Dissolved Gases in Seawater

- Fundamentals
- Solubility Relationships
- Air-Sea Exchange
- Departures from Ideality
- O_2 Dynamics (Intro)

DISSOLVED GASES IN THE OCEANS

SOURCES

1. Atmosphere (Major Term)
   (N_2, O_2, Ar, etc.)

2. Volcanic Activity (H_2S)

3. Marine Production & Consumption Processes

   a) Biological Activity
      ($NO_3^- \rightarrow N_2O$, respiration)

   b) Radioactive Decay
      ($^{226}Ra \rightarrow {}^{222}Rn$)

BASIC CONCEPTS

I. Dalton’s Law

$$P_T = \Sigma P_i \sim P_{N2} + P_{O2} + P_{Ar} + P_{H2O} + P_{CO2}$$

II. Ideal Gas Law

$$P_i = n_i RT/V \quad \text{where } R = 82.05 \text{ cm}^3 \text{ atm mol}^{-1} \text{deg}^{-1}$$

III. $P_i = X_i [P_T - P_{H2O}]$, $P_{H2O} = (h/100)\, P_{H2O\text{-Sat}}$

IV. Henry’s Law

$P_i = H_i [C_i]$ $\qquad$ $[C_i] = P_i/H_i$

at equilibrium $\quad P_i \text{ (soln)} = P_i \text{ (air)}$

$H_i = f\,(T,S,P)$

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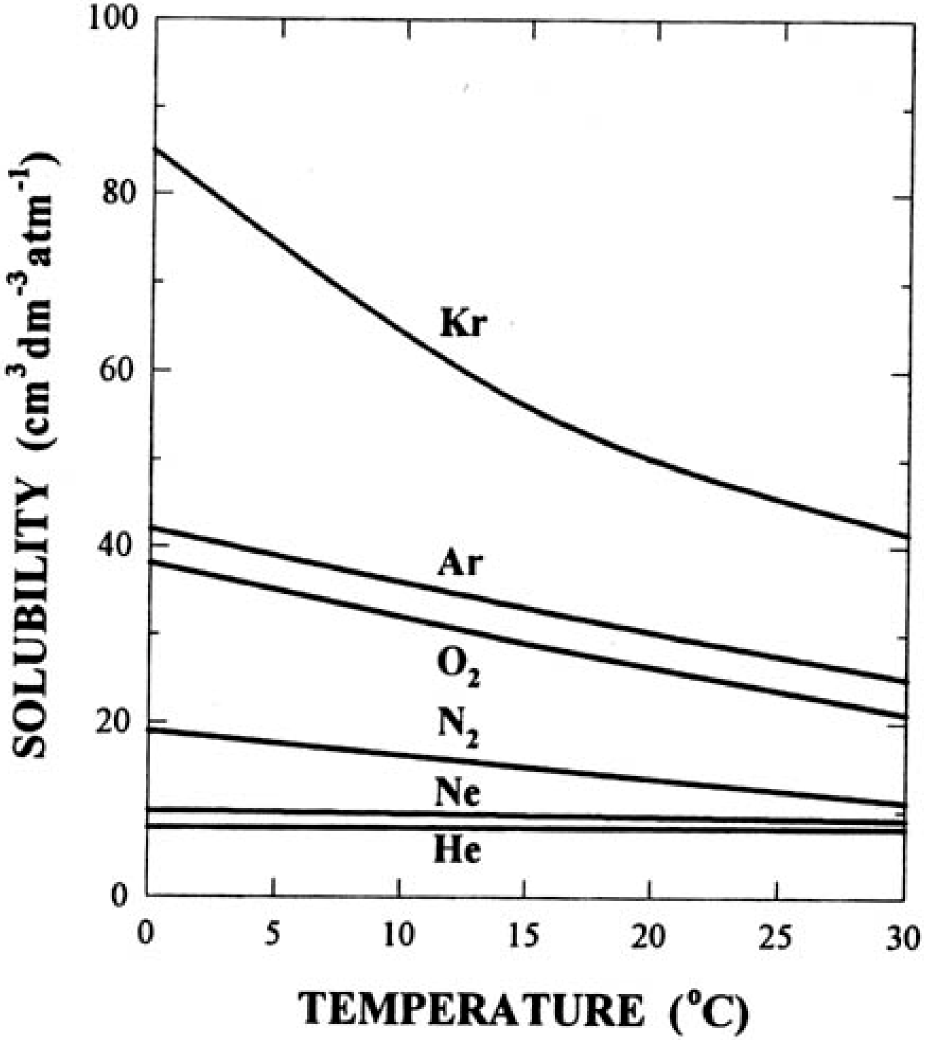

FIGURE 6.5. The effect of temperature on the solubility of gases in seawater.

EFFECT OF TEMPERATURE ON SOLUBILITY OF GASES IN SEAWATER

Gas	0°C	25°C
He	1.8 nM	1.7 nM
Ne	7.9	6.6
Kr	4.0	2.3
Xe	0.6	0.4
N_2	616 µM	383 µM
O_2	349	206
Ar	17	10
N_2O	14	6
CO_2	20	9

EFFECT OF SALINITY ON SOLUBILITY OF GASES (0° C)

Gas	Water	Seawater
He	2.2 nM	1.8 nM
Ne	10	7.9
Kr	5.8	4.0
Xe	0.9	0.2
N_2	823 µM	616 µM
O_2	456	349
Ar	22	17
CO_2	23	20

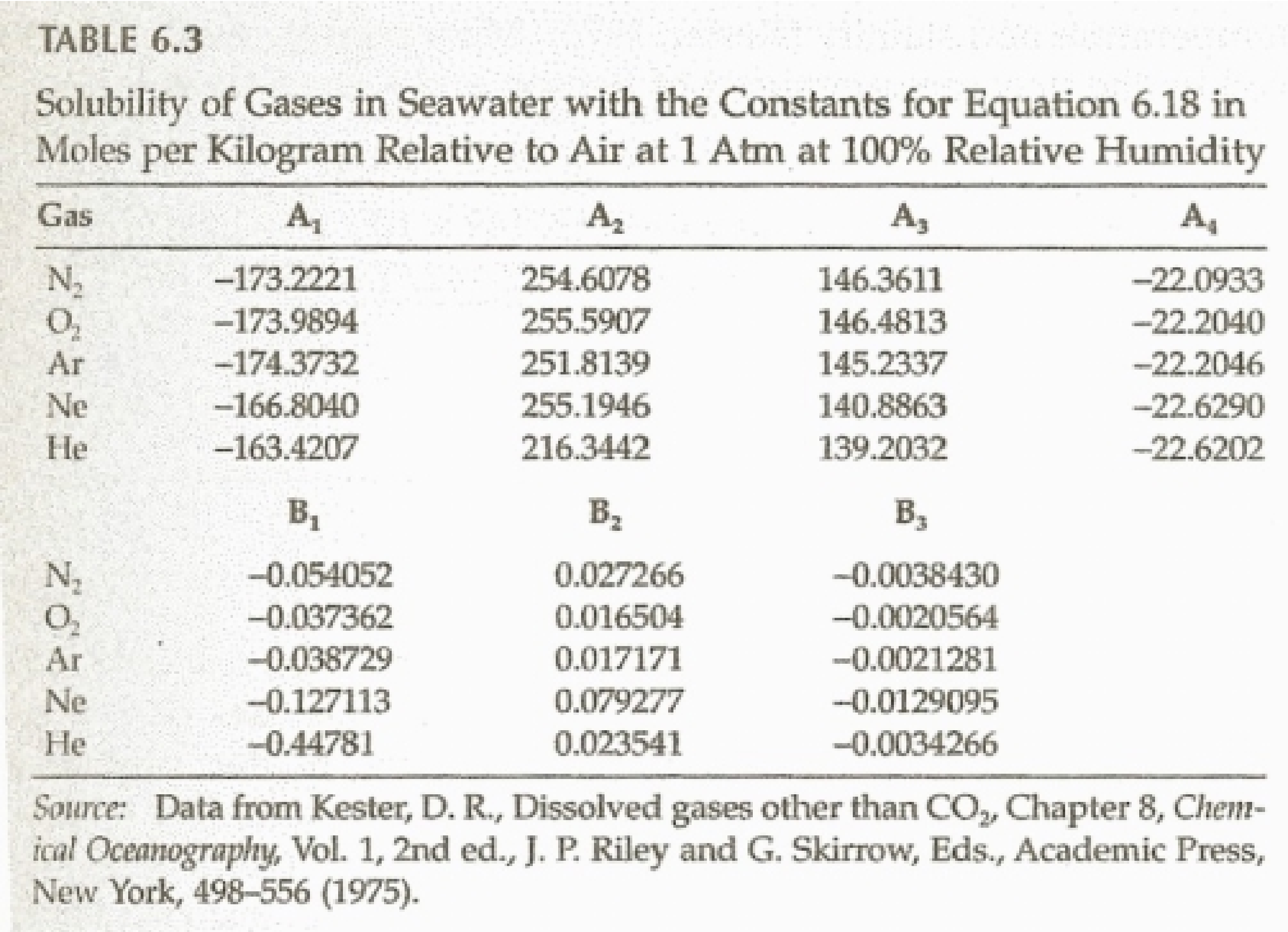

TABLE 6.3

Solubility of Gases in Seawater with the Constants for Equation 6.18 in Moles per Kilogram Relative to Air at 1 Atm at 100% Relative Humidity

Gas	A_1	A_2	A_3	A_4
N_2	–173.2221	254.6078	146.3611	–22.0933
O_2	–173.9894	255.5907	146.4813	–22.2040
Ar	–174.3732	251.8139	145.2337	–22.2046
Ne	–166.8040	255.1946	140.8863	–22.6290
He	–163.4207	216.3442	139.2032	–22.6202
	B_1	B_2	B_3	
N_2	–0.054052	0.027266	–0.0038430	
O_2	–0.037362	0.016504	–0.0020564	
Ar	–0.038729	0.017171	–0.0021281	
Ne	–0.127113	0.079277	–0.0129095	
He	–0.44781	0.023541	–0.0034266	

Source: Data from Kester, D. R., Dissolved gases other than CO_2, Chapter 8, *Chemical Oceanography,* Vol. 1, 2nd ed., J. P. Riley and G. Skirrow, Eds., Academic Press, New York, 498–556 (1975).

(see Hamme & Emerson [2004 DSR I] and Garcia & Gordon [1992, L&O] for improved coefficients

$$\ln C_i = A_1 + A_2\,(100/T) + A_3\,\ln(T/100) + A_4\,(T/100)$$
$$+\; S[B_1 + B_2\,(T/100) + B_3\,(T/100)^2]$$

T is in °K

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Fick’s First Law

$$dC_i/dt = A\ D_i\ (dC_i/dz)$$

Where:

A = area

C_i = concentration species i

D_i = diffusion coefficient

Z = thickness of diffusion layer

DIFFUSION COEFFICIENTS OF GASES

Gas	MW	D (10^5 cm^2 s^{-1}) 0°C	24°C
He	4	2.0	4.0
Ne	20	1.4	2.8
N_2	28	1.1	2.1
O_2	32	1.2	2.3
Ar	40	0.8	1.5
CO_2	44	1.0	1.9
N_2O	44	1.0	2.0
Kr	84	0.7	1.4
Xe	131	0.7	1.4
Rn	222	0.7	1.4

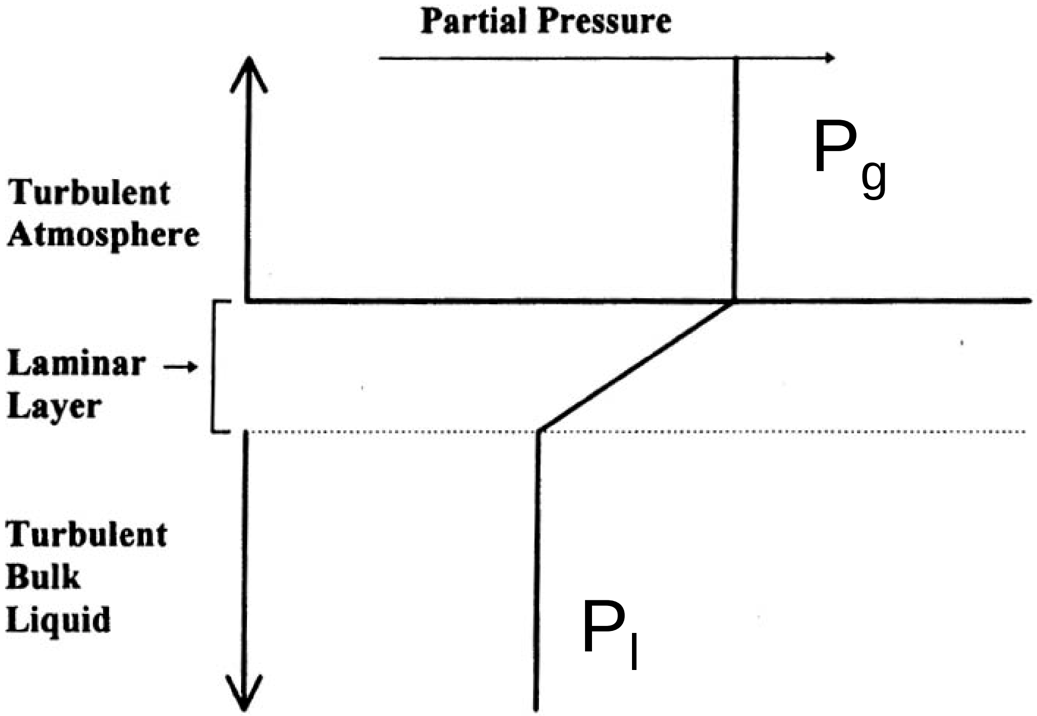

FIGURE 6.1. The laminar layer for the transport of gases across the air-sea interface.

Combining Henry's and Fick's Laws:

$$dC_i/dt = (A\ D_i/\tau\ H_i)\ [P_i\ (\text{gas})\ - (P_i\ (\text{liquid})]$$

where:

τ = thickness of boundary layer

More simply:

$$F_i = dC_i/dt = k_t \Delta C_i$$

Where:

F = flux (mol cm^{-2} s^{-1})

ΔC = change in concentration across interface (mol cm^{-3})

k_t = transfer velocity (cm s^{-1})

= permeability coefficient

= mass transfer coefficient

= absorption coefficient

= exit coefficient

= piston velocity

$k \propto D_i/(\tau\ H_i)$ for thin layer model

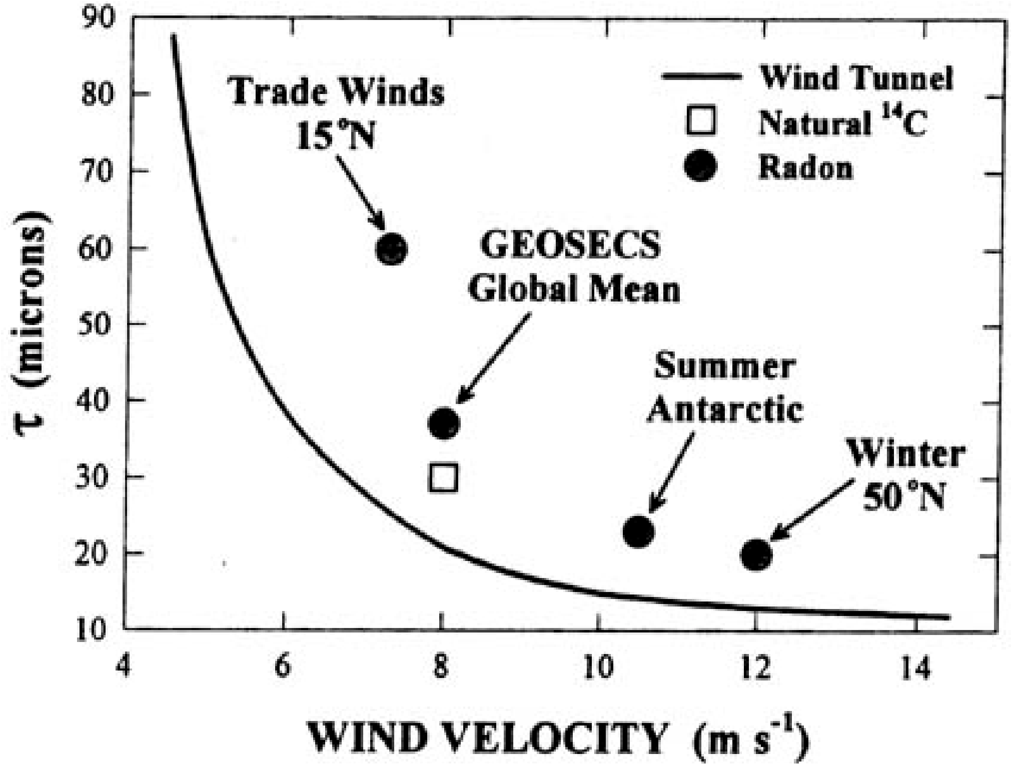

FIGURE 6.2. The thickness of the laminar layer as a function of the wind speed.

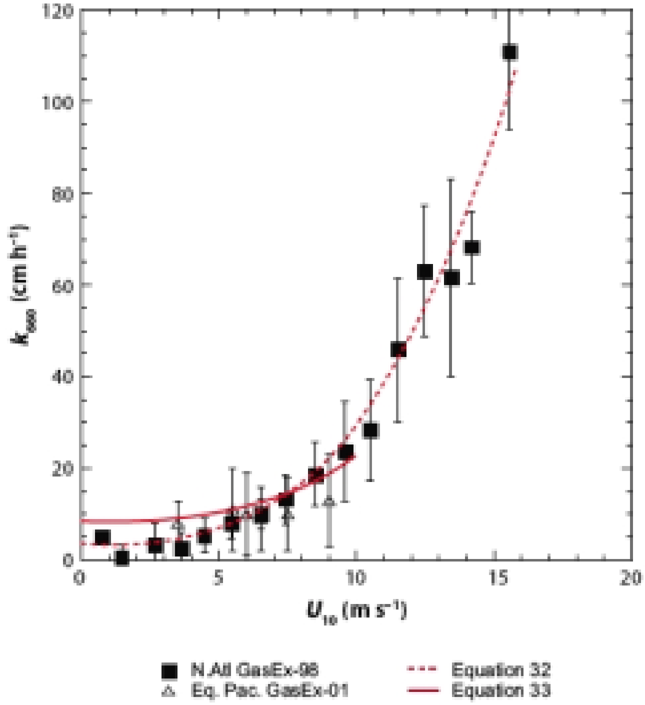

Figure 4

Comparison of CO_2 covariance flux measurements in the North Atlantic (*solid squares*) (McGillis et al. 2001) and Equatorial Pacific (*open triangles*) (McGillis et al. 2004b, Hare et al. 2004). The results are binned in nominally 1 m s^{-1} wind speed bins and the error bars indicate the standard deviation of the points in each interval that range from as few as 4 at low and high winds to more than 200 at intermediate winds. The dashed red line is the parameterization expressed in Equation 32 and the solid red line is that in Equation 33.

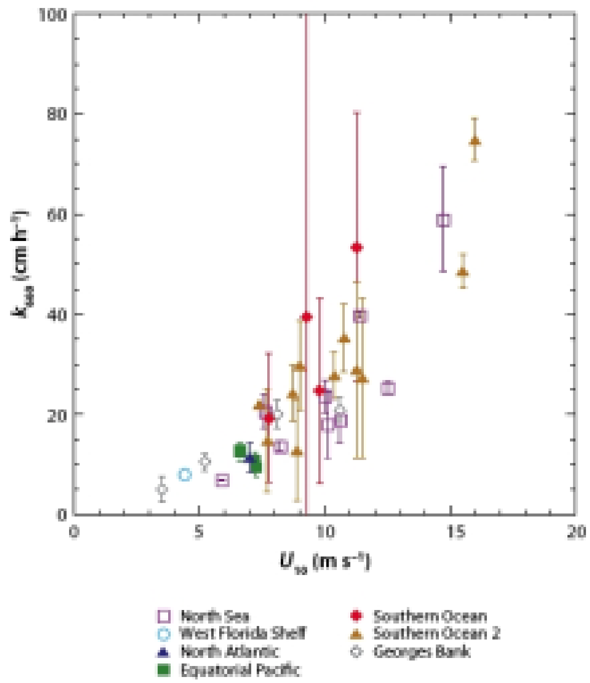

Figure 3

Summary of $^3He/SF_6$ dual-deliberate tracer results normalized to $Sc = 660$ and plotted against wind speed. The open symbols are for the experiments in the coastal oceans, while the solid symbols depict the studies in the open ocean. The error bars are based on the variation of $^3He/SF_6$ in the mixed layer at each sampling time propagated through Equation 18. References are as follows: North Sea, Nightingale et al. (2000b); West Florida Shelf, Wanninkhof et al. (1997); North Atlantic, Wanninkhof & McGillis (1999); Equatorial Pacific, Nightingale et al. (2000a); Southern Ocean, Wanninkhof et al. (2004); Southern Ocean 2, Ho et al. (2006); Georges Bank, Wanninkhof et al. (1993).

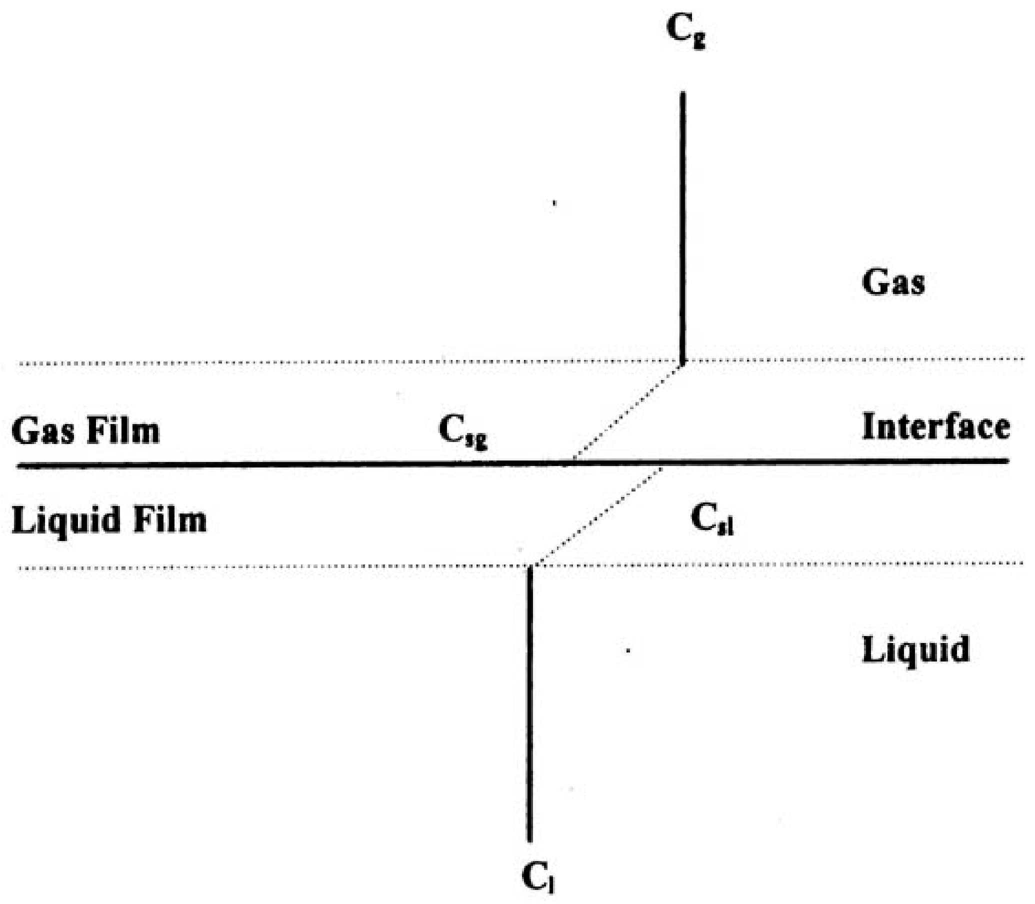

FIGURE 6.3. The gas film model for the transport of gases across the air-sea interface.

“Resistance” to Gas Exchange

$$1/k_r = R = R_g + R_l$$

Where:

k_r = exchange coefficient (yes - yet another definition!)

R = Total resistance

R_g= Resistance to transfer in gas boundary layer

R_l = Resistance to transfer in liquid boundary layer

For Reactive Gases (SO_2, HNO_3)

$$R_g \gg R_l$$

For Inert Gases (O_2, CO_2)

$$R_l \gg R_g$$

$$1/K_l = 1/k_l\alpha \; (C_g/H - C_l)$$

(α = modifying factor allowing for contributions of reactions of gas in aqueous phase)

For most gases R_l most important

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Causes of Non-Reactive Gases Departing from Expected Solubility

1. Departures from Standard Atmosphere
2. Dissolution of Air Bubbles
3. Air Injection
4. Differential Heating and Gas Exchange
5. Mixing of Waters of Different Temperatures
6. Radiogenic or Primordial Addition

BUBBLE INJECTION EFFECTS

1. Less soluble gases become more enriched in bubbles

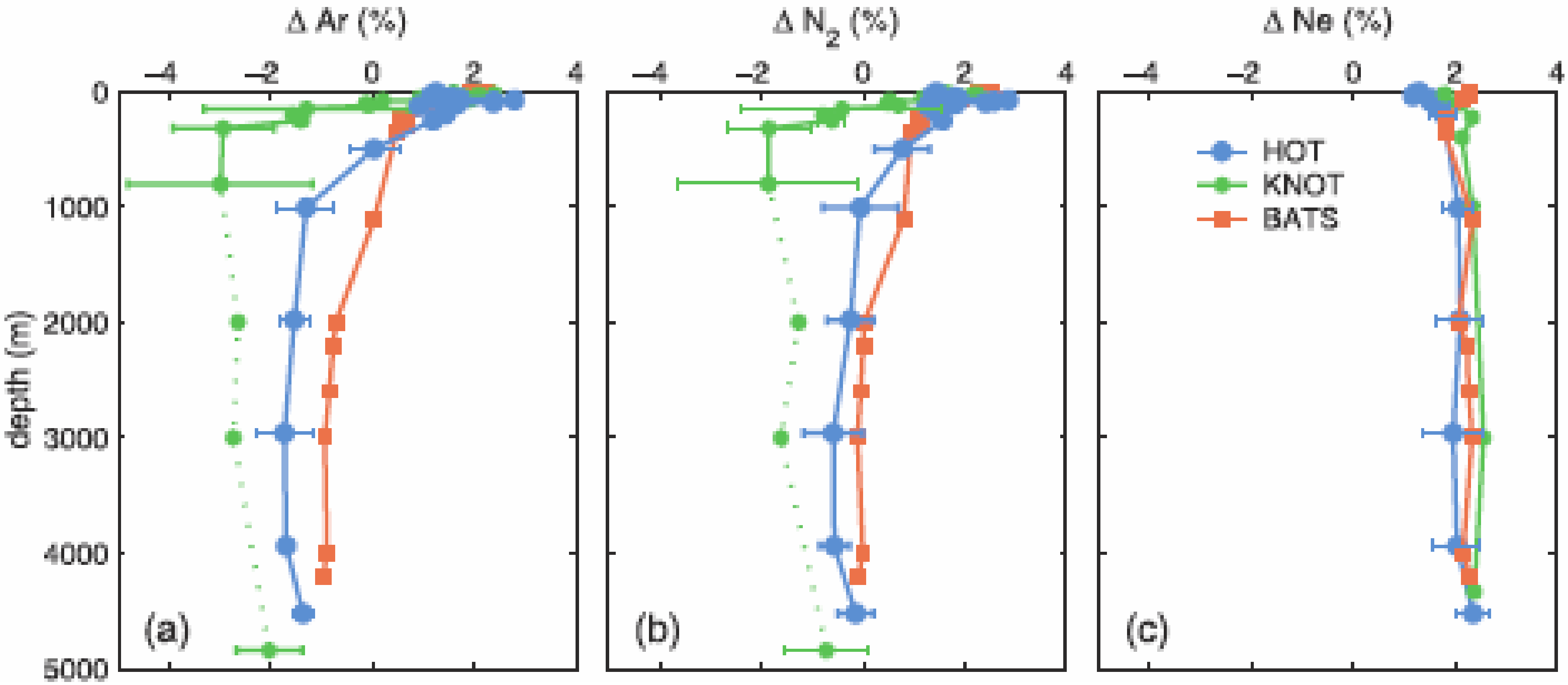
2. Diffusion coefficients are approximately double in bubbles

3. Bubbles are pushed to depths of 20 m (P_t ~ 3 atm)

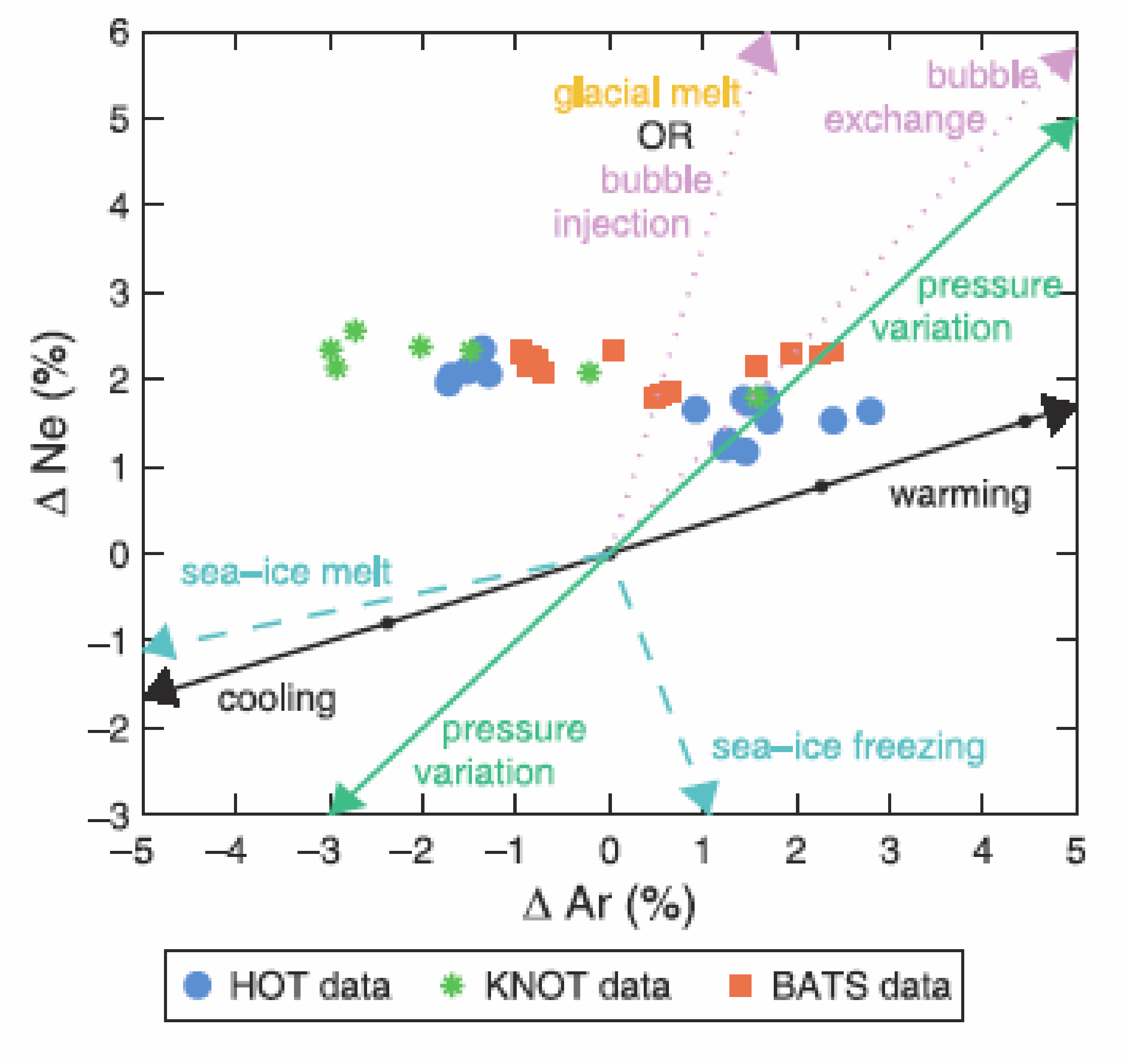
4. Air Injection- the total dissolution of the air in a bubble due to hydrostatic pressure

Gas	N_2	O_2	Ar	CO_2	Ne	He	Kr
Δ% sat	+7.7	+3.8	+3.5	+0.1	+11.6	+13.8	+1.8

From the total dissolution of a bubble (1 cm^3) of air at STP (15°C and S =35) in 1 m^3


Δ Ar (%)
Δ N$_2$ (%)
Δ Ne (%)
−4
−2
0
2
4
depth (m)
0
1000
2000
3000
4000
5000
(a)
(b)
(c)
HOT
KNOT
BATS

Hamme & Emerson, 2002



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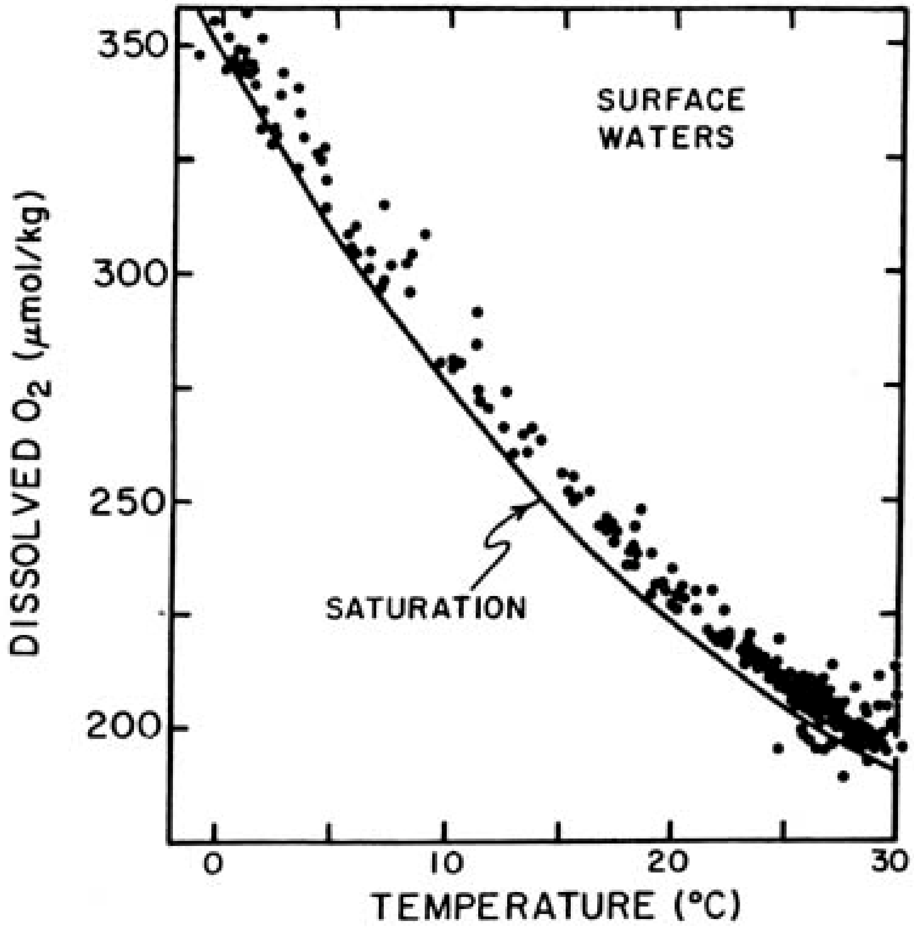
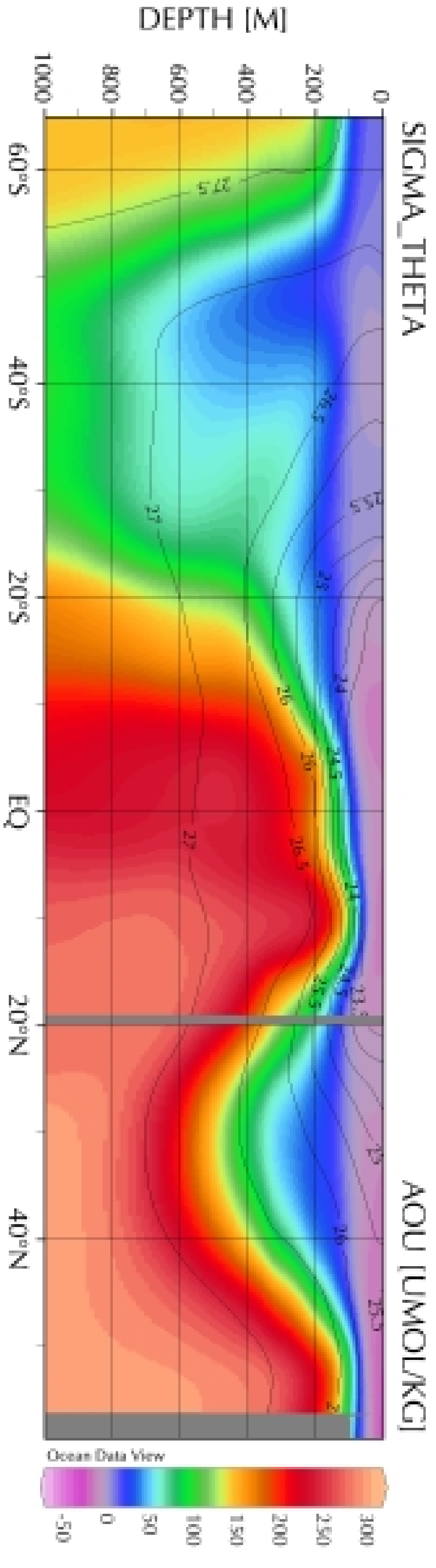
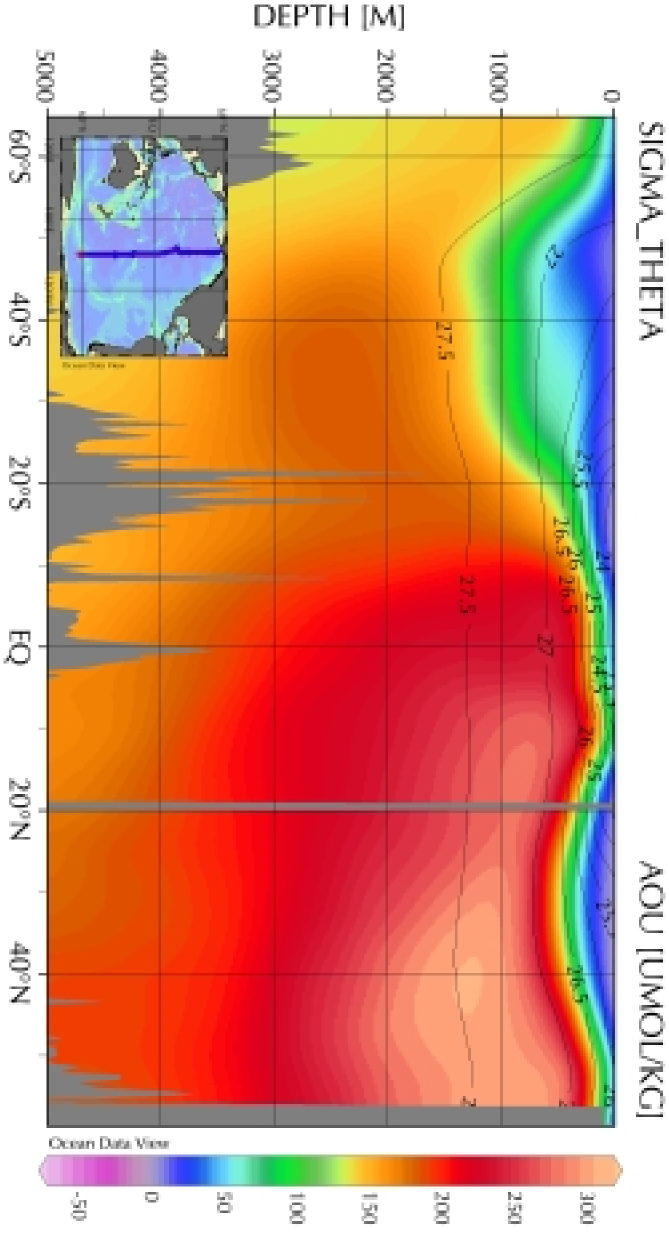
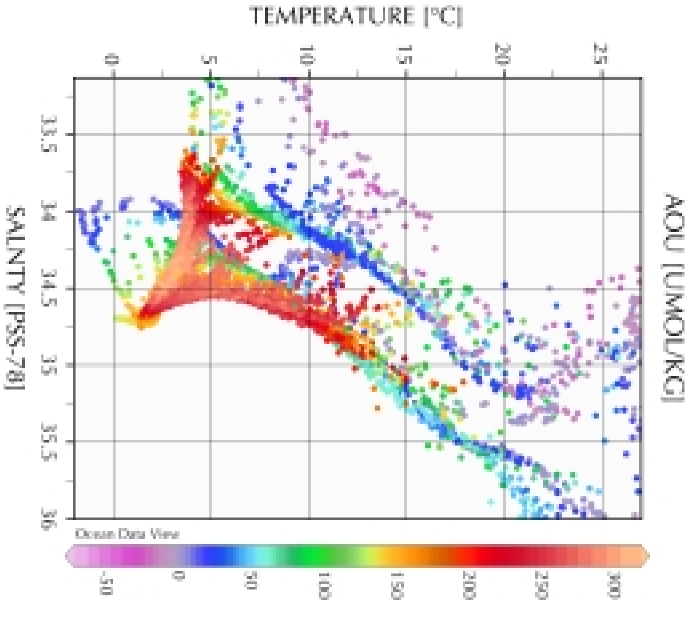
$$\% \ O_2 \text{ sat} = O_2 \text{ obs}/O_2 \text{ sat} \times 100$$

AOU = O2 sat - O2 obs




DEPTH [M]
0
200
400
600
800
1000
SIGMA_THETA
AOU [UMOL/KG]
60°S
40°S
20°S
EQ
20°N
40°N
27.5
26.5
25.5
27
25
26
24
24.5
23.5
Ocean Data View
-50
0
50
100
150
200
250
300


DEPTH [M]
0
1000
2000
3000
4000
5000
SIGMA_THETA
AOU [UMOL/KG]
60°S
40°S
20°S
EQ
20°N
40°N
27
27.5
25.5
26.5
26
25
24.5
Ocean Data View
-50
0
50
100
150
200
250
300


TEMPERATURE [°C]
0
5
10
15
20
25
SALNTY [PSS-78]
33.5
34
34.5
35
35.5
36
AOU [UMOL/KG]
Ocean Data View
-50
0
50
100
150
200
250
300

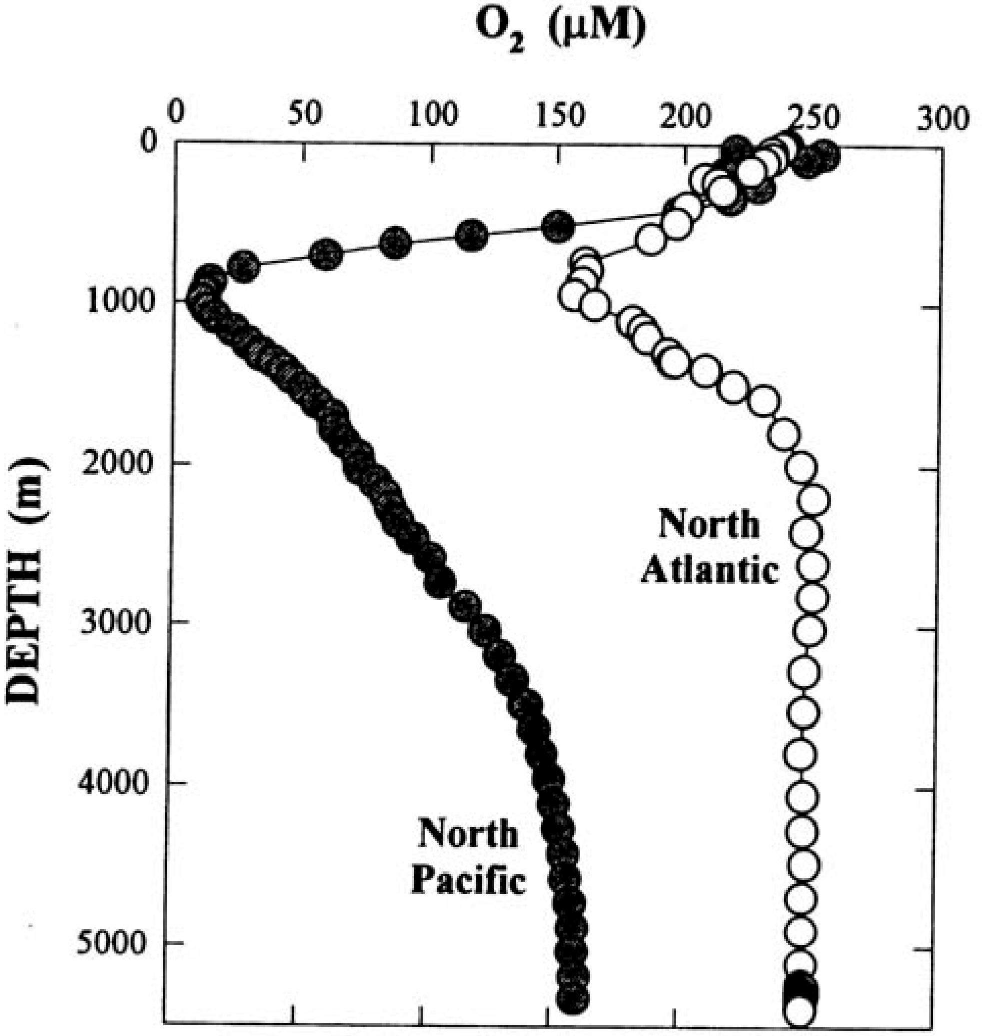


FIGURE 6.9. Profiles of oxygen in the North Atlantic and Pacific Oceans.

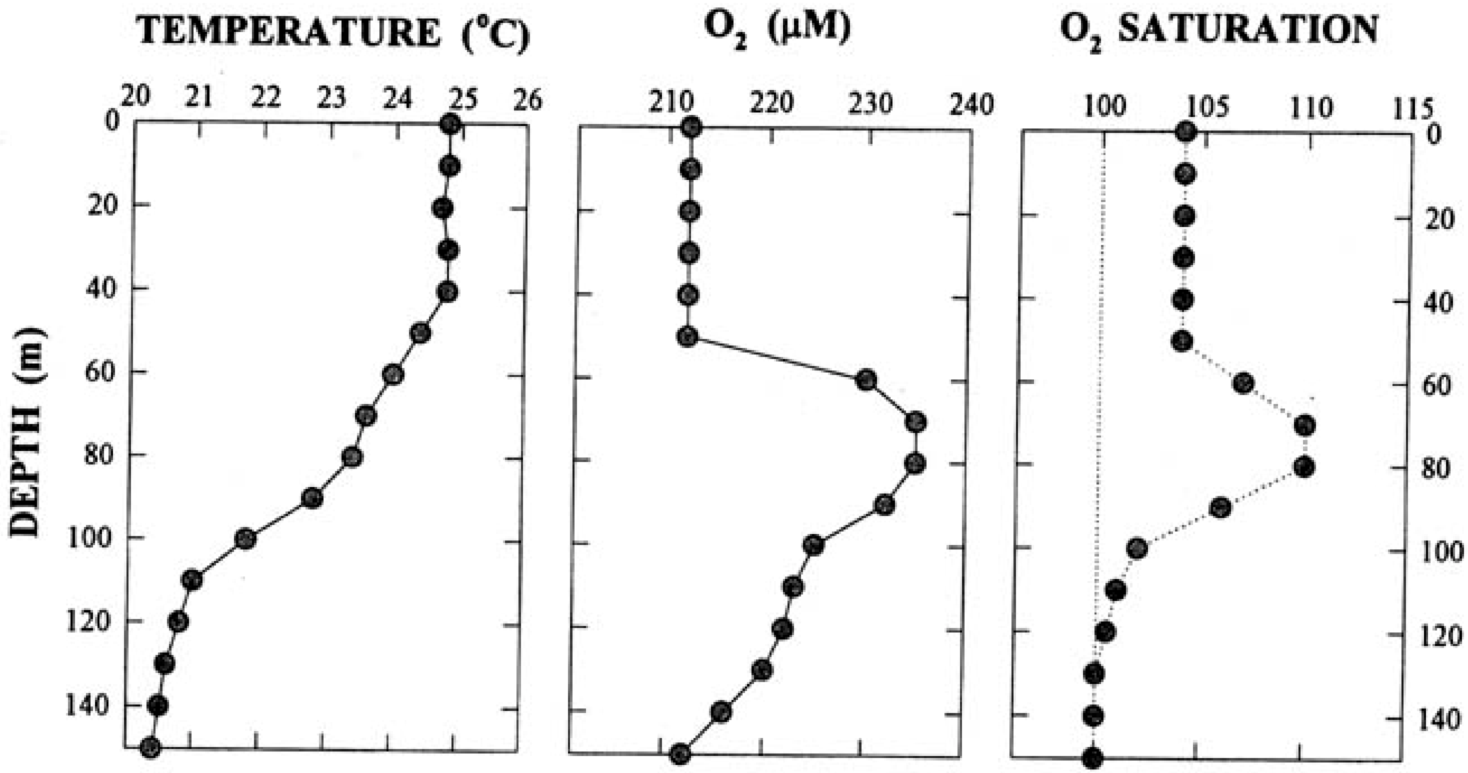


FIGURE 6.11. Profiles of temperature and oxygen in Pacific waters showing increases due to photosynthesis.

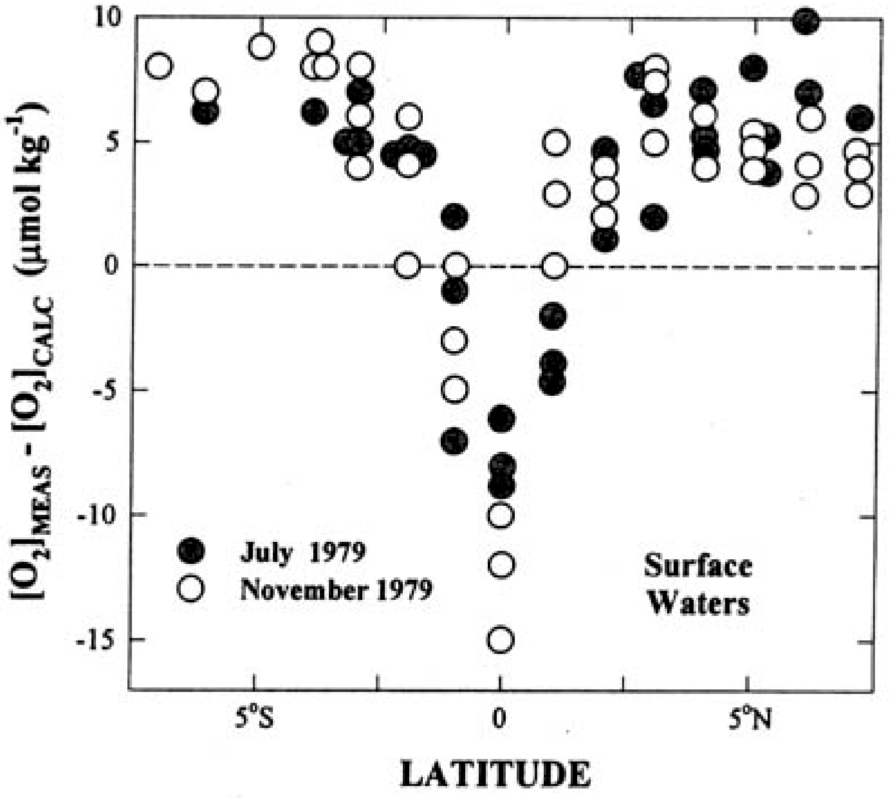


FIGURE 6.15. Differences in the measured and calculated dissolved oxygen concentrations in surface waters.

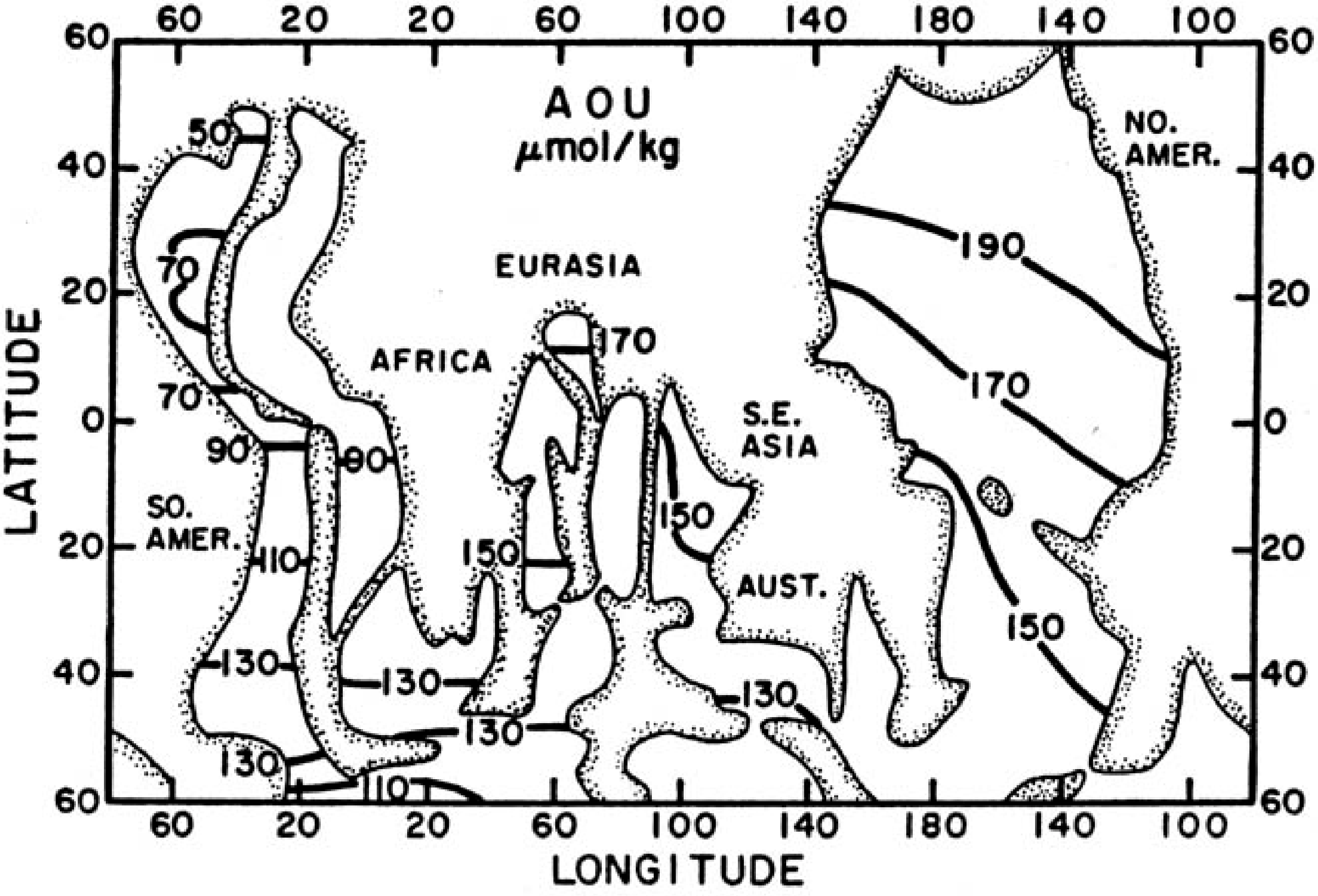


FIGURE 6.16. Apparent oxygen utilization in deep waters of the world oceans.

METHODS OF MEASUREMENT

1. Direct measurement in solution

   (O_2). Winkler Method for Oxygen

   A. $MnSO_4$ + NaOH Fixing Agent

   $$Mn^{2+} + 2\,OH^- \rightarrow Mn(OH)_2$$
   $$2\,Mn(OH)_2 + O_2 \rightarrow 2\,MnO(OH)_2$$

   B. Add KI, HCl and titrate with $S_2O_3^{2-}$

   $$MnO(OH)_2 + 4H^+ + 2\,I^- \rightarrow$$
   $$Mn^{2+} + I_2 + 3H_2O\,,\; I_2 + I^- \rightarrow I_3^-$$

   $$I_3^- + 2\,S_2O_3^{2-} \rightarrow 3\,I^- + S_4O_6^{2-}$$

2. Gas Chromatography (O_2,N_2,Ar,CO,CH_4)

3. Mass Spectrometry (low or non-reactive gases)