Inorganic carbon in the ocean: Basics

Introduction
Equilibrium and Measurement
Biogeochemical Processes and the CO$_2$ system
-- organic matter formation / destruction
-- CaCO$_3$ precipitation / dissolution
Why study carbonate in the ocean? (stating the obvious)

Life on earth is carbon-based!

*pH is a key master variable for many processes - and carbonate equilibria play an important role in determining ocean pH*

*HCO₃⁻ is the 3rd most concentrated anion in the ocean*

*The marine carbon cycle is a key factor in determining the fate of anthropogenic CO₂*

...

*And if the pursuit of knowledge isn’t enough: MC&G students: I guarantee you’ll have a carbonate question on your general exam!*
Carbon cycling in the ocean
(an overview)

Atmosphere

Land

Ocean

HCO₃⁻ → CO₂

CO₂ + H₂O ⇌ H₂CO₃

H₂CO₃* ⇌ H⁺ + HCO₃⁻

HCO₃⁻ ⇌ H⁺ + CO₃²⁻

CO₂ → Corg

Ca²⁺ + CO₃²⁻ → CaCO₃(s)

Corg → CO₂

CaCO₃(s) → Ca²⁺ + CO₃²⁻
Earth surface carbon cycle - Time Scales

Increasing...

Surface ocean ~ atmosphere

Deep ocean: large reservoir!

Largest reservoir: long time scales

Sundquist, 1993
Dissolved Carbonate Equilibria

\[ \Sigma CO_2 = [H_2CO_3^\ast] + [HCO_3^-] + [CO_3^{2-}] \]

\[ K_1 = \frac{[H^+]\left[HCO_3^-\right]}{[H_2CO_3^\ast]} \]

\[ K_2 = \frac{[H^+]\left[CO_3^{2-}\right]}{[HCO_3^-]} \]

\( K_1, K_2 \) known…

-- 3 equations, 5 unknowns…

Specify (or measure) 2 things - \( \Sigma CO_2 \), pH … to get :
pH = - log($H^+$)

Seawater pH

Concentration (moles/kg)
Speciation as $f(pH)$ on log-log plot:
A “Bjerrum” Plot

$K_1 = \frac{[H^+] [HCO_3^-]}{[H_2CO_3^*]}$

$log\{K_1\} = log\{H^+\} + log\left(\frac{[HCO_3^-]}{[H_2CO_3^*]}\right)$
Are $\sum \text{CO}_2$ and pH an ideal pair to measure?

Sometimes, but note:

50 : 50 mix of A and B

$\sum \text{CO}_2(\text{mix}) = 0.5 \times \sum \text{CO}_2(\text{A}) + 0.5 \times \sum \text{CO}_2(\text{B})$

** Not true for pH !! **
How about a quantity that is related to the major ion composition?

The charge balance in seawater:

An apparent excess of positive charge of ~ 2.2 mmol / kg

What are the missing anions?
The **Alkalinity**

The missing anions: $\text{HCO}_3^-$, $\text{CO}_3^{2-}$, $\text{B(OH)}_4^-$

The **conjugate bases** of the weak acids, $\text{H}_2\text{CO}_3$ and $\text{B(OH)}_3$

$$HA \Rightarrow H^+ + A^-$$

**Acid**  
**Conjugate base**

Alkalinity (mol/kg) = the amount of strong acid that must be added to a 1 kg (sea)water sample to make its pH equal to that of the second equivalence point of the dissolved CO$_2$ system, pH = 4.3
Total Alkalinity:
seawater, pH = 8

"Practical Alkalinity":

\[
PA = \left[ HCO_3^- \right] + 2 \left[ CO_3^{2-} \right] + \left[ B(OH)_4^- \right] + \left[ OH^- \right] - \left[ H^+ \right]
\]

\[ \Sigma = PA = 2300 \text{ mmol kg}^{-1} \]

Figure by MIT OCW.
What does the definition mean?
The titration of seawater with a strong acid (HCl)
dpH / dVa

titration endpoint at inflection of pH vs Vₐ curve
At the titration endpoint,

\[ [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [B(OH)_4^-] + [OH^-] \]

That is, the endpoint is the point at which Alk = 0

So: the moles of acid added to reach the endpoint = Alk
Alkalinity: A precise definition
Dickson, 1981; 19994

“The total alkalinity of a natural water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at $25^\circ$ C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample.”

Remember:

(1) predominant species at $pH = 4.5$ does not contribute to Alkalinity

(2) How do you estimate $pK$ for an acid from this diagram?
Alkalinity

So we have:

Carbonate Alkalinity: \( CA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \)

“Water Alkalinity” = \([\text{OH}^-] - [\text{H}^+]\)

“Borate Alkalinity” = \([\text{B(OH)}_4^-]\)

For most applications, can use:

\[
\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B(OH)}_4^-]
\]

But in some applications, you need to add minor contributors, such as

\( \text{NH}_3, \text{PO}_4^{3-}, \text{HPO}_4^{2-}, \text{H}_3\text{SiO}_4^- , \text{HS}^- , \ldots \)

• Remember, when you titrate a seawater sample to the 2nd CO₂ endpoint, The result is “Titration Alkalinity”, which includes all conjugate bases of weak Acids in the sample. The approximation in the Alk expression above is the Neglect of the contribution of minor constituents to the result.
Measurements: Summary

\( \Sigma CO_2 \)

(i) Titration + curve fitting
(ii) Acidify; strip CO\(_2\);
Measure CO\(_2\) by gas chromatography, Coulometry, IR analyzer

± 2 µmol/kg

Calibration: reference seawater (Dickson)

Alkalinity

(i) Titration + curve fitting
(ii) Gran titration

± 2 µmol/kg

Calibration: reference seawater (Dickson)

pH

(i) Electrochemical measurement
(ii) pH-sensitive dyes

±0.002 pH units

Calibration: buffers for seawater
The “more-than-I-ever-wanted-to-know” section: pH scales

(1) Laboratory chemistry: the NBS pH scale

\[ pH = -\log a_{H^+} \]

** Defined relative to low-ionic strength buffers -- abandoned for measurements in seawater

(2) Seawater: An analysis of “[H+]” in seawater yields

\[ [H^+]_{\text{free}} + [HSO_4^-] + [HF] \]

[HF] is small; in order to determine \([H^+]_{\text{free}}\), need to know K for \(HSO_4^-\) dissociation WELL.

“They” have decided it is better to define a new pH scale:

The “Total pH scale”:

\[ H^+_T = \left[ H^+ \right]_{\text{free}} + [HSO_4^-] \]

Or the “seawater pH scale”:

\[ H^+_T = \left[ H^+ \right]_{\text{free}} + [HSO_4^-] + [HF] \]
pH scales, cont.

So that:

1. pH measurements are reported on the pH\textsubscript{T} scale
2. equilibrium constants are reported on the pH\textsubscript{T} scale

Can convert between the scales with $K_{HSO4}$ and $K_{HF}$

**The difference between pH\textsubscript{sws} and pH\textsubscript{T} is ~ 0.01 unit ~ 2\% at pH 8
The difference between pH\textsubscript{NBS} and pH\textsubscript{T} is ~ 0.1 unit ~ 20\% at pH 8

The precision of good pH measurements is ~ 0.002 pH units
On equilibrium constants for calculations in seawater

Consider the reaction: \[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]

In an “ideal” solution: \[ K = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \]

In an “ideal” solution, all concentrations \( \rightarrow 0 \), so there are no ion-ion or ion-solvent interactions.

In a real solution, these interactions are important, so…
On equilibrium constants for calculations in seawater

Consider the reaction:

\[ HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \]

In an “ideal” solution:

\[ K = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \]

In an “ideal” solution, all concentrations \( \rightarrow 0 \), so there are no ion-ion or ion-solvent interactions.

In a real solution:

\[ K = \frac{\gamma_{H^+}\gamma_{CO_3^{2-}}[H^+][CO_3^{2-}]}{\gamma_{HCO_3^-}[HCO_3^-]} \]

The \( \gamma \) are “activity coefficients”, and are generally <1 for ions in solution because of electrostatic interactions between ions and between and ions and solvent.

In addition, some ions (esp. \( CO_3^{2-} \)) form complexes with other ions in seawater.
Equilibrium constants for calculations in seawater

For a solution with the ionic strength of seawater \( I = \sum c_i z_i^2 \sim 0.7 \), it is difficult to calculate the \( \gamma \) values. Therefore:

“Constant ionic medium” equilibrium constants are used. They are:

-- measured in solutions with the same proportions of major ions as seawater
-- measured as functions of \( T \) and \( S \)
-- pressure dependence is calculated from thermodynamic data

So:

\[
K' = \frac{[H^+]_T [CO_3^{2-}]_T}{[HCO_3^-]_T}
\]

The “\( T \)” denote “total” concentrations, including complexes…

And remember, for \( H^+ \), the “\( T \)” denotes the “total” pH scale.

These “seawater” constants are available from the literature as \( f(T,S,P) \)
Working with the carbonate system in seawater

\[ \Sigma CO_2 = \left[ H_2CO_3^* \right] + \left[ HCO^- \right] + \left[ CO^-_3 \right] \]

\[ Alk = \left[ HCO^-_3 \right] + 2\left[ CO^-_3 \right] + \left[ B(OH)^-_4 \right] + \left[ OH^- \right] - \left[ H^+ \right] \pm \text{minor components} \]

\[ TB = \left[ B(OH)_3 \right] + \left[ B(OH)^-_4 \right] = \text{constant} \times \text{Salinity} \]

\[ K_1 = \frac{\left[ H^+ \right] \left[ HCO^-_3 \right]}{\left[ H_2CO_3^* \right]} \quad K_2 = \frac{\left[ H^+ \right] \left[ CO^-_3 \right]}{\left[ HCO^-_3 \right]} \]

\[ K_B = \frac{\left[ H^+ \right] \left[ B(OH)^-_4 \right]}{\left[ B(OH)_3 \right]} \quad K_W = \frac{\left[ H^+ \right] \left[ OH^- \right]}{\left[ H_2O \right]} \]

Measure \( \Sigma CO_2, \text{Alk, S} \implies 7 \text{equations in 7 unknowns} \)

\[ \implies \text{you can solve for speciation!} \]
Useful approximations for back-of-the-envelope calculations

At seawater pH,

\[ \Sigma \text{CO}_2 \sim [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]

\[ \text{Alk} \sim [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] \]

And

\[ [\text{CO}_3^{2-}] \sim \text{Alk} - \Sigma \text{CO}_2 \]
The effect of biogeochemical processes on $\Sigma CO_2$ and Alk

(1) The incorporation of $CO_2$ into organic matter (i.e., production of o.m.)

$CO_2 \rightarrow "C_{org}" + O_2$

$\Delta \Sigma CO_2 = -1$
$\Delta Alk = 0$

... and a small (usually negligible) increase in Alk due to $NO_3^-$ assimilation, $\Delta Alk = (16/106) *$ mol $C_{org}$ formed

(2) The precipitation of $CaCO_3$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

$\Delta \Sigma CO_2 = -1$
$\Delta Alk = -2$

How do these processes affect the ability of the ocean to take up $CO_2$ from the atmosphere?

Taking into account Henry’s law relating $[CO_2]$ in the water to the $PCO_2$ in equilibrium with the water,

$[CO_2] = K_H PCO_2$

System approaches equilibrium after Perturbation: lower ocean $[CO_2]$ --> ocean absorbs $CO_2$
Contours of $[CO_2]$ vs. Alk and $\sum CO_2$

- o.m. formation: decrease $[CO_2]$
- $CaCO_3$ pptn: increase $[CO_2]$
Biogeochemical processes and the carbonate system

How do decomposition and dissolution processes affect the carbonate system?

(3) Organic matter dissolution... reverses (1),
\[ C_{org} + O_2 \rightarrow CO_2 + \ldots \]
\[ \Delta \Sigma CO_2 = +1 \]
\[ \Delta \text{Alk} = 0 \]
(and, as before, there's a small drop in Alk due to NH$_3$ oxidation to NO$_3^-$)

(4) CaCO$_3$ dissolution... reverses (2),
\[ CaCO3 \rightarrow Ca^{2+} + CO_3^{2-} \]
\[ \Delta \Sigma CO_2 = +1 \]
\[ \Delta \text{Alk} = +2 \]

How do these processes affect the [CO$_3^{2-}$] of seawater as it “ages” during its transit through the deep sea?
Question: what can you use this contour plot for if you have actual data?
Using data and theory to calculate relative rates of organic matter oxidation and carbonate dissolution
see Broecker and Peng, Tracers in the Sea

\[
\frac{\Delta A L K}{\Delta \Sigma CO_2} = \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{15}{105} = 0.93
\]

\[
\frac{\Delta A L K}{\Delta \Sigma CO_2} = \frac{1}{5} \cdot \frac{4}{5} \cdot \frac{15}{105} = 0.29
\]

Figure by MIT OCW.
And…

We’ve shown how biogeochemical processes affect $\Sigma CO_2$ and Alk in the ocean…
We’ve started to show how distributions of $\Sigma CO_2$ and Alk can be used to learn about biogeochemical processes...

We’ve not discussed the biological and chemical processes that control formation and decomposition of organic matter
formation and dissolution of CaCO$_3$

Those discussions will follow…