Carbon Dioxide, Alkalinity and pH

OCN 623 – Chemical Oceanography

21 February 2017

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")

Student Learning Outcomes (SLOs)

At the completion of today's section, students should be able to:

1. Identify the chemical species involved in the marine CO_2/carbonate system
2. Explain CO_2 dissolution in seawater and subsequent reactions
3. Explain the concepts of pH, alkalinity, and dissolved inorganic carbon, and write the equations defining these quantities
4. Calculate the concentrations of components of the marine CO_2/carbonate system
5. Explain the relationship between carbonate dissolution/precipitation and pCO_2.

Outline

1. CO_2 speciation
2. Dissolved inorganic carbon (DIC)
3. Partial pressure of CO_2 (P_{CO2})
4. pH
5. Alkalinity
6. Calculation of composition of marine CO_2 system
7. Oceanographic applications

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

CO_2 Speciation

- CO_2(g) has many possible transformations upon dissolution in H_2O
- Major dissolved forms:
  - **$CO_{2(aq)}$ (*aqueous carbon dioxide* – a dissolved gas)**
  - **H_2CO_3 (*carbonic acid* – trace amount)**
  - **HCO_3^- (*bicarbonate ion*)**
  - **CO_3^{-2} (*carbonate ion*)**
- Species interconvert readily
- Perturbations to one part of CO_2 system leads to redistribution of species
- Reactions not always intuitive!

Seawater pH

- **pH = - log {H^+}** {H^+} = *Hydrogen ion activity*
- The pH of seawater varies only between about 7.5 and 8.4 (*i.e.*, slightly alkaline)

Equations for CO_2 Speciation

The equilibrium of gaseous and aqueous CO_2:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

Subsequent hydration and dissociation reactions:

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

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

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

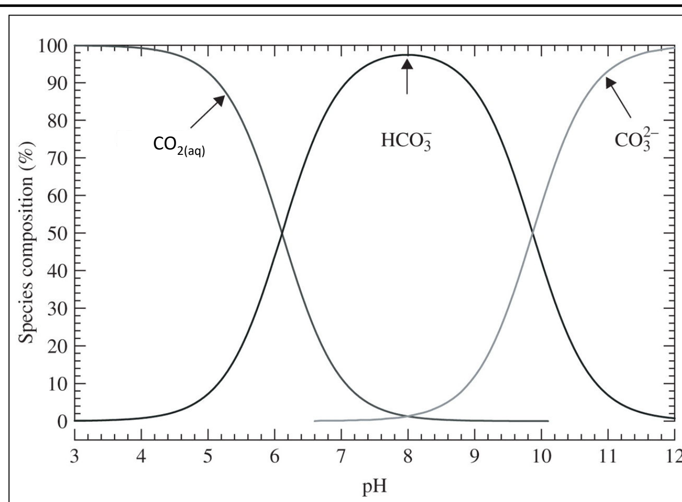
$$K_2^* = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]}$$

Hint: When you add a CO_2 species to the system, follow the H^+. Thus, the following is a reasonable approximation when pH is between 7.5 and 8.5:

$$CO_{2(aq)} + CO_3^{-2} + H_2O \leftrightarrow 2HCO_3^-$$

Asterisk (*) indicates a "stoichiometric" constant

Distribution of CO_2 Species at Different pH Values



Seawater values shown --- freshwater curves are shifted left

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

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Group Task

How does seawater pH change when atmospheric CO_2 is added to the ocean?

What are the reactions??

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What are the reactions??

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

$$CO_{2(g)} \rightarrow CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O \rightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftarrow CO_3^{-2} + H^+$$

⇐ The limited amount of CO_3^{2-} available means that not all of the H^+ produced by the middle reaction can be consumed

Effects of Pressure on Carbonate Speciation

	1 atm	1000 atm
K_1*	$10^{-5.89}$	$10^{-5.55}$
K_2*	$10^{-9.13}$	$10^{-8.93}$

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$

$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$ ← $K_1* = \frac{\{H^+\}[HCO_3^-]}{[CO_2]}$

$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$ ← $K_2* = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]}$

As you raise a sample from depth:

- Ks' decrease
- Reactions shift to left
- pH increases
- $CO_{2(g)}$ releases

Group Task

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

What exactly is happening?

Hint: What happens to the dissolved CO_2?

Group Task

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

$$HCO_3^- \leftarrow CO_3^{-2} + H^+$$

$$CO_{2(aq)} + H_2O \leftarrow HCO_3^- + H^+$$

$$CO_{2(g)} \leftarrow CO_{2(aq)}$$

Dissolved Inorganic Carbon

(DIC, Total CO_2, ΣCO_2)

$$DIC \equiv [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}]$$

At seawater pH, >99% of CO_2 species are HCO_3^- and CO_3^{-2}, so we can simplify:

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

Partial Pressure of CO_2

(P_{CO2})

In the atmosphere:

P_{CO2} ≡ partial pressure of CO_2 in the atm,

out of a total pressure of 1 atm (at sea level)

Measurement:

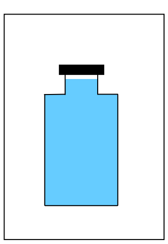
Determine fraction of atm that is CO_2

$P_{CO2} = P_{total} \cdot \text{fraction}_{CO2}$

In water:

P_{CO2} ≡ partial pressure of CO_2 in a gas when in equilibrium with the water

(Henry's Law: $P_{CO2,\ gas} = K \cdot [CO_2]_{water}$)



Measurement:

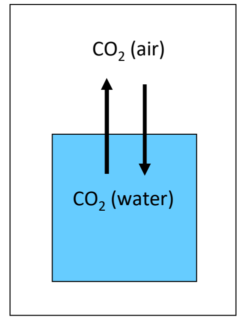
Equilibrate water with a small gas headspace

Determine fraction of headspace gas that is CO_2

$P_{CO2} = P_{total} \cdot \text{fraction}_{CO2}$

Uses of P_{CO2}

- A common unit for **comparing CO_2 concs in water and the atmosphere**
- Evaluation of the **direction of gas fluxes**



- $P_{CO2(air)} > P_{CO2(water)}$ Flux of CO_2 from air to water
- $P_{CO2(air)} = P_{CO2(water)}$ No net flux of CO_2 (equilibrium)
- $P_{CO2(air)} < P_{CO2(water)}$ Flux of CO_2 from water to air

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)

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

- TA usually reported in meq/L or meq/kg (an "equivalent" is a mole of charge)

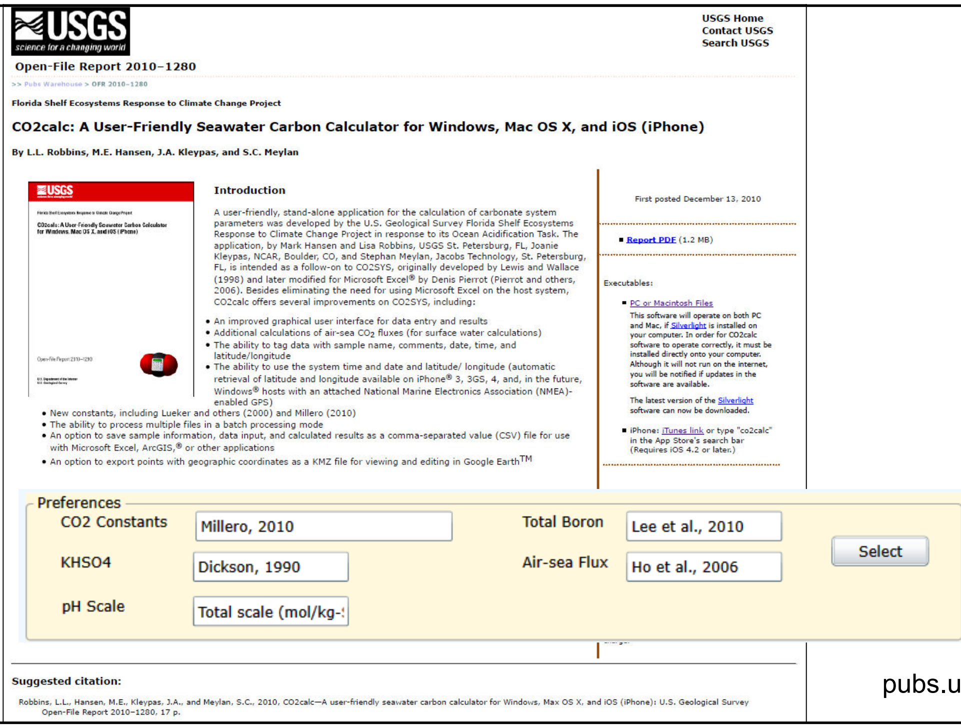
Carbonate Alkalinity (CA)

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

- Typically, HCO_3^- and CO_3^{-2} are present at ~1000x conc of other proton acceptors
- Hence: CA nearly equals TA

CO_2 System Calculations

- There are four CO_2 properties that can be measured:
  DIC, P_{CO2}, pH, and alkalinity
- Any two of these properties can be used to determine the composition of the CO_2 system in water (*i.e.,* concs of $CO_{2(aq)}$, HCO_3^-, and CO_3^{-2})
- These calculations are simple for some pairs of data, but are difficult for others
- Applications/apps are available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Florida Shelf Ecosystems Response to Climate Change Project

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 CO_2 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, ArcGIS,® or other applications
- An option to export points with geographic coordinates as a KMZ file for viewing and editing in Google Earth™

First posted December 13, 2010

- Report PDF (1.2 MB)

Executables:

- PC or Macintosh Files
  This software will operate on both PC and Mac, if Silverlight is installed on your computer. In order for CO2calc software to operate correctly, it must be installed directly onto your computer. Although it will not run on the internet, you will be notified if updates in the software are available.
  The latest version of the Silverlight software can now be downloaded.
- iPhone: iTunes link or type "co2calc" in the App Store's search bar (Requires iOS 4.2 or later.)

Suggested citation:

Robbins, L.L., Hansen, M.E., Kleypas, J.A., and Meylan, S.C., 2010, CO2calc—A user-friendly seawater carbon calculator for Windows, Max OS X, and iOS (iPhone): U.S. Geological Survey Open-File Report 2010–1280, 17 p.

pubs.usgs.gov/of/2010/1280/

Group Task

CO_2/Carbonate System Calculation

Assume these conditions: S = 30 g/kg T=20°C Depth = 0 m
DIC = 2200 µmol/kg

• How do the concentrations of CO_2(aq), HCO_3^-, and CO_3^{2-} change if pH changes from 8.0 to 7.7?

• How can this be explained using the CO_2/carbonate reactions?

Group Task

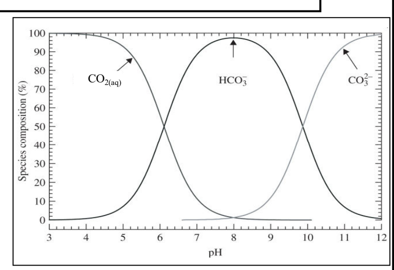
CO_2/Carbonate System Calculation

Assume these conditions: S = 30 g/kg T=20°C Depth = 0 m DIC = 2200 µmol/kg

• How do the concentrations of CO_2(aq), HCO_3^-, and CO_3^{2-} change if pH changes from 8.0 to 7.7?

• How can this be explained using the CO_2/carbonate reactions?

	pH 8.0	*pH 7.7*
$CO_{2(aq)}$, µmol/kg	16	34
HCO_3^-, µmol/kg	2020	2082
CO_3^{2-}, µmol/kg	164	85



$HCO_3^- \leftarrow CO_3^{-2} + H^+$

$CO_{2(aq)} + H_2O \leftarrow HCO_3^- + H^+$

$CaCO_3$ Precipitation/Dissolution

A tricky subject when discussing "CO_2"
(or, more properly, P_{CO2})

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (consumption of CO_3^{2-})

Does this reduce the CO_2 (P_{CO2}) level of the seawater?

No! Lost CO_3^{2-} will be replaced:

$HCO_3^- \rightarrow CO_3^{2-} + H^+$

But this H^+ release causes:

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$

$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$

$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$

Thus, $CaCO_3$ precipitation causes a decrease in DIC, but an <u>increase</u> in P_{CO2}

Hint: when pH is between 7.5 and 8.5:

$CO_{2(aq)} + CO_3^{-2} + H_2O \leftrightarrow 2HCO_3^-$

What processes affect Alk and ΣCO_2?

- CO_2 exchange between the atmosphere and surface seawater changes ΣCO_2, but doesn't affect Alk
- Photosynthesis / respiration also changes ΣCO_2, but doesn't affect Alk (loss of HCO_3^- is balanced by loss of H^+)

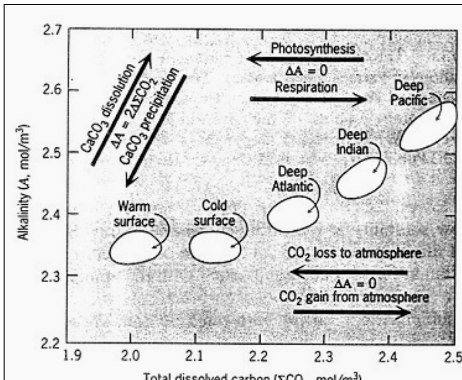


FIGURE 15.7. Relationship between the total dissolved inorganic carbon content and the alkalinity of waters from various parts of the ocean. The arrows indicate the effects of various processes occurring within the sea.

- $CaCO_3$ dissolution / precipitation changes both ΣCO_2 and Alk ⟶

Calcification

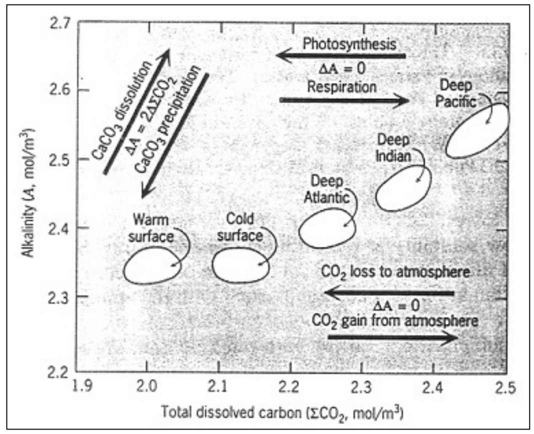
Effects on Alk-pH-ΣCO_2

- Surface-ocean plankton remove CO_3^{2-} and Ca^{2+} from seawater to form $CaCO_3$ tests (*calcification*):

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

- Calcification alters both Alk and ΣCO_2, but not pH

- Amount of Alk decrease is 2x the effect on ΣCO_2 because of double negative charge of CO_3^{2-}



$CO_{2(aq)} + CO_3^{-2} + H_2O \leftrightarrow 2HCO_3^-$

Homework

Due: Tues, February 28, 2017

(Put in my Inbox in MSB 205)

Consider a surface seawater with these characteristics (Be careful of units!):

S = 35 g/kg ΣCO_2 = 2.2 mM Total alkalinity = 2.45 meq L^{-1} T = 25°C

1) What is the P_{CO2} of this seawater?

2) Is this seawater under- or super-saturated with respect to atmospheric CO_2? What is the basis for your answer? What direction is the air-sea flux?

3) How do the results change if ΣCO_2 = 2.3 mM? Why?

State All Assumptions! Explain how you performed calculations!

Carbon Dioxide – Oceans and Atmosphere

Air-Sea Gas Exchange

OCN 623 – Chemical Oceanography

23 February 2017

Reading: Libes, Chapter 15, pp. 389 – 394

Chapter 6 – pp. 158 -168