

Lecture 23

The Oceans

Reading: White, Digital Chapter 15

Today

1. The oceans: currents, stratification and chemistry

Next Time

2. the marine carbon cycle

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We now turn to marine chemistry, primarily from the perspective of understanding the ocean's role in Earth's carbon cycle and its climate.

Interesting factsoids about the world's oceans:

- ❖ They are **>97%** of the total **mass** of the hydrosphere.
- ❖ They are **the main repository on Earth** for **liquid water** and its dissolved constituents.
- ❖ They contain a significant amount of the worlds **easily accessible carbon**.
- ❖ They're where **most of Earth's photosynthesis/respiration** occurs.
- ❖ They play a major role in **regulating Earth's climate**.
- ❖ Within the ocean's basins is the integrated history of some **100 million years of hydrospheric processes**.
- ❖ The **overturn** rate for the oceans is every **~1500-2000** years in its present configuration and sea level.

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Chemicals in the Oceans

Sea water has accumulated elements in proportion to their solubility and stability in sea water over the age of the earth.

Conservative elements have T_{res} up to 10^7 yr (50000x the overturn rate; they are *well-mixed* in the oceans).

* Oceanic elemental concentration varies with depth and geographic location but the ratio of one conservative element to another is essentially constant throughout.

Non-conservative elements

* Abundances are highly variable in the oceans. These elements have $T_{res} < 5x$ oceanic turnover rate.

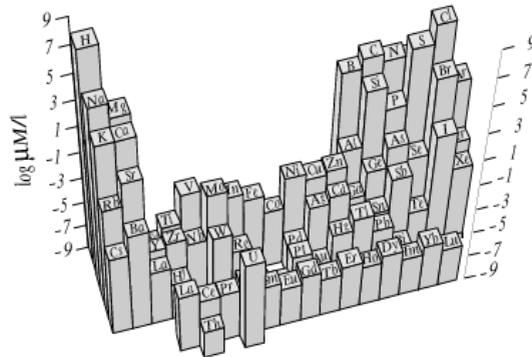


Figure 15.5. The composition of seawater. The most abundant elements are those on the sides of the periodic table. Elements in the interior tend to be less abundant. *from White, "Geochemistry"*

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The Composition of Seawater

Table 10.9 Average Composition of Water in Streams and in the Oceans in micrograms per gram

source: Faure, *Geochemistry*

| Element | Classification ^a | Stream water | Seawater | Seawater enrichment | T _{res} MORT ^b | Element | Classification ^a | Stream water | Seawater | Seawater enrichment | T _{res} MORT ^b |
|---------|-----------------------------|--------------------|-----------------------|---------------------|------------------------------------|---------|-----------------------------|----------------------|-----------------------|---------------------|------------------------------------|
| Li | I | 3×10^{-3} | 1.7×10^{-1} | 56.7 | 2.5×10^6 | Sn | IV | 4×10^{-3} | 5×10^{-7} | 0.013 | 1.3×10^2 |
| Be | IV | 1×10^{-5} | 2×10^{-7} | 0.02 | 6.3×10^1 | Sb | III | 7×10^{-3} | 1.5×10^{-4} | 2.1 | 1.3×10^3 |
| B | I | 1×10^{-2} | 4.5 | 450 | 1.6×10^7 | I | I | 7×10^{-3} | 5.6×10^{-2} | 8 | $<4.0 \times 10^6$ |
| F | I | 1×10^{-3} | 1.3 | 1300 | 7.9×10^5 | Cs | I | 2×10^{-5} | 2.9×10^{-4} | 14.5 | 4.0×10^4 |
| Na | I | 6.3 | 1.08×10^4 | 1714 | 2.0×10^8 | Ba | III | 2×10^{-2} | 1.4×10^{-2} | 0.7 | 5.0×10^3 |
| Mg | I | 4.1 | 1.29×10^3 | 315 | 5.0×10^7 | La | III | 4.8×10^{-3} | 4.5×10^{-6} | 0.094 | 7.9×10^1 |
| Al | IV | 5×10^{-2} | 8×10^{-4} | 0.016 | 7.0 | Pr | III | 7.3×10^{-6} | 1.0×10^{-6} | 0.14 | 7.9×10^1 |
| Si | II | 6.5 | 2.8 | 0.43 | 7.9×10^3 | Nd | III | 3.8×10^{-6} | 4.2×10^{-6} | 0.11 | 7.9×10^1 |
| P | II | 2×10^{-2} | 7.1×10^{-2} | 3.6 | 4.0×10^6 | Sm | III | 7.8×10^{-6} | 8.0×10^{-7} | 0.10 | 7.9×10^1 |
| S | I | 3.7 | 9.0×10^2 | 243 | 5.0×10^8 | Eu | III | 1.5×10^{-6} | 1.5×10^{-7} | 0.10 | 6.3×10^1 |
| Cl | I | 7.8 | 1.95×10^4 | 2500 | 6.3×10^8 | Gd | III | 8.5×10^{-6} | 1.0×10^{-6} | 0.11 | 1.0×10^2 |
| K | I | 2.3 | 3.99×10^2 | 173 | 1.3×10^7 | Tb | III | 1.2×10^{-6} | 1.7×10^{-7} | 0.14 | 1.0×10^2 |
| Ca | I | 15 | 4.13×10^2 | 27.5 | 1.3×10^6 | Dy | III | 7.2×10^{-6} | 1.1×10^{-6} | 0.15 | 1.0×10^2 |
| Se | IV | 4×10^{-6} | 6.7×10^{-7} | 0.17 | 2.5×10^1 | Ho | III | 1.4×10^{-6} | 2.8×10^{-7} | 0.20 | 1.3×10^2 |
| Ti | IV | 3×10^{-3} | $<9.6 \times 10^{-4}$ | 0.32 | $<1.6 \times 10^2$ | Er | III | 4.2×10^{-6} | 9.2×10^{-7} | 0.22 | 1.6×10^2 |
| V | IV | 9×10^{-4} | 1.2×10^{-3} | 1.3 | 7.9×10^3 | Tm | III | 6.1×10^{-7} | 1.3×10^{-7} | 0.21 | 1.6×10^2 |
| Cr | IV | 1×10^{-3} | 2×10^{-4} | 0.2 | 1.6×10^3 | Yb | IV | 3.6×10^{-6} | 9.0×10^{-7} | 0.25 | 2.0×10^2 |
| Mn | III | 7×10^{-3} | 3×10^{-4} | 0.04 | 3.2×10^1 | Lu | IV | 6.4×10^{-7} | 1.4×10^{-7} | 0.22 | 2.0×10^2 |
| Fe | IV | 4×10^{-2} | 6×10^{-5} | 0.0015 | 6.9×10^{-1} | Hf | IV | — | $<7 \times 10^{-6}$ | — | $<1.3 \times 10^3$ |
| Co | III | 1×10^{-4} | 2×10^{-6} | 0.02 | 2.0×10^1 | Ta | IV | — | $<2.5 \times 10^{-4}$ | — | $<2.0 \times 10^4$ |
| Ni | III | 3×10^{-3} | 5×10^{-4} | 1.7 | 1.6×10^3 | W | IV | 3×10^{-3} | 1×10^{-4} | 3.3 | 7.9×10^4 |
| Cu | III | 7×10^{-4} | 3×10^{-4} | 0.04 | 1.0×10^3 | Re | IV | — | 4×10^{-6} | — | 3.2×10^6 |
| Zn | III | 2×10^{-2} | 4×10^{-4} | 0.02 | 1.3×10^3 | Au | III | 2×10^{-6} | 4.9×10^{-6} | 2.5 | 1.6×10^6 |
| Ga | IV | 9×10^{-5} | 2×10^{-5} | 0.2 | 7.9×10^3 | Hg | III | 7×10^{-5} | 1×10^{-6} | 0.14 | 7.9×10^3 |
| Ge | IV | 5×10^{-6} | 5×10^{-6} | 1 | 2.0×10^3 | Tl | IV | — | 1×10^{-5} | — | 6.3×10^3 |
| As | IV | 2×10^{-3} | 1.7×10^{-3} | 0.85 | 1.0×10^5 | Pb | III | 1×10^{-3} | 2×10^{-5} | 0.002 | 5.0×10^1 |
| Se | III | 6×10^{-2} | 1.3×10^{-4} | 2.2 | 6.3×10^5 | Bi | IV | — | 2×10^{-5} | — | 2.5×10^4 |
| Br | I | 2×10^{-2} | 6.7×10^1 | 3350 | 7.9×10^8 | Th | IV | $<1 \times 10^{-4}$ | 6×10^{-8} | ~ 0.0006 | 3.4 |
| Rb | I | 1×10^{-3} | 1.2×10^{-1} | 120 | 7.9×10^5 | U | I | 4×10^{-3} | 3.1×10^{-3} | 2.7 | 1×10^6 |
| Sr | I | 7×10^{-2} | 7.6 | 109 | 5.0×10^6 | | | | | | |
| Y | III | 4×10^{-5} | 7×10^{-6} | 0.18 | 1.3×10^2 | | | | | | |
| Zr | IV | — | 3×10^{-5} | — | 1.6×10^2 | | | | | | |
| Nb | IV | — | $<5 \times 10^{-6}$ | — | $<2.5 \times 10^2$ | | | | | | |
| Mo | I | 6×10^{-4} | 1.1×10^{-2} | 18.3 | 3.2×10^5 | | | | | | |
| Ag | III | 3×10^{-4} | 2.7×10^{-6} | 0.009 | 2.0×10^4 | | | | | | |
| Cd | IV | 1×10^{-5} | 8×10^{-5} | 8 | 7.9×10^4 | | | | | | |
| In | IV | — | 1×10^{-7} | — | 1.0×10^3 | | | | | | |

^a I. Conservative element whose concentration is directly related to the salinity of seawater.

II. Nonconservative element whose concentration varies with depth or regionally within the oceans, or both, generally because of involvement in biological activity.

III. Nonconservative element whose concentration varies irregularly and is not related to salinity, depth, or geographic factors.

IV. Unclassified, but probably nonconservative.

^b Mean oceanic residence time in years.

source: Taylor and McLennan (1985).

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Chemical Mass Balances in the Oceans

Elements are added to and subtracted from the oceans by geological, biological, physical, and chemical processes.

Net elemental input/output fluxes (mass/time) are small relative to the oceanic reservoir size (mass), so that small flux changes take a long time to show up as measurable differences in sea water concentration.

chemical fluxes **into** the oceans

on the top

- ◆ rivers ◆ precipitation
- ◆ dry deposition ◆ gas exchange

on the bottom

- ◆ sea floor volcanism

chemical fluxes **out of** the oceans

on the top

- ◆ gas exchange,
- ◆ aerosol formation

on the bottom

- ◆ sedimentation ◆ alteration of the basaltic oceanic crust

chemical fluxes **within** the oceans

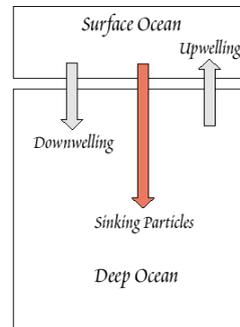


Figure 15.3. The two box model of the ocean and the fluxes between them.
White, Geochemistry

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Salinity

Remember that the salinity of seawater causes it to have a fairly high ionic strength ($I = \frac{1}{2} \sum m_i z_i^2 \approx 0.7$).

Salt content is one of two fundamental controls on sea water density (along with temperature), which in turn control marine stratification and circulation.

The salt content of water is almost entirely from conservative elements.

Salinity is given units of g/kg (parts per thousand, ‰). Typical sea water Salinity ranges from 33 to 35.5‰ .

Marine (conservative ion)/(total salinity) ratios = constant.

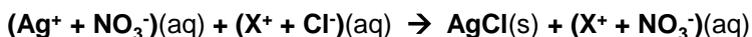
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Salinity

•Historically, salinity was determined by measuring **chlorinity** (which is g Cl⁻/kg H₂O) and then converting to salinity. Salinity and true chlorinity are related by a fixed ratio:

$$\text{salinity (S)} = 0.03 + 1.805 \times \text{chlorinity}$$

•Chlorinity is easy to measure by adding a known number of moles of AgNO₃ to seawater to precipitate silver chloride, centrifuging or filtering the solids, then drying and weighing, and converting to chlorinity using the atomic weight of Cl and the molecular weight of AgCl.



•A slight correction must be made to chlorinity measured this way because (Ag⁺ + NO₃⁻)(aq) removes all the halogens in seawater (Cl, F, Br, I), not just Cl (we call this the “chlorine equivalent” of seawater). It turns out that **[total halogens]/[Cl] ≈ 1.0004** (by mass). Today we usually measure salinity directly by measuring **electrical conductivity**, as salinity is directly proportional to conductivity.

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Salinity Effects

Salinity not only affects density but also the **freezing and boiling points** of seawater relative to pure water. Freezing produces sea ice in the polar regions.

T_{fus} = the freezing/melting point of pure water = 0°C at 1 atm pressure.

ΔT_{fus}, the **freezing point depression** of a solution caused by the solutes it contains, is

$$\Delta T_{\text{fus}} = T_{\text{fus}} - T_{\text{depr}} = k_{\text{fus}} \cdot (\text{molality of solute})$$

k_{fus} is called the freezing-point depression constant. It is *solvent-specific* but applies for any solute in that solvent.

$$k_{\text{fus}} = (RT^2 \cdot \text{MW}_{\text{solvent}} / 1000 \Delta H_{\text{fus}}) \quad \text{where MW is molecular weight.}$$

$$k_{\text{fus}} = 1.86 \quad \text{for H}_2\text{O}$$

Let's do a T_{depr} calculation for seawater with S = 35‰.

A **first approximation** is to assume that all the salts in seawater are NaCl. Then...

35 g NaCl/kg sw ÷ 58.44 g NaCl/mole = 0.60 molal, and...

$$\Delta T_{\text{fus}} = T_{\text{fus}} - T_{\text{depr}} = 0 - T_{\text{depr}} = 1.86 \times 0.60; \quad \text{so } T_{\text{depr}} = \mathbf{-1.12^\circ\text{C}}$$

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Salinity Effects

The "solute" in seawater is actually a mixed salt of NaCl, MgSO₄, CaCO₃, etc... We can refine our approximation by trying to account for this when converting salinity to solute molality. If we assume for instance that the 35 ‰ salinity is composed of 90% by moles of NaCl and 10% by moles of MgSO₄, we could derive T_{fus} in two ways

- calculate T_{fus} due to each component and add together
- convert salinity into a total molality using the mean molecular weight of the solute mixture.

Let's work through this example using technique b.

$$MW_{\text{NaCl}} = 58.44 \text{ g/mol}; MW_{\text{MgSO}_4} = 120.37 \text{ g/mol}$$

$$\text{mean } MW_{\text{solute}} = 0.9(58.44) + 0.1(120.37) = 64.63 \text{ g/mol}$$

then, molality at 35 ‰ salinity is

$$35\text{g NaCl/kg sw} \times 1 \text{ mol salts}/64.63 \text{ g} = 0.542 \text{ molal and...}$$

$$T_{\text{fus}}^{\circ} - T_{\text{fus}} = 0 - T_{\text{fus}} = 1.86 \times 0.542 = \boxed{-1.007 \text{ }^{\circ}\text{C}}$$

Further approximations can be done, but will have smaller effects.

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The pH of sea water

At pH ~8.0 - 8.2, sea water is basic: This results largely from by CO₂ dissolution AND CaCO₃ precipitation. We have previously discussed the CO₂ system equilibria:

- $\text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{aq})$ ($K_{\text{H}} = 10^{-6.48}$)
- $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^-(\text{aq}) + \text{H}^+$ ($K_{\text{a}1} = 10^{-6.4}$)
- $\text{HCO}_3^-(\text{aq}) \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$ ($K_{\text{a}2} = 10^{-10.3}$)
- $\text{CaCO}_3 \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$ ($K_{\text{sp}} = 10^{-8.3}$)

Using also $K_{\text{w}} = 10^{-14}$, atmospheric $P_{\text{CO}_2} \sim 10^{-3.5} \text{ atm} = 32 \text{ Pa}$ ($1 \text{ Pa} \sim 10^{-5} \text{ atm} = 1 \text{ kg/ms}$), and CaCO₃ saturation (which is true for the surface oceans) yields pH = 8.4

8.4 differs slightly from the actual pH of the oceans but this analysis is pretty close. Two other important reactions are:

- * photosynthesis-respiration [$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{CH}_2\text{O} + \text{O}_2$]
- * the element B which forms boric acid in sea water (0.450 g/kg ~ 0.0073 m, from sea water slide).

B helps buffer sea water pH of because it's concentration is ~ 3x that of HCO₃⁻ and because



$$\text{@ pH} = 8.2, m_{\text{H}^+} = 10^{-8.2} \quad K_{\text{a}1} = 10^{-9} = \frac{(10^{-8.2} m_{\text{B}(\text{OH})_4^-})}{m_{\text{B}(\text{OH})_3}}$$

$$\boxed{m_{\text{B}(\text{OH})_4^-} / m_{\text{B}(\text{OH})_3} = 0.158}$$

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The Charge balance of Sea Water

sea water has a **slight "excess" of positive** charge between its major cations (Na^+ , Mg^{2+} , K^+ , Ca^{2+}) and major anions (Cl^- , Br^- , SO_4^{2-}).

This **excess is "balanced" by dissolved CO_2** ($\Sigma \text{CO}_2(\text{aq})$, as HCO_3^- and CO_3^{2-} , the proportions of which are pH dependent.)

Table 2-3 Charge balance in sea water: the excess cation charge is balanced by the dissociation of carbonic acid (H_2CO_3) into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions.

| Positive | | |
|------------------|----------------------------|------------------------------|
| Cation | Mass, moles/m ³ | Charge, moles/m ³ |
| Na^+ | 470 | 470 |
| K^+ | 10 | 10 |
| Mg^{++} | 53 | 106 |
| Ca^{++} | 10 | 20 |
| Σ | — | 606 |

note: that this table uses the obscure unit m^3 for volume. One liter is 1 dm^3 so a m^3 is simply $10 \times 10 \times 10$ (= 1000 liters).

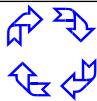
| Negative | | |
|---|----------------------------|------------------------------|
| Anion | Mass, moles/m ³ | Charge, moles/m ³ |
| Cl^- | 547 | 547 |
| SO_4^{--} | 28 | 56 |
| Br^- | 1 | 1 |
| Σ | — | 604 |
| HCO_3^- + CO_3^{--} | — | Balance 2 |
| Σ' | — | 606 |

The balance of charge and ion population in mean sea water is given in Table 2-3. Notice that to balance Σ anions = Σ cations, we need **2 mole/m³, or 2 mmol/L, of dissolved inorganic carbon.**

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The Ocean Currents affect sea water chemistry

Oceanic water masses move in fairly regular patterns ... and acquire specific compositional signatures along the way.



"Gyrospheric" (circular) flow of surface ocean currents reflects dominant wind patterns at the base of the atmosphere, oceanic boundaries at continental margins, and the Coriolis force of Earth's rotation.

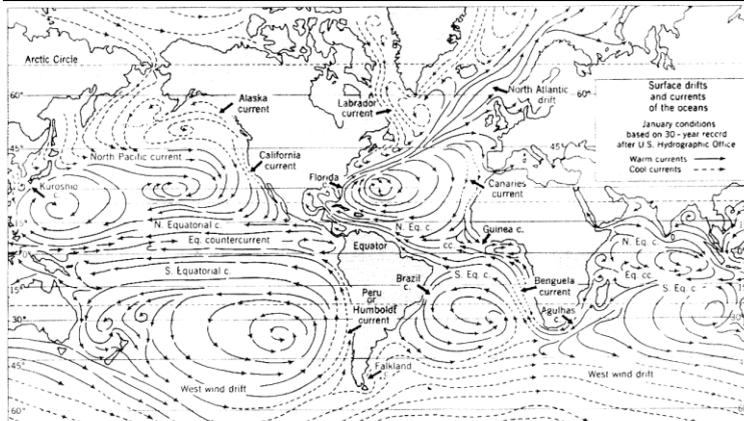


Figure 14.5. Surface ocean currents. (Strahler 1971, p. 269; Fig. 16.6.)

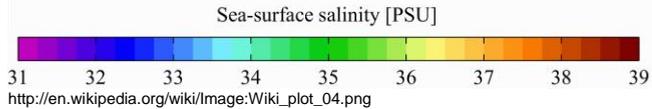
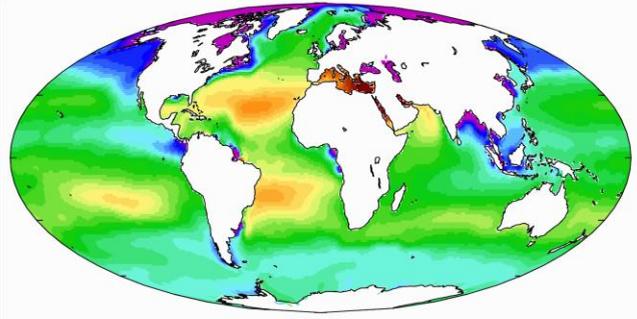
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The Ocean Currents affect sea water chemistry

Salinity (S) and Temperature (T) variations reflect physical processes mostly because S is dominated by the long-residence-time, conservative constituents of sea water.

* **Surface patterns** result from latitudinal climate variations and surface currents.

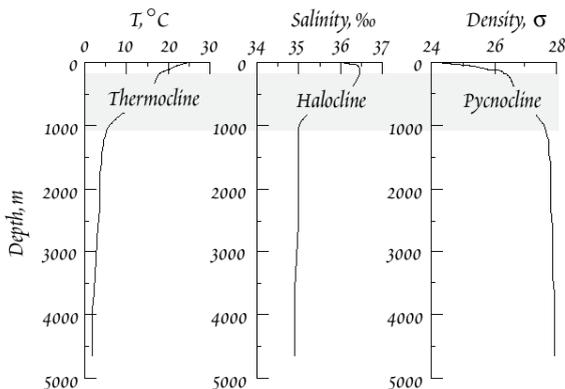
Annual mean sea surface salinity from the World Ocean Atlas 2001.



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The Ocean Currents affect sea water chemistry

* **Deep patterns** result from density (saltiest/coldest waters settle to the bottoms of the world's oceans).



Visible light penetrates to ~100 m in low turbidity sea water away from coastal areas, and to ~10 m in the murkiest coastal waters.

The mean depth is about 4km, so the layer(s) that are not in contact with the atmosphere are a much greater proportion of the total volume in the oceans than in lakes.

Figure 15.2. Temperature, salinity, and density variations at GEOSECS station 25 at 58° N in the North Atlantic. The station was occupied in September, and summer heating has extended the thermocline and pycnocline nearly to the surface. Gray area shows the position of the permanent thermocline and pycnocline. An inversion in the salinity profile near the surface indicates an excess of precipitation over evaporation. *White, Geochemistry*

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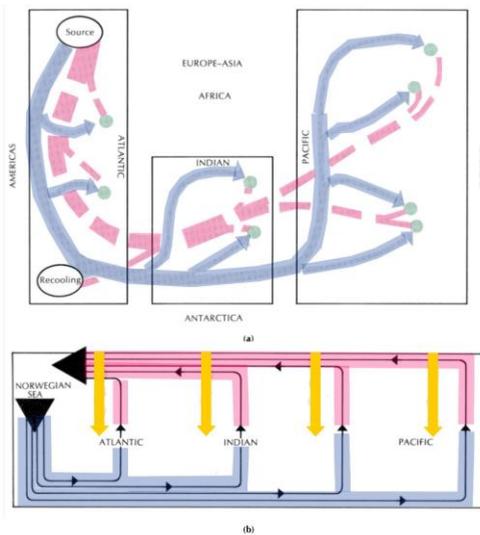


Figure 1-6 (a) is an idealized map of the patterns of deep water flow (solid lines) and surface water flow (dashed lines). The large circles designate the sinking of NADW in the Norwegian Sea and the recooling of water along the perimeter of the Antarctic Continent; the shaded circles indicate the distributed upwelling which balances this deep water generation. (b) is an idealized vertical section running from the North Atlantic to the North Pacific showing the major advective flow pattern (solid lines) and the rain of particles (shy lines). The combination of these two cycles leads to the observed distribution of nutrients.

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Recall the plan view (top) and side on view (bottom) **schematic representation of deep ocean circulation** that we discussed last week, with both bottom water formation and shallow return flow depicted.

Also shown is the export of particle from surface waters to deep waters (yellow arrows).

The slowness of ocean circulation means that most of the oceans are isolated from the atmosphere on decade to century time scales and thus have plenty of time to develop the signature of excess respiration.

Mixing and sea water chemistry

Oceanic water masses slowly mix in a roughly 2000-yr cycle, affecting the abundances of all the elements in seawater.

Conservative Elements are well mixed in sea water since their residence times are \gg the oceanic mixing time scale.

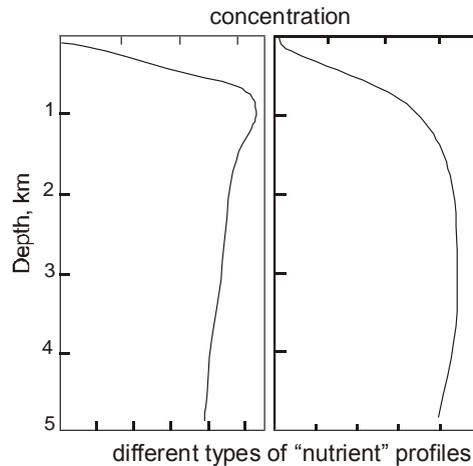
Non-conservative elements - Biological and other processes produce elemental concentrations that deviate from salinity-normalized concentrations in sea water. This can include large vertical as well as horizontal variations.

Photosynthesis-respiration results in changes of C, O, N and P in Redfield Ratio proportions and other “elements of life” in similar fashion.

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Deep Ocean Currents and Stratification:

The oceans are stratified. Like stratified lakes, the oceans support “excess” photosynthesis in their surface layer and “excess” respiration in their deep layers, giving rise for instance to *nutrient profile* composition vs depth relationships.



Oceanic stratification lasts longer than in lakes but it leads to familiar "nutrient profiles" for the depth distribution of NO_3^- and PO_4^{3-} in the oceans.

Other elements involved in the cycle of life also display "nutrient" profiles.

These include Si, which is used by some marine phytoplankton to produce shells, and micronutrients like Cd and Zn.

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Ocean Convection and the chemical elements of life

As we discussed before, “just-formed” North Atlantic deep water has very low nutrient content (since it was just in the photic zone) and relatively low ΣCO_2 (reflecting exchange with the atmosphere and the operation of photosynthesis).

As the deep waters migrate, they acquire more prominent signatures of the effects of excess respiration over photosynthesis, (e.g., more exaggerated nutrient-profiles)

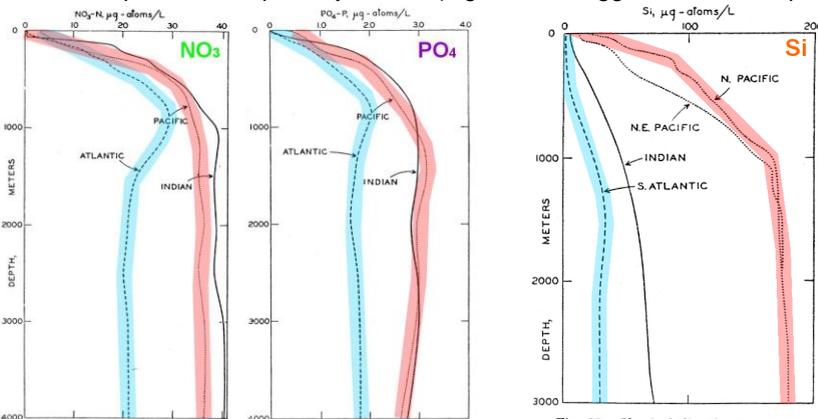


Fig. 50. Vertical distribution of nitrate in the Atlantic, Pacific, and Indian Oceans based on data from the stations shown in fig. 44.

Fig. 48. Vertical distribution of phosphate in the Atlantic, Pacific, and Indian Oceans based on data from the stations shown in fig. 44.

Fig. 55. Vertical distribution of silicate at individual localities in the North Pacific, South Atlantic, and Indian Oceans.

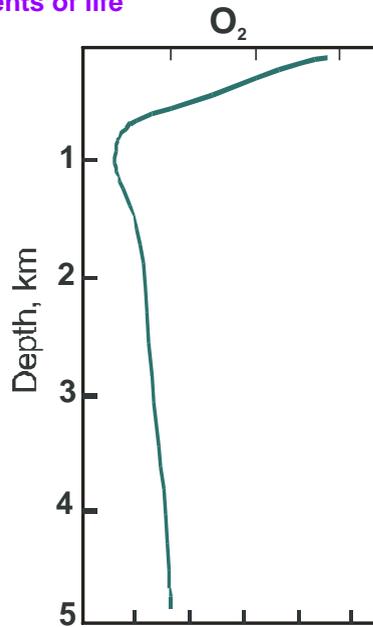
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Ocean Convection and the chemical elements of life

Dissolved O₂ also behaves predictably during deep water migration. DOx profiles look very similar to those in a stratified lake except that O₂ reaches a prominent minimum in intermediate depth waters.

Deepest waters are more variable: the younger the oceanic water mass is, the higher the dissolved O₂ is, since this is effectively replenished by young deep water masses.

This effect is mostly lost by the time deep waters make it to the Pacific Ocean and a close to straight depth profile in the intermediate and deep layers is observed.



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Ocean Convection and the chemical elements of life

Summarizing, deep seawater masses change composition as they migrate through the oceans. **Along this deep circulation flow path, they acquire:**

| | |
|------------------|--|
| <i>increased</i> | ΣCO_2 nutrients silica CA |
| <i>decreased</i> | O ₂ |

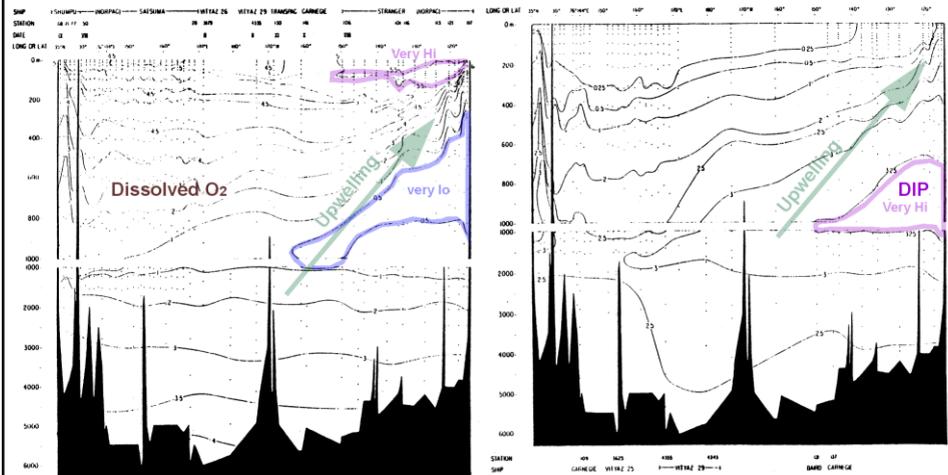
ΣCO_2 and CA (carbonate alkalinity) also increase in older deep waters from sinking marine particulate matter, which affects CaCO₃ solubility and seafloor carbonate sediment preservation patterns, as we see next lecture.

North Pacific deep waters have the highest nutrient content, highest ΣCO_2 and lowest dissolved O₂.

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The upwelled waters are very enriched in nutrients because north pacific deep waters are so old. (Upwelled waters in the North Atlantic have a more limited effect on surface productivity because they are younger).

North Pacific Transects from Japan to N. America at ~27° N



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Upwelling

Dissolved O₂ is especially low beneath the upwelling zone off of California. This is so low because there is a greater excess of dead phytoplankton (photosynthesizers) settling out of the rich upwelling-influenced surface waters.

This sinking biomass feeds a vigorous community of respiring organisms, which consume the oxygen.

Some isolated submarine basins off of Southern California actually go anoxic (eutrophic) during all or part of the year due to this excess of organic matter settling through the water column, leading to conditions that are ideal for accumulation of organic matter, which is necessary to form petroleum precursor deposits in the underlying sediments.

Off-shore oil drilling in Southern California is exploiting previously deposited (Miocene) organic matter that has been transformed to oil through diagenesis of the sediments.

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