Alkalinity is 'conservative', ie. not a function of pH, pressure, T. If we consider Carbonate Alkalinity, this property seems counter intuitive. $[H^+]$ and $K_1, K_2$ all change with ↗. However, the sum is constant

$$\sum\{\text{charge of conservative positive ions}\} - \sum\{\text{charge of conservative negative ions}\} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] - [H^+]$$

When thinking of changes in alkalinity in the ocean, easier to imagine how conservative ions are changing.

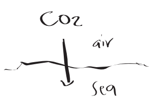
★ A solution where $[HCO_3^-] \simeq [H^+]$ will have an Alkalinity of ~0. (this happens ~pH 4.3 in the ocean at T = 25°C and Salinity of 35)

Some examples:

carbonate precipitation

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

what is the change in alkalinity associated with this reaction? ... decreases by 2. −1 mol DIC

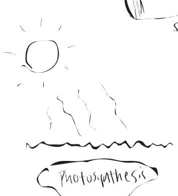



$$CO_2(g) \longleftrightarrow CO_2(a) + H_2O \longleftrightarrow H_2CO_3$$

No change in alkalinity, +1 mol DIC


$$CaSiO_3 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$$

increase in alkalinity by 2, increase DIC by 2




$$H_2O + CO_2 \rightarrow CH_2O + O_2$$

−1 DIC Alkalinity is tricky...

these bugs use nutrients to create organic matter

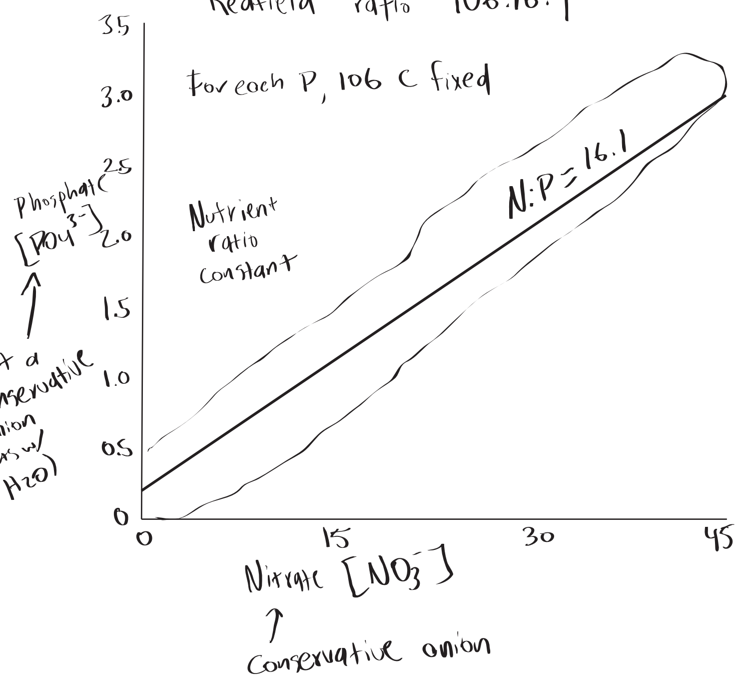
C:N:P = 106:16:1

each $NO_3^-$ counts towards alkalinity

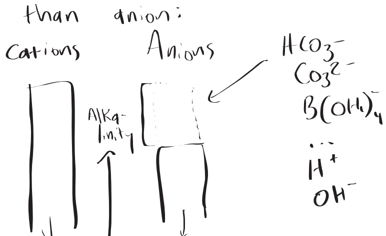
– So alkalinity increases by $\frac{16}{106}$ to make one $CH_2O$

Note the increase is due to the negative charge

"Redfield" ratio C:N:1 106:16:1




Ocean has more conservative cation charge than anion:




increases when cation ↑ or anion ↓

decreases when cation ↓ or anion ↑

Recall: 
$$pCO_2 \simeq \frac{K_2}{K_0K_1}\frac{(2DIC - Alk)^2}{Alk - DIC}$$

approximate; really includes $B(OH)_4^-$, $H^+$, $OH^-$

Alk = 2350
DIC 1900 → 2000
$pCO_2$ 140 → 233 ppm

Alk 2300 → 2400
DIC 1950
$pCO_2$ 219 → 150 ppm