

Inorganic carbon in the ocean: Basics

Introduction

Equilibrium and Measurement

Biogeochemical Processes and the CO₂ system

- organic matter formation / destruction
- CaCO₃ precipitation / dissolution

Why study carbonate in the ocean? (stating the obvious)

Life on earth is carbon-based!

pH is a key master variable for many processes - and carbonate equilibria play an important role in determining ocean pH

HCO₃⁻ is the 3rd most concentrated anion in the ocean

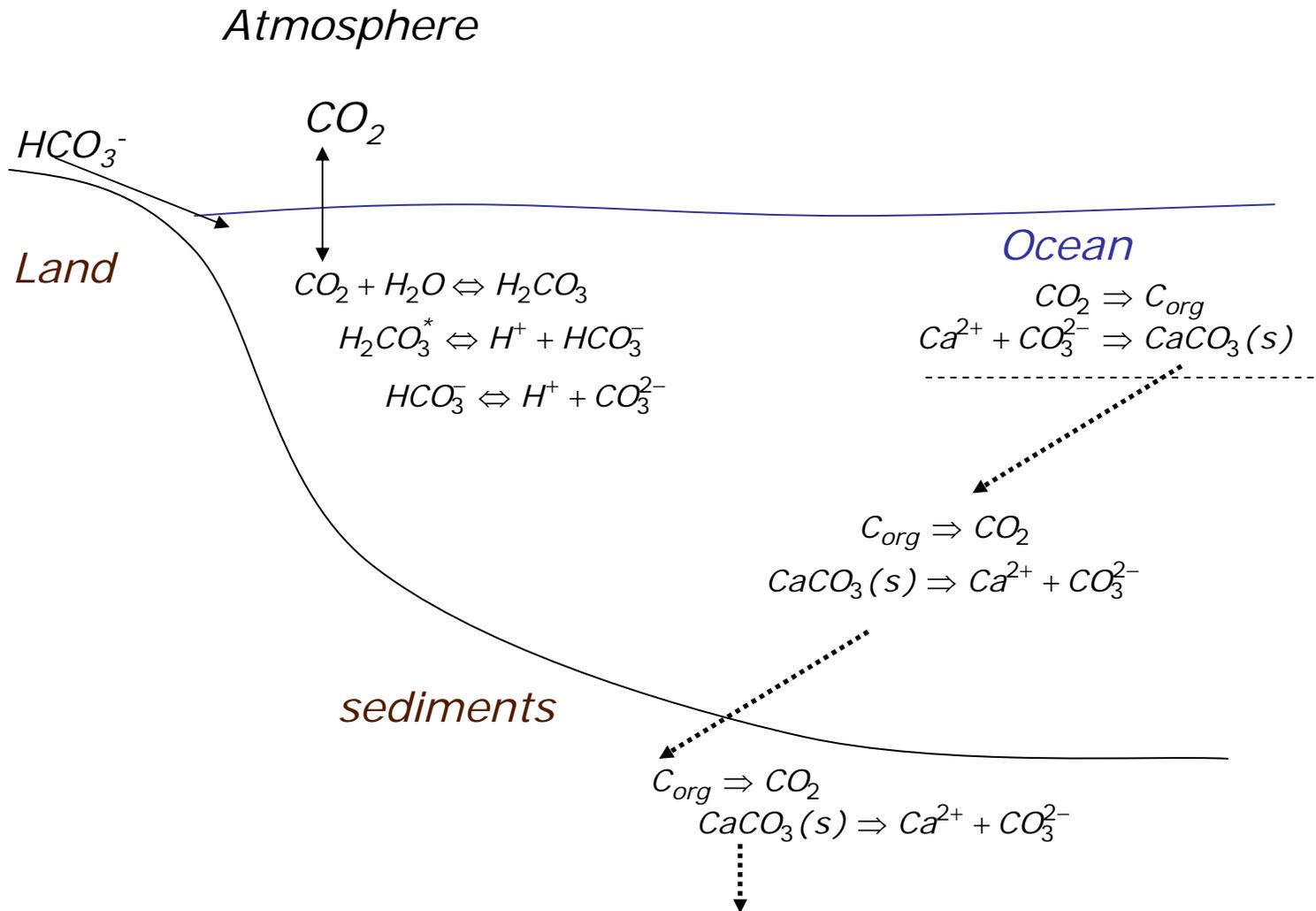
The marine carbon cycle is a key factor in determining the fate of anthropogenic CO₂

...

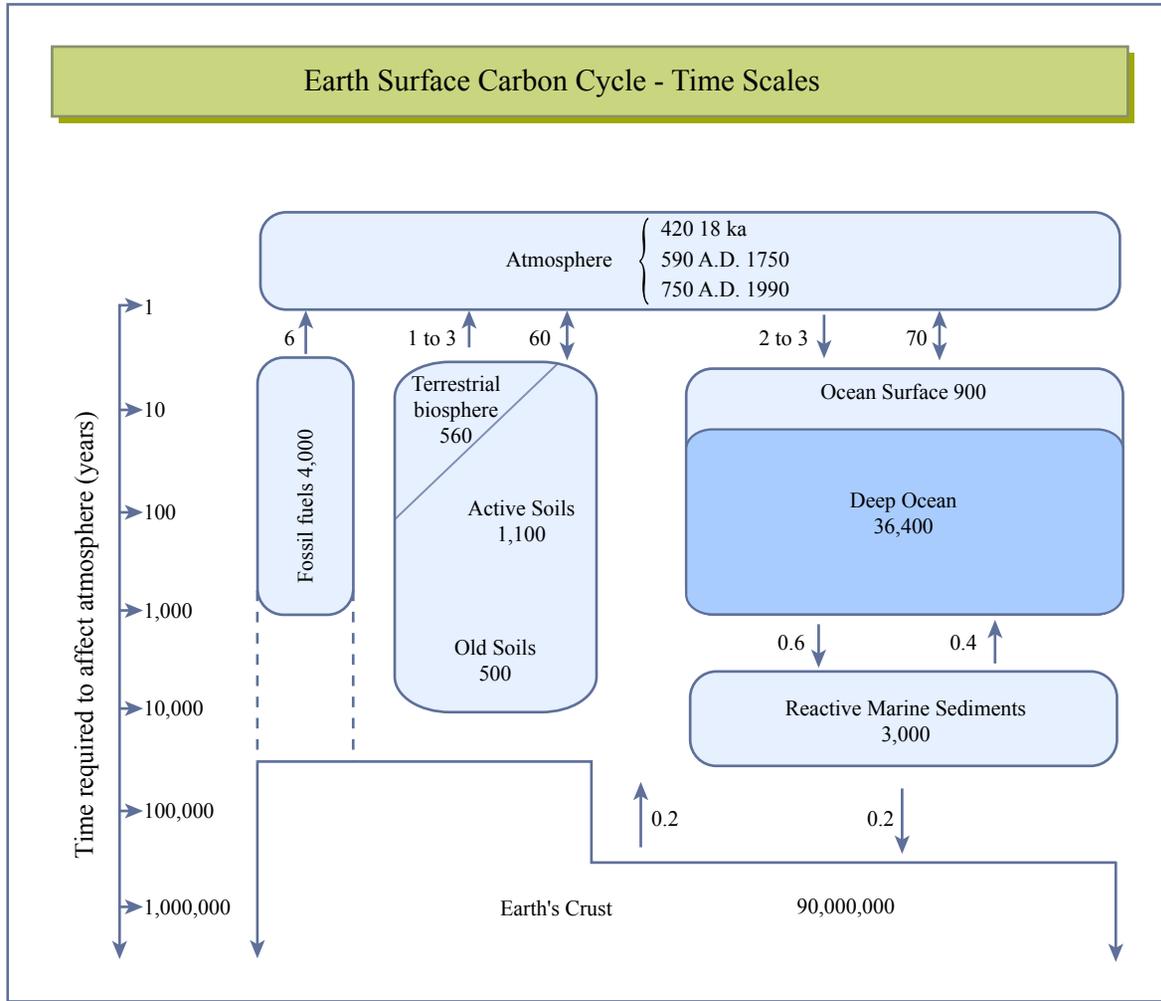
And if the pursuit of knowledge isn't enough:

MC&G students: I guarantee you'll have a carbonate question on your general exam!

Carbon cycling in the ocean (an overview)



Earth surface carbon cycle - Time Scales



Increasing...

*Surface ocean
~ atmosphere*

*Deep ocean :
large reservoir!*

*Largest reservoir:
long time scales*

Figure by MIT OCW.

Dissolved Carbonate Equilibria

$$\Sigma CO_2 = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

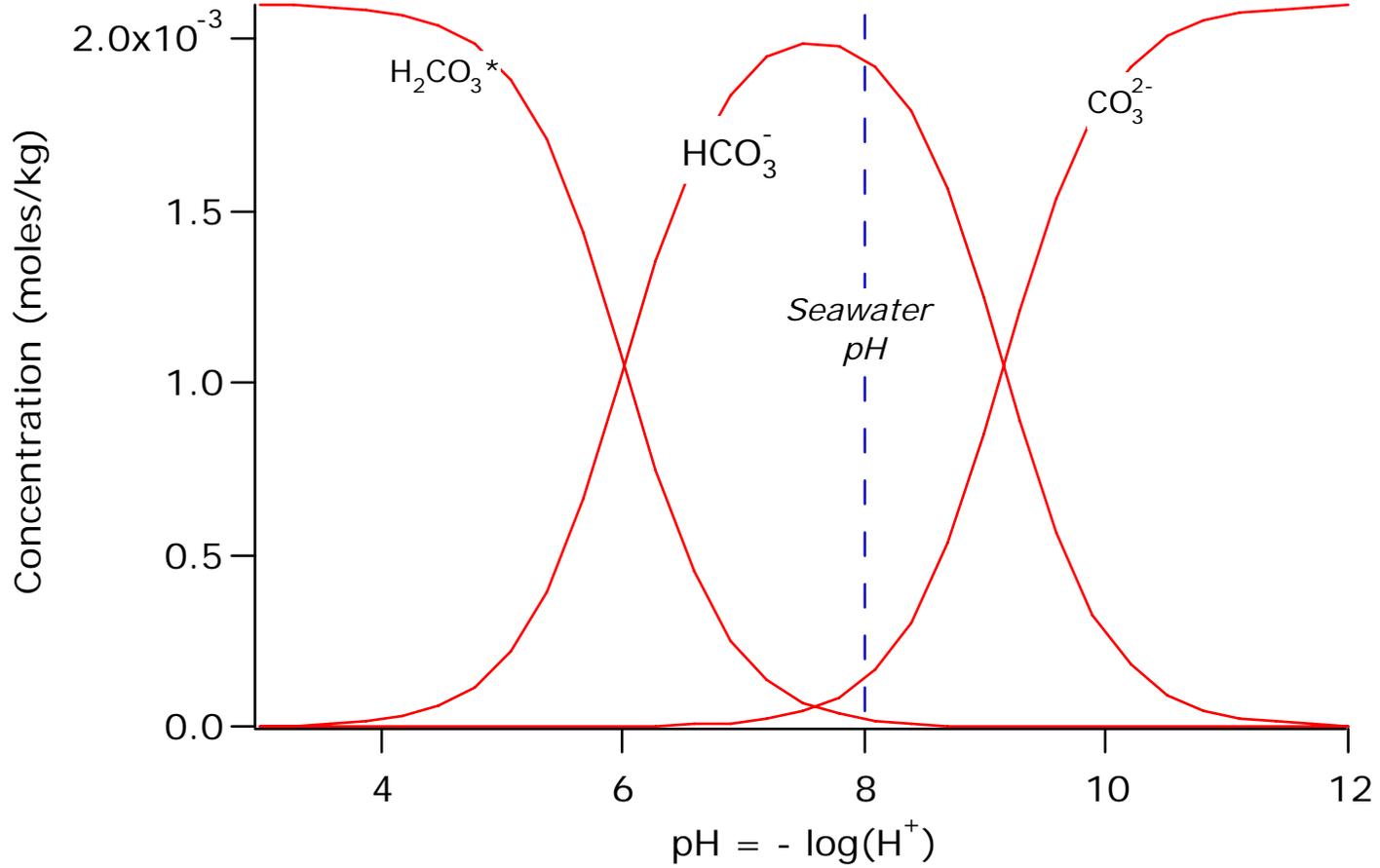
$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

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

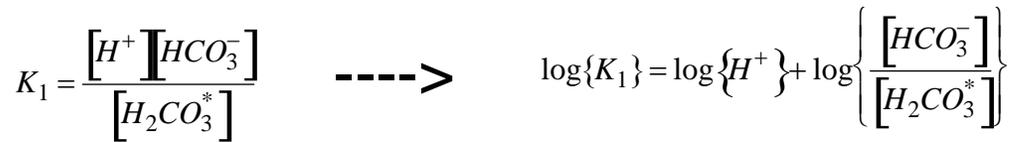
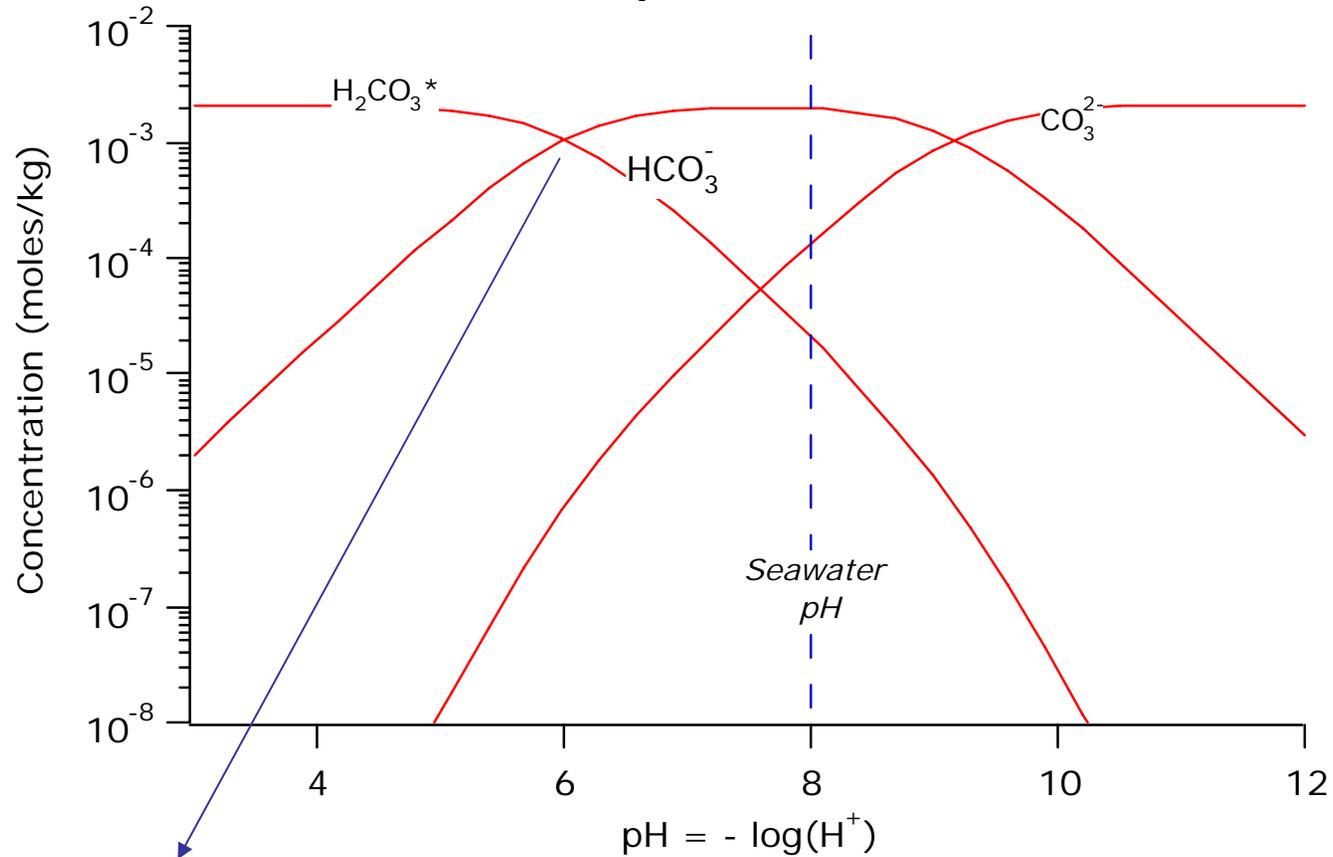
K_1 , K_2 known...

-- 3 equations, 5 unknowns...

Specify (or measure) 2 things - ΣCO_2 , pH ... to get :



Speciation as $f(\text{pH})$ on log-log plot: A "Bjerrum" Plot



Are ΣCO_2 and pH an ideal pair to measure?
Sometimes, but note:

Water mass A
pH_A
 $\Sigma \text{CO}_2\text{A}$

Water mass B
pH_B
 $\Sigma \text{CO}_2\text{B}$

50 : 50 mix of A and B

$$\Sigma \text{CO}_2(\text{mix}) = 0.5 * \Sigma \text{CO}_2(\text{A}) + 0.5 * \Sigma \text{CO}_2(\text{B})$$

**** Not true for pH !! ****

How about a quantity that is related to the major ion composition?

The charge balance in seawater:

Concentrations, $[c_i]$ (mmol kg ⁻¹), and charge concentrations, $[q_i] = z_i \cdot [c_i]$ (mmol kg ⁻¹), of conservative ions in seawater at S = 35.						
Cations	$[c_i]$	$[q_i]$		Anions	$[c_i]$	$[q_i]$
Na ⁺	467.8	467.8		Cl ⁻	545.5	545.5
Mg ²⁺	53.3	106.5		SO ₄ ²⁻	28.2	56.4
Ca ²⁺	10.3	20.6		Br ⁻	0.8	0.8
K ⁺	9.9	9.9		F ⁻	0.1	0.1
Sr ²⁺	0.1	0.2			.	.
Total	.	605.0		Total	.	602.8

Figure by MIT OCW.

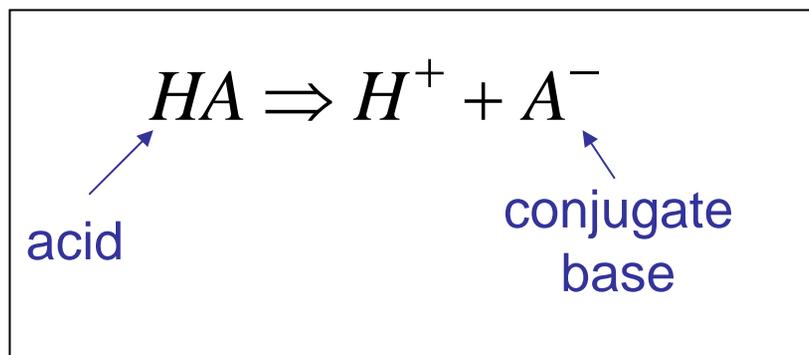
An apparent excess of positive charge of ~ 2.2 mmol / kg

What are the missing anions?

The Alkalinity

The missing anions: HCO_3^- , CO_3^{2-} , B(OH)_4^-

The conjugate bases of the weak acids,
 H_2CO_3 and B(OH)_3



Alkalinity (mol/kg) = the amount of strong acid that must be added to a 1 kg (sea)water sample to make its pH equal to that of the second equivalence point of the dissolved CO_2 system, $\text{pH} = 4.3$

Total Alkalinity: seawater, pH = 8

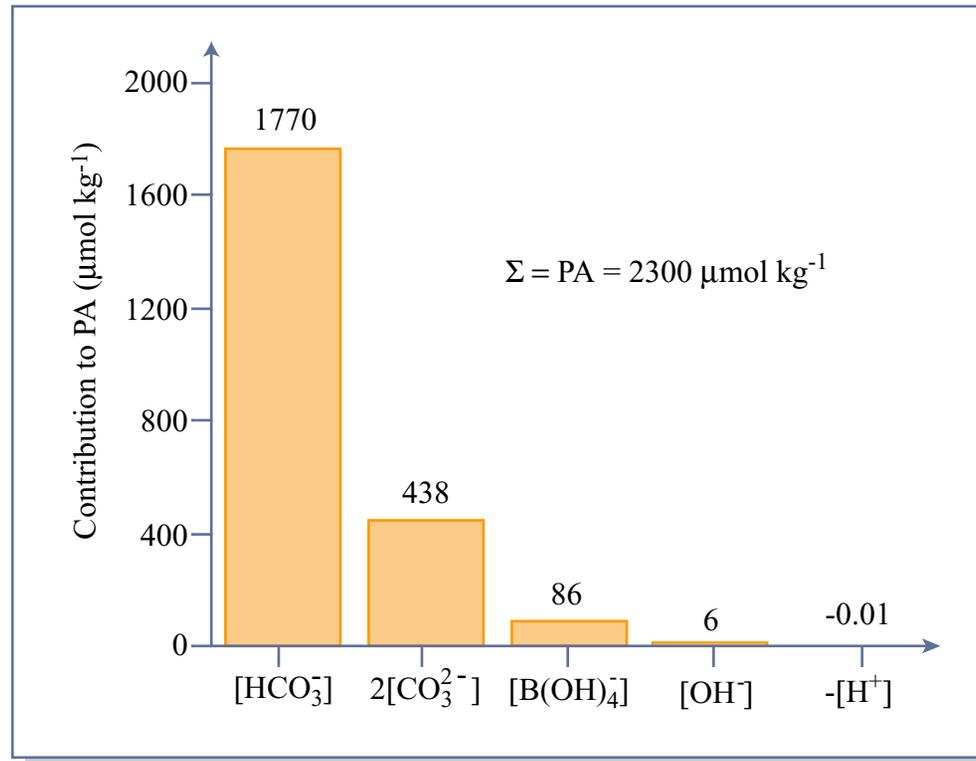
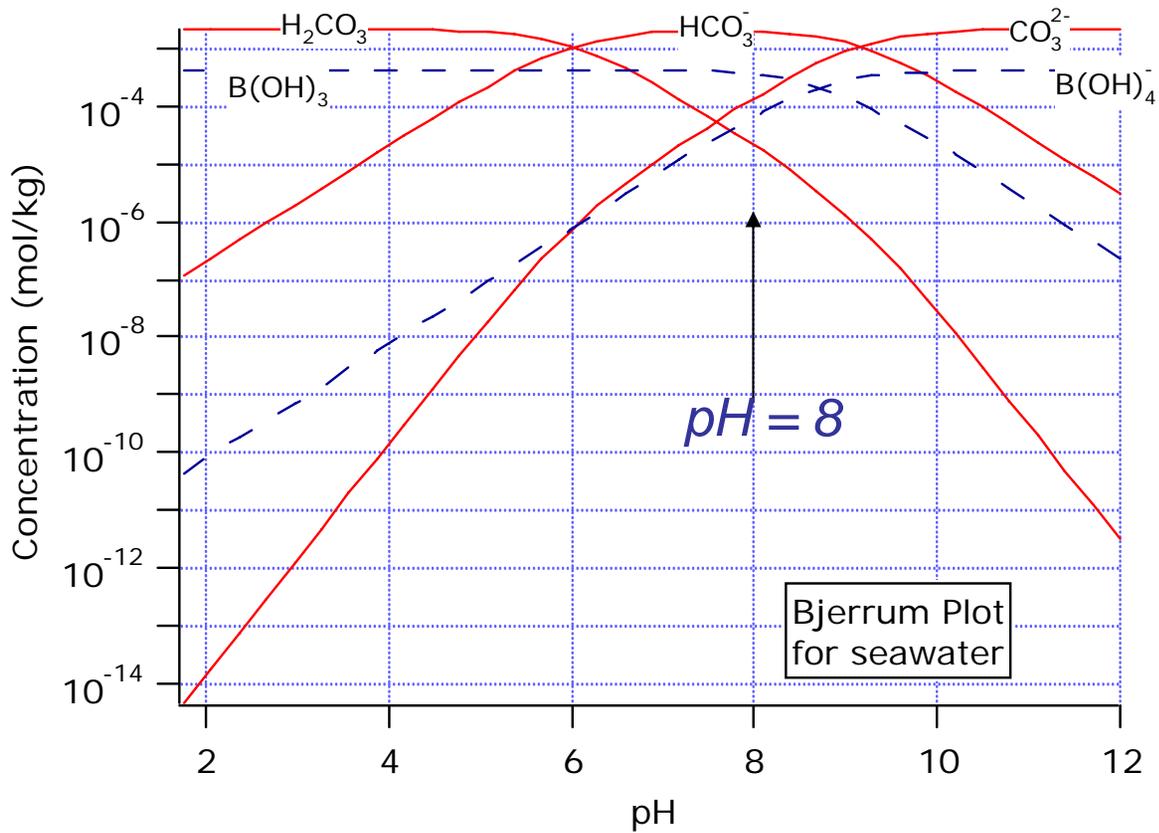


Figure by MIT OCW.

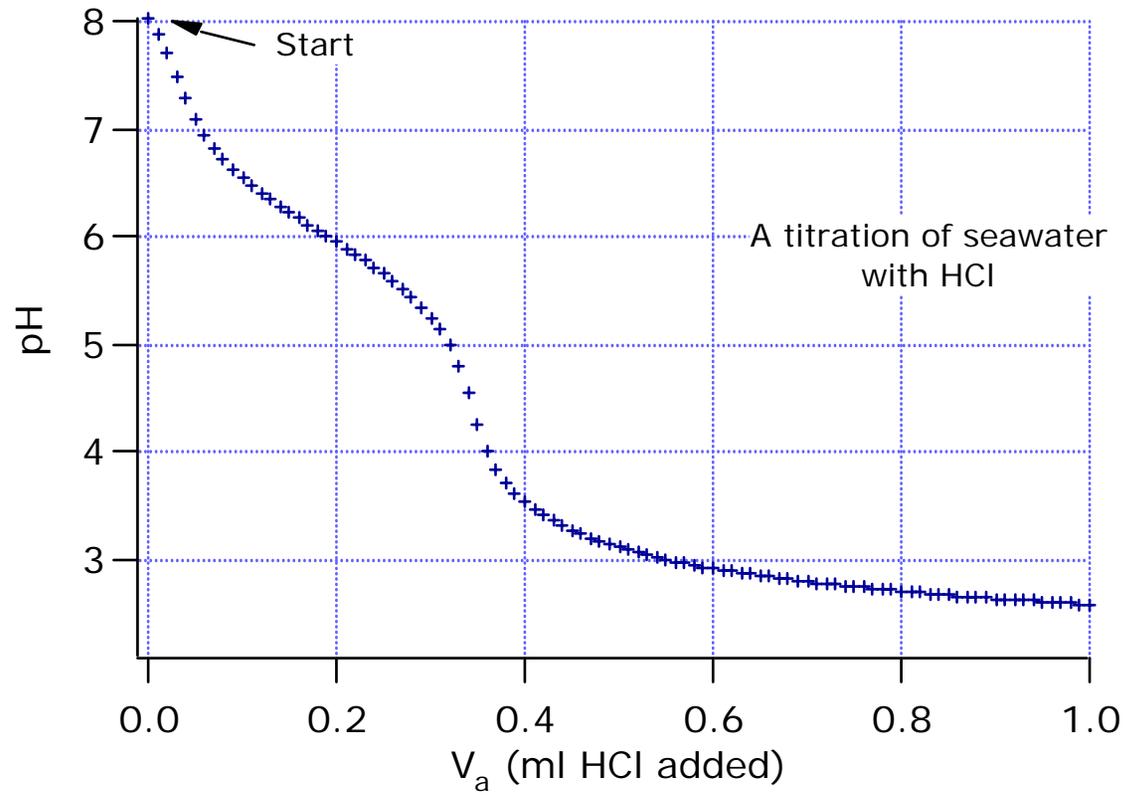
“Practical Alkalinity”:

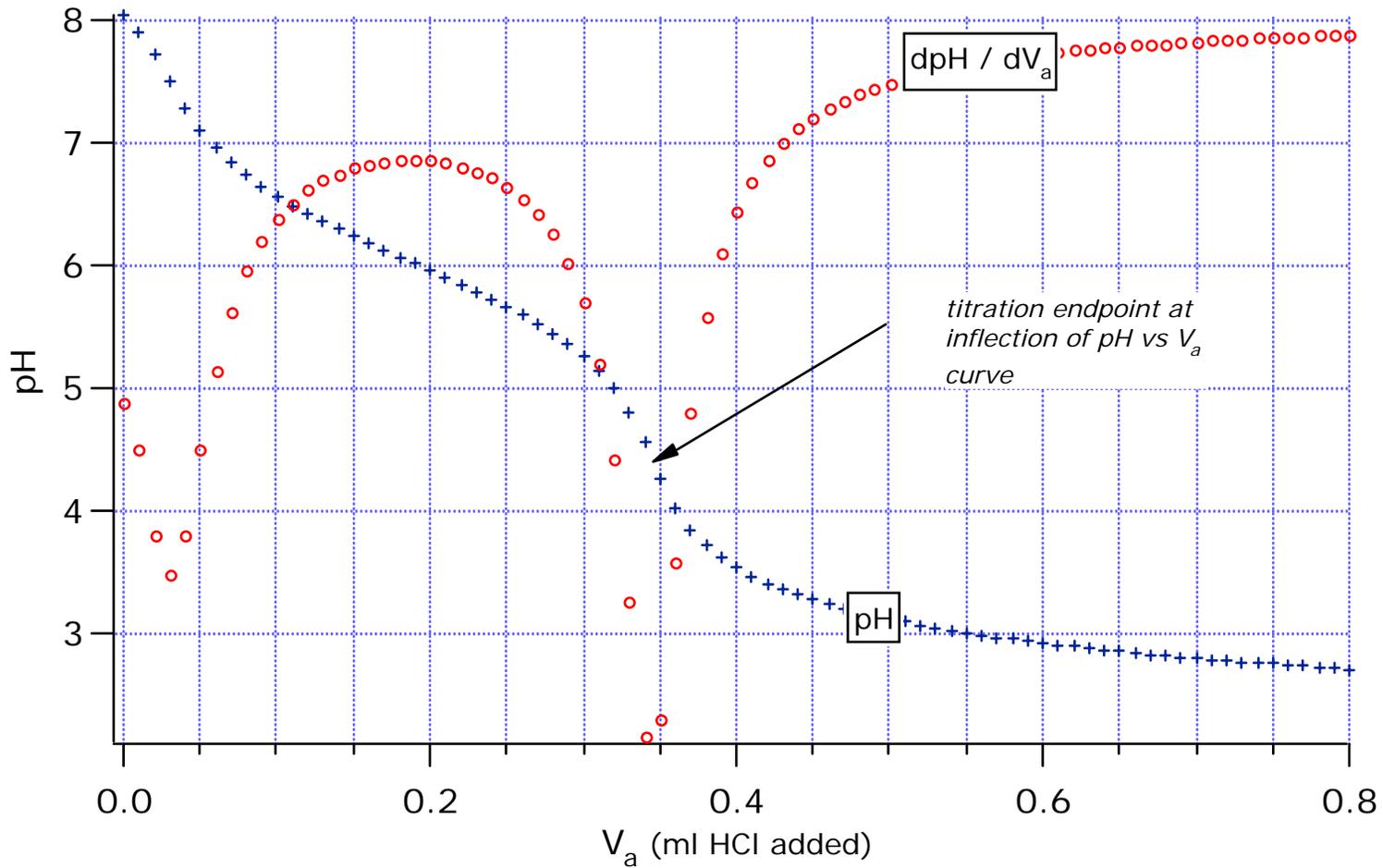
$$PA = \left[HCO_3^- \right] + 2 \left[CO_3^{2-} \right] + \left[B(OH)_4^- \right] + \left[OH^- \right] - \left[H^+ \right]$$

What does the definition mean?

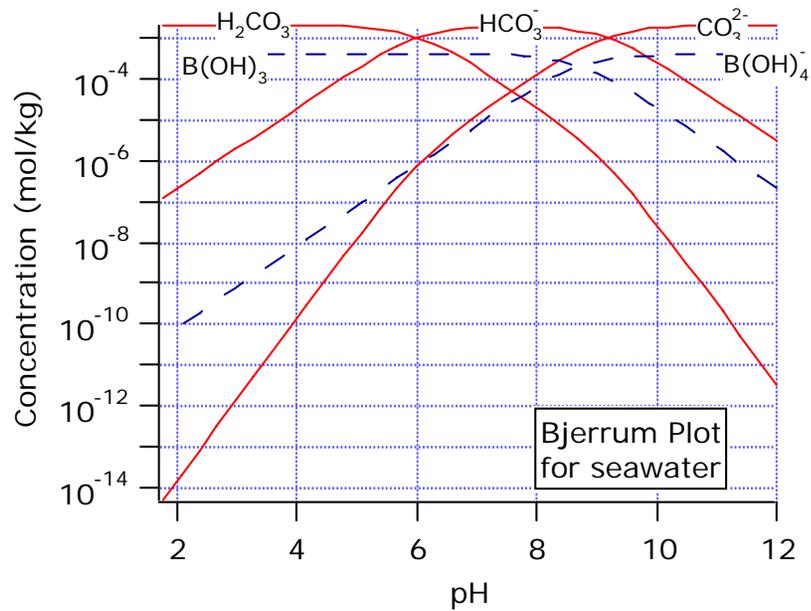


The titration of seawater with a strong acid (HCl)





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



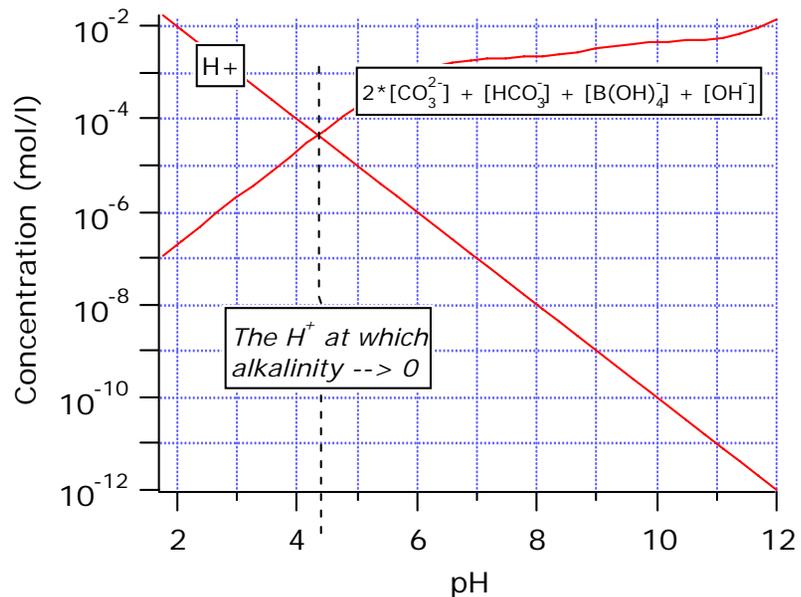
At the titration endpoint,

$$[H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [B(OH)_4^-] + [OH^-]$$

That is, the endpoint
Is the point at which
 $Alk = 0$

So: the moles of acid
added to reach the
endpoint = Alk

Concentrations during the titration:



Alkalinity: A precise definition

Dickson, 1981 ; 19994

“The total alkalinity of a natural water is thus defined 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 one kilogram of sample.”

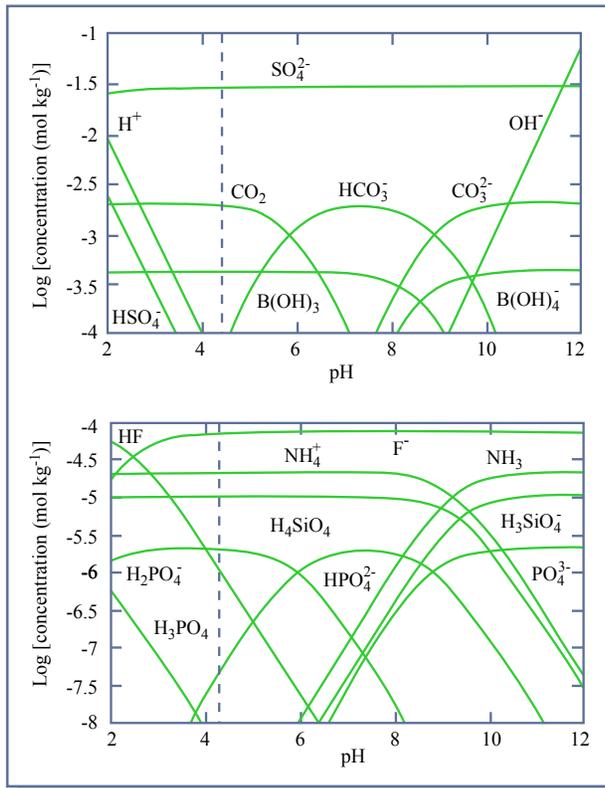


Figure by MIT OCW.

Remember:

(1) predominant species at pH = 4.5 does not contribute to Alkalinity

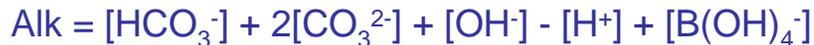
(2) How do you estimate pK for an acid from this diagram?

Alkalinity

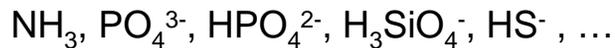
So we have:



For most applications, can use:



But in some applications, you need to add minor contributors, such as



- Remember, when you titrate a seawater sample to the 2nd CO_2 endpoint, The result is “Titration Alkalinity”, which includes all conjugate bases of weak Acids in the sample. The approximation in the Alk expression above is the Neglect of the contribution of minor constituents to the result.

Measurements: Summary

ΣCO_2

(i) *Titration + curve fitting*

(ii) *Acidify ; strip CO_2 ;*

*Measure CO_2 by gas chromatography,
Coulometry, IR analyzer*

$\pm 2 \mu\text{mol/kg}$

Calibration: reference seawater (Dickson)

Alkalinity

(i) *Titration + curve fitting*

(ii) *Gran titration*

$\pm 2 \mu\text{mol/kg}$

Calibration: reference seawater (Dickson)

pH

(i) *Electrochemical measurement*

(ii) *pH-sensitive dyes*

$\pm 0.002 \text{ pH units}$

Calibration: buffers for seawater

The “more-than-I-ever-wanted-to-know” section : pH scales

(1) Laboratory chemistry: the NBS pH scale

$$pH = -\log a_{H^+}$$

** Defined relative to low-ionic strength buffers --
abandoned for measurements in seawater

(2) Seawater: An analysis of “[H+]” in seawater yields



[HF] is small; in order to determine $[H^+]_{\text{free}}$, need to know
K for HSO_4^- dissociation WELL.

“They” have decided it is better to define a new pH scale:

The “Total pH scale” :

$$H_T^+ = [H^+]_{\text{free}} + [HSO_4^-]$$

Or the “seawater pH scale” :

$$H_T^+ = [H^+]_{\text{free}} + [HSO_4^-] + [HF]$$

pH scales, cont.

So that:

- (1) pH measurements are reported on the pH_T scale
- (2) equilibrium constants are reported on the pH_T scale

Can convert between the scales with K_{HSO_4} and K_{HF}

**The difference between pH_{SWS} and pH_T is ~ 0.01 unit $\sim 2\%$ at pH 8
The difference between pH_{NBS} and pH_T is ~ 0.1 unit $\sim 20\%$ at pH 8

The precision of good pH measurements is ~ 0.002 pH units

On equilibrium constants for calculations in seawater

Consider the reaction: $HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$

In an “ideal” solution:

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

In an “ideal” solution, all concentrations $\rightarrow 0$, so there are no ion-ion or ion-solvent interactions.

In a real solution, these interactions are important, so...

On equilibrium constants for calculations in seawater

Consider the reaction: $HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$

In an “ideal” solution:

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In an “ideal” solution, all concentrations $\rightarrow 0$, so there are no ion-ion or ion-solvent interactions.

In a real solution:

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

The γ are “activity coefficients”, and are generally < 1 for ions in solution because of electrostatic interactions between ions and between ions and solvent .

In addition, some ions (esp. CO_3^{2-}) form complexes with other ions in seawater.

Equilibrium constants for calculations in seawater

For a solution with the ionic strength of seawater ($I = \sum c_i z_i^2 \sim 0.7$), it is difficult to calculate the γ values.

Therefore:

“Constant ionic medium” equilibrium constants are used. They are:

- measured in solutions with the same proportions of major ions as seawater
- measured as functions of T and S
- pressure dependence is calculated from thermodynamic data

So:

$$K' = \frac{[H^+]_T [CO_3^{2-}]_T}{[HCO_3^-]_T}$$

The “T” denote “total” concentrations, including complexes...

And remember, for H^+ , the “T” denotes the “total” pH scale.

These “seawater” constants are available from the literature as $f(T,S,P)$

Working with the carbonate system in seawater

$$\Sigma CO_2 = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \pm \text{minor components}$$

$$TB = [B(OH)_3] + [B(OH)_4^-] = \text{constant} \times \text{Salinity}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

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

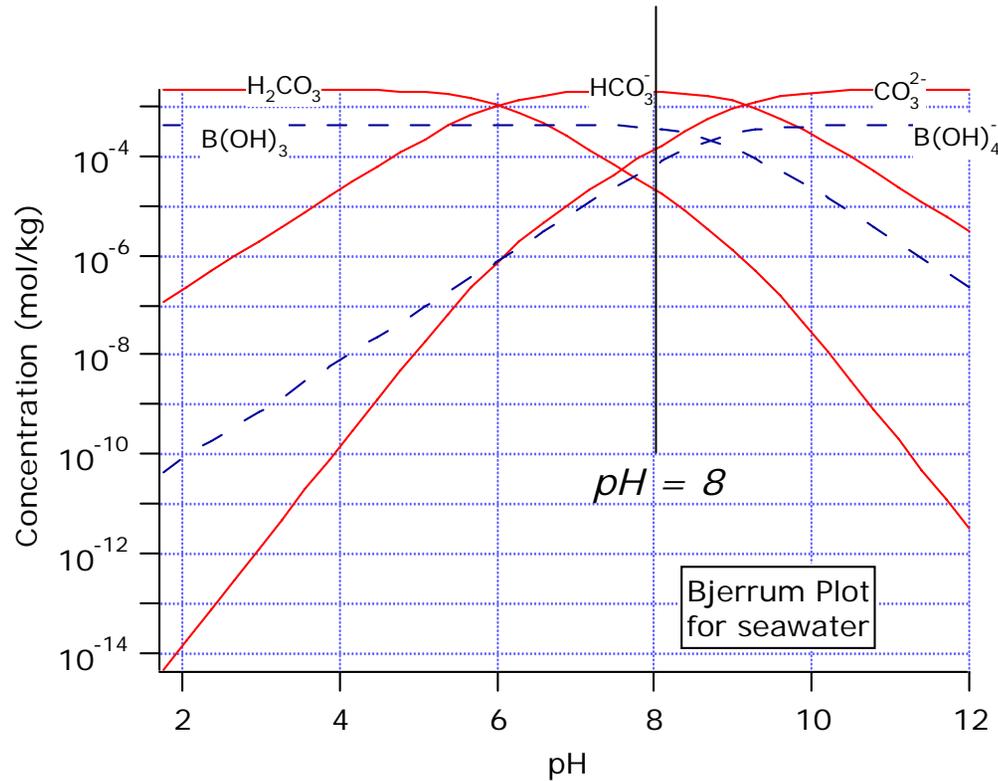
$$K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]}$$

$$K_W = [H^+][OH^-]$$

Measure ΣCO_2 , Alk, S \Rightarrow 7 equations in 7 unknowns

\Rightarrow you can solve for speciation!

Useful approximations for back-of-the-envelope calculations



At seawater pH,

$$\Sigma \text{CO}_2 \sim [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\text{Alk} \sim [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}]$$

And

$$[\text{CO}_3^{2-}] \sim \text{Alk} - \Sigma \text{CO}_2$$

The effect of biogeochemical processes on ΣCO_2 and Alk

- (1) The incorporation of CO_2 into organic matter (I.e., production of o.m.)

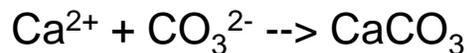


$$\Delta \Sigma \text{CO}_2 = -1$$

$$\Delta \text{Alk} = 0$$

... and a small (usually negligible) increase in Alk due to NO_3^- assimilation, $\Delta \text{Alk} = (16/106) * \text{mol C}_{\text{org}} \text{ formed}$

- (2) The precipitation of CaCO_3



$$\Delta \Sigma \text{CO}_2 = -1$$

$$\Delta \text{Alk} = -2$$

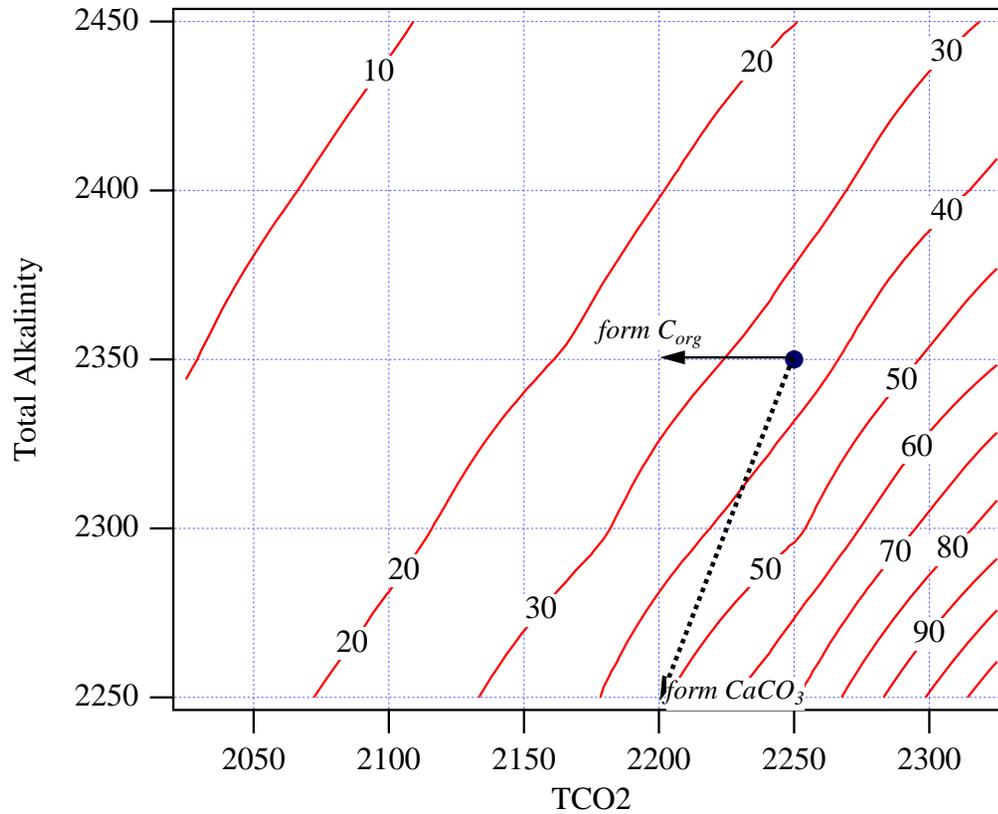
How do these processes affect the ability of the ocean to take up CO_2 from the atmosphere?

Taking into account Henry's law relating $[\text{CO}_2]$ in the water to the PCO_2 in equilibrium with the water,

$$[\text{CO}_2] = K_H \text{PCO}_2$$

*System approaches equilibrium after
Perturbation: lower ocean $[\text{CO}_2]$ -->
ocean absorbs CO_2*

Contours of $[\text{CO}_2]$ vs. Alk and ΣCO_2



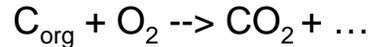
o.m. formation:
decrease $[\text{CO}_2]$

CaCO₃ pptn:
increase $[\text{CO}_2]$

Biogeochemical processes and the carbonate system

How do decomposition and dissolution processes affect the carbonate system?

(3) Organic matter dissolution... reverses (1),



$$\Delta \Sigma CO_2 = +1$$

$$\Delta \text{Alk} = 0$$

(and, as before, there's a small drop in Alk due to NH_3 oxidation to NO_3^-)

(4) $CaCO_3$ dissolution... reverses (2),

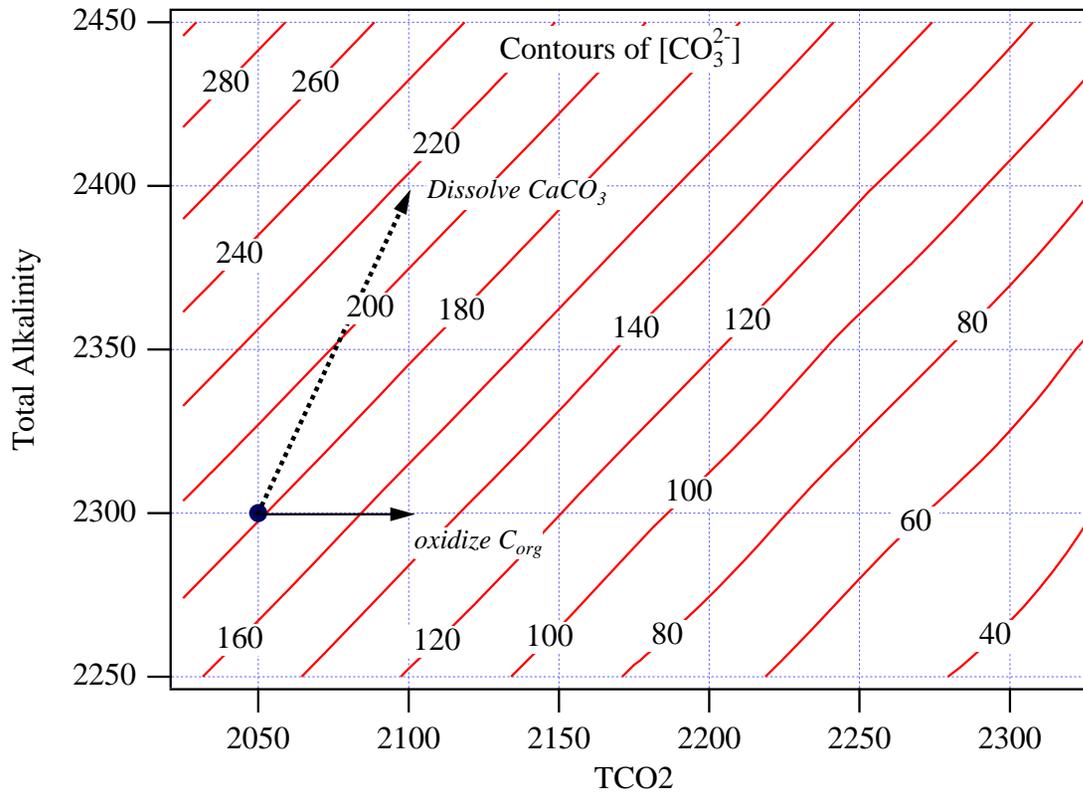


$$\Delta \Sigma CO_2 = +1$$

$$\Delta \text{Alk} = +2$$

How do these processes affect the $[CO_3^{2-}]$ of seawater as it “ages” during its transit through the deep sea?

Contours of $[\text{CO}_3^{2-}]$

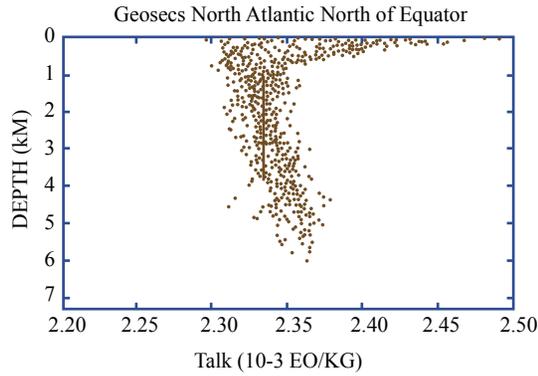


Oxidize o.m.:
decrease $[\text{CO}_3^{2-}]$

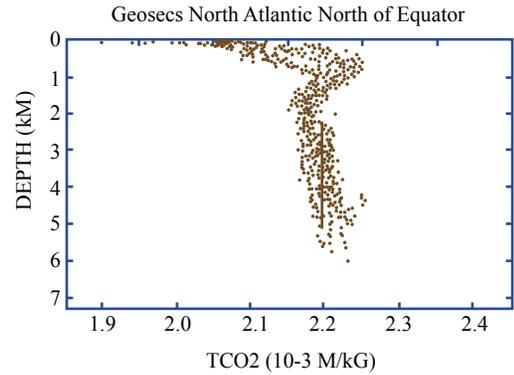
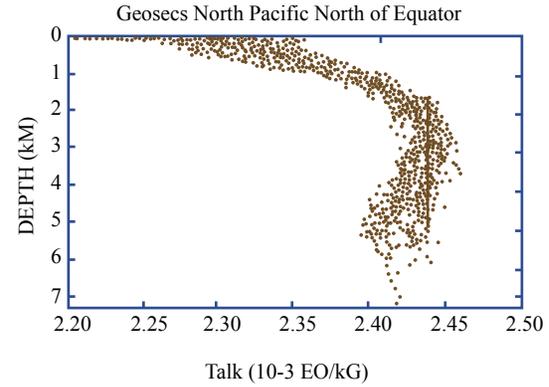
Dissolve CaCO_3 :
increase $[\text{CO}_3^{2-}]$

Question: what can you use this contour plot for if you have actual data?

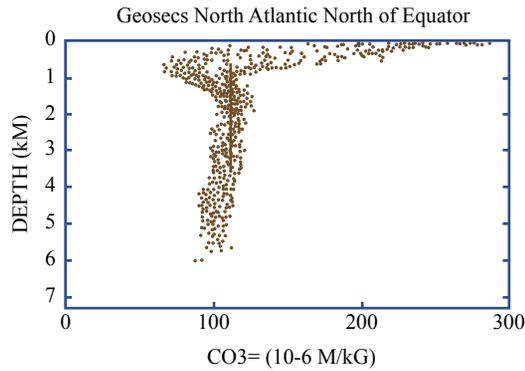
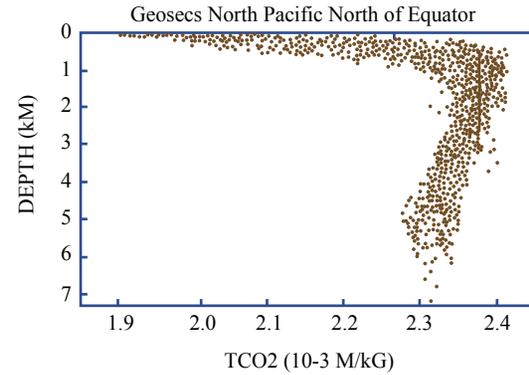
OBSERVATION



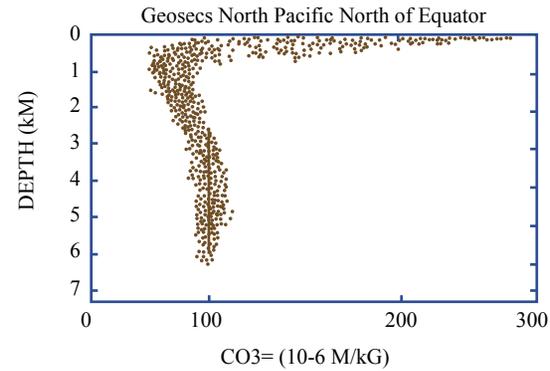
Alk



TCO₂



CO₃²⁻



NORTH ATLANTIC

NORTH PACIFIC

Using data and theory to calculate relative rates
of organic matter oxidation and carbonate dissolution
see Broecker and Peng, Tracers in the Sea

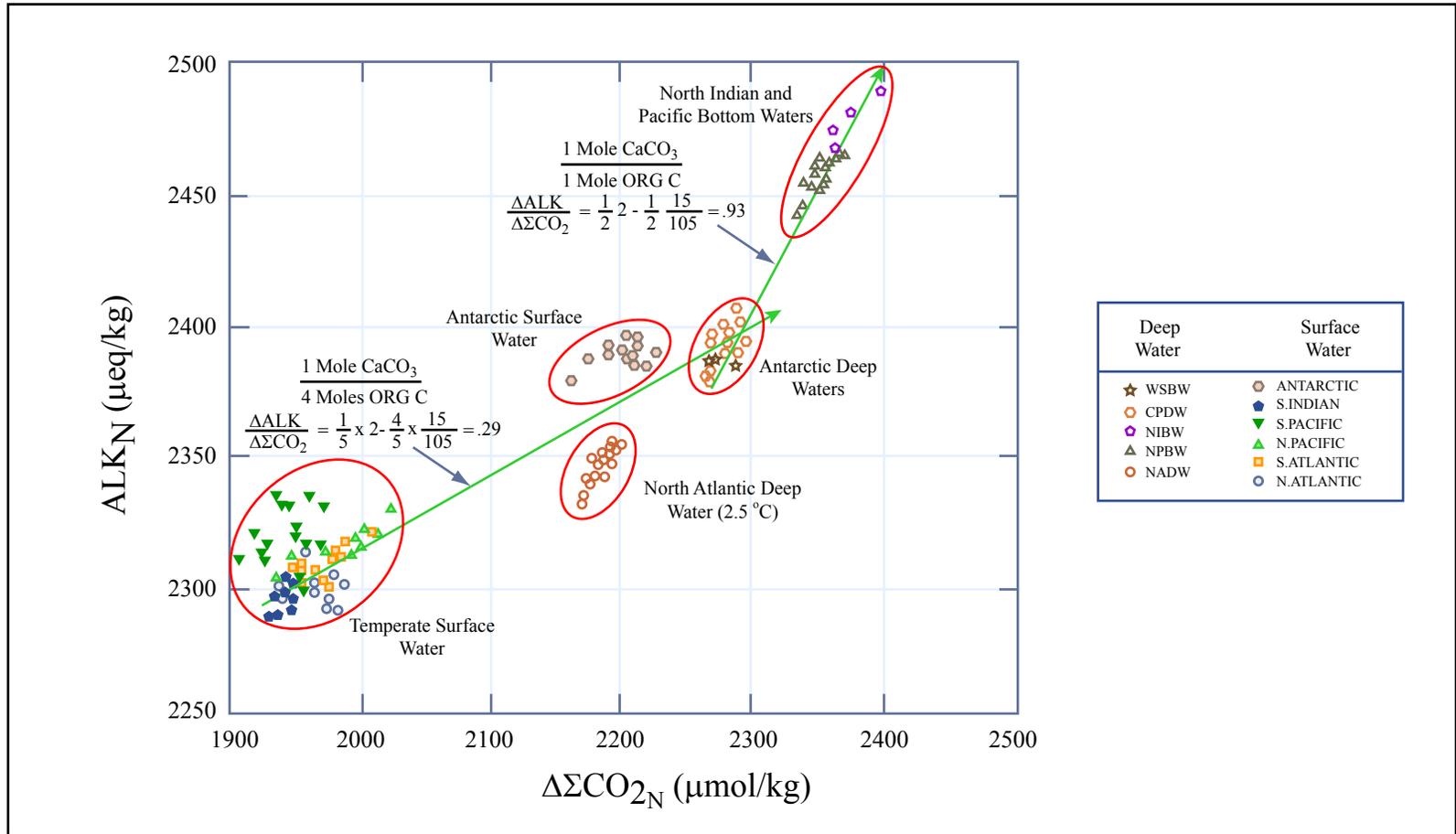


Figure by MIT OCW.

And...

We've shown how biogeochemical processes affect ΣCO_2 and Alk in the ocean...

We've started to show how distributions of ΣCO_2 and Alk can be used To learn about biogeochemical processes...

*We've not discussed the biological and chemical processes that control
formation and decomposition of organic matter*

formation and dissolution of CaCO_3

Those discussions will follow...