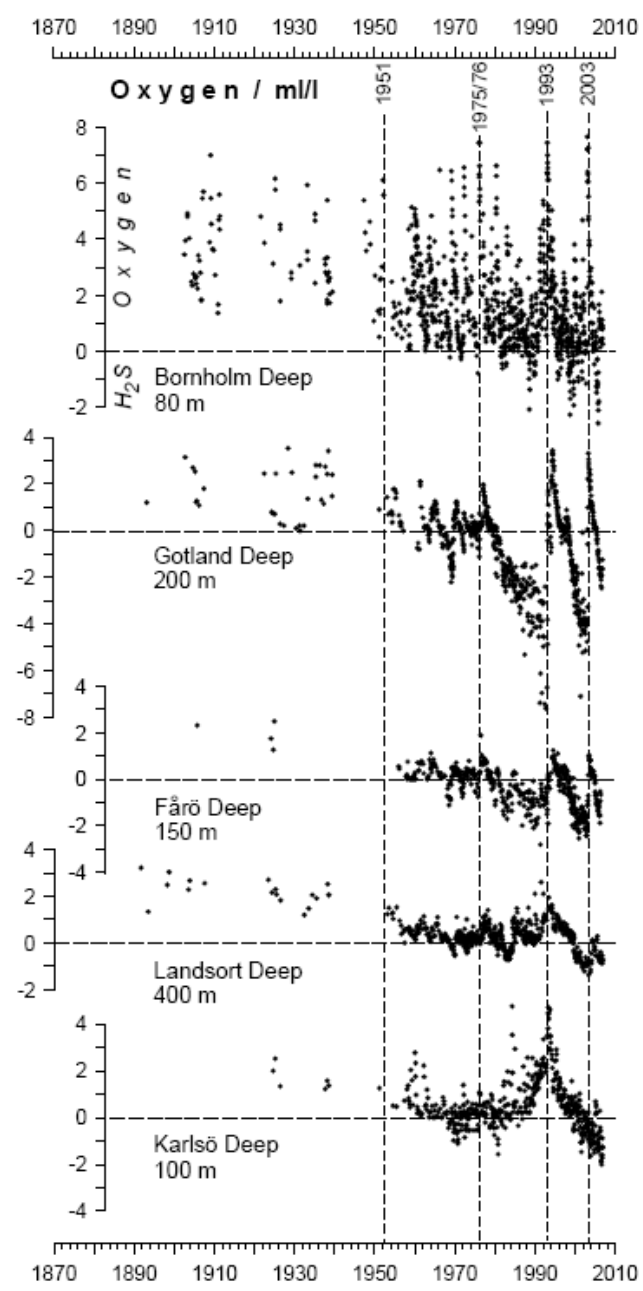
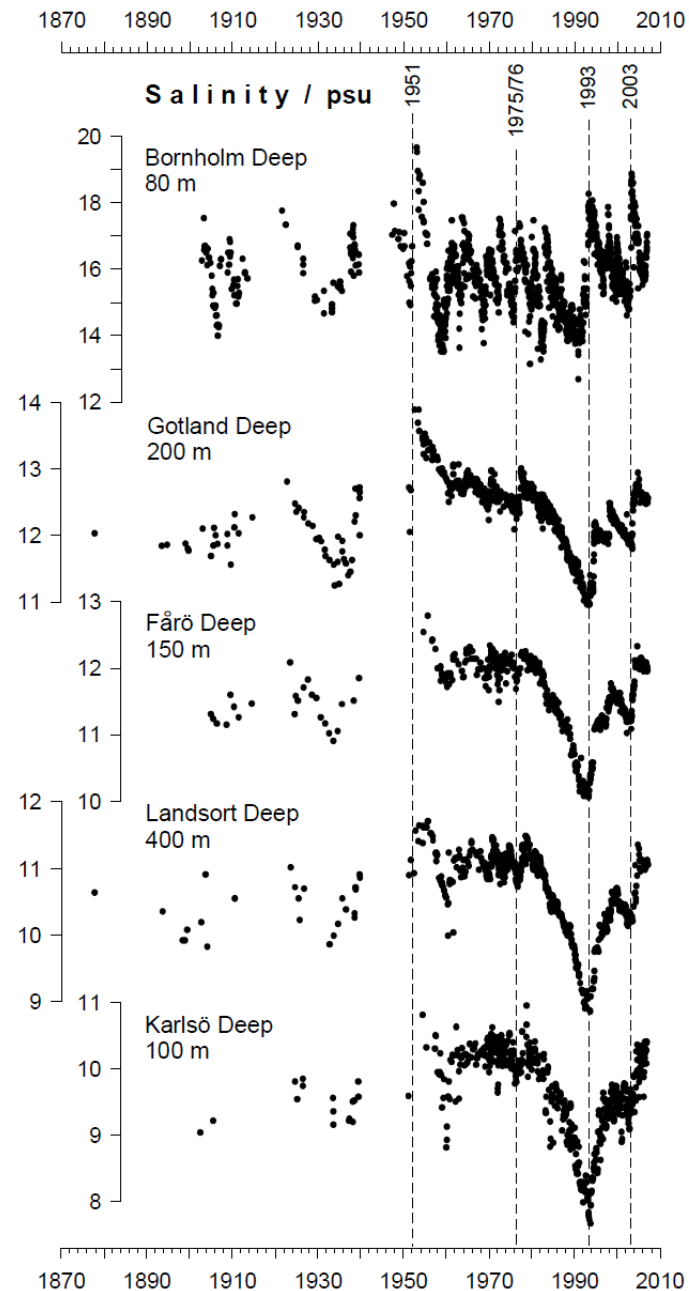
- Addition of organic matter represents an enrichment of the ecosystem
- If rate of input > bacterial degradation = accumulation
- Rate of bacterial action depends on temperature, oxygen availability
- Lead to de-oxygenation
- Therefore: If organic waste is within capacity = enrichment and if accumulation > development of anoxic conditions<



# Fertilizers

- **Agricultural fertilizers** – may have similar effect to organic wastes
- Nitrates and phosphates
- Leached from arable land
- Carried by rivers to the sea
- Can enhance phytoplankton production
- Anoxic conditions
- Eutrophication?

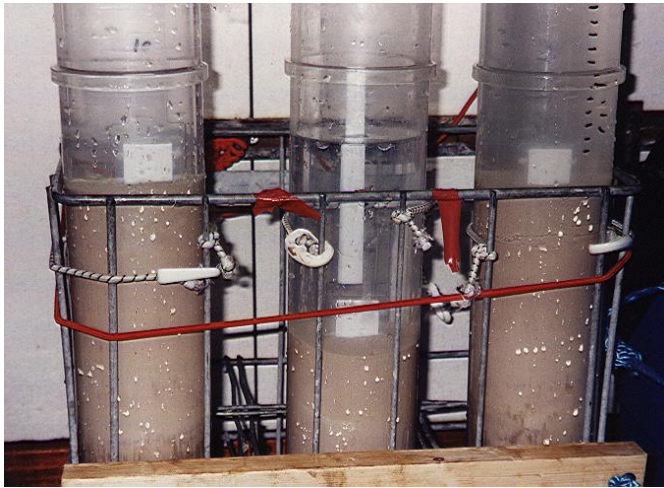






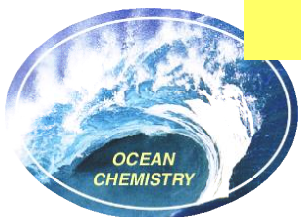
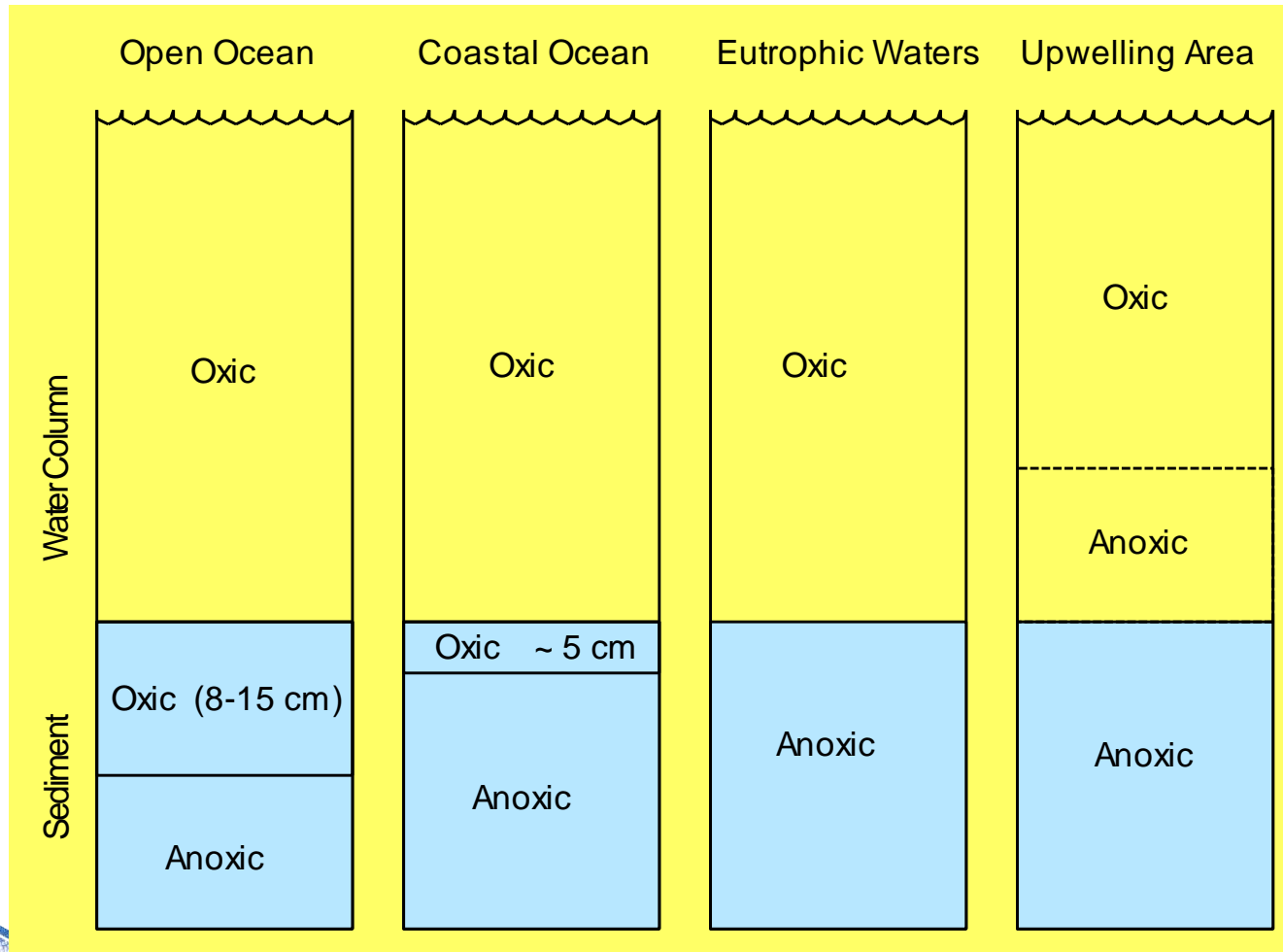
## 2. In Sediments:

- Relatively high organic carbon content
- Below a near-surface layer: relatively little mixing (molecular diffusion along long, TORTUOUS, path)  
(in near surface sediment layer: BIOTURBATION and IRRIGATION)



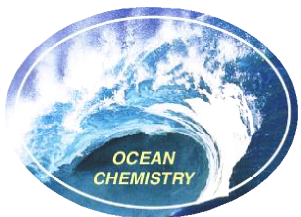


# Variation in sediment processes



# Post depositional changes in sediments, or **Diagenesis**

- Oxidation reactions in sediments break down organic carbon
- A sequence of terminal electron acceptors carry out these reactions: microbial strategies shift depending on the available oxidants
- These reactions are energetically favourable for various microbes and are microbially catalysed



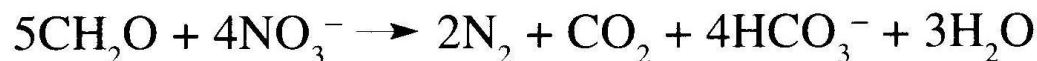




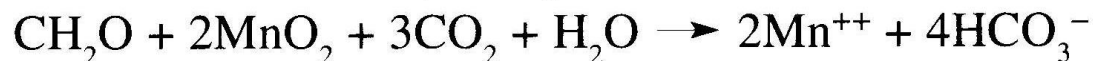
Oxygenation (oxic)



Nitrate reduction (mainly anoxic)



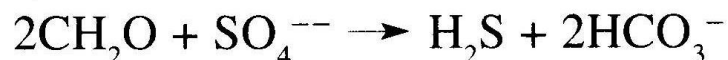
Manganese oxide reduction (mainly anoxic)



Ferric oxide (hydroxide) reduction (anoxic)



Sulfate reduction (anoxic)



Methane formation (anoxic)



---

*Note:* Organic matter schematically represented as  $\text{CH}_2\text{O}$ .

*Major processes of organic matter decomposition in marine sediments. Reactions succeed one another in the order written as each oxidant is completely consumed.*

**Table 12.2** *Stoichiometry and energy yield (Gibbs free energy,  $\Delta G^{\circ'}$ ) for the oxidation of marine organic matter using a variety of natural oxidants*

Reaction	Gibbs Free Energy
[1] $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16} + 175 \text{ O}_2 \rightarrow$ $122 \text{ CO}_2 + 16 \text{ NO}_3^- + 16 \text{ H}^+ + 138 \text{ H}_2\text{O}$	$\Delta G^{\circ'} = -73.2 \text{ MJ}$
[2] $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16} + 114.4 \text{ NO}_3^- + 114.4 \text{ H}^+ \rightarrow$ $122 \text{ CO}_2 + 57.2 \text{ N}_2 + 16 \text{ NH}_3 + 179.2 \text{ H}_2\text{O}$	$\Delta G^{\circ'} = -65.6 \text{ MJ}$
[3] $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16} + 286 \text{ MnO}_2 + 572 \text{ H}^+ \rightarrow$ $122 \text{ CO}_2 + 286 \text{ Mn}^{++} + 16 \text{ NH}_3 + 408 \text{ H}_2\text{O}$	$\Delta G^{\circ'} = -65.2 \text{ MJ}$
[4] $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16} + 286 \text{ Fe}_2\text{O}_3 + 1144 \text{ H}^+ \rightarrow$ $122 \text{ CO}_2 + 572 \text{ Fe}^{++} + 16 \text{ NH}_3 + 694 \text{ H}_2\text{O}$	$\Delta G^{\circ'} = -33.7 \text{ MJ}$
[5] $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16} + 71.5 \text{ SO}_4^{--} + 71.5 \text{ H}^+ \rightarrow$ $122 \text{ CO}_2 + 16 \text{ NH}_3 + 71.5 \text{ HS}^- + 122 \text{ H}_2\text{O}$	$\Delta G^{\circ'} = -12.8 \text{ MJ}$
[6] $(\text{CH}_2\text{O})_{80}(\text{CH}_2)_{42}(\text{NH}_3)_{16} \rightarrow$ $40 \text{ CO}_2 + 40 \text{ CH}_4 + 16 \text{ NH}_3 + (\text{C}_{42}\text{H}_{84})$	$\Delta G^{\circ'} = -6.0 \text{ MJ}$

All the reactions are thermodynamically favourable.

However ALL (except #1) are mediated **only** by bacteria (or bacteria-protoczoa consortia).

Specialized enzymes are required. Usually multiple species are required for each step.

Reactions take place sequentially – most energy favorable first, then.....



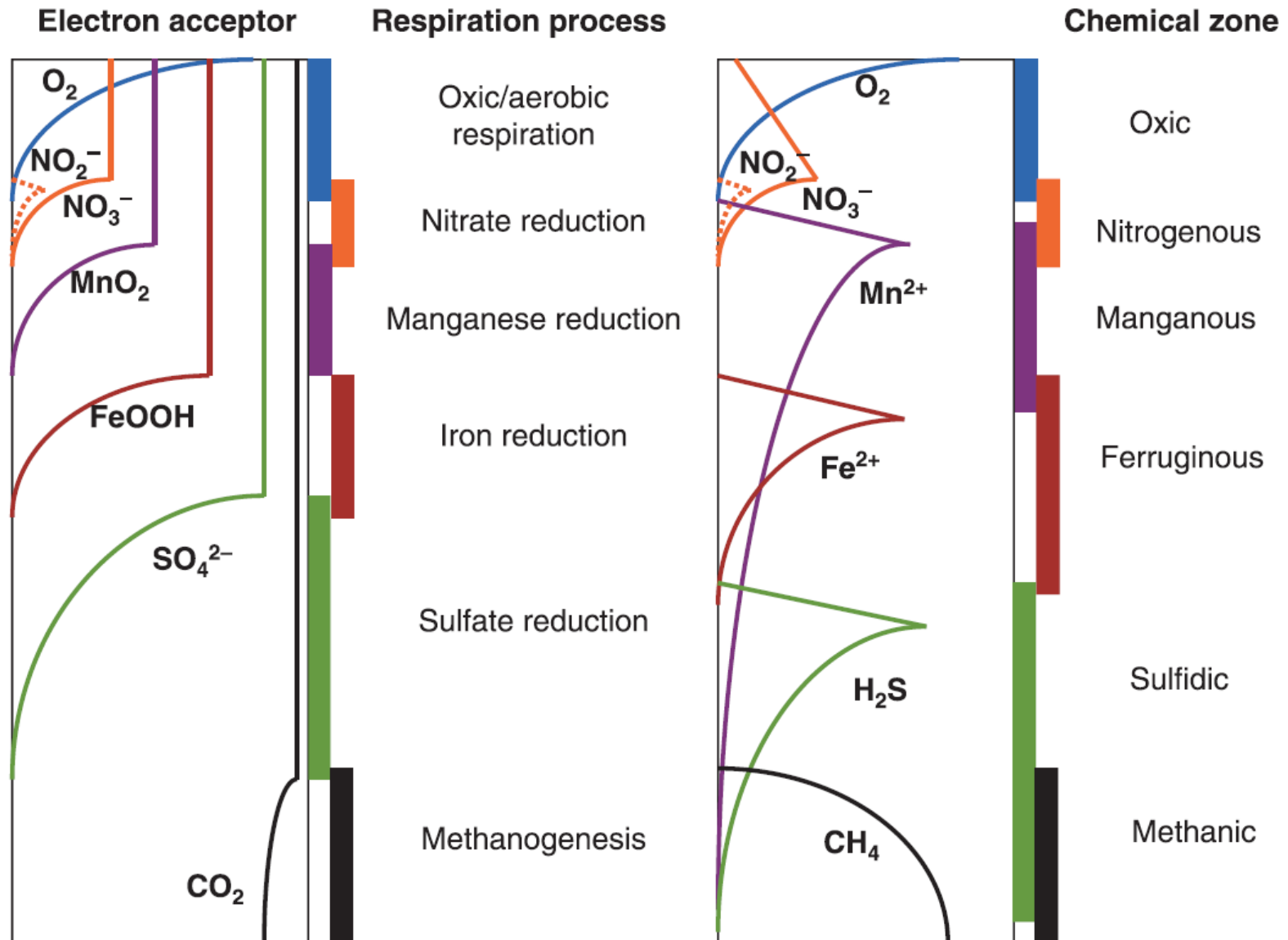
## ***Availability of oxidants***

In seawater:

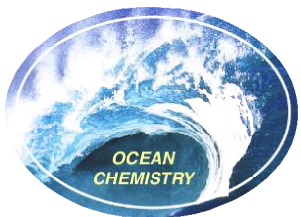
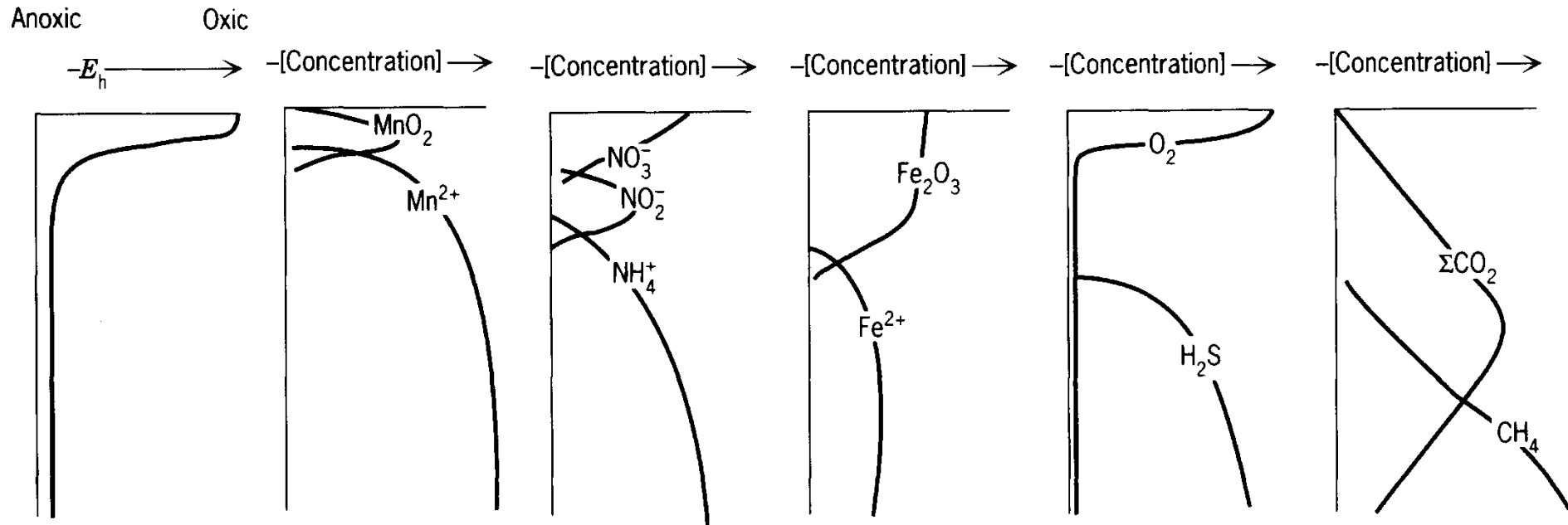
[O <sub>2</sub> ]	< 400 x 10 <sup>-6</sup> mol kg <sup>-1</sup>
[NO <sub>3</sub> ]	< 20 x 10 <sup>-6</sup> mol kg <sup>-1</sup>
[MnO <sub>2</sub> ] [Fe <sub>2</sub> O <sub>3</sub> ]	very low in oxic seawater
[SO <sub>4</sub> ]	28 x 10 <sup>-3</sup> mol kg <sup>-1</sup>

Therefore sulphate has the potential to be the most important oxidant..

In sediments, the manganese and iron oxides supplied from ***mineral*** phases can play a much larger role as oxidants.



# Vertical segregation in sediments





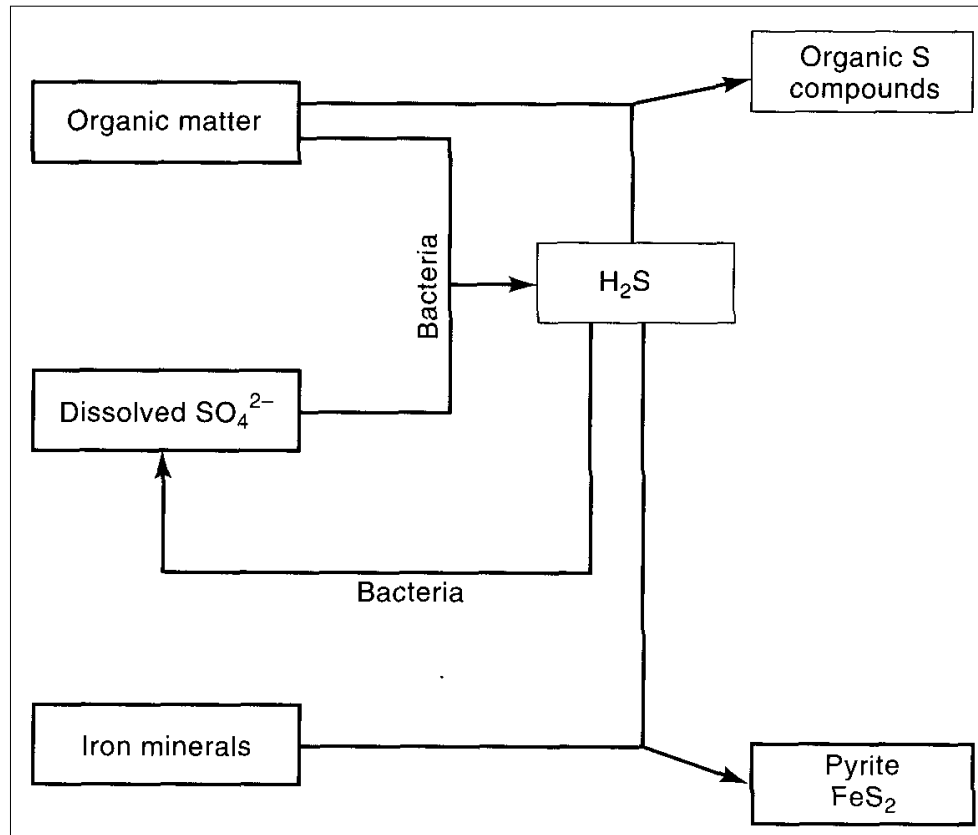
# ***Sulphate Removal***

- Supply of organic material, respiration and restricted diffusion of  $O_2$  from overlying water uses up all  $O_2$  at some depth in sediments
- Most ocean sediments (e.g. >10-20cm below interface) are ANOXIC
- Organic matter can continue to be bacterially decomposed using other oxidants (electron acceptors): e.g.  $NO_3^-$ ,  $NO_2^-$ , Mn and Fe oxides, and then  $SO_4$
- In locations where organic matter supply to sediments is high, (e.g. underneath shallower productive regions of the ocean), then all the sulphate in sediment pore waters can be used up



# ***What happens to the $H_2S$ produced in sediments***

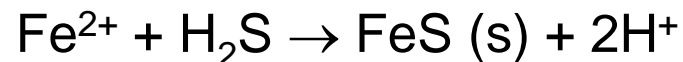
- some diffuses upwards and is re-oxidised to sulphate (cycle)
- some reacts with iron minerals to form pyrite and is buried in the sediments



*Simplified version of the process of sedimentary pyrite formation*



- Additional sulphate can then diffuse into the sediment from overlying waters and be reduced
- Most of the  $\text{H}_2\text{S}$  produced diffuses upwards to the sediment-water interface, reacts with  $\text{O}_2$  and reforms  $\text{SO}_4^{2-}$  there
- About 10% of the  $\text{H}_2\text{S}$  reacts with  $\text{Fe(II)}$  from (land-derived) iron-containing minerals and precipitates as sulfides:



- Slowly, these sulphides are transformed to pyrite ( $\text{FeS}_2$ ) and buried



# Thermodynamics versus Kinetics

- Thermodynamics tell us how things are at equilibrium;
- The oceans are far from equilibrium due to Life;
- Kinetics tells us how fast or slow a reaction occurs;
- Many redox reactions occur very slowly in the absence of microbial catalysis;

