Carbon Dioxide, Alkalinity and pH

OCN 623 – Chemical Oceanography

12 February 2015

Reading: Libes, Chapter 15, pp. 383 – 394

(Remainder of chapter will be used with the lecture: “Biogenic production, carbonate saturation and sediment distributions”)

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Outline

1. CO₂ speciation
2. pH
3. Alkalinity
4. Calculation of composition of marine CO₂ system
5. Oceanographic applications
6. Global CO₂
Why is it important to understand the CO$_2$ system?

- CO$_2$ controls the fraction of inbound radiation that remains trapped in the atmosphere (greenhouse effect), which in turn strongly influences planetary climate.

- CO$_2$ is the raw material used to build organic matter.

- CO$_2$ controls the pH of the oceans.

- Distribution of CO$_2$ species affects preservation of CaCO$_3$ deposited on the sea floor.
CO₂ Speciation

- CO₂(g) has many possible transformations upon dissolution in H₂O

- Major dissolved forms:
  - CO₂(aq) (*aqueous carbon dioxide* – a dissolved gas)
  - H₂CO₃ (*carbonic acid* – trace amount)
  - HCO₃⁻ (*bicarbonate ion*)
  - CO₃⁻² (*carbonate ion*)

- Species interconvert readily

- Perturbations to one part of CO₂ system leads to redistribution of species

- Reactions not always intuitive!
Equations for CO₂ Speciation

The equilibrium of gaseous and aqueous CO₂:

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

Subsequent hydration and dissociation reactions:

\[ \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

\[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

\[ K_1^* = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \]

\[ K_2^* = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \]

Asterisk (*) indicates a “stoichiometric” constant

Hint: when pH is between 7.5 and 8.5:

\[ \text{CO}_2(\text{aq}) + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- \]
\[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \]

\[ \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

\[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

Seawater values shown --- freshwater curves are shifted left
How to Calculate $K_1^*$ and $K_2^*$

\[ pK = - \log K \]


For: $S = 0 – 50 \text{ g/kg}, \ T = 0 – 50^\circ\text{C}$

At $S = 35 \text{ g/kg}$ and $T = 25^\circ\text{C}$:

\[ pK_1^* = 5.8401 \quad pK_2^* = 8.9636 \]
Effects of Pressure on $K_1^*$ and $K_2^*$

As you raise a sample from depth:
- Ks’ decrease
- Reactions shift to left
- pH increases
- $CO_2(g)$ release

Decreasde pressure shifts reactions to left

$$K_1^* = \frac{\{H^+\}[HCO_3^-]}{[CO_2]}$$

<table>
<thead>
<tr>
<th></th>
<th>1 atm</th>
<th>1000 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_1^*$</td>
<td>5.89</td>
<td>5.55</td>
</tr>
<tr>
<td>$pK_2^*$</td>
<td>9.13</td>
<td>8.93</td>
</tr>
</tbody>
</table>

As you raise a sample from depth:

<table>
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<tr>
<th>Depth (m)</th>
<th>$0^\circ$C</th>
<th>$5^\circ$C</th>
<th>$10^\circ$C</th>
<th>$0^\circ$C</th>
<th>$5^\circ$C</th>
<th>$10^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.12</td>
<td>1.11</td>
<td>1.11</td>
<td>1.07</td>
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<td>1.23</td>
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<td>1.50</td>
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<tr>
<td>10,000</td>
<td>2.91</td>
<td>2.80</td>
<td>2.70</td>
<td>2.07</td>
<td>2.03</td>
<td>1.99</td>
</tr>
</tbody>
</table>

“1” = 1 atm
Dissolved Inorganic Carbon
(DIC, Total CO₂, ΣCO₂)

\[
\text{DIC} \equiv [\text{CO}_2(aq)] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

• At seawater pH, >99% of CO₂ species are HCO₃⁻ and CO₃⁻², so we can simplify:

\[
\text{DIC} \equiv [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

• Equilibrium equations can be combined to allow us to calculate the concentration of any of the CO₂ species
Partial Pressure of CO$_2$ ($P_{\text{CO}_2}$)

In the atmosphere:

$P_{\text{CO}_2} \equiv$ partial pressure of CO$_2$ in the atm,
out of a total pressure of 1 atm (at sea level)

\textit{Measurement:}

Determine fraction of atm that is CO$_2$

$P_{\text{CO}_2} = P_{\text{total}} \cdot \text{fraction}_{\text{CO}_2}$
In water:

\[ \text{PCO}_2 \equiv \text{partial pressure of CO}_2 \text{ in atm when in equilibrium with the water} \]

(Henry’s Law: \( \text{PCO}_2 = K \cdot [\text{CO}_2]_{\text{water}} \))

Measurement:

Equilibrate water with a small gas headspace

Determine fraction of headspace gas that is CO\(_2\)

\[ \text{PCO}_2 = \text{P}_{\text{total}} \cdot \text{fraction}_{\text{CO}_2} \]
$P_{\text{CO}_2}$ provides a common unit for comparing CO$_2$ concs in water and the atmosphere, which allows a quick evaluation of gas fluxes.

- $P_{\text{CO}_2(\text{air})} > P_{\text{CO}_2(\text{water})}$: Flux of CO$_2$ from air to water
- $P_{\text{CO}_2(\text{air})} = P_{\text{CO}_2(\text{water})}$: No net flux of CO$_2$ (equilibrium)
- $P_{\text{CO}_2(\text{air})} < P_{\text{CO}_2(\text{water})}$: Flux of CO$_2$ from water to air
Seawater pH

• pH = - log \{H^+\}

• The pH of seawater varies only between about 7.5 and 8.4 (i.e., slightly alkaline)

• Over geological time, pH is thought to be controlled by water/mineral equilibria on a global scale

• Over shorter time scales (10^4 to 10^5 yrs) the CO_2 system (and its shifting equilibria) regulates seawater pH

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+
\]
Seawater pH – T and P Effects

For temperatures $T_1$ and $T_2$:

$$pH_{T_2} = pH_{T_1} + 0.011(T_2 - T_1)$$

Increased T causes pH to increase

“1” = 1 atm

Increased P causes pH to decrease
Definitions of Alkalinity

- GENERAL DEFINITION: The acid-buffering capacity of seawater

- Total Alkalinity (TA) represents ability of seawater to resist pH change upon addition of acid

- Remember the concept of a “buffer” (from basic chemistry): a substance that resists pH change upon addition of acid or base

- For seawater we focus on its ability to absorb H⁺
Total Alkalinity (TA)

$$TA \equiv 2[CO_3^{-2}] + [HCO_3^{-}] + [H_2BO_3^{-}] + 2[HBO_3^{-2}] + 3[BO_3^{-3}]$$
$$+ [OH^{-}] + [\text{organic/inorganic } H^{+} \text{ acceptors}] - [H^{+}]$$

• **End point** of an alkalinity titration (using acid titrant) is when:

  $$\text{Added } [H^{+}] = 2[CO_3^{-2}] + [HCO_3^{-}] + [H_2BO_3^{-}] + 2[HBO_3^{-2}] +$$
  $$3[BO_3^{-3}] + [OH^{-}] + [H^{+}\text{acceptors}]$$

• TA usually reported in **meq/L** or **meq/kg** (an “equivalent” is a mole of charge)
Carbonate Alkalinity (CA)

\[ CA \equiv 2[\text{CO}_3^{\text{-2}}] + [\text{HCO}_3^-] \]

- Typically, \( \text{HCO}_3^- \) and \( \text{CO}_3^{\text{-2}} \) are present at ~1000x conc of other proton acceptors

- Hence: CA nearly equals TA
CO₂ System Calculations

• There are four CO₂ properties that can be measured:
  DIC, P_{CO₂}, pH, and carbonate alkalinity

• Any two of these properties can be used to determine the composition of the CO₂ system in water (i.e., concs of CO₂(aq), HCO₃⁻, and CO₃⁻²)

• Traditionally, pH and alkalinity were measured

• Now: also use ΣCO₂ and P_{CO₂} to better constrain calculations, improving accuracy
Example Calculation #1

Use DIC and Carbonate Alkalinity data to calculate the concentrations of each inorganic carbon species ($CO_2(aq)$, $HCO_3^-$, and $CO_3^{2-}$) assuming $CO_2(aq)$ is negligible.

Two equations & two unknowns:

$$CA \equiv 2[CO_3^{2-}] + [HCO_3^-]$$

$$[HCO_3^-] = CA - 2[CO_3^{2-}]$$

$$DIC \equiv [HCO_3^-] + [CO_3^{2-}]$$

$$= CA - 2[CO_3^{2-}] + [CO_3^{-2}]$$

$$= CA - [CO_3^{-2}]$$

$$[CO_3^{2-}] = CA - DIC$$

$$[HCO_3^-] = CA - 2(CA - DIC)$$

$$= 2DIC - CA$$
Calculate the concentration (in mM) of each inorganic carbon species (CO$_2$(aq), HCO$_3^-$, and CO$_3^{2-}$) if:

DIC = 2.3 mM,  pH = 8.0,  T = 10°C,  P = 1 atm,  S = 35

At T = 10°C,  S = 35:

\[
pK_1^* = 6.08 \quad K_1^* = 10^{-6.08} = 8.318 \times 10^{-7}
\]

\[
pK_2^* = 9.28 \quad K_2^* = 10^{-9.28} = 5.248 \times 10^{-10}
\]

\[
pH = 8.0 \quad \{H^+\} = 10^{-8.0}
\]

From the definition of stoichiometric equilibrium constants:

\[
[CO_2] = \frac{\{H^+\}[HCO_3^-]}{K_1^*} = 0.01202 \quad [HCO_3^-]
\]

\[
[CO_3^{2-}] = \frac{K_2^*[HCO_3^-]}{\{H^+\}} = 0.05248 \quad [HCO_3^-]
\]
From the definition of DIC:

\[ \text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]

\[
2.3 = (0.01202 \times [\text{HCO}_3^-]) + [\text{HCO}_3^-] + (0.05248 \times [\text{HCO}_3^-])
\]

\[
2.3 = 1.0645 \times [\text{HCO}_3^-]
\]

\[
[\text{HCO}_3^-] = 2.16 \text{ mM}
\]

\[
[\text{CO}_2] = (0.01202)(2.16) = 0.026 \text{ mM}
\]

\[
[\text{CO}_3^{2-}] = (0.05248)(2.16) = 0.113 \text{ mM}
\]
CO2calc: A User-Friendly Seawater Carbon Calculator for Windows, Mac OS X, and iOS (iPhone)

By L.L. Robbins, M.E. Hansen, J.A. Kleypas, and S.C. Meylan

Introduction
A user-friendly, stand-alone application for the calculation of carbonate system parameters was developed by the U.S. Geological Survey Florida Shelf Ecosystems Response to Climate Change Project in response to its Ocean Acidification Task. The application, by Mark Hansen and Lisa Robbins, USGS St. Petersburg, FL, Joanie Kleypas, NCAR, Boulder, CO, and Stephan Meylan, Jacobs Technology, St. Petersburg, FL, is intended as a follow-on to CO2SYS, originally developed by Lewis and Wallace (1998) and later modified for Microsoft Excel® by Denis Pierrot (Pierrot and others, 2006). Besides eliminating the need for using Microsoft Excel on the host system, CO2calc offers several improvements on CO2SYS, including:

- An improved graphical user interface for data entry and results
- Additional calculations of air-sea CO₂ fluxes (for surface water calculations)
- The ability to tag data with sample name, comments, date, time, and latitude/longitude
- The ability to use the system time and date and latitude/longitude (automatic retrieval of latitude and longitude available on iPhone® 3, 3GS, 4, and, in the future, Windows® hosts with an attached National Marine Electronics Association (NMEA)-enabled GPS)
- New constants, including Lueker and others (2000) and Millero (2010)
- The ability to process multiple files in a batch processing mode
- An option to save sample information, data input, and calculated results as a comma-separated value (CSV) file for use with Microsoft Excel®

First posted December 13, 2010

- Report PDF (1.2 MB)

Executables:
- PC zip file (742 KB; dated February 3, 2011)
- Macintosh disk image file (4.9 MB)
- iPhone: iTunes link or type “co2calc” in the App Store’s search bar (Requires iOS 4.2 or later.)

For additional information contact:
Lisa Robbins
U.S. Geological Survey
St. Petersburg Coastal and Marine Science Center
600 4th Street South
St. Petersburg, FL 33701
http://coastal.er.usgs.gov/flash
**CaCO₃ Precipitation/Dissolution**

A tricky subject when discussing “CO₂”
(or, more properly, Pₐₐ₇C0₂)

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \]

Does this reduce the CO₂ (Pₐₐ₇C0₂) level of the seawater?

No! Lost CO₃²⁻ will be replaced:
\[ \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+ \]

But this H⁺ release causes:
\[ \text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

Thus, CaCO₃ precipitation causes a decrease in DIC, but an increase in Pₐₐ₇C0₂

Hint: when pH is between 7.5 and 8.5:
\[ \text{CO}_2(aq) + \text{CO}_3^{-2} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- \]
What processes affect Alk and $\Sigma$CO$_2$?

- CO$_2$ exchange between the atmosphere and surface seawater changes $\Sigma$CO$_2$, but doesn’t affect Alk

- Photosynthesis / respiration also changes $\Sigma$CO$_2$, but doesn’t affect Alk (loss of HCO$_3^-$ is balanced by loss of H$^+$)

- CaCO$_3$ dissolution / precipitation changes both $\Sigma$CO$_2$ and Alk
Calcification
Effects on Alk-pH-ΣCO₂

- Surface-ocean plankton remove \( \text{CO}_3^{2-} \) and \( \text{Ca}^{2+} \) from seawater to form \( \text{CaCO}_3 \) tests (calcification):
  \[
  \text{CO}_3^{2-} + \text{Ca}^{2+} \rightarrow \text{CaCO}_3
  \]

- Calcification alters both Alk and \( \Sigma\text{CO}_2 \), but not pH

- Amount of Alk decrease is 2x the effect on \( \Sigma\text{CO}_2 \) because of double negative charge of \( \text{CO}_3^{2-} \)

\[
\text{CO}_2(\text{aq}) + \text{CO}_3^{-2} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^{-}
\]
### Processes Affecting Alkalinity

<table>
<thead>
<tr>
<th>Process</th>
<th>Alkalinity Change for Forward Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photosynthesis and Respiration:</strong></td>
<td></td>
</tr>
<tr>
<td>(1a) $n\text{CO}_2 + n\text{H}_2\text{O} \xrightarrow{\text{photos}} (\text{CH}_2\text{O})_n + n\text{O}_2$</td>
<td>No change</td>
</tr>
<tr>
<td>(1b) $106\text{CO}<em>2 + 16\text{NO}<em>3^- + \text{HPO}<em>4^{2-} + 122\text{H}<em>2\text{O} + 18\text{H}^+ \xrightarrow{\text{photos}} {C</em>{106}\text{H}</em>{263}\text{O}</em>{110}\text{N}</em>{16}\text{P}_1} + 138\text{O}_2$</td>
<td>Increase</td>
</tr>
<tr>
<td>(1c) $106\text{CO}<em>2 + 16\text{NH}<em>4^+ + \text{HPO}<em>4^{2-} + 108\text{H}<em>2\text{O} \xrightarrow{\text{photos}} {C</em>{106}\text{H}</em>{263}\text{O}</em>{110}\text{N}</em>{16}\text{P}_1} + 107\text{O}_2 + 14\text{H}^+$</td>
<td>Decrease</td>
</tr>
<tr>
<td><strong>Nitrification:</strong></td>
<td></td>
</tr>
<tr>
<td>(2) $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+$</td>
<td>Decrease</td>
</tr>
<tr>
<td><strong>Denitrification:</strong></td>
<td></td>
</tr>
<tr>
<td>(3) $5\text{CH}_2\text{O} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{CO}_2 + 2\text{N}_2 + 7\text{H}_2\text{O}$</td>
<td>Increase</td>
</tr>
<tr>
<td><strong>Sulfide Oxidation:</strong></td>
<td></td>
</tr>
<tr>
<td>(4a) $\text{HIS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+$</td>
<td>Decrease</td>
</tr>
<tr>
<td>(4b) $\text{FeS}_2(s) + \frac{14}{3}\text{O}_2 + 3\frac{1}{3}\text{H}_2\text{O} \xrightarrow{\text{pyrite}} \text{Fe(OH)}_3(s) + 4\text{H}^+ + 2\text{SO}_4^{2-}$</td>
<td>Decrease</td>
</tr>
<tr>
<td><strong>Sulfate Reduction:</strong></td>
<td></td>
</tr>
<tr>
<td>(5) $\text{SO}_4^{2-} + 2\text{CH}_2\text{O} + \text{H}^+ \rightarrow 2\text{CO}_2 + \text{HS}^- + \text{H}_2\text{O}$</td>
<td>Increase</td>
</tr>
</tbody>
</table>
Vertical $\Sigma CO_2$ and Alkalinity Profiles

Figure 15.10
Current Status of Global CO$_2$

- Anthropogenic CO$_2$ input to atmosphere is primarily through oxidation of fossil organic matter (i.e., oil, coal and natural gas) and cement production.

- We are currently adding considerably to the CO$_2$ inventory of the atmosphere and the oceans, while stimulating terrestrial biomass production.

- There is $\sim$53x as much CO$_2$ in the ocean as in the atmosphere, but it is uncertain at what rate anthropogenic CO$_2$ is being added.
Ocean CO$_2$ Increase Tracks Atmosphere

“Ocean Acidification”

Time series of atmospheric CO$_2$ at Mauna Loa and surface ocean pH and pCO$_2$ at Ocean Station Aloha in the subtropical North Pacific Ocean. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL; HOTS/Aloha data: Dr. David Karl, University of Hawaii (modified after Feely, 2008).
In More Detail...

Figure 1. Ocean carbon dioxide and pH measurements near Hawaii at Station ALOHA 1988-2007

This figure demonstrates that as carbon dioxide in the air and ocean increases over time, the pH in the seawater decreases (Dore et al., 2009). Top: Calculated partial pressure of carbon dioxide in seawater (blue ●), and in air at nearby Mauna Loa (red ●)*. Bottom: Direct measurement of pH in surface seawater (orange ●) compared with calculated pH (green ●)*. Scientists measure “partial pressure” of carbon dioxide (pCO₂), the pressure that carbon dioxide gas exerts if it were alone in a container instead of being a component of the mixture of gases in the atmosphere or ocean, in units called microatmospheres.
Figure 1. North Pacific Ocean pH along 152°W in 2006 (pH_T, 25°C).

Byrne et al. 2010, Geophys. Res. Lett. 37
Change in seawater pH between 1991 and 2006

Change in seawater pH attributed to natural interdecadal/interannual DIC variability between 1991 and 2006 (due mostly to slowdown in downwelling, with more respiration at given depths)

Change in seawater pH attributed to the uptake of anthropogenic carbon between 1991 and 2006
Global Oceanic CO₂ Flux

- High values at equator (esp. in the Pacific) and along west coasts are from *upwelling* and subsequent *gas evasion to atmosphere*
- Low values where there is high bioproductivity
- Low values where cooling of ocean increases solubility of gas and causes *gas infusion to surface ocean*

Sabine et al. 2009
Ocean Water-column Anthropogenic Carbon ($C_{ant}$)

Can you identify the globally important sources and sinks, and when they are most active?

Note how the arctic “traps” large amounts of N. Hemisphere CO$_2$ during winter.
Here are mean surface-ocean values for two ocean basins:

<table>
<thead>
<tr>
<th>TA (ueq/kg)</th>
<th>DIC (umol/kg)</th>
<th>Salinity</th>
<th>T (°C)</th>
<th>TA (ueq/kg)</th>
<th>DIC (umol/kg)</th>
<th>Salinity</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>2100</td>
<td>34</td>
<td>20</td>
<td>2400</td>
<td>2000</td>
<td>35</td>
<td>24</td>
</tr>
</tbody>
</table>

1) Using these data, determine the values for the following in each seawater:
   - $\text{CO}_2$ (aq) (umol/kg)
   - pH
   - $\text{HCO}_3^-$ (umol/kg)
   - $\text{pCO}_2$ (uatm)
   - $\text{CO}_3^{2-}$ (umol/kg)

2) Are these seawaters sources or sinks of atmospheric $\text{CO}_2$? Why?

3) Extra credit: Why might the $\text{CO}_2$ chemistry be so different between these two waters?

EXPLAIN EXACTLY HOW YOU OBTAINED YOUR RESULTS!