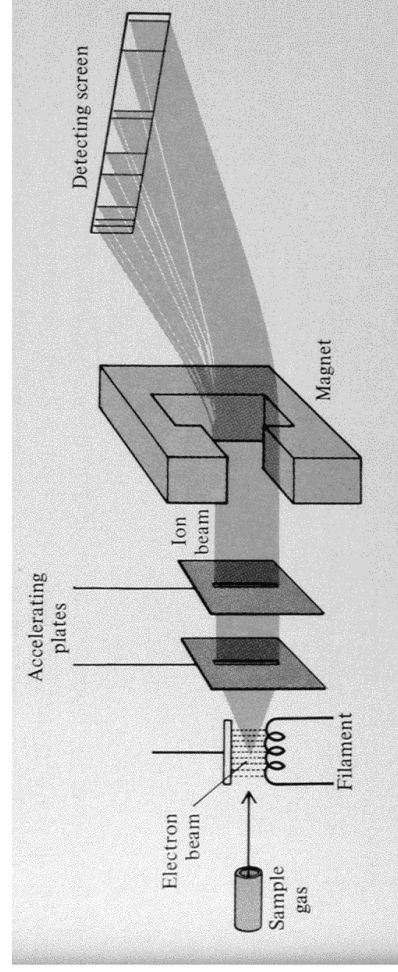


Supplemental Materials for the 2006 CIDER
lecture on the stable isotope geochemistry of the mantle

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Isotopes

- Term coined in 1914 by Frederick Soddy; means 'same place' [in periodic table]
- Isotopes = Nuclides of a single element having different atomic weights; i.e., they have the same Z (number of protons), but different mass
- 3/4 of naturally occurring isotopes discovered by 1919, most by FW Aston using the 'positive ray device' (a forerunner of the modern sector mass spectrometer).



Language

Stable Isotopes: Nuclides of a single element having different masses, and that are neither the product of nor undergo radioactive decay

^{16}O , ^{17}O and ^{18}O are the stable isotopes of oxygen
 ^{12}C ($t^{1/2} \sim 10^{-21}$ s) is not

Isotopologues: ‘Versions’ of a single molecule having different proportions of isotopes

The stable isotopologues of molecular oxygen include:

$^{16}\text{O}^{16}\text{O}$, $^{17}\text{O}^{16}\text{O}$, $^{18}\text{O}^{16}\text{O}$, $^{18}\text{O}^{17}\text{O}$, $^{17}\text{O}^{17}\text{O}$, $^{18}\text{O}^{18}\text{O}$
 “normal” “singly substituted”
 “doubly substituted”

Isotopomers: ‘Versions’ of an isotopologue having non-equivalent locations of isotopes within the molecule (think of ‘isomers’)

$^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ are isotopomers of each other
 $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ are *not* isotopomers, as they are equivalent (related by simple symmetry operations)

Nomenclature

Convention for reporting isotopic ratios:

$$R^i = \frac{[\text{isotope } i]}{[\text{reference isotope}]}$$

Where $[i]$ denotes the concentration (mole fraction) of isotope i in a population of atoms

- Usual convention is that the reference isotope is the most abundant stable isotope of that element, so that R^i values approximately equal mixing proportions of i
- In general, the most abundant stable isotope of elements of interest is also the lightest, so R^i values always ratio a heavy isotope to a light one
- This rule is violated for Li, B and some transition metals. Nomenclature is mixed in these cases. The best (least confusing) thing to do for such elements is to place heavier isotopes in the numerator and the lightest one in the denominator
- The identity of the element whose isotopes are being ‘ratioed’ is generally not indicated. One must figure out what element is meant from memory or context.

$$R^{\text{D}} = \frac{\text{D}}{\text{H}} \quad R^7 = \frac{^7\text{Li}}{^6\text{Li}} \quad R^{11} = \frac{^{11}\text{B}}{^{10}\text{B}} \quad R^{13} = \frac{^{13}\text{C}}{^{12}\text{C}} \quad R^{15} = \frac{^{15}\text{N}}{^{14}\text{N}} \quad R^{17} = \frac{^{17}\text{O}}{^{16}\text{O}} \quad R^{34} = \frac{^{34}\text{S}}{^{32}\text{S}}$$

$$\dots \text{ or } R^6 = \frac{^6\text{Li}}{^7\text{Li}} \quad R^{18} = \frac{^{18}\text{O}}{^{16}\text{O}}$$

The δ value

$$\delta^i_{\text{standard}} = \left\{ \frac{R^i_{\text{sample}}}{R^i_{\text{standard}}} - 1 \right\} \times 1000$$

Where i is an isotope of interest (e.g., ^{18}O or D)

- $\delta^i_{\text{standard}}$ values have meaning only in the context of their known reference frame (R^i_{standard})
- Always, always, always write δ^i values with the subscript denoting its standard
- A $\delta^i_{\text{standard}}$ value without a known reference frame is worse than meaningless: It is often also misleading
- Never, ever, ever, for any reason, even after suffering a head blow, treat $\delta^i_{\text{standard}}$ values as if they were R^i or $[i]$ values.

Some commonly used R^i_{standard} values:

$$\begin{aligned} R^{\text{D}}_{\text{VSMOW}} &= 0.00015575 \\ R^7_{\text{L-SVEC}} &= 12.019 \\ R^{11}_{\text{NBS 951}} &= 4.04362 \\ R^{13}_{\text{PDB}} &= 0.0112372 \end{aligned}$$

$$\begin{aligned} R^{15}_{\text{Air}} &= 0.0036747 \\ R^{17}_{\text{VSMOW}} &= 0.0003799 \\ R^{18}_{\text{VSMOW}} &= 0.0020052 \\ R^{34}_{\text{CDT}} &= 0.0450045 \end{aligned}$$

The α_{j-k} and Δ_{j-k} values

$$\alpha_{j-k} = \frac{R^j_j}{R^j_k}$$

$$\Delta^i_{j-k} = \delta^i_j - \delta^i_k$$

e.g., $\Delta^{18}\text{O}_{j-k} = \delta^{18}\text{O}_{\text{VSMOW of } j} - \delta^{18}\text{O}_{\text{VSMOW of } k}$

$$\Delta^i_{j-k} \sim 1000x(\alpha_{j-k} - 1)$$

$$\Delta^i_{j-k} \sim 1000x(\ln\alpha_{j-k})$$

The error in these approximations is small ($\sim 0.02\%$) if δ^i_j and δ^i_k are both within 10 ‰ of 0, and within 10 ‰ of each other

$$\alpha_{j-k} = \frac{1000 + \delta^i_j}{1000 + \delta^i_k}$$

Other nomenclatures and variables

[⁵⁰O₃]: The fraction of all ozone molecules that have a mass of 50 AMU (mostly ¹⁶O¹⁶O¹⁸O)

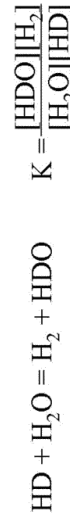
R⁴⁶: The ratio of the concentration of CO₂ molecules having mass 46 (mostly ¹⁶O¹²C¹⁸O) to the concentration of 'normal' CO₂ molecules (¹⁶O¹²C¹⁶O)

Δ¹⁷O: Deviation in δ¹⁷O_{VSMOW} from the 'terrestrial mass fractionation line' (a trend defined by the relationship δ¹⁷O_{VSMOW} = 0.52xδ¹⁸O_{VSMOW})

ε: Isotopic fractionation in units of per mil. = (α_{j-k}-1)x1000

Note ε approximately (but not exactly) equals Δ_{j-k}

K: Equilibrium constant for an isotope exchange reaction



Note K is related to α_{H₂O-H₂} (dependence varies with # of atoms exchanged)

Equilibrium fractionations

Some definitions:

Equilibrium: A state wherein temperature, pressure and chemical potentials of all chemical species are equal among all co-existing phases, and the system is in its lowest possible free-energy state at that T and P

Homogeneous equilibrium: The equilibrium state in a system containing only one phase (e.g., air), although it may contain several chemical species

Heterogeneous equilibrium: The equilibrium state in a system containing two or more phases (e.g., water and a precipitated mineral)

Geothermometry: Determination of the temperature of a geological system, generally at some time in the past and based on application of equilibrium thermodynamics to one or more phases that you think were part of an equilibrated system at that time.

Statistical Thermodynamics: Calculation of the bulk thermodynamic properties of a population of atoms or molecules based on quantum mechanical models for the properties of individual atoms or molecules and the Boltzmann-Maxwell models for distributions of energies in such populations.

Partition Function (Q): The sum of energies corresponding to all possible quantum-mechanical states of a given atom or molecule. A key concept in Statistical Thermodynamics.

Exchange Reactions

$$\text{General model: } aA_1 + bB_2 = aA_2 + bB_1$$

Where A and B are molecules or formula units (for condensed phases), subscripts 1 and 2 denote different isotopologues of A and B (usually 1 is 'normal' and 2 'exotic'), and a and b are stoichiometric coefficients required for a balanced reaction



$$A_1 = H_2^{16}O; A_2 = H_2^{18}O; B_1 = C^{16}O; B_2 = C^{18}O; a = b = 1$$

For more complex cases, unless you have a special reason to do otherwise, write the reaction so it involves exchange of one atom between isotopically pure end-members



$$A_1 = MgSi^{16}O_3; A_2 = MgSi^{18}O_3; B_1 = Mg_2Si^{16}O_4; B_2 = Mg_2Si^{18}O_4; a = 1/3; b = 1/4$$



$$A_1 = MgSi^{16}O_3; A_2 = MgSi^{16}O_2^{18}O; B_1 = Mg_2Si^{16}O_4; B_2 = Mg_2Si^{16}O_3^{18}O; a = b = 1$$

Reasons are twofold: relations between a and k are usually simpler, and (more importantly) it is easier to estimate the properties of the isotopic end members rather than their partially-substituted relatives.

Properties of the equilibrium constant

$$aA_1 + bB_2 = aA_2 + bB_1$$

$$K = \frac{(a_{A_2})^a (a_{B_1})^b}{(a_{A_1})^a (a_{B_2})^b}$$

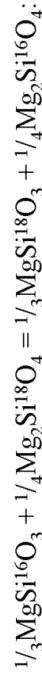
$$\alpha_{A-B} = \frac{R^2_A}{R^2_B}$$

(where $R^2_i = \frac{[\text{isotope } 2]}{[\text{isotope } 1]}$ in compound i)

$a_i = \gamma_i [i]^n$, where γ_i is the activity coefficient, $[i]$ is proportion of isotope i contributing to the pool of an element of interest in phase A or B (e.g., $[^{18}O]$ in water) and n is number of sites in compound A or B in which the isotope of interest mixes (e.g., 1 for O in H_2O , 3 for O in $CaCO_3$). If $\gamma_i = 1$ (ideal mixing):

Usually $a = K^{1/x}$, where x = the number of atoms exchanged (see eqn. 2.20 in Criss)

$$H_2^{16}O + C^{18}O = H_2^{18}O + C^{16}O: K = \frac{[H_2^{18}O][C^{16}O]}{[H_2^{16}O][C^{18}O]} = \frac{[H_2^{18}O]}{[H_2^{16}O]} \frac{[C^{16}O]}{[C^{18}O]} = \alpha_{H_2O-CO}$$



$$K = \frac{[[18]_{En}]^3 [[16]_{Fo}]^4}{[[16]_{En}]^3 [[18]_{Fo}]^4} = \frac{[18]_{En} [[16]_{Fo}]}{[16]_{En} [[18]_{Fo}]} = \alpha_{En-Fo}$$

Classical thermodynamics

$$-RT \ln K = \Delta G_{\text{rxn}}^{\text{T,P}} = \Delta H_{\text{rxn}}^0 - T \Delta S_{\text{rxn}}^0 + P \Delta V_{\text{rxn}}^0$$

Systems are driven toward the lowest G state

ΔH_{rxn}^0 : Isotopologues with relatively low heats of formation from the elements (i.e., relatively strong bonds) are favored
 $T \Delta S_{\text{rxn}}^0$: Random sharing of isotopes among all co-existing species is increasingly favored at higher temperatures (i.e., $\alpha \rightarrow 1$ as $T \rightarrow \infty$)
Competition between ΔH and $T \Delta S$ terms is source of T sensitivity to K. If H, S and V are insensitive to T, K will vary with T^{-1}
 $P \Delta V_{\text{rxn}}^0$: Isotopologues with the lowest partial molar volumes are increasingly favored at higher pressure.

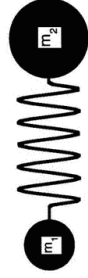
This effect long thought to be negligible; actually as important as T for hydrogen isotope fractionations between water or brine and minerals at geological P and T.

$\Delta G_{\text{rxn}}^{\text{T,P}}$ for stable isotope exchange reactions are generally on the order of 10^{-3} kcal, while errors in measuring H, S and V are equivalent to ca. 1-10 kcal. Therefore calorimetry and cell refinements cannot be used to calibrate rxns of interest.

Turn to:

- Statistical mechanics
- Experiments producing nominally equilibrated model systems
- Empirical calibration using nominally equilibrated natural assemblages

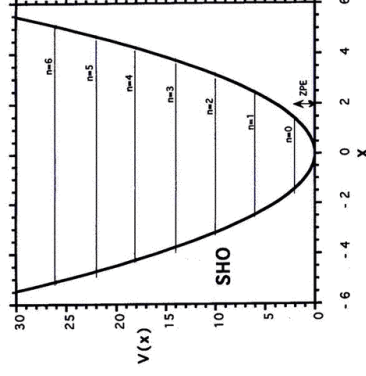
Core of the statistical mechanical approach:
 A model for the internal energy of molecules



$$F = -kx$$

$$P.E. = 1/2 kx^2$$

At rest (lowest energy state), bond will take on a characteristic distance where the potential energy stored in the spring is at a minimum



If you 'tweak' a harmonic oscillator, it will vibrate with the frequency:

$$\nu = \frac{1}{2\pi} \left[\frac{k}{\mu} \right]^{1/2}$$

- k is the spring constant (in Kg s^{-2}) on the bond. Intra-molecular bonds generally have spring constants of ca. 10^5 to 100 Kg s^{-2} . Intermolecular bonds (e.g., van der Waal's forces) generally have spring constants of ca. $1-10 \text{ Kg s}^{-2}$. A slinky is 1 Kg s^{-2}
- ν is the frequency in s^{-1} ; note $\omega = \nu c$ (i.e., wave numbers in cm^{-1} = frequency in $\text{s}^{-1} \times c$ in cm/s)
- μ is the 'reduced mass':

For dimers and vibrational modes where only 2 atoms move (e.g., CO_2 symmetric stretch)

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

For vibrations involving three or more atoms

$$\frac{\sum m_i m_j}{\sum m_k}$$

for all i-j bonds
for all k atoms
(see CO_2 example, below)

This simple model is the core of all 1st-order calculations of equilibrium isotope effects, despite other complexities.

Recall that the energy content of a classical harmonic oscillator that is 'tweaked' from its energy minimum by a distance, x, will increase in energy by the amount:

$$\Delta E = 1/2 kx^2$$

So the energy of the system is independent of mass

Isotope effect comes from the expression for the energy of a harmonic oscillator
In which energy is quantized (derived from integration of the Schrodinger eqn.)

$$E_i = (n_i + 1/2) h\nu$$

Where E_i is the energy of quantum state $n_i = 0, 1, 2, 3, \dots$, h is Planck's constant
and ν is the vibration frequency of the harmonic oscillator.

All members of a population of molecules will be in quantum state 0 when temperature is absolute 0; at higher temperatures, the population will contain members having a range of quantum states, with a distribution described by the Boltzmann law:

$$P_{ni} = A e^{-E_i/kT}$$

Where P_{ni} is the probability that a molecule is in quantum state n_i , k is the Boltzmann constant and A is a constant have a value such that $\sum P_{ni} = 1$

We now need to know one thing to calculate the effect of isotopic substitution on the energies of intramolecular bonds: How does isotopic substitution effect the spring constant on the bond? This field generally follows the Born-Oppenheimer approximation, which states that potential surfaces of bonds are independent of isotopic mass (i.e., ignore this part of the problem). Therefore:

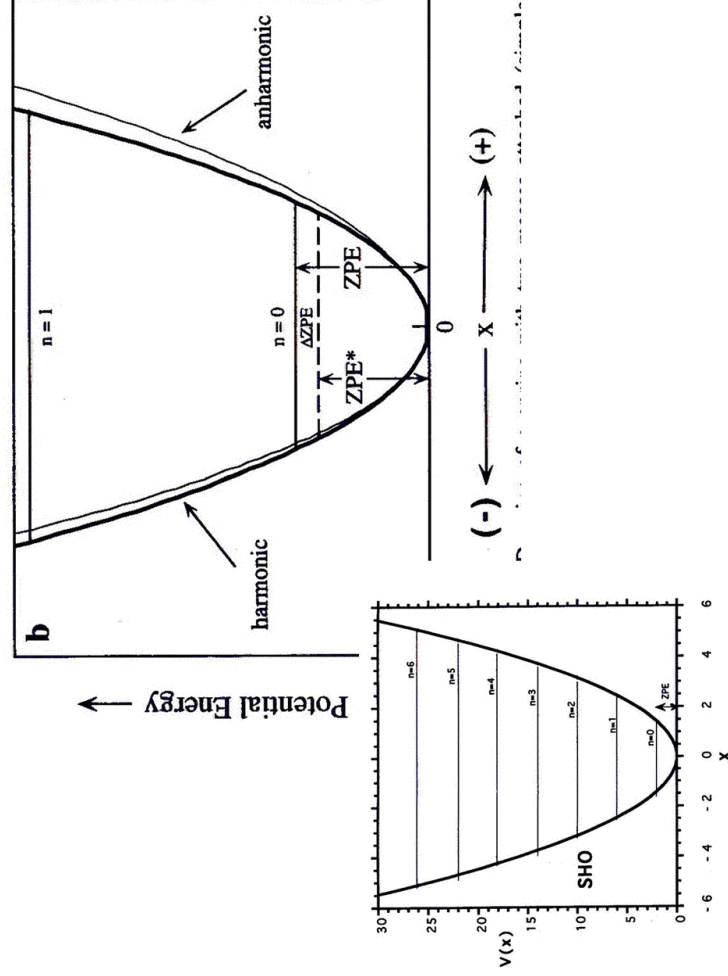
$$v = \frac{1}{2\pi} \left[\frac{k}{\mu} \right]^{1/2} \quad v' = \frac{1}{2\pi} \left[\frac{k}{\mu'} \right]^{1/2}$$

$$\frac{v'}{v} = \left[\frac{\mu}{\mu'} \right]^{1/2}$$

$$E_i - E_i' = [(n_i + 1/2)h] (v - v')$$

For order-of-magnitude estimates, we usually ignore the high-energy states and simply calculate the difference in energy between the $n_i = 0$ states, called the ‘Zero Point Energies’, or ZPE’s.

$$ZPE - ZPE' = \frac{1}{2}h(v - v')$$



Exchange reactions are driven in the direction of decreasing total ZPE's:

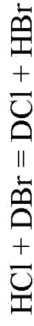
The reaction: $aA + bB' = aA' + bB$, is driven to the right if:

$$\Delta ZPE_{rxn} = (aZPE_A' + bZPE_B') - (aZPE_A + bZPE_B) < 0$$

That is, heavy isotopes are concentrated in materials for which $(ZPE - ZPE')$ is a large number, i.e., for which $(v-v')$ is a large number.

$$\text{Note: } (v-v') = v \left(1 - \left[\frac{\mu}{\mu'} \right]^{1/2} \right)$$

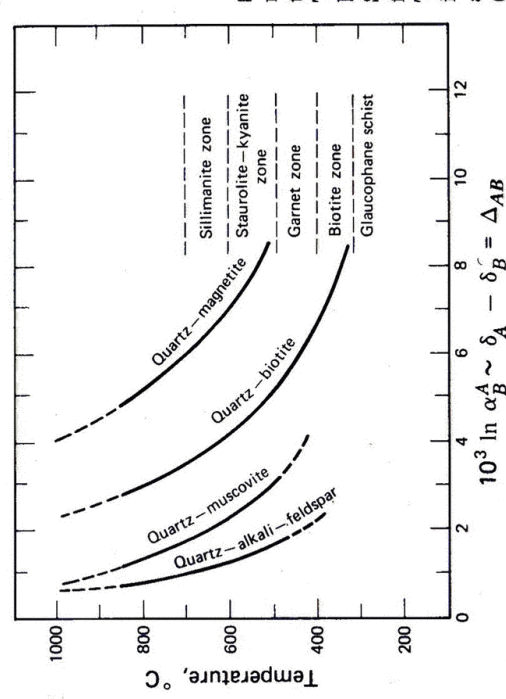
So, in any exchange reaction between A and B, the heavy isotope will be concentrated in the compound with the higher frequency of molecular vibration.



The HCl stretch has a frequency of 2988.95 cm^{-1} ; HBr of 2649.67 cm^{-1} ; so D should be concentrated in hydrochloric acid, and the reaction is driven to the right.

Si-O stretch: 1000 cm^{-1}

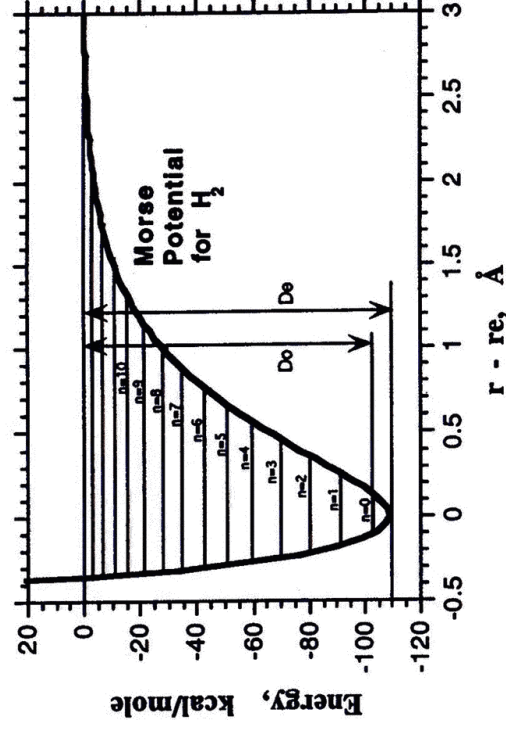
Fe-O stretch: 600 cm^{-1}



General rule: $v_{\text{m-O}}$ varies with $(\text{mass of cation } m)^{-1}$

Calculating the right values for k or α of exchange reactions requires several things:

- A more accurate potential surface for bonds (i.e., they are not harmonic oscillators)
- Consider energetic terms associated with $n_i = 1, 2, 3, \dots$ states (i.e., Boltzmann law)
- Add terms for quantum particle translations and rotations



The partition function (Q)

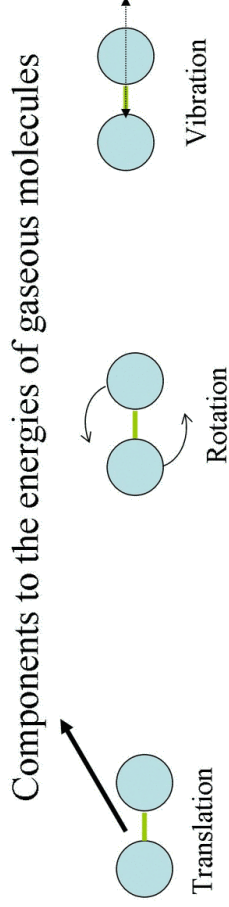
$$Q = \sum n_i e^{-E_i/kT}$$

where n_i = the number of particles, in the population of interest. So, Q is a sort of weighted average of the energies of all molecules in a population—a statistical-mechanical equivalent of a , the chemical activity.

For the reaction: $aA + bB' = aA' + bB$

$$k = \frac{(Q_A')^a (Q_B)^b}{(Q_A)^a (Q_B')^b} = \frac{(Q_A'/Q_A)^a}{(Q_B'/Q_B)^b}$$

Knowing Q'/Q values of substances (ratios in energy between isotopically substituted and isotopically normal populations) is all you need to calculate k or α values.



Quantum theory predicts isotope effects for all of these energies, analogous to the ZPE effect

$$Q = Q_{\text{trans}} \times Q_{\text{rot}} \times Q_{\text{vib}}$$

$$Q_{\text{trans}} = \frac{(2\pi M k T)^{3/2}}{h^3} V$$

Where M is molecular weight, k is Boltzmann's constant, h is Planck's constant, and V is the system volume.

$$\frac{Q_{\text{trans}}'}{Q_{\text{trans}}} = \left(\frac{M'}{M} \right)^{3/2}$$

Similarly:
$$\frac{Q_{\text{rot}}'}{Q_{\text{rot}}} = \left(\frac{\sigma I'}{\sigma^* I} \right)$$

Where σ is the symmetry number and I the moment of inertia (this term is more complex for tri-atomic and higher-order molecules)

And, drawing on theory we discussed earlier:

The ZPE contribution

$$\frac{Q_{\text{vib}}'}{Q_{\text{vib}}} = \prod \frac{e^{-U_i'/2}}{e^{-U_i/2}} \frac{1 - e^{-U_i}}{1 - e^{-U_i'}}$$

Contributions from higher-energy quantum states of each vibration

Where $U_i = h\nu_i/kT$ for each vibrational mode, i

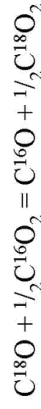
There is 1 mode for diatomic molecules, 3a-5 for linear polyatomic molecules and 3a-6 for non-linear polyatomic molecules, where a is the number of atoms. e.g., CO₂ has 4 modes (see below).

Combining the rotational and translational terms using the Teller-Redlich spectroscopic theorem, and simplifying:

$$\frac{Q'}{Q} = \left(\frac{m'}{m} \right)^{3r/2} \frac{\sigma'}{\sigma} \prod \frac{\nu_i'}{\nu_i} \frac{e^{-U_i'/2}}{e^{-U_i/2}} \frac{1 - e^{-U_i}}{1 - e^{-U_i'}}$$

Where m is the mass of the isotope exchanged, and r is the number of atoms of the Element of interest in the molecule (e.g., 2 for O in CO₂)

An example: Exchange of ^{18}O and ^{16}O between CO and CO_2 at 0°C

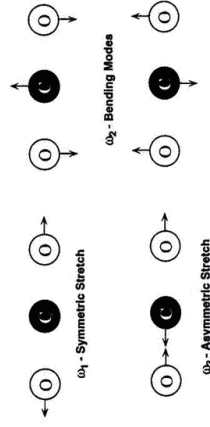


CO : asymmetric dimer ($\sigma/\sigma' = 1$); one stretching vibration with $\omega = 2140.8\text{ cm}^{-1}$

CO_2 : Linear polyatomic molecule ($\sigma/\sigma' = 1$); four vibration modes:

Symmetric stretch ($\omega = 1342.5\text{ cm}^{-1}$), two equivalent ('degenerate') bending

Modes ($\omega = 667.0\text{ cm}^{-1}$) and one asymmetric stretch ($\omega = 2355.0\text{ cm}^{-1}$)



ω'/ω can be calculated using harmonic oscillator approximation in all cases.

$$\mu = \frac{16 \cdot 16}{16+16} \quad \text{for symmetric stretch of } \text{CO}_2 \quad = \frac{2 \cdot 16 \cdot 12}{2 \cdot 16+12} \quad \text{for other modes}$$

$$1.1937 \quad 0.9758 \quad 1.000004$$

$$\text{CO: } \frac{Q'}{Q} = \left[\frac{m'}{m} \right]^{3r/2} \frac{\sigma}{\sigma'} \prod \frac{v_i'}{v_i} \frac{e^{-U_i'/2}}{e^{-U_i/2}} \frac{1 - e^{-U_i}}{1 - e^{-U_i'}}$$

$$1.3349 \quad 1 \quad 1.1459$$

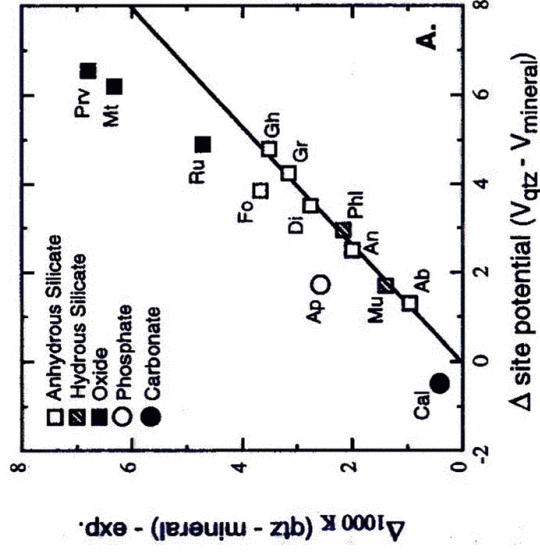
$$1.4250 \quad \frac{0.9427}{0.9847} \quad \frac{0.9847 (\times 2)}{0.9847} \quad 1.000001$$

$$\text{CO}_2: \frac{Q'}{Q} = \left[\frac{m'}{m} \right]^{3r/2} \frac{\sigma}{\sigma'} \prod \frac{v_i'}{v_i} \frac{e^{-U_i'/2}}{e^{-U_i/2}} \frac{1 - e^{-U_i}}{1 - e^{-U_i'}}$$

$$1.8295 \quad 1 \quad 1.2247 \quad 1.0275 (\times 2) \quad 1.0996$$

$$K = \alpha_{\text{CO}_2\text{-CO}} = \frac{(1.8295)^{1/2}}{(1.3349)} = 1.01328; \quad \epsilon = 13.3 \text{ ‰}$$

Site-potential models for solids



Carbon Isotopes

The Good

- Tracer of subducted sediment
- Discriminant of organic matter vs. marine carbonate vs. primitive volatiles
- Monitor of extents and mechanisms of degassing

The Bad and the Ugly

- Most common sample types (glass+silicate minerals) susceptible to contamination
- Most data generated on interesting but exotic objects (mantle diamonds)
- Relative importance of subducted signatures vs. mantle redox chemistry unclear

Major Reservoirs:

Sedimentary organics marine carbonate normal' mantle carbon	$\delta^{13}\text{C}_{\text{PDB}}$	Size
	-25 ‰	≡ 1 'crust'
	0 ‰ -5 ‰	~ 5

Important fractionations:

CH_4/CO_2	α 0.996 to 0.990
$\text{C}_{\text{melt}}/\text{CO}_2$	0.9975 to 0.9955

Representative references:

Taylor, 1986 (review of work up to 1986)
 Javoy, 1978 (submarine basalts)
 Deines et al, 1973-1993 (diverse)

Hydrogen Isotopes

The Good

- Tracer of subducted and primordial H in the mantle
 - Monitor of extents and mechanisms of volcanic degassing
- The Bad and the Ugly
- Sensitive to sub-solidus alteration
 - Contrast between mantle and subducted rocks can be subtle
 - 'Specialty' measurement; small data sets and poor inter-laboratory calibration

Major Reservoirs:

δ_{DSMOW}	\equiv 0 ‰	Size
Seawater	-50 to -80	\equiv 1 'ocean'
'normal' mantle hydrogen	-15 to -70	\sim 0.1 to 2
altered ocean crust	-90 to -120	\sim 0 to 0.1
'exotic' mantle hydrogen		?

Important fractionations:

	α
CH ₄ /H ₂ O	0.94 to 0.92
H ₂ /H ₂ O	0.85 to 0.70
OH ⁻ /H ₂ O	0.98 to 0.94

Representative references:

- Craig, Kyser, Poreda (early work on lavas)
- Boetcher and O'Neil (early work on rocks)
- Deloule, Graham (recent SIMS work on rocks)

Nitrogen Isotopes

The Good:

- Tracer of subducted pelagic sediment
 - Monitor of metasomatic reactions??
- The Bad and the Ugly:
- Most common sample types (glass+silicate minerals) almost unanalyzable and very susceptible to contamination
 - Most data generated on interesting but exotic objects (mantle diamonds)
 - Relative importance of subducted signatures vs. mantle redox chemistry unclear

Major Reservoirs:

$\delta^{15}\text{N}_{\text{AIR}}$	\equiv 0 ‰	Size
Air	\sim 0-20 ‰	\equiv 1 'atmosphere'
Sedimentary organic matter	< 0 ‰	\sim 0.1-0.5
'normal' mantle nitrogen		\sim 1

Important fractionations:

sedimentary fixed N is ¹⁵N enriched
 metamorphism enriches ¹⁵N in residue
 $\delta^{15}\text{N}$ of diamond independent of habit

Representative references:

- Cartigny et al., 1997-2001 (recent work on mantle diamonds)
- Boyd et al., 1987-1995; Javoy 1984(previous work on diamonds)
- Marty, 1995, 1997 (basalts)

Sulfur Isotopes

The Good:

- Monitor of volcanic degassing (including oxidation state of magma)
- Isotopic contrast between mantle and subducted sediments
- Isotopic contrast between sedimentary sulfate and sulfide

The Bad and the Ugly:

- Small ranges in mantle materials
- Dominance of degassing signatures in shallowly-erupted lavas

Major Reservoirs:

Crustal (sulfide and sulfate)
Mantle (sulfide and sulfate)
Core (large, but isolated...?)

Important fractionations:

SO₂ vapor vs. SO₄²⁻melt: 0.996 to 0.998
SO₂ vs. H₂S: 1.002 to 1.004

Representative references:

Taylor 1986 (review up to 1986)
Sakai et al., 1982 (degassing models)
Mandeville, 1998 (recent application)