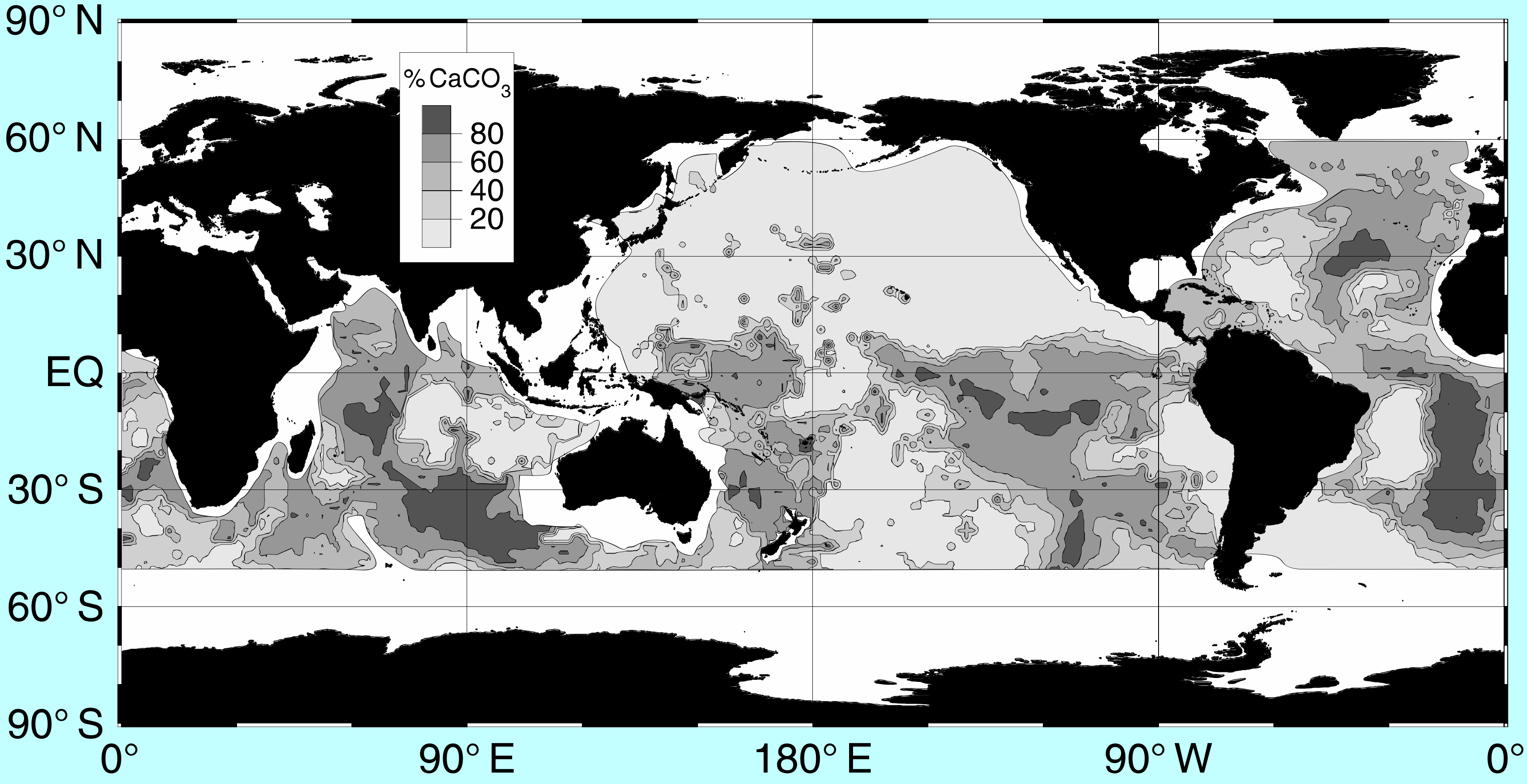
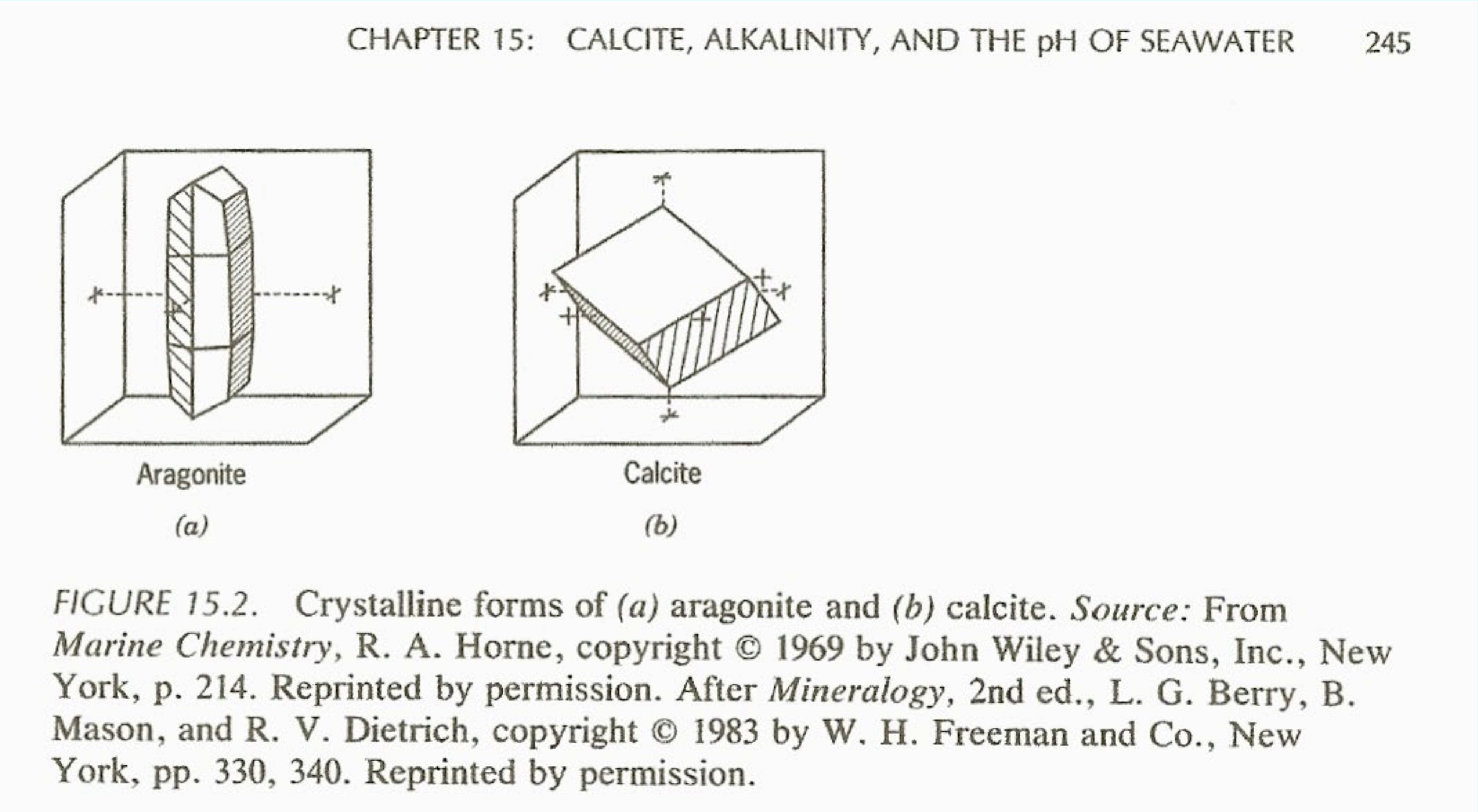
$CaCO_3$ Distribution in Sediments



$CaCO_3$ 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.



Aragonite

(a)

Calcite

(b)

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

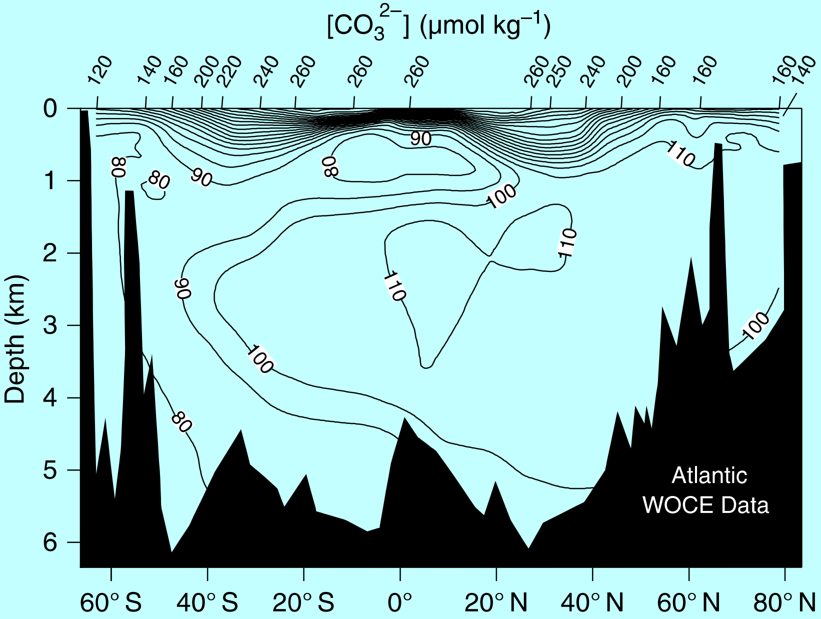
$\Omega = [Ca^{2+}]\,[CO_3{}^{2-}]/K_{sp}'$

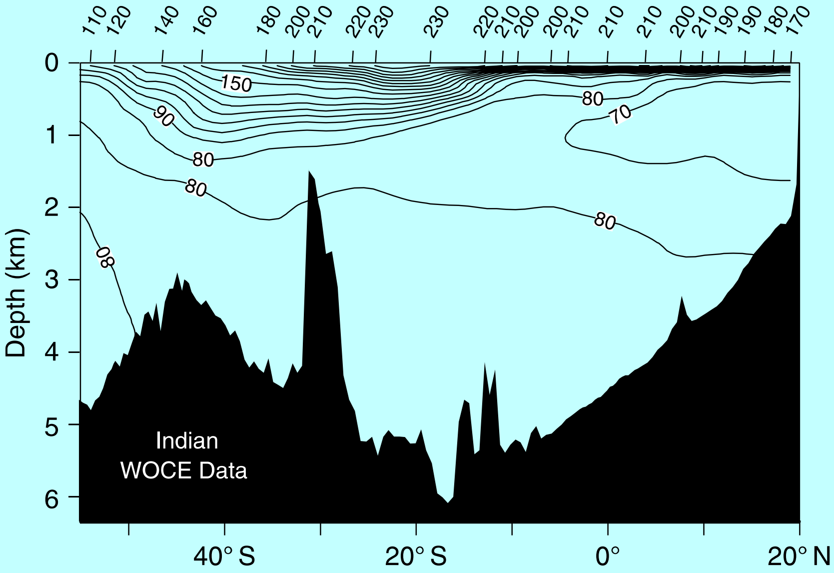
$\Omega > 1$, supersaturated $\Omega <$ undersaturated

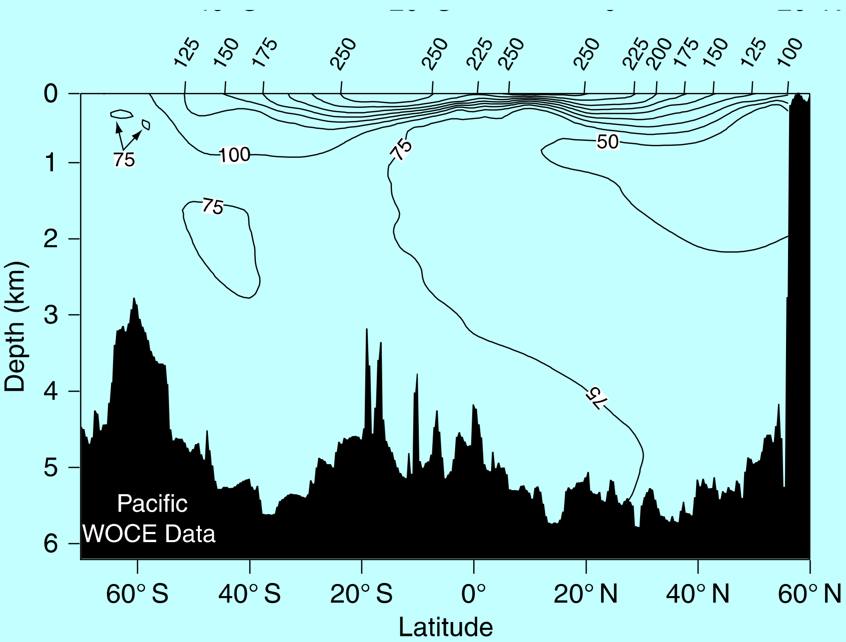
K_{sp}' is greater for aragonite than calcite and at higher P and lower T

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

$CO_3^{=}$ Sections







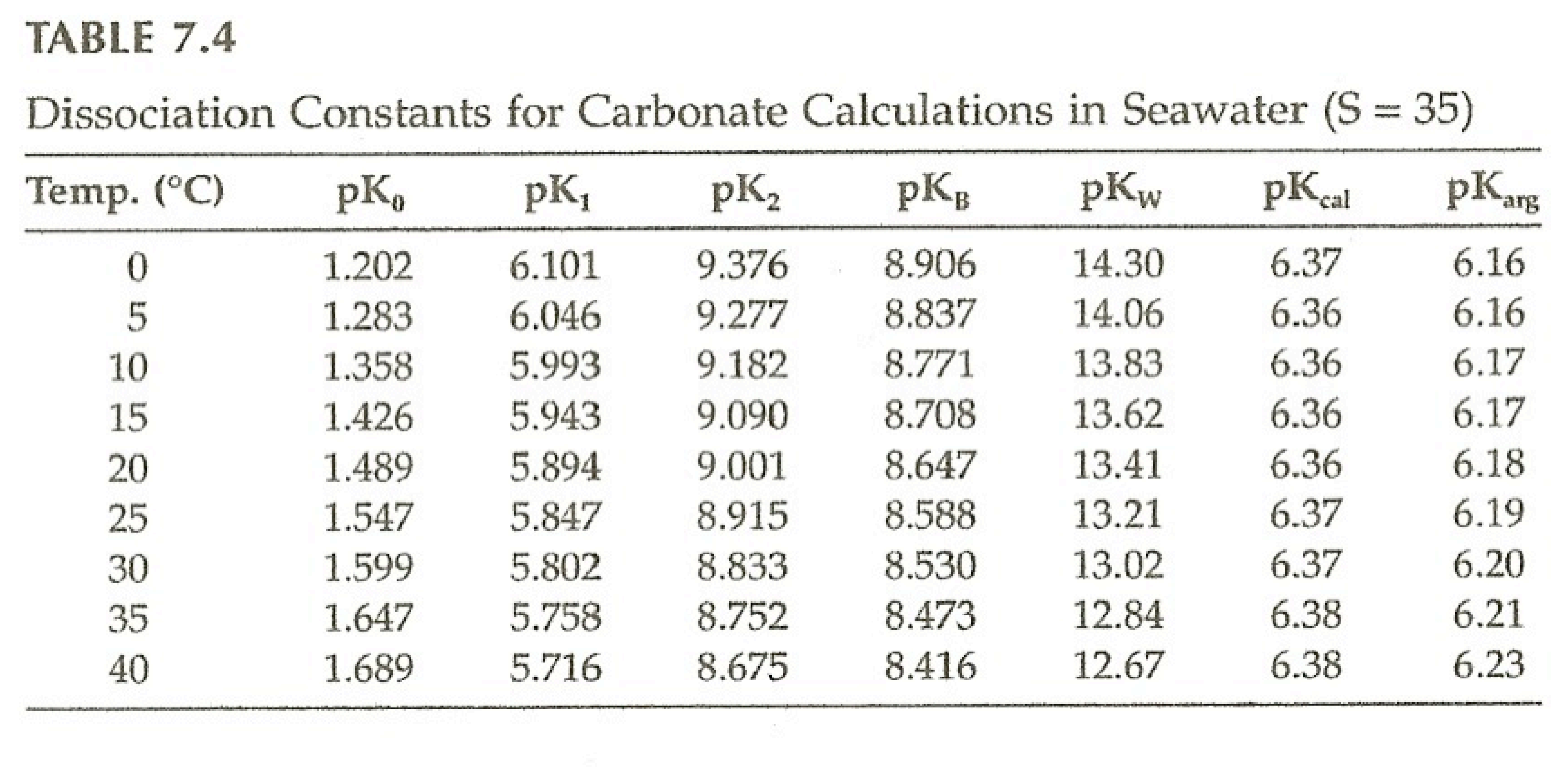


TABLE 7.4

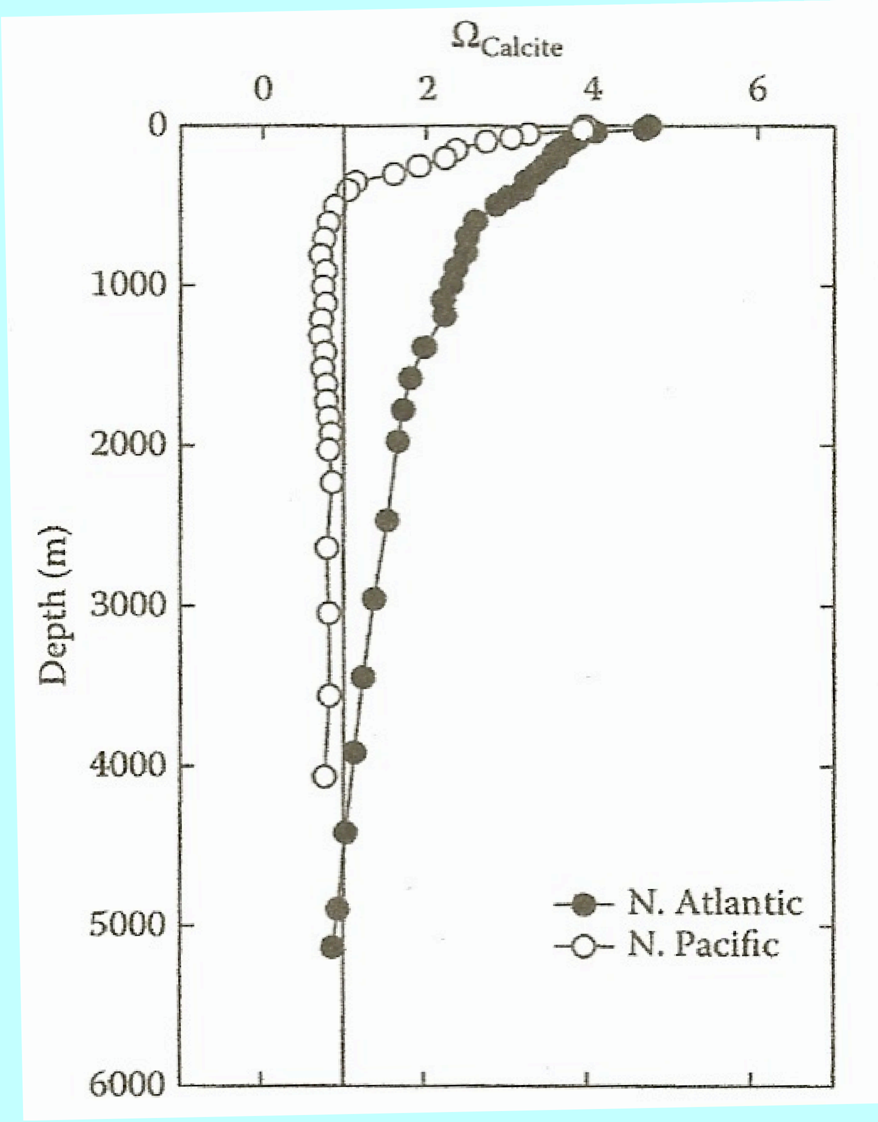
Dissociation Constants for Carbonate Calculations in Seawater (S = 35)

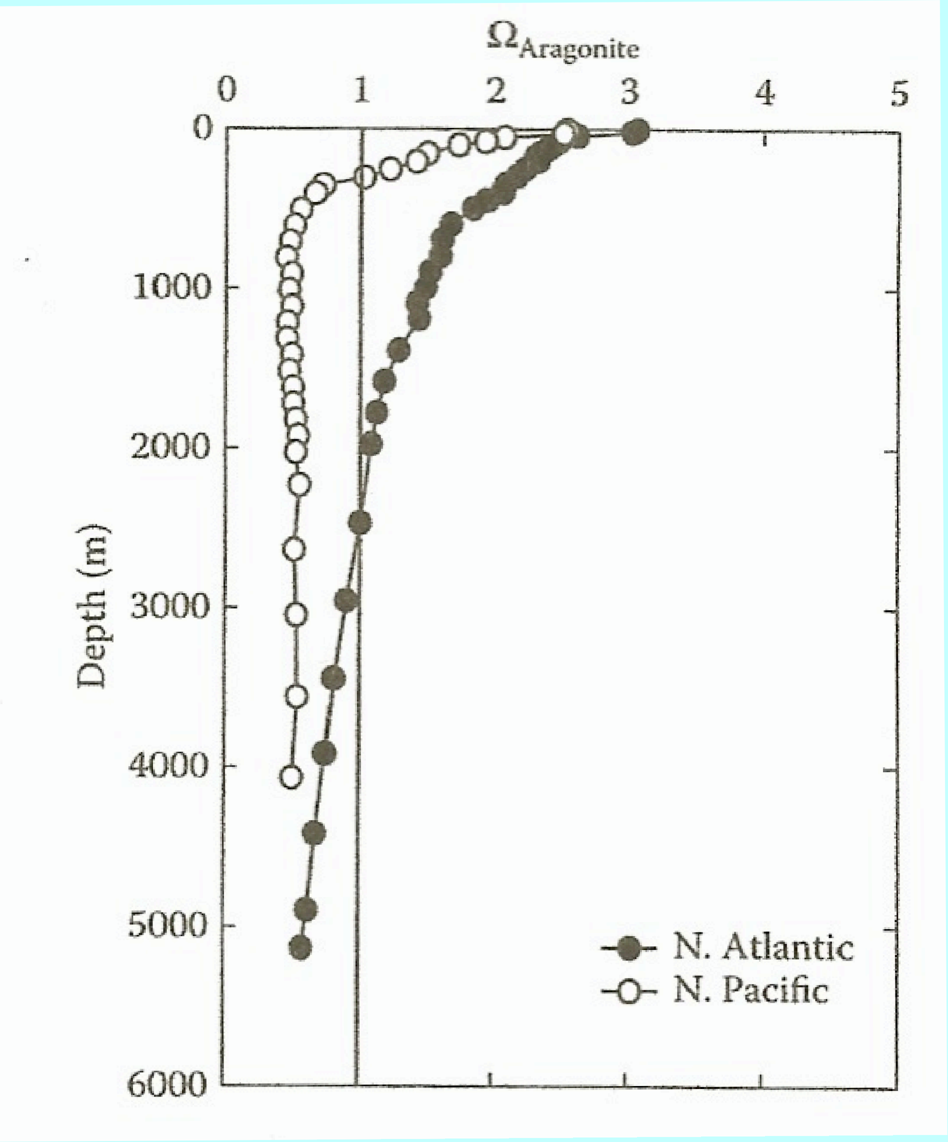
Temp. (°C)	pK_0	pK_1	pK_2	pK_B	pK_W	pK_{cal}	pK_{arg}
0	1.202	6.101	9.376	8.906	14.30	6.37	6.16
5	1.283	6.046	9.277	8.837	14.06	6.36	6.16
10	1.358	5.993	9.182	8.771	13.83	6.36	6.17
15	1.426	5.943	9.090	8.708	13.62	6.36	6.17
20	1.489	5.894	9.001	8.647	13.41	6.36	6.18
25	1.547	5.847	8.915	8.588	13.21	6.37	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

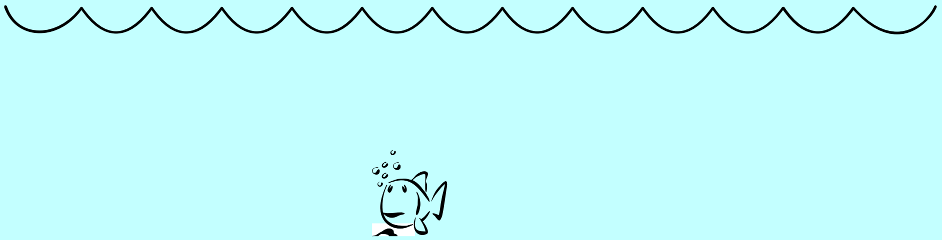
Use concentrations in mol/kg when using these K values.

$CaCO_3$ Saturation

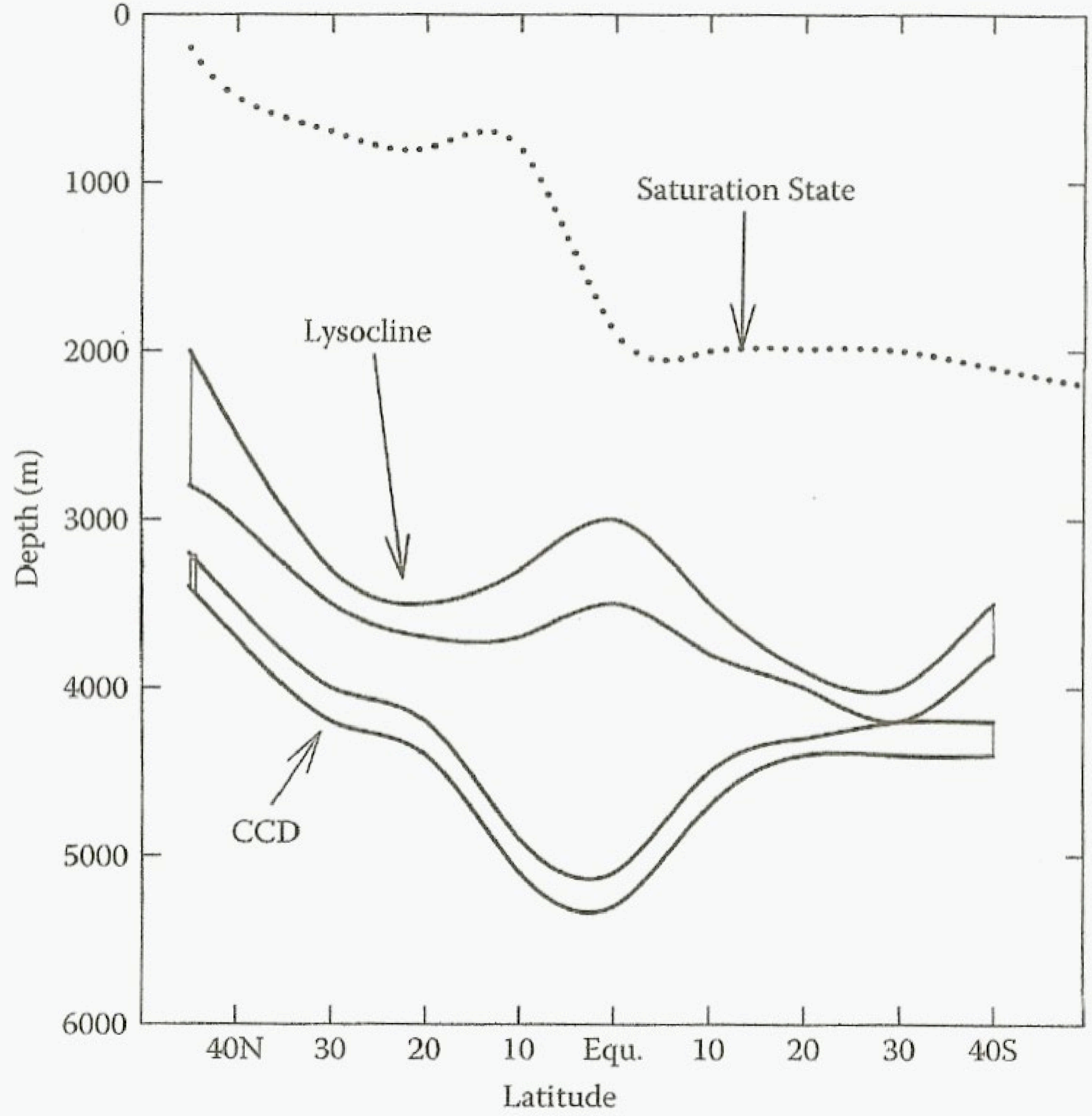
- $CaCO_3$ supersaturated in surface waters, under-saturated in deep waters [K_2, $K_{sp} = f(P,T,S)$]
  - Calcite
  - Aragonite
- Saturation Depth - depth below which seawater is under-saturated with respect to calcite or aragonite
- Lysocline – depth of rapid increase in solubility and dissolution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


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

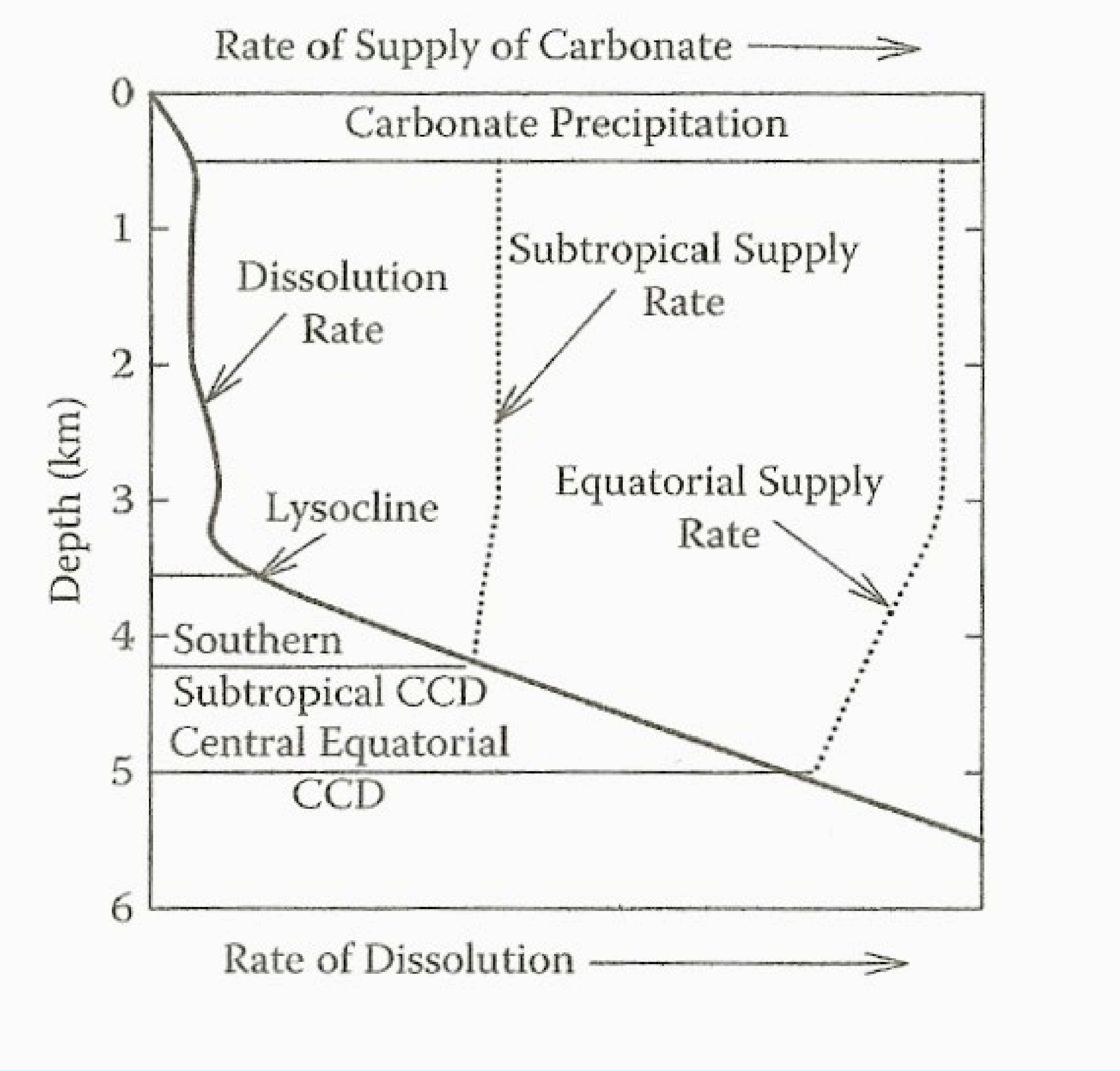

$\Omega_{Aragonite}$
0
1
2
3
4
5
0
1000
2000
3000
4000
5000
6000
Depth (m)
N. Atlantic
N. Pacific

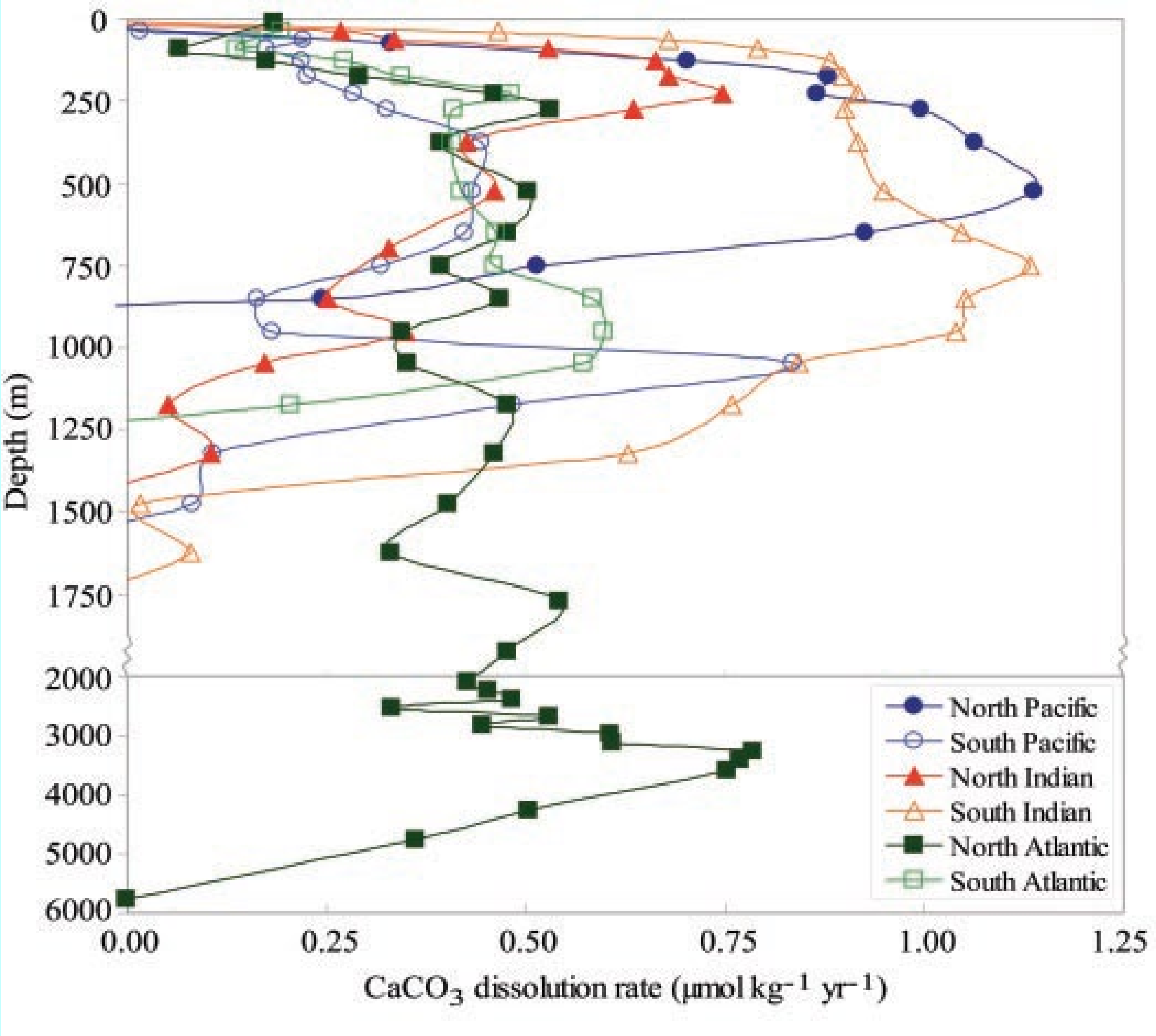


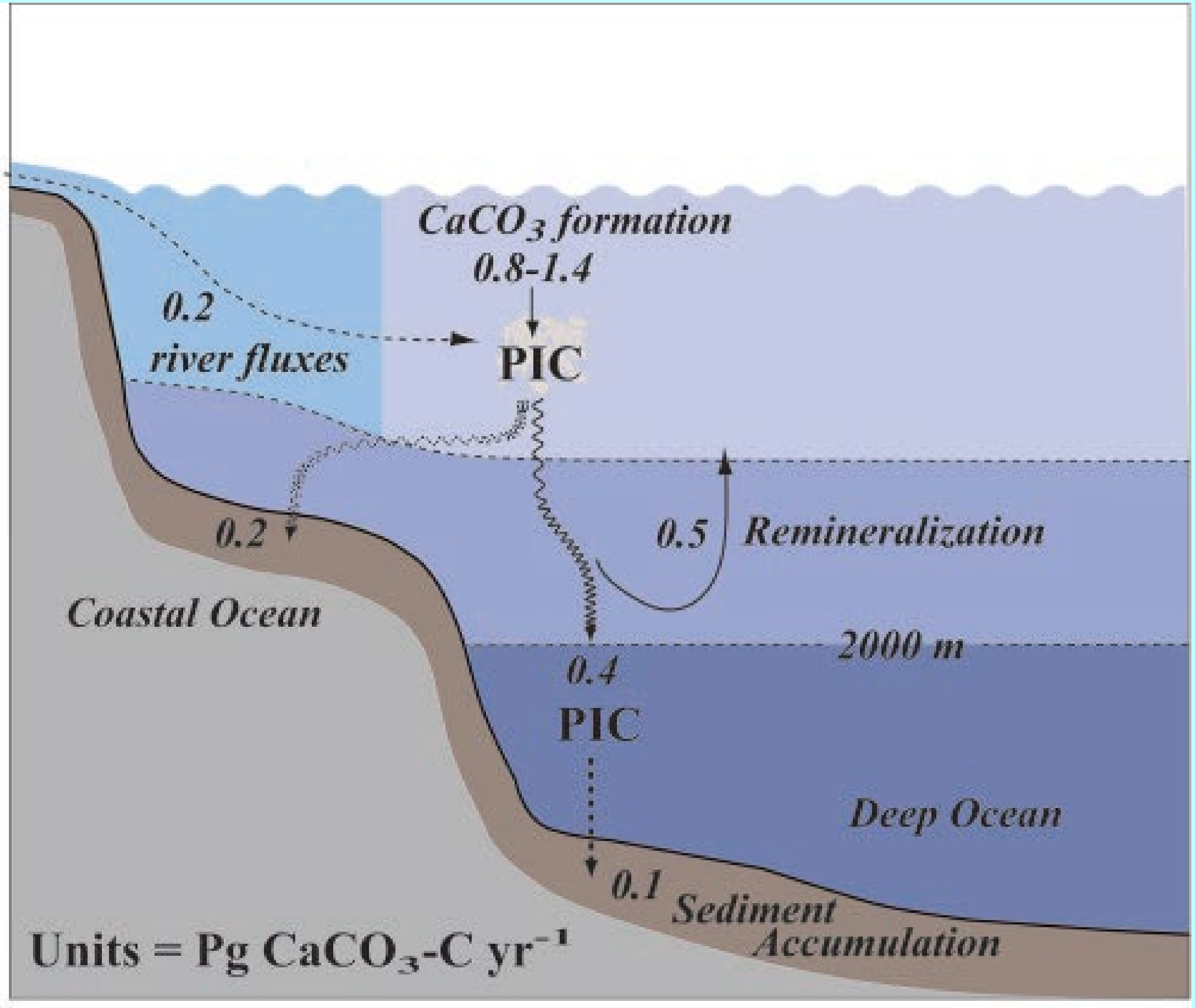
arrows indicate theoretical relations among the depths of the lysocline (where $CaCO_3$% shows visible signs of dissolution), the carbonate compensation depth, CCD (where the $CaCO_3$ concentration drops to zero) and the saturation horizon ($\Omega = 1$).

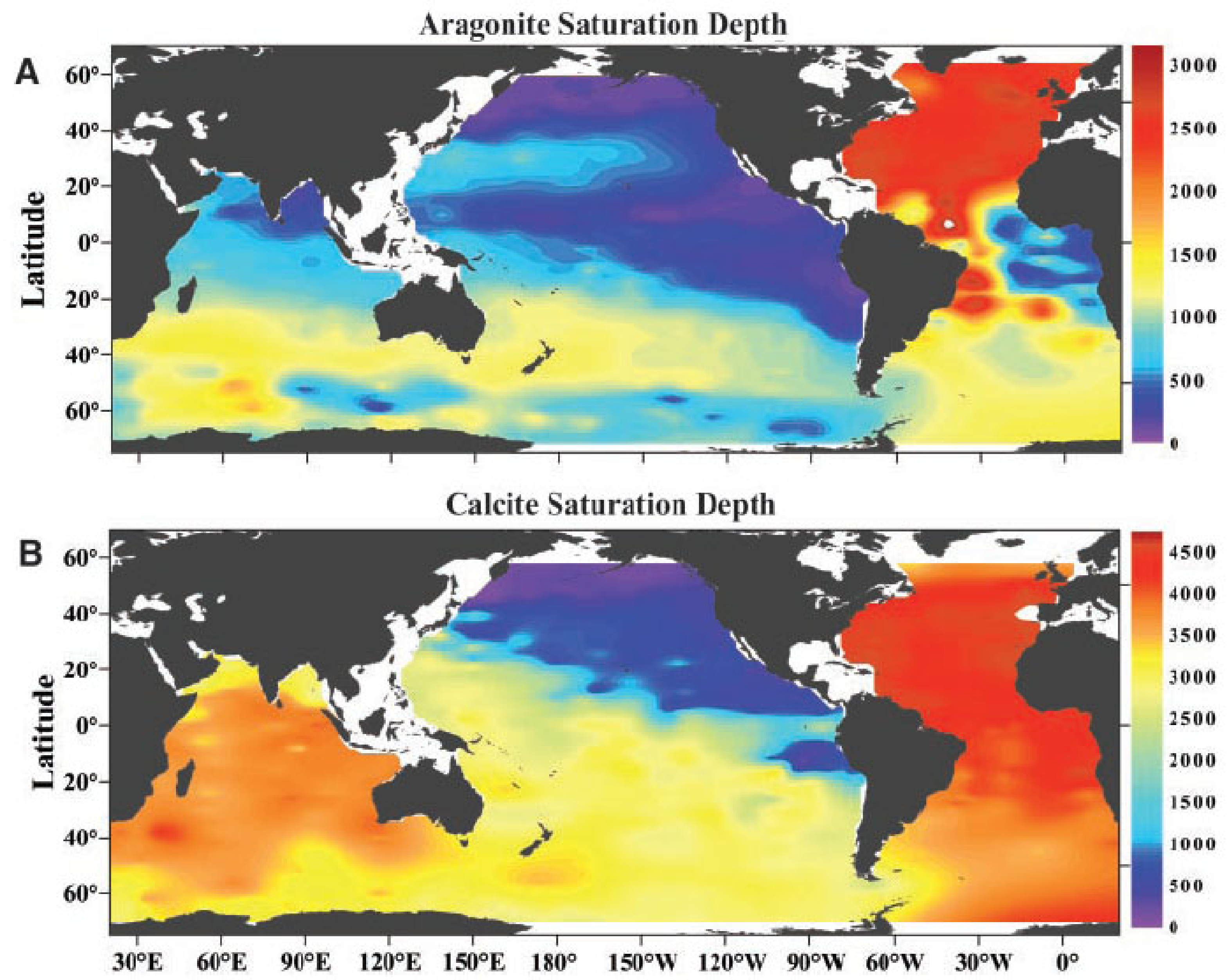

0
1000
2000
3000
4000
5000
6000
Depth (m)
Saturation State
Lysocline
CCD
40N
30
20
10
Equ.
10
20
30
40S
Latitude

Kinetic Considerations

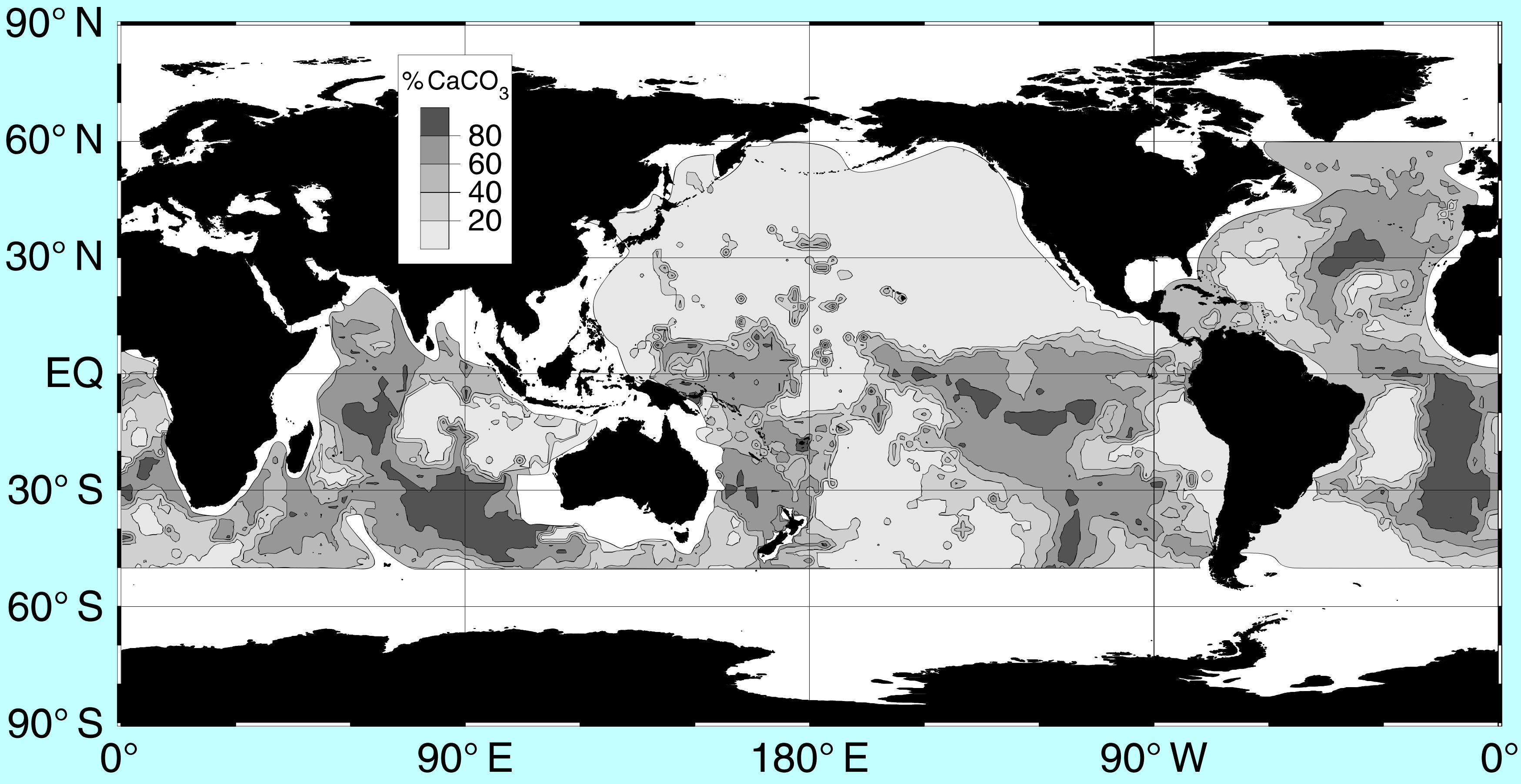



0
250
500
750
1000
1250
1500
1750
2000
3000
4000
5000
6000
Depth (m)
0.00
0.25
0.50
0.75
1.00
1.25
CaCO$_3$ dissolution rate (µmol kg^{-1} yr^{-1})
North Pacific
South Pacific
North Indian
South Indian
North Atlantic
South Atlantic


CaCO3 formation
0.8-1.4
0.2
river fluxes
PIC
0.2
0.5
Remineralization
Coastal Ocean
2000 m
0.4
PIC
Deep Ocean
0.1
Sediment
Accumulation
Units = Pg CaCO3-C yr-1


Aragonite Saturation Depth
A
60°
40°
20°
0°
20°
40°
60°
Latitude
3000
2500
2000
1500
1000
500
0
Calcite Saturation Depth
B
60°
40°
20°
0°
20°
40°
60°
Latitude
4500
4000
3500
3000
2500
2000
1500
1000
500
0
30°E
60°E
90°E
120°E
150°E
180°
150°W
120°W
90°W
60°W
30°W
0°

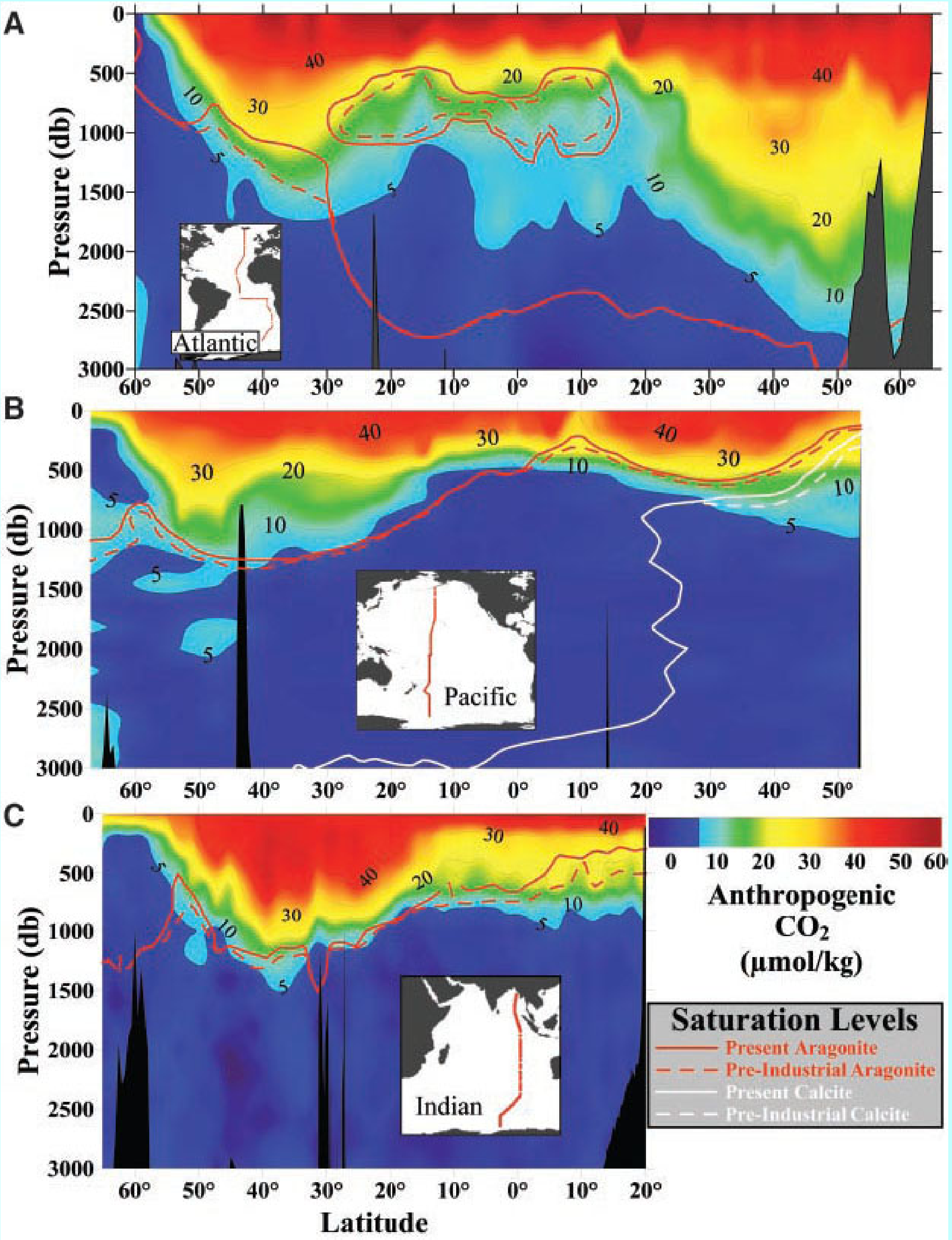
$CaCO_3$ Distribution in Sediments



Anthropogenic CO_2 Invasion and $CaCO_3$

A negative feedback?

(Feely et al., *Science* 2004)



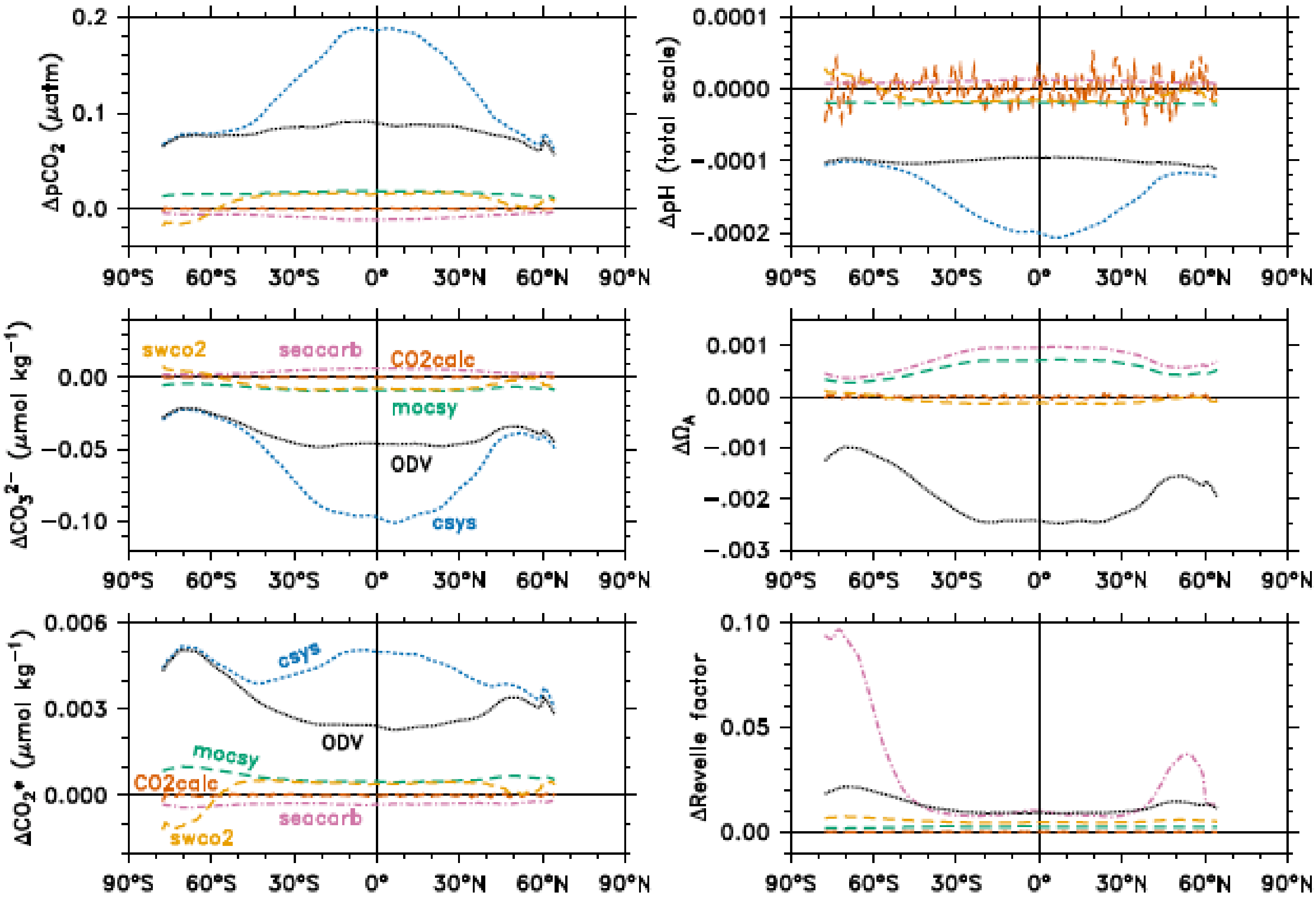


Figure 2. Global zonal-mean surface values for variables computed from gridded data products for A_T and C_T from GLODAP (Key et al., 2004) combined with T, S, and nutrients from the 2009 World Ocean Atlas (WOA2009) (Locarnini et al., 2010; Antonov et al., 2010; Garcia et al., 2010). Curves are shown for each package and variable after subtracting off corresponding results for the CO2SYS-MATLAB reference. The csys package does not provide results for Ω_A and the Revelle factor. It also neglects nutrient alkalinity, but its curves were adjusted to include the effects of P_T and Si_T as computed by mocsy.

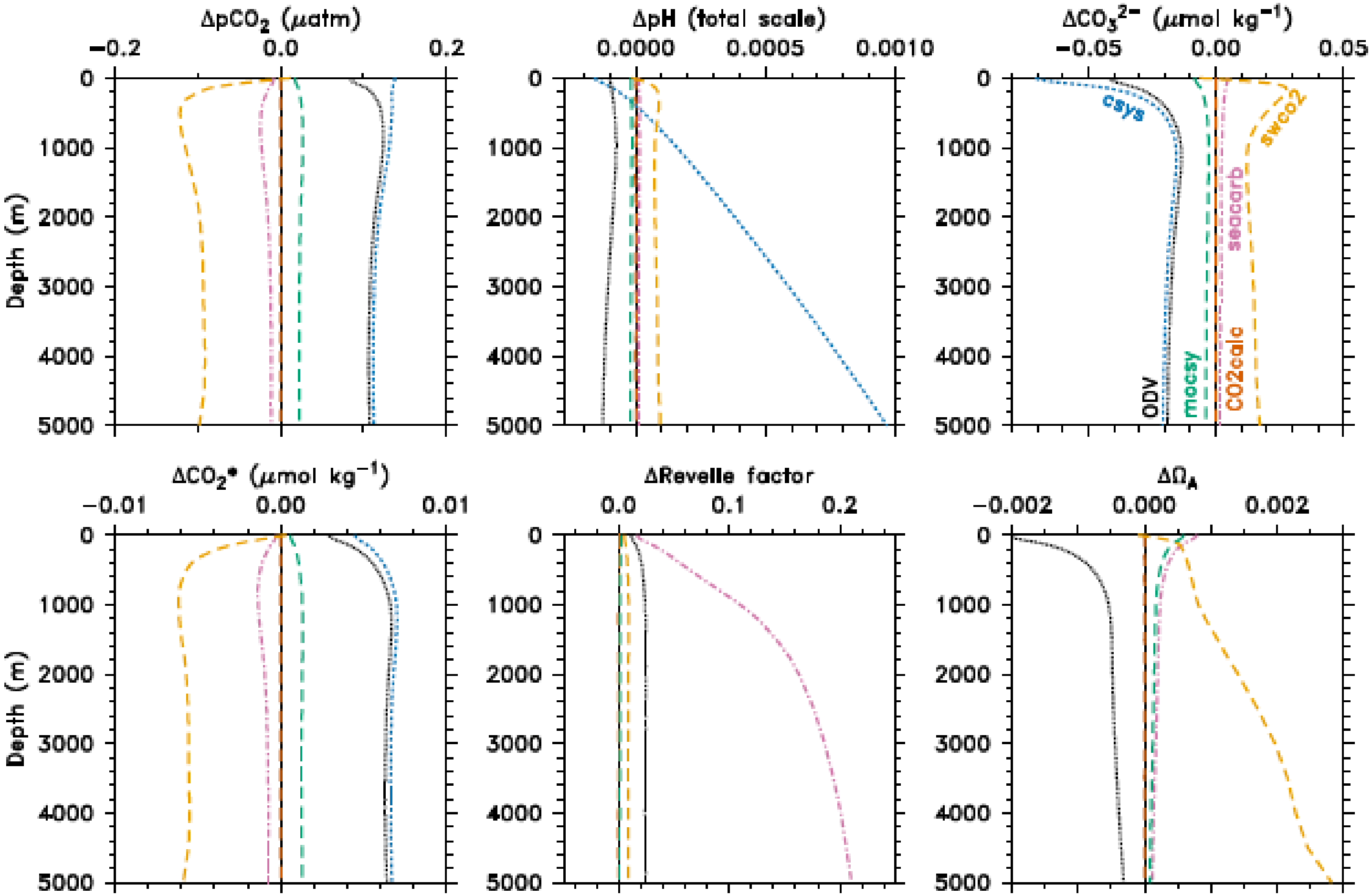


Figure 3. Global-mean vertical profiles of variables computed from the same gridded data products as in Fig. 2. For each software package, corresponding results from the reference (CO2SYS-MATLAB) have been subtracted. The csys curves are adjusted as in Fig. 2. In all comparisons, the csys results are computed with the option ocdflag = 1; its discrepancies would be larger with ocdflag = 0.