INTRODUCTION TO CO_2 CHEMISTRY IN SEA WATER

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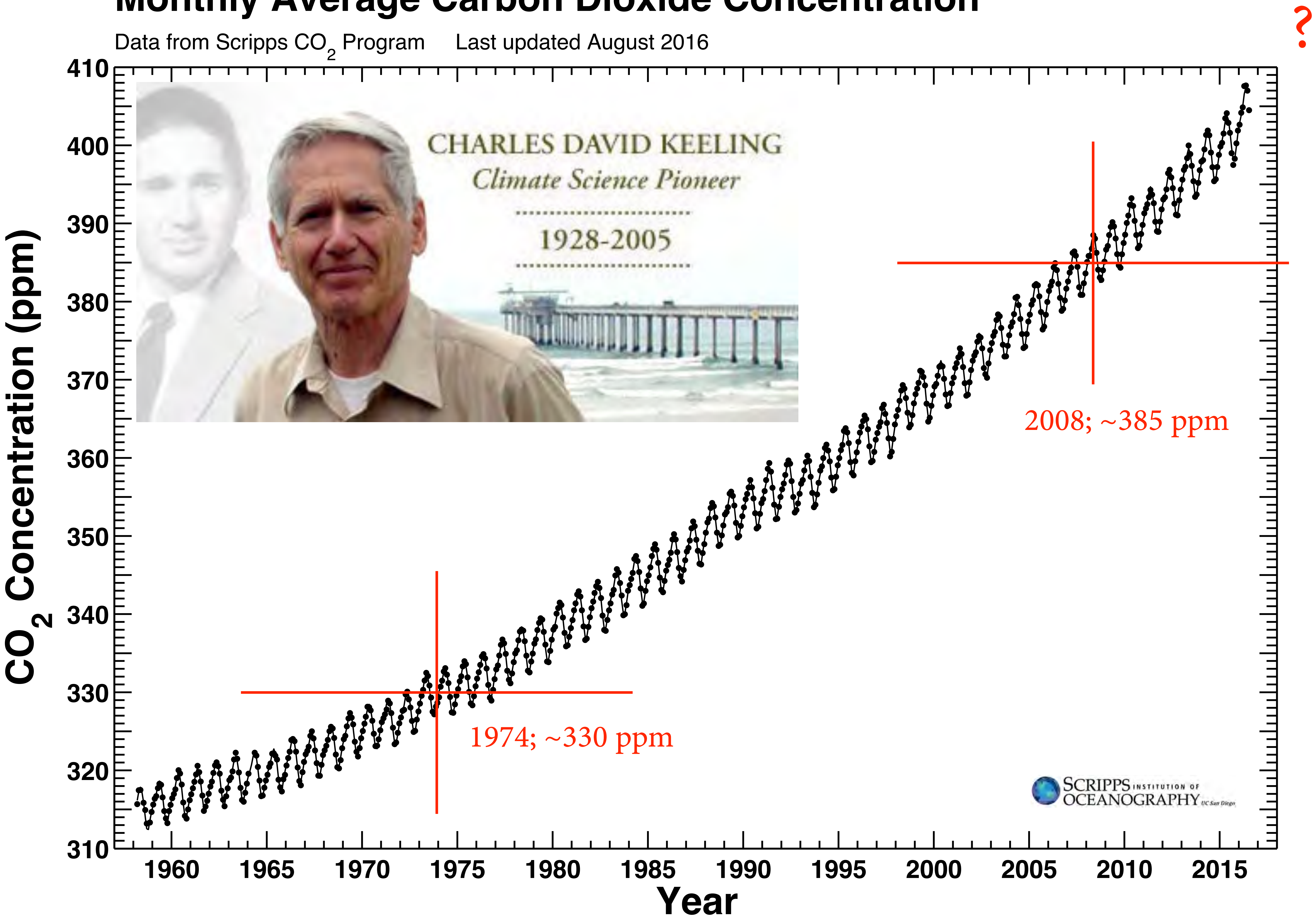
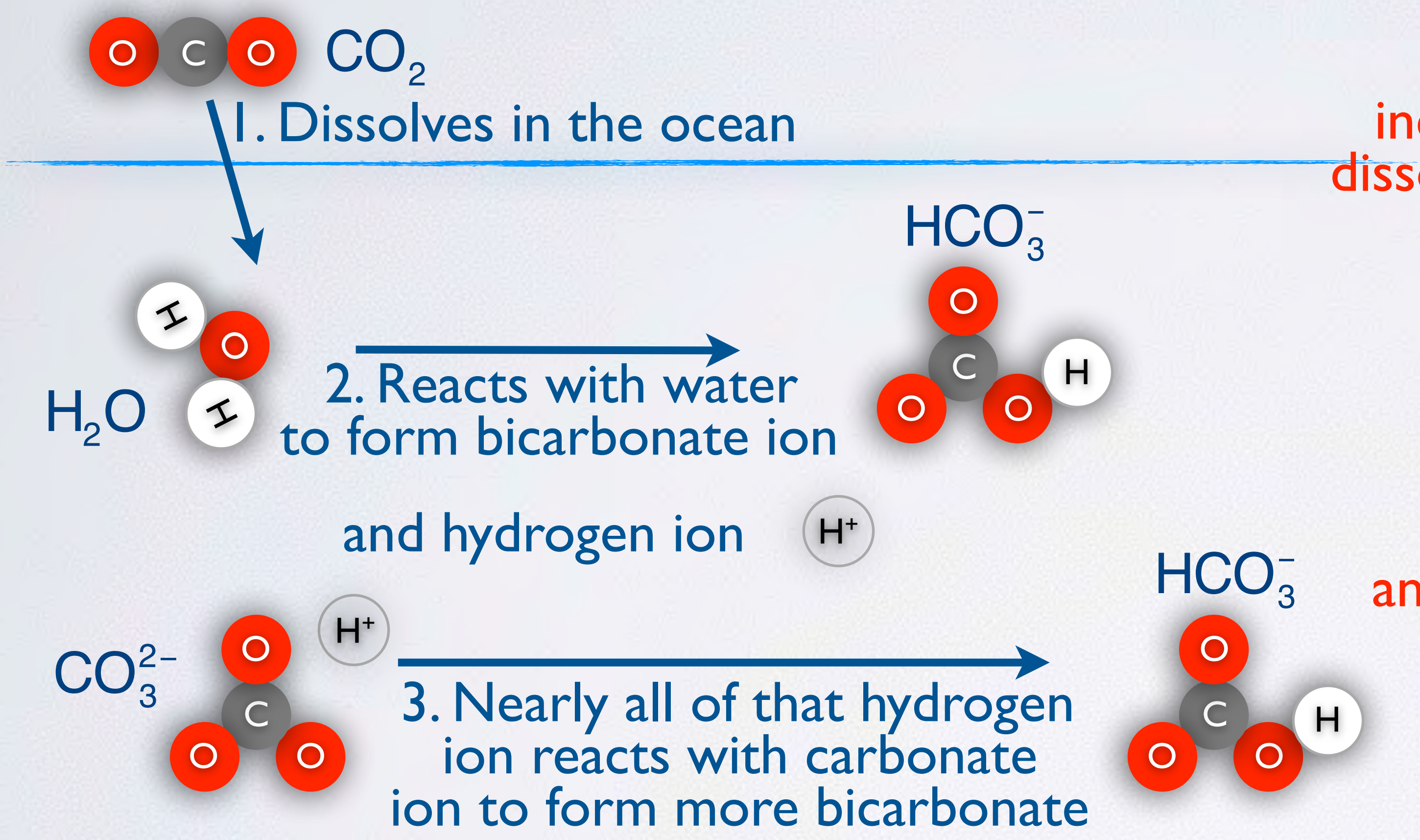
2nd Latin-American Course in Ocean Acidification
Ensenada, Baja California
CICESE IAEA UABC
MÉXICO • September 2016

Mauna Loa Observatory, Hawaii
Monthly Average Carbon Dioxide Concentration

Data from Scripps CO_2 Program Last updated August 2016



EFFECT OF ADDING CO_2 TO SEA WATER



CO_2

1. Dissolves in the ocean

H_2O

2. Reacts with water to form bicarbonate ion

HCO_3^-

and hydrogen ion H^+

CO_3^{2-} H^+

3. Nearly all of that hydrogen ion reacts with carbonate ion to form more bicarbonate

HCO_3^-

$$CO_2 + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^-$$

increase in dissolved CO_2 ↑

↓ decreases carbonate

↑ increases bicarbonate

also hydrogen ion concentration increases

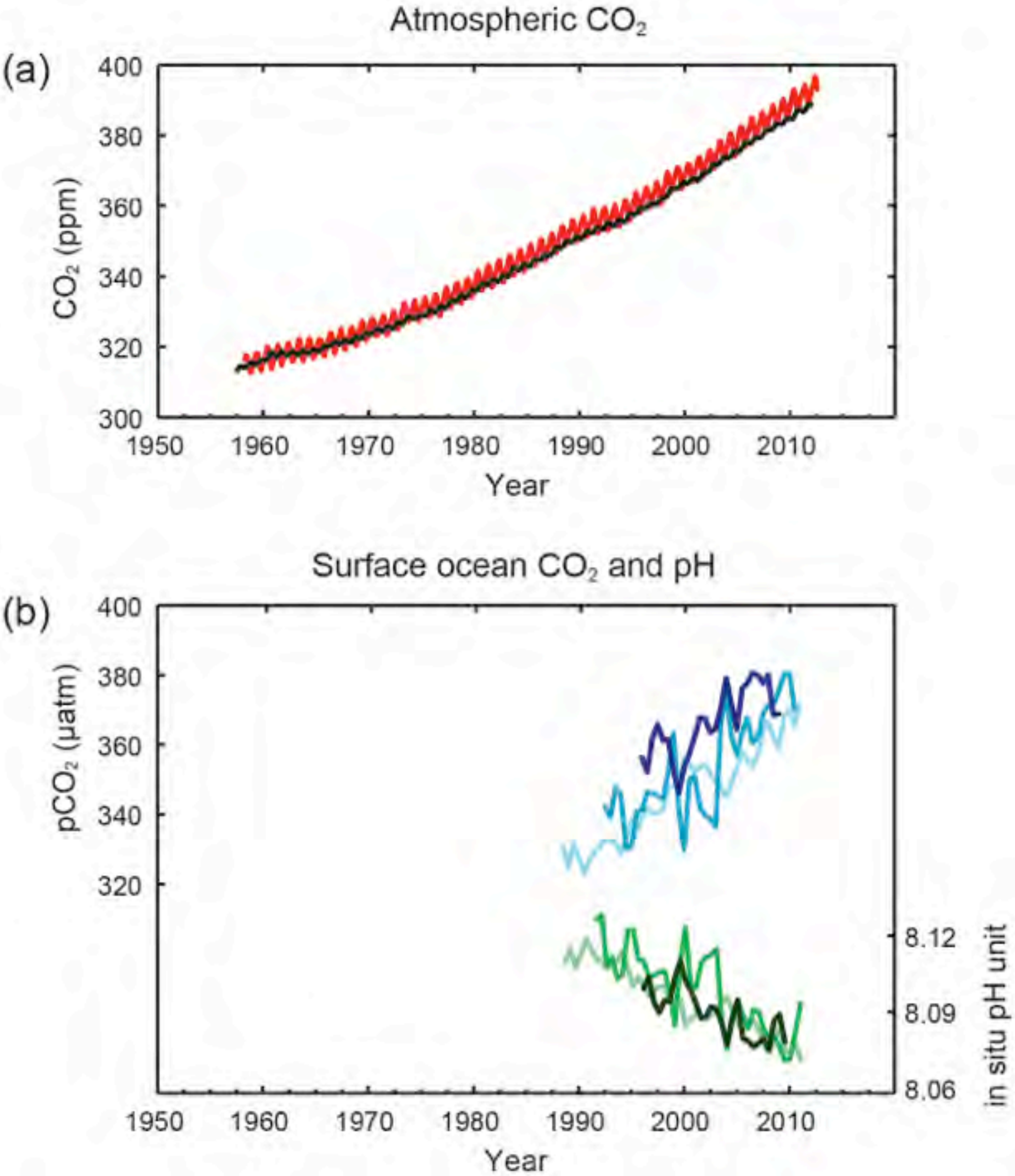
i.e., pH = –lg [H^+] decreases

and saturation state of calcium carbonate decreases

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

(a measure of how "easy" it is to form a shell)

Multiple observed indicators of a changing global carbon cycle: (a) atmospheric concentrations of carbon dioxide (CO_2) from Mauna Loa (19°32′N, 155°34′W – red) and South Pole (89°59′S, 24°48′W – black) since 1958; (b) partial pressure of dissolved CO_2 at the ocean surface (blue curves) and in situ pH (green curves), a measure of the acidity of ocean water. Measurements are from three stations from the Atlantic (29°10′N, 15°30′W – dark blue/dark green; 31°40′N, 64°10′W – blue/green) and the Pacific (22°45′N, 158°00′W – light blue/light green) Oceans. — Figure from IPCC AR5.



THE KINDS OF CHEMICAL QUESTIONS WE NEED TO BE ABLE TO ANSWER

- How can I estimate the CO_2 composition of a sample of sea water?
- If the CO_2 level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?
- What will be the consequent change in the saturation state of aragonite?
- Will this be the same all over the oceans? Why?
- How should I modify the CO_2 composition of a sample of sea water to reach a desired target composition?

REQUIRES ACCESS TO VARIOUS "TOOLS"

- Understanding of acid-base (and especially CO_2) equilibria in sea water.
- Understanding of which CO_2 parameters in sea water are usually measured, and how.
- Access to suitable computational tools for the CO_2 system such as CO2calc.
- Access to suitable analytical equipment (and training) to make any CO_2 measurements desired.

Part 1: Seawater carbonate chemistry

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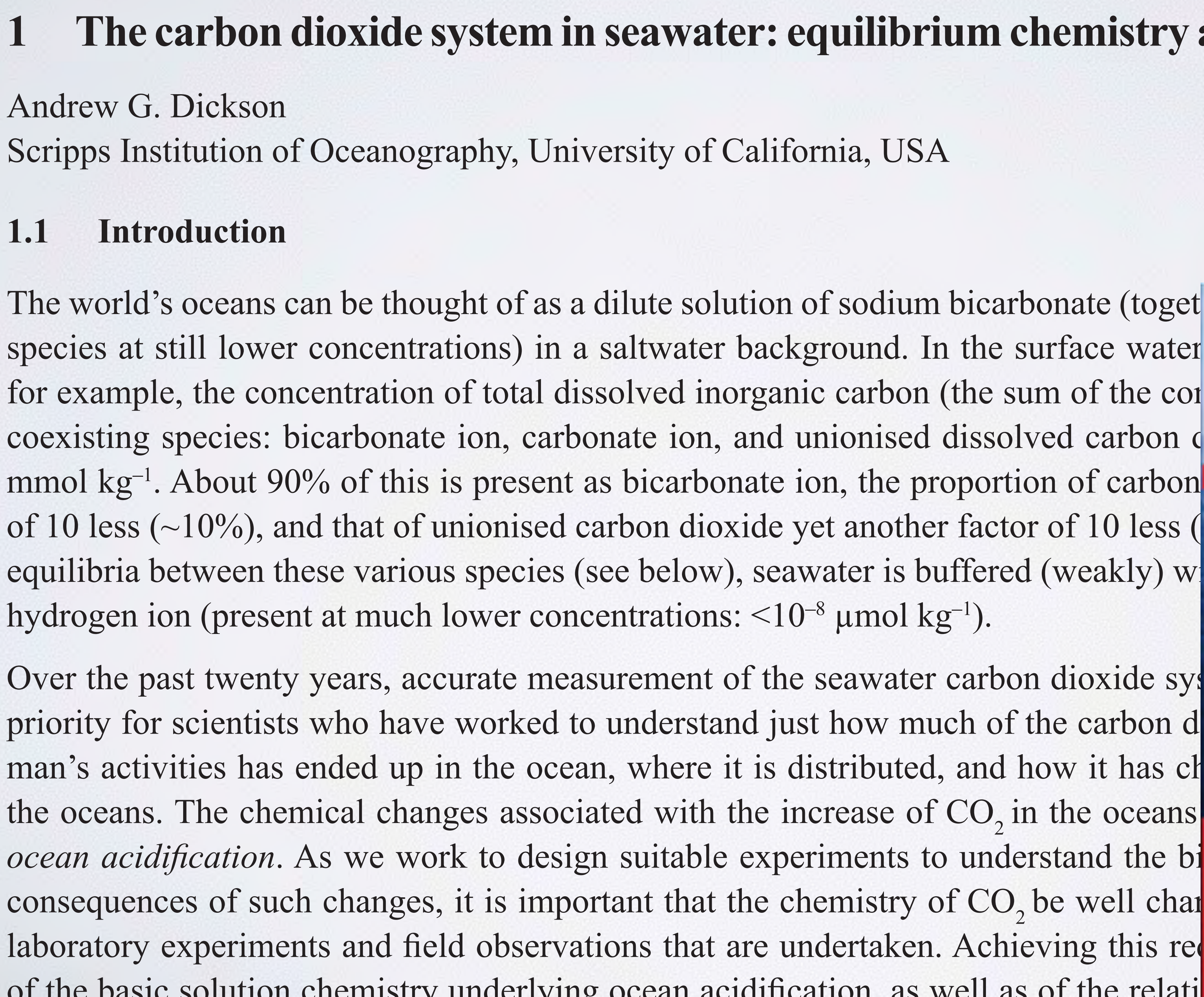


1 The carbon dioxide system in seawater: equilibrium chemistry and measurements

Andrew G. Dickson
Scripps Institution of Oceanography, University of California, USA

1.1 Introduction

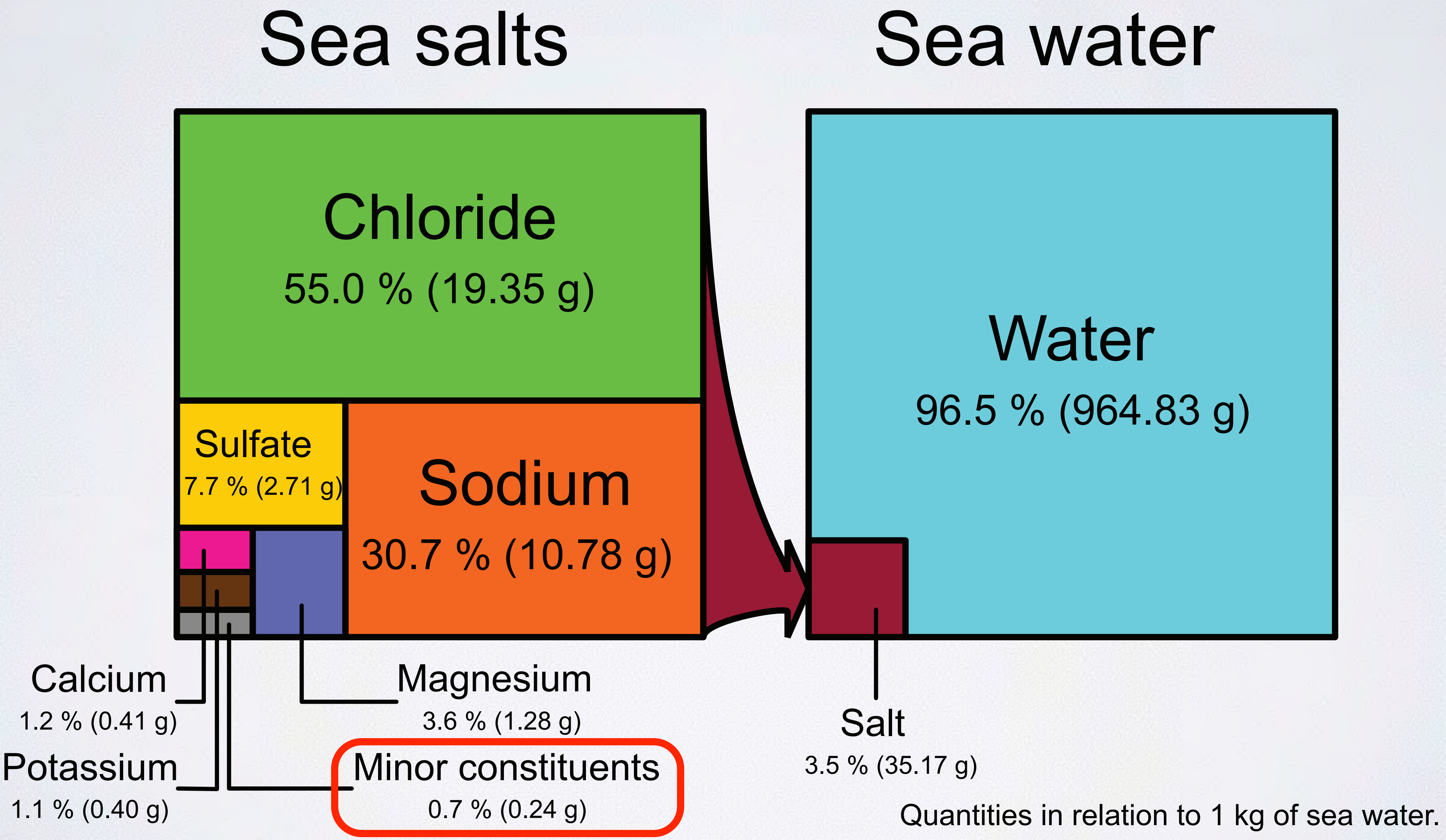
The world's oceans can be thought of as a dilute solution of sodium bicarbonate (toget
species at still lower concentrations) in a saltwater background. In the surface water
for example, the concentration of total dissolved inorganic carbon (the sum of the co
coexisting species: bicarbonate ion, carbonate ion, and unionised dissolved carbon d
mmol kg^{-1}. About 90% of this is present as bicarbonate ion, the proportion of carbon
of 10 less (~10%), and that of unionised carbon dioxide yet another factor of 10 less (
equilibria between these various species (see below), seawater is buffered (weakly) w
hydrogen ion (present at much lower concentrations: <10^{-8} µmol kg^{-1}).

Over the past twenty years, accurate measurement of the seawater carbon dioxide sys
priority for scientists who have worked to understand just how much of the carbon d
man's activities has ended up in the ocean, where it is distributed, and how it has ch
the oceans. The chemical changes associated with the increase of CO_2 in the oceans
ocean acidification. As we work to design suitable experiments to understand the bi
consequences of such changes, it is important that the chemistry of CO_2 be well char
laboratory experiments and field observations that are undertaken. Achieving this re
of the basic solution chemistry underlying ocean acidification, as well as of the relati

Guide
to best practices
for ocean acidification
research
and data reporting

INTRODUCTION TO CO_2 EQUILIBRIA IN SEA WATER

COMPOSITION OF SEA WATER ($S = 35$)


Sea salts
Sea water
Chloride
55.0 % (19.35 g)
Sulfate
7.7 % (2.71 g)
Sodium
30.7 % (10.78 g)
Water
96.5 % (964.83 g)
Calcium
1.2 % (0.41 g)
Potassium
1.1 % (0.40 g)
Magnesium
3.6 % (1.28 g)
Minor constituents
0.7 % (0.24 g)
Salt
3.5 % (35.17 g)

Quantities in relation to 1 kg of sea water.

ACID-BASE SPECIES COMPRISE A SUBSET OF THE "MINOR CONSTITUENTS" PRESENT IN SEAWATER

HCO_3^-

$SiO(OH)_3^-$

H^+

H_2O

CO_2

CO_3^{2-}

$H_2PO_4^-$

H_3PO_4

NH_4^+

organic acids

OH^-

$B(OH)_3$

organic bases

HF

PO_4^{3-}

NH_3

$Si(OH)_4$

HPO_4^{2-}

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; A_T = 2300 µmol kg^{-1}; t = 18 °C; S = 35

ACID-BASE SPECIES COMPRISE A SUBSET OF THE "MINOR CONSTITUENTS" PRESENT IN SEAWATER

HCO_3^-

$SiO(OH)_3^-$

H^+

10^{-2} µmol kg^{-1}

CO_2

~54 mol kg^{-1}

H_2O

CO_3^{2-}

$H_2PO_4^-$

H_3PO_4

NH_4^+

organic acids

OH^-

3.2 µmol kg^{-1}

$B(OH)_3$

organic bases

HF

PO_4^{3-}

NH_3

$Si(OH)_4$

HPO_4^{2-}

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; t = 18 °C; S = 35

ACID-BASE SPECIES COMPRISE A SUBSET OF THE "MINOR CONSTITUENTS" PRESENT IN SEAWATER

1900 µmol kg⁻¹

HCO_3^-

$SiO(OH)_3^-$

H^+

H_2O

CO_2

15.5 µmol kg⁻¹

CO_3^{2-}

158 µmol kg⁻¹

$H_2PO_4^-$

H_3PO_4

NH_4^+

organic acids

OH^-

$B(OH)_3$

organic bases

HF

PO_4^{3-}

NH_3

$Si(OH)_4$

HPO_4^{2-}

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; t = 18 °C; S = 35

ACID-BASE SPECIES COMPRISE A SUBSET OF THE "MINOR CONSTITUENTS" PRESENT IN SEAWATER

HCO_3^-

$SiO(OH)_3^-$

H^+

H_2O

CO_2

CO_3^{2-}

$H_2PO_4^-$

H_3PO_4

NH_4^+

organic acids

358 μmol kg⁻¹ → $B(OH)_3$

OH^-

organic bases

HF

PO_4^{3-}

NH_3

$Si(OH)_4$

HPO_4^{2-}

$B(OH)_4^-$ ← 75 μmol kg⁻¹

other acid/base species

Average ocean water; pH = 8; t = 18 °C; S = 35

ACID-BASE SPECIES COMPRISE A SUBSET OF THE “MINOR CONSTITUENTS” PRESENT IN SEAWATER

$SiO(OH)_3^-$

3 µmol kg⁻¹

HCO_3^-

H_2O

CO_2

CO_3^{2-}

$H_2PO_4^-$

H_3PO_4

NH_4^+

organic acids

OH^-

$B(OH)_3$

organic bases

HF

PO_4^{3-}

NH_3

97 µmol kg⁻¹

$Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Average ocean water; pH = 8; *t* = 18 °C; *S* = 35

ACID-BASE SPECIES COMPRISE A SUBSET OF THE “MINOR CONSTITUENTS” PRESENT IN SEAWATER

$SiO(OH)_3^-$

H^+

HCO_3^-

2.10^{-2} µmol kg^{-1}

H_2O

CO_2

CO_3^{2-}

$H_2PO_4^-$

10^{-8} µmol kg^{-1} H_3PO_4

NH_4^+

organic acids

OH^-

$B(OH)_3$

organic bases

HF

0.2 µmol kg^{-1} PO_4^{3-}

NH_3

1.8 µmol kg^{-1} HPO_4^{2-}

$Si(OH)_4$

$B(OH)_4^-$

other acid/base species

Note that these various equilibrium constants are functions of salinity, temperature, & pressure.

CARBON DIOXIDE EQUILIBRIA IN SEA WATER

Gas solubility

$$CO_2(g) = CO_2(aq)$$

concentration of unionized CO_2 in sea water (mol kg^{-1})

$$K_0 = \frac{[CO_2]}{x(CO_2) \cdot p}$$

mole fraction of CO_2

equilibration pressure

Acid Dissociation

total hydrogen ion concentration

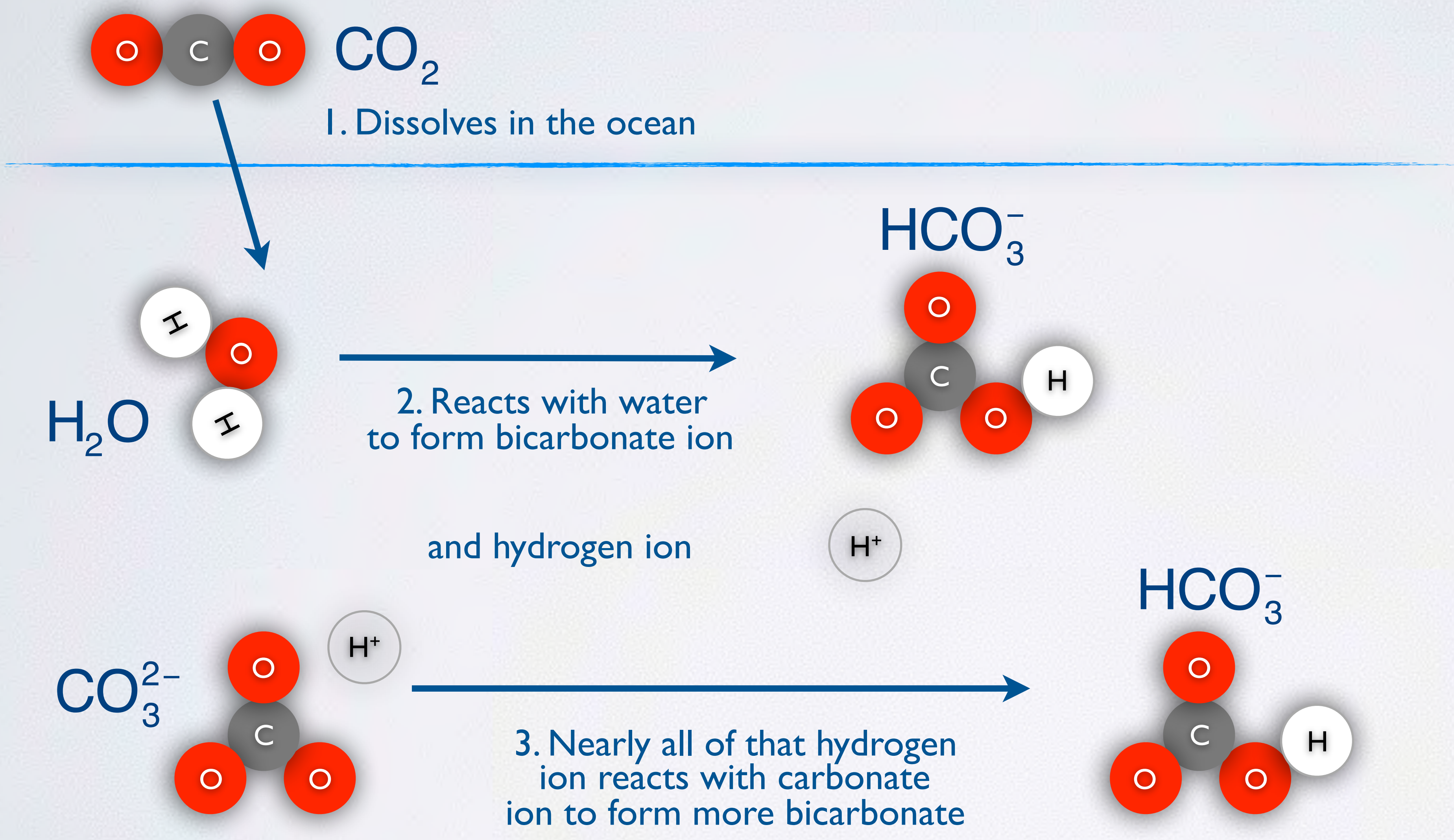
$$CO_2 + H_2O = H^+ + HCO_3^-$$

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

$$HCO_3^- = H^+ + CO_3^{2-}$$

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

CARBON DIOXIDE EQUILIBRIA IN SEA WATER



CO_2

1. Dissolves in the ocean

H_2O

2. Reacts with water to form bicarbonate ion

HCO_3^-

and hydrogen ion

H^+

CO_3^{2-}

H^+

3. Nearly all of that hydrogen ion reacts with carbonate ion to form more bicarbonate

HCO_3^-

$$K_0 = \frac{[CO_2]}{x(CO_2) \cdot p}$$

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

$$\frac{1}{K_2} = \frac{[HCO_3^-]}{[H^+][CO_3^{2-}]}$$

$$CO_2 + CO_3^{2-} + H_2O \rightleftarrows 2HCO_3^-$$

$$K_1 / K_2 = \frac{[HCO_3^-]^2}{[CO_2][CO_3^{2-}]}$$

CARBON DIOXIDE PARAMETERS IN SEA WATER

- Total Dissolved Inorganic Carbon

$$C_T = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

T, p independent

UNITS: moles per kilogram of solution (usually μmol kg^{-1})

- Total Hydrogen Ion Concentration (pH)

$$pH = -\lg\left([H^+]/(\text{mol kg}^{-1})\right)$$

T, p dependent

UNITS: pH is dimensionless; BUT, [H$^+$], total hydrogen ion concentration is in moles per kilogram of solution

- Partial Pressure of CO_2
  (in air that is in equilibrium with the water sample)

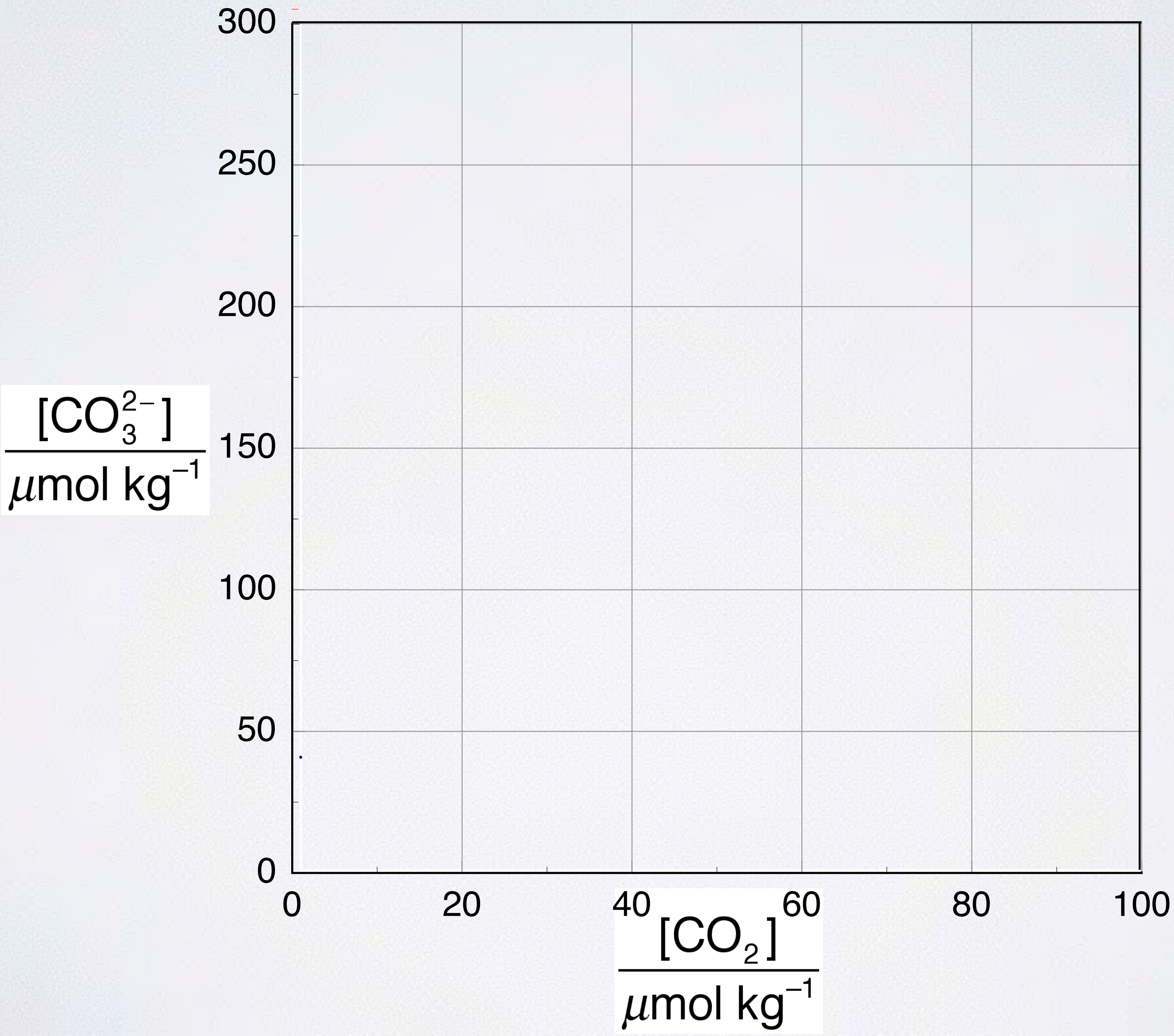
$$p(CO_2) = x(CO_2)\,p = [CO_2]/K_0$$

T, p dependent

UNITS: pressure units (usually μatm)

CO_2 SYSTEM RELATIONSHIPS IN SEA WATER

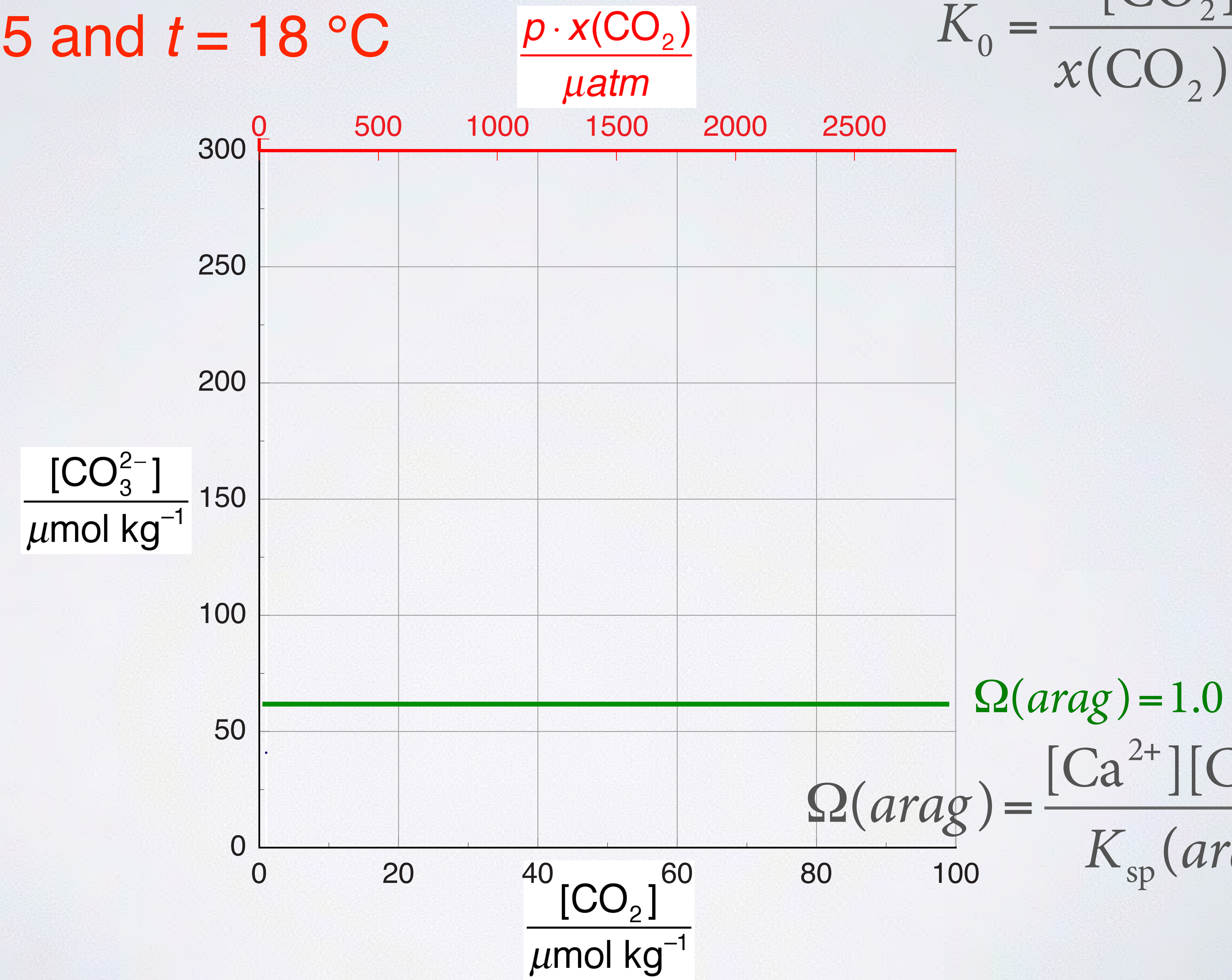
$$K_0 = \frac{[CO_2]}{x(CO_2)\cdot p}$$



CO_2 SYSTEM RELATIONSHIPS IN SEA WATER

At *S* = 35 and *t* = 18 °C

$$K_0 = \frac{[CO_2]}{x(CO_2)\cdot p}$$

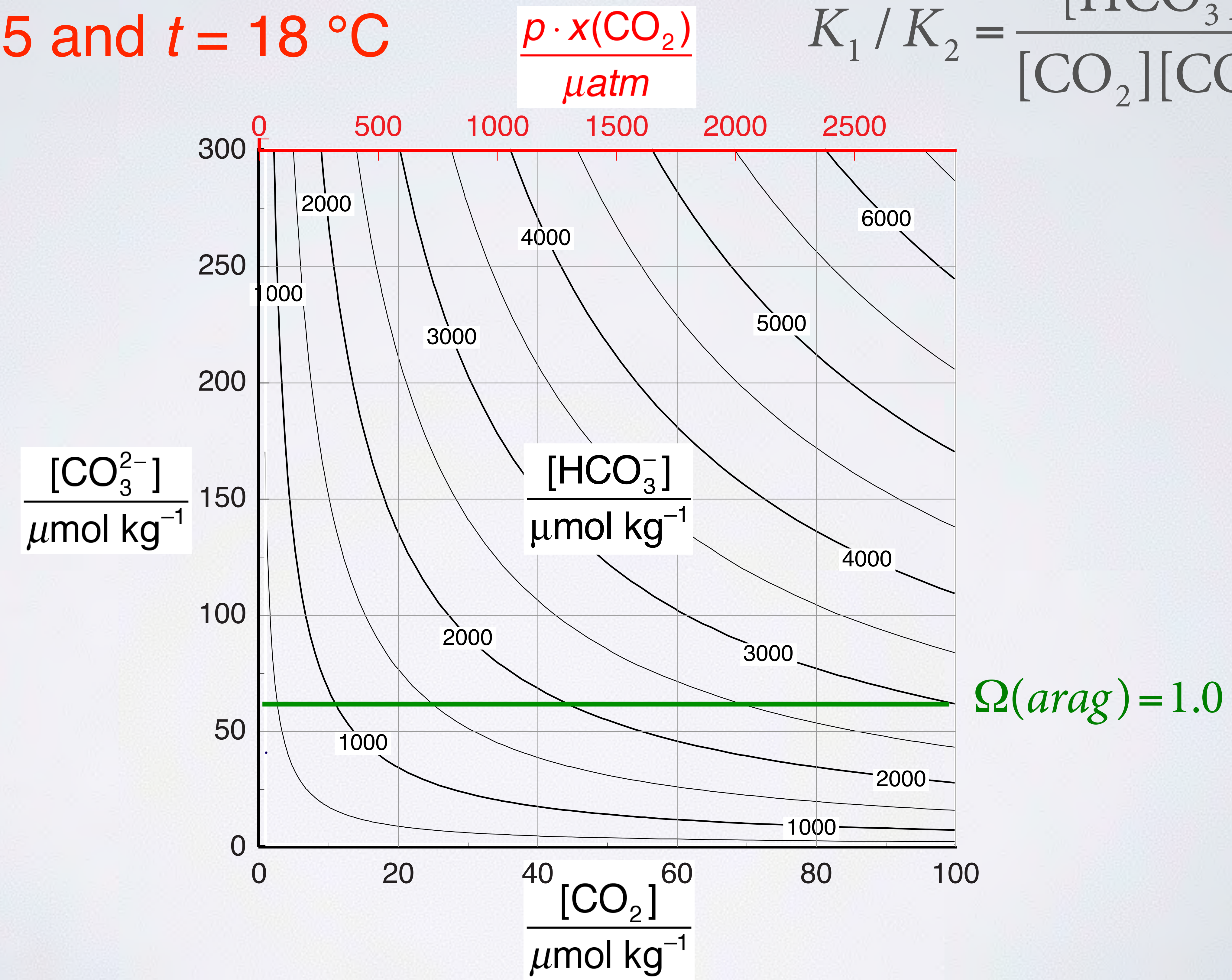


$$\Omega(arag) = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}(arag)}$$

CO_2 SYSTEM RELATIONSHIPS IN SEA WATER

At *S* = 35 and *t* = 18 °C

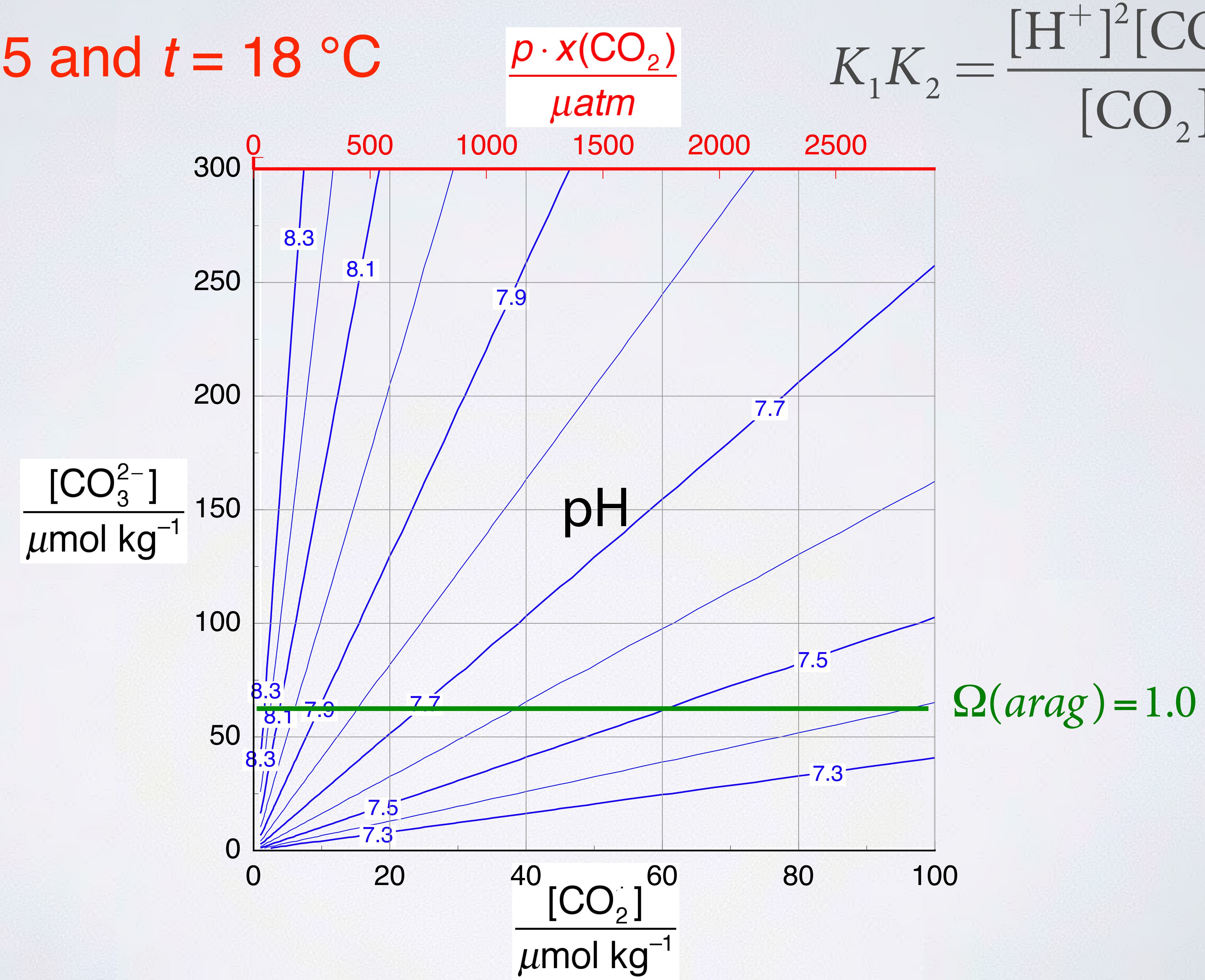
$$K_1/K_2 = \frac{[HCO_3^-]^2}{[CO_2][CO_3^{2-}]}$$



CO_2 SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18$ °C

$$K_1 K_2 = \frac{[H^+]^2[CO_3^{2-}]}{[CO_2]}$$



IMPORTANT CONSEQUENCE OF CO_2 EQUILIBRIA

- In a system at equilibrium, with both a gaseous and an aqueous phase, the state of the CO_2 system is described by a knowledge of the $p(CO_2)$ in the gas phase, and of the four concentrations: $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[H^+]$, in the aqueous phase.

- However, there are three equilibrium relationships between these various concentrations:

$$K_0 = \frac{[CO_2]}{x(CO_2)\cdot p} \qquad K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \qquad K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

- Hence there are only two degrees of freedom.

This implies that only **two** of the aqueous concentrations can be varied independently of one another.

OTHER ACID-BASE SYSTEMS IN SEA WATER

OTHER ACID-BASE SYSTEMS IN SEA WATER

Water Dissociation

$$H_2O = H^+ + OH^- \qquad K_W = [H^+][OH^-]$$

Boric Acid Dissociation

$$B(OH)_3 + H_2O = H^+ + B(OH)_4^- \qquad K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]}$$

Total Dissolved Boron (depends on salinity)

$$B_T = [B(OH)_3] + [B(OH)_4^-]$$

For every other acid-base system considered, you need the total concentration and the equilibrium constant. The species concentrations can then be inferred from a knowledge of the pH.

DANGER
CO2
HAZARD AREA
AHEAD

TOTAL ALKALINITY

$$A_T \boxed{\approx} [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

T, p independent

UNITS: moles per kilogram of solution (usually μmol kg^{-1})

1. What species are missing?
2. Why is this particular sum of species concentrations independent of temperature and pressure though each of the individual species contributions is itself a function of T and p?
3. A key aspect of total alkalinity: it does not change when CO_2 is added to or removed from sea water. Why?

FORMAL DEFINITION FOR ALKALINITY IN SEAWATER

The total alkalinity of a sample of sea water is a form of mass-conservation relationship for hydrogen ion. It is rigorously defined (Dickson, 1981) as

> "... the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample."

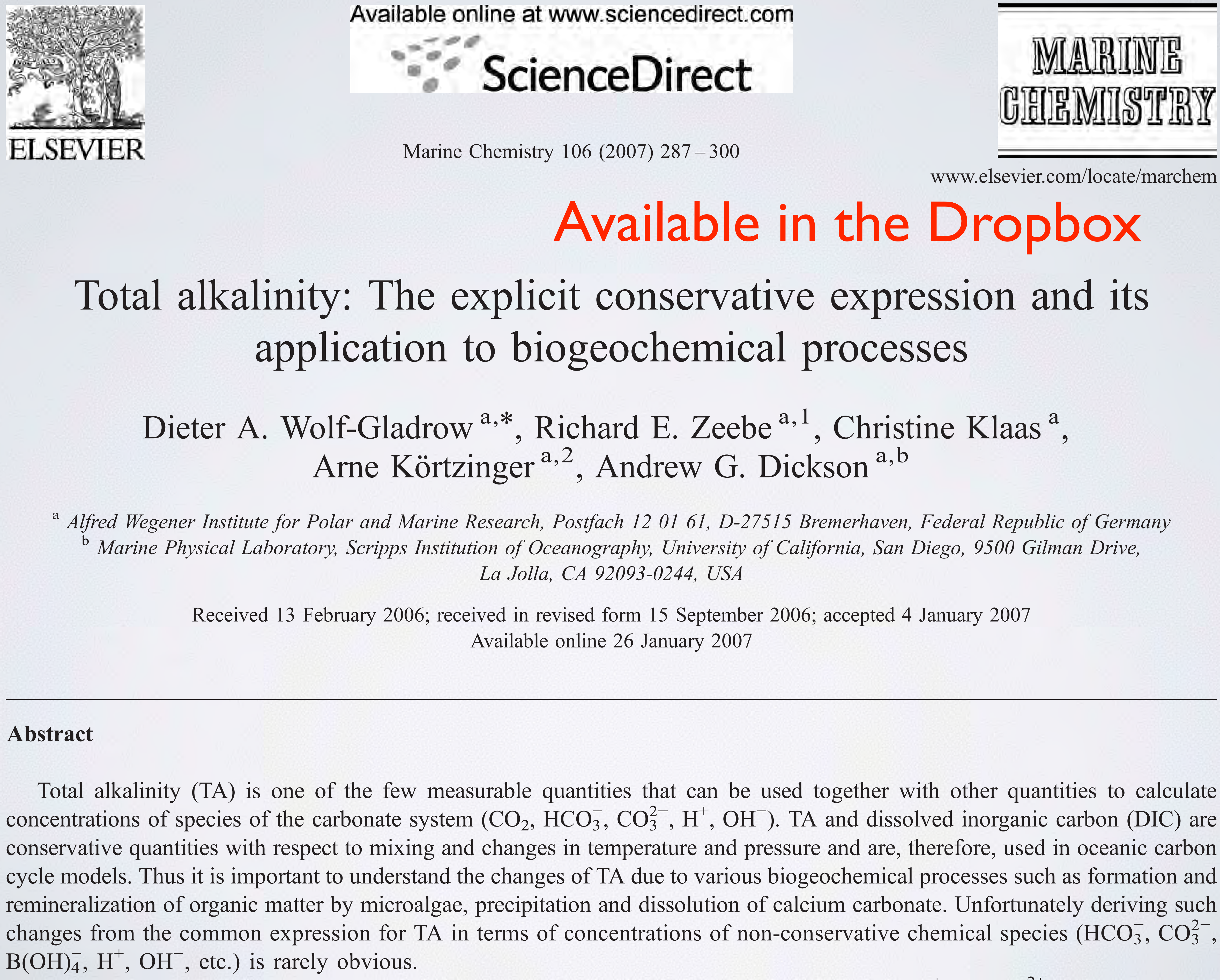
$$\begin{aligned} A_\mathrm{T} = {} & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] + [\mathrm{HPO_4^{2-}}] \\ & + 2[\mathrm{PO_4^{3-}}] + [\mathrm{SiO(OH)_3^-}] + [\mathrm{NH_3}] + [\mathrm{HS^-}] + \ldots \\ & - [\mathrm{H^+}]_\mathrm{F} - [\mathrm{HSO_4^-}] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] - \ldots \end{aligned}$$

Formal definition of alkalinity

If we choose to omit those species that are typically present at low concentration, we then get the expression we have used so far.

$$\begin{aligned} A_\mathrm{T} = {} & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] + [\mathrm{HPO_4^{2-}}] \\ & + 2[\mathrm{PO_4^{3-}}] + [\mathrm{SiO(OH)_3^-}] + [\mathrm{NH_3}] + [\mathrm{HS^-}] + \ldots \\ & \underbrace{- [\mathrm{H^+}]_\mathrm{F} - [\mathrm{HSO_4^-}]}_{-[\mathrm{H^+}]} - [\mathrm{HF}] - [\mathrm{H_3PO_4}] - \ldots \end{aligned}$$

The definition of hydrogen ion concentration we have been using has been the “total” hydrogen ion concentration (i.e., implicitly including the concentration of the hydrogen sulfate species together with the *free* hydrogen ion concentration).



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Total alkalinity: The explicit conservative expression and its application to biogeochemical processes

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Abstract

Total alkalinity (TA) is one of the few measurable quantities that can be used together with other quantities to calculate concentrations of species of the carbonate system (CO_2, HCO_3^-, CO_3^{2-}, H^+, OH^-). TA and dissolved inorganic carbon (DIC) are conservative quantities with respect to mixing and changes in temperature and pressure and are, therefore, used in oceanic carbon cycle models. Thus it is important to understand the changes of TA due to various biogeochemical processes such as formation and remineralization of organic matter by microalgae, precipitation and dissolution of calcium carbonate. Unfortunately deriving such changes from the common expression for TA in terms of concentrations of non-conservative chemical species (HCO_3^-, CO_3^{2-}, $B(OH)_4^-$, H^+, OH^-, etc.) is rarely obvious.

IMPLICATIONS FOR THE DEGREES OF FREEDOM FOR ACID-BASE SYSTEMS IN SEAWATER

- We stated earlier that there are only two *degrees of freedom* and that only **two** of the aqueous concentrations of the CO_2 species can be varied independently of one another.

- However, for each additional acid-base system (except water) that is added in, there are two additional species concentrations and one equilibrium relationship. Thus there will be an additional *degree of freedom* for each new acid/base pair.

- Furthermore, one does not have to limit oneself to simple species concentrations when thinking of "concentrations" that can be varied independently. It also applies to combinations of species concentrations such as C_T or A_T.

COMPUTER PROGRAMS EXIST FOR THESE CALCULATIONS

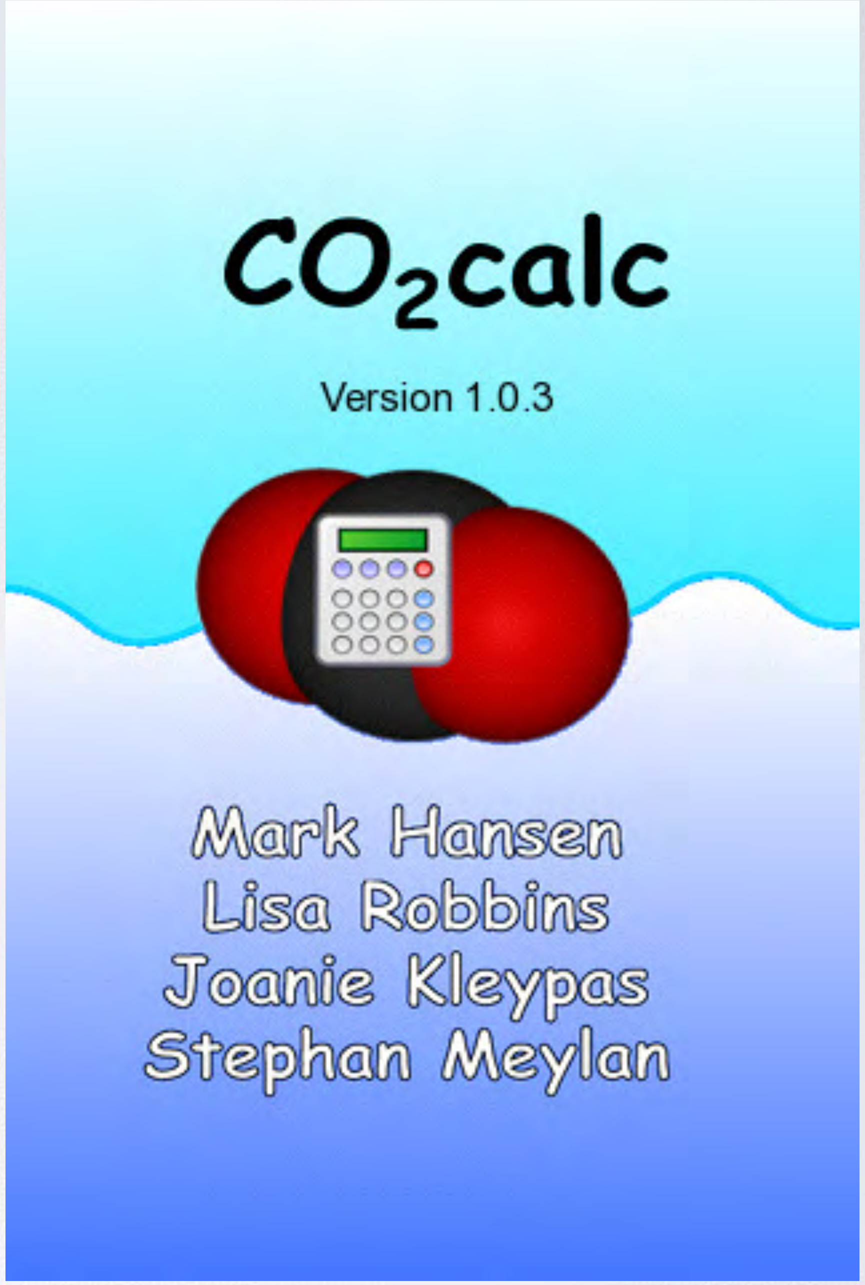
- Provide built in data for the various equilibrium constants which are functions of salinity, temperature, and pressure as well as for total concentrations such as boron that are proportional to salinity.

- Allow some additional acid-base information to be added (*e.g.* total phosphate and/or total silicate concentrations)

- Allow calculation of CO_2 speciation
  (typically from 2 analytical parameters, salinity & temperature)

Florida Shelf Ecosystems Response to Climate Change Project

CO2calc: A User-Friendly Seawater Carbon Calculator for Windows, Mac OS X, and iOS (iPhone)



CO_2calc

Version 1.0.3

Mark Hansen
Lisa Robbins
Joanie Kleypas
Stephan Meylan

http://pubs.usgs.gov/of/2010/1280/

Open-File Report 2010–1280

U.S. Department of the Interior
U.S. Geological Survey

If you have a laptop, bring it this afternoon

If you can, download the program CO2calc pubs.usgs.gov/of/2010/1280/

If you don't have a laptop here, work with someone who does

CAN USE ANY TWO (OR MORE) OF THESE PARAMETERS TO DESCRIBE THE CO_2 SYSTEM IN A SEA WATER SAMPLE

Mathematically, all choices should be equivalent.

In practice that is not the case. Every one of these terms is an experimental quantity with an associated uncertainty. These uncertainties propagate through the calculations resulting in uncertainties in the various calculated values.

In addition to uncertainties in the measured CO_2 parameters, there are also uncertainties in the various equilibrium constants, and in the total concentrations of other acid-base systems such as boron, *etc.*

(Also, the expression used for alkalinity may be incomplete.)

CAN USE ANY TWO (OR MORE) OF THESE PARAMETERS TO DESCRIBE THE CO_2 SYSTEM IN A SEA WATER SAMPLE

As yet it is not straightforward to carry out a rigorous consideration of such uncertainties. Thus they are often – mistakenly – ignored.

WARNING
CO2

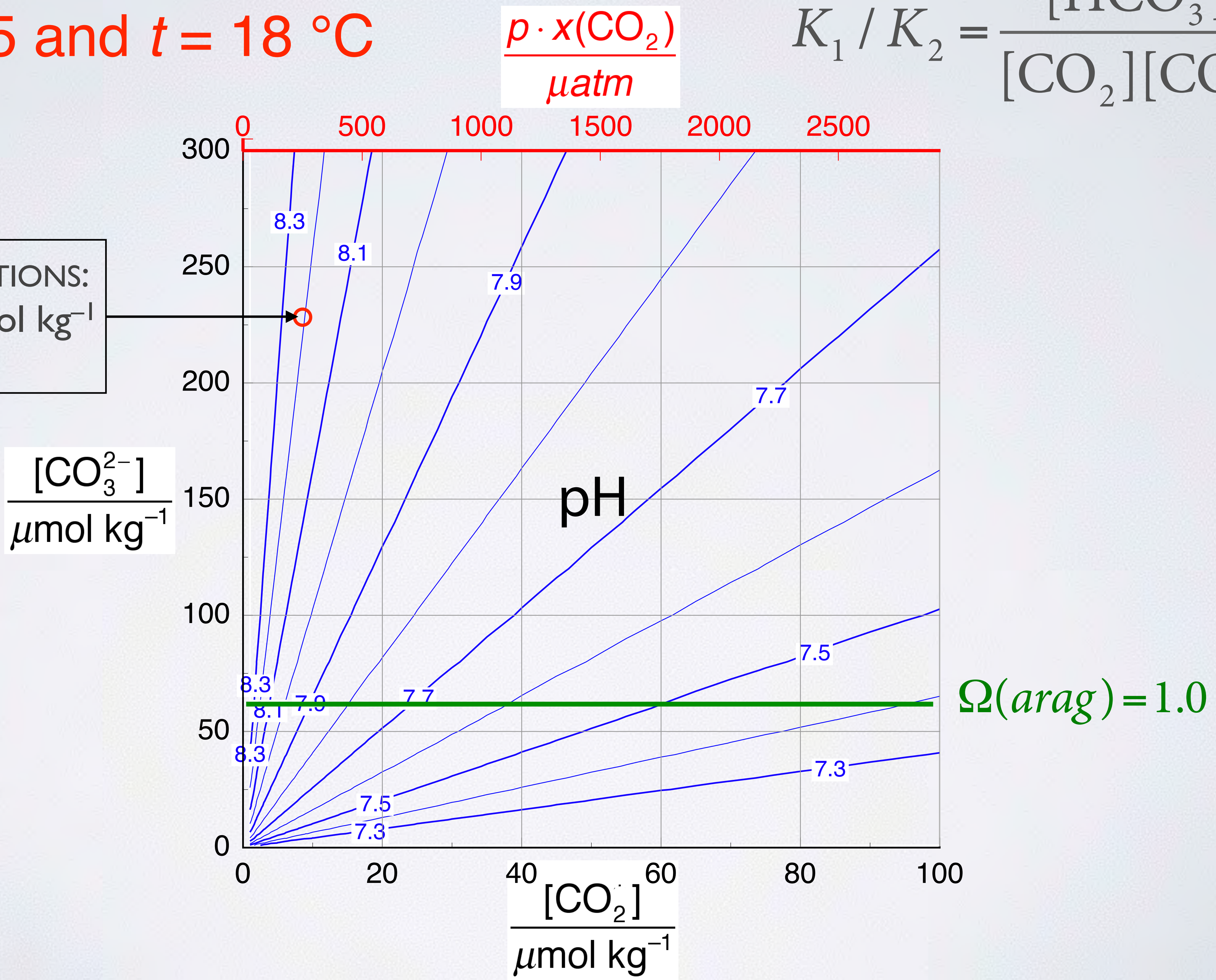
IMPLICATIONS FOR THE "ACIDIFICATION" OF SEA WATER

ACIDIFICATION TO pH 7.3

At $S = 35$ and $t = 18$ °C

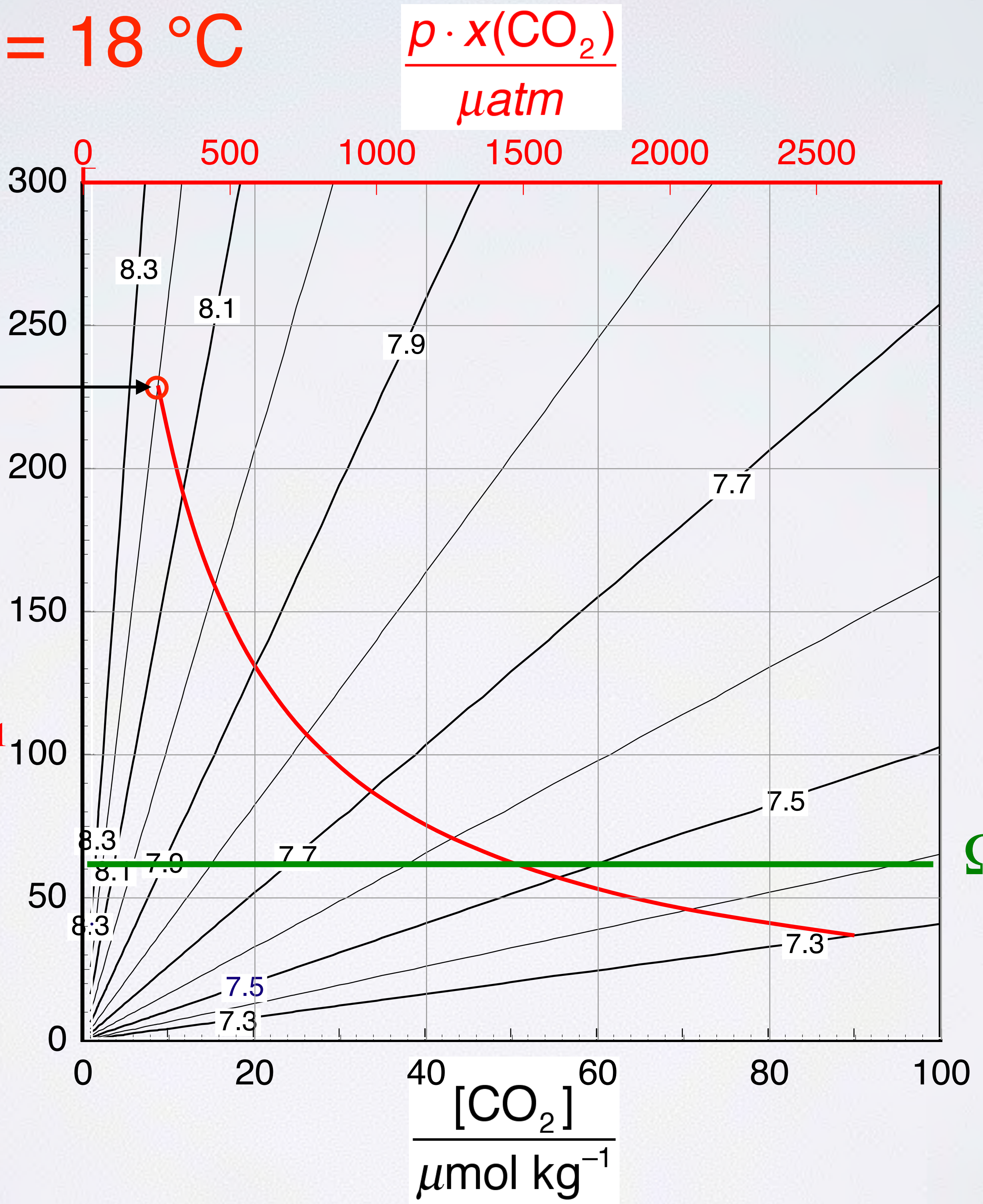
$$K_1 / K_2 = \frac{[\mathrm{HCO_3^-}]^2}{[\mathrm{CO_2}][\mathrm{CO_3^{2-}}]}$$

INITIAL CONDITIONS:
A_T = 2300 µmol kg⁻¹
pH = 8.2



Acidification to pH 7.3 (by addition of CO_2)

At $S = 35$ and $t = 18$ °C



Initial conditions:
$A_T = 2300\ \mu mol\ kg^{-1}$
pH = 8.2

$$\Delta C_T \approx +368\ \mu mol\ kg^{-1}$$

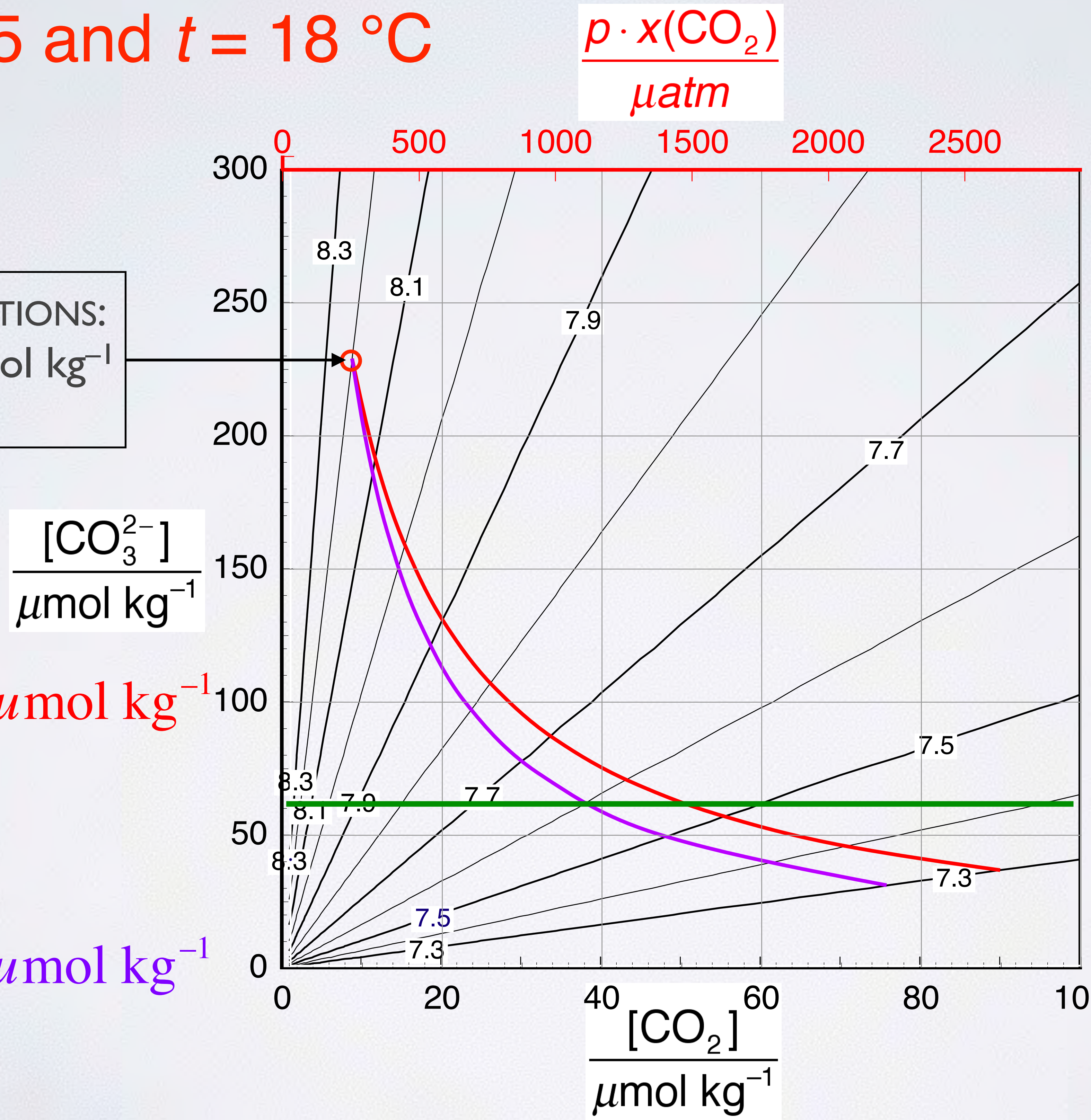
Final conditions:
$p(CO_2) = 2635\ \mu atm$
$[CO_3^{2-}] = 37\ \mu mol\ kg^{-1}$
$\Omega(arag) = 0.57$

$\Omega(arag) = 1.0$

Acidification to pH 7.3 (by addition of HCl)

At $S = 35$ and $t = 18$ °C

Initial conditions:
A_T = 2300 μmol kg^{-1}
pH = 8.2



$\Delta C_T \approx +368\ \mu mol\ kg^{-1}$

$\Delta A_T \approx -359\ \mu mol\ kg^{-1}$

Final conditions:
$p(CO_2)$ = 2635 μatm
$[CO_3^{2-}]$ = 37 μmol kg^{-1}
$\Omega(arag) = 0.57$

$\Omega(arag) = 1.0$

Final conditions:
$p(CO_2)$ = 2220 μatm
$[CO_3^{2-}]$ = 31 μmol kg^{-1}
$\Omega(arag) = 0.48$

WHAT HAPPENS AT A DIFFERENT TEMPERATURE?

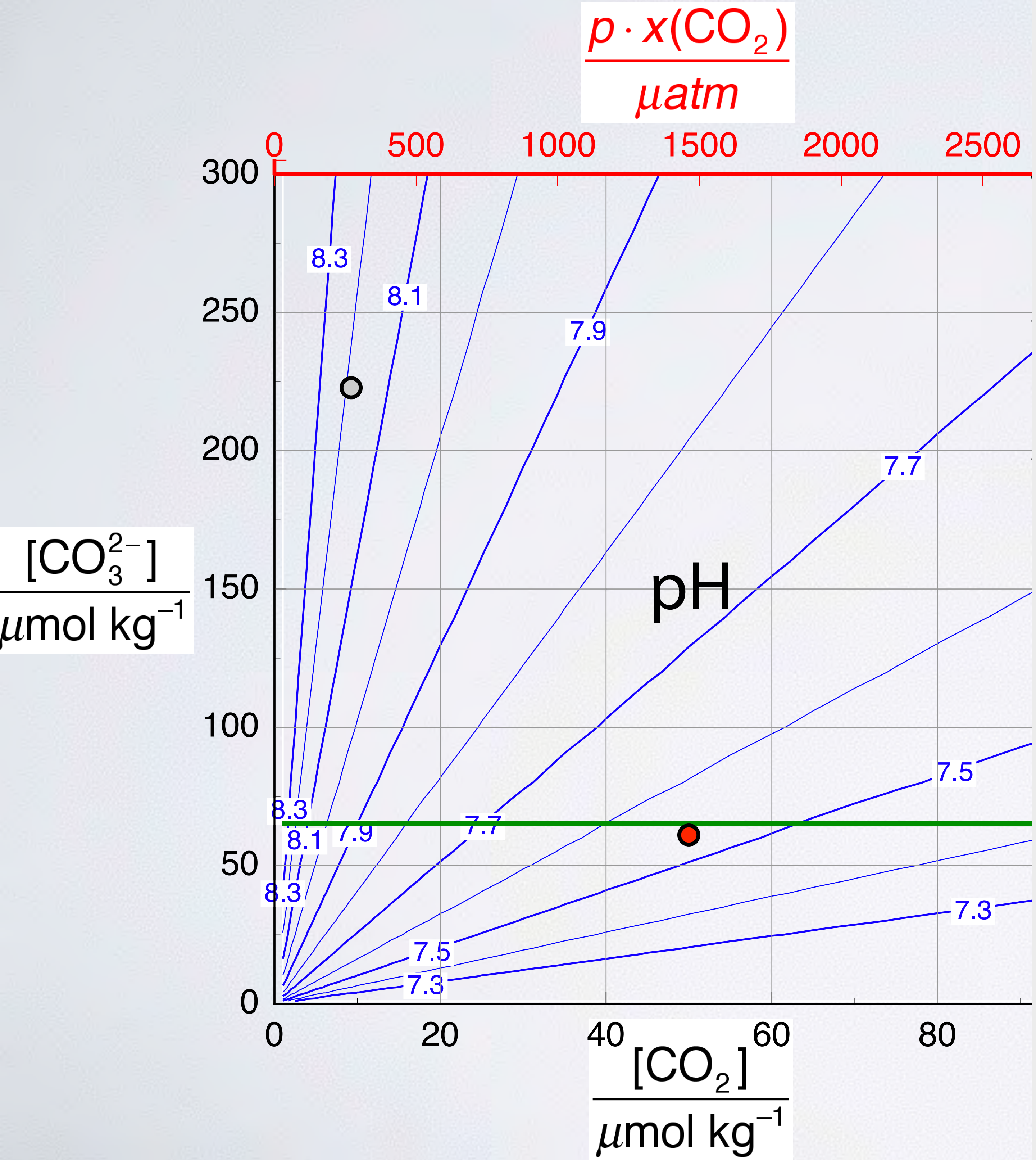
INITIAL CONDITIONS:
A_T = 2300 μmol kg^{-1}
$p(CO_2)$ = 280 μatm

→

FINAL CONDITIONS:
A_T = 2300 μmol kg^{-1}
$p(CO_2)$ = 1500 μatm

DANGER
C0₂
HAZARD AREA
AHEAD

18 °C

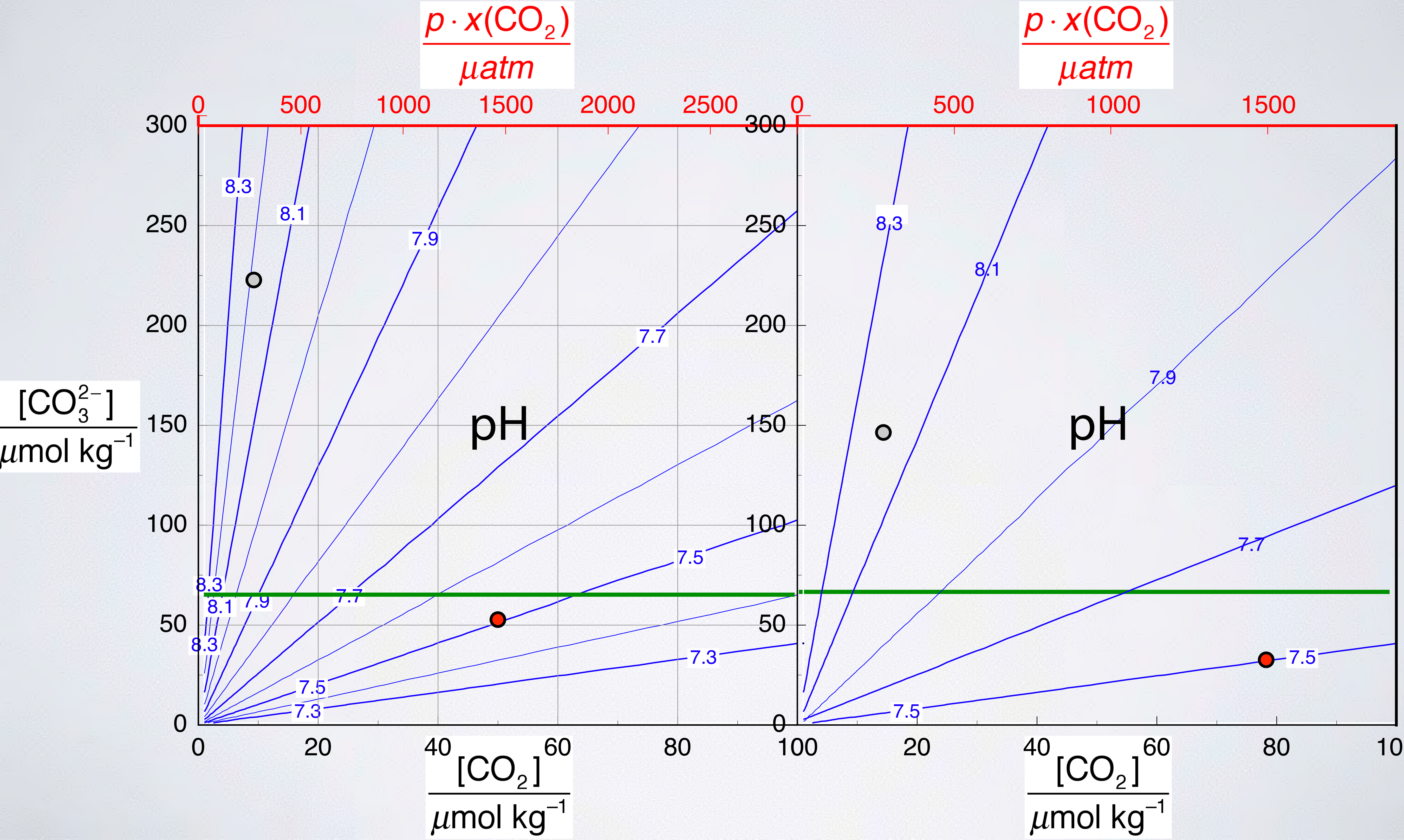


INITIAL CONDITIONS:
A_T = 2300 µmol kg^{-1}
$p(\mathrm{CO_2})$ = 280 µatm

FINAL CONDITIONS:
A_T = 2300 µmol kg^{-1}
$p(\mathrm{CO_2})$ = 1500 µatm

18 °C

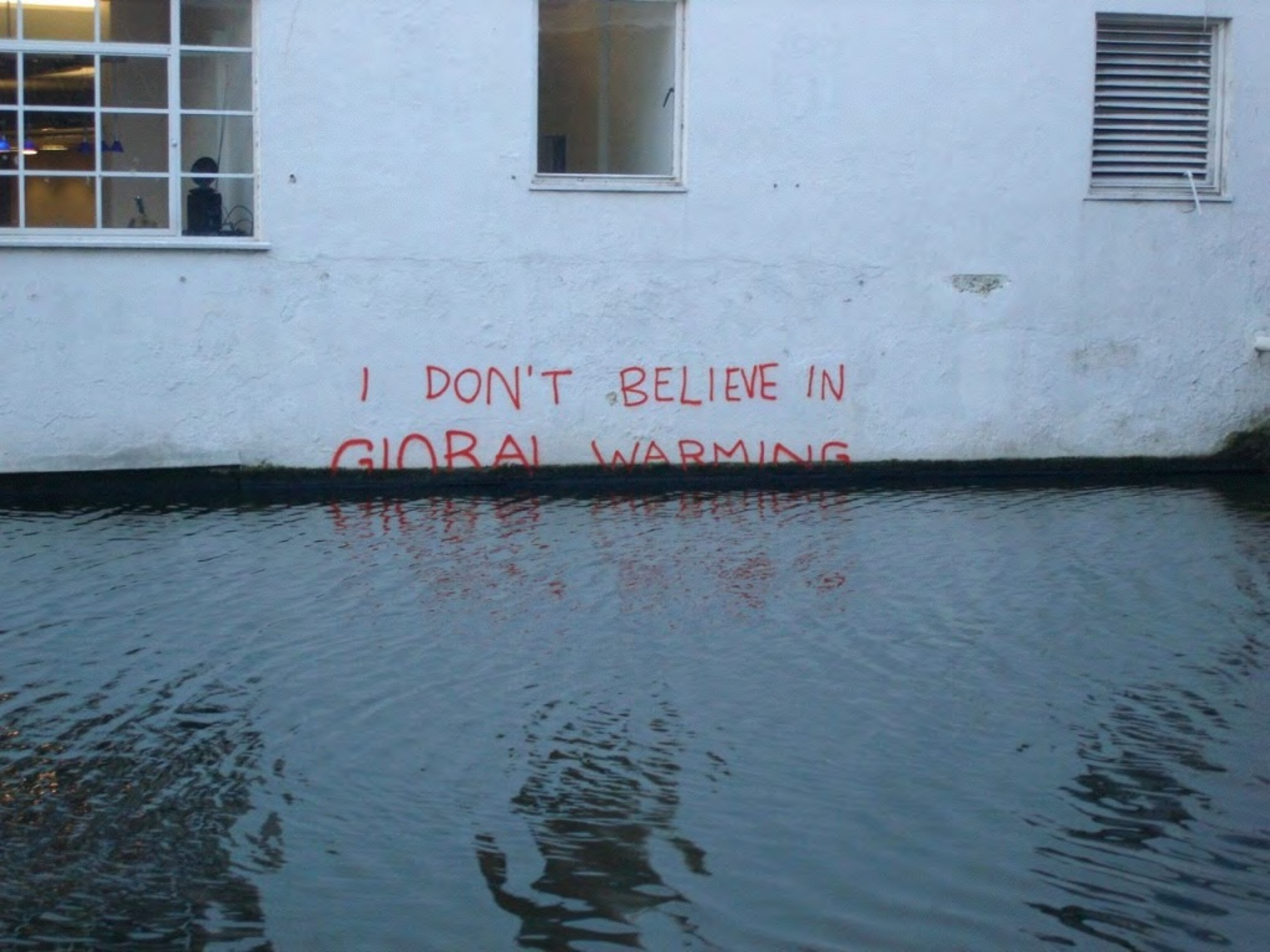
5 °C


$\frac{p \cdot x(CO_2)}{\mu atm}$
0
500
1000
1500
2000
2500
0
500
1000
1500
$\frac{[CO_3^{2-}]}{\mu mol\ kg^{-1}}$
300
250
200
150
100
50
0
8.3
8.1
7.9
7.7
7.5
7.3
pH
8.3
8.1
7.9
7.7
7.5
$\frac{[CO_2]}{\mu mol\ kg^{-1}}$
0
20
40
60
80
100
20
40
60
80
100
$\frac{[CO_2]}{\mu mol\ kg^{-1}}$

$S = 35$	18 °C	5 °C
$A_T = 2300$ µmol kg^{-1}		
$p(CO_2)$	280 µatm	
pH	8.17	8.18
$\Omega(arag)$	3.37	2.19
C_T	1984 µmol kg^{-1}	2092 µmol kg^{-1}
$p(CO_2)$	1500 µatm	
pH	7.53	7.51
$\Omega(arag)$	0.94	0.53
C_T	2260 µmol kg^{-1}	2323 µmol kg^{-1}
ΔC_T	276 µmol kg^{-1}	230 µmol kg^{-1}

IMPLICATIONS OF CO_2 EQUILIBRIA FOR DESIGN OF OCEAN ACIDIFICATION EXPERIMENTS

- Only two of the concentrations of the aqueous CO_2 species can be varied independently of one another. Thus we cannot design *perfect* experiments to study organismal physiology, however we only need to control **two** CO_2 parameters.
- If you know what sea water composition you have to start with, and know the composition you want to get to, it is often simpler to think about the changes as if they occur in total alkalinity and in total dissolved inorganic carbon.
- In many systems, it is not convenient to alter the sea water alkalinity to a target value; one just uses the alkalinity of the source sea water as is.
- It is often best to monitor and control pH – by varying $p(CO_2)$. This is less demanding of temperature control than monitoring $p(CO_2)$.


I DON'T BELIEVE IN
GLOBAL WARMING

If you have a laptop, bring it this afternoon

If you can, download the program CO2calc
pubs.usgs.gov/of/2010/1280/

If you don't have a laptop here, work with someone who does