Lectures 18: CO2 in seawater

1. The carbonate system
2. Alkalinity
    A. Examples

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.

The Carbonate System (at equilibrium)

$CO_2(g) \xleftrightarrow[K_0]{} CO_2(a)$

$$K_0 = \frac{CO_2(a)}{CO_2(g)}$$

(1) $CO_2(a) + H_2O \xleftrightarrow[K_1]{} H^+ + HCO_3^-$

$$K_1 = \frac{\underset{①}{[H^+]}\,\underset{②}{[HCO_3^-]}}{\underset{③}{[CO_2]}\,\cancel{[H_2O]} \to 1}$$

recall:
$pH = -\log_{10}[H^+]$
$K_1, K_2 = f(P, T, \text{salinity})$

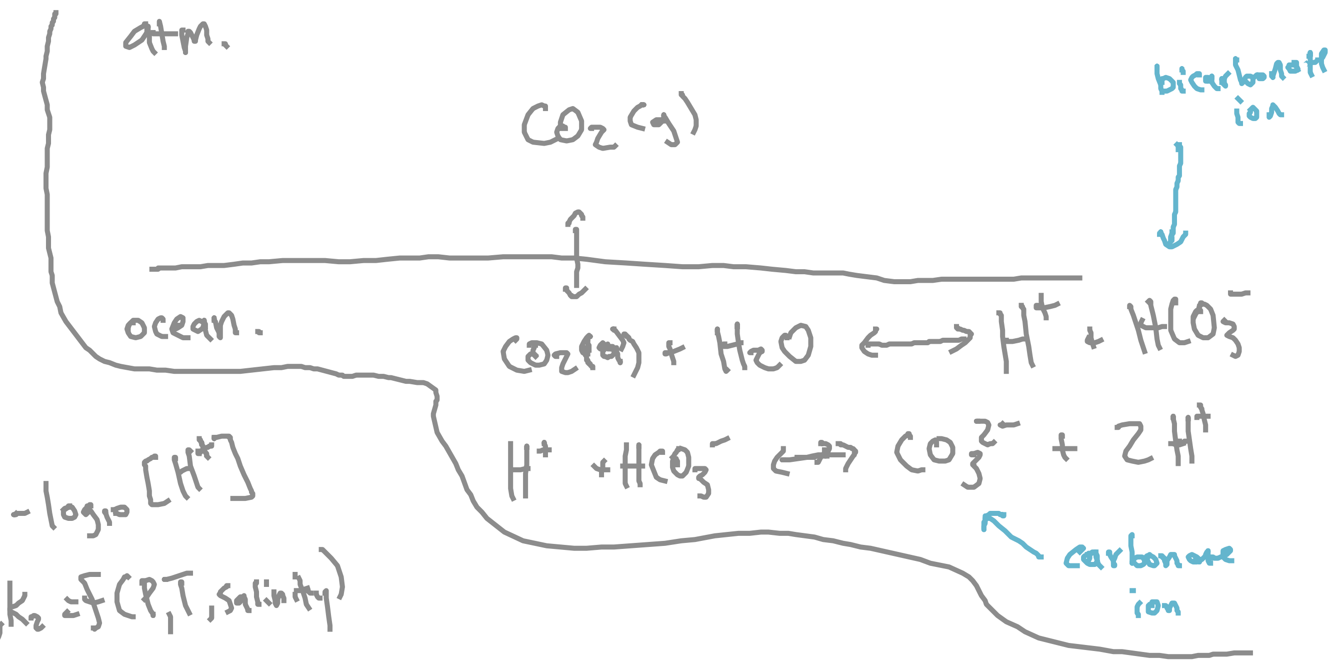
6 unknowns, 4 eqs.

(2) $HCO_3^- + H^+ \xleftrightarrow[K_2]{} CO_3^{2-} + 2H^+$

$$K_2 = \frac{④[CO_3^{2-}][H^+]^{\cancel{2}}}{[HCO_3^-]\cancel{[H^+]}} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}$$

(3) Dissolved inorganic carbon / D.I.C. $= \underset{⑤}{\sum CO_2} = [CO_3^{2-}] + [HCO_3^-] + [CO_2(a)]$

(4) Carbonate Alkalinity $\approx$ $\underset{⑥}{\text{Total Alkalinity}}$ $= [HCO_3^-] + 2[CO_3^{2-}]$



Brief Total Alkalinity Intro

Total Alkalinity, TA $= [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]$

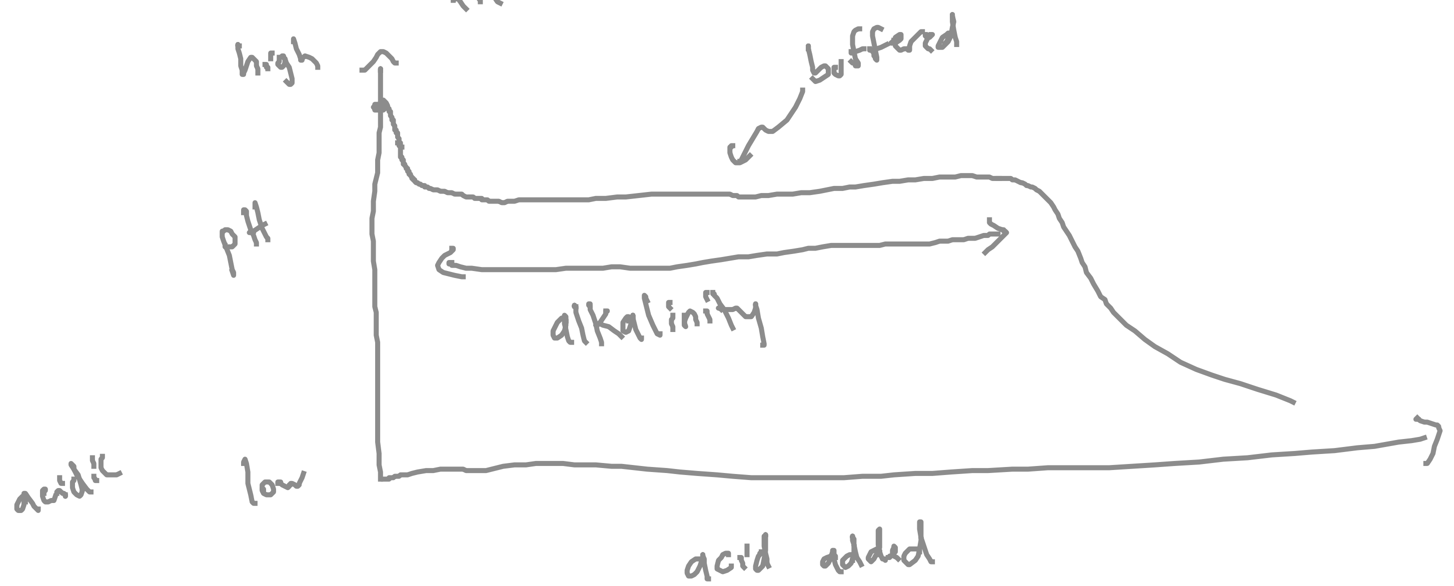
$+$ minor components $- [H^+]$

conservative:
not a function of
T, pH, P

TA $=$ charge from all dissolved "conservative" anions $-$ charge from all dissolved "conservative" cations

$[Cl^-]$ $[Na^+]$

recall titrations



An exercise: relative abundance of carbon species in seawater

$CA \simeq TA$

Four eqs., six unknowns $\longrightarrow$ measure two things to fully describe the system

unknowns: $[H^+][CO_3^{2-}][HCO_3^-][CO_{2(aq)}][DIC][TA]$

determine the relative abundances of carbon species in the ocean w/ the following measurements: pH = 8.1, DIC = 2.1 mol/kg

$K_1 = e^{-13.4847}$

$K_2 = e^{-20.5504}$

hint: Start w/ DIC eq. and replace $[CO_2]$ and $[CO_3^{2-}]$

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

$[CO_{2(aq)}] \approx$

$[HCO_3^{2-}] \approx$

$[CO_3^{2-}] \approx$

An exercise: relative abundance of carbon species in seawater

CA ≃ TA

Four eqs., six unknowns ⟶ measure two things to fully describe the system

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determine the relative abundances of carbon species in the ocean w/ the following measurements: $pH = 8.1$, $DIC = 2.1\ mol/kg$

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hint: Start w/ DIC eq. and replace $[CO_2]$ and $[CO_3^{2-}]$

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

$[CO_{2(aq)}] \simeq 0.5\%$

$[HCO_3^{-}] \simeq 86.5\%$

$[CO_3^{2-}] \simeq 13\%$

$$DIC = \frac{[HCO_3^-][H^+]}{K_1} + [HCO_3^-] + \frac{K_2[HCO_3^-]}{[H^+]}$$

$a = [HCO_3^-]$

$$DIC = a\left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right) = 1.82\ mol/kg$$

An exercise: relative abundance of carbon species in seawater

recall:

$$pCO_2 \cdot K_0 = [CO_2(aq)]$$

$$pCO_2 = \frac{[CO_2(aq)]}{K_0}$$ replace w/ eq 1

$$pCO_2 = \frac{1}{K_0} \cdot \frac{[HCO_3^-][H^+]}{K_1}$$ replace w/ eq 2

$$pCO_2 = \frac{1}{K_0} \frac{[HCO_3^-]}{K_1} \cdot \frac{K_2[HCO_3^-]}{[CO_3^{2-}]}$$

$$pCO_2 = \frac{K_2}{K_0 K_1} \cdot \frac{2[HCO_3^-]^2}{[CO_3^{2-}]}$$

$$pCO_2 = \frac{K_2}{K_0 K_1} \cdot \frac{(2DIC - CA)^2}{CA - DIC}$$

only constant at fixed T, P, salinity

$$DIC = \cancel{[CO_2(aq)]}^{\to 0} + \underbrace{[HCO_3^-]}_{a} + \underbrace{[CO_3^{2-}]}_{b}$$

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

$$CA \approx TA$$

$$DIC = a + b$$

$$CA = a + 2b$$

$$DIC - b = a$$

$$CA = DIC - b + 2b$$

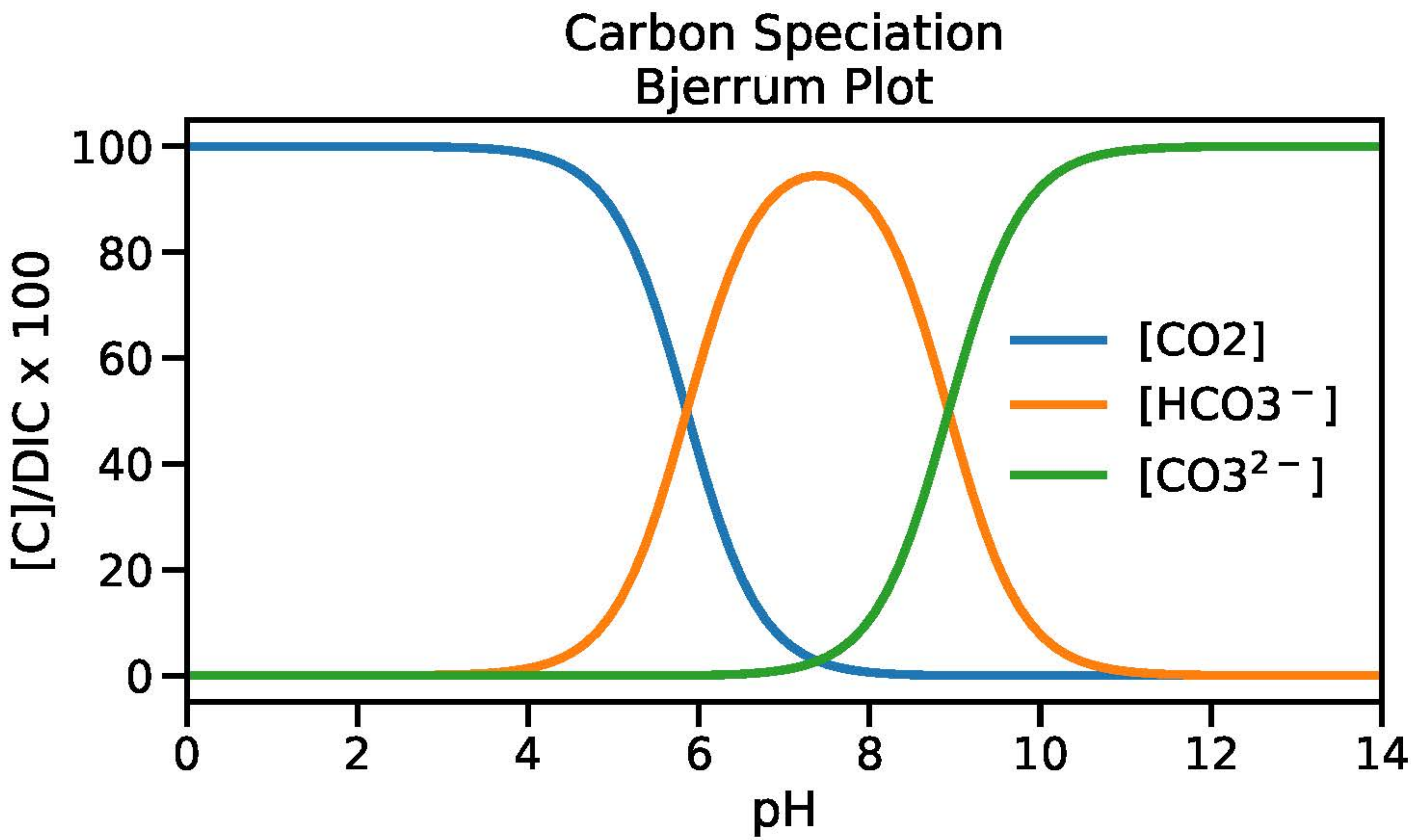
$$CA = DIC + b$$

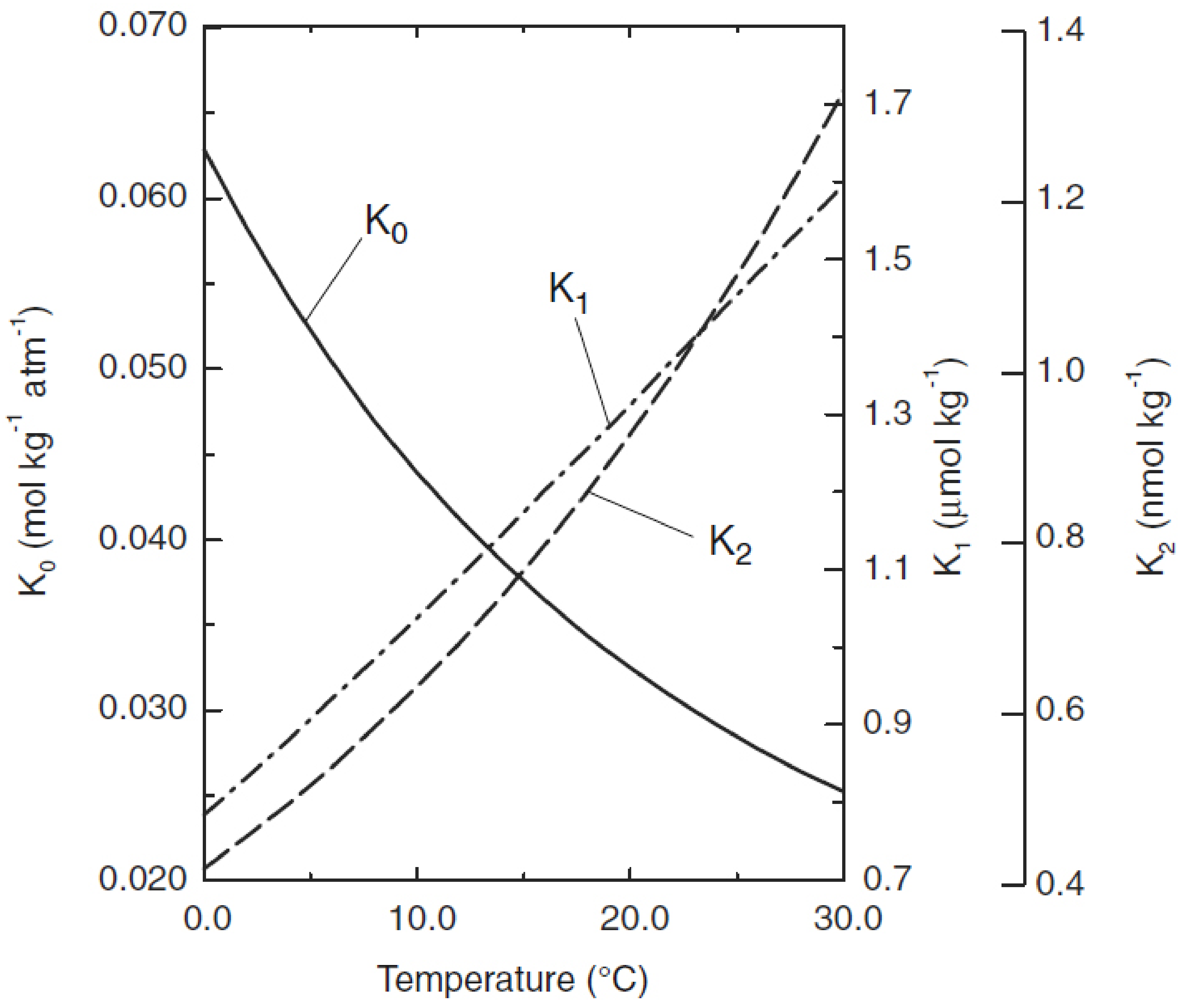
$$b = CA - DIC$$

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

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

calculation from previous slide


Carbon Speciation
Bjerrum Plot
[C]/DIC x 100
100
80
60
40
20
0
0
2
4
6
8
10
12
14
pH
[CO2]
[HCO3$^-$]
[CO3^{2-}]



0.070
0.060
0.050
0.040
0.030
0.020
K_0 (mol kg^{-1} atm^{-1})
0.0
10.0
20.0
30.0
Temperature (°C)
K_0
K_1
K_2
1.7
1.5
1.3
1.1
0.9
0.7
K_1 (µmol kg^{-1})
1.4
1.2
1.0
0.8
0.6
0.4
K_2 (nmol kg^{-1})

$$\frac{K_2}{K_0 K_1} \propto pCO_2 \approx \frac{1}{K_0}$$

- Assume fixed ALK and DIC. How does pCO_2 change when T increases?

$pCO_2 \nearrow$ as $T \nearrow$