Introduction to CO$_2$ chemistry in sea water

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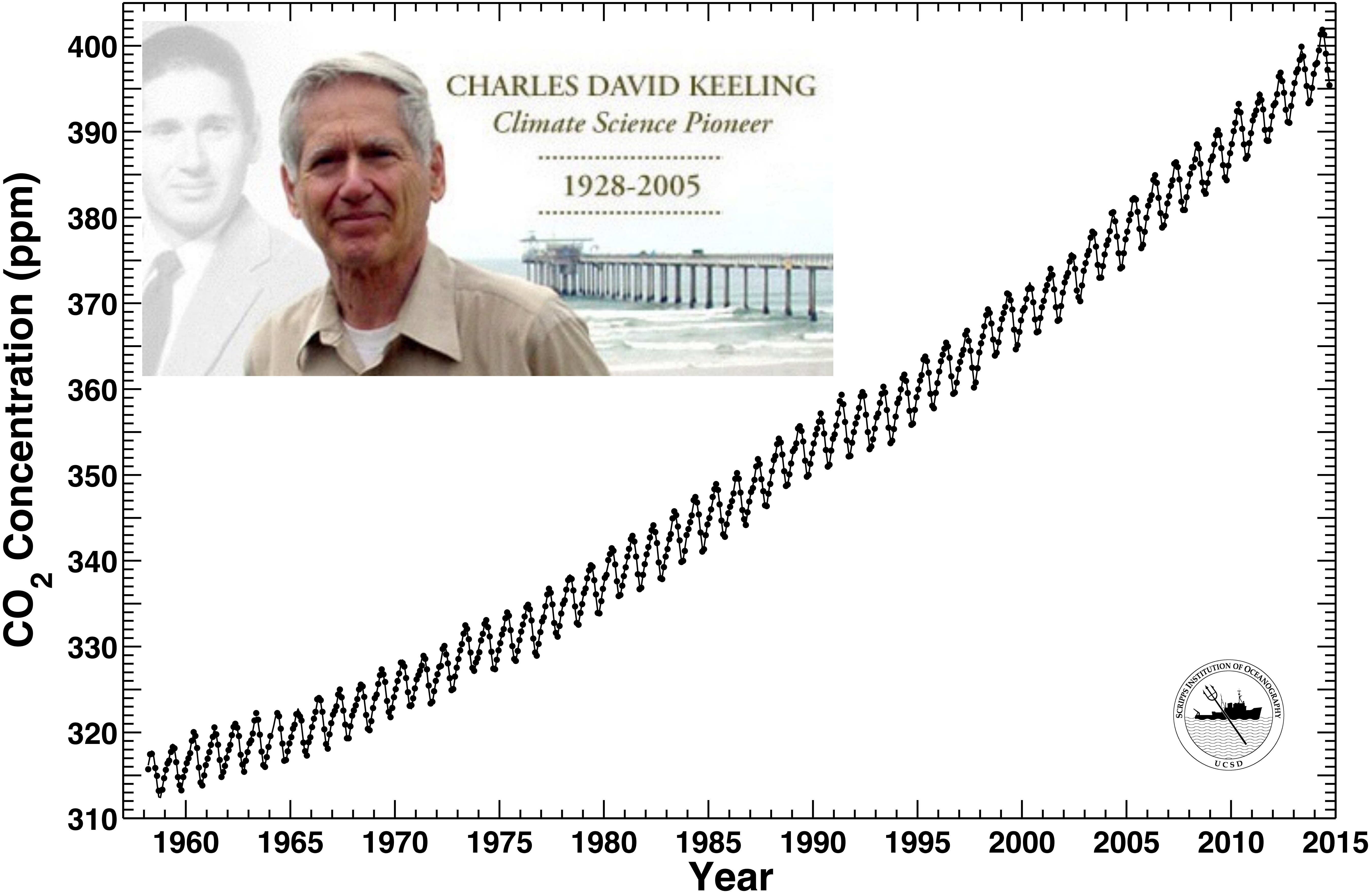
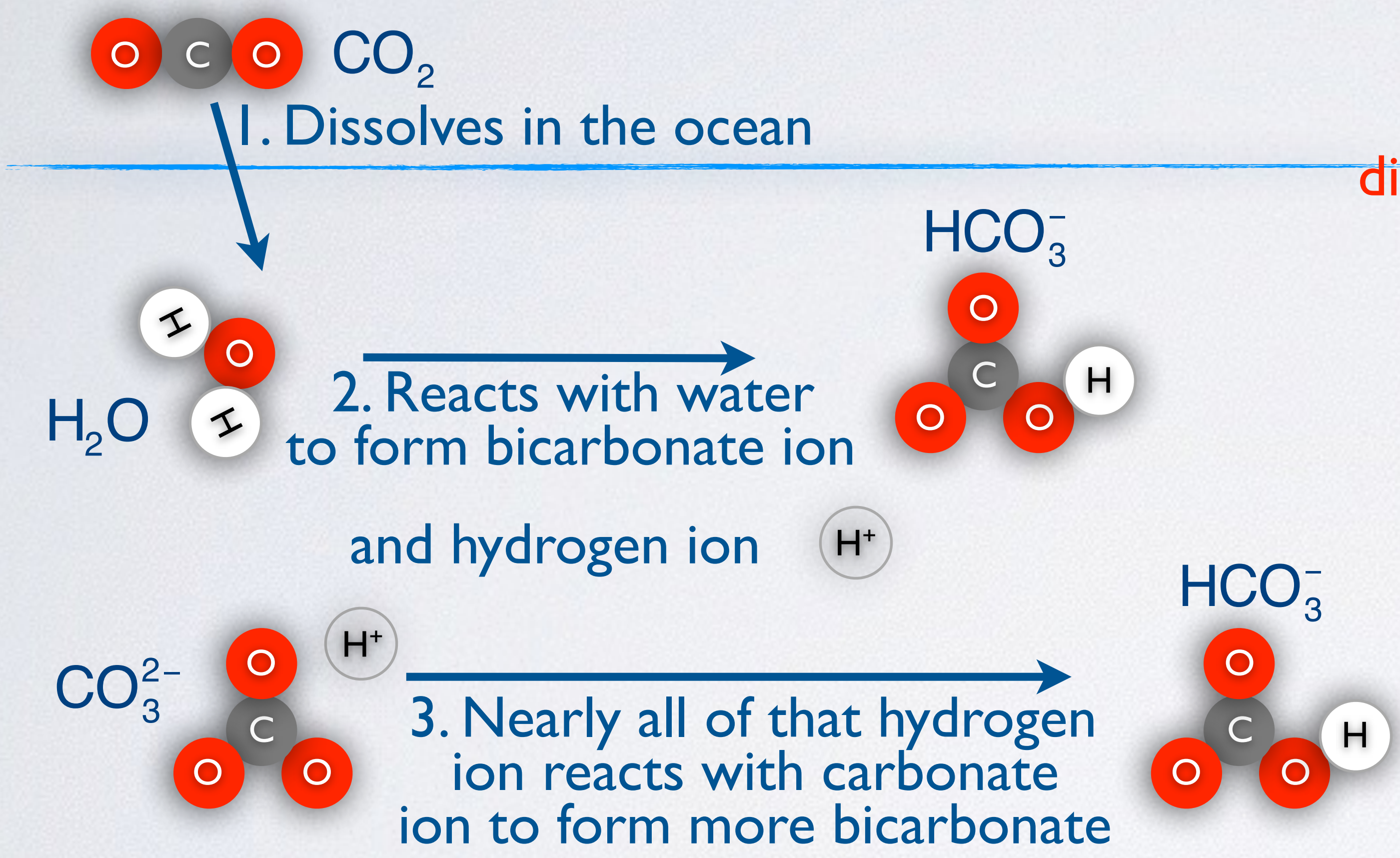
Monthly Average Carbon Dioxide Concentration

Data from Scripps CO_2 Program   Last updated November 2014



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

CO_3^{2-}

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

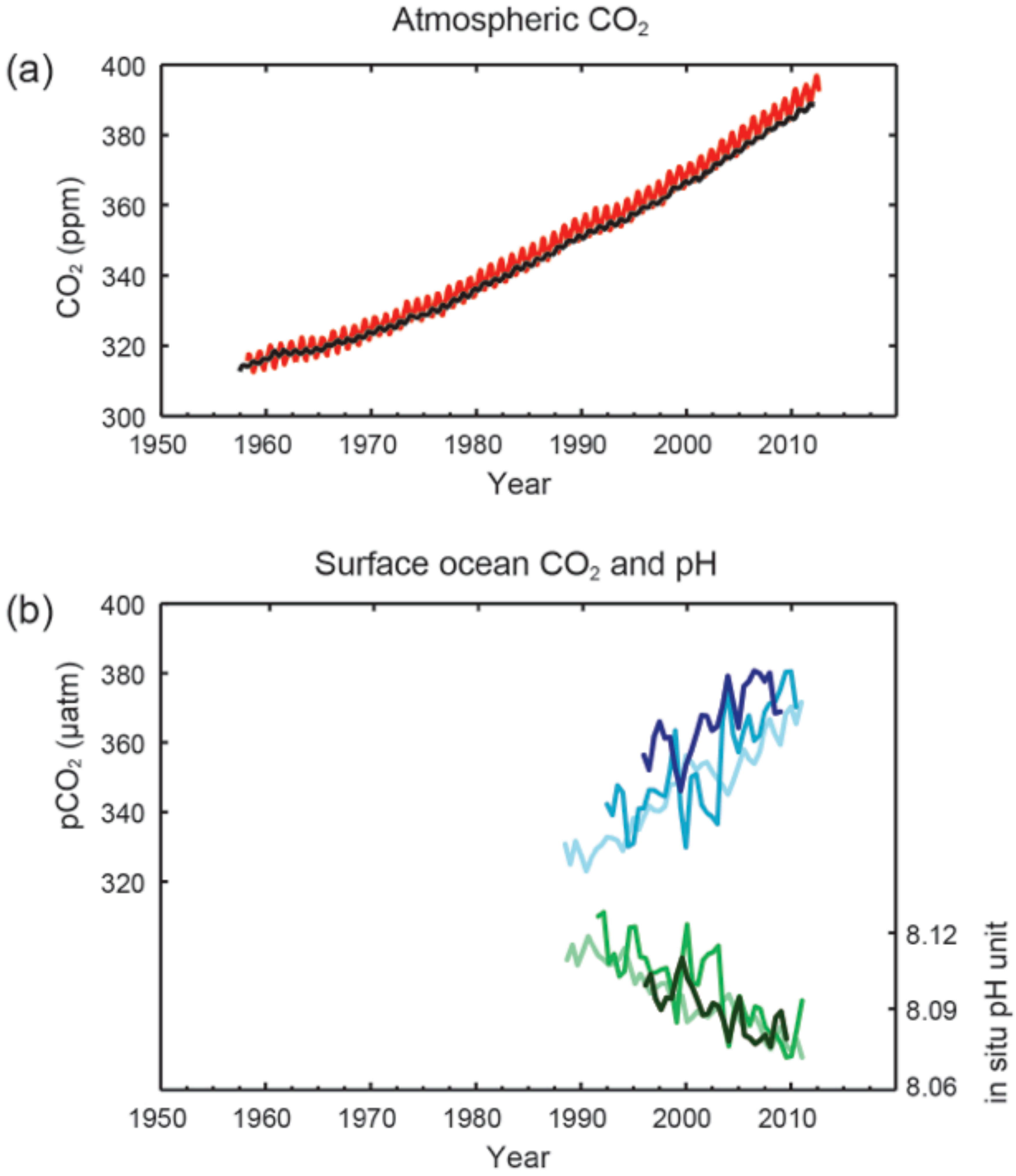
i.e., $pH = -\lg [H^+]$ decreases

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

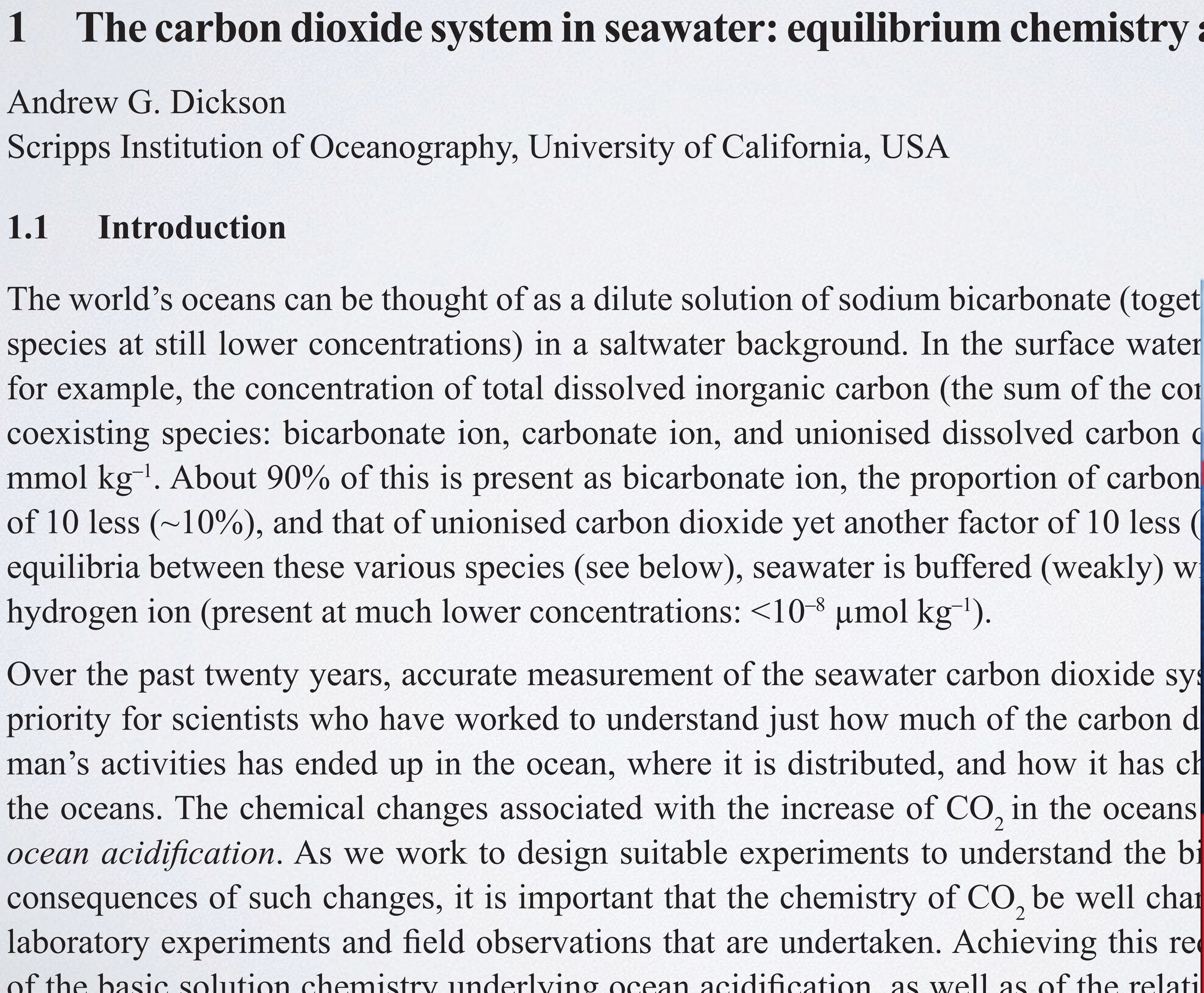
- If the CO_2 level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?
- What will be the consequent change in the saturation state of aragonite?
- Will this be the same all over the oceans? Why?
- How can I estimate the CO_2 composition of a sample of sea water?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

Available in the Dropbox



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

Andrew G. Dickson
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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

EUROPEAN COMMISSION
European Research Area

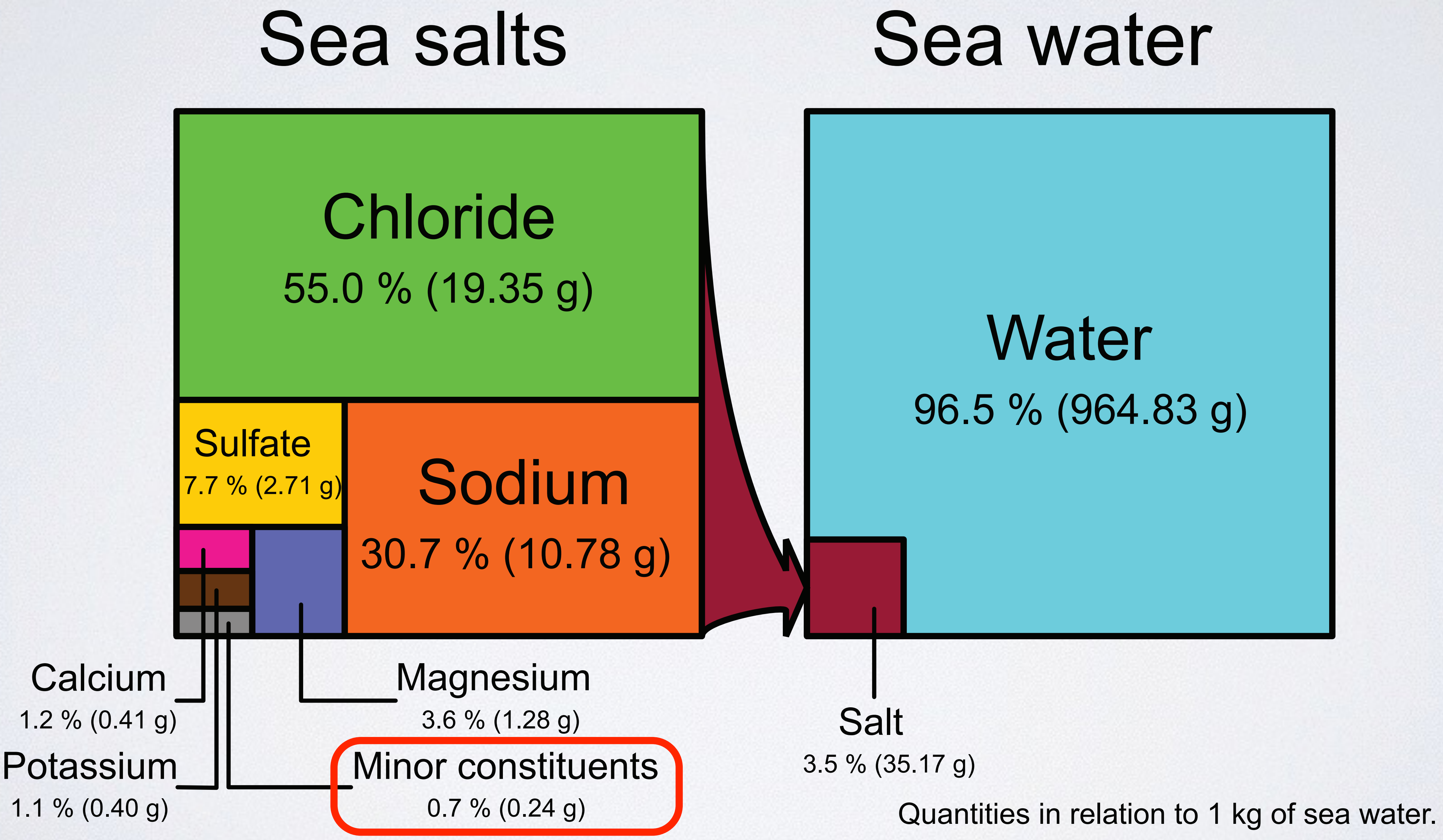
Guide
to best practices
for ocean acidification
research
and data reporting

EUR 24328 EN

GENERAL INFORMATION

INTRODUCTION TO CO_2 EQUILIBRIA IN SEA WATER

COMPOSITION OF SEA WATER ($S = 35$)



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; *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_3PO_4

$H_2PO_4^-$

NH_4^+

organic acids

OH^-

3.2 μmol kg^{-1}

$B(OH)_3$

organic bases

HF

PO_4^{3-}

NH_3

HPO_4^{2-}

$Si(OH)_4$

$B(OH)_4^-$

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

1903 µmol kg^{-1}

HCO_3^-

$SiO(OH)_3^-$

H^+

CO_2

15 µmol kg^{-1}

H_2O

CO_3^{2-}

$H_2PO_4^-$

H_3PO_4

NH_4^+

159 µmol kg^{-1}

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

344 µmol kg⁻¹

$B(OH)_3$

OH^-

organic bases

HF

PO_4^{3-}

NH_3

$Si(OH)_4$

HPO_4^{2-}

$B(OH)_4^-$

72 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

$H_2PO_4^-$

CO_3^{2-}

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

$Si(OH)_4$

1.8 µmol kg⁻¹

HPO_4^{2-}

$B(OH)_4^-$

other acid/base species

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

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

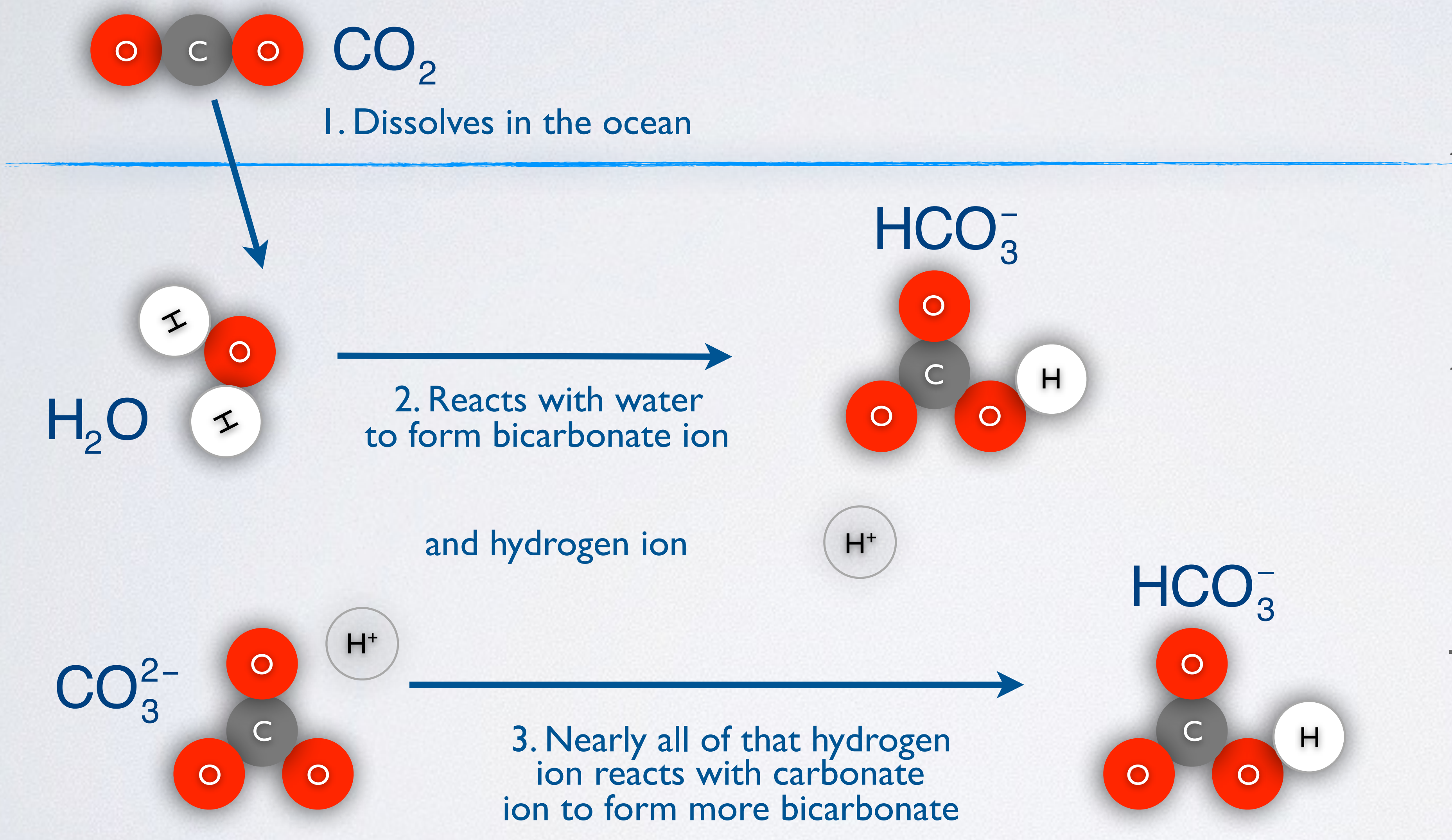
total hydrogen
ion concentration

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

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

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

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

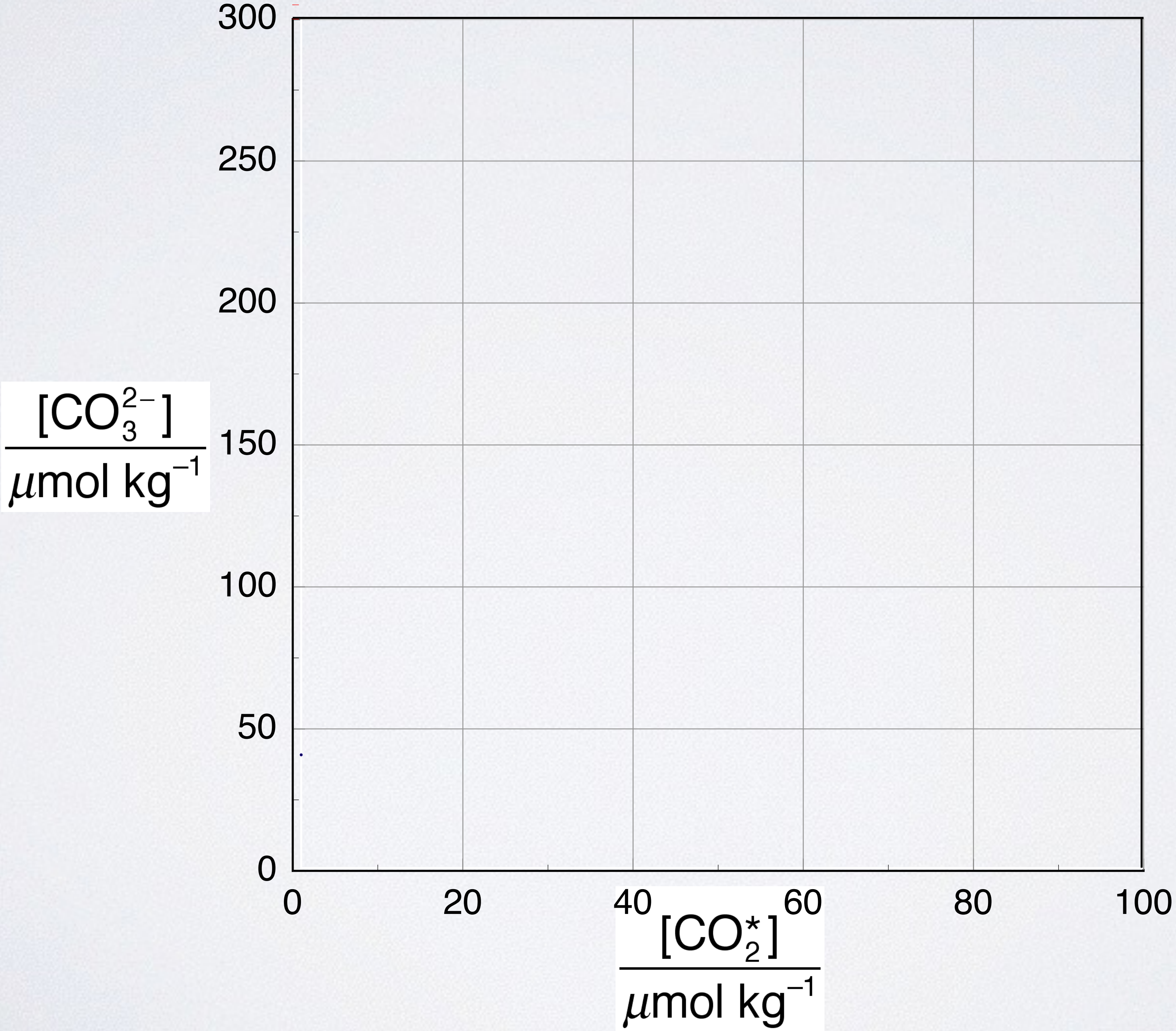
(in air that is in equilibrium with the water sample)

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

T, p dependent

UNITS: pressure units (usually μatm)

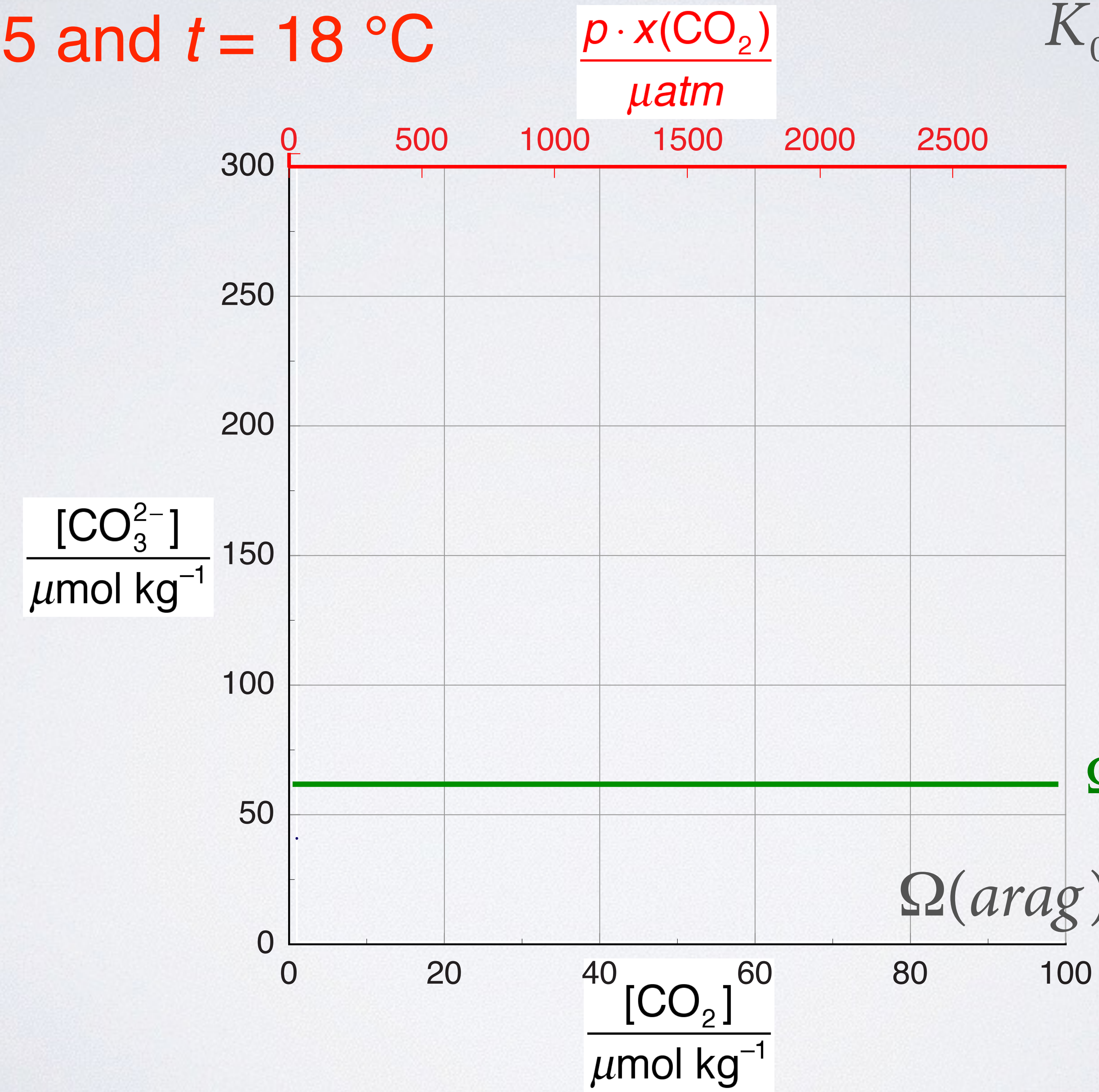
CO_2 SYSTEM RELATIONSHIPS IN SEA WATER



CO2 SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18$ °C

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



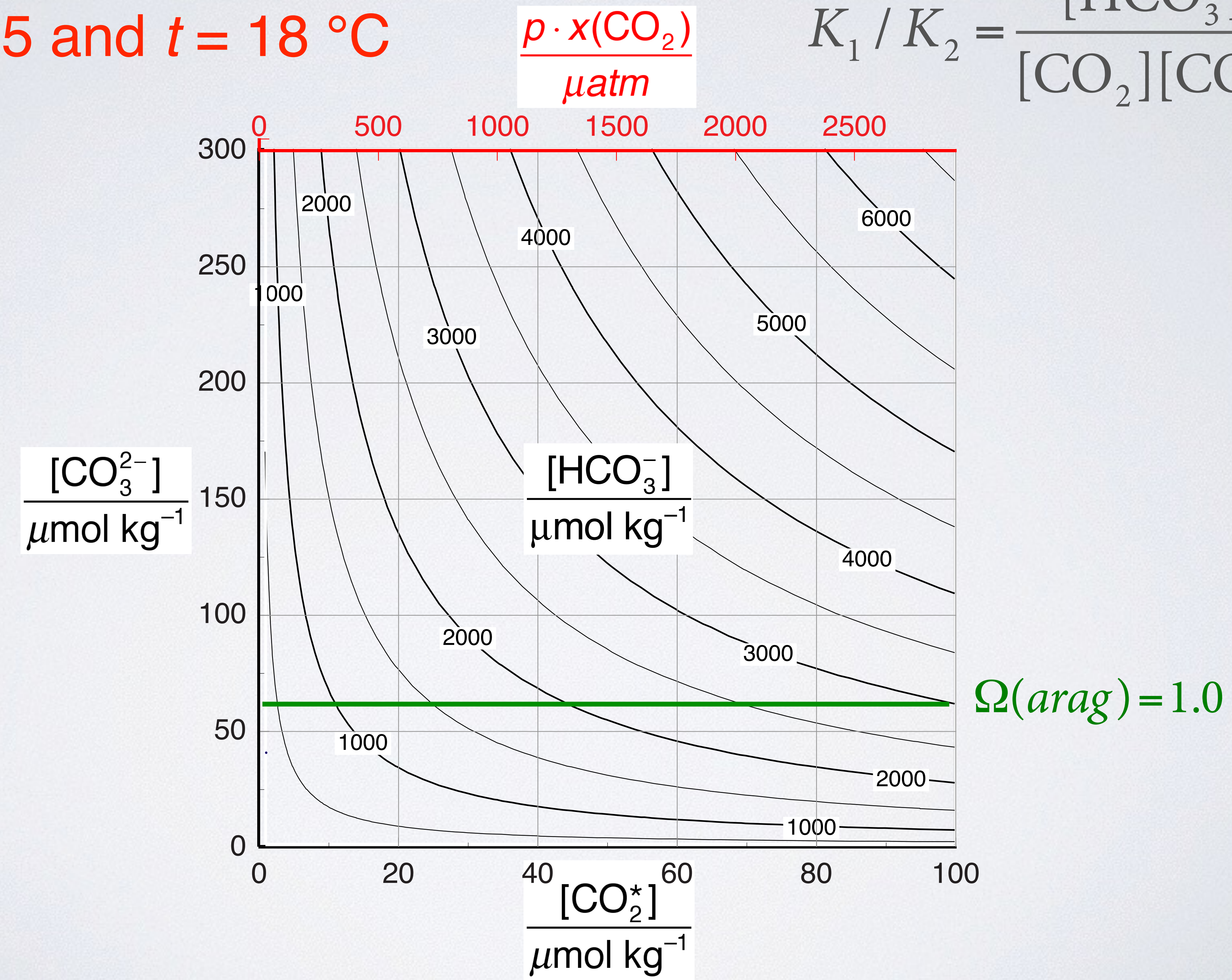
$\Omega(arag) = 1.0$

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

CO_2 SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18$ °C

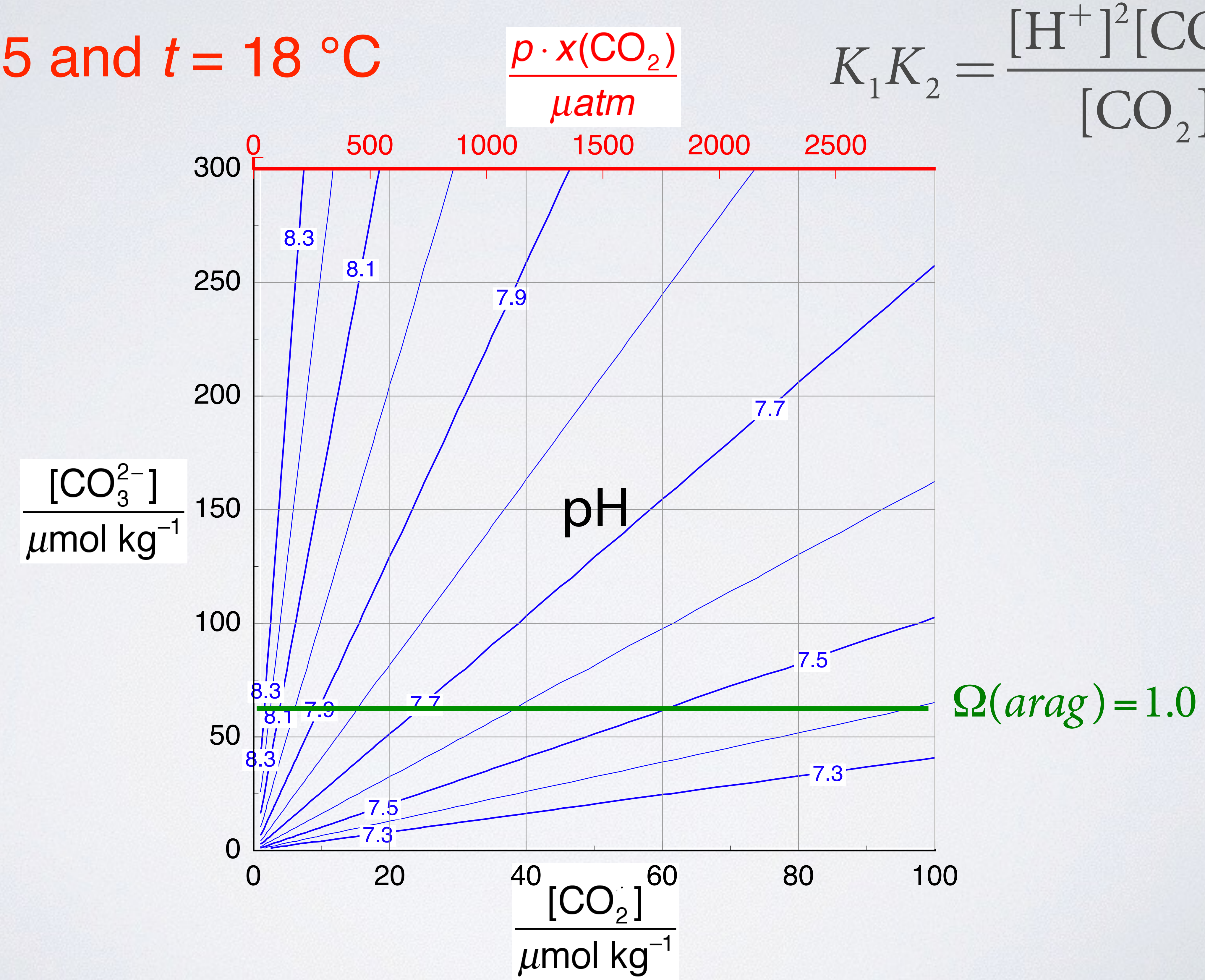
$$K_1 / K_2 = \frac{[HCO_3^-]^2}{[CO_2][CO_3^{2-}]}$$



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.

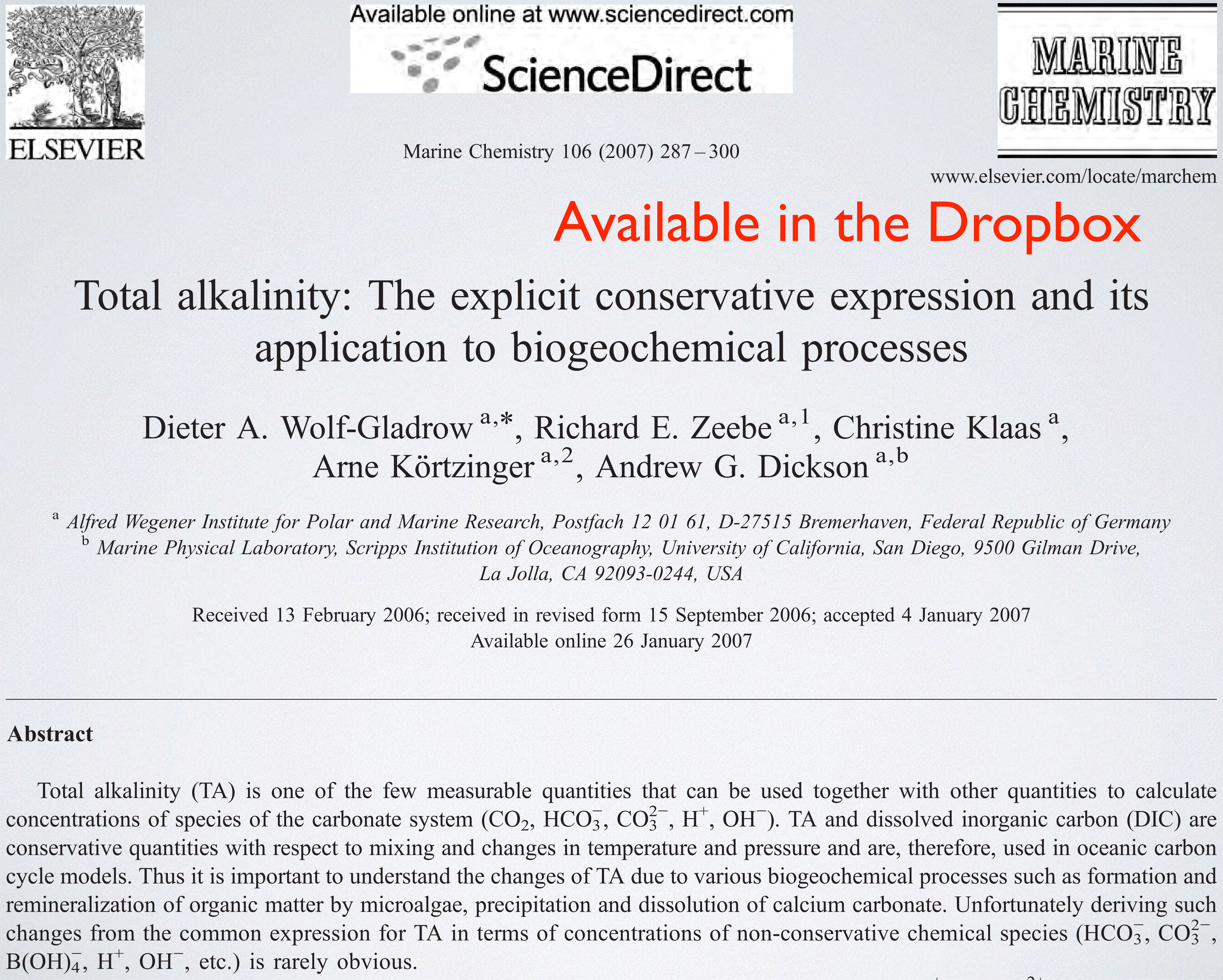
TOTAL ALKALINITY

$$A_{\mathrm{T}} \enclose{circle}{\approx} [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}]$$

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?



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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 and for total concentrations such as boron that are proportional to salinity.

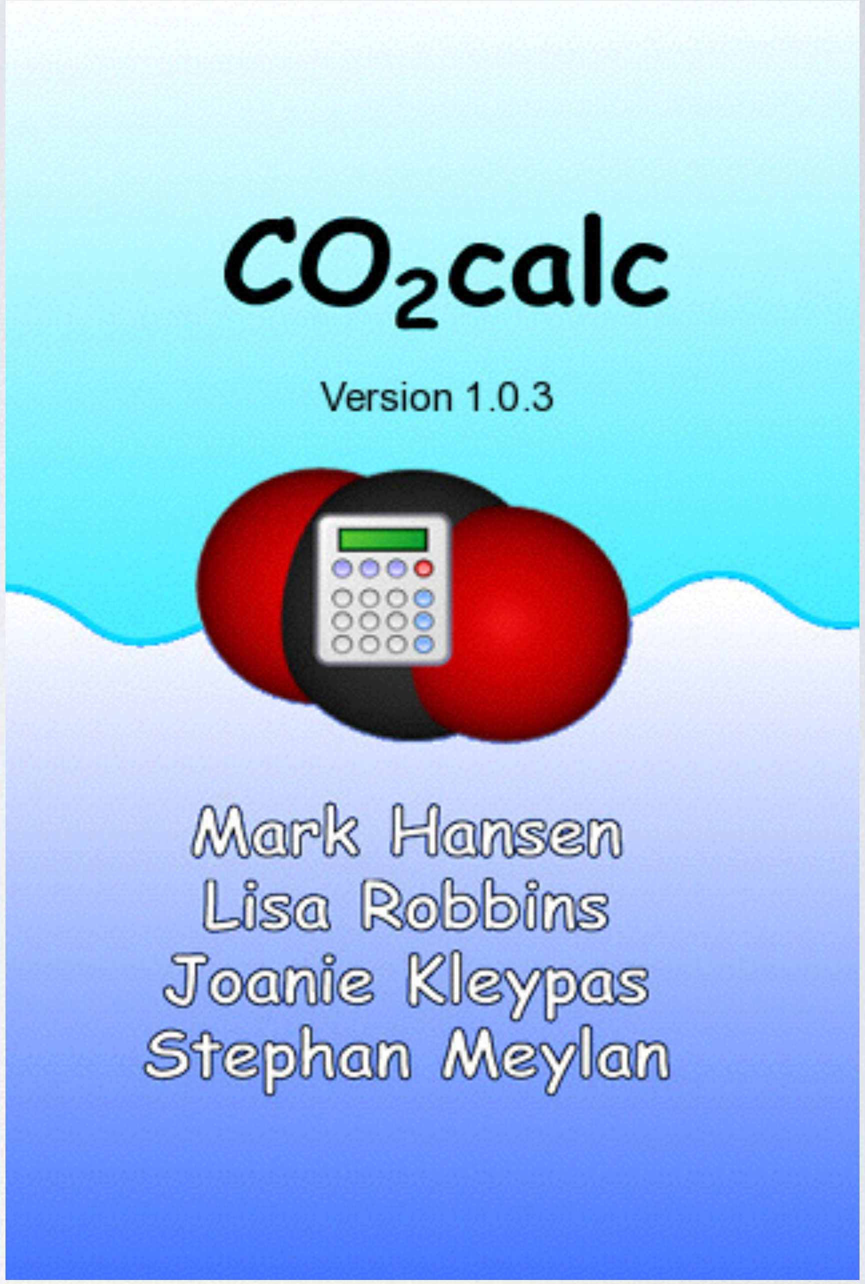
- Allow some additional acid-base information to be added (*e.g.* total phosphate and/or total silicate concentrations)

- 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)

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



CO_2calc

Version 1.0.3

Mark Hansen
Lisa Robbins
Joanie Kleypas
Stephan Meylan

Open-File Report 2010–1280

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

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.

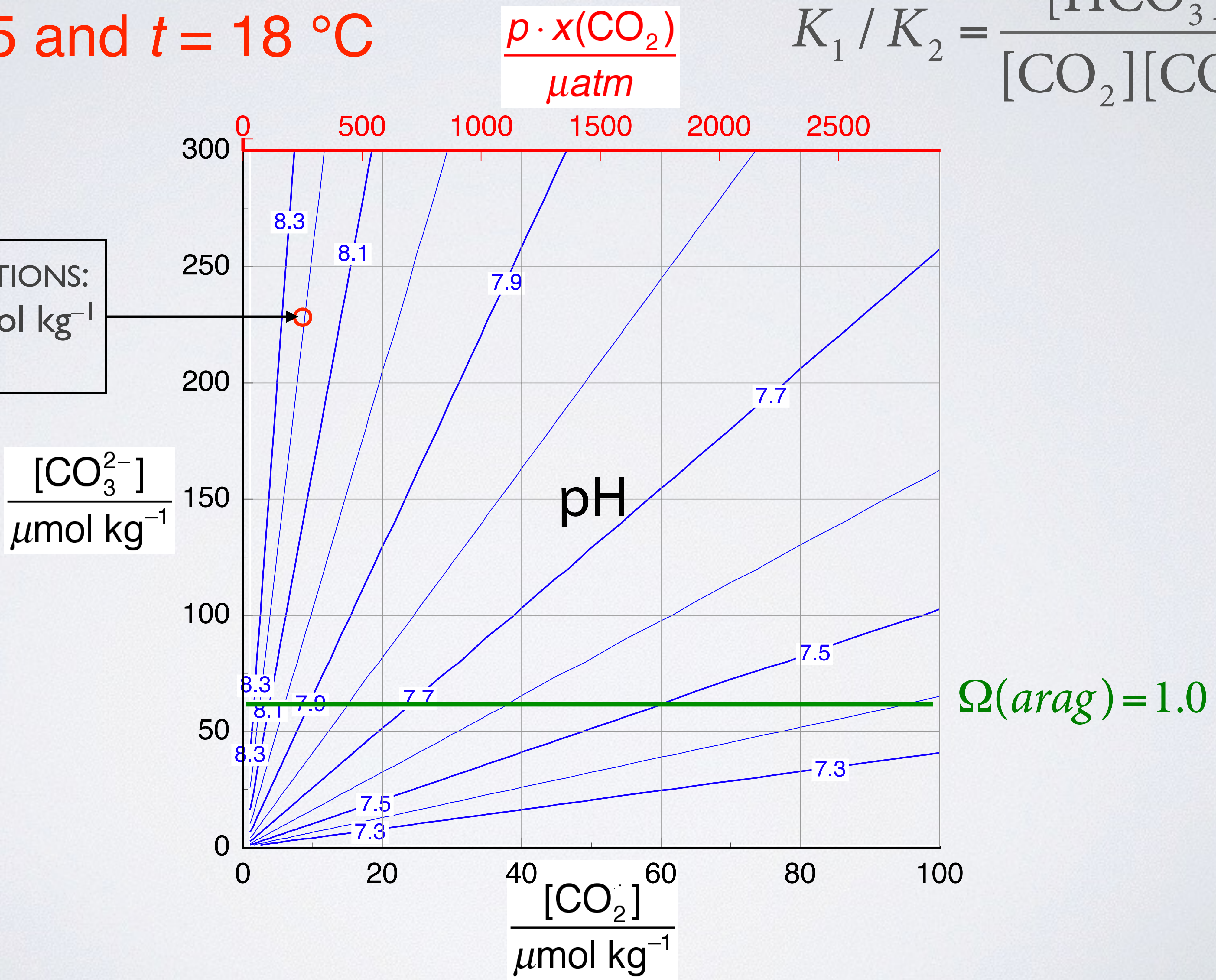
IMPLICATIONS FOR THE "ACIDIFICATION" OF SEA WATER

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



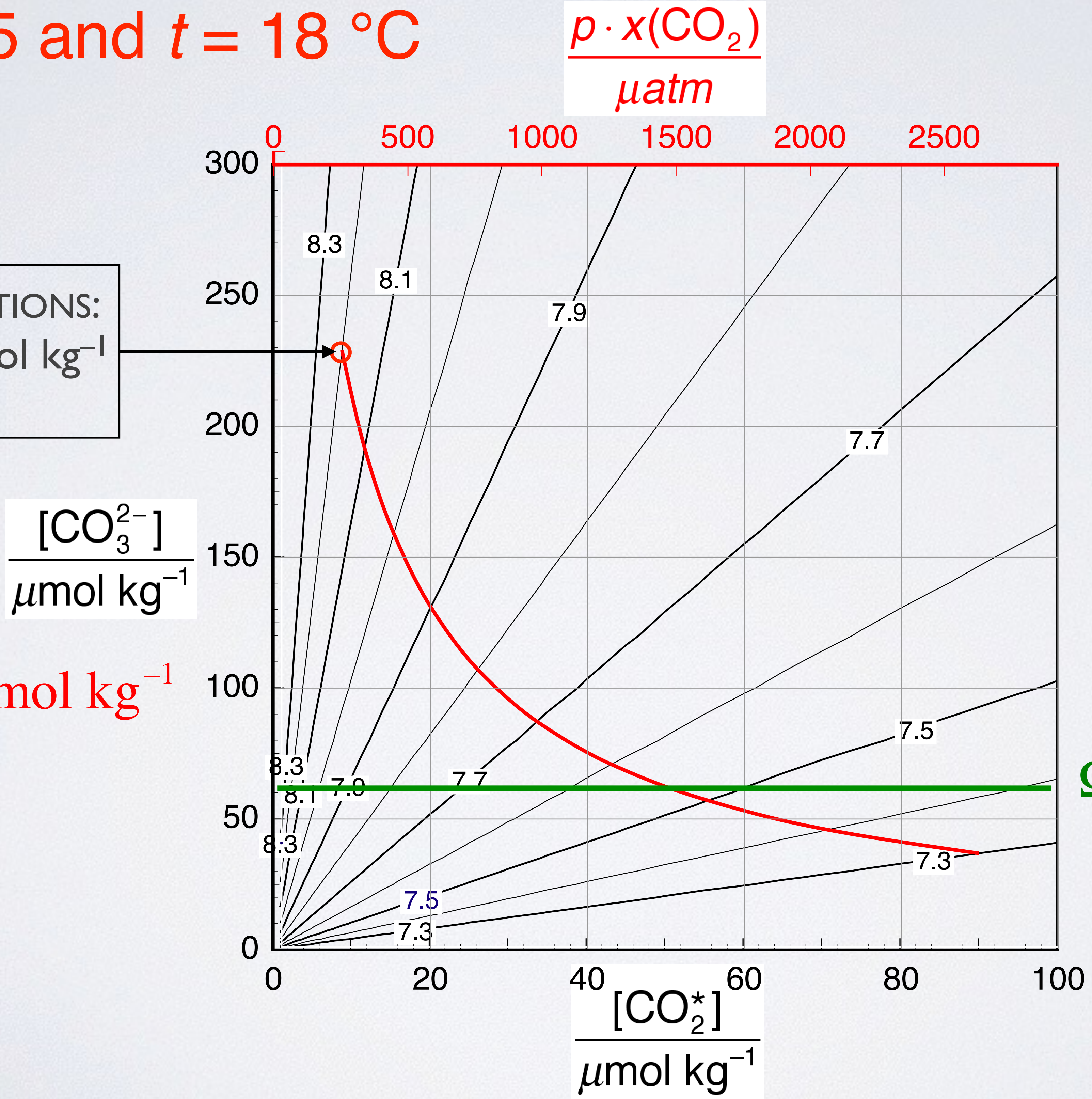
ACIDIFICATION TO PH 7.3 (BY ADDITION OF CO_2)

At $S = 35$ and $t = 18$ °C

INITIAL CONDITIONS:

$A_T = 2300$ μmol kg^{-1}

pH = 8.2



$\Delta C_T \approx +360\ \mu mol\ kg^{-1}$

FINAL CONDITIONS:

$p(CO_2) = 2630$ μatm

$[CO_3^{2-}] = 37$ μmol kg^{-1}

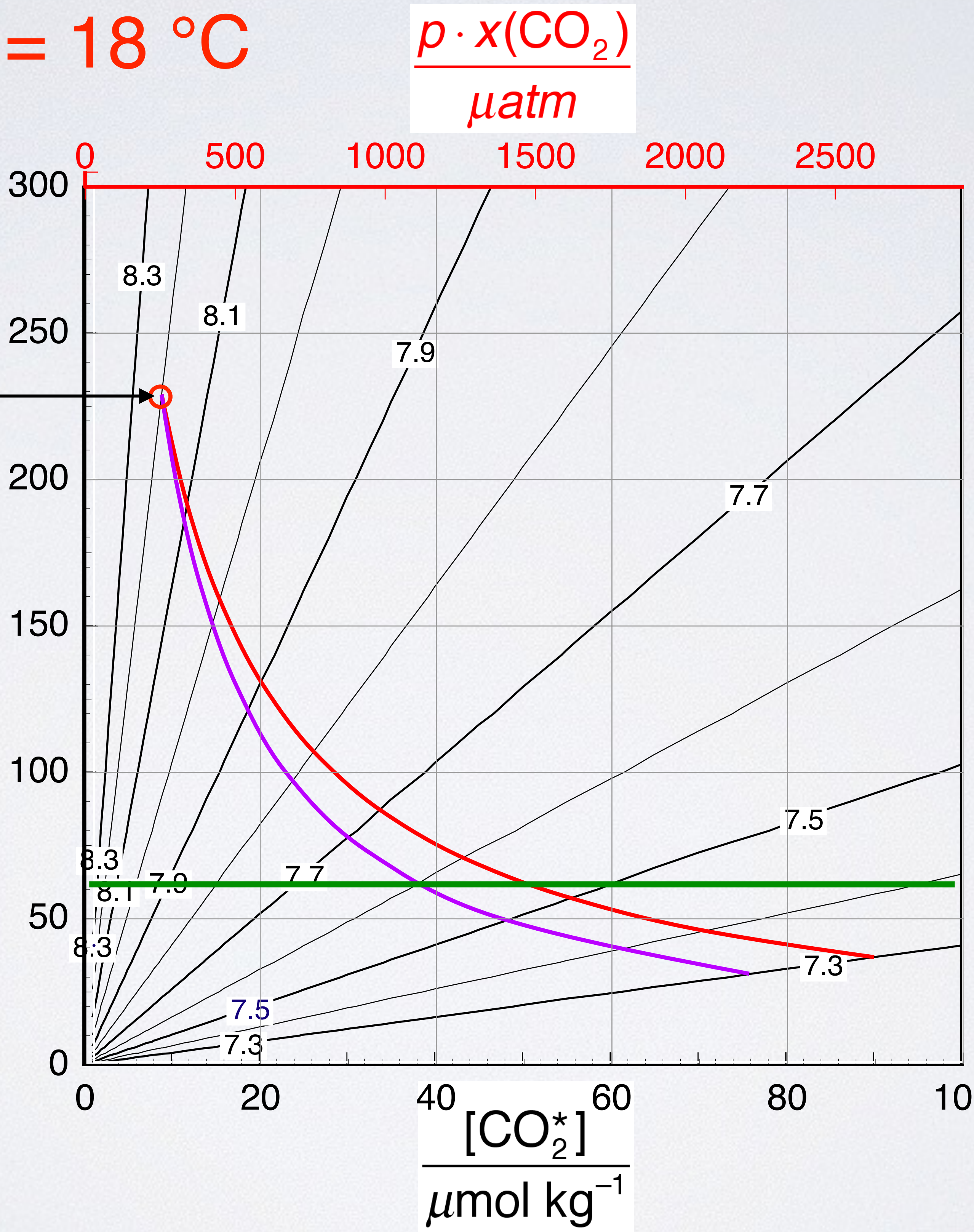
$\Omega(arag) = 0.57$

$\Omega(arag) = 1.0$

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



$\Delta C_T \approx +365\ \mu$mol kg^{-1}

$\Delta A_T \approx -358\ \mu$mol kg^{-1}

FINAL CONDITIONS:
$p(\mathrm{CO_2})$ = 2630 µatm
$[\mathrm{CO_3^{2-}}]$ = 37 µmol kg^{-1}
$\Omega(arag)$ = 0.57

$\Omega(arag)$ = 1.0

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

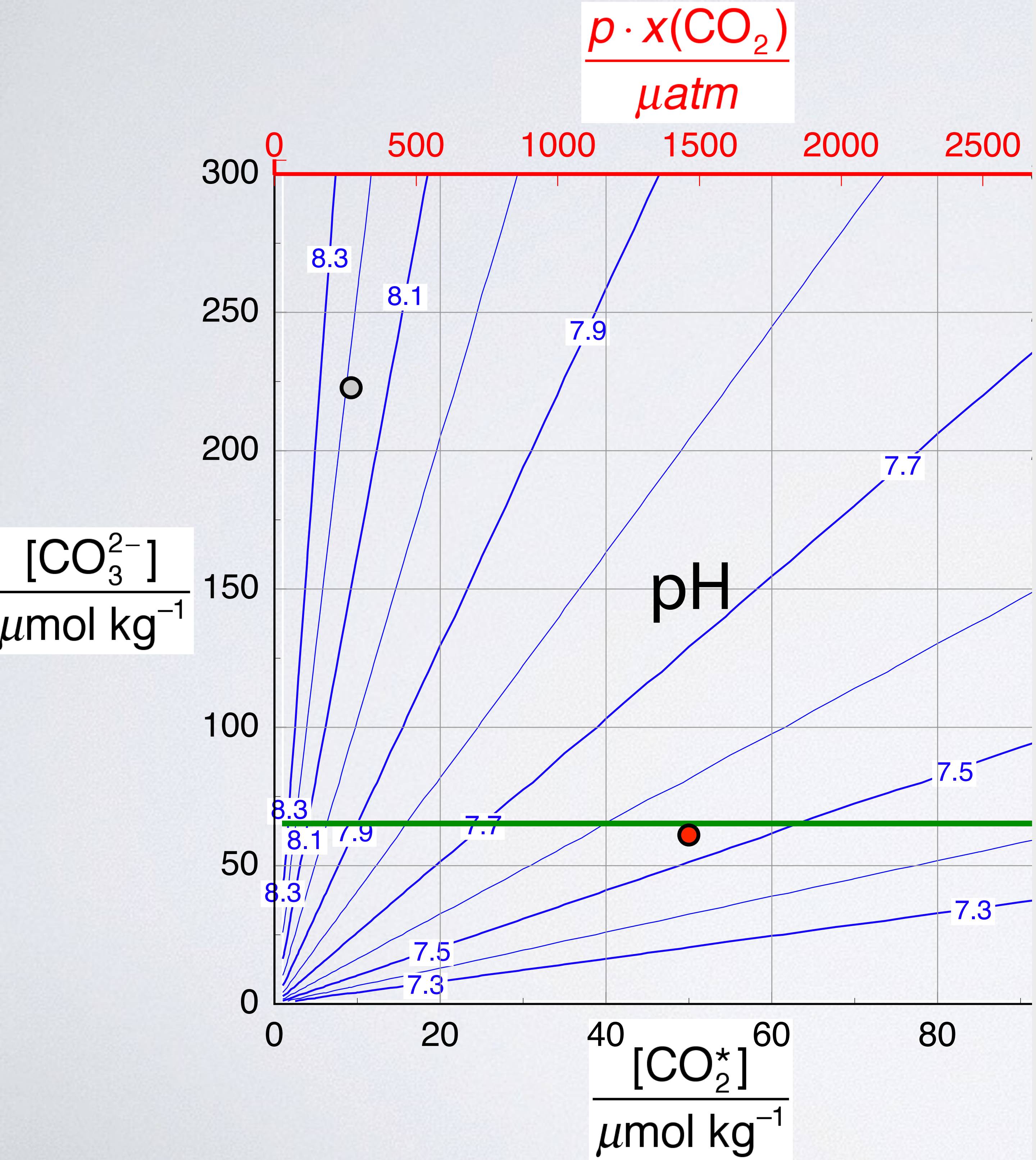
What happens at a different temperature?

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

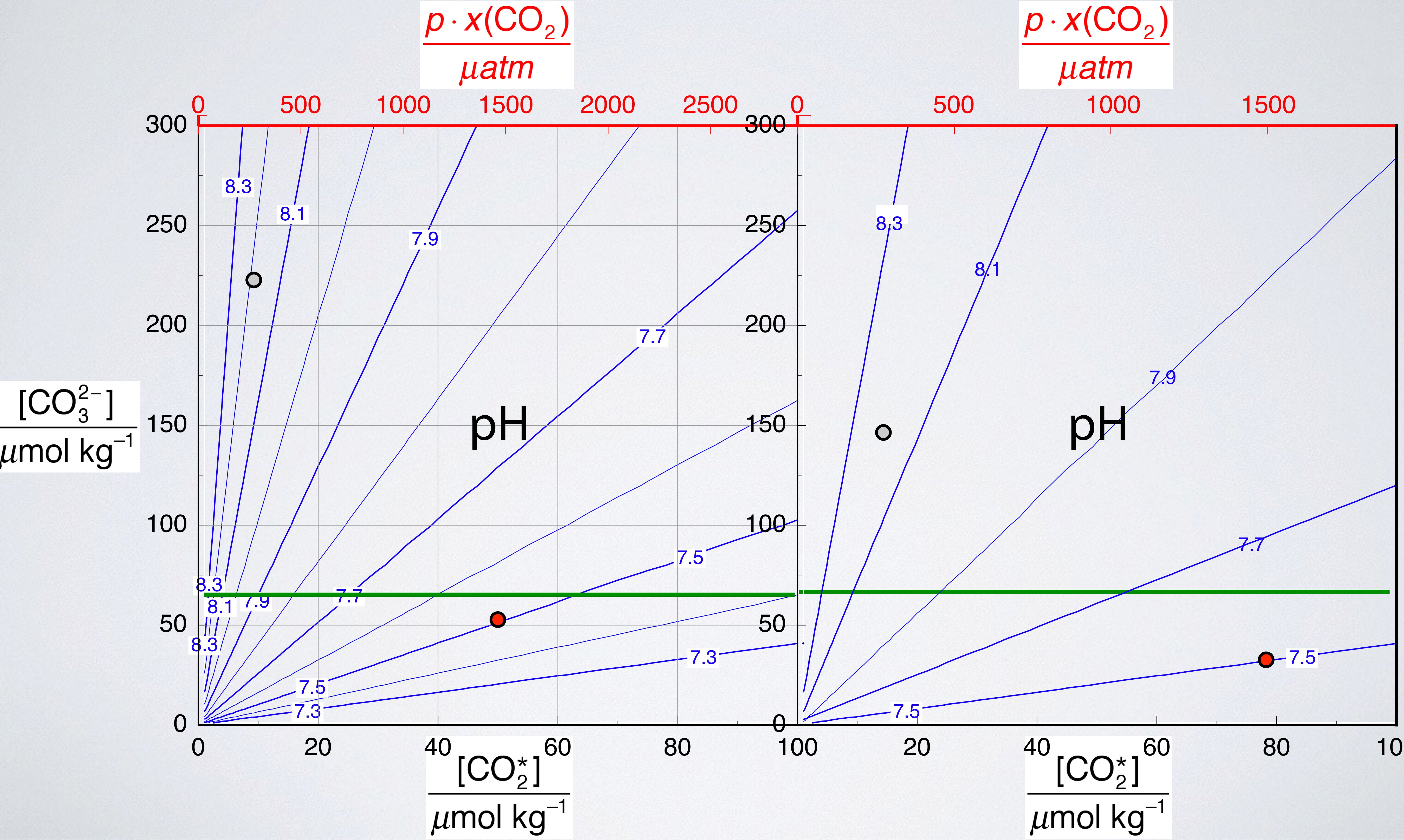
18 °C



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

18 °C 5 °C



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

$S = 35$	18 °C	5 °C
$A_T = 2300$ µmol kg^{-1}		
$p(\mathrm{CO_2})$	280 µatm	
pH	8.17	8.18
$\Omega(arag)$	3.37	2.19
C_T	1984 µmol kg^{-1}	2092 µmol kg^{-1}
$p(\mathrm{CO_2})$	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, and one just uses the alkalinity of the source sea water as is.
- It is often best to 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