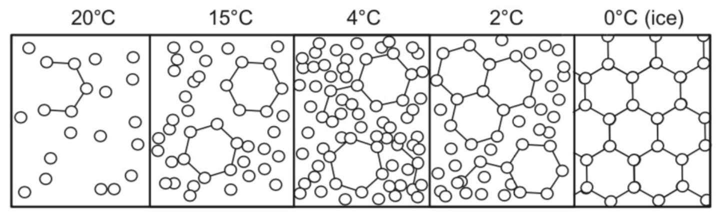
Chemical composition of seawater

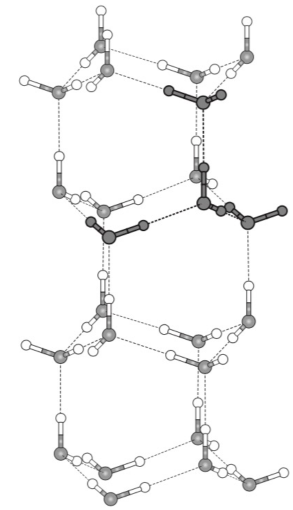
- Learning objectives:
  - Describe the properties of saltwater that are important to how the ocean circulates
  - Understand differences between units and why it matters
  - Broadly distinguish physical / circulation differences between different ocean basins
  - Identify different elemental behavior and explain the rationale for classification

Chemical composition of seawater

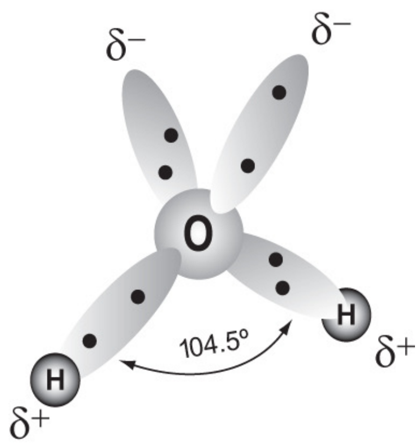
- Hydrogen bonds – why water works the way it does
- Salinity
  - Past and current ways to measure
  - Salt content of the oceans
  - Evaporation and precipitation
- Potential temperature and potential density
- Units
- Ions in the ocean
- Gases in the ocean
- Types of elements

Fresh water





Emerson and Hamme, 2021



Unequal charge on a water molecule

How does this affect ventilation of a water body?

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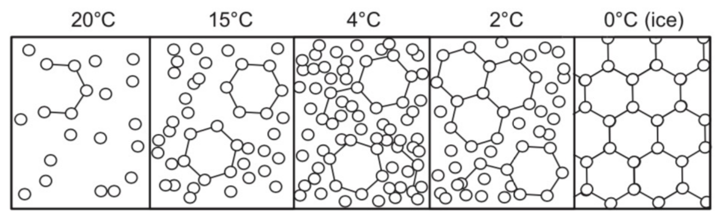
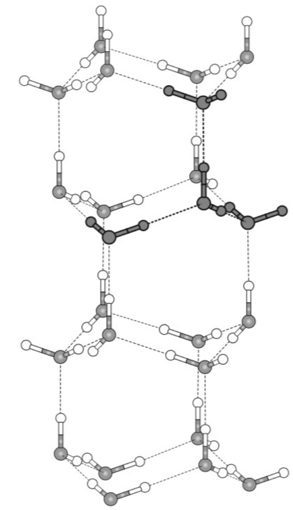
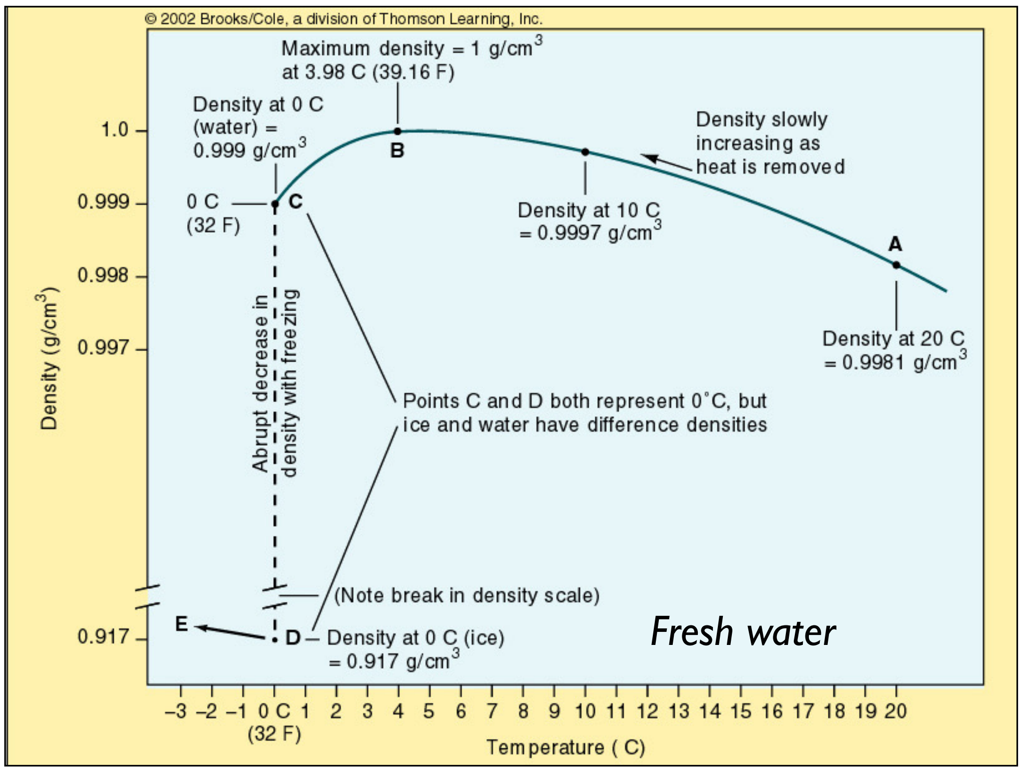
Fresh water





Emerson and Hamme, 2021



Salt water

Electrostriction: contraction of water volume w/ ions added

The "density anomaly" of seawater is designated by the symbol "σ" (sigma)

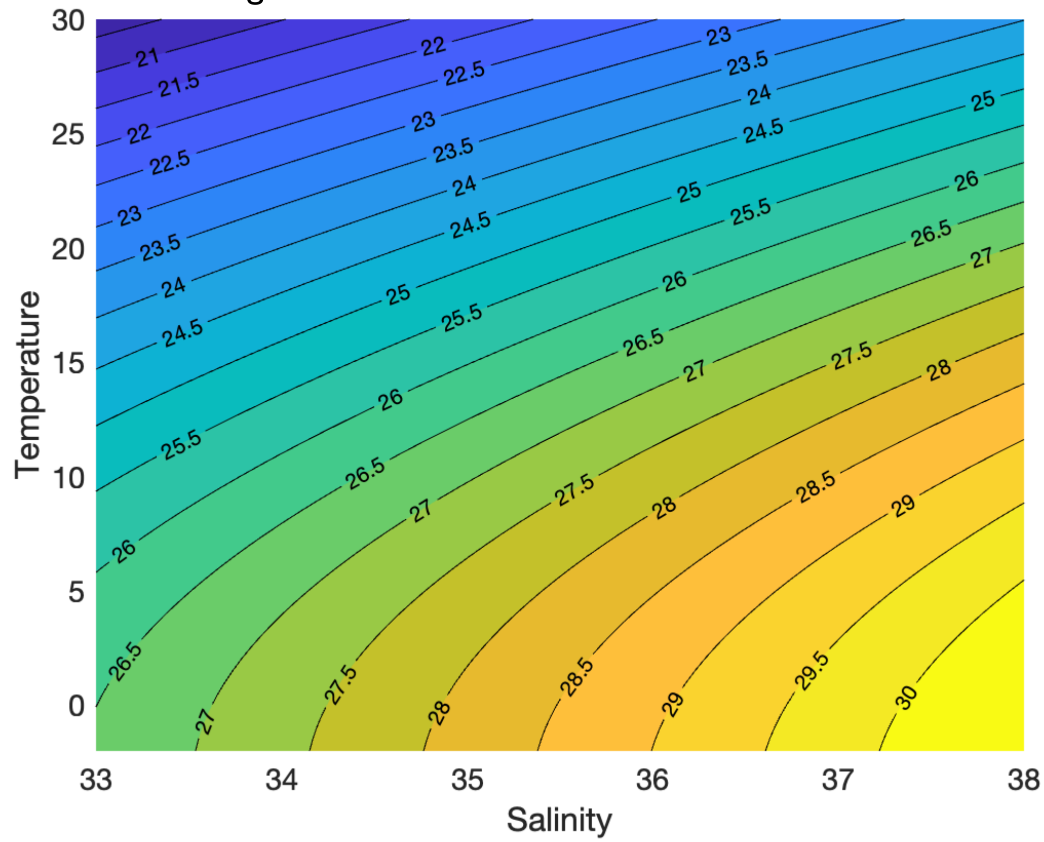
$$\sigma = \left(\frac{\rho}{\rho_0} - 1\right)1000,$$

ρ = density (kg m^{-3})

ρ_0 = maximum density of seawater (999.974 kg m^{-3})

In this notation , a density of 1025 kg/m^3 is expressed as σ = 25 kg m^{-3}

"T-S" diagram:



- Calculated using CSIRO Matlab seawater properties toolbox

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- What do you notice about density of SW as it cools?

How does this affect ventilation of a water body?

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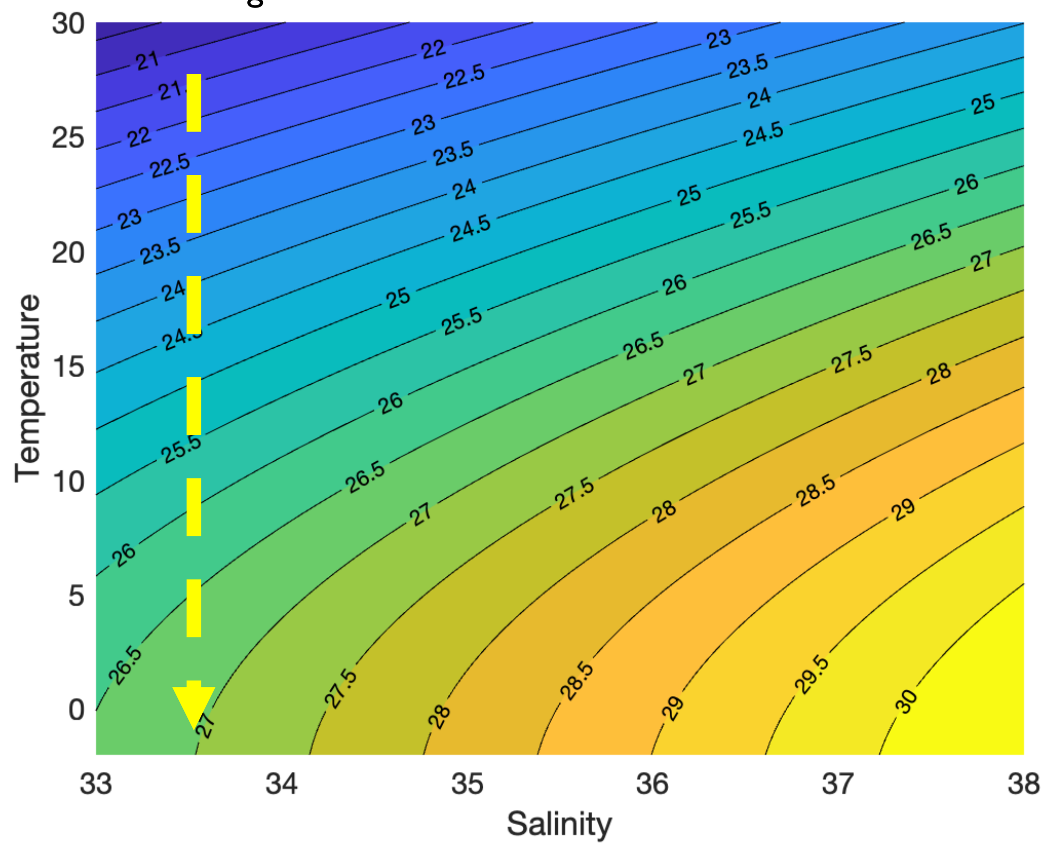

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Ventilation:
Exposure of a water parcel to the atmosphere (air-sea heat/chemical fluxes)

- What do you notice about density of SW as it cools?

How does this affect ventilation of a water body?

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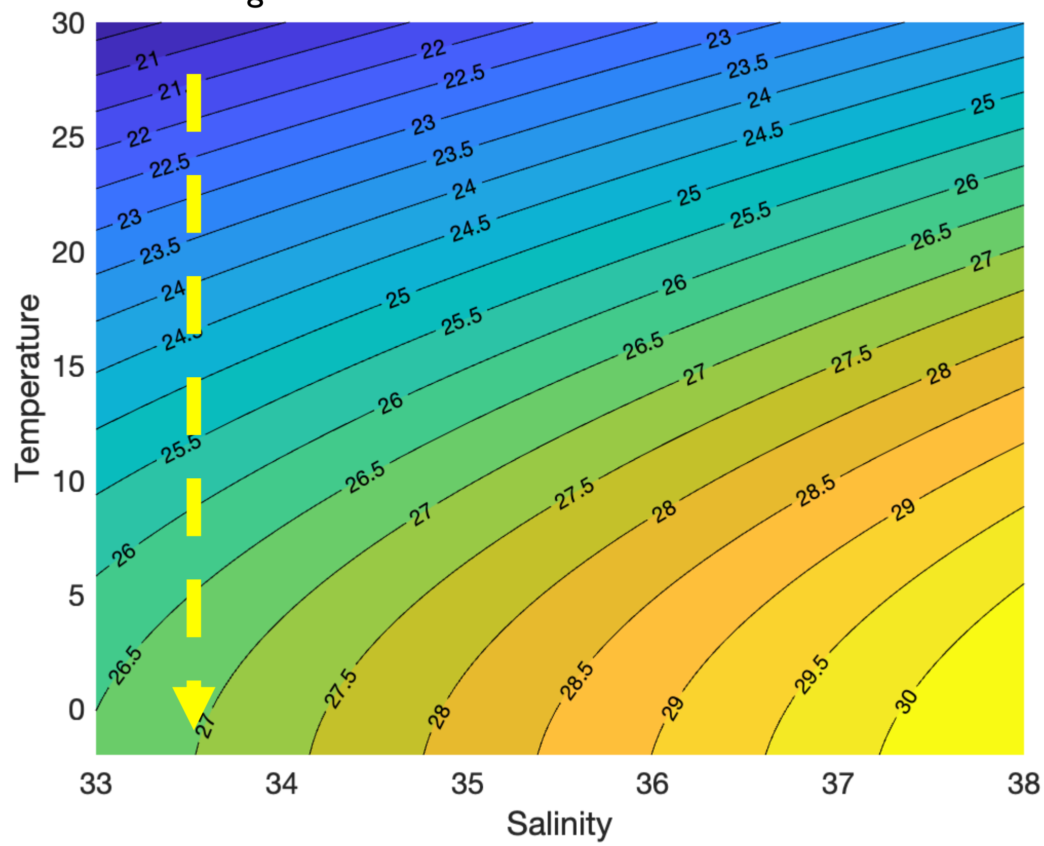

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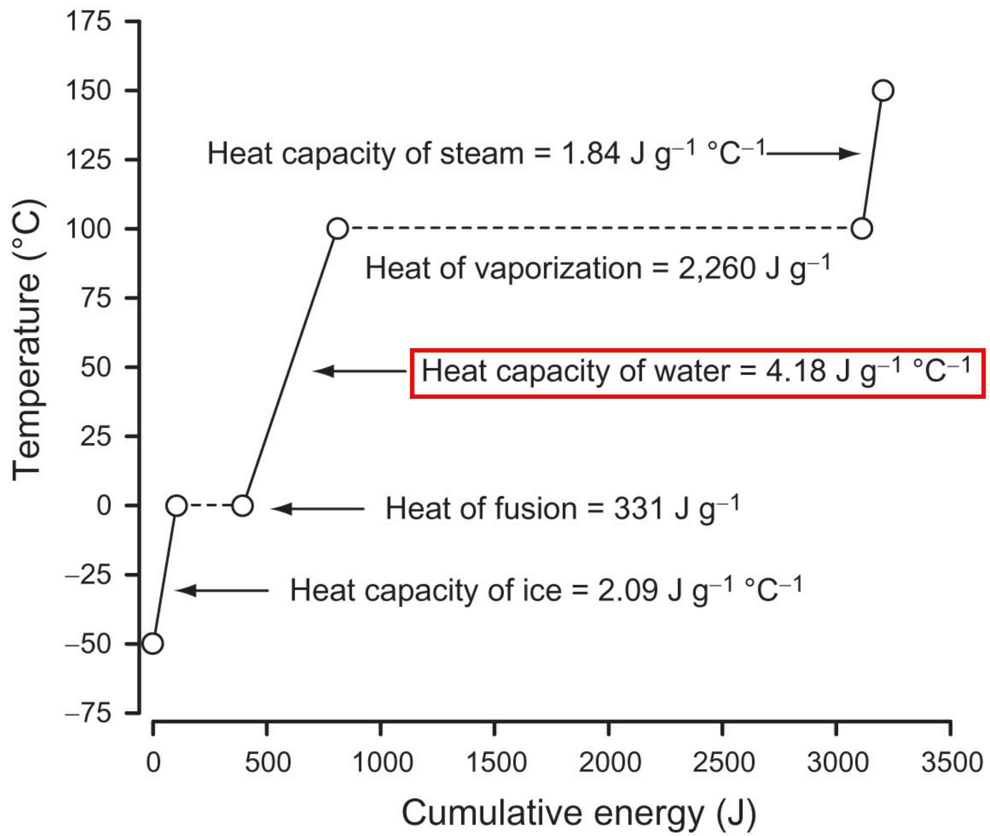
Heat capacity

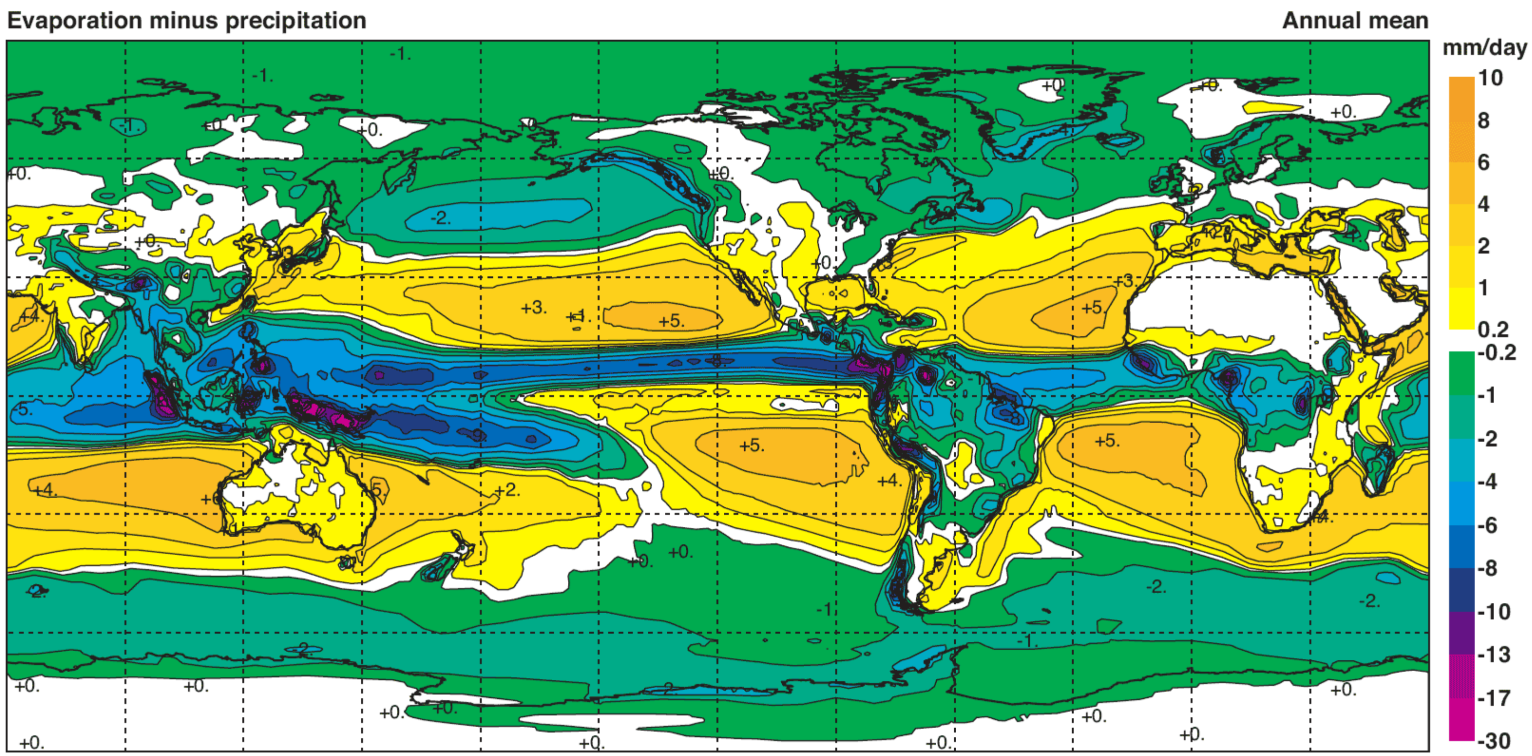


Emerson & Hamme, 1.2

Salinity

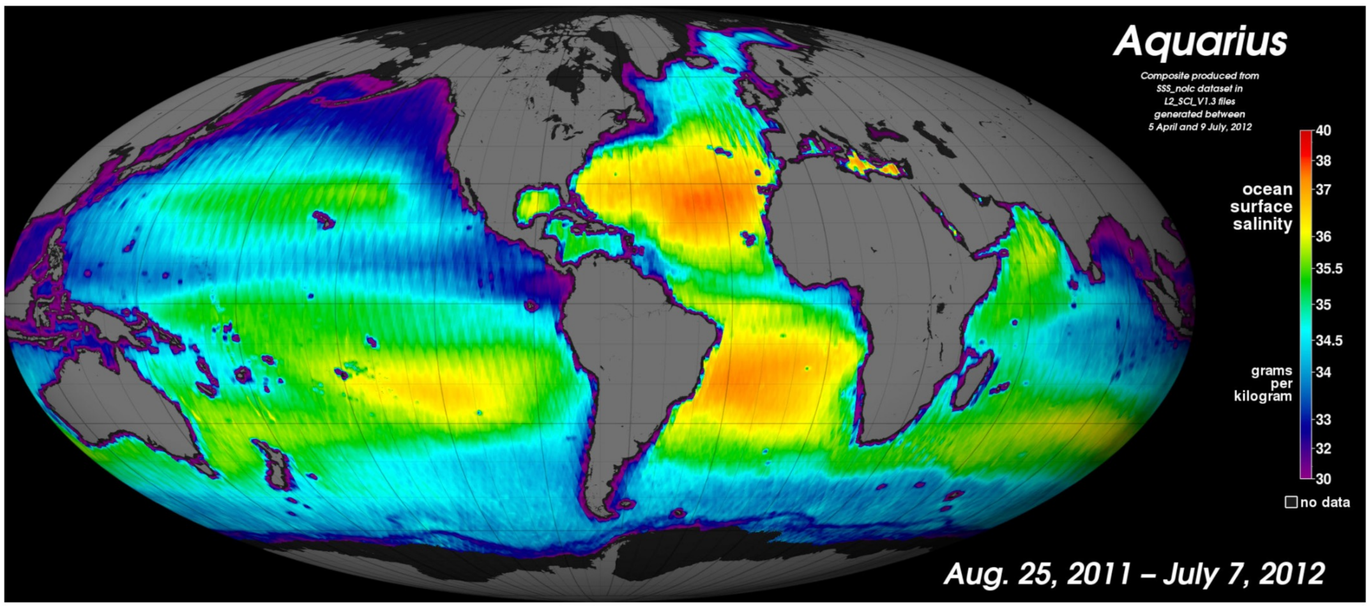
- Salinity is the amount of dissolved solids in seawater (effectively g solute / kg sw)
- Used for determining the density of seawater
- Affects the freezing point and maximum density of seawater
- Changes in salinity drive thermohaline circulation
- Temperature and salinity characteristics fingerprint origin of water masses
- Accuracy of determination needed is a function of the problem being addressed, e.g. estuaries vs deep ocean

Global Evaporation - Precipitation



Global Sea Surface Salinity

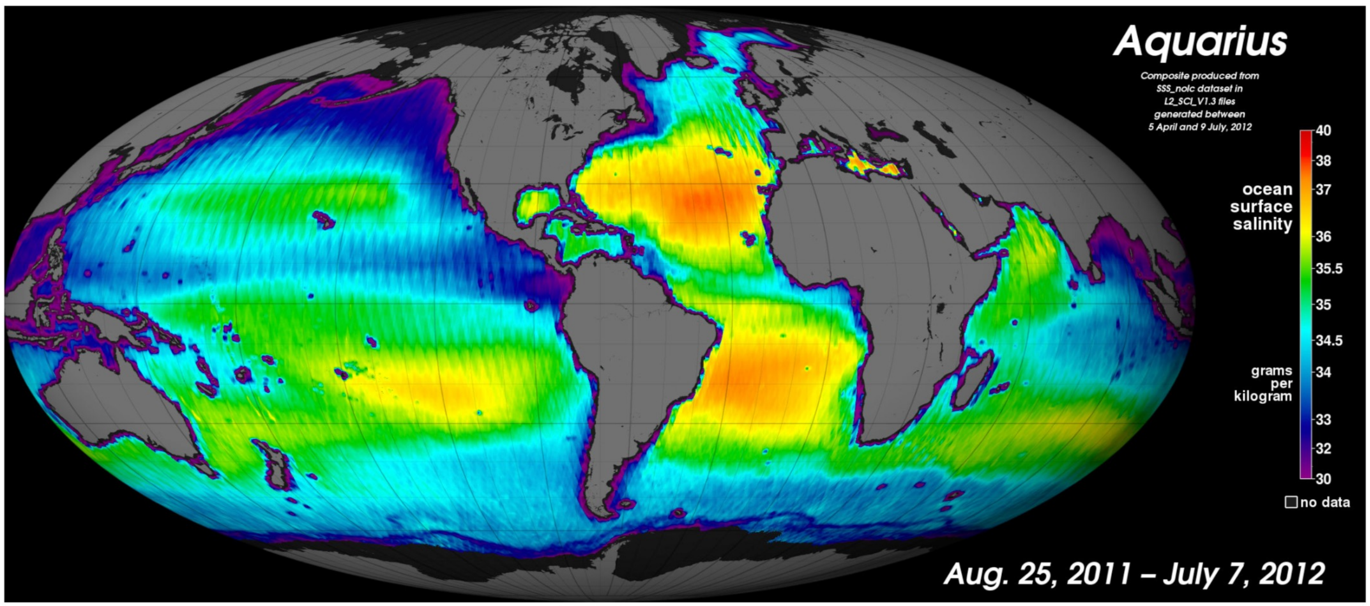
Radiometer-derived sea-surface salinity
- Aquarius spacecraft



- Set of three radiometers -- sensitive to salinity (1.413 GHz; L-band)
- Scatterometer -- corrects for the surface roughness (1.2 GHz; L-band)

Global Sea Surface Salinity

Radiometer-derived sea-surface salinity
- Aquarius spacecraft



Where would you expect the densest water?

Salinity Measurement – Historical

- Salinity is roughly the number of grams of dissolved matter per kilogram of seawater

- Salinity is difficult to measure gravimetrically because many of the salts are hydrophilic, and some decompose on heating to dryness
- From about 1900 to the 1960's, salinity was calculated from *chlorinity Cl*, as determined by titration with silver ion
  - **Salinity = 1.80655 x [Cl^-] (ppt)**

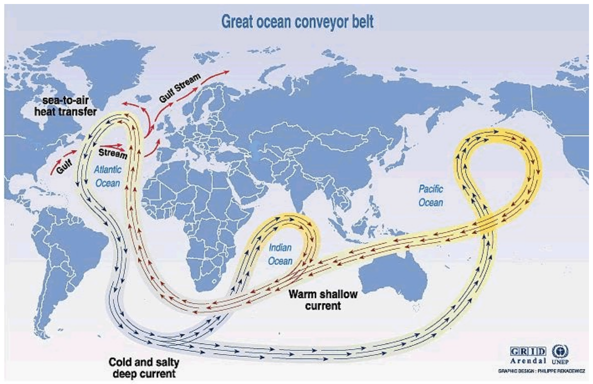
- As of 1978, it became standard to calculate "practical salinity" S from measured conductivity (PSS-78)
- Note: practical salinity is unit-less, and is not a SI quantity!

Standard Mean Ocean Water (SMOW): $S \approx 35$, $Cl \approx 19‰$

- A salinity measure (g-salt/kg) is needed that is more accurate than conductivity-based Practical Salinity
- Handles spatial variations in the composition of seawater upsets the relationship between
  - Practical Salinity Sp (which is a function of conductivity, temperature and pressure) and
  - Absolute Salinity S_A (defined as the mass of dissolved material {'salt'} per mass of seawater solution)…a true 'mass fraction'

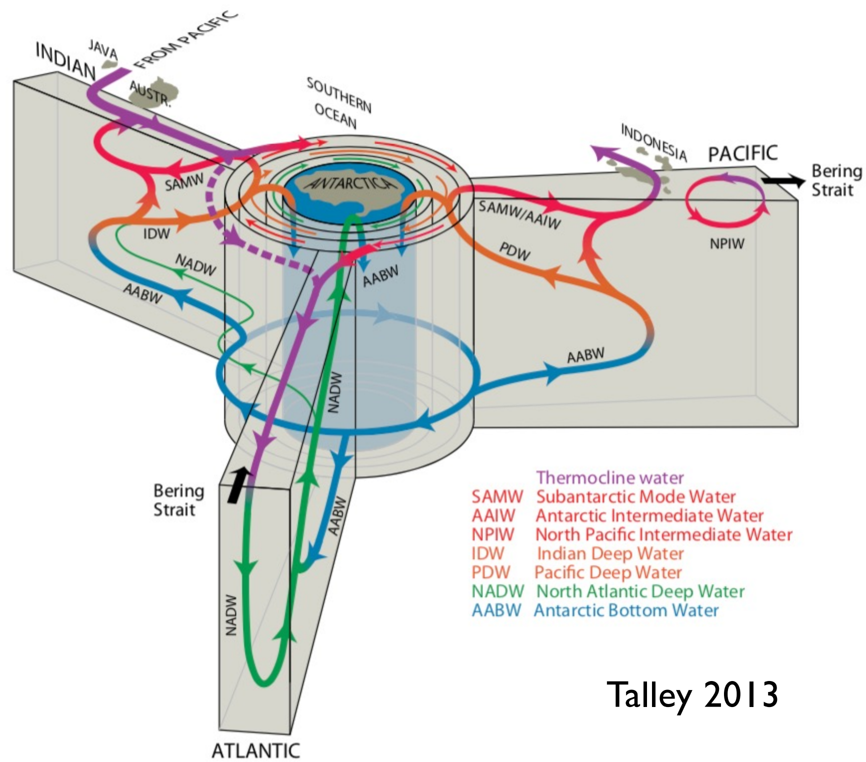
Salinity and circulation

Water mass	Temp.	Sal.
AABW	-0.7	34.65
NADW	2.3	34.9
AAIW	3.5	34.1



Source: Broecker, 1991, in Climate change 1995, Impacts, adaptations and mitigation of climate change: scientific-technical analyses, contribution of working group 2 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

- Freezing point of seawater is ~ -1.8˚C
- Density continually increases to freezing point



Talley 2013

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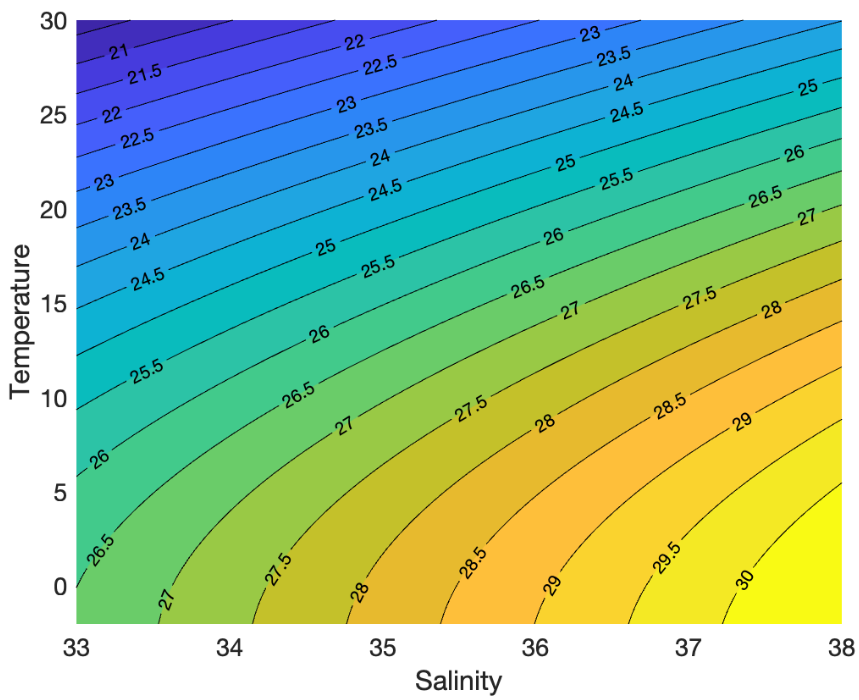

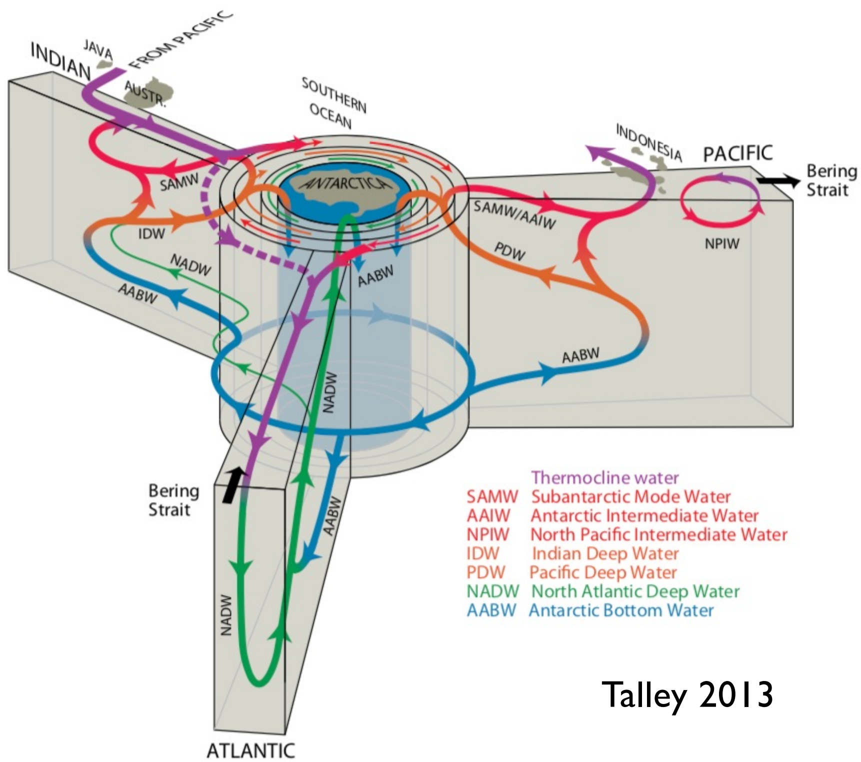

Talley 2013

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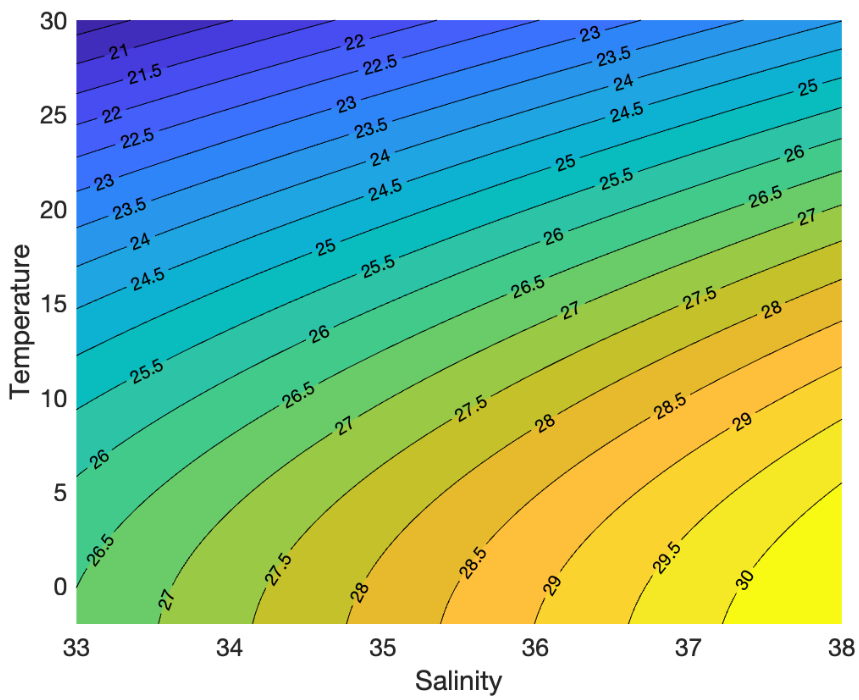
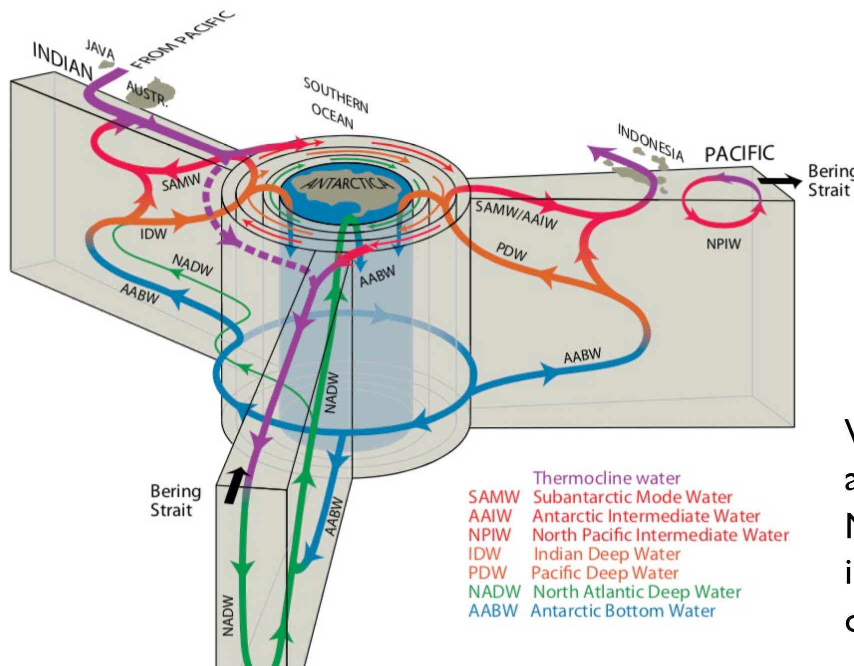




Talley 2013

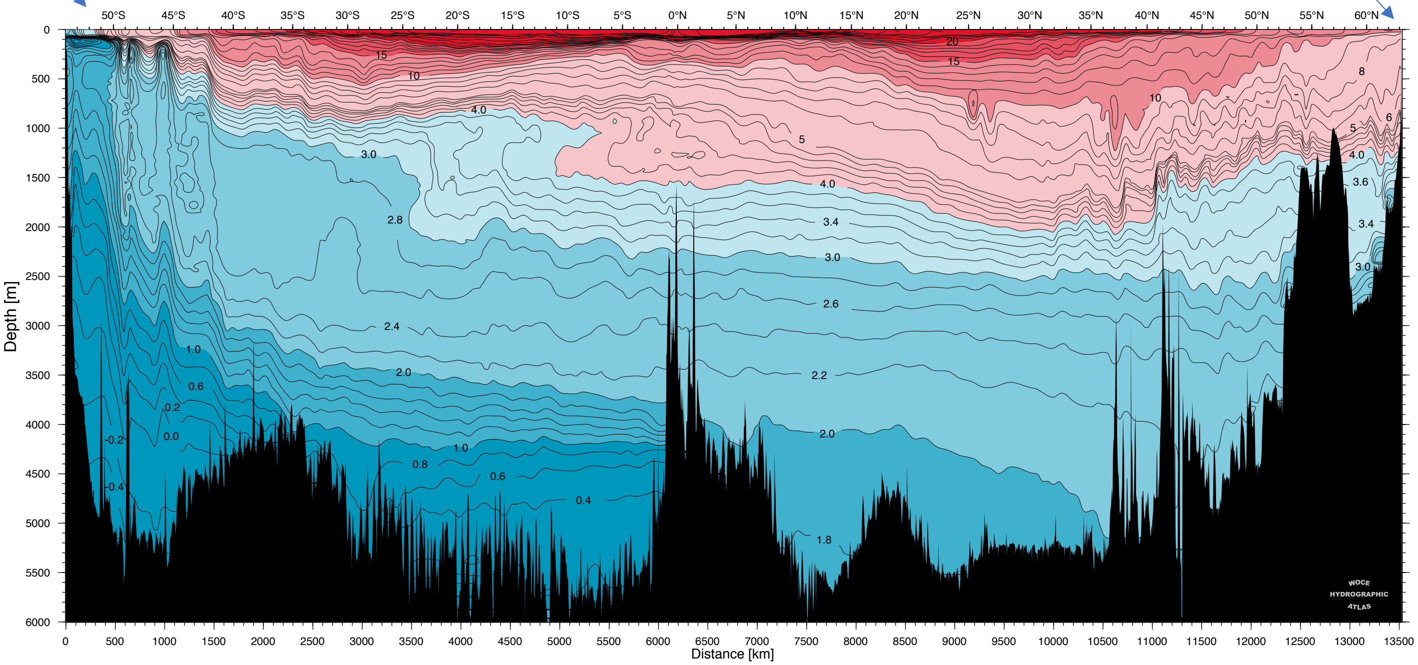
Why is there no arrow from the North Pacific into the deep ocean?

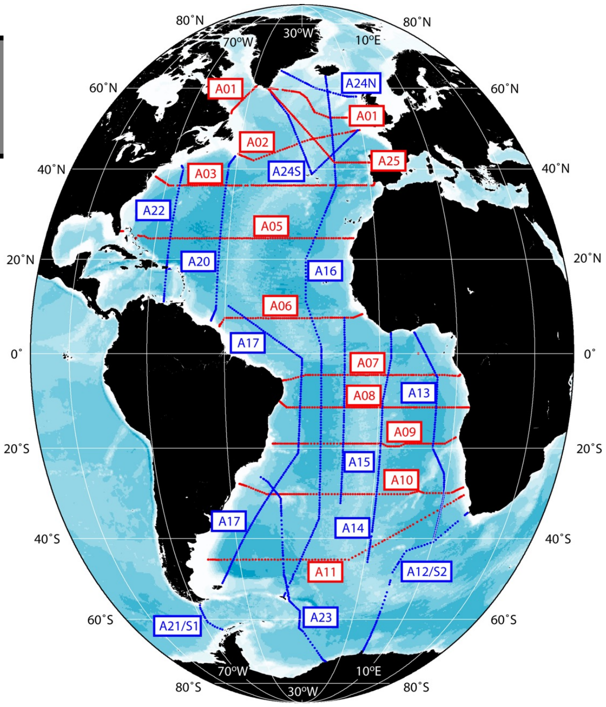
Stratification and mixing

Ventilation

Atlantic WOCE line A16 – potential temperature

Ventilation





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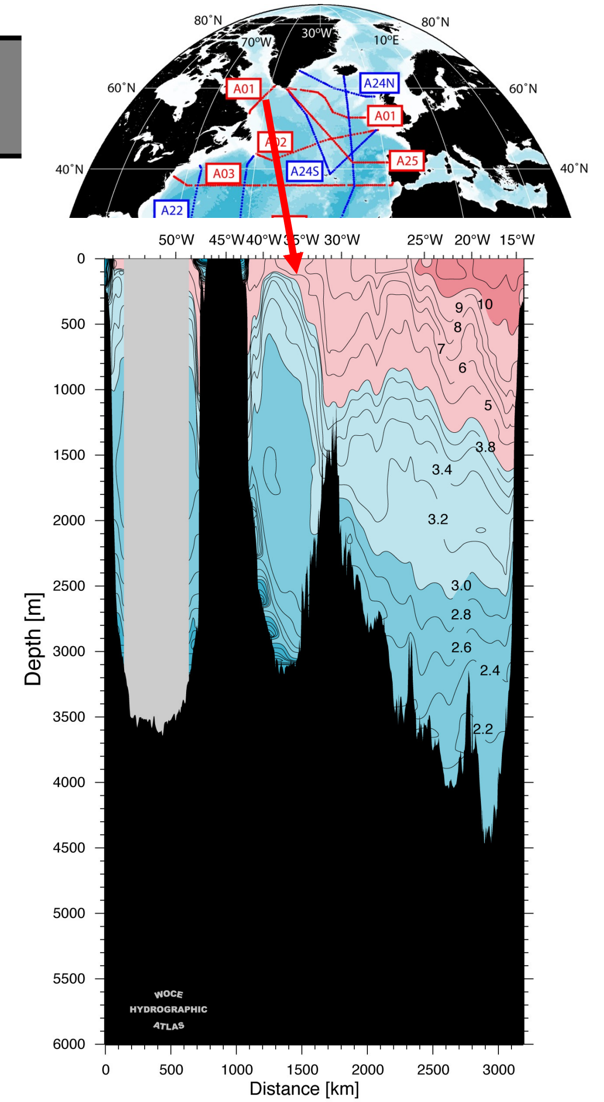
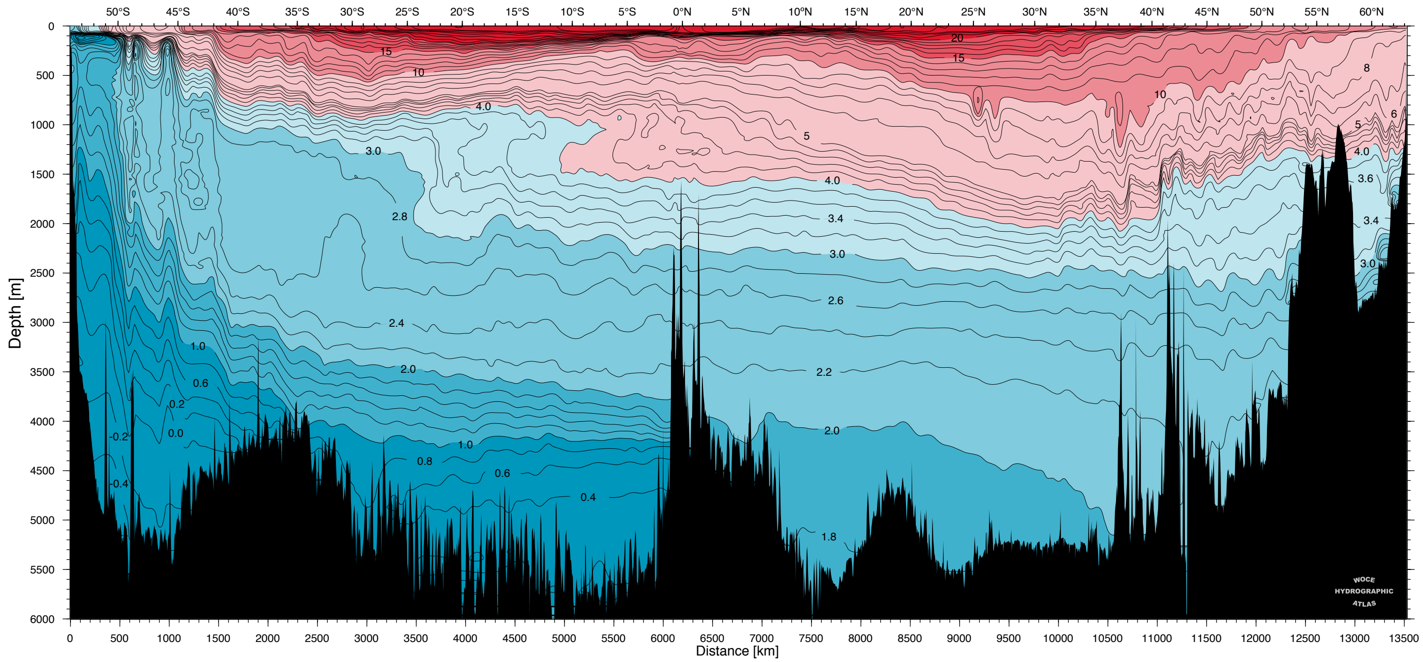
http://whp-atlas.ucsd.edu/whp_atlas/atlantic_index.html

Stratification and mixing



Atlantic WOCE line A16 – potential temperature



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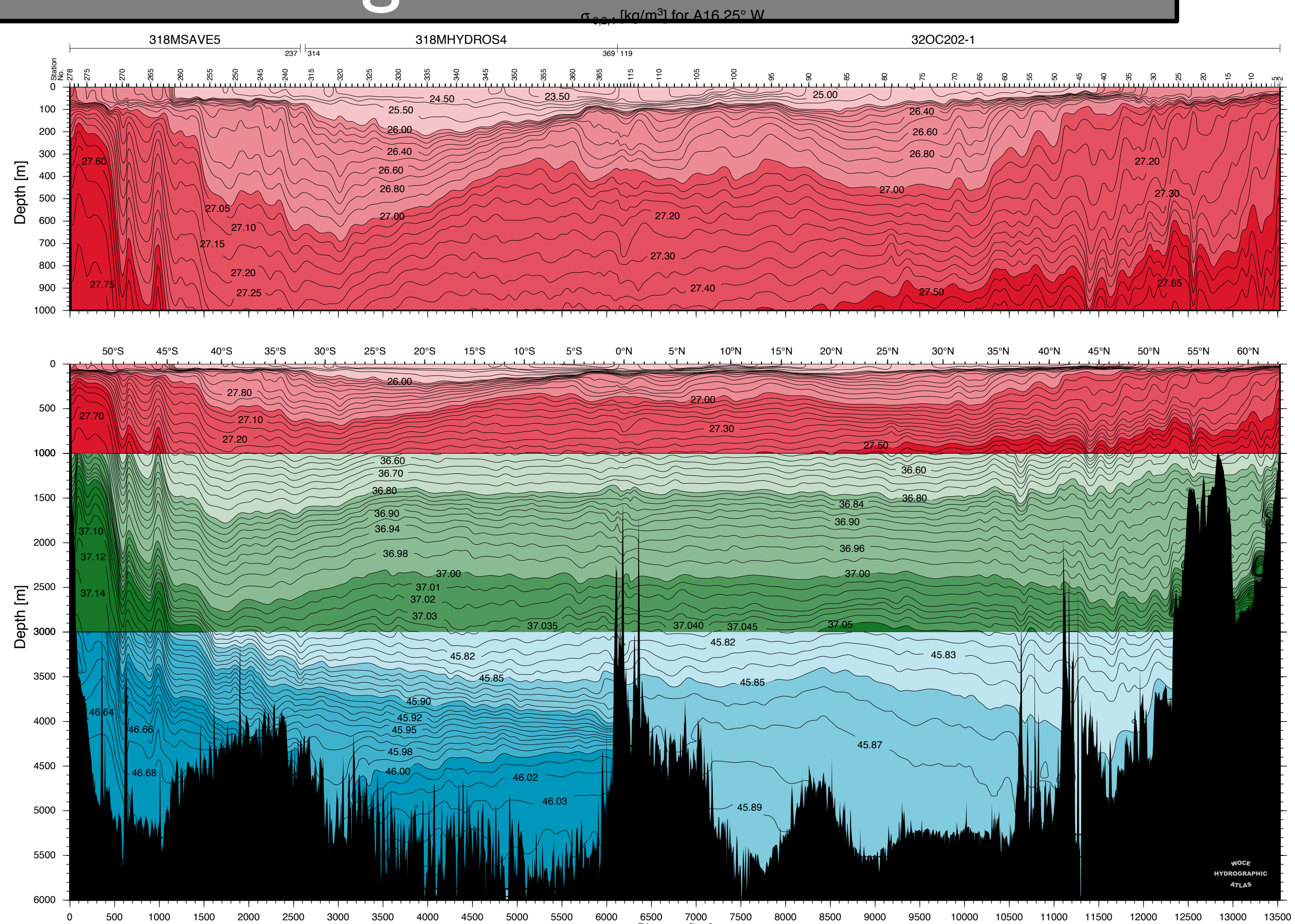
http://whp-atlas.ucsd.edu/whp_atlas/atlantic_index.html

Stratification and mixing

Atlantic WOCE line A16 – potential density (mult. ref depths)



Mixing happens along isopycnals much faster than across

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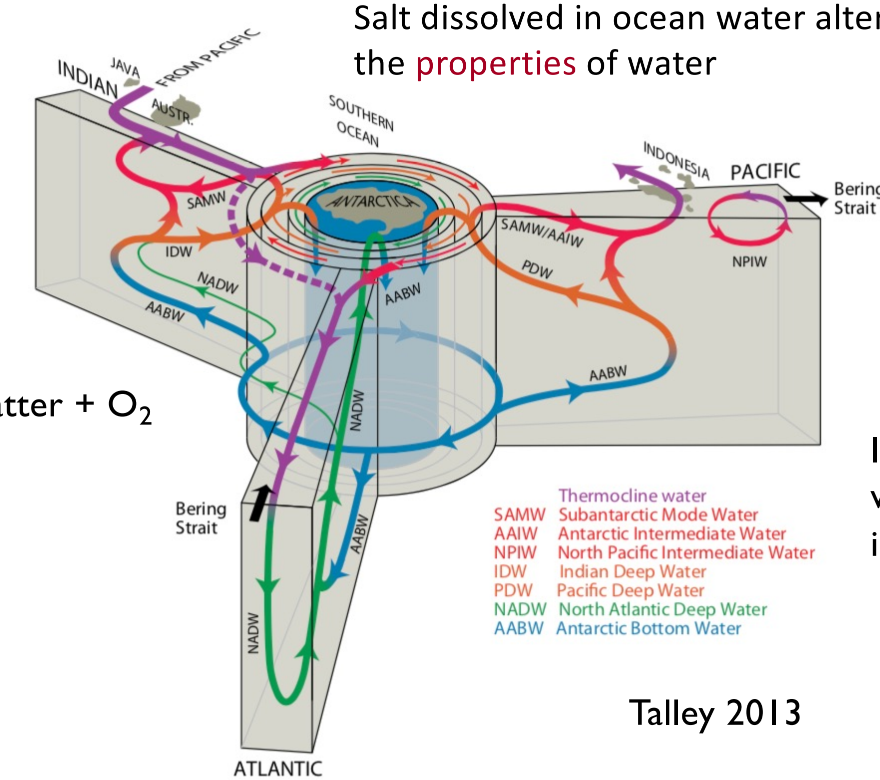
Circulation and biology

Water mass	Temp.	Sal.
AABW	-0.7	34.65
NADW	2.3	34.9
AAIW	3.5	34.1

Salt dissolved in ocean water alters the properties of water

The impact of biology accumulates with water mass age:

$$CO_2 + H_2O + \text{nutrients (N, P, trace)} \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} \text{Organic matter} + O_2$$



Talley 2013

Is there deep water formation in the Pacific?

Circulation and biology

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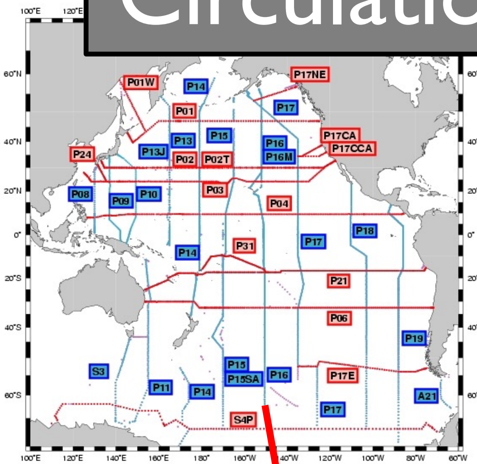
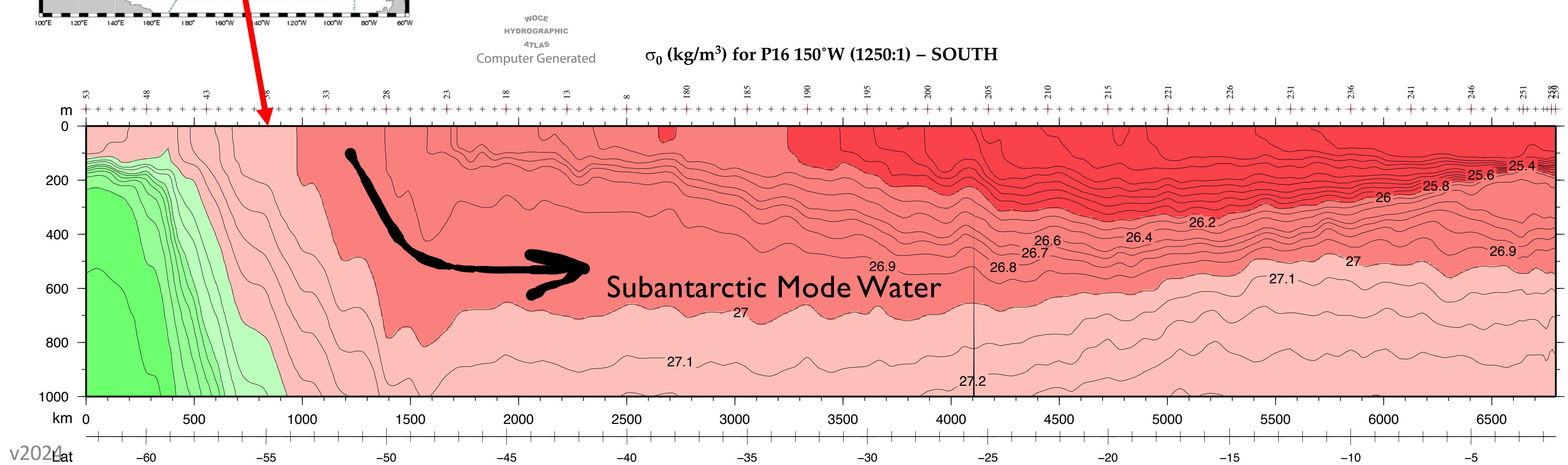
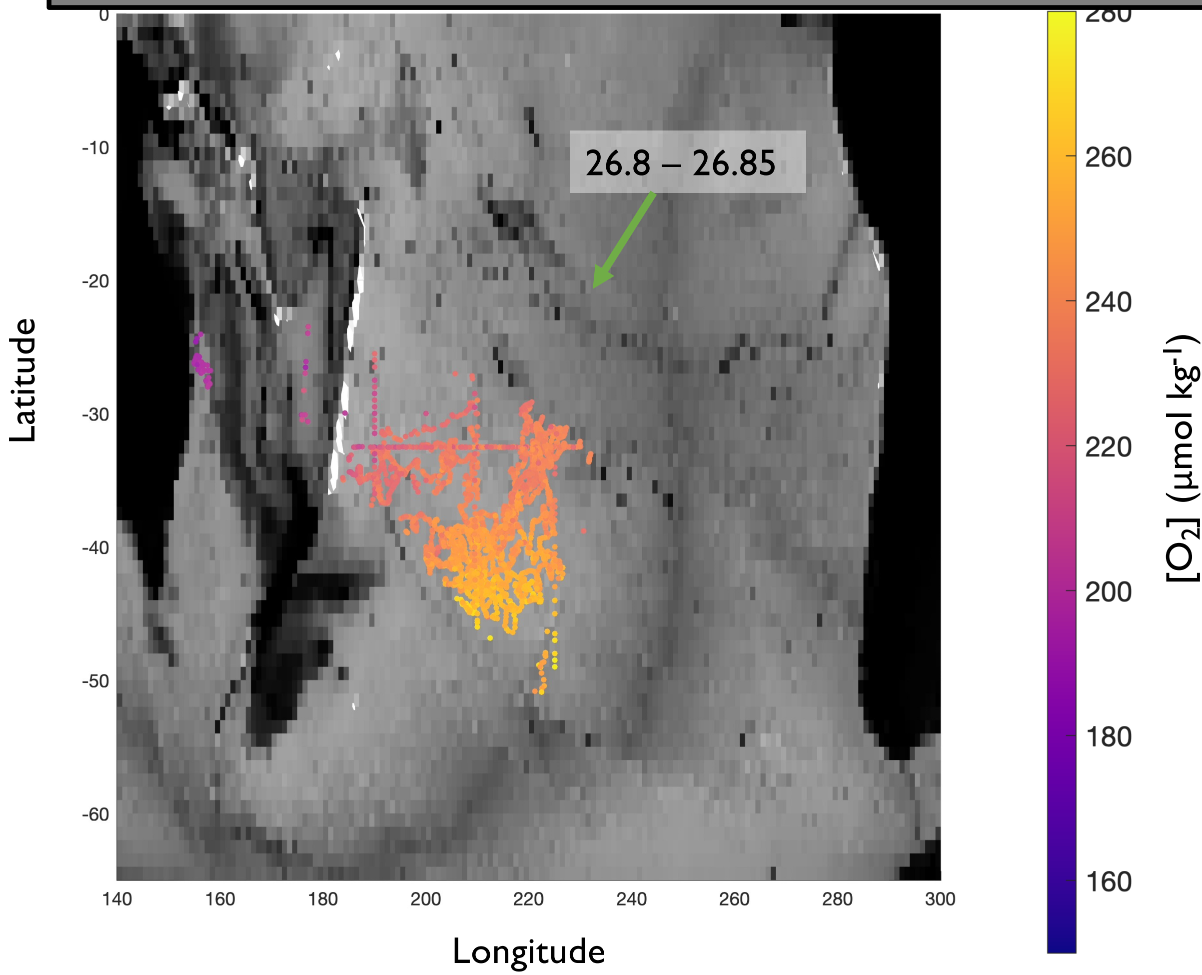


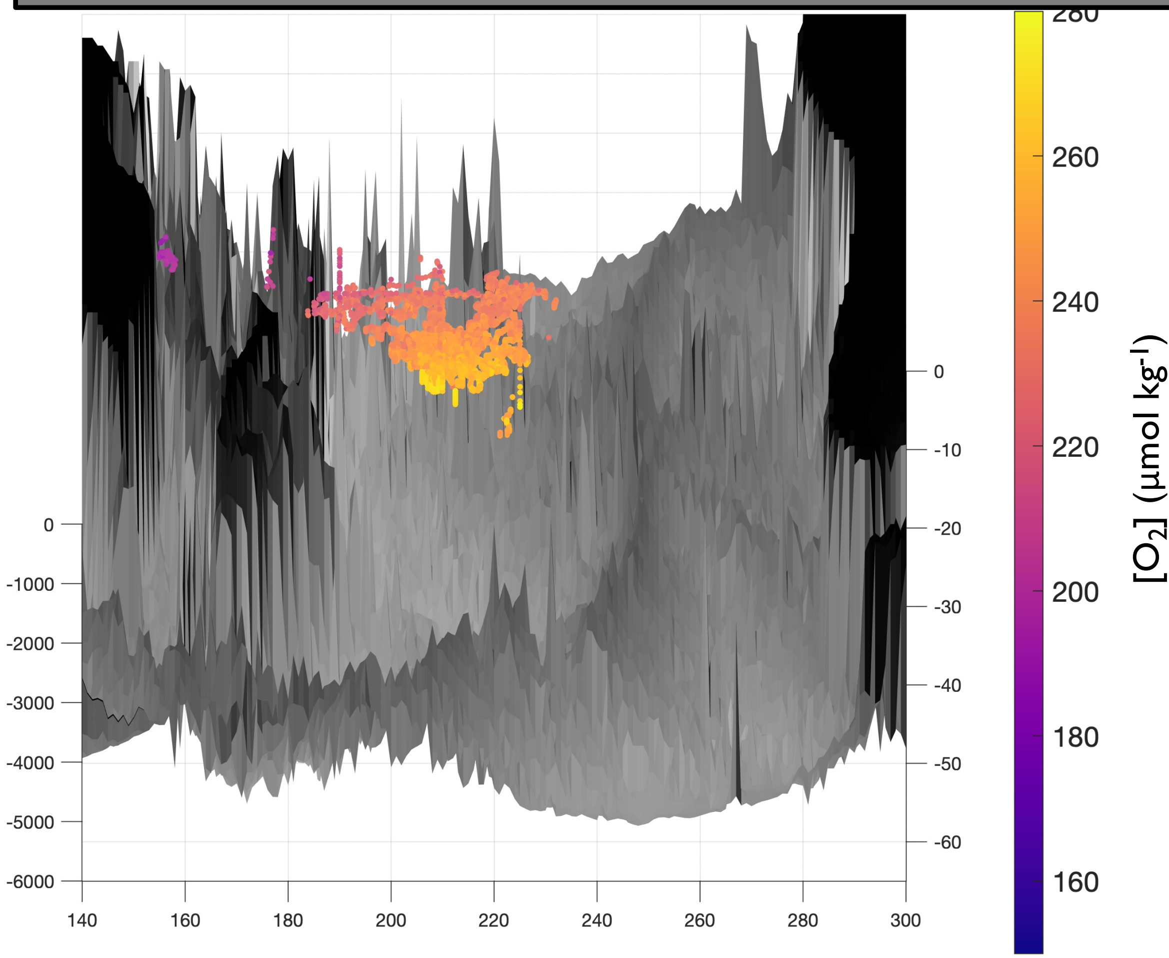


Spatial patterns of SAMW density layers



- The lightest SAMW mostly recirculates in the subtropics

Spatial patterns of SAMW density layers



- The lightest SAMW mostly recirculates in the subtropics
- Formation is in the central Pacific, oxygen is lost as the water moves northward

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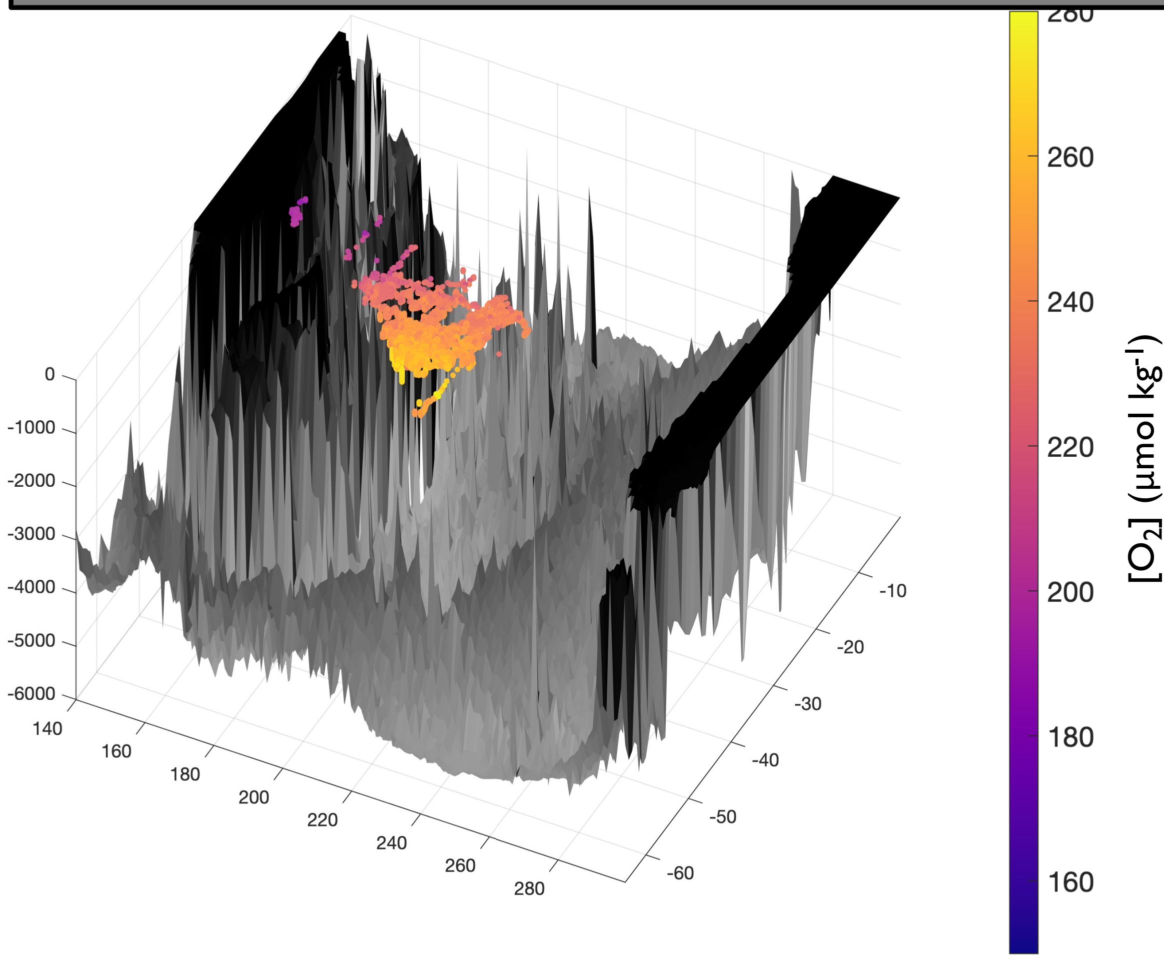

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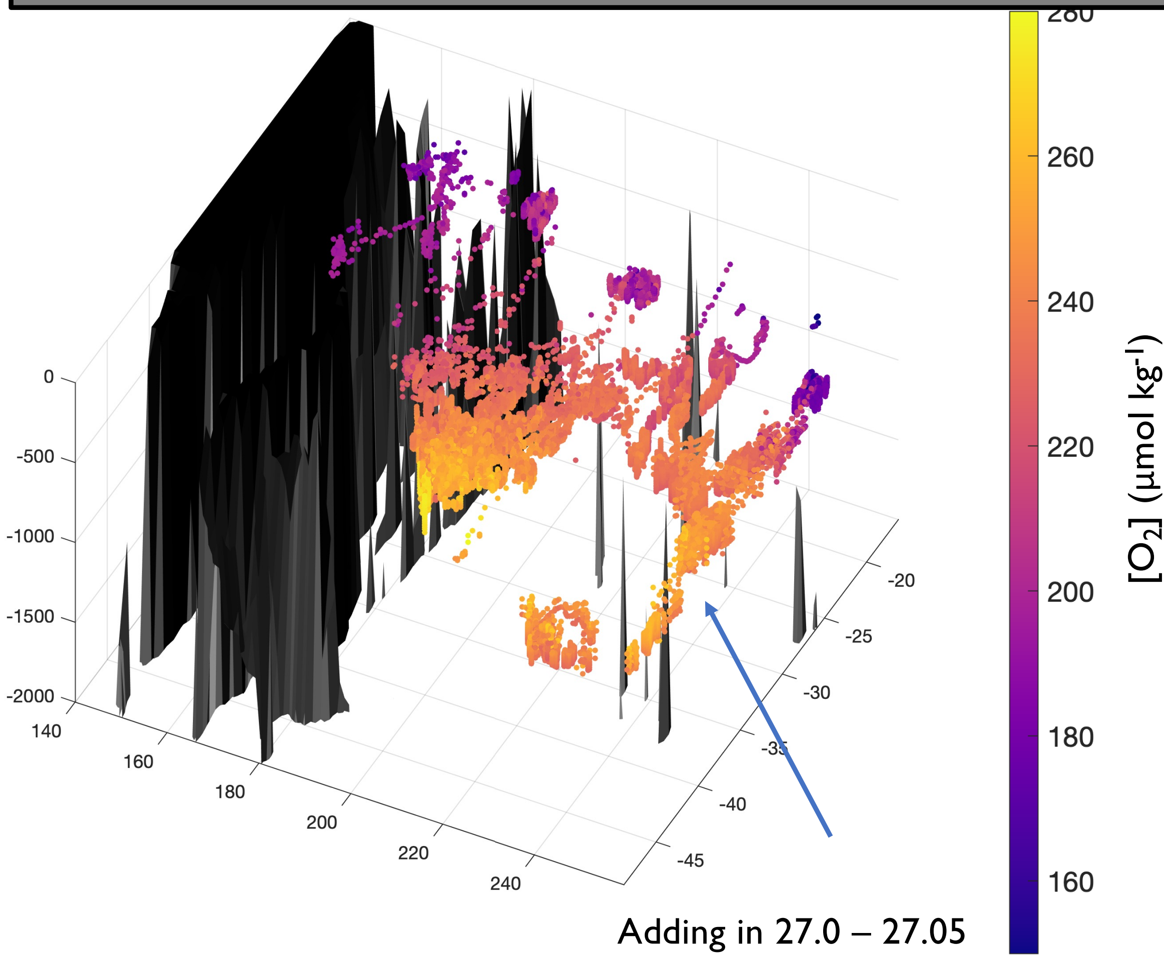

Adding in 27.0 – 27.05

- The lightest SAMW mostly recirculates in the subtropics
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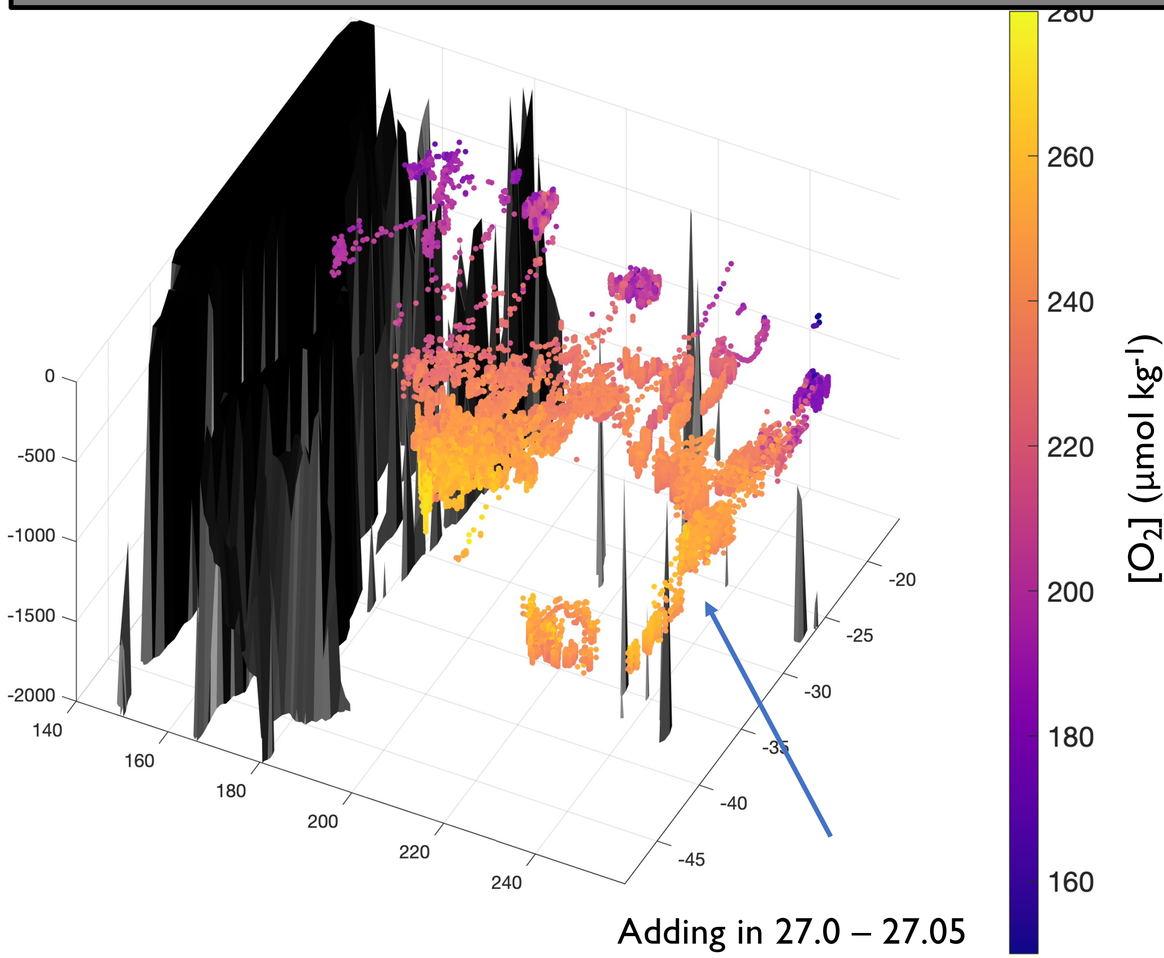
- The densest water forms in the southeast Pacific and takes a longer track northward before circulating to the west

Spatial patterns of SAMW density layers



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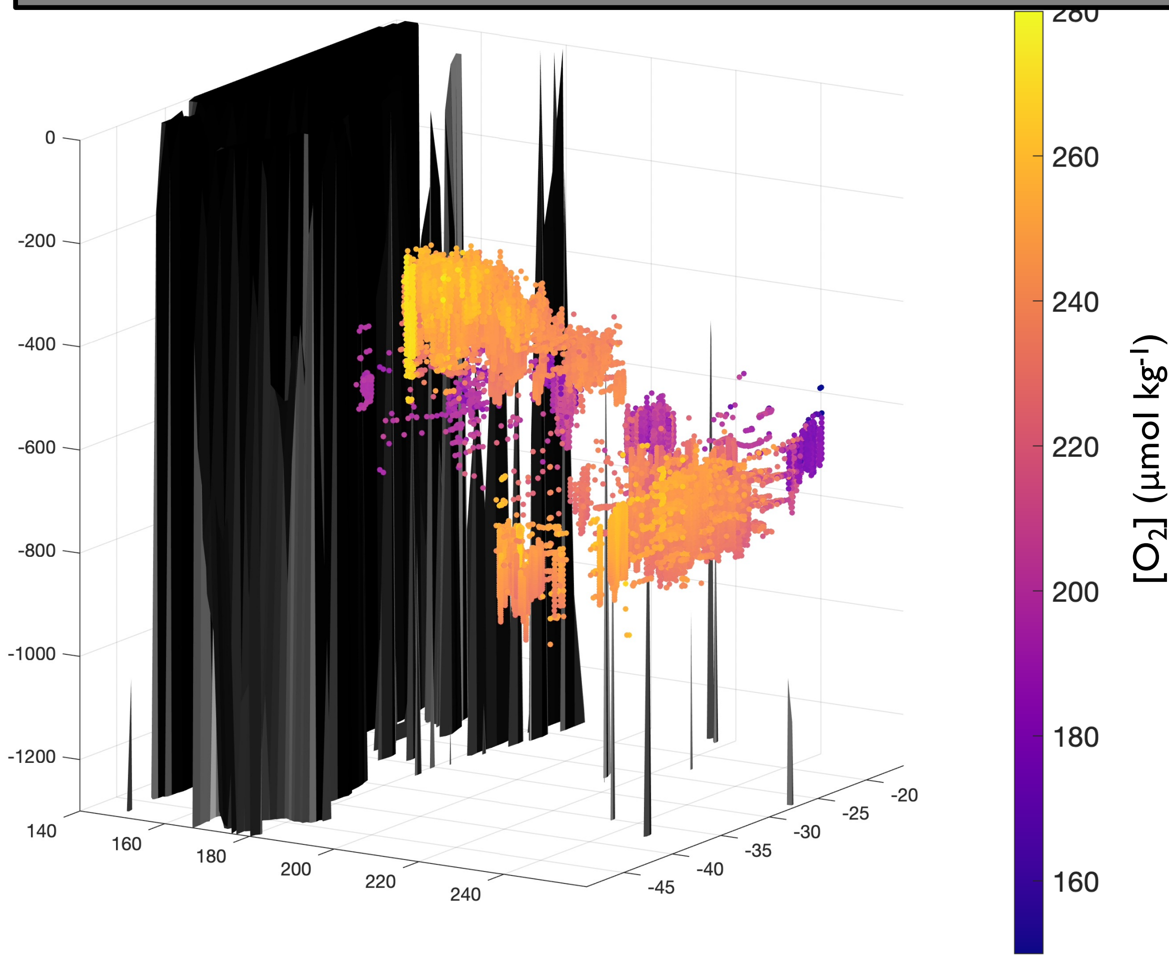

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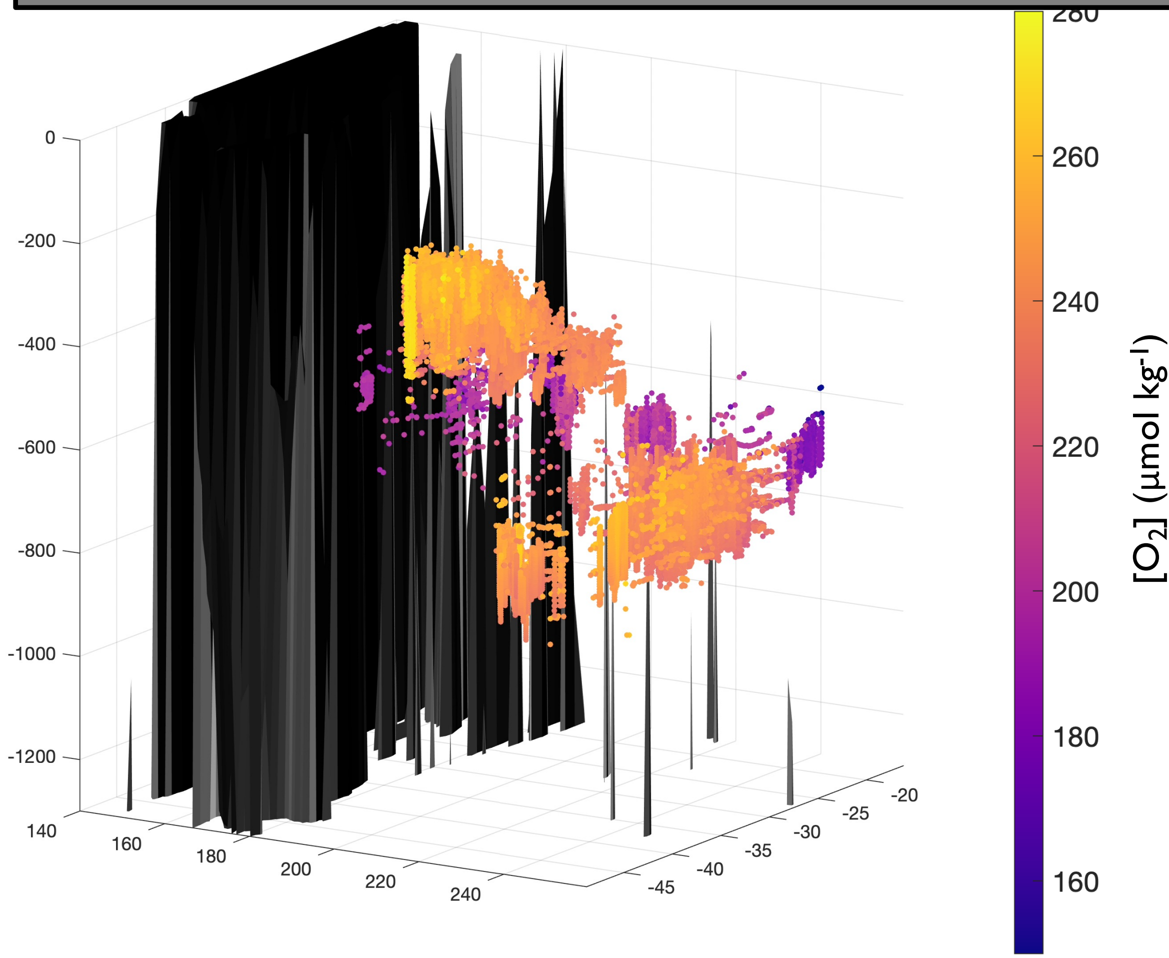
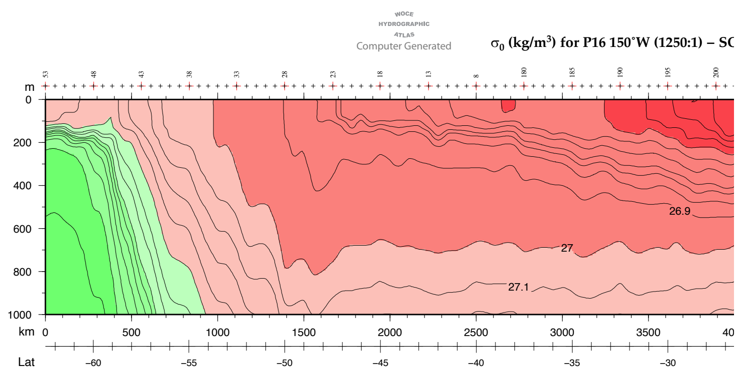
- Viewed from the east, lighter water sinks into the ocean interior, densest water starts to upwell toward the tropics

Spatial patterns of SAMW density layers





Units

Table 1.2. Concentration units encountered in oceanography. (a) Molality, molarity, normality and volume ratio all have a long history of use in classical chemistry because of their convenience for laboratory preparations. Equivalents, eq, is equal to moles × absolute value of the charge of the species. Units indicated as "seawater units' are those preferred in oceanography. (b) Exponential terminology used in chemical oceanography.

(a)

Name	Basis	Dimensions	Symbol	Definition
Concentrations in aqueous solution				
Molal	Mass	mol kg^{-1}	m	Moles per kilogram of solvent
Molar	Volume	mol l^{-1}	M	Moles per liter of solution
Normal	Volume	eq l^{-1}	N	Equivalents per liter of solution
Weight ratio	Mass	g kg^{-1}		Mass of solute per mass solution
Volume ratio	Volume	ml l^{-1}		Volume solute per volume of solution
Seawater Units	Mass	mol kg^{-1}		Moles per kilogram of solution
Seawater Units	Mass	eq kg^{-1}		Equivalents per kilogram of solution
Concentrations in the atmosphere				
Mole Fraction	Moles	mol mol^{-1}	X	Moles gas per moles of dry air (= volume fraction, e.g. ppmv., for ideal gas)
Fugacity	Pressure	bar bar^{-1}, atm	f	Gas pressure per atmospheric pressure (=partial pressure, p, for ideal gas)
Partial Pressure	Pressure	bar bar^{-1}, atm	p	Gas pressure per atmospheric pressure

(b)

Name (symbol)	Peta (P)	Terra (T)	Giga (G)	Mega (M)	Kilo (k)	Milli (m)	Micro (μ)	Nano (n)	Pico (p)	Femto (f)	Atto (a)
Unit multiplier	10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}

Emerson and Hamme, 2021

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Partial Pressure	Pressure	bar bar^{-1}, atm	*p*	Gas pressure per atmospheric pressure

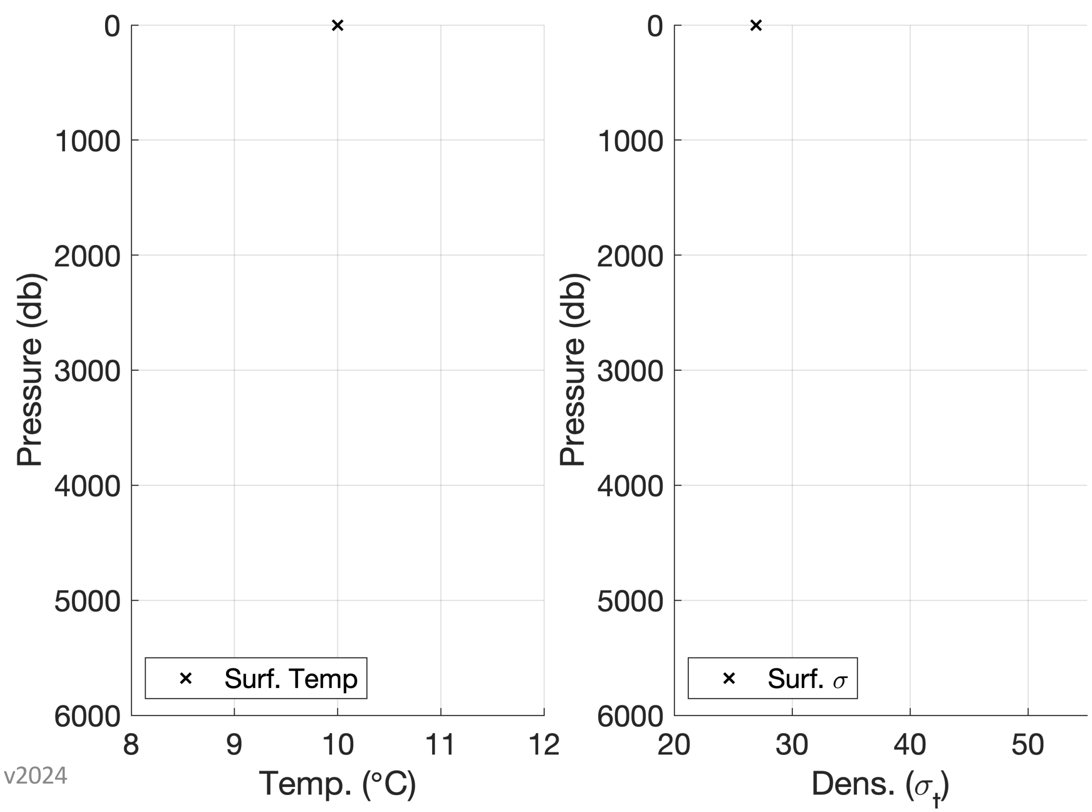
(b)

Name (symbol)	Peta (P)	Terra (T)	Giga (G)	Mega (M)	Kilo (k)	Milli (m)	Micro (μ)	Nano (n)	Pico (p)	Femto (f)	Atto (a)
Unit multiplier	10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}

What is the difference between the denominators here?

Emerson and Hamme, 2021

In situ vs. potential density and temperature

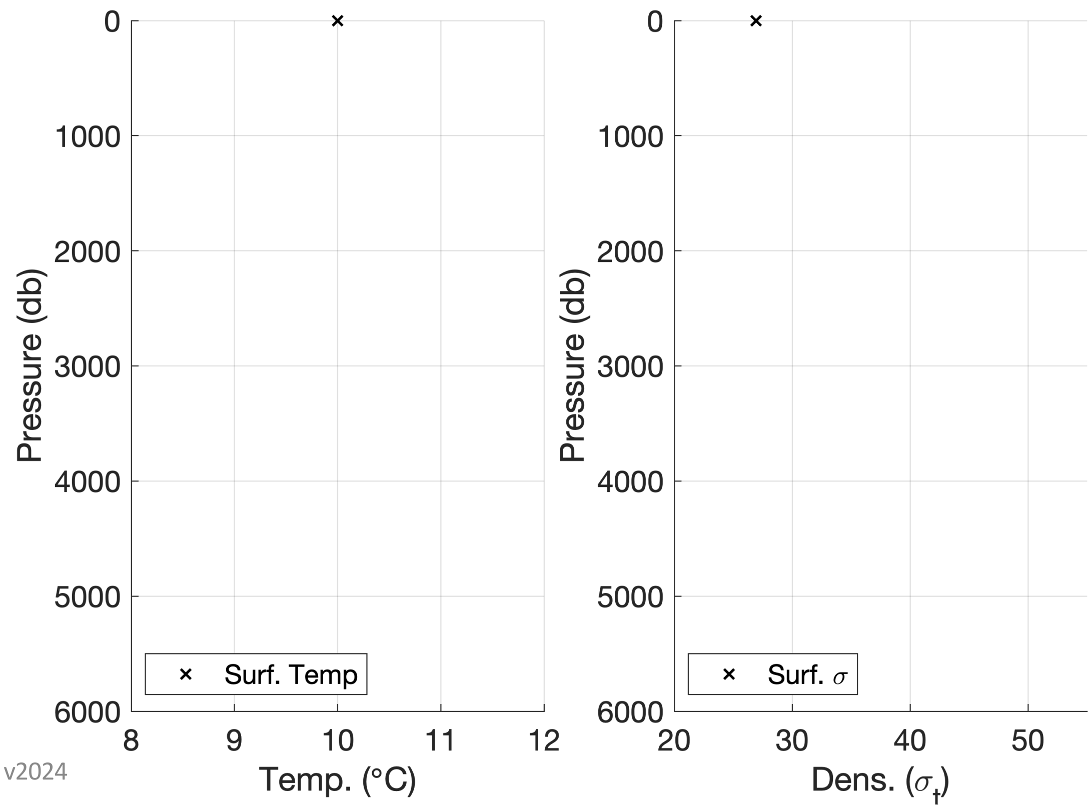


Example: imagine a parcel of water at the surface of the ocean.

- Starting T = 10, S=35, σ = 26.95;

(note that salinity is being held constant)

In situ vs. potential density and temperature



Example: imagine a parcel of water at the surface of the ocean.

- Starting T = 10, S=35, σ = 26.95;
- Assuming no heat is added or removed, what will the temperature be if that water parcel is brought down to 6000 m?

(note that salinity is being held constant)

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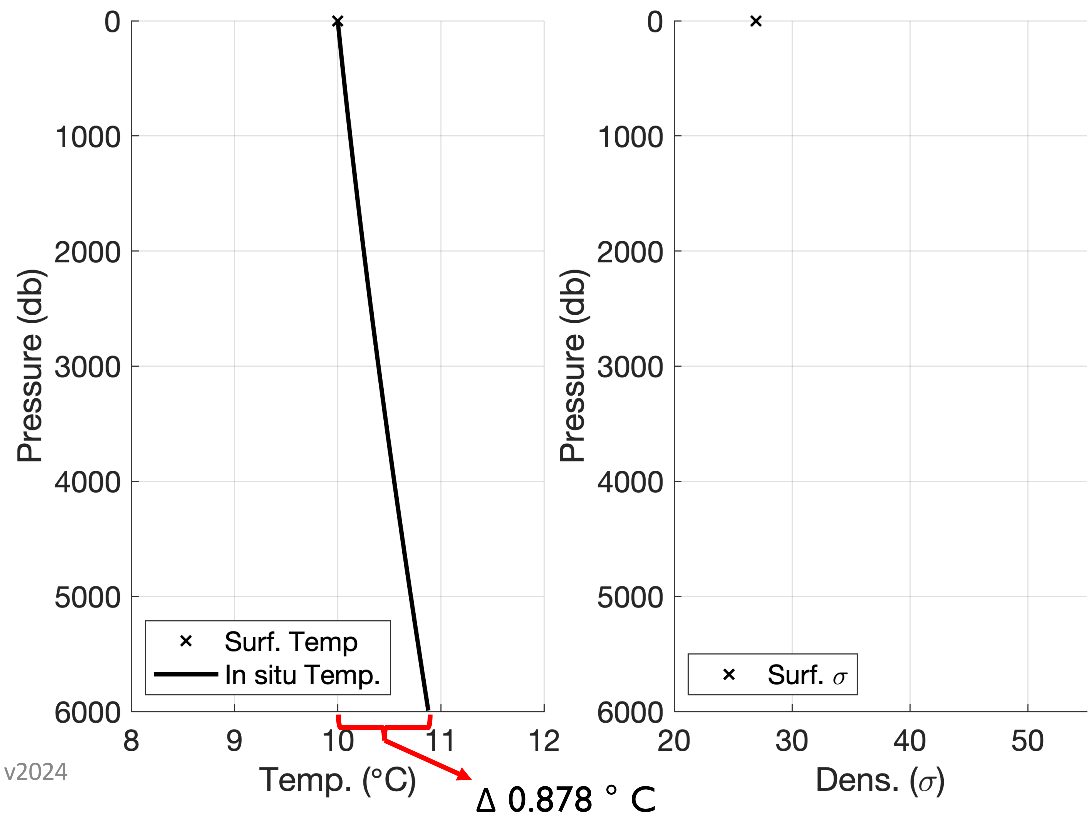
In situ vs. potential density and temperature



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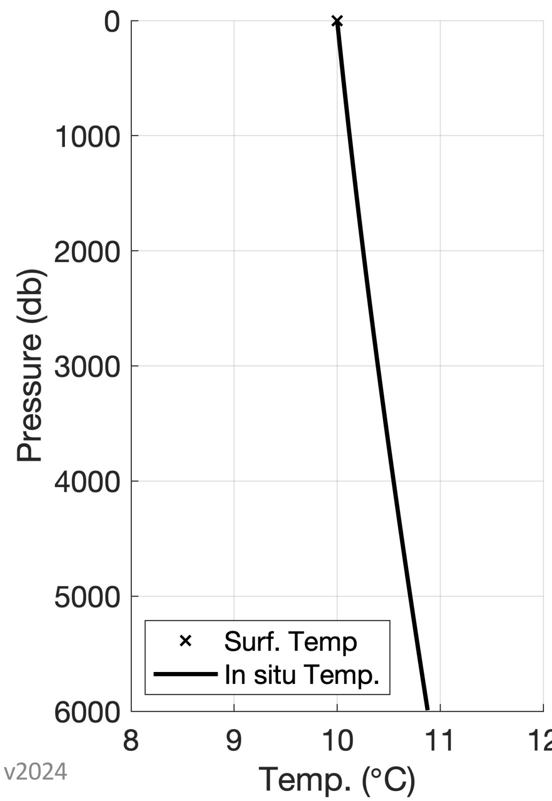
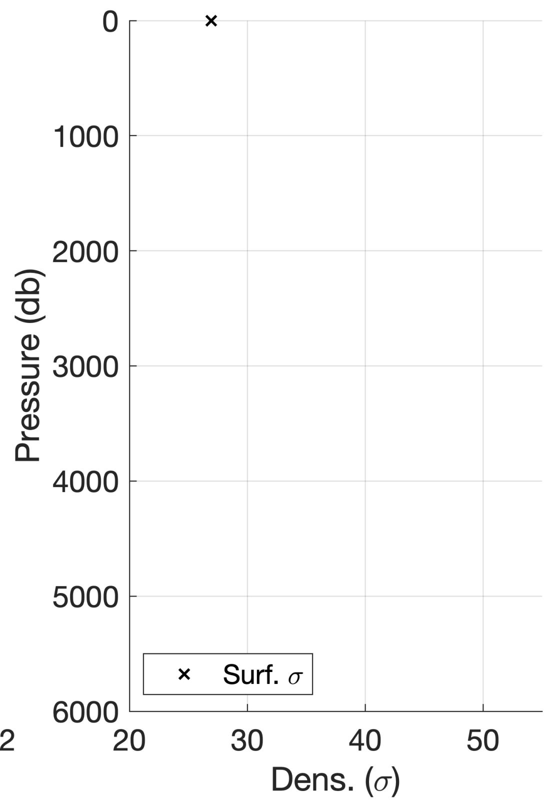
Example: imagine a parcel of water at the surface of the ocean.

- Starting T = 10, S=35, σ = 26.95;
- In-situ temp. reflects the influence of pressure on temperature
  - No change in heat, but molecules are squished together and temperature goes up

(note that salinity is being held constant)

In situ vs. potential density and temperature





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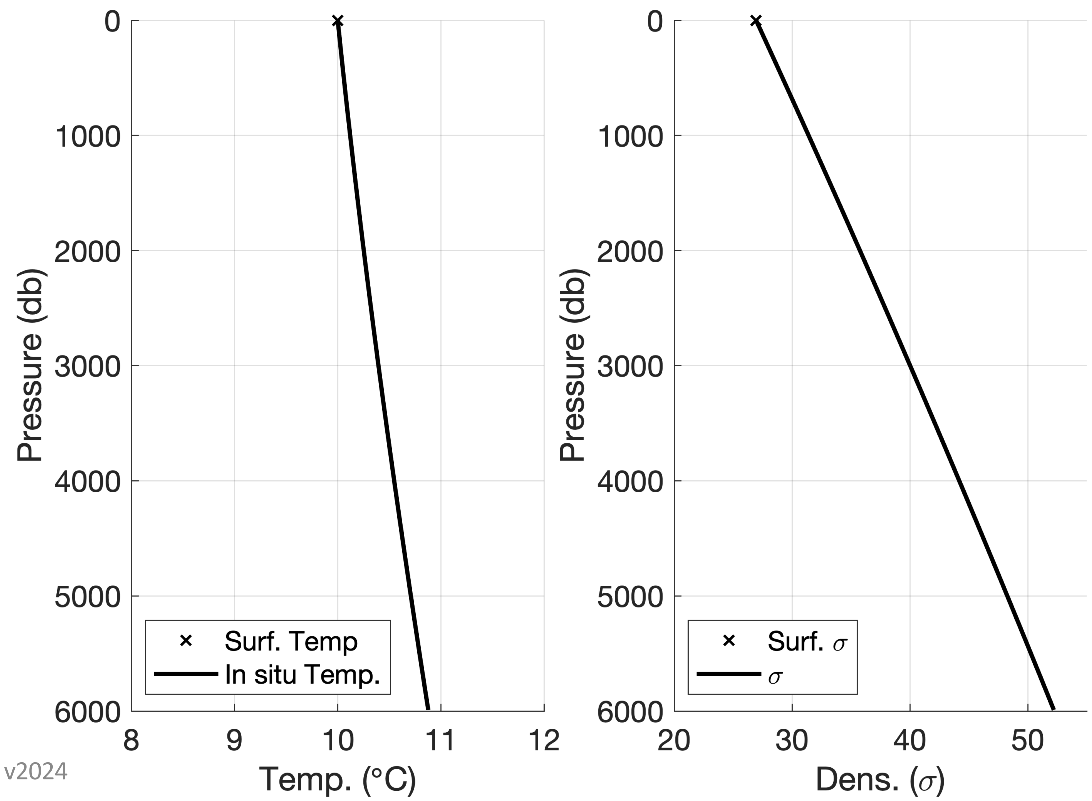
- In-situ temp. reflects the influence of pressure on temperature
  - No change in heat, but molecules are squished together and temperature goes up
- What should the density look like as you bring that water parcel down?

(note that salinity is being held constant)

In situ vs. potential density and temperature



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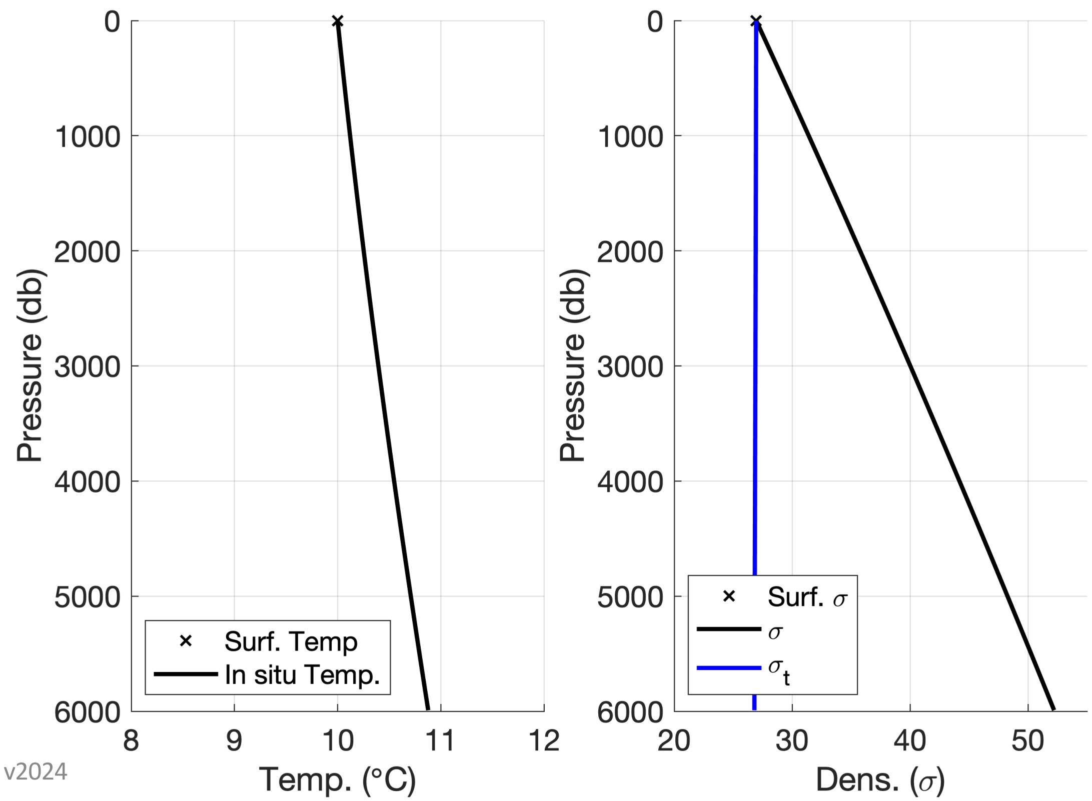
Example: imagine a parcel of water at the surface of the ocean.

- Starting T = 10, S=35, σ = 26.95;
- In-situ temp. reflects the influence of pressure on temperature
  - No change in heat, but molecules are squished together and temperature goes up
- In situ density reflects impact of pressure
  - σ : in situ density

(note that salinity is being held constant)

In situ vs. potential density and temperature

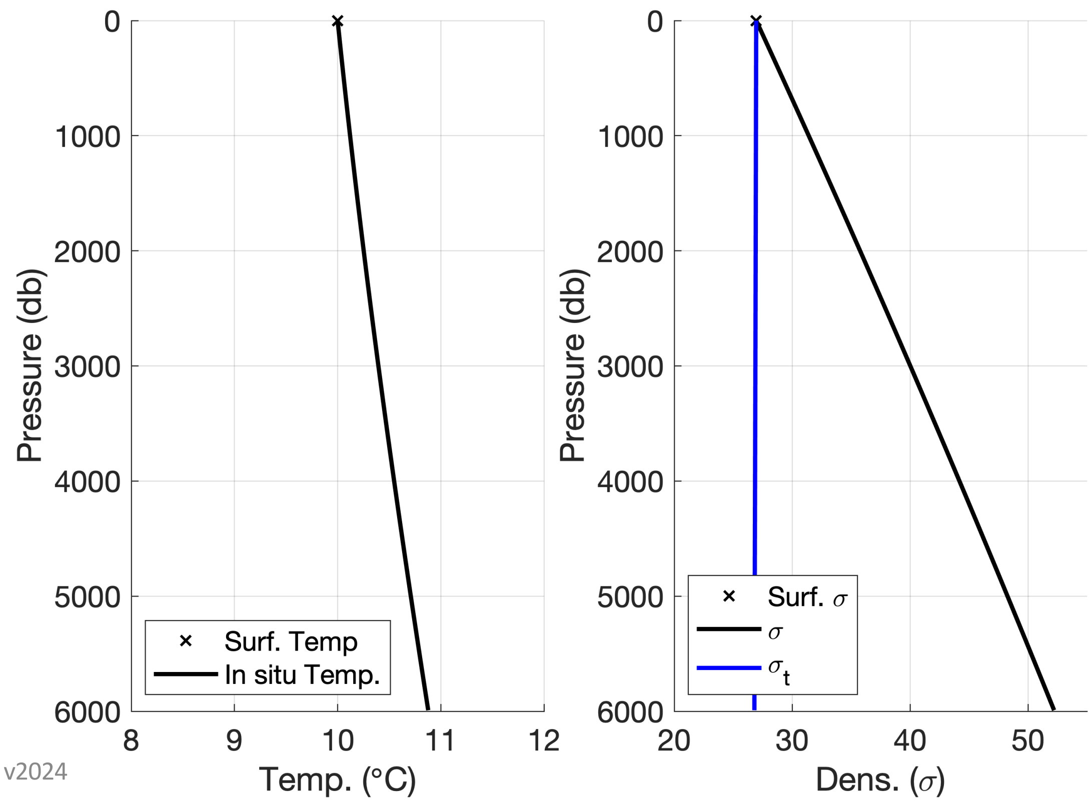


Example: imagine a parcel of water at the surface of the ocean.

- Starting T = 10, S=35, σ = 26.95;
- In-situ temp. reflects the influence of pressure on temperature
  - No change in heat, but molecules are squished together and temperature goes up
- In situ density reflects impact of pressure
  - σ : in situ density
  - σ_t : density calculated using in situ temperature but pressure effect on density removed

(note that salinity is being held constant)

In situ vs. potential density and temperature



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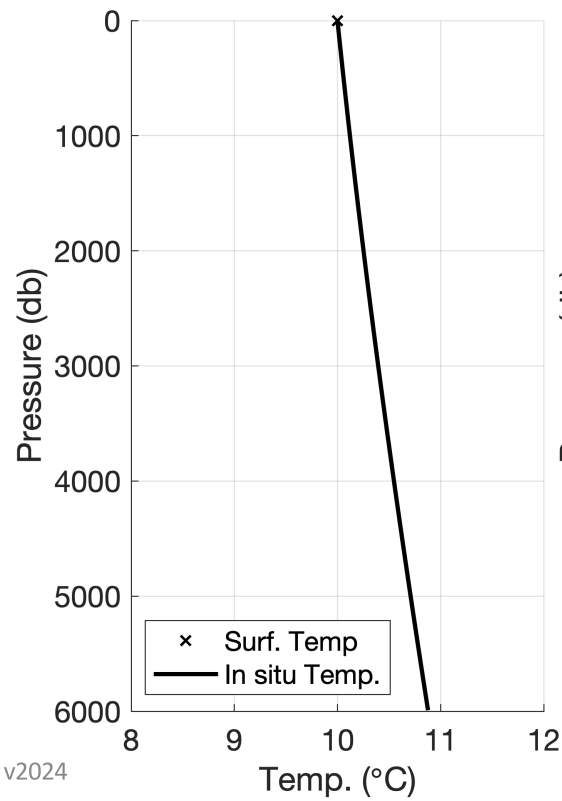
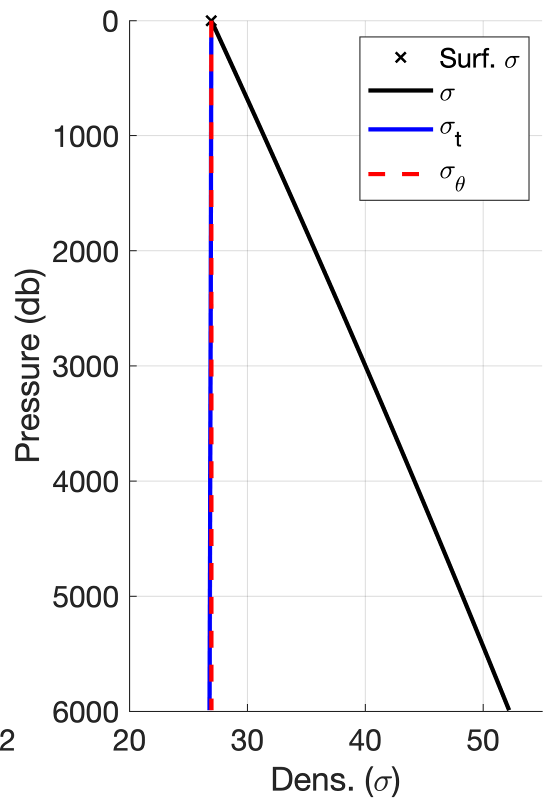
What impact will removing the pressure effect on temperature have?

(note that salinity is being held constant)

In situ vs. potential density and temperature





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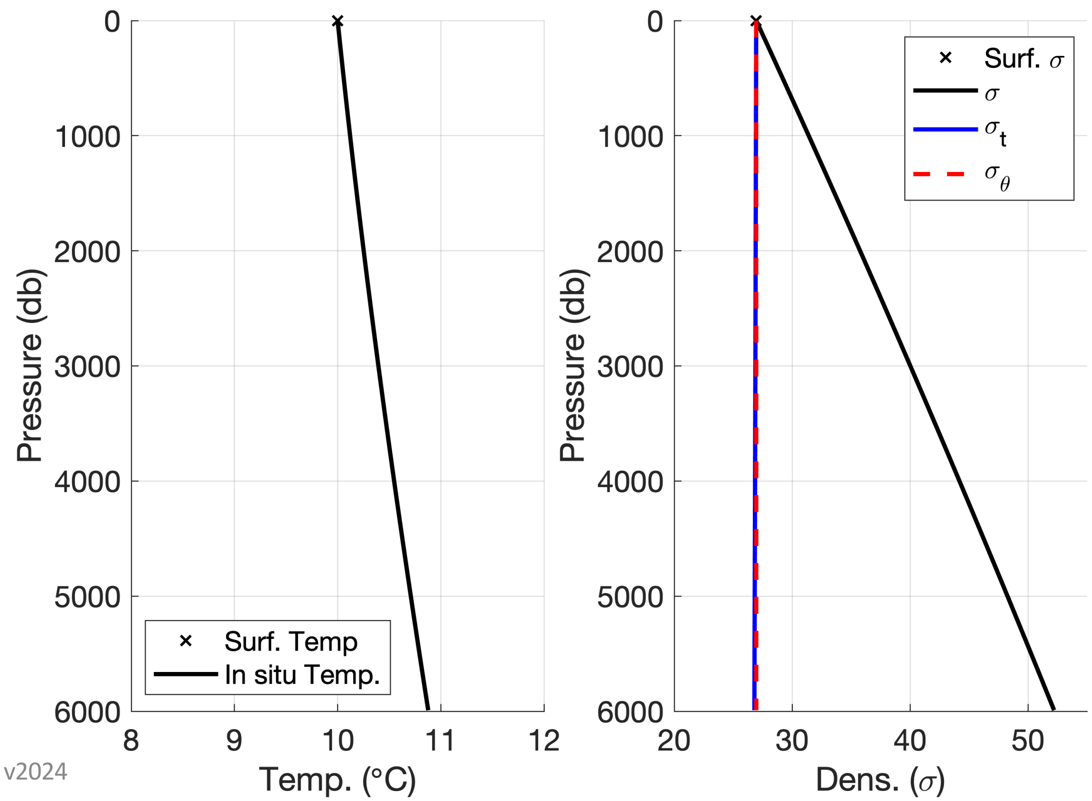
- In situ density reflects impact of pressure
  - σ : in situ density
  - σ_t : density calculated using in situ temperature but pressure effect on density removed
  - **σ_θ : density calculated using "potential" temperature (θ) but pressure effect on density removed**
    - **Known as "potential density"**

(note that salinity is being held constant)

In situ vs. potential density and temperature



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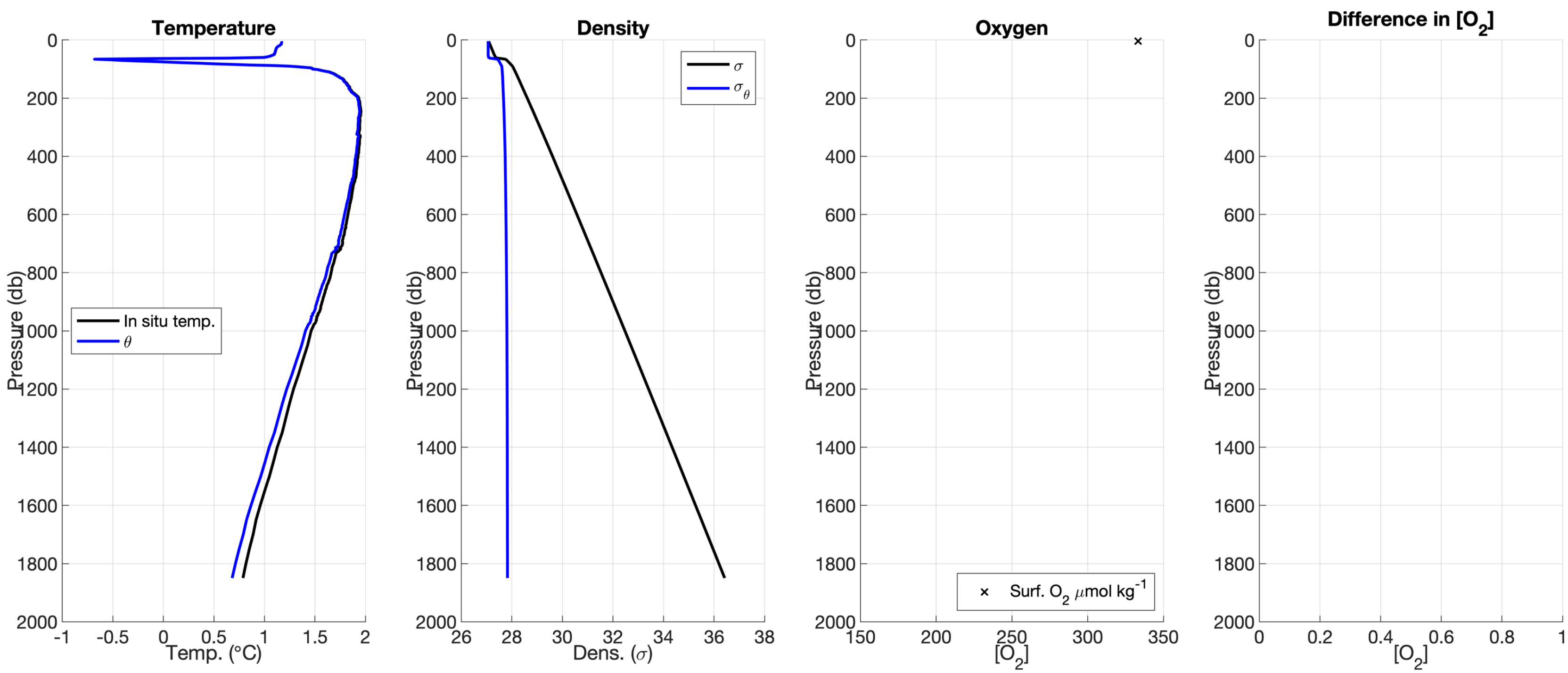
So why go into all this detail when we're talking about units of concentration?

What happens to a given number of water molecules when you move them up or down in the water column?

(note that salinity is being held constant)

In situ vs. potential density and temperature

Example from a profiling float near Antarctic sea ice:



In situ vs. potential density and temperature

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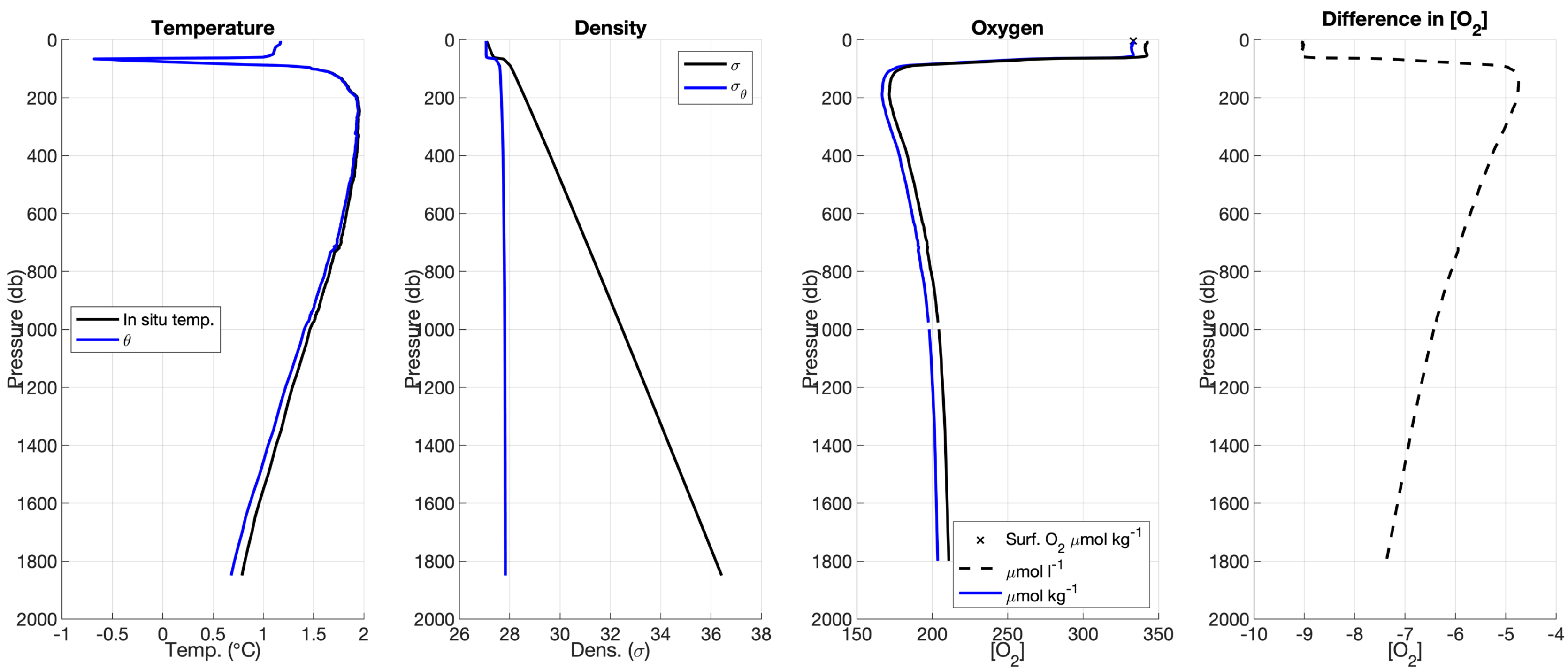

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In situ vs. potential density and temperature

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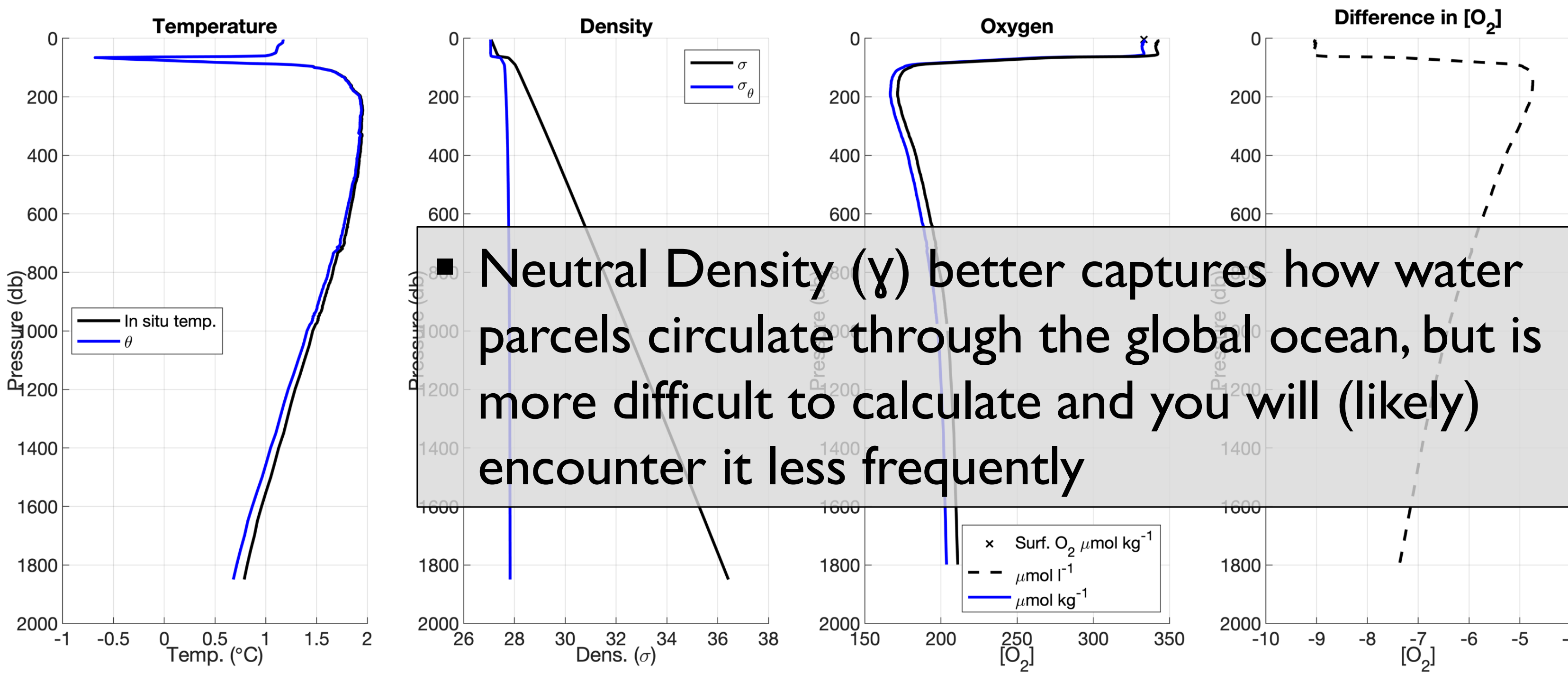


- Neutral Density (ɣ) better captures how water parcels circulate through the global ocean, but is more difficult to calculate and you will (likely) encounter it less frequently

Units

Emerson and Hamme, 2021

Table 1.2. Concentration units encountered in oceanography. (a) Molality, molarity, normality and volume ratio all have a long history of use in classical chemistry because of their convenience for laboratory preparations. Equivalents, eq, is equal to moles × absolute value of the charge of the species. Units indicated as "seawater units' are those preferred in oceanography. (b) Exponential terminology used in chemical oceanography.

(a)

Name	Basis	Dimensions	Symbol	Definition
Concentrations in aqueous solution				
Molal	Mass	mol kg^{-1}	*m*	Moles per kilogram of solvent
Molar	Volume	mol l^{-1}	M	Moles per liter of solution
Normal	Volume	eq l^{-1}	N	Equivalents per liter of solution
Weight ratio	Mass	g kg^{-1}		Mass of solute per mass solution
Volume ratio	Volume	ml l^{-1}		Volume solute per volume of solution
Seawater Units	Mass	mol kg^{-1}		Moles per kilogram of solution
Seawater Units	Mass	eq kg^{-1}		Equivalents per kilogram of solution
Concentrations in the atmosphere				
Mole Fraction	Moles	mol mol^{-1}	*X*	Moles gas per moles of dry air (= volume fraction, e.g. ppmv., for ideal gas)
Fugacity	Pressure	bar bar^{-1}, atm	*f*	Gas pressure per atmospheric pressure (=partial pressure, p, for ideal gas)
Partial Pressure	Pressure	bar bar^{-1}, atm	*p*	Gas pressure per atmospheric pressure

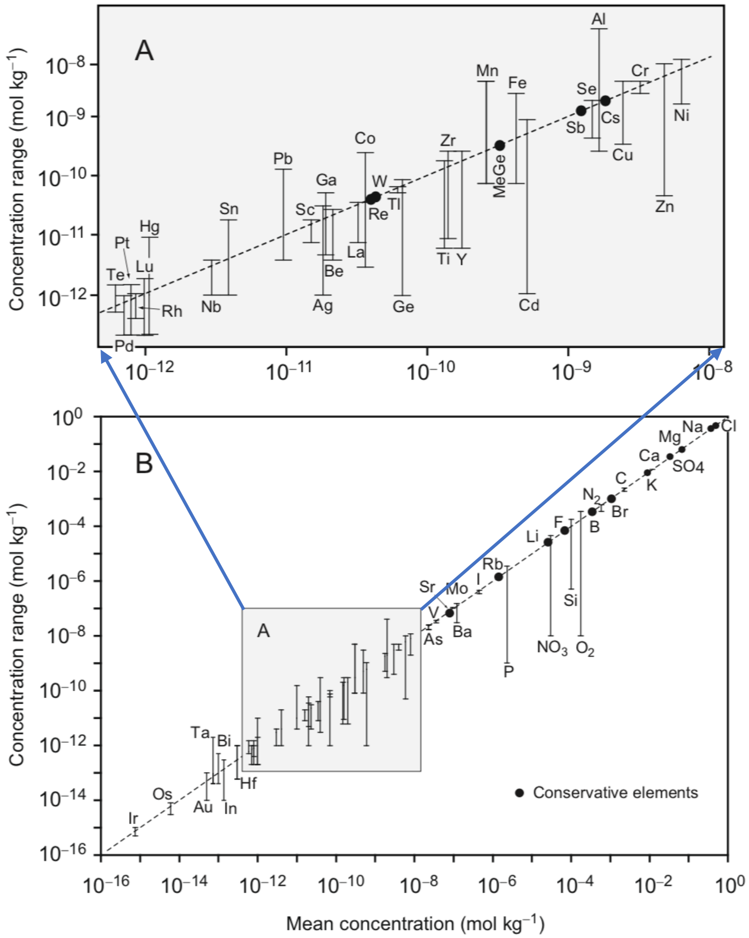
(b)

Name (symbol)	Peta (P)	Terra (T)	Giga (G)	Mega (M)	Kilo (k)	Milli (m)	Micro (µ)	Nano (n)	Pico (p)	Femto (f)	Atto (a)
Unit multiplier	10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-18}

Preferred units

Note that your problem sets will use a range of units, not just preferred units

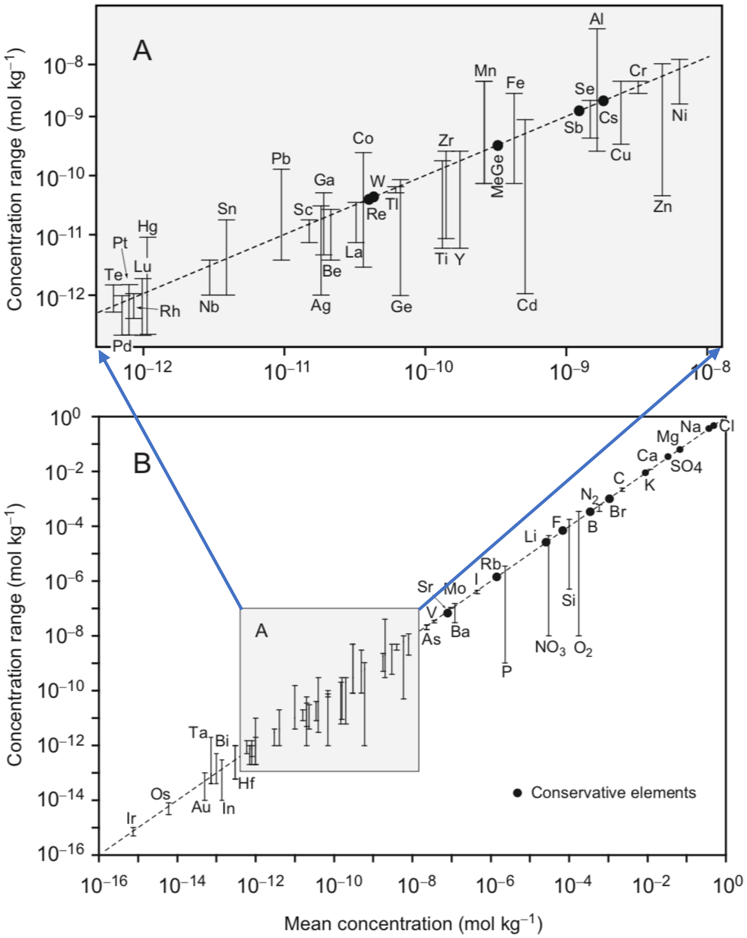
Element classification



Types of elements

- **Conservative**: constant concentration ratio w/ salinity
- **Biologically active**: taken up by biology in the surface, returned to the water from respiration at depth
- **Adsorbed**: removed by particulates through adsorption or scavenging
- **Anthropogenic**: changed distribution due to human activities
- **Dissolved gases**: can be either conservative (near atmospheric equilibrium) or biologically active

Element classification



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What processes result in elements above the 1:1 line?

What about below?

Major ions in seawater of salinity 35

Table 1.4 Major ions[a] in seawater at S=35. Major ions are defined here as those charged constituents of seawater with concentrations greater than 10 μmol kg^{-1}, excluding the nutrient nitrate which varies in concentration.

Cations			Anions		
Species	mmol kg^{-1}	meq kg^{-1}	Species	mmol kg^{-1}	meq kg^{-1}
Na^+	469.06	469.06	Cl^-	545.86	545.86
Mg^{2+}	52.82	105.64	SO_4^{2-}	28.24	56.48
Ca^{2+}	10.28	20.56	HCO_3^-	1.80	1.80
K^+	10.21	10.21	Br^-	0.84	0.84
Sr^{2+}	0.09	0.18	CO_3^{2-}	0.25	0.51
Li^+	0.02	0.02	$B(OH)_4^-$	0.11	0.11
			F^-	0.07	0.07
ΣCations	542.48	605.67	ΣAnions	577.17	605.67

[a]The concentration cut-off for the definition of major ions traditionally consists of elements with concentrations greater than 1 mg kg^{-1}. The concentration of Li^+ is below this threshold, but it is added here to create the charge balance

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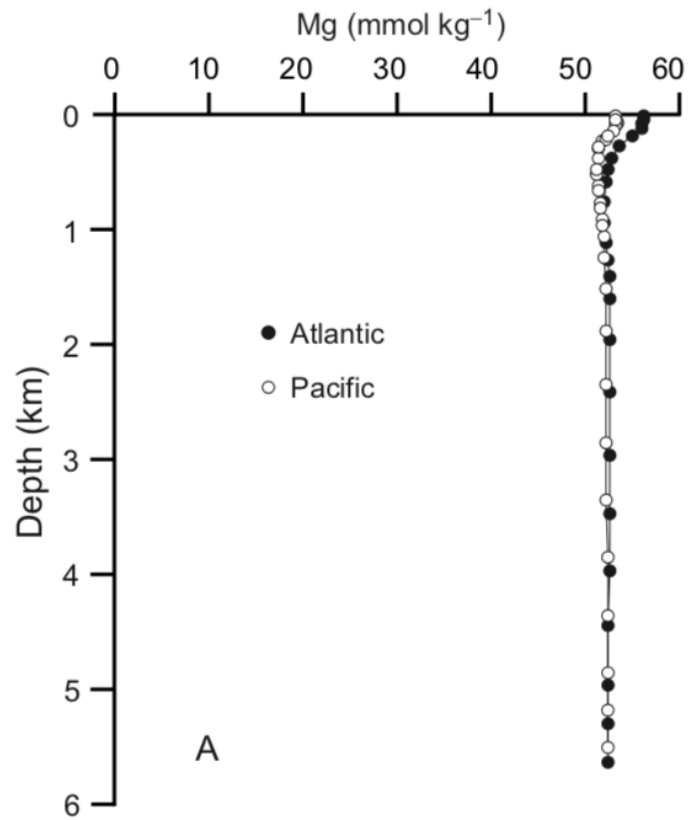
Species	mmol kg^{-1}	meq kg^{-1}	Species	mmol kg^{-1}	meq kg^{-1}
Na^{+}	469.06	469.06	Cl^{-}	545.86	545.86
Mg^{2+}	52.82	105.64	SO_4^{2-}	28.24	56.48
Ca^{2+}	10.28	20.56	HCO_3^{-}	1.80	1.80
K^{+}	10.21	10.21	Br^{-}	0.84	0.84
Sr^{2+}	0.09	0.18	CO_3^{2-}	0.25	0.51
Li^{+}	0.02	0.02	$B(OH)_4^{-}$	0.11	0.11
			F^{-}	0.07	0.07
ΣCations	542.48	605.67	ΣAnions	577.17	605.67

[a]The concentration cut-off for the definition of major ions traditionally consists of elements with concentrations greater than 1 mg kg^{-1}. The concentration of Li^{+} is below this threshold, but it is added here to create the charge balance

Most major ions are conservative, with exceptions in red

Conservative vs. Nonconservative Elements



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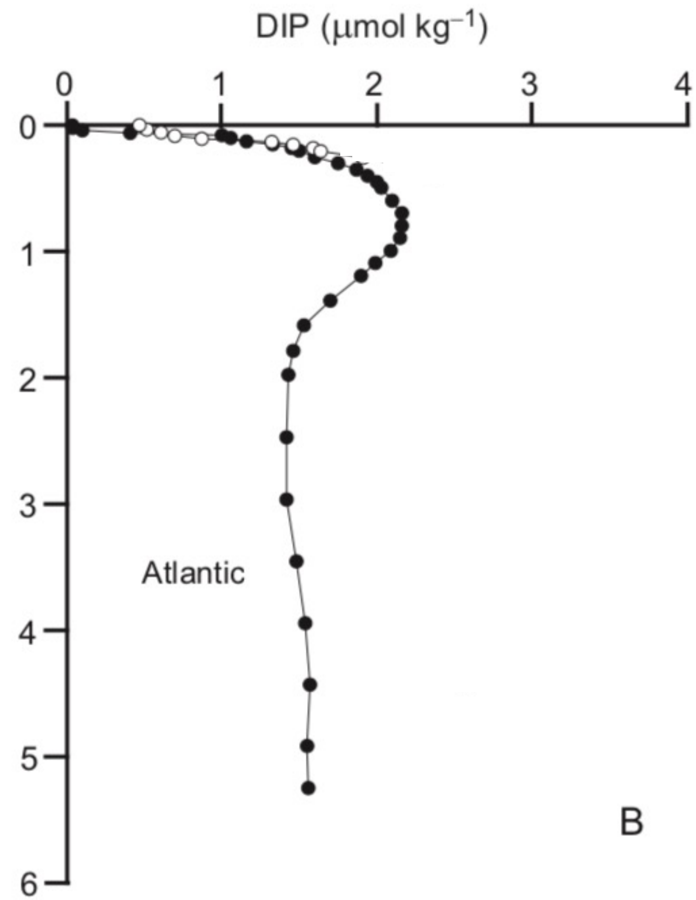
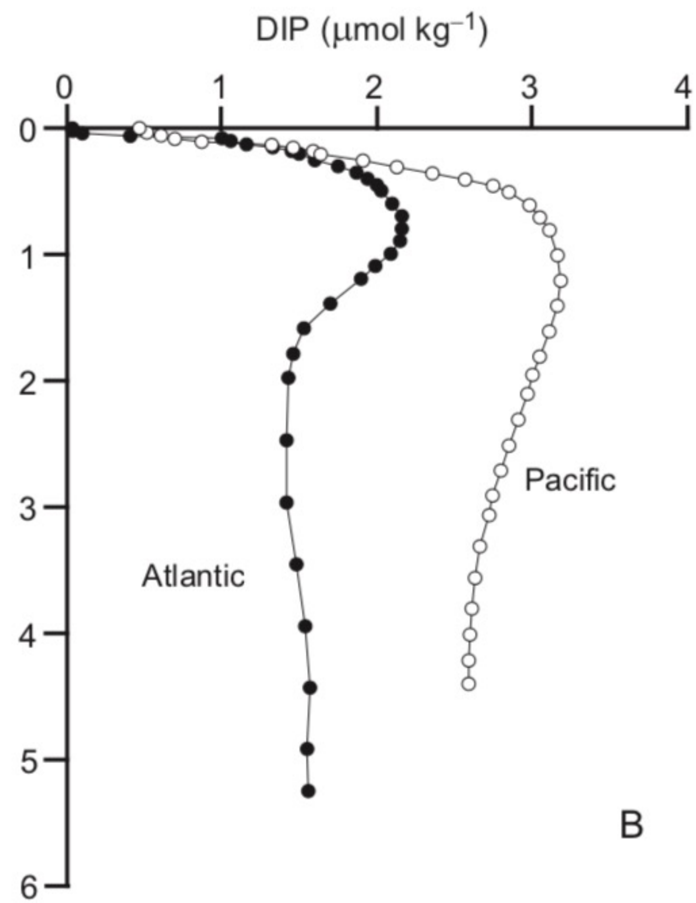
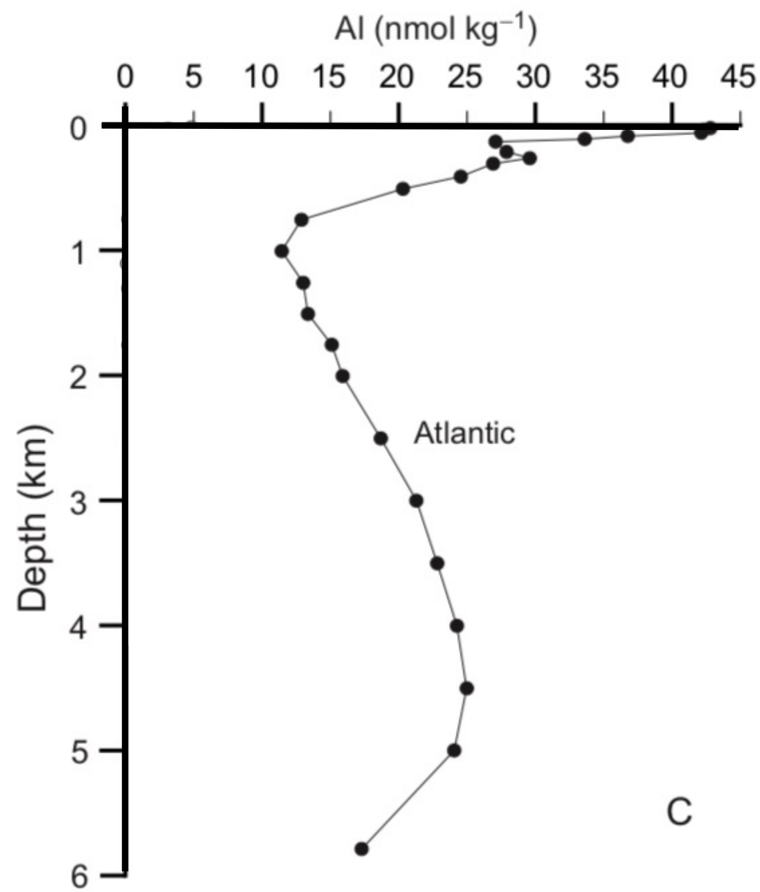
Conservative vs. Nonconservative Elements



Conservative vs. Nonconservative Elements



Conservative vs. Nonconservative Elements



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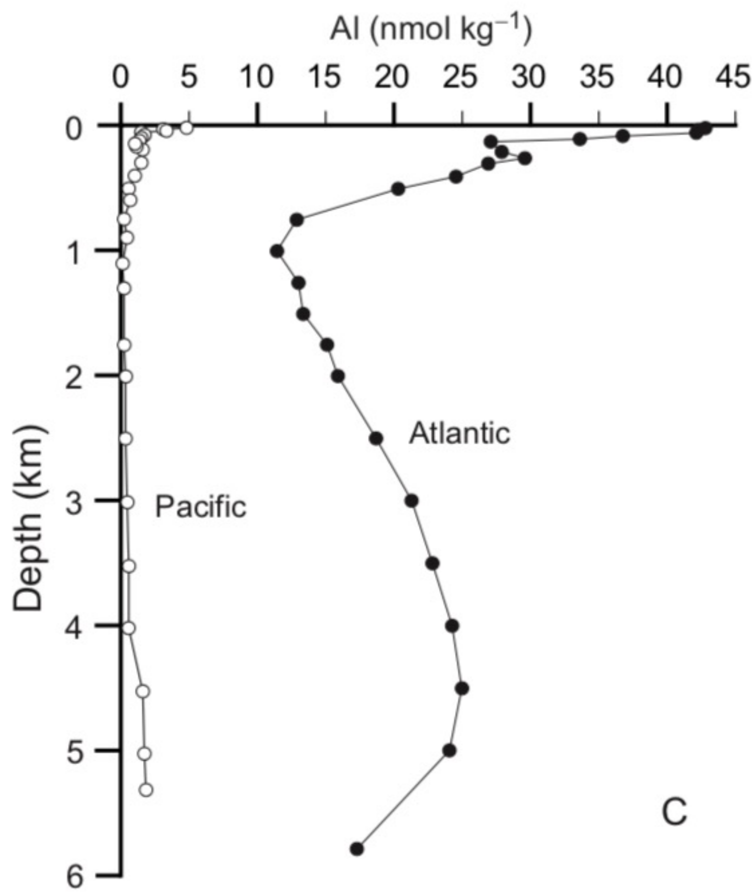

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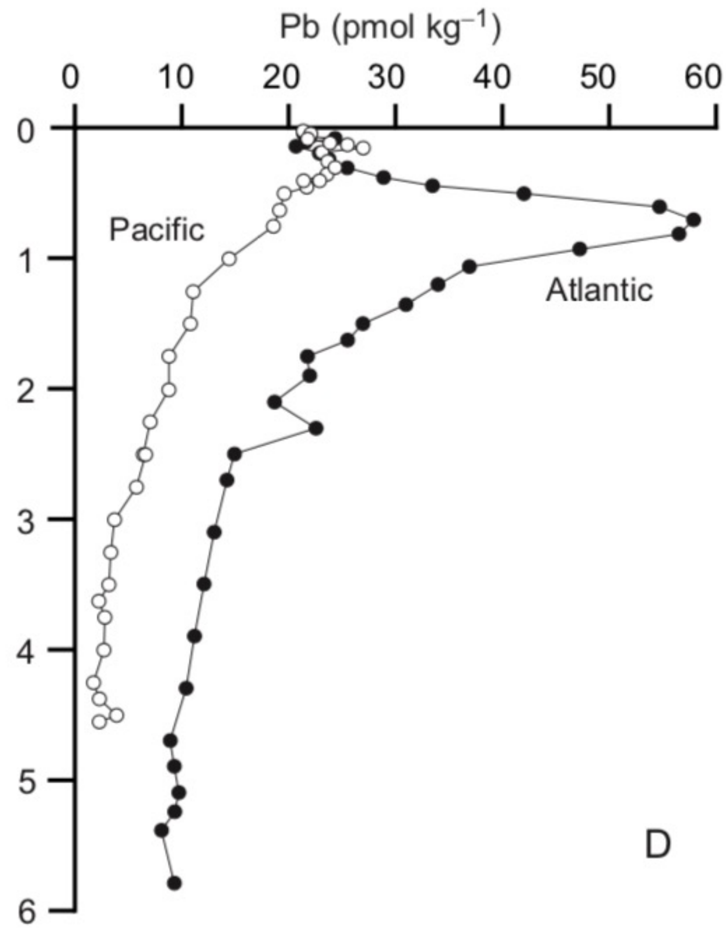


Composition of the atmosphere / ocean

Table 1.5. *The major gases of the atmosphere excluding water vapor, which has a concentration of a few percent at saturation in the atmosphere*

Seawater equilibrium concentrations were calculated from the Henry's Law coefficients at 20 °C and $S = 35$.

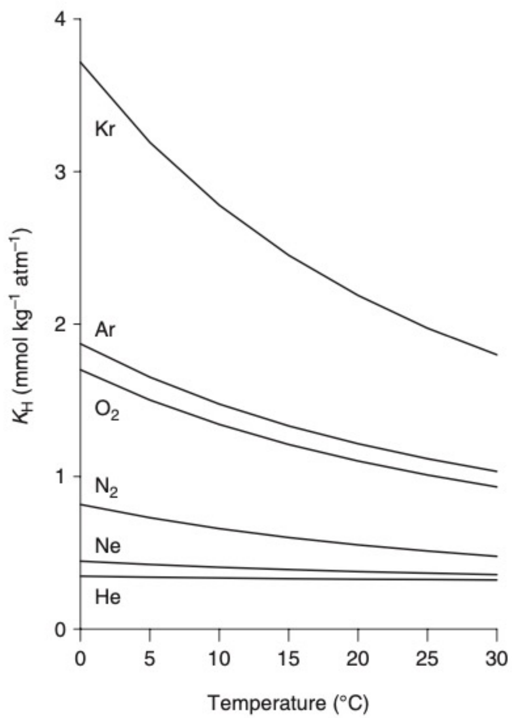
Gas	Atmospheric mole fraction (atm)	Seawater equilibrium concentration (μmol kg^{-1})
N_2	7.808×10^{-1}	4.18×10^{2}
O_2	2.095×10^{-1}	2.25×10^{2}
Ar	9.34×10^{-3}	1.10×10^{1}
CO_2	3.65×10^{-4}	1.16×10^{1}
Ne	18.2×10^{-6}	7.0×10^{-3}
He	5.24×10^{-6}	2.0×10^{-3}
Kr	1.14×10^{-6}	2.0×10^{-3}
Xe	0.87×10^{-7}	3.0×10^{-4}

~ 99%

Mole fraction is the amount (atm or moles) of a gas relative to atmosphere as a whole
Often denoted using X_i (e.g. X_{O2})

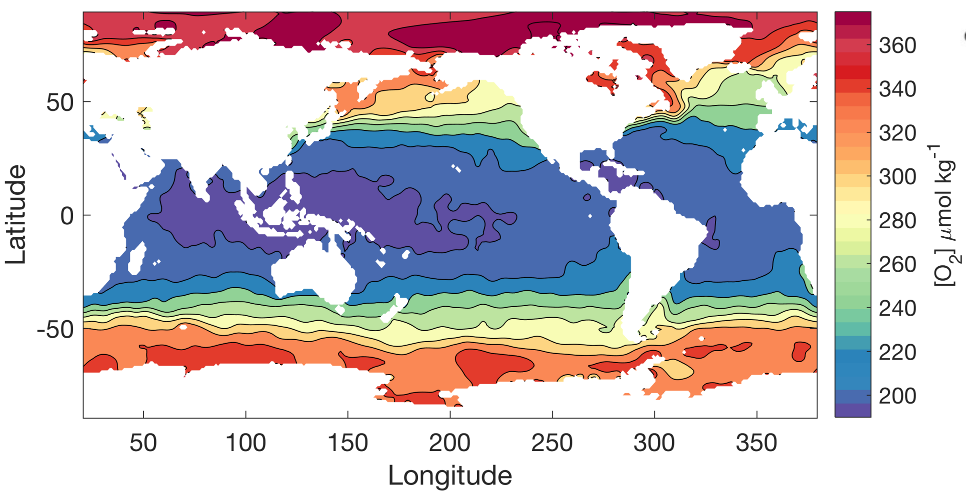
Emerson and Hedges

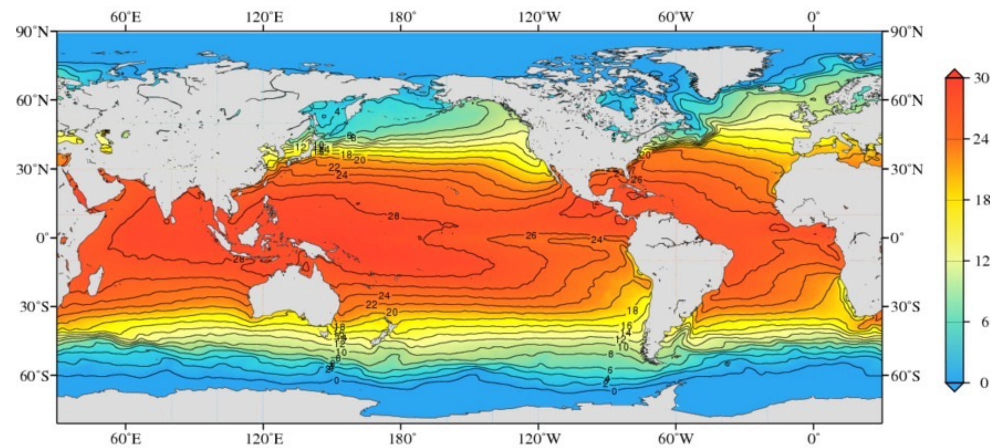
Gas solubility as a function of temperature



- Solubility decreases as temperature increases
- Solubility increases with molecular weight
- Solubility of molecular gases such as CO_2 usually have a greater solubility than atomic gases (N_2, O_2) of similar molecular weight
- The temperature dependence of solubility increases with increasing molecular weight
- Adding salt decreases solubility (salting out effect)

Temperature is a first order control on gas concentrations





Annual temperature [°C] at the surface (quarter-degree grid)