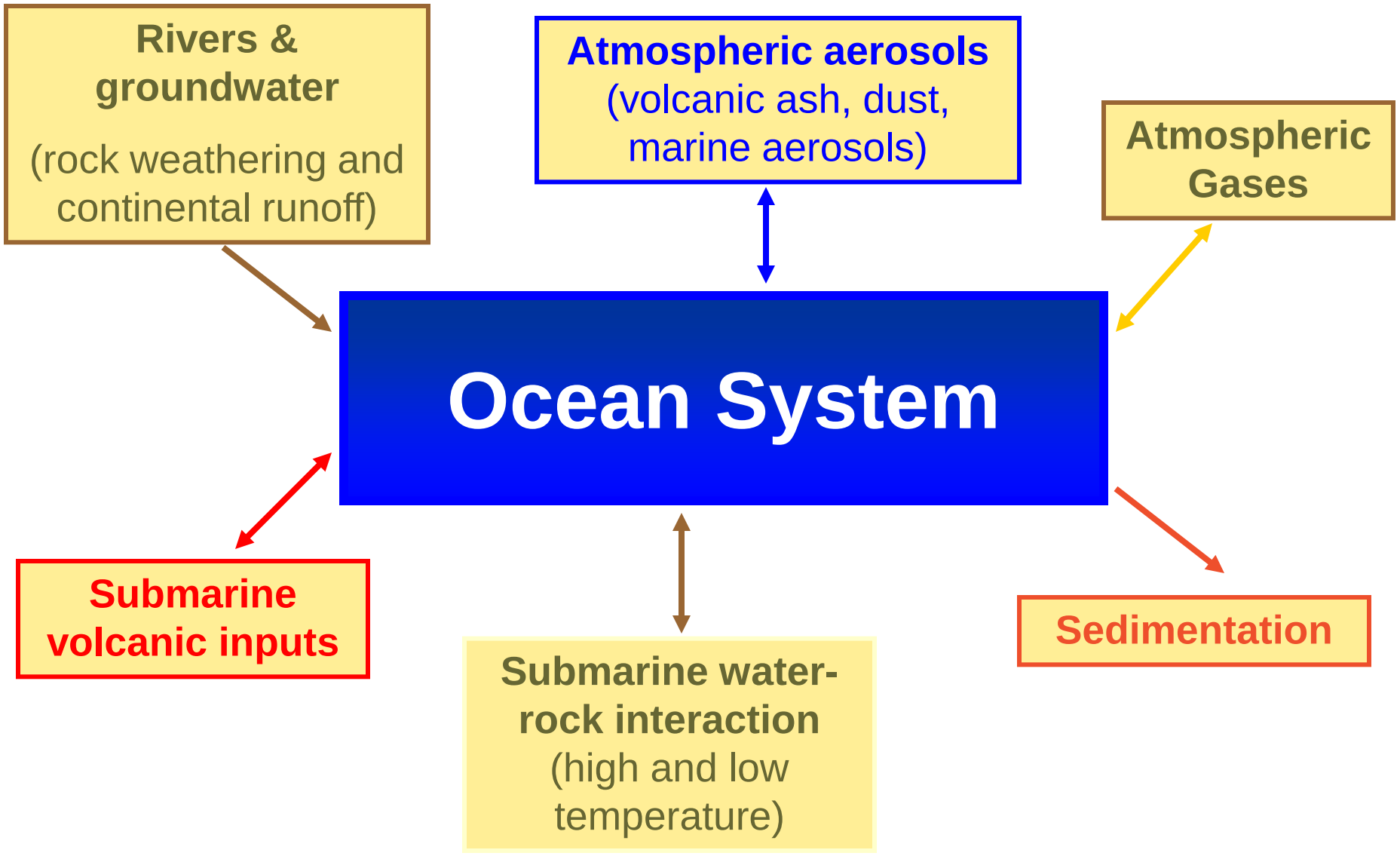
Ocean as a chemical system



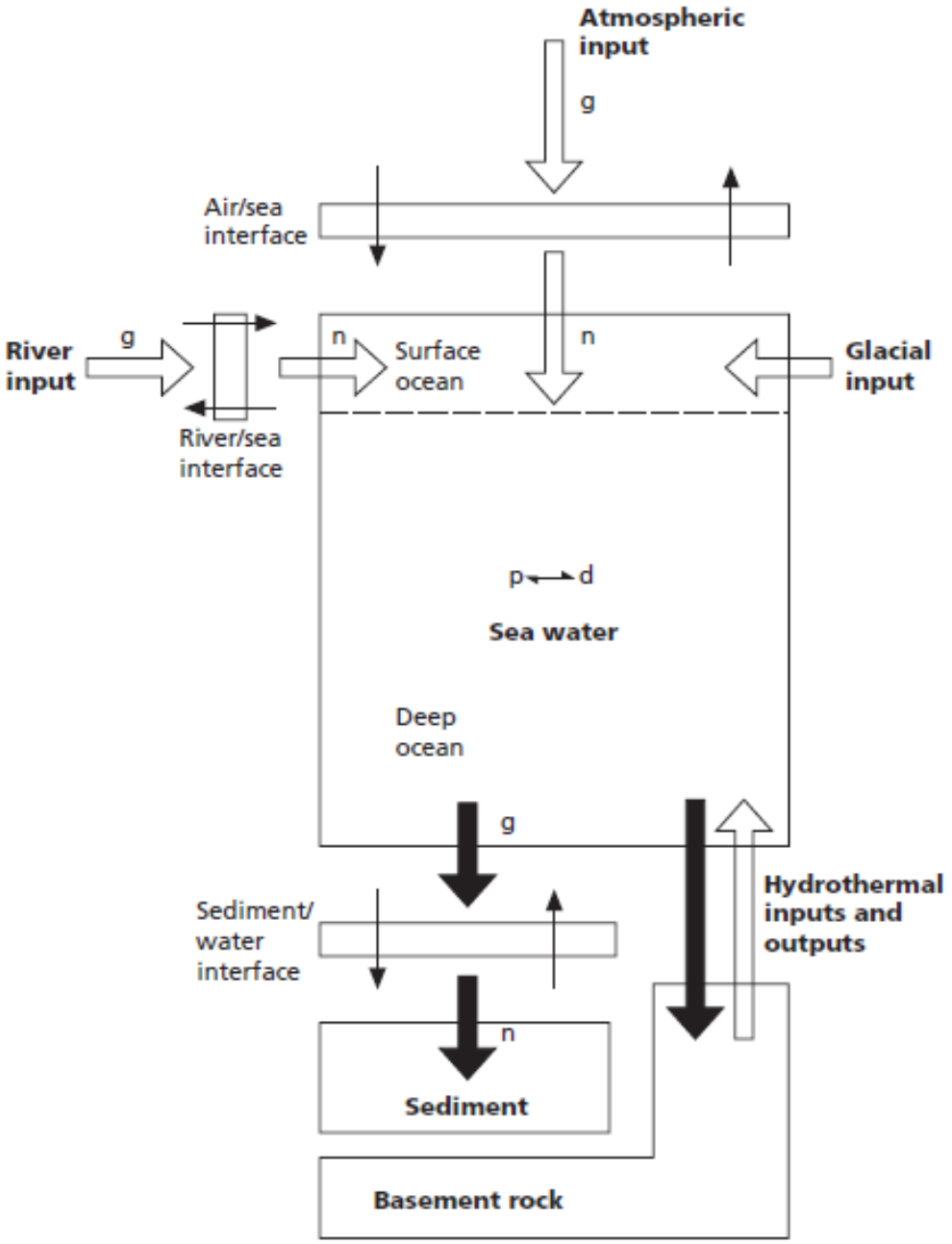
Ocean as a chemical system

source/input →

internal reactivity →

sink/output

transport cycle



Marine geochemistry

- **How do the oceans work as a chemical system?**

  describing chemical processes

  identifying pathways (source to sink journey)

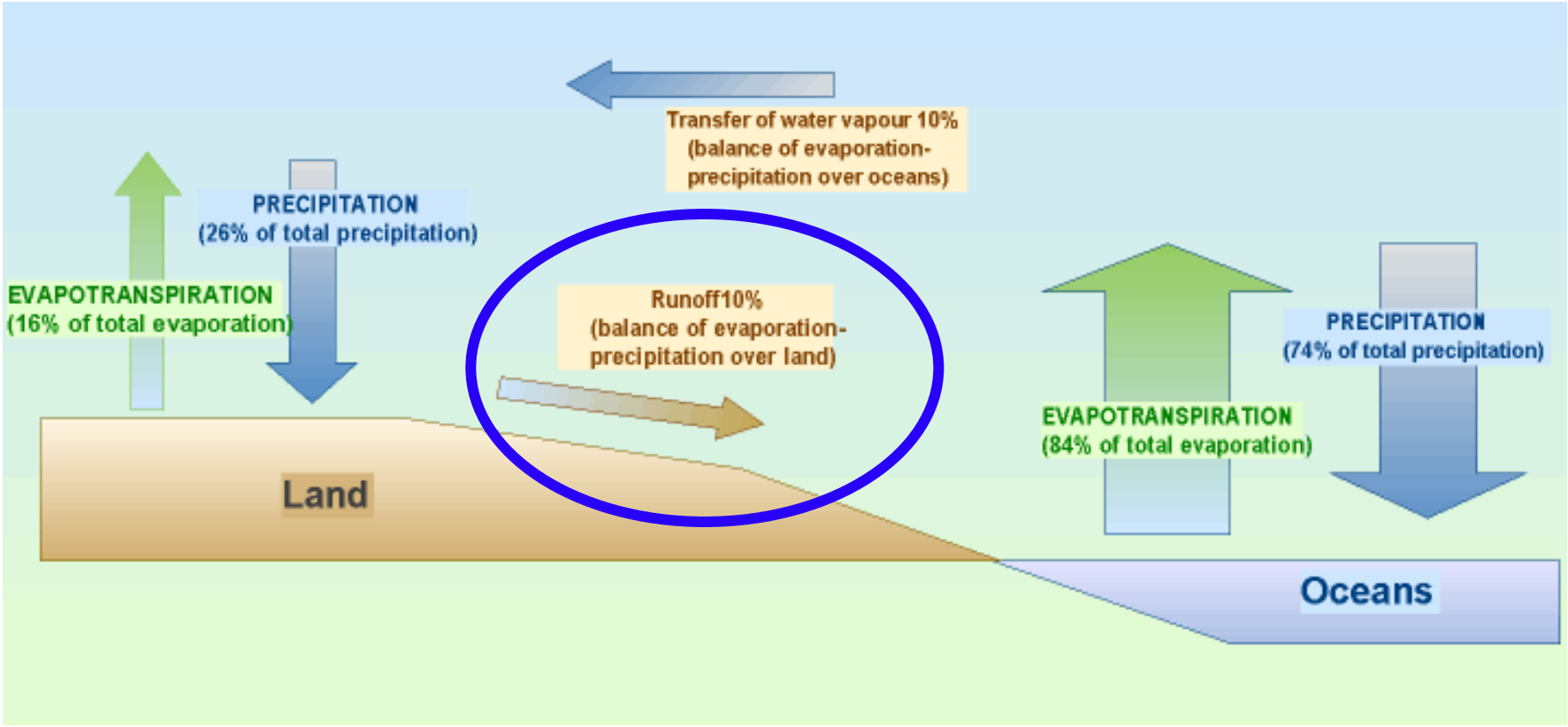
  relate them to fluxes

  particulate – dissolved interaction

  transport – removal process

  marine mass balances

World Water Balance



Waugh 1990

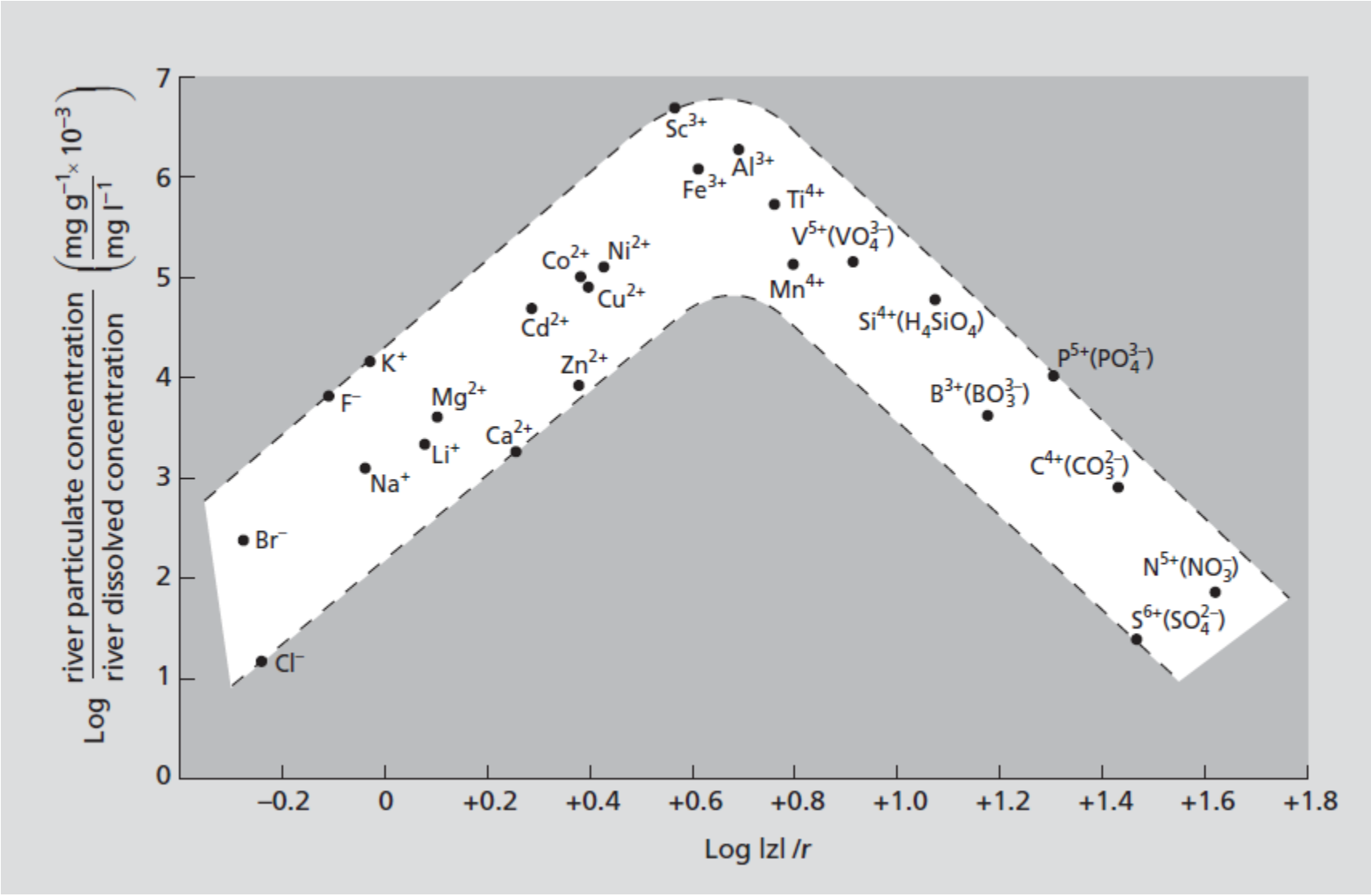
River water drainage

Table 3.1 The major element composition of rivers draining into the oceans; units, mg l^{-1} (data from Martin & Whitfield (1983) and Riley & Chester (1971)).

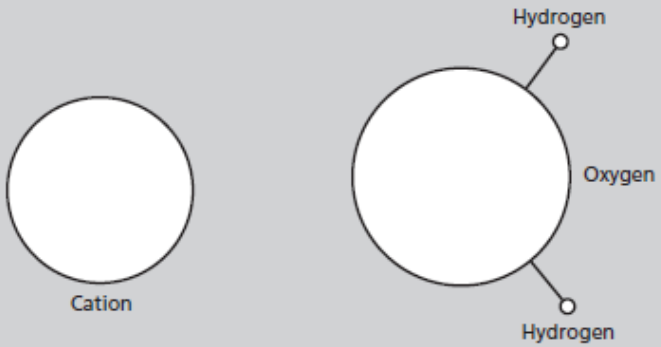
Element	Atlantic	Indian	Arctic	Pacific	World average river water	Sea water
Na^+	4.2	8.5	8.8	5.2	5.3	10 733
K^+	1.4	2.5	1.2	1.2	1.5	399
Ca^{2+}	10.5	21.6	16.1	13.9	13.3	412
Mg^{2+}	2.5	5.4	1.3	3.6	3.1	1 294
Cl^-	5.7	6.8	11.8	5.1	6.0	19 344
SO_4^{2-}	7.7	7.9	15.9	9.2	8.7	2 712
HCO_3^-	37	94.9	63.5	55.4	51.7	142
SiO_2^{3-}	9.9	14.7	5.1	11.7	10.7	—
TDS*	78.9	154.9	123.7	105.3	101.6	—

* TDS = total dissolved solids.

Pattern of element solubility in river waters

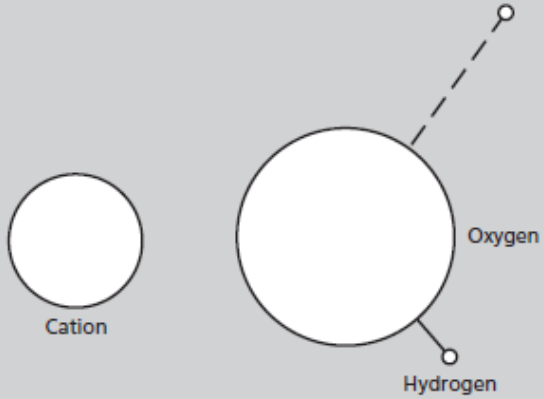


(a)



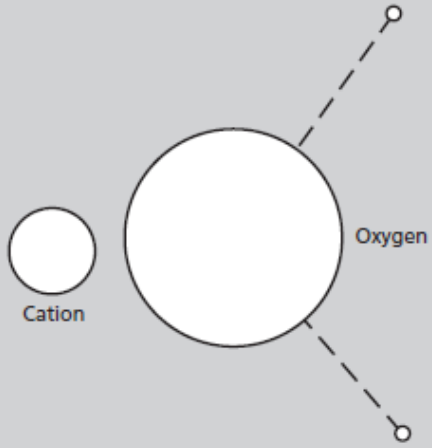
Cation log $z/r < +0.48$
Cation electronegativity < 1.2

(b)



Cation log z/r between +0.48 and +1.08
Cation electronegativity between 1.2 and 1.9

(c)



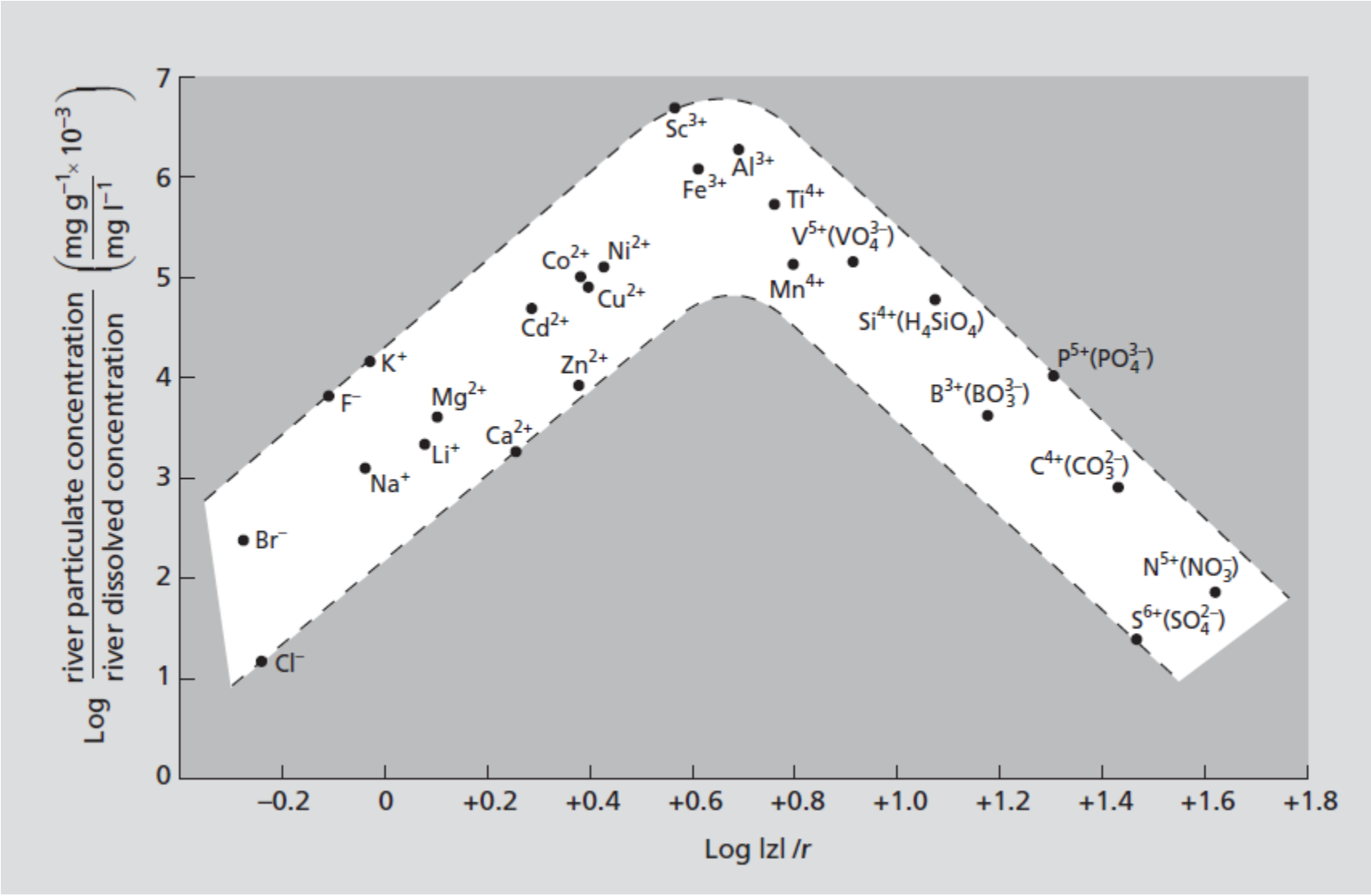
Cation log $z/r > +1.08$
Cation electronegativity > 1.9

Ca^{2+}, Na^{+}, K^{+} and Mg^{2+}

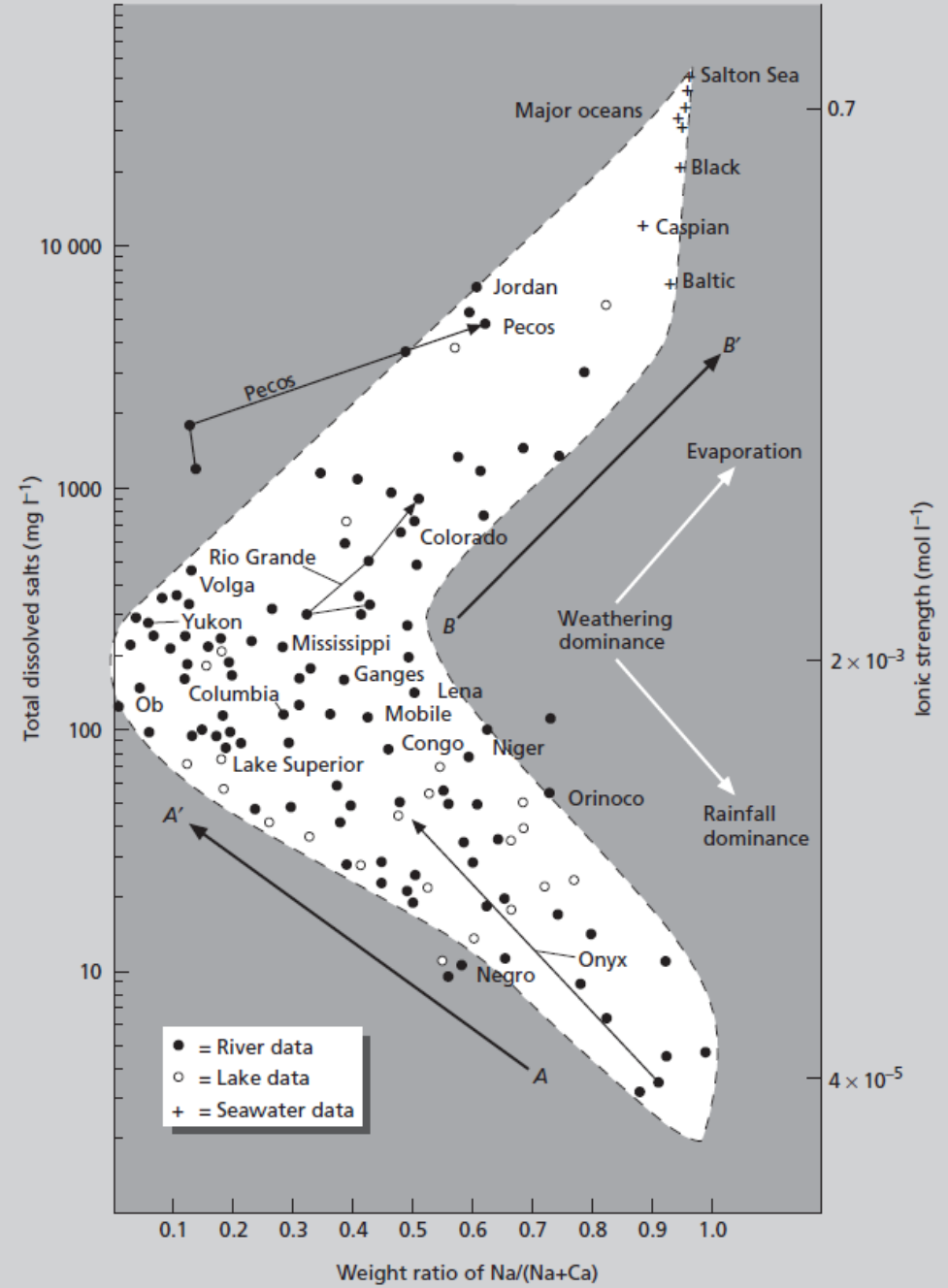
$$Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow FeOH_{3(s)} + 3H^{+}_{(aq)}$$

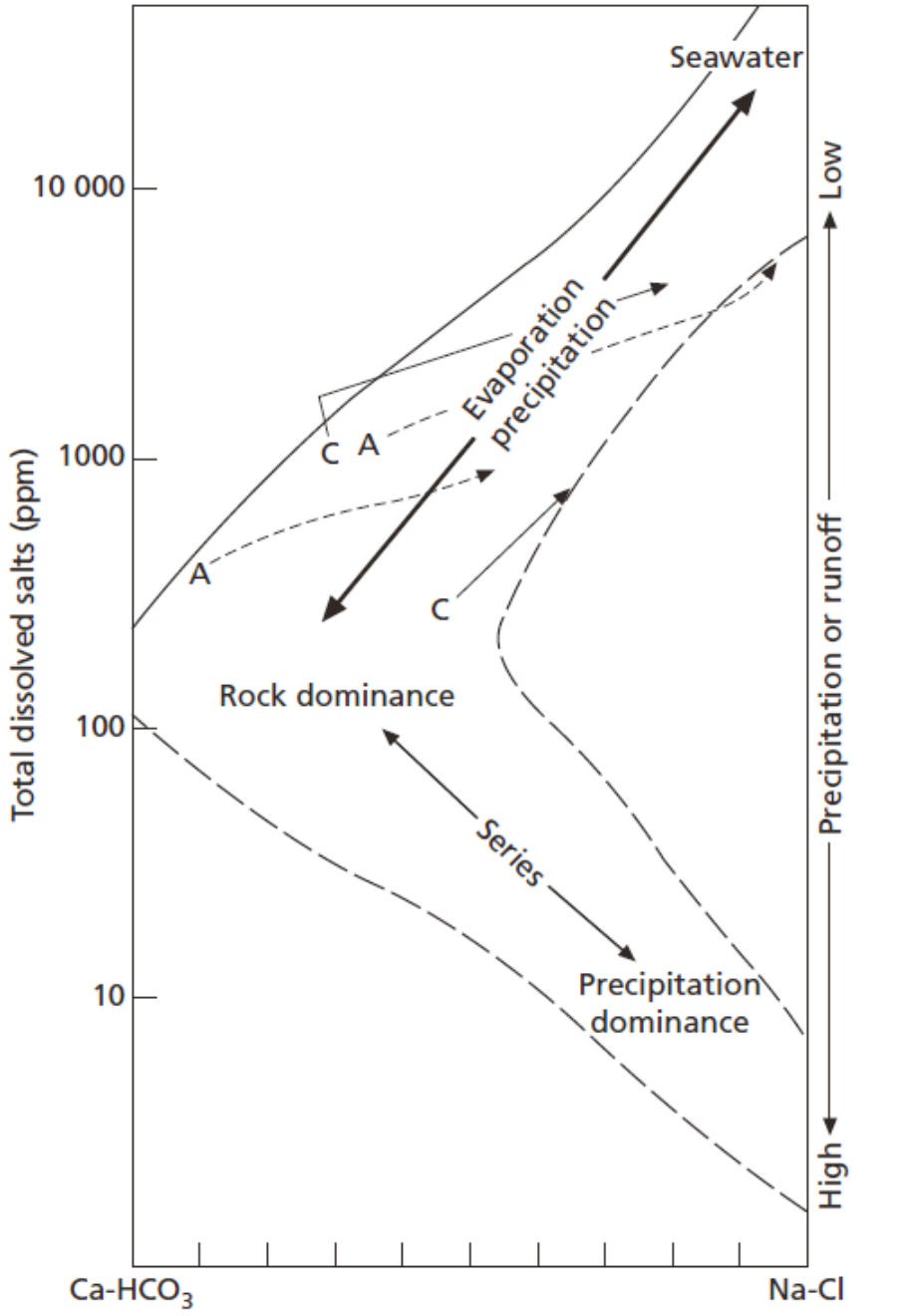
$$S(VI)_{(s)} + 4H_2O_{(l)} \rightarrow SO^{2-}_{4(aq)} + 2H^{+}_{(aq)}$$

Pattern of element solubility in river waters

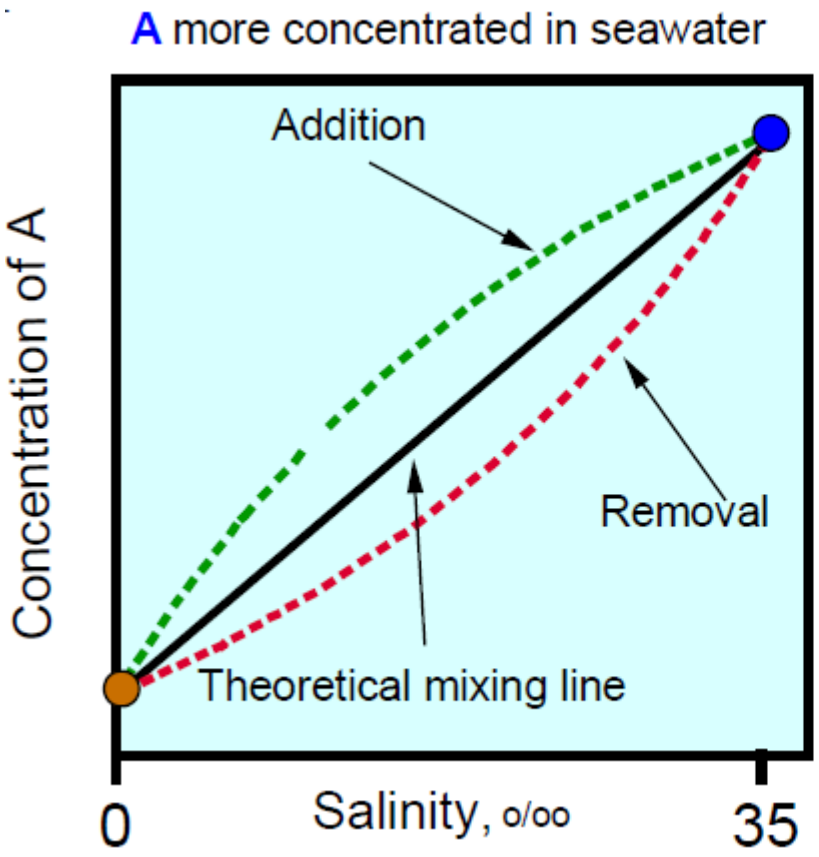


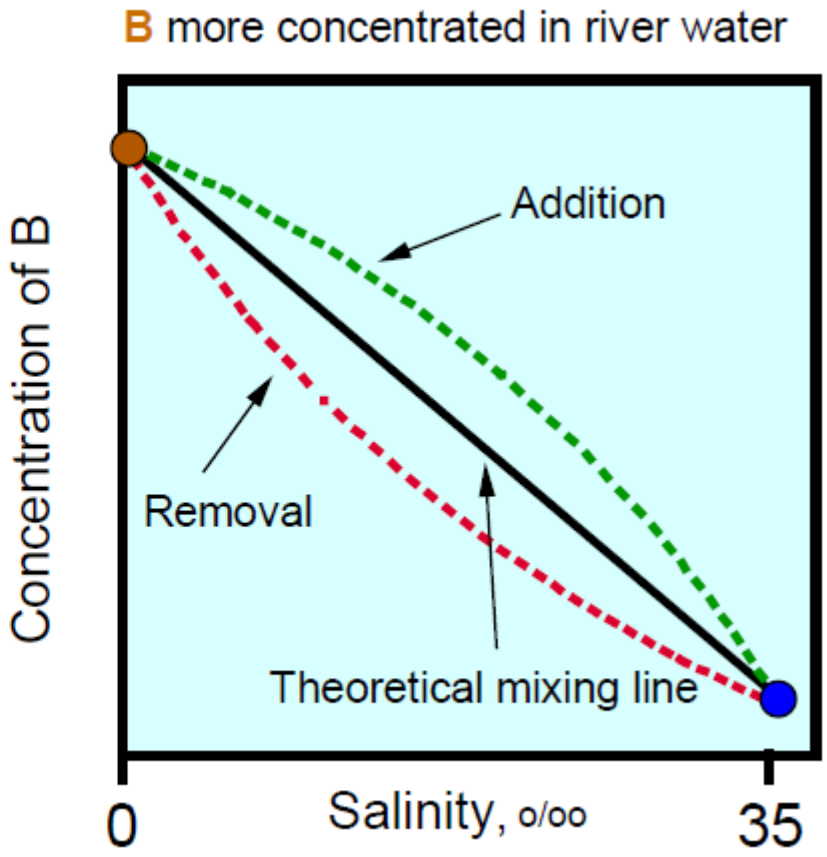
Chemical signals transported by rivers



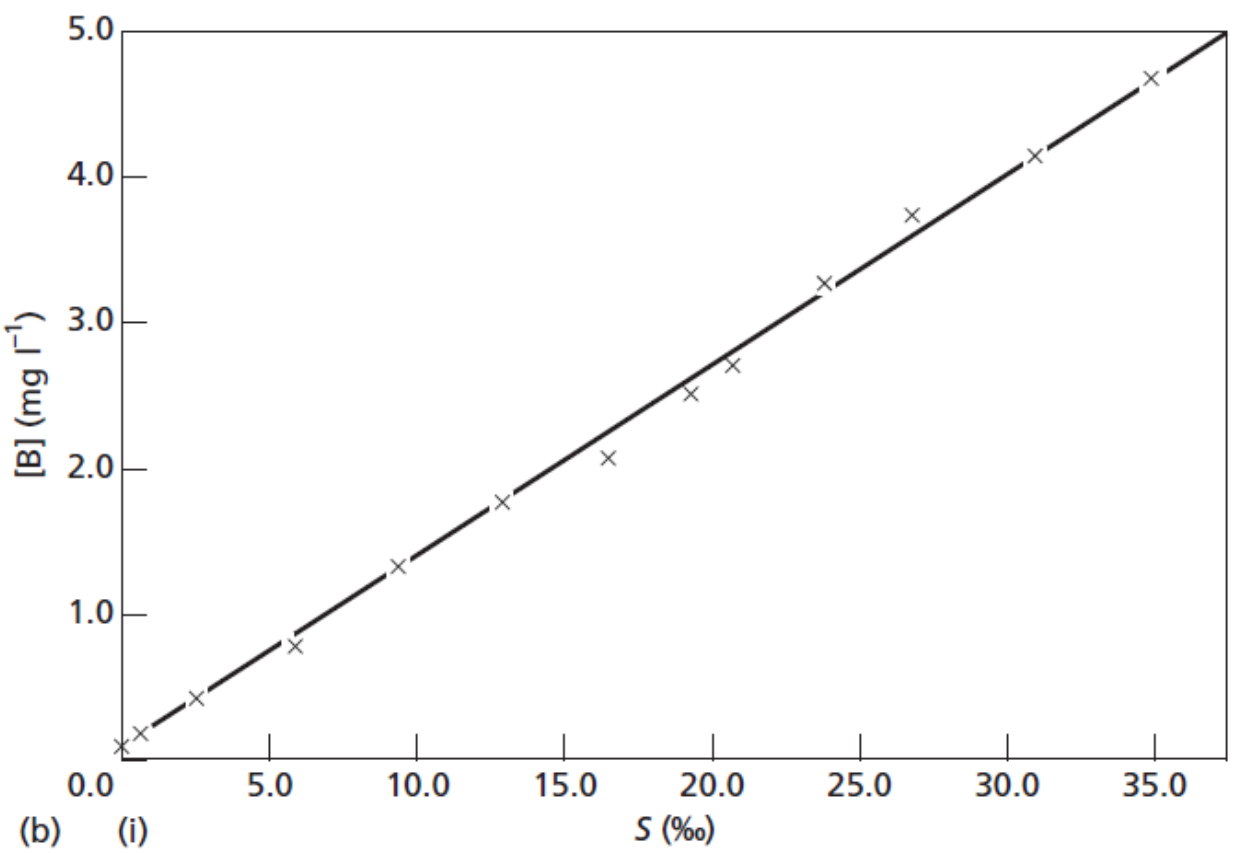


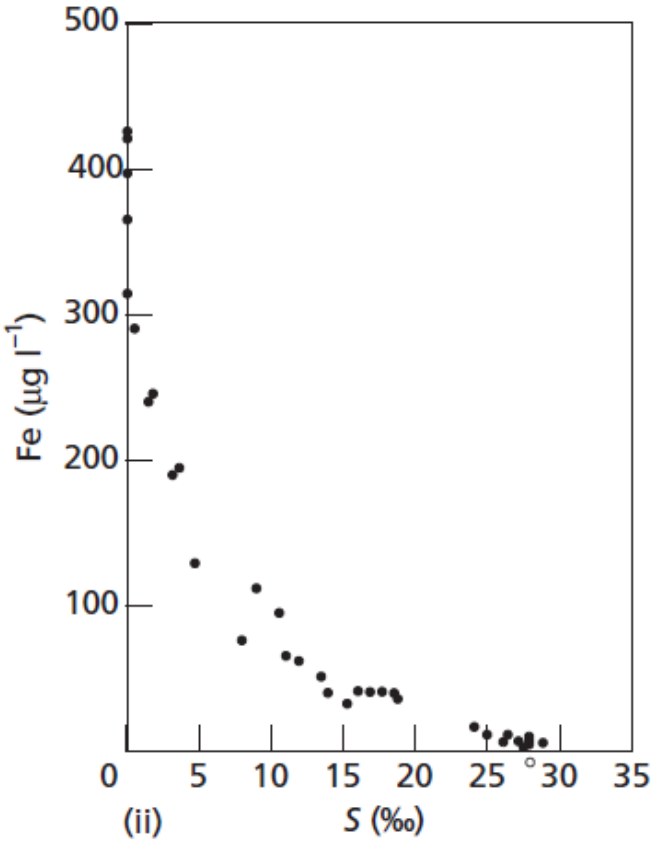
Water mixing in estuaries





Water mixing in estuaries





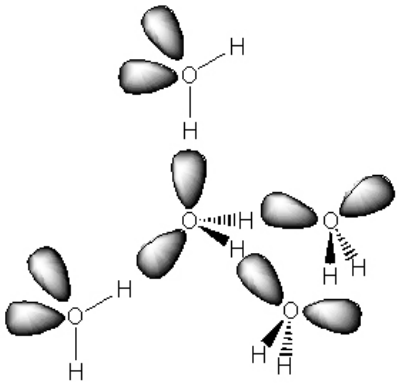
Ocean Geochemistry

- Oceans are the main reservoir of water on the Earth ~97% by volume.
- Much higher contents of dissolved solids than most other natural waters (35 g / kg water)
- Compared to other natural waters, seawater is remarkably homogeneous in composition

Total dissolved solids (g/kg)	
Rain	0.005
River	0.1
Ocean	35

Properties of Seawater

- Water covers 71% of the earth's surface
- 97% of the water is contained in the oceans
- Water molecules – hydrogen bridge bond
- High solubility (except oil)
- High heat capacity
- High heat of vaporisation
- Transport medium
- Salinity varies around 35g salt/kg

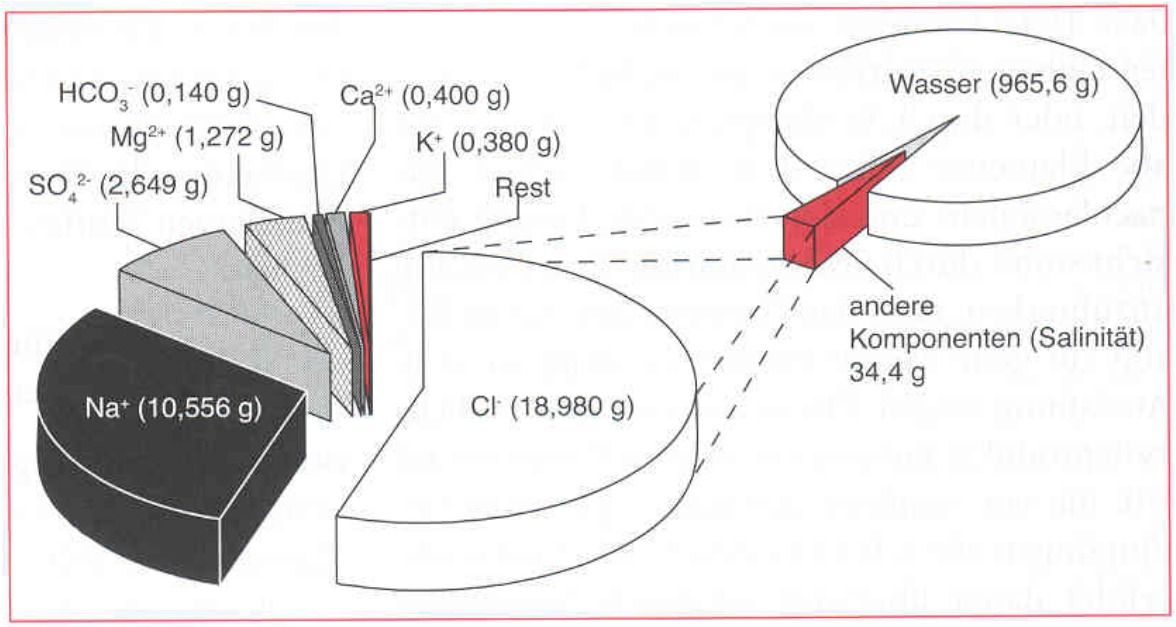


Ocean as a chemical system

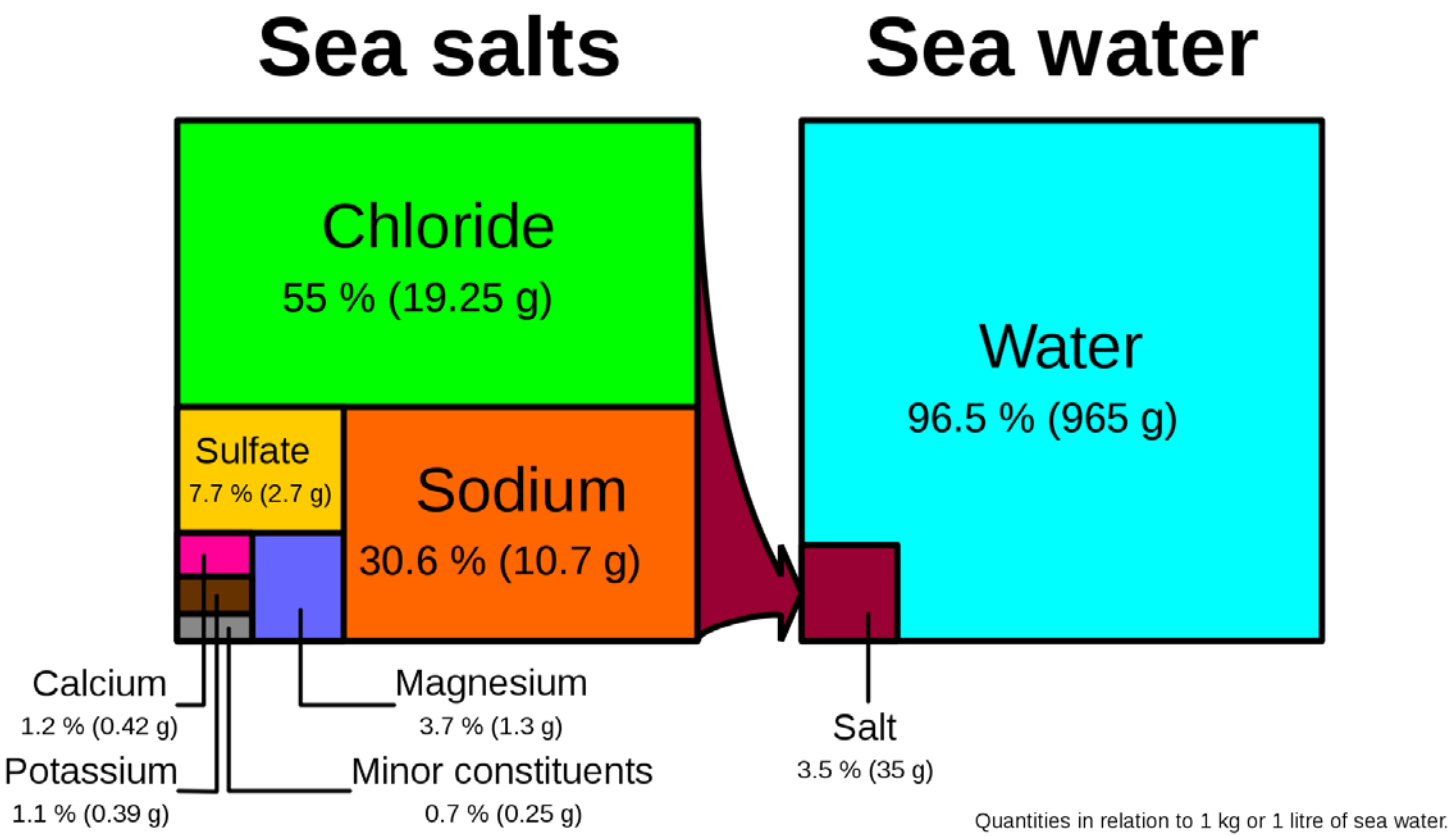
Ocean reservoir

Chemical composition of seawater differs largely from that of stream water

Element budget of seawater depends on input and output/discharge



Composition of Seawater



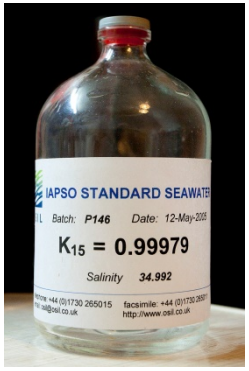
Salinity

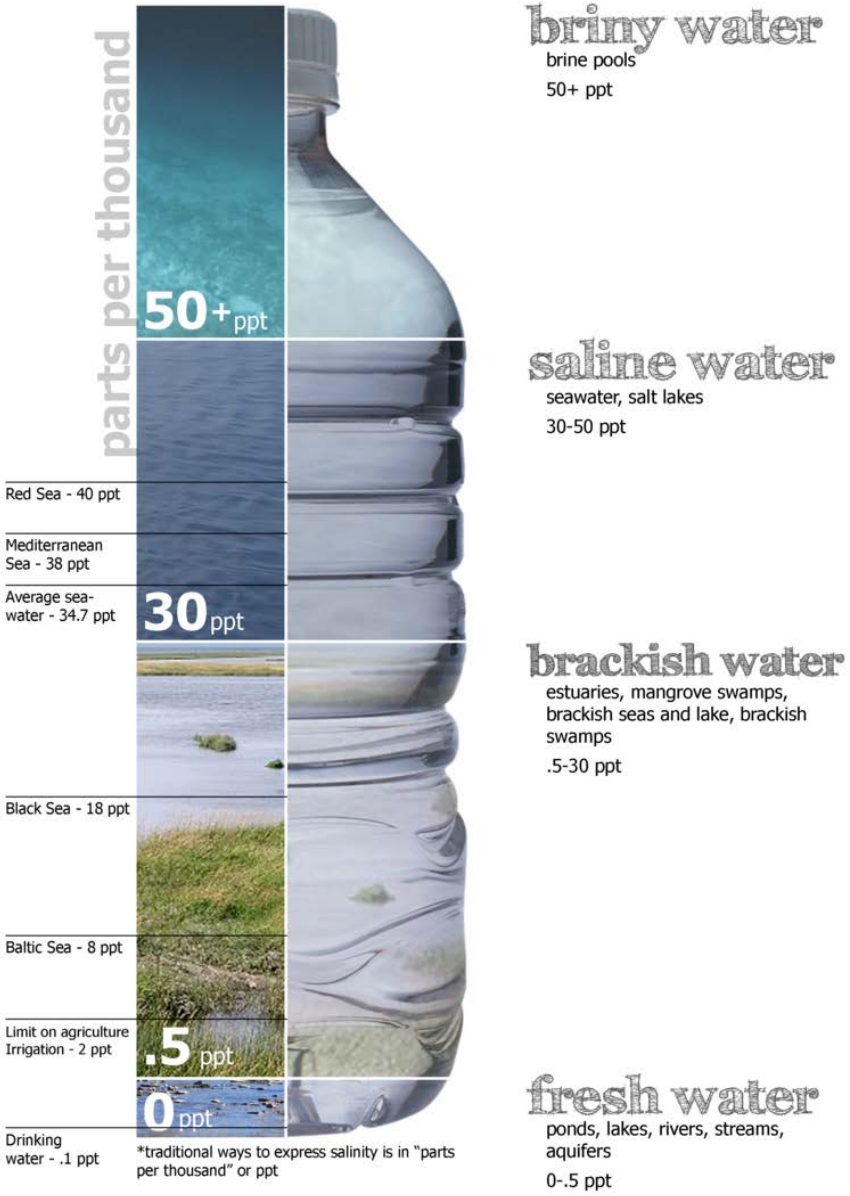
Quantity of dissolved salt content of the water
(weight in grams of the dissolved inorganic matter in one kilogram of water)

Chlorinity: concentration of dissolved chloride

$$S‰ = 1.80655\ Cl‰$$

Standard seawater has a salinity of 34.99 ppt (or ‰) and a chlorinity of 19.37 ‰.
The electrical conductivity of this water at T=15 °C is 42.9 mS/cm





Electrical conductivity

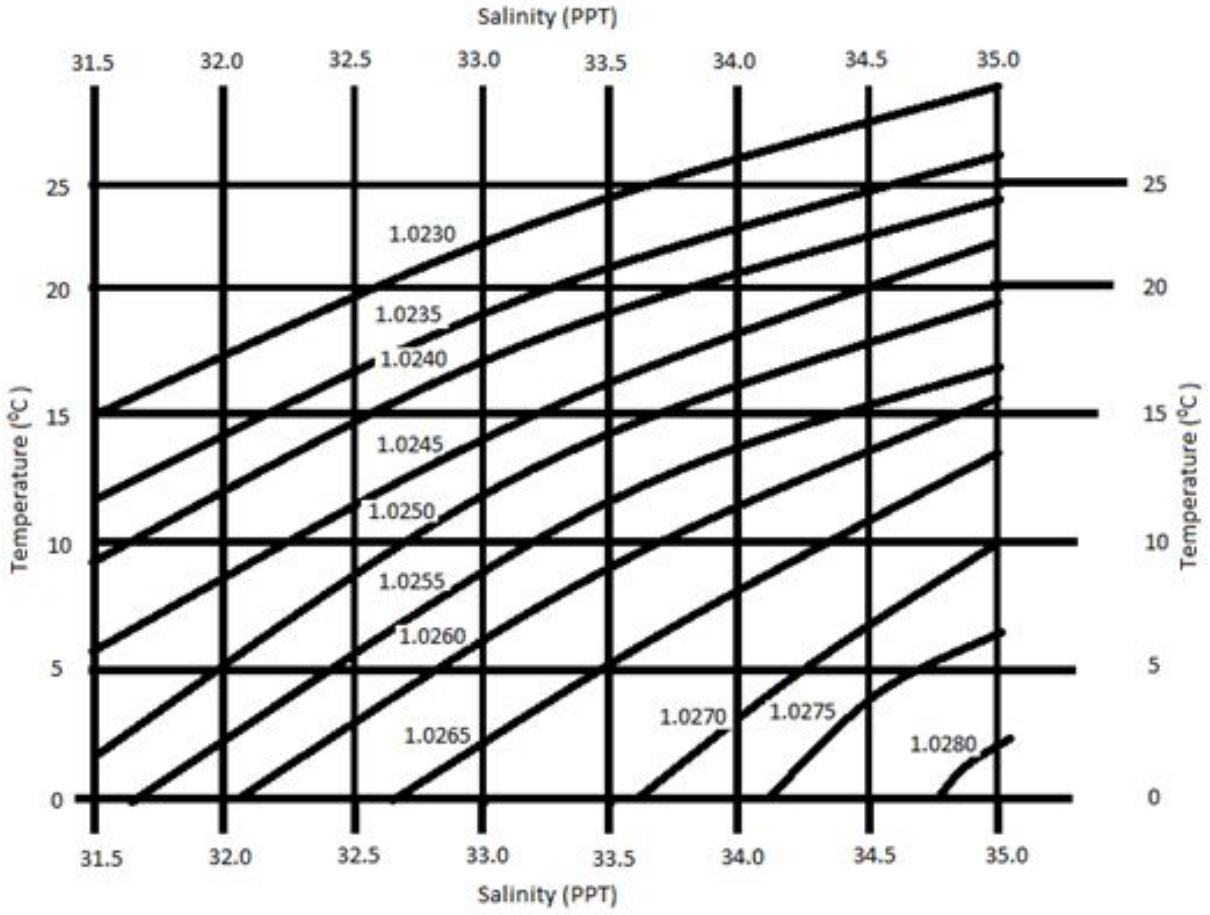
Milli-Q water	0.054 µS/cm
rainwater	30-60 µS/cm
GW Silicates	130 µS/cm
GW Carbonates	260 µS/cm
Ocean water	43000 µS/cm

1 °dH = 33 µS/cm

Temperature-salinity-density variation

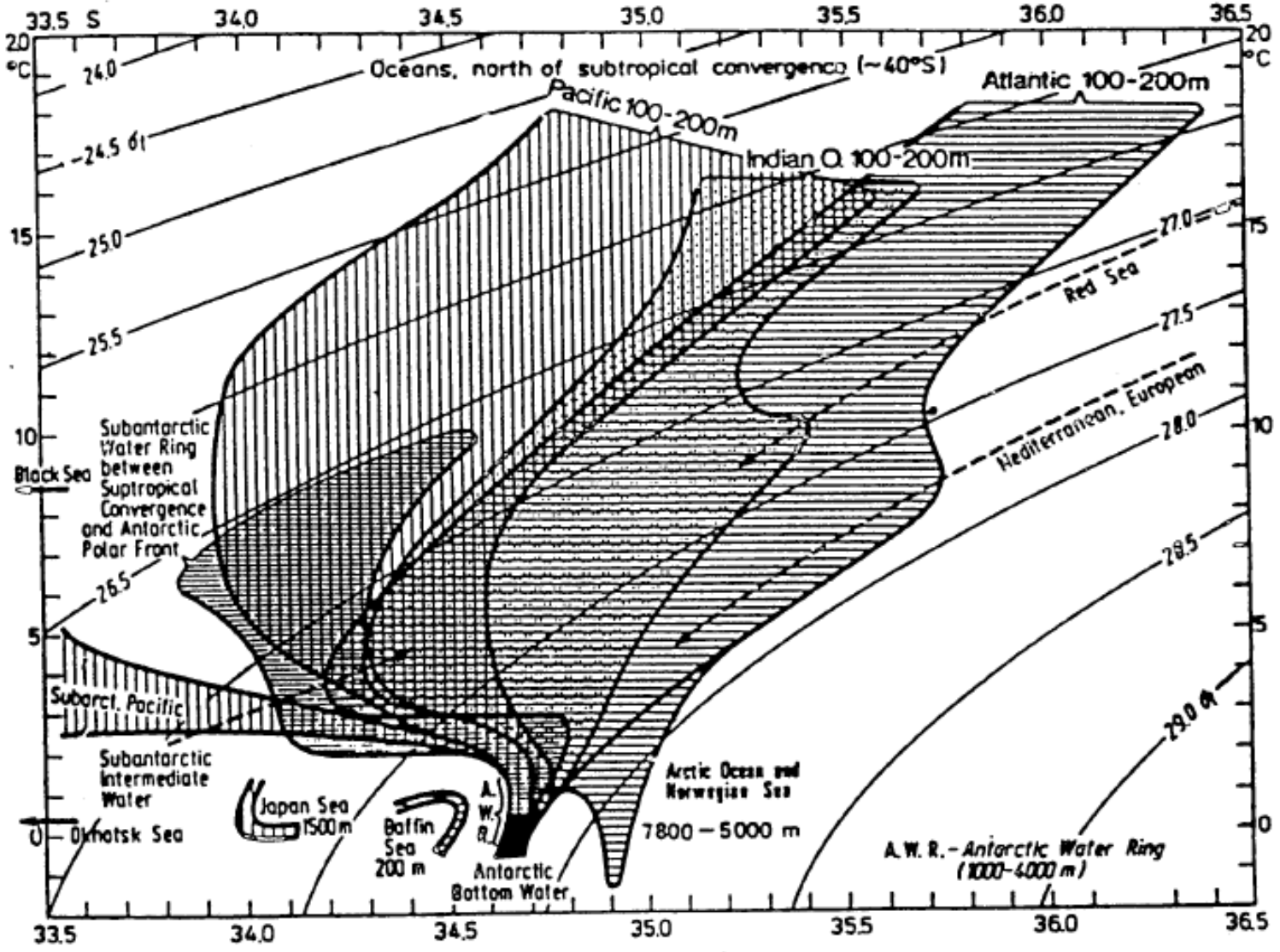
1. Seawater density is controlled by temperature and salinity

2. T of seawater is fixed at the sea surface by heat exchange with atmosphere

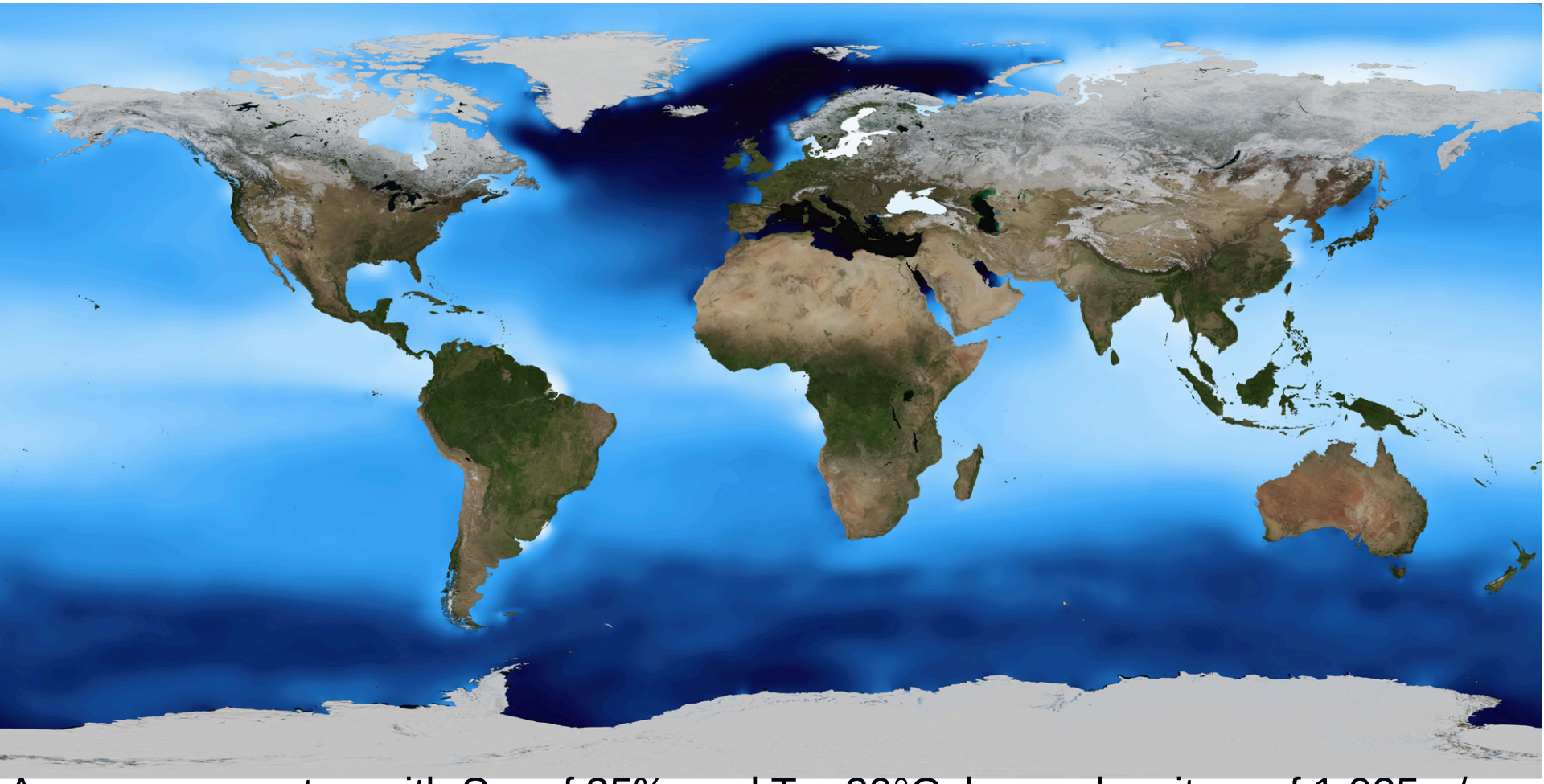


Temperature and salinity can only be changed at the surface → conservative properties

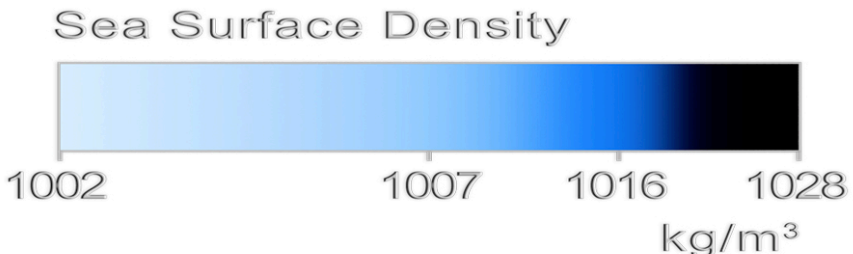
Temperature-salinity-density variation



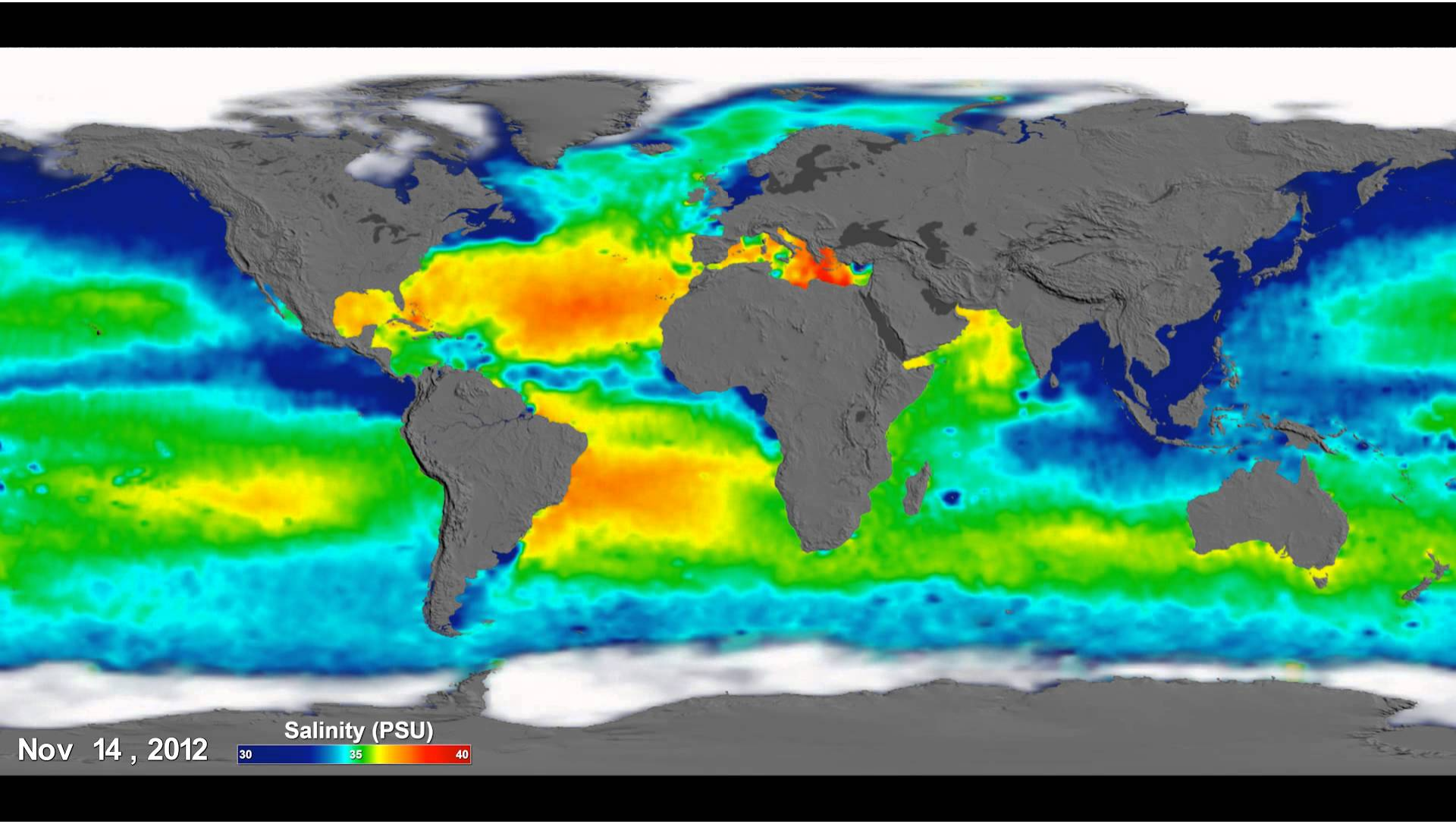
Sea surface density



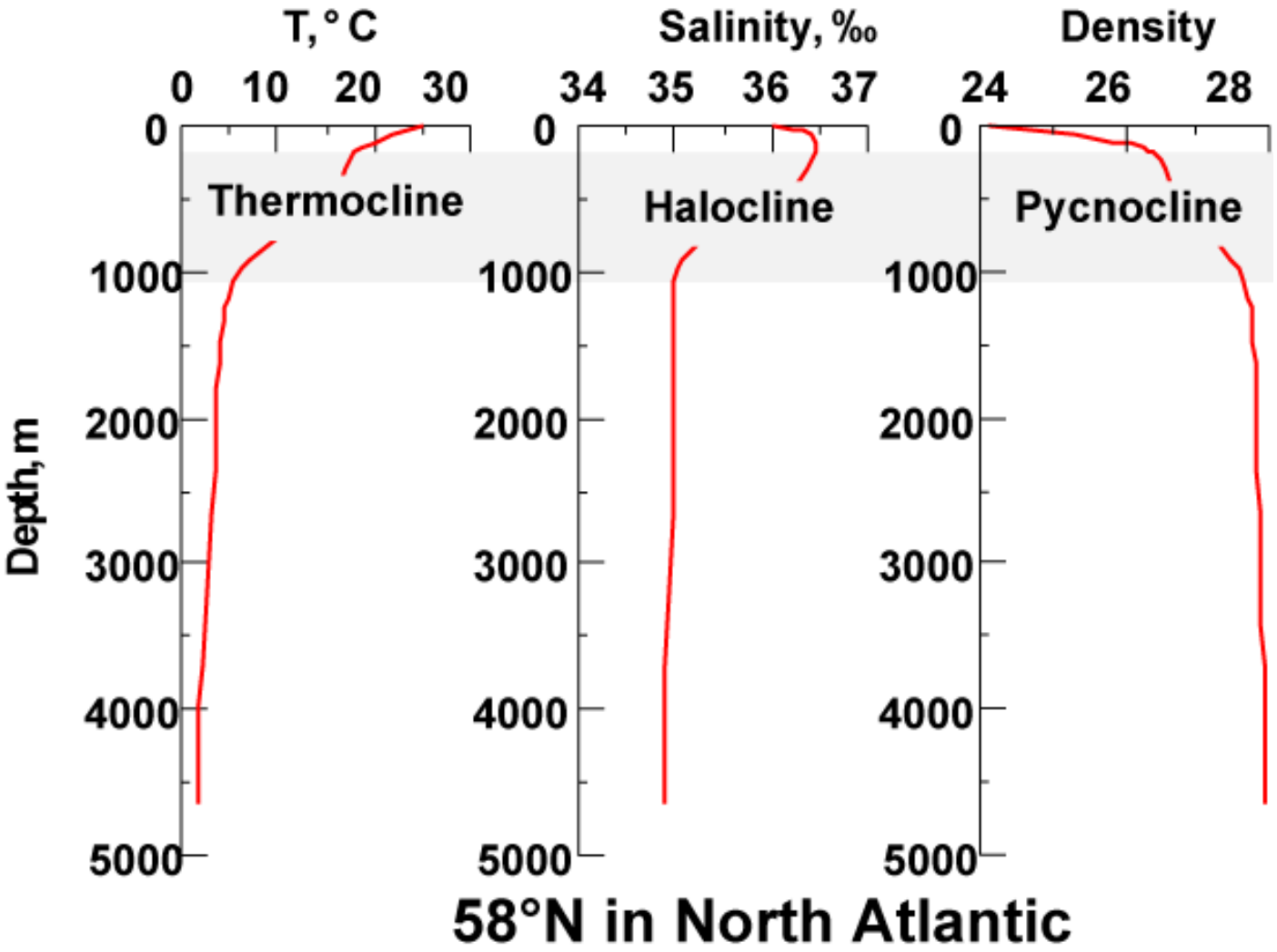
Average seawater, with S = of 35‰ and T = 20°C, has a density σ of 1.025 g/cc



Sea surface salinity



Temperature-salinity-density variation



Pycnocline:

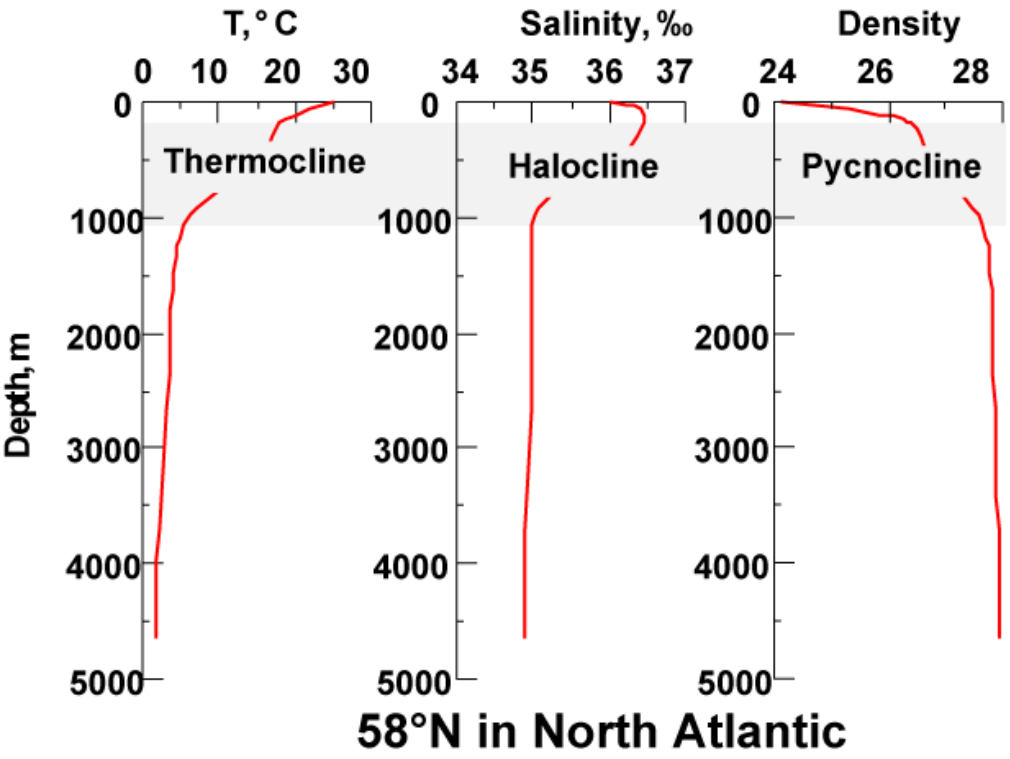
strong boundary to vertical mixing

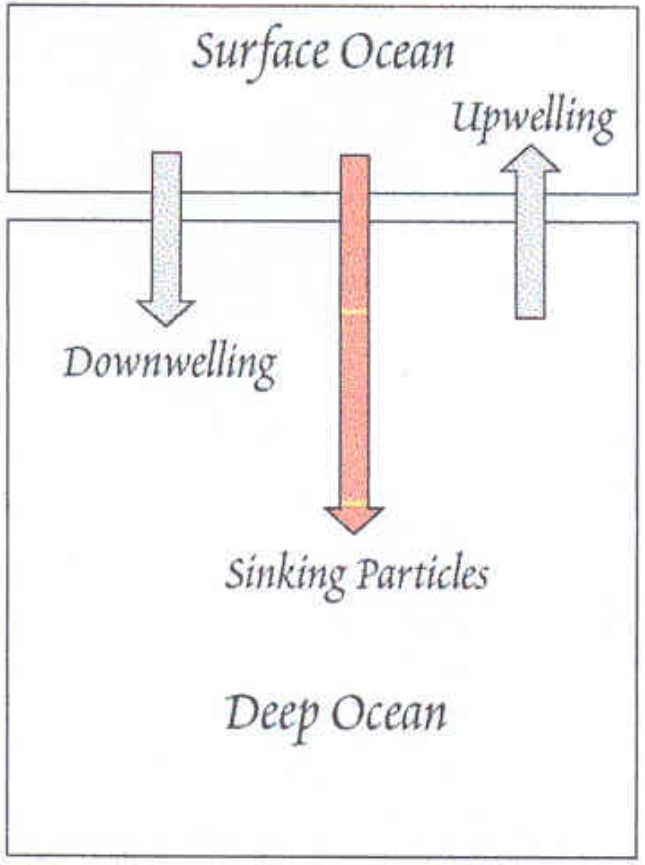
from: White *Geochemistry*

Thermohaline circulation

Thermohaline circulation driven by density differences

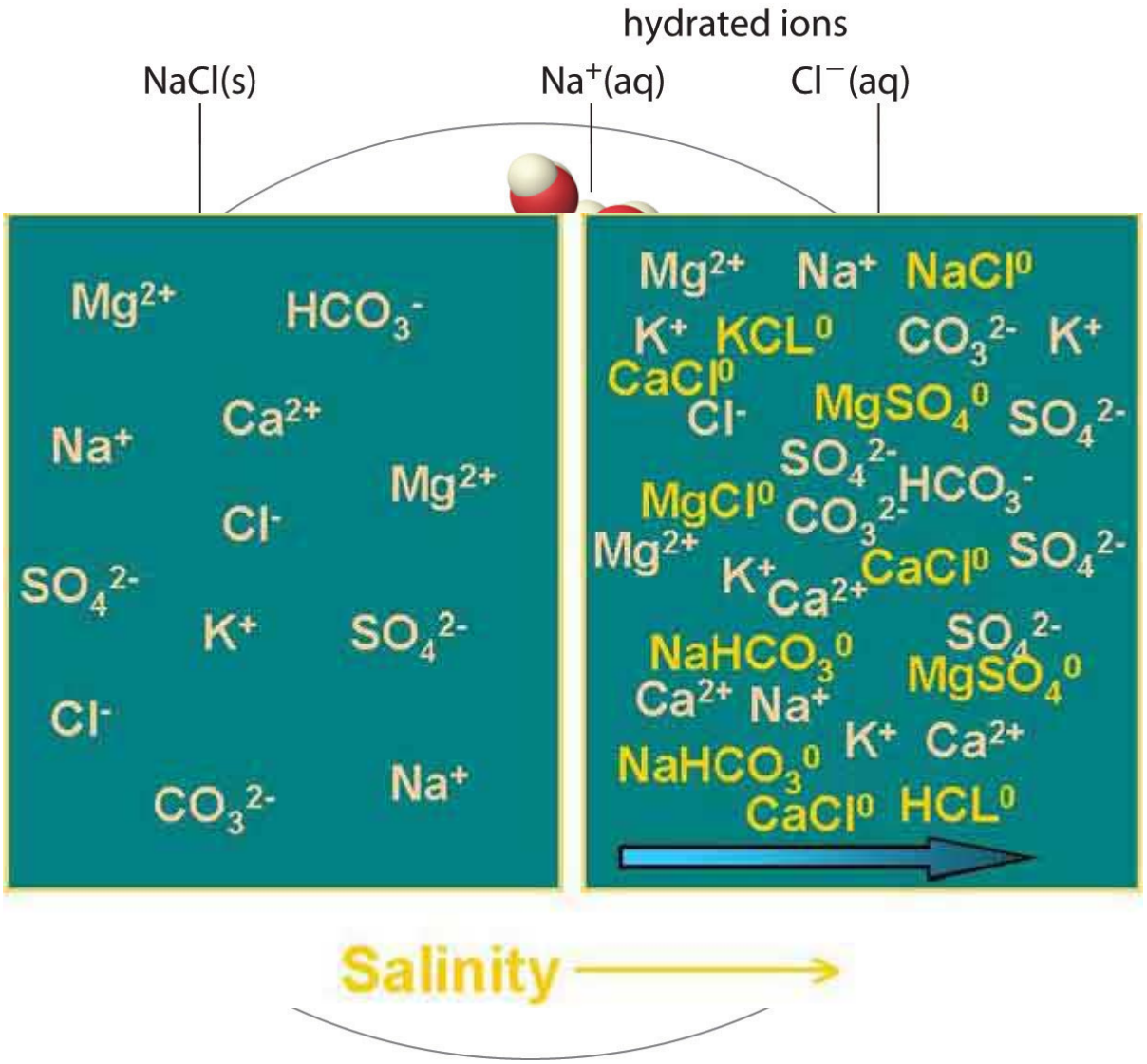
→ exchange of surface water and deep water masses





from: White *Geochemistry*

Speciation and complexation in Seawater



Complex:

$MgCO_3^0$
$MgHCO_3^+$
$MgSO_4^0$
$CaSO_4^0$
$NaSO_4^-$

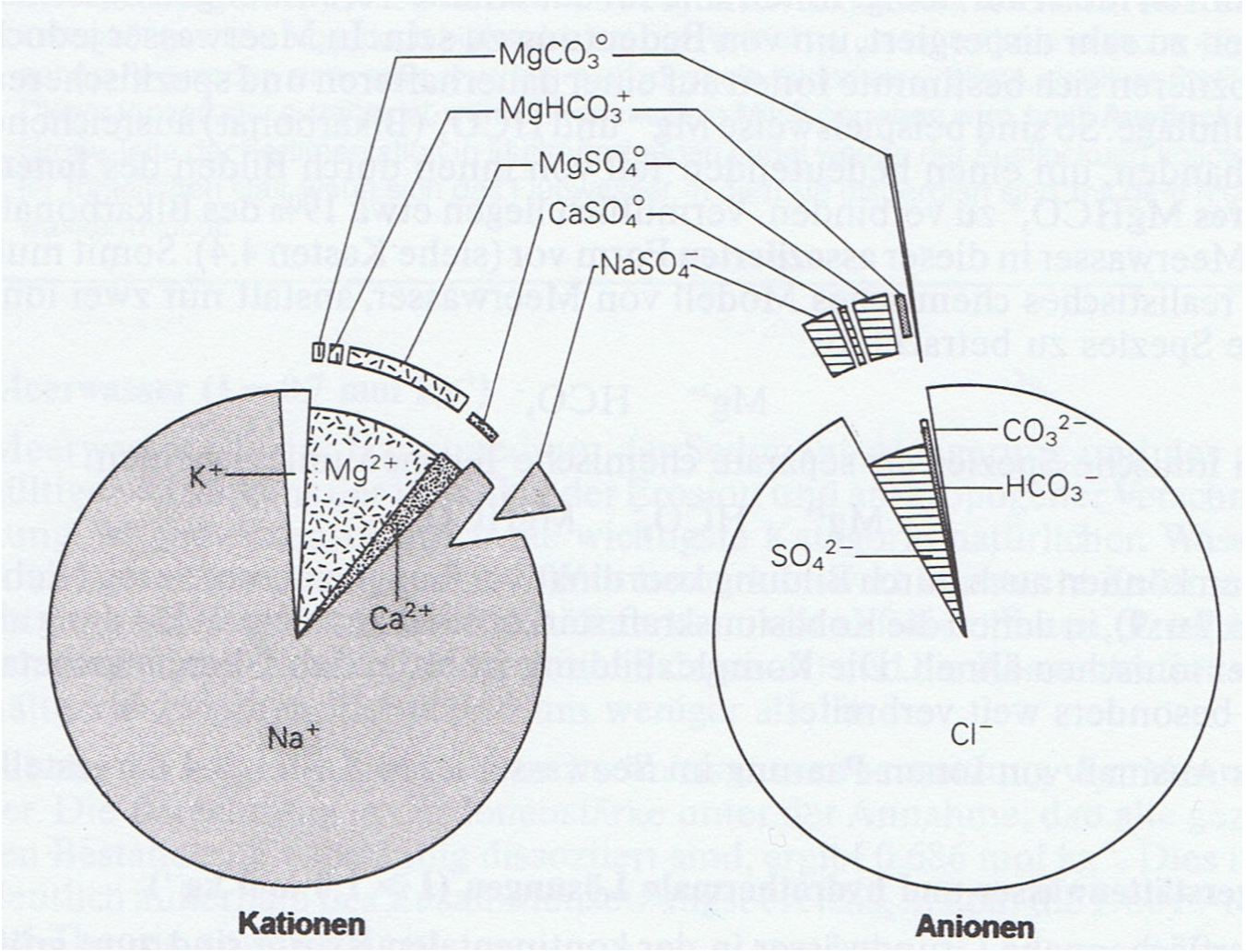
Speciation and complexation in Seawater

illustration: ion-pairing of magnesium

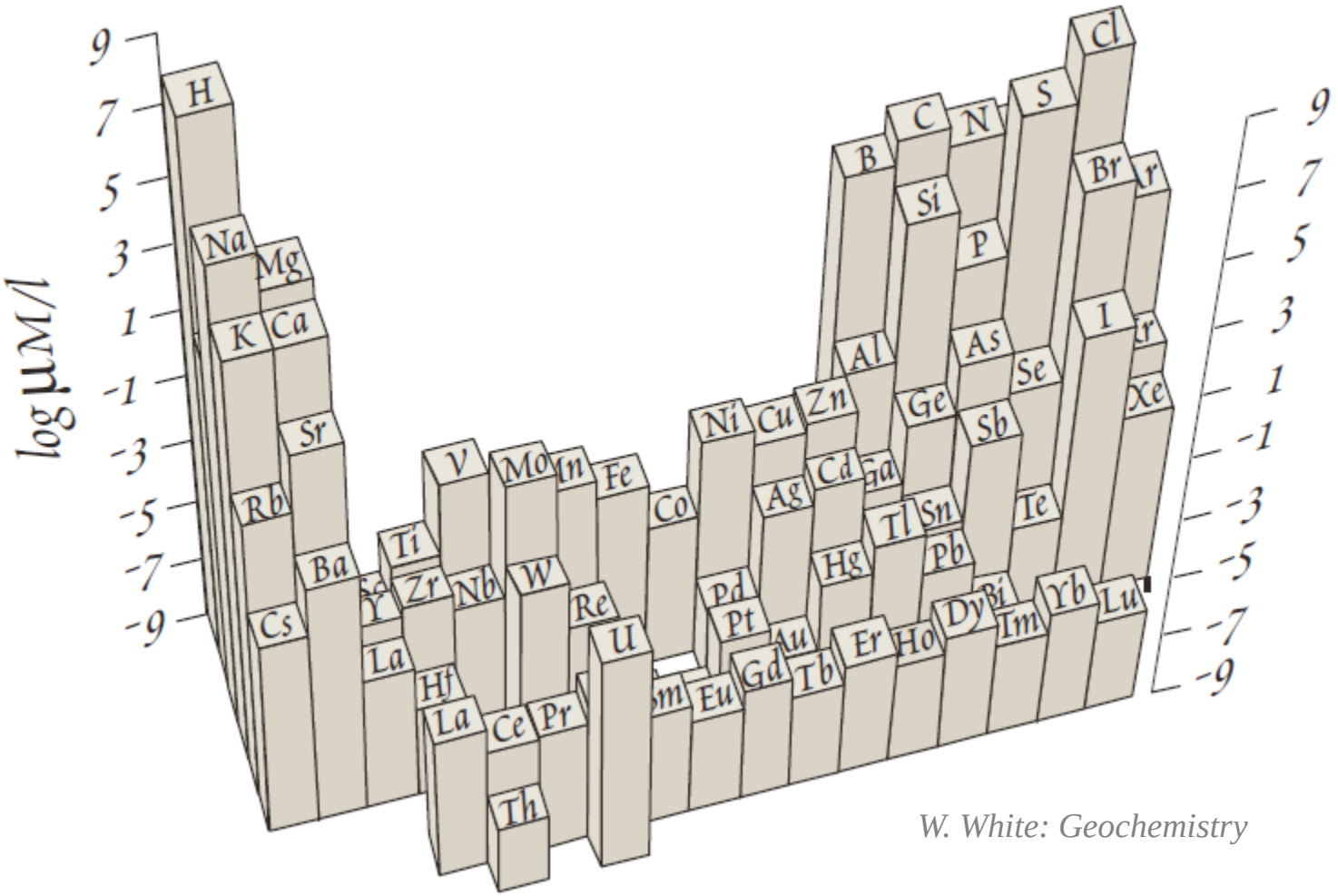
as free ion:
Mg^{2+}

as ion pair
$MgSO_4$
$MgCO_3$

as complex
$MgHCO_3^-$



Major elements in seawater



W. White: Geochemistry

Properties of elements in seawater

Conservative elements – occur in constant proportion in seawater; their distribution depends only on transport of water

Non-conservative elements – undergo a variety of reactions:

biogeochemical cycling,

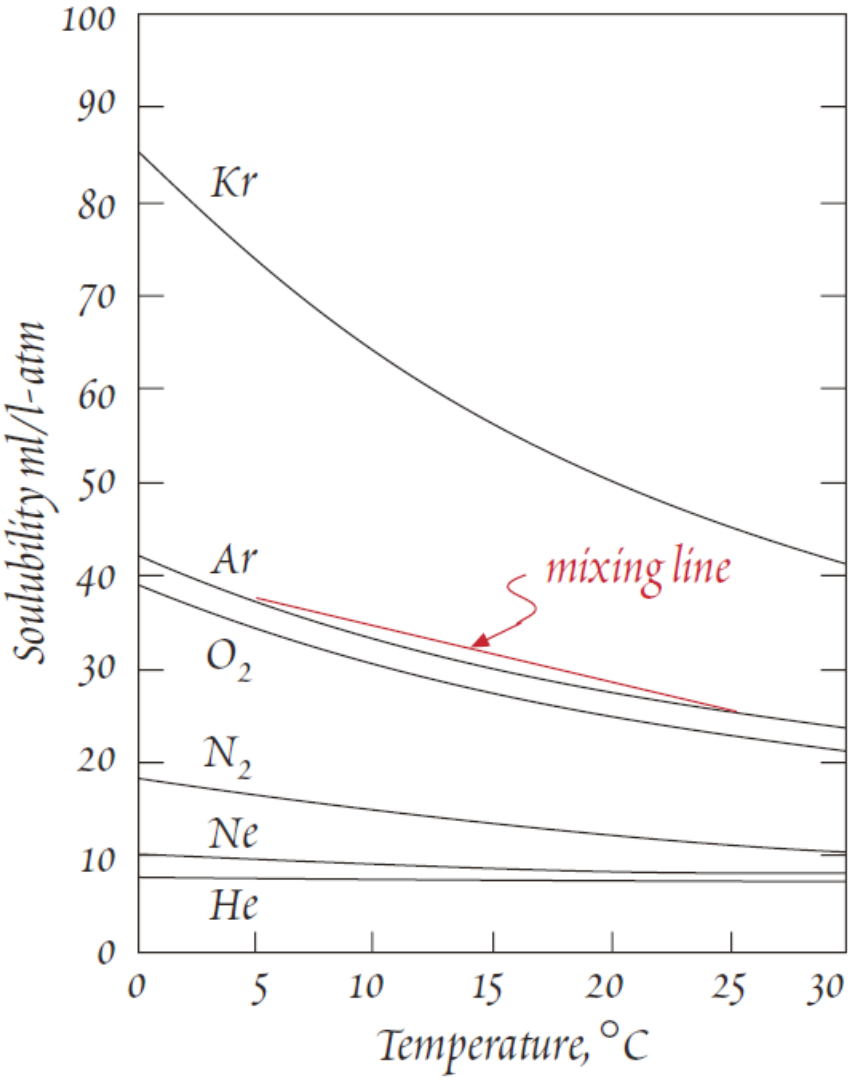
radioactive decay,

isotope fractionation,

exchange with the atmosphere

Ion	g/kg (ppt) at S = 35‰	Percent of Dissolved solids
Cl^-	19.354	55.05
SO_4^{2-}	2.649	7.68
HCO_3^-	0.140	0.41
$B(OH)_4^-$	0.0323	0.07
Br^-	0.0673	0.19
F^-	0.0013	0.00
Na^+	10.77	30.61
Mg^{2+}	1.290	3.69
Ca^{2+}	0.412	1.16
K^+	0.399	1.10
Sr^{2+}	0.008	0.03

Dissolved gases in seawater

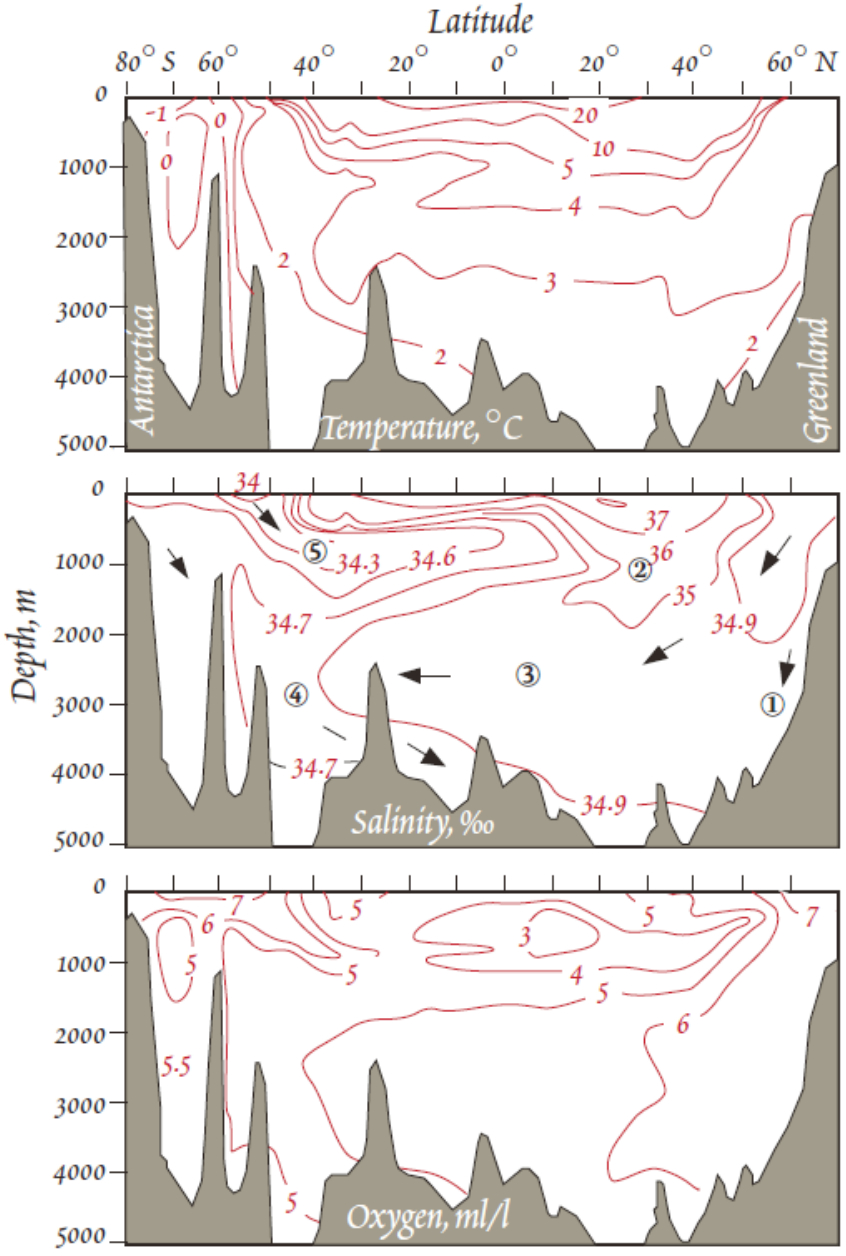


	Atmospheric Partial Pressure	Equilibrium Conc. in Seawater (ml/l) 0°C	24°C
He	5.2	4.1×10^{-5}	3.8×10^{-5}
Ne	1.8	1.8×10^{-4}	1.5×10^{-4}
N_2	0.781	14.3	9.2
O_2	0.209	8.1	5.0
Ar	9.3×10^{-3}	0.39	0.24
Kr	1.1×10^{-6}	9.4×10^{-5}	8.5×10^{-5}
Xe	8.6×10^{-8}	1.7×10^{-5}	8.5×10^{-6}
CO_2	3.6×10^{-4}	0.47	0.24
N_2O	3×10^{-7}	3.2×10^{-4}	1.4×10^{-4}

solubility of gas in ocean: **C = kp**
C = concentration in seawater,
k = Henrys law constant,
p is the partial pressure of the gas in atmosphere

W. White: Geochemistry

Oxygen variation in seawater



oxygen variation due to *respiration* and *photosynthesis*

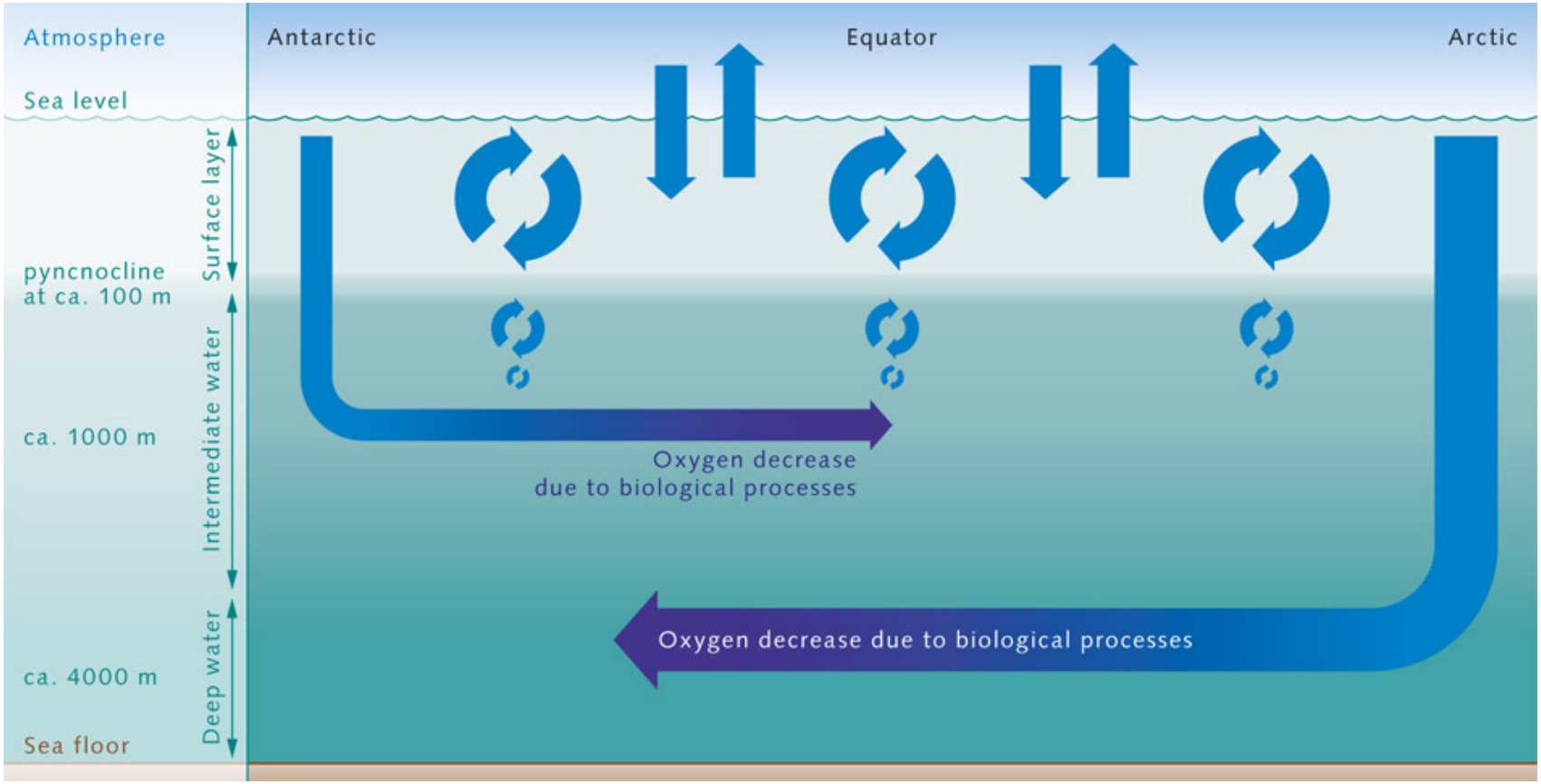
in the surface ocean, rate of photosynthesis exceeds that of respiration → net O_2 production in surface layer

1 North Atlantic Bottom Water
2 Mediterranean Water
3 North Atlantic Deep Water
4 Antarctic Bottom Water
5 Antarctic Intermediate Water

oxygen minimum typically occurs within the thermocline

W. White: Geochemistry

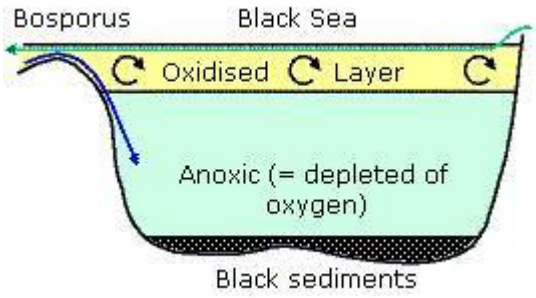
Distribution of O_2



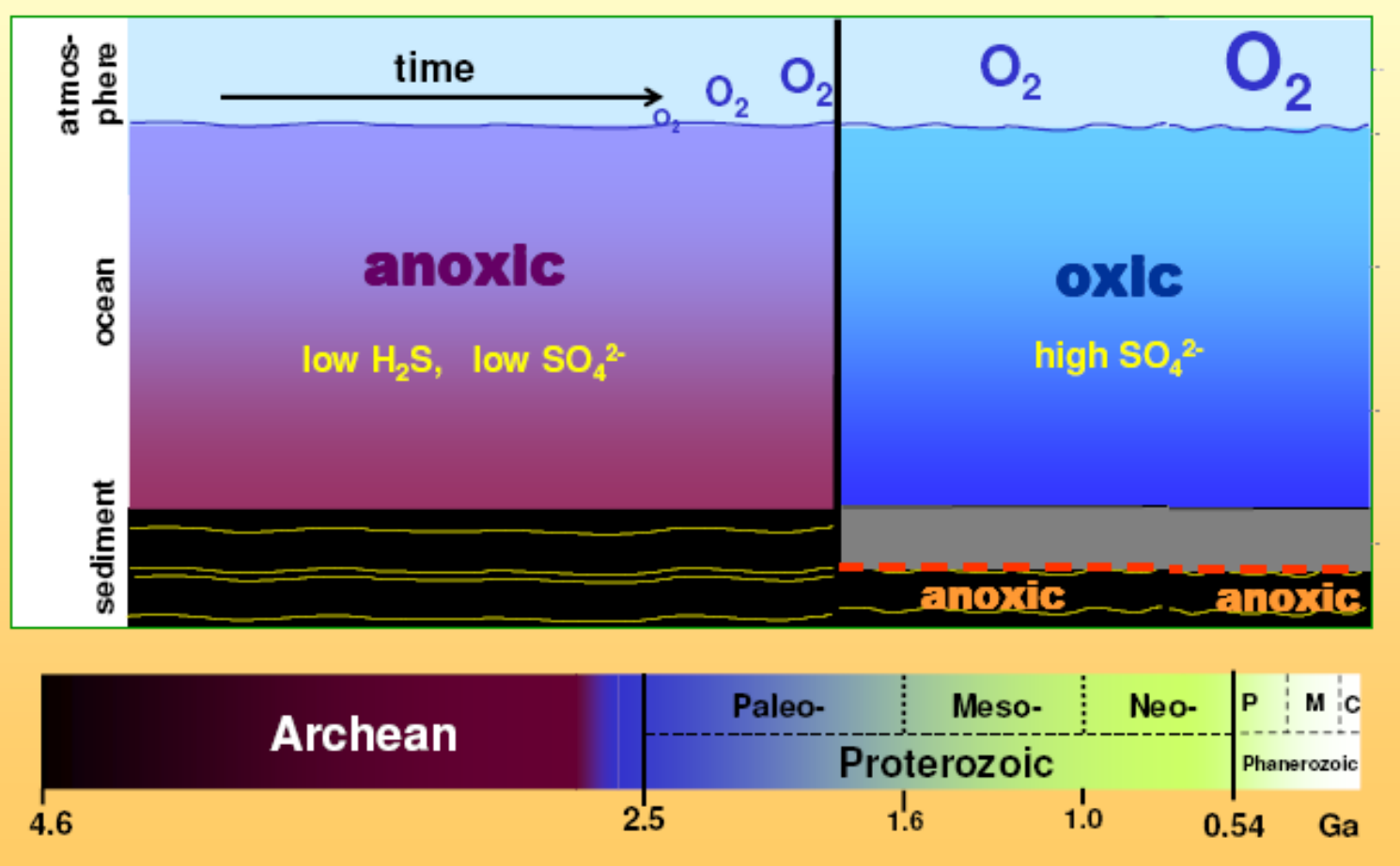
Anoxic waters

When oxygen is depleted, bacteria will turn to reducing nitrate and sulfate:

$SO_4^{-2} + H^{+1} \rightarrow H_2S + H_2O$ + chemical energy (**euxinic** conditions)

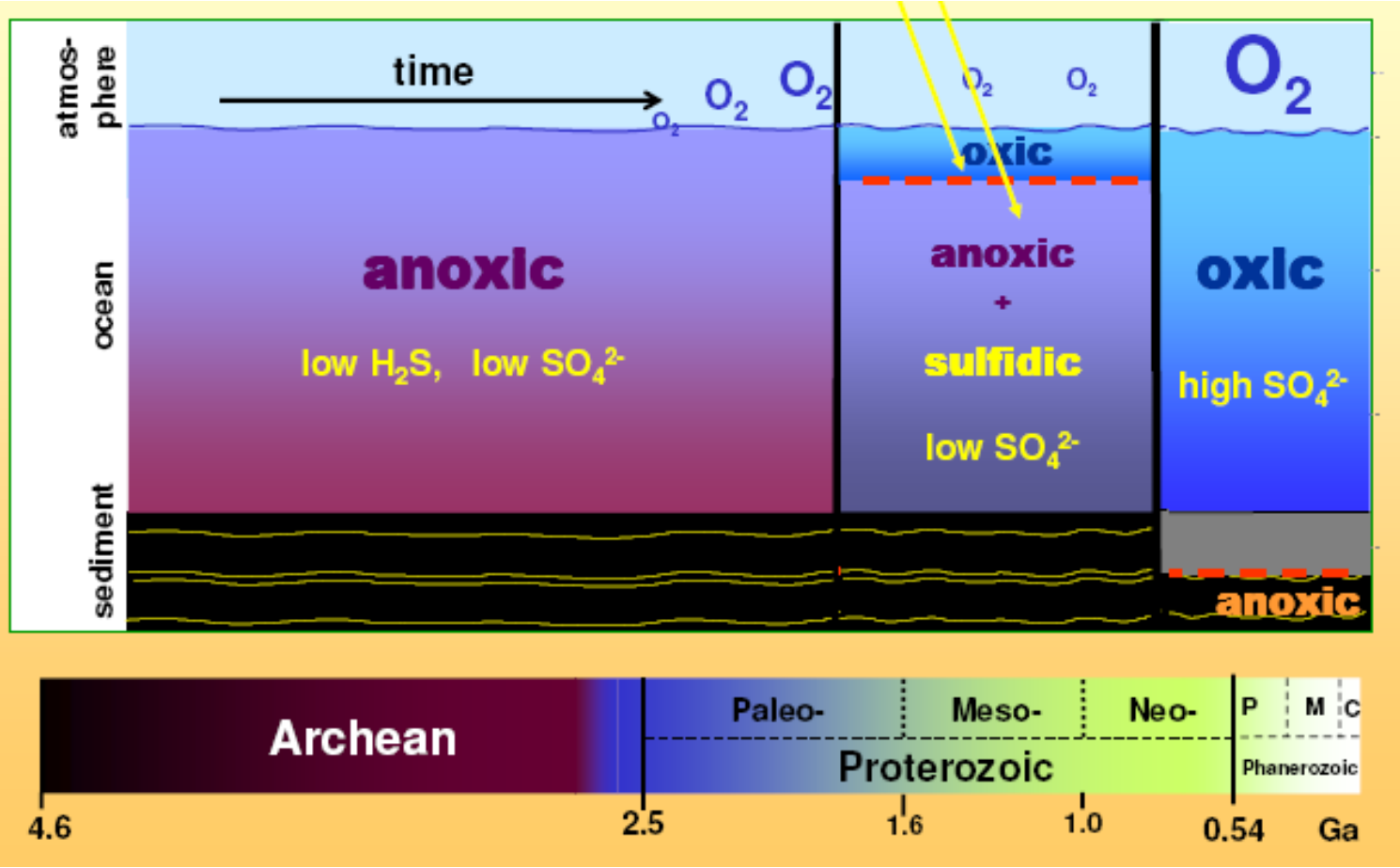


Primeval oceans



http://www.goldschmidt2007.org/plenary.php Plenaries - Jochen BROCKS “Molecular Fossils and Early Life on Earth”

Primeval oceans



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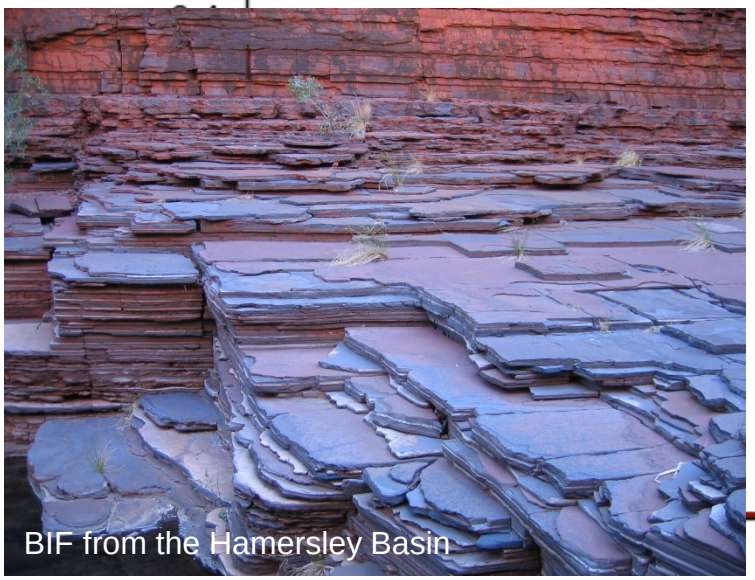
O_2 build-up in the Earth's atmosphere


BIF from the Hamersley Basin

Stage 1: 3.85–2.45 Ga: no O_2 in atmosphere. Oceans were also largely anoxic
Stage 2: 2.45–1.85 Ga: **Great oxygenation event**. Formation of **BIFs**. O_2 produced and rose to values of 0.02 and 0.04 atm, but absorbed in oceans and seabed
Stage 2: 1.85–0.85 Ga: O_2 starts to gas out of the oceans, but is absorbed by land surfaces. No significant change in oxygen level
Stage 2: 0.85–present: O_2 sinks filled and the gas accumulates