Seawater Chemistry and Chemical Oceanography

The Universal Solvent

- Polarity of molecule makes water very effective at "hydrating" even weakly charged ions

Sphere of Hydration

- Polarity of water molecules allows interactions with solute molecules
  - Example NaCl
    - Ionic bond
    - Water's polarity can break this bond and retain the ions that result in solution
- Water is the universal solvent
Seawater has everything dissolved in it. 13ppm Au $\times$ 1.12e21 kg H$_2$O = 1.5e10 kg Au @ $43,052/\text{kg}* = $646 trillion

*Gold prices as of 5 Oct 2010

Seawater Salinity

- **Salinity** – the amount ions dissolved in water, including dissolved gases
  - Not including
    - Suspended material (floating grains of clay, for instance)
    - Sediment settled from water
- Average ocean salinity
  - 3.5%
  - 35%
  - 35 g/kg
  - 35 permil
### Changing Salinity

- **Sources**
  - Runoff
  - Hydrothermal Vents
  - Volcanoes
- **Sinks**
  - Sea Spray
  - Biology
  - Hydrothermal Vents
  - Chemical Precipitation

### Other Seawater Constituents

- **Gases**
  - CO₂
  - O₂
  - N₂
  - Ar
- **Important Trace Constituents**
  - I₂
  - PO₄⁻³
  - NO₃⁻¹
  - Fe

### Measuring Salinity

- **Salinity is measured as conductivity of the water**
  - Since the dissolved constituents are ions, they facilitate the conductance of an electric current
- **Units**
  - psu – practical salinity units
  - 1 psu = 1 permil
Salinity Variations

**Freshwater** – 0.16 psu
**Saltwater** – 35 psu average

**Hypersaline water** – 40 psu and greater
- Semi-enclosed seas
- Red Sea, Mediterranean Sea

Salinity values can be any mixture of these values

**Brackish** – between 0 psu and 35 psu
- River estuaries
- Bays
Cause of Salinity Variation

• Decrease Salinity
  – Precipitation (H₂O)
  – Runoff
  – Melting Ice • Increase Salinity
  – Evaporation
  – Ice formation

Salinity Profiles

• Halocline
  – Rapidly changing salinity
• Surface processes control salinity

Salinity and Density

• What determines the salinity of deep water?
  – We need to ask how the water gets there.
Seawater Density

- \( \rho = f(T, S) \)
- \( \frac{d\rho}{dT} < 0 \)
- \( \frac{d\rho}{dS} > 0 \)
- Density units
  - Pure water
  - 1000 g/L
  - \( \sigma = \rho - 1000 \)

Salinity and Temperature

- 1022-1030 g/L
Salinity and Temperature

- Used to characterize seawater
- Representative of surface processes and thus region of origin

Depth Profiles

- Pycnocline
  - Rapid change in density
- Mixed layer
  - Above thermocline

Acidity and Alkalinity

- pH of oceans = 8.2
  - $10^{-8.2}$ mol H⁺/L
- Carbonate buffering
Changing Alkalinity

- Oceans are absorbing more CO₂
- This mitigates CO₂’s effect on climate change
- Ocean pH is lowered

![Map showing ocean pH changes](image)

Chemical Oceanography

- Use of chemicals to track ocean circulation
  - Natural chemicals
    - ¹⁴C
    - Nitrates
    - Phosphates
  - Anthropogenic chemicals
    - CFC’s
    - ¹⁴C (from nuclear bombs)
    - ³H (from nuclear bombs)
Chem O – a ‘dye’ experiment

The ‘dye’ doesn’t always need to be visible – a change in salinity, a measurable solute or nutrient, a man-made chemical can all help in tracing currents.

Chemical Oceanography

• Use of chemicals to track ocean circulation
  – Some circulation is too subtle to measure directly
  – GeoSecs (1970’s)
  – WOCE (1990’s)

GeoSECS

• Geochemical Ocean Section Study
  – 1973 to 1976
  – International Decade of Ocean Exploration
  – Application of geochemical and hydrographic data to study circulation and mixing process in the ocean
    • Atlantic – R.V. Knorr (WHOI)
    • Pacific – R.V. Melville (Scripps)
    • Atlantic – F.S. Meteor (Germany)
    • Pacific and Indian – R.V. Hakuho-Maru (Japan)
GeoSECS

- Measured:
  - CTD
  - Radioactive tracers
  - Stable isotope tracers
  - Dissolved salts
    - Ba
    - Sr
    - Mg
  - Alkalinity

GeoSECS

- Sparse data, but invaluable to this day
- Southern Hemisphere not as well represented in data

WOCE

- World Ocean Chemistry Experiment
  - 1990 to 2002
  - World Climate Research Program
  - 30 nations participated
WOCE

• World Ocean Chemistry Experiment
  – More coverage geographically
Nitrates and Phosphates

- **Nutrients**

Seasonal Productivity Variations

- Nitrates used in productive seasons
- Upwelling and currents

GeoSECS and WOCE

- Both expeditions left a legacy of important discoveries.
- Classification of ocean transport and circulation that is nearly impossible to measure directly
  - Dye experiments – use of anthropogenic chemicals to trace movement of deep ocean
  - Thermohaline circulation
    - Density driven – salt and temperature
Thermohaline Circulation

- Thermo... – temperature
- ...haline – salt
  - Density-driven flow of surface water to deep ocean and vice versa

Global Conveyor Belt

- ...of heat and carbon

Subtropical Atlantic
Subtropical Atlantic

- Evaporation over isthmus of Panama
- Gulf Stream transport of water poleward

Subtropical Atlantic

- Cold, salty water becomes ‘unstable’ – density is higher than water below it.
Observation of the N. Atlantic Overturn

• Subduction of heat and salt (and carbon) into deep water masses

Observability of Thermohaline Circulation

• Major ocean current system that can’t be measured directly from moving ship
• Use of chemicals dissolved in ocean to “trace” it – passive tracers.

Anthropogenic Tracers

• Man-made chemicals enter the ocean and allow us to trace ocean currents passively
Radiocarbon ($^{14}$C)

Late 1950’s, early 1960’s

Radiocarbon Bomb Curve
Tritium

- Produced in 1950’s and 1960’s
- $^3$H half life = 12.32 y
- Demonstration of sinking N. Atlantic waters

Key Concepts

- All chemicals dissolve into the ocean
- Salinity and temperatures are the “currency” of oceanography
- Thermohaline circulation only observable using chemical oceanography
- Other tracers can be used – oil?