

Carbonate Equilibrium

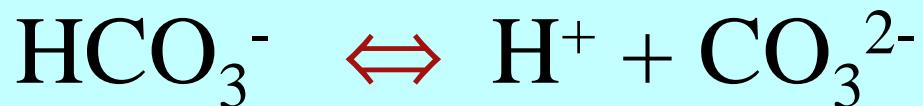
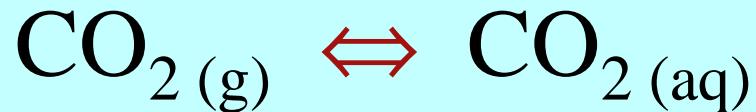
-Key Concepts-

- 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 CO₂ on >1000 yr timescales (60 times more 'CO₂' in ocean)

Species of Importance

- $\text{CO}_{2(\text{aq})}$
- H_2CO_3 (+ $\text{CO}_{2(\text{aq})}$) = H_2CO_3^* or ‘ CO_2 ’)
- HCO_3^-
- CO_3^{2-}
- H^+
- OH^-

Carbonate Equilibrium Equations



CONCEPT OF pH



$$K_w = (a\text{H}^+ a\text{OH}^-)/a\text{H}_2\text{O} = [\text{H}^+][\text{OH}^-] \gamma_{\text{H}^+} \gamma_{\text{OH}^-}$$

$$K_w' = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$pK_w (\text{pure water}) = 14.00$$

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

$$\text{pH} = -\log [\text{H}^+] = 7.0 \text{ in pure water}$$

$$p\text{OH} = 14 - \text{pH}$$

$$pK_w (\text{seawater}) = 13.19 \quad [\text{H}^+]_{\text{Total}} = [\text{H}^+]_{\text{Free}} + [\text{HF}] + [\text{HSO}_4^-]$$

85% of H₊ is Free 34% of OH⁻ is Free

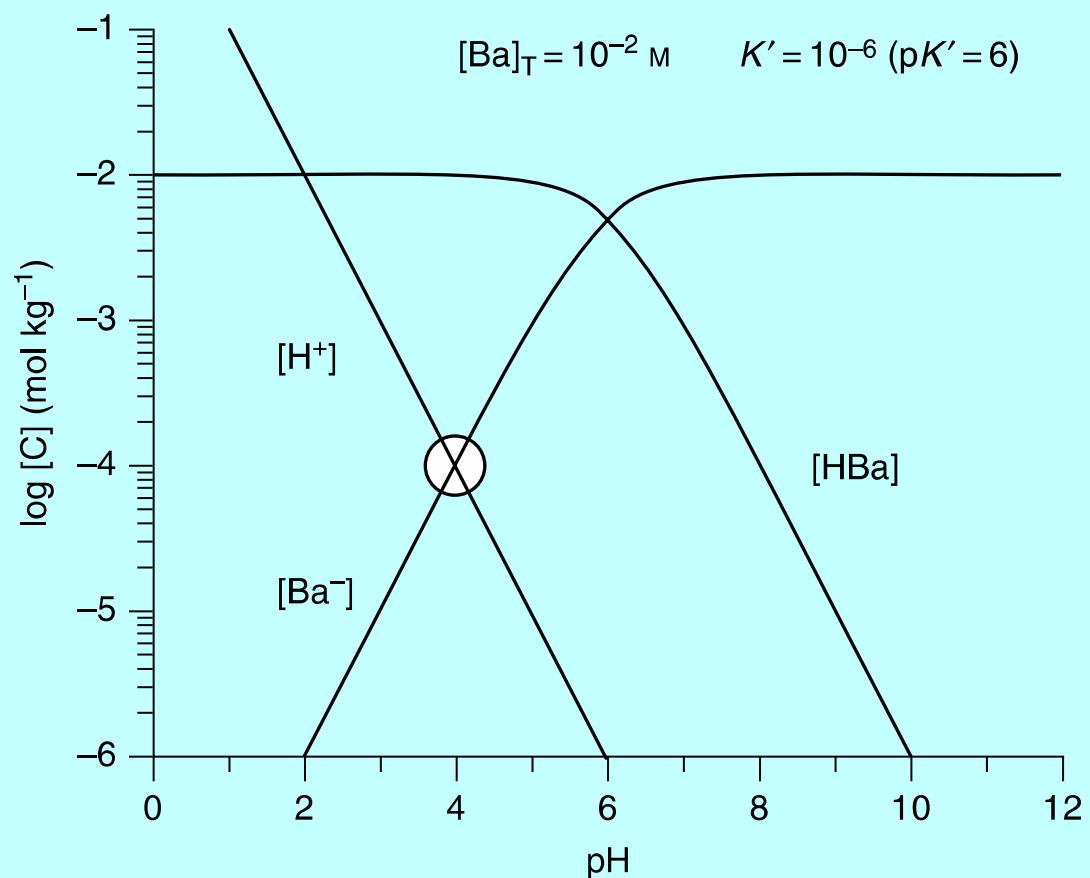


Figure 4.1. Concentrations of the acidic $[\text{HBA}]$ and basic $[\text{Ba}^-]$ forms of an acid with total concentration $[\text{Ba}]_T = 10^{-2} \text{ mol kg}^{-1}$ and an equilibrium constant $K = 10^{-6}$, as a function of pH. The concentrations are equal at the point where $\text{pH} = \text{p}K$.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

Equilibrium Constants

$$K_0 \text{ (or } K_H) = [\text{CO}_2]/f\text{CO}_2 \sim [\text{CO}_2]/p\text{CO}_2$$

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

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

$$K_{\text{sp}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

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

(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

Ionization Fractions

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

$$\alpha_{H_2CO_3^*} = (1 + K_1/[H^+] + K_1K_2/[H^+]^2)^{-1}$$

$$\alpha_{HCO_3^-} = (1 + [H^+]/K_1 + K_2/[H^+])^{-1}$$

$$\alpha_{CO_3^{2-}} = (1 + [H^+]/K_2 + [H^+]^2/K_1K_2)^{-1}$$

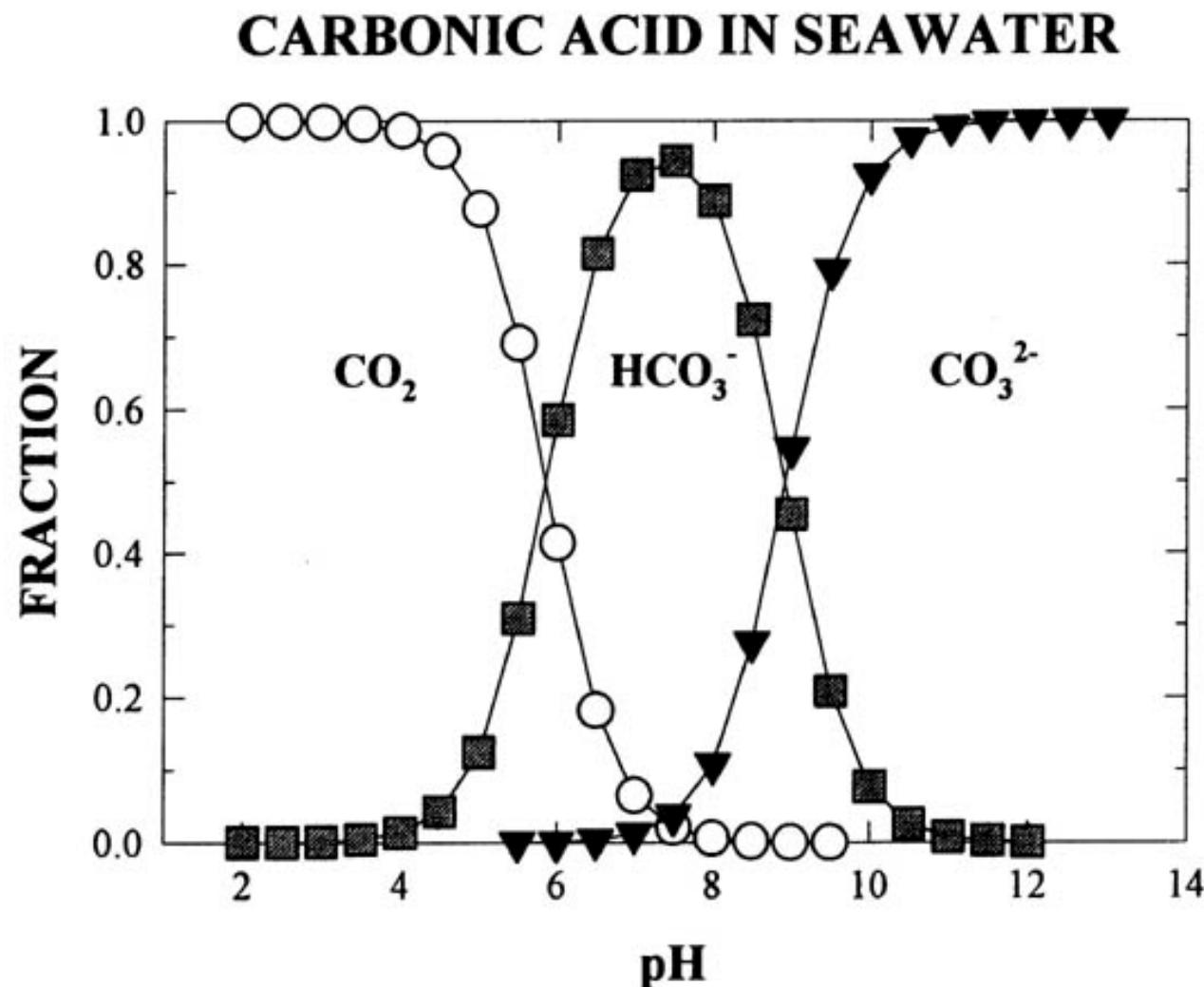


FIGURE 7.6. The fractions of carbonic acid as a function of pH.

Parameters of the CO₂ System in Seawater

- pH
- Total Alkalinity (A_T)
- TCO₂ (C_T , ΣCO_2)
- pCO₂
- Any two of above parameters can define carbonate speciation

METHODS OF ANALYSIS

pH	Potentiometry	± 0.005
	Spectrophotometry	± 0.002
A_T	Potentiometry	$\pm 2 \mu M$
	Spectrophotometry	$\pm 2 \mu M$
TCO ₂	Potentiometry	$\pm 3 \mu M$
	Coulometry	$\pm 1 \mu M$
pCO ₂	Gas Chromatography	$\pm 0.5 \mu Atm$
	Infrared Spect.	$\pm 0.5 \mu Atm$
	Batch Surface	$\pm 2 \mu Atm$
	Batch Deep	$\pm 2 \mu Atm$

What's Alkalinity?

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

Practical Definition : Excess acid (eq) 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	<u>2.3</u>
		2300.0 μM

ANOXIC WATERS

HS⁻ and NH₃ are Important

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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 $\mu\text{mol kg}^{-1}$ range and variable. ($\text{pK}' = -\log K'$)

Species	Reaction	Concentration		pK'
		(mol kg^{-1})	$-\log C_T$	
H_2O	$\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$			13.2
DIC	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$\approx 2.04 \times 10^{-3}$	2.69	5.85
	$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$			8.97
B	$\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{B}(\text{OH})_4^- + \text{H}^+$	4.16×10^{-4}	3.38	8.60
Si	$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+$	*	*	9.38
	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$	*	*	1.61
P	$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+$	*	*	5.96
	$\text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-} + \text{H}^+$	*	*	8.79
SO_4^{2-}	$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$	2.824×10^{-2}	1.55	1.00
F	$\text{HF} \rightleftharpoons \text{F}^- + \text{H}^+$	7.0×10^{-5}	4.15	2.52
Anoxic water				
N	$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$	*	*	9.19
HS ^{??}	$\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$	*	*	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.

$$\Sigma \text{cations} - \Sigma \text{anions} = 0.605\ 67 - 0.603\ 25 = 0.002\ 42.$$

$$\begin{aligned}
 A_T &= \text{cation charge} - \text{anion charge} = 0.605\ 67 - 0.603\ 25 \text{ (eq kg}^{-1}) \\
 &= 0.002\ 42 \text{ (eq kg}^{-1}\text{).}
 \end{aligned}$$

Carbonate Species at Fixed A_C & pH

$$[\text{HCO}_3^-] = A_C [\text{H}^+]/([\text{H}^+] + 2K_2)$$

$$[\text{CO}_3^{2-}] = A_C K_2/([\text{H}^+] + 2K_2)$$

$$[\text{CO}_2] = A_C [\text{H}^+]^2/([\text{H}^+]K_1 + 2K_1K_2)$$

$$\text{pCO}_2 = [\text{CO}_2]/K_0$$

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

Carbonate Species at Fixed pH and C_T

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

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

$$CO_3^{2-} = C_T K_1 K_2 / [H^+]^2 + K_1[H^+] + K_1K_2$$

$$pCO_2 = [CO_2]/K_0$$

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

Carbonate Species at Fixed pCO₂ & pH

$$[\text{CO}_2] = K_0 \text{ pCO}_2$$

$$[\text{HCO}_3^-] = K_1 K_0 \text{ pCO}_2 / [\text{H}^+]$$

$$[\text{CO}_3^{2-}] = K_1 K_2 K_0 \text{ pCO}_2 / [\text{H}^+]^2$$

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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 $\mu\text{mol kg}^{-1}$ and alkalinity values, A_T , are in $\mu\text{eq kg}^{-1}$.

Parameter	Surface Water	North Atlantic Deep Water		Antarctic Deep Water		North Pacific Deep Water		
<i>Measured concentrations</i>								
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	
<i>Calculated carbonate parameters (Models I and II)</i>								
	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

^aCalculated 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).

^bCalculated 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 CO₂ IN OCEAN WATERS

REMOVAL

- 1.) Photosynthesis CO₂ → CHO₂
- 2.) Formation of CaCO₃ CO₃²⁻ + Ca²⁺ → CaCO₃
- 3.) Solar Heating CO₂(aq) → CO₂(g)

ADDITION

- 1.) Oxidation of Organic C
- 2.) Dissolution of CaCO₃
- 3.) Dissolution of CO₂ from Atm from Fossil Fuel Burning

TABLE 7.6
Changes in the CO₂ 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

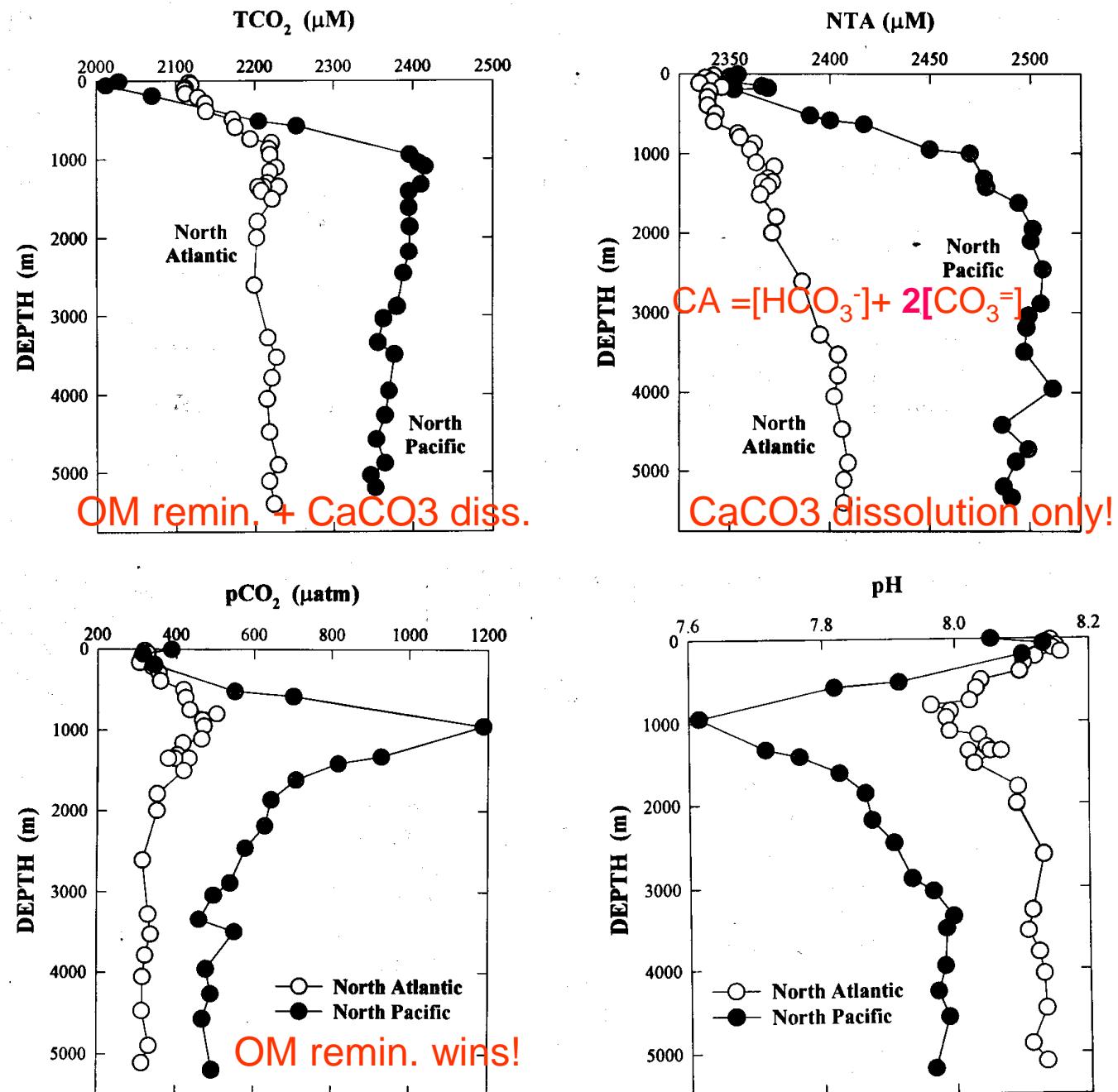
^a All the concentrations are mM.

TABLE 7.7
Changes in the CO₂ System Due to the
Dissolution of CaCO₃

	Initial^a	ΔCaCO₃ (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.

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Carbonate System 1 #

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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.

