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

Carbonate Equilibrium Equations

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

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

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

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

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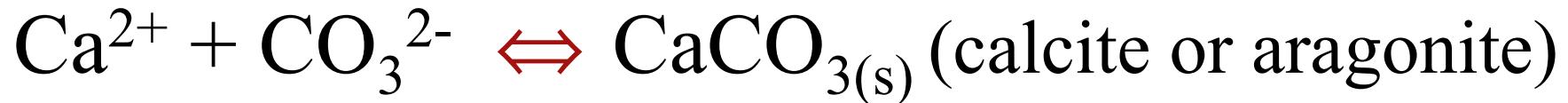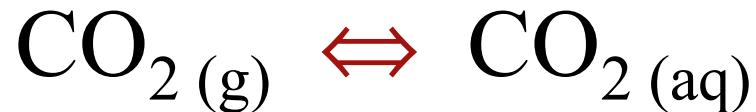
CONCEPT OF pH

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

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

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

pK_W (pure water) $= 14.00$

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

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

$pOH = 14 - pH$

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

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

Equilibrium Constants

$$K_0 \text{ (or } K_H) = [H_2CO_3*]/pCO_2$$

$$K_1 = [H^+][HCO_3^-]/[H_2CO_3^*]$$

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

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

$$C_T = TCO_2 = \Sigma CO_2 = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

(for practical calculations K's 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

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

$$(CO_2^* \text{ in Millero})$$

$$[CO_2]_{(aq)} + [H_2O] \longleftrightarrow [H_2CO_3] \qquad \text{(slow)}$$
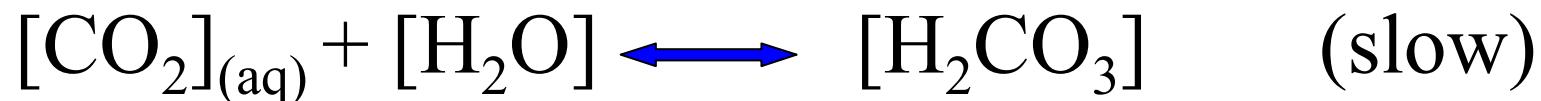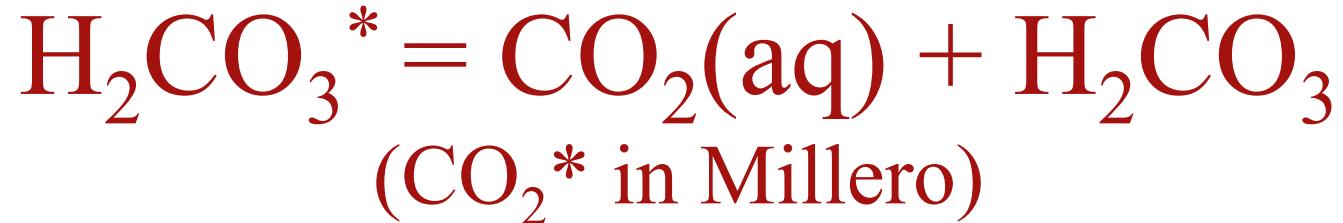
$$K = [H_2CO_3]/[CO_2]_{(aq)} [H_2O] \qquad = 10^{-2.7}$$

$$[H_2CO_3] \longleftrightarrow [H^+] + [HCO_3^-] \qquad \text{(fast)}$$

$$K_{(H2CO3)} = [H^+] [HCO_3^-]/[H_2CO_3] \qquad = 10^{-3.6}$$

$H_2CO_3^*$ (cont.)

$$[CO_2]_{(aq)} + [H_2O] \overset{K}{\longleftrightarrow} [H_2CO_3] \overset{K_{H2CO3}}{\longleftrightarrow} [H^+] + [HCO_3^-]$$

$$H_2CO_3 + CO_{2(aq)} = H_2CO_3^*$$
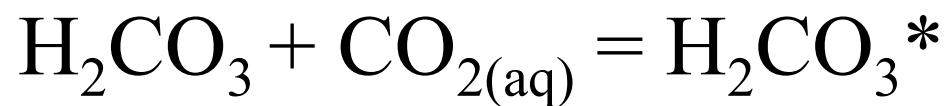
$$K_1 = K\, K_{H2CO3} = 10^{-6.3}$$

$$K_1 = [H^+]\,[HCO_3^-]/[H_2CO_3^*]$$

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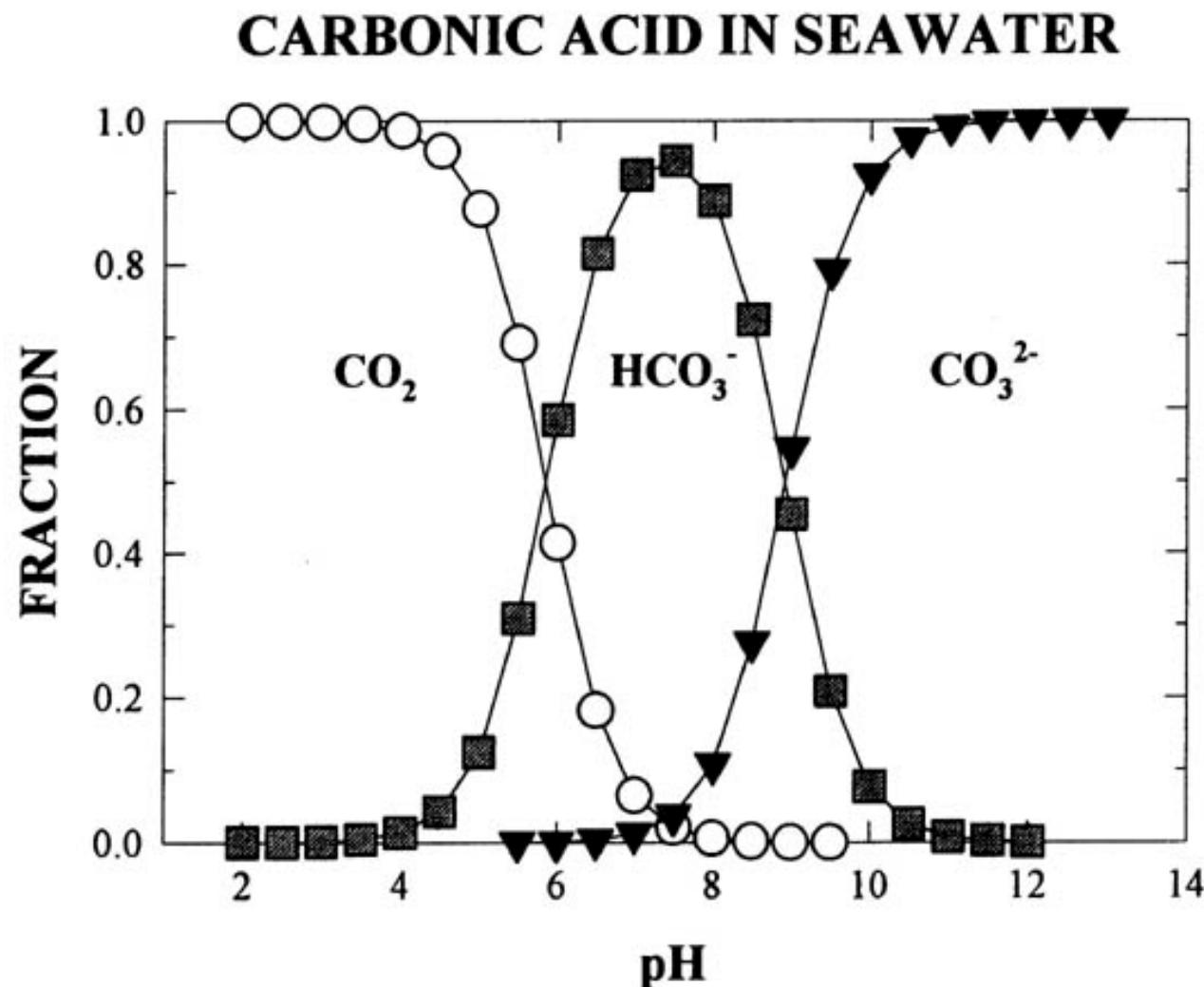
FIGURE 7.6. The fractions of carbonic acid as a function of pH.

Parameters of the CO_2 System in Seawater

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

- Any two of above parameters can define carbonate speciation

METHODS OF ANALYSIS

pH	Potentiometry	± 0.005
	Spectrophotometry	± 0.002
TA	Potentiometry	± 2 µM
	Spectrophotometry	± 2 µM
TCO_2	Potentiometry	± 3 µM
	Coulometry	± 1 µM
pCO_2	Gas Chromatography	± 0.5 µAtm
	Infrared Spect.	± 0.5 µAtm
	Batch Surface	± 2 µAtm
	Batch Deep	± 2 µAtm

MEASURABLE PARAMETERS

Parameter	Precision	Accuracy
pH	± 0.0004	± 0.002
TA	± 1 μM	± 2 μM
TCO_2	± 1 μM	± 2 μM
pCO_2	± 0.5 μAtm	± 1 μAtm

What's Alkalinity?

- Carbonate alkalinity (CA, A_c)

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

- Total alkalinity

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]$$
$$- [H^+] + [SiO(OH)_3^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] +$$
$$[Organics]$$

Total Alkalinity

Definition 1: The sum of the anions of weak acids as determined by titration by HCl to the carbonic acid endpoint

Definition 2: the excess positive charge from the cations of strong bases

COMPONENTS OF TOTAL ALKALINITY

SPECIES	%	TA
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

Carbonate Species at Fixed CA & pH

$$[HCO_3^-] = CA\,[H^+]/([H^+] + 2K_2)$$

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

$$[H_2CO_3*] = CA[H^+]^2/([H^+]K_1 + 2K_1K_2)$$

$$pCO_2 = [H_2CO_3*]/K_0$$

$$C_T = TCO_2 = [H_2CO_3] + [HCO_3^-]+[CO_3^{2-}]$$

Carbonate Species at Fixed pH and C_T

$$H_2CO_3{}^* = C_T[H^+]^2 \quad /[H^+]^2 + K_1[H^+] + K_1K_2$$

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

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

$$pCO_2 = [H_2CO_3{}^*]/K_0$$

$$C_T = TCO_2 = [H_2CO_3] + [HCO_3{}^-] + [CO_3{}^{2-}]$$

Carbonate Species at Fixed pCO$_2$ & pH
(K$_H$ = K$_0$ in Millero)

$$[H_2CO_3{}^*] = K_0 \, pCO_2$$

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

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

(a)

(b)
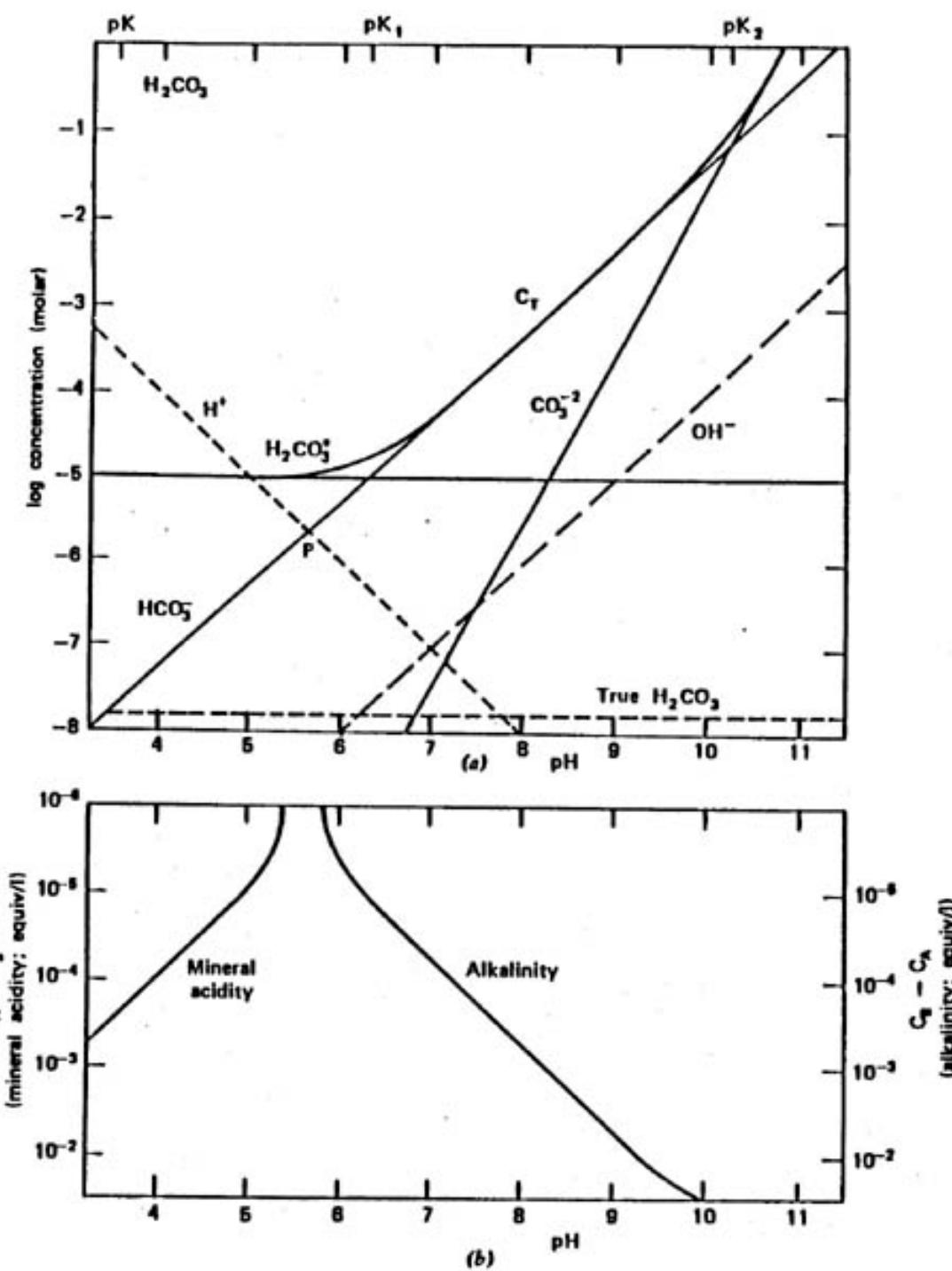
CHANGES IN CO_2 IN OCEAN WATERS

REMOVAL

1.) Photosynthesis $CO_2 \rightarrow CHO_2$

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.) 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

		ΔAOU (mM)		
	Initial[a]	0.13	0.26	% Change
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 $CaCO_3$

		$\Delta CaCO_3$ (mM)		
	Initial[a]	0.05	0.10	% Change
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.
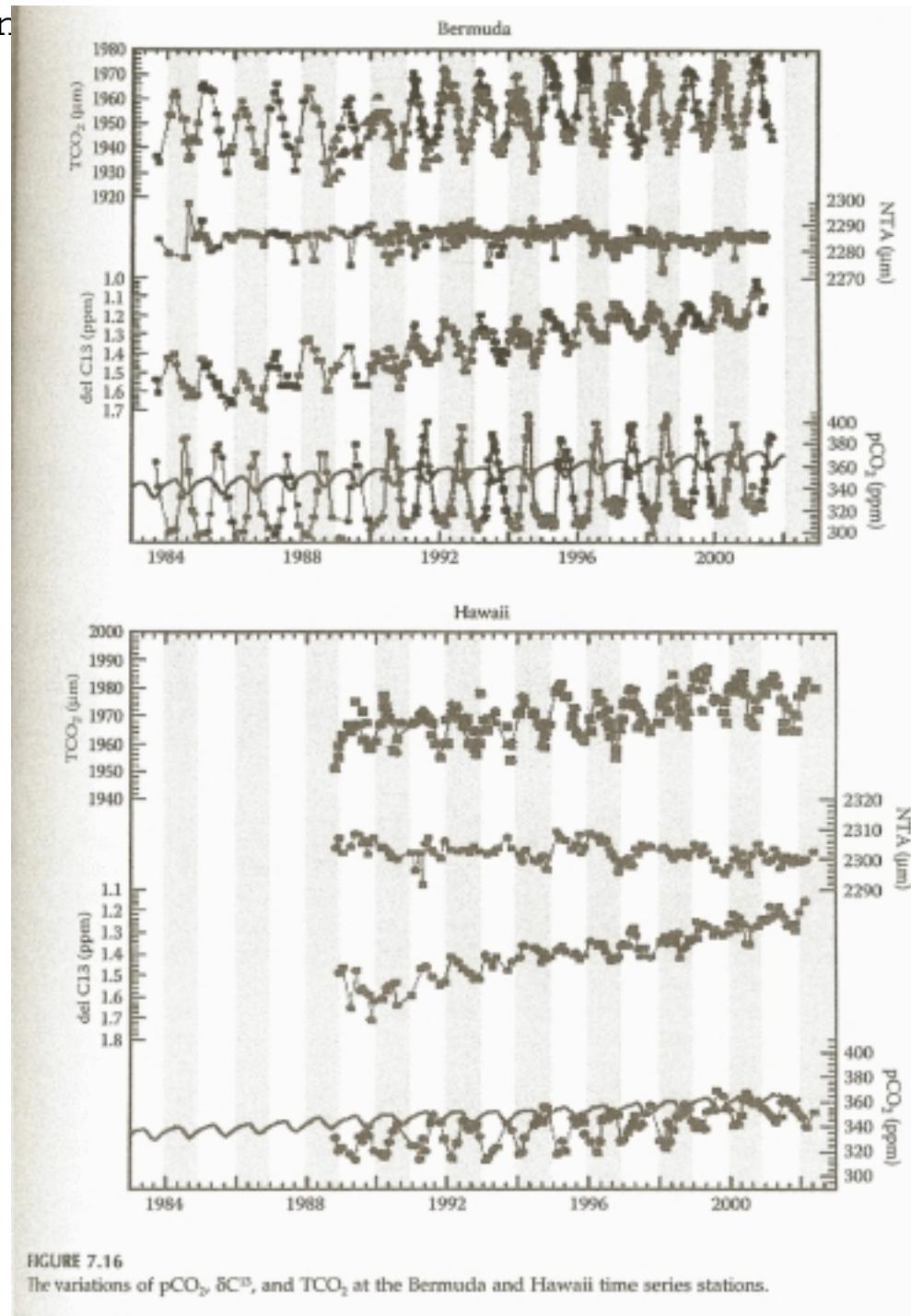
FIGURE 7.16
The variations of pCO_2, δC^{13}, and TCO_2 at the Bermuda and Hawaii time series stations.

TCO$_2$ (μM)

North Atlantic

North Pacific

OM remin. + CaCO3 diss.

NTA (μM)

North Pacific

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

North Atlantic

CaCO3 dissolution only!

pCO$_2$ (μatm)

○ North Atlantic
● North Pacific

OM remin. wins!

pH

○ North Atlantic
● North Pacific
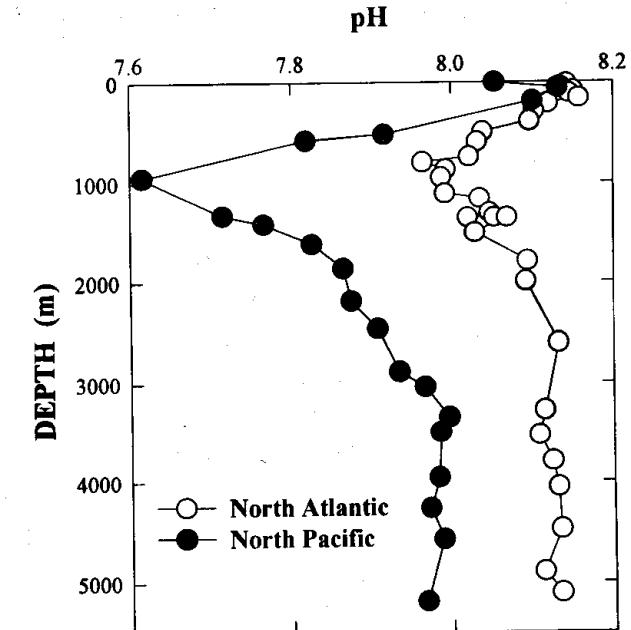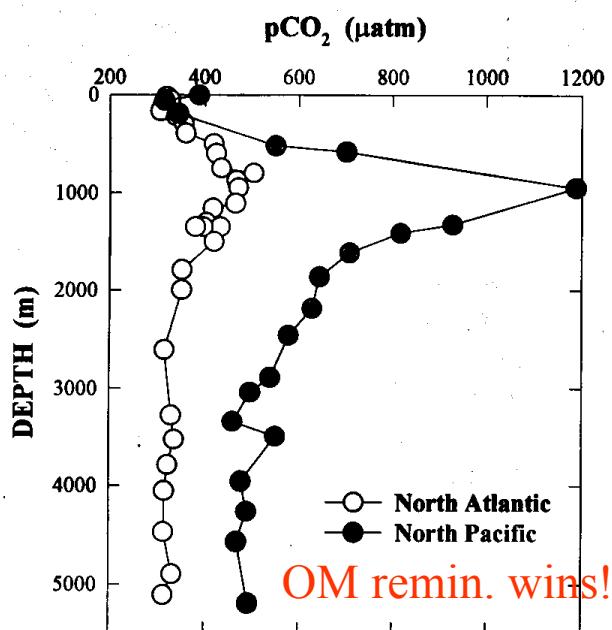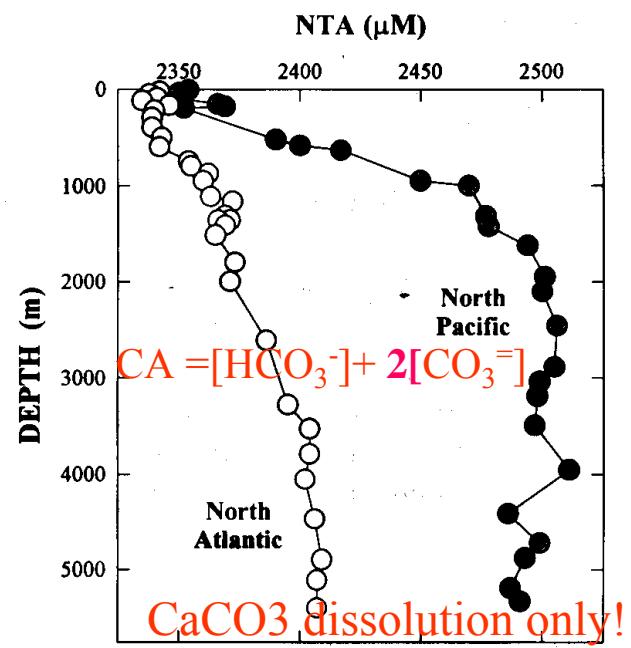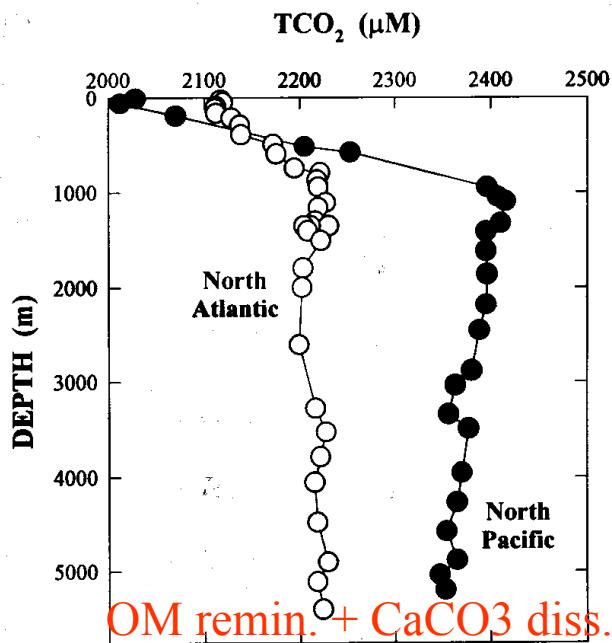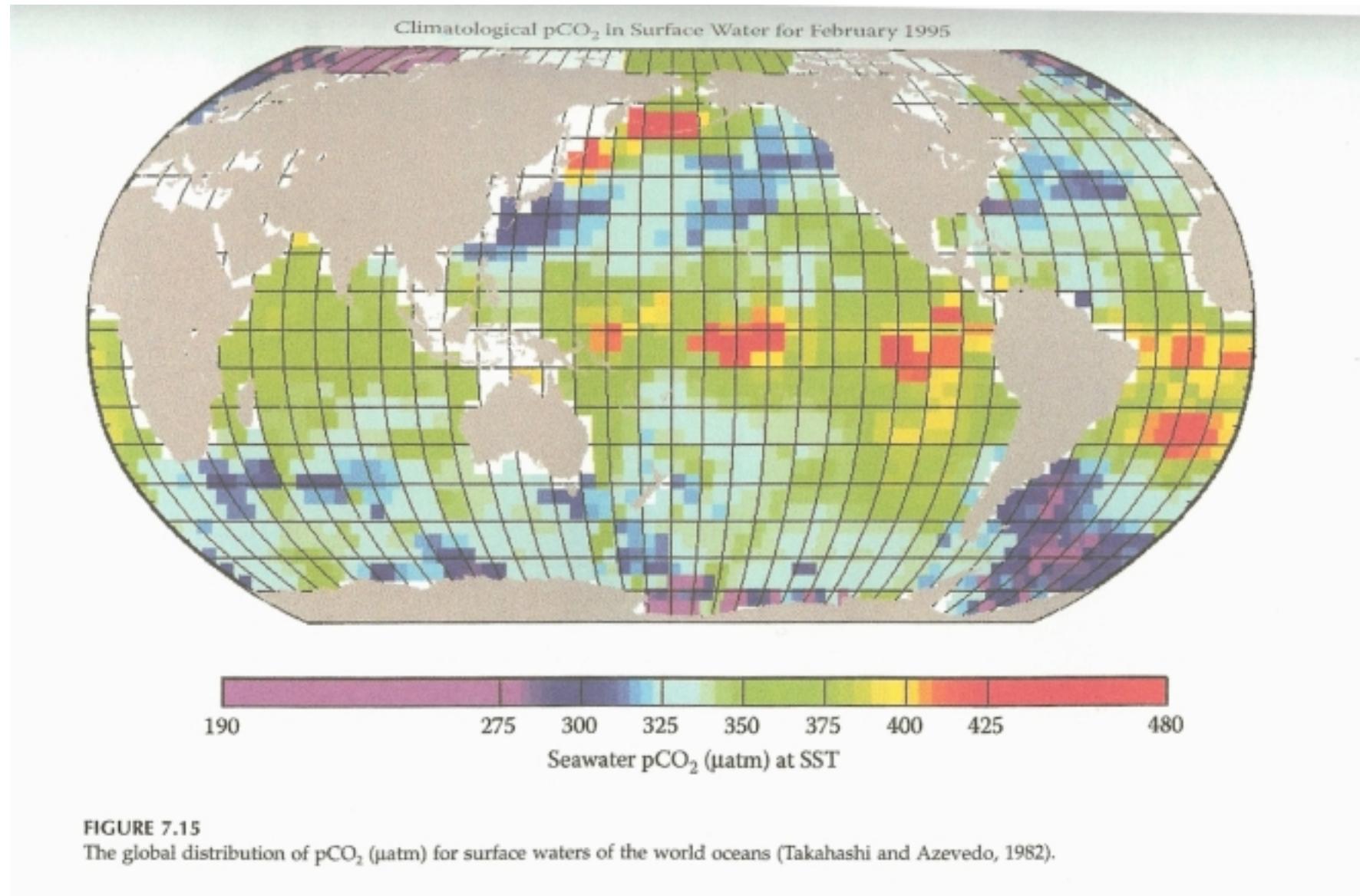
FIGURE 7.15
The global distribution of pCO_2 (µatm) for surface waters of the world oceans (Takahashi and Azevedo, 1982).