Dissolved Gases other than Carbon Dioxide in Seawater

OCN 623 – Chemical Oceanography

Reading: Libes, Chapter 6 – pp. 147-158

Outline

1. Basic concepts
   - Gas laws
   - Gas solubility and air-sea equilibrium

2. Dissolved oxygen variability in the ocean

3. "Unusual" gases in the ocean
   - Hydrogen sulfide
   - Methane hydrates

Fundamental Gas Laws

1) $C_G = [G]$ = gas concentration (mole/L) of gas "G" in solution

2) P_G = partial pressure (atm or kPa) of gas "G" in a gas mixture or a liquid

3) $P_{Total} = P_{N_2} + P_{O_2} + P_{Ar} + P_{H_2O} + ...$ (in gas phase)   (Dalton's Law)

$$P_G = P_{Total} \cdot \text{(mole fraction of "G" in a gas mixture)}$$

In the atmosphere (at 1atm TOTAL pressure and 100% relative humidity):

$$P_{N_2} = 0.78 \text{ atm} \qquad P_{CO_2} = 0.00032 \text{ atm}$$

$$P_{O_2} = 0.21 \text{ atm} \qquad P_{CH_4} = 0.0000014 \text{ atm}$$

4) IDEAL GAS LAW: $P_{Total}V = nRT$

(T = ^{0}K, n = # of moles, V = volume, R = ideal gas constant)

AT STP (0^{0}C, 1atm) in the gaseous state:

1 mole = 22.4 L
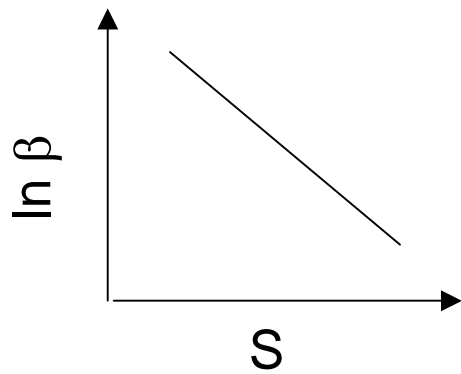
5) HENRY'S LAW: $P_G = K_G \cdot C_G$ (under equilibrium conditions)

K_G = "Henry's Law Constant" (a function of S and T)

$1/K_G = \beta_G$ = "Bunsen Coefficient" = Amount of gas which can be dissolved in a unit of volume of water at a given T and S, when P_G is given (assume 1atm if not stipulated)

$$(\text{Units}: \frac{mL_{GAS}}{mL_{S.W.} \cdot atm})$$

6) **Setchenow Relationship** ("Salting-out Effect"):

$$\ln \beta = b_1 + (b_2 \cdot S)$$

where b_1 and b_2 are constants for each gas for a given temp.

Lower salinity -- higher solubility

S

7) **Effect Of Salinity And Temperature:**

$$\ln C_G = A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4 (T/100)$$

$$+ S [B_1 + B_2 (T/100) + B_3 (T/100)^2]$$

$T = {}^0K$ $S = $ salinity   (Weiss, 1970)

Lower temp -- higher solubility

Constants are quoted for a given P_{Tot} (*e.g.*, Table 8.3)

Gas Solubility - Empirical Data

$$\ln C_G = A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100) + S\left(B_1 + B_2(T/100) + B_3(T/100)^2\right)$$

where: T = Absolute temperature (°K)

S = Salinity

TABLE 8.3

Solubility of gases in sea water with the constants for equation (8.11) to yield c_G^* in µmol kg^{-1} (values in parentheses yield cm^3 l^{-1}) relative to air at 760 mm Hg total pressure at 100% relative humidity.

Gas	Source of experimental data	A_1	A_2	A_3	A_4	B_1	B_2	B_3
N$_2$	Douglas (1964, 1965)	− 173·2221	254·6078	146·3611	− 22·0933	− 0·054052	0·027266	− 0·0038430
	Murray et al. (1969)	(− 172·4965)	(248·4262)	(143·0738)	(− 21·7120)	(− 0·049781)	(0·025018)	(− 0·0034861)
O$_2$	Carpenter (1966)	− 173·9894	255·5907	146·4813	− 22·2040	− 0·037362	0·016504	− 0·0020564
	Murray and Riley (1969)	(− 173·4292)	(249·6339)	(143·3483)	(− 21·8492)	(− 0·033096)	(0·014259)	(− 0·0017000)
Ar	Douglas (1964, 1965)	− 174·3732	251·8139	145·2337	− 22·2046	− 0·038729	0·017171	− 0·0021281
	Weiss (1971a)	(− 173·5146)	(245·4510)	(141·8222)	(− 21·8020)	(− 0·034474)	(0·014934)	(0·0017729)
Ne	Weiss (1971b)	− 166·8040	225·1946	140·8863	− 22·6290	− 0·127113	0·079277	− 0·0129095
		(− 160·2630)	(211·0969)	(132·1657)	(− 21·3165)	(− 0·122883)	(0·077055)	(− 0·0125568)
He	Weiss (1971b)	− 163·4207	216·3442	139·2032	− 22·6202	− 0·44781	0·023541	− 0·0034266
		(− 152·9405)	(196·8840)	(126·8015)	(− 20·6767)	(− 0·040543)	(0·021315)	(0·0030732)

Seawater Gas Concentrations in Equilibrium With the Atmosphere

Table 6.2 NAECs of Gases in Seawater at a Salinity of 35.0.							
T(°C)	0	5	10	15	20	25	30
Saturation Water Vapor Pressure $\left(\frac{P_{H_2O}}{P_T} \times 100\right)$							
	0.6%	0.8%	1.2%	1.6%	2.3%	3.1%	4.1%
Concentrations in mmol/m^3							
N_2	635.7	565.6	508.3	460.7	420.4	385.7	355.1
O_2	355.6	313.2	278.7	250.0	225.9	205.1	186.9
CO_2	23.37	19.26	16.09	13.6	11.61	10.00	8.66
Ar	17.01	14.98	13.33	11.96	10.81	9.81	8.93
Concentrations in μmol/m^3							
N_2O	14.84	12.16	10.09	8.46	7.16	6.10	5.23
Ne	8.45	8.03	7.66	7.33	7.04	6.79	6.56
Kr	4.31	3.68	3.18	2.78	2.44	2.16	1.93
CH_4	3.44	3.00	2.64	2.35	2.12	1.92	1.76
He	1.81	1.76	1.73	1.68	1.67	1.62	1.62

NAEC = normal atmospheric equilibrium concentration

8) $\%\ \text{Saturation}_{G_{\text{sw}}} = \dfrac{P_{G(seawater)}}{P_{G(atmosphere)}} \cdot 100\,\% \quad = \quad \dfrac{C_G}{NAEC} \cdot 100\,\%$

Examples:

100% Saturation: Gas and liquid phases in equilibrium

$$(P_{G(seawater)} = P_{G(atmosphere)})$$
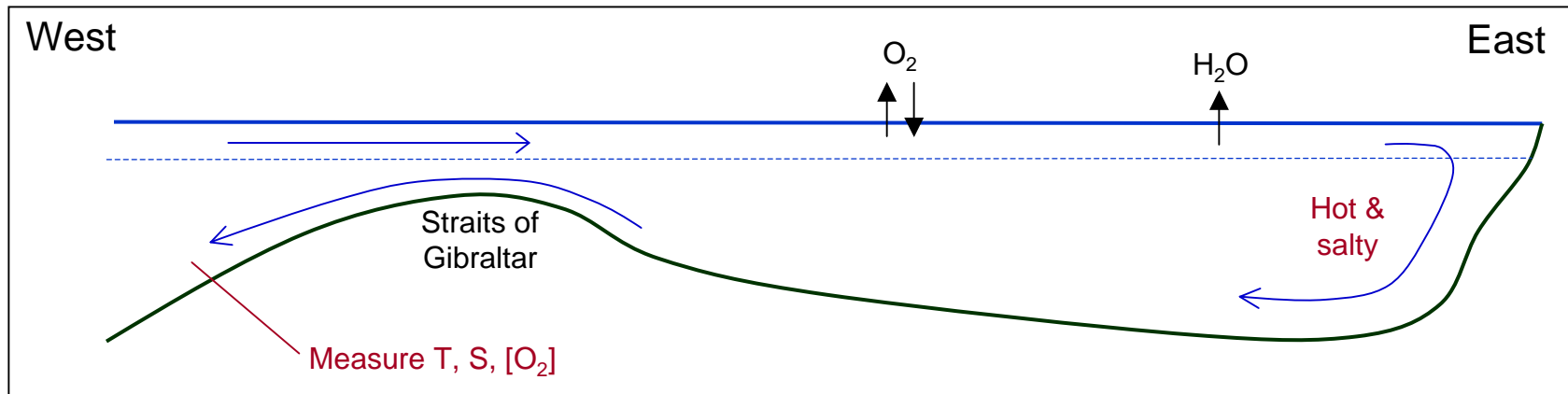
<100% Saturation: Gas transfer into solution   (undersaturated)

$$(P_{G(seawater)} < P_{G(atmosphere)})$$

>100% Saturation: Gas transfer out of solution   (supersaturated)

$$(P_{G(seawater)} > P_{G(atmosphere)})$$

Example: Calculation of % Saturation of Mediterranean Outflow Water

Loss of O_2 in Mediterranean bottom waters =

$$NAEC_{\text{Original watermass}} - [O_2]_{\text{Measured in outflow}}$$

From Table 6.2 or 8.3, T and S data

VALUES FOR THE IDEAL GAS CONSTANT "R" IN VARIOUS UNITS:

$8.3143 \ J \cdot K^{-1} \cdot mol^{-1}$ (SI)

$82.058 \ cm^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$

$0.082058 \ l \cdot atm \cdot K^{-1} \cdot mol^{-1}$

$1.9872 \times 10^{-3} \ Kcal \cdot K^{-1} \cdot mol^{-1}$

Conversion factors for pressure:

$$
\begin{aligned}
1 \ atm &= 760 \ torr = 760 \ mm \ Hg \\
&= 1.013 \times 10^5 \ N \cdot m^{-2} = 1.013 \times 10^5 \ Pa \\
&= 1.013 \ bar \\
&= 14.70 \ lb \ in^{-2} \\
&= 1.013 \times 10^6 \ dyne \ cm^{-2}
\end{aligned}
$$

0.1 bar = 1 decibar

In seawater:

1 dbar ≈ 1 m depth

Table 7.3. *Factors for the interconversion of dissolved oxygen data*

1 mmol O_2 = 2 mg-at O = 31.9988 mg O_2 = 22.3916 ml O_2 (STP)

Vertical Distribution of O$_2$

Dominant trends:

- Sub-thermocline O$_2$ minimum

- O$_2$ depletion at depth: Atlantic < Indian < Pacific

- High O$_2$ solubility in cold high-latitude water
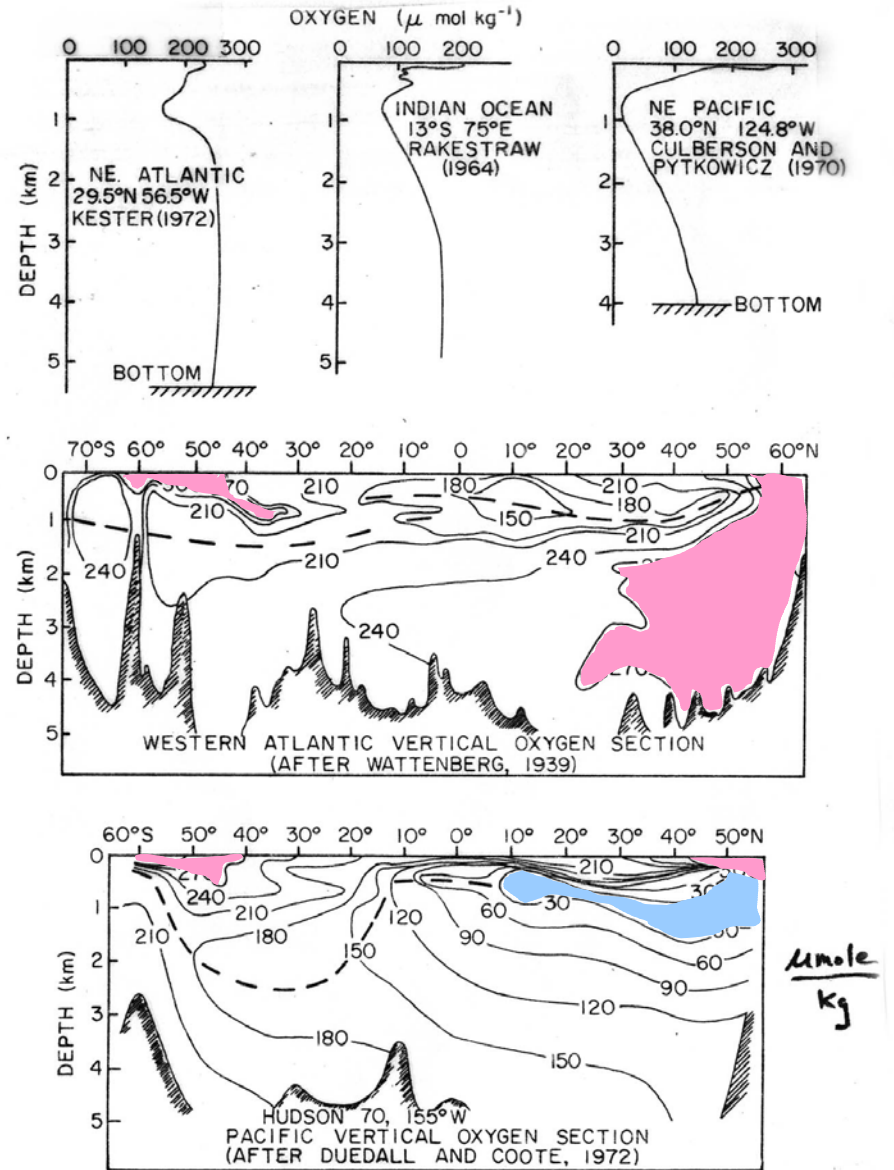
- Low O$_2$ concs in upwelled waters

FIG. 8.7. Vertical distribution of oxygen in the ocean. Upper: profiles from three ocean basins; Centre: north–south vertical section through the western Atlantic: Lower: north–south vertical section through the central Pacific. The dashed line represents the depth of the oxygen minimum surface.
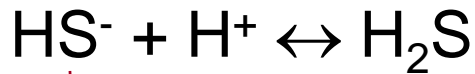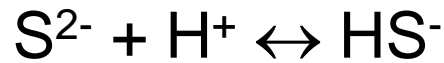
Horizontal Distribution of O₂
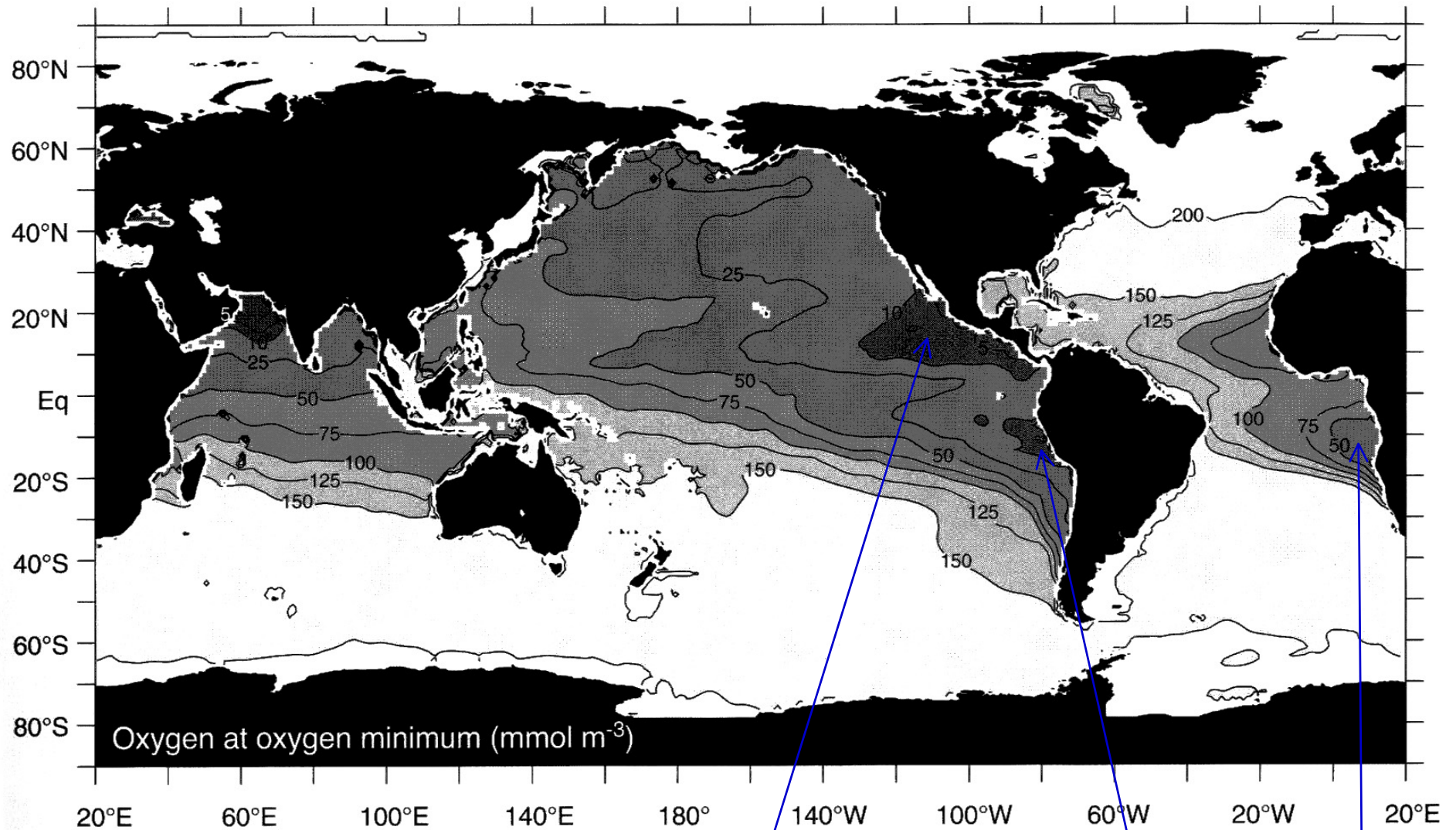
FIGURE 5.3.7: Oxygen concentration at the depth of the vertical oxygen minimum. Data are from the World Ocean Atlas 2001. [*Conkright et al.*, 2002]

West-coast upwelling systems: Eastern Tropical North Pacific (ETNP)   Peru   Namibia

Eastern Tropical North Pacific (ETNP)

Line denotes 9.9 μM dissolved oxygen contour at 400m depth

O₂ Concentrations (uM)
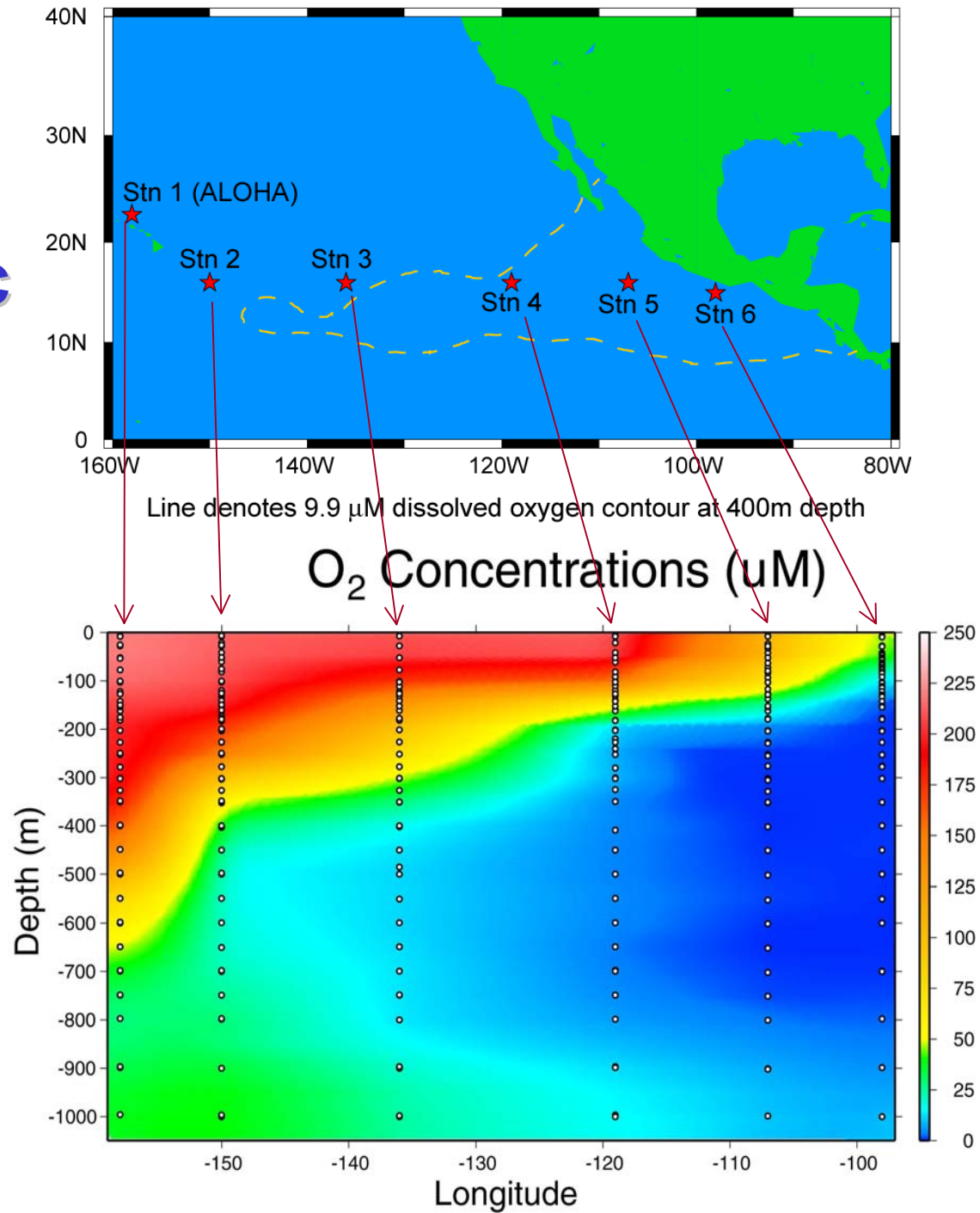
Hydrogen Sulfide – a gas under certain conditions

$$S^{2-} + H^+ \leftrightarrow HS^-$$

$$HS^- + H^+ \leftrightarrow H_2S$$

Ion

Dissolved gas

Under acidic conditions: neutral species that obeys gas laws

Hydrogen sulphide

As with dissolved oxygen the concentrations of hydrogen sulphide present in water samples may be expressed in a number of units depending on the purpose of the investigation. Hydrogen sulphide is usually produced in estuarine waters by bacterial reduction of sulphate and occurs in the water mainly as undissociated H_2S and HS^-. At pH values below 11 only minute amounts of S^{2-} are present and H_2S dominates at pH values less than about 7 (Almgren *et al.*, 1976). Thus the concentrations of the dissolved species are often expressed as in terms of the volume of the un-dissociated gas at STP per litre of solution, although mg S^{2-} l^{-1} is also used. As with oxygen and nutrient data, however, there is much to be gained from using molar units, in this case mmol S^{2-} l^{-1}. Table 7.4 provides a summary of the relationships between the various units to be found in the literature.

Table 7.4. *Factors for the interconversion of dissolved hydrogen sulphide data*

1 mmol H_2S = 34.076 mg H_2S = 32.06 mg S^{2-} = 22.40 ml H_2S (STP)
0.2935 mmol H_2S = 1 mg H_2S = 0.9408 mg S^{2-} = 0.657 ml H_2S (STP)
0.3119 mmol H_2S = 1.0629 mg H_2S = 1 mg S^{2-} = 0.699 mg H_2S (STP)
0.04464 mmol H_2S = 1.5213 mg H_2S = 1.4313 mg S^{2-} = 1 ml H_2S (STP)

(HEAD, 1985)
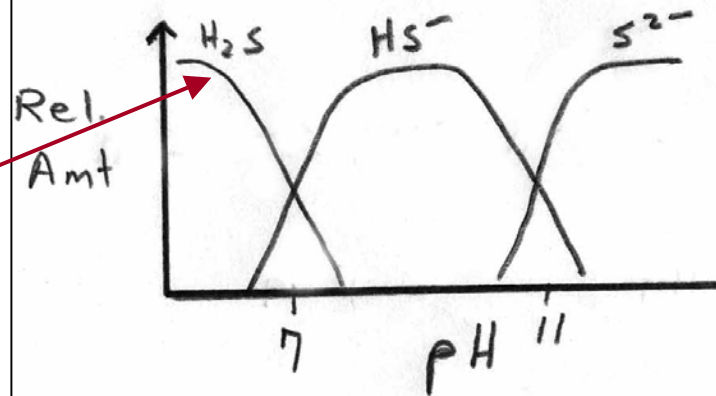
Gas Hydrates (Clathrates)

Hydrate: Crystalline structure of water in which hydrocarbon or CO_2 "gas" molecules are physically trapped (not bonded).

At appropriate T and P (<u>above</u> the freezing point of water) many gas hydrates are possible (up to iso-butane, C_5).
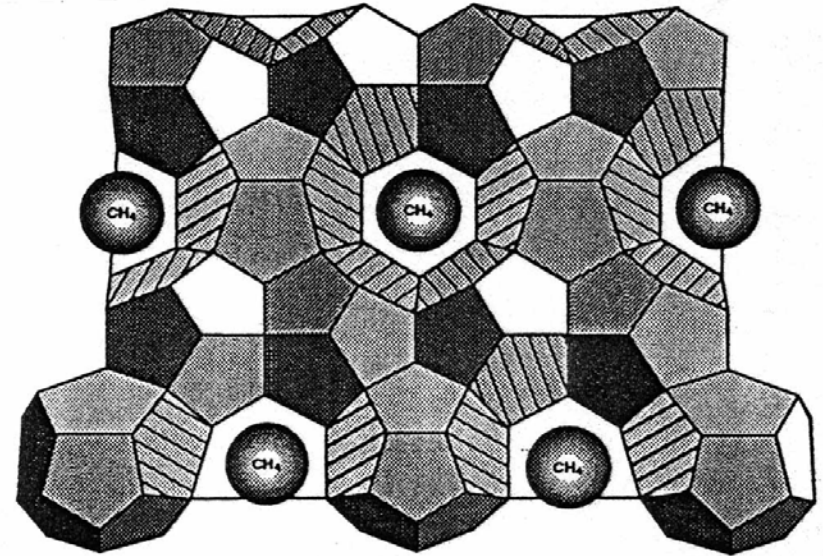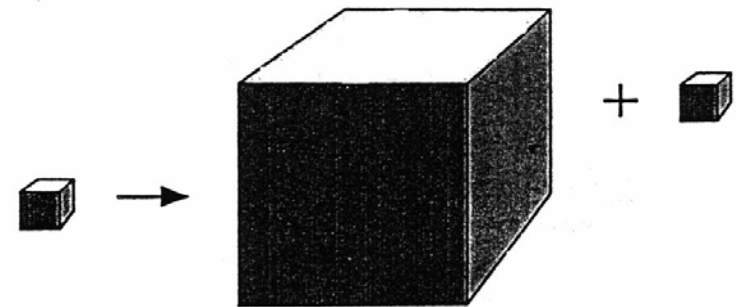
Of special interest: *Methane hydrate*

Figure 1. Gas hydrate structure. In this <u>structure I methane hydrate</u> the rigid cages are composed of hydrogen-bonded water molecules, and each cage, both exposed and covered in this figure, contains a methane molecule. Modified from *Hitchon* [1974].

1 m³   164 m³   0.8 m³

Gas Hydrate   Gas   Water

Figure 2. One cubic meter of gas hydrate yields 164 m³ of gas and 0.8 m³ of water at standard temperature and pressure.

Methane Hydrate Stability-Field Diagram
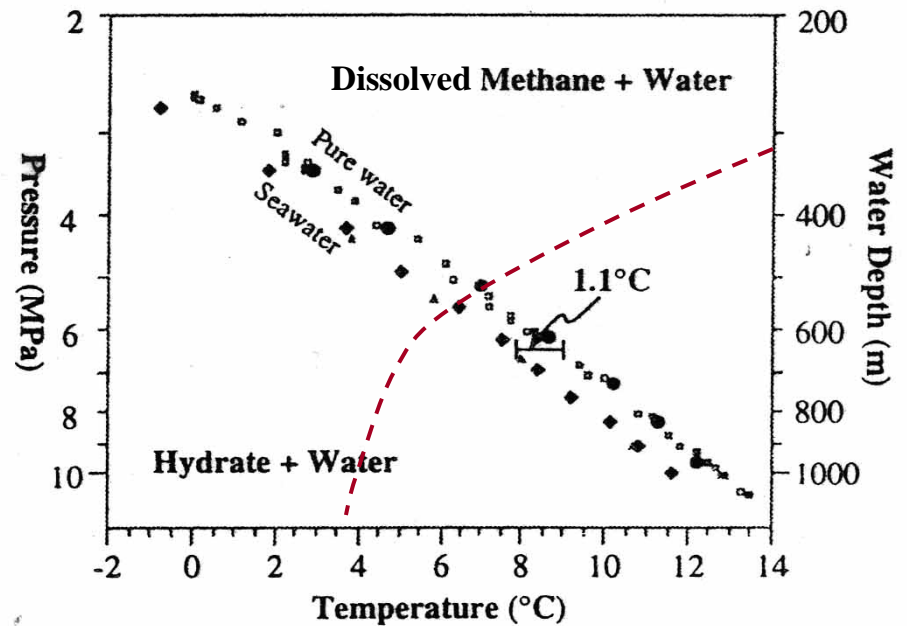
Figure 1. Methane hydrate stability conditions for the <u>pure methane-pure water</u> and <u>pure methane-seawater</u> (S ≈ 33.5 ‰) systems over the pressure range of 2.56-12.0 MPa. Data for the pure methane-pure water system are from this study as well as those compiled in *Sloan* [1990]. Data for "synthetic" seawater (S ≈ 35 ‰) are from *Dholabhai et al.* [1991]. As shown in this figure, at any given pressure, the temperature at which methane hydrate dissociates in the pure methane-seawater system is depressed by approximately -1.1 °C relative to the pure methane-pure water system. Note the pressure axis is reversed in order to reflect increasing pressure with depth along continental margins, and that the temperature axis is expressed in °C (rather than K) for convenience. The depth axis assumes a hydrostatic pressure gradient of 0.010 MPa/m.

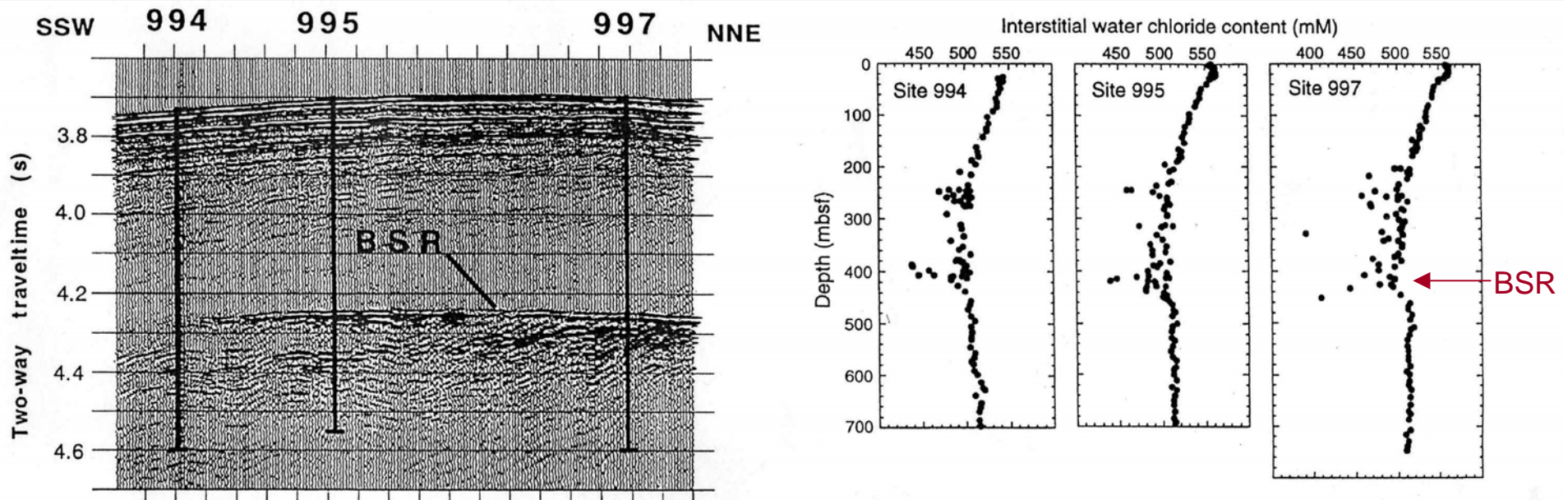# Seismic and Geochemical Evidence for Hydrates

Fig. 1. (Left) Seismic reflection profile across the Blake Ridge showing locations of sites 994, 995, and 997 with respect to the bottom-simulating reflector. (Right) Interstitial water chloride values at these sites are shown.

Seismic profiles – *Bottom-simulating reflector (BSR)* seen cutting across bedding planes (at the base of the hydrate stability field).
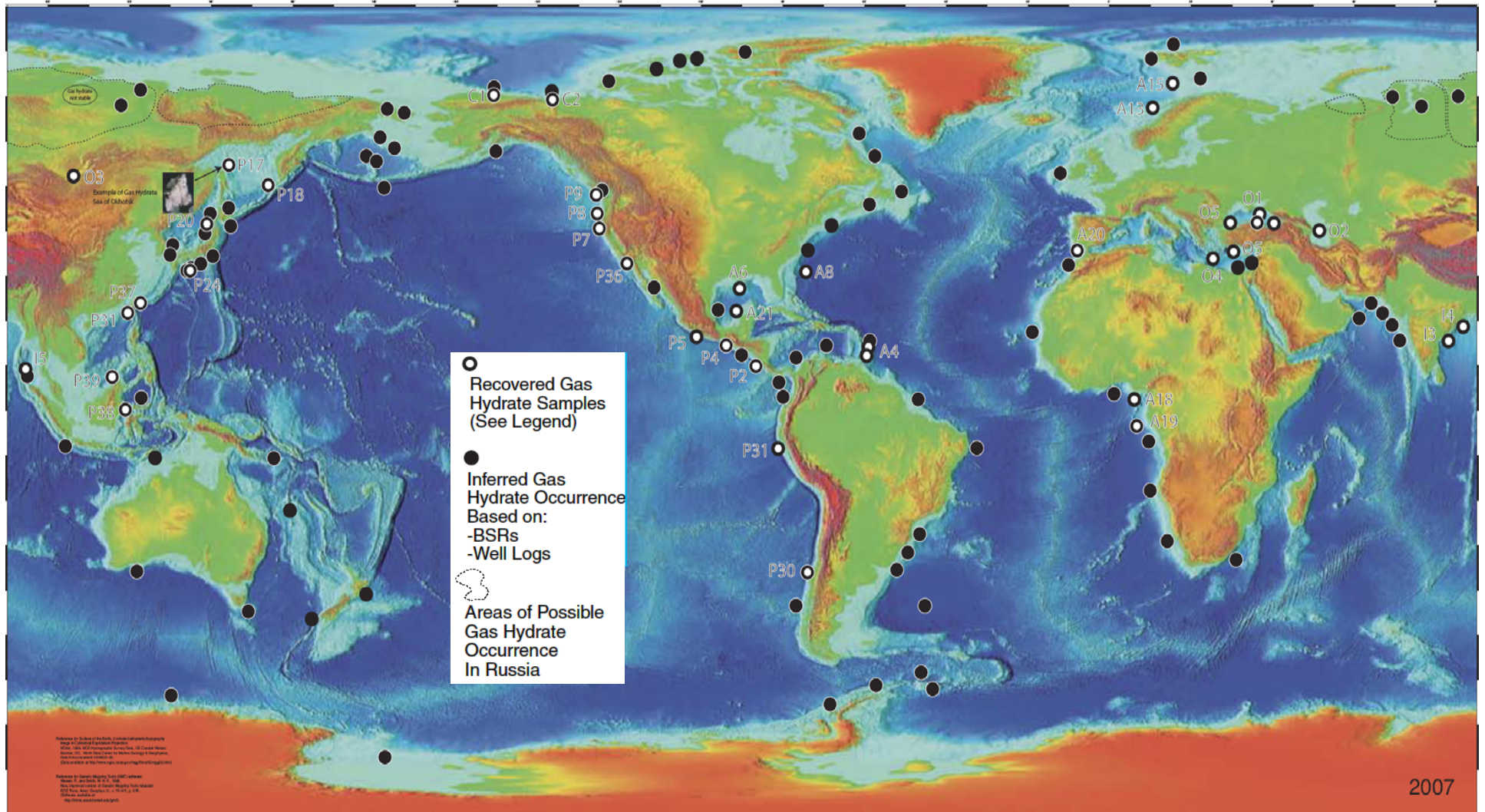
Sediment cores:

- Will degas and "self-extrude" when brought to the ocean surface

- "Burning ice"
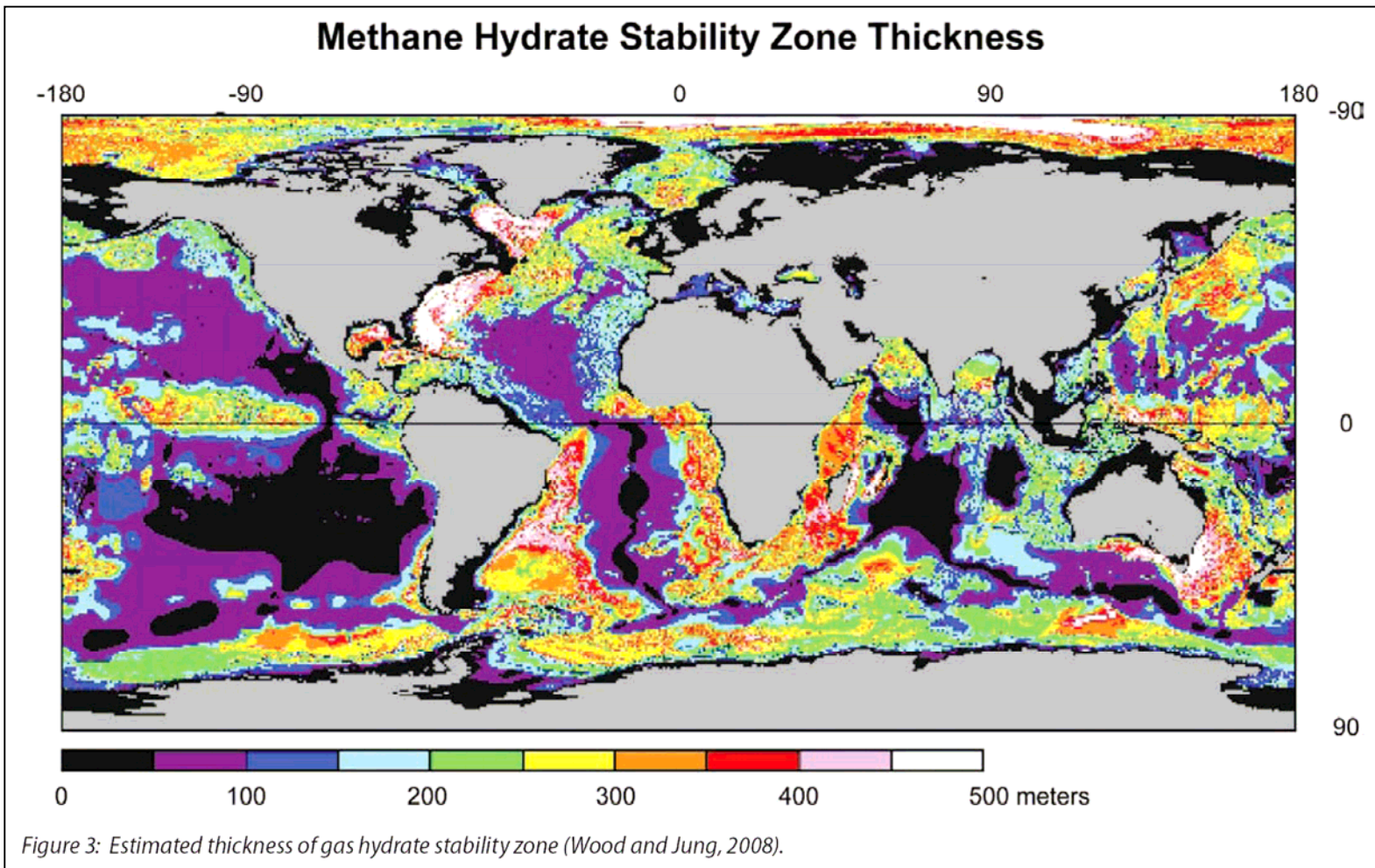
- Negative chloride anomalies ⟶

Hydrate-Associated Chloride Anomalies

- During hydrate formation: water + methane are removed from pore water – leaves chloride-enriched pore water

- Over time, locally elevated chloride concentrations diffuse away

- During core recovery: hydrate decomposes, releasing methane and water – leaves chloride-depleted pore water

A Global Inventory of Methane Hydrate Occurrence

http://walrus.wr.usgs.gov/globalhydrate/

Figure 3: Estimated thickness of gas hydrate stability zone (Wood and Jung, 2008).

Largest reservoirs:

- East coast of North America

- Arctic Ocean

- East coast of Australia

Importance of Methane Hydrates

- Energy source: Blake Plateau (off SE U.S.) alone contains enough methane to meet US natural gas needs for 100 years

- Methane is a potent greenhouse gas

- Climatic change or tectonic events may lead to catastrophic methane release via positive feedback:

  Increased global temp causes hydrate decomposition

  Release of methane to atm increases global warming
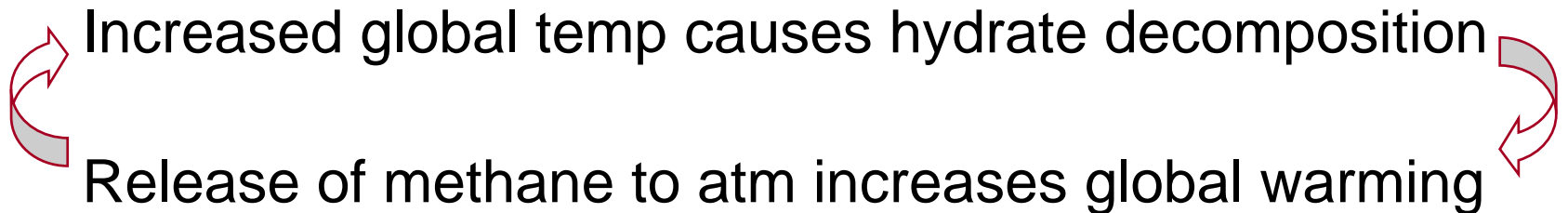
Homework due: Feb 14, 2012

Show your calculations, and cite any sources of data used:

1) Seawater in an area of upwelling off the coast of Peru was found to contain 2.91 mL O_2 / liter at a depth of 10 m. The temperature was 15°C, and S = 35. What was the percent saturation of oxygen compared to a water vapor-saturated atmosphere at 1 atm pressure?

2) After following the water mass as it moved offshore for four days, a sample taken at 10 m contained 6.05 ml O_2/liter. The temperature was 16°C, and S = 35. What was the percent saturation now? Why did the oxygen concentration change?