

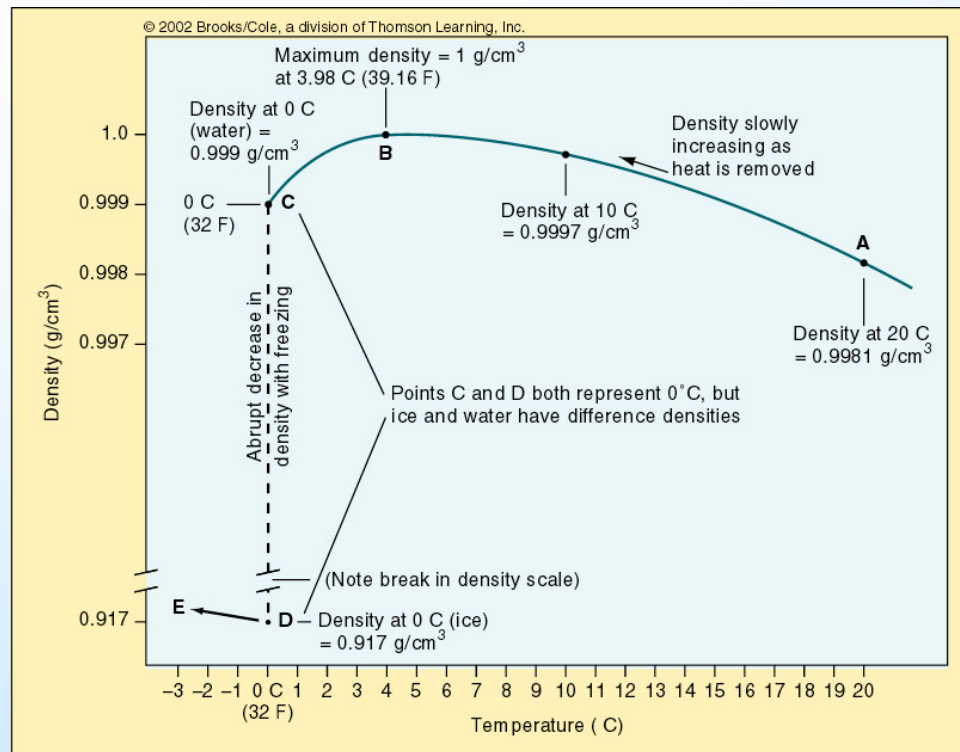
Chemical composition of seawater; Salinity and the major constituents

OCN 623 – Chemical Oceanography

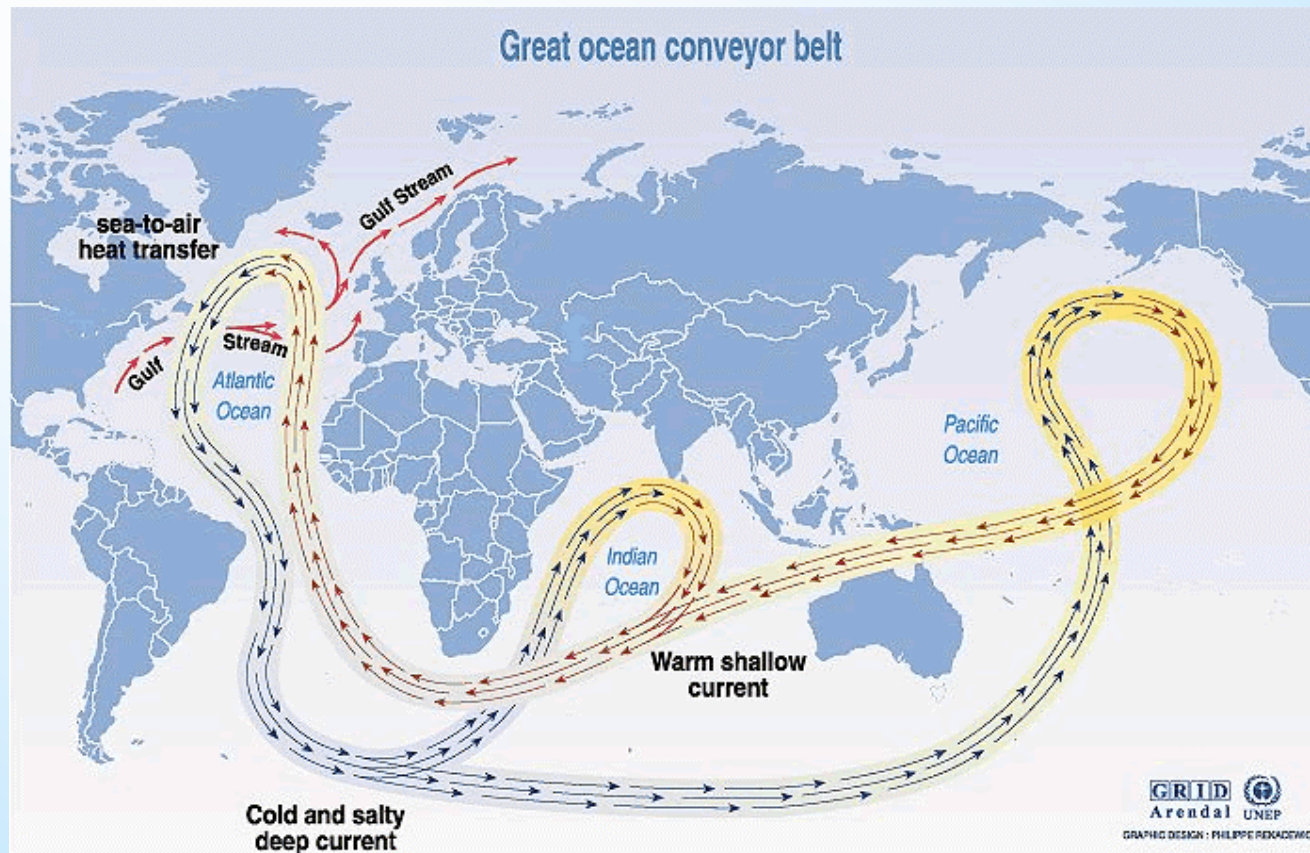
Salt dissolved in ocean water alters the **properties** of water

Freezing point of seawater is $\sim -1.8^{\circ}\text{C}$

Density continually increases to freezing point



Drives the **circulation mode** of the oceans
-completely different from freshwater in lakes



Source: Broecker, 1991, in Climate change 1996, 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.

Concentration units for aqueous solutions, gases, and solids

Molar units

1. *Molarity = moles per litre of solution = M*

- Commonly used terms include:

mM = millimolar = millimoles per litre = 10^{-3} moles per litre

μ M = micromolar = micromoles per litre = 10^{-6} moles per litre

nM = nanomolar = nannomoles per litre = 10^{-9} moles per litre

pM = picomolar = picomoles per litre = 10^{-12} moles per litre

fM = femtomolar = femtomoles per litre = 10^{-15} moles per litre

aM = attomolar = attomoles per litre = 10^{-18} moles per litre

gM?

2. *Molality = moles per kilogram of solvent = m*

- No longer in common use except in some computer programs that calculate distribution of chemical species

3. Moles per kilogram of solution

- The preferred usage in geochemistry, if not in marine chemistry, about 1.024 smaller than M
- Sometimes defined as "formality"; however, this latter term has been inconsistently defined in the past and is in disuse

4. *Normality = moles of charge equivalents per litre of solution* (analogous to molarity, except that it refers to charge)

Comes from acidity, i.e. moles H^+ per litre

- Can also use equivalents per kg of solution (meq/kg)

5. g-atom/litre = mole/litre (a gram-atom is a mole)

6. Mole fraction (used for mixtures of gases and for solid solutions) = $n_1/n_1+n_2+n_3+\dots$

Mass concentration units

1. **wt.% = “weight percent”** (actually, mass percent)
= g per 100 g
 - Used for solids

2. **‰ = parts per thousand**
= g/kg for liquids and solids
= mL/L for gas mixtures

3. **Per mil = parts per thousand**
 - Term is analogous to “per cent”
 - Is used extensively for isotopic analyses – specifies the *deviation* from an isotopic *standard reference material* (SRM)

4. ppm = parts per million

= $\mu\text{g/g}$ or mg/kg for liquids and solids

= $\mu\text{L/L}$ for mixtures of gases = ppmv

- "ppm" is commonly used for solids, whereas "mg/kg" is generally preferred for liquids

5. ppb = parts per billion

= ng/g or $\mu\text{g/kg}$

6. mg/L = milligrams per litre

- commonly used for solutions

Conservative vs. Nonconservative Elements

- *Conservative*
 - Non-reactive
 - Thus, remain in ocean for long periods (long residence time)
 - Examples: Na, K, S, Cl, Br, Sr, B (“*conservative major elements*”)
- *Nonconservative*
 - Biologically and/or chemically reactive
 - Examples: C, P, Fe

Chemical composition of seawater

Major ions in seawater of salinity 35

Symbol	Name	% of total	mmoles	gms /kg
Cl ⁻	Chloride	55.29	546	19.353
Na ⁺	Sodium	30.74	469	10.76
Mg ²⁺	Magnesium	3.69	53	1.292
SO ₄ ²⁻	Sulphate	7.75	28	2.712
Ca ²⁺	Calcium	1.18	10.3	0.412
K ⁺	Potassium	1.14	10.2	0.399
Total		99.8		

CONSTANCY OF MAJOR ELEMENT RATIOS

- 1776 - Lavoisier - Analyzed English Channel deep seawater
- First seawater analysis
- 1819 - Marcet - "Specimens of seawater contain the same ingredients all over the world.....these (ingredients) bear nearly the same proportion to each other.....(the samples) differ only as to the total amount of their saline content."
- 1884 - Dittmar - Analysed 77 samples from the HMS *Challenger* (1872-76)
- Confirmed Marcet's finding, except Ca/Cl was lower in surface seawater as compared to deep seawater (i.e., nonconservative)

Salinity

- Salinity is the **amount** of dissolved solids in seawater
- Used for determining the **density** of seawater
- Affects the **freezing point** of seawater
- Affects the temperature of **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

Salinity Measurement – The Past

- 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

$$\text{Salinity} = 1.80655 \text{ Cl}$$

- 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 ≈ 35, Cl ≈ 19‰**

Salinity Measurement – The Future?

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

Improved seawater thermodynamics:- How should the proposed change in salinity be implemented?

by SCOR/IAPSO Working Group 127

February 2008

Background

The SCOR/IAPSO Working Group 127 on the “Equation of State and Thermodynamics of Seawater” is charged with providing improved algorithms and descriptions of the thermodynamic properties of seawater. The working group has made significant progress on many of its goals, and it is now time to seek the advice of the oceanographic community regarding the best practical ways of adopting these developments into oceanographic practice. The Working Group has met twice to date, once in Warnemünde in 2006, then in Reggio Calabria in 2007. Our next meeting is in Berlin in September 2008.

The working group will soon provide the most accurate algorithms to date for the thermodynamic properties of seawater (such as density, entropy, enthalpy, specific heat capacity, etc). In order to achieve such accuracy it became evident that a salinity variable is required that more accurately represents absolute salinity than does the conductivity-based Practical Salinity. Spatial variations in the composition of seawater upsets the relationship between Practical Salinity S (which is a function of conductivity, temperature and pressure) and Absolute Salinity S_A (defined as the mass of dissolved material per mass of seawater solution). If the thermodynamic properties of seawater are to be written in terms of just one type of salinity, then they are much closer to being functions of (S_A, t, p) than being functions of (S, t, p) . Moreover, Absolute Salinity is a conservative property (that is, it is conserved when turbulent mixing occurs) whereas Practical Salinity is not conservative.

Absolute salinity for seawater of Reference Composition

In order to progress toward evaluating Absolute Salinity our first task was to define the relative concentrations of the constituents of Standard Seawater. This we have done, and this work is published in Millero et al (2008a). The abstract of this paper is as follows.

Fundamental determinations of the physical properties of seawater have previously been made for Atlantic surface waters, referred to as “Standard Seawater”. In this paper a Reference Composition consisting of the major components of Atlantic surface seawater is determined using these earlier analytical measurements. The stoichiometry of sea salt introduced here is thus based on the most accurate prior determination of the composition, adjusted to achieve charge balance and making use of the 2005 atomic weights. Reference Seawater is defined as any seawater that has the Reference Composition and a new Reference-Composition Salinity S_R is defined to provide the best available estimate of the Absolute Salinity of both Reference Seawater and the Standard Seawater that was used in the measurements of the physical properties. From a practical point of view, the value of S_R can be related to the Practical Salinity S by

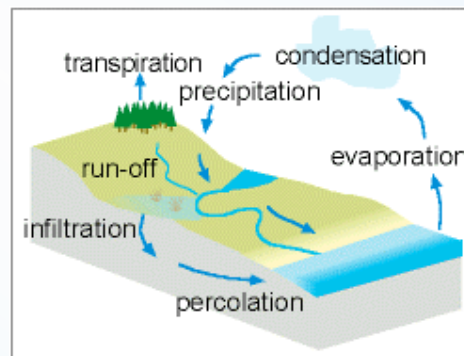
$$S_R = (35.165\,04 / 35) \text{ g kg}^{-1} \times S.$$

Reference Seawater that has been “normalized” to a Practical Salinity of 35 has a Reference-Composition Salinity of exactly $S_R = 35.165\,04 \text{ g kg}^{-1}$.

- Absolute Salinity would:
 - end the ongoing debate in the oceanographic literature about the use of “psu” or “pss”
 - make research papers more readable to the outside scientific community
 - be consistent with SI
- A Reference Composition consisting of the major components of Atlantic surface seawater is being determined using existing analytical measurements
- A new **Reference-Composition Salinity** S_R is defined to provide the best available estimate of the Absolute Salinity
- The value of S_R can be related to Practical Salinity S by
$$S_R = (35.165\,04 / 35) \text{ g kg}^{-1} \times S$$
- An algorithm will account for the variation of seawater composition from the standard composition – using either measured parameters (e.g., total alkalinity, silicate and nitrate) or simply the spatial location (longitude, latitude and pressure)

Why are major ion distributions so consistent?

Source of major ions to ocean is **continental weathering**



Reservoirs and fluxes

Ocean	$1.4 \times 10^{21} \text{ L}$
Evap from ocean	$43 \times 10^{16} \text{ L yr}^{-1}$
Precip over ocean	38×10^{16}
Precip over land	11×10^{16}
River flow	3.7×10^{16}
Hydrothermal	0.017×10^{16}

Continental materials are unlike seawater or river water

Most common ions in seawater and river water and the elemental composition of the Earth's crust* listed in order of abundance

Seawater
(as ions)

Chloride (Cl^-)
Sodium (Na^+)
Sulphate (SO_4^{2-})
Magnesium (Mg^{2+})
Calcium (Ca^{2+})
Potassium (K^+)
Bicarbonate (HCO_3^-)
Bromide (Br^-)
Borate (H_2BO_3^-)
Strontium (Sr^{2+})

Earth's crust
(as elements)

Silicon (Si)
Aluminium (Al)
Iron (Fe)
Calcium (Ca)
Sodium (Na)
Potassium (K)
Magnesium (Mg)
Titanium (Ti)
Manganese (Mn)
Phosphorous (P)

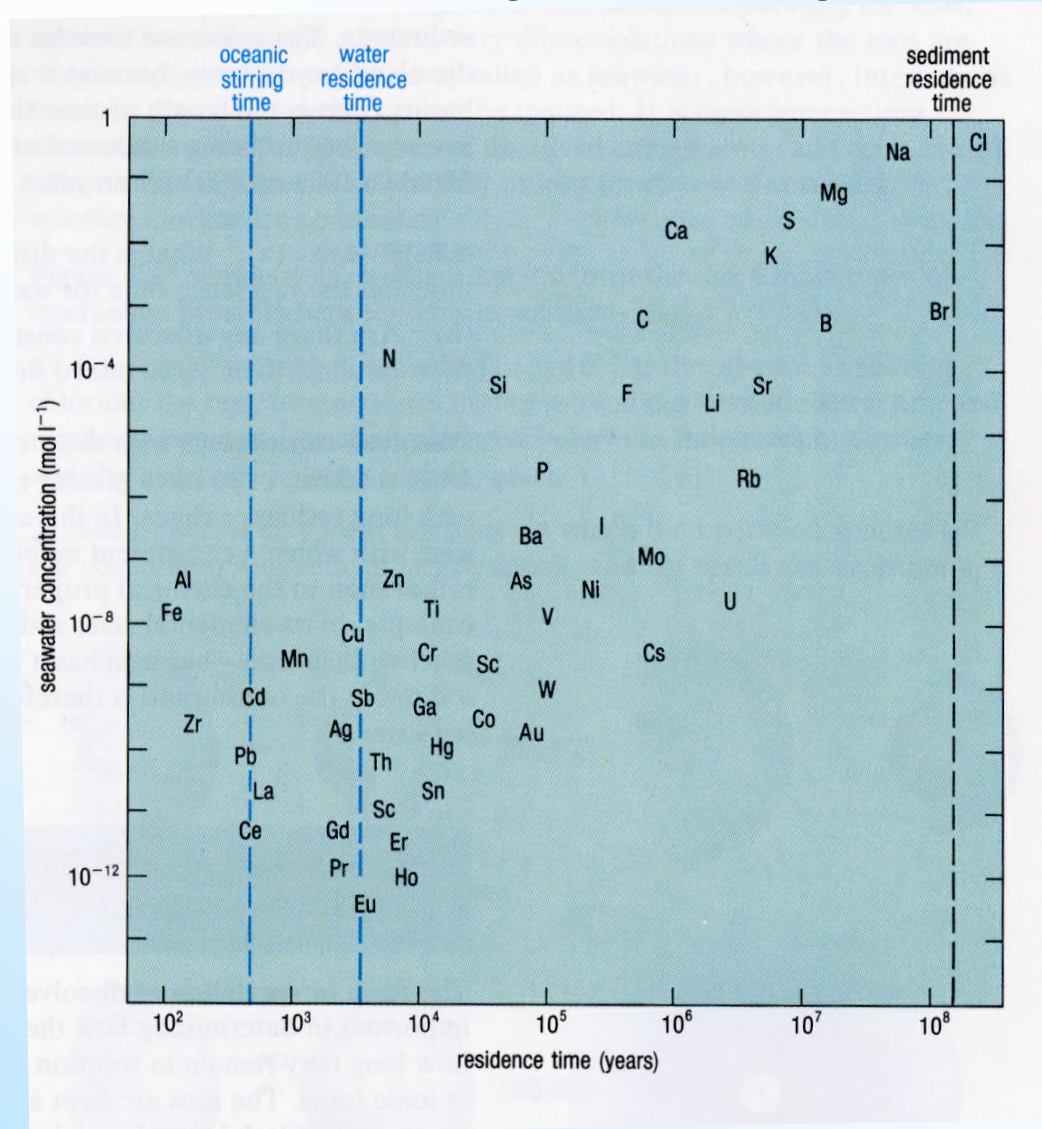
River water
(as ions)

Bicarbonate (HCO_3^-)
Calcium (Ca^{2+})
Silicate (SiO_2)
Sulphate (SO_4^{2-})
Magnesium (Mg^{2+})
Potassium (K^+)
Sodium (Na^+)
Iron (Fe^{3+})

* Excluding oxygen

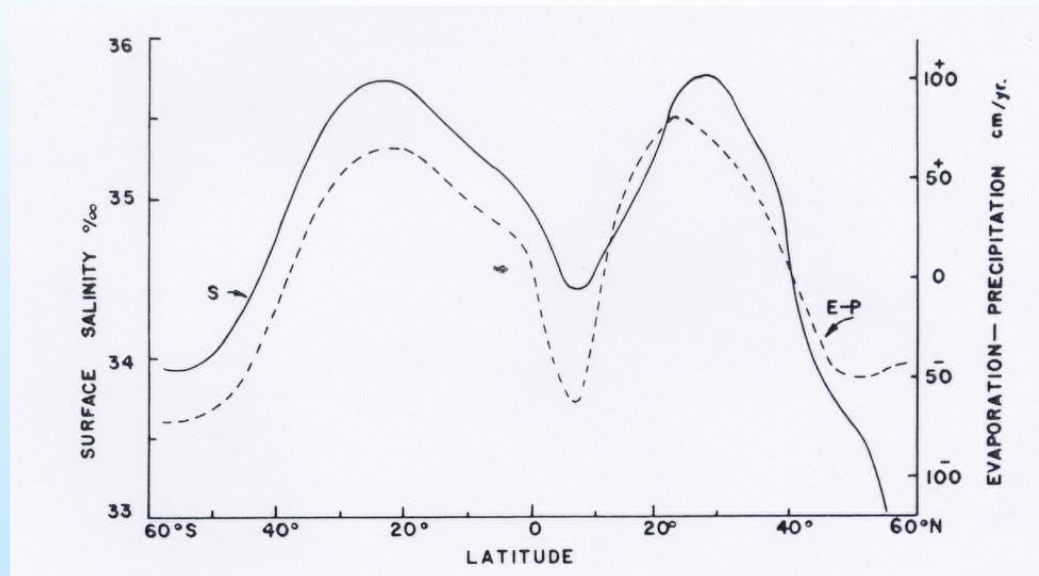
Residence time of species in seawater affects concentration

Long residence time facilitates good mixing ---**Marcel's principle**



Salinity Variability

- Variations in salinity depend almost entirely on:
 - Balance between **evaporation** and **precipitation**
 - Extent of **mixing** between surface and deeper waters
- The salinity of surface sea water:
 - High (up to 37.5) in **mid-latitudes** due to net evaporation
 - Low at **high latitudes** (to ~33 above 40°N and S) and at the **equator** (~35) due to net precipitation

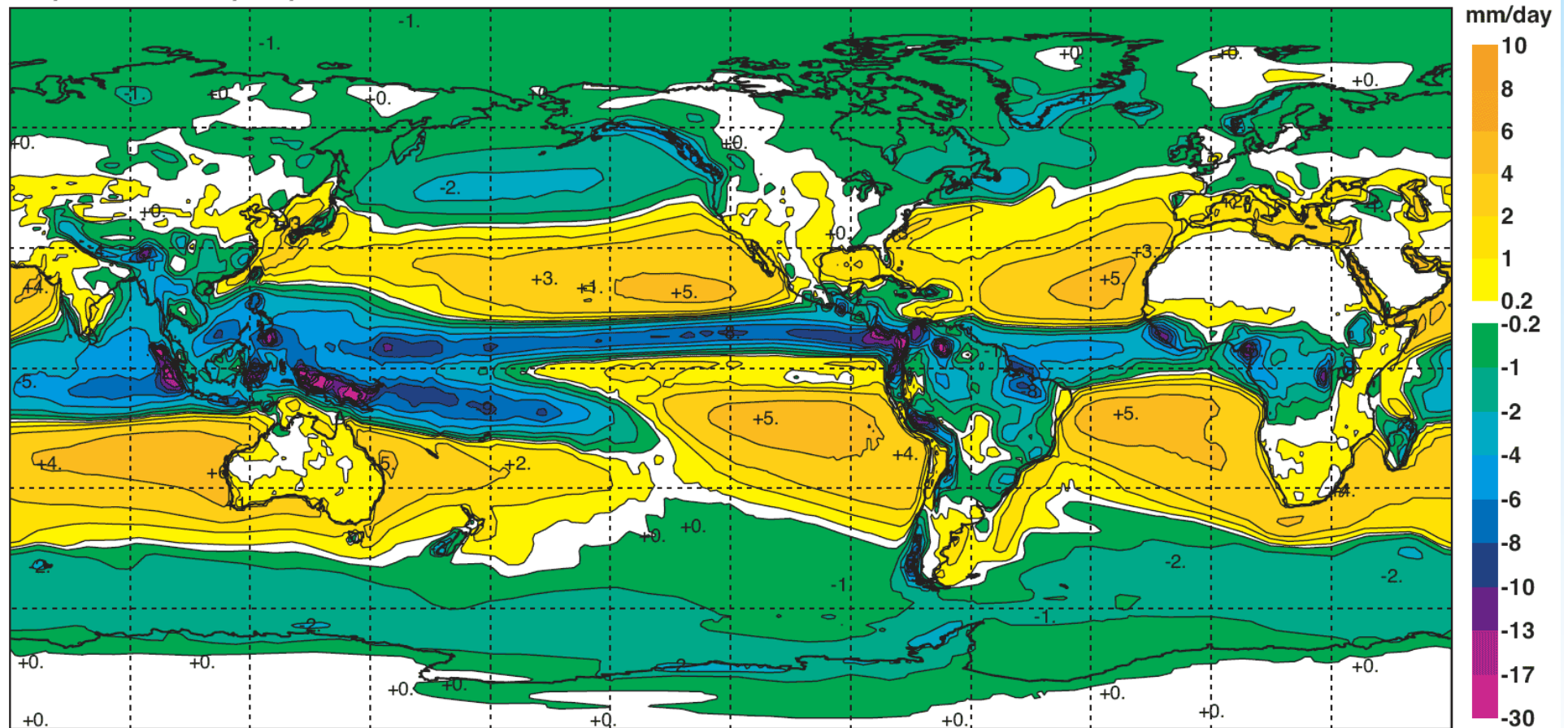




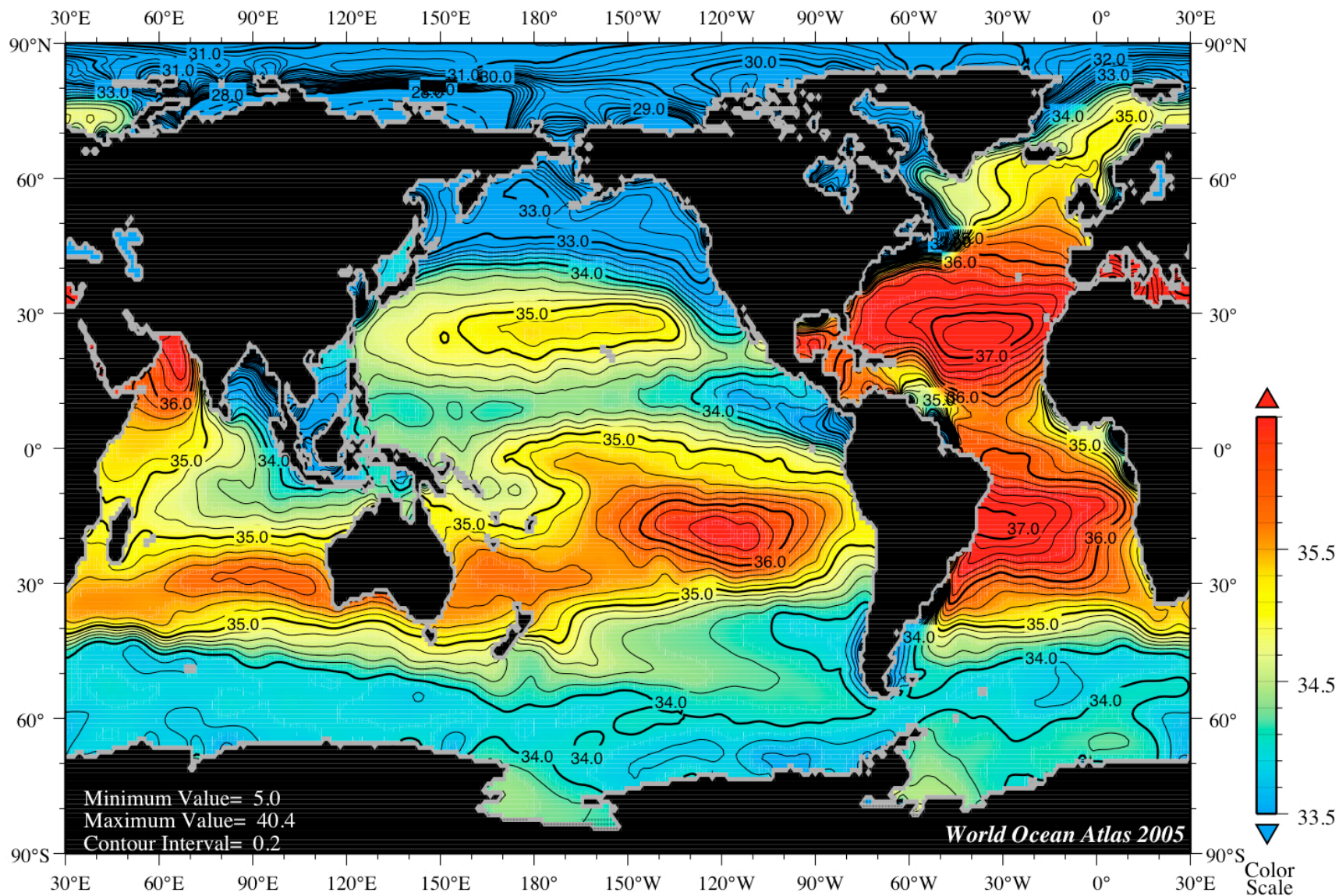
Global Evaporation - Precipitation

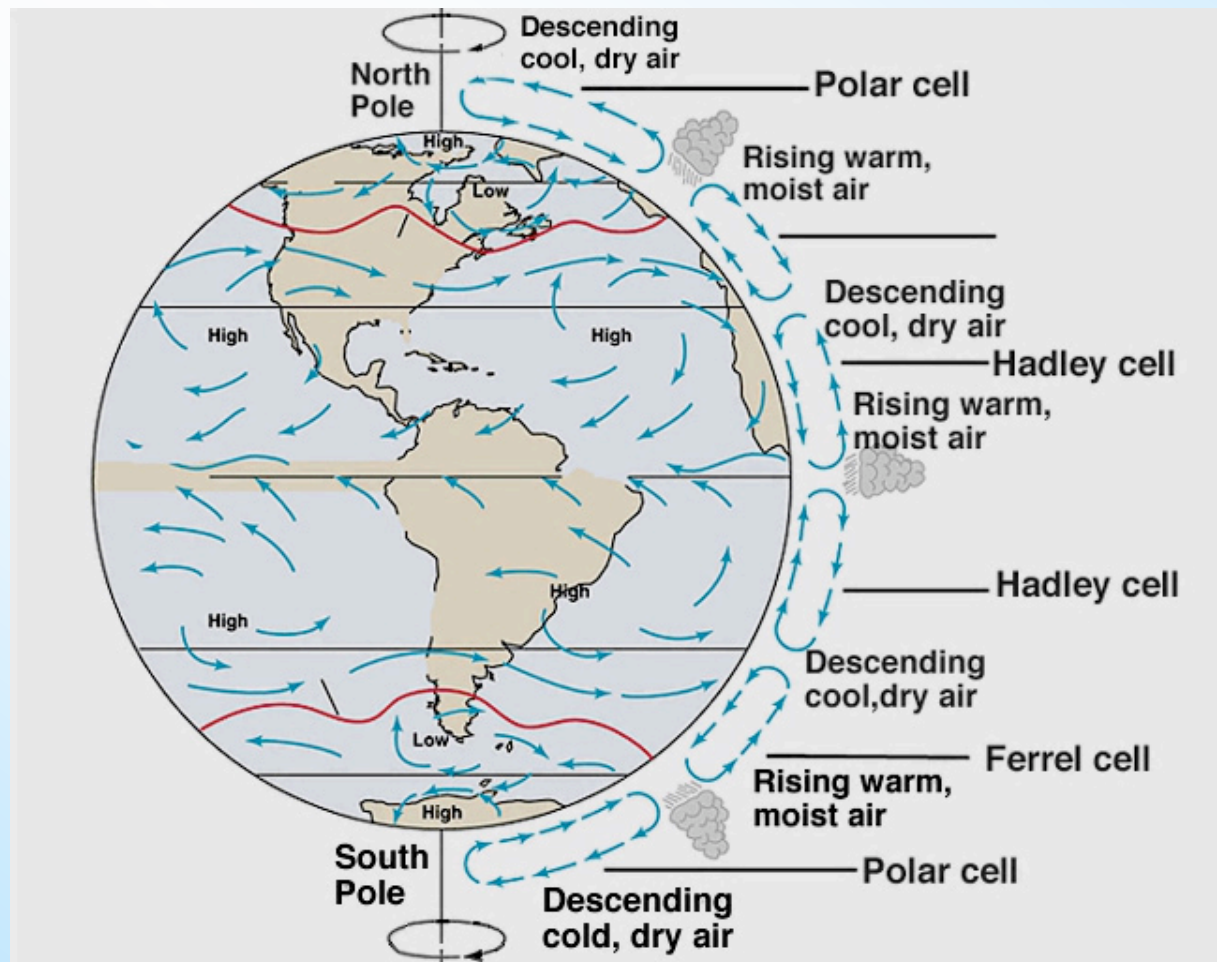
Evaporation minus precipitation

Annual mean



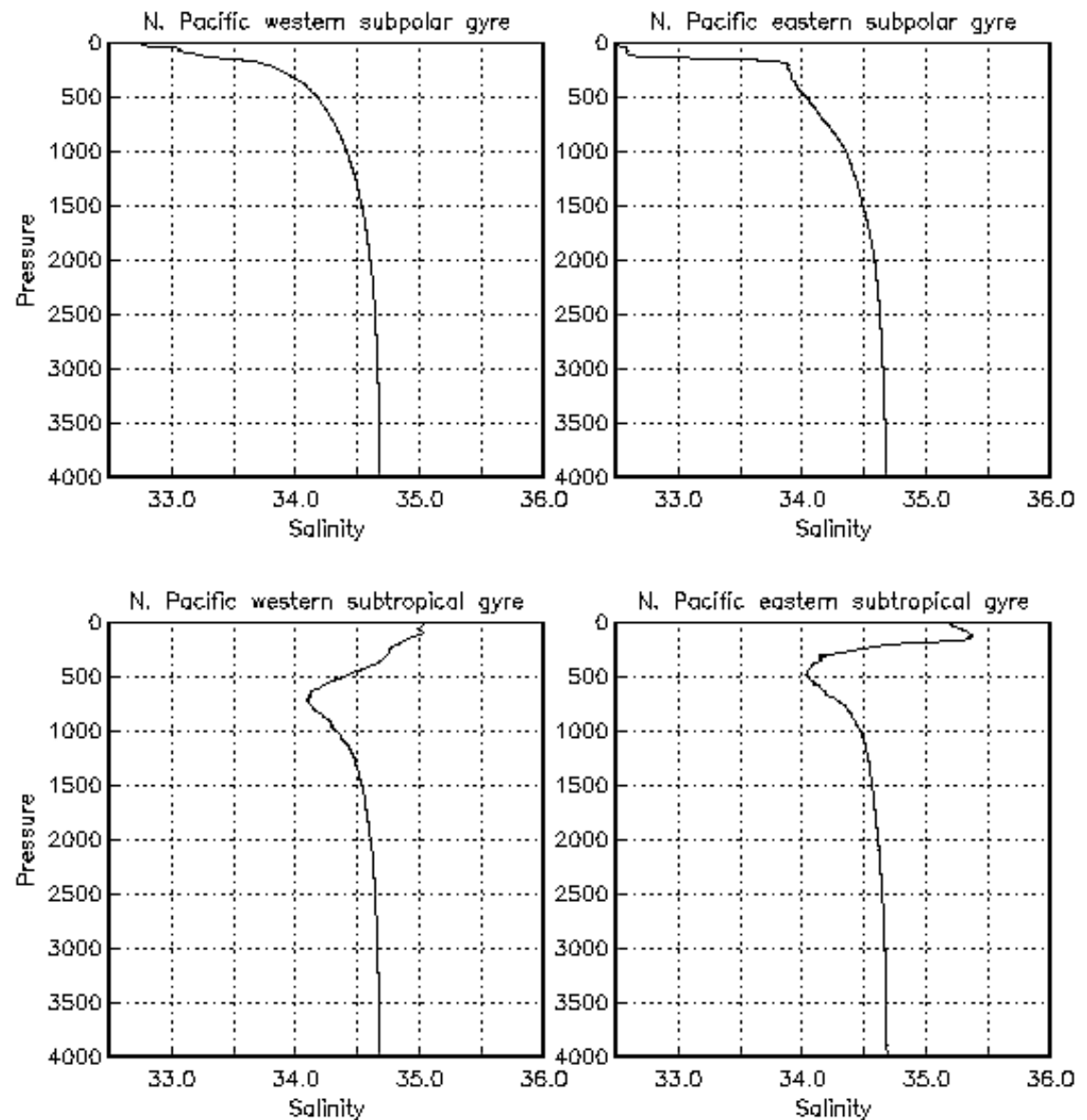
Annual salinity [PSS] at the surface.



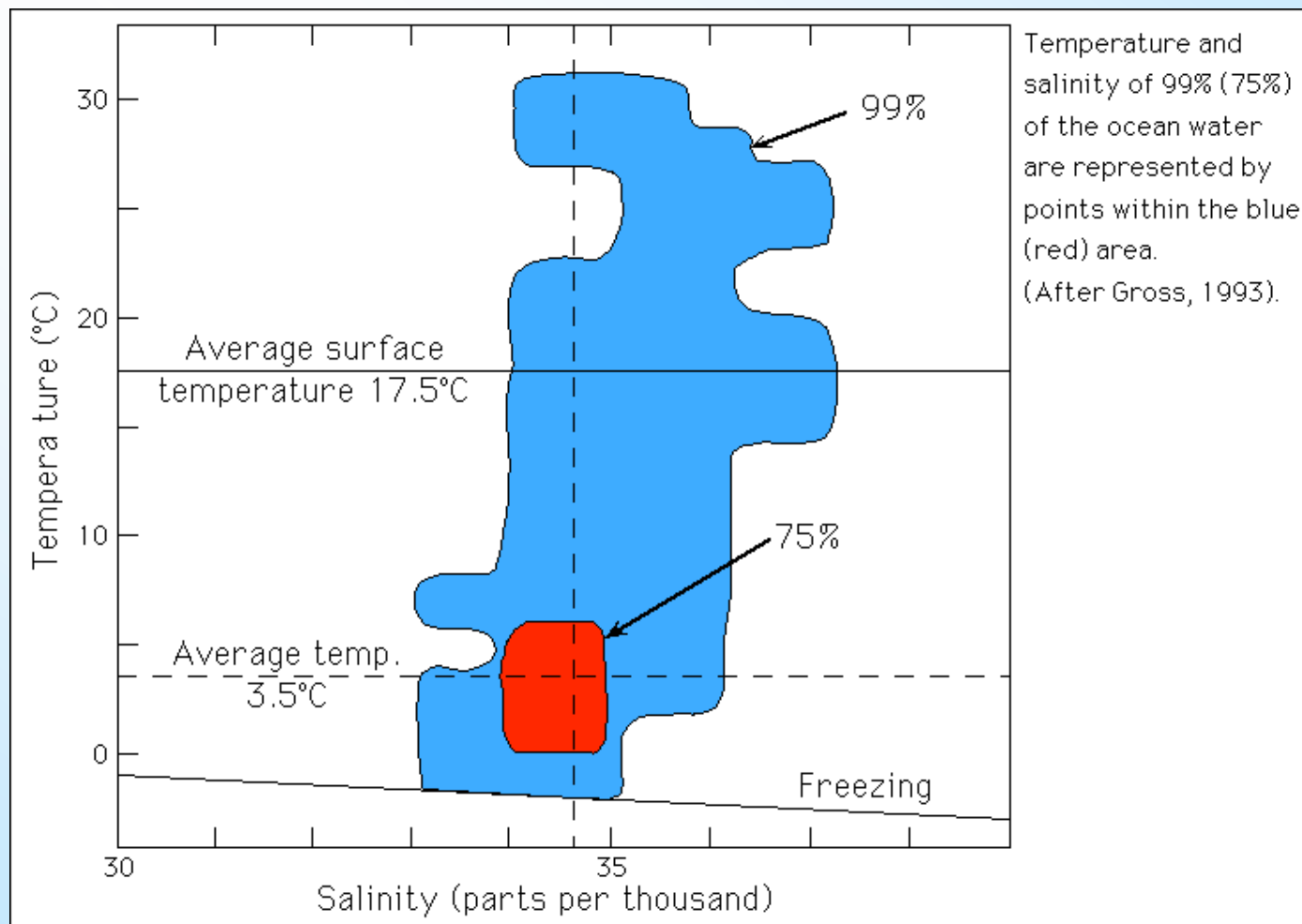


There typically is a *halocline* from the base of the mixed surface layer to about 1000 m depth

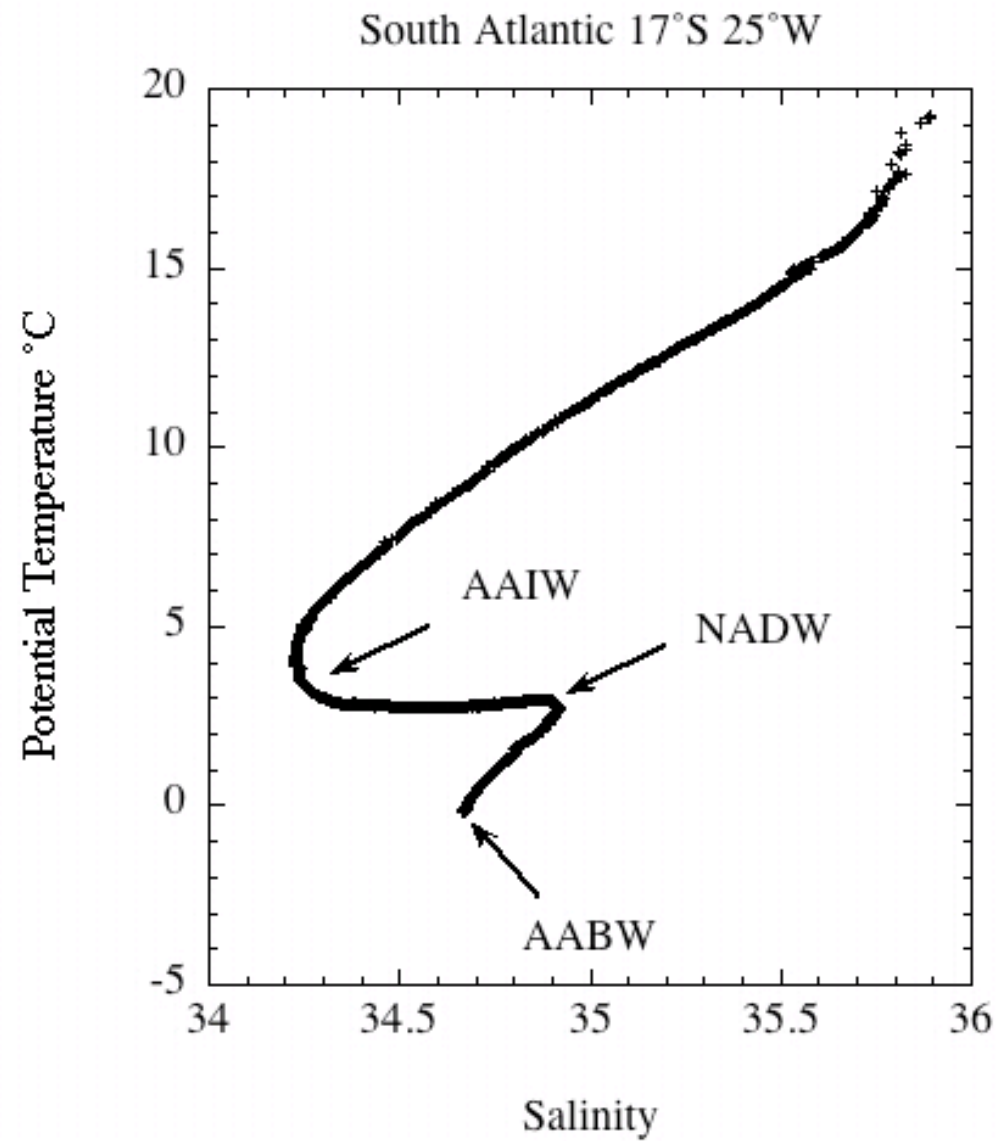
- At **high latitudes**: salinity increases with depth
- At **mid and low latitudes**: salinity decreases with depth
- Below 1000 m, salinities are generally between 34 and 35 at all latitudes

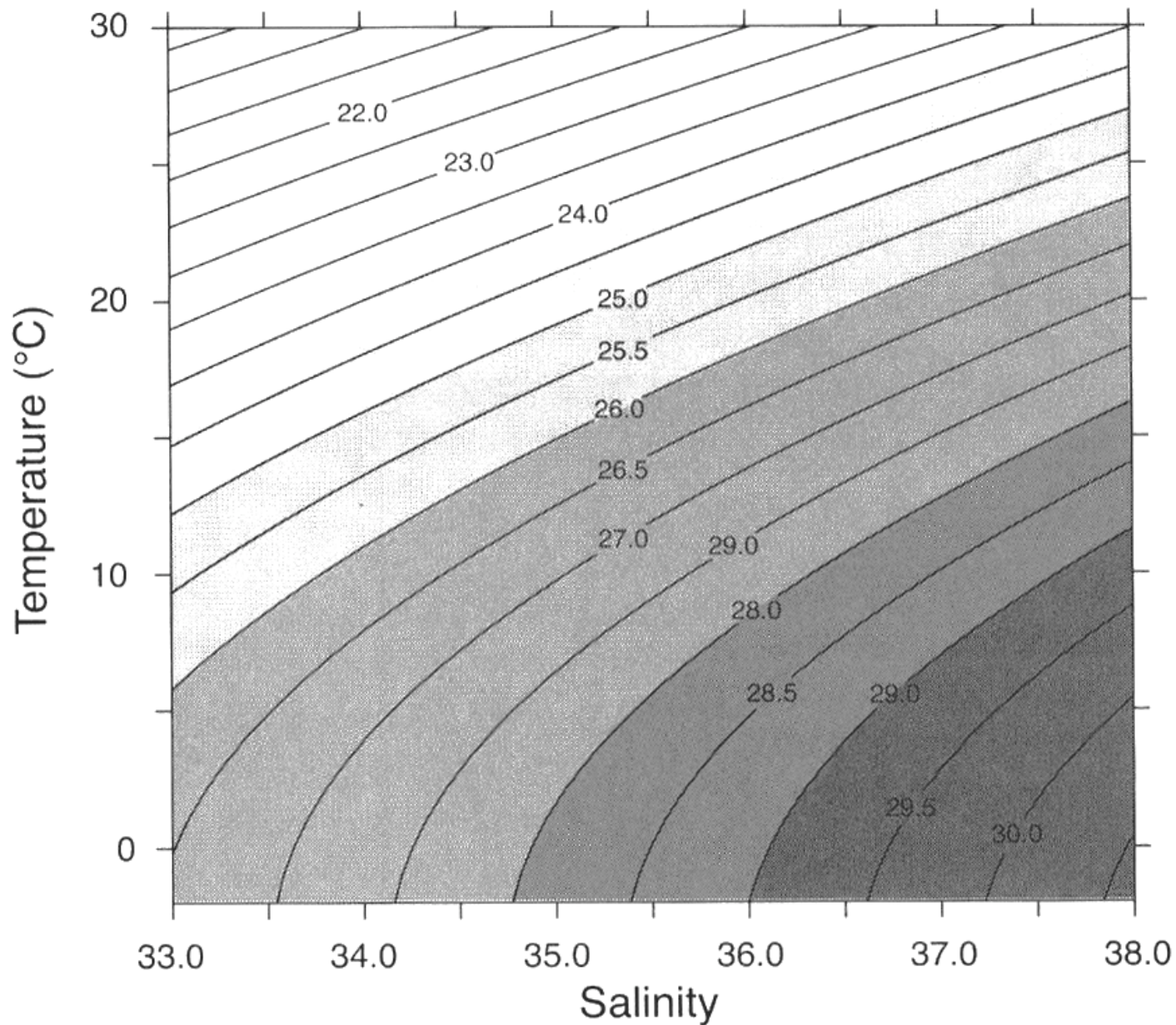


Most ocean water falls in a narrow salinity range



Temperature and salinity
are fingerprint characteristics
of seawater origin





The “**density anomaly**” of seawater in “**mass per volume in excess of 1 kg/m³, multiplied by 1000**”, is designated by the symbol “**σ**” (sigma)

In this notation, a specific gravity of 1.025 kg/m³ is expressed as $\sigma = 25$

