Lecture 20: Alkalinity

1. Alkalinity
    A. Examples and practice

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.

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

$DIC = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}]$ ($[CO_{2(aq)}] \to 0$; $a = [HCO_3^-]$, $b = [CO_3^{2-}]$)

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

$CA \approx TA$

$DIC = a + b$

$CA = a + 2b$

$DIC - b = a$

$CA = DIC - b + 2b$

$CA = DIC + b$

$b = CA - DIC$

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

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

↑ calculation from previous slide

CO2, Alkalinity, and DIC

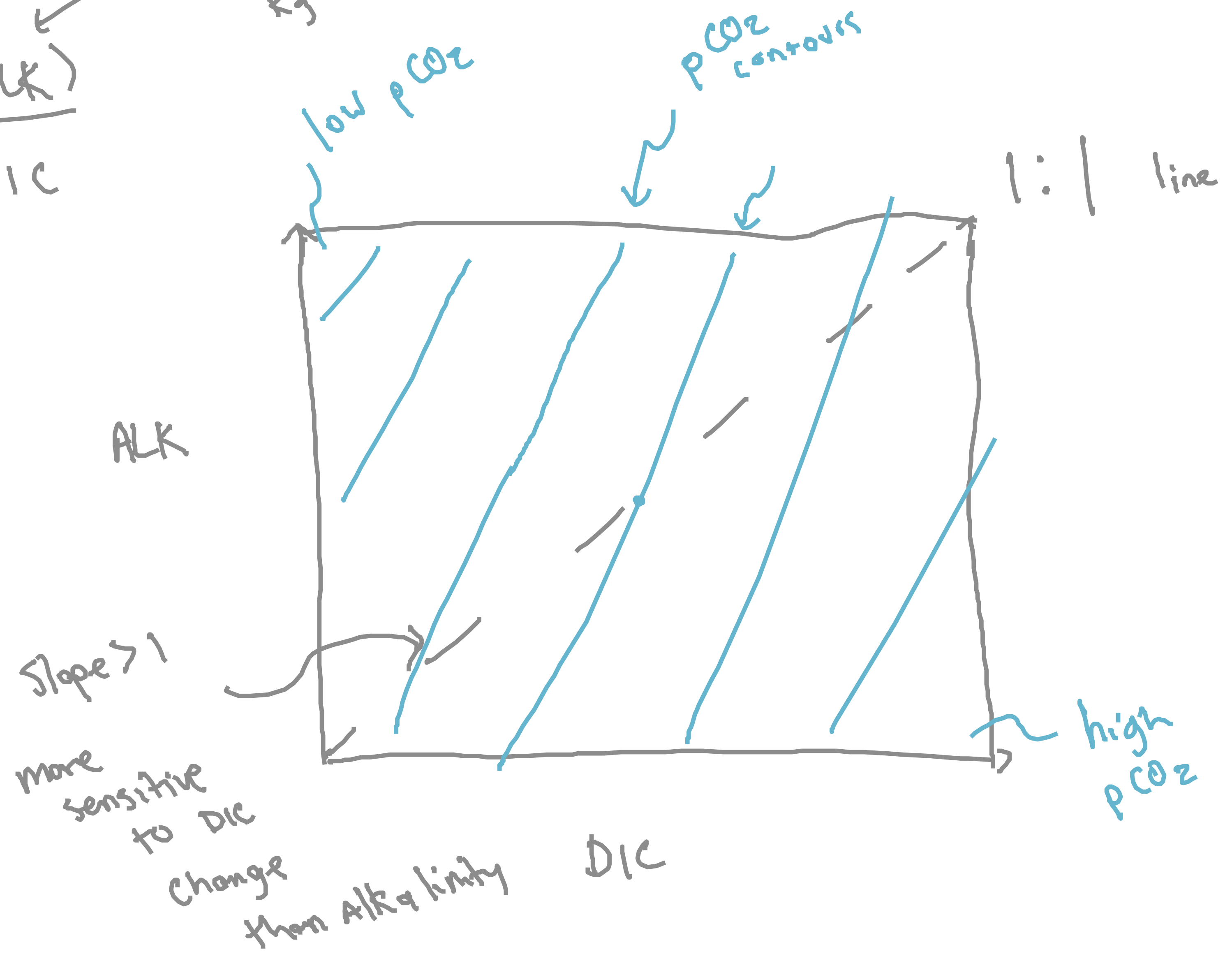
recall:

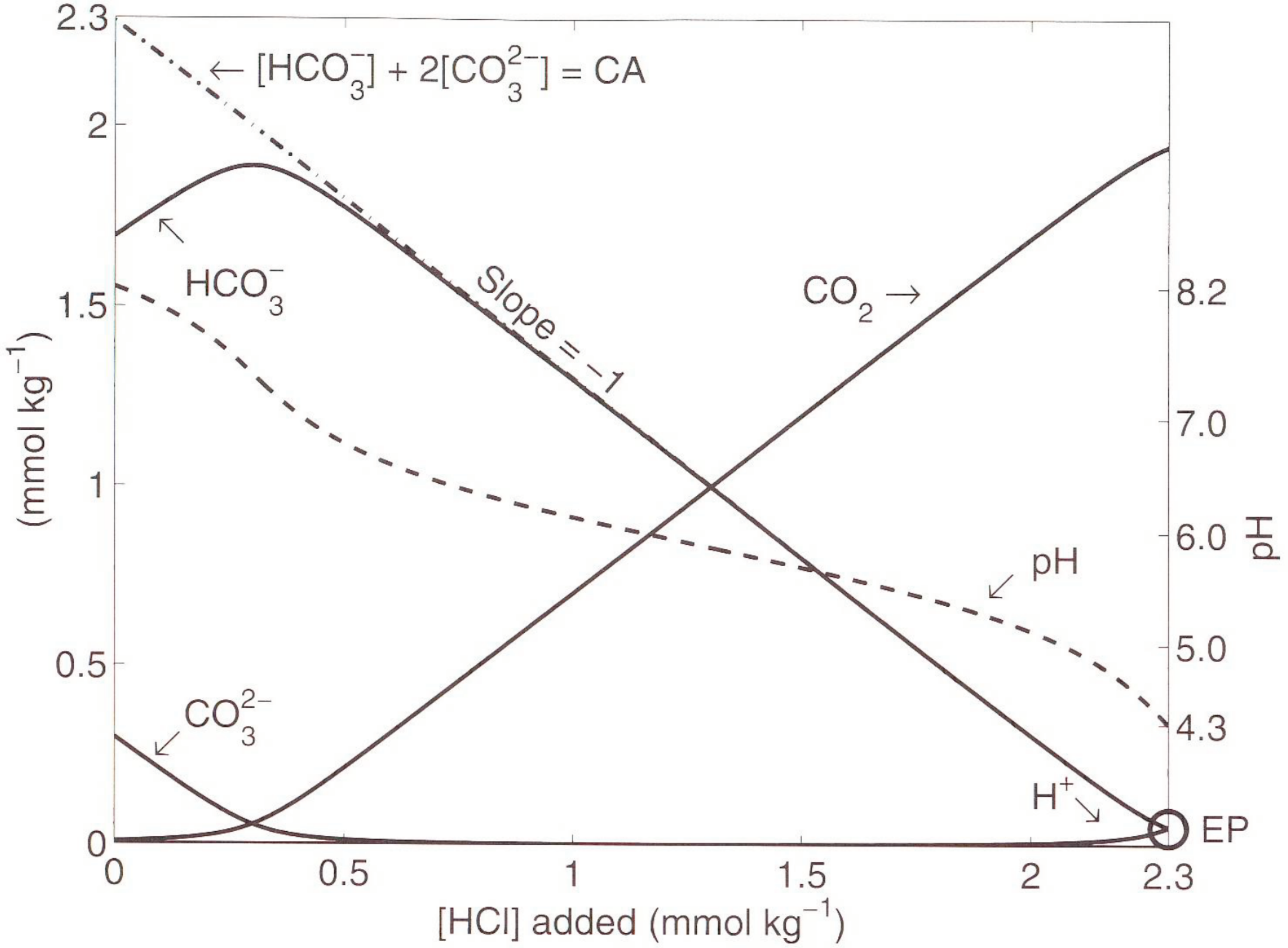
$$pCO_2 \approx \frac{K_2}{K_0 K_1} \cdot \frac{(2\,DIC - ALK)}{ALK - DIC}$$

in SW: DIC ~2100 µmol/kg; ALK ~2300 µmol/kg

$$[HCO_3^-] \approx 2\,DIC - ALK$$

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





2.3
2
1.5
1
0.5
0
← [HCO3−] + 2[CO32−] = CA
HCO3−
Slope = −1
CO2 →
CO32−
pH
H+
EP
8.2
7.0
6.0
5.0
4.3
pH
(mmol kg−1)
0
0.5
1
1.5
2
2.3
[HCl] added (mmol kg−1)

Total Alkalinity (TA)

TA is the excess of proton-accepting species over proton-donating species in seawater. These are the species that react with seawater and contribute to its ability to resist a drop in pH.

$$\text{TA} \approx [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [H_3SiO_4^-] + [HS^-]$$
$$+ [H_2PO_4^-] + 2[HPO_4^{2-}] - [H^+]$$

Total alkalinity can also be tracked as the net charge difference between conservative cations and conservative (non-reactive) anions in seawater.

- **Conservative cations** contribute positive charge
- **Conservative anions** contribute negative charge
- Their **net excess positive charge** is balanced by the seawater acid-base system (above)

TA behaves like a conserved charge balance quantity during many mixing processes, even though its chemical expression is often written in terms of acid-base species such as bicarbonate and carbonate.

$\sum$ charge of positive ions

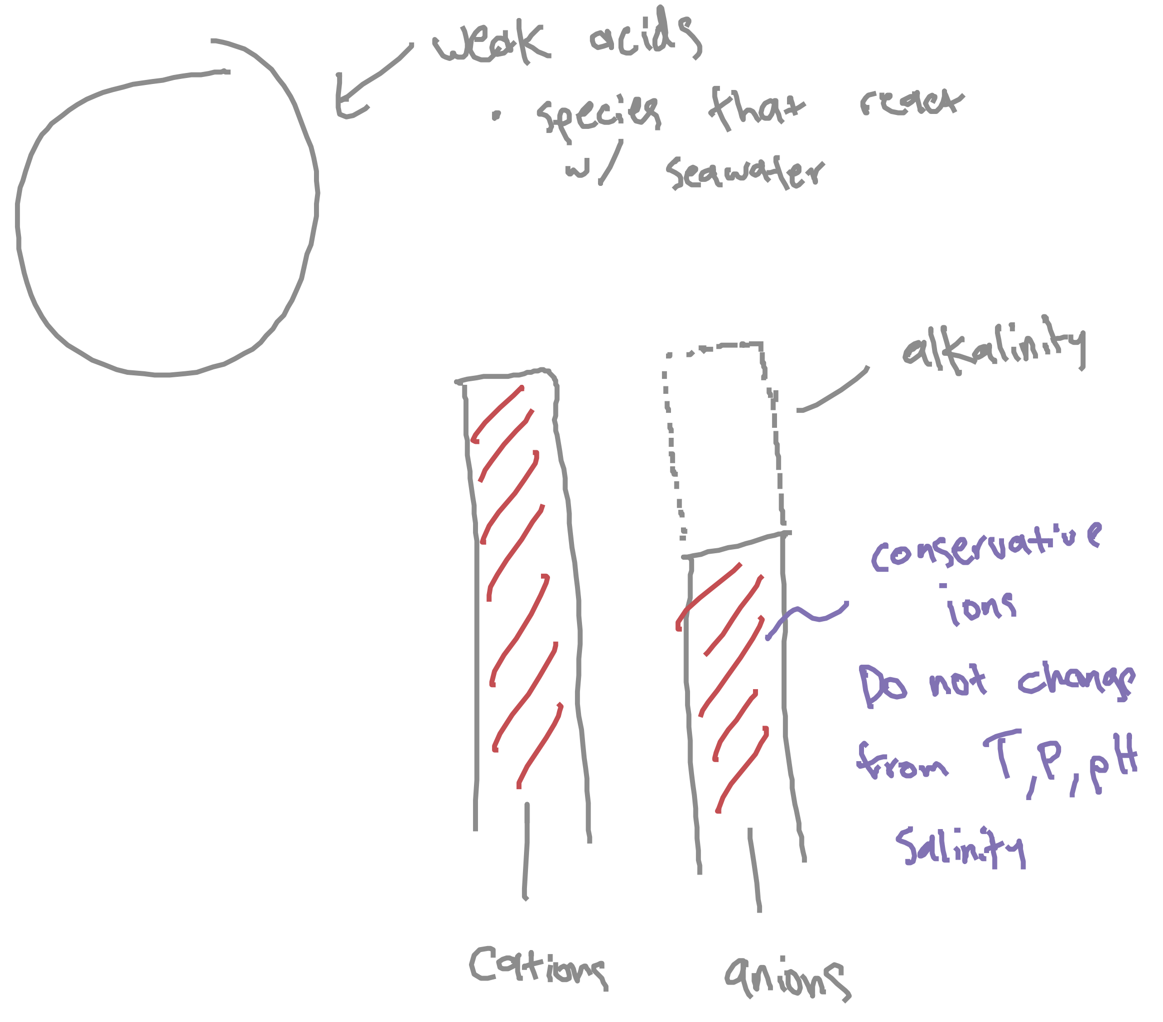
minus

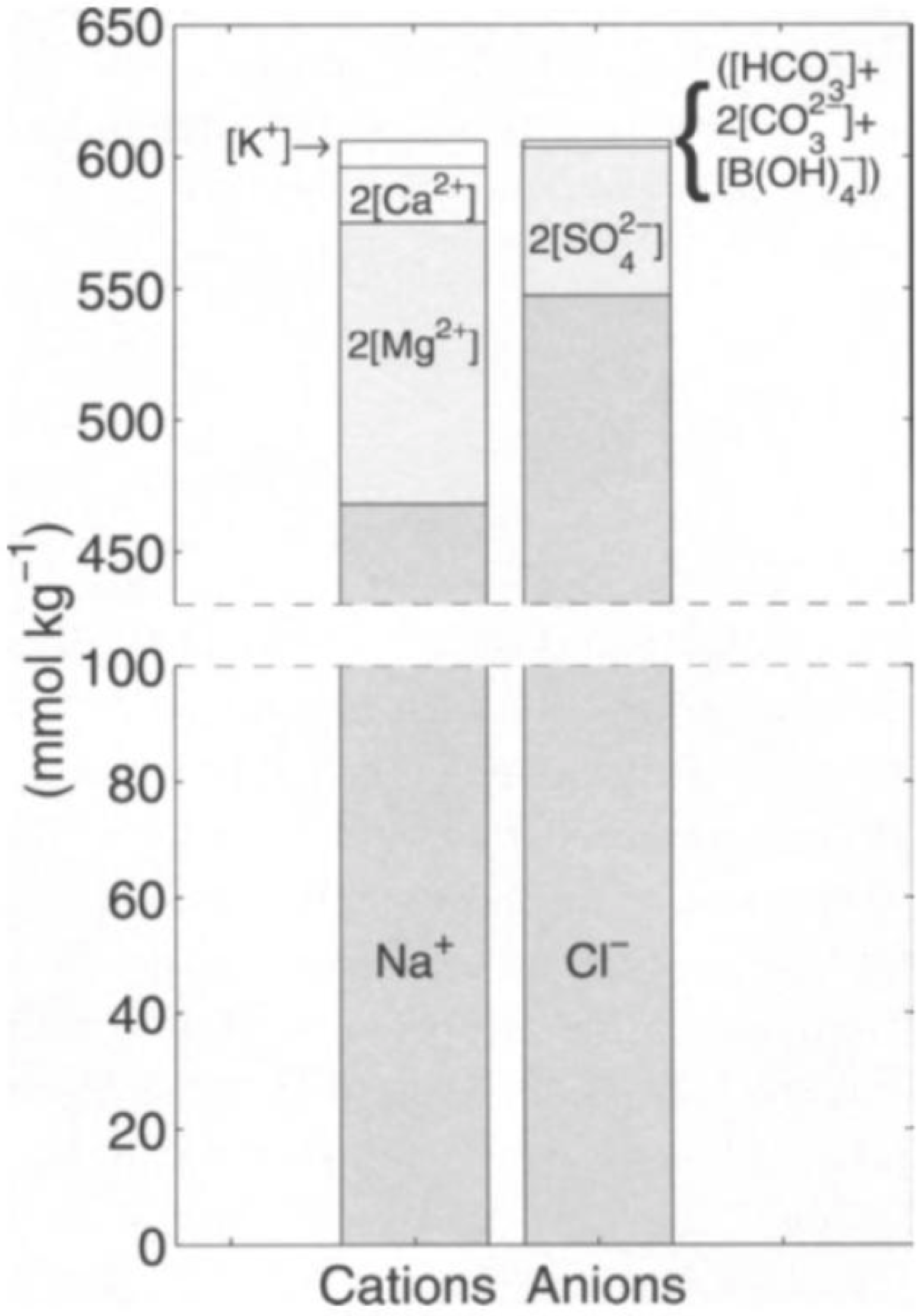
$\sum$ charge of negative ions

CA ≈ TA

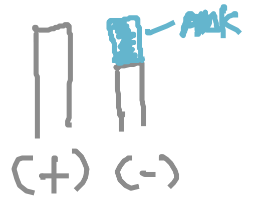
complicated form for (alkalinity)

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [B(OH)_4^-] + [H_3SiO_4^-] + [HS^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] - [H^+]$$




650
600
550
500
450
100
80
60
40
20
0
(mmol kg^{-1})
[K$^+$]→
2[Ca^{2+}]
2[Mg^{2+}]
Na$^+$
([HCO$_3^-$]+
2[CO$_3^{2-}$]+
[B(OH)$_4^-$])
2[SO$_4^{2-}$]
Cl$^-$
Cations
Anions

Alkalinity: real world examples



① Carbonate precipitation

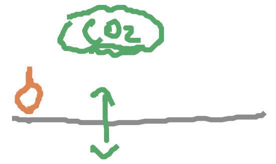
$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$

How does DIC change? -1 mol DIC

How does ALK change? -2 mol ALK

② air-sea gas exchange $CO_2(g) \rightarrow CO_2(a) + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow$

$[HCO_3^-]$ $[CO_3^{2-}]$



ΔDIC: +1 mol

ΔALK: 0 change

③ Silicate weathering

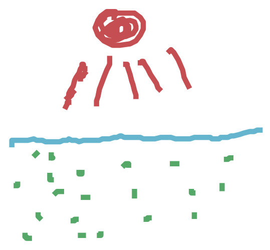
$CaSiO_3$ (silicate mineral) $+ 2\,CO_2(g)$ (atm.) $+ 2\,H_2O$ (rain) $\rightarrow Ca^{2+} + 2\,HCO_3^- + SiO_2$ (dissolved in seawater)

ΔDIC: +2

ΔALK: +2

Alkalinity: real world examples

(4) Photosynthesis



consume nutrients

(organic matter)

$H_2O + CO_{2(aq)} \rightarrow CH_2O + O_2$

DIC: −1 mol

ALK: 0?

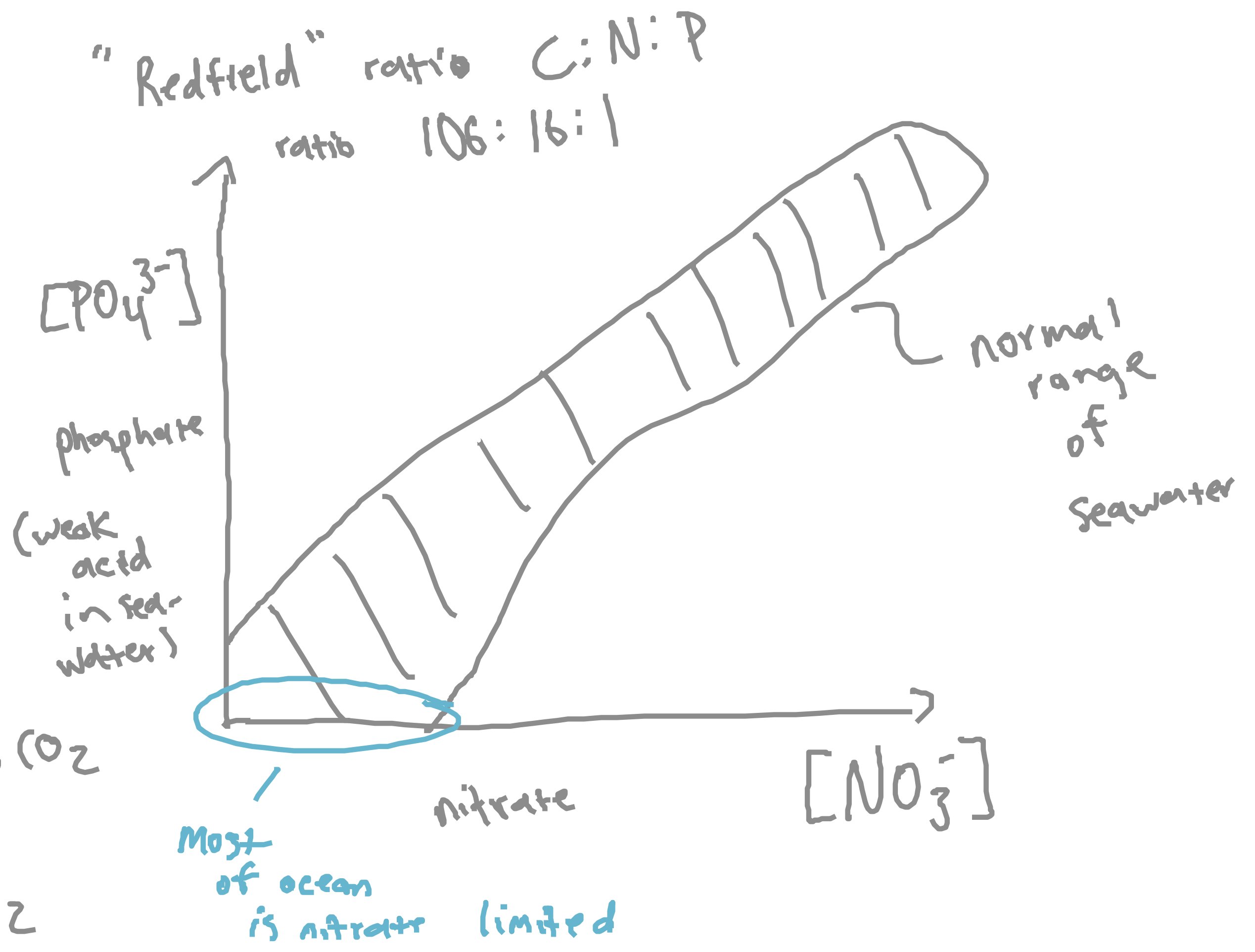
$1[PO_4^{3-}] + 16[NO_3^-] + 106 H_2O + 106 CO_2$

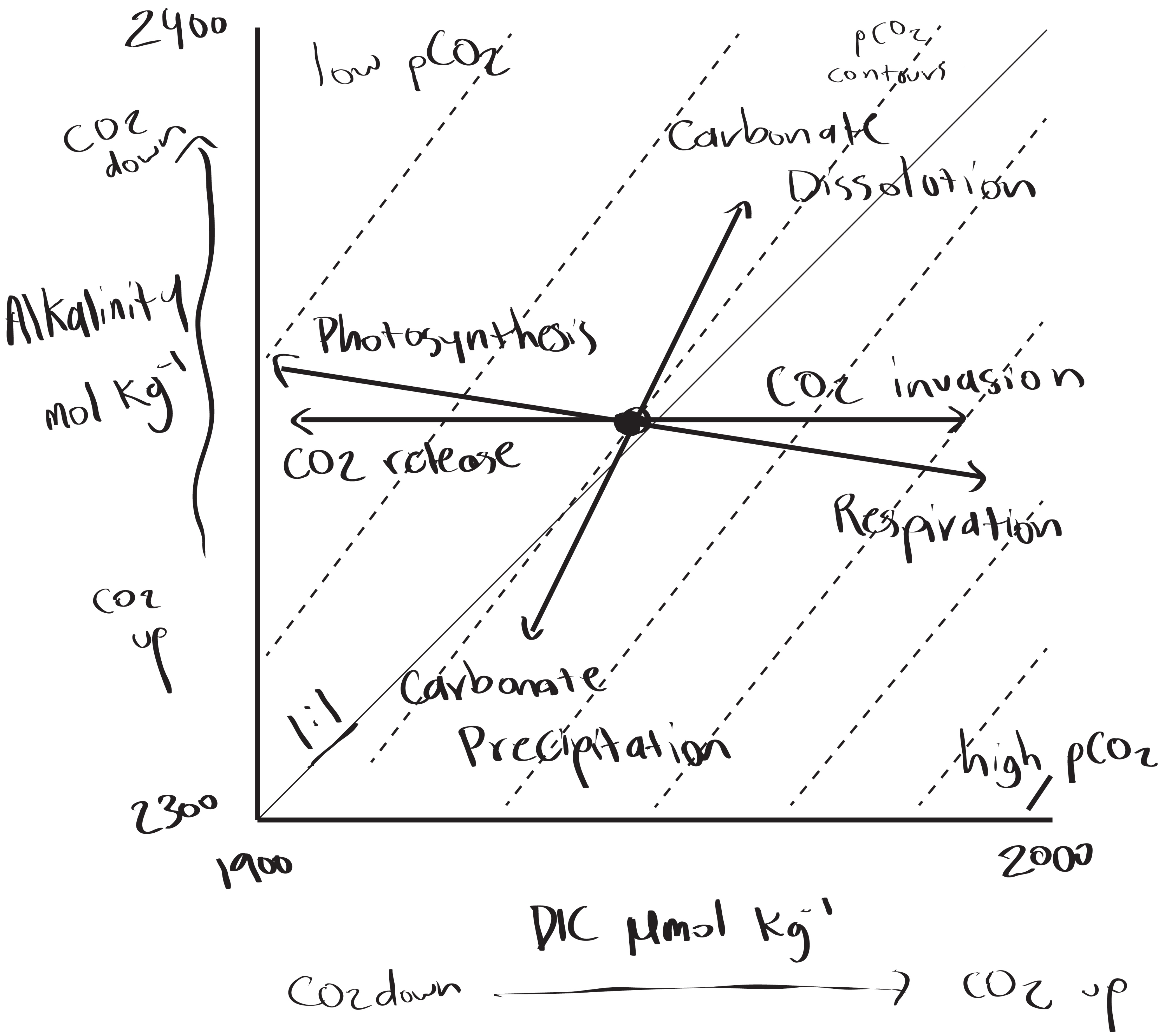
$\rightarrow 106 CH_2O + O_2$

DIC: −106 mol C / −1

ALK: +16 mol / $+\frac{16}{106}$

ignore weak acid




2400
2300
1900
2000
low pCO2
pCO2 contours
high pCO2
CO2 down
CO2 up
Alkalinity mol Kg-1
DIC μmol Kg-1
CO2 down
CO2 up
Carbonate Dissolution
Photosynthesis
CO2 invasion
CO2 release
Respiration
Carbonate Precipitation
1:1