Lecture 17: CO2 in seawater

1. Stable isotope fractionation example
2. Climate wrap up
3. CO2 in seawater

We acknowledge and respect the lək^{w}əŋən 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.

Stable isotopes: equilibrium example

$$H_2O(l) + HDS(g) \rightleftharpoons HDO(l) + H_2S(g)$$

K is equilibrium constant $K = \frac{[HDO][H_2S]}{[HDS][H_2O]} \neq 1 = \alpha$ "fractionation factor"

* $\Delta G^{\circ} = \Delta G_0 + RT \ln Q$

at equilibrium $\Delta G_0 = -RT \ln K$

$\Delta E_2 - \Delta E_1 \approx -RT \ln K$

$-1(\Delta E_2 - \Delta E_1) \approx -RT \ln K$

$\frac{\Delta E_1 - \Delta E_2}{RT} \approx \ln K$

to get to products ΔG_0 reactants

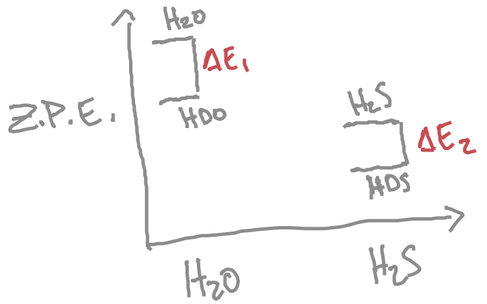
$H_2S + HDO - HDS - H_2O$

$H_2S - HDS + HDO - H_2O$

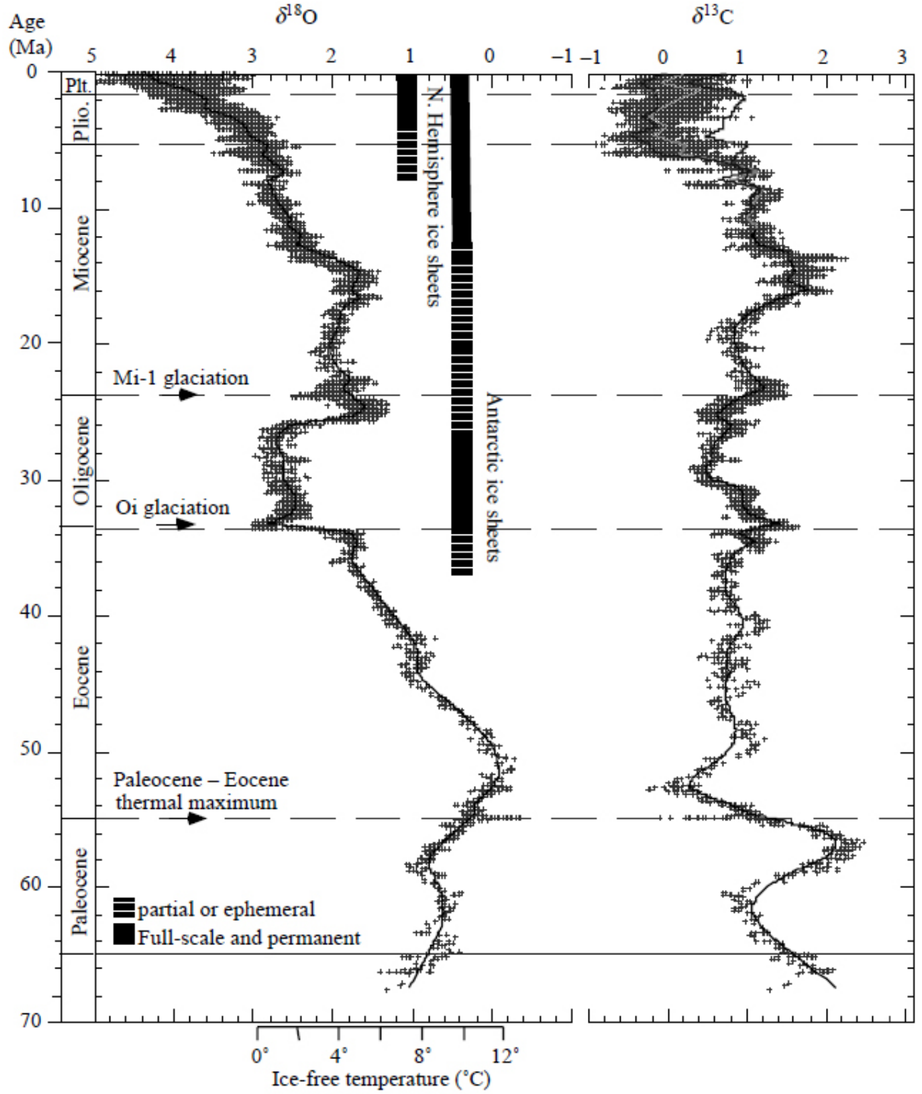
$-1(H_2O - HDO)$

$(H_2S - HDS) - (H_2O - HDO)$

$\Delta E_2 \quad \Delta E_1$



General Rule: heavy isotopes prefer to go into the chemical compound that is more strongly bonded



Compilation from Zachos *et al.*, 2001

colder
+

warmer
−

$\delta^{18}O$ of forams ↗

↳ ice volume ↗

↳ lower temp.

icehouse

greenhouse

hot

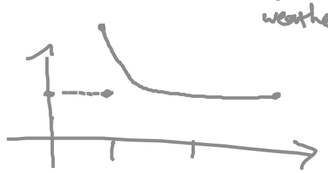
hypothesis 1: Volcanic degassing decreases over the last 50 mA

recall

mass of CO_2

$$\frac{dM}{dt} = F_{in} - KM$$

↑ weatherability

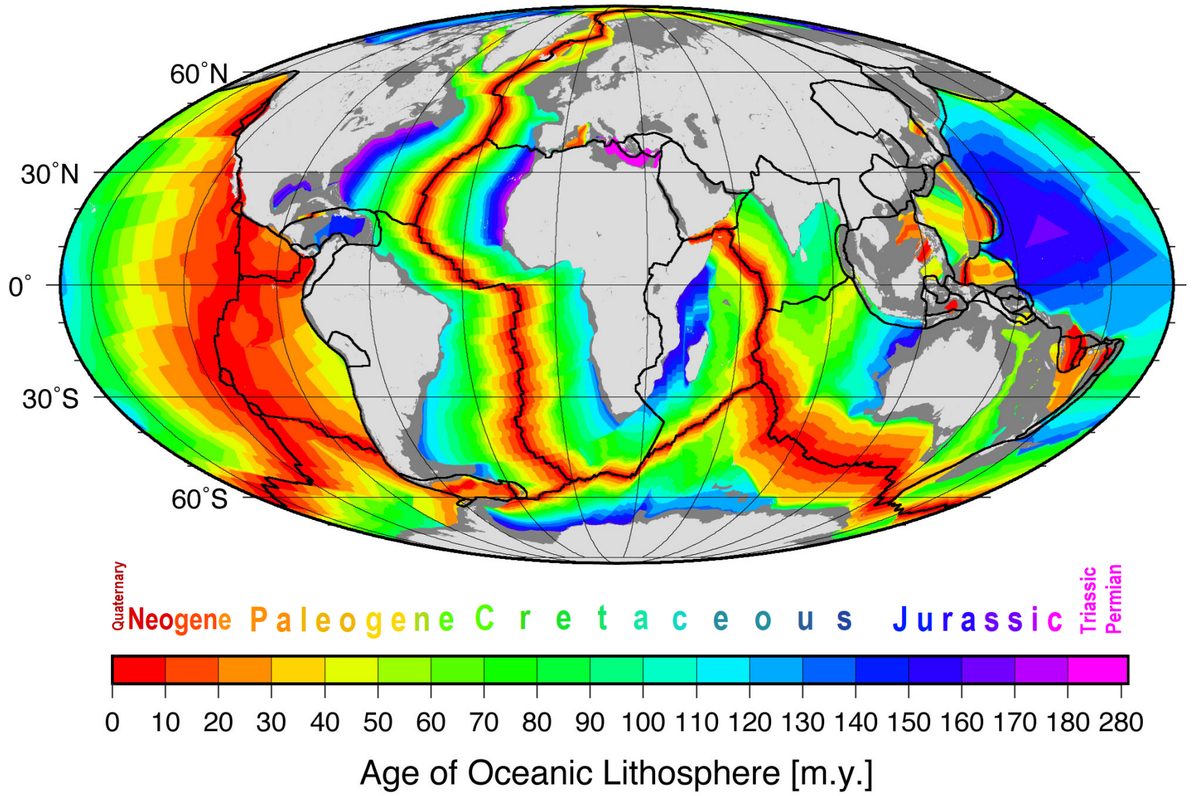


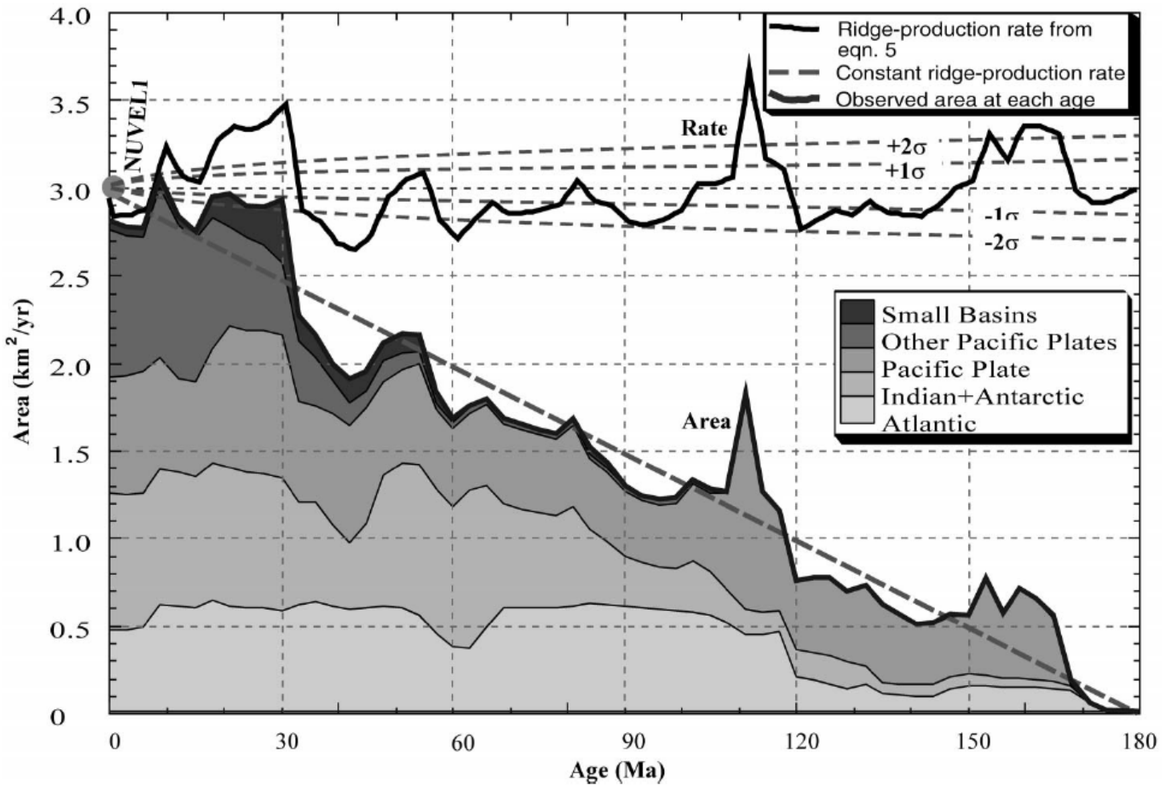
$$\frac{dM}{dt} = 0 \quad \text{at steady state}$$

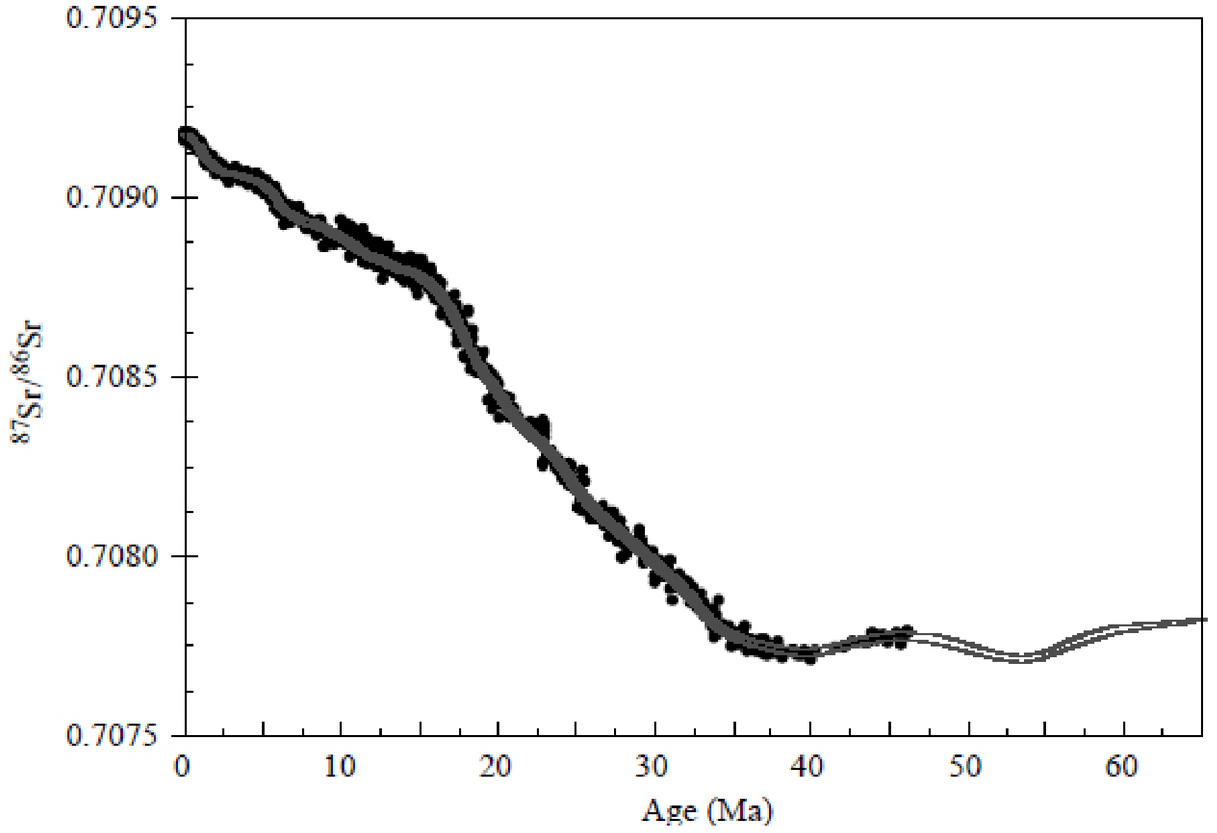
$$0 = F_{in} - K \cdot M$$

$$F_{in} = KM$$

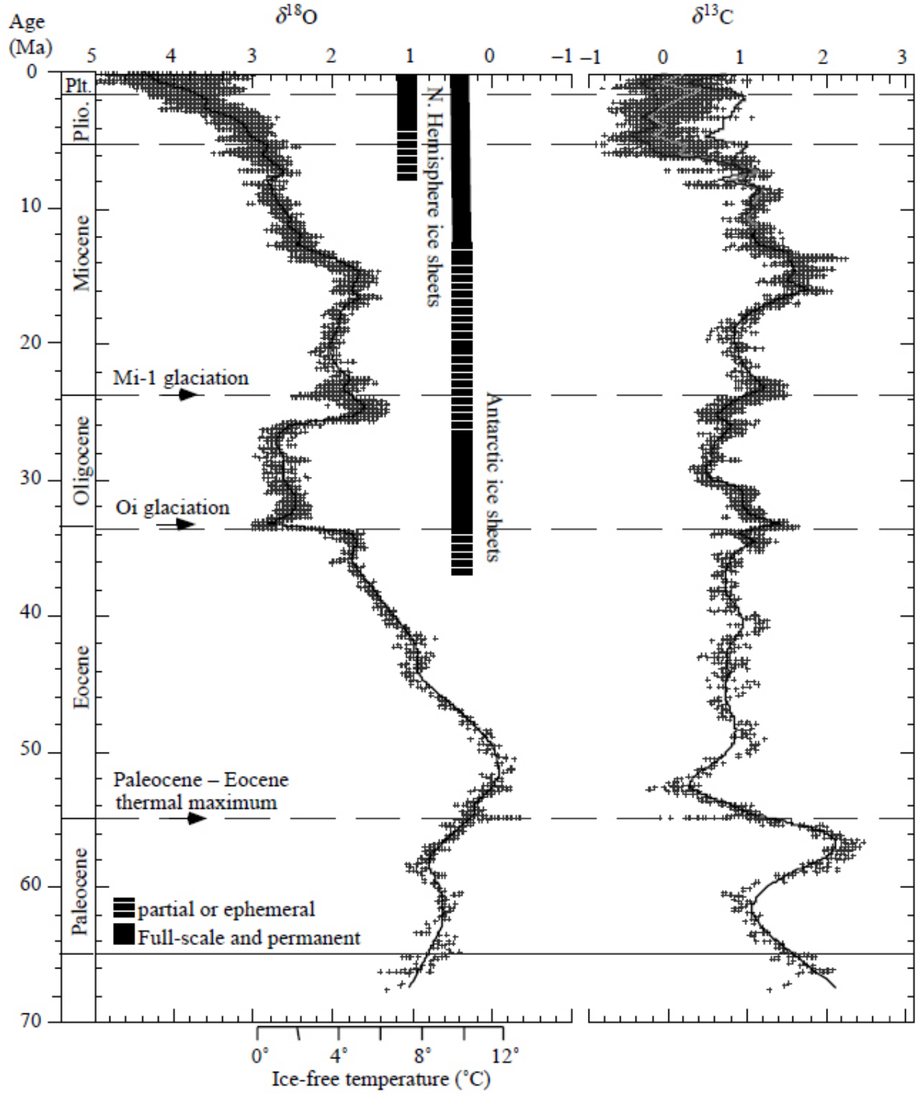
$$\frac{F_{in}}{K} = M$$


60˚N
30˚N
0˚
30˚S
60˚S
Quaternary
Neogene
Paleogene
Cretaceous
Jurassic
Triassic
Permian
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 280
Age of Oceanic Lithosphere [m.y.]

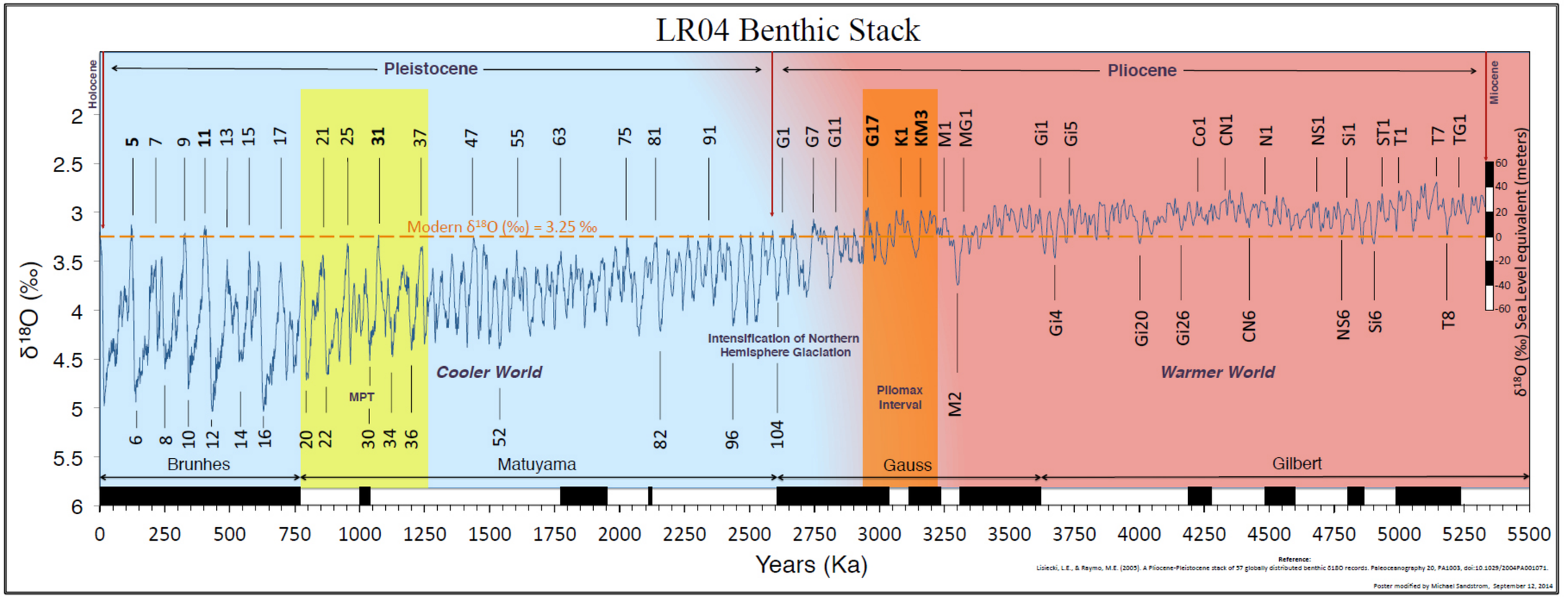

Ridge-production rate from eqn. 5
Constant ridge-production rate
Observed area at each age
Rate
+2σ
+1σ
-1σ
-2σ
NUVEL1
Area
Small Basins
Other Pacific Plates
Pacific Plate
Indian+Antarctic
Atlantic
Area (km²/yr)
Age (Ma)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
30
60
90
120
150
180



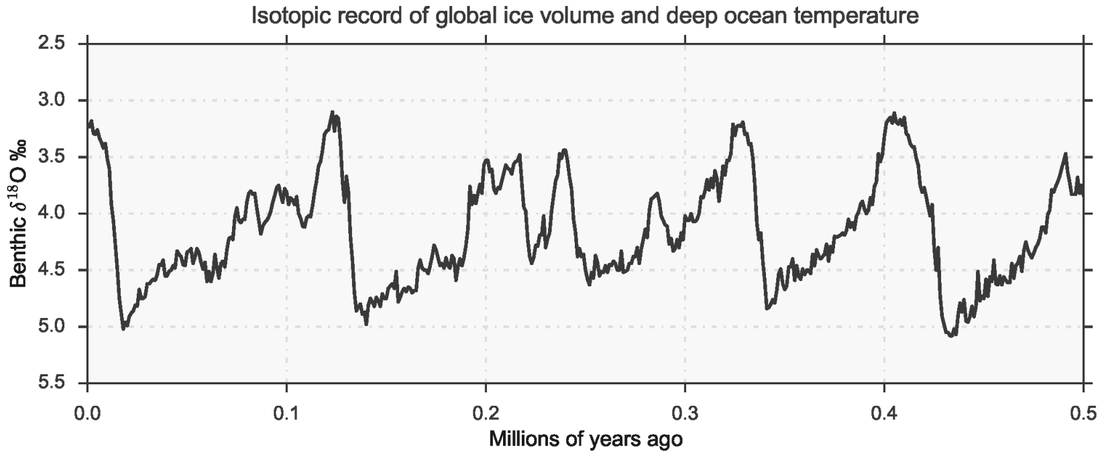
Compilation from Ravizza and Zachos, 2003



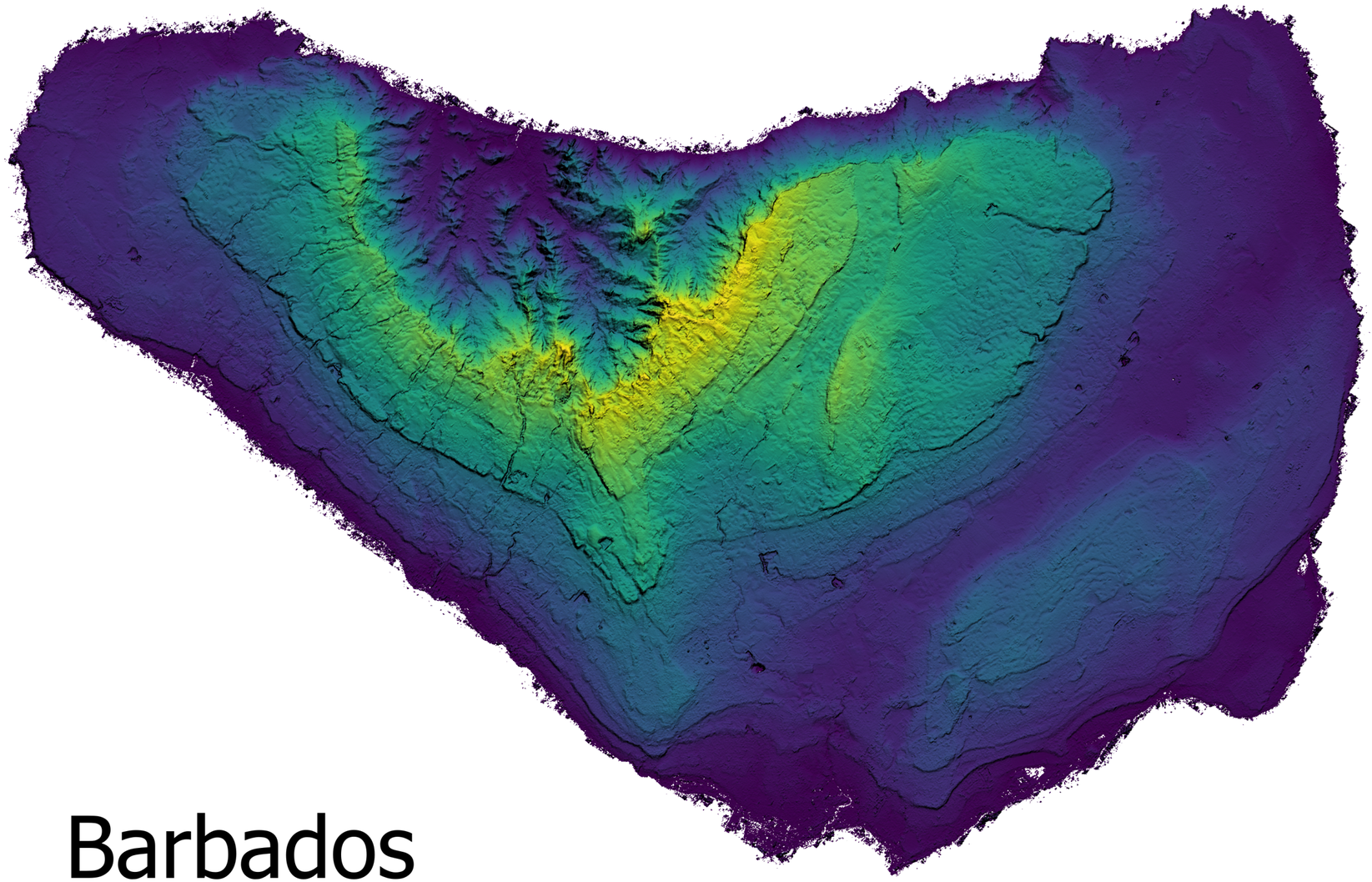
Compilation from Zachos *et al.*, 2001



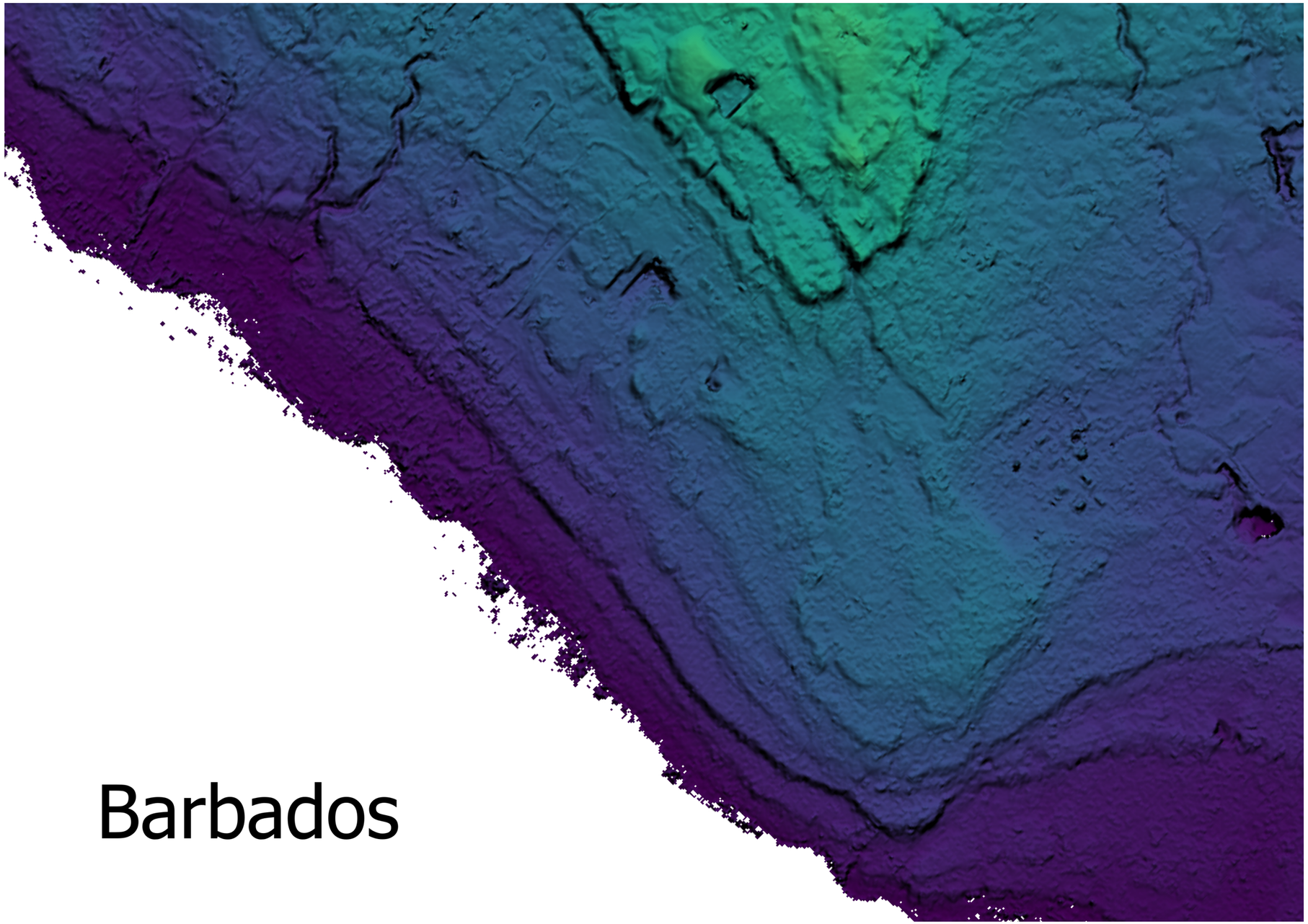
from Lisiecki and Raymo, 2004


Isotopic record of global ice volume and deep ocean temperature
Benthic $\delta^{18}O$ ‰
2.5
3.0
3.5
4.0
4.5
5.0
5.5
0.0
0.1
0.2
0.3
0.4
0.5
Millions of years ago

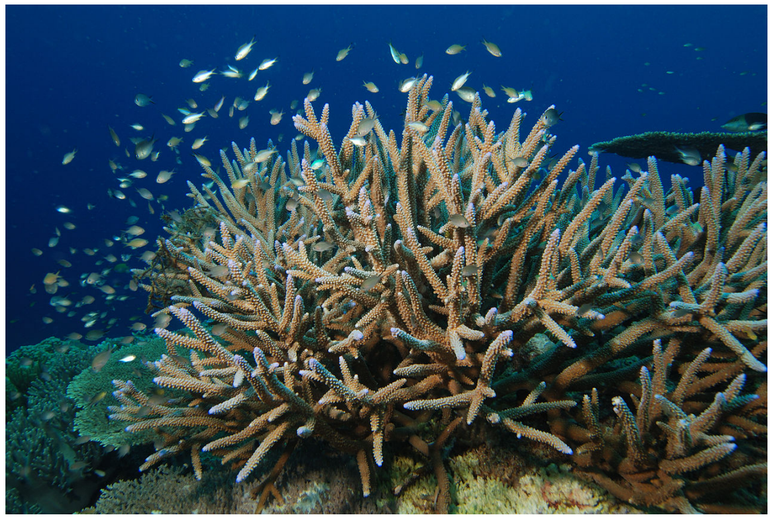

Barbados

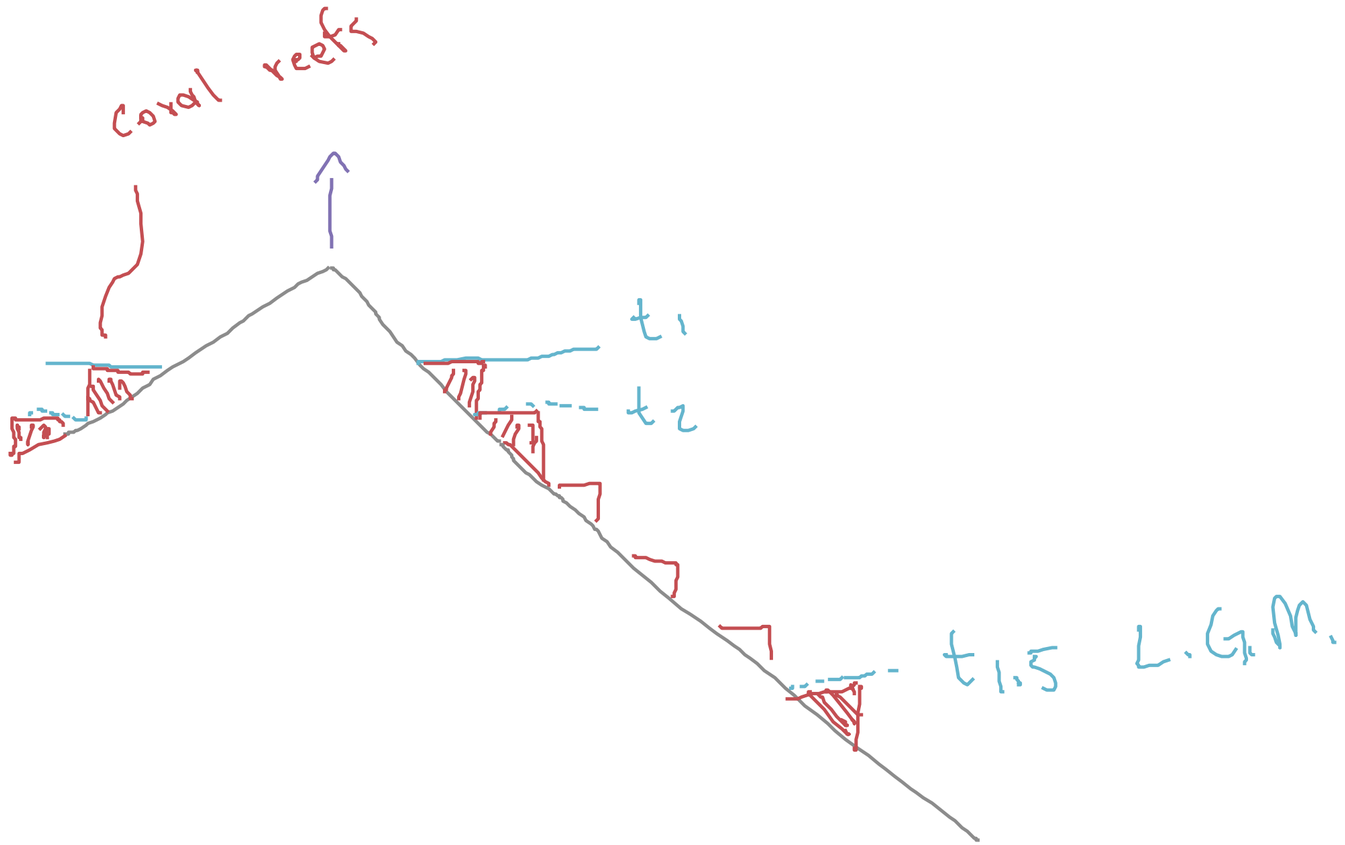


Barbados

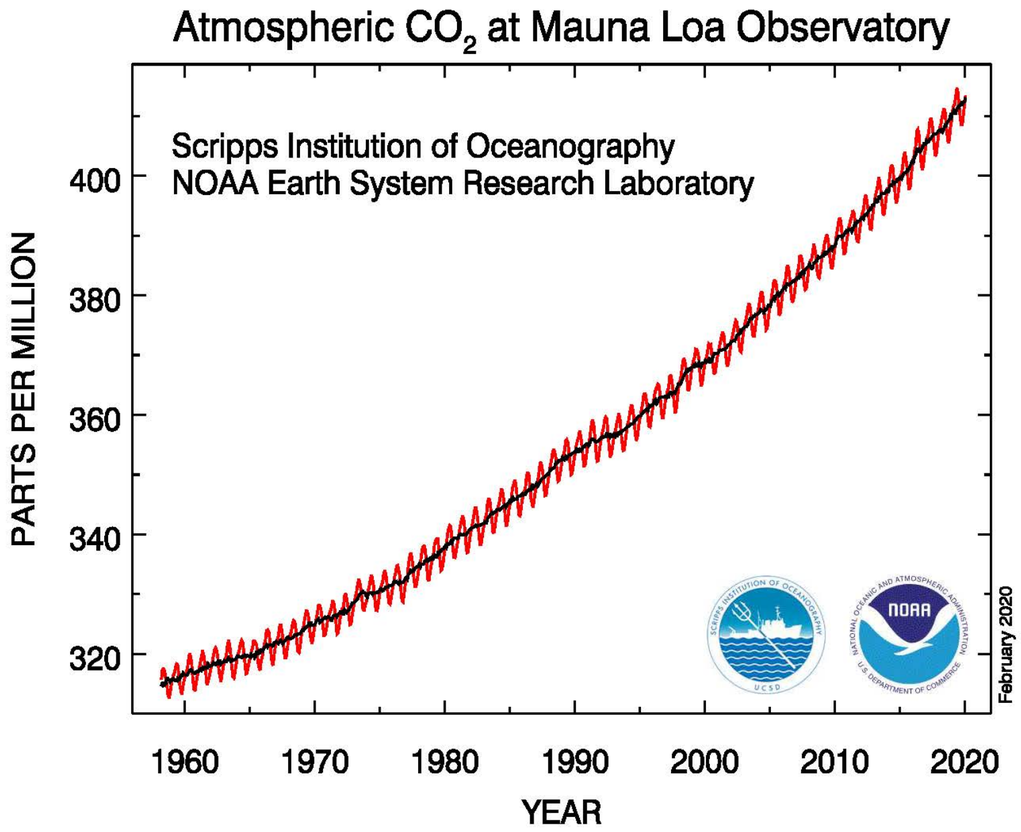


Barbados




Coral reefs
t1
t2
t1.5
L.G.M.

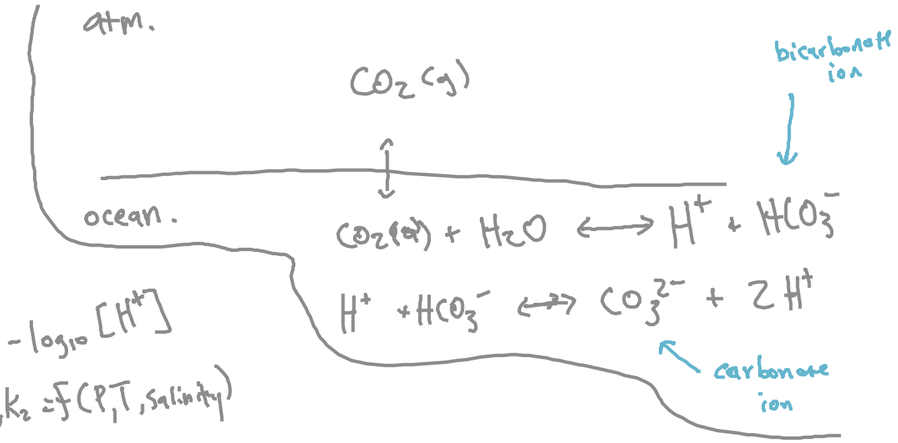
Motivation:


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)

$CO_2(g) \overset{K_0}{\longleftrightarrow} CO_2(aq)$

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



① $CO_2(aq) + H_2O \overset{K_1}{\longleftrightarrow} H^+ + HCO_3^-$

$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2][H_2O]}$ ≈ 1

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

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

6 unknowns, 4 eqs.

② $HCO_3^- + H^+ \overset{K_2}{\longleftrightarrow} CO_3^{2-} + 2H^+$

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

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

④ Carbonate Alkalinity ≈ Total Alkalinity ⑥ $= [HCO_3^-] + 2[CO_3^{2-}]$