



Lectures 19: Alkalinity and DIC

1. The carbonate system
2. Alkalinity
 - A. Examples
3. Carbonate Saturation

We acknowledge and respect the lək̓ʷəŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.



Practice Problem: relative abundance of carbon species in seawater

Q1: Determine the relative abundances of carbon species in the ocean with the following measurements:

- pH: 8.1
- DIC: 2.1 mmol/kg
- $k_1 = e^{-13.4847}$
- $k_2 = e^{-20.5504}$



An exercise: relative abundance of carbon species in seawater

Start w/ DIC

$$\sum \text{CO}_2 = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$$

DIC →

$$\sum \text{CO}_2 = \frac{[\text{HCO}_3^-] K_2}{[\text{H}^+]} + [\text{HCO}_3^-] + \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1}$$

replace

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]}$$
$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

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

Solve for $[\text{HCO}_3^-]$

$$\text{H}_2\text{CO}_3 \approx 0.5\% \text{ DIC}$$

$$\text{HCO}_3^- \approx 86.5\% \text{ DIC}$$

$$\text{CO}_3^{2-} \approx 13\% \text{ DIC}$$



Practice Problem: relative abundance of carbon species in seawater (isotopic composition)

Q2: Using the ratios from the previous question, determine the isotopic composition of each carbon bearing species assuming that:

- $\delta^{13}\text{C}$ of H_2CO_3 is 10 per mil less than HCO_3^-
- $\delta^{13}\text{C}$ of CO_3^{2-} is 4 per mil less than HCO_3^-
- $\delta^{13}\text{C}$ of DIC is 7 per mil



Relative abundance of carbon species in seawater (isotopic composition)

Set up:

$$\delta^{13}\text{C of } \text{HCO}_3^- = X$$

$$\delta^{13}\text{C of } \text{H}_2\text{CO}_3 = X - 10$$

$$\delta^{13}\text{C of } \text{CO}_3^{2-} = X - 4$$

$$\delta^{13}\text{C of DIC} = 7\text{‰}$$

From Q1:

$$\text{H}_2\text{CO}_3 \approx 0.5\% \text{ DIC}$$

$$\text{HCO}_3^- \approx 86.5\% \text{ DIC}$$

$$\text{CO}_3^{2-} \approx 13\% \text{ DIC}$$

$$100\% \cdot 7\text{‰} = 86.5\% (X) + 13\% (X - 4) + 0.5\% (X - 10)$$

Solve for X ...



An exercise: relative abundance of carbon species in seawater

recall:

$$p\text{CO}_2 \cdot K_0 = [\text{CO}_2(\text{aq})]$$

$$p\text{CO}_2 = \frac{[\text{CO}_2(\text{aq})]}{K_0} \quad \leftarrow \text{replace w/ eq 1}$$

$$p\text{CO}_2 = \frac{1}{K_0} \cdot \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1} \quad \leftarrow \text{replace w/ eq 2}$$

$$p\text{CO}_2 = \frac{1}{K_0} \cdot \frac{[\text{HCO}_3^-]}{K_1} \cdot \frac{K_2[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

$$p\text{CO}_2 = \frac{K_2}{K_0 K_1} \cdot \frac{2[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]}$$

$$p\text{CO}_2 = \frac{K_2}{K_0 K_1} \cdot \frac{2(\text{DIC} - \text{CA})^2}{\text{CA} - \text{DIC}}$$

only constant at fixed T, P, salinity

$$\text{DIC} = \cancel{[\text{CO}_2(\text{aq})]} + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad \text{CA} \approx \text{TA}$$

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

$$\text{DIC} = a + b$$

$$\text{CA} = a + 2b$$

$$\text{DIC} - b = a$$

$$\text{CA} = \text{DIC} - b + 2b$$

$$\text{CA} = \text{DIC} + b$$

$$b = \text{CA} - \text{DIC}$$

$$[\text{CO}_3^{2-}] = \text{CA} - \text{DIC}$$

$$2\text{DIC} - \text{CA} = [\text{HCO}_3^-]$$

↑ calculation from previous slide



CO₂, Alkalinity, and DIC

recall:

$$pCO_2 \approx \frac{K_2}{K_0 K_1} \cdot \frac{(Z \text{ DIC} - \text{ALK})}{\text{ALK} - \text{DIC}}$$

in SW $\approx 2100 \frac{\mu\text{mol}}{\text{kg}}$ \leftarrow $2300 \frac{\mu\text{mol}}{\text{kg}}$

$$[HCO_3^-] \approx Z \text{ DIC} - \text{ALK}$$

$$[CO_3^{2-}] \approx \text{ALK} - \text{DIC}$$

