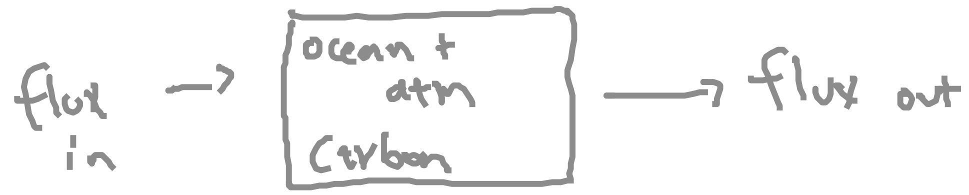
Lectures 19-22: CO2 in seawater

1. The carbonate system
2. Alkalinity
3. Carbonate Saturation
4. Oceanic uptake of anthropogenic CO_2 (Revelle factor)

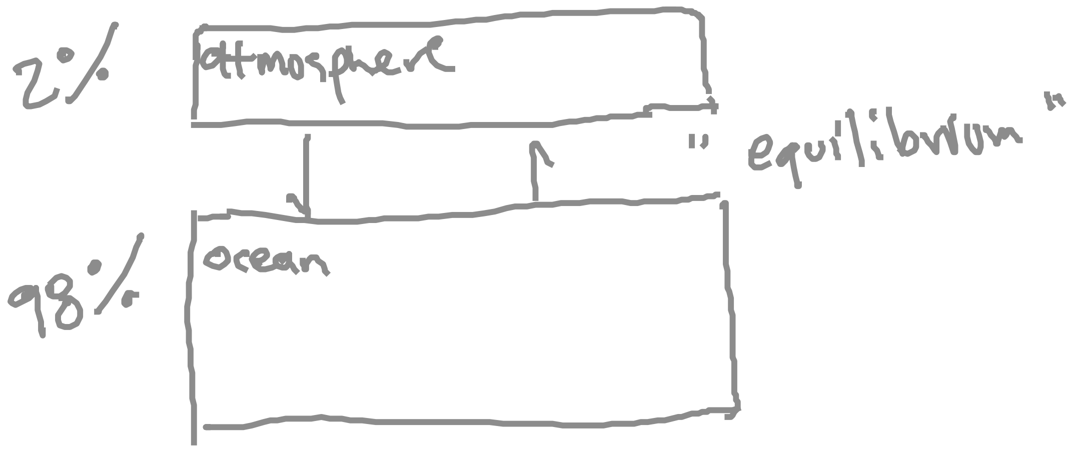
We acknowledge and respect the lək̓ʷəŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.

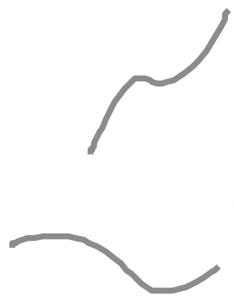
Carbon on a new timescale..

>1 Ma timescale



Now, we will consider:

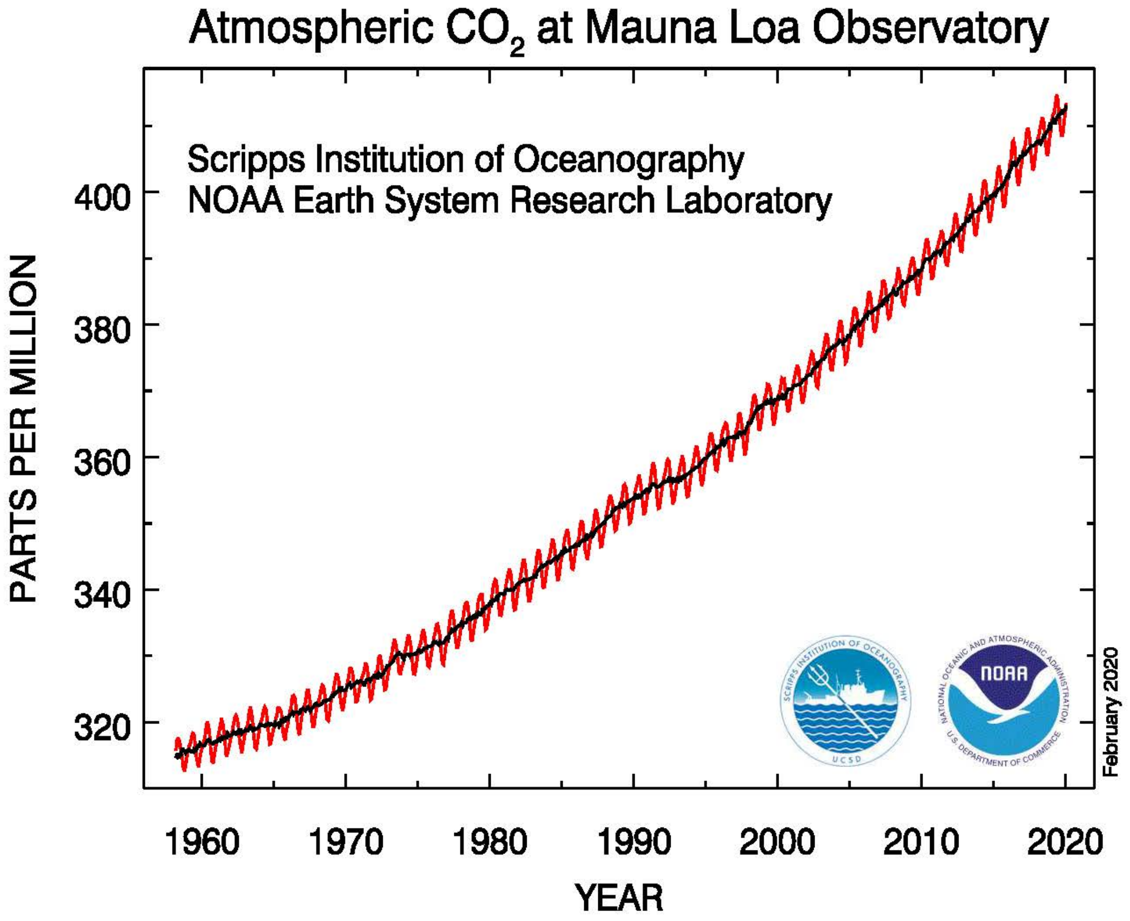




- How much C has to be added to the ocean/atmosphere for a given rise in pCO_2?
- Will that rate of <u>change</u> in the future?

(Yes)

Motivation:


Atmospheric CO_2 at Mauna Loa Observatory
Scripps Institution of Oceanography
NOAA Earth System Research Laboratory
PARTS PER MILLION
400
380
360
340
320
1960
1970
1980
1990
2000
2010
2020
YEAR
February 2020

The Carbonate System (at equilibrium)

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

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

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

$$K_1 = \frac{\overset{\textcircled{1}}{\underline{[H^+]}}\,\underline{[HCO_3^-]}\,\textcircled{2}}{\textcircled{3}\,\underline{[CO_2]}\,\cancel{[H_2O]} \rightarrow 1}$$

recall:

$pH = -\log_{10}[H^+]$

$K_1, K_2 = f(P, T, \text{salinity})$

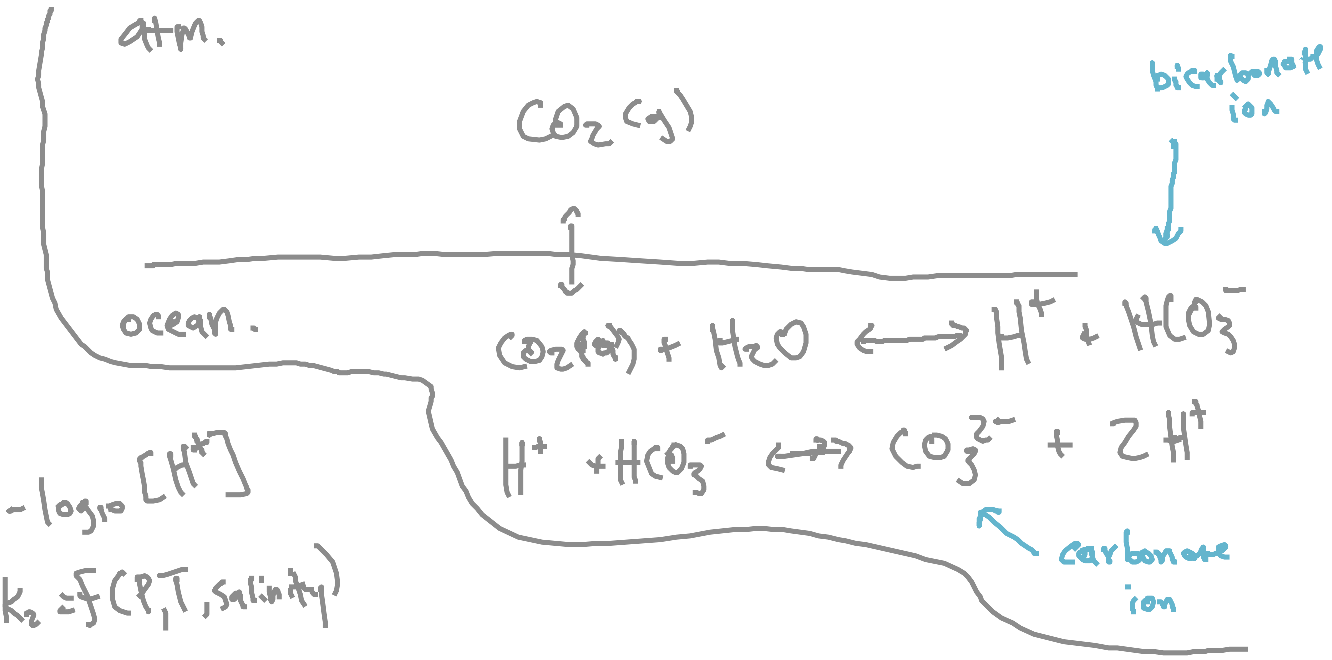
6 unknowns, 4 eqs.

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

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

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

④ Carbonate Alkalinity ≈ $\underset{\textcircled{6}}{\underline{\text{Total Alkalinity}}} = [HCO_3^-] + 2[CO_3^{2-}]$



Brief Total Alkalinity Intro

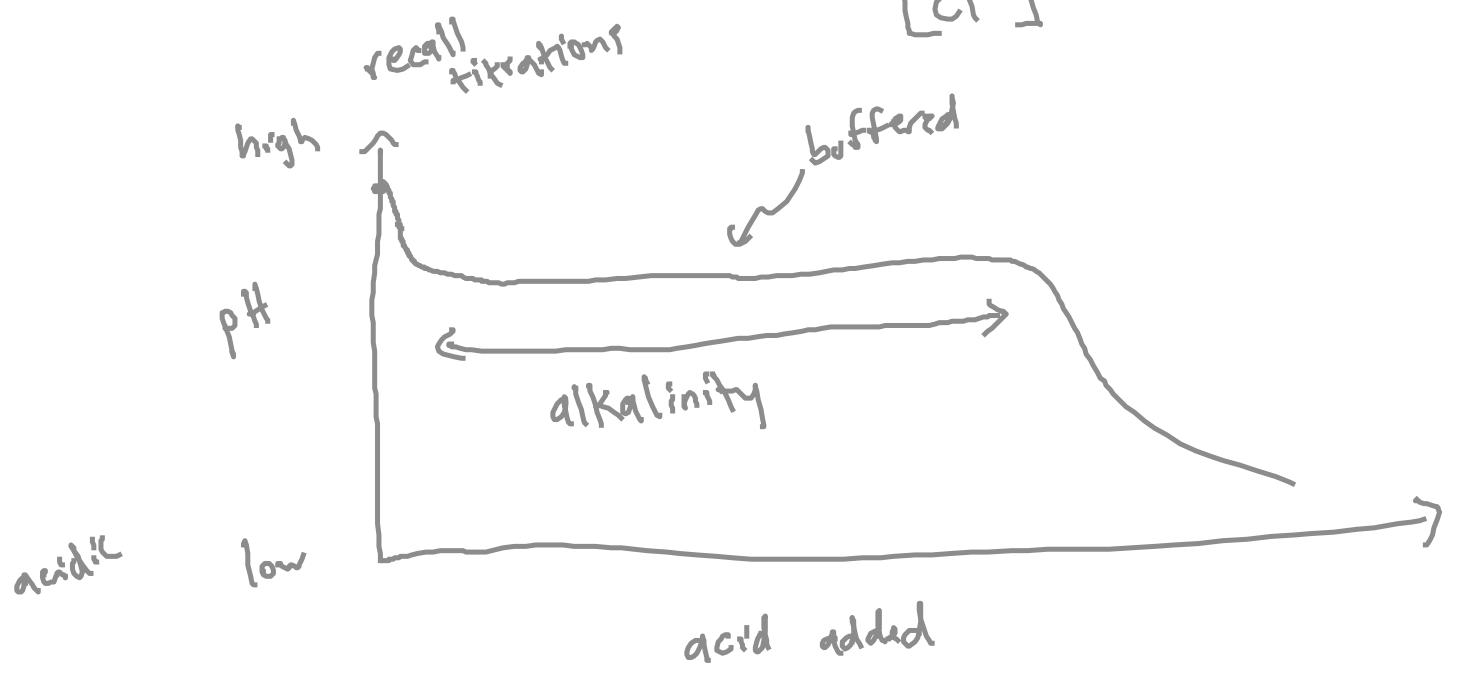
Total Alkalinity, $TA = [HCO_3^-] + 2[CO_3^{2+}] + [B(OH)_4^-] + [OH^-]$

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

conservative: not a function of T, pH, P

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

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



An exercise: relative abundance of carbon species in seawater

CA ≃ TA

Four eqs., six unknowns ⟶ 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: $[CO_2] = \frac{[HCO_3^-][H^+]}{K_1}$

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

$[HCO_3^{-}] \approx$

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

An exercise: relative abundance of carbon species in seawater

$CA \simeq TA$

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

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

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

$a = [HCO_3^-]$

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

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

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

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

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/ eq1

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

replace w/ eq2

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

$$pCO_2 = \frac{K_2}{K_0K_1} \cdot \frac{2[HCO_3^-]^2}{[CO_3^{2-}]}$$

$$pCO_2 = \frac{K_2}{K_0K_1} \cdot \frac{(2DIC - CA)^2}{CA - DIC}$$

only constant at fixed T, P, salinity

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

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

$$CA \approx TA$$

$$DIC = a + b$$

$$CA = a + 2b$$

$$DIC - b = a$$

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

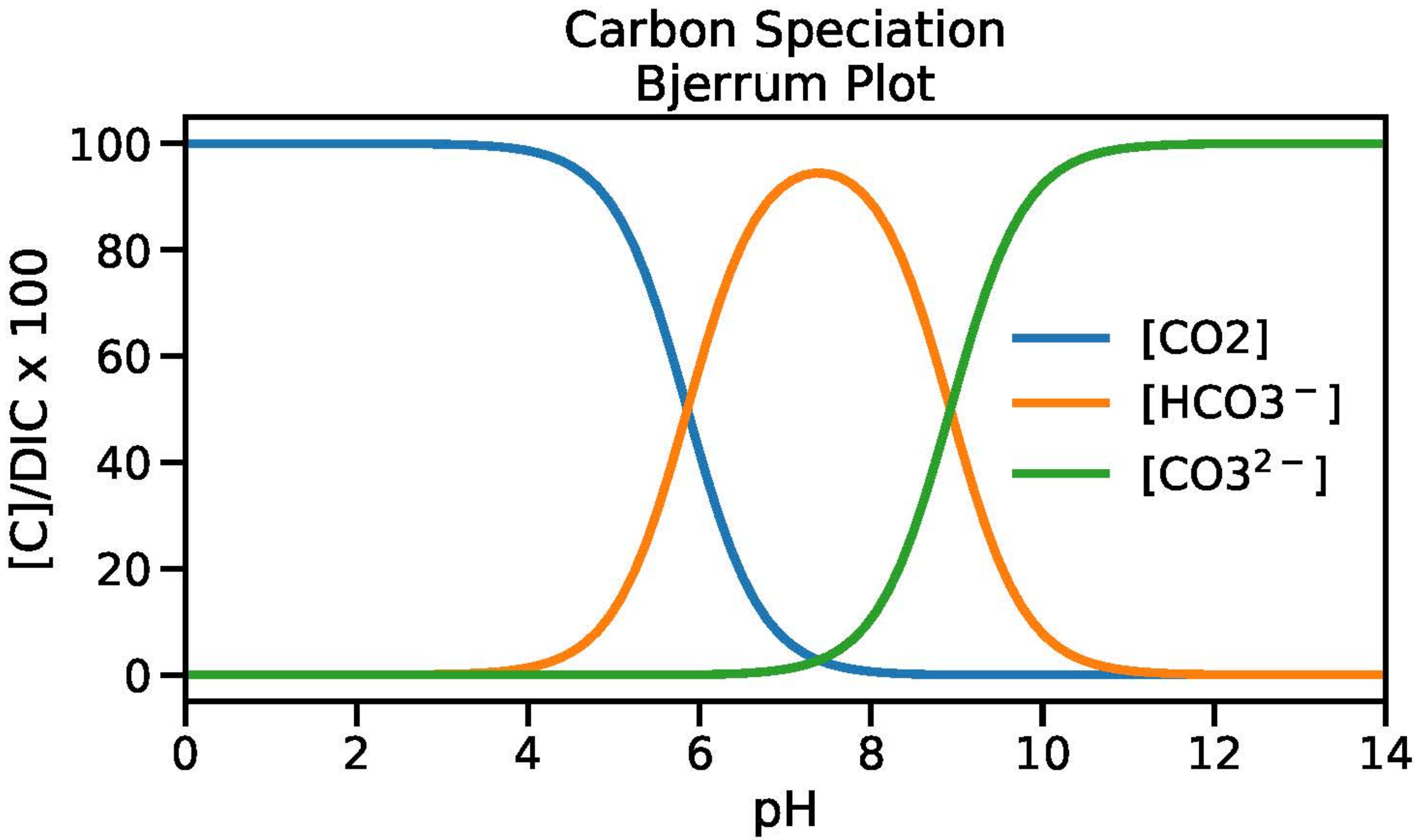
$$CA = DIC + b$$

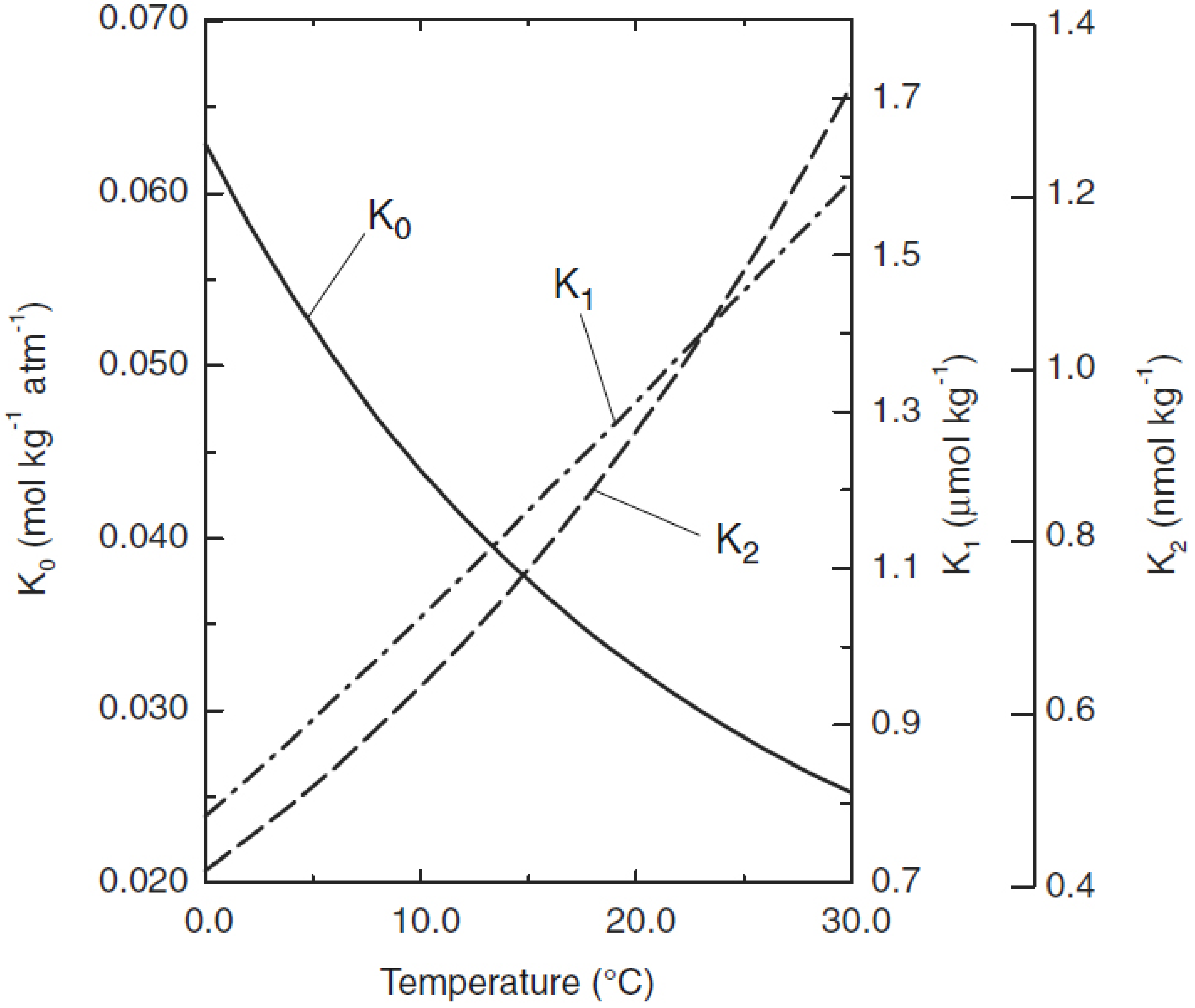
$$b = CA - DIC$$

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

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

calculation from previous slide

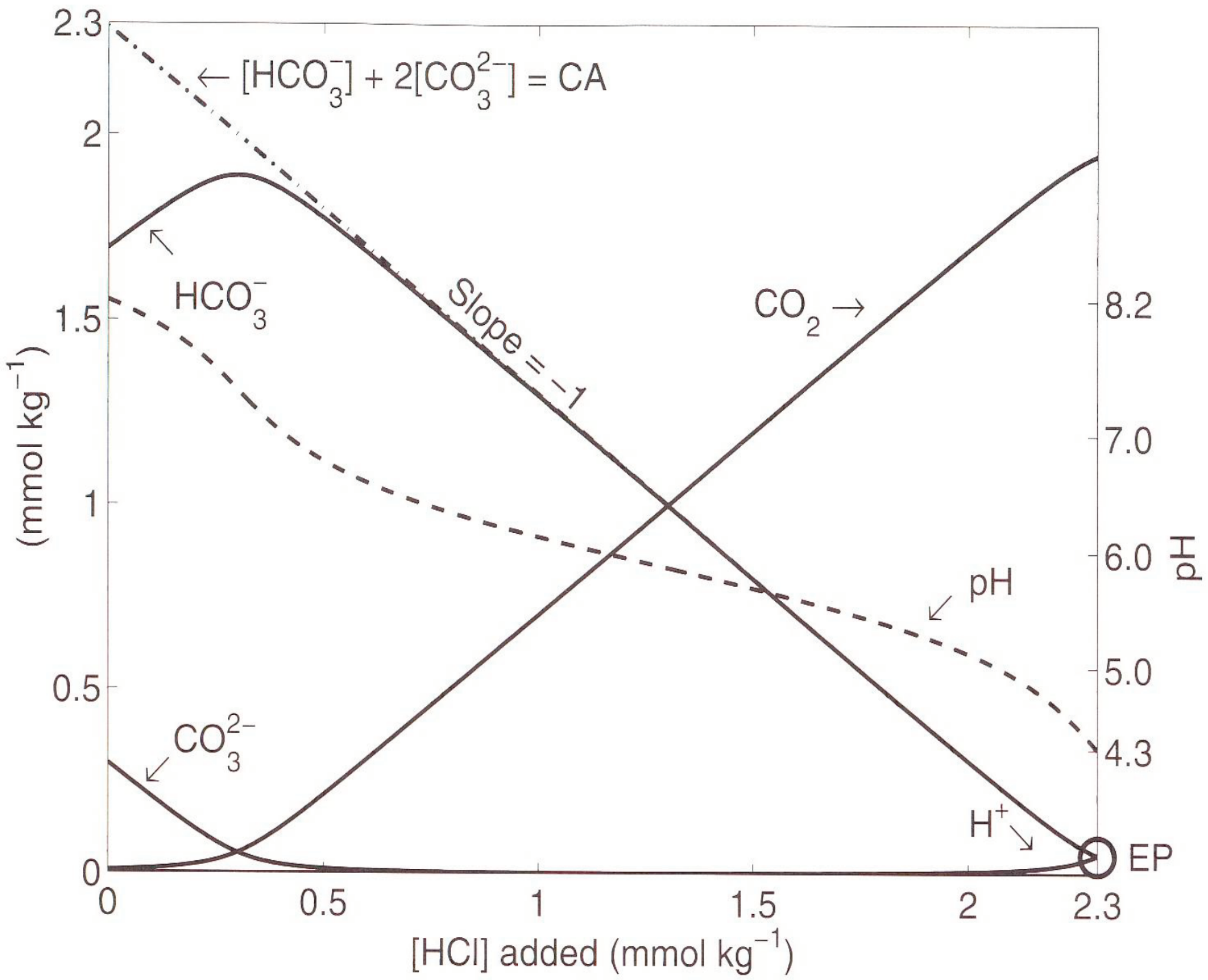

Carbon Speciation
Bjerrum Plot
[C]/DIC x 100
100
80
60
40
20
0
0
2
4
6
8
10
12
14
pH
[CO2]
[HCO3$^-$]
[CO3^{2-}]

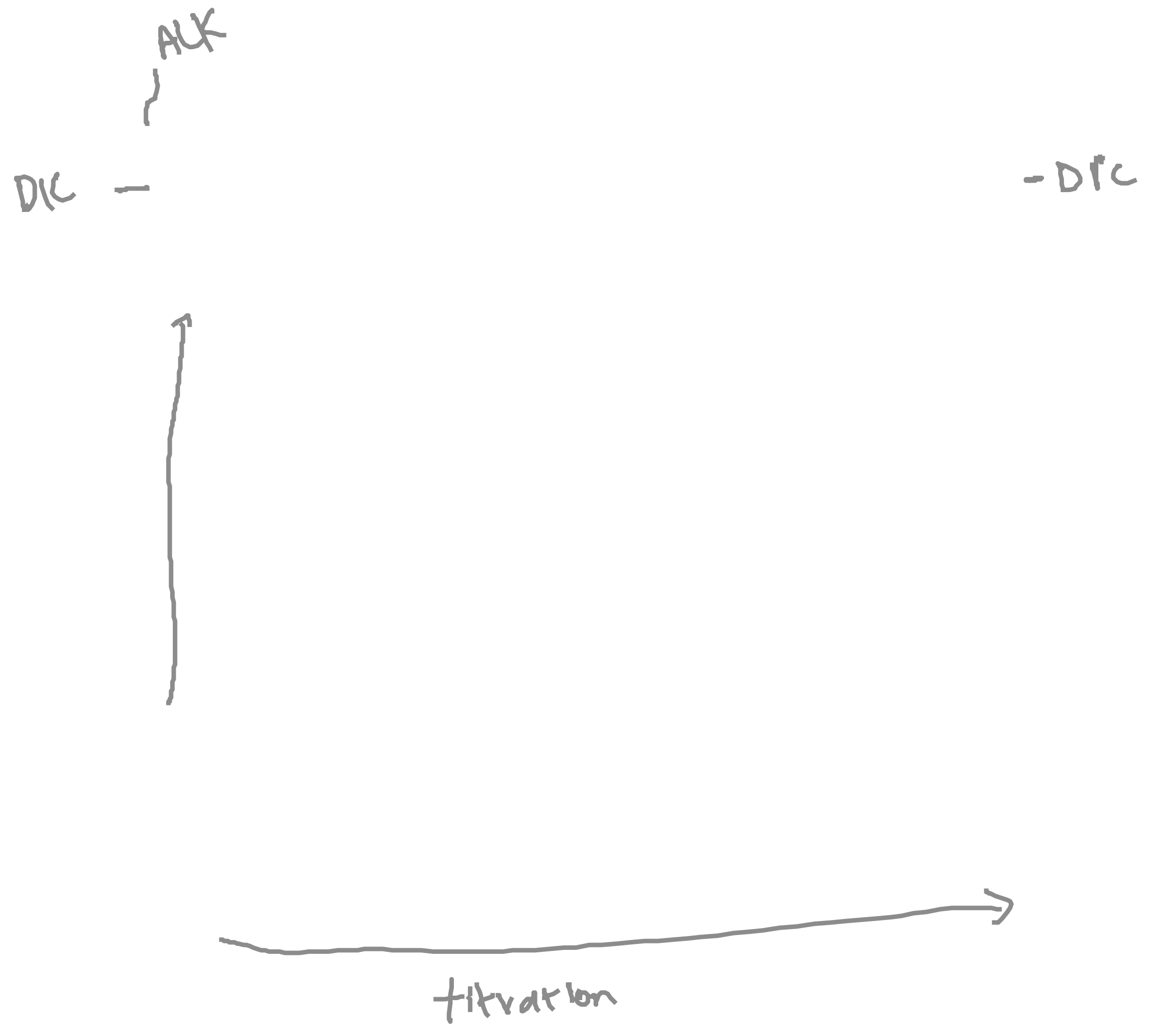


$$\frac{K_2}{K_0 K_1} \propto pCO_2 \approx \frac{1}{K_0}$$

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

pCO_2 ↗ as T ↗





[illegible] $[HCO_3^-]$ and $[CO_3^{2-}]$ to CO_2

$\sum$ charge of positive ions

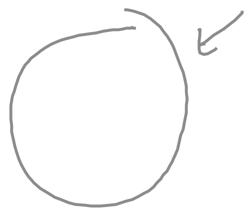
minus

$\sum$ charge of negative ions

$CA \approx TA$

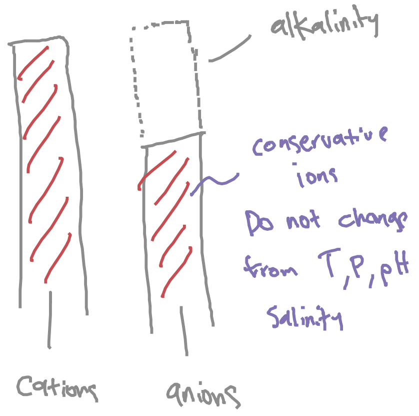
complicated form for (alkalinity)

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



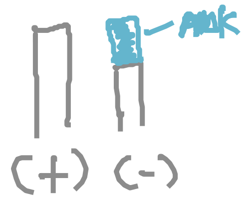
weak acids

- species that react w/ seawater



Do not change from T, P, pH Salinity

Alkalinity: real world examples



① Carbonate precipitation

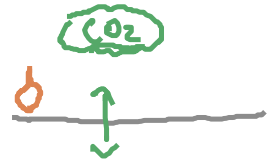
$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3 + H_2O + CO_2$$

How does DIC change?, -1 mol DIC

How does ALK change?, -2 mol ALK

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

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



ΔDIC: +1 mol

ΔALK: 0 change

③ Silicate weathering

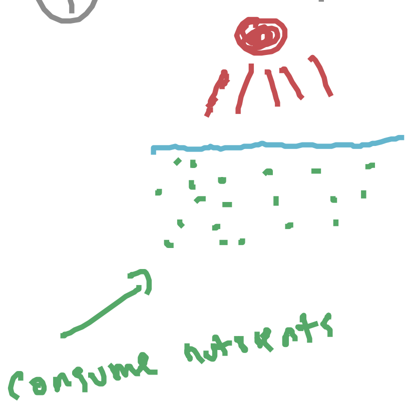
$$\overset{\text{silicate mineral}}{CaSiO_3} + 2\overset{\text{atm.}}{CO_2(g)} + 2\overset{\text{rain}}{H_2O} \longrightarrow \underbrace{Ca^{2+} + 2HCO_3^- + SiO_2}_{\text{dissolved in seawater}}$$

ΔDIC: +2

ΔALK: +2

Alkalinity: real world examples

④ Photosynthesis



(organic matter)

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

DIC: −1 mol

ALK: 0?

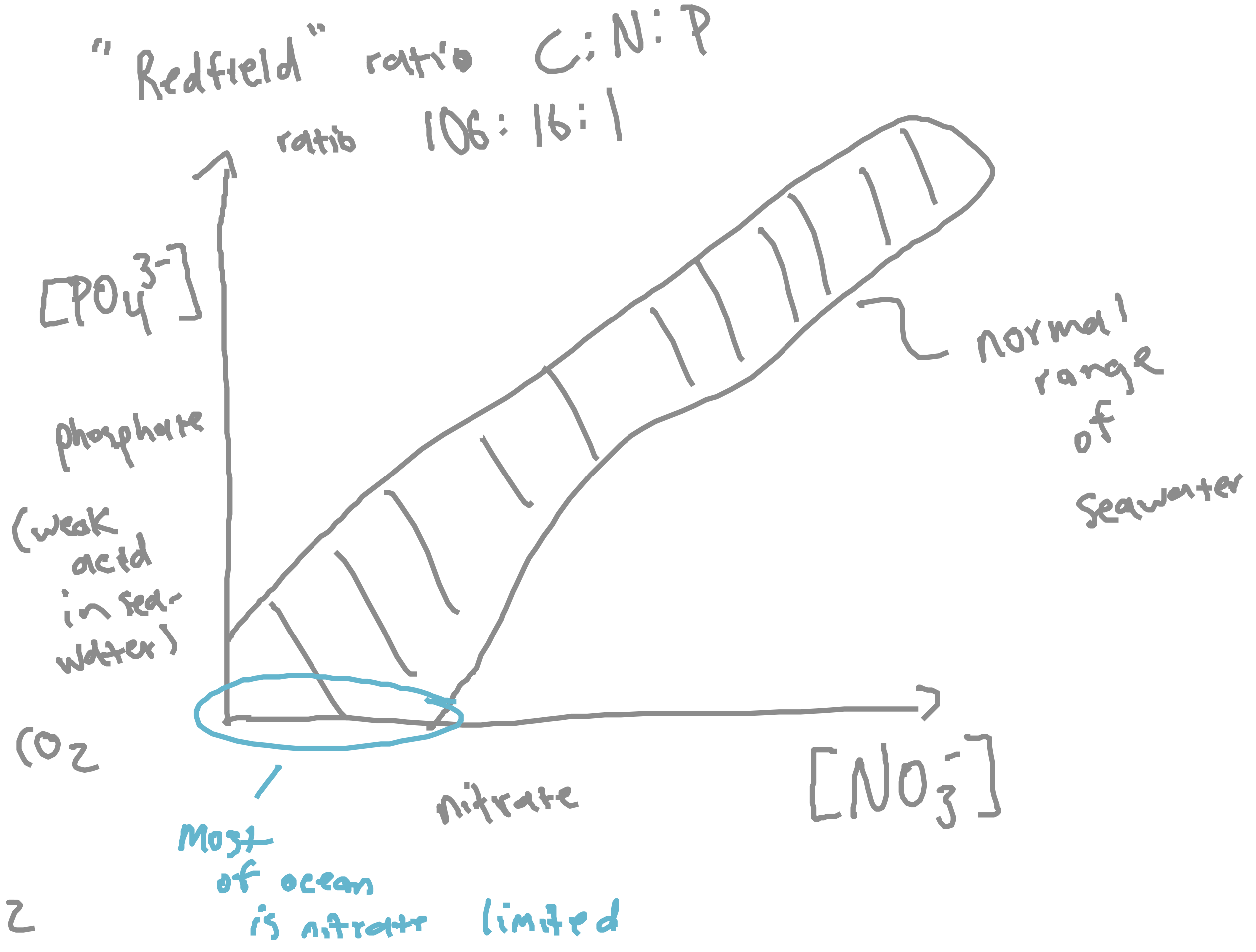
$1[PO_4^{3-}] + 16[NO_3^-] + 106 H_2O + 106 CO_2$

$\longrightarrow 106 CH_2O + O_2$

DIC: −106 mol / −1

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

ignore weak acid



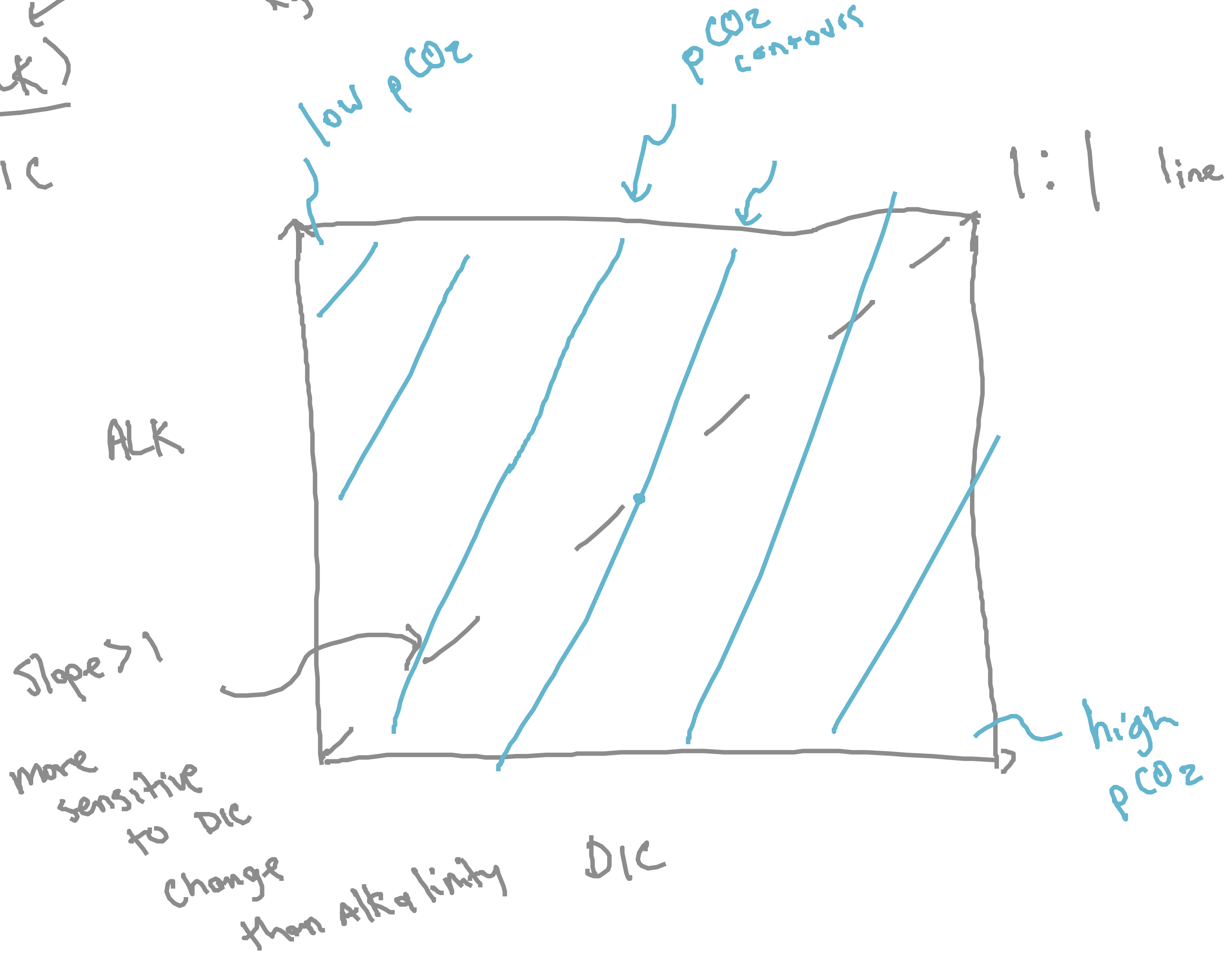
CO2, Alkalinity, and DIC

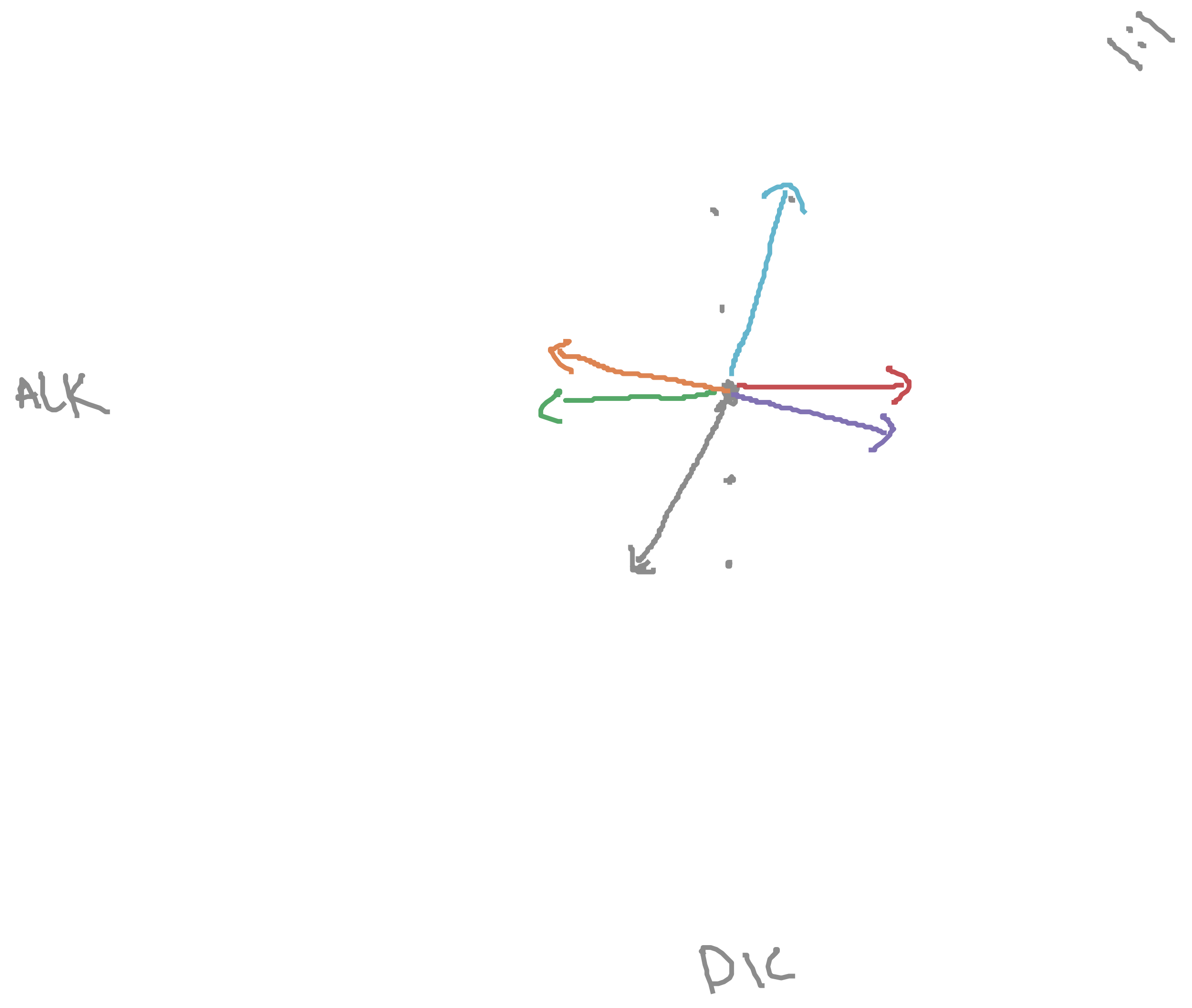
recall:

$$pCO_2 \approx \frac{K_2}{K_0 K_1} \cdot \frac{(2\,\overset{\text{in SW} \approx 2100\,\mu mol/kg}{DIC} - \overset{2300\,\mu mol/kg}{ALK})}{ALK - DIC}$$

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

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

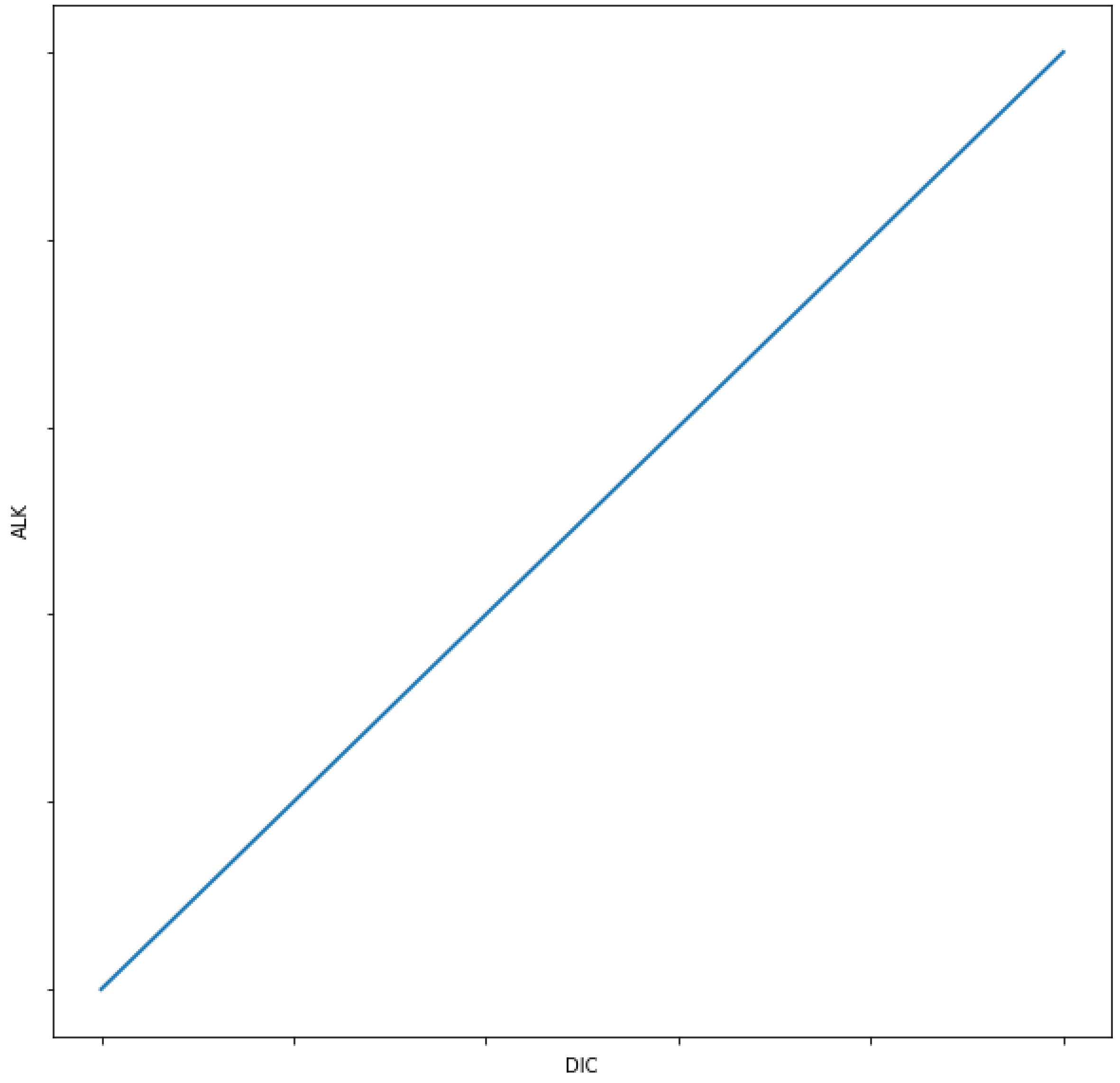


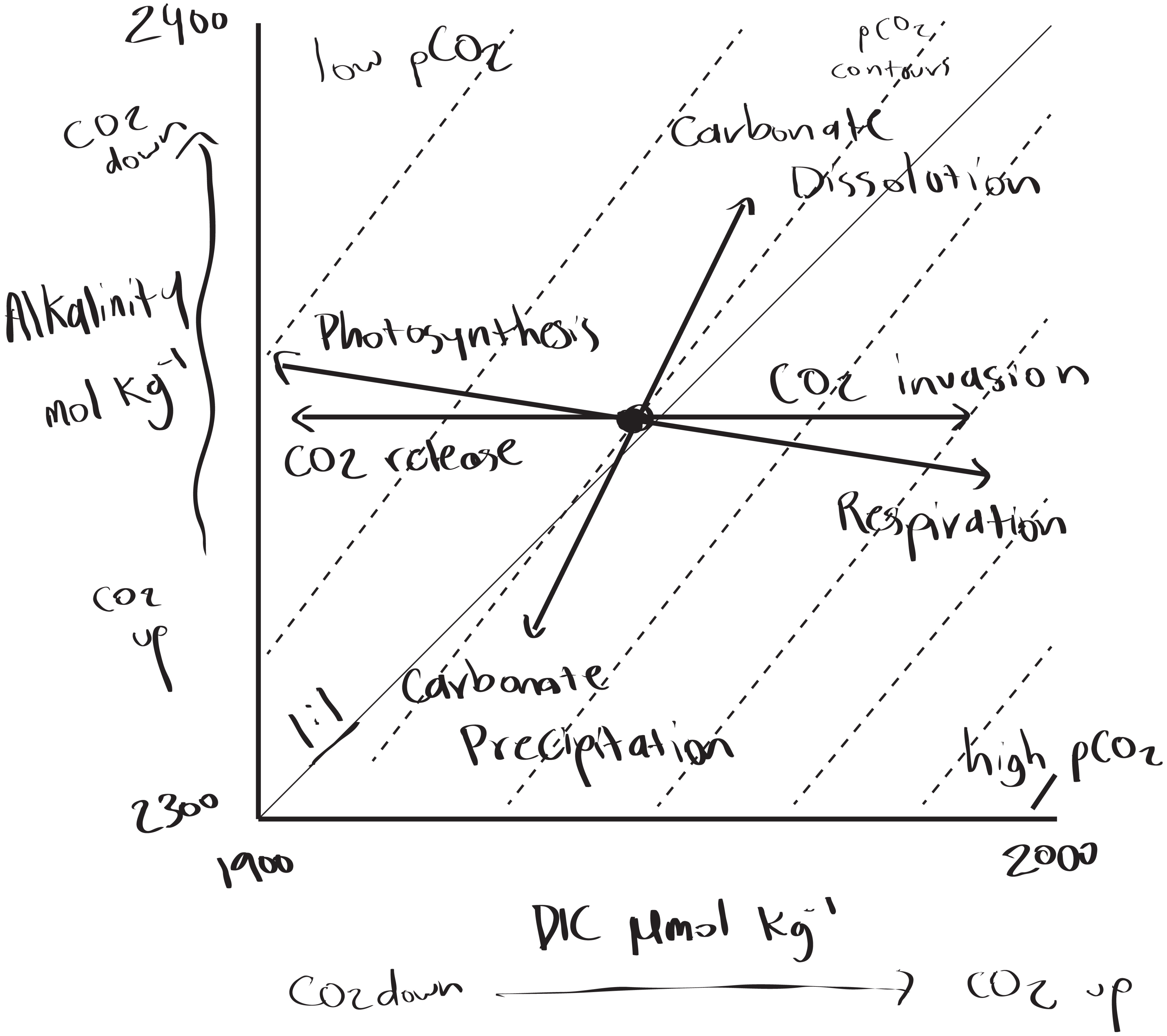


① carbonate precipitation
② carbonate dissolution
③ CO2 invasion
④ CO2 degassing
⑤ photosynthesis
⑥ respiration

In [4]:

```
fig = plt.figure(figsize=(10, 10))
plt.plot([0, 1], [0, 1], "-", lw=2)
_ = plt.gca().set_xticklabels([])
_ = plt.gca().set_yticklabels([])
plt.gca().set_xlabel("DIC")
plt.gca().set_ylabel("ALK")
sns.set_context("poster")
```




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

Carbonate Saturation State

$$CaCO_3 \underset{K_{sp}}{\longleftrightarrow} [Ca^{2+}] + [CO_3^{2-}]$$

$$K_{sp} = \frac{[Ca^{2+}] \cdot [CO_3^{2-}]}{1}$$

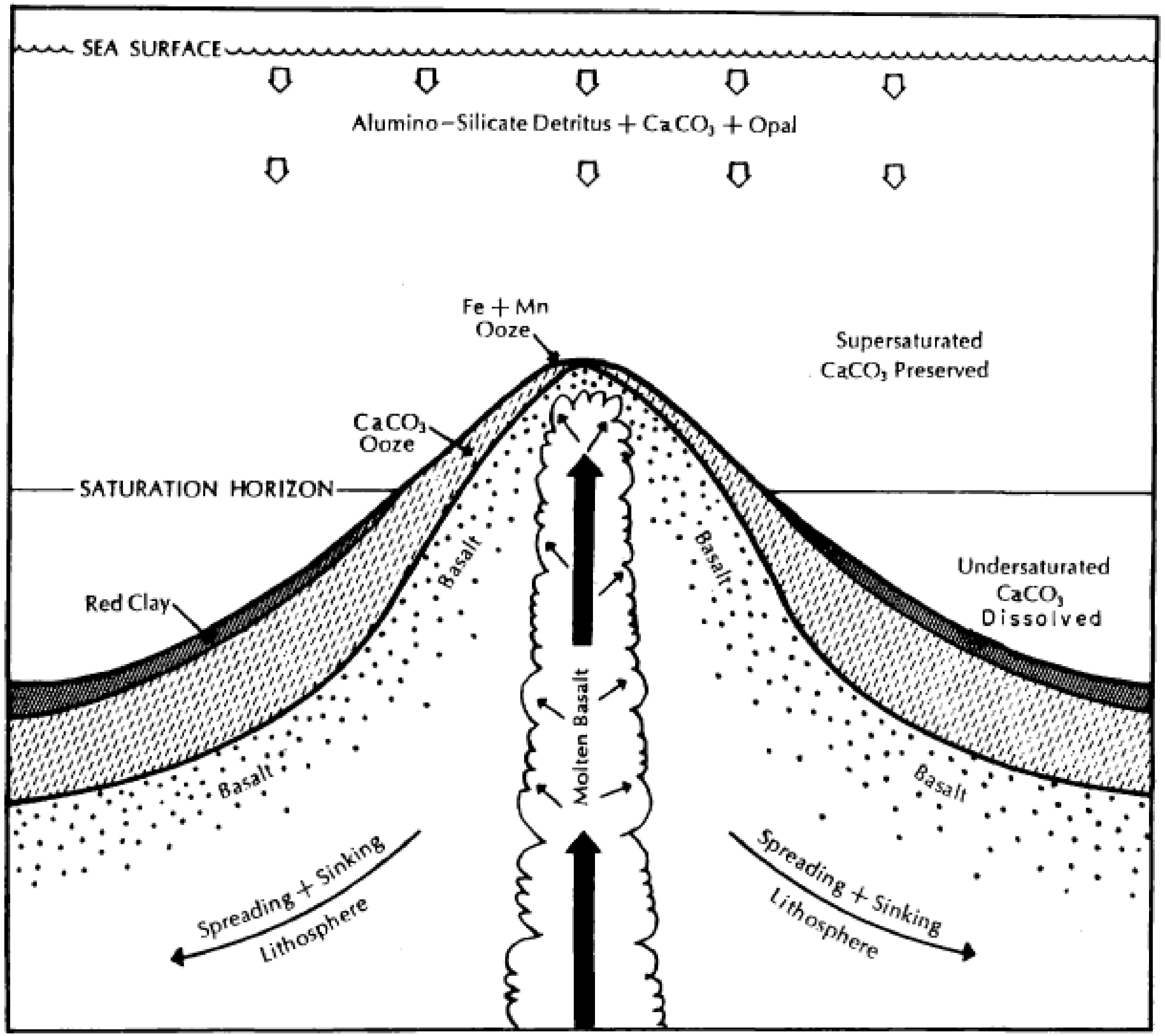
$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}}$$

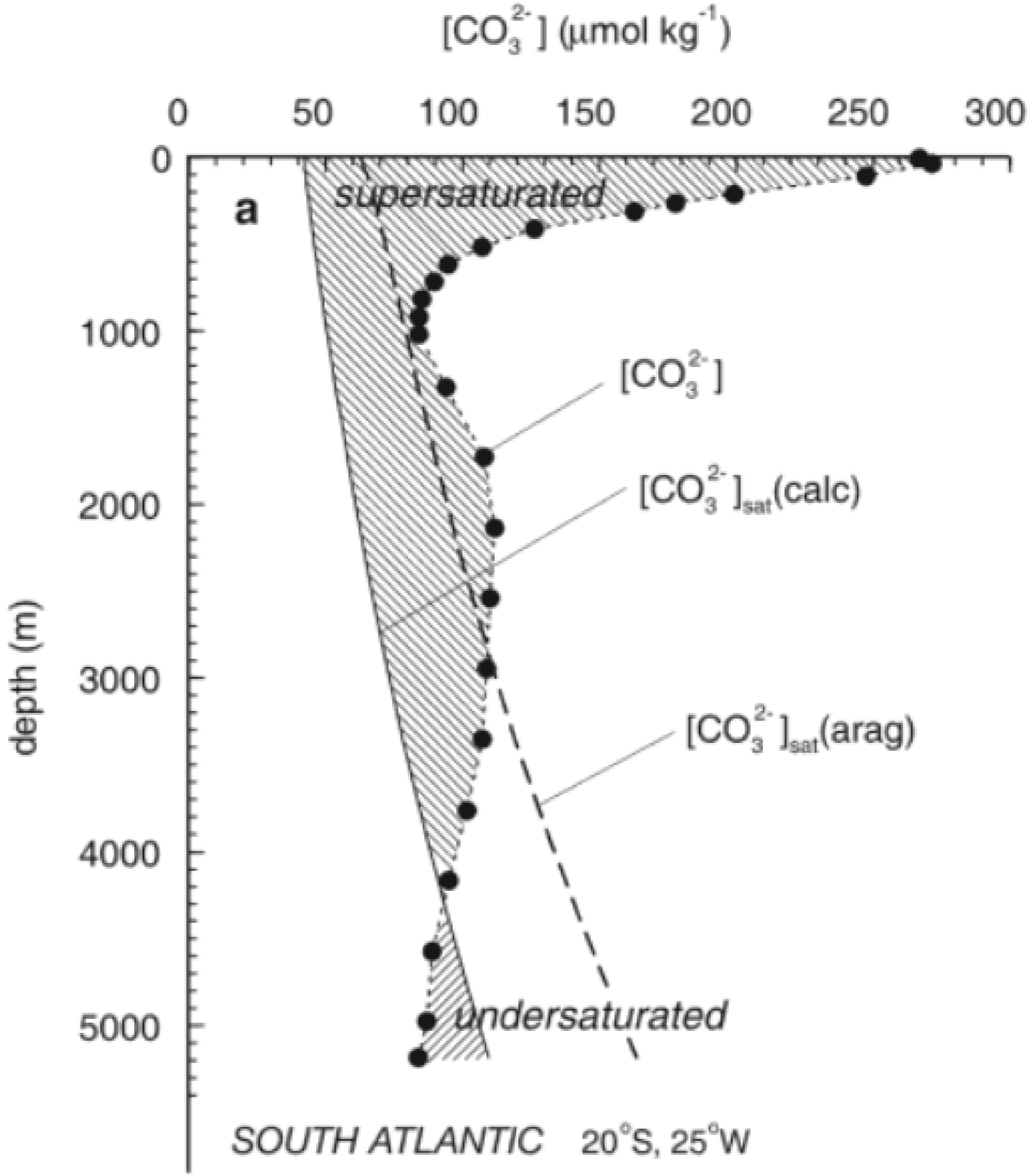
Ω, saturation state

$\Omega = 1$, equilibrium, saturated

$\Omega < 1$, undersaturated

$\Omega > 1$, supersaturated


SEA SURFACE
Alumino – Silicate Detritus + CaCO₃ + Opal
Fe + Mn Ooze
Supersaturated CaCO₃ Preserved
CaCO₃ Ooze
SATURATION HORIZON
Basalt
Basalt
Red Clay
Undersaturated CaCO₃ Dissolved
Molten Basalt
Basalt
Basalt
Spreading + Sinking Lithosphere
Spreading + Sinking Lithosphere


[CO$_3^{2-}$] (μmol kg^{-1})
0
50
100
150
200
250
300
0
1000
2000
3000
4000
5000
depth (m)
a
supersaturated
[CO$_3^{2-}$]
[CO$_3^{2-}$]$_{sat}$(calc)
[CO$_3^{2-}$]$_{sat}$(arag)
undersaturated
SOUTH ATLANTIC 20°S, 25°W