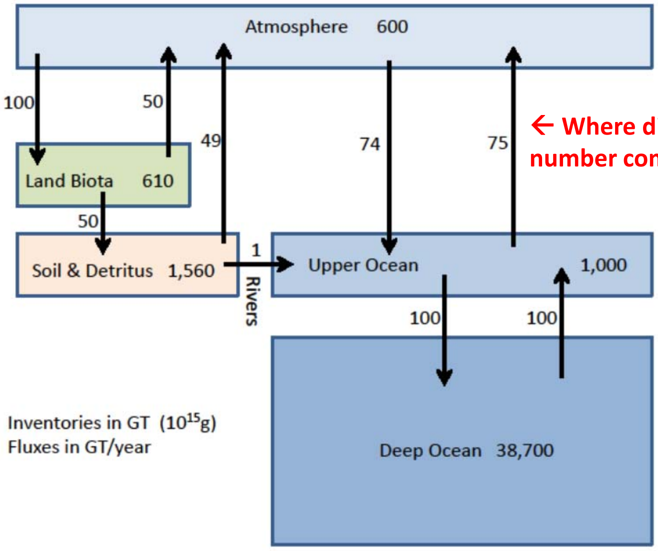
Isotopes and Gases

Isotopes as constraints to air-sea gas exchange, gas exchange time-scales, the various time-scales of carbon (isotope) exchange

Isotope effects in gas solution and molecular diffusion



← **Where did this number come from??**

Using the natural radiocarbon budget

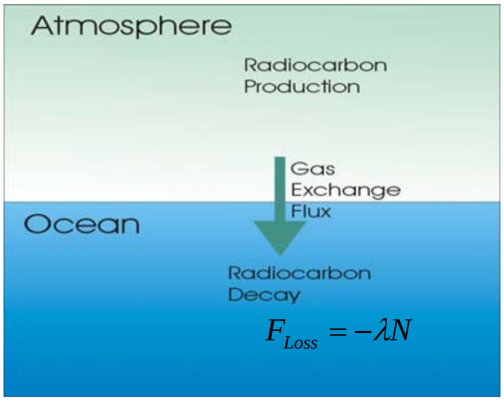
- A long term, large scale average
- Natural radiocarbon is…
  - very slow exchanger (T ~ 10 y)*
  - globally distributed
  - produced by cosmic rays in the atmosphere only
  - basic premise:

    flux in = decay of inventory

*more later…

Challenges:

1. Gas exchange model?
2. Isotope effects
   a) In solution
   b) During gas exchange



$$F_{Loss} = -\lambda N$$

A gas exchange model

- Gas exchange is a “first order” process
  - flux proportional to degree of disequilibrium
- Slabs of water presented to atmosphere
  - to be removed in time “T” before reaching equilibrium
  - volume “filled” = Area x thickness “L” reached by diffusion (*D*)
    - depth reached in time T related to molecular diffusion rate
    - Scales like a random walk effect $L = \sqrt{DT}$
  - mass flux related to frequency of slab replacement (θ) times the volume replaced each time $F = \sqrt{DT}\Delta C = \sqrt{\frac{D}{\theta}}\Delta C$ $\quad \Delta C \equiv C - C^*$
  - frequency of slab replacement is related to viscosity of water (ν)

    (where *k* is a constant of proportionality) $F = k\sqrt{\frac{D}{\nu}}\Delta C$
  - Define the Schmidt Number: $S_c \equiv \frac{\nu}{D}$

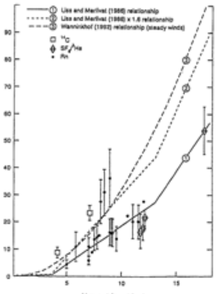
    So now the G.E.R. becomes $F = \left(k\,Sc^{-0.5}\right)\Delta C$

A gas exchange model

$$F = \left(k\, Sc^{-0.5}\right)\Delta C$$

$kSc^{-0.5}$ is commonly called a "**piston velocity**" and is modeled as a function of **U_{10}** (wind speed at 10 m height above ocean)* →

Usually plotted for Sc = 600 →



- Premises
  - A first order process
  - Separate "water" (*k, T*) and "gas" (*Sc*, Δ*C*) dependencies
    - So you can derive a "general" relationship and predict for various gases
    - Generally formulate *k* as a non-linear function of wind-speed
      - Also dependent on surfactants, fetch, wave spectra, etc.
- Schmidt number for various gases and temperatures

T(°C)	He	Ne	Kr	Xe	Rn	H_2	CH_4	CO_2
0	378	767	2045	2700	3168	633	1908	1922
5	292	578	1477	1929	2234	472	1399	1396
10	230	445	1090	1408	1610	360	1047	1036
20	150	276	626	793	885	219	618	**600**
30	102	180	380	472	516	141	385	369

*Wanninkhof, 1992. Journal of Geophysical Research 97, 7373-7382.

$$F = \left(k\, Sc^{-n}\right)\Delta C$$

In more general terms…

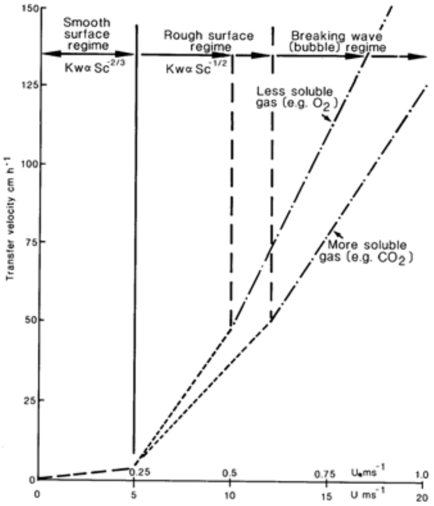
Range of physical models & situations dependent on wind speed

(a) Beaker: stagnant film ***n=1***

(b) Weak turbulence ***n=2/3***

(c) "Normal" oceanic ***n=1/2***

(d) Strong forcing: bubble dynamics & spray (all hell breaks loose)



Beware:
1. Wind speed measured at 10 m above sea level
2. Choice of paremeterization depends on whether "instantaneous" or "average" wind speed

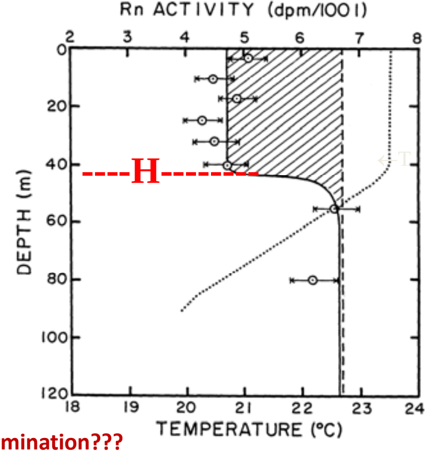
The Radon Deficit Technique

- Gas Exchange Flux = Production - Decay

F = H(A_{226} - A_{222})

$$F = \left(k\,Sc^{-0.5}\right)\Delta C$$

$$H\left(A_{226} - A_{222}\right) = kSc^{-1/2}\,\frac{A_{222}}{\lambda_{222}}$$



What is the characteristic timescale of this determination???

If determined *k* using Rn at 10°C, using ***n=1***

- flux of CO_2 would differ by 25%
- flux of N_2 would differ by a factor of 1.9
- flux of He would differ by a factor of 2.6

Warning: original literature (1974) used *stagnant film model (n=1),* which is **morally incorrect** and punishable by revocation of J.P. PhD

Gas exchange timescales

- Adjustment time w.r.t. a change $T_{GE}=H/K$ where ***K*** is piston velocity = $kSc^{-0.5}$, ***H*** is mixed layer depth
  - a physical time-scale
  - examples U_{10} = 10 m/s, H = 100 m, Temp = 20 C
    - He (Sc = 150), T_{GE} ~ 11 days
    - O_z (Sc = 450), T_{GE} ~ 18 days
    - CO_2 (Sc = 600), T_{GE} ~ 23 days???*
- CO_2 is actually much longer due to "chemical inertia" of huge buffer system effect

$$T_{GE} = \left(\frac{H}{kSc^{-0.5}}\right)\times\frac{\partial\left[\Sigma CO_2\right]}{\partial\left[pCO_2\right]} = \left(\frac{H}{kSc^{-0.5}}\right)\times R$$

R is "Revelle Factor" and is a function of pCO_2 and carbon system parameters, as well as temperature ~ 10

So T_{GE} ~ 0.7 years for CO_2

CO_2 Gas Exchange and Radiocarbon

- $^{14}CO_2$ has an even larger "**isotopic inertia**"
  - to change $p^{14}CO_2$ you have to flux much more $^{14}CO_2$ into the water due to huge ΣCO_2 reservoir

$$T = \left(\frac{H}{kSc^{-0.5}}\right) \times \frac{[\Sigma CO_2]}{[pCO_2]} = \left(\frac{H}{kSc^{-0.5}}\right) \times 180$$

  - this "Broecker Factor" arises because you have to move ^{14}C throughout the entire carbon reservoir (unlike CO_2 and the Revelle factor)
  - the gas exchange residence time for $^{14}CO_2$ is

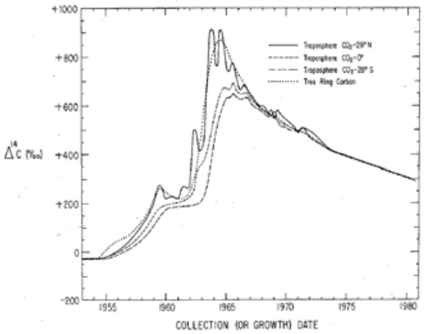
180 X 23 days ~ 10 years!!!

Observation of the Broecker Factor?

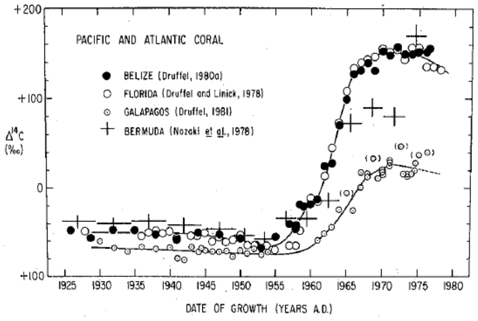
Surface ocean response to bomb ^{14}C transient seen in coral records

Long time-scale related to "reservoir age"

Atmospheric "Forcing"



Surface Ocean "Response"



Druffel, E. R. M. and Suess, H. E., 1983. *Journal of Geophysical Research* ***88, 1271-1280.***

Isotope effects in solution and diffusion
Gas Solubility

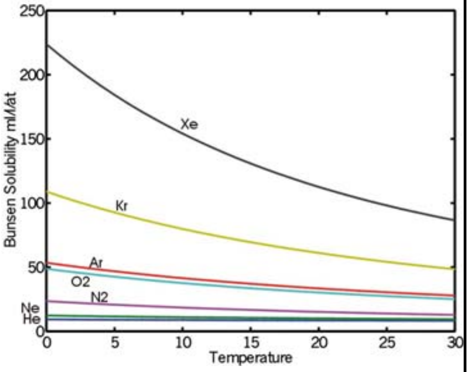
- Dalton's Law of Partial Pressures:
  - individual "partial pressures" are additive
  - gases behave *independently*
- Henry's Law:
  - gas concentration in water proportional to partial pressure of gas above the water $$\left[A_{Aq}\right]=\frac{K_{eq}}{RT}P_A$$
  - $[A_{aq}]$ = "aqueous activity" (gas concentration)
    - expressed in molar units
- Solubility expressed in terms of Bunsen Solubility Coefficient*
$$\left[A_{Aq}\right]=\beta_A P_A$$
  - Relates concentration directly to partial pressure in gas phase

*sometimes referred to as α

Gas Solubilities

"heat of solution" depends on

1. work required to create cavity in solvent
2. work required to contain solute in the cavity
3. energy gained from solute-solvent attraction



Unlike in rocks, smaller atoms or molecules are *less* soluble than the larger ones!

- Gas solubility generalities:
  - heavier, more polar gases are more soluble (3rd)
  - all gases are more soluble at ***lower*** temperatures*
    - more soluble gases have greater temperature dependence
  - Increasing salinity *depresses* solubility $$\ln\left(\frac{\beta_0}{\beta_S}\right)=k_S S$$

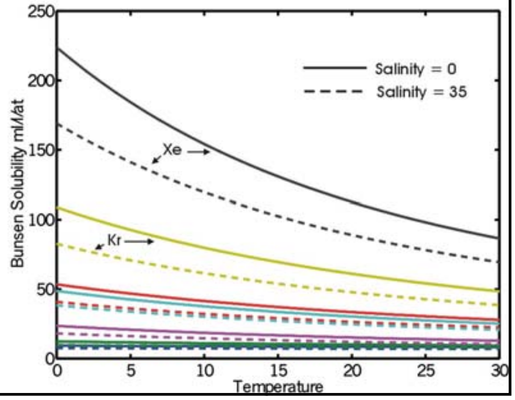
*unlike salts, for example

Gas Solubility

- Solubilities determined in the laboratory under controlled conditions
  - reported in quasi-thermodynamic equations, e.g.,

$$\ln\beta = A_1 + A_2\left(\frac{1}{T}\right) + A_3 \ln T + S\left[B_1 + B_2 T + B_3 T^2\right]$$

  - just a convenient form to calculate solubility as a function of T& S



Isotope Effects in Solution

- Heavier isotopes are more soluble (enriched in water)
  - Due to 2nd (solute) and 3rd (solute-solvent) energy terms (former more important?)

Gas	**Molecular Wt**	**Isotope Ratio**	**Mass Difference**	**Isotope Effect**
Helium	4	$^{3}He/^{4}He$	-28.6%	-1.5%
Neon	20.2	$^{20}Ne/^{22}Ne$	-9.5%	-0.5%
Oxygen	32	$^{18}O^{16}O/^{16}O_2$	6.1%	+0.1%
Argon	40	$^{40}Ar/^{36}Ar$	10.5%	+0.05%

  - Proportional to fractional mass difference, inversely to solubility (more soluble gases less affected)

$^{14}CO_2/^{12}CO_2$ → 1.5%

Isotope Effects in Diffusion

- Heavier isotopes move more slowly
  - Related to but not explicable by kinetic gas theory (complicated reduced mass effect with multiple water molecules) $\sqrt{\frac{\Delta m}{m}}$

Gas	**Molecular Wt**	**Isotope Ratio**	**Mass Difference**	**Isotope Effect**
Helium	4	$^3He/^4He$	-28.6%	5.0%
Neon	20.2	$^{20}Ne/^{22}Ne$	-9.5%	1.4%
Oxygen	32	$^{18}O^{16}O/^{16}O_2$	6.1%	-0.3%
Argon	40	$^{40}Ar/^{36}Ar$	10.5%	-0.8%

  - Proportional to fractional mass difference, inversely to solubility (more soluble gases less affected)

$^{14}CO_2/^{12}CO_2$ → -0.2%

Bourg and Sposito (2008) *GCA*, *72*, 2237-2247* Knox et al (1992) *JGR*, *97* 20335-20343

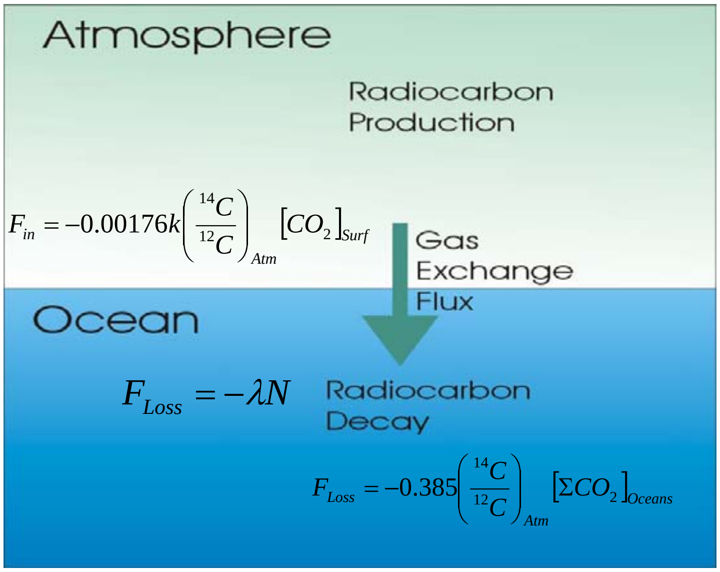
Revisiting the global ocean radiocarbon mass balance calculation

- Using an appropriate Sc number for area weighted average ocean surface temperature $F_{in} = 0.027k\Delta C$
- Or $F_{in} = 0.027k\left(C_{Surf} - C_0\right)$
- Substituting what we now know :

$$F_{in} = 0.027k\left\{0.95\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf} - 1.015\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf}\right\}$$

- This becomes $F_{in} = -0.00176k\left(\frac{^{14}C}{^{12}C}\right)_{Atm}\left[CO_2\right]_{Surf}$
- Which must balance decay in the ocean interior

Global ocean radiocarbon mass balance



Atmosphere

Radiocarbon Production

$$F_{in} = -0.00176k\left(\frac{^{14}C}{^{12}C}\right)_{Atm}[CO_2]_{Surf}$$

Gas Exchange Flux

Ocean

$$F_{Loss} = -\lambda N$$

Radiocarbon Decay

$$F_{Loss} = -0.385\left(\frac{^{14}C}{^{12}C}\right)_{Atm}[\Sigma CO_2]_{Oceans}$$