Understanding Ocean Acidification (OA): Chemical and Oceanographic Basics

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Outline

I. What is OA?

II. What makes seawater effective absorbers of anthropogenic CO$_2$?

III. What are the known consequences of OA?

IV. What are the possible effect(s) of OA on the oceanic carbon cycle?

Caldeira and Wickett (2003)
Not an “any old” phenomenon

A. glacial-interglacial CO$_2$ changes

B. Slow changes over the past 300 million years

C. Historical changes in ocean surface waters

D. Unabated fossil-fuel burning over the next few centuries

Caldeira and Wickett (2003)
Pre-Industrial Carbon Cycle

Units: $10^{15}$ gC or $10^{15}$ gC yr$^{-1}$

Human-Induced Carbon Fluxes (averaged over 1980s)

<table>
<thead>
<tr>
<th>Flux Source/Process</th>
<th>Carbon Flux (10^15 gC)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel burning</td>
<td>590 +161</td>
<td></td>
</tr>
<tr>
<td>Weathering</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Land use change</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Vegetation</td>
<td>2300 +65 -124</td>
<td></td>
</tr>
<tr>
<td>Soil &amp; Detritus</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Rivers</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Fossil fuels</td>
<td>3700 -220</td>
<td></td>
</tr>
<tr>
<td>Fossil fuel burning</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>Weathering</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Uplift and Weathering</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Sedimentary rocks</td>
<td>15,000,000</td>
<td></td>
</tr>
<tr>
<td>Human-induced carbon fluxes</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Marine Biota</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Surface ocean</td>
<td>900 +18</td>
<td></td>
</tr>
<tr>
<td>Ocean Degassing</td>
<td>70.6</td>
<td></td>
</tr>
<tr>
<td>Ocean Uptake</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Respiration</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Deep ocean</td>
<td>37100 +100</td>
<td></td>
</tr>
<tr>
<td>Surface sediment</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Weathering</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>


Note that anthropogenic fluxes are not balanced.
Net Changes in C Stocks ($10^{15}$ gC)

1800 to 1994

- Atmosphere: +165
- Land Net: -39
  - Land use change: -100 to -180
  - Biosphere: +61 to +141
- Oceans: +118
- Fossil Fuels: -244

1980 to 1999

- Atmosphere: +65
- Land Net: +15
  - Land use change: -24
  - Biosphere: +39
- Oceans: +37
- Fossil Fuels: -177

The oceans have been consistent sinks for anthropogenic CO$_2$ since the industrial revolution.

Why so much dissolved CO\(_2\) in seawater?

Total dissolved inorganic carbon \(\geq 2000 \ \mu\text{M}\)

Total dissolved inorganic carbon = \(\sim 2.5 \ \mu\text{M}\) at room temp.
Forms of Inorganic Carbon

Gas phase

\[ \text{CO}_2(g) \]

Aqueous phase

Dissolved Inorganic Carbon (DIC) = \([\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]\)

\[
\begin{align*}
0.5 \% & \quad 88.6 \% & \quad 10.9 \%
\end{align*}
\]

\([\text{H}_2\text{CO}_3^*] = \text{CO}_2(aq) + [\text{H}_2\text{CO}_3] \]

[\text{CO}_2] is also used instead of \([\text{H}_2\text{CO}_3^*] \]

Solid phase

Primarily \text{CaCO}_3 (calcite, aragonite)
Alkalinity Defined

Alkalinity ≈ [HCO₃⁻] + 2[CO₃²⁻] + [OH⁻] − [H⁺]

Carbonate Alkalinity = [HCO₃⁻] + 2[CO₃²⁻]

POP QUIZ:

1. What is the alkalinity of pure H₂O?
2. What is the alkalinity of pure H₂O bubbled with CO₂?
3. What is the alkalinity of a 1 mM NaHCO₃ solution?
4. What is the alkalinity of a 1 mM Na₂CO₃ solution?
DIC and Alkalinity Profiles in the Water Column

TCO$_2$ = total CO$_2$ = DIC
TA = total alkalinity
The “N” prefix indicates that the values have been normalized to salinity of 35.

Millero (2006)

What happens to atmospheric CO$_2$ when it dissolves in seawater? Write out the reaction(s).
Acidification Lowers the Carbonate Ion Concentration

![Graph showing pH and dissolved CO₂ and CO₃²⁻ concentrations over time.](image)

**Fig. 2.** Seawater pH and the dissolved carbon dioxide (CO₂) and carbonate ion (CO₃²⁻) concentrations in the surface layer of the ocean assuming a “business as usual” (IS92a) anthropogenic CO₂ emission scenario (Houghton et al. 1995). Dashed lines represent the predicted changes in carbonate chemistry if CO₂ emissions are reduced according to the Kyoto Protocol (modified after Wolf-Gladrow et al. 1999).
Acidification Lowers the Saturation State of CaCO$_3$

CaCO$_3$(s) $\leftrightarrow$ Ca$^{2+}$ + CO$_3^{2-}$

**Ion Product**

\[ [\text{Ca}^{2+}]_{\text{observed}} + [\text{CO}_3^{2-}]_{\text{observed}} \]

**Solubility Product**

\[ [\text{Ca}^{2+}]_{\text{sat}} + [\text{CO}_3^{2-}]_{\text{sat}} \]

**Saturation State** = $\Omega$

\[ \frac{\text{Ion Product}}{\text{Solubility Product}} \approx \frac{[\text{CO}_3^{2-}]_{\text{observed}}}{[\text{CO}_3^{2-}]_{\text{sat}}} \]

Feely et al. (2004)
CaCO₃ Saturation Horizon is Shoaling

Figure 3.2 Curves of $\text{CO}_3^{2-}$ concentration versus depth for saturation of CaCO₃ (calcite and aragonite). Dots represent a profile of seawater $[\text{CO}_3^{2-}]$ for a station in the Atlantic. Dashed lines denote the depth of the saturation horizon (see text for details).

Feely et al. (2004)
The aragonite and calcite saturation horizons have shoaled by 10s to 100s of meters since the industrial revolution (figure).

Orr et al. (2005)
“some polar and subpolar surface waters will become undersaturated at ~2 x CO$_2$, probably within the next 50 years”
(“2 x CO$_2$” being twice the preindustrial level)
Without these pumps, atmospheric CO$_2$ will increase by about 50% relative to pre-industrial values (Marinov and Sarmiento, 2004).
Biological Pumps

Primary Production:

$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{“CH}_2\text{O”} + \text{O}_2$

Calcium Carbonate Precipitation:

$\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$

Soft Tissue Pump:

$\text{“CH}_2\text{O”} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

Carbonate Pump:

$\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$
Effects of Acidification on the Oceanic Carbon Cycle??

1. What might happen to the soft tissue pump?
2. What might happen to the carbonate pump?
3. Are the two pumps “coupled”? 
References Cited (*available in pdf)


Relationship between pH and carbonate species (log C – pH Diagram)

Figure 3. A distribution diagram of carbonic acid with CT = 2.0 x 10-3 (-log CT = 2.7). In this case the apparent seawater constants of pK\textsuperscript{'}\textsubscript{1} = 6.0 and pK\textsuperscript{'}\textsubscript{2} = 9.1 were used. The species for boric acid are also shown (pK\textsuperscript{'}\textsubscript{B} = 8.7; -log CB = 3.3).