

INTRODUCTION TO CO₂ CHEMISTRY IN SEA WATER

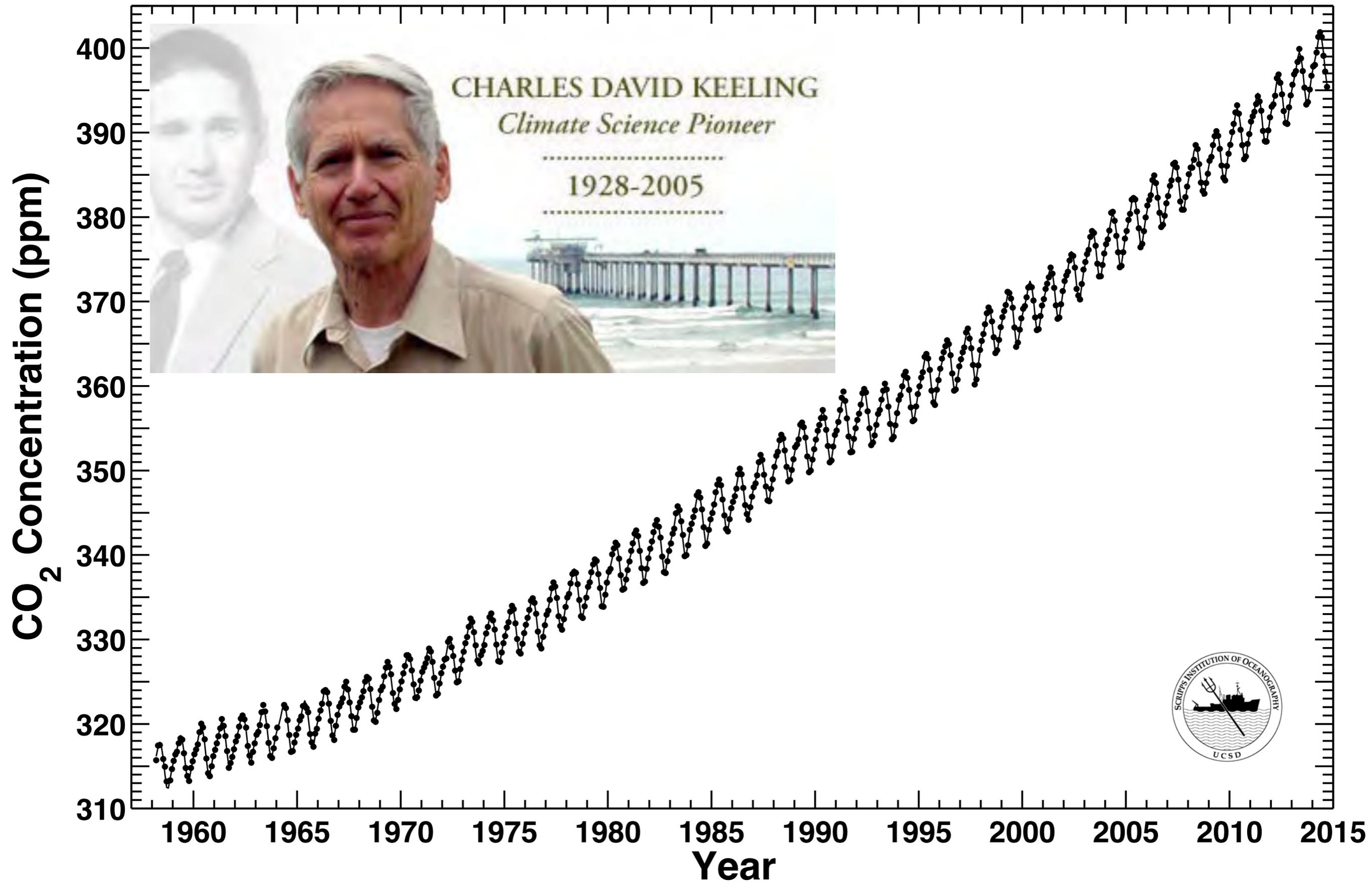
ANDREW G. DICKSON
SCRIPPS INSTITUTION OF OCEANOGRAPHY, UC SAN DIEGO



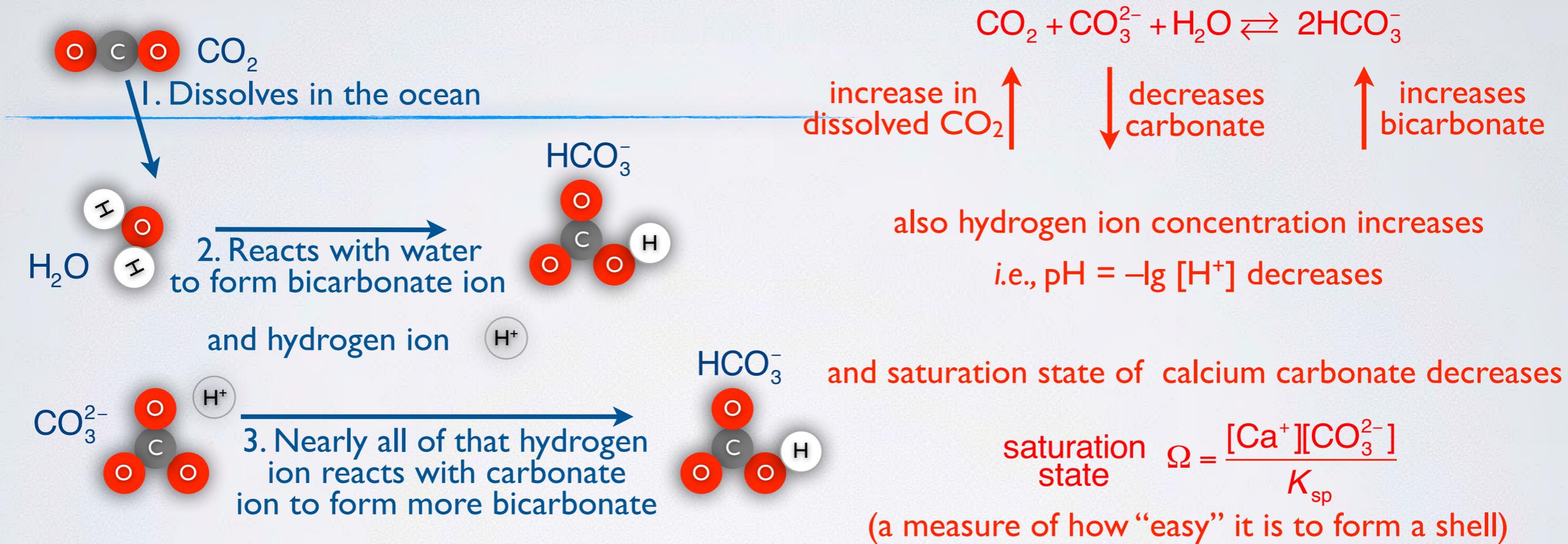
Mauna Loa Observatory, Hawaii

Monthly Average Carbon Dioxide Concentration

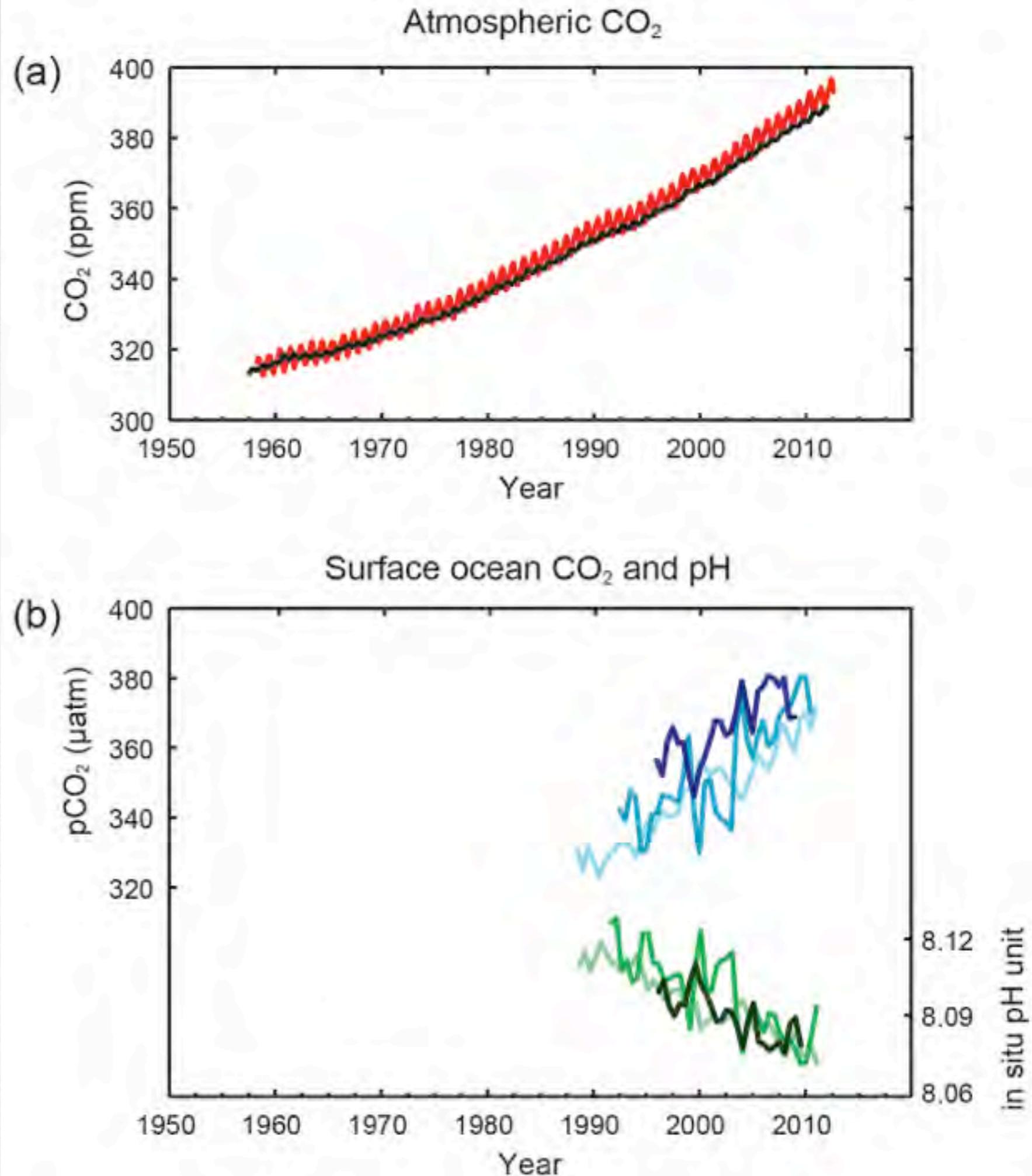
Data from Scripps CO₂ Program Last updated November 2014



EFFECT OF ADDING CO₂ TO SEA WATER



Multiple observed indicators of a changing global carbon cycle: (a) atmospheric concentrations of carbon dioxide (CO_2) from Mauna Loa ($19^\circ 32' \text{N}$, $155^\circ 34' \text{W}$ – red) and South Pole ($89^\circ 59' \text{S}$, $24^\circ 48' \text{W}$ – 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 ($29^\circ 10' \text{N}$, $15^\circ 30' \text{W}$ – dark blue/dark green; $31^\circ 40' \text{N}$, $64^\circ 10' \text{W}$ – blue/green) and the Pacific ($22^\circ 45' \text{N}$, $158^\circ 00' \text{W}$ – 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 200 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 CO₂) equilibria in sea water.
- Understanding of which CO₂ parameters in sea water are usually measured, and how.
- Access to suitable computational tools for the CO₂ system such as CO2calc.
- Access to suitable analytical equipment (and training) to make any CO₂ measurements desired.

Part 1: Seawater carbonate chemistry

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

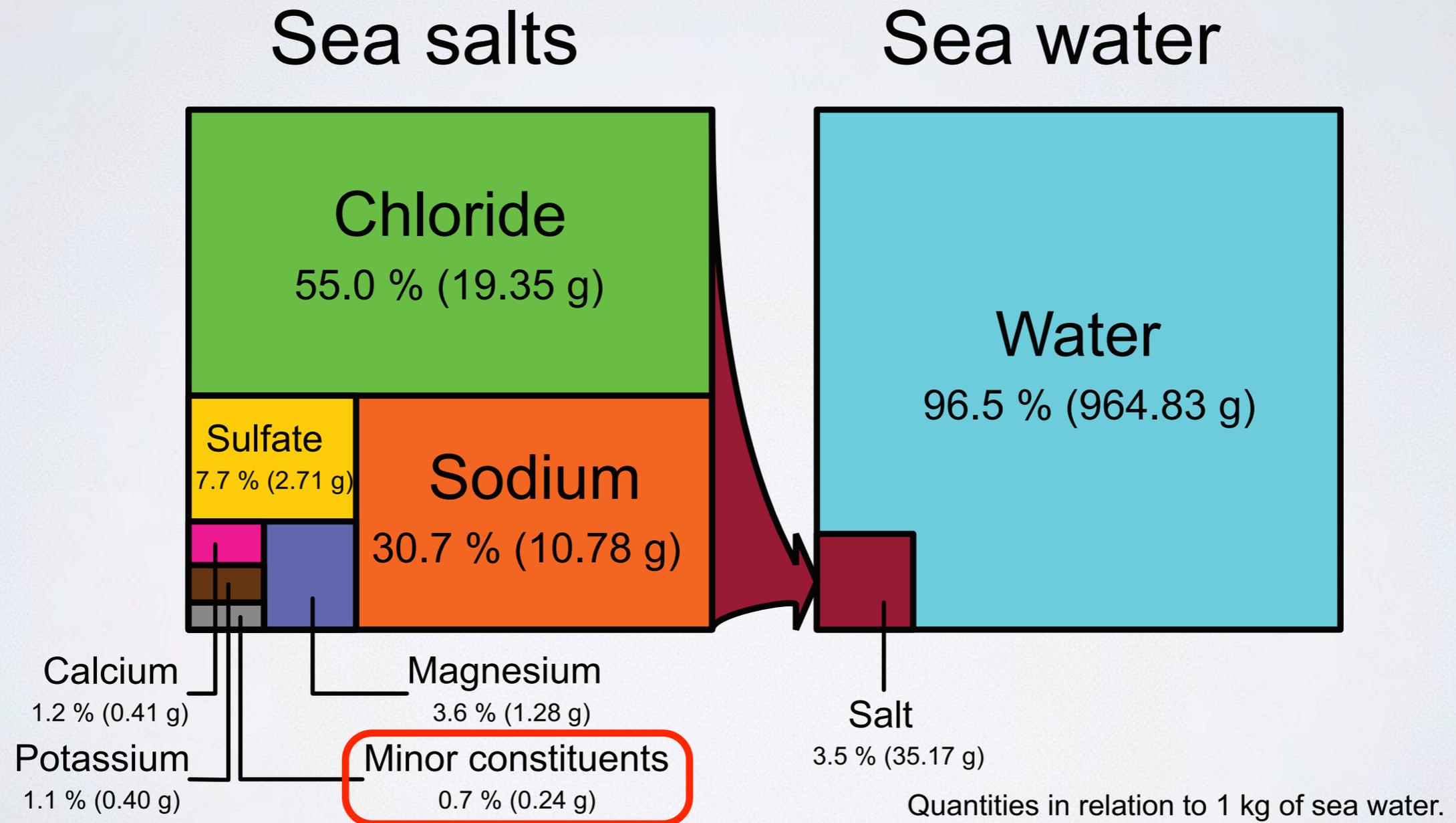
The world's oceans can be thought of as a dilute solution of sodium bicarbonate (together with other carbonate species at still lower concentrations) in a saltwater background. In the surface water, for example, the concentration of total dissolved inorganic carbon (the sum of the carbonate species: bicarbonate ion, carbonate ion, and unionised dissolved carbon dioxide) is about 2 mmol kg⁻¹. About 90% of this is present as bicarbonate ion, the proportion of carbonate ion is about 10% less (~10%), and that of unionised carbon dioxide is yet another factor of 10 less (1%). Because of the equilibria between these various species (see below), seawater is buffered (weakly) against changes in hydrogen ion concentration (present at much lower concentrations: <10⁻⁸ μmol kg⁻¹).

Over the past twenty years, accurate measurement of the seawater carbon dioxide system has become a high priority for scientists who have worked to understand just how much of the carbon dioxide from human's activities has ended up in the ocean, where it is distributed, and how it has changed the chemistry of the oceans. The chemical changes associated with the increase of CO₂ in the oceans are known as *ocean acidification*. As we work to design suitable experiments to understand the biological and chemical consequences of such changes, it is important that the chemistry of CO₂ be well characterised through laboratory experiments and field observations that are undertaken. Achieving this requires a good understanding of the basic solution chemistry underlying ocean acidification, as well as of the relative

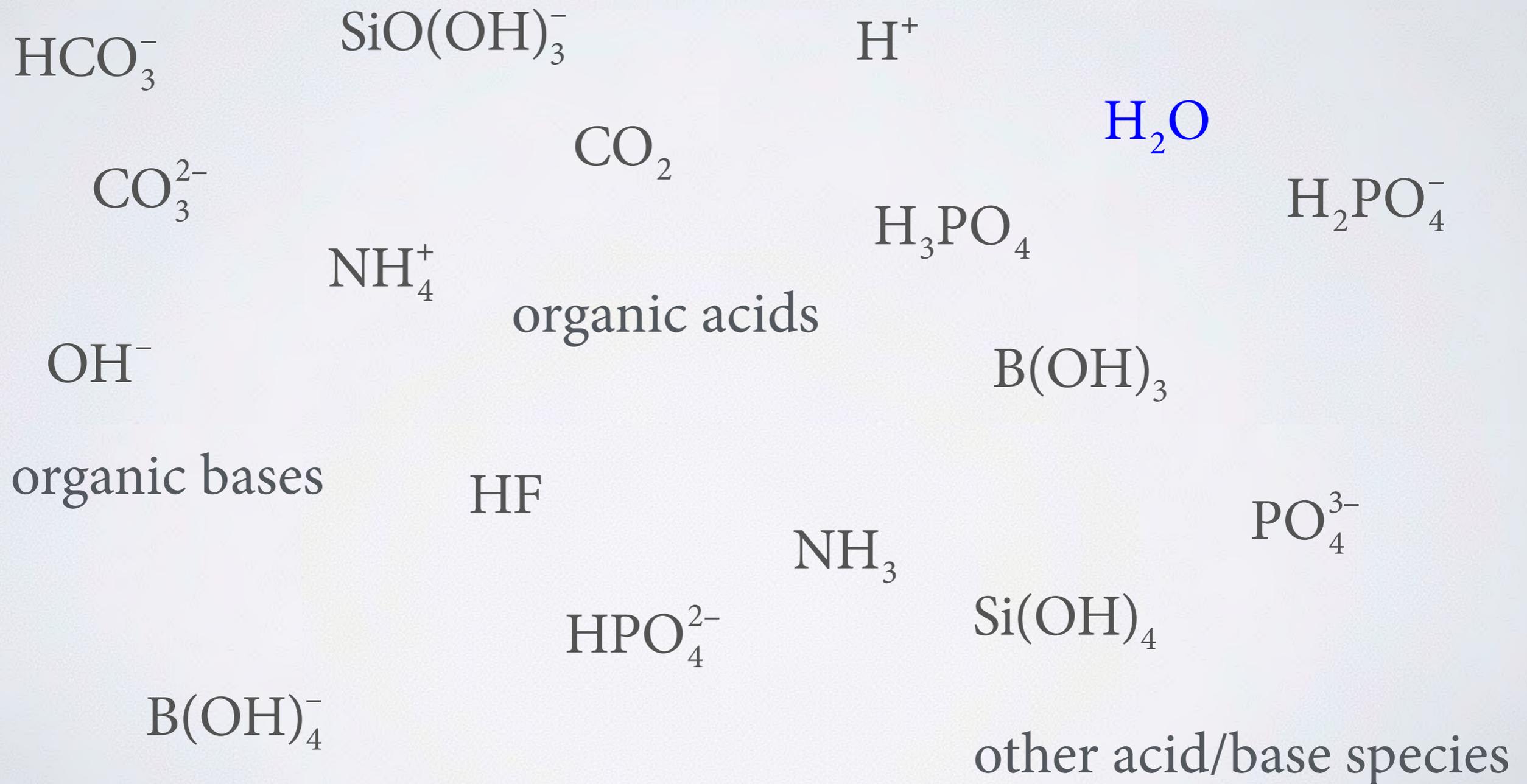


INTRODUCTION TO CO₂ EQUILIBRIA IN SEA WATER

COMPOSITION OF SEA WATER ($S = 35$)

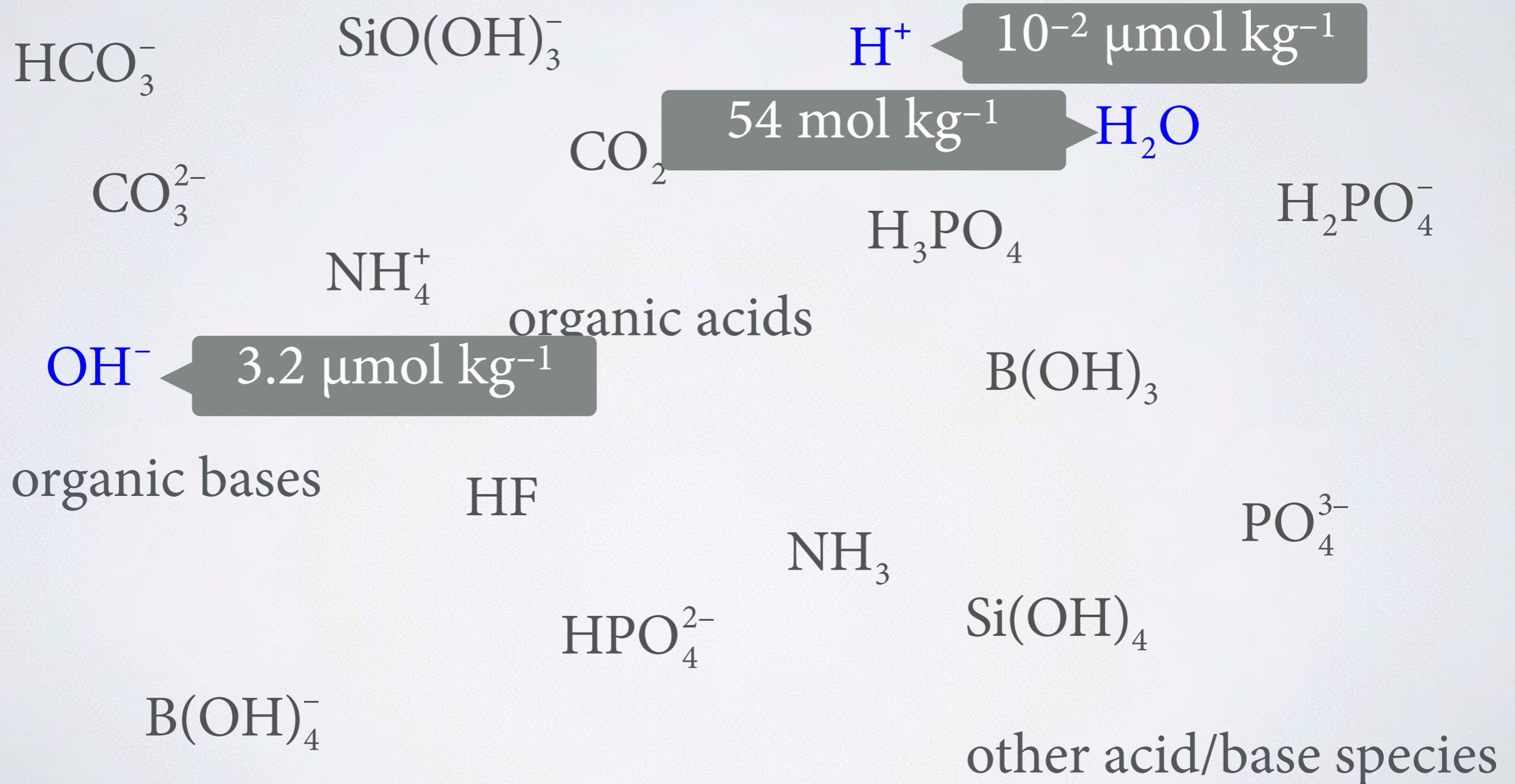


ACID-BASE SPECIES COMPRISE A SUBSET OF THE “MINOR CONSTITUENTS” PRESENT IN SEAWATER



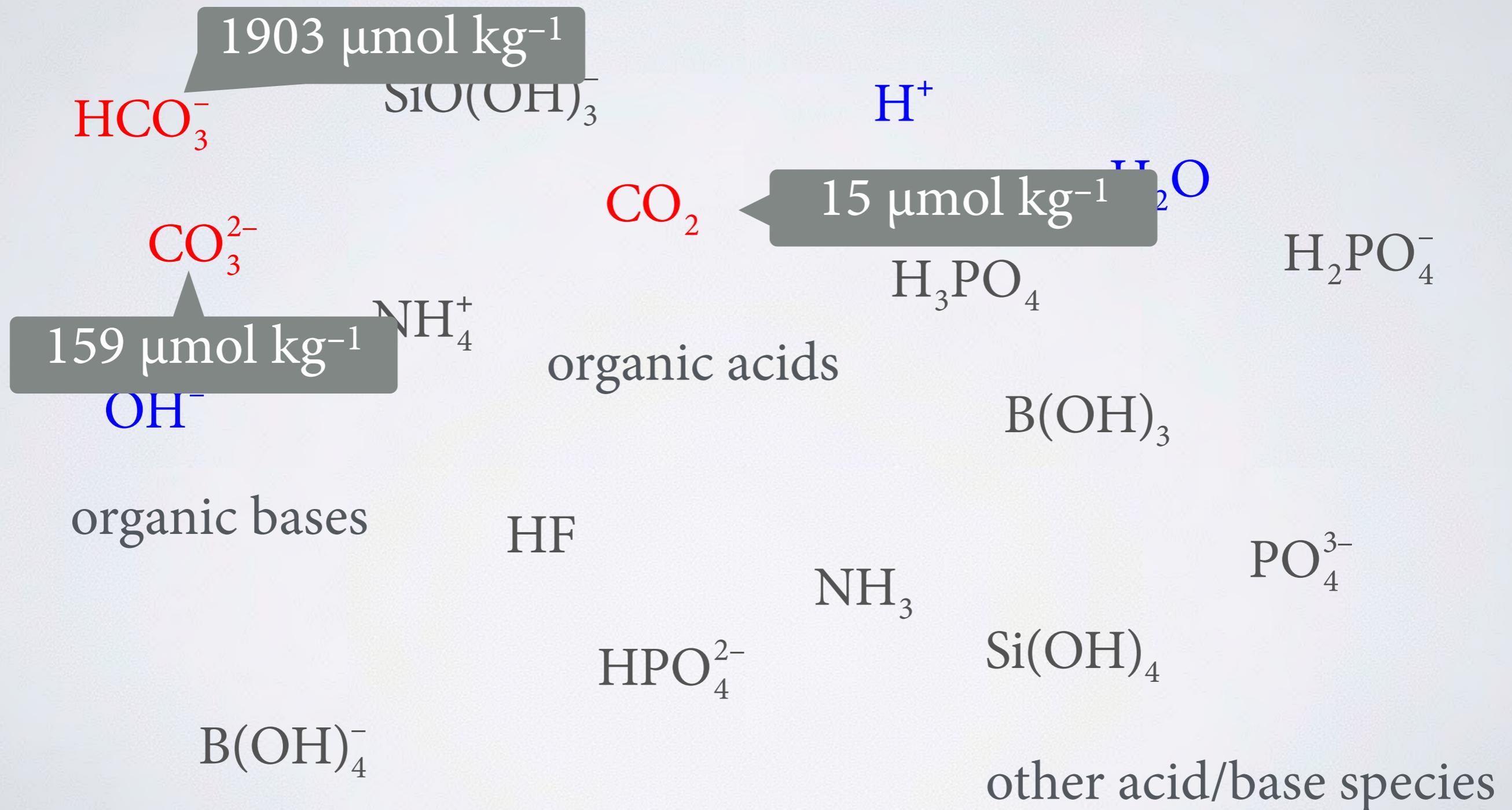
Average ocean water; pH = 8; $t = 18\text{ }^\circ\text{C}$; $S = 35$

ACID-BASE SPECIES COMPRISE A SUBSET OF THE
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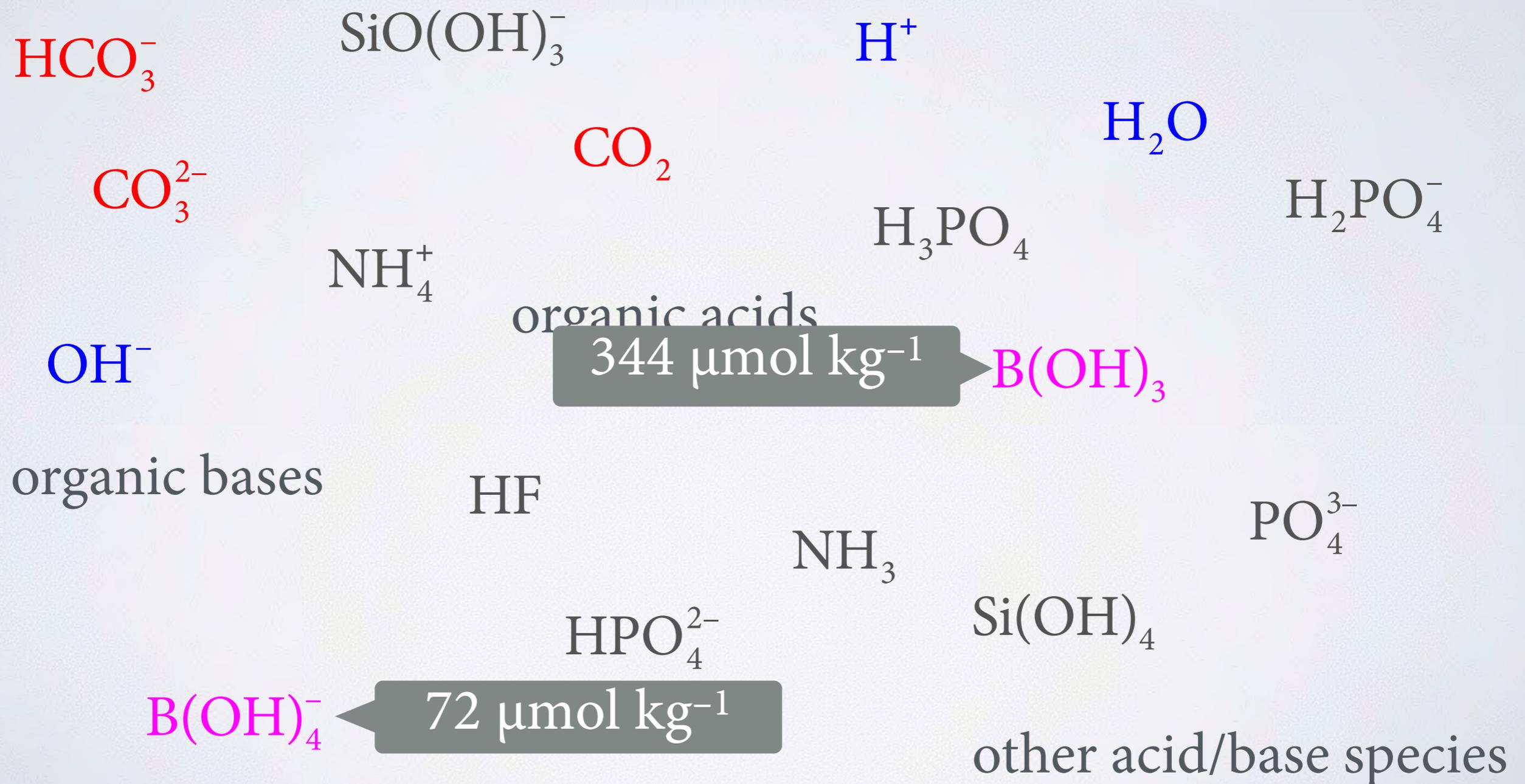
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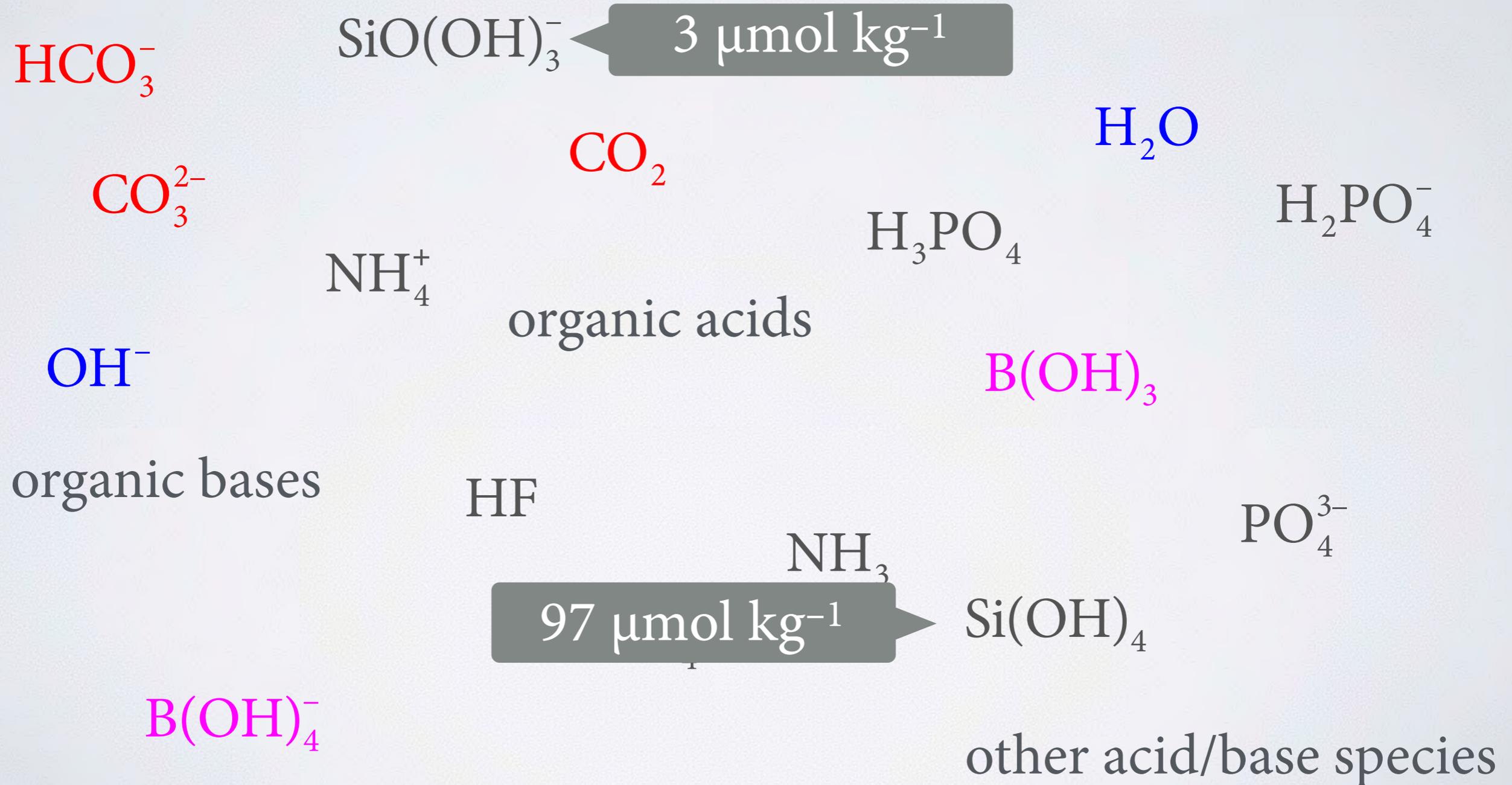
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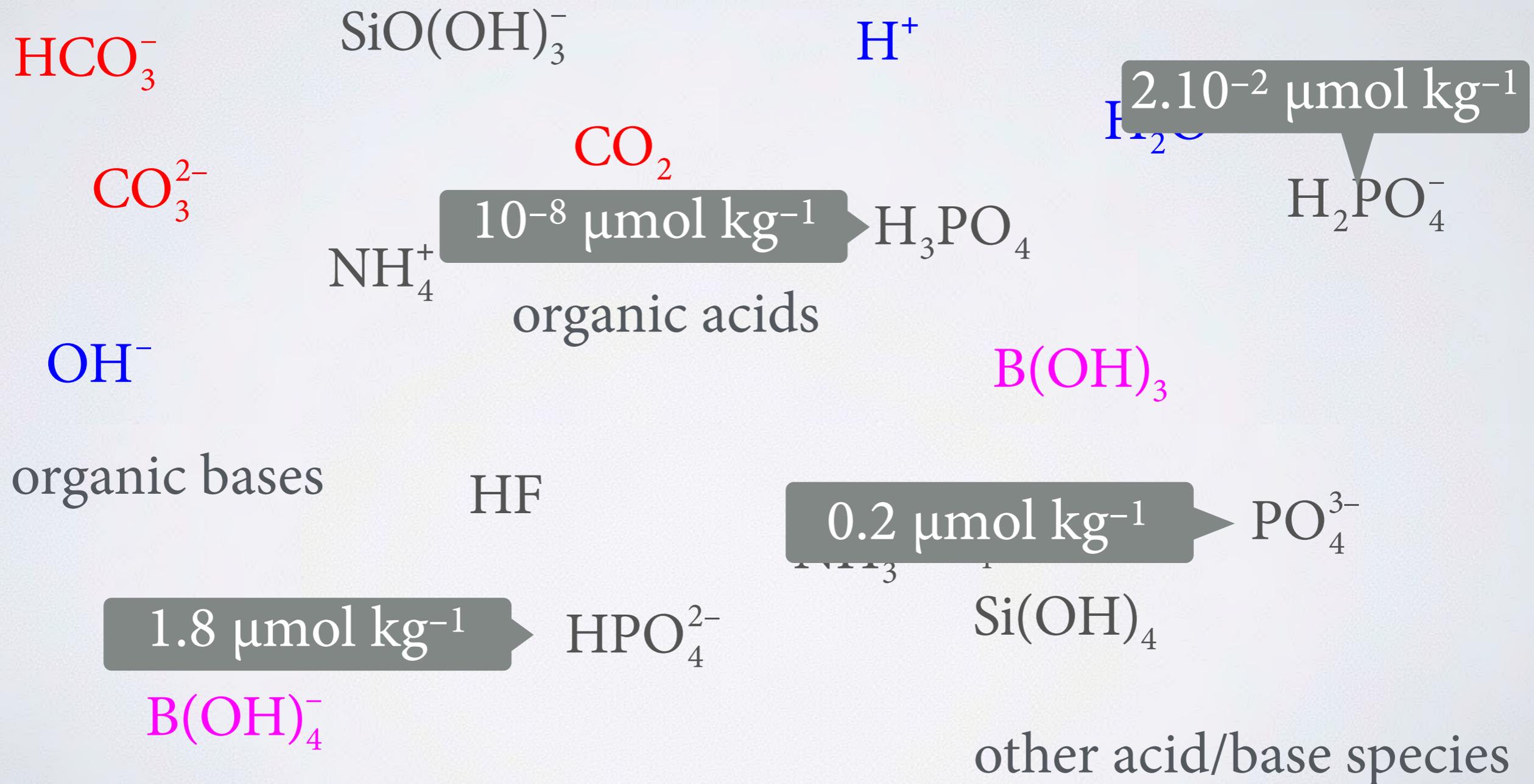
Average ocean water; pH = 8; $t = 18\text{ }^\circ\text{C}$; $S = 35$

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



Average ocean water; pH = 8; $t = 18\text{ }^\circ\text{C}$; $S = 35$

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



CARBON DIOXIDE EQUILIBRIA IN SEA WATER

Gas solubility

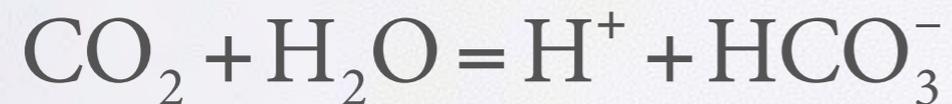


$$K_0 = \frac{\text{concentration of unionized CO}_2 \text{ in sea water (mol kg}^{-1}\text{)}}{x(\text{CO}_2) \cdot p}$$

mole fraction of CO_2

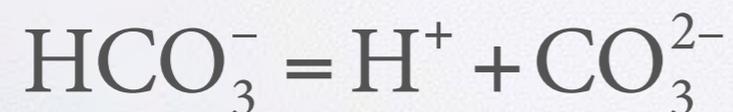
equilibration pressure

Acid Dissociation



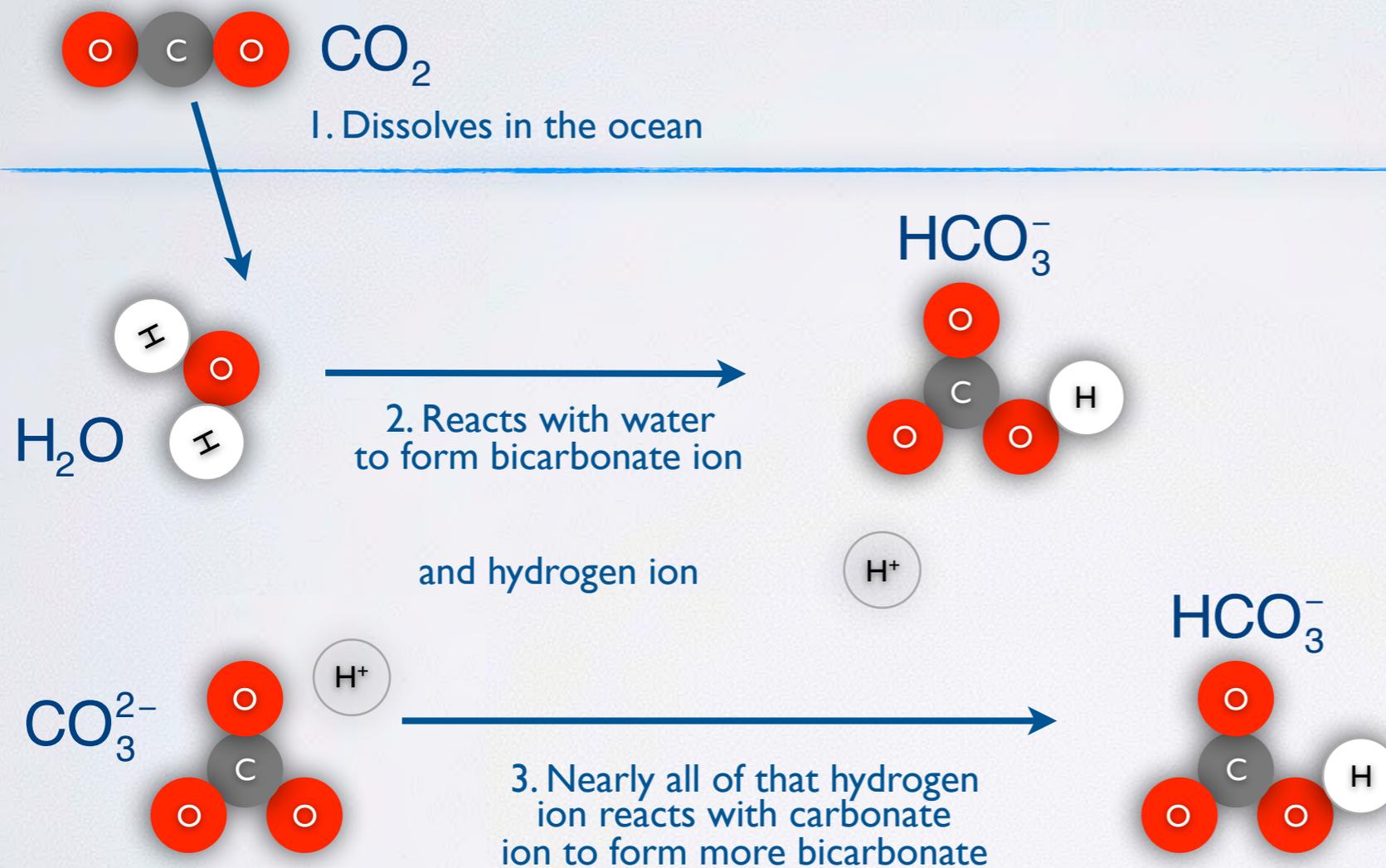
total hydrogen ion concentration

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$



$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

CARBON DIOXIDE EQUILIBRIA IN SEA WATER



$$K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p}$$

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

$$\frac{1}{K_2} = \frac{[\text{HCO}_3^-]}{[\text{H}^+][\text{CO}_3^{2-}]}$$



CARBON DIOXIDE PARAMETERS IN SEA WATER

- Total Dissolved Inorganic Carbon

$$C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

T, p independent

UNITS: moles per kilogram of solution (usually $\mu\text{mol kg}^{-1}$)

- Total Hydrogen Ion Concentration (pH)

$$\text{pH} = -\lg [\text{H}^+]$$

T, p dependent

UNITS: pH is dimensionless

But, total hydrogen ion concentration is in moles per kilogram of solution

- Partial Pressure of CO_2

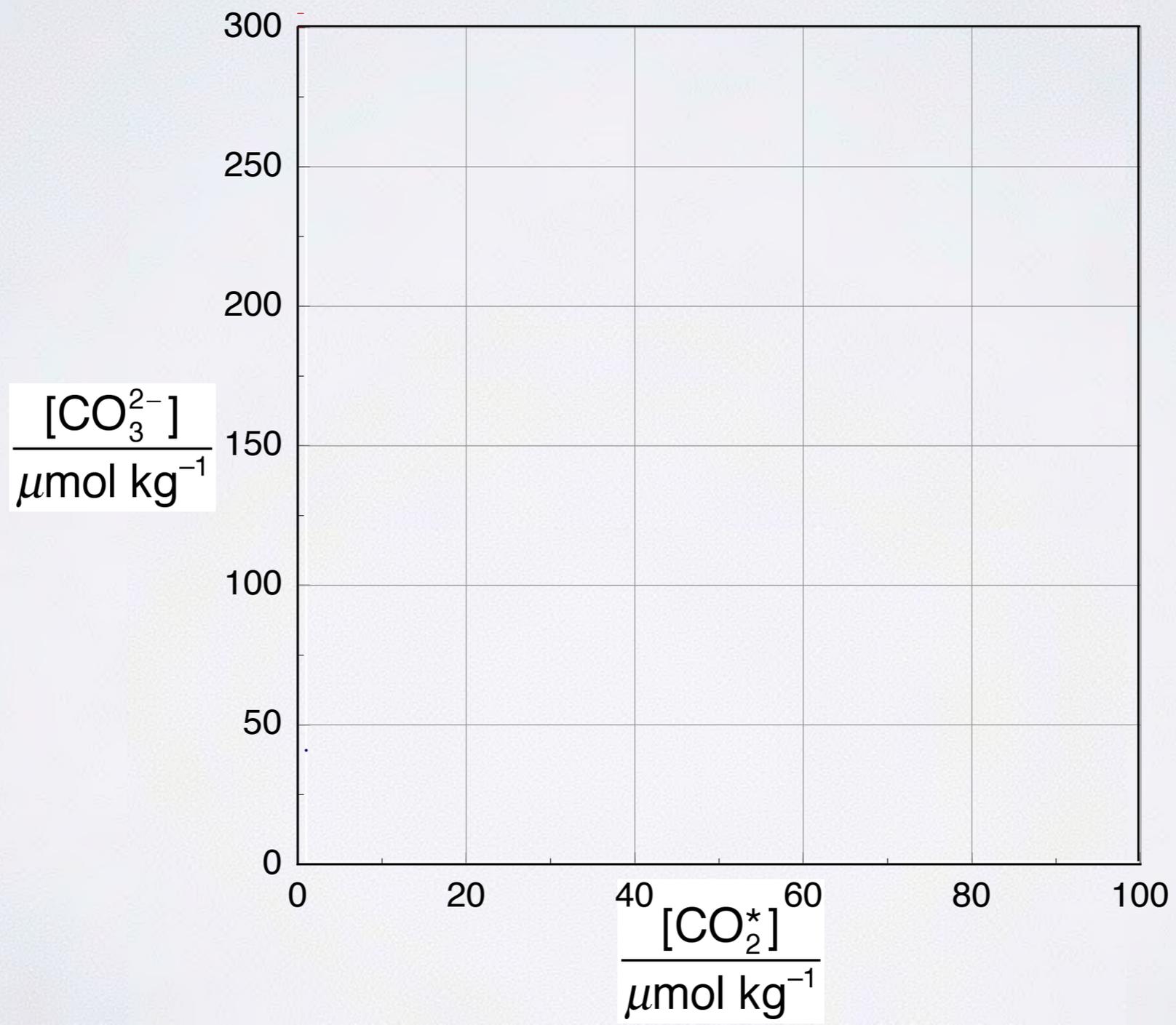
(in air that is in equilibrium with the water sample)

$$p(\text{CO}_2) = x(\text{CO}_2) p = [\text{CO}_2] / K_0$$

T, p dependent

UNITS: pressure units (usually μatm)

CO₂ SYSTEM RELATIONSHIPS IN SEA WATER

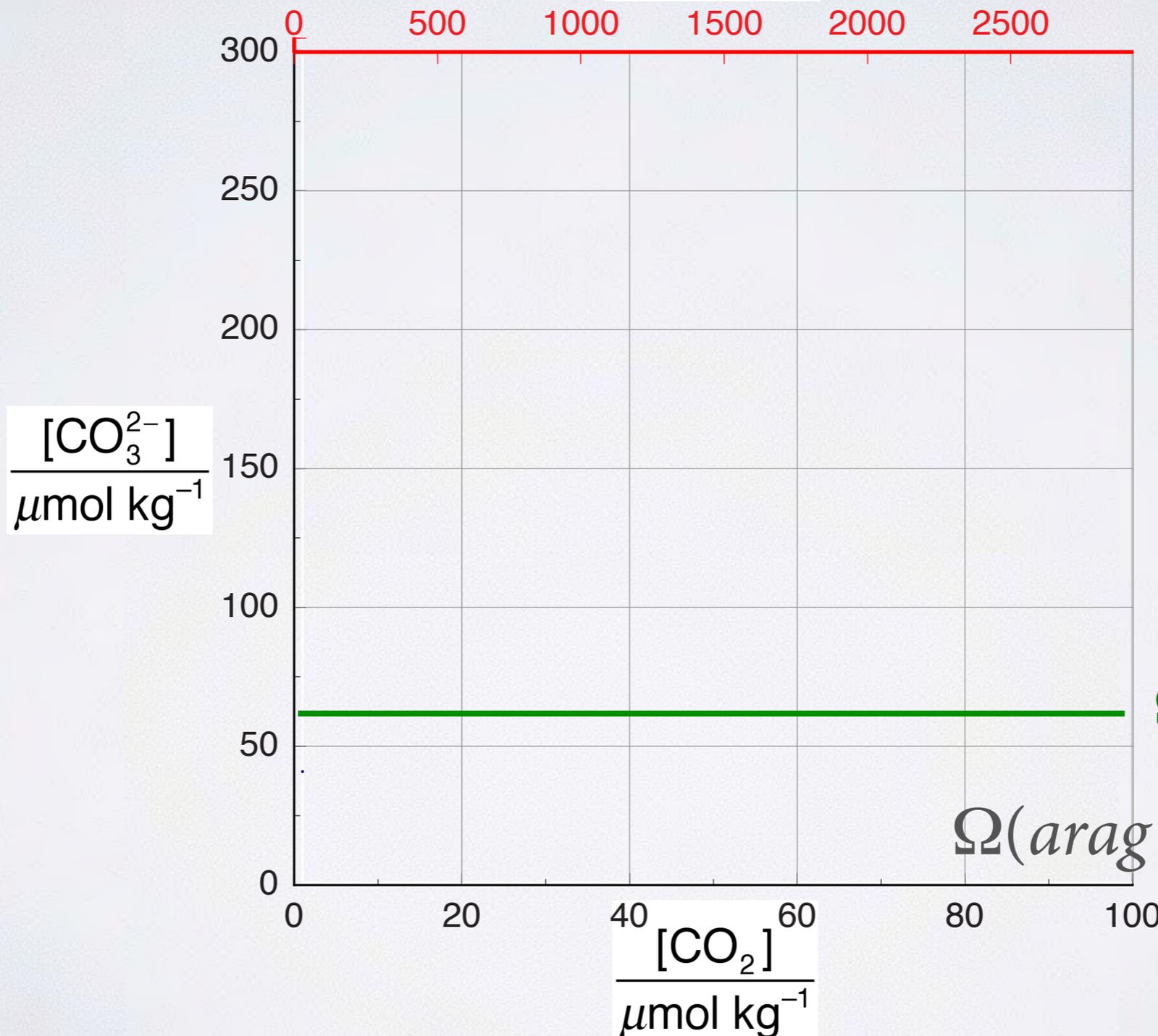


CO₂ SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18$ °C

$$\frac{p \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

$$K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p}$$



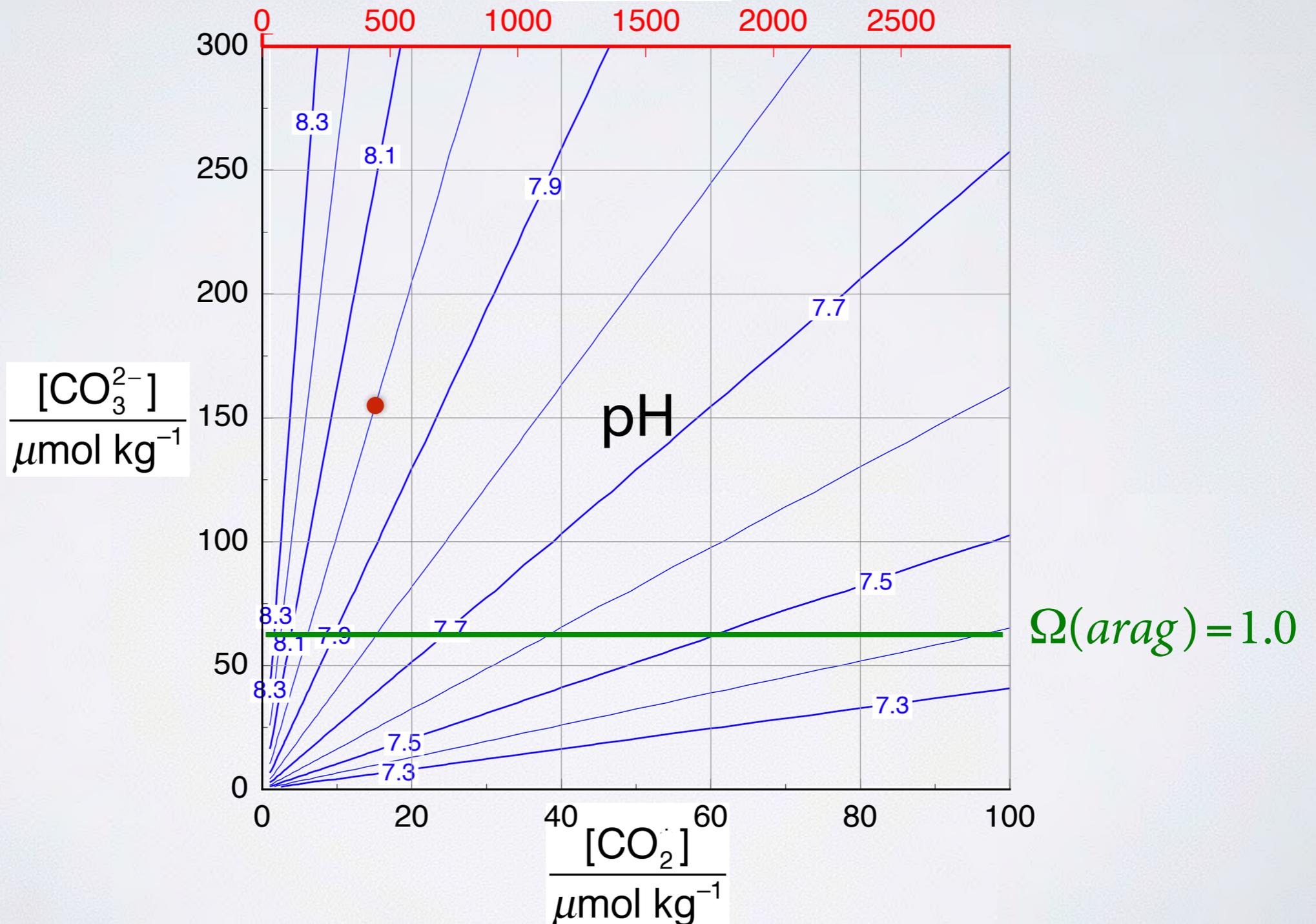
$$\Omega(\text{arag}) = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{sp}}(\text{arag})}$$

CO₂ SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18$ °C

$$\frac{p \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

$$K_1 / K_2 = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$$

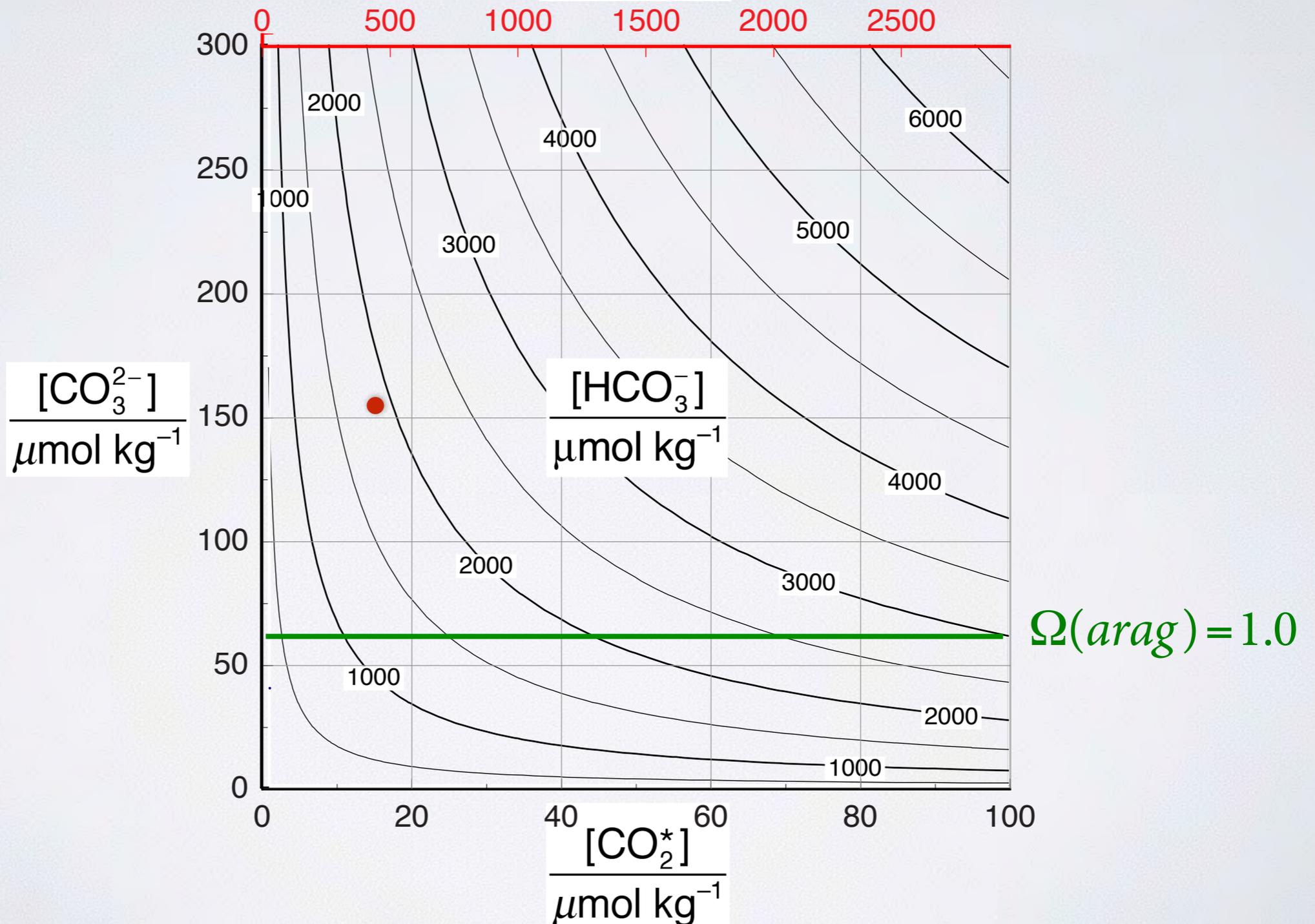


CO₂ SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18$ °C

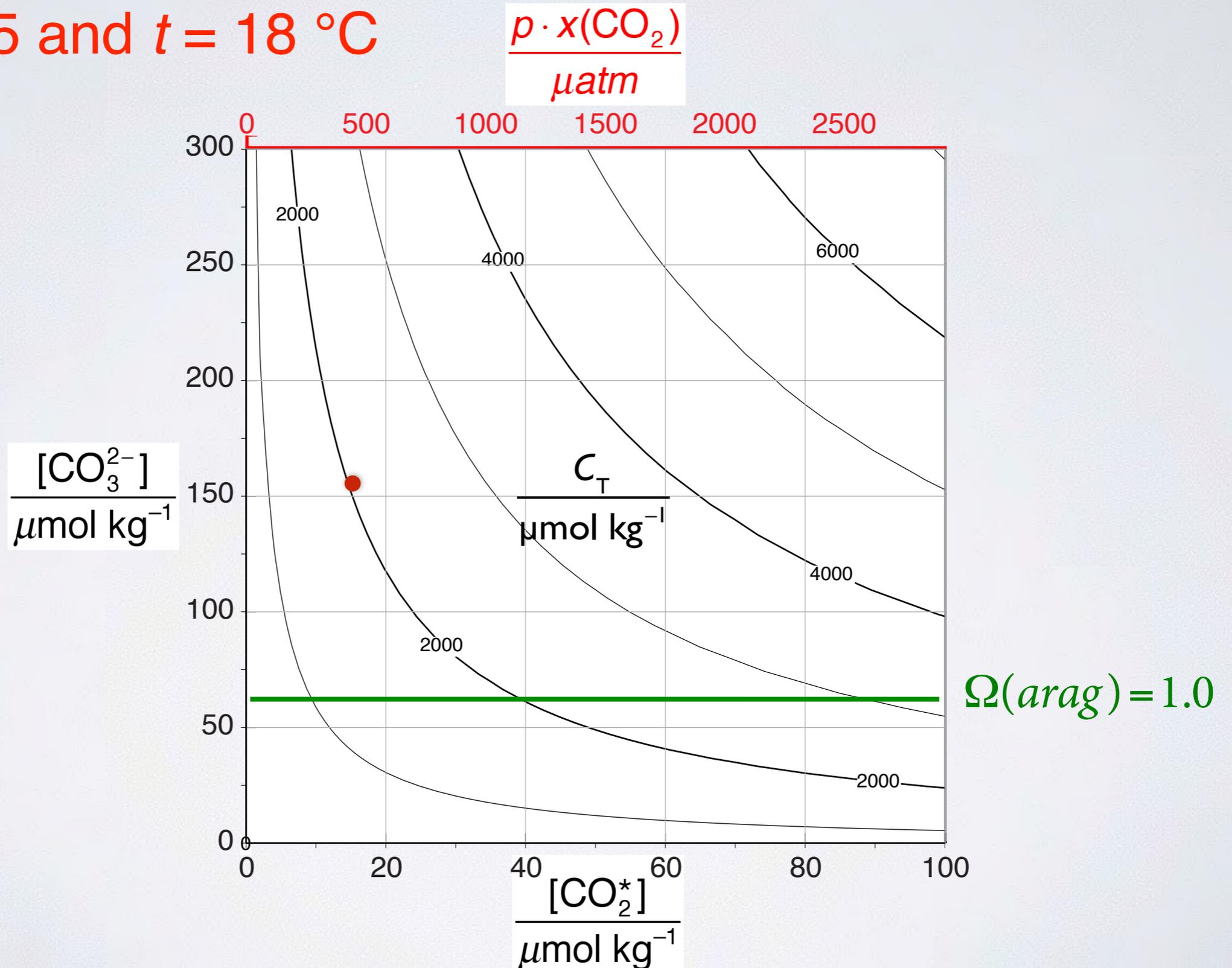
$$\frac{p \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

$$K_1 / K_2 = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$$



CO₂ SYSTEM RELATIONSHIPS IN SEA WATER

At $S = 35$ and $t = 18\text{ }^{\circ}\text{C}$



IMPORTANT CONSEQUENCE OF CO₂ EQUILIBRIA

- In a system at equilibrium, with both a gaseous and an aqueous phase, the state of the CO₂ system is described by a knowledge of the $p(\text{CO}_2)$ in the gas phase, and of the four concentrations: $[\text{CO}_2]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, and $[\text{H}^+]$, in the aqueous phase.
- However, there are three equilibrium relationships between these various concentrations:

$$K_0 = \frac{[\text{CO}_2]}{x(\text{CO}_2) \cdot p} \quad K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

- 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

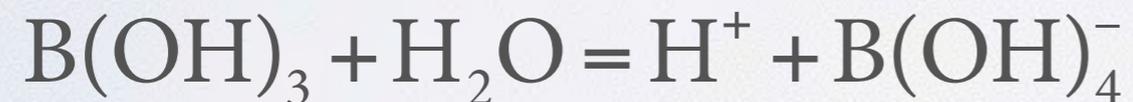
OTHER ACID-BASE SYSTEMS IN SEA WATER

Water Dissociation



$$K_{\text{W}} = [\text{H}^+][\text{OH}^-]$$

Boric Acid Dissociation



$$K_{\text{B}} = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]}$$

Total Dissolved Boron (depends on salinity)

$$B_{\text{T}} = [\text{B}(\text{OH})_3] + [\text{B}(\text{OH})_4^-]$$

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

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+]$$

T, p independent

UNITS: moles per kilogram of solution (usually $\mu\text{mol kg}^{-1}$)

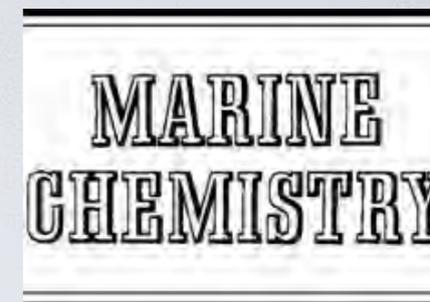
Why is this particular sum of species concentrations independent of temperature and pressure though each of the individual species contributions is itself a function of T and p ?



One key aspect of total alkalinity: it does not change when CO_2 is added to or removed from sea water.



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Will make available in the Dropbox

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-} , $\text{B}(\text{OH})_4^-$, 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 CO₂ species can be varied independently of one another.
- However, for each additional acid-base system that is added in, there are two additional species concentrations and one equilibrium relationship. Thus an additional *degree of freedom*.
- 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.

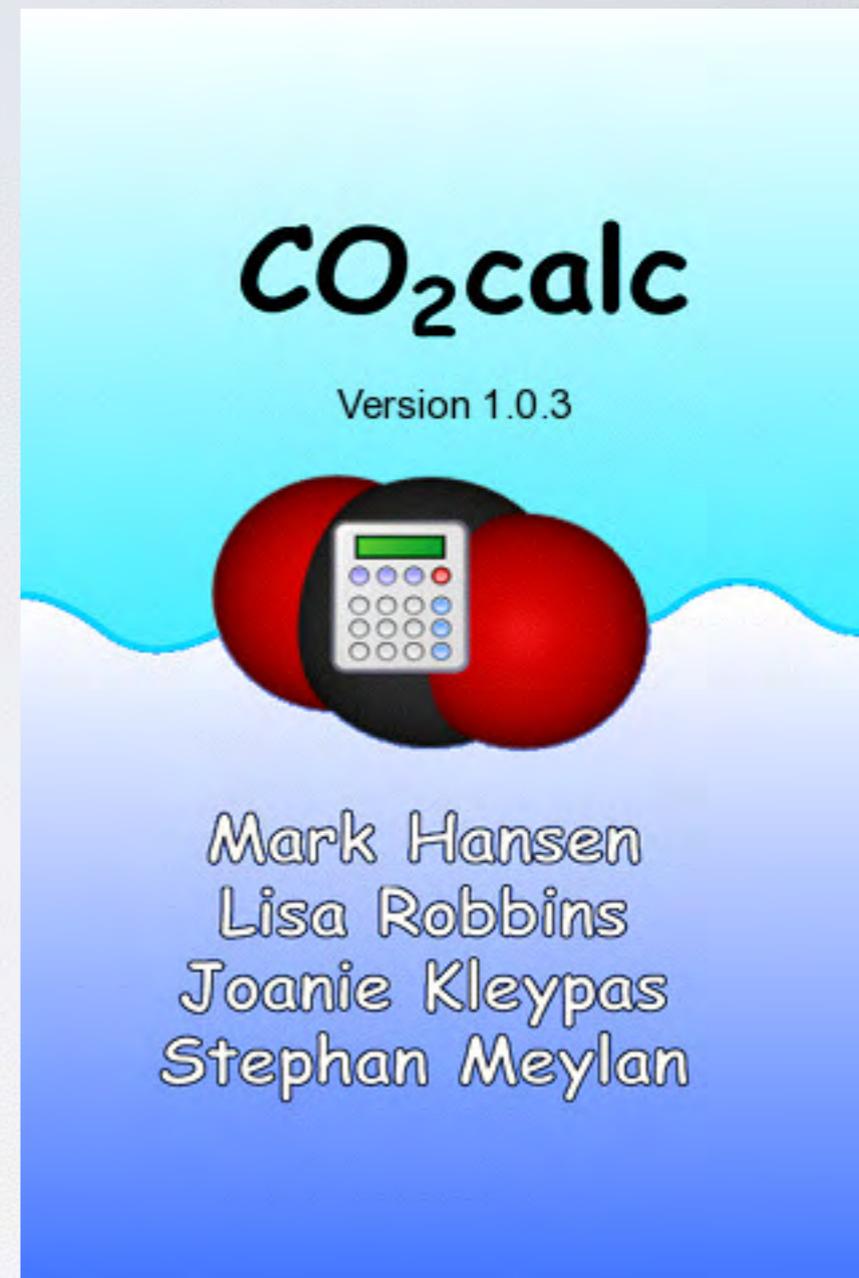
COMPUTER PROGRAMS EXIST FOR THESE CALCULATIONS

- 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 CO₂ 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/>



Open-File Report 2010–1280



CAN USE ANY TWO (OR MORE) OF THESE PARAMETERS TO DESCRIBE THE CO₂ 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 CO₂ 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 CO₂ 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

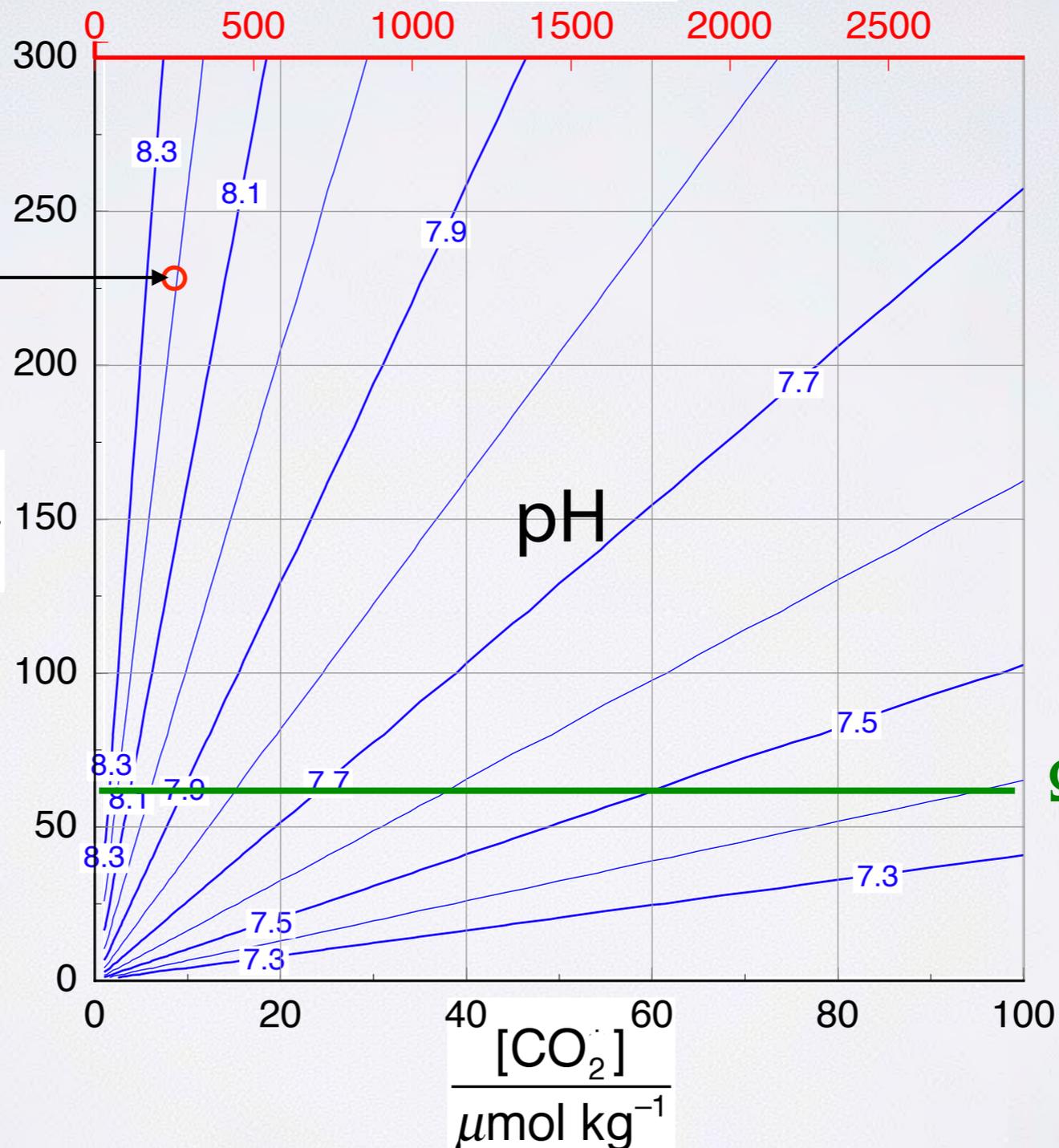
At $S = 35$ and $t = 18\text{ }^\circ\text{C}$

$$\frac{p \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

$$K_1 / K_2 = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_2][\text{CO}_3^{2-}]}$$

INITIAL CONDITIONS:
 $A_T = 2300\ \mu\text{mol kg}^{-1}$
 $\text{pH} = 8.2$

$$\frac{[\text{CO}_3^{2-}]}{\mu\text{mol kg}^{-1}}$$



$\Omega(\text{arag}) = 1.0$

ACIDIFICATION TO pH 7.3 (BY ADDITION OF CO₂)

At $S = 35$ and $t = 18$ °C

$$\frac{p \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

INITIAL CONDITIONS:
 $A_T = 2300 \mu\text{mol kg}^{-1}$
 $\text{pH} = 8.2$

$$\frac{[\text{CO}_3^{2-}]}{\mu\text{mol kg}^{-1}}$$

FINAL CONDITIONS:

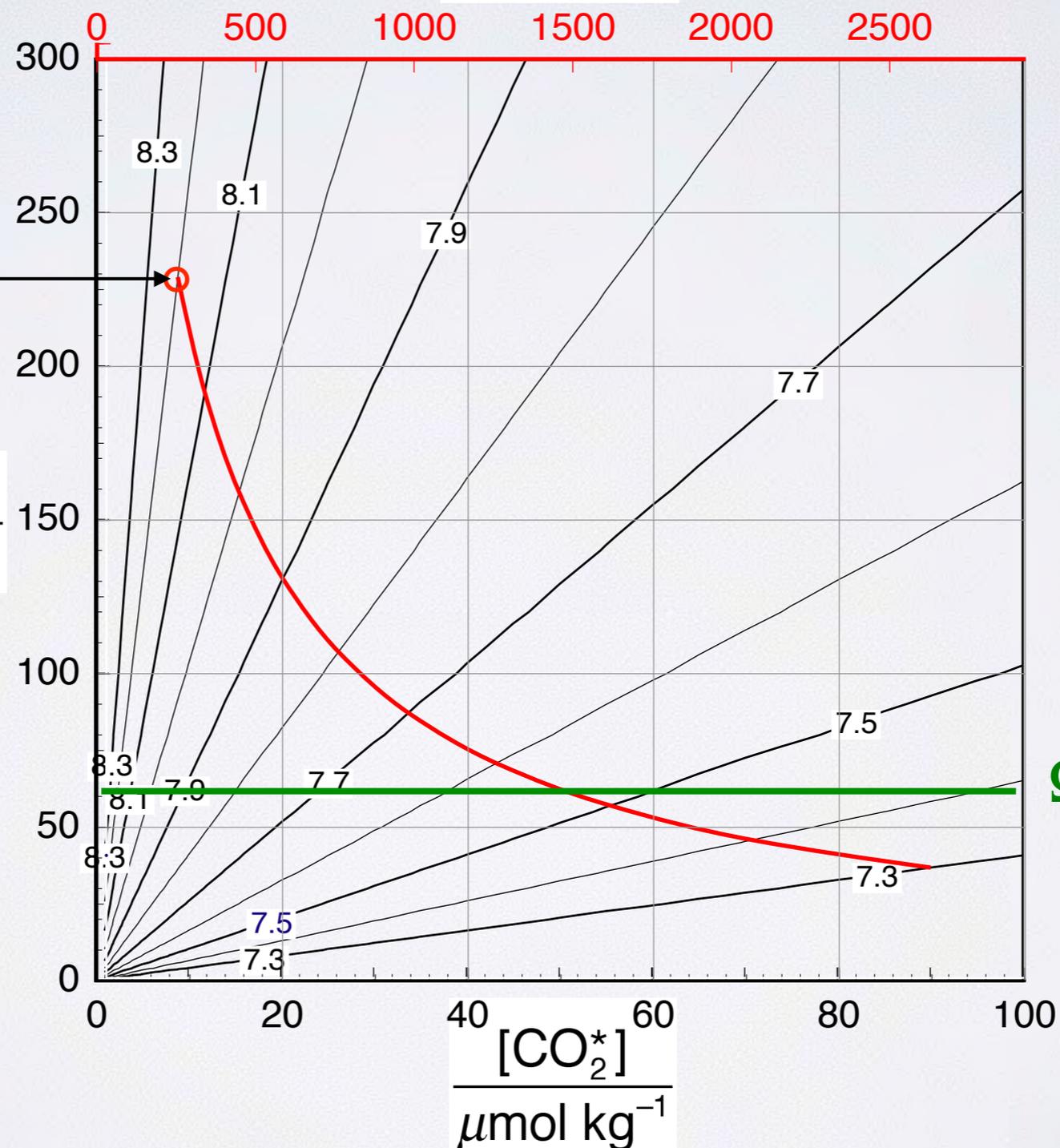
$$p(\text{CO}_2) = 2630 \mu\text{atm}$$

$$[\text{CO}_3^{2-}] = 37 \mu\text{mol kg}^{-1}$$

$$\Omega(\text{arag}) = 0.57$$

$$\Omega(\text{arag}) = 1.0$$

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



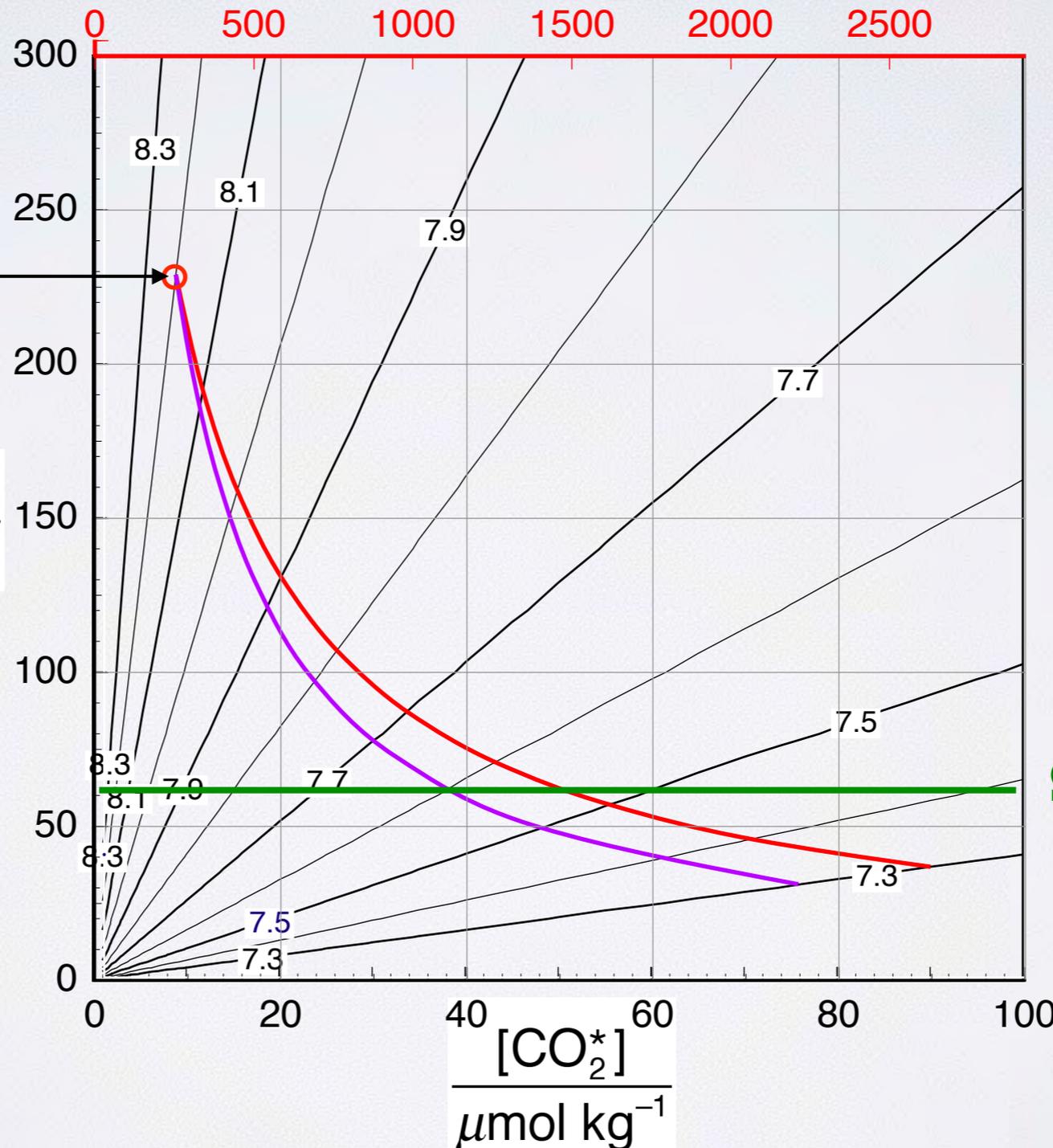
ACIDIFICATION TO pH 7.3 (BY ADDITION OF HCL)

At $S = 35$ and $t = 18\text{ }^\circ\text{C}$

$$\frac{p \cdot x(\text{CO}_2)}{\mu\text{atm}}$$

INITIAL CONDITIONS:
 $A_T = 2300\ \mu\text{mol kg}^{-1}$
 $\text{pH} = 8.2$

$$\frac{[\text{CO}_3^{2-}]}{\mu\text{mol kg}^{-1}}$$



FINAL CONDITIONS:

$$p(\text{CO}_2) = 2630\ \mu\text{atm}$$

$$[\text{CO}_3^{2-}] = 37\ \mu\text{mol kg}^{-1}$$

$$\Omega(\text{arag}) = 0.57$$

$$\Omega(\text{arag}) = 1.0$$

FINAL CONDITIONS:

$$p(\text{CO}_2) = 2220\ \mu\text{atm}$$

$$[\text{CO}_3^{2-}] = 31\ \mu\text{mol kg}^{-1}$$

$$\Omega(\text{arag}) = 0.48$$

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

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

WHAT HAPPENS AT A DIFFERENT TEMPERATURE?

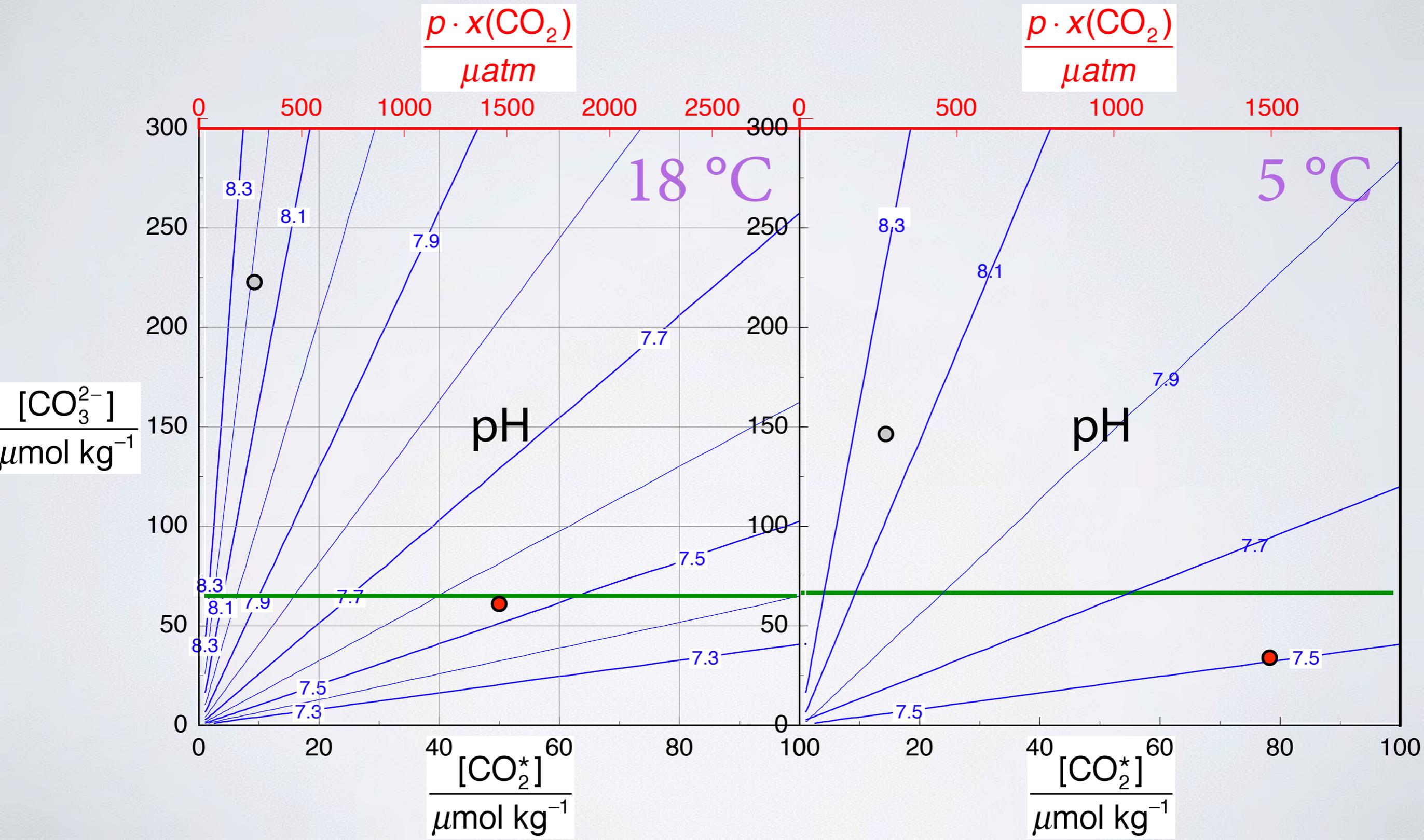


These changes are due to changes in the various equilibrium constants with T

$$A_T = 2300 \mu\text{mol kg}^{-1}$$

$$p(\text{CO}_2) = 280 \mu\text{atm}$$

$$\text{or } 1500 \mu\text{atm}$$



$S = 35$

18 °C

5 °C

$A_T = 2300 \mu\text{mol kg}^{-1}$

$p(\text{CO}_2)$ 280 μatm

pH 8.17 8.18

$\Omega(\text{arag})$ 3.38 2.19

C_T 1987 $\mu\text{mol kg}^{-1}$ 2095 $\mu\text{mol kg}^{-1}$

$p(\text{CO}_2)$ 1500 μatm

pH 7.53 7.50

$\Omega(\text{arag})$ 0.94 0.53

C_T 2262 $\mu\text{mol kg}^{-1}$ 2342 $\mu\text{mol kg}^{-1}$

ΔC_T 275 $\mu\text{mol kg}^{-1}$ 247 $\mu\text{mol kg}^{-1}$

IMPLICATIONS OF CO₂ EQUILIBRIA FOR DESIGN OF OCEAN ACIDIFICATION EXPERIMENTS

- Only two of the concentrations of the aqueous CO₂ 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 CO₂ 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, however, 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.
- Then it is often best to control pH – by varying $p(\text{CO}_2)$. This is less demanding of temperature control.



I DON'T BELIEVE IN
GLOBAL WARMING