



Lectures 19: Alkalinity and DIC

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

We acknowledge and respect the $lək'wəṇ$ 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.



An exercise: relative abundance of carbon species in seawater

recall:

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

replace w/ eq 1

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

replace w/ eq 2

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

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

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

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

only constant at fixed T, P, salinity

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

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

CA $\approx$ TA

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

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

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

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

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

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

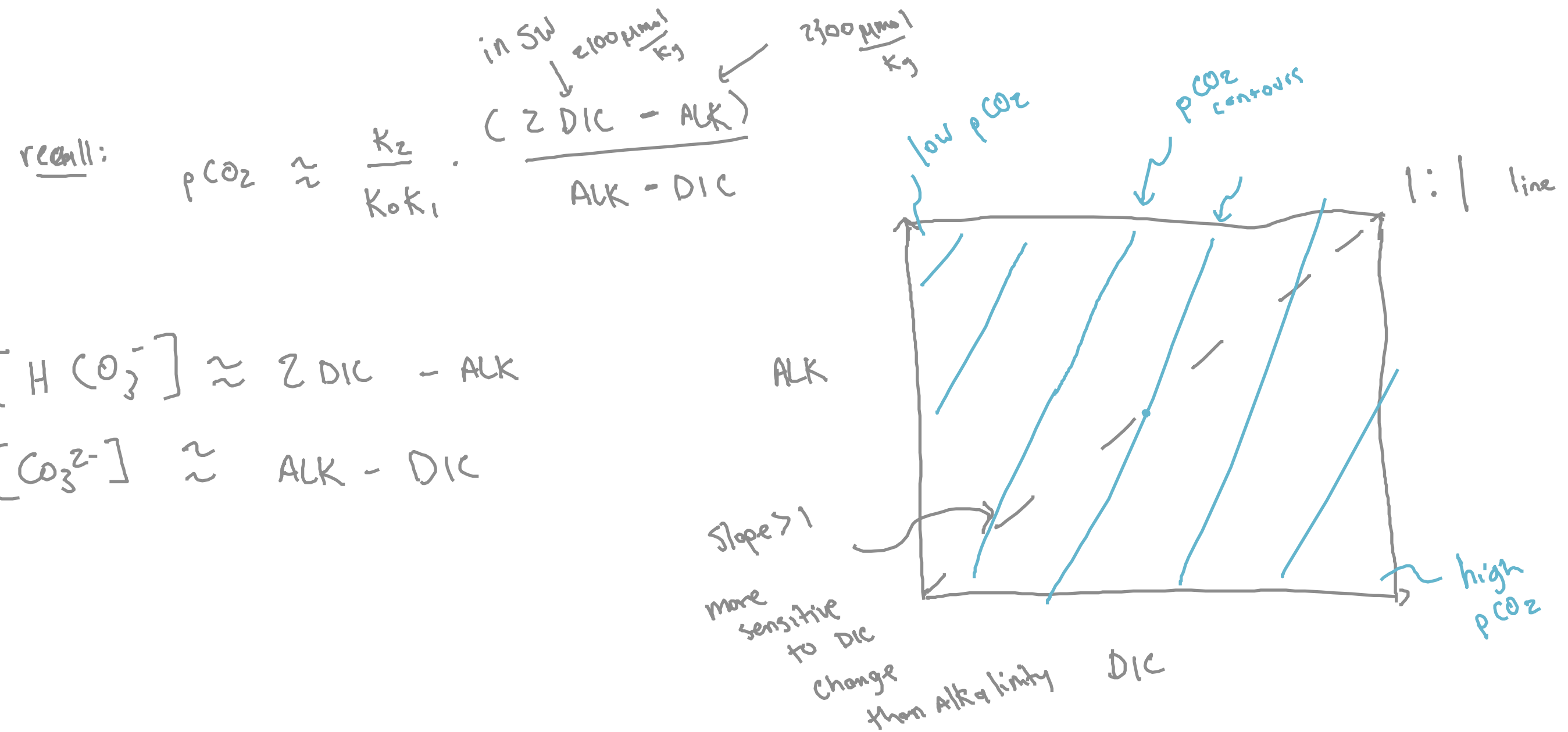
$$[\text{CO}_3^{2-}] = \text{CA} - \text{DIC}$$

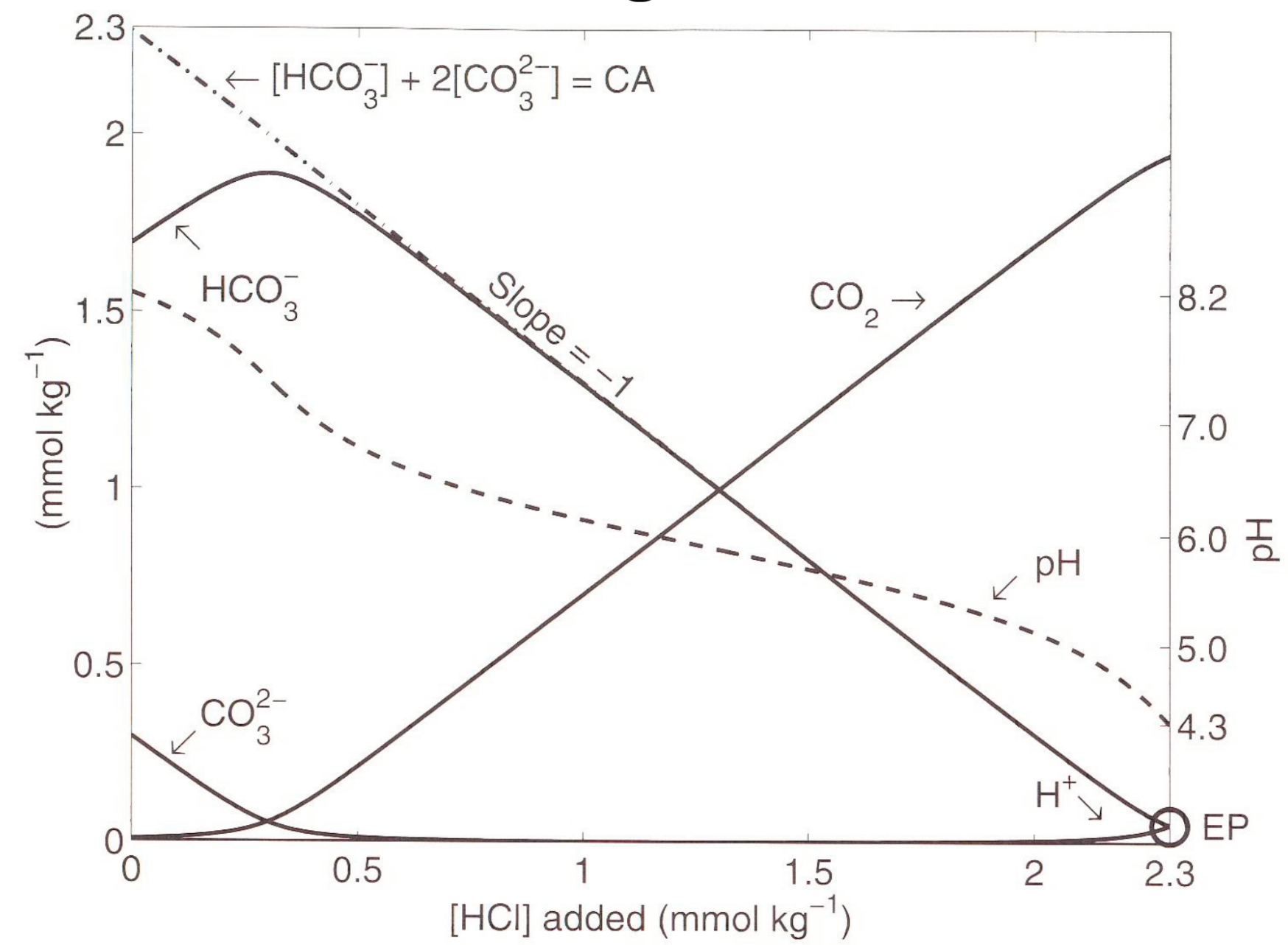
$$2\text{DIC} - \text{CA} = [\text{HCO}_3^-]$$

↑
calculation from previous slide



CO₂, Alkalinity, and DIC





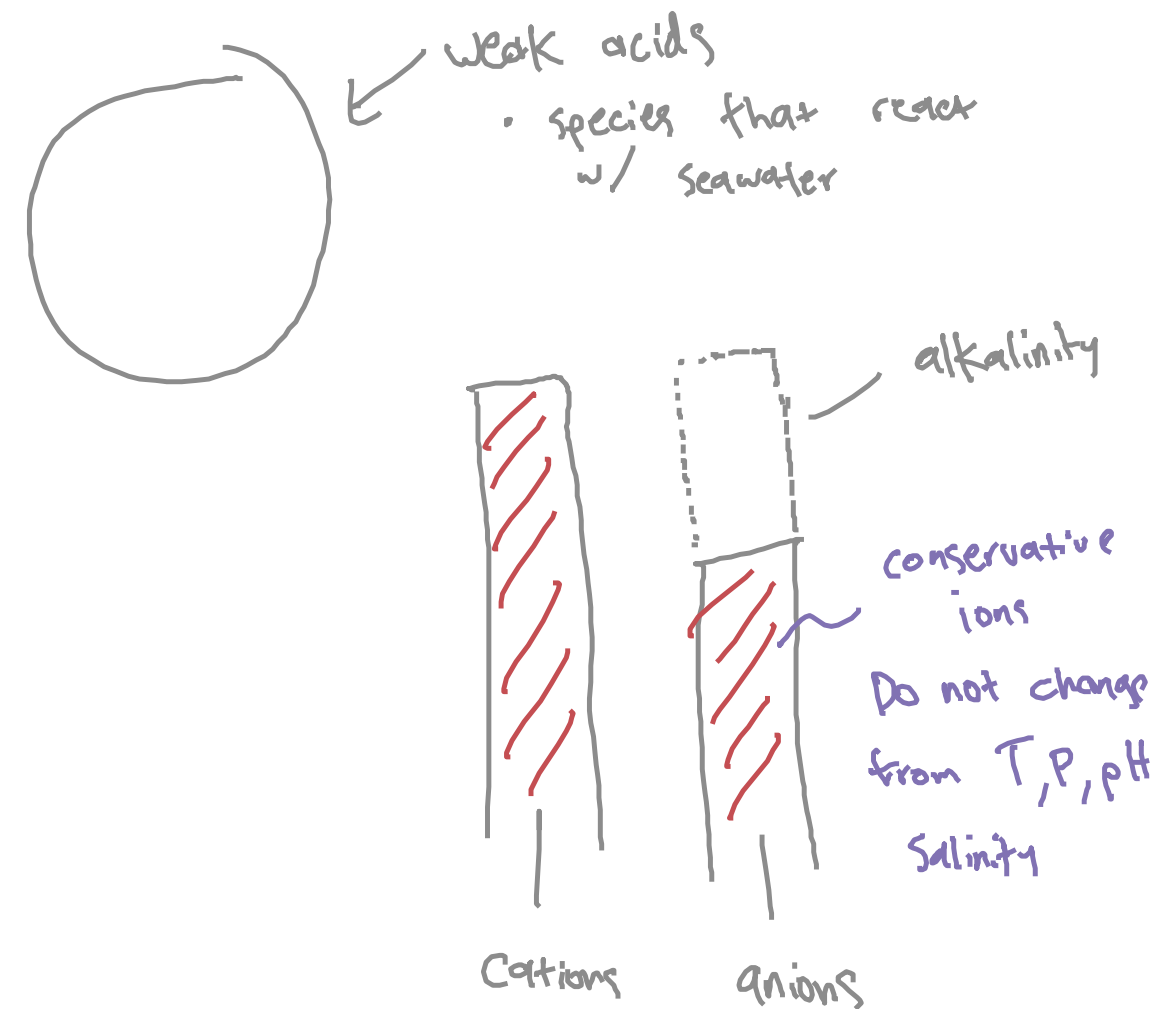
$\sum$ charge of positive ions

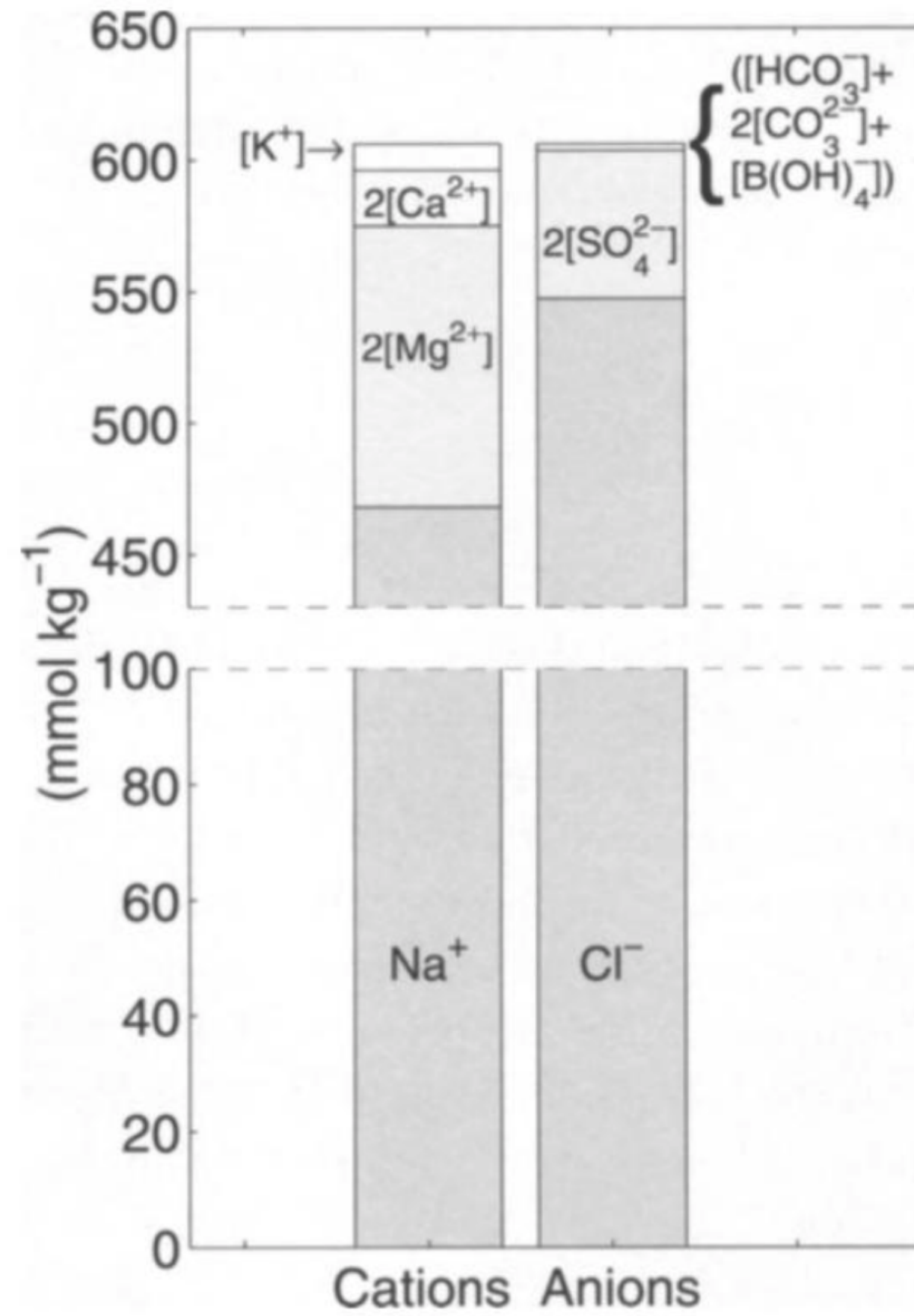
minus

$\sum$ charge of negative ions

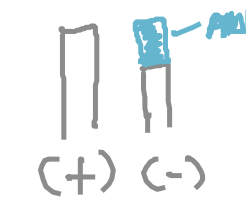
CA & TA
complicated form for (alkalinity)

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \\ & + [\text{B(OH)}_4^-] + [\text{H}_3\text{SiO}_4^-] + [\text{HS}^-] \\ & + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] - [\text{H}^+] \end{aligned}$$





Alkalinity: real world examples



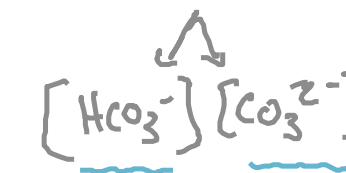
① Carbonate precipitation



How does DIC change? -1 mol DIC

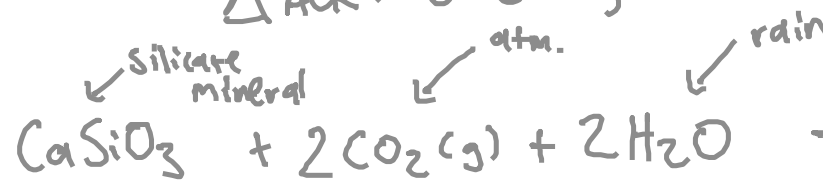
How does ALK change? -2 mol ALK

② air-sea gas exchange $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons$



$\Delta \text{DIC}: +1 \text{ mol}$

$\Delta \text{ALK}: 0 \text{ change}$



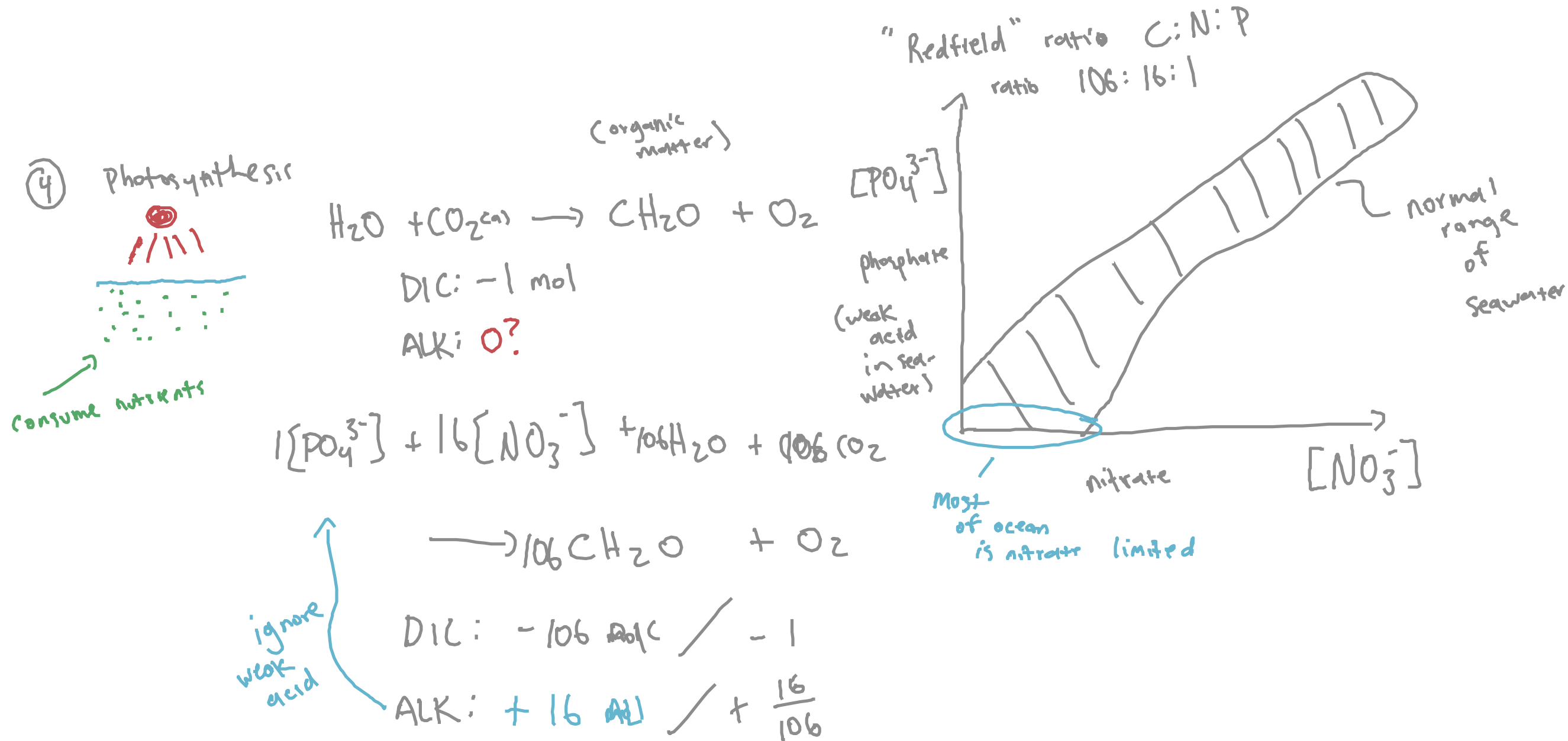
$\Delta \text{DIC}: +2$

$\Delta \text{ALK}: +2$

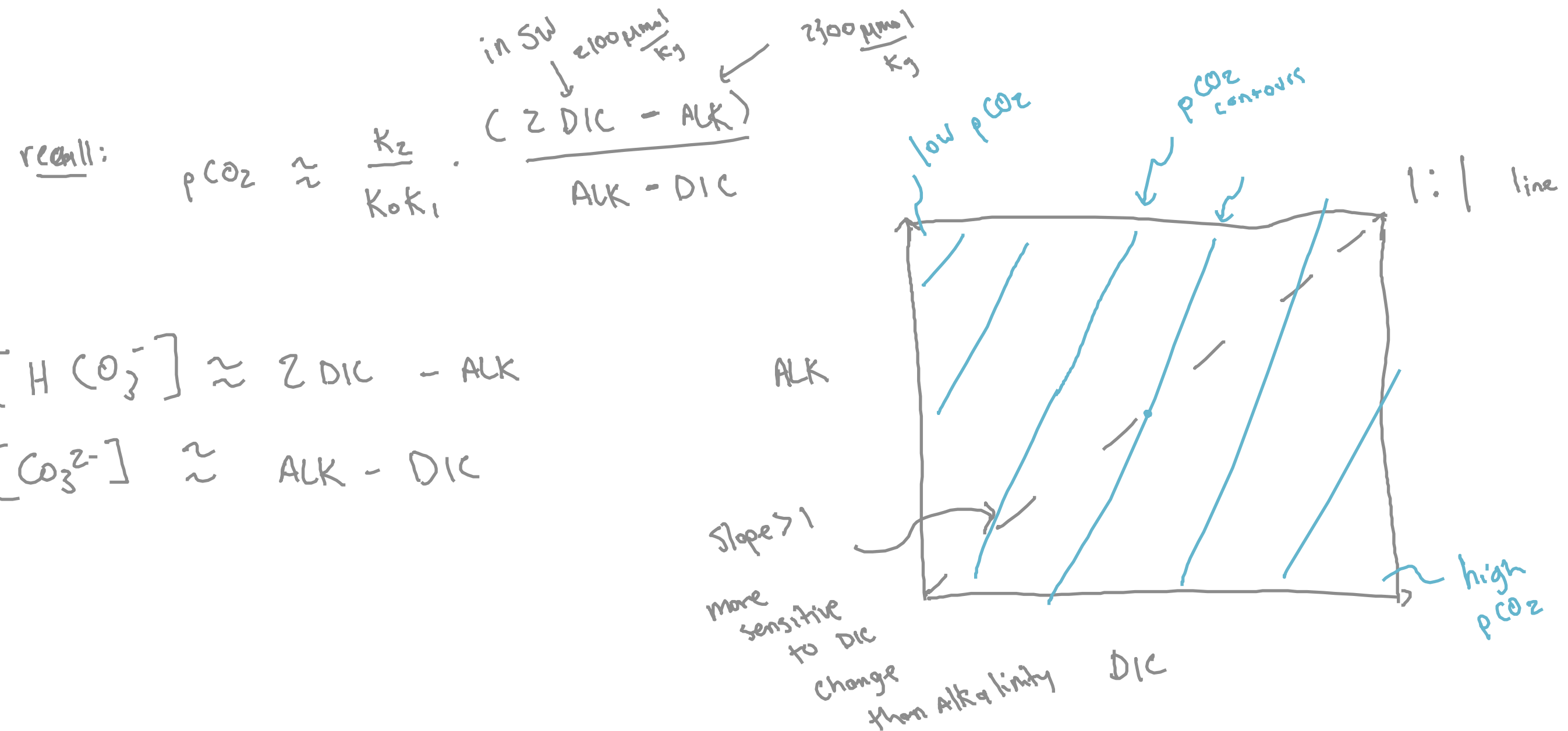
dissolved in seawater

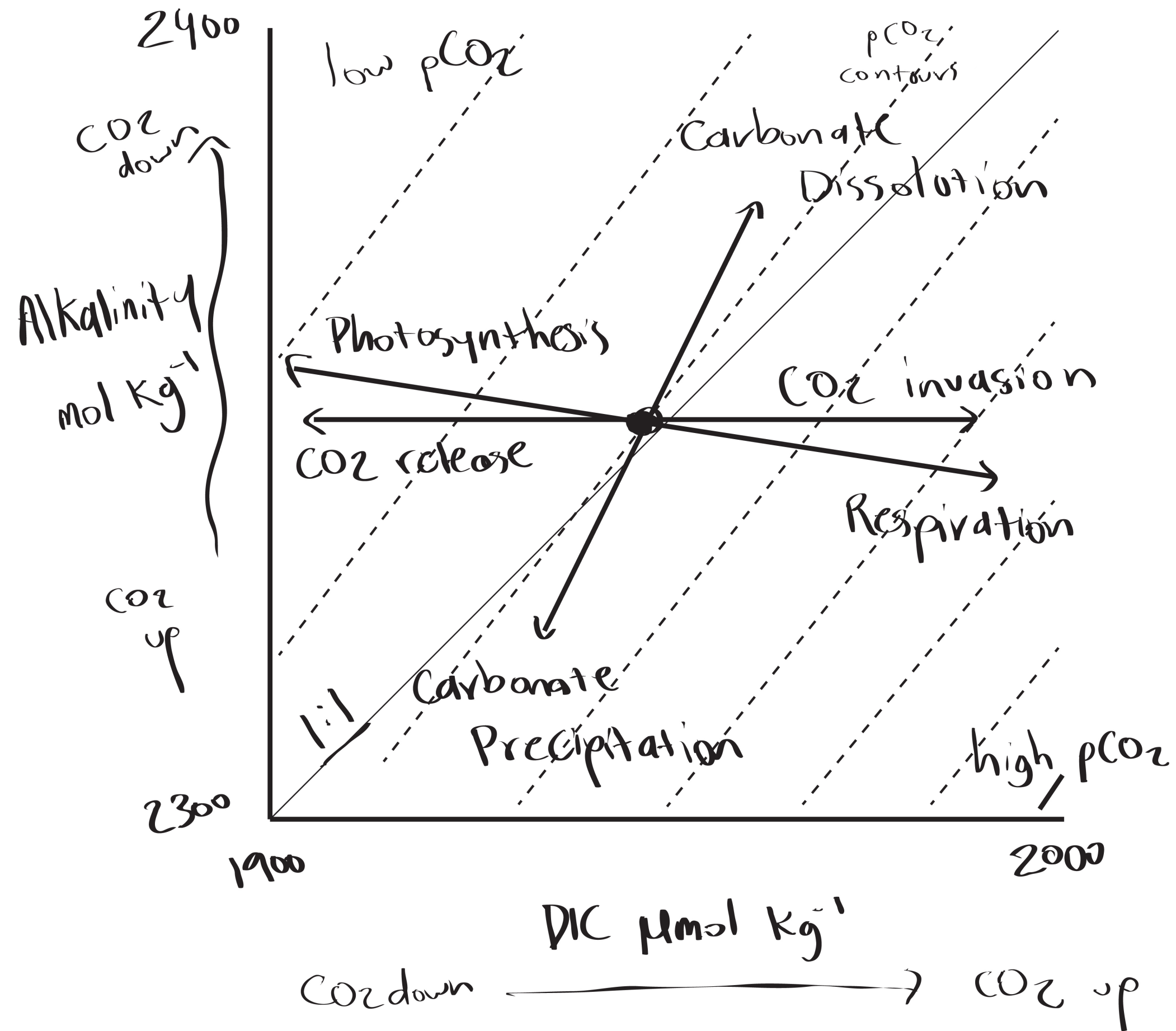


Alkalinity: real world examples

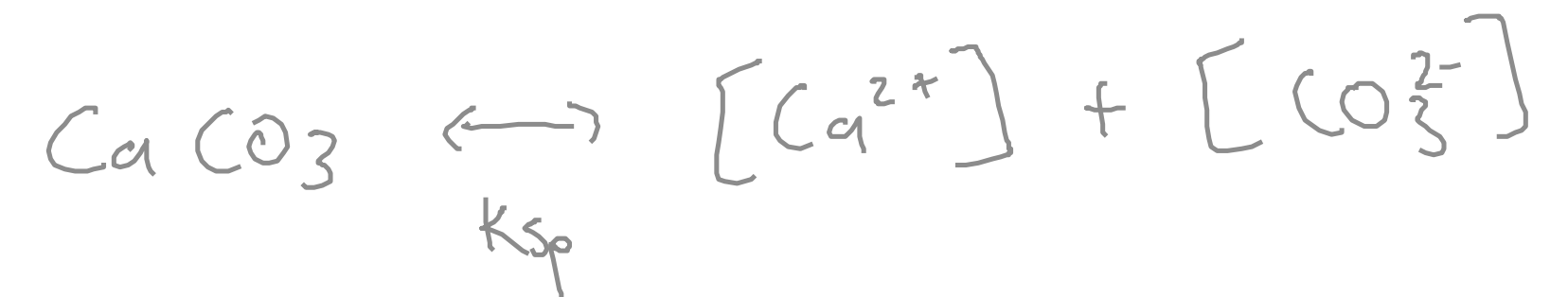


CO₂, Alkalinity, and DIC





Carbonate Saturation State



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

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

Ω , saturation state

$\Omega = 1$, equilibrium, saturated

$\Omega < 1$, undersaturated

$\Omega > 1$, supersaturated

