Lecture 16
Physical Principles of Isotopic Fractionation II:
Mass dependent and mass independent fractionation

Lecture 16
Isotopic Fractionation II

- A quick review of general aspects
- Reviewing ZPE effects (SHO approximation)
  - Why is $\alpha_D \gg \alpha_{18}$ for water?
- Revisiting open system fractionation
  - The Rayleigh equation
- Combined kinetic/equilibrium fractionation
  - The Dole Effect as an example
  - Gravitational fractionation in soil gases
- Triple (and more) Isotope systems
  - Mass dependent and mass independent effects

Why Look at Isotope Fractionation?

- Process identification
  - Comparison of relative importance
  - Quantification of rates
- Proxy records of the past
  - E.g. in sediments, ice cores
  - Climate changes:
    - temperature, hydrology, circulation, productivity
- Diagnose & correct for artifacts in records
  - One investigators noise is another's signal
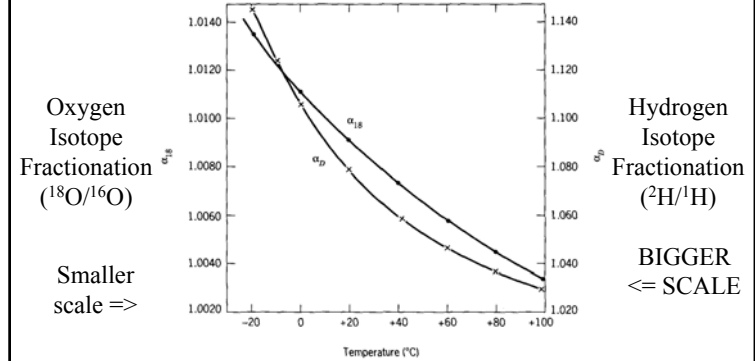

Types of Isotope Fractionation

1. Non-equilibrium (unidirectional) effects
   a. Diffusion/effusion
   b. Evaporation/condensation
   c. Kinetic (bond breaking/making)
   d. Metabolic (combination of all the above)
2. Equilibrium effects
   a. Bond strength
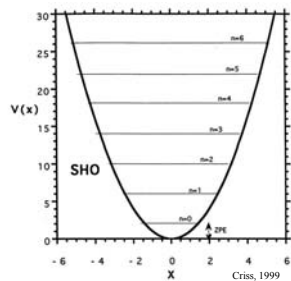   b. Availability of states (statistical mechanics)

General Rules

- Lighter isotopes move faster
- lighter isotopes form weaker bonds
  - effect strongly depends on binding energy
  - covalent bonds generally weaker, more strongly affected
- isotope effects generally stronger for bigger relative mass differences
  - directly proportional for same element
    - e.g. ^{16}O, ^{17}O, ^{18}O : $\delta^{18}O = 2 \times \delta^{17}O$
- isotope effects stronger at lower temperatures
  - as T >>, $\alpha \rightarrow 1$
  - for low T, $\alpha \sim 1/T^2$
  - for high T, $\alpha \sim 1/T$

Partitioning between phases

- Vapour-droplet partitioning in a cloud $R_L = \alpha R_V$

Oxygen Isotope Fractionation ($^{18}O/^{16}O$)

Smaller scale =>

Hydrogen Isotope Fractionation ($^2H/^1H$)

BIGGER <= SCALE

Energy Levels for a Simple Harmonic Oscillator

Criss, 1999

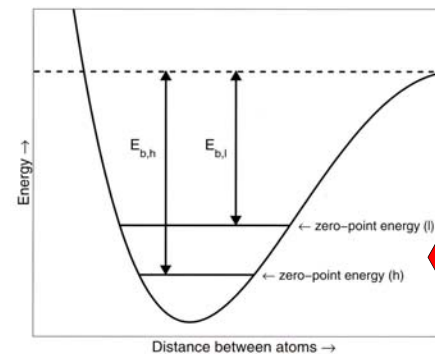Lowest level, $n = 0$, has energy = $h\nu/2$. This is the Zero-Point Energy, ZPE.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$
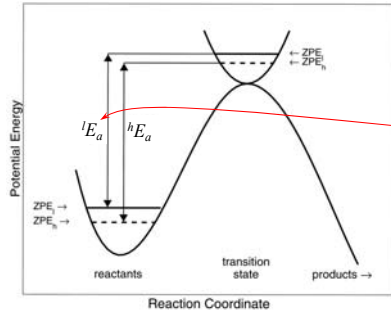
k is the force constant

μ is the reduced mass

ν, and in turn the ZPE, is thus mass-dependent.

Energy Levels in Isotopically Substituted Molecules

Zeebe & Wolf-Gladrow, 2001

The ZPE of the bond with the light isotope is greater than that of the bond with the heavy isotope.

2

Kinetic Isotope Effects

Zeebe & Wolf-Gladrow, 2001

Bonding in transition state is weaker than in reactants.

Activation energy for light isotopic species is therefore smaller.

$$k = A\mathrm{e}^{\frac{-E_a}{RT}}$$

Light isotopic species react more rapidly.

Isotope fractionation: the Rayleigh Equation

- Describes how the ratio changes with progressive removal of material, e.g. by evaporation from a water droplet:

  f = fraction left

$$R_L = \alpha R_V \qquad \frac{R_V}{R_{V_0}} = f^{\alpha-1}$$

But where did this come from????

The Rayleigh Equation

$$\frac{R_V}{R_{V_0}} = f^{\alpha-1}$$

- For a vapor where droplets are forming … α = 1.008

$$R_L = \alpha R_V = \alpha R_{V_0} f^{\alpha-1}$$

f	$f^{\alpha-1}$	δ_V	$\alpha f^{\alpha-1}$	δ_L
1.000	1.00000	0.00	1.00800	8.00
0.800	0.99822	-1.78	1.00620	6.20
0.640	0.99644	-3.56	1.00441	4.41
0.512	0.99466	-5.34	1.00262	2.62
0.410	0.99288	-7.12	1.00083	0.83
0.328	0.99111	-8.89	0.99904	-0.96
0.262	0.98935	-10.65	0.99726	-2.74
0.210	0.98758	-12.42	0.99548	-4.52
0.168	0.98582	-14.18	0.99371	-6.29
0.134	0.98406	-15.94	0.99193	-8.07
0.107	0.98231	-17.69	0.99017	-9.83
0.086	0.98055	-19.45	0.98840	-11.60
0.069	0.97881	-21.19	0.98664	-13.36
0.055	0.97706	-22.94	0.98488	-15.12
0.044	0.97532	-24.68	0.98312	-16.88
0.035	0.97358	-26.42	0.98137	-18.63
0.028	0.97184	-28.16	0.97962	-20.38
0.023	0.97011	-29.89	0.97787	-22.13
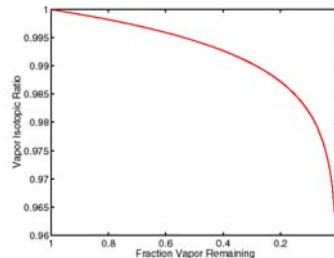
For evaporation

- For the backwards reaction, then the effect is $1/\alpha$

$$R_2 = \alpha_{1\to2} R_1$$

$$R_1 = \alpha_{2\to1} R_2 = \frac{1}{\alpha_{1\to2}} R_2$$

$$\therefore \alpha_{2\to1} = \alpha_{1\to2}^{-1}$$

- e.g. for evaporation of a droplet
  $$\frac{R_L}{R_{L_0}} = f^{\frac{1}{\alpha}-1}$$
  – the remaining liquid is given by

  – the vapour is given by
  $$\frac{R_V}{R_{L_0}} = \frac{1}{\alpha}\frac{R_L}{R_{L_0}} = \frac{1}{\alpha}f^{\frac{1}{\alpha}-1}$$

The Dole Effect

- The global ocean contains 3.9×10^{22} mol O_2
  - In the form of H_2O
- The atmosphere contains 3.6×10^{19} mol O_2
  - i.e., about 0.1% as much as the ocean
- Atmospheric O_2 is isotopically heavy w.r.t. the ocean
  - $\delta^{18}O \sim 23.5$‰ (w.r.t. SMOW)
  - Known as the "Dole Effect"

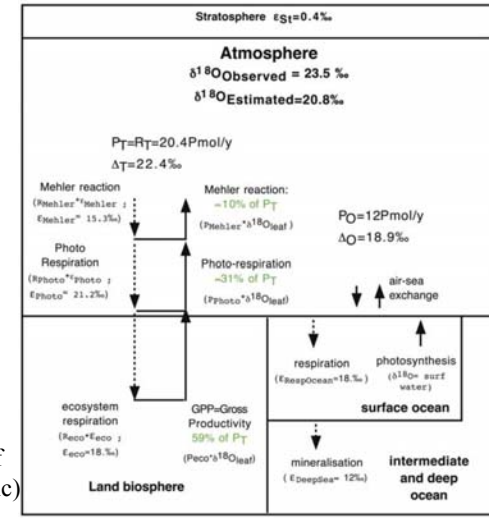Dole (1936) J. Chem. Phys. 4 p268-275

Bender et al (1994) GBC 8(3) 363-376

The Dole Effect

- Marine:
  - Photo ~0‰
  - Resp^n ~18‰
  - Remin ~12‰
- Terrestrial
  - Mehler ~15‰
  - Photo ~21‰
  - Resp^n ~18‰
- Net ~ 21‰

Key enhancement is leaf water enrichment (kinetic)

Stratosphere $\varepsilon_{St}=0.4$‰

Atmosphere
$\delta^{18}O_{Observed} = 23.5$‰
$\delta^{18}O_{Estimated}=20.8$‰

$P_T=R_T=20.4$Pmol/y
$\Delta_T=22.4$‰

$P_O=12$Pmol/y
$\Delta_O=18.9$‰

Past variations in Dole Effect?

- Changing balance between terrestrial & marine productivity
- Ice core O_2 →

Expect an aridity overprint due to leaf water fractionation?
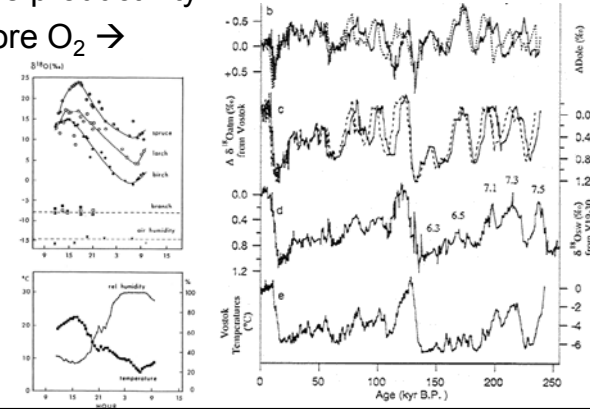

Gravitational Fractionation in Soil Gases

- Also an issue in ice core bubbles
  - Wherever you have "trapped" gas column
- General principles:
  - Hydrostatic equilibrium requires $\dfrac{dP}{dz} = -\rho g$
    - For an ideal gas we have $\dfrac{d(\ln P)}{dz} = \dfrac{-gM}{RT}$
    - Which integrates to $\ln \dfrac{P}{P_0} = \dfrac{-gzM}{RT}$
    - For two isotopes we have $\ln \dfrac{R}{R_0} = -\dfrac{(\Delta M)gz}{RT}$

Fractionation in soil gases

Upward flux of water vapor (derived from groundwater) through soil (in an arid climate) pushes gases out of soil, back diffusion of gases favor lighter isotopes, offset from gravitational fractionation profile
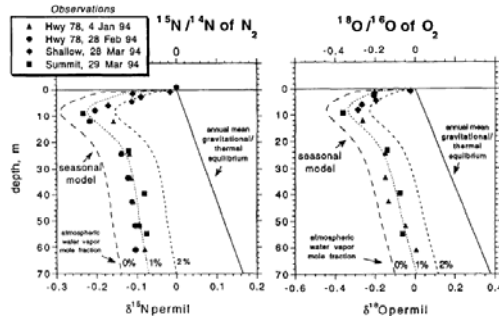
Severinghaus et al (1996) GCA 60, 1005-1018.

Triple Isotope Systems

Expect mass dependency (with subtle differences)
– e.g., for ^{16}O, ^{17}O, ^{18}O, that $\delta^{17}O \sim 0.5\ \delta^{18}O$

$$\theta_{Kinetic} = \frac{\ln\left(^{17}\alpha\right)}{\ln\left(^{18}\alpha\right)} = 0.511$$

$$\theta_{Eqm} = \frac{\ln\left(^{17}\alpha\right)}{\ln\left(^{18}\alpha\right)} = 0.523$$

Angert *et al*, (2004), *GCA*, *68*(17), 3487-3495.

- Θ_{Eqm} Can vary with marine species (0.518-0.538)
  – Luz, B., and E. Barkan (2011), GBC *25*(GB3001), doi:10.1029/2010GB003883.
– Nobody really ever looked for these deviations because
  - Extra work to make measurements
  - Differences would be small/subtle (mass spec is hard to do)
  - Not expected

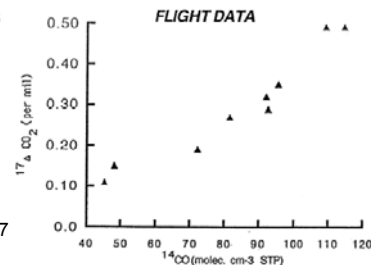## "Mass Independent" Fractionation
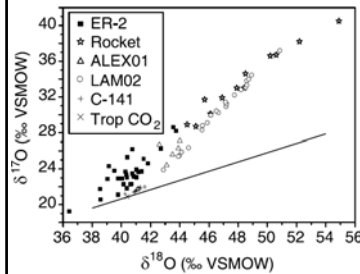
← Significant deviations from the "mass dependent" line observed in upper atmospheric CO_2
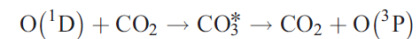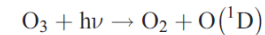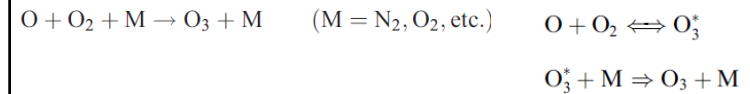
Define: $\Delta^{17}O = \delta^{17}O - 0.516 \times \delta^{18}O$

$\Delta^{17}O$ correlates with radiocarbon in CO_2 →

Boering et al (2004) *GRL 31*, L03109
Thiemens et al (1995) GRL 22(3) 255-257

"Mass Independent" Fractionation

- Linked to ozone formation
- Huge (~150‰) fractionations
- Very similar values for ^{18}O and ^{17}O
- Originally thought to be related to doubling of rotational states in asymmetric molecules

$$O + O_2 + M \to O_3 + M \qquad (M = N_2, O_2, etc.)$$

$$O + O_2 \Longleftrightarrow O_3^*$$

$$O_3^* + M \Rightarrow O_3 + M$$

$$O_3 + h\nu \to O_2 + O(^1D)$$

$$O(^1D) + CO_2 \to CO_3^* \to CO_2 + O(^3P)$$

Subsequent exchange with CO_2 carries "signal" out of stratosphere
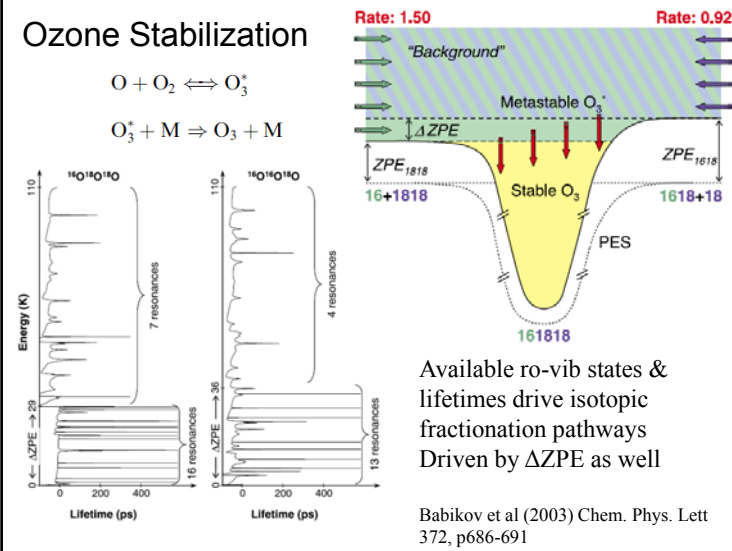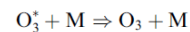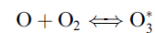
Ozone and molecular oxygen isotopomers

Ozone & molecular oxygen obviously linked →
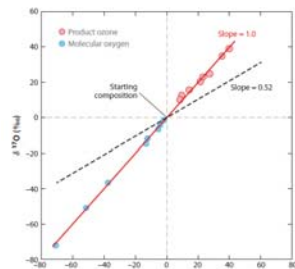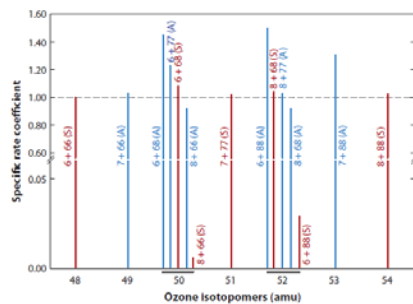
Substantial formation rate dependence on isotope *position* within a given isobar indicating strong ro-vib state influence

Thiemens et al (2012) Annu. Rev. Phys. Chem. 63, 155-177

Ozone Stabilization

$$O + O_2 \Longleftrightarrow O_3^*$$

$$O_3^* + M \Rightarrow O_3 + M$$

Available ro-vib states & lifetimes drive isotopic fractionation pathways
Driven by ΔZPE as well

Babikov et al (2003) Chem. Phys. Lett 372, p686-691

"Mass independent" fractionation in heavy isotopes

ICPMS & TIMS has seen MIF in at least 19 isotope systems, including…

– Hg, Sn, Cd, Zn, Te, Sr, Pb, Cr, U, Ti…

1. Either due to nuclear field shift
   – Overlap of electron s-orbitals with larger volume nuclei (hence n-effect)
     • Most significant for odd-A nuclei
       – Nuclear volume smaller than interpolated between even-A neighbors

2. Or nuclear spin effects
   – Coupling of electron spin angular momentum with non-zero nuclear spin
     • Typically magnetic coupling during photodissociation

Epov et al (2011) J. Anal. A. Spectrom. 26, 1142-1156
Bergqyust et al (2007) Science 318, 417-420.