Carbon Dioxide, Alkalinity and pH

OCN 623 – Chemical Oceanography

15 March 2018

Reading: Libes, Chapter 15, pp. 383 – 389

(Remainder of chapter will be used with the classes “Global Carbon Dioxide” and “Biogenic production, carbonate saturation and sediment distributions”)

<table>
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<th>Student Learning Outcomes (SLOs)</th>
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<td>2. Explain <strong>CO$_2$ dissolution</strong> in seawater and subsequent <strong>reactions</strong></td>
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<td>3. Explain the concepts of <strong>pH, alkalinity, and dissolved inorganic carbon</strong>, and write the equations defining these quantities</td>
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<td>4. Explain the relationship between <strong>carbonate dissolution/precipitation</strong> and <strong>pCO$_2$</strong></td>
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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.
Ocean Carbon Cycle in a Global Context

- **Land sink**
- **Fossil fuel and cement emissions**
- **Land-use change**

**Atmosphere**

- CaCO₃ formation
- NPP
- Respiration
- Export
- Remineralization
- Transport/mixing

**Coastal ocean**

- a+ decreased buffer capacity
- b+ decreased solubility in warm ocean
- c+ enhanced recycling in warm ocean
- d- carbon overconsumption
- e? DOM recycling/export
- f+ increased denitrification
- g+ increased nitrogen fixation
- h- reduced calcification
- i+ reduced particle ballast
- j+ increased stratification
- k? increased Southern Ocean winds
- l+ reduced deep water formation
- m- reduced upwelling
- n- increased carbonate dissolution

**Deep ocean**

**Mixed layer**

**Interior ocean**

Sabine and Tanhua 2009
There are many forms of dissolved inorganic carbon in water. Perturbations to one species leads to a redistribution of all the other species. Individual dissolved species can not be measured directly.

Using the thermodynamic constants ($K_x$), any two measured parameters can be used to calculate the concentration of all the species.
There are four measurable carbon parameters in water.

Measurable parameter:

**CO₂ fugacity**
Based on ~3 million measurements since 1970 and NCEP/DOE/AMIP II reanalysis.
Global flux is 1.4 ±0.7 Pg C/yr

Takahashi et al., Deep Sea Res. II, 2009
Surface observations have large variability over a wide range of time and space scales making it very difficult to properly isolate the anthropogenic increases. Uptake of 2 Pg C yr$^{-1}$ only requires a DpCO$_2$ of 8ppm.

The global mean air-sea CO$_2$ flux for the period from 1982 to 2009 gives an average contemporary net uptake of 1.47±.23 Pg C yr$^{-1}$
There are four measurable carbon parameters in water:

- **Total Alkalinity (TA)**
  - Represents the ability of seawater to resist pH change upon addition of acid.
  - Measurable parameter:
    \[
    TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + \ldots + [\text{OH}^-] - [\text{H}^+]\]

- **Carbonate Alkalinity (CA)**
  - Typically, \(\text{HCO}_3^-\) and \(\text{CO}_3^{2-}\) are present at \(~\)1000x conc of other proton acceptors.
  - Measurable parameter:
    \[
    CA = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]
    \]
  - Hence: CA nearly equals TA

**GENERAL DEFINITION:**

The acid-buffering capacity of seawater.

*Total Alkalinity (TA)* represents ability of seawater to resist pH change upon addition of acid.
Surface TA/Talk/Alk/A<sub>T</sub> Distribution is Very Similar to Salinity
Shallow Indian Ocean Data (depth < 100 m)
There are four measurable carbon parameters in water:

- \( x_{CO_2} \)
- \( p_{CO_2} \)
- \( f_{CO_2} \)

Inorganic Carbon is stored in the ocean as Total CO₂ (a.k.a. DIC).

DIC and TA are state variables, meaning they are not a function of temperature or pressure.

**Total CO₂**

\[
TCO₂ = \left[ CO₂ \right]^* + \left[ H₂CO₃ \right] + \left[ HCO₃^- \right] + \left[ CO₃^{2-} \right]
\]
TCO$_2$/DIC/C$_T$: Surface Distribution is Similar to Nutrient Distributions
Shallow Indian Ocean Data (depth < 100 m)
There are four measurable carbon parameters in water:

- $pCO_2$ (partial pressure of carbon dioxide)
- $fCO_2$ ( fugacity of carbon dioxide)
- $pH$ (hydrogen ion activity)
- $K_{0}$ (equilibrium constant for the reaction $CO_2 + H_2O = H_2CO_3$)

The pH of seawater is slightly basic; acidification is a process, not a state.

The measurable parameter is:

$$pH = -\log_{10}\{H^+\}$$

There are 5 different pH scales. The most common are $pH_{sws}$ and $pH_T$.

- $[H^+]_{sws} = [H^+]_f + [HSO_4^-] + [HF]$
- $[H^+]_T = [H^+]_f + [HSO_4^-]$
Surface pH distribution reflects combined patterns of alkalinity and TCO$_2$.
Group Task

How does seawater pH change when atmospheric CO$_2$ is added to the ocean?
What are the reactions??
How does seawater pH change when atmospheric CO$_2$ is added to the ocean?

What are the reactions??

Answer: The pH decreases because of the release of hydrogen ions:

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

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

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

The limited amount of CO$_3^{2-}$ available means that not all of the H$^+$ produced by the middle reaction can be consumed.
Take home message:
Each of the 4 measurable carbon parameters can tell us something different about the basic processes operating in the Ocean.
Question:
How will ocean carbon system respond to changes in ocean processes?
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:

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

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

Hint: When you add a CO₂ species to the system, follow the H⁺. Thus, the following is a reasonable approximation when pH is between 7.5 and 8.5:

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

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

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

Asterisk (*) indicates a "stoichiometric" constant.
**Distribution of CO$_2$ Species at Different pH Values**

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

Seawater values shown --- freshwater curves are shifted left
Effects of Pressure on Carbonate Speciation

As you raise a sample from depth:
- $K_s$'s decrease
- Reactions shift to left
- pH increases

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<th>1 atm</th>
<th>1000 atm</th>
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<td>$K_1^*$</td>
<td>$10^{-5.89}$</td>
<td>$10^{-5.55}$</td>
</tr>
<tr>
<td>$K_2^*$</td>
<td>$10^{-9.13}$</td>
<td>$10^{-8.93}$</td>
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\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq)
\]

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

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

Why is raising a sample of seawater from depth to the surface like opening a can of soda???

What exactly is happening?

How does the pH change?

Hint: What happens to the dissolved CO$_2$?
Why is raising a sample of seawater from depth to the surface like opening a can of soda???

**Answer:** In both cases there is:

1) An aqueous solution containing a large amount of dissolved CO$_2$

2) Pressure is released, causing the CO$_2$/carbonate reactions to shift to the left (due to decreased Ks)

3) CO$_2$ gas is released and pH increases

\[
\begin{align*}
\text{HCO}_3^- & \leftrightharpoons \text{CO}_3^{2-} + \text{H}^+ \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \leftrightharpoons \text{HCO}_3^- + \text{H}^+ \\
\text{CO}_2(g) & \leftrightharpoons \text{CO}_2(aq)
\end{align*}
\]
CaCO$_3$ Precipitation/Dissolution

A tricky subject when discussing “CO$_2$”
(or, more properly, pCO$_2$)

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \quad \text{(consumption of CO}_3^{2-})$$

Does this reduce the CO$_2$ (pCO$_2$) level of the seawater?

No! Lost CO$_3^{2-}$ 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, CaCO$_3$ precipitation causes a decrease in DIC and TA, but an **increase** in pCO$_2$
Chemical Reactions of Carbonate Species in Seawater

$[\text{Ca}^{2+}]$ is one of the 6 major ions in seawater

To a first order it is considered conservative with salinity ($\sim$10.3 mmol/kg at salinity of 35)

Therefore, $[\text{CO}_3^{2-}]$ primarily controls the saturation state of the waters with respect to aragonite, calcite, magnesian calcite

$K_{sp} = \text{solubility product of a solid}$

$K_{sp}' = \text{apparent solubility product}$

Solubility of CaCO$_3$ increases with decreasing temperature and increasing pressure.

Increasing Solubility from left to right: dolomite < calcite < aragonite < high-magnesian calcite
At the completion of today’s section, students should be able to:

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