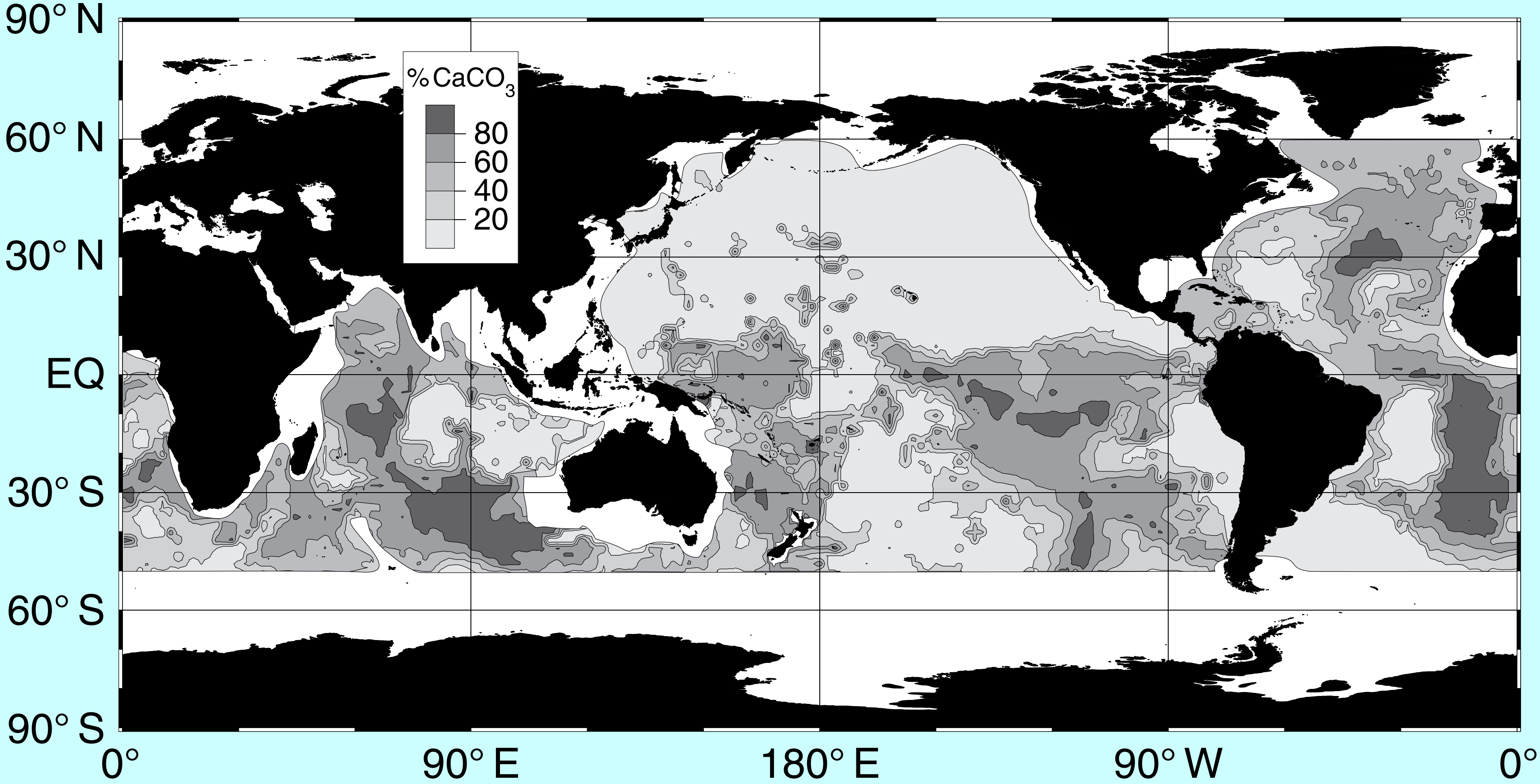
$CaCO_3$ Distribution in Sediments



$CaCO_3$ production almost all biogenic in the ocean

FIGURE 15.1. Calcareous remains found in deep-sea sediments: *(a)* forams, *(b)* coccoliths, *(c)* pteropod pens. *Source:* From *The Sea,* vol. 3, W. R. Reidel (ed.: M. N. Hill), copyright © 1963 by John Wiley & Sons, Inc., New York, pp. 869, 872–873. Reprinted by permission.

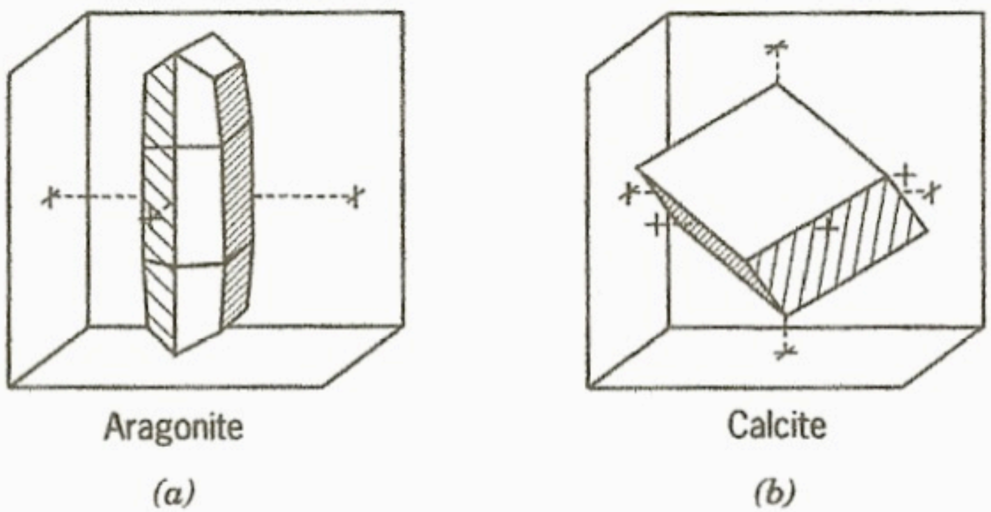


FIGURE 15.2. Crystalline forms of *(a)* aragonite and *(b)* calcite. *Source:* From *Marine Chemistry*, R. A. Horne, copyright © 1969 by John Wiley & Sons, Inc., New York, p. 214. Reprinted by permission. After *Mineralogy*, 2nd ed., L. G. Berry, B. Mason, and R. V. Dietrich, copyright © 1983 by W. H. Freeman and Co., New York, pp. 330, 340. Reprinted by permission.

Carbonate Equilibrium Equations

$$CO_{2\,(g)} + H_2O \overset{K_0}{\Leftrightarrow} H_2CO_3^*$$

$$H_2CO_3^* \overset{K_1}{\Leftrightarrow} H^+ + HCO_3^-$$

$$HCO_3^- \overset{K_2}{\Leftrightarrow} H^+ + CO_3^{2-}$$

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

$CaCO_3$ Saturation State - Ω

$\Omega = [Ca^{2+}]\,[CO_3^{2-}]/K_{sp}'$

Ω > 1, supersaturated   Ω < undersaturated

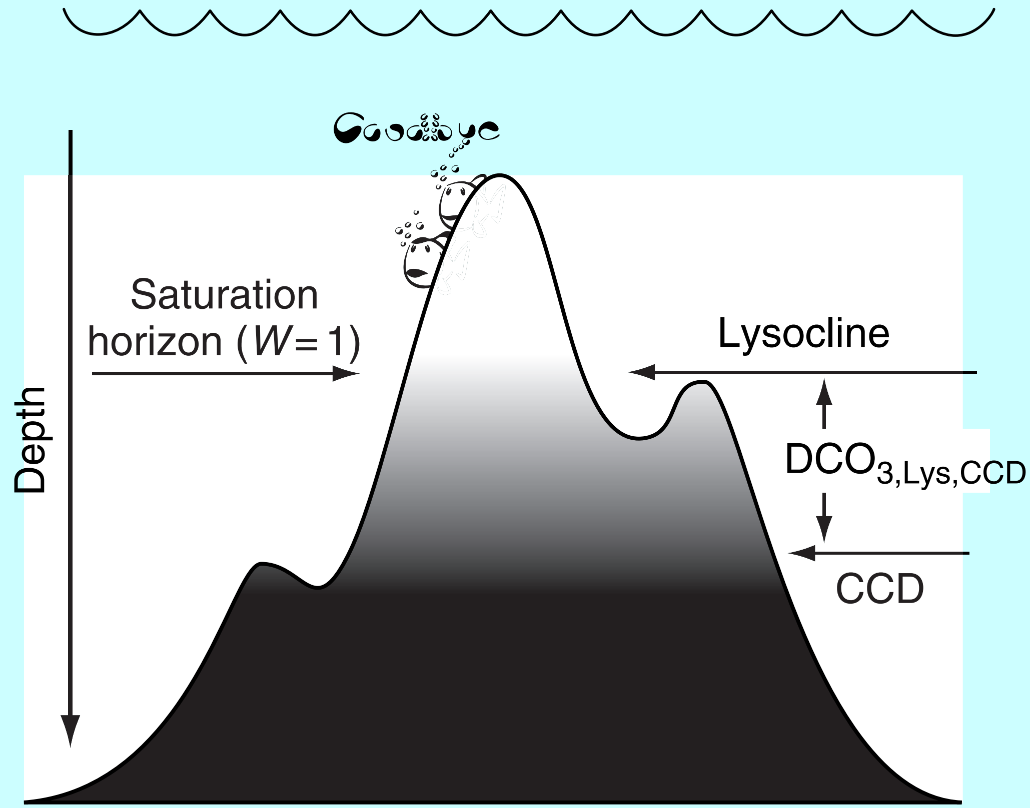
K_{sp}' is greater for aragonite than calcite and at higher P and lower T

Since $[Ca^{2+}]$ in mol/kg = 2.934×10^{-4} S, Ω > is a function of $[CO_3^{2-}]$ and K_{sp}'

$CaCO_3$ Saturation

- $CaCO_3$ supersaturated in surface waters, under-saturated in deep waters [K_2, K_{sp} = f(P,T,S)]
  - Calcite
  - Aragonite
- Saturation Depth - depth below which seawater is under-saturated with respect to calcite or aragonite
- Lysocline – depth of rapid increase in solubility and dissolution rate
- Compensation Depth (CCD) – depth at which sediments are >5% $CaCO_3$

Figure 12.12. A sketch of the carbonate content of deep sea sediments as a function of depth. Lighter shades indicate greater $CaCO_3$ content in the sediments. Horizontal arrows indicate theoretical relations among the depths of the lysocline (where $CaCO_3$% shows visible signs of dissolution), the carbonate compensation depth, CCD (where the $CaCO_3$ concentration drops to zero) and the saturation horizon ($\Omega = 1$).



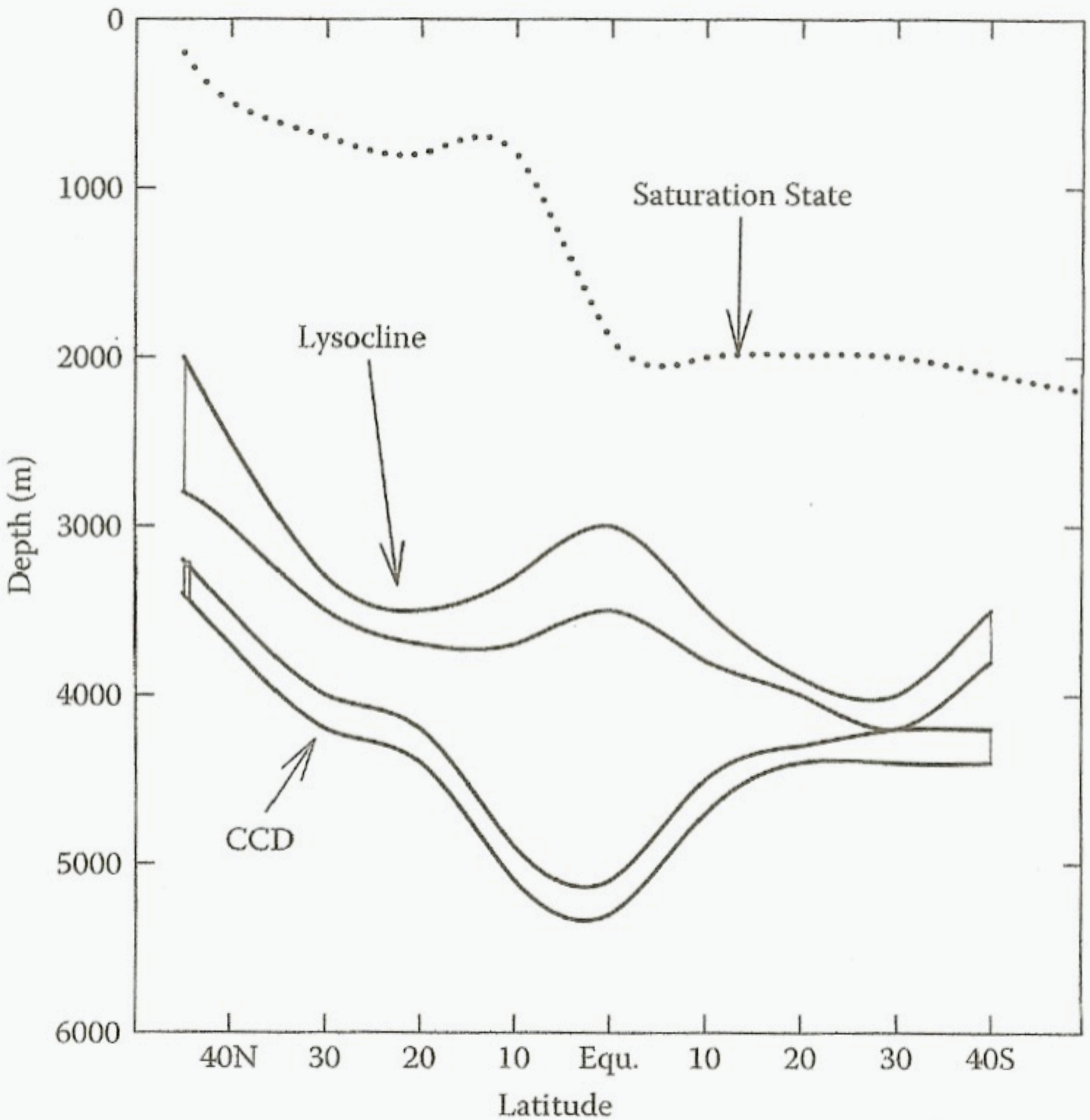
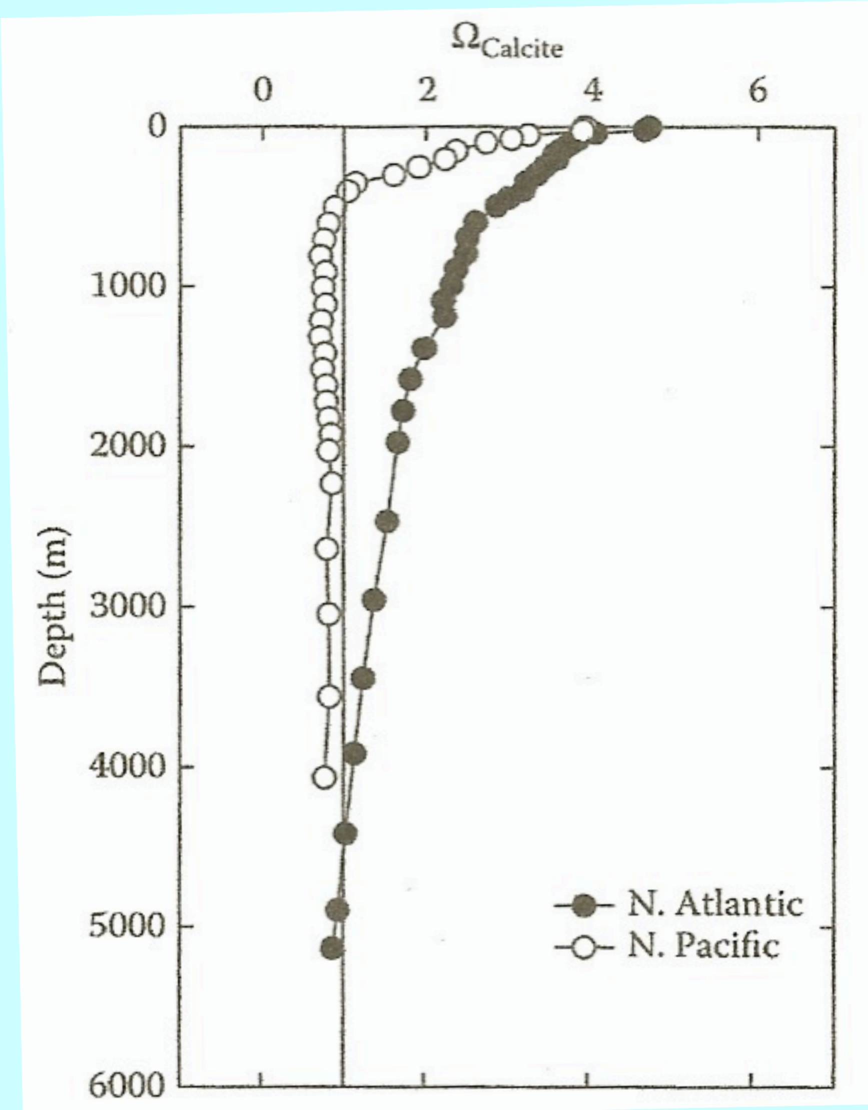

0
1000
2000
3000
4000
5000
6000
Depth (m)
Saturation State
Lysocline
CCD
40N
30
20
10
Equ.
10
20
30
40S
Latitude

TABLE 7.4

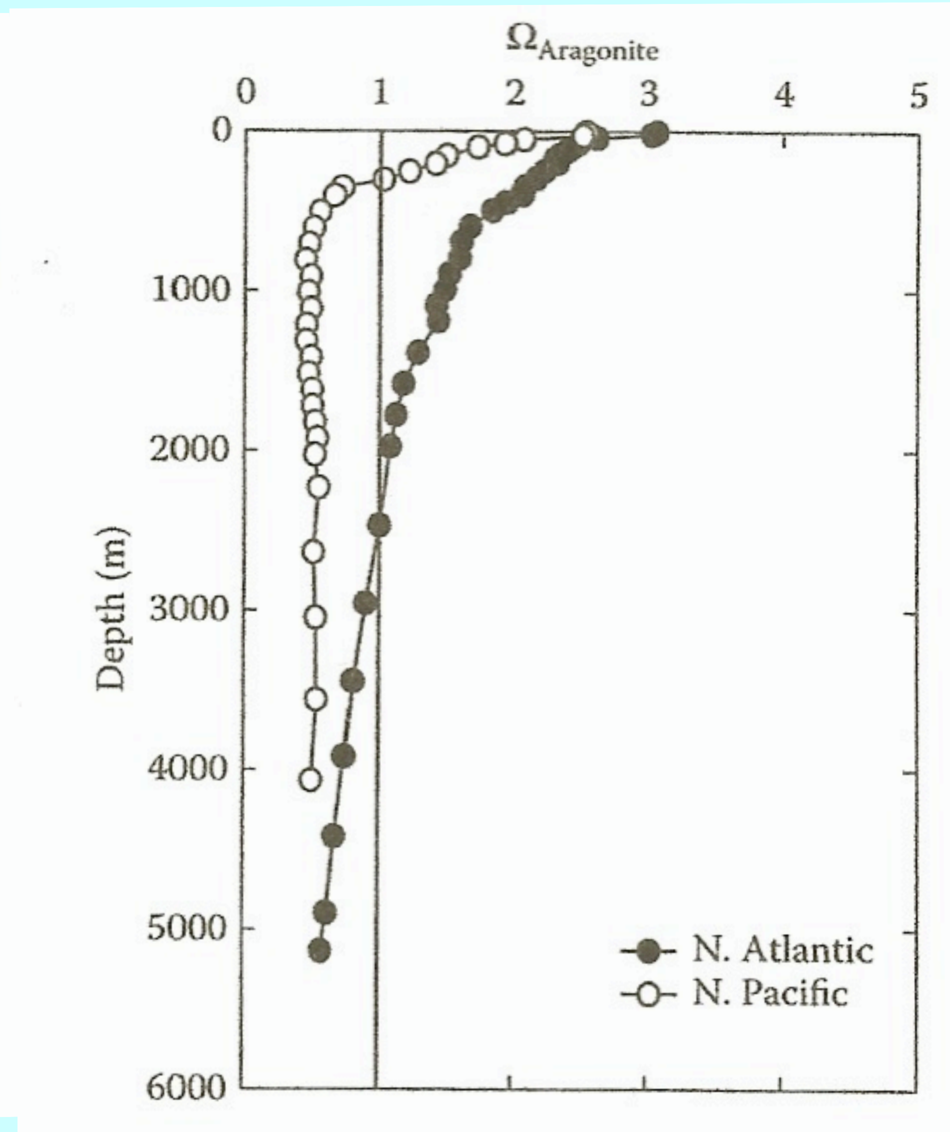
Dissociation Constants for Carbonate Calculations in Seawater (S = 35)

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

Use concentrations in mol/kg when using these K values.



$\Omega_{Calcite}$
0
2
4
6
0
1000
2000
3000
4000
5000
6000
Depth (m)
N. Atlantic
N. Pacific



$\Omega_{Aragonite}$
0
1
2
3
4
5
0
1000
2000
3000
4000
5000
6000
Depth (m)
N. Atlantic
N. Pacific