Carbonate Equilibrium
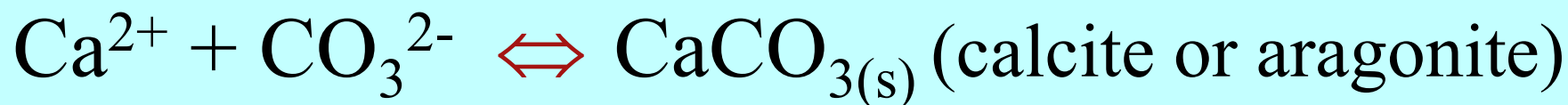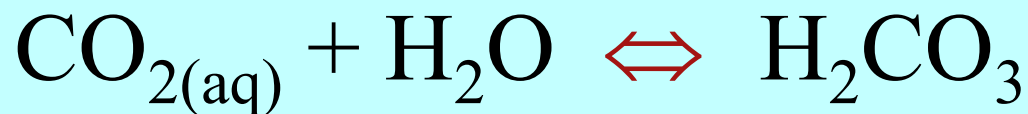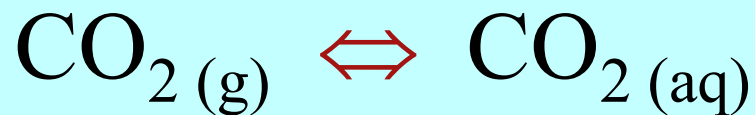# -Key Concepts-

- Major buffer system influencing pH (master variable)

- Linked to geological, biological and climatological cycles

- Complex chemistry involving gaseous, dissolved, and solid phases

- Cycle undergoing significant anthropogenic perturbation mostly from fossil fuel burning

- Oceanic Carbonate System controls atmospheric CO_2 on >1000 yr timescales (60 times more 'CO_2' in ocean)

Species of Importance

- $CO_{2(aq)}$
- H_2CO_3 (+ $CO_{2(aq)}$ = H_2CO_3* or 'CO_2')
- HCO_3^-
- CO_3^{2-}
- H^+
- OH^-

Carbonate Equilibrium Reactions

$$CO_{2\,(g)} \Leftrightarrow CO_{2\,(aq)}$$

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_3$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_{3(s)} \text{ (calcite or aragonite)}$$

CONCEPT OF pH

$H_2O \iff H^+ + OH^-$

$Kw = (aH^+aOH^-)/aH_2O = [H^+][OH^-] \gamma H^+ \gamma OH^-$

$Kw^* = [H^+][OH^-] = 10^{-14}$

pKw (pure water) $= 14.00$

$[H^+] = [OH^-] = 10^{-7}$

$pH = - \log [H+] = 7.0$ in pure water

$pOH = 14 - pH$

pKw (seawater) $= 13.19$ $\qquad [H^+]_{Total} = [H^+]_{Free} + [HF] + [HSO_4^-]$

85% of H+ is Free   34% of OH- is Free

$[Ba]_T = 10^{-2}$ M $\quad K' = 10^{-6}$ (p$K' = 6$)
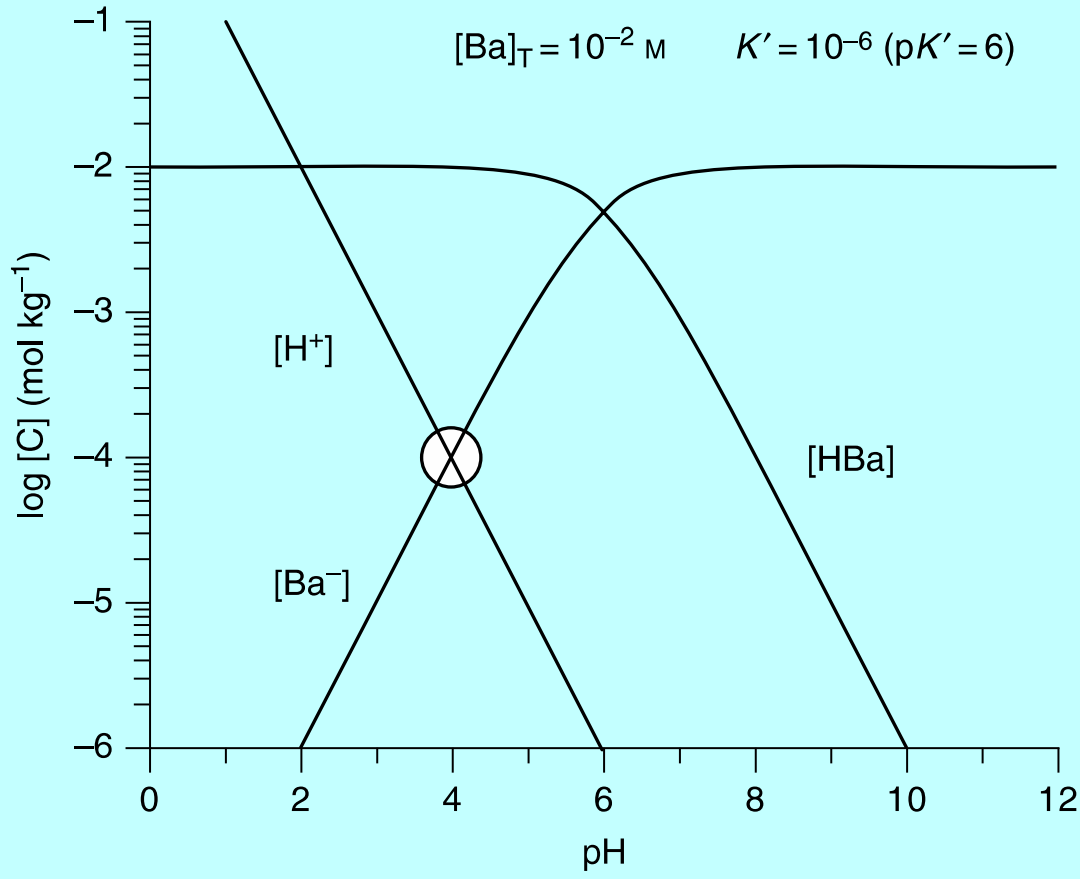
Figure 4.1. Concentrations of the acidic [HBa] and basic [Ba$^-$] forms of an acid with total concentration $[Ba]_T = 10^{-2}$ mol kg^{-1} and an equilibrium constant $K = 10^{-6}$, as a function of pH. The concentrations are equal at the point where pH = pK. When the criteria of charge balance is included in the equations, the system is defined at a single pH where $[H^+] = [Ba^-]$, indicated by the small circle.

Equilibrium Equations

$$K_0 \text{ (or } K_H) = [CO_2]/fCO_2 \sim [CO_2]/pCO_2$$

$$K_1 = [H^+] [HCO_3^-]/[CO_2]$$

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

$$K_{sp} = [Ca^{2+}] [CO_3^{2-}]$$

$$C_T = TCO_2 = \Sigma CO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

(for practical calculations K values are K's and a function of T,S, & P)

TABLE 7.4

Dissociation Constants for Carbonate Calculations in Seawater (S = 35)

Temp. (°C)	pK_0	pK_1	pK_2	pK_B	pK_W	pK_{cal}	pK_{arg}
0	1.202	6.101	9.376	8.906	14.30	6.37	6.16
5	1.283	6.046	9.277	8.837	14.06	6.36	6.16
10	1.358	5.993	9.182	8.771	13.83	6.36	6.17
15	1.426	5.943	9.090	8.708	13.62	6.36	6.17
20	1.489	5.894	9.001	8.647	13.41	6.36	6.18
25	1.547	5.847	8.915	8.588	13.21	6.37	6.19
30	1.599	5.802	8.833	8.530	13.02	6.37	6.20
35	1.647	5.758	8.752	8.473	12.84	6.38	6.21
40	1.689	5.716	8.675	8.416	12.67	6.38	6.23

Note; for calculations using these pK values, if data is inputed in units of atm and moles/kg, results are in moles/kg
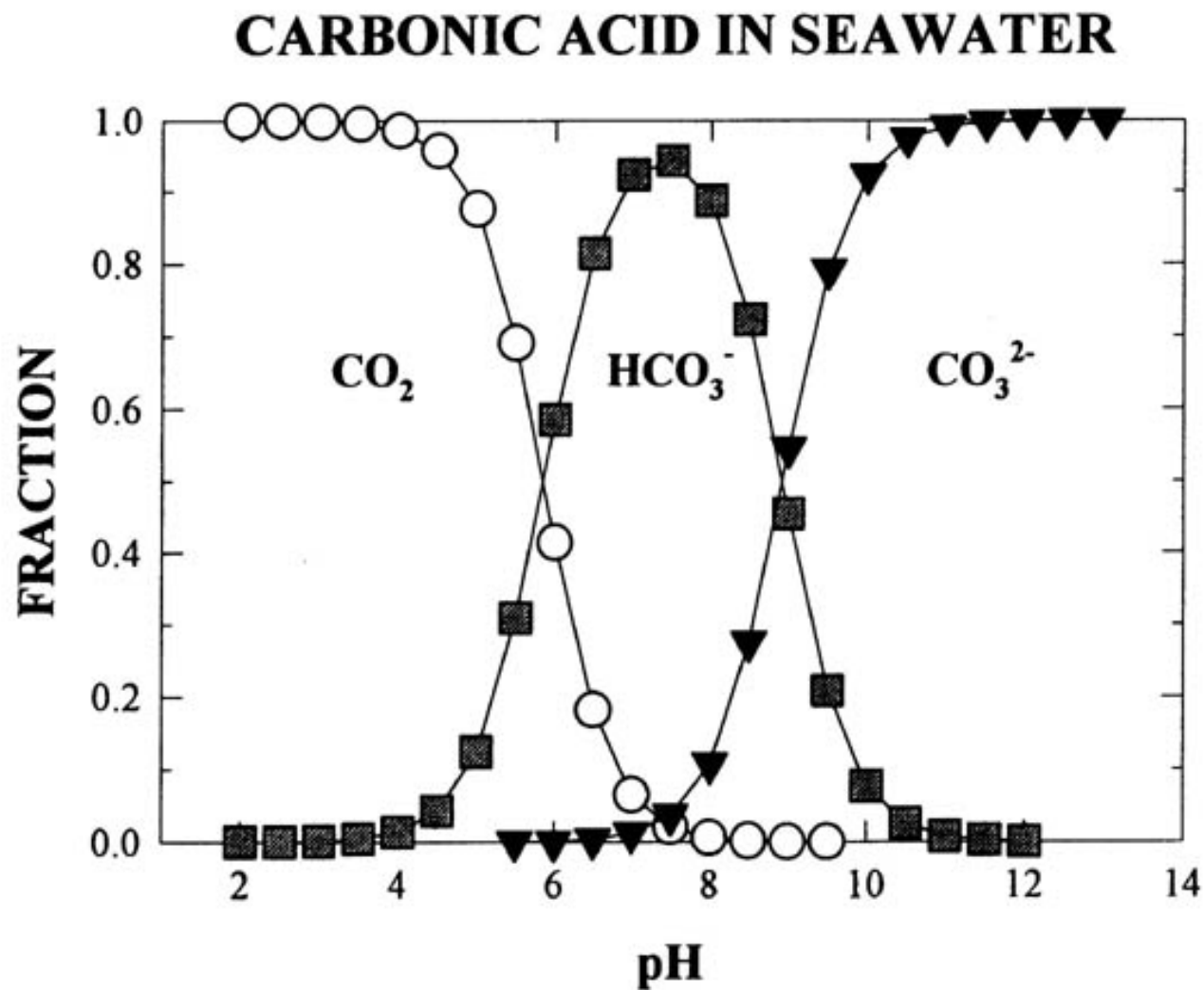
Ionization Fractions

(e.g. $[H_2CO_3^*] = C_T \, \alpha_{H2CO3*}$)

$$\alpha_{H2CO3*} = (1 + K_1/[H^+] + K_1K_2/[H^+]^2)^{-1}$$

$$\alpha_{HCO3} = (1 + [H^+]/K_1 + K_2/[H^+])^{-1}$$

$$\alpha_{CO3} = (1 + [H^+]/K_2 + [H^+]^2/K_1K_2)^{-1}$$

CARBONIC ACID IN SEAWATER

FIGURE 7.6. The fractions of carbonic acid as a function of pH.

Parameters of the CO_2 System in Seawater

- pH
- Total Alkalinity (A_T)
- TCO_2 (C_T, ΣCO_2)
- pCO_2

- Any two of above parameters can define carbonate speciation

METHODS OF ANALYSIS

pH	Potentiometry	$\pm$ 0.005
	Spectrophotometry	$\pm$ 0.002
A_T	Potentiometry	$\pm$ 2 μM
	Spectrophotometry	$\pm$ 2 μM
TCO2	Potentiometry	$\pm$ 3 μM
	Coulometry	$\pm$ 1 μM
pCO2	Gas Chromatography	$\pm$ 0.5 μAtm
	Infrared Spect.	$\pm$ 0.5 μAtm
	Batch Surface	$\pm$ 2 μAtm
	Batch Deep	$\pm$ 2 μAtm

What's Alkalinity?

Theoretical Definition: the excess of bases (proton acceptors) over acids (proton donors) in solution

 Practical Definition : Excess acid (eqivalents) needed to titrate solution to the carbonic acid endpoint

Alkalinity's Components

- Carbonate alkalinity (A_C)

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

- Carbonate & Borate alkalinity ($A_{C\&B}$)

  $$A_{C\&B} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$$

- Total alkalinity (A_T)

  $$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]$$
  $$- [H^+] + [SiO(OH)^{3-}] + [HPO_4^{2-}] + 2[PO_4^{3-}] +$$
  $$-[HSO_4^-] - [HF] - [H_3PO_4]$$

COMPONENTS OF TOTAL ALKALINITY

SPECIES	%	A_T
HCO_3^-	89.9	2067.7 µM
CO_3^{2-}	6.7	154.1
$B(OH)_4^-$	2.9	66.7
$SiO(OH)_3^-$	0.2	4.6
OH^-	0.2	4.6
HPO_4^{2-}	0.1	2.3
		2300.0 µM

ANOXIC WATERS

HS^- and NH_3 are Important

Table 4.1. Compounds that exchange protons in the pH range of seawater

Equilibrium constants are for 25 °C and $S = 35$ from the equations in Appendix 4.2 and Millero (1995) for nitrogen and sulfur species. An asterisk (*) indicates the concentration is in the $\mu mol\ kg^{-1}$ range and variable. ($pK = -\log K$.)

Species	Reaction	Concentration (mol kg^{-1})	$-\log C_T$	pK'
H_2O	$H_2O \rightleftharpoons OH^- + H^+$			13.2
DIC	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	$\approx 2.04 \times 10^{-3}$	2.69	5.85
	$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$			8.97
B	$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$	4.16×10^{-4}	3.38	8.60
Si	$H_4SiO_4 \rightleftharpoons H_3SiO_4^- + H^+$	*	*	9.38
P	$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	*	*	1.61
	$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	*	*	5.96
	$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	*	*	8.79
SO_4^{2-}	$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$	2.824×10^{-2}	1.55	1.00
F	$HF \rightleftharpoons F^- + H^+$	7.0×10^{-5}	4.15	2.52
Anoxic water				
N	$NH_4^+ \rightleftharpoons NH_3 + H^+$	*	*	9.19
HS	$H_2S \rightleftharpoons HS^- + H^+$	*	*	6.98

Table 4.2. Concentrations of cation and anion species that do not significantly exchange protons in the pH range of seawater (35‰)

Cation	eq kg^{-1}	Anion	eq kg^{-1}
Na^+	0.469 06	Cl^-	0.545 86
Mg^{2+}	0.105 64	SO_4^{2-}	0.056 48
Ca^{2+}	0.020 56	Br^-	0.000 84
K^+	0.010 21	F^-	0.000 07
Sr^{2+}	0.000 18		
Li^+	0.000 02		
Total cations	0.605 67	Total anions	0.603 25

Source: From the compilation in Table 1.4.
Σcations − Σanions = 0.605 67 − 0.603 25 = 0.002 42.

A_T = cation charge − anion charge = 0.605 67 − 0.603 25 (eq kg^{-1})
= 0.002 42 (eq kg^{-1}).

Carbonate Species at Fixed A_C & pH

$$[HCO_3^-] = A_C [H^+]/([H^+] + 2K_2)$$

$$[CO_3^{2-}] = A_C K_2/([H^+] + 2K_2)$$

$$[CO_2] = A_C [H^+]^2/([H^+]K_1 + 2K_1K_2)$$

$$pCO_2 = [CO_2]/K_0$$

$$C_T = TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

Carbonate Species at Fixed pH and C_T

$$CO_2 = C_T[H^+]^2 \ /[H^+]^2 + K_1[H^+] + K_1K_2$$

$$HCO_3^- = C_TK_1[H^+] \ /[H^+]^2 + K_1[H^+] + K_1K_2$$

$$CO_3^{2-} = C_TK_1K_2 \ /[H^+]^2 + K_1[H^+] + K_1K_2$$

$$pCO_2 = [CO_2]/K_0$$

$$C_T = TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

Carbonate Species at Fixed pCO$_2$ & pH

$$[CO_2] = K_0 \, pCO_2$$

$$[HCO_3^-] = K_1 \, K_0 \, pCO_2/[H^+]$$

$$[CO_3^{2-}] = K_1 K_2 K_0 pCO_2/[H^+]^2$$

Table 4.4. | Carbonate system parameters calculated for different conditions in the surface and deep oceans at 35‰ salinity using two different methods

Column (I)[a] is the calculation utilizing all species in the total alkalinity, A_T. A_{Si} and A_P (bottom row) are the alkalinities due to silicate and phosphate species. Column (II)[b] is the calculation assuming the total alkalinity does not include Si and P species, $A_T = A_{C\&B}$. Concentrations and DIC are in units of $\mu mol\ kg^{-1}$ and alkalinity values, A_T, are in $\mu eq\ kg^{-1}$.

Parameter	Surface Water		North Atlantic Deep Water		Antarctic Deep Water		North Pacific Deep Water	
Measured concentrations								
Z (km)	0.0		4.0		4.0		4.0	
T (°C)	20.0		2.0		2.0		2.0	
A_T	2300		2350		2390		2460	
DIC	1950		2190		2280		2370	
[Si]	0.0		60		130		160	
[P]	0.0		1.5		2.2		2.5	
Calculated carbonate parameters (Models I and II)								
	I	II	I	II	I	II	I	II
pH	8.19	8.20	7.95	8.11	7.80	7.98	7.74	7.92
f_{CO_2} (μatm)	256	255	316	333	462	478	562	575
$[HCO_3^-]$	1698	1698	2064	2052	2171	2161	2264	2254
$[CO_3^{2-}]$	244	244	108	118	82	91	73	83
$[CO_2]$	8	8	18	19	27	28	33	33
$[B(OH)_4]$	108	108	67	60	50	46	44	40
A_{Si}	0.0	0.0	1.3	0.0	2.0	0.0	2.1	0.0
A_P	0.0	0.0	1.6	0.0	2.3	0.0	2.5	0.0

[a] Calculated by using the program of Lewis and Wallace (1998) with the K_1 and K_2 of Mehrbach et al. (1973) as reinterpreted by Dickson and Millero (1987).
[b] Calculated by using the program in Appendix 4.1, with the K_1 and K_2 of Mehrbach et al. (1973) as refitted by Luecker et al. (2000).

CHANGES IN CO_2 IN OCEAN WATERS

REMOVAL

1.) Photosynthesis $CO_2 \rightarrow CH_2O$

2.) Formation of $CaCO_3$ $CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3$

3.) Solar Heating $CO_2(aq) \rightarrow CO_2(g)$

ADDITION

1.) Oxidation of Organic C

2.) Dissolution of $CaCO_3$

3.) Surface Cooling and Adsorption of Atmospheric CO_2

4.) Via #3, dissolution of CO_2 from Atm from Fossil Fuel Burning

TABLE 7.6
Changes in the CO_2 System Due to the Oxidation of Plant Material

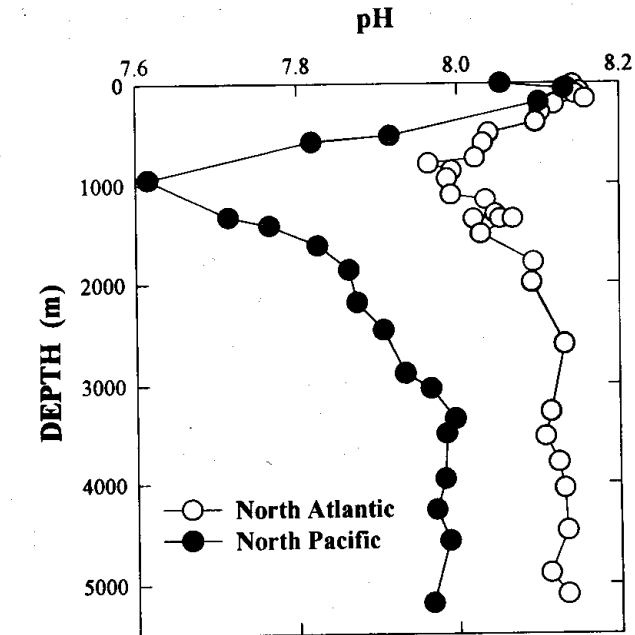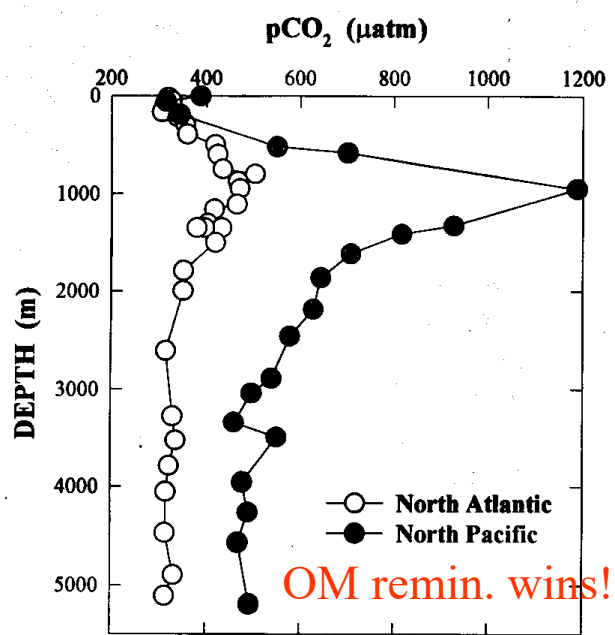|	Initial[a]	ΔAOU (mM)		% Change
		0.13	0.26	
ΔCO_2	0	0.10	0.20	—
TCO_2	2.200	2.300	2.400	9.1 ± 0.1
CA	2.487	2.487	2.487	0
pCO_2	350	610	1160	231 ± 1.0
pH	8.200	8.001	7.753	-5.5 ± 0.04
$[CO_2]$	0.012	0.021	0.040	233
$[HCO_3^-]$	1.889	2.072	2.234	18
$[CO_3^{2-}]$	0.299	0.208	0.126	-58

[a] All the concentrations are mM.

TABLE 7.7
Changes in the CO_2 System Due to the Dissolution of $CaCO_3$

	Initial[a]	$\Delta CaCO_3$ (mM)		% Change
		0.05	0.10	
ΔCO_2	0	0.05	0.10	—
TCO_2	2.200	2.250	2.300	4.5 ± 0.1
CA	2.487	2.587	2.687	72 ± 0.05
pCO_2	350	310	290	-17 ± 1.0
pH	8.200	8.264	8.321	1.5 ± 0.04
$[CO_2]$	0.012	0.011	0.010	-17
$[HCO_3^-]$	1.889	1.892	1.844	0.3
$[CO_3^{2-}]$	0.299	0.348	0.397	33

[a] All the concentrations are mM.

TCO$_2$ (µM)

NTA (µM)

DEPTH (m)

North Atlantic

North Pacific

CA =[HCO$_3^-$]+ **2**[CO$_3^=$]

North Atlantic

North Pacific

OM remin. + CaCO3 diss.

CaCO3 dissolution only!

pCO$_2$ (µatm)

pH

DEPTH (m)

○ North Atlantic
● North Pacific

○ North Atlantic
● North Pacific

OM remin. wins!
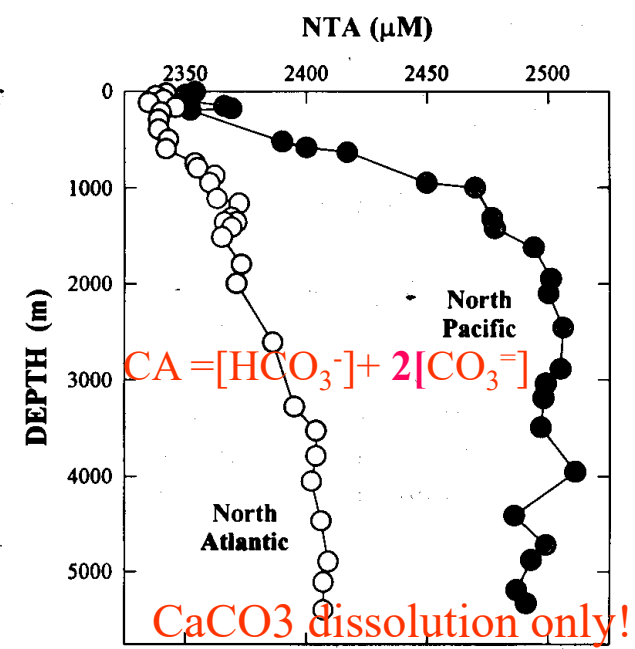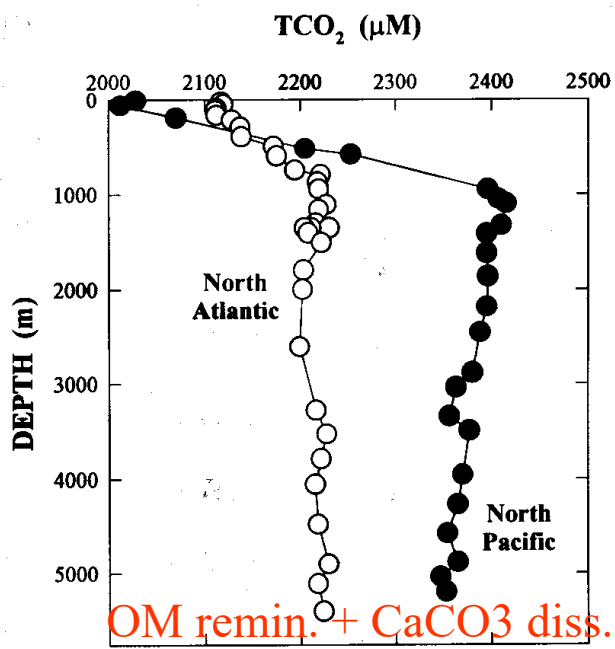
Plate 2 Salinity-normalized ($S = 35$) total alkalinity, $A_{T,N}$, versus salinity-normalized dissolved inorganic carbon, DIC_N, for the world's ocean. Data are for the deep ocean at depths >2.5 km except for the section labeled "North Atlantic Shallow", which is 100–1000 m in the North Atlantic Ocean. Lines indicate different $DIC_N : A_{T,N}$ ratios.
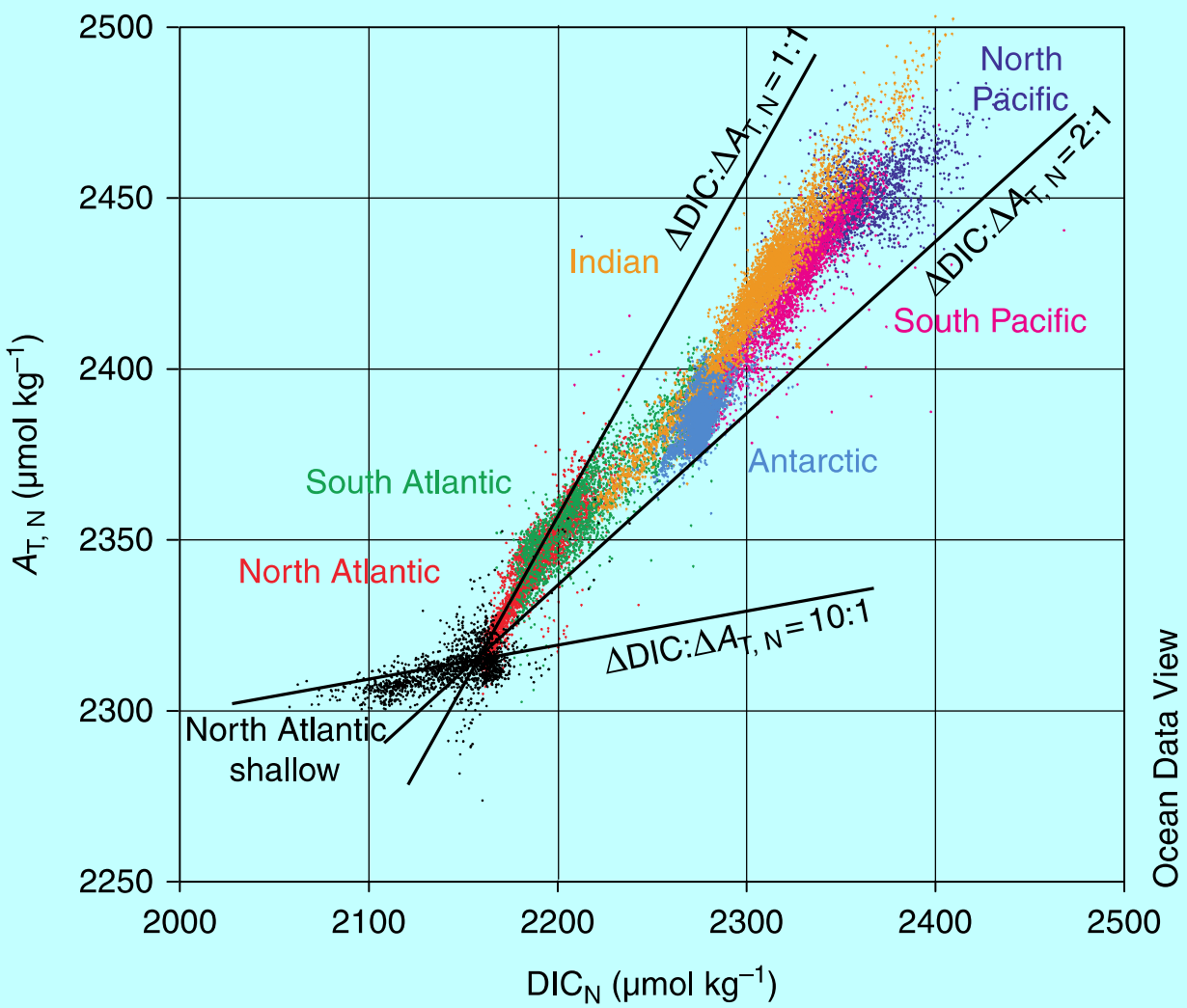
Mean annual air–sea flux for 1995