The Chemical Composition of Seawater

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Seawater Chemistry Supports:

• \( \frac{1}{2} \text{O}_2 \) production

• \( \text{CO}_2 \) sink

• Food production
Topics

- Salts
- Carbonate system
- Inorganic Nutrients
- Trace Metals
- Organic Matter
Salts

• Density
• Freezing point
• Ionic strength
• Complexes with other ions
• Analytical challenges
## Salt in the Ocean

35 grams of salt / liter of seawater

<table>
<thead>
<tr>
<th>Cations</th>
<th>mmol/kg</th>
<th>Anions</th>
<th>mmol/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>469.06</td>
<td>Cl⁻</td>
<td>545.86</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>52.82</td>
<td>SO₄²⁻</td>
<td>28.24</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>10.28</td>
<td>Br⁻</td>
<td>0.84</td>
</tr>
<tr>
<td>K⁺</td>
<td>10.21</td>
<td>F⁻</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Sources and Sinks of Chemical Constituents
Residence Time

Assume steady state: inputs = outputs

Residence Time (years) = ocean inventory (mol) / river inflow rate (mol y\(^{-1}\))

\[ \tau = \frac{\text{reservoir}}{\text{input or output}} \]

Residence Time of Water = \(1.35 \times 10^{18} \text{ m}^3 \div 3.5 \times 10^{13} \text{ m}^3 \text{ y}^{-1} = 40,000 \text{ years}\)

Residence Time of Na\(^+\) = \(647 \times 10^{18} \text{ moles} \div 8.1 \times 10^{12} = 80 \times 10^6 \text{ years}\)

Residence Time of Cl\(^-\) = \(753 \times 10^{18} \text{ moles} \div 7.7 \times 10^{12} = 98 \times 10^6 \text{ years}\)

These ions reside in the ocean \sim 3000 \text{ times longer than the water}
Evaporation and Precipitation Drive Sea Surface Salinity

Levitus, 1982
Global Sea Surface Salinity

Emerson & Hedges, 2008
Section View of Salinity

Salinity [pss-78]

Data: M. Arhan, IFREMER/LPO

A13
Feb/Mar 1995

www.ewoce.org
Topics

• Salts
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Carbonate System: Ocean Storage of Carbon

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \]

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \]
As Atmospheric CO$_2$ Increases Ocean Chemistry Responds

For 650,000 years, atmospheric carbon dioxide had never been above this line.

Current level

1950 level

NASA
Ocean Acidification

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3
\]

\[
\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+
\]

\[
\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+
\]
Ocean Acidification Can Impact Ocean Life

CaCO$_3$ $\rightarrow$ Ca$^{2+}$ + CO$_3^{2-}$

<table>
<thead>
<tr>
<th>Physiological response</th>
<th>Major group</th>
<th>Species studied</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calcification</strong></td>
<td>Coccolithophores$^1$</td>
<td>4 2 1 1 1</td>
</tr>
<tr>
<td></td>
<td>Planktonic Foraminifera</td>
<td>2 2</td>
</tr>
<tr>
<td></td>
<td>Molluscs</td>
<td>4 4</td>
</tr>
<tr>
<td></td>
<td>Echinoderms$^1$</td>
<td>3 2 1</td>
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<tr>
<td></td>
<td>Tropical corals</td>
<td>11 11</td>
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<td></td>
<td>Coralline red algae</td>
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<td><strong>Photosynthesis$^2$</strong></td>
<td>Coccolithophores$^3$</td>
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<tr>
<td></td>
<td>Prokaryotes</td>
<td>2 1</td>
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<td></td>
<td>Seagrasses</td>
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<td><strong>Nitrogen Fixation</strong></td>
<td>Cyanobacteria</td>
<td>1 1</td>
</tr>
<tr>
<td><strong>Reproduction</strong></td>
<td>Molluscs</td>
<td>4 4</td>
</tr>
<tr>
<td></td>
<td>Echinoderms</td>
<td>1 1</td>
</tr>
</tbody>
</table>

1) Increased calcification had substantial physiological cost; 2) Strong interactive effects with nutrient and trace metal availability, light, and temperature; 3) Under nutrient replete conditions.

Doney et al., 2009
Oysters

- affects development of oysters

- already a problem on Northwest Coast of U.S.
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Nitrogen vs. Phosphorus Limitation

Karl et al., 2001
Nitrogen Cycle

Marine Nitrogen Cycle

- NO$_2^-$ → NO → N$_2$O
- NO → NH$_3$/NH$_4^+$ → N$_2$
- N$_2$ Fixation
- N$_2$ Fixation
- N$_2$ Fixation
- Assimilation
- Ammonification
- ANAMMOX
- Denitrification
- N$_2$ Fixation
- N$_2$ Fixation
Phosphorus Cycle

$\text{PO}_4^{3-}$

Organic Phosphorus
Increased Inputs of Nutrients: Eutrophication
Harmful Algal Blooms

• Toxins
  – Shellfish poisoning
  – Fish kills

• Hypoxia
  – Blooms drawdown oxygen so quickly that an area becomes anoxic driving organisms away or killing them
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Trace Metals

- Micronutrients
- Iron can limit nitrogen fixation
- Human contamination
Trace Metal Profiles

1. Conservative

2. Nutrient-like Profile

3. Particle-scavenged
Also hydrothermal sources of metals: iron coming off a hydrothermal vent on the mid-Atlantic ridge.
Human Contributions to Trace Metal Concentrations also Detectable: Higher Concentrations of Lead in North Atlantic Deepwater
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Conclusions

• Many marine chemical constituents including trace metals, nutrients, and the carbonate system underlie a delicate balance that supports the productivity of the ocean.

• Chemicals also act as tracers of physical processes occurring in the ocean including deepwater circulation, inputs from hydrothermal vents, and upwelling.

• The chemistry of the ocean is influenced by humans in many ways.
Questions?