Lecture 10 - Acids and Bases: Ocean Carbonate System

Carbonate chemistry is the most intensely studied subject of marine chemistry. It is central to:

- The control of seawater pH;
- Regulation the CO_2 content of the atmosphere via the biological pump;
- Determining the ocean's influence on fossil fuel CO_2 uptake;
- Determining the extent of burial of $CaCO_3$ in marine sediments.

We will review acids and bases and how this relates to the carbonate chemistry of seawater, we will discuss:

- Acids and Bases in Seawater
- Alkalinity and Dissolved Inorganic Carbon (DIC)
- $CaCO_3$ preservation in marine sediments

Acids and Bases

Arrhenius (1887) proposed that an acid is a substance whose water solution contained an excess of hydrogen ions. The excess H^+ ions resulted from dissociation of the acid as it was introduced into water. The fact that H^+ ions cannot exist un-hydrated in water solution led to the Bronsted Concept in which acids are compounds that can donate a proton to another substance which is a proton acceptor. Thus, an acid is considered a proton donor (and a base is a proton acceptor). Proton transfer can only occur if an acid reacts with a base such as:

$$Acid_1 = Base_1 + Proton$$
$$Proton + Base_2 = Acid_2$$

$$Acid_1 + Base_2 = Acid_2 + Base_1$$

For example:

$$HCl + H_2O = H_3O^+ + Cl^-$$
$$H_2O + H_2O = H_3O^+ + OH^-$$
$$H_2CO_3 + H_2O = H_3O^+ + HCO_3^-$$

In the first reaction, HCl transfers a proton to H_2O.
Note that water (H_2O), in the second reaction, can be both an acid (proton donor) and a base (proton acceptor).

To simplify this presentation we will write acids as Arrhenius Acids, in which acids simply react to produce excess hydrogen ions in solution. Such as:

$$HCl = H^+ + Cl^-$$

Monoprotic Acids

Let's use acetic acid (CH_3COOH) as an example of a monoprotic acid and we will abbreviate it as HA. The base form (CH_3COO^-) will be A^-.
We need to determine the concentrations of 4 species. These are the acid (HA) and base

(A^-) forms of acetic acid and H^+ and OH^-.

When there are four unknowns we need four equations.
To simplify matters we will neglect activity corrections and assume that activities are equal to concentrations ( ) = [ ]

The 4 key equations are:

(1) $HA \Leftrightarrow H^+ + A^-$	HA = acid; H^+ = hydrogen ion; A^- = anion (conjugate base)
(2) $K = (H^+)(A^-)/(HA)$	K = thermodynamic equilibrium (K = equilibrium constant)
(3) $C_T = [HA] + [A^-]$	C_T = total anion inventory
(4) $0 = [H^+] + [A^-]$	Charge Balance

(Note that mass and charge balances are written in terms of concentrations, not activities)

To solve for a given concentration in terms of the others, one must have equations for:

a. Acid / Base equilibrium
b. Total anion inventory
c. Charge Balance

pH ($-\log(H^+)$) is used as a master variable (e.g. the parameter against which other concentrations are expressed) for acid-base reactions because it is the variable that determines the distribution of acid and base forms. In addition it is easily measured.

The pK of an acid base couple (-log K) tells you at what pH the acid, HA, and base, A^-, are equal in concentration and half the total concentration of the anion, C_T.

$$K_{HA} = \frac{(H^+)(A^-)}{(HA)} \qquad \log K_{HA} = \log (H^+) + \log (A^-) - \log (HA); \quad pK = - \log K$$

So $$pH = pK_{HA} + \log \frac{(A^-)}{(HA)}$$

Using this equation, we can predict the extent of protonation of an acid dissolved in water. Or describe the distribution of the species HA, A^-, H^+ and OH^- as a function of pH.

We need to be able to solve for the concentration of these species. We can do this by two methods. One is algebraic and one is graphical.

Algebraic Method
By combining equations 2 and 3 given above we can write algebraic expressions to solve for the main species of acetic acid (HA) and acetate (A^-) as functions of K, C_T and pH.

$[HA] = C_T [H^+] / (K + [H^+])$; $\qquad \log [HA] = \log C_T + \log [H^+] – \log (K + [H^+])$
$[A^-] = C_T K / (K + [H^+])$; $\qquad \log [A^-] = \log C_T + \log K – \log (K + [H^+])$

The equation for HA is derived using simple algebra as follows:

(1) We start with: $K = (H^+)(A^-)/(HA)$

(2) Rearrange the mass balance to solve for $A = C_T - HA$ and substitute for A in the equilibrium expression.
(3) We now have: $K = (H^+)(C_T - HA) / (HA)$
(4) Rearranging this equation gives: $(HA) = (H^+)C_T / (K + (H^+))$

The equation for (A) is derived using the same approach but using $HA = C_T - A$ in step b. If this is not clear please derive this relation yourself.

For such calculations when you know K and the total concentration (C_T) you can calculate the concentration of HA and A^- for any pH (or H^+).

Graphical Approach
This approach is to construct a graph or distribution diagram showing how the concentrations of all the species vary with pH. Such graphs are constructed using the equations for HA and A given above. The graph is a plot of –log [conc.] as the Y-axis and pH as the X-axis.

There are three regions for these graphs as discussed below.

For example take acetic acid:
$K = 10^{-4.7}$ (this is the equilibrium constant for acetic acid, CH_3COOH); pK = 4.7
$C_T = 10^{-2}$
( ) = [ ] (e.g. activities equal concentrations for simplification).

If we make a plot of the concentration of each species as a function of pH there will be three regions

a) pH = pK (e.g. $H^+ = K$) (this pH is called the system point in the diagram).
If we look at the equilibrium constant:

$$K = (H^+)(A^-)/(HA) \text{ and rearrange it to: } K / (H^+) = (A^-) / (HA)$$

We see that when K = (H), at the system point pH, the ratio $K / (H^+)$ is equal to one and thus: $[HA] = [A^-]$ and since $CT = [HA] + [A^-]$ then $[HA] = [A^-] = 1/2\ C_T$
or in log form: $\log [HA] = \log [A^-] = \log (C_T/2) = \log C_T - \log 2 = \log C_T - 0.3$
in other words the point where $\log [HA] = \log [A^-]$ is 0.3 log units lower than $\log C_T$ and that is where pH=pK.

b) When pH << pK the solution is acidic and $(H^+) >> K$
For this condition the algebraic equations for HA and A can be simplified as follows:

$[HA] = C_T [H^+] / (K + [H^+]) \cong C_T [H^+] / ([H^+]) \cong C_T$
$[HA] \cong C_T$ and $\log [HA] \cong \log C_T$ (The line for HA has no slope and is equal to CT)

Similarly: since $[A^-] = C_T K / (K + [H^+]) \cong C_T K / ([H^+])$
So $\log [A^-] \cong \log C_T + \log K - \log H^+ \cong \log CT + \log K + pH$
Note that change in $\log [A^-]$ is proportional to +1 change in pH or:
$\delta \log [A^-] / \delta pH = +1$ (The line for $[A^-]$ has a slope of +1)

Note that in this case:
$K = (H^+)(A^-)/(HA)$; so $K/(H^+) = (A^-)/(HA)$; and since $H^+ > K$ then $[HA] > [A^-]$

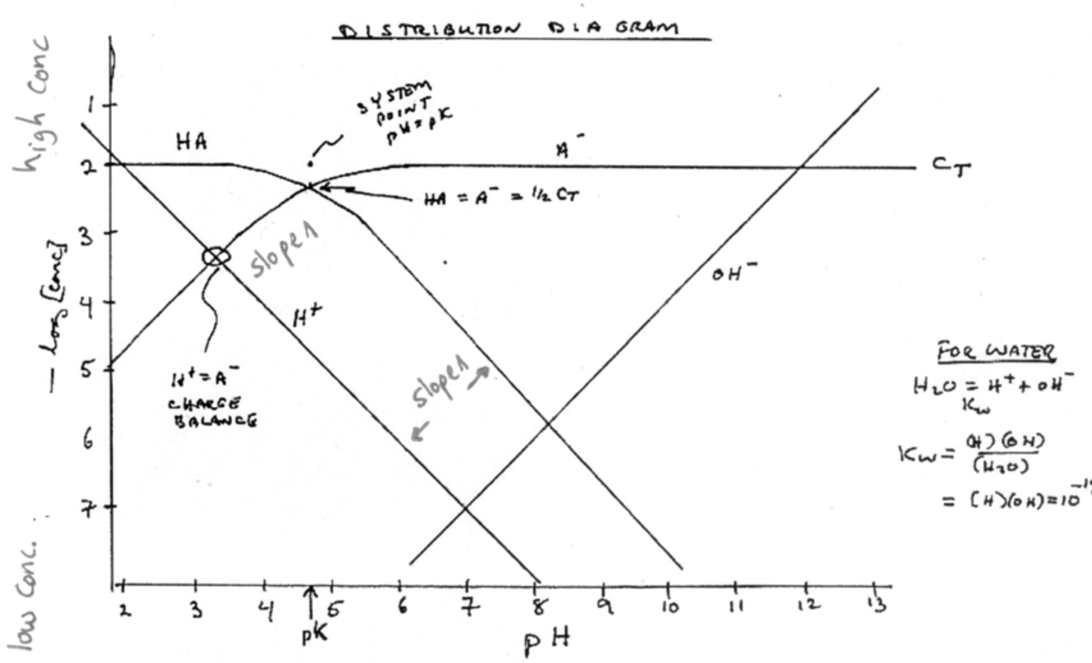
c) pH >> pK (e.g. basic solution, $H^+ << K$)
From: $[A^-] = C_T K / (K + [H^+]) \cong C_T K / (K) \cong C_T$ and $\log [A^-] = \log C_T$
From: $[HA] = C_T [H^+] / (K + [H^+]) \cong C_T [H^+] / (K)$
$\log [HA] = \log C_T + \log H^+ - \log K = \log C_T - pH - \log K$
The slope for [HA] is -1; $\delta \log [HA] / \delta pH = -1$

The steps for constructing the graph are:

(1) Label axes (pH and –log [C])
(2) Draw a horizontal line for total concentration; (at $-\log C_T$), for the acetic acid above this will be at 2
(3) Locate system point, pH = pK and $HA = A^-$; note that the cross over is 0.3 log units below the C_T line, for the acetic acid above this is at pH 4.7
(4) Draw lines for the species, slope = +1 for $[A^-]$ and slope = -1 for [HA]; remember that at a pH lower than the system point $HA > A^-$, at a pH higher than the system point $A^- > HA$
(5) Draw lines for H^+ and OH^-; remember $H^+ = OH^-$ at pH = pK = 7.

The lines for H^+ and OH^- can be obtained as follows. Write the acidity reaction for H_2O.
$H_2O = H^+ + OH^-$ $\quad K_w = (H^+)(OH^-) / (H_2O) = (H^+)(OH^-)$ (because we can assume the activity of pure water solvent is equal to one). The value of $K_w = 10^{-14}$.

Thus: $\log (H^+) + \log (OH^-) = -14.0$
Or $\quad -pH + -pOH = -14.0$
Or $\quad pH + pOH = 14.0$
Thus at pH = 4.0, the pOH = 10.0



Apparent Equilibrium Constants

The difference between concentrations and activities can't be ignored for seawater and chemical oceanographers often use a second approach. Oceanographers frequently use an equilibrium constant defined in terms of concentrations. These are called apparent or operation equilibrium constants. We use the symbol K' to distinguish them from K. Formally they are equilibrium constants determined on the seawater activity scale. Apparent equilibrium constants (K') are written in the same form as K except that all species are written as concentrations. The exception is H^+, which is always written as the activity (H^+). For the monoprotic acid HA we write:

$$HA = H^+ + A^- \qquad \text{and} \qquad K' = (H^+)[A^-] / [HA]$$

The apparent equilibrium constants cannot be calculated from standard free energies of reaction. They have to be determined experimentally in the lab. They must be determined in the same medium or solution to which they will be applied. Thus, if we need a value of K' for the acid HA in seawater, someone must have experimentally determined the K for the acidity reaction in a seawater solution with a known salinity (S) at the temperature and pressure of interest. This sounds complicated, and it is. It is a lot of work, but fortunately, it has been done for several important acids in seawater. There are pros and cons for both the K and K' approaches. When we use K the pro is that we can calculate the K from ΔG_r and one value can be used for all problems in all solutions (one K fits all). The cons are that to use K we need to obtain values for the free ion activity coefficients (γi) and the % free (f_i) for each solution. For K' there needs to have been experimental determination of this constant for enough values of S, T and P that equations can be derived to calculate K' for the S, T and P of interest. The good news is that when this has been done the values of K' are usually more precise than the corresponding value of K. We also do not need values of γ_i and f_i when we use K'.

Example:

The difference between K and K' can be illustrated by this simple example.

$$K = (H^+)(A^-) / (HA) = (H^+)[A\text{-}]\ \gamma_{T,A-} / [HA]\ \gamma_{T,HA}$$

Rearrange to get:

$$\frac{K\ \gamma_{T,HA}}{\gamma_{T,A-}} = \frac{(H+)\ [A\text{-}]}{[HA]} \qquad\qquad K' = \frac{K\ \gamma_{T,HA}}{\gamma_{T,A-}}$$

You see that the difference in magnitude of K and K' is the ratio of the total activity coefficients of the base to the acid.

For: $H_2CO_3 = HCO_3^- + H^+$

$$K_1 = (HCO_3^-)(H^+) / (H_2CO^3)$$

or

$$K_1 = \frac{[HCO_3^-]\ \gamma_{T,HCO3}\ (H^+)}{[H_2CO_3]\ \gamma_{T,H2CO3}} = \frac{[HCO_3^-]\ (H^+)}{[H_2CO_3]}\ \frac{\gamma_{T,HCO3}}{\gamma_{T,H2CO3}} = 10^{-6.3} \text{ (from tables)}$$

The value of K' has been determined for the same reaction. At S = 35, 25°C and 1 atm

$$K_1' = \frac{[HCO_3^-]\,(H^+)}{[H_2CO_3]} = 10^{-6.0}$$

If we set $K_1 = K_1' (\gamma_{T,HCO3} / \gamma_{T,H2CO3})$
We can solve for $\gamma_{T,HCO3} / \gamma_{T,H2CO3} = K_1 / K_1' = 10^{-6.3} / 10^{-6.0} = 10^{-0.3} =$ **5.0×10^{-1}**
The difference between K and K' is due to the activity coefficient ratios.

The acids of Seawater. There are many acid/base pairs in seawater. However, very few have a pK or a significant concentration in the pH range of seawater (pH 7-9). The concentrations and apparent constants in the table below were taken from Edmond (1970). Some elements form more than one acid.

SPECIES	REACTION	CONCENTRTION		pK'
		(moles / kg)	-log C_T	
H_2O	$H_2O \Leftrightarrow OH + H^+$			13.9
C	$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$	2.4×10^{-3}	2.6	6.0
	$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$			9.1
B	$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + H^+$	4.25×10^{-4}	3.37	8.7
Si	$H_2SiO_3 \Leftrightarrow HSiO_3^- + H+$	1.5×10^{-4}	3.82	9.4
	$HSiO_3^- \Leftrightarrow SiO_3^{2-} + H^+$			
P	$H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+$	3.0×10^{-6}	5.52	1.6
	$H_2PO_4^- \Leftrightarrow HPO_4^{2-} + H+$			6.0
	$HPO_4^{2-} \Leftrightarrow PO_3^{3-} + H^+$			8.6
Mg	$Mg^{2+} + H_2O \Leftrightarrow MgOH^+ + H^+$	5.32×10^{-2}	1.27	12.5
Ca	$Ca^{2+} + H_2O \Leftrightarrow CaOH^+ + H^+$	1.03×10^{-2}	1.99	13.0
S	$HSO_4^- \Leftrightarrow SO_4^{2-} + H^+$	2.82×10^{-2}	1.55	1.5
F	$HF \Leftrightarrow F^- + H^+$	5.2×10^{-5}	4.28	2.5
Anoxic Water				
N	$NH_4^+ \Leftrightarrow NH_3(aq) + H^+$	10×10^{-6}	5.0	9.5
S	$H_2S \Leftrightarrow HS^- + H^+$	$10\text{-}100 \times 10^{-6}$	5.0-4.0	7.0
	$HS^- \Leftrightarrow S^{2-} + H^+$			13.4

The Most Important Acids in Seawater are Carbonic Acid and Boric Acid:

Carbonic Acid
Carbonic acid is a diprotic acid and it can have a gaseous form.

There are 6 species we need to solve for:

$CO_2(g)$	Carbon Dioxide Gas
$H_2CO_3^*$	Carbonic Acid ($H_2CO_3^* = CO_2(aq) + H_2CO_3$)
HCO_3^-	Bicarbonate
CO_3^{2-}	Carbonate
H^+	Proton
OH^-	Hydroxide

To solve for six unknowns we need six equations.
Four of these are equilibrium constants. These are written here as K but could also be expressed as K'.

1. $CO_2(g) + H_2O = H_2CO_3^*$ $K_H = (H_2CO_3^*) / P_{CO2}$ (Henry's Law)
(gas concentrations are given as partial pressure; e.g. atmospheric $P_{CO2} = 10^{-3.5}$)
2. $H_2CO_3^* = H^+ + HCO_3^-$ $K_1 = (HCO_3^-)(H^+) / H_2CO_3^*)$
3. $HCO_3^- = H^+ + CO_3^{2-}$ $K_2 = (H^+)(CO_3^{2-}) / (HCO_3^-)$
4. $H_2O = H^+ + OH^-$ $K_w = (H^+)(OH^-)$

Representative values for these constants are given below. Equations are given in Millero (1995) from with which you can calculate all K's for any salinity and T, P conditions. The values here are for S = 35, 25°C and 1 atm.

Constant	Thermodynamic Constant (K)	Apparent Seawater Constant (K')
K_H	$10^{-1.47}$	$10^{-1.53}$
K_1'	$10^{-6.35}$	$10^{-6.00}$
K_2'	$10^{-10.33}$	$10^{-9.10}$
K_w	$10^{-14.0}$	$10^{-13.9}$

We can also define total CO_2 (also referred to as DIC, C_T or ΣCO_2)

$$C_T = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] = 10^{-2.6}$$

At equilibrium, the concentration of CO_2 is about 1000 times more than H_2CO_3, so, in practice, the first two equilibria are usually combined by defining:

$$CO_2(aq) = CO_2 + H_2CO_3 = H_2CO_3^*$$

(It is not always stated and I may sometimes forget the (aq), but in all cases the dissolved concentration of CO_2 in water refers to both $CO_2 + H_2CO_3$ unless explicitly stated differently)

Combining equations (1), (2) and (3) and solving for $CO_2(aq)$:

(4) $C_T = [CO_2(aq)] + \{K_1' ([CO_2(aq)]/a_{H+}\} + \{K_2'K_1'([CO_2(aq)]/a_{H+}^2)\}$
$= [CO_2(aq)]\{1+K_1'/a_{H+} + K_1'K_2'/a_{H+}^2\}$

for HCO_3^-:

(5) $C_T = [HCO_3^-]\, a_{H+} / K_1' + [HCO_3^-] + K_2'[HCO_3^-]/a_{H+} = [HCO_3^-]\{a_{H+}/K_1' + 1 + K_2'/a_{H+}\}$

for CO_3^{2-}:

(6) $C_T = [CO_3^{2-}]\, a_{H+}^2/K_1'K_2' + [CO_3^{2-}]a_{H+}/K_2' + [CO_3^{2-}] = [CO_3^{2-}]\{a_{H+}^2/K_1'K_2' + a_{H+}/K_2' + 1\}$

when $a_{H+} >> K_1'$ $C_T = [CO_2(aq)]$ (from eq. 4)
$K_1' > a_{H+} > K_2'$ $C_T = [HCO_3^-]$ (from eq. 5)
$K_2' > a_{H+}$ $C_T = [CO_3^{2-}]$ (from eq. 6)

at $[CO_2(aq)] = [HCO_3^-]$ $C_T \cong 2[CO_2(aq)] = 2[HCO_3^-]$ (from eq. 4 and 5)

$[CO_3^{2-}] = [HCO_3^-]$ $\qquad C_T \cong 2[CO_3^{2-}] = 2[HCO_3^-]$ $\qquad$ (from eq. 5 and 6)
$[CO_2(aq)] = [CO_3^{2-}]$ $\qquad C_T \cong [CO_2(aq)\{2 + K_1'/(K_1'K_2')^{1/2}$ $\qquad$ (from eq. 4 and 6)

Water (The solvent)

$K_W' = a_{H+} [OH^-] / [H_2O];$ $\qquad K_W' = 10^{-13.9}$
$\log a_{H+} + \log[OH^-] = -13.9$ $\qquad a_{H2O} = 1$
$pH = -\log a_{H+} = \log [OH^-] + 13.9$

Construct a Distribution Diagram (Home Work!! bring to class)

a. Specify the total CO_2 (e.g. $C_T = 2.0 \times 10^{-2.6}$)
b. Locate C_T on the graph and draw a horizontal line for that value.
c. Locate the two system points on that line where $pH = pK_1$ and $pH = pK_2$.
d. Make the crossover point, which is 0.3 log units less than C_T
e. Sketch the lines for the species.

The Carbonate System in Seawater

For calculations such as CO_2 gas exchange or $CaCO_3$ solubility, we need to know the concentrations of H_2CO_3 or CO_3^{2-}. We cannot measure these species directly. The four parameters that can be measured are used to define all other variables in the carbonate system these are: pH, Total CO_2, Alkalinity and P_{CO2}.

Measurements

pH is defined in terms of the activity of H^+ or as $pH = -\log (H^+)$. The historical approach was to measure pH using a glass electrode calibrated with buffer solutions prepared by the National Bureau of Standards. Thought the precision can be quite good (+0.003) the accuracy is no better than about +0.02. New colorimetric methods have been developed where the ratio of the acid to base is determined using a H^+ sensitive dye. See Millero (1995) for discussion and references.

Total CO_2 (expressed as C_T or DIC or ΣCO_2) is defined as the sum of the concentrations of the three carbonate species: $C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$
It is determined by acidifying a seawater sample to about a pH of 2. This converts all the carbonate species to H_2CO_3, which is essentially equivalent to $CO_2(aq)$, which can be driven off with an inert carrier gas (e.g. He) and analyzed with an infrared (IR) detector.

Alkalinity there are two definitions for alkalinity:
- The alkalinity of seawater is the sum of the concentrations of anions that accept protons at the pH of seawater.
- Another definition for the alkalinity is that it is the difference between the concentrations of total cation and total anion that do NOT exchange H^+ in the pH range of seawater. This is an important concept because it helps explain the origin of alkalinity in terms of charge balance in seawater.

Species	-log C	Concentration		% of Alkalinity
		mmol / kg	meq / kg	
HCO_3^-	2.87	1.960	1.960	84
CO_3^{2-}	3.84	0.144	0.288	12
$B(OH)_4^-$	4.19	0.064	0.064	3
$HSiO_3^-$	5.30	0.005	0.005	0.2
HPO_4^{2-}	5.68	0.002	0.004	0.2
OH^-	6.00	0.001	0.001	0.0
		Total Alkalinity (TA) =	2.322 meq / kg	

Generally: TA (or Alk) = $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [HSiO_3^-] + [HPO_4^-] + [OH^-]$
Carbonate alkalinity: $A_C = [HCO_3^-] + 2[CO_3^{2-}]$

Cations		Anions	
Equivalents / kg			
Na^+	0.46847	Cl^-	0.54591
Mg^{2+}	0.10616	SO_4^{2-}	0.05646
Ca^{2+}	0.02066	Br^-	0.00084
K^+	0.0102	F^-	0.00014
Sr^{2+}	0.00018		
Total Cations	0.60567	Total Anions	0.60335

TA = Cation charge – Anion charge = 0.60567 – 0.60335 = 0.00232= 2.32 meq/kg

Since alkalinity is defined as the amount of acid necessary to titrate all the weak bases in seawater (e.g. HCO_3^-, CO_3^{2-}, $B(OH)_4^-$) it is determined using an acid titration. The concentration is expressed as equivalents kg^{-1}, rather than moles kg^{-1}, because each species is multiplied by the number of protons it consumes. For example, when acid is added HCO^{3-} consumes one proton as it is converted to H_2CO_3. CO_3^{2-} consumes two protons, thus its concentration is multiplied by two ($CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$).

P_{CO2} is defined as the partial pressure of CO_2 that a water mass would have if it were in equilibrium with a gas phase. It is determined by equilibrating a known volume of water with a known volume of gas and measuring the CO_2 in the gas phase, again by IR detection.

Ocean Distributions of pH, DIC, Alk and P_{CO2}

pH – The surface values in both oceans are just slightly higher than pH = 8.1. This is close to the value expected for water of seawater alkalinity in equilibrium with the atmosphere with $P_{CO2} = 10^{-3.5}$. pH then decreases to a minimum in both oceans, however the minimum is much more intense in the Pacific (to about pH = 7.3) than the Atlantic (pH = 7.75). The depth of this pH minimum corresponds to the depth of the oxygen minimum. In the deep sea the pH increases slowly, but at all depths the pH in the Pacific (pH ~7.5) is less than that in the Atlantic (pH ~7.8). This is a result from CO_2 produced by respiration.

DIC – The total CO_2 is about 1950 µmol kg^{-1} in the surface Atlantic and Pacific. It then increases with depth. The increase is steep in the upper 1000m and then is more gradual in the deeper water. All subsurface DIC concentrations in the deep Pacific (about 2350 µmol kg^{-1}) are higher than in the deep Atlantic (about 2200 µmol kg^{-1}). This is a result of organic matter respiration and carbonate dissolution.

Alkalinity – Total alkalinity (includes the concentrations of all titratable bases) in the surface Atlantic is about 2300 µeq kg^{-1}, while the surface Pacific is slightly lower at 2250 µeq kg^{-1}. Alkalinity increases less steeply than does DIC. The deep values are lower in the Atlantic (2350 µeq kg^{-1}) than in the Pacific (2425 µeq kg^{-1}).

P_{CO2} – In most regards, the distribution of P_{CO2} is a mirror image of pH. When pH goes down, P_{CO2} goes up. The surface values in both oceans are about 350 µatm, which is about the value of the atmosphere. P_{CO2} increases to a maximum of about 800 µatm in the Atlantic and over 2000 µatm in the Pacific.

Controls on Ocean Distributions.

A) Photosynthesis/Respiration

Organic matter (approximated as CH_2O) is produced and consumed as follows:
$CH_2O + O_2 \Leftrightarrow CO_2 + H_2O$

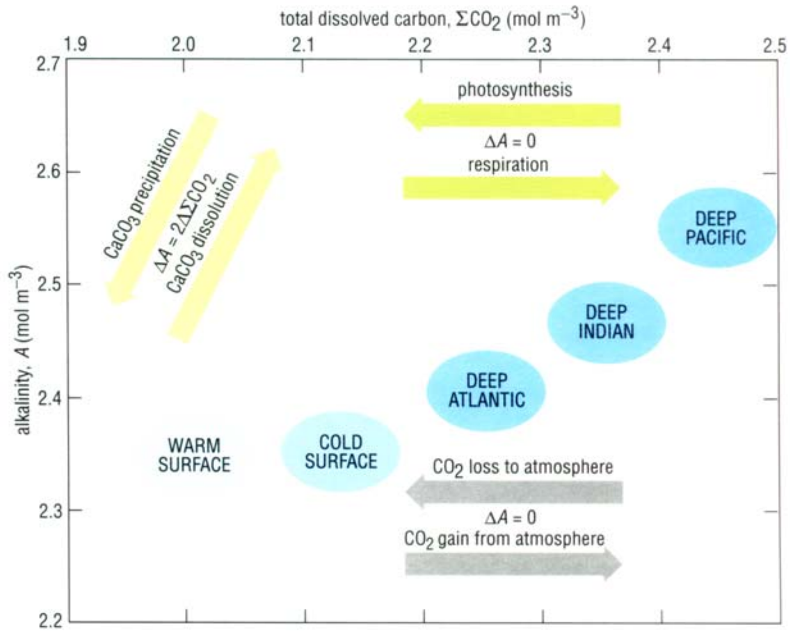
Then:
$CO_2 + H_2O \rightarrow H_2CO_3^*$
$H_2CO_3^* \rightarrow H^+ + HCO_3^-$
$HCO_3^- \rightarrow H+ + CO_3^{2-}$

As CO_2 is produced during respiration we should observe:
pH ↓; DIC ↑; Alk =; P_{CO2}↑ ΔDIC =1; ΔAlk=0
The trends will be the opposite for photosynthesis.

B) $CaCO_3$ dissolution/precipitation
$CaCO_3(s) \rightarrow Ca^{2+} + CO_3^{2-}$
Also written as:
$CaCO_3(s) + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$

As $CaCO_3(s)$ dissolves, $CO3^{2-}$ is added to solution. We should observe:
pH↑; DIC↑; Alk↑; P_{CO2}↓ ΔDIC =1; ΔAlk=2

The trends predicted by these processes can be seen in the 6 vector diagrams in the following figure.



C) Weathering Processes

On the global scale, an imbalance of cations and nonprotonating anions is caused by weathering of rocks.

$$\text{Rock} + H^+ + H_2O \rightarrow \text{cations}^+ + \text{clay} + H_2SiO_3(aq)$$

$$\underline{CO_2(aq) + H_2O \Leftrightarrow HCO_3^- + H^+}$$

$$\text{Rock} + CO_2(aq) + 2H_2O \rightarrow \text{cations}^+ + \text{clay} + HCO_3^- + H_2SiO_3(aq)$$

Examples:

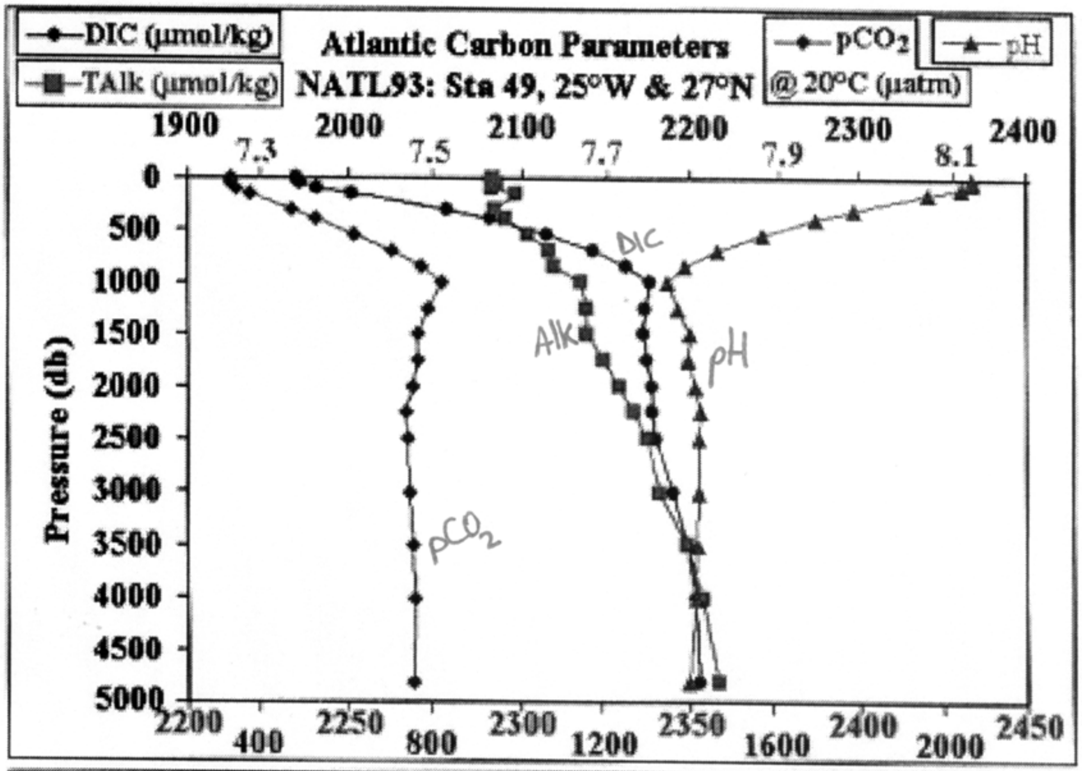
Dissolution of silicates (Potassium Feldspar)

$$\underset{\text{(K-feldspar)}}{KAlSi_3O_8(s)} + H^+ + 4.5H_2O \rightarrow K^+ + \underset{\text{(kaolinite)}}{0.5Al_2Si_2O_5(OH)_4(s)} + 2\ H_4SiO_4(aq)$$

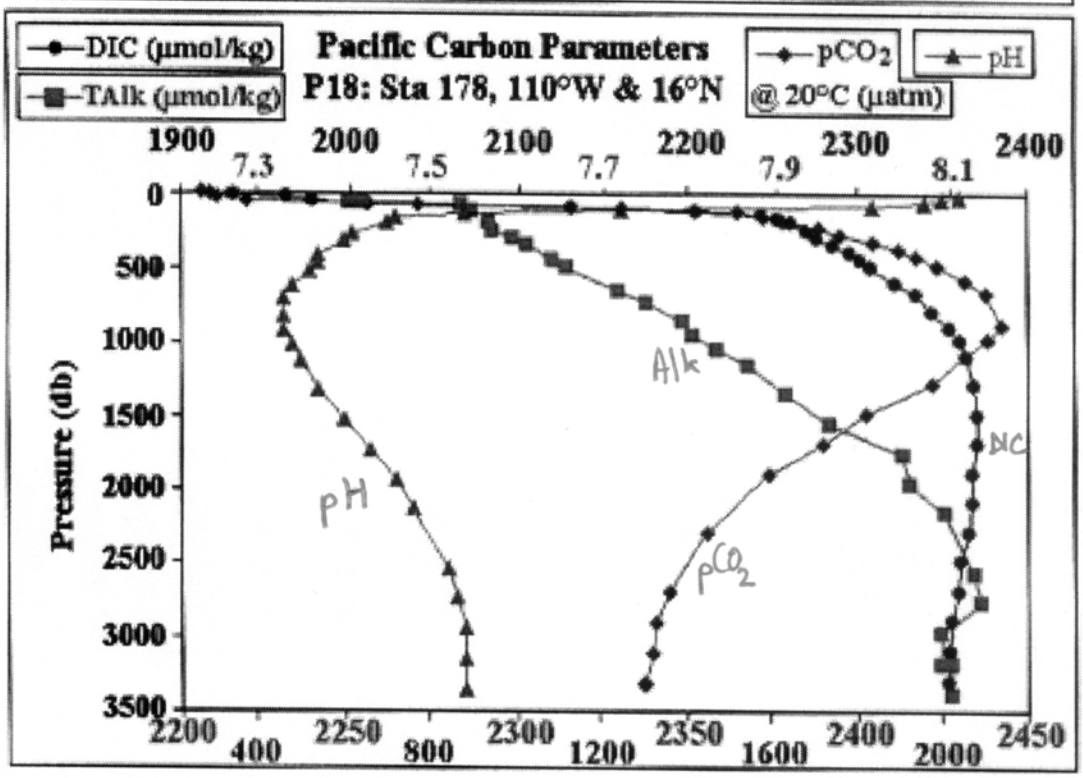
$$\underline{CO_2(aq) + H_2O \Leftrightarrow HCO_3^- + H^+}$$

$$\text{K-feldspar} + CO_2(aq) + 5.5H_2O \rightarrow \text{kaolinite} + K^+ + HCO_3^- + 2H_4SiO_4$$

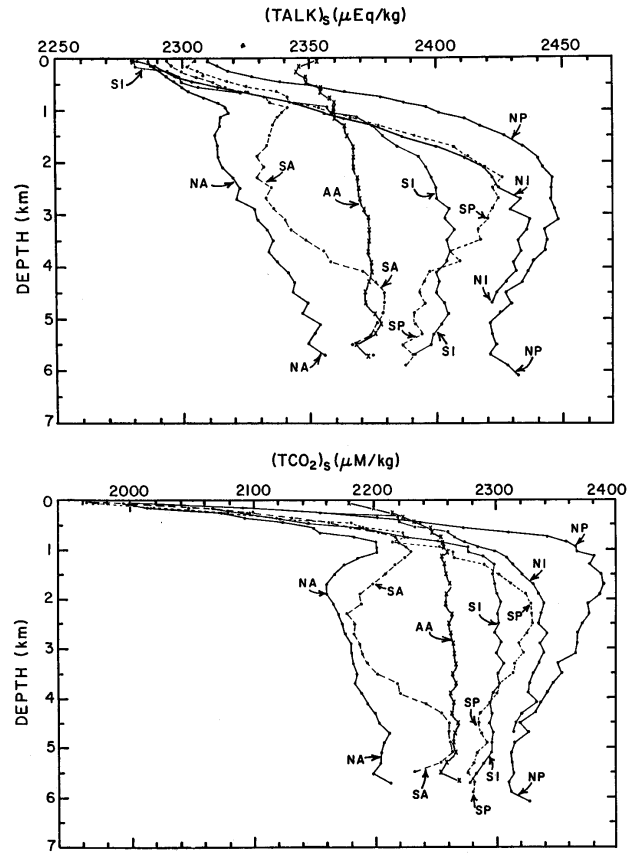
Neutralization of acid (H^+) during weathering creates excess cations that are balanced by anions of weak acids (the alkalinity). Both the composition of the rocks and the atmosphere determine the alkalinity and the overall pH. Note that weathering of carbonate rock is a similar reaction to that written above for carbonate dissolution in the ocean. The weathering reactions control the overall alkalinity in seawater but the biological processes (A and B above) determine the internal distribution within the ocean.



Atlantic Carbon Parameters
NATL93: Sta 49, 25°W & 27°N
DIC (µmol/kg)
TAlk (µmol/kg)
pCO2
@ 20°C (µatm)
pH
1900 2000 2100 2200 2300 2400
7.3 7.5 7.7 7.9 8.1
Pressure (db)
0 500 1000 1500 2000 2500 3000 3500 4000 4500 5000
2200 2250 2300 2350 2400 2450
400 800 1200 1600 2000
DIC
Alk
pH
pCO2



Pacific Carbon Parameters
P18: Sta 178, 110°W & 16°N
DIC (µmol/kg)
TAlk (µmol/kg)
pCO2
@ 20°C (µatm)
pH
1900 2000 2100 2200 2300 2400
7.3 7.5 7.7 7.9 8.1
Pressure (db)
0 500 1000 1500 2000 2500 3000 3500
2200 2250 2300 2350 2400 2450
400 800 1200 1600 2000
Alk
DIC
pH
pCO2



Vertical distribution of (a) alkalinity and (b) DIC (or ΣCO_2) NA = North Atlantic; SA = South Atlantic; AA = Antarctic; SI = South Indian; NI = North Indian; SP = South Pacific; NP = North Pacific (Takahashi et al., 1981)

Carbonate System Calculations

Unknowns:

P_{CO2}, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, H^+, OH^-

Equations: K_w, K_H, K_1, K_2

(1) $CO_2(g) \Leftrightarrow [CO_2(aq)]$ $\quad K_H' = [CO_2aq(aq)] / ppCO_2$

(2) $CO_2(aq) + H_2O \Leftrightarrow HCO_3^- + H^+$ $\quad K_1' = [HCO_3^-]\, a_{H+} / [CO_2(aq)]$

(3) $HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$ $\quad K_2' = [CO_3^{2-}]\, a_{H+} / [HCO_3^-]$

$H_2O \Leftrightarrow H^+ + OH^-$ $\quad K_W' = a_{H+}\, [OH^-] / [H_2O]$

Mass Balance:

(4) $DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2]$

Charge Balance:

(5) $ALK = [HCO_3^-] + 2\,[CO_3^{2-}] + [B(OH)_4^-]$ + minor anions

or for carbon only: $A_C = [HCO_3^-] + 2[CO_3^{2-}]$

Calcium Carbonate precipitation/dissolution (K_{sp})

(6) $CaCO_3(s) \Leftrightarrow Ca^{2+} + CO_3^{2-}$

DIC and Alk are independent of temperature and pressure, thus they are often the measured parameters. The rest are dependent on T and P because equilibrium constants are a function of (T,P); but, if any two of the variables (P_{CO2}, Alk, DIC, pH) are known (measured) all the system is defined.

Equations can be derived to solve for each species in terms of two of these variables.

Example 1: Measure pH and C_T
A useful shorthand is the alpha notation, where the alpha (α) express the fraction each carbonate species is of the C_T. These values are a function of pH only for a given set of acidity constants. Thus:

$$H_2CO_3 = \alpha_0 C_T$$
$$HCO_3^- = \alpha_1 C_T$$
$$CO_3^{2-} = \alpha_2 C_T$$

The derivations of the equations are as follows:

$$\alpha_0 = H_2CO_3 / C_T = H_2CO_3 / (H_2CO_3 + HCO_3 + CO_3)$$
$$= 1 / (1 + HCO_3/H_2CO_3 + CO_3/H_2CO_3)$$
$$= 1 / (1 + K_1/H + K_1K_2/H^2)$$
$$= H^2 / (H^2 + HK_1 + K_1K_2)$$

The values for α_1 and α_2 can be derived in a similar manner.

$$\alpha_1 = HCO_3^-/C_T = HK_1 / (H^2 + HK_1 + K_1K_2)$$
$$\alpha_2 = CO_3^{2-}/C_T = K_1K_2 / (H^2 + HK_1 + K_1K_2)$$

For example:
Assume pH = 8, $C_T = 10^{-3}$, $pK_1' = 6.0$ and $pK_2' = 9.0$
Using the above relations you can solve for the C system distribution.

$[H_2CO_3^*] = 10^{-5}$ mol kg^{-1} (note the answer is in concentration because we used K')
$[HCO_3^-] = 10^{-3}$ mol kg^{-1}
$[CO3^{2-}] = 10^{-4}$ mol kg^{-1}

Example 2: We know alkalinity and P_{CO2}. What is the pH?

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

For this problem neglect H and OH (a good assumption), then:

$$Alk = C_T\alpha_1 + 2C_T\alpha_2$$
$$= C_T(\alpha_1 + 2\alpha_2)$$

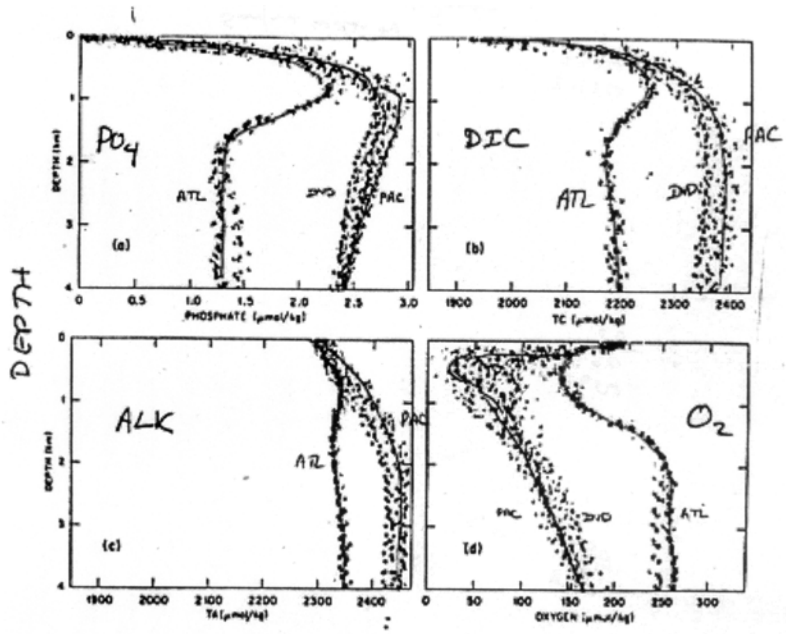
We can use this equation if we know 2 of the 3 variables (Alk, C_T or pH). Remember that α_1 and α_2 are expressed H, K1 and K2 only.

Similar equations can be derived for a system that is open to equilibration with the atmosphere. Now:

$$Alk = (K_H P_{CO2} / \alpha_0)(\alpha_1 + 2\alpha_2)$$
$$Alk = K_H P_{CO2} ((\alpha_1 + 2\alpha_2) / \alpha_0)$$
$$Alk = K_H P_{CO2} (HK_1 + 2K_1K_2 / H^2)$$

Ocean Carbonate System: Control

The ocean profiles of PO_4, dissolved inorganic carbon (DIC or ΣCO_2), alkalinity and oxygen in the Atlantic, Indian and Pacific Oceans are shown below.



The main features are:
1. Uniform surface values
2. Increase with depth
3. Deep ocean values increase from the Atlantic to the Pacific
4. DIC < Alk and ΔDIC > ΔAlk
5. Profile of pH is similar in shape to O_2.
6. Profile of P_{CO2} (not shown) mirrors O_2.

Note that CO_3^{2-} decreases from the Atlantic to the Pacific by a factor of four. Because CO_3^{2-} is lower in the Pacific we expect $CaCO_3$ to be more soluble and therefore less $CaCO_3$ will be preserved in the sediments. This is generally true.

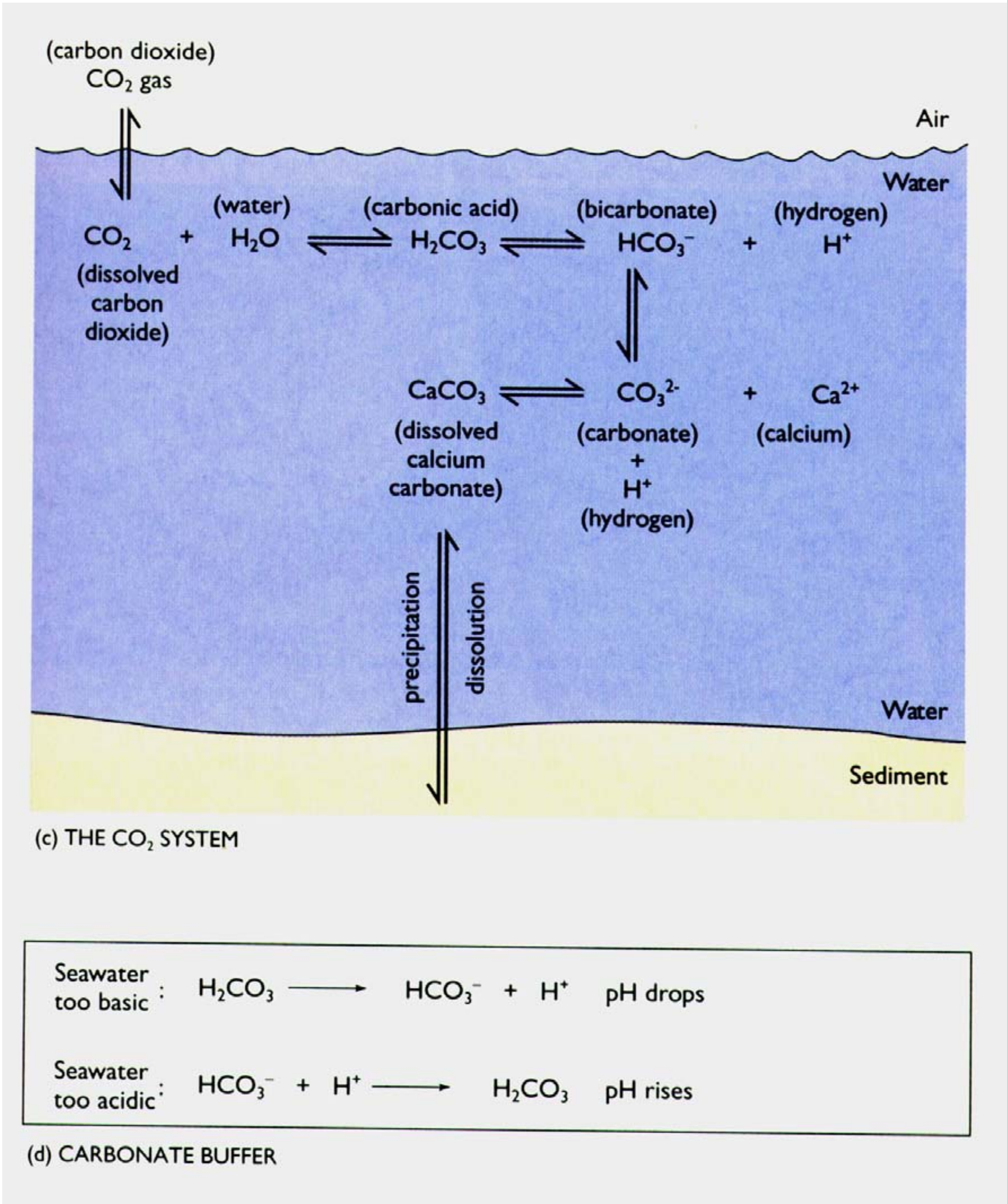
	Alk x 10^{-3}	ΣCO_2 x10^{-3}	CO_3^{2-} x 10^{-6}	pH (in situ)
Surface Waters	2.300	1.950	242	8.30
North Atlantic Deep Water	2.350	2.190	109	8.03
Antarctic Water	2.390	2.280	84	7.89
North Pacific Deep Water	2.420	2.370	57	7.71

What controls the pH of seawater? pH is controlled by alkalinity and DIC; therefore, on long time scales it is controlled by the weathering (sources) and burial (sinks) of silicate and carbonate rocks. Internal (short time scale) variations of pH in the ocean are controlled by internal variations in DIC and alkalinity that are controlled by photosynthesis, respiration and $CaCO_3$ dissolution and precipitation. pH can be calculated from Alk and DIC as shown below.

$$Alk \approx HCO_3^- + 2CO_3^{2-}$$
$$Alk \approx C_T\,\alpha_1 + 2C_T\,\alpha_2$$
$$Alk = C_T\,(H^+ K_1' + 2K_1' K_2') / (H^2 + HK_1' + K_1'K_2')$$

Rearranging, we can calculate pH from Alk and C_T.

$$(H^+) = \{-K_1'\,(Alk-C_T) + [(K_1')^2\,(Alk-C_T)^2 - 4Alk\,K_1'\,K_2'\,(Alk - C_T)]\,\}/\,2Alk$$



(c) THE CO_2 SYSTEM

(d) CARBONATE BUFFER

The Carbonate Chemistry in Seawater a Buffers System

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