

Dissolved Gases in Seawater

- Fundamentals
- Solubility Relationships
- Air-Sea Exchange
- Departures from Ideality
- O₂ Dynamics (Intro)

DISSOLVED GASES IN THE OCEANS

SOURCES

1. Atmosphere (Major Term)

(N₂, O₂, Ar, etc.)

2. Marine Production & Consumption Processes

a) Biological Activity

(NO₃⁻ → N₂O, respiration)

b) Radioactive Decay

(²²⁶Ra → ²²²Rn)

3) Submarine Volcanic Activity (³He)

BASIC CONCEPTS

I. Dalton's Law

$$P_T = \sum P_i \sim P_{N_2} + P_{O_2} + P_{Ar} + P_{H_2O} + P_{CO_2}$$

II. Ideal Gas Law

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

$$\text{III. } P_i = X_i [P_T - P_{H_2O}], \quad P_{H_2O} = (h/100) P_{H_2O-Sat}$$

IV. Henry's Law

$$C_i = K_i [P_i] \quad P_i \sim f_i$$

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

$$K_i = f(T, S, P)$$

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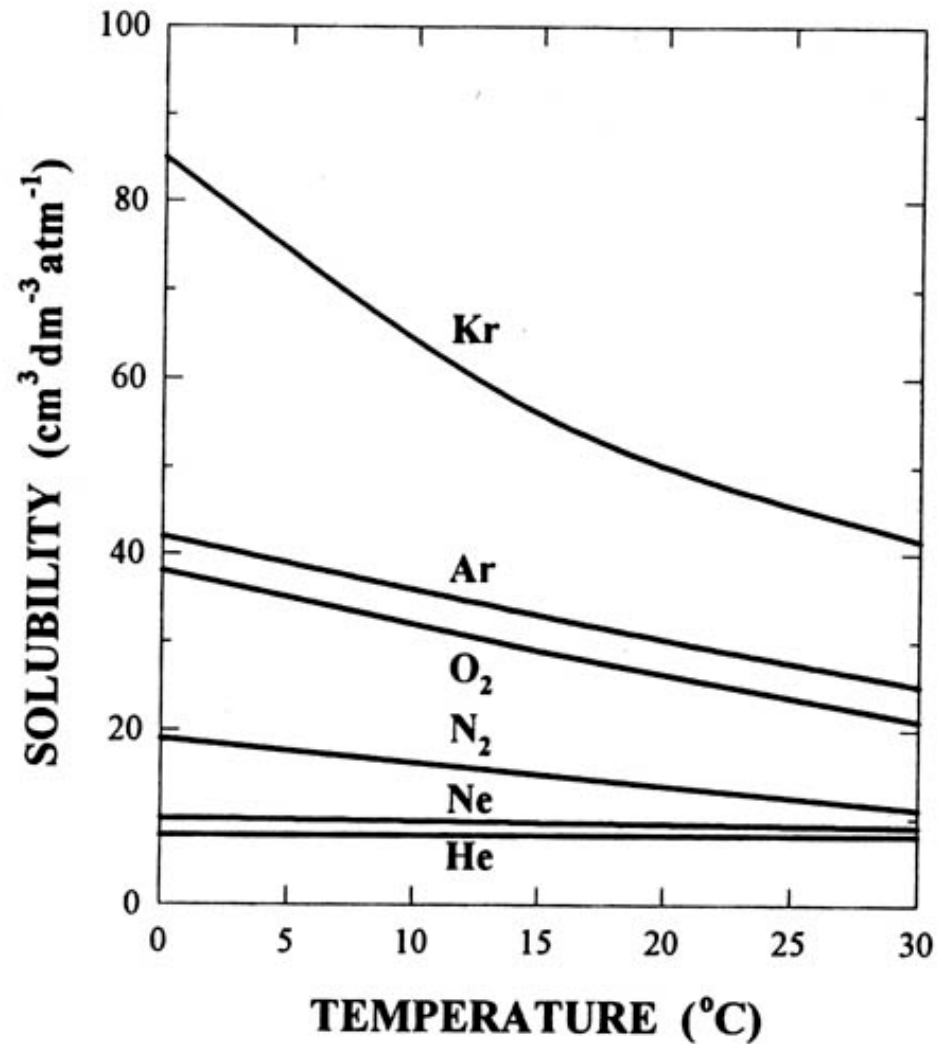


FIGURE 6.5. The effect of temperature on the solubility of gases in seawater.

Table 3.6. Solubilities of the major atmospheric gases in seawater ($s=35$) at one atmosphere pressure and 20°C

X_c is the mole fraction in a dry atmosphere (Glueckauf, 1951); $K_{H,C}$, the Henry's Law coefficient; C^s , the concentration in seawater at saturation equilibrium with the atmosphere. Saturation concentrations and Henry's Law coefficients for N_2 , O_2 , Ar, CO_2 , Ne and He are calculated by using the equations in Table 3A1.1. Values for Kr, CH_4 and N_2O are from the compilation in Wanninkhof (1992). No correction was made here for the difference between the volume of the solvent and the solution in β and α (see text).

Gas	X_c	$K_{H,C}$	C^s	β^b	α^c
	($\text{mol}_g \text{mol}_{atm}^{-1}$)	($\text{mol kg}^{-1} \text{atm}^{-1}$)	($\mu\text{mol kg}^{-1}$)	$(\text{cm}^3_g)/(\text{cm}^3_{sw})$	
N_2	7.8084×10^{-1}	5.51×10^{-4}	4.21×10^2	1.27×10^{-2}	1.36×10^{-2}
O_2	2.0946×10^{-1}	1.10×10^{-3}	2.25×10^2	2.53×10^{-2}	2.71×10^{-2}
Ar	9.34×10^{-3}	1.21×10^{-3}	1.10×10^1	2.78×10^{-2}	2.98×10^{-2}
CO_2	3.65×10^{-4}	3.24×10^{-2}	1.16×10^1	7.44×10^{-1}	7.98×10^{-1}
Ne	1.818×10^{-5}	3.84×10^{-4}	6.83×10^{-3}	8.82×10^{-3}	9.47×10^{-3}
He	5.24×10^{-6}	3.29×10^{-4}	1.66×10^{-3}	7.47×10^{-3}	8.01×10^{-3}
Kr	1.14×10^{-6}	2.20×10^{-3}	2.44×10^{-3}	5.05×10^{-2}	5.42×10^{-2}
CH_4	1.6×10^{-6}	1.21×10^{-3}	1.89×10^{-3}	2.78×10^{-2}	2.97×10^{-2}
N_2O	5.0×10^{-7}	2.34×10^{-2}	1.14×10^{-2}	5.37×10^{-1}	5.77×10^{-1}

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 ₂ O	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 3A1.1. Coefficients used in the fitting equations for air saturation (C^s) and Henry's Law coefficients (K_H) of gases in seawater (Table 3.6)

The coefficients and fitting equations in the footnotes are for saturation values of O_2 , N_2 , Ar, Ne, and He in units of $\mu\text{mol kg}^{-1}$ and ml kg^{-1} . Values can be transformed between these units by using the real gas molar volumes calculated from Van der Waals constants (22.385 9, 22.391 9, 22.386 9, 22.422 4 and 22.436 9 mol^{-1} for O_2 , N_2 , Ar, Ne, and He, respectively). The fitting equation for CO_2 is for the Henry's Law coefficient, K_H ($\text{mol kg}^{-1} \text{atm}^{-1}$) instead of the saturation concentration.

Coefficient	O_2^a	N_2^b	Ar ^b	Ne ^b	He ^c	K_{H,CO_2}^d
		($\mu\text{mol kg}^{-1}$)		(nmol kg^{-1})	(ml kg^{-1})	($\text{mol kg}^{-1} \text{atm}^{-1}$)
A_0	5.808 710	6.432 41	2.791 63	2.181 40		
A_1	3.202 910	2.927 58	3.177 14	1.289 31	-67.217 8	-60.240 9
A_2	4.178 870	4.303 51	4.136 58	2.122 35	216.344 2	93.451 7
A_3	5.100 060	4.266 73	4.866 32		139.203 2	23.358 5
A_4	-0.098 664				-22.620 2	
A_5	3.803 690					
B_0	-0.007 016	-0.007 443 16	-0.006 963 17	-0.005 947 22		
B_1	-0.007 700	-0.007 999 36	-0.007 683 87	-0.005 093 70	-0.044 781	0.023 517
B_2	-0.013 86	-0.001 529 48	-0.001 190 78		0.023 541	-0.023 656
B_3	-0.009 515				-0.0034266	0.0047035
C_0	$-2.759 150 \times 10^{-7}$					
$[C]^s$ at 20 °C 35 ppt	225.5	420.5	11.08	6.826	3.729×10^{-5}	0.0324

^a Garcia and Gordon (1992): $\ln C^s = A_0 + A_1 T_s + A_2 T_s^2 + A_3 T_s^3 + A_4 T_s^4 + A_5 T_s^5 + S(B_0 + B_1 T_s + B_2 T_s^2 + B_3 T_s^3) + C_0 S^2$;

where $T_s = \ln \{(298.15 - t)(273.15 + t)^{-1}\}$ and t is temperature (°C).

^b Hamme and Emerson (2004): same equation as in ^a.

^c Weiss (1971): $\ln C^s = A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100) + S\{B_1 + B_2(T/100) + B_3(T/100)^2\}$, where T is absolute temperature.

^d Weiss (1974): $\ln K_{H,CO_2} = A_1 + A_2(100/T) + A_3 \ln(T/100) + S\{B_1 + B_2(T/100) + B_3(T/100)^2\}$, where T is absolute temperature.

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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

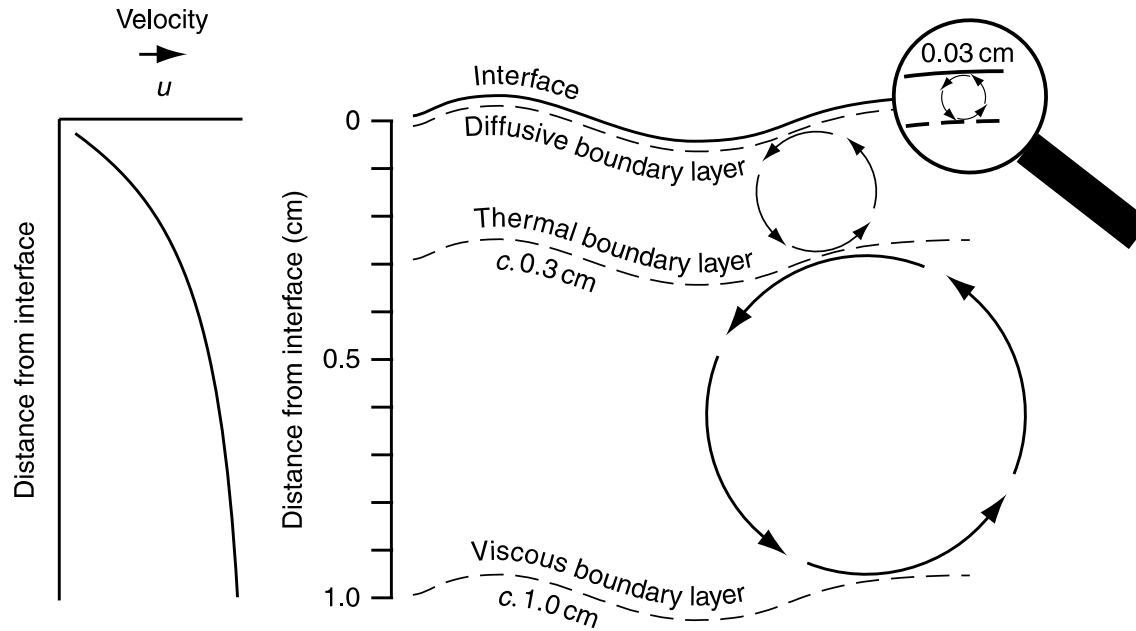
D_i = diffusion coefficient

Z = thickness of diffusion layer

Table 10.1. Molecular diffusion coefficients, D , and Schmidt numbers, Sc , for gases

The molecular diffusion coefficients, D (in units of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$; see note ^a), were determined from the equations presented in Chapter 9, Table 9.1. The kinematic viscosity of water is from Pilson (1998). The kinematic viscosity is 3%–5% greater in seawater than in freshwater, and we assume here that this is the only factor causing a salinity dependence on Sc . Opposite trends with T for diffusion coefficients and kinematic viscosity create greater temperature dependence for Schmidt numbers than for the molecular diffusion coefficients.

Gas	$D (\times 10^5)^a$ ($\text{cm}^2 \text{ s}^{-1}$)		Sc^b ($S=0$)		Sc^c ($S=35$)	
	5 °C	20 °C	5 °C	20 °C	5 °C	20 °C
N ₂	1.63	2.52	931	398	958	415
O ₂	1.49	2.24	1019	448	1048	467
Ar	1.42	2.23	1070	450	1100	469
CO ₂	1.09	1.68	1394	598	1433	623
Ne	2.62	3.65	580	275	596	287
He	5.19	6.73	293	149	310	155
Kr	1.03	1.61	1475	624	1516	650
Xe	0.79	1.27	1923	791	1977	823
CH ₄	1.09	1.63	1394	616	1433	642



erent distances from the wall where molecular motions become as important as eddy motions for transport. The scales are called the viscous (momentum), thermal (heat) and diffusive (molecular) boundary layers near the interface.

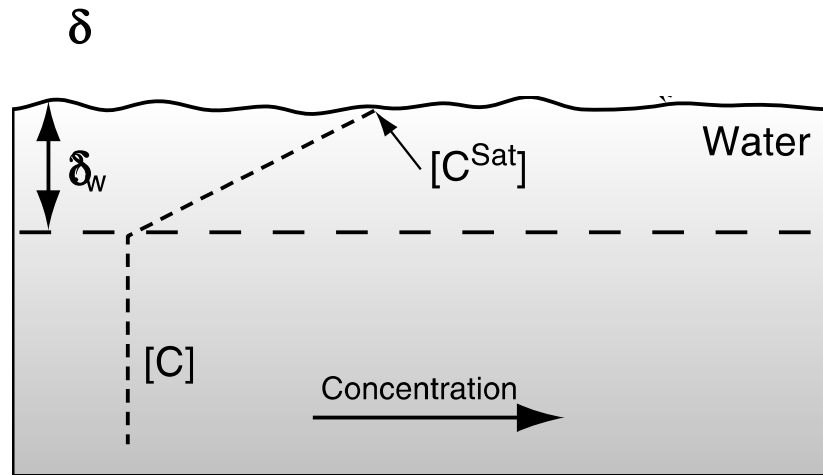
Models for Air-Sea Gas Exchange

1) Stagnant Film (simplest)

2) Surface Renewal

3) Rigid Wall (Mathematically complex)

ion in the water are indicated by f^a and $[C]$, respectively. Chemical equilibrium at the air–water interface is described by Henry’s Law, where $K_H f^a = [C^{Sat}]$.



Combining Henry's and Fick's Laws:

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

where:

τ = thickness of boundary layer

More simply:

$$F_i = dC_i/dt \times A^{-1} = G_c K_i \Delta P_i$$

$$G_c = G^* (D_i/\nu)^n = G^* (Sc_i)^{-n}$$

Where:

F = flux (mol cm⁻² s⁻¹)

ΔP_i = change in partial pressure across interface (atm)

Sc_i = Schmidt number

ν = kinematic viscosity

G* = transfer velocity (cm s⁻¹)

= permeability coefficient

= mass transfer coefficient

= exit coefficient

= piston velocity

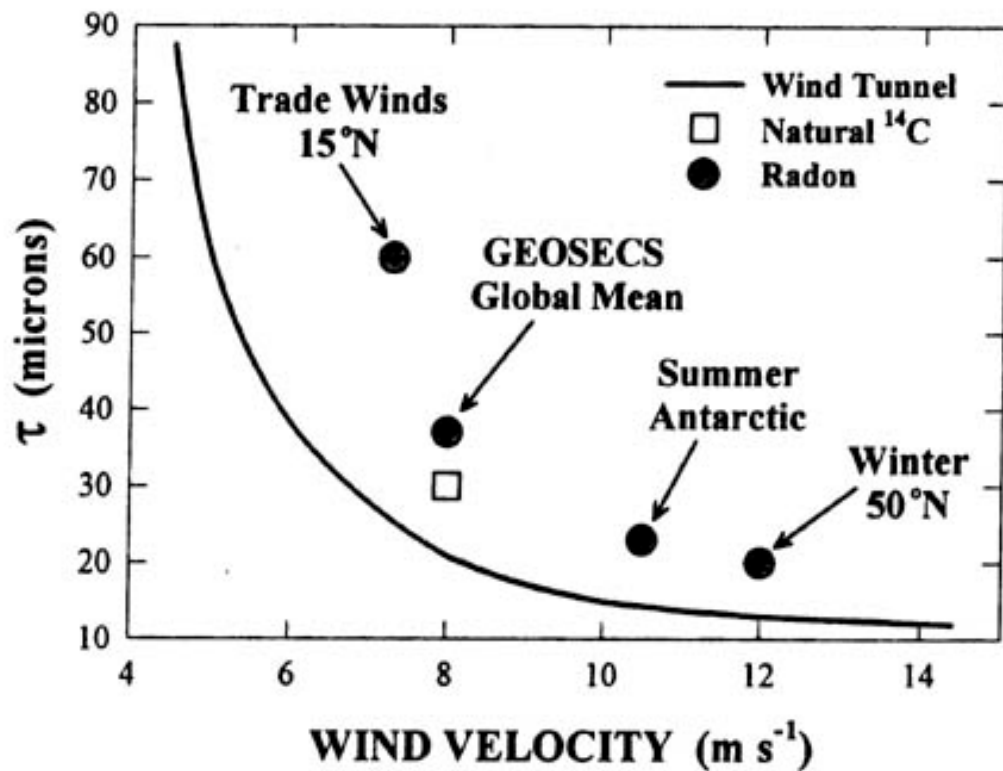


FIGURE 6.2. The thickness of the laminar layer as a function of the wind speed.

Models for Air-Sea Gas Exchange

1) Stagnant Film $G_c = D_i/\delta$

2) Surface Renewal $G_c = 2 (D_i/\pi \theta)^{0.5}$

θ is renewal time

3) Rigid Wall $G_c = U^* /12 (D_i/\nu)^{2/3}$
 $= U^* /12 (Sc_i)^{-2/3}$

U^* is the friction velocity at the interface

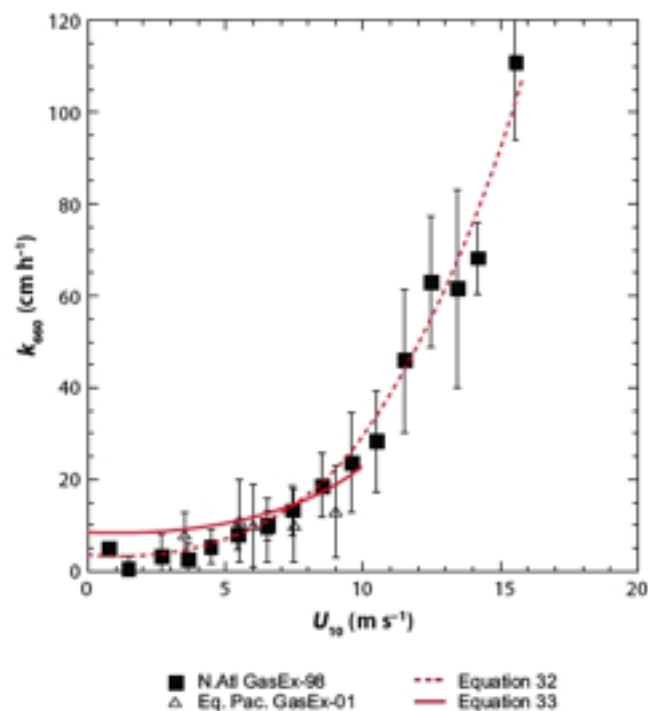


Figure 4

Comparison of CO_2 covariance flux measurements in the North Atlantic (*solid squares*) (McGillis et al. 2004) 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 a 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 Equati

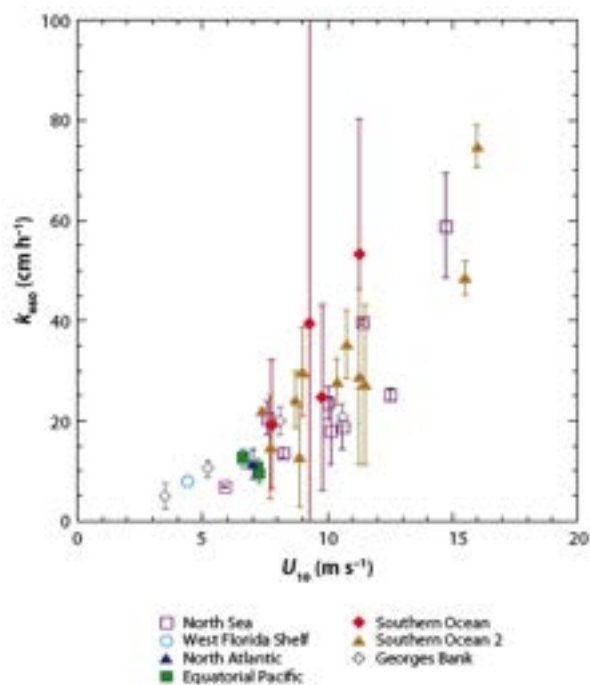


Figure 3

Summary of $^3\text{He}/\text{SF}_6$ dual-deliberate tracer results normalized to $\text{Sc} = 660$ 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 $^3\text{He}/\text{SF}_6$ 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).

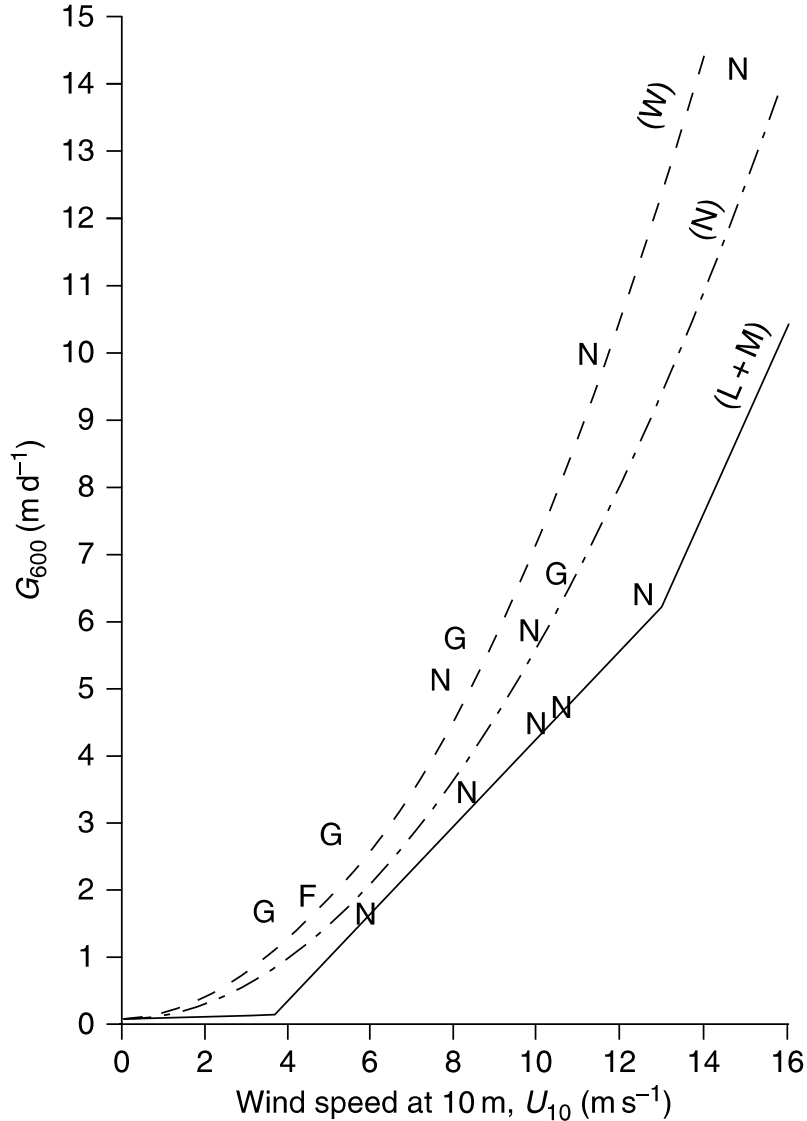


Figure 10.7. Gas transfer velocity, G_{600} , as a function of wind speed, U_{10} , for all dual tracer experiments. N is from the North Sea, G is from the Georges Bank and F from the Florida Shelf. Lines are the same as those described in the caption to Figure 10.6, with the addition of the one in the middle, which is the best fit through the dual tracer data ($G_{600} = \{0.23 \times U^2 + 0.1 \times U\} (Sc/600)^{-1/2}$, where U is in m s^{-1} and G is in cm h^{-1}). Redrawn from Nightingale *et al.* (2000).

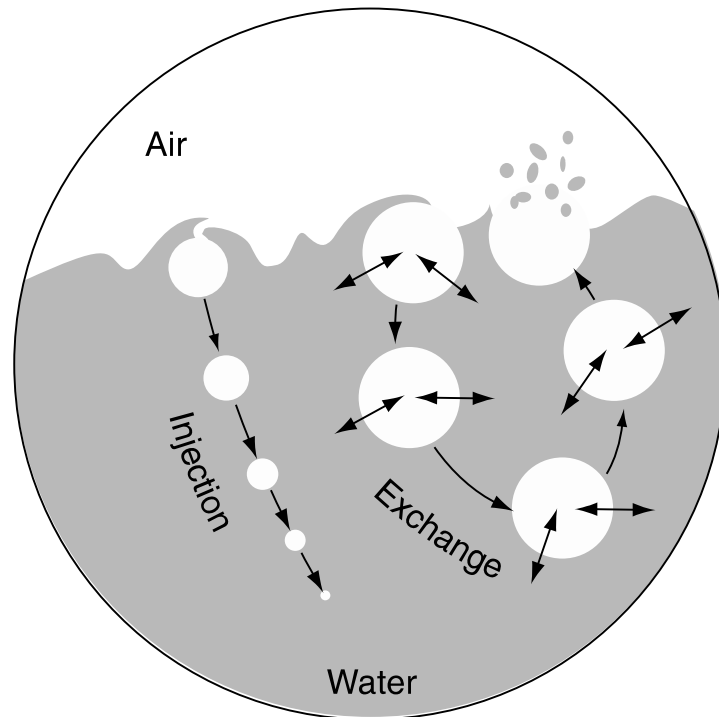
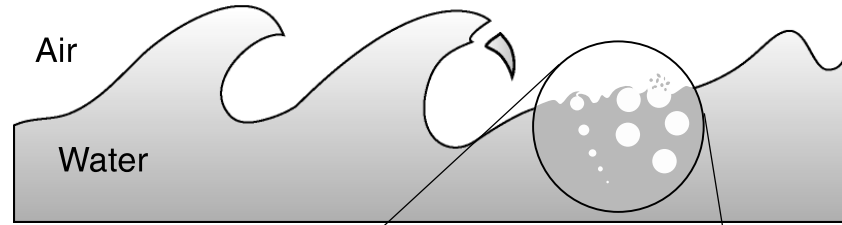
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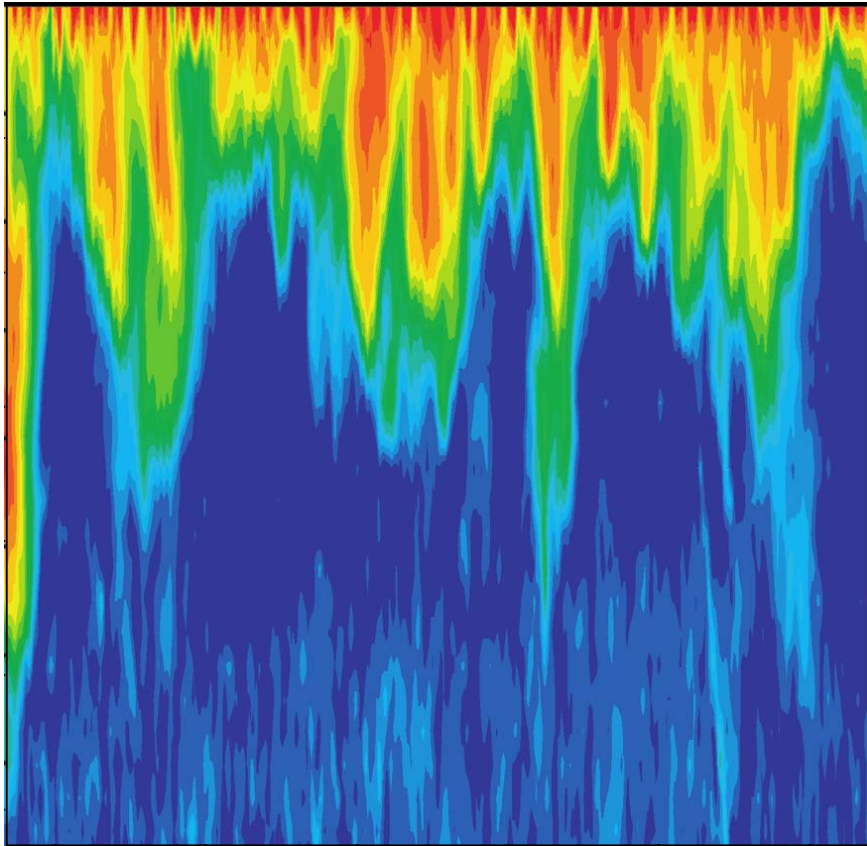
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Causes of Non-Reactive Gases Departing from Expected Solubility

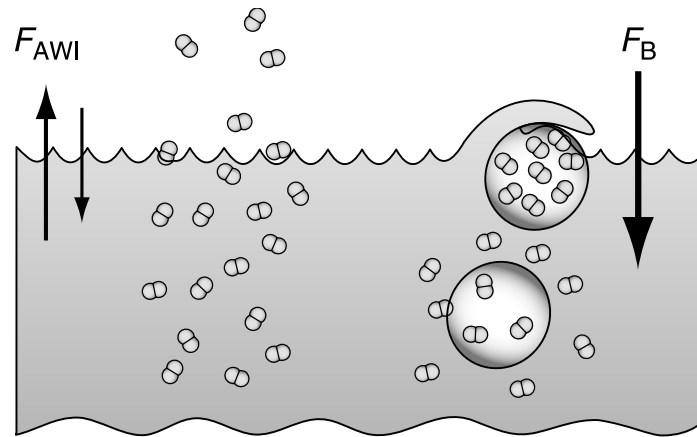
1. Departures from Standard Atmosphere
2. Dissolution and/or Collapse (Injection) of Air Bubbles
4. Heating/Cooling and Incomplete Gas Exchange
5. Mixing of Waters of Different Temperatures/Salinities

are submerged by waves and exchange their contents partly with the surrounding water before they resurface at the interface.





an indication of the depth of penetration of bubbles caused by breaking waves. (Data courtesy of Sven Vogel of the Institute of Ocean Sciences, Sidney, B. C.).



interface, F_{AWI} , indicated on the left side.

gram, is balanced by a diffusive flux across the air-water

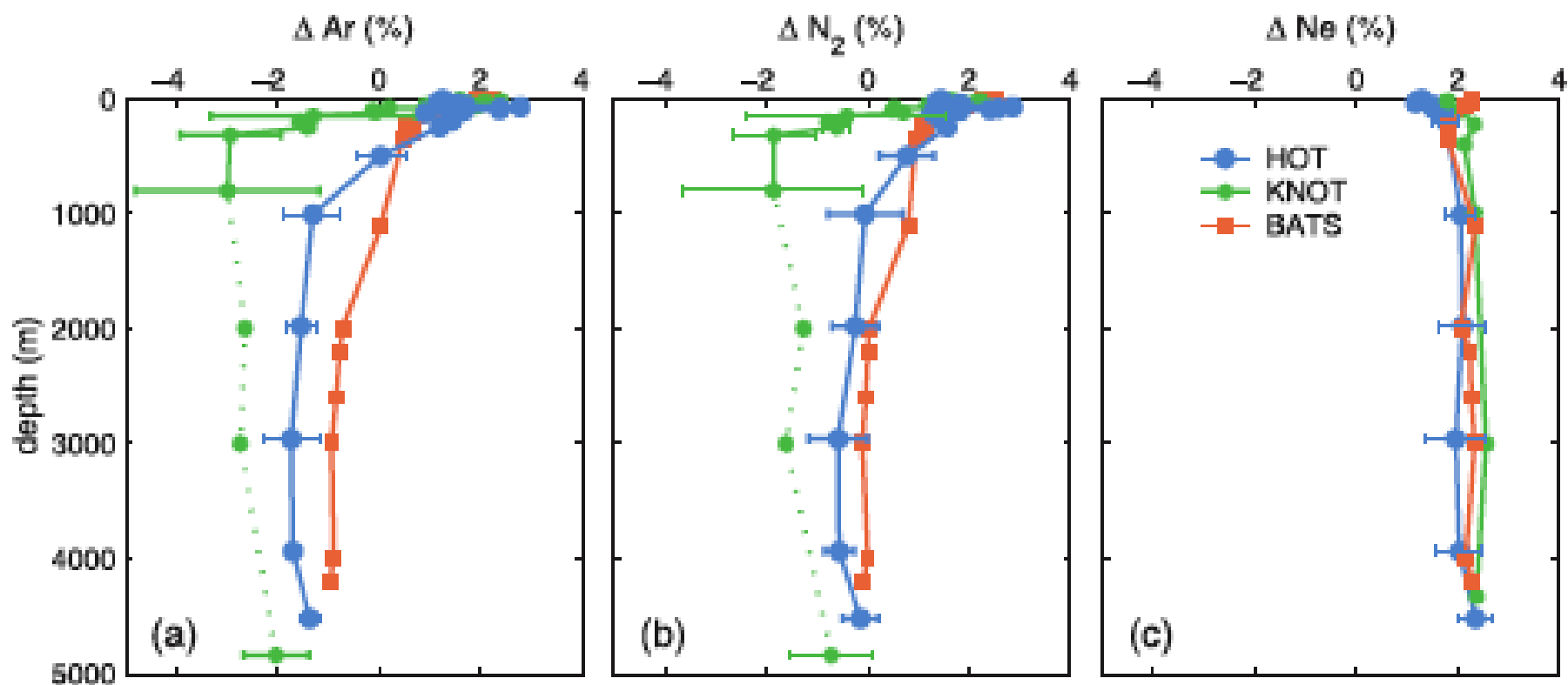
BUBBLE INJECTION EFFECTS

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 ($P_t \sim 3$ atm)
4. Air Injection- the total dissolution of the air in a bubble due to hydrostatic pressure

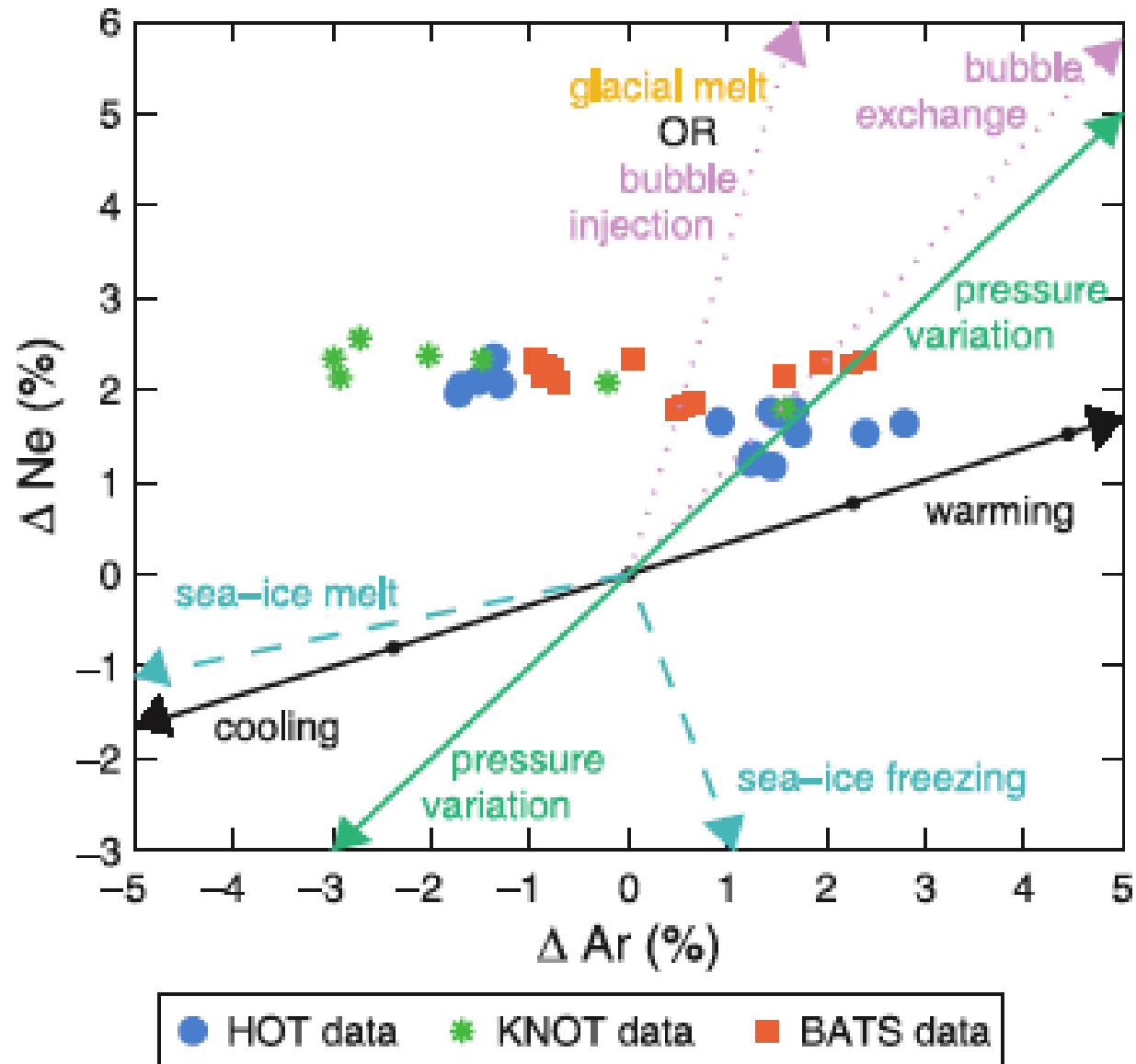
Gas	N ₂	O ₂	Ar	CO ₂	Ne	He	Kr
Δ% sat	+7.7	+3.8	+3.5	+0.1	+11.6	+13.8	+1.8

From the total dissolution of a bubble (1 cm³) of air at STP (15° C and S =35) in 1 m³

HAMME AND EMERSON: CONTROLS ON INERT GAS SATURATIONS



Hamme & Emerson, 2002

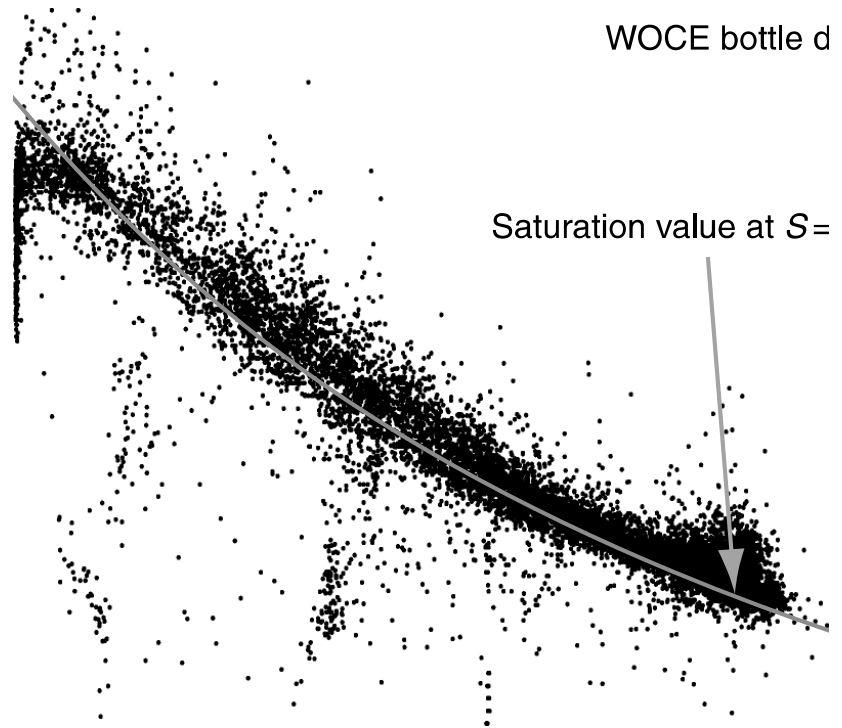


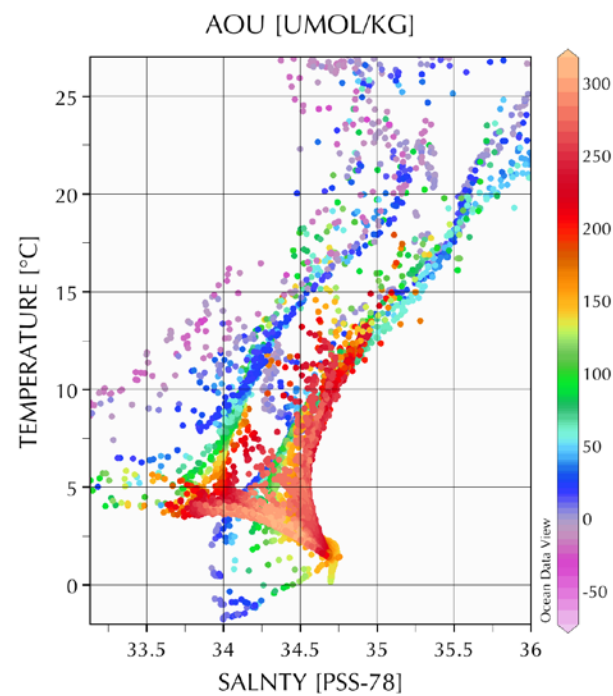
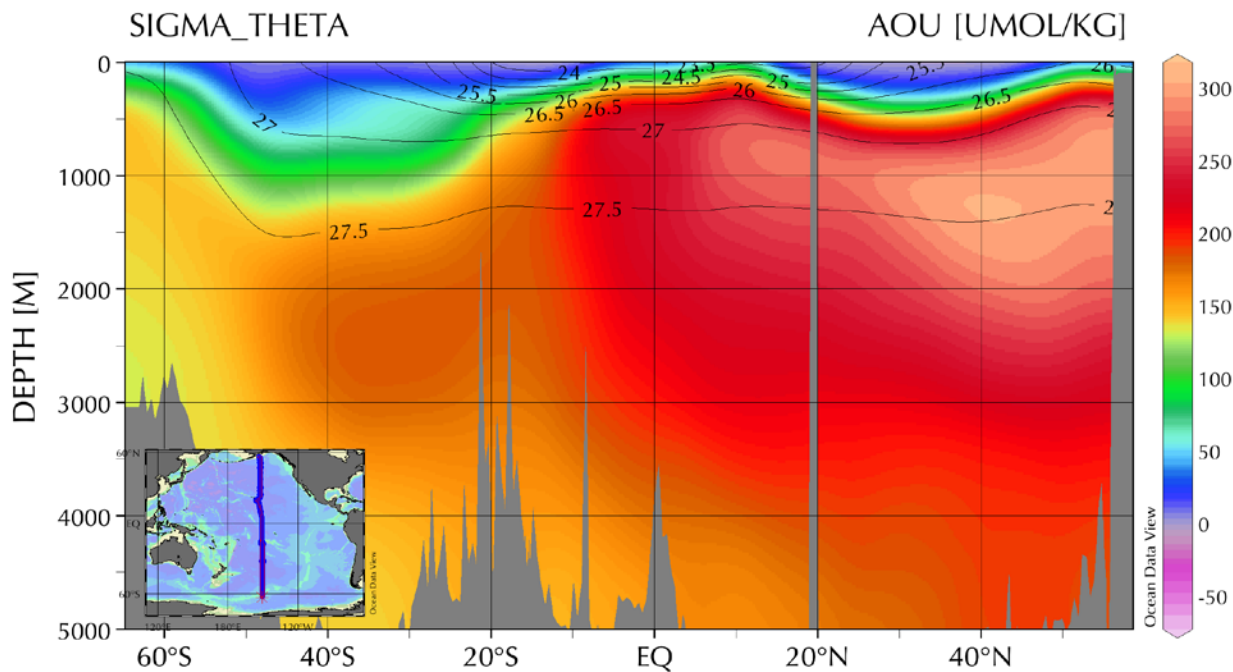
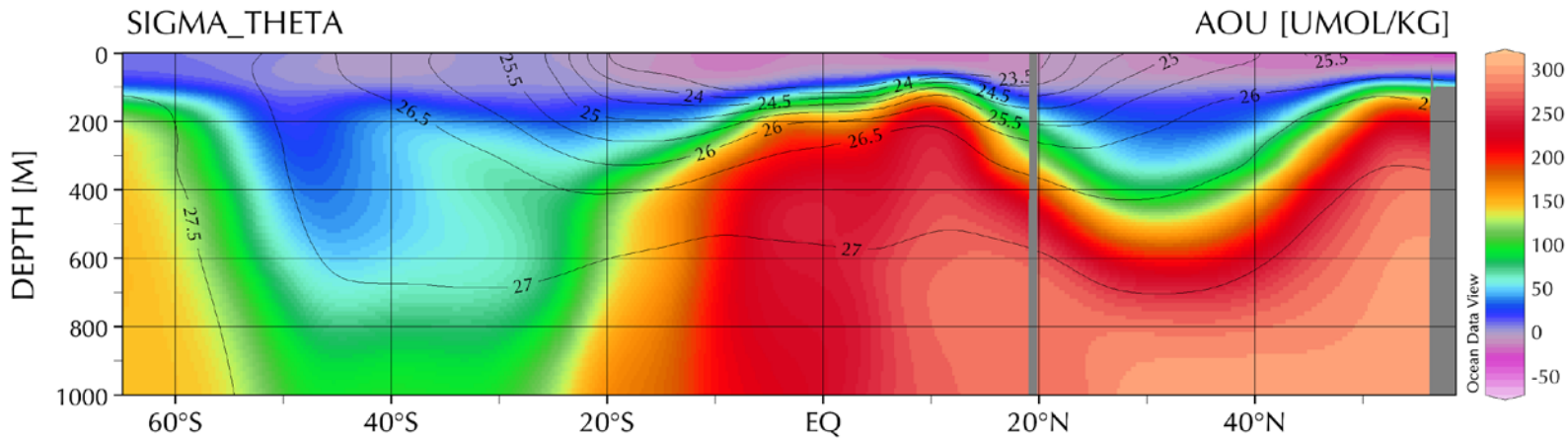
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$$\% \text{ O}_2 \text{ sat} = \text{O}_2 \text{ obs} / \text{O}_2 \text{ sat} \times 100$$
$$\text{AOU} = \text{O}_2 \text{ sat} - \text{O}_2 \text{ obs}$$

e saturation value with
atmospheric oxygen at a salinity
of 35.





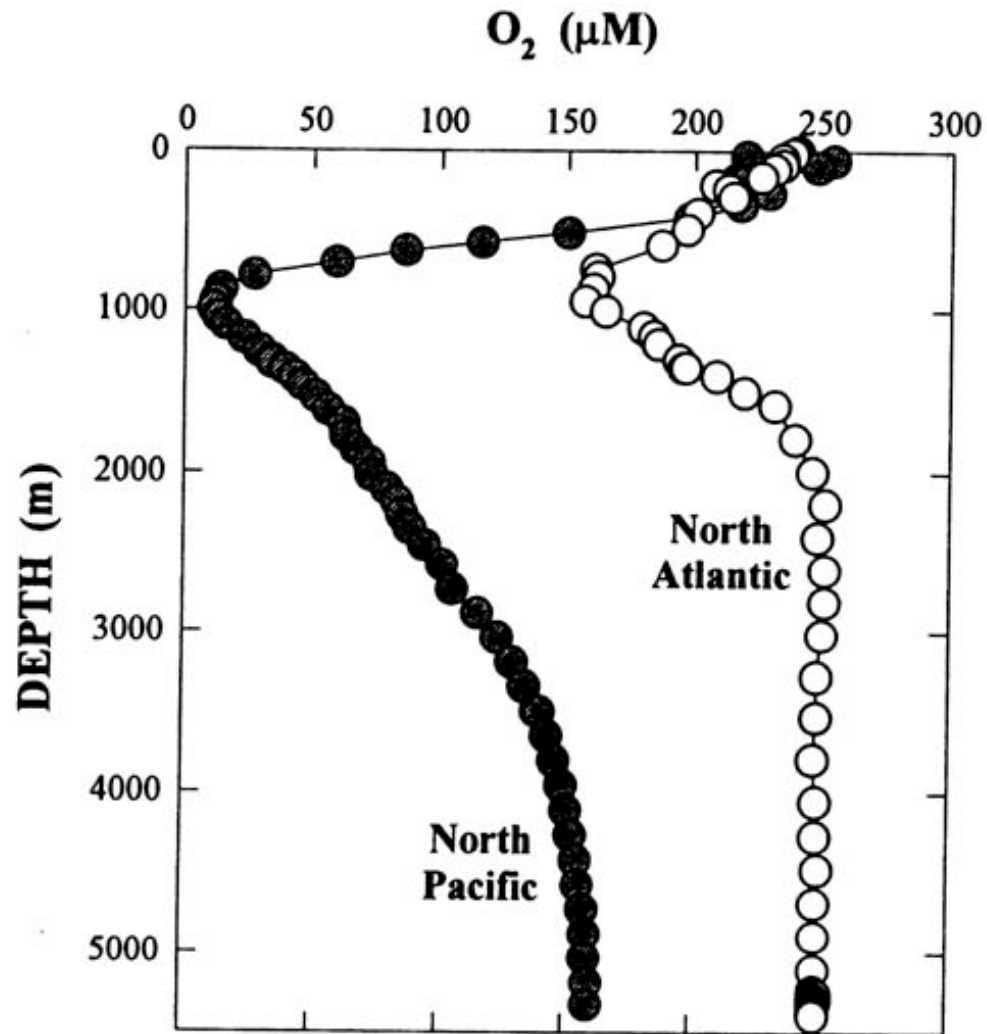


FIGURE 6.9. Profiles of oxygen in the North Atlantic and Pacific Oceans.

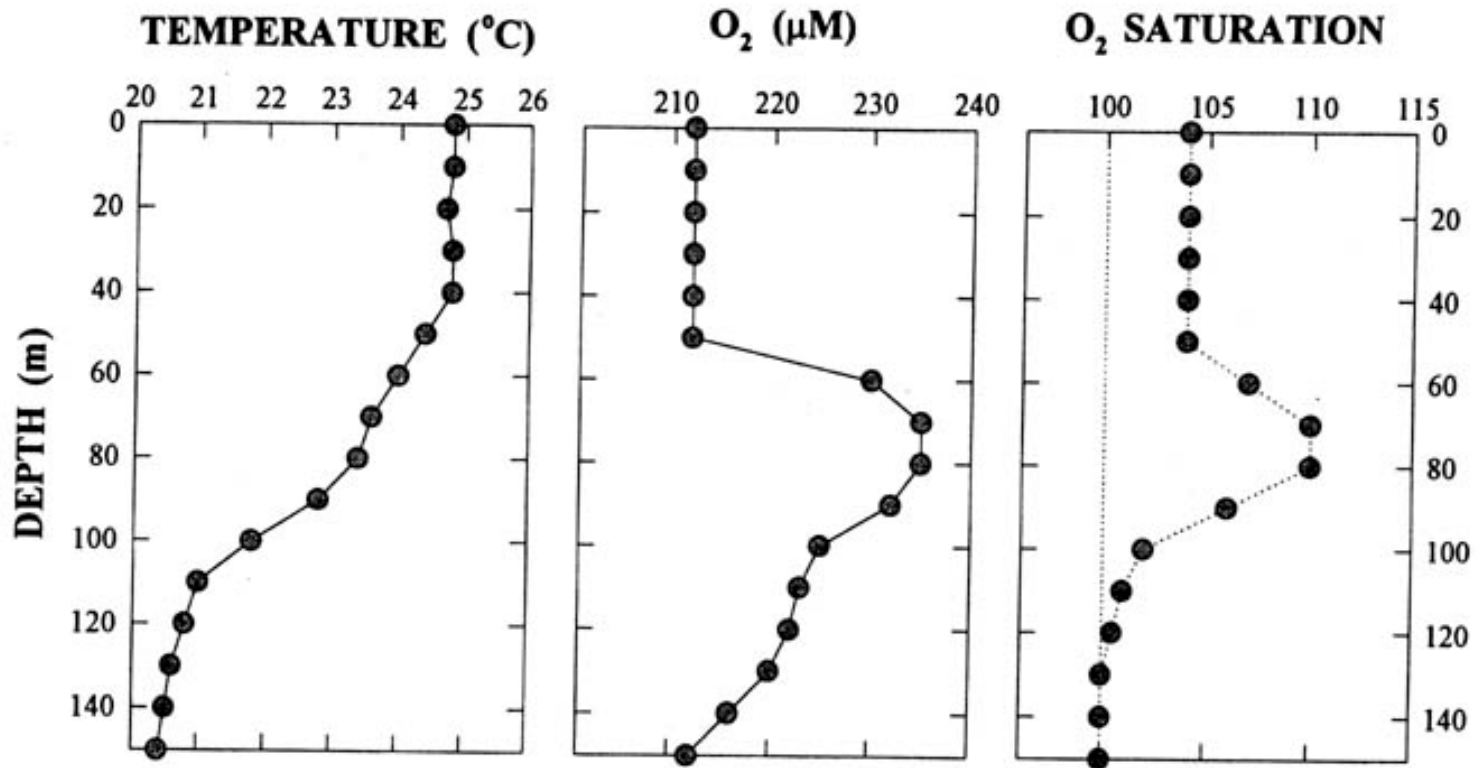


FIGURE 6.11. Profiles of temperature and oxygen in Pacific waters showing increases due to photosynthesis.

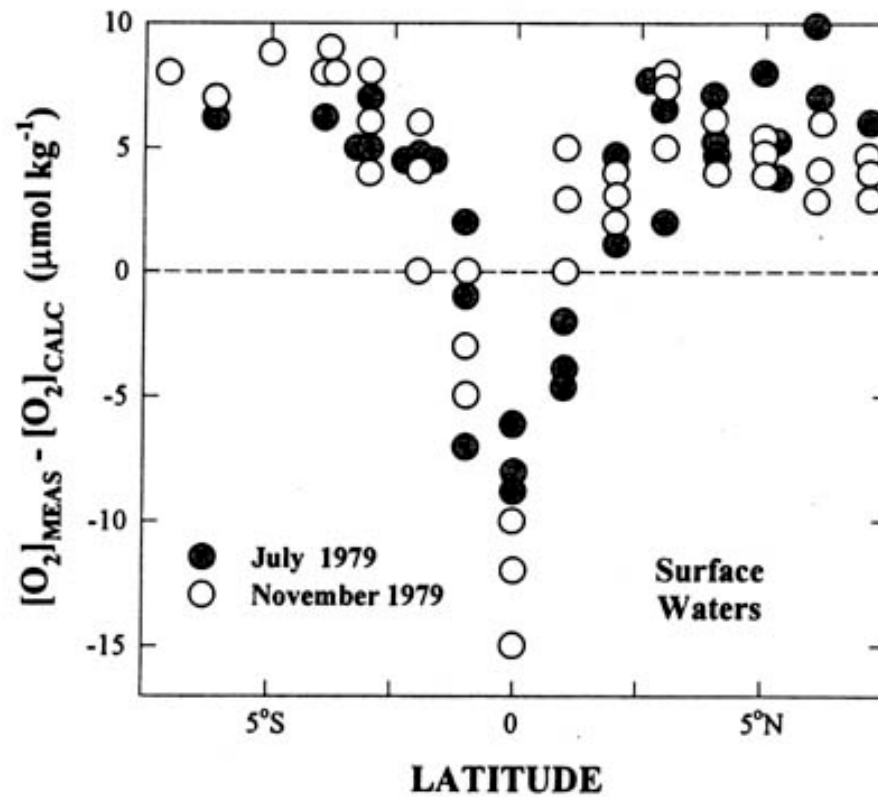


FIGURE 6.15. Differences in the measured and calculated dissolved oxygen concentrations in surface waters.

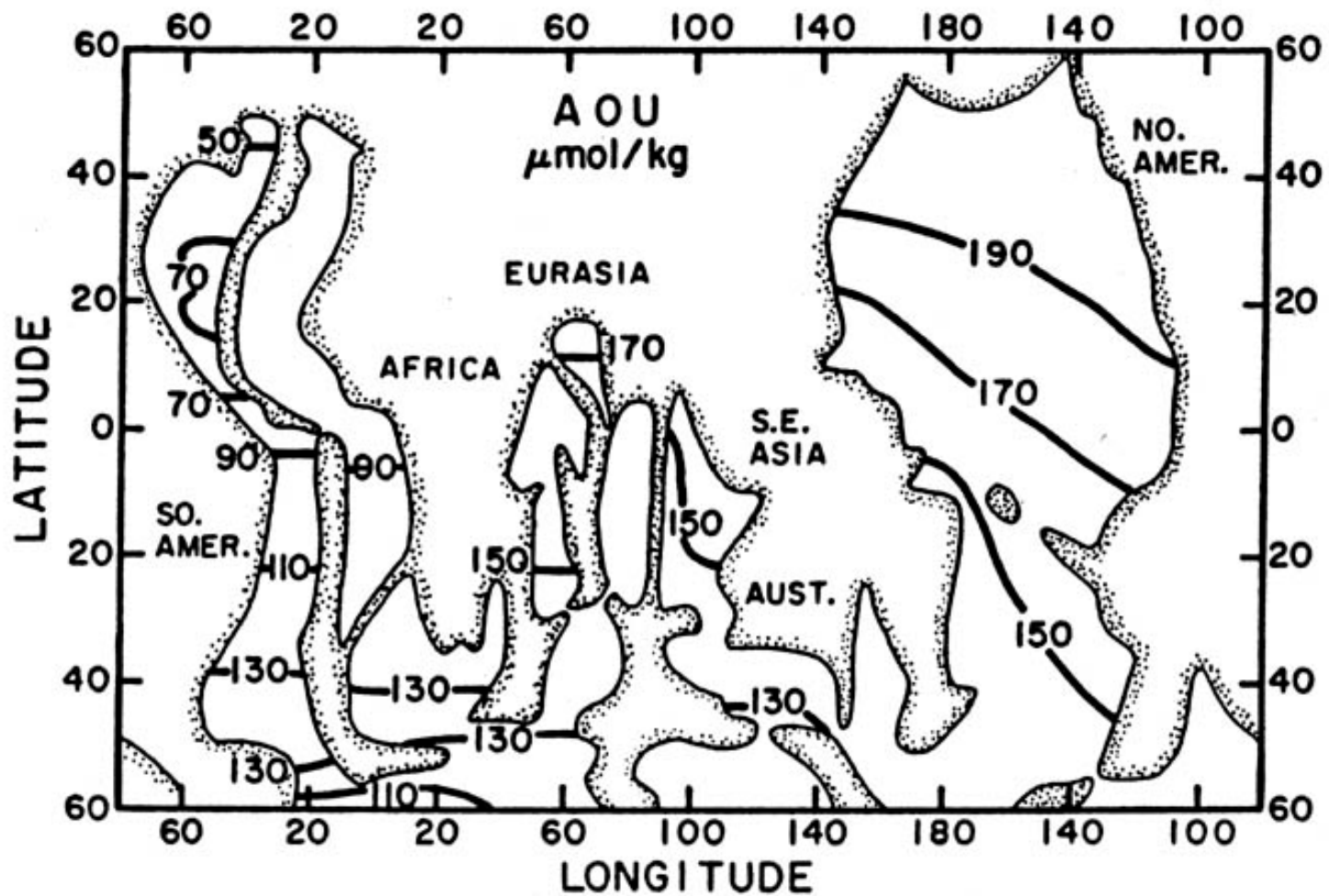


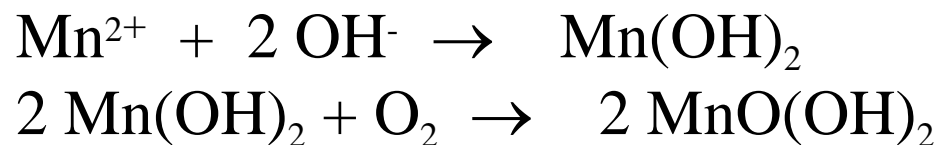
FIGURE 6.16. Apparent oxygen utilization in deep waters of the world oceans.

METHODS OF MEASUREMENT

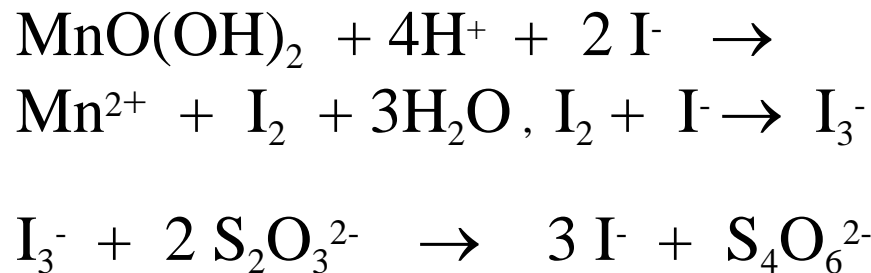
1. Direct measurement in solution

(O₂). **Winkler Method for Oxygen**

A. MnSO₄ + NaOH Fixing Agent



B. Add KI, HCl and titrate with S₂O₃²⁻



2. Gas Chromatography (O₂,N₂,Ar,CO,CH₄)

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