**Biogeochemical Systems** 

(10.21.10)

(Schlesinger: Chapter 9)

# Part 1. Ocean Composition, Circulation, El Nino

#### **Lecture Outline**

- 1. Introduction
- 2. Ocean Circulationa) Global Patternsb) El Niño
- 3. Seawater Composition: Major Ions
- 4. Summary

#### Introduction

- The Earth's waters constitute its hydrosphere.
- The oceans dominate, freshwaters contribute small amounts only.
- The ocean is a major player in global biogeochemical cycles.

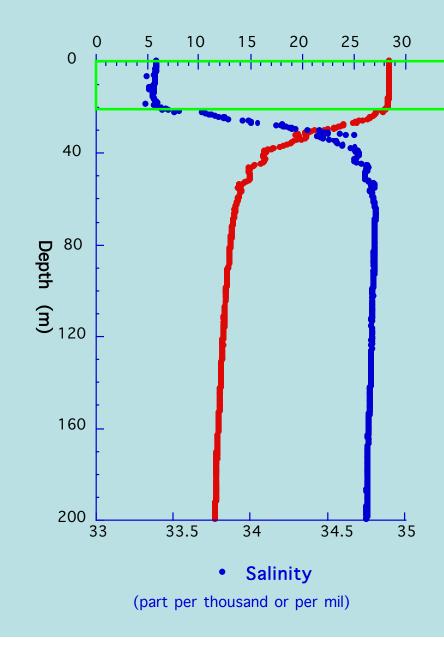
Reservoir	Volume (10 <sup>6</sup>	Percent of
	km <sup>3</sup> )	Total
Oceans	1400	95.96
Ice Caps & Glaciers	43.4	2.97
Groundwater	15.3	1.05
Lakes	0.125	0.009
Rivers	0.0017	0.0001
Soil Moisture	0.065	0.0045
Atmosphere	0.0155	0.001
Biosphere	0.002	0.0001
Approximate Total	1459	

# Table 1.1. Inventory of Water at the Earth's Surface (afterBerner and Berner 1996).

#### **Global Circulation Patterns: Stratification**

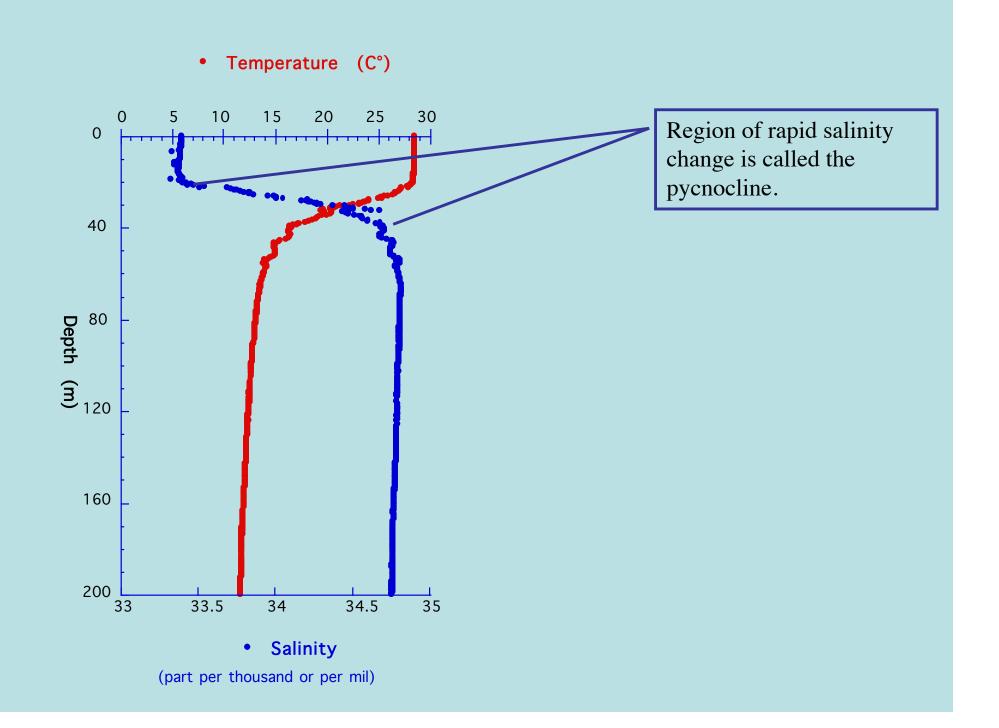
- Thermal Stratification confers Stability to Water Column.
  - Solar energy heats the surface ocean
  - Warm surface waters are less dense than colder deeper waters
  - This thermal stratification prevents mixing of surface and deep waters
  - Opposite of atmospheric circulation! (Chap. 3)
- The surface oceans layer is relatively well-mixed, can be from 75-200 m thick, with a mean temperature of 18°C (30°C maximum).
- The deep ocean contains 95% of the total ocean volume, with a mean temperature of 3°C.
- The zone of rapid temperature increase between the surface and deep ocean is called the *thermocline*.
- Due to the temperature change, there is also a rapid change in density that roughly parallels the thermocline, called the *pycnocline*.

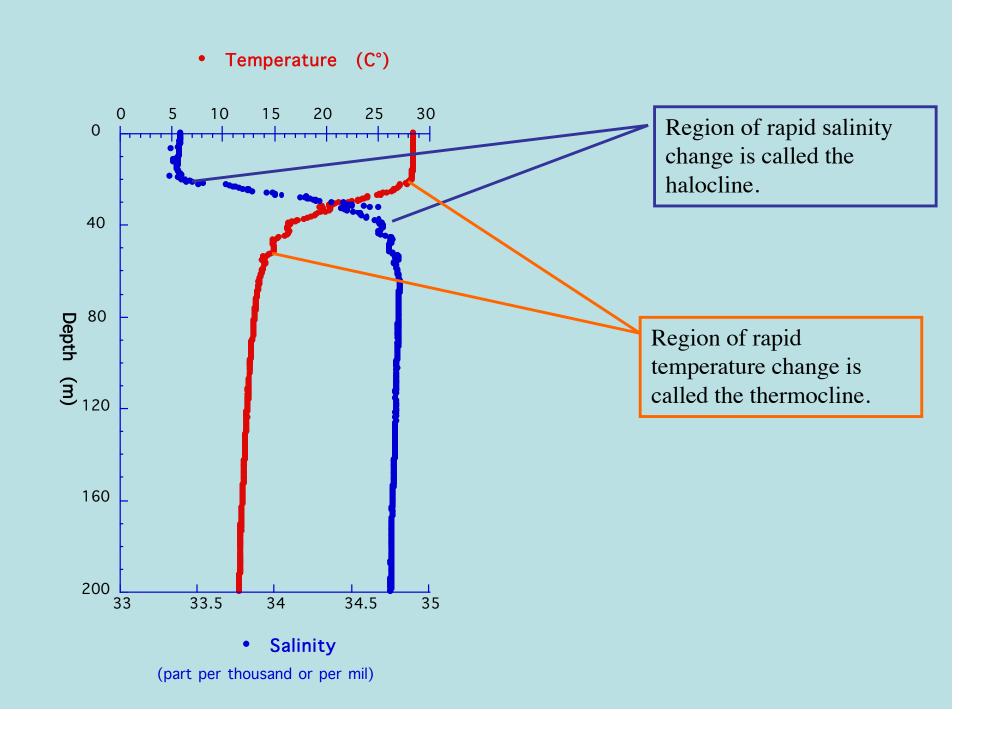
• Temperature (C°)



#### Surface Mixed Layer

Note that both temperature & salinity are very nearly constant. This is the result of physical mixing of the near surface by winds (Equatorial Pacific data from Ravizza, unpubl.).





# Wind-Driven Major Surface Water Currents

- Trade winds drive surface currents E-to-W along equator.
- Currents deflect N or S when continents are encountered, and move toward the poles.
- As they move pole-ward, they are deflected by the Coriolis force (Chap. 3).

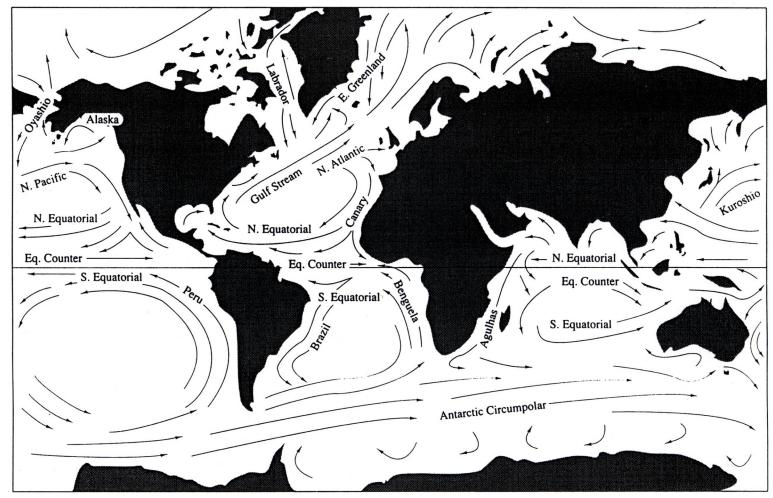


Figure 9.1 Major currents in the surface waters of the world's oceans. From Knauss (1978).

# Wind-Driven Major Surface Water Currents (cont'd.)

- Surface currents along the W side of continents return cold water to tropics.
- These surface currents create the circular gyre circulation in each major ocean.
- This global circulation transfers heat from tropics to poles, redistrib. >50% of xs heat.

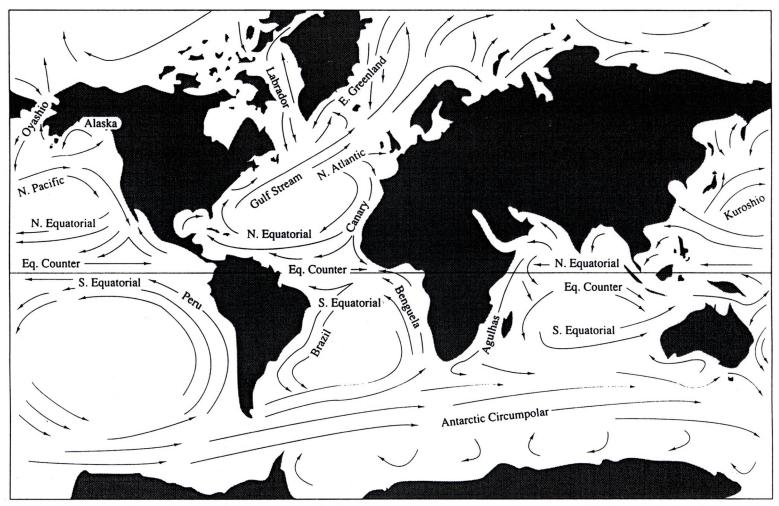
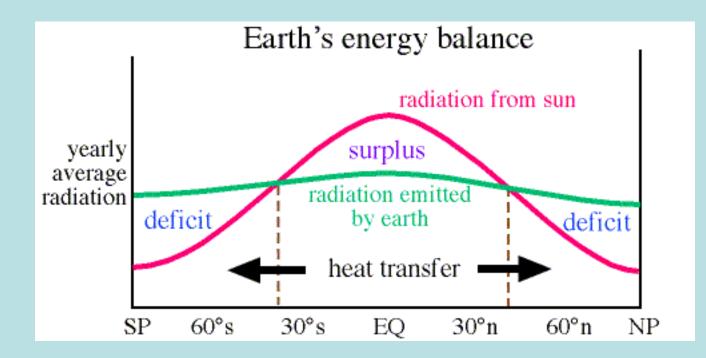


Figure 9.1 Major currents in the surface waters of the world's oceans. From Knauss (1978).

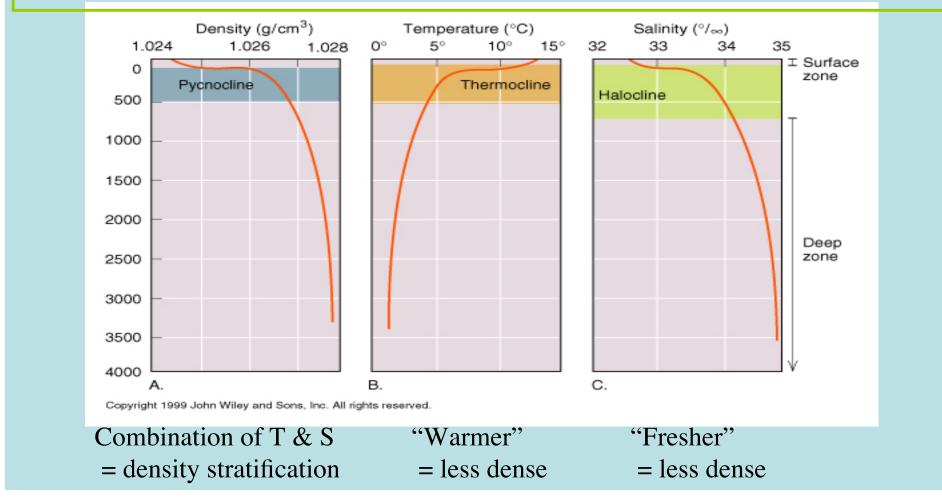
Recall that for Earth to maintain a stable average temperature, energy supplied by sun (annual average) must be balanced by an equal amount of energy lost to space.



At high latitudes (near the poles) more heat is lost than is supplied by the sun, at low latitudes (near the equator) the opposite is true. This requires redistribution of heat by the circulation of the ocean & atmosphere (Ch. 3).

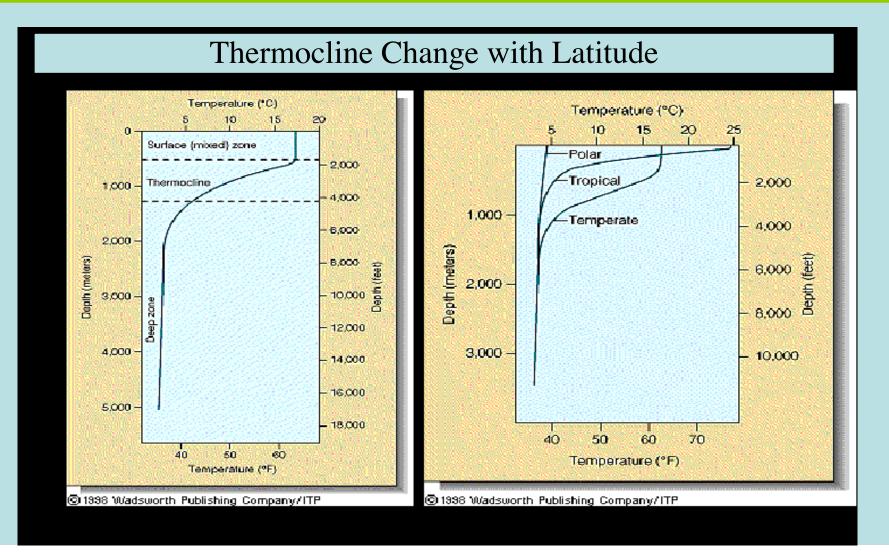
# **Thermohaline Circulation**

- In the polar oceans in winter, fresh water freezes out of surface waters, leaving behind saltier, higher density seawater that can sink to the deep ocean.
- In summer, due to ice melt, surface waters are fresher and more stable.
- Because seasonal *downwelling* of cold polar surface waters is driven both by temperature and salinity, it is called *thermohaline circulation*.



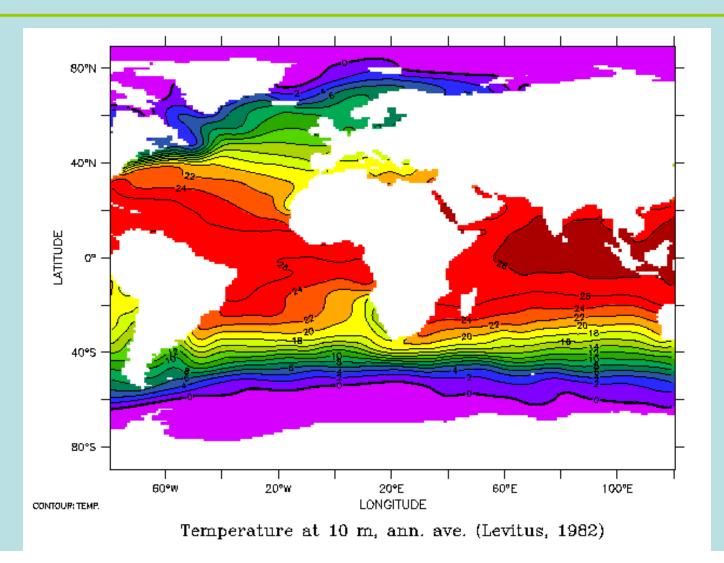
# Thermohaline Circulation (cont'd.)

- Heat loss at polar latitudes causes increased density of surface waters.
- When surface water density equals that of underlying deep waters, mixing occurs.
- Mixing of waters of equal density = *isopycnal mixing*.



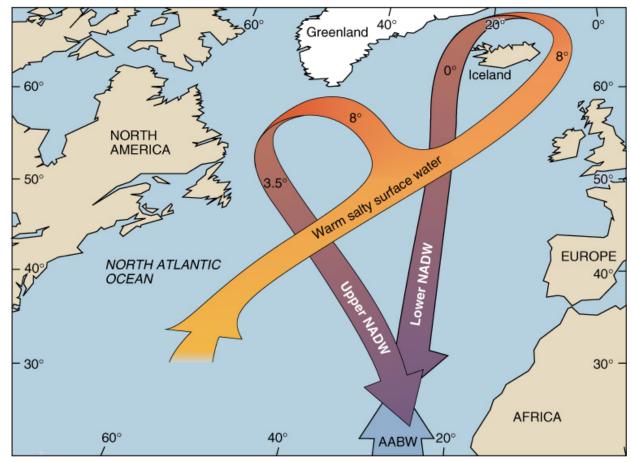
#### **Thermohaline Circulation (cont'd.)**

- Cold water near the poles makes seawater more dense at high latitudes.
- *Downwelling* of cold surface waters at the poles creates deep sea currents.



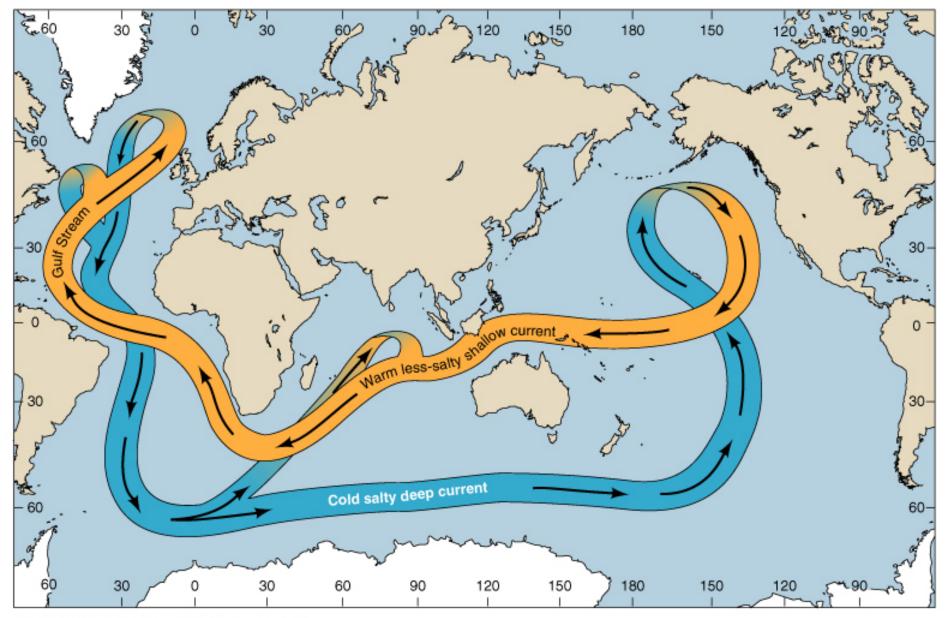
# **Thermohaline Circulation (cont'd.)**

- North Atlantic Deep Water (NADW) forms near Greenland, moves south through the deep Atlantic and then into the Indian and Pacific Oceans.
- Major zones of upwelling occur in the Pacific and the circumpolar Southern Ocean.
- Deep waters are nutrient-rich, so high NPP is found in upwelling zones.



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## **Global Thermohaline Circulation**



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#### **Oceanic Water Residence Times**

- *Residence Time*  $(T_R) = Mass / Flux In, or T_R = Mass / Flux Out.$
- Residence time with respect to river flow:

 $T_R$  = total ocean volume / annual river flow = 3400 years

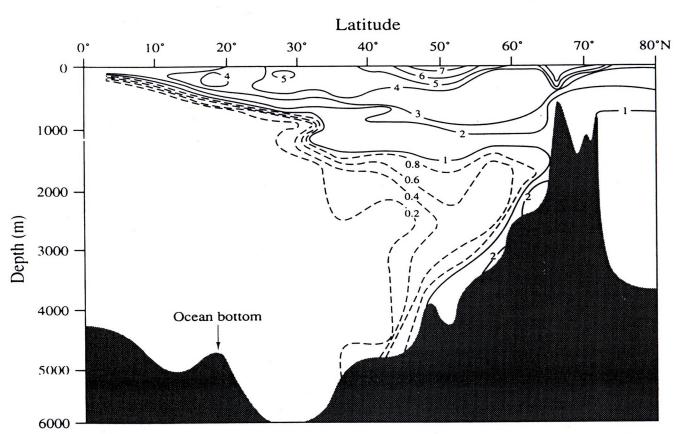
- However, most rivers mix only with surface waters, which have  $T_R = 1700$  years with respect to river waters.
- Considering rain water and upwelling input to surface waters reduces the  $\mathrm{T}_{\mathrm{R}}$  even more.
- For example, the mean  $T_R$  of North Pacific surface waters is *ca*. 9-15 years.
- Surface waters are also in rapid gaseous equilibrium with the atmosphere.

- The mean  $T_R$  of CO<sub>2</sub> in the surface ocean is *ca*. 6 years.

#### **Oceanic Water Residence Times (cont'd.)**

Transient tracers (bomb tritium: <sup>3</sup>H, bomb carbon 14: <sup>14</sup>C) constrain  $T_R$ .

- ${}^{3}\text{H}_{2}\text{O}$  dating of downwelling polar waters reveals that NADW transport toward the equator is *ca*. 10 x faster than the annual rate of riverine input to the ocean.
- Downwelling also occurs in southern ocean.



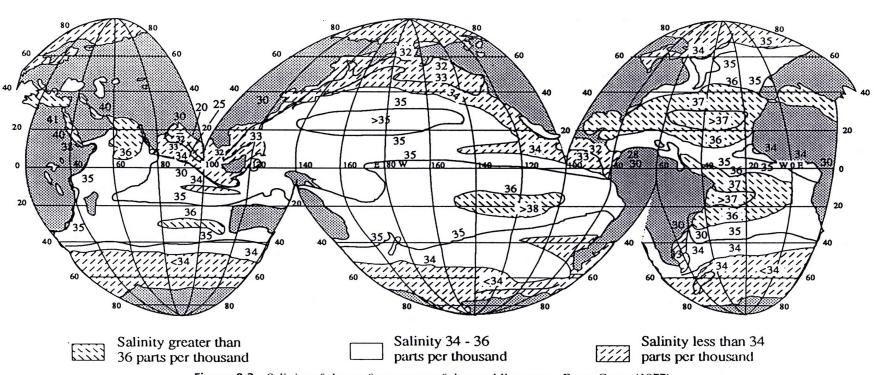
**Figure 9.2** Penetration of bomb-derived tritium ( ${}^{3}H_{2}O$ ) into the North Atlantic Ocean. Data are expressed as the ratio of  ${}^{3}H/H \times 10^{-18}$  for samples collected in 1972. From Ostlund (1983).

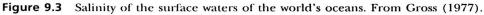
#### **Oceanic Water Residence Times (cont'd.)**

- Volume of water entering deep ocean >>> riverine inflow, so  $T_R <<< 3400$  years.
- <sup>14</sup>C dating of dissolved CO<sub>2</sub> yields residence times that range from 275 years for the Atlantic Ocean to 510 years for the Pacific Ocean.
  - Deep waters maintain an historical record of surface ocean conditions back several centuries.

# **Deep Water Currents and Ocean Salinity**

- Deep currents also transfer seawater between ocean basins as a result of the Antarctic circumpolar current (Fig. 9.1).
- In the Atlantic, evaporation > precipitation + river inflow
  - Atlantic Ocean is more saline than the Pacific Ocean.
  - Less saline waters are returned to the Atlantic from the Pacific
  - Dense saline waters flows out of deep Atlantic to Pacific and Indian Oceans.





#### **Deep Water Currents and Climate Change**

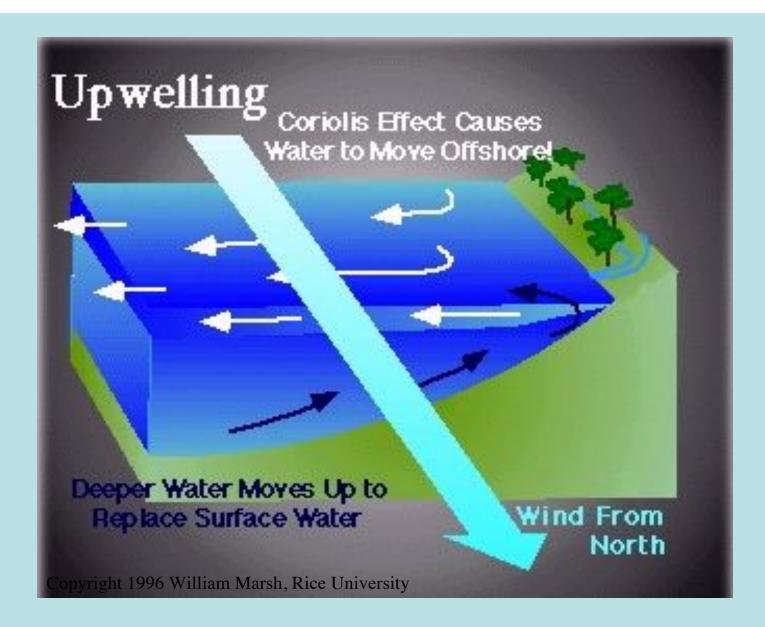
- Formation of deep waters may be associated with changes in global climate.
- For example, an increase in the rate of downwelling of cold, saline N. Atlantic waters at the start of the last glacial epoch may have resulted in a lowering of atmospheric  $CO_2$ .
  - $CO_2$  is more soluble in cold waters.
  - Atm CO<sub>2</sub> during last glacial was 200 ppm, vs pre-industrial 280 ppm.
- However, because deep water formation depends on the contrast in temperature and density between surface and deep waters, once the glacial epoch was fully developed the production of NADW was likely to have declined.
  - causing a reduction in transport of atmospheric  $CO_2$  to the deep ocean
  - allowing warmer conditions to return.

# 2b. El Niño

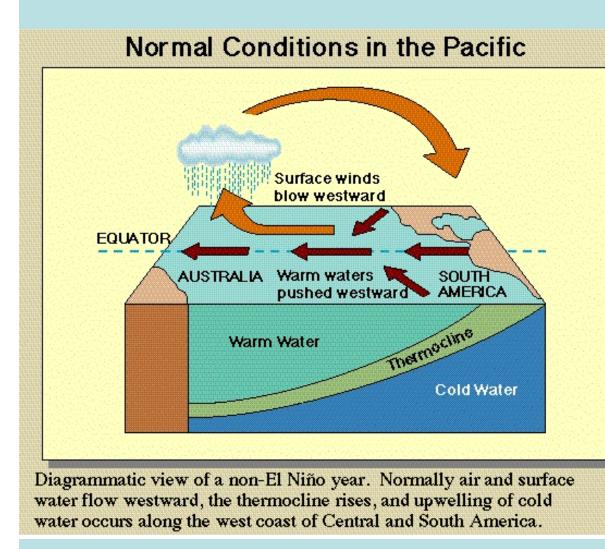
- El Niño is one example of shorter time-scale (year-to-year) variations in ocean currents that can affect biogeochemistry and global climate.
- El Niño occurs in the central Pacific Ocean.
  - Under normal conditions, trade winds blow warm surface waters E to W
  - Displacement of warm surface waters in the E. Pac. drives upwelling of cold bottom waters along the west coast of S. America & southern N. America.

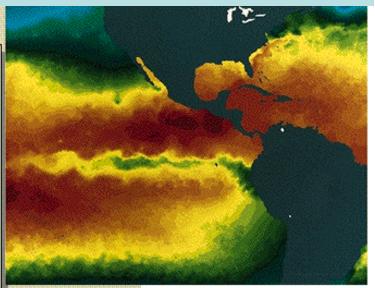
- High nutrients are carried with the deep upwelled waters, fueling phytoplankton growth and important fisheries industries, especially in Peru.

- Periodically (every 3-5 years), this surface transport breaks down in an event called: the *El Niño-Southern Oscillation (ENSO)*.
- During El Niño years, warm surface waters remain along the coast of Peru, preventing upwelling of nutrient rich bottom waters; fisheries collapse.



http://www.brookes.ac.uk/geology/sedstruc/upwell/ocean.htm

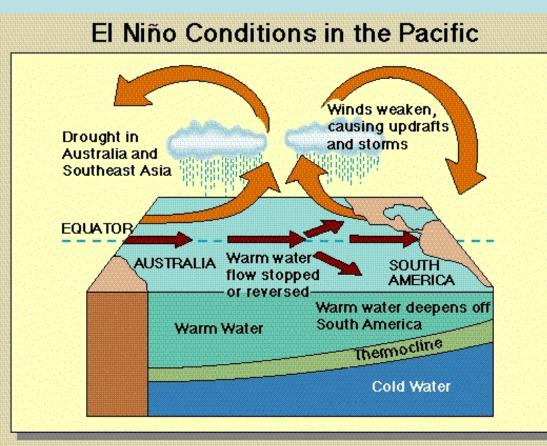




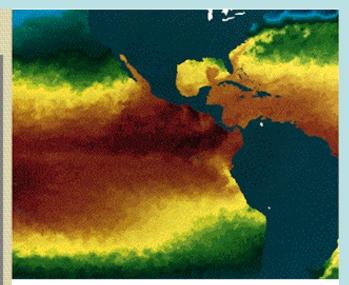
Surface water temperature in a non-El Niño year. This map, produced from satellite data, shows the surface temperature of the equatorial Pacific on 31 May 1988. The warmest water is indicated by the dark red, and progressively cooler water by yellow and green. Note the coastal upwelling along the South American coast at the lower right of the map, and the tongue of recently upwelled water extending westward along the equator from the South American coast.

(Figures and figure links listed refer to figures in Garrison, Oceanography: An Invitation to Marine Science 4th Ed.)

http://www.geology.wmich.edu/kominz/C9normaleqPac.gif



Diagrammatic view of an El Niño year. When the Southern Oscillation develops, the trade winds diminish and then reverse, leading to an eastward movement of surface waters along the equator. The surface waters of the central and eastern Pacific become warmer, coastal upwelling along the South and Central American coast decreases, and storms over land may increase.



Surface water temperature in an El Niño year. This map, produced from satellite data, shows the surface temperature of the equatorial Pacific on 13 May 1992. The thermocline was deeper than normal, and equatorial upwelling was suppressed. Note the absence of coastal upwelling along the coast and the lack of the tongue of recently upwelled water extending westward along the equator.

(Figures and figure links listed refer to figures in Garrison, Oceanography: An Invitation to Marine Science 4th Ed.)

http://www.geology.wmich.edu/kominz/C9elnino1.gif

# 2b. El Niño (cont'd.)

- Other climatic changes associated with El Niño:
  - exceptionally warm winters and high rainfall in western N. America.
  - absence of warm surface waters in the W. Pac reduces monsoons intensity in S. E. Asia and India.
- El Niño events are part of a cycle, alternating with opposite but equally extreme conditions during non-El Niño years, known as La Niña conditions.
  - Upwelling of cold, deep waters during La Nina years results in lower atmospheric temperatures over much of the N. hemisphere.
  - The trigger for the switch between El Niño and La Niña is poorly understood.
- Some consequences of the El Niño-La Niña cycles:
  - Add variation to global temperature, making it difficult to perceive atmospheric warming due to the Greenhouse Effect.
  - Affects atmospheric CO<sub>2</sub>, since CO<sub>2</sub> release from cold, upwelled waters is lower during El Niño years.
  - Denitrification rates 25% lower during El Niño years vs. 25% La Niña years.

#### Seawater Composition: Major Ions

- $T_R$  for these major ions are much longer than  $T_R$  for water in the oceans, so they are uniformly distributed.
- These ions are *conservative*; maintain the same ratio to each other throughout oceanic waters, even if salinity changes.

Constituent	Concentration in seawater <sup>a</sup> (mg/kg)	Chlorinity ratio <sup>a</sup>	Concentration in river water <sup>b</sup> (mg/kg)	Mean residence time (10 <sup>6</sup> yr)
Sodium	10,760	0.5561	5.15	75
Magnesium	1,294	0.0668	3.35	14
Calcium	412	0.0213	13.4	1.1
Potassium	399	0.0206	1.3	11
Strontium	7.9	0.00041	0.03	12
Chloride	19,350	1.0000	5.75	120
Sulfate	2,712	0.1400	8.25	12
Bicarbonate	145	0.0075	52	0.10
Bromide	67	0.0035	.02	100
Boron	4.6	0.00024	0.01	10.0
Fluoride	1.3	0.000067	0.10	0.5
Water				0.034

**Table 9.1**Major Ion Composition of Seawater, Showing Relationships to Total Salinity<br/>and Mean Residence Times for the Elements with Respect to River Water Inputs

<sup>a</sup> Holland (1978).

<sup>b</sup> Meybeck (1979) and Holland (1978).

#### Seawater Composition: Major Ions (cont'd.)

• Because these elements are conservative, can calculate total salinity from the concentration of a single ion, typically Chloride is used:

salinity % = 1.81 (Chloride %), where % = parts per thousand (ppt) = g/kg of water

- Mass Balance of Major Elements in Seawater (e.g. Steady State):
  - Major element composition has remained constant for long periods of time.
  - -This requires processes that remove ions from the oceans to balance new riverine inputs.
  - Residence times for major elements (Table 9.1) vary from 120 Ma for Cl to 1.1 Ma for Ca;  $T_R$  provides a measure of how reactive an element is.
  - The shorter  $T_R$  for Ca reflects biological removal as calcium carbonate, and deposition in sediments; there is no similar removal process for Cl.

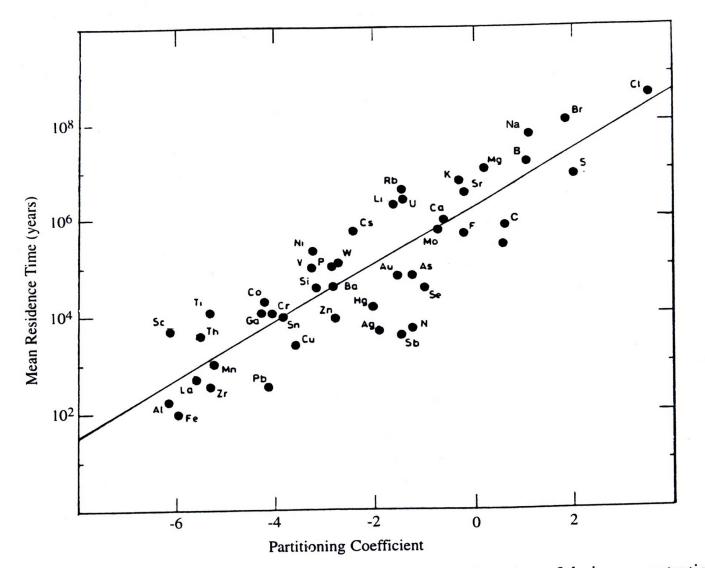
#### Examples of Processes that Remove Ions from Seawater

- Cyclic Sea Salts.
  - Wind blown sea-spray forms aerosols containing seawater ions (Chap. 3)
  - A significant portion of river-transported Cl derives from these aerosols, returning them to the sea -- *cyclic seasalts*.
  - This process removes ions in proportion to their concentration in seawater.
- Ion Exchange on River-borne Clays Entering the Ocean
  - Most of the cation exchange sites on clays are occupied by Ca<sup>2+</sup>.
  - Upon exposure to seawater, Ca<sup>2+</sup> is released, and replaced by other seawater cations, especially Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>.
  - Most deep sea clays have higher Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>. concentrations than riverine clays (Martin and Meybeck 1979).
  - When these clays settle out onto the seafloor these ions are removed from sw.
- Burial of dissolved ions (particularly Na<sup>+</sup> and Cl<sup>-</sup>) in sediment pore waters.
- Deposition of biogenic CaCO<sub>3</sub>.is the major process removing Ca<sup>2+</sup> from seawater.

# Examples of Processes that Remove Ions from Seawater (cont'd.)

- Biogenic removal resulting from sulfate reduction and formation of pyrite (FeS<sub>2</sub>), a secondary, *authigenic* mineral.
- Evaporite minerals (salt flats, sabkhas)
  - During some periods in the geologic past, vast deposits of evaporite minerals formed when seawater evaporated from shallow, enclosed basins.
  - Although limited in areal extent, this process has been important for Na<sup>+</sup>, Cl<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> removal from seawater during certain periods of Earth's history.
- Reverse Weathering, an old idea recently (mid-1990s) confirmed.
  - Formation of secondary, authigenic silicate minerals within sediments
  - Important for removing Mg<sup>2+</sup>, K<sup>+</sup>, H<sub>4</sub>SiO<sub>4</sub>.
- Removal at Hydrothermal Vents.
  - Particularly important for  $Mg^{2+}$  (Mg-silicate formation), but also for  $SO_4^{2-}$ .

#### Mean Seawater T<sub>R</sub> correlates with Tendency to Form Solid-Phase



**Figure 9.4** Mean residence time of elements in seawater as a function of their concentration in seawater divided by their mean concentration in the Earth's crust—with high values of the index indicating elements that are very soluble. From Whitfield and Turner (1979).

# Summary of Major Processes that Remove Ions from Seawater (cont'd.)

- Summary of Removal Processes:
  - Most Na <sup>+</sup> and Cl<sup>-</sup> are removed in pore water burial, sea spray, and in evaporitic deposits.
  - Mg<sup>2+</sup> is largely removed in hydrothermal exchange.
  - $Ca^{2+}$  and  $SO_4^{2-}$  are removed by deposition in biogenic sediments.
  - K<sup>+</sup> is removed by exchange with clay minerals and reverse weathering.
- Eventually, over long periods of time, ocean sediments are subducted into the Earth's mantle
  - Non-volatile components are melted under pressure and converted into primary silicate minerals.
  - volatile components are released as volcanic gases (H<sub>2</sub>O, CO<sub>2</sub>, Cl<sub>2</sub>, SO<sub>4</sub>)

## **Lecture Summary**

- Temperature and salinity differences between surface and deep water result in stable stratification of the water column; reduction of this contrast in high latitudes leads to *isopycnal* mixing and deep water formation.
- Thermohaline circulation is driven by downwelling of cold, dense surface waters at high latitudes to form deep waters; transport of cold, deep waters equator-ward, with a counter-balancing flow of warm surface waters from equator to pole.
- Thermohaline circulation is an important mechanism for redistributing heat energy on the Earth's surface.
- Wind driven surface currents lead to formation of *central ocean gyres* and *upwelling*.
- El Niño-Southern Oscillation results from changes in surface current and upwelling patterns, and leads to global climate change.
- Residence time  $(T_R)$  of elements in the ocean reflects how much time an element spends in the ocean before removal, ranges from <100 to >100 Ma
- T<sub>R</sub> indicates relative reactivity of elements, i.e. efficacy of removal processes.