



Lectures 19: Alkalinity and DIC

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

We acknowledge and respect the *lək'ʷəŋən* peoples on whose traditional territory the university stands and the Songhees, Esquimalt and *WSÁNEĆ* peoples whose historical relationships with the land continue to this day.



An exercise: relative abundance of carbon species in seawater

recall:

$$pCO_2 \cdot K_0 = [CO_2^{ca}]$$

$$pCO_2 = \frac{[CO_2^{ca}]}{K_0}$$

$$pCO_2 = \frac{1}{K_0} \cdot \frac{[HCO_3^-][H^+]}{K_1}$$

replace w/ eq1
replace w/ eq2

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

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

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

only constant at fixed $T, P, \text{ salinity}$

$$\begin{aligned} DIC &= [CO_2^{eq}] + [HCO_3^-] + [CO_3^{2-}] \\ CA &= [HCO_3^-] + 2[CO_3^{2-}] \end{aligned}$$

$CA \approx TA$

$$\begin{aligned} DIC &= a + b \\ CA &= a + 2b \end{aligned}$$

$$DIC - b = a$$

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

$$CA = DIC + b$$

$$b = CA - DIC$$

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

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

↑
calculation from previous slide



CO₂, Alkalinity, and DIC

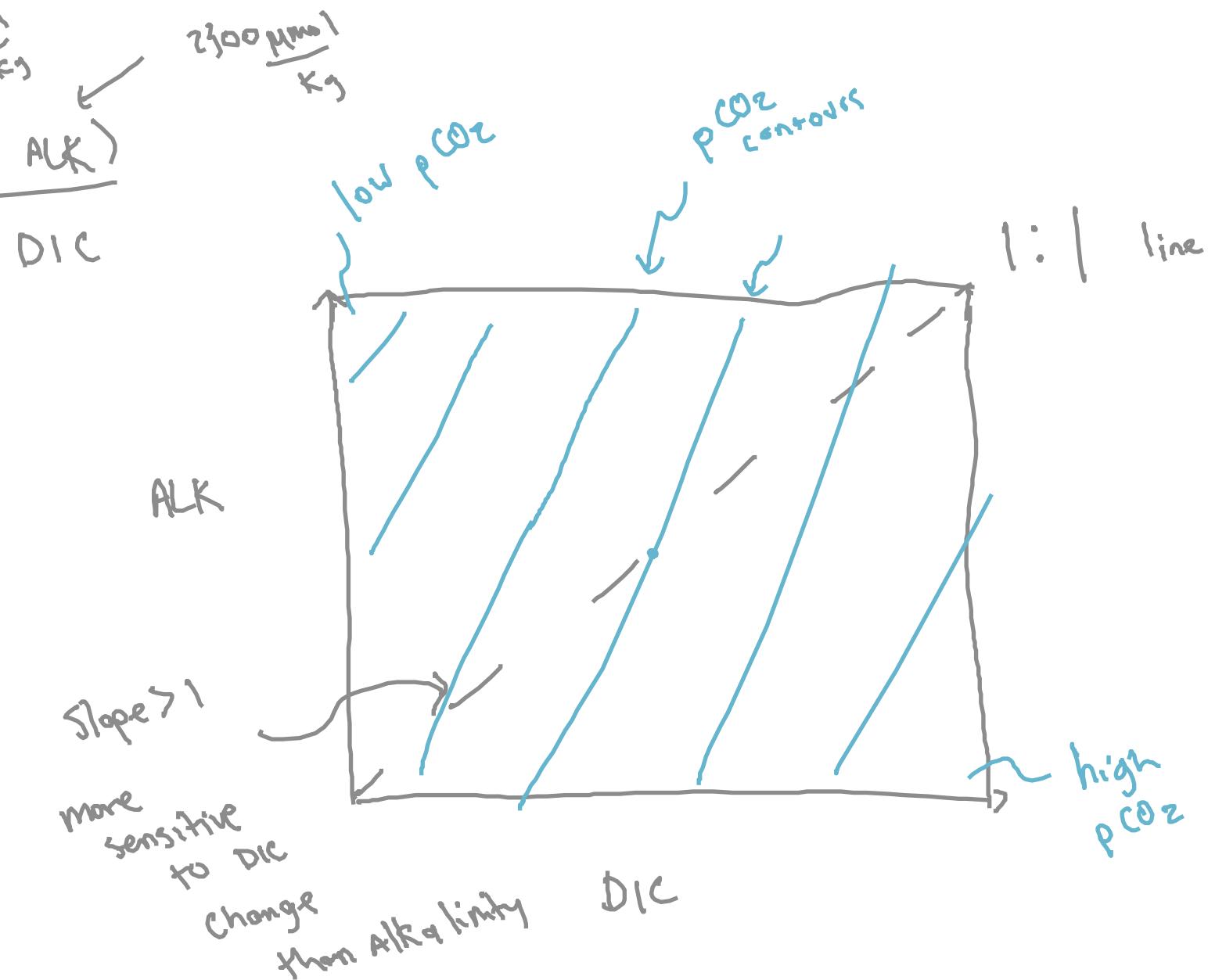
recall:

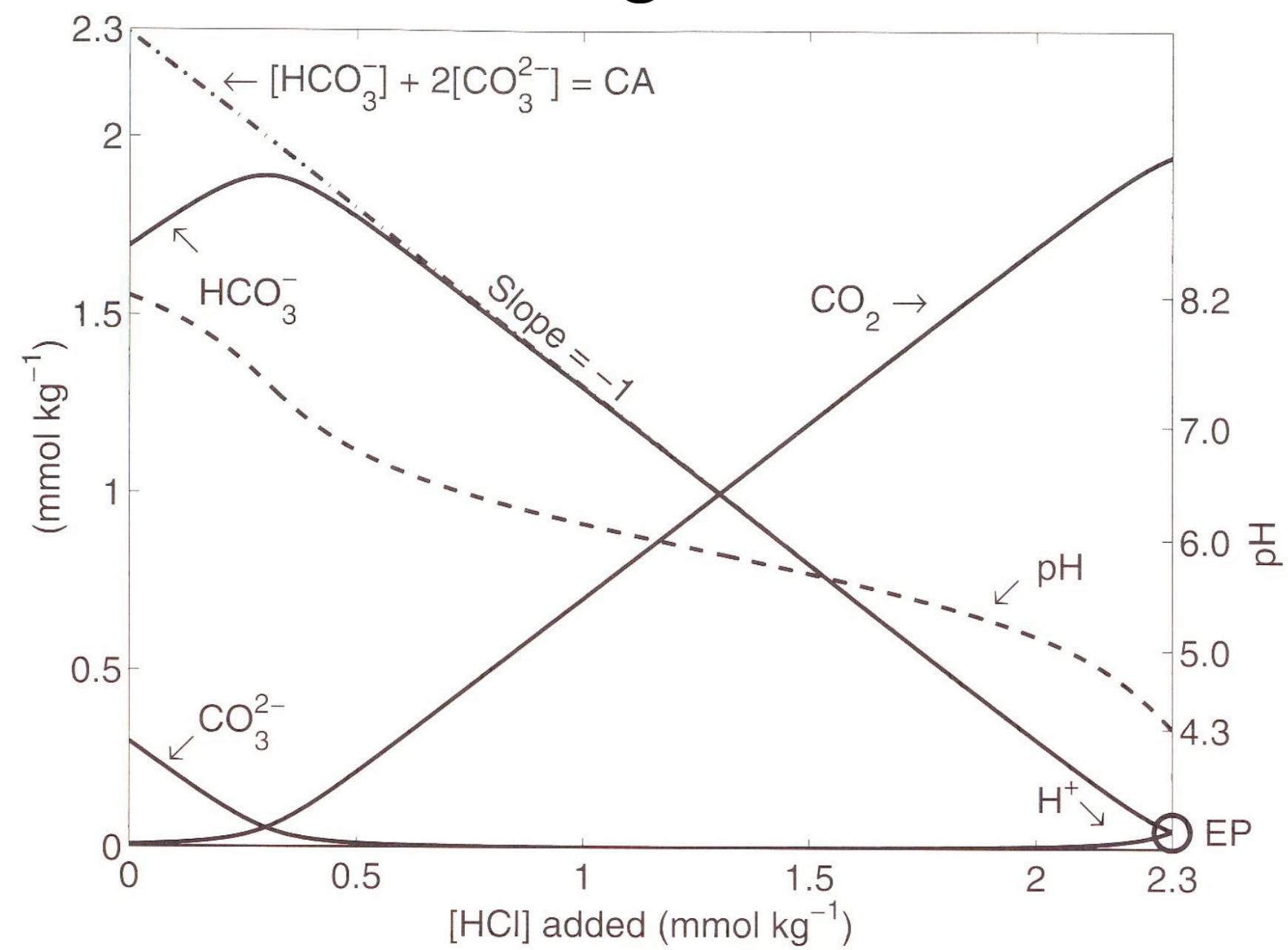
$$p\text{CO}_2 \approx \frac{\kappa_2}{\kappa_1} \cdot \frac{(2\text{DIC} - \text{ALK})}{\text{ALK} - \text{DIC}}$$

in SW
↓ 100 μmol/kg
↓ 200 μmol/kg

$$[\text{HCO}_3^-] \approx 2\text{DIC} - \text{ALK}$$

$$[\text{CO}_3^{2-}] \approx \text{ALK} - \text{DIC}$$

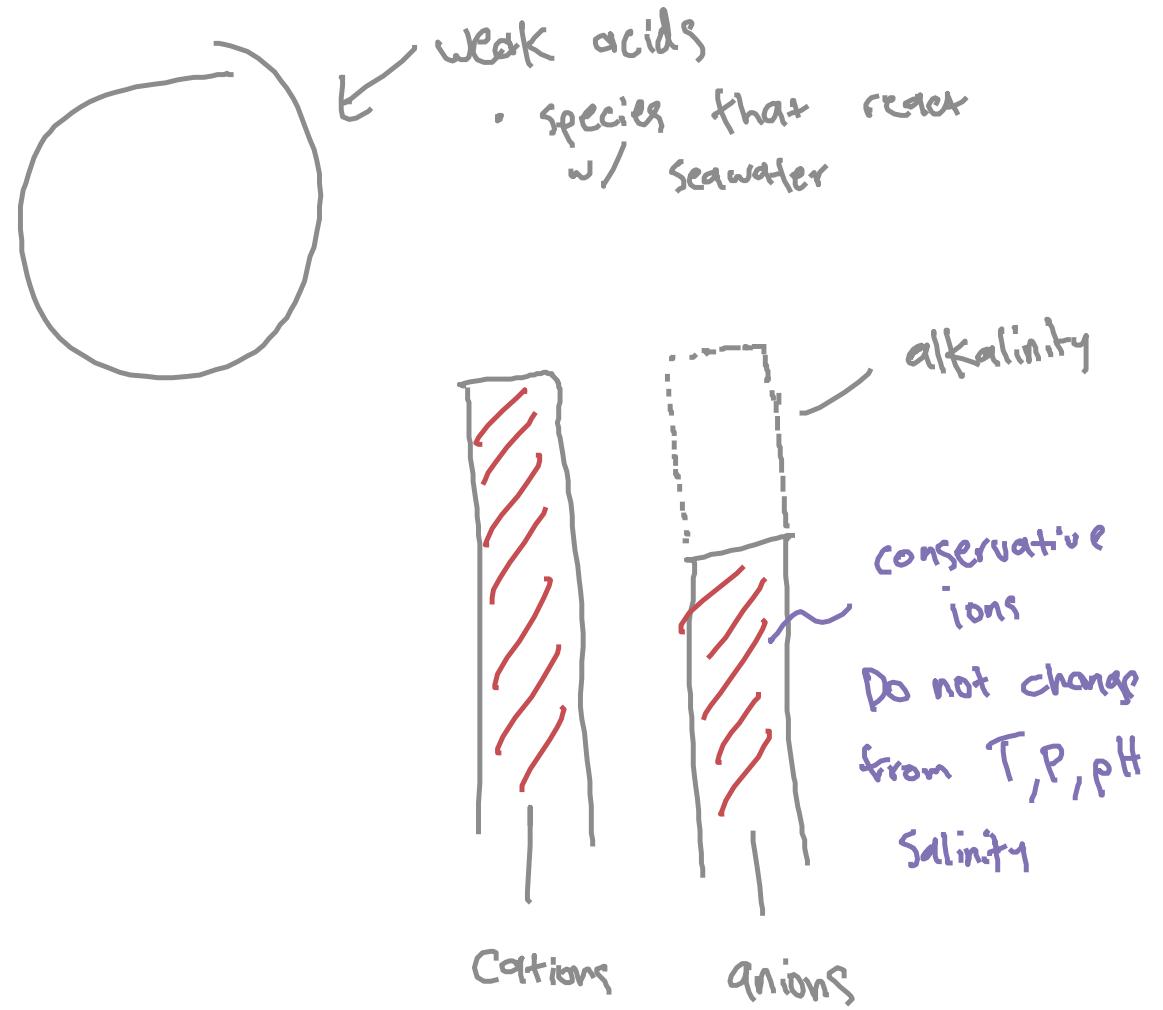


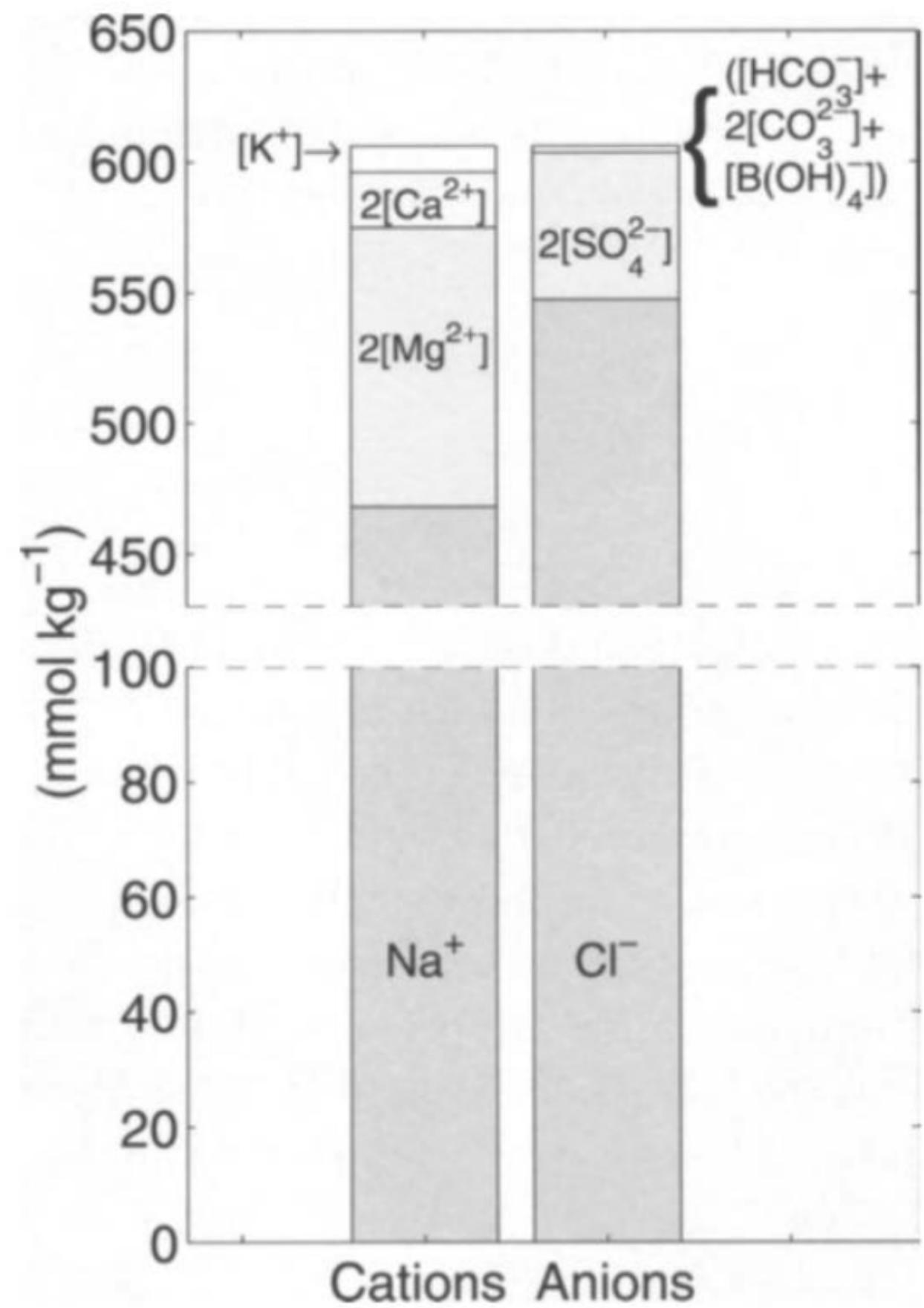


\sum charge of positive ions

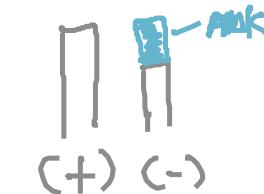
minus
 \sum charge of negative ions

$$\begin{aligned} CA &\approx TA \\ &\text{complicated form for (alkalinity)} \\ TA = & [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \\ & + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] \\ & + [H_2PO_4^-] + 2[HPO_4^{2-}] - [H^+] \end{aligned}$$





Alkalinity: real world examples



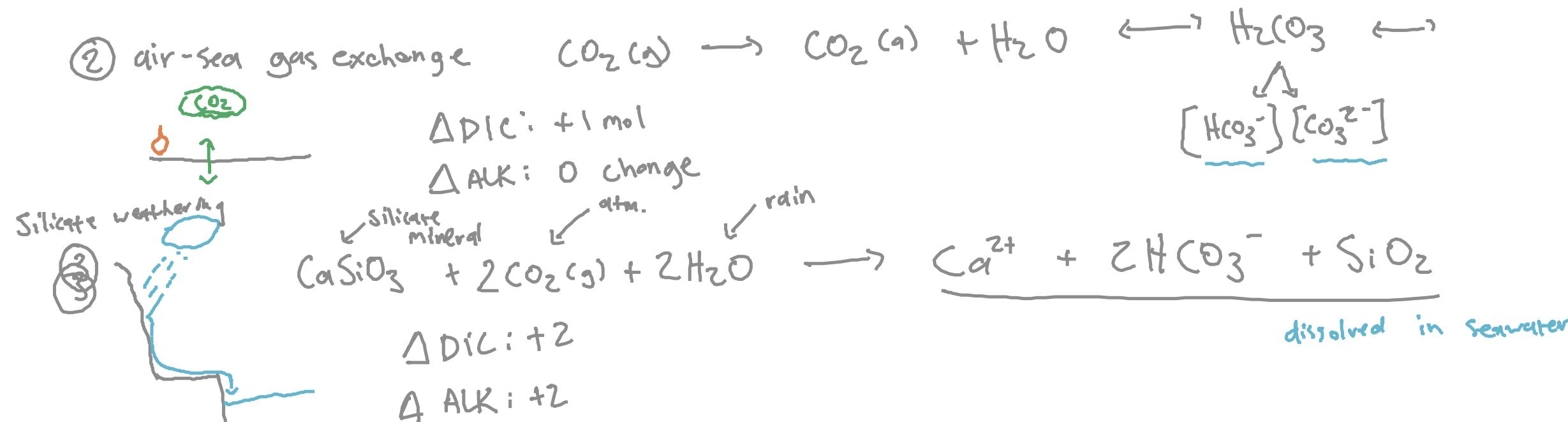
① Carbonate precipitation



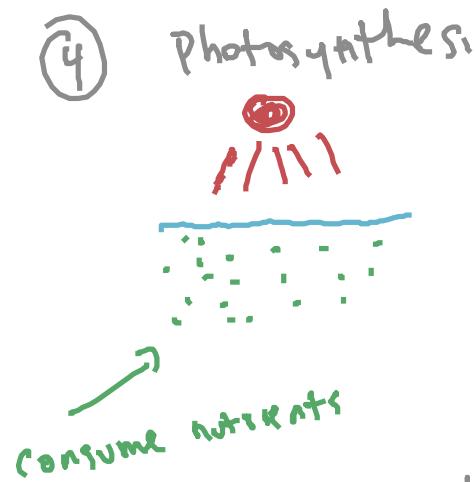
How does DIC change? -1 mol DIC

How does ALK change? -2 mol ALK

② air-sea gas exchange

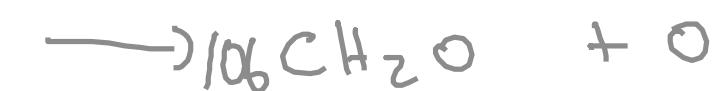


Alkalinity: real world examples

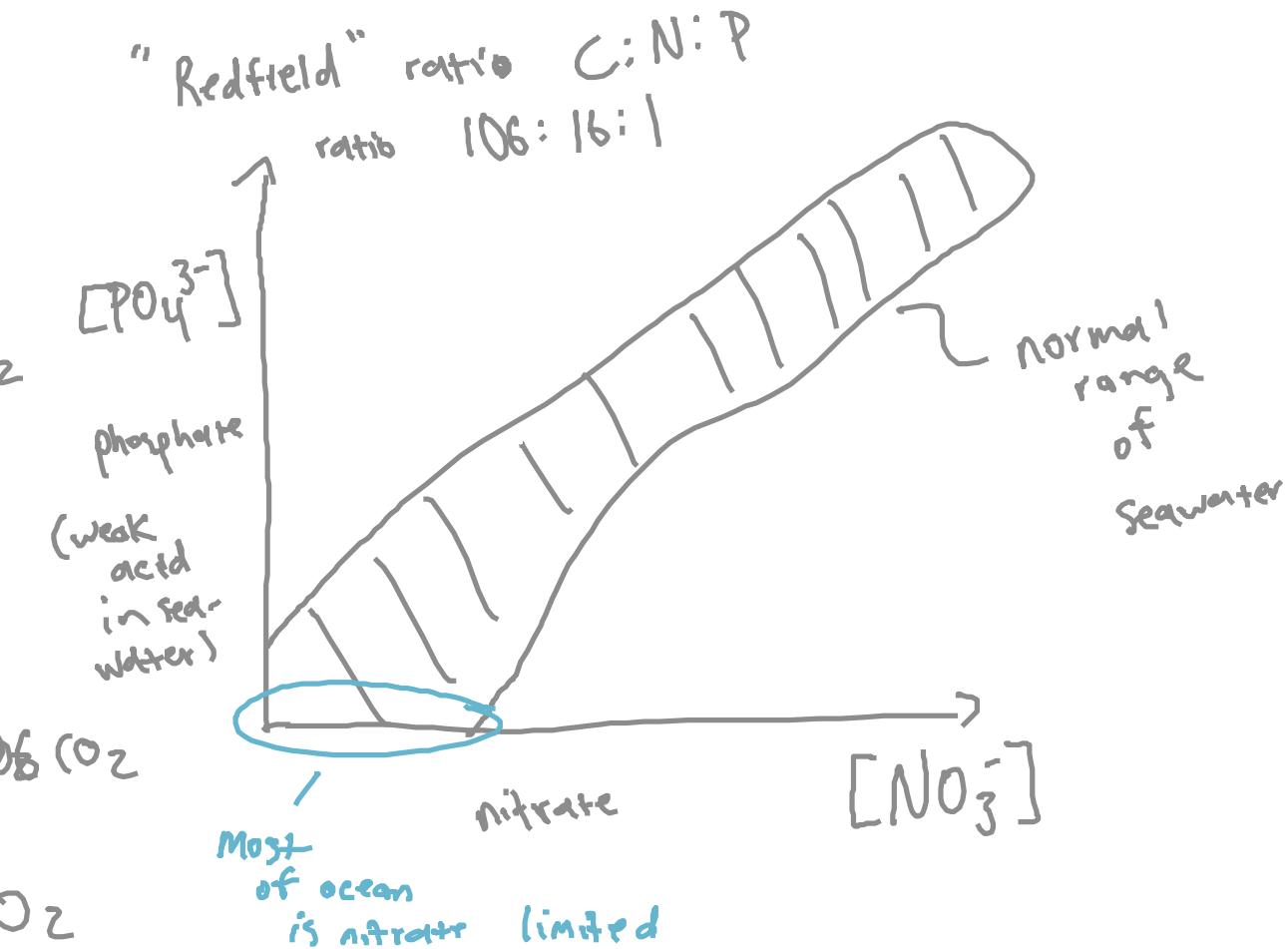
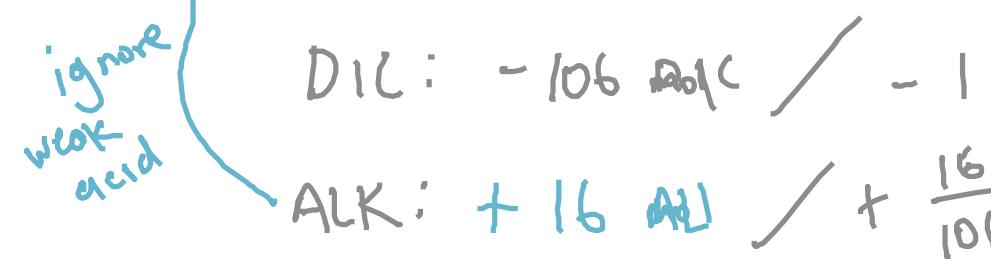


DIC: -1 mol

ALK: 0?



DIC: -106 mol C / -1



CO₂, Alkalinity, and DIC

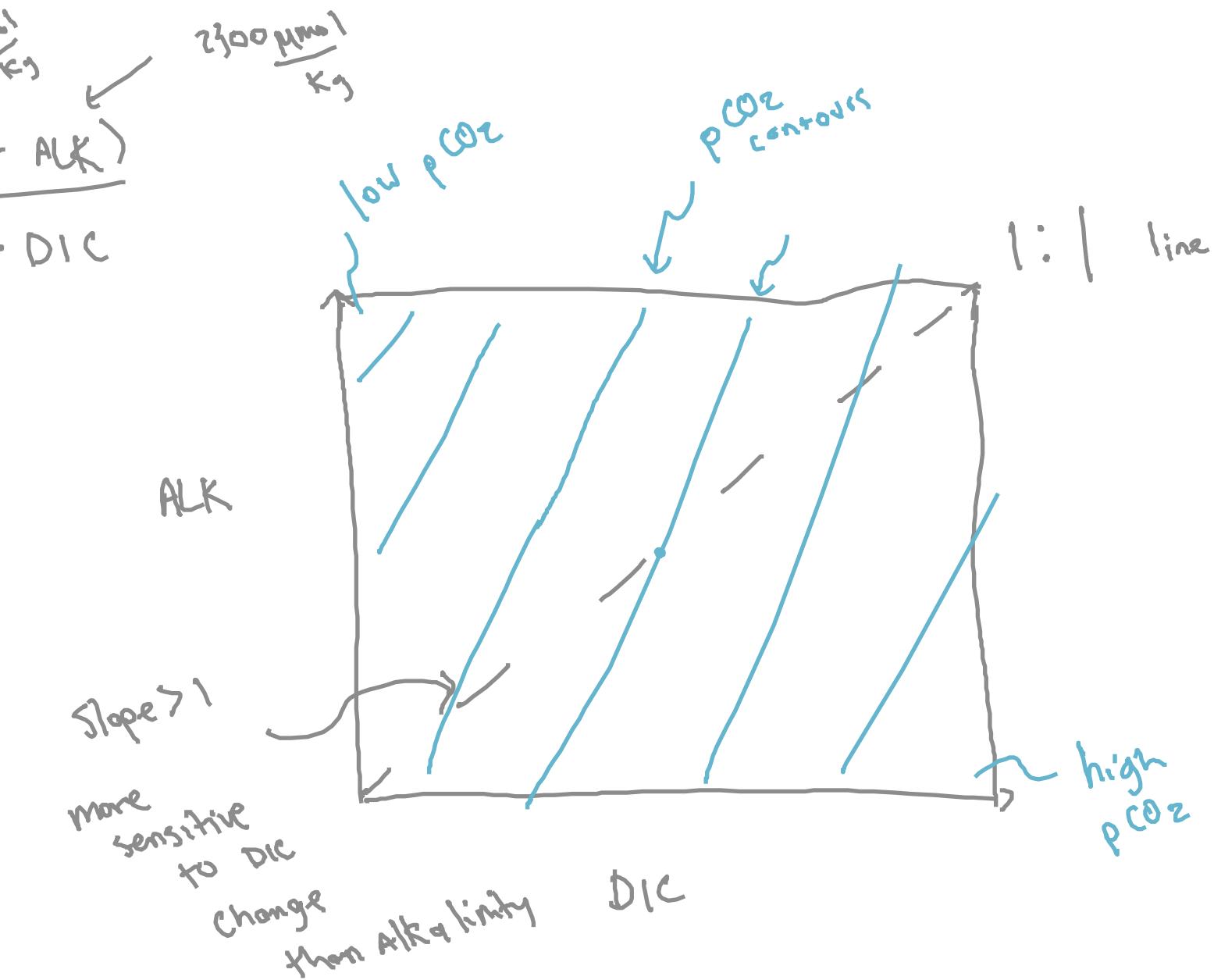
recall:

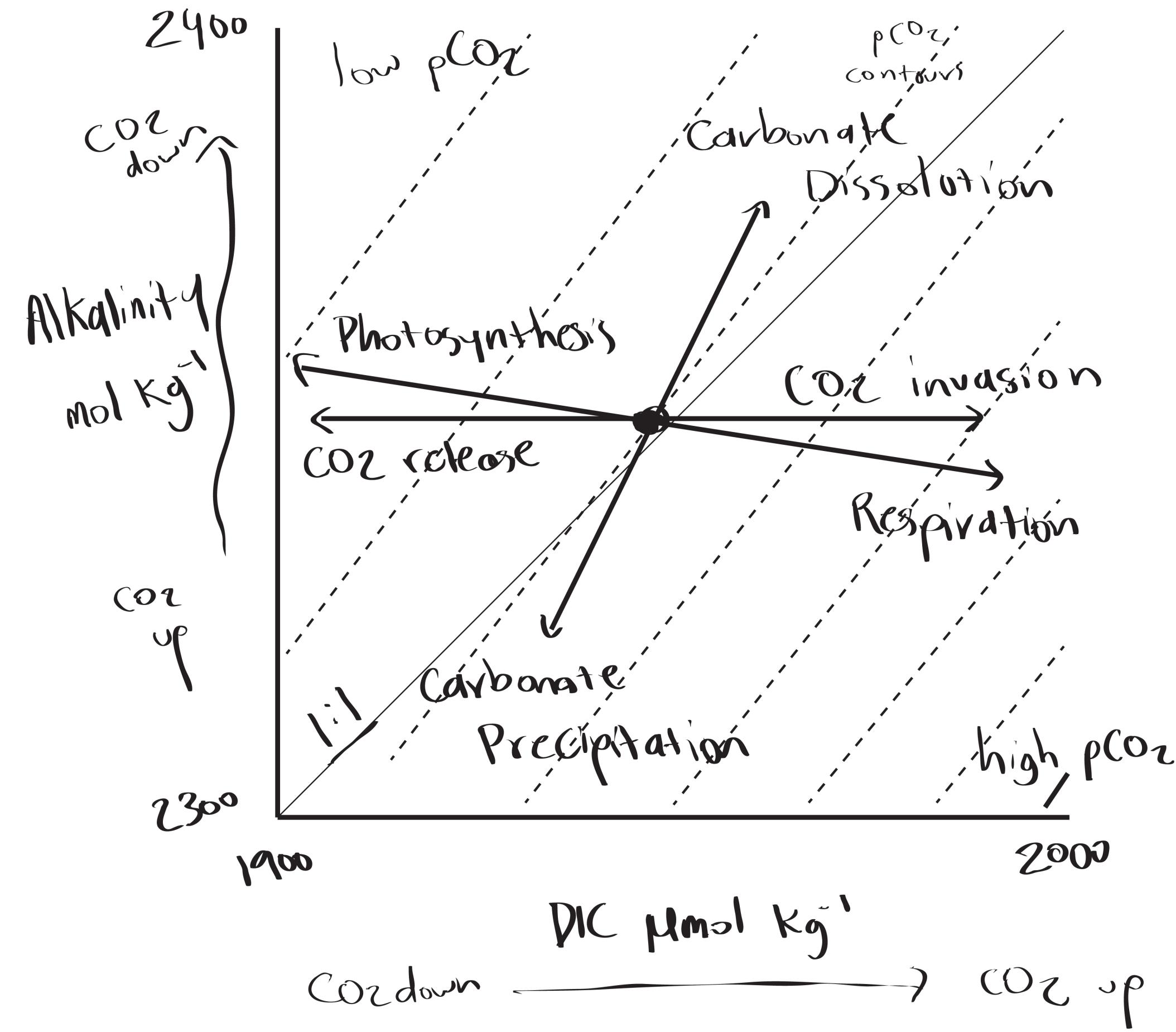
$$p\text{CO}_2 \approx \frac{\kappa_2}{\kappa_1} \cdot \frac{(2\text{DIC} - \text{ALK})}{\text{ALK} - \text{DIC}}$$

in SW
↓
 $\frac{100 \mu\text{mol}}{\text{kg}}$

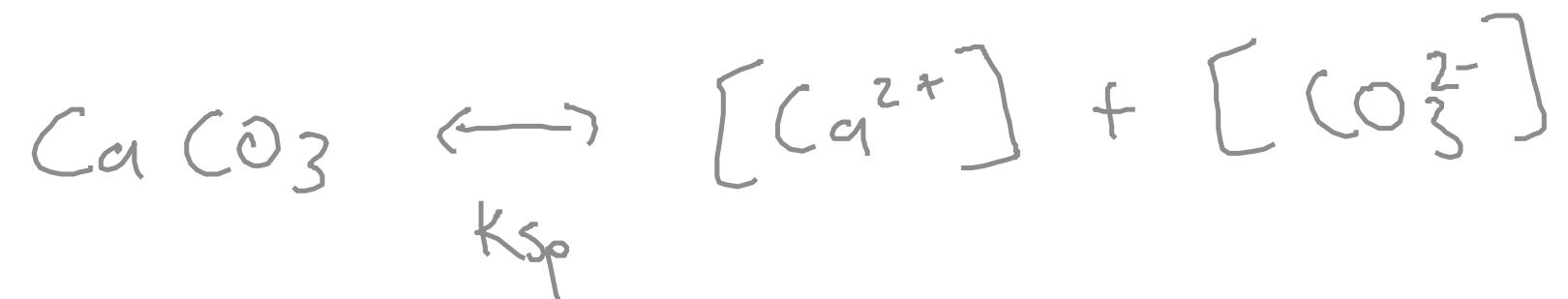
$$[\text{HCO}_3^-] \approx 2\text{DIC} - \text{ALK}$$

$$[\text{CO}_3^{2-}] \approx \text{ALK} - \text{DIC}$$





Carbonate Saturation State



$$K_{sp} = \frac{[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]}{1} \quad \Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}}$$

Ω , saturation state

$\Omega = 1$, equilibrium, saturated

$\Omega < 1$, undersaturated

$\Omega > 1$, supersaturated

