

# 12.744: Lecture 1

## Chart of the Nuclides

### Some definitions

We start with the concept of isotopes, which are forms of elements that exists with different atomic weights (given a different in neutrons) but where chemically indistinguishable. Some important units are as follows:

- $N$ : number of neutrons
- $Z$ : number of protons (same as the atomic number, as  $Z$  dictates the chemical properties of the atom)
- $A = N + Z$ : the mass number
- $M$ : atomic mass
- $I = N - Z$ : neutron excess number

Following our first discussion, we also define:

- Isotopes: same number of protons, different number of neutrons
- Isobars: same mass number,  $A$
- Isotones: same number of neutrons, different number of protons

The basic unit of nuclear mass is the unified atomic mass unit,  $u$  or dalton, Da, which is one-twelfth the mass units of  $^{12}\text{C}$ .

### Nuclear Forces

It is important to note that not all combinations of  $N$  and  $Z$  are stable, where we define nucleons as either protons or neutrons. For those that are stable, it is generally the case that  $N \sim Z$ . Given the positive charge of protons, it is clear that there must be an equal and opposite force that allows for the coulombic or electrostatic force to be overcome in the nuclear. This is called the strong (nuclear) force. This is one of four fundamental forces of nature, which we define now along with their relative strengths:

- Strong (nuclear) force: 1, mediated by the pion
- Electromagnetic force:  $10^{-2}$ , mediated by the photon
- Weak force:  $10^{-5}$
- Gravitational:  $10^{-39}$

The mediation particle carries 1 quantum of its respective force.

### Nuclear Masses

Interestingly, if we add up the masses of protons, neutrons, and electrons in an atom, you will find that you are at more mass than the element's known mass. This additional mass is converted into binding energy holding together the nucleus. As a general principle, we have that the lowest energy configuration is the most stable. Therefore, we can take the case that an atom must be relatively more stable, and have less energy, than the sum of its constituent parts. Thus, we can use Einstein's mass-energy equivalence of  $E = mc^2$  to get the mass decrement between this sum  $W$  and the mass given by Einstein's relation as:

$$\delta = W - M.$$

We can then determine the binding energy, per nucleon, as;

$$E_B = \left( \frac{W}{M} \right) c^2.$$

### Models

One model is the liquid-drop model, which assumes that all nucleons in a nucleus have equivalent states. The model treats the binding between nucleons in a way similar to the binding between molecules in a liquid drop. There are four effects of differing power laws that effect total binding energy:

1. volume energy
2. surface energy
3. excess neutron energy
4. coulomb energy

We can write this as:

$$B(A, I) \sim \underbrace{A}_{\text{volume}} - \underbrace{A^{2/3}}_{\text{surface}} - \underbrace{I^2 A^{-1}}_{\text{excess neutron}} - \underbrace{Z^2 A^{-1/3}}_{\text{coulomb}} + \underbrace{\epsilon}_{\text{parity fudge factor}}.$$

Here, we let  $\epsilon$  be the even-odd fudge factor with the binding energy greatest for the even-even factor and least for the odd-odd factor, that is:

$$\epsilon(A, Z) = \begin{cases} \epsilon_0 & \text{for even } Z, N, \\ 0 & \text{for odd } A, \\ -\epsilon_0 & \text{for odd } Z, N. \end{cases}$$

The solution to this equation at constant  $A$ , that is for isobars, are hyperbolas in  $I$ . For odd  $A$ , we get that there is a single energy well with a nuclei near the bottom. For even  $A$ , we get that there are two energy wells, with the even one having less energy and is therefore more stable. These nucleci will decay into a stable number of neutrons. This then shows the branched decay in which an unstable nucleus can branch into two possible daughters.

Another model is the shell model, which uses Schrödinger's equation together with the Pauli exclusion principle that only one particle can have a distinct set of quantum numbers give the characteristics of each shell of the atom. Important to this is the total nuclear angular momentum, or spin or  $j$ , which is the sum of the intrinsic angular momentum for nucleons given as  $0.5\hbar$  and the orbital angular momentum which arises from the rotation of the nucleus  $l$ :  $j = l \pm 0.5$ . As an aside, we note that total angular momentum and magnetic moment of pairs of nucleons cancel because the vectors of each member pair are in opposite directions.

## Magic Numbers

We note that this model does not take into consideration is the even-odd effect. From the chart of the nuclides, we get that even combinations are more likely to be stable than odd ones. Additionally, we note that this model does not include the magic numbers, which are: 2, 8, 20, 28, 50, 82, and 126. The first part of this series turns out to be solutions to the Schrödinger equation for a three-dimensional harmonic oscillator, which fails for 28 and beyond as  $f$  is the only allowable state in the fourth shell. We present the following observations:

1. Magic number nuclides are unusually common in nature
2. There are many different nuclides in cases where  $N$  or  $Z$  are magic
3. The heaviest stable nuclide occurs at  $N = 126$
4. Nuclear properties change when a magic number is reached, like: spin, magnetic and quadrupole moment, and isomeric states.
5. Neutron-capture cross-sections for magic number are anomalously low
6. Neutron emission is delayed in fission product nuclei containing  $N^* + 1$  neutrons for  $N^*$  magic, for which the binding energy for the last neutron or proton drops

We note further that nuclei with magic numbers of  $N, Z$  are stable and unreactive, analogous to the noble gases. Additionally, the properties of these nuclei can be dominated by the last nucleon, analogous to the valence electron.

## Decay

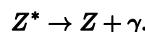
We start with the decay equation:

$$\frac{dN}{dt} = -\lambda N,$$

which is mediated by a few kinds of decay, described below:

### Gamma decay

A  $\gamma$  ray is a high energy photon, which can be absorbed by nuclei to become excited, which subsequently decay, releasing this photon. The reaction is written as:



### Alpha decay

An  $\alpha$  particle is simply a helium nucleus, a particularly stable configuration. This decreases the mass of the parent nucleus by the mass of the  $\alpha$  particle plus the kinetic energy of the  $\alpha$  particle and the daughter nucleus, from conservation of momentum stemming from the recoil of the parent nucleus. A subsequent  $\gamma$  might occur, as the daughter is often excited. The "valley of stability" is traversed diagonally, 2:2, by this decay.

### Beta decay

This is the process by which the nucleus changes the charge but has no change in mass, which occurs when either an electron or positron is emitted from the nucleus (if  $Z < N$  or  $Z > N$ , that is which side of the "valley" the parent is). We call these  $\beta^-$  and  $\beta^+$  decay. Correspondingly, we have that a neutrino is released, to conserve energy, which is a massless neutral particle with 0.5 spin. The "valley of stability" is thus traversed orthogonally along either constant  $Z$  or  $N$ .  $\beta$  decay involves the weak force, which transforms the proton into a neutron or vice versa, which is mediated by the  $W$  boson (i.e., neutrino lost then converted to positron or antineutrino lost then converted to electron).

### Electron capture

This is similar to  $\beta^+$  decay, in which an electron is added to a nucleus to produce a nucleus which less mass than the parent, with the difference in mass being carried off as energy in a neutrino or a  $\gamma$  ray. There is a dependency on pressure here, which forces electrons closer to the nucleus, increasing probability of capture.

### **Spontaneous fission**

This is the process by which a nucleus splits into two or more fairly heavy daughter nuclei, which are of unequal size of ratio 1.45, in addition to releasing two free neutrons.

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# 12.744: Lecture 2

## Stellar Nucleosynthesis

### Nucleon Decay

We consider the neutron decay into a proton:

$$n \rightarrow p.$$

We need to balance this, however, following:

1. charge
2. baryons
3. leptons

Therefore, the above becomes:

$$\begin{array}{c} n \rightarrow p + e + \bar{\nu}_e \\ \hline o \rightarrow 1 -1 o \quad (\text{charge}) \\ \hline 1 \rightarrow 1 o o \quad (\text{baryon numbers}) \\ \hline o \rightarrow o +1 -1 \quad (\text{lepton numbers}) \end{array}$$

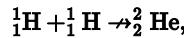
Here, the antineutrino is  $\bar{\nu}_e$ . The etymology is that baryons comes from "heavy" and leptons means "light".

### Production of the Elements

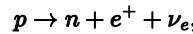
We start with the Big Bang, in which the produced elements were 75% H and 25% He. This comes from a large production of  $n$  and  $p$ , for which we note from above that the  $n$  are unstable and decay, as well as a minor percentage of  $p$ , in so doing producing a smattering of other lighter elements, such as, in order of decreasing log mass fraction:

- $^4\text{He}$
- $^2\text{H}$
- $^3\text{He}$
- $^3\text{H}$
- $^7\text{Be}$
- $^7\text{Li}$
- $^6\text{Li}$

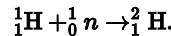
We can tackle this quantitatively. First, we note that:



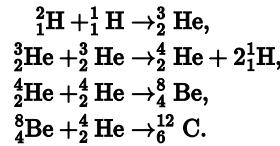
given that the coulomb repulsion of like-charged particles is too strong. However, we note that the above is akin to the opposite of our initial discussion, namely:



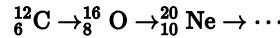
where  $e^+$  is a positron and  $\nu_e$  is a neutrino. Thus, we can get:



We can go down the ladder as follows:



and so on. This is happening in a star, and only in those stars at which the  $(T, P)$  is strong enough to produce these elements, i.e., overcome the repulsion. We note that the Be production is not energetically favourable as it has a tendency to split into 2 helium, given the binding energy of Be is much smaller than He. Once we get to the conditions to form  $^{12}\text{C}$ , we get the  $\alpha$ -ladder with the addition of the  $\alpha$  particles:



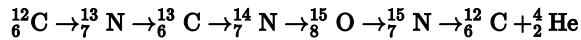
These can be produced only in stars that are massive enough to produce the  $T, P$  conditions, as stated above, but for those that are, we can get successive rings within the stars that are burning, from the outside in (with increasing mass):

1. H: 7 million years
2. He: 500,000 years
3. C: 600 years
4. Ne: 1 year
5. O: 6 months
6. Si: 1 day

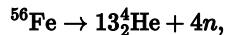
This occurs as it is energetically favourable to do so, that is we are on the left side of the energy binding curve, namely left of  $^{56}\text{Fe}$ . At this point, we have reached the maximum binding energy, and it becomes energetically less favourable to produce elements. There is no energy to be gained from additional burning. We end stellar nucleosynthesis here. As an aside, there is an inverse relationship between mass of star and a lifetime of star.

## C-N-O Cycle

We have the following important synthesis cycle:



Therefore, we have a catalytic cycle that produces  $\alpha$ -particles that can be used to produce heavier and heavier elements. We note that this only occurs in so called "Second Generation Stars", those that were formed after the first stars composed mainly of H and He exploded into supernovae after  $^{56}\text{Fe}$  conditions are reached. We note that when  $^{56}\text{Fe}$  can be broken down as follows:



therefore these supernovae produce large numbers of  $\alpha$ -particles and neutrons.

## Other Production Pathways: *s, r* processes

We have two different main pathways that produce most of our elements:

- slow addition of neutrons: *s*-process,  $t_{1/2} \sim 10^4$  years. This occurs during the burning of stable stars, which produce *n* at slow rates
- fast addition of neutrons: *r*-process,  $t_{1/2} \sim 0.1$  seconds. This occurs at the supernovae stage at fast rates during collapse.

First, the *s*-process follows along the stability line within the valley of stability. Second, the *r*-process overshoots the stability line, which will eventually decay back to the valley of stability. We note from relative mass abundances that there are always two peaks, the *r* peak and the *s* peak, for which the *r* process is always at lower masses. This is because in the decay toward the stability line of the *r*-process, it eventually ends up at a lower mass than the slow addition. We can also note that the isotopes on the neutron-rich side of the valley of stability were often created by *r*-processes, while those on the proton rich side were produced by *s*-processes. There is also shielding effects, in which *r*-process produced elements shield other elements from being produced by the same process, thus making these shielded elements to be produced by the *s*-process. There is also the proton addition, or *p*-process, that can produce elements on the proton rich side, but these are low abundance and less favourable to make.

Fission is the last production pathway, that occurs when atoms get so big that they can spontaneously split a part and form two or more daughter particles with different masses, as discussed previously. This occurs when the Coulombic forces are too great for the atoms to remain intact and stable.

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# **12.744: Lecture 3**

## **Mass Spectrometry**

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This lecture involved a discussion on the basics of design and use of mass spectrometry.

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# 12.744: Lecture 4

## Mass-dependent Fractionation

There are two different kind of fractionation processes: equilibrium and kinetic. We start with the experiment in Fig. 1.

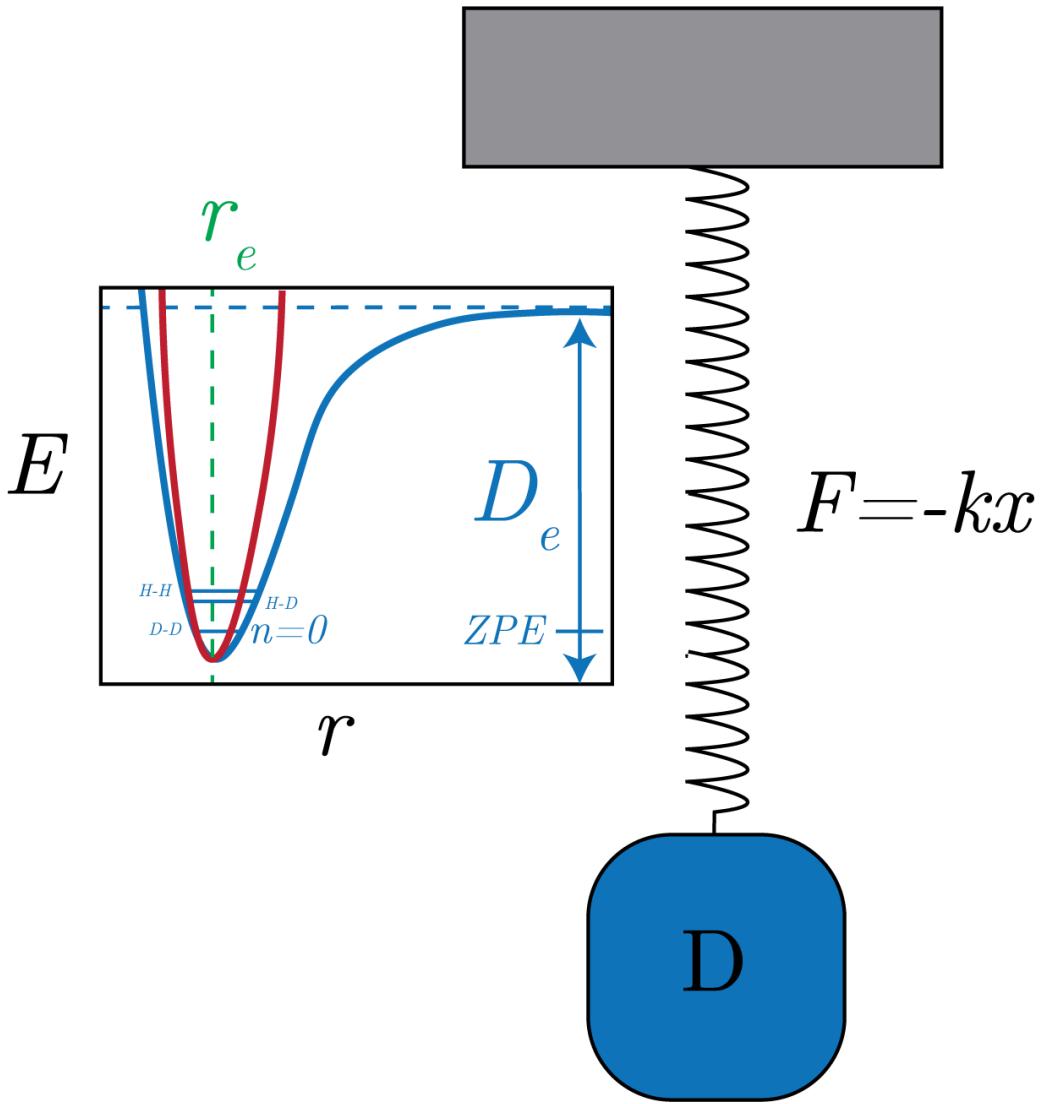


Fig. 1: A diagram of Hooke's Law and a simple harmonic oscillator (SHO).

Equilibrium isotope fractionation is a consequence of difference in the vibrational frequencies of molecules participating in isotope exchange reactions. For diatomic molecules, the simplest model is that of the simple harmonic oscillator (SHO), in which the bond between the two atoms is considered to be an ideal spring. The set-up for this is presented in Fig. 1, and assumes that there is an atom of finite mass  $m$  bound to another atom of infinite mass, such as a ball attached by a spring to a wall. We know from classical physics that we can represent this system by Hooke's Law (or the law of Elasticity) given by:

$$F = -kx,$$

where we have that  $k$  is the spring constant that represents the bond strength of the molecule. We consider the equilibrium position to be  $x_0$ . We can integrate this equation over  $x$  to get:

$$E_p = \frac{1}{2}kx^2,$$

which is the potential energy, or the red parabola or well in Fig. 1. We can rearrange Hooke's Law, using Newton's Second Law to get:

$$\ddot{x} = -\frac{k}{m}x.$$

This is a second order homogeneous linear differential equation which we assume has a solution (an *ansatz* if you like) of the form:

$$x(t) = x_0 \cos [\omega t],$$

in which we note that if we differentiate this twice with respect to  $t$  we get an equation proportional to the re-written Hooke's Law. To nondimensionalize  $\cos$ , we define:

$$\omega = \frac{2\pi}{T} [\text{radians s}^{-1}],$$

which is the angular frequency and  $T$  is the period of one oscillation. Plugging this into our equation we wish to solve, we get:

$$\ddot{x} = -\omega^2 x_0 \cos [\omega t],$$

which implies that:

$$\omega^2 = \frac{k}{m}.$$

We can then translate angular frequency to frequency  $\nu$  via:

$$\omega = 2\pi\nu,$$

where we can think of this as the arc length traversed by  $\omega$  for an angle  $\nu$ , as we know that we relate linear and angular distances from geometry. Now, if we want to consider two finite masses, say of  $m_1$  and  $m_2$ , then we introduce the reduced mass of the form:

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

which gives upon substitution:

$$\nu^2 = \frac{k}{\mu 2\pi}.$$

This then allows us to relate vibrational frequencies of isotopologues, say by solving the above system for two different masses and taking the ratio:

$$\frac{\nu_1}{\nu_2} = \left( \frac{\mu_2}{\mu_1} \right)^{1/2}.$$

In Fig. 1, we have that the red function is the SHO, which has equal spacing between energy levels  $n$ , with the lowest being:

$$E_0 = \frac{1}{2}\hbar\omega, \quad \text{for } \omega = \sqrt{k/m},$$

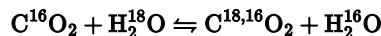
which means that you can never get to the value of the potential at  $r_e$ . We note that this is opposed to the Morse Potential, which does not have equal spacing (asymmetric solution) between energy levels  $\nu$ . We further note that  $r_e$  is the same for both, and that it takes a force in order to change  $r$  toward and away from  $r_e$ . Also, see that it is impossible to disassociate with the SHO, as there are an infinite number of  $n$ , versus in the Morse potential which has a certain energy threshold, as shown in Fig. 1.

The Zero Point Energy (ZPE) is an important part of these potentials and is lower for the heaviest isotopologues (i.e., D-D, H-D, H-H). We define ZPE as:

$$\text{ZPE} = \frac{1}{2}\hbar\omega,$$

and thus we see that heavier isotopes have lower ZPE, and thus more energy is needed to get them out of the energy well. This means that to get out of this potential well ("do chemistry"), you need to apply more energy. So, out of all of the isotopes, the lighter ones will be more reactive, or more readily able to do chemistry and react in chemical reactions. An example is CO<sub>2</sub>, for which <sup>12</sup>C will react first before <sup>13</sup>C or <sup>14</sup>C.

This model explains kinetic isotope effects, which are non-equilibrium isotope effects. Each system energetically gains from having heavier isotopes in a reaction. An example of this is:



The question then becomes: where does the <sup>18</sup>O go, as it will make each bonding environment more favorable for each compound. The answer to this is from ZPE. Specifically, we can define the difference in the ZPE for the two isotopes with vibrational frequencies  $\nu$  and  $\nu'$ :

$$\Delta\text{ZPE} = \frac{1}{2}\hbar(\nu - \nu') \sim \nu \left( \frac{\nu}{\nu'} \right)^{1/2}.$$

So, the molecular with the greater **ΔZPE** will get the heavier isotope (in this case  $\nu'$ ). From this, we can get, after calculation:

$$\begin{aligned} \Delta G^\circ(\text{H}_2\text{O}) &= -56.7 \text{ [kcal mol}^{-1}], \\ \Delta G^\circ(\text{CO}_2) &= -92.3 \text{ [kcal mol}^{-1}], \end{aligned}$$

which then means that the difference between the ZPE for water is less than that for carbon dioxide. Therefore, CO<sub>2</sub> is the more favorable as it has the most to gain, and therefore the heavier O isotope ends up with the carbon dioxide.

This leads us to some qualitative rules for isotope fractionation:

1. Degree of fractionation goes down with increasing temperature T
2. Degree of fractionation increases with increasing mass, described by the fractional mass difference:  $\mu = (m_h \cdot m_l) / (m_h + m_l)$
3. Heavy isotopes are concentrated in substances with the stiffest bonds (i.e., high spring constant, stiffest bonds). These often correlate with the following environments:
  - High oxidation state: Fe<sup>3+</sup> vs. Fe<sup>2+</sup>, remembering that the oxidation state is the hypothetical charge of an atom if all of its bonds to other atoms were fully ionic)
  - Bonds with elements near the top of the periodic table: F, Cl, Br
  - Strongly covalent bonds (bonds formed by sharing valence electrons vs. the complete transfer of valence electrons in ionic bonding)
  - Low-spin configuration (specifically for transition metals), which are based on the molecular geometries of the complexes of interest
  - Low coordination numbers: B(OH)<sub>3</sub> vs. B(OH)<sub>4</sub><sup>-</sup>, which becomes important when reconstructing paleo pH with B isotopes. We note that the heavier isotope <sup>11</sup>B will end up in B(OH)<sub>3</sub> and so we can get the pH from the forams that incorporate these heavy isotopes (or not). Remember that the coordination number is the number of atoms bonded to a central atom, the ligand.

Let's look at this all in play. For O<sub>2</sub> with O atoms of mass 16, there is a vibrational frequency of about 1580 [cm<sup>-1</sup>], as opposed to O<sub>2</sub> of one 16 and one 18, which has a frequency of about 1235 [cm<sup>-1</sup>]. This shows us that the heavier the mass, the lower the frequency, therefore the closer to the bottom of the potential energy well determined above. We can see this in our calculation of  $\nu$  in the negative square root dependence on the reduced mass. As the energy of a vibrational model is directly related to the frequency, then the heavier the molecule the less energy in the bond, as it is deeper into the energy well. Conversely, we see that the higher the force constant, such as the  $k$  above related to a stiffer bond, then the higher the vibrational frequency and energy will be. We note that the force constant is unaffected by isotope substitution but rather the orbital electrons which are closer to the interatomic distance (think the cloud of electrons), therefore we get that no matter the isotope of a given element the spring constant the same within a given molecular for a given atom. We remember that the overarching principle of isotope fractionation is to lower the overall energy of the system (reach a minimum, equilibrium state, i.e. resting in the bottom of the well), this means that all molecules are competing for the heaviest isotopes and therefore the lowest energy. The molecule that successfully receives this heavier isotope is the one that has the greatest energetic benefit (or the greatest reduction of energy) of the incorporation, which is usually the compound with the higher force constant as this would translate to a higher energy level (and thus a greater difference between the bottom of the well). An example would be that <sup>18</sup>O would preferentially choose the smaller, higher charged silicon to the larger, lesser charged iron (silicates instead of oxides).

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# **12.744: Lecture 5**

## **Instrumental Mass Bias**

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This lecture involved a discussion of instrumental mass bias and other practicalities of isotope measurements.

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# 12.744: Lecture 6

## Stable Isotope Systematics

### Stable Isotopes

We will be specifically talking about: C, H, O, N, and S. We will consider Li later. The isotopes are:

C :  $^{12}\text{C}$ ,  $^{13}\text{C}$ .

H :  $^1\text{H}$ ,  $^2\text{H}$  (Deuterium, D).

O :  $^{16}\text{O}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ .

N :  $^{14}\text{N}$ ,  $^{15}\text{N}$ .

S :  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ ,  $^{36}\text{S}$ .

We note that the first of each presented above are by far the most abundant in the Earth system. Important is the relative mass difference here, which we define as:

$$\mu = \frac{\Delta m + m}{m},$$

where  $m$  is the abundant isotope and  $\Delta m$  is the mass difference between the less abundant isotope of interest and the abundant isotope. (i.e.,  $^1\text{H}$  is the abundant and  $^2\text{H}$  is the less abundant). We note that the fractionation scales as these relative mass differences, so doing out the math we can get that:

$$\begin{aligned} D &: 0.015\% \Rightarrow \mu = 2 \\ ^{13}\text{C} &: 1.11\% \Rightarrow \mu = 1.08 \\ ^{15}\text{N} &: 0.36\% \Rightarrow \mu = 1.07 \\ ^{18}\text{O} &: 0.2\% \Rightarrow \mu = 1.12 \\ ^{34}\text{S} &: 4.22\% \Rightarrow \mu = 1.06 \end{aligned}$$

So, we can see that the H system is going to fractionate much more than the other systems.

### Notation

#### $\delta$ Notation

We define the  $\delta$ -notation as, for  $A$  the heavy isotope and  $C$  the light isotope (as is the standard now and happens in the CHONS that  $C$  is also the most abundant):

$$\delta_A = \left( \frac{(A/C)_{sample}}{(A/C)_{standard}} - 1 \right) \times 10^3.$$

Note that we are in per mille. Then, we have the isotope ratio:

$$R_A = \frac{A}{C}.$$

Next, we have the fractionation factor:

$$\alpha_{A/B} = \frac{R_A}{R_B},$$

and we say then that:

$$\delta_A - \delta_B \simeq \log \alpha_{A/B} \times 10^3.$$

We call this difference the approximate fractionation. We can derive this as follows, starting with the definition:

$$\delta_{A,B} = \left( \frac{R_{A,B}}{R_S} - 1 \right) \times 10^3,$$

for  $R_S$  our standard ratio as in the  $\delta$  notation above. Then, we can plug this into our definition of  $\alpha_{A/B}$  to get, after simplifying:

$$\alpha_{A/B} - 1 = \frac{\delta_A - \delta_B}{\delta_b + 10^3} \simeq \frac{\delta_A - \delta_B}{10^3},$$

where we have used that  $\delta_B \ll 10^3$ . Using the Taylor Series expansion:

$$\log x = \sum_n \frac{(x-1)^n}{n} = x-1 + \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 + \dots,$$

for  $x \in (-1, 1]$ . Then, as  $|\alpha - 1| \ll 1$ , we can approximate as:

$$\log x \simeq x - 1.$$

There are a few things that we assume here:

1.  $\alpha$  is very near 1
2.  $\delta_B \ll 10^3$

The ranges of these values are as follows, in [%]:

$$\begin{aligned}\delta D &\in -200 : +20 \\ \delta^{18}\text{O} &\in -40 : +40 \\ \delta^{13}\text{C} &\in -60 : +10 \\ \delta^{34}\text{S} &\in -50 : +40\end{aligned}$$

The hydrogen system might break down these assumptions, as we see that the range of  $\delta D$  ranges from -200 to +20 [%], with the extrema existing in Carbanaceous chondrites (primitive meteors) and meteoric water. The meteoric water also has the highest in the oxygen system as well. The lowest carbon is in biogenic methane. These relationships can be seen (and the departure that can be propagated to large values given certain system conditions) in Fig. 1.

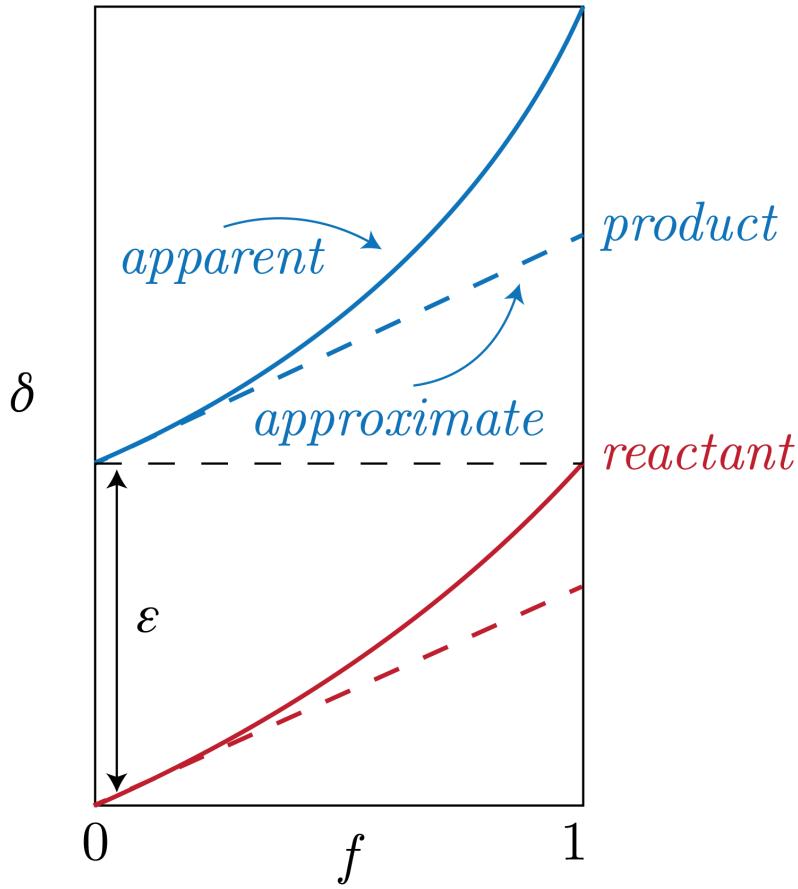


Fig. 1: The difference between the approximate and apparent fractionation.

#### ε Notation

We define the apparent fractionation as:

$$\epsilon = (\alpha_{A/B} - 1) \times 10^3.$$

## Standards

There are a few standards that are of interest to us. These are normally historical and are as follows:

1. H, O: VSMOW (Vienna Standard Mean Ocean Water)
2. N: Air
3. C: VPDB (Belemnite)
4. S: VCDT

We note that we there is no more VPDB and VCDT, but we anchored the current standard to those so that we can extrapolate back to the original standard. These are come from the fact that it was once very hard to measure so the standards helped to achieve the precision needed.

## Fractionations

### Mass Differences

The first that causes fractionation is mass difference. We can think of all of the different configurations of  $\text{H}_2\text{O}$  with H, D, and  $^{18,16}\text{O}$ . Now, we can do out the masses of each of these configurations. Then, the molecular velocity of an ideal gas is given by:

$$v = \left( \frac{8KT}{\pi m} \right)^{1/2}.$$

So, we see that:

$$v \sim \frac{1}{\sqrt{m}}.$$

Therefore, any process that involves a gas moving around, we can get that the relative velocities  $v_1/v_2$  for different masses. This then means that the diffusion is going to happen at different rates, and therefore the fractionation is proportional to this ratio in a system.

### Bonding Strength

We can recall the ZPE differences discussed previously here. We can then say additionally that:

$$\alpha \sim \frac{1}{T^n}.$$

### Kinetic Isotope Effect

This occurs in addition to the equilibrium effect. This occurs when there are incomplete or unidirectional reactions. A good example of this is the condensation of water from vapour. We assume first order kinetic reactions here of the form:

$$K = A \exp[-E_a/T],$$

with  $K$  being the reaction constant and  $E_a$  the activation energy. This is known as the Arrhenius equation. Then, we can say that:

$$\begin{aligned} \frac{dA}{dt} &= K_A A, \\ \frac{dB}{dt} &= K_B B. \end{aligned}$$

Now, we can let  $A, B$  be different isotopologues of water, say:  $\text{H}_2^{16}\text{O}, \text{H}_2^{18}\text{O}$ . From above, we know then that we can get the isotope fractionation as, dropping the subscript for clarity:

$$\alpha = \frac{K_A}{K_B},$$

which then means that:

$$\frac{dB}{dA} = \alpha \frac{B}{A}.$$

Then, we can get from our definitions of  $A, B$ :

$$\log \left[ \frac{B}{B_0} \right] = \alpha \log \left[ \frac{A}{A_0} \right],$$

which becomes, for  $B \ll A$ :

$$\frac{B/A}{B_0/A_0} = \left( \frac{A}{A_0} \right)^{\alpha-1},$$

and note that  $A/A_0$  is our fraction of the reactant remaining, or  $f$  as we will see later.

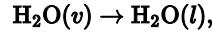
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# 12.744: Lecture 7

## Water Cycle

### Rayleigh Distillation

We start by assuming an open system of the form:



with a first order equation of the form:

$$\frac{dA}{dt} = K_A A$$

with:

$$K_A = A \exp[-E_a/T],$$

We can take a similar set of equations for a species  $B$ . We then get:

$$\alpha = \frac{K_A}{K_B}.$$

Dividing out  $t$ , we get:

$$\frac{dB}{dA} = \alpha \frac{B}{A}.$$

Then, if you then solve:

$$\log\left[\frac{B}{B_0}\right] = \alpha \log\left[\frac{A}{A_0}\right],$$

for  $A_0, B_0$  the initial amounts for  $A, B$ . We want to find something of the form  $A/B$ . We then take the Taylor Series to get:

$$\frac{B/A}{B_0/A_0} = \left(\frac{A}{A_0}\right)^{\alpha-1}.$$

Here, we assumed that  $B \ll A$  (where we have that  $A$  is the lighter isotopologue than  $B$  of water, i.e. has  $^{16}\text{O}$  vs.  $^{18}\text{O}$ ). Then, this means that  $A \sim B + A$ . We note that the fraction remaining of the reactant is:

$$f = \frac{A}{A_0}.$$

After all of this, we get that:

$$\frac{A}{A_0} = f \frac{B/A}{B_0/A_0} f^{\alpha-1}.$$

This then gives:

$$\frac{B}{A} = \frac{B_0}{A_0} f^{\alpha-1}.$$

This is an isotope ratio that we care about, and here with heavy over light as is the standard. Then, switching to  $\delta$  notation, we get:

$$\delta^{18}\text{O}(l) = f^{\alpha-1} - 1.$$

Plotting this out looks like the top panel of Fig. 1.

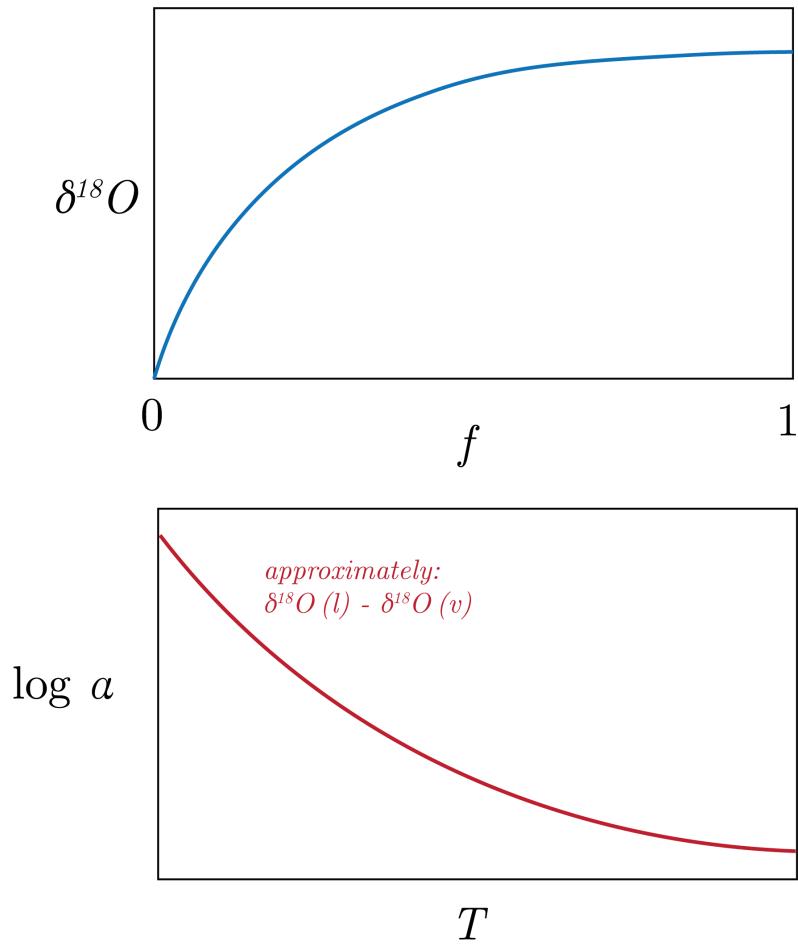


Fig. 1: A diagram of Rayleigh distillation dynamics.

We also note the inverse relationship between fractionation and temperature in the lower panel. We can see this also in the latitudinal variation of temperature, as in Fig. 2.

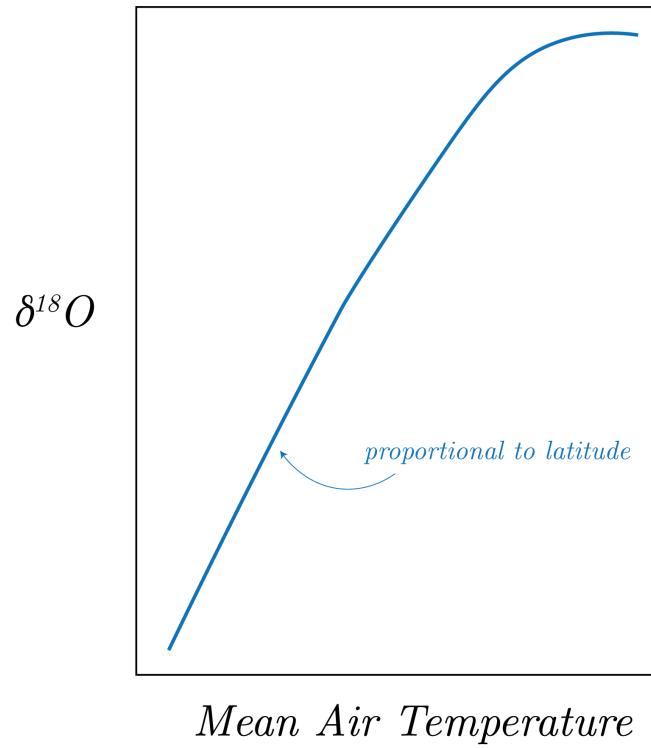


Fig. 2: The inverse relationship with temperature and  $\delta^{18}\text{O}$  with latitude.

We start with the idea of water vapour pressure. Here, we first start with the inset of Fig. 3, in which we note that you can fit in more water vapour with increasing temperature. So, this means that we can change  $f$  with the temperature. Now, let's look at Fig. 3.

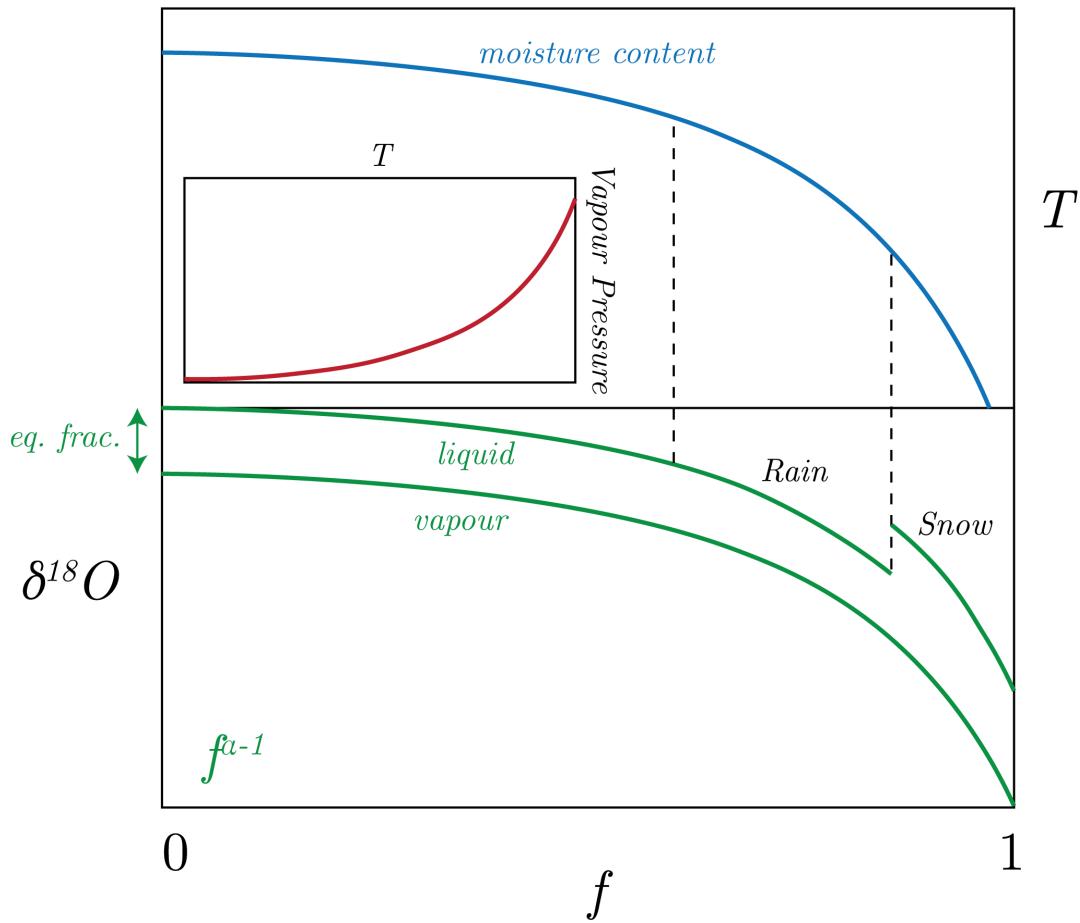


Fig. 3: The effect of temperature on oxygen in both liquid and vapour phases.

We can see the proportional effect with temperature, as well as the Rayleigh Equation of  $f^{\alpha-1}$  in the  $\delta^{18}\text{O}$  plot with fraction remaining. We now explore just why the ranges of  $\delta\text{D}$  are so much greater than that for O, as in the Global Meteoric Water Line (remembering that this subset has the greatest range in the  $\delta$  values for CHONS). We present the GMWL in Fig. 3.

# Global Meteoric Water Line

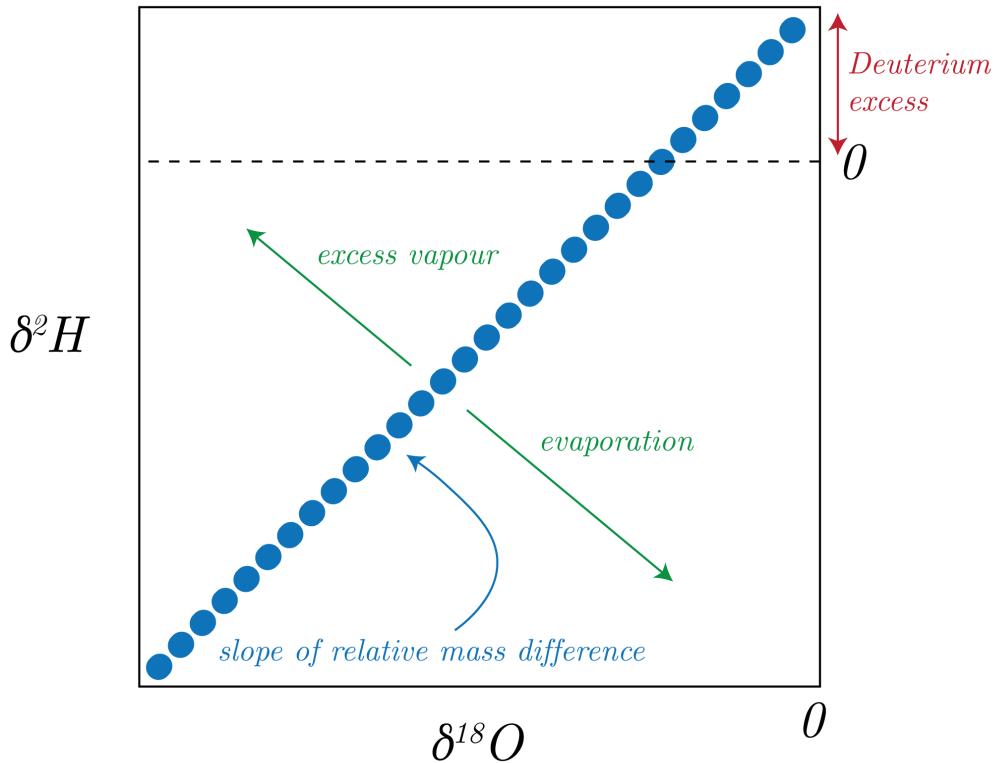


Fig. 3: The Global Meteoric Water Line.

The slope of the relative mass difference we defined as  $\mu$  is understandable given that we can take the approximate fractionation as:

$$\delta_B - \delta_A \sim \log \alpha \times 10^3.$$

Then, with  $\delta_A = 0$  by VSMOW, we get that:

$$\delta_B \sim \log \alpha \times 10^3.$$

Therefore, we can get, plugging in for  $B$  both D and  $^{18}\text{O}$  and taking the ratio, we get:

$$\delta\text{D} = \frac{\log \alpha_{\text{D}}}{\log \alpha_{^{18}\text{O}}} \delta^{18}\text{O}.$$

Then, we get that the slope is:

$$\frac{\log \alpha_{\text{D}}}{\log \alpha_{^{18}\text{O}}} \sim 8.$$

However, from Fig. 3, we note that there is a non-zero  $y$ -intercept, which we call the "deuterium excess." This is from the kinetic isotope effect, which preferentially happens in D over  $^{18}\text{O}$  which cause this excess (as we saw in the  $\mu$  calculations). This is usually about 10 but can be found from:

$$d = \delta\text{D} - 8\delta^{18}\text{O}.$$

We can then look at deviations from the GMWL to determine the processes that the isotope fractionated sample came from. For a smaller  $d$  than expected we get that there is evaporation and greater  $d$  means that there is excess vapour.

## Ice Core Temperature Reconstructions

We can look at some  $\delta\text{D}$  ice cores, such as in Fig. 4.

## Vostok Ice Core

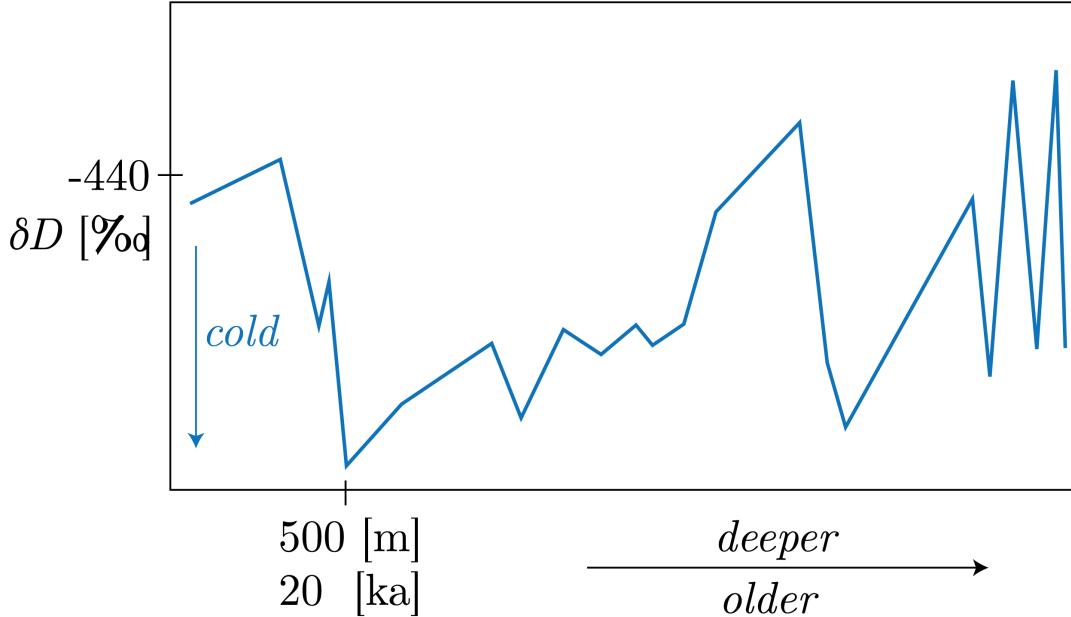


Fig. 4: The Vostok Ice Core used for temperature reconstructions.

We note that ice has a non-negligible effect on the isotope composition of the ocean, which allows us to reconstruct temperature. Specifically, we will talk about mixing here to understand this.

### Mixing

We start with 2 pools with isotope composition  $\delta_A$  and  $\delta_B$ . With mass conservation, we can write the mixing equation as:

$$\delta_{\text{mix}} = f_A \delta_A + f_B \delta_B \quad \text{where } f_A + f_B = 1.$$

This then means that we can write this all as:

$$\delta_{\text{mix}} = f_A \delta_A + (1 - f_A) \delta_B = f_A (\delta_A - \delta_B) + \delta_B,$$

which implies that:

$$f_A = \frac{\delta_{\text{mix}} - \delta_B}{\delta_A - \delta_B}.$$

Now, we can assume that all water is either in the ice or in the ocean. So, applying the equations above, we get:

$$\delta_{\text{mix},i} = f_{\text{ice},i} \delta_{\text{ice},i} + f_{\text{ocean},i} \delta_{\text{ocean}} = \text{constant},$$

for  $i$  either the PI or the LGM. With all of this, we get:

---


$$\delta_{\text{ocean,LGM}} = \delta_{\text{ice}} \frac{(f_{\text{ice,PI}} - f_{\text{ice,LGM}})}{f_{\text{ocean,LGM}}}.$$

# 12.744: Lecture 8

## Mass-independent Fractionation

### Spiking

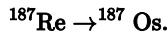
We are looking at the issue of spiking in this lecture for systems that have 3 or more isotope ratios of interest, and are specifically using the Osmium system. We first look at the Osmium system:

**184, 186, 187, 188, 189, 190, 192**

which are corresponding relative abundances of:

**0.02, 1.6, variable, 16, 16, 26, 41.**

In this system, we are interested in the variable abundance of  $^{187}\text{Os}$ , which is variable given:



We normalize to  $^{188}\text{Os}$  given its median abundance, and we use  $^{192}\text{Os}$  as the independent variable given it is the most abundant, and we are finally using  $^{190}\text{Os}$  due to the fact that it is usually used as a spike isotope in experiments. By spike here, we mean that this is a standardized sample that we can use as a tracer of sorts, that we can get from national labs, for example.

Now, we consider a set-up as in Fig. 1.

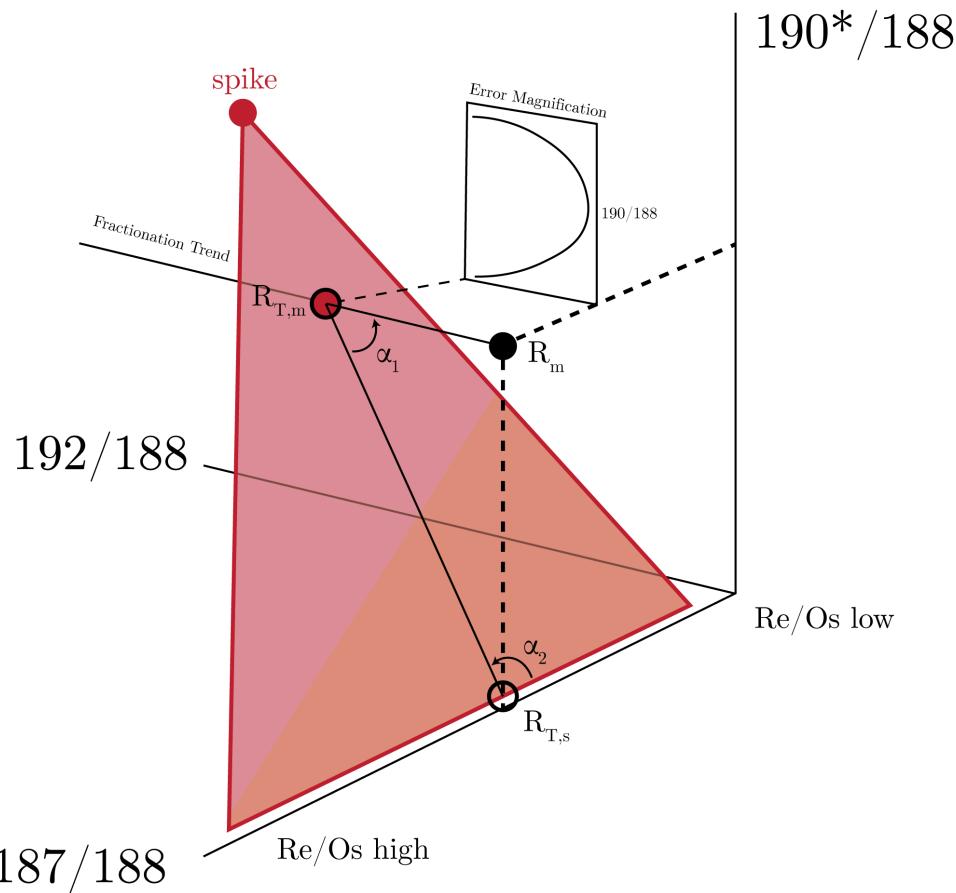


Fig. The Spiking of Osmium.

The trick here is to design the spike such that we are minimizing the angles  $\alpha_1, \alpha_2$  and therefore getting the lowest error magnification, shown in the inset plot of Fig. 1. This is essentially a slice through the red region, with  $190/180$  being the independent variable. The result from this optimization problem is the following rule:

$$\text{EM}_{\min} = \sqrt{R_{\text{sample}} \cdot R_{\text{spike}}}.$$

## Mass-independent Fractionation

We can think of this fractionation effect as in Fig. 2.

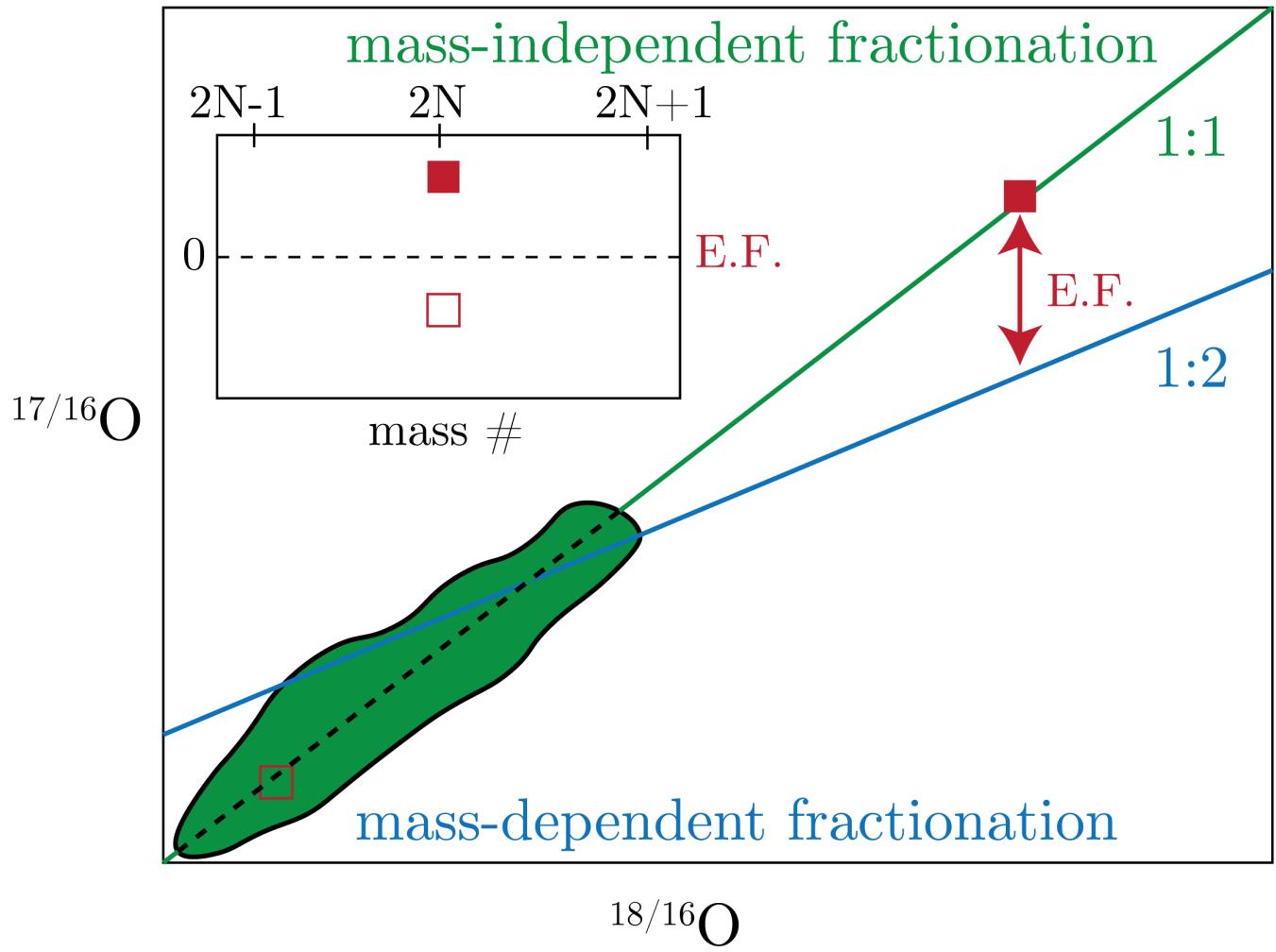


Fig. Mass-dependent fractionation for the O system. The green region is observational data.

We note that in this figure we consider the enrichment factor (EF) that is the difference between the mass dependent fractionation (MDF) line and the measured value. We define the MDF as:

$$\Delta m = m_1/m_2,$$

where the index 1 represents the numerator mass of the ratio and 2 the denominator. We now look at the various contributions to the isotope fractionation factor,  $\alpha$ :

$$\log \alpha = \underbrace{\log \alpha_0}_{\text{Urrey}} + \underbrace{\log k_{anh}}_{\text{Anharmonic} \ll 1} + \underbrace{\log k_{BO}}_{\text{Born-Oppenheimer Approximation} \ll 1} + \underbrace{\log k_{hf}}_{\text{Magnetic Isotope Effect} \ll 1}$$

We note that MIE could also be known as the nuclear spin isotope effect and is purely a kinetic effect that applies only to isotopes with odd masses in paramagnetic species. This comes from these species having a single unpaired electron in the valence shell. This only applies to chemical reactions that are selective to spin, such as reactions that involve transition states in atmospheric reactions, such as ozone (think reactions with UV light).

### An example: Sulfur

We can use S to determine the oxygen concentration in deep time. To do this, we will consider the following S isotopes:

$$32, 33, 34, 36$$

with relative abundances:

$$95, 0.8, 4, 0.02.$$

We note that  $^{33}\text{S}$  is the only odd element and therefore is susceptible to MIE. There are two varying hypothesis to how  $\text{O}_2$  has developed in deep time. These are presented as the blue lines in the main plot of Fig. 3.

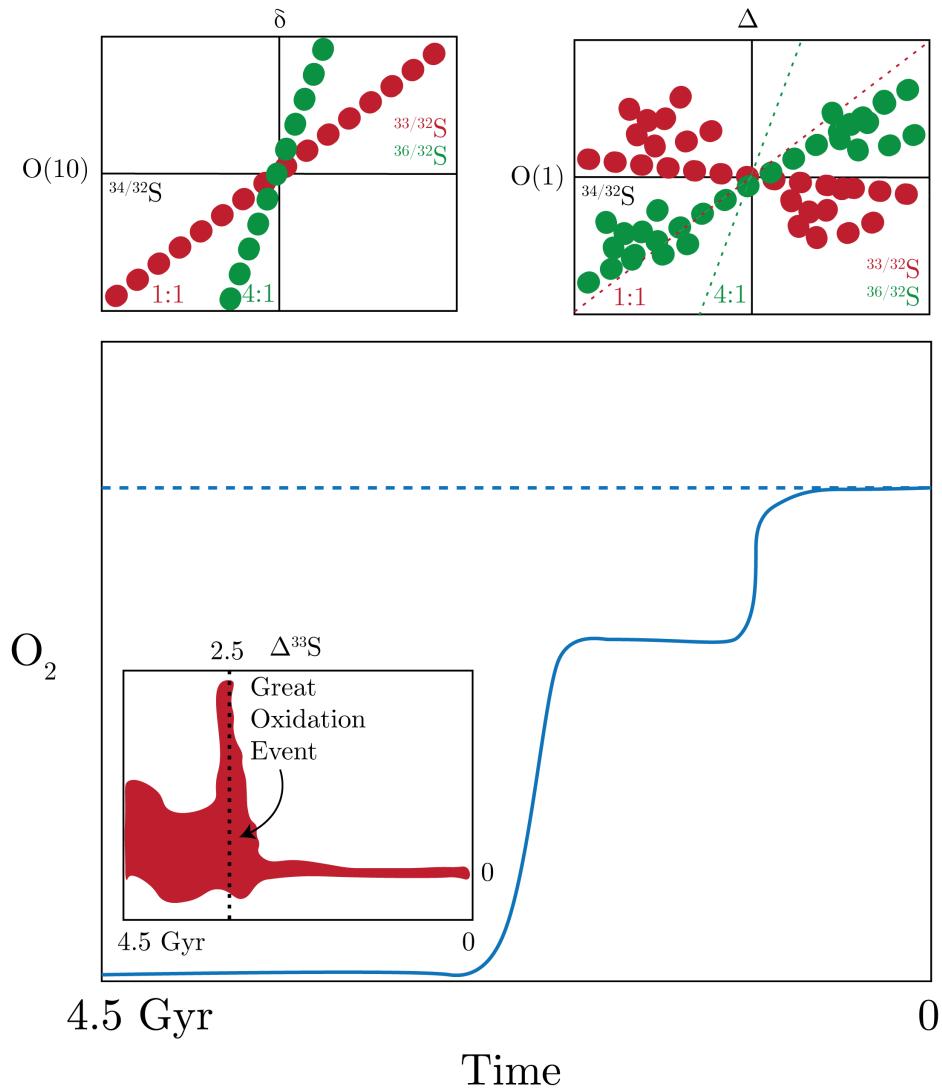
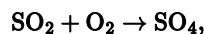


Fig. 3: MDF and varying precision measurement of S to extract oxygen levels in deep time.

The first is a constant value (dashed) and the second is a stepwise action. Now, the top two plots of Fig. 3 show S isotope ratios, with the line representing the general trend of the data. Of interest to us is the difference between the  $\delta$  plot on the LHS and the  $\Delta$  plot on the RHS. We note the LHS top plot have data that fall directly on the MDF line. However, the  $\delta$  plot was made using a less precise MS (read: old) versus the  $\Delta$  plot made with a very precise MS. We see that the  $\Delta$  plot, which is the deviation from the MDF, shows that  $^{33}\text{S}$  demonstrates MIE, and a negative correlation, as compared to the  $\delta$  plot (the dashed lines are the expected MDF lines). The y-scales are orders of magnitude less on the  $\Delta$  plot than the  $\delta$  plot.

Now, the inset plot is something interesting. This is the experimental evidence for the "Great Oxidation Event". We can see that before 2.5 billion years ago, we have a complete lack of oxygen and after which point we have abundant oxygen, the inverse of the  $\Delta^{33}\text{S}$  data shown in the inset. It is still debated whether it was an event or a process. The reason this data is connected to oxygen is from atmospheric chemistry of sulfur, specifically  $\text{SO}_2$ , which is emitted from volcanoes, becomes part of the upper atmosphere, and interacts with UV radiation. It undergoes photolysis and the thinking is that this process depends on the UV light from the sun and if there is sufficient  $\text{SO}_2$  in the atmosphere, there is something called the self-shielding effect. This effect is dependent on the isotope, for which only certain wavelengths provide the adequate energy to proceed with the reaction. Therefore, it is the sulfur isotope that drives whether or not this process takes place in the atmosphere. Thus, this effect is dependent on the spin effect (MIE), which only exists for odd masses. There might also be photoexcitation on the  $\text{SO}_2$ .

So, what happens is that:



which then is super soluble, which is stripped out of the atmosphere and put into the land and ocean reservoirs. We do not see the effect nearly as much any more in the atmosphere, with the currently thinking being that the reaction above has been fully oxidized out of the atmosphere, so we are only dealing with sulfate and sulfides in the sediments.

### Kinds of Mixing and Fractionation

Consider Fig. 4. We go over the different kinds of lines given the spaces.

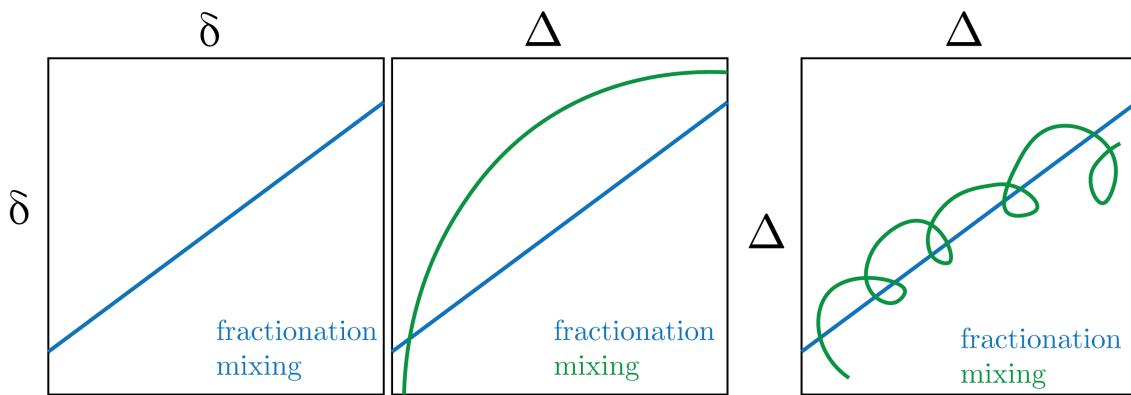


Fig. 4: Kinds of lines for mixing and fractionation given  $\Delta$  and  $\delta$  spaces.

### Nuclear Volume Effect

We care about the Nuclear Volume Effect now, which mostly takes place in large atoms. This is also known as the Nuclear Field Shift Effect, though this is not as common as this almost includes the geometry of the effect (though it is less important to the effect than the change in the size). So, this effect occurs when the radius of the nucleus is so great that it can no longer be considered a positive point charge but rather a distributed charge that can interact with the electrons, particularly the inner shell electrons. Specifically, we get that inner electrons overlap with the nucleus, which means that those negative charges are compensated by part of the nucleus, which changes the charge of the atom, causing the other electrons to be less tightly bound to the nuclear. We can see this in Fig. 5

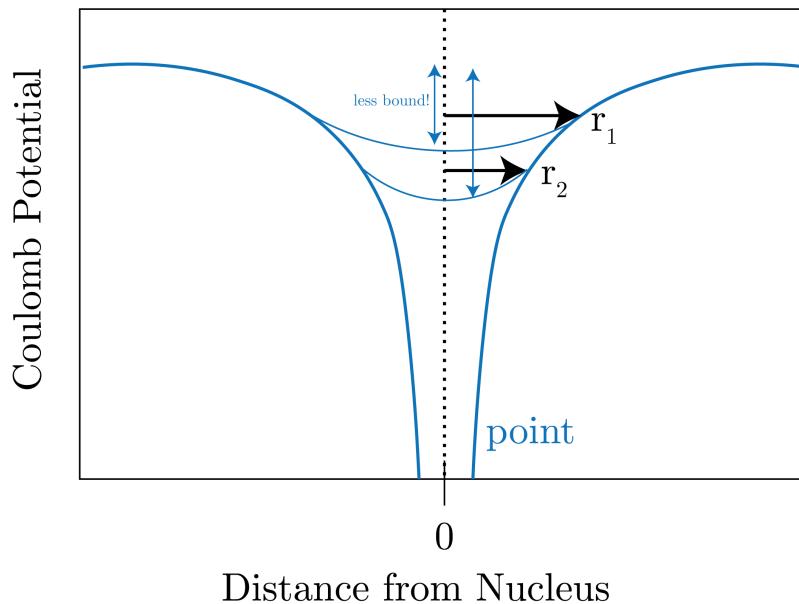


Fig. 5: The Nuclear Volume Effect in practice.

From Fig. 5, we note that the larger radius has more potential energy, therefore the electrons are less bound than the smaller radius, which has a minimum that is deeper into the well meaning more tightly bound electrons (more energy needed to disassociate). In Fig. 6, we can see that the odd mass isotopes have this effect, as well.

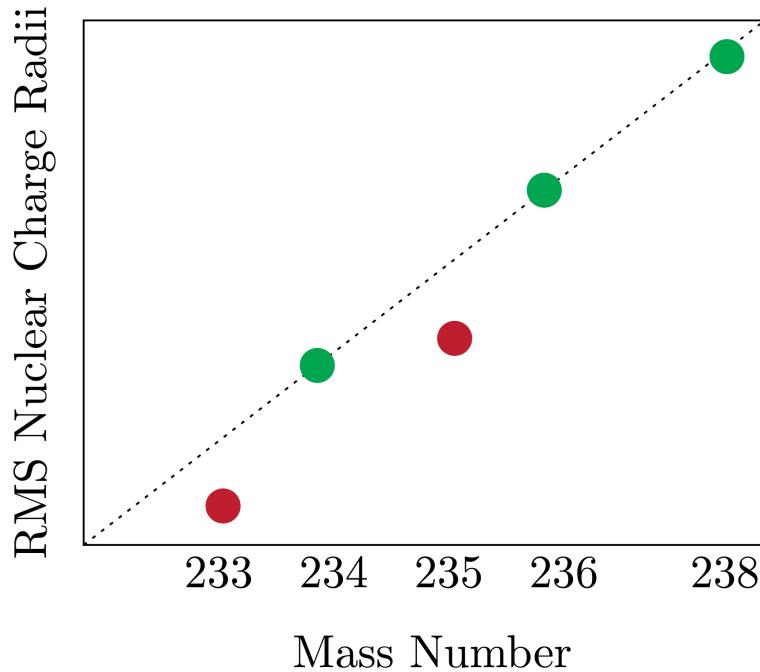


Fig. 6: The Nuclear Volume Effect in action.

Some examples of this are in Mercury, Chromium (for 52 being doubly magic), and Platinum (though very small). We also see that the nuclear binding energy traces the nuclear size very well, as we use the binding energy of  $H_2$  to calculate the binding energy. We can see these in Clacium and Molybdenum. Finally, we get that the net effect from the MDF and the NVE agrees well with observations, as shown in Fig. 7.

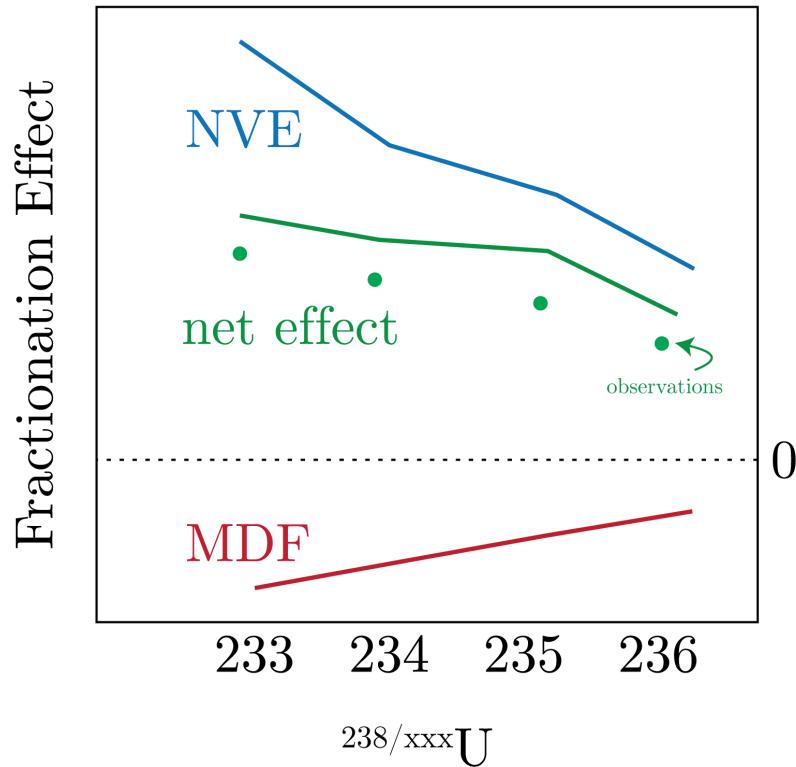


Fig. 7: The net effect from MDf and NVE for U.

# 12.744: Lecture 9

## Stable Isotopes meet Biology I

### Models of Isotope Dynamics and Behavior

We will introduce four major types of models for differing systems, as follows:

#### Reversible, Closed System

In general, we have that "reversible" means equilibrium dynamics. This is to say that we have equations, for system  $\mathbf{A}$  and  $\mathbf{B}$ , of the form:

$$\mathbf{A} \rightleftharpoons \mathbf{B}.$$

Some examples of systems that obey this kind of dynamic are:

1. Water vapor:  $\text{H}_2\text{O}$  (O, H)
2. Carbonate system:  $\text{CaCO}_3$ , DIC (C, O)
3. Silicates:  $\text{Si(OH)}_4$  (O)
4. Nitrite:  $\text{NO}_2^-$  (*aq*) (O)
5. Sulfite:  $\text{SO}_3^{2-}$  (*aq*) (O)
6. Carbon:  $\text{CO}_2$ ,  $\text{CH}_4$  (C)

We note here that some of these species can be at chemical equilibrium but not at isotopic equilibrium. This is to say that there could be equilibrium amounts of each species present, but there is a gradient toward a more favorable isotopic composition of those species. Some key components that lead to this distinction are **time** and **temperature**, which will change the reaction kinetics of our system.

First, we derive the measured isotope ratio of a phase  $\mathbf{A}$ ,  $R_A$ , for a given element  $\mathbf{X}$  with a reference phase  $\mathbf{C}$  from:

$$\delta_A = \left[ \frac{R_A - R_{STD}}{R_{STD}} \right] \times 10^3 = \left[ \frac{R_A}{R_{STD}} - 1 \right] \times 10^3,$$

where we have that, for concentration  $[X]$ :

$$R_A = \frac{[X_A]}{[X_C]}.$$

Note that we are in per mille here and that the subscript  $STD$  refers to a standard value. Now, we can rearrange this equation for  $R_A$  to get:

$$R_A = (\delta_A + 10^3) \times R_{STD}/10^3.$$

To make this all concrete, we can think of a system such as:  $X = \text{O}$ , where  $A = 18$ , and  $B = 16$ .

We then define an important factor in stable isotope geochemistry, which is the fractionation factor defined as follows:

$$\alpha_{A/B} = \frac{R_A}{R_B},$$

which, from above, becomes:

$$\alpha_{A/B} = \frac{\delta_A + 10^3}{\delta_B + 10^3}.$$

This then implies that:

$$\delta_A = \alpha_{A/B}\delta_B + (\alpha_{A/B} - 1) \times 10^3.$$

We introduce the variable  $\epsilon$ :

$$\epsilon_{A/B} = (\alpha_{A/B} - 1) \times 10^3,$$

which in this lecture we use to define the Kinetic Isotope Effect (KIE). Therefore, we have that:

$$\delta_A = \alpha_{A/B}\delta_B + \epsilon_{A/B} \sim \delta_B + \epsilon_{A/B},$$

where we have used that  $\alpha_{A/B} \sim 1$ .

## Reversible, Open System

Again, we note that "reversible" implies that we are dealing with equilibrium dynamics. As the system is "open", this means that we are seeing a loss products along the way, such as through distillation and rainout. Oftentimes, we see this in the hydrological cycle or in hydrothermal vent systems. Some explicit examples of this include:

1. Rainout during cloud transport, which leads to increasingly depleted vapor.
2. Weather patterns that follow temperature, altitude, latitude, and humidity (e.g.,  $\delta^{18}\text{O}$  will go down as we get to the higher latitudes)

## Irreversible, Closed System

We start by assuming some system of the form:

$$\mathbf{R}_0 \rightarrow \mathbf{R} + \mathbf{P},$$

where we have  $\mathbf{R}_0$  is the initial concentration of the reactant,  $\mathbf{R}$  is the concentration of the reactant, and  $\mathbf{P}$  is the product of the reaction. This is an irreversible system, so this is a one-way reaction, and it is a closed system, therefore there is not additional product or reactant to the system other than what is described by mass continuity in the equation above. We next define:

$$\Delta_{A/B} = \delta_A - \delta_B.$$

From our definition of  $\alpha_{A/B}$ , we can subtract  $1 = (\delta_B + 10^3)/(\delta_B + 10^3)$  from both sides and note that  $\delta \ll 10^3$ , which gives:

$$\alpha_{A/B} - 1 = \frac{\delta_A - \delta_B}{10^3}.$$

Then, we recall the Taylor expansion:

$$\log[x+1] = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots, \quad \text{for } x \in (-1, 1].$$

So, to first order, we have that, for  $x = \alpha_{A/B} - 1$ :

$$\Delta_{A/B} \sim (\alpha_{A/B} - 1) \times 10^3 \sim \log[\alpha_{A/B}] \times 10^3.$$

Now, in this system we can derive, for:

$$\alpha_{P/R} = \frac{R_P}{R_R} \epsilon_{P/R} \log \left[ f \frac{1 + R_{R_0}}{1 + R_R} \right] = \log \left[ \frac{R_R}{R_{R_0}} \right],$$

that:

$$\epsilon_{P/R} \log \left[ f \frac{1 + R_{R_0}}{1 + R_R} \right] = \log \left[ \frac{R_R}{R_{R_0}} \right],$$

where we define:

$$f = \frac{R}{R_0},$$

or the fraction reacted. Given that  $(1 + R_{R_0})/(1 + R_R) \sim 1$ , for an abundance of rare isotopes assumed to be low, we can approximate this as:

$$\epsilon_{P/R} \log[f] = \log \left[ \frac{R_R}{R_{R_0}} \right].$$

We can rearrange this to get:

$$f^{\epsilon_{P/R}} = \frac{R_R}{R_{R_0}},$$

which is known as the "Rayleigh Equation". We now make the Mariotti Approximation, in which we re-write the Rayleigh Equation using  $\delta$  notation and rearrange to get:

$$\log[\delta_R + 1] \sim \log[R_{R_0} + 1] + \epsilon_{P/R} \log[f].$$

We note that this is essentially a line of the form:  $y \sim mx + b$  in  $\log$  space. Therefore, we can get the slope of this line, if we have data, say, to get  $\epsilon_{P/R}$  of the reaction described above. From the equation above, we can also get, by again remembering our Taylor Expansion and taking the first order, we get:

$$\begin{aligned}\delta_R &= \delta_{R_0} - \epsilon_{P/R} \log [f], \\ \delta_P &= \delta_{R_0} + \epsilon_{P/R} \left( \frac{f}{1-f} \right) \log [f],\end{aligned}$$

where we have derived the second form by substituting in the mass conservation equation:

$$\delta_{R_0} = f\delta_R + (1-f)\delta_P.$$

Of some interest might be:

$$\delta_{P'} = \delta_R - \epsilon_{P/R},$$

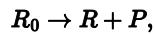
where we have that  $P'$  is the instantaneous  $\delta$  value. We note that these are approximations and have errors that scale with  $f$  and  $\epsilon$ .

### Irreversible, Open System

We start deriving the equations of this model system by assuming a steady state, this is to say that the fluxes in are equal to the fluxes out:

$$F_{in} = F_{out}.$$

Now, for an irreversible reaction of the form:



we have:

$$F_{R_0} \delta_{R_0} = F_R \delta_R + F_P \delta_P.$$

We can rearrange this to get:

$$\delta_R = \delta_{R_0} + \frac{F_P}{F_R + F_P} \epsilon_{R/P}.$$

Noting that:

$$F_R + F_P = 1 - f,$$

we get finally that:

$$\delta_R = \delta_{R_0} + (1-f)\epsilon_{R/P},$$

and correspondingly:

$$\delta_P = \delta_{R_0} - f\epsilon_{R/P}$$

We can look at diagram of these two models of an irreversible system in Fig. 1.

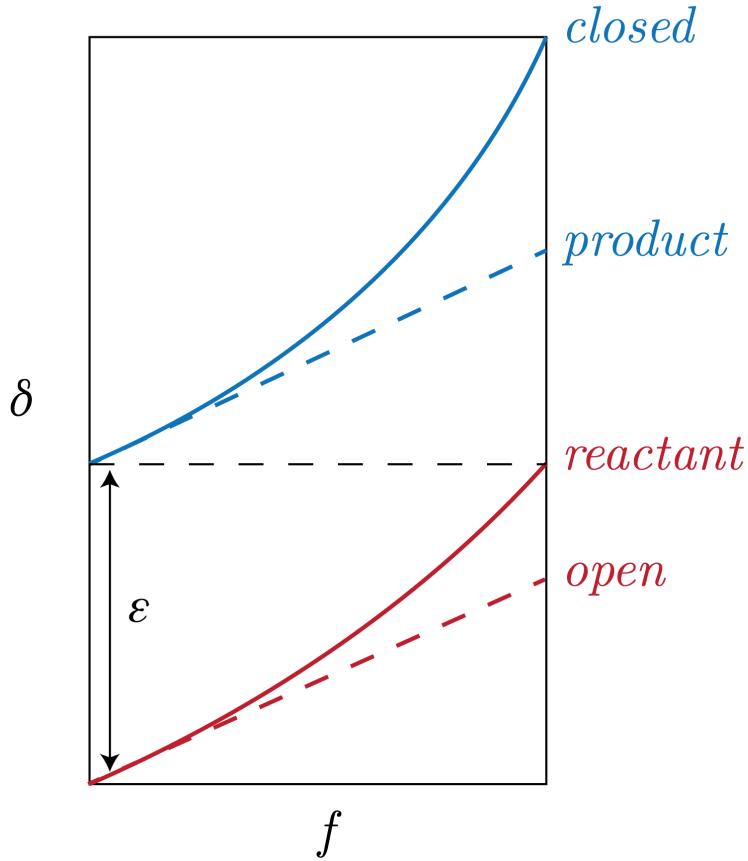


Fig. 1: Two varying models of irreversible systems for fractionation, with specific interest in the fractionation factor  $\epsilon_{P/R}$ .

## Introduction to the Nitrogen Cycle

We will use the N cycle to understand a few of these concepts, as there is a lot of N in on the Earth, like  $205 - 330 \cdot 10^{18}$  [kg N]. Wow. There are a few important parts of the N cycle that we will consider. The first is **denitrification**, or  $\text{NO}_3^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ , which contributes about 250 [Tg N  $\text{y}^{-1}$ ] to the atmosphere. This has an isotope fractionation of  $\epsilon \sim 25$  [%]. Two important values to remember are that mean and deep ocean nitrate  $\text{NO}_3^-$  has  $\delta^{15}\text{N}$  of 5 [%] while atmospheric  $\text{N}_2$  has  $\delta^{15}\text{N}$  of 0 [%], as does the sedimentary  $\text{NO}_3^-$ .

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# 12.744: Lecture 10

## Stable Isotopes meet Biology II

### Mixing Dynamics

We consider the following system:

$$\mathbf{A} + \mathbf{B} = \mathbf{C},$$

where we have that  $\mathbf{A}$  and  $\mathbf{B}$  are mixed to make  $\mathbf{C}$ . We have then that mixing dynamics use the following equation, following mass balance for moles  $\mathbf{M}_i$ :

$$M_C \delta_C = M_A \delta_A + M_B \delta_B.$$

Therefore, we get that for  $f$  the fraction:

$$\delta_C = f_A \delta_A + (1 - f_A) \delta_B.$$

An important concept is that in this kind of mixing, we have that mixing is not linear, this is to say that this is not conservative. We can make a "Keeling Plot", in which we plot  $1/M_i$ , in which we case we have linear mixing. An example of this is plotted in Fig. 1 below.

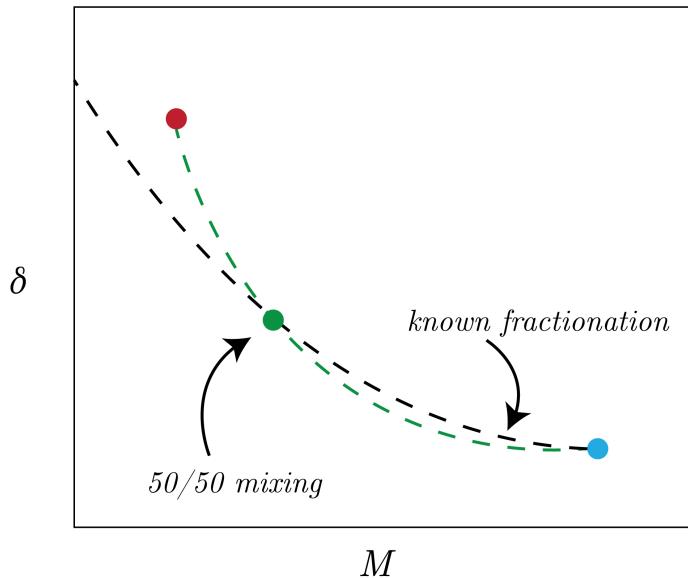


Fig. 1: Mixing of two different states that follow a nonlinear (nonconservative) mixing pattern and land on a known isotope fractionation ( $\epsilon$  value).

### A Mixing Example

#### Case I

We consider two states. The first state is  $[\text{NO}_2^-] = 40 \text{ } [\mu\text{M}]$  with a  $\delta^{15} = 5 \text{ [‰]}$ . The second state is denitrified water, for which we remember that  $\epsilon_{DNF} = 25 \text{ [‰]}$ , of  $[\text{NO}_2^-] = 10 \text{ } [\mu\text{M}]$ . Using our open, irreversible system equations, for  $f = \frac{10}{40}$ , we get:

$$\delta^{15}\text{N} = \delta^{15}\text{N}_0 - \log[f]\epsilon_{DNF} \simeq 39.7 \text{ [‰].}$$

Then, we apply our mixing equation to get:

$$\delta_{mix} = \frac{(20 \cdot 5) + (10 \cdot 39.7)}{(40 + 10)/2} \simeq 23.9 \text{ [‰].}$$

#### Case II

We have the same setup but with the denitrification drawdown to  $4 \text{ } [\mu\text{M}]$ . This then gives  $\delta^{15}\text{N} \simeq 62.5 \text{ [‰]}$  and a  $\delta_{mix} = 20.5 \text{ [‰]}$ . Therefore, we see that the levers can really matter, i.e., you can change both the concentration as well as the isotope values, which can have counteracting effects.

## -Simulation

We consider the following system:

$$A \rightarrow \text{System} \rightarrow B.$$

Here, we have the following definitions:

1. Assimilatory:  $A$  (i.e., biomass)
2. Dissimilatory:  $B$  (i.e., energy conservation turning one substance into another)

In a closed study of cells described by the top panel of Fig. 2, we want to compare the intracellular and extracellular nitrate. They were limited by different nutrients, such as Fe such that they would consume all of the nitrate. The results are presented in the bottom panel of Fig. 2 and summarized below:

1. Low Fe, Low T: small  $\epsilon_p$ , large difference between  $\delta^{15}\text{N}$  in the cell and outside the cell. This is to say that the **efflux/uptake  $\ll 1$** .
2. Low light: large  $\epsilon_p$ , small difference between internal and external pools.

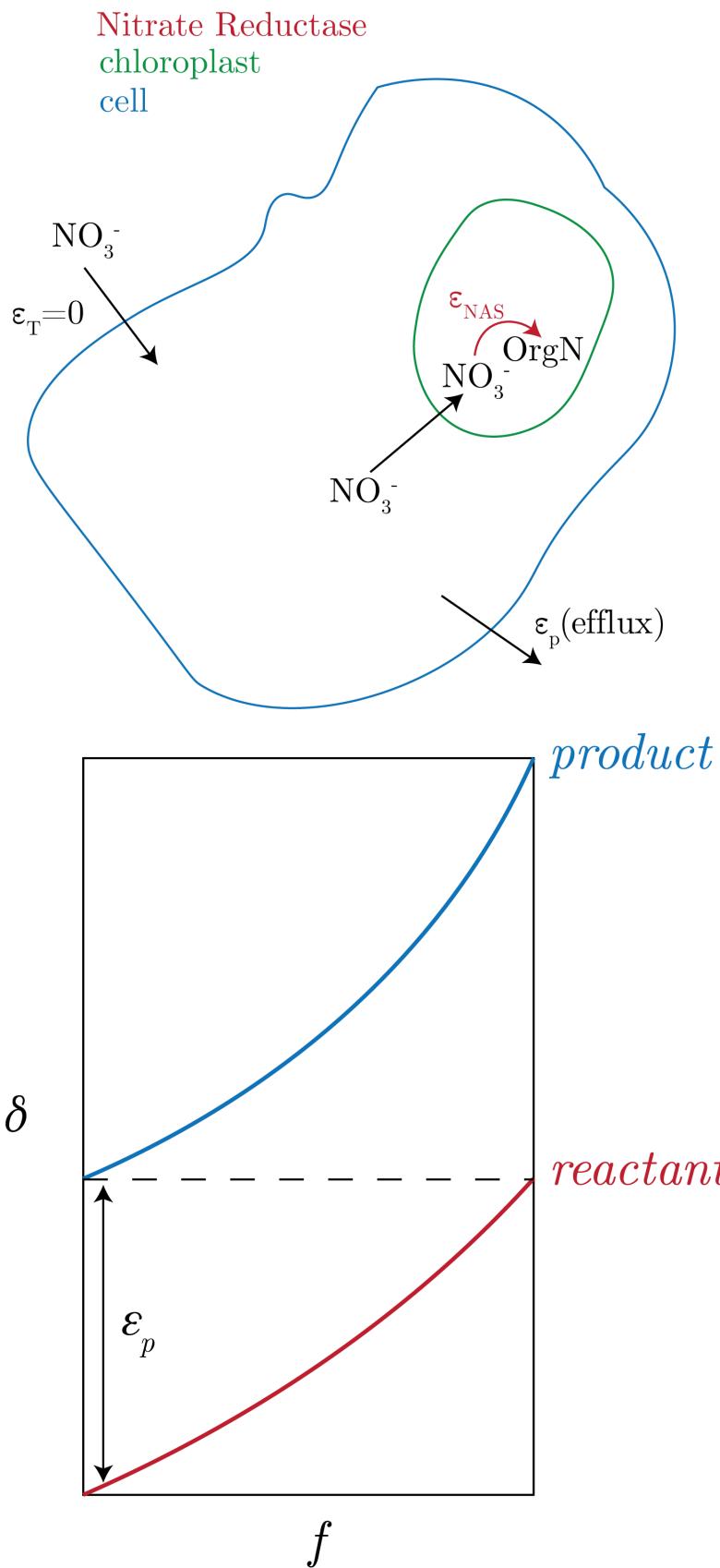


Fig. 2: Experimental setup and results from nitrate cell experiments.

We consider another setup, presented in Fig. 3, where we have a similar experiment but with CO<sub>2</sub>, in which the rate limiting step is the CO<sub>2</sub> → OrgC, which has a signature of  $\delta^{13}\text{C}$ .

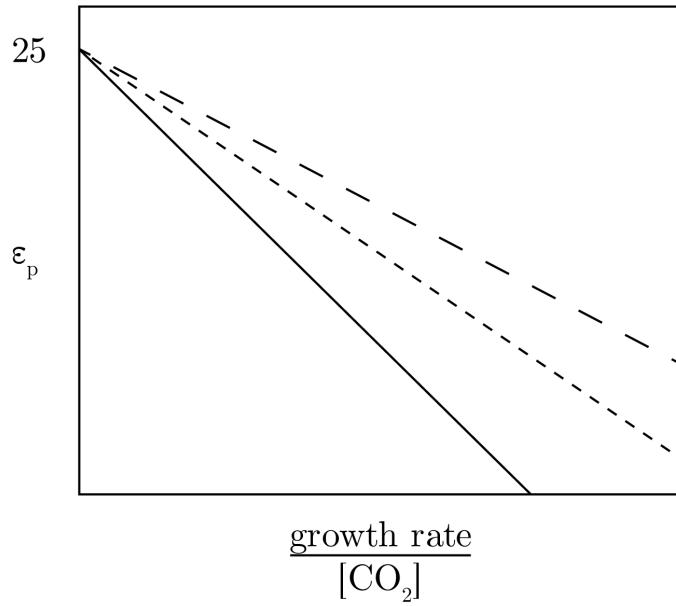
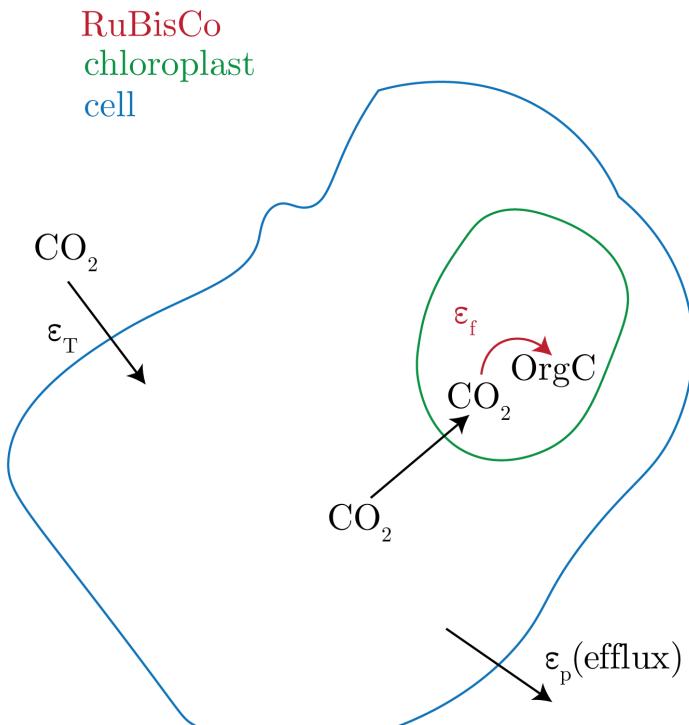


Fig. 3:  $\text{CO}_2$  experiment in cell showing isotope effect. The lines in the lower panel are for different species of cells.

The model to describe this is, for  $\mu$  the growth rate:

$$\epsilon_p = \epsilon_T - (\epsilon_f - \epsilon_T) \left[ \frac{K_1}{K_2} - \frac{\mu}{K_2 [\text{CO}_2]} \right].$$

We note that  $K_1/K_2 \sim 1$  and that as  $\mu \rightarrow 0$ , that  $\epsilon_p \rightarrow \epsilon_f$  as  $[\text{CO}_2] \rightarrow \infty$  all determined by the RuBisCo. This is called the Passive Diffusion Model. It has been updated to include the co-uptake of bicarbonate into the cell, at which RuBisCo is the most down-stream enzyme acting on the system.

## Biosynthesis

We assume a system in **steady state (SS)** as shown in Fig. 4 below.

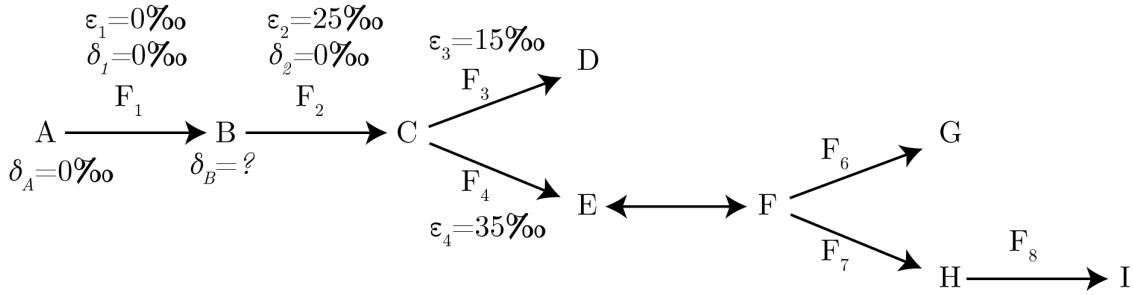


Fig. 4: Steady state biosynthetic test case that we are considering.

We first want to, given the conditions given in the figure, determine what  $\delta_B$  is. To do this, we note that SS means  $\delta_1 = \delta_2$ . Therefore, we get that:

$$\delta_2 = \delta_B - \epsilon_2,$$

which means that  $\delta_B = 25\text{‰}$ . We know this as what goes in,  $\delta_B$ , must equal what does out,  $\delta_2$ , offset by the isotope effect,  $\epsilon_2$ , so we can equilibriantly write this as:

$$[\text{IN}] \delta_B = \delta_2 + \epsilon_2 [\text{OUT}].$$

Here we note that the time to reach steady state,  $\tau$ , is proportional to the size of your isotope pool over the flux of that pool, as presented in Fig. 5.

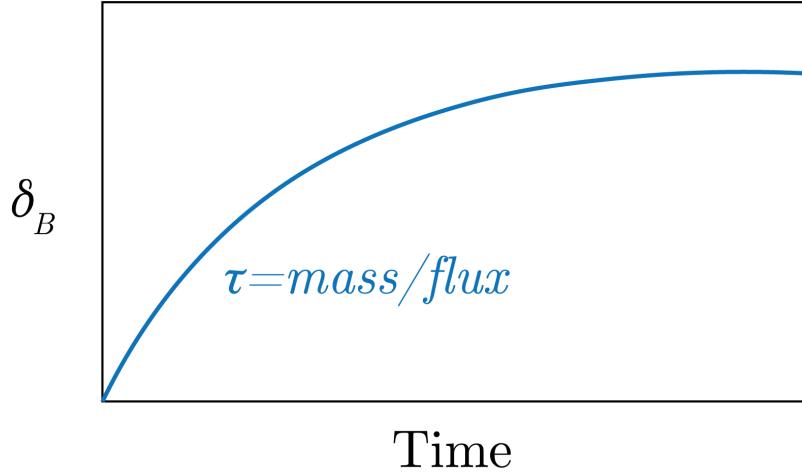


Fig. 5: A schematic showing the approach to steady state.

How, we want to know what happens at Point C in Fig. 4. Again, as we are at steady state, we know that:

$$F_2 = F_3 + F_4,$$

which then means that:

$$\delta_2 F_2 = \delta_3 F_3 + \delta_4 F_4.$$

Now we can change this into  $f_3 = F_3 / (F_3 + F_4)$  notation to get the mixing equation:

$$\delta_2 = f_3 \delta_3 + (1 - f_3) \delta_4.$$

We can think og this as in Fig. 6.

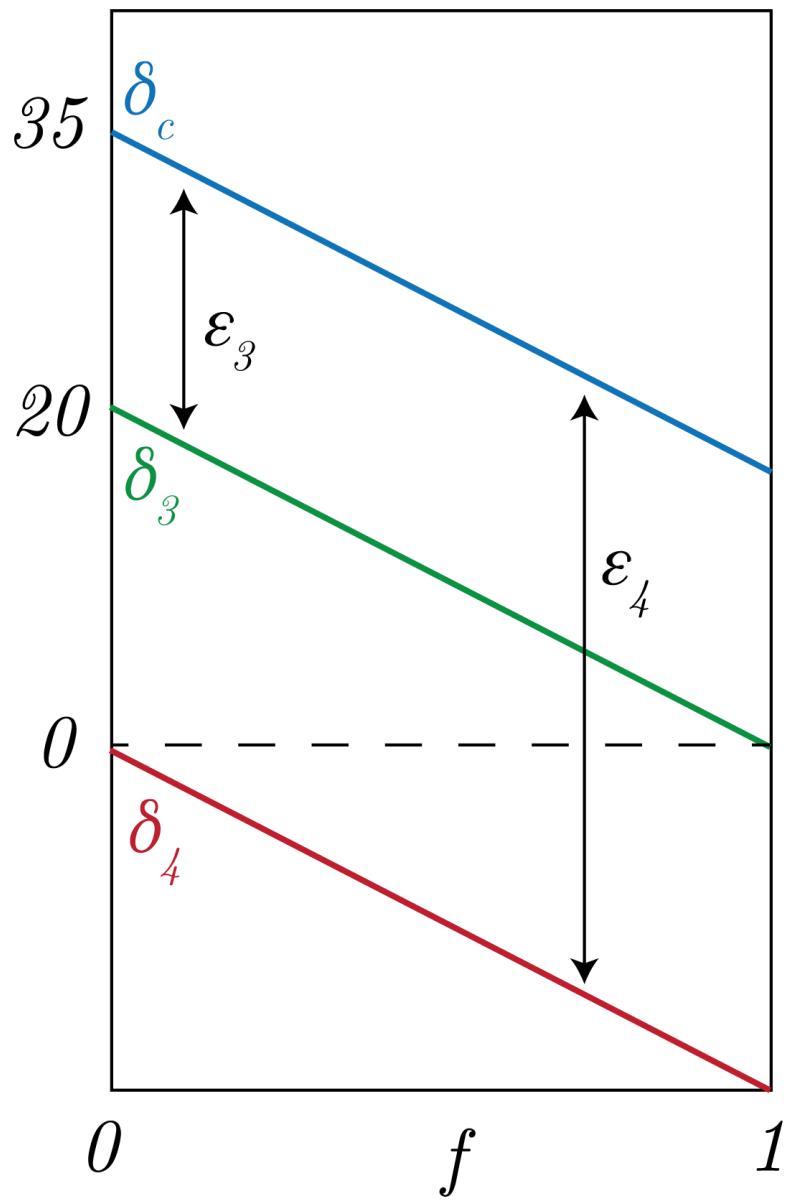


Fig. 6: How to think about the branching equation above.

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# 12.744: Lecture 11

## Stable Isotopes meet Biology III

### Dual Isotope Systems

#### Sulfate

We will start with  $\text{SO}_4^{2-}$ . Specifically, we note that this is an electron acceptor of heterotrophy and the consumption of organic matter. Just go out to a marsh and take a deep breath! A diagram of this system is in Fig. 1.

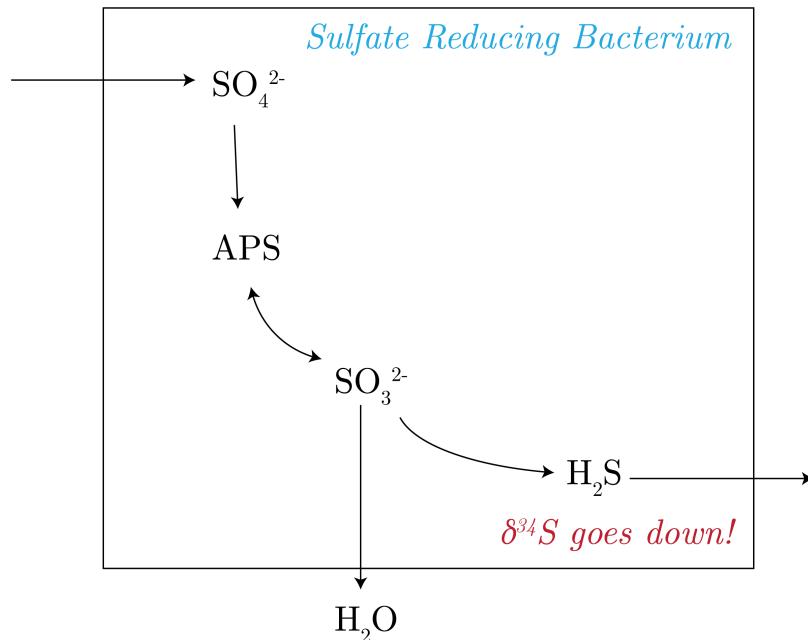


Fig. 1: A sulfate reduce bacterium and the effect on  $\delta^{34}\text{S}$ .

However, we saw that there was a change in the curvature of the  $\delta^{18}\text{O}$  to  $\delta^{34}\text{S}$  plots, as seen in Fig. 2

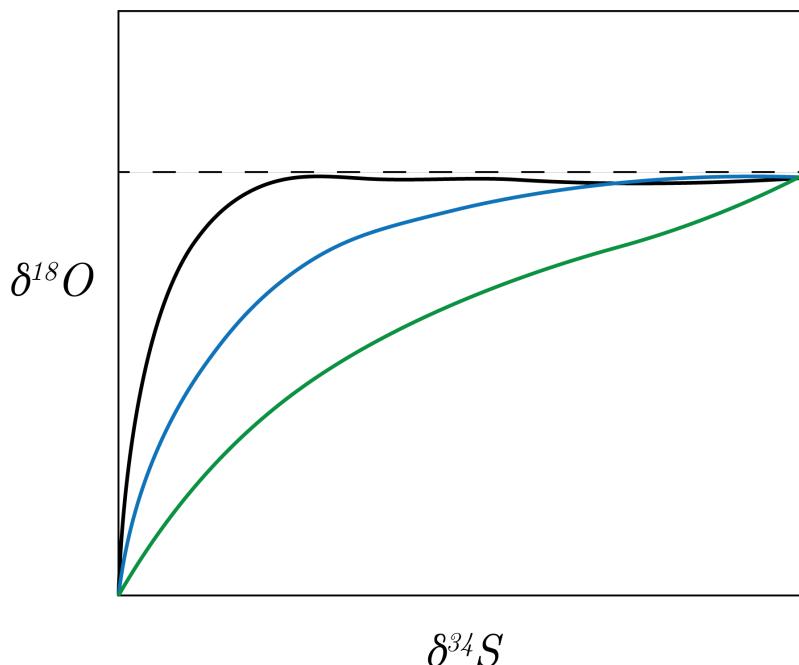
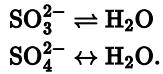


Fig. 2: Change in the curvature of oxygen-sulfur system.

We see that this curvature is proportional to how often the back reaction between sulfite and APS (kinetic isotope effect) and between sulfite and water (equilibrium isotope effect), that is the greater the curvature, the higher the reversibility of the reaction. The steady state between these three competing systems is what we get as the ultimate value offset from water (the asymptote in Fig. 2 above). We can write this as:



We look at systems now of the form:

$$A \rightleftharpoons_{\epsilon_b}^{\epsilon_f} B,$$

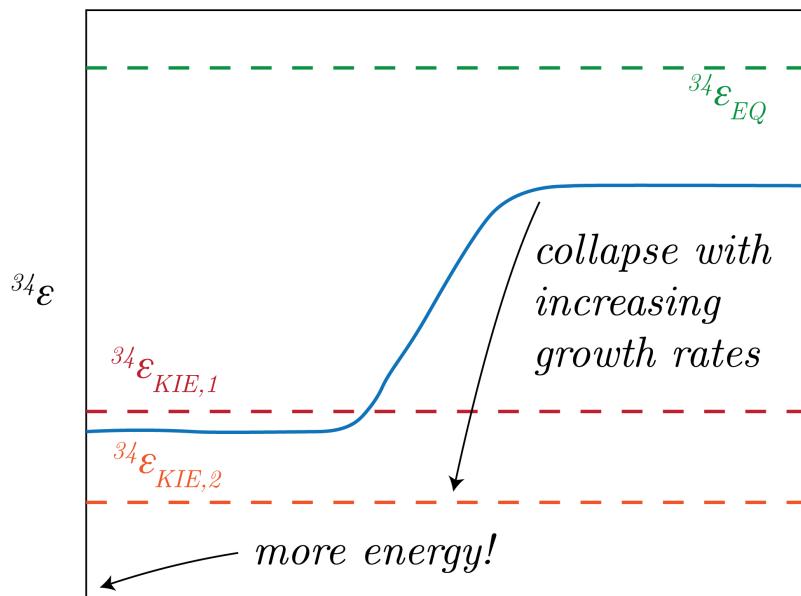
which ends up with some, in the case of  $\text{SO}_4^{2-}$ , with some  $\epsilon_{eq} = 70$  [%]. This is **enzyme reversibility**. Specifically, we can define:

$${}^{34}\alpha_{net} = ({}^{34}\alpha_{eq} - {}^{34}\alpha_{KIE})f + {}^{34}\alpha_{KIE},$$

where we define  $f$  with the Gibbs Free energy:

$$f = \exp[\Delta G/RT],$$

\ where  $\Delta G$  is a ratio of the electron acceptor to electron donor (i.e., in heterotrophic environments where there is a competition between supply and demand of energy). From these equations, we can see that as  $\Delta G \rightarrow 0$ , we get that there is less energy, therefore  $f \rightarrow 1$  and  ${}^{34}\alpha_{net} \rightarrow {}^{34}\alpha_{eq}$ . Conversely, as  $\Delta G \rightarrow -\infty$  we have that there is more energy in the system,  $f \rightarrow 0$ , and  ${}^{34}\alpha_{net} \rightarrow {}^{34}\alpha_{KIE}$ , which makes intuitive sense given the kinds of reactions taking place in each regime. We can look at data to see that, with new experiments showing this understanding in data, as presented in Fig. 3.



## Electron Potential

Fig. 3: Sulfur system dynamics and the limiting regimes discussed previously graphically shown.

### Nitrogen

We will specifically be interested in looking how nitrogen is coupled and decoupled with oxygen. Presently, in the ocean the abundant form of nitrogen is nitrate,  $\text{NO}_3^{2-}$ . We can look at the major reservoirs of nitrate in Fig. 4.

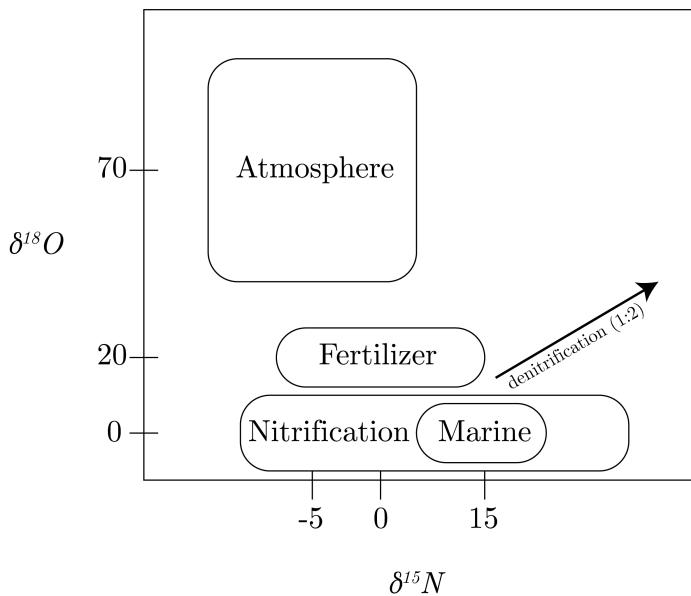


Fig. 4: Nitrate and Oxygen reservoirs on earth.

We note that mixing in this phase space is linear. The high atmospheric nitrate-oxygen pool is from reactions with ozone, O<sub>3</sub>. The high fertilizer nitrate values is from ammonia volatilization, in which ammonia is exchanged with ammonium, which is exchanged with its gaseous form, leaving ammonia in the aqueous pool. This is presented in Fig. 5 below.

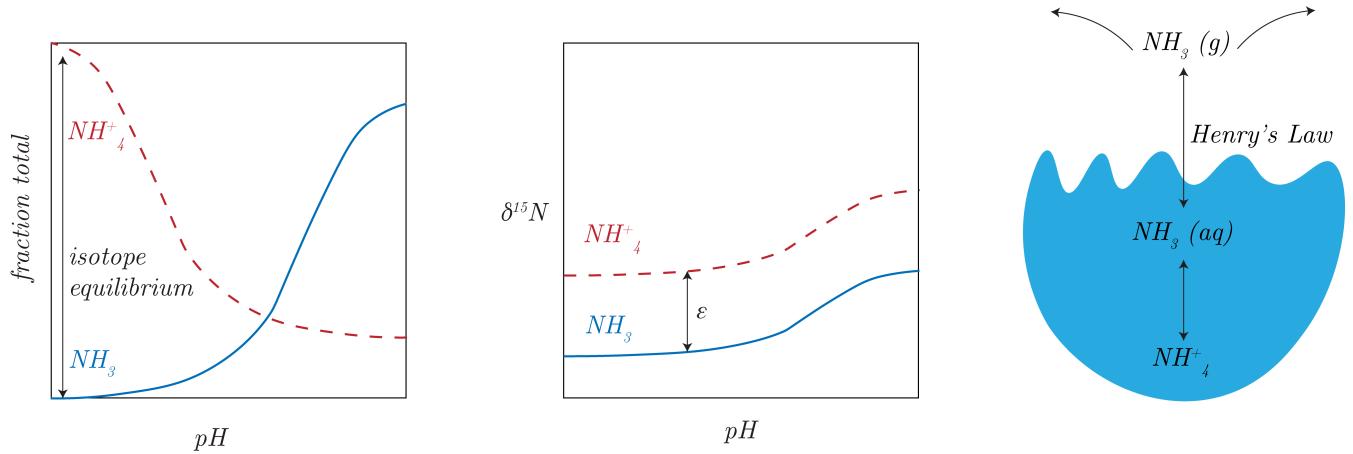


Fig. 5: Graphical and diagrammatic understanding of ammonia volatilization.

Many species were then raised and under many different regimes of conditions (that did change the isotope effects), they saw a 1:1, that was controlled by the enzymes within the species that were causing the isotope fractionation, i.e.,  $\delta^{18}\text{O}_{\text{NH}_3} : \delta^{15}\text{N}_{\text{NH}_3}$ . However, when observations were taking in an ocean ODZ, we see that the data is above the 1:1 line. We present this in Fig. 6.

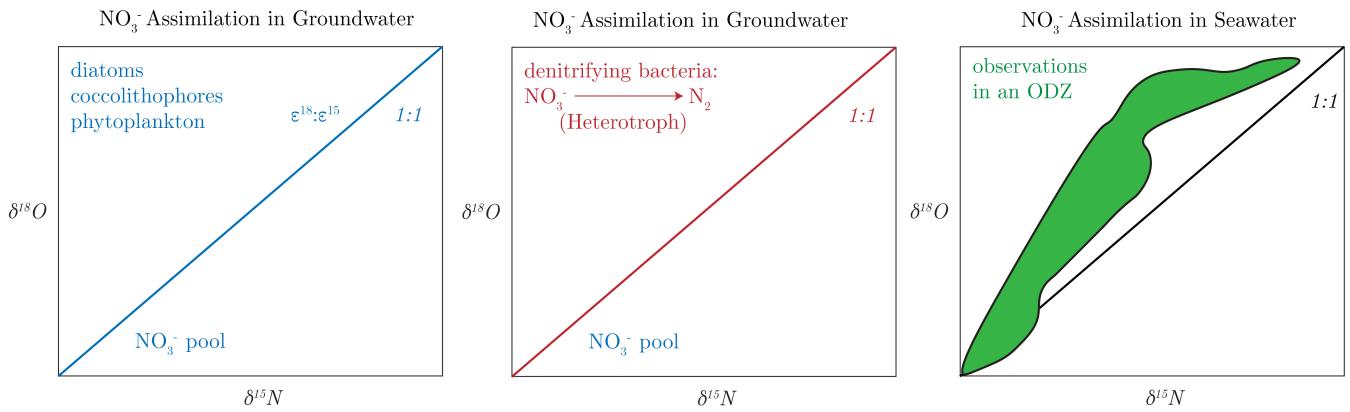


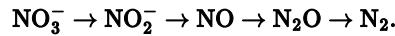
Fig. 6: The difference between groundwater and seawater nitrate assimilation in the oxygen-nitrogen system.

The difference here is possibly due to:

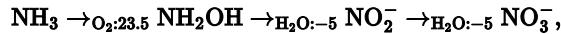
1. Freshwater vs. saltwater
2. Different cycling of processes

### 3. Different organisms

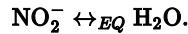
So, we can start with describing denitrification:



We can see is that the cycling of nitrate and nitrite can explain the differences seen between groundwater and seawater. What happens is:



determined from labelling experiments, which gives a mixing ratio, assuming equipartition:  $(23.5 - 5 - 5)3 = 4.5 [\%]$ . However, this neglects any kinetic isotope effects. We would also like to note that there are equilibrium effects with:



We note that this only happens, as with sulfate, that the equilibration with water is on the order of billion of years, so we can neglect any equilibrium effects. Therefore, we see that there is a decoupling of N and O, this is to say that not only are the biological effects of N being taken into consideration here but also the isotope effects from the equilibration with O from the surrounding water. We show this decoupling in Fig. 7.

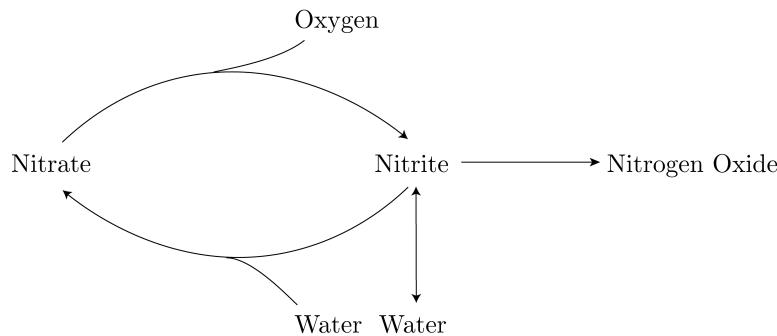


Fig. 7: The Nitrogen-Oxygen decoupling in denitrification.

We finally cover the **branching effect** in the nitrogen cycle. To begin, we note the process described in Fig. 8, where preliminarily note that the concentration of nitrate before entering the cell is going to be less than the  $\text{N}_2$  leaving the cell, given -similation.

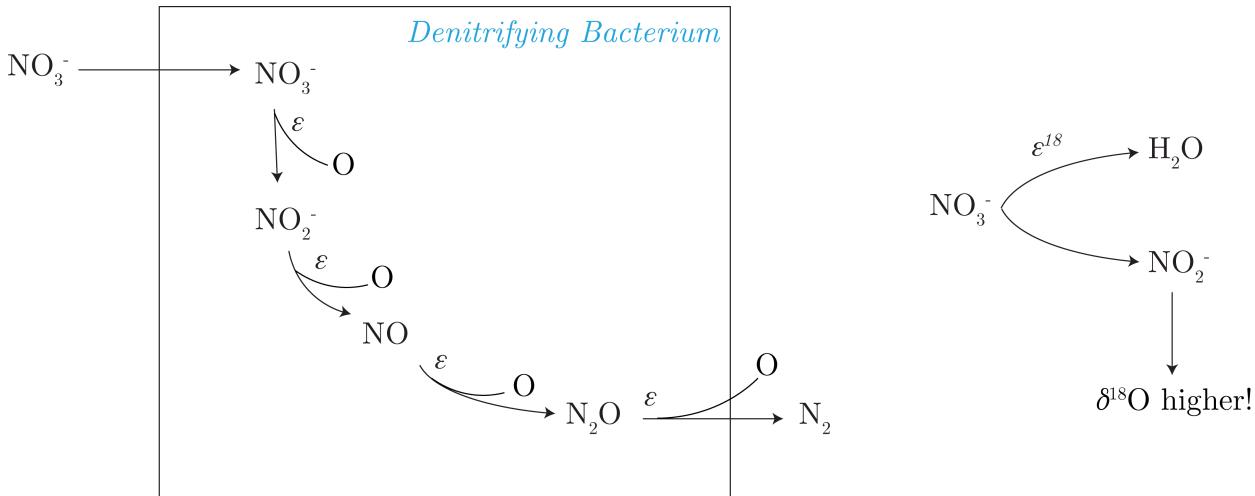


Fig. 8: The branching of the nitrogen cycle with in a denitrifying bacterium.

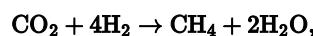
This is called "O atom abstraction." It means that for O containing intermediates, we will get:

1.  $\delta^{15}\text{N}$  will be lower in the reactant pool
2.  $\delta^{18}\text{O}$  will be higher in the reactant pool

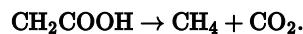
This is because the light isotope reacts faster than the heavy isotope, therefore leaving the reactant sooner, or a lower  $\delta$  value. In the abstraction, it is easier for the heavier to react given the isotope effect, making is so that the  $\delta$  value for O will be higher.

### Methane

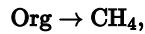
Methane is produced by methanogenesis:



This has a large isotope effect. There is also fermentation, or acetoclastic methanogenesis:



This process has a lesser isotope effect. There is also a geologic component, which is:



as we know that at high temperatures, isotopes are reduced. We can look at all of this in Fig. 9.

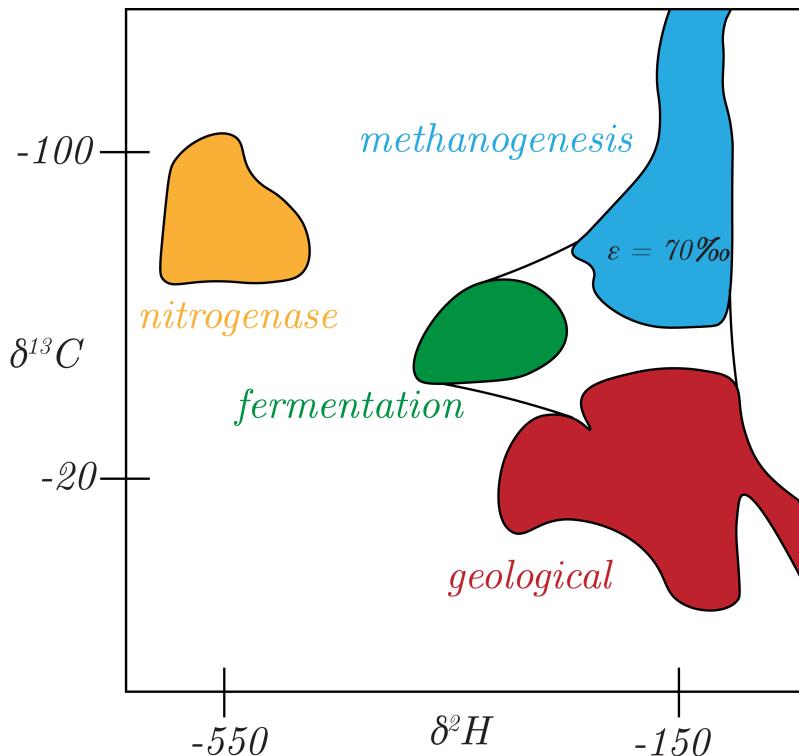


Fig. 9: End members of H, including methanogenesis.

And lastly, we can wrap this all up by seeing in Fig. 10 that there is an increase in the fractionation factor with decreasing (less negative)  $\Delta G$ , which gets at the equilibrium of:

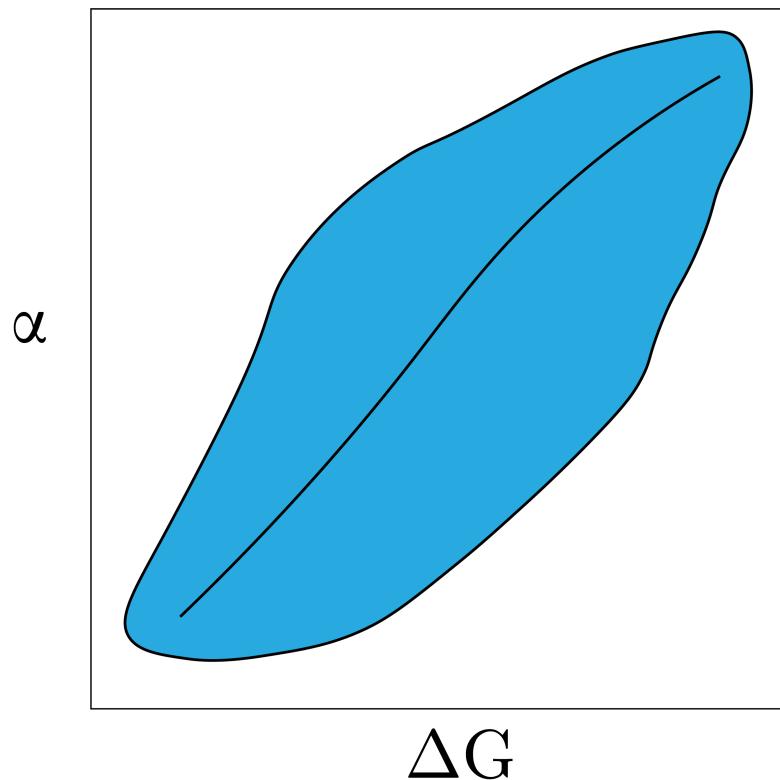
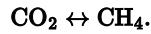


Fig. 10: The relationship between Gibbs Free Energy and Methanogenesis. Blue is the spread of the data and the center black line is the mean of the data.

So, when  $\Delta G$  is low, there is very little energy to be gained from methane production, there is a lot of fractionation (this is an equilibrium effect). When there is more energy around, we see something akin to a kinetic isotope effect. As methane is at the bottom of the redox ladder, methanogenesis normally takes place where there is not a lot of energy around.

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# 12.744: Lecture 12

## Clumped Isotopes

### Oxygen: an introduction

We can look  $\delta^{18/16}\text{O}$  to  $\delta^{17/16}\text{O}$  fractionation. This is a mass dependent fractionation line has a slope given by 0.5, as would be expected given the differences in the masses of the two isotopes, which we call the terrestrial fractionation line. Additionally, if we look at meteoric contributions, we note that they fall on a mass independent fractionation line, as does ozone, that is along a line that has a slope of 1. We show this is Fig. 1.

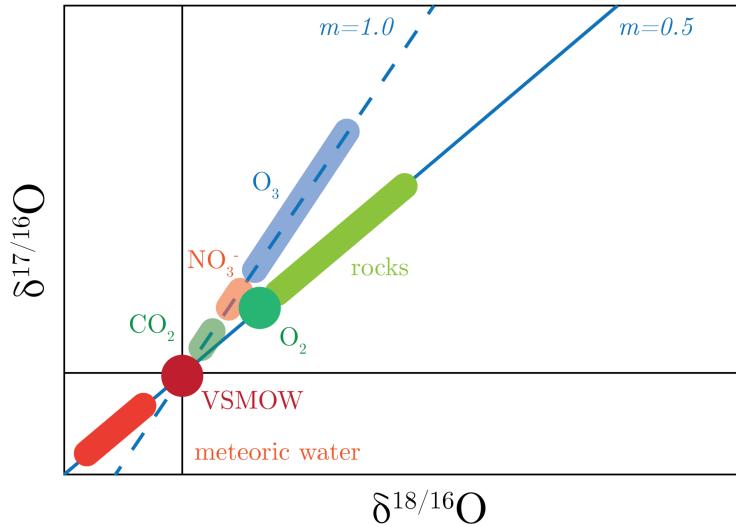


Fig. 1: Terrestrial fractionation line.

This fractionation of ozone has to do with the symmetry of the molecule. We can also see that this anomaly from ozone can be inherited by other species, such as  $\text{NO}_3^-$  and  $\text{CO}_2$ . Of importance here is how we define the deviations from this line, which we define as:

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O},$$

where we have that the true value of the slope is given by  $m = 0.52$ . For all compounds that do inherit this signal, we get that their fractionation is kinetic, i.e. mass independent, and will thus fall along the 1:1 line initially. However, if there is any change in this signal, it is going to change along the mass dependent fractionation line. We define this effect as:

$$\epsilon_{KIE}^{17} \simeq 0.52\epsilon_{KIE}^{18}.$$

You can also conservatively mix between end members between these fractionations.

### Current Definitions

We have a few definitions, which change the relation between these isotopes if you can measure small deviations:

1.  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$
2.  $\Delta^{17}\text{O} = (\delta^{17}\text{O} + 1) - (\delta^{18}\text{O} + 1)^{0.52}$
3.  $\Delta^{17}\text{O} = (\delta^{17}\text{O} + 1)/(\delta^{18}\text{O} + 1)^{0.52}$
4.  $\Delta'^{17}\text{O} = \delta^{17}\text{O}' - C\delta^{18}\text{O}'$

where the prime in the fourth definition denotes:

$${}^i\text{O}' = \log \left[ \frac{{}^iR_{\text{samp}}}{{}^iR_{\text{ref}}} \right].$$

The fourth definition is the most common and there are a few important things to consider when defining the  $C$ . In addition to  $\delta, \alpha, \epsilon$ , we introduce  $\theta$  which is an intrinsic property of the process, that is for the equilibrium and kinetic effects:  $\theta_{eq}$  and  $\theta_{KIE}$ . We have  $s$  the slope in the reference frame, which ranges from meteoric water which evaporates through Rayleigh distillation to form a slope of  $s = 0.528$  or  $\text{O}_2$  respiration in aquatic systems that produce a slope of  $0.5179$ . Lastly, we have  $c$ , which is a coefficient and is basically an arbitrary number used to define a reference frame. Oftentimes, we let  $c = 0.5305$ , which is the thermodynamic maximum value. We present a schematic of this in Fig. 2.

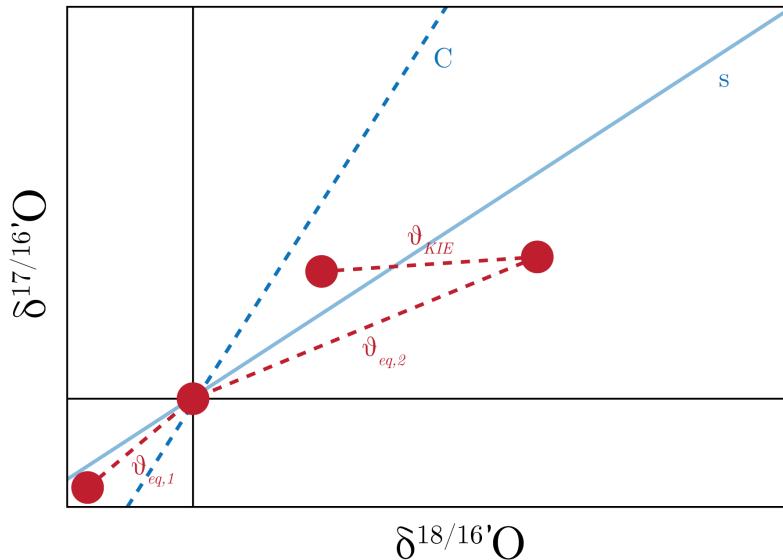


Fig. 2: Disentangling the definitions of  $\theta$ ,  $c$ , and  $s$ .

We can imagine then  $s$  the best fit line through the datapoints above, all of which are mass dependent fractionation.

## Applications

We care about:

$$\text{ANCP} = \text{GPP} - \text{Resp.}$$

Now, this is an underconstrained problem if we do not consider  $^{17}\text{O}$ , however, with this additional isotope we are able to constrain more systems, such as GPP. We show this in Fig. 3.

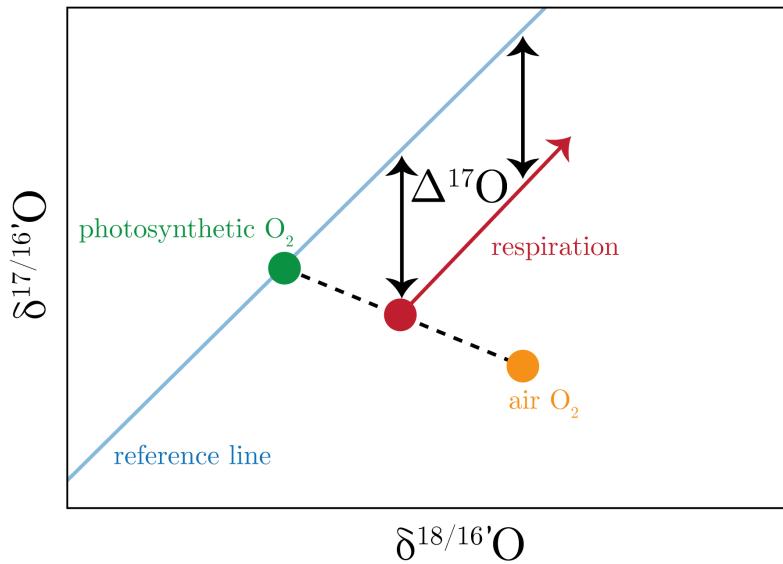


Fig. 3: The use of triple oxygen isotopes to determine GPP.

What we note is that respiration does not affect the  $\Delta^{17}\text{O}$ , and therefore allow us to calculate the mixing ratios of the photosynthetic and atmospheric oxygen.

## Polyatomic Isotope Ratios

Let's take  $\text{CO}_2$ . Then, for  $iF$  the relative fraction of a different species  $i \in [12, 13, 16, 17, 18]$ . The corresponding isotope ratios are, for the common species:

$$\begin{aligned} {}^{44}F &= {}^{12}F {}^{16}F {}^{16}F, \\ {}^{45}F &= {}^{13}F {}^{16}F {}^{16}F + 2{}^{12}F {}^{16}F {}^{17}F, \\ {}^{46}F &= {}^{12}F {}^{17}F {}^{17}F + 2{}^{12}F {}^{16}F {}^{18}F + 2{}^{13}F {}^{16}F {}^{17}F, \end{aligned}$$

where we determine the "clumping" as the aggregation of isotope substitutions within the molecule beyond a random distribution. We can then determine the following ratios:

$$\begin{aligned} 45/44 : {}^{45}\text{R} &= {}^{13}\text{R} + 2{}^{17}\text{R}, \\ 46/44 : {}^{46}\text{R} &= 2{}^{18}\text{R} + 2{}^{13}\text{R} + {}^{17}\text{R}^2. \end{aligned}$$

These are the ratios that our mass spectrometer measures. We recall from our mass dependent fractionation discussion that:

$${}^{17}\text{R} \simeq {}^{18}\text{R}^{0.52},$$

which allows us to correct out the  ${}^{17}\text{O}$  contribution and just have the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .

### An example: carbonates

As background, we note that there is a linear relationship between  $K_{eq}$  for the carbonate-water system and  $T$ , namely the  $\epsilon = \delta_c - \delta_w$  of  $\delta^{18}\text{O}$ . The new frontier is in the 47-clumped isotopes, for which new resolving power has allowed us to measure these data. Historically, there might not have been any value to measuring the abundance of this isotope, as we already know how much of the 16, 17, and 18 is in this molecule from other clumped isotope. But we note that the distribution of the 47-clumped isotope is powerful because it allows us to go further with the carbonate paleothermometer discussed previously, in so far as we no longer have to assume that we know the  $\delta_w$  in the paleorecord. We know that the  $\delta^{18}\text{O}$  also changes as a function of ice, via Rayleigh distillation.

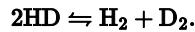
Now, to get at this, we define:

$$\Delta_{47} = \left[ \left( \frac{\{47/44\}_{sample}}{\{47/44\}_{random}} \right) - 1 \right] \times 10^3.$$

From our  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements, we should be able to get at the relative speciation of the isotopes from our fractional abundances defined above (for that random distribution). Research has shown that at higher temperature, there is a higher degree of clumping, with a linear relationship to  $T^{-2}$ . Why is this the case?

### Clumping

Let's take the  $\text{H}_2$  and  $\text{D}_2$  example, namely:



We note that this is a Binomial distribution, so that we are dealing with the distribution function:

$$1 = [\text{H}]^2 + 2[\text{H}][\text{D}] + [\text{D}]^2.$$

We then can define the equilibrium constant:

$$K_{eq} = \frac{[\text{H}_2][\text{D}_2]}{2[\text{HD}]},$$

and we note that our rearrangement of the PDF for our binomial distribution is given as:

$$\frac{[\text{H}]^2[\text{D}]^2}{(2[\text{H}][\text{D}])^2}.$$

Therefore, we can equate these and get that  $K_{eq} = 0.25$  for the random binomial distribution. However, we note that this is the theoretical minimum, which is approached as  $T \rightarrow \infty$ . The system will favour clumping when the energy difference between the  $\text{HD}$  and  $\text{H}_2$  is smaller than  $\text{HD}$  and  $\text{D}_2$ , as the net effect of not clumping will increase the dissociation energy.

### An example: methane

Of interest is the 18-clumped isotopes for methane, which are  ${}^{13}\text{CH}_3\text{D}$  and  ${}^{12}\text{CH}_2\text{D}_2$ , that gives a temperature relationship. The definitions are the same as above. It has recently allowed us to tease apart the KIE from microbial activity.

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# 12.744: Lecture 13

## Box model perturbations

### The Basic Setup

We consider the model presented in Fig. 1, in which there is some isotope fractionation process that is occurring within the box with fractionation  $\epsilon$ .

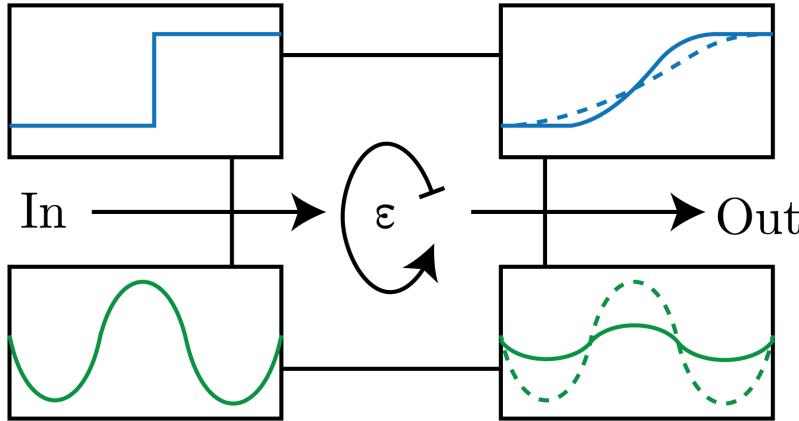


Fig. 1: A schematic of our box model.

We first start with the conservation of mass, that is:

$$\frac{dN}{dt} = \sum J_{in} - \sum J_{out}.$$

We can then move this to include the ratios:

$$\frac{d}{dt}[NR_{box}] = \sum J_{in}R_{in} - \sum J_{out}R_{out},$$

where we note that we can have  $R \rightarrow \delta$  only when  $\langle \delta \rangle_c^2 \ll 1$ . Oftentimes we consider the steady state, which allows us to set the LHS of the above equations to 0. Therefore, we get:

$$R_{box_{ss}} = \frac{\sum J_{in}R_{in}}{\sum J_{out}},$$

for which we do not consider fractionation yet. We note that the determination of steady state, and whether our system is steady, is non-trivial.

### Step-wise Forcing Function

For a step-wise forcing function of the form  $J = J_0 + J'$  is given by:

$$R_{box}(t) = R_{box_{ss}} - (R_{box_{ss}} - R_{box}(t_0)) \exp[(t - t_0)/\tau],$$

where we have that  $\tau$  is the e-folding time scale of the system, or the residence-time. We can see these are the top set of input and output functions in Fig. 1.

### Periodic Forcing Function

We consider the general equation:

$$\frac{dM}{dt} = J_0 + b \sin[\omega t] - kM,$$

for  $\omega = 2\pi/T$ ,  $T$  the period, and  $k = 1/\tau$ . This is a first order linear nonhomogeneous differential equation. This has a solution of the form:

$$M = M_0 \exp[-kt] + \frac{J_0}{k} (1 - \exp[-kt]) + \frac{b\omega}{k^2\omega^2} \exp[-kt] + \left( \frac{bk}{k^2 + \omega^2} \sin[\omega t] \right) - \left( \frac{b\omega}{k^2 + \omega^2} \cos[\omega t] \right).$$

We can simplify this for a range of different initial BCs, such as  $M(0) = 0, b = 0$ , which gives:

$$M = \frac{J_0}{k} (1 - \exp[-kt]),$$

which doesn't really do much for this scenario as we have neglected the periodic boundary forcing. We can then assume that  $t \gg 1$ , which then means that:

$$M = \frac{J_0}{k} + \frac{bk}{k^2 + \omega^2} \sin[\omega t] - \frac{b\omega}{k^2 + \omega^2} \cos[\omega t].$$

Now, let's say that  $\omega \ll k$ , or that  $T \gg \tau$ . We can make an analogy to oxygen in glacial-interglacial forcing. This then gives:

$$M = \frac{J_0}{k} + \frac{b}{k} \sin[\omega t].$$

We can then say that the system responds in phase. Next, let's consider the opposite of the above, or that  $\omega \gg k$  or that  $\tau \gg T$ . This is the case of Sr in the glacial-interglacial forcing. The solution is then:

$$M = \frac{J_0}{k} - \frac{b}{\omega} \cos[\omega t] = \frac{J_0}{k} + \frac{b}{\omega} \sin\left[\omega - \frac{\pi}{2}\right].$$

Therefore, we have a solution that is of the form in the previous case but with a phase shift of  $\pi/2$ . Thus, the response is delayed by a maximum of 1/4 of the forcing oscillation and the amplitude is damped. We note that this effect increases for increased response time,  $\tau$ . Therefore, we find that the response is driven by the response time, the magnitude of the forcing function, and the period of forcing oscillation. We note that this shows us that we have not shown at that Sr varies on glacial-interglacial timescales... even today!

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# 12.744: Lecture 14

## Cosmogenic nuclides

### An introduction

Cosmogenic nuclides form from the interaction of nuclei and cosmic rays. Cosmic rays are rays that come from space and decline in abundance from the top of the atmosphere to about 1 [km], and then increase to the surface of the ocean, as shown in Fig. 1. We show this in Fig. 1.

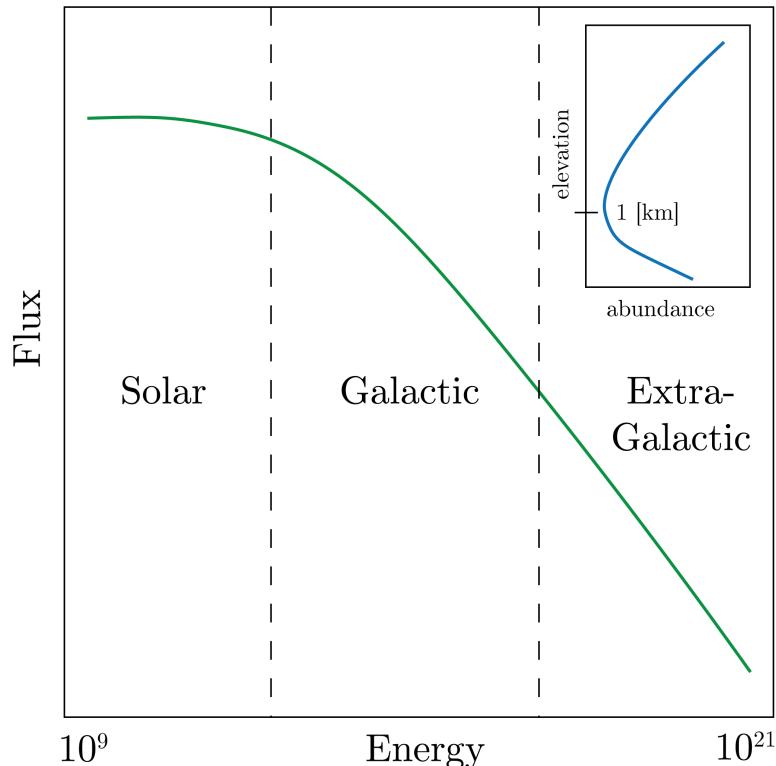


Fig. 1: The flux of cosmic rays at the top of the atmosphere, with the inset plot being the abundance from the top of the atmosphere to the surface elevation.

The make up of rays at the top of the atmosphere are the so-called primary particles:

1.  $p \sim 83\%$
2.  $\alpha \sim 13\%$
3.  $e^- \sim 3\%$

The secondary particles are primarily  $n$  and  $\mu$ , neutrons and muons. If we look at the ratio of primary to secondary, we get:

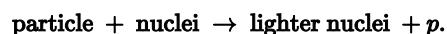
- 19 [km]: 87%
- 12 [km]: 5%
- 0 [km]:  $10^{-5}\%$

So, clearly we are really dealing with  $n$ th particles at the surface. In terms of the secondary particles, there are only 0.1% left at the surface. This is about 500 spallation event per gram per year at the surface. This is not that abundant...

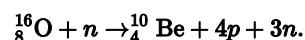
### Production pathways

These are:

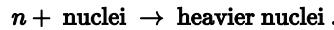
1. Spallation – this is defined by:



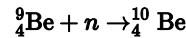
And example of this is, for  $n$  a secondary particle:



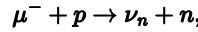
2. Neutron capture - this is defined by:



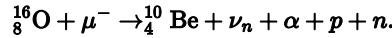
And example of this:



3. Muon capture - this is defined by:



where we define  $\nu_n$  as a muon neutrino and  $\mu^-$  the muon. This is not a common process in the atmosphere, but occurs at the surface in rocks. An example is:



This is on about 2% of making  ${}^{10}_4\text{Be}$ , but it increases at the surface with depth.

We then remember the earth magnetic field lines and that the magnetic field force is greatest when the incoming ray is perpendicular with the field lines. This then means that the magnetic field is weakest at the poles, which we can describe by the Lorenz Force:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{V} \times \mathbf{B}).$$

This then means that there is less attenuation at the poles, and therefore the maximum number of cosmogenic rays produced.

## Production Rates

These are a function of the following:

1. Latitude, which is mostly a quadratic function that is empirical.
2. Atmosphere thickness, or altitude, as there is more attenuation of the cosmogenic rays. We model this as:  $N = N_0 \exp[-d/\lambda]$ , for  $\lambda$  the attenuation length scale and  $d$  the atmosphere depth.
3. Depth in the subsurface, which we define as:  $P(z) = P_0 \exp[-\rho z/\lambda]$ , where we can define absorption coefficient  $\mu = \rho/\lambda$ .
4. Time, driven by solar wind and variations in the sun production.

## Main cosmogenic isotopes

The main players are:

1.  ${}^3\text{He}$ ,  $t_{1/2} = \text{stable}$
2.  ${}^{21}\text{Ne}$ ,  $t_{1/2} = \text{stable}$
3.  ${}^{10,7}\text{Be}$ ,  $t_{1/2} = 1.5 \times 10^6$  [y]
4.  ${}^{26}\text{Al}$ ,  $t_{1/2} = 7.3 \times 10^5$  [y]
5.  ${}^{36}\text{Cl}$ ,  $t_{1/2} = 3 \times 10^5$  [y]
6.  ${}^{14}\text{C}$ ,  $t_{1/2} = 5730$  [y]

which then means that we can trace different processes with different tracers with applicable timescales.

## Applications

We consider in situ production in rocks. We care about production  $P$ , erosion  $\epsilon$ , decay  $\lambda$ , and initial concentration  $N_0$ . From this, we can write down the equation as:

$$N(z, t) = N(z, 0) \exp[-\lambda t] + \frac{P(0)}{\lambda + \mu\epsilon} \exp[-\mu z] (1 - \exp[-(\lambda + \mu\epsilon)t]).$$

If the erosion rate is 0 at the surface, we get something like:

$$N(z, t) = N(z, 0) \exp[-\lambda t] + \frac{P(0)}{\lambda} (1 - \exp[-\mu t]).$$

We can then solve for  $t$  and get the surface age. An example of this is in volcanic lava flow or in Antarctica. Another handy simplification is for when  $t \gg 1$ , which then means that  $t \gg 1/(\lambda + \mu\epsilon)$ . Therefore, we can get:

$$N(z) = \frac{P_0}{\lambda + \mu\epsilon} \exp[-\mu z].$$

We can then solve for  $\epsilon$  here. These are the two extremes.

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# 12.744: Lecture 15

## Radiocarbon I

### Analytical Methods

We note that:

$$\begin{aligned} {}^{10}\text{B} &\sim 10.012938 \\ {}^{10}\text{Be} &\sim 10.01432 \end{aligned}$$

and then see that:

$$R = \frac{m}{\Delta m} \sim 7 \times 10^3.$$

Therefore, if we have an isotope system as in Fig. 1, we need a super high-resolution machine in order to resolve the second peak.

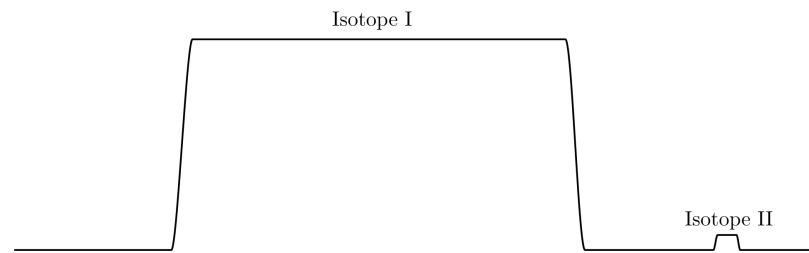
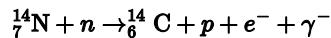


Fig. 1: Comparison of analytical isotope peaks.

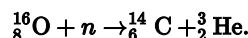
### Radiocarbon ( $^{14}\text{C}$ )

This is produced in the upper atmosphere. There are two main production paths:

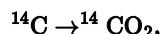
1. Neutron Capture: By far the most important, this is N is super abundant in the atmosphere. The equation is:



2. Spallation: This is described by:



In the atmosphere, what we have is:



by oxidation.

From all of this, the natural abundance is  ${}^{14}\text{C} \sim 1 \times 10^{-12}$ . This means, that in the modern atmosphere there is less than 1 ton of  ${}^{14}\text{C}$  is in the atmosphere. The decay is of the form:



which is a  $\beta^-$  decay. The half-life is  $t_{1/2} = 5730$  [yr]. This is specifically called the "true half-life", because there is another half-life that is in use, known as the "Libby Number". This is defined as  $t_{l,1/2} = 5568$  [yr]. This is the half-life is from the 1960's, but it is not exactly correct. We can describe the decay as:

$$N = N_0 \exp[-\lambda t],$$

where  $\lambda = \log 2 / t_{1/2}$  is the decay constant and  $N_0$  is the initial concentration. As we know the characteristics of this equation so well, we can use it as a dating tool. The standard for  ${}^{14}\text{C}$  is oxalic acid, Ox I, synthesized in 1950. What is really used is the activity of Ox I  $\times 0.95$ . In practice, we measure:

$$\frac{{}^{14}\text{C}}{{}^{12}\text{C}},$$

and then normalize to:

$$\frac{^{13}\text{C}}{^{12}\text{C}},$$

where  $\delta^{13}\text{C}$  of **-25** [%]. Then, we have the equation:

$$A_{sn} = A_s \left( 1 - 2 \times \left( \frac{25 + \delta^{13}\text{C}_{ms}}{1000} \right) \right).$$

The **2** comes from an assumption that the 14:12 fractionation is **2**× 13:12 fractionation, which is an approximation but it works really well.

## Notations

There are a few notations in radiocarbon literature. The first is  $F_m$ , or the fraction modern. This is defined as:

$$F_m = \frac{A_{sn}}{A_{\text{OxI}}} = \frac{R_{sn}}{R_{\text{OxI}}},$$

where we have that  $R = 14 : 13\text{C}$ . We get that  $F_m \in [0, 1]$ , where  $F_m = 1$  is the radiocarbon is from 1950. When  $F = 0$ , this is when you cannot tease a part radiocarbon from the measurement background. This is called "radiocarbon dead", and occurs at about 60,000 [yr]. To get the age, we use:

$$^{14}\text{C}_{age} = -8033 \log [F_m],$$

which uses the Libby half-life. Importantly,  $^{14}\text{C} \neq$  the age of the radiocarbon. This is because the atmosphere is constantly evolving, therefore the age is translating the age using the conditions for radiocarbon in the modern atmosphere backward in time. Therefore, true time/calendar age needs to correct for the evolution of radiocarbon in the atmosphere. \par Lastly, we use:

$$\Delta^{14}\text{C} = (F_m \exp[-\lambda(t_{ms} - 1950)] - 1) \times 1000 [\text{\%}],$$

which includes a correction of decay from the measurement date to the reference point of 1950. Usually, we have  $\Delta^{14}\text{C} \in [-1000, 0]$ , for dates pre-1950. It then belongs to **[0, 600]**.

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# 12.744: Lecture 16

## Radiocarbon II

### The Levers of Radiocarbon

We remember the decay equation:

$$N = N_0 \exp [-\lambda t].$$

The big question is about the variations in  $N_0$  over time, specifically in the atmosphere of CO<sub>2</sub>. There are two major processes that affect this:

1. Production rate: variation in geomagnetic field and solar activity (Milankovitch Cycles)
2. Carbon cycle: reorganization of carbon reservoirs
3. Anthropocene: human influence

Now, we remember that:

$$^{14}\text{C age} = -8033 \times \log F_m.$$

We can translate this to calendar age as described by Fig. 1, the "calibration curve"

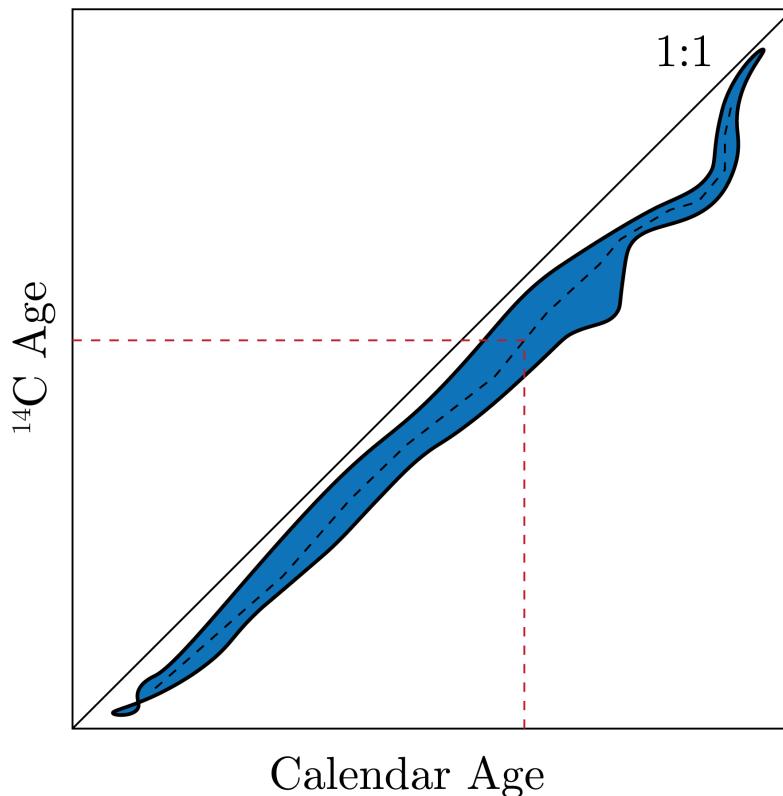


Fig. 1: The  $^{14}\text{C}$  Calibration Curve. The blue region is uncertainty around the dashed best fit line.

### Production Rate Change

Of importance is the production rate change of cosmogenic isotopes, which we diagramize in Fig. 2. Here, we can look at the production rate of another radiogenic isotope  $^{10}\text{Be}$ , which we know has cyclical changes in production given the deflection of cosmic rays by the Earth's magnetic field.

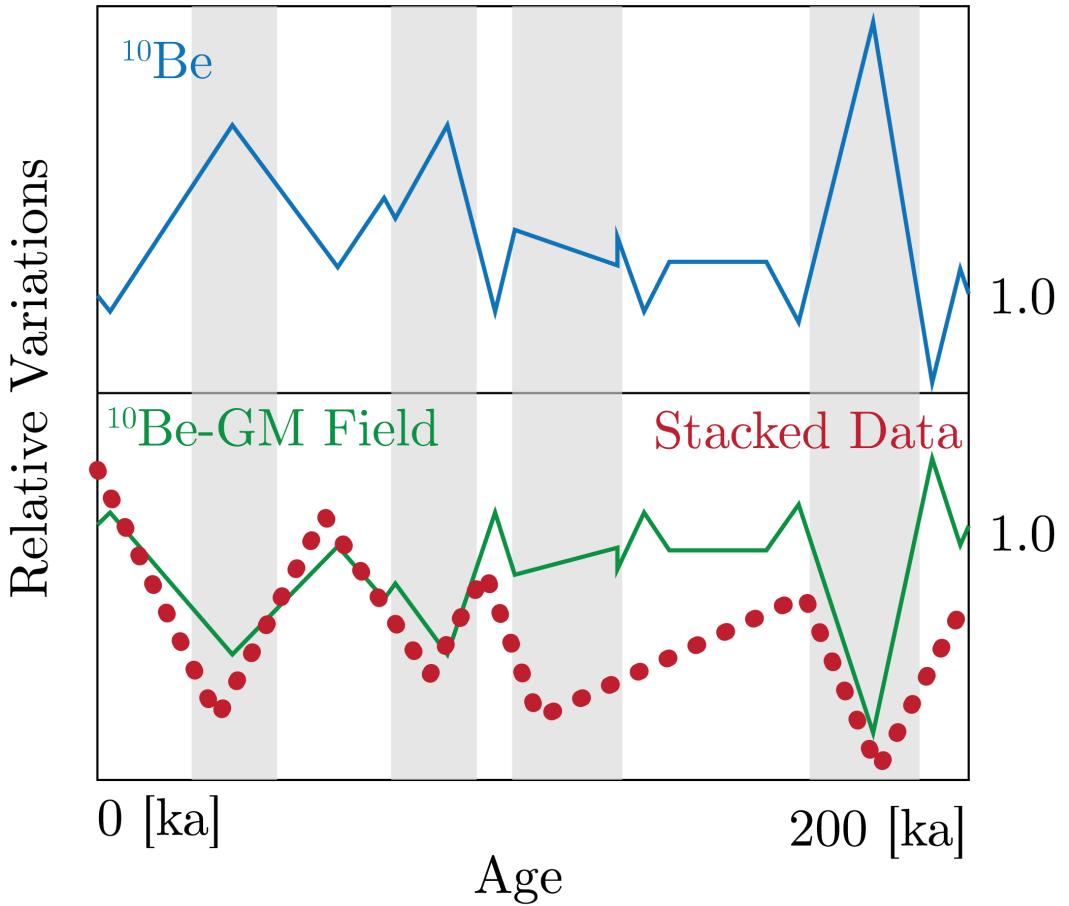


Fig. 2: The production rate of  $^{10}\text{Be}$  used to derive geomagnetic changes (GM), that compares well with stacked data.

Additionally we can see that there is a large effect on  $^{14}\text{C}$ , such as in Fig. 3 and the relation of the virtual dipole moment (GM field variations), there is a large variation that we need to correct for in  $^{14}\text{C}$ .

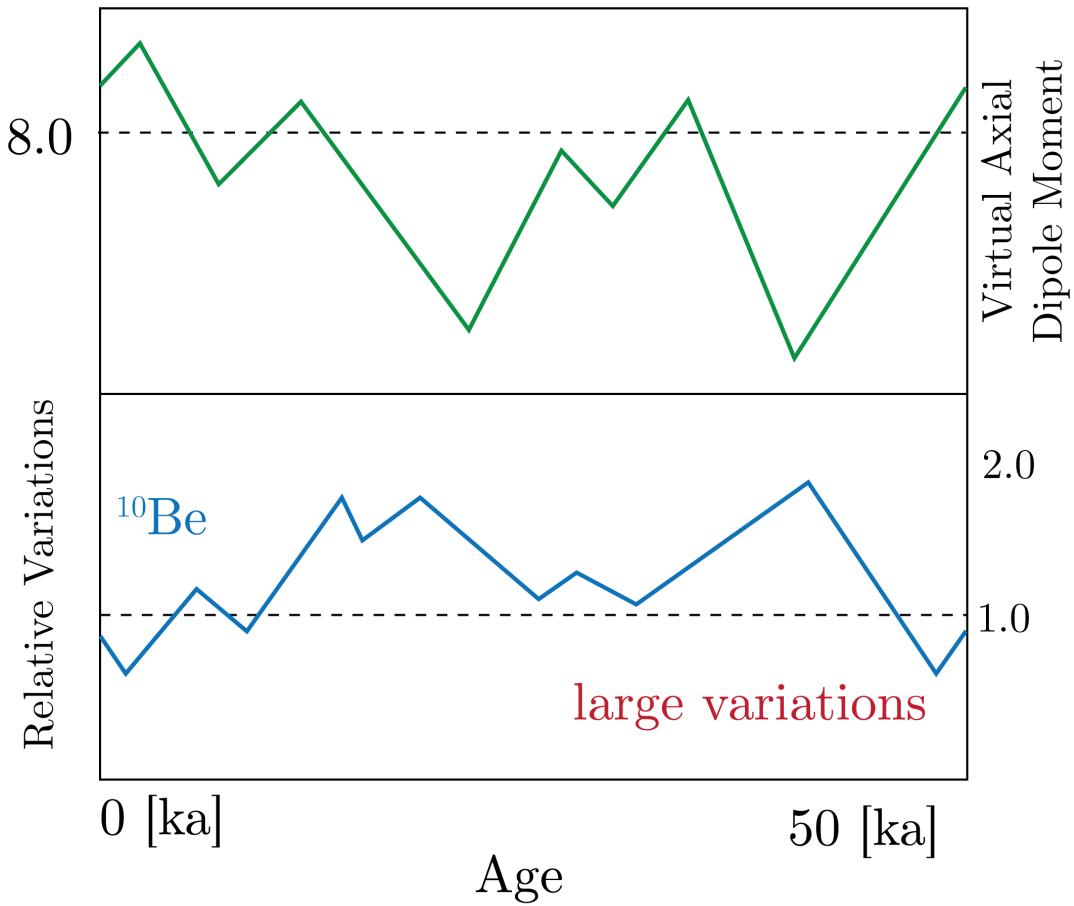


Fig. 3: The Virtual Dipole Moment (a measure of the GM field) causes large variations in <sup>14</sup>C.

We correct for this by removing the trends from the geometric field and solar variations to then look at the changes in the Earth's Carbon cycle, as roughly shown in Fig. 4. The residuals show that about half the variation is from these planetary changes, with the rest from the Carbon Cycle internal drives itself.

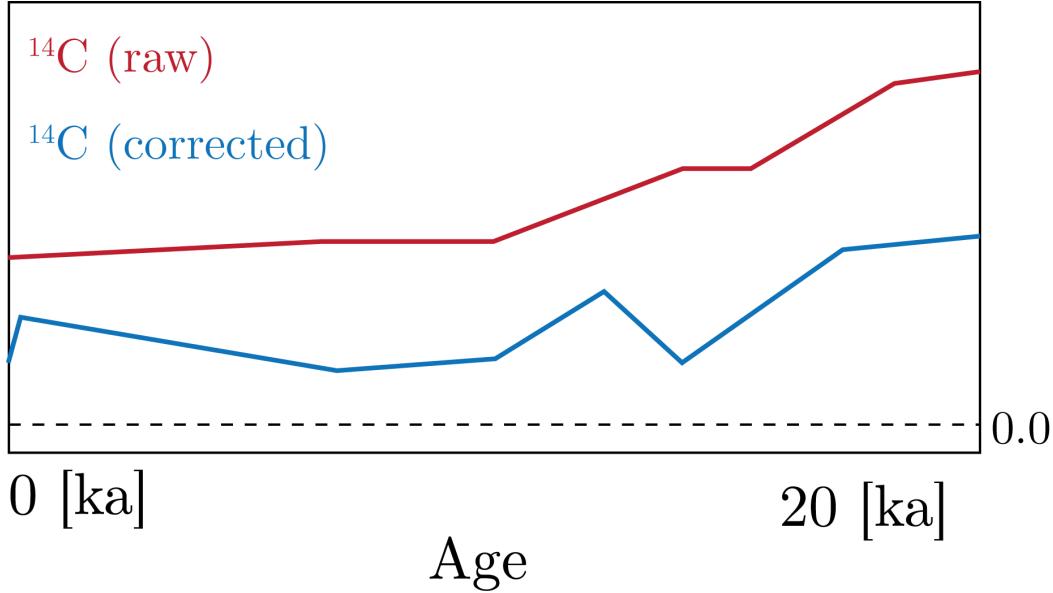


Fig. 4: Removal of geomagnetic and solar activity from <sup>14</sup>C data.

## Carbon Cycles

Now, all the changes in <sup>14</sup>C are from changes in the Earth's carbon cycle, with the major reservoirs presented in Fig. 5.

# The Carbon Cycle

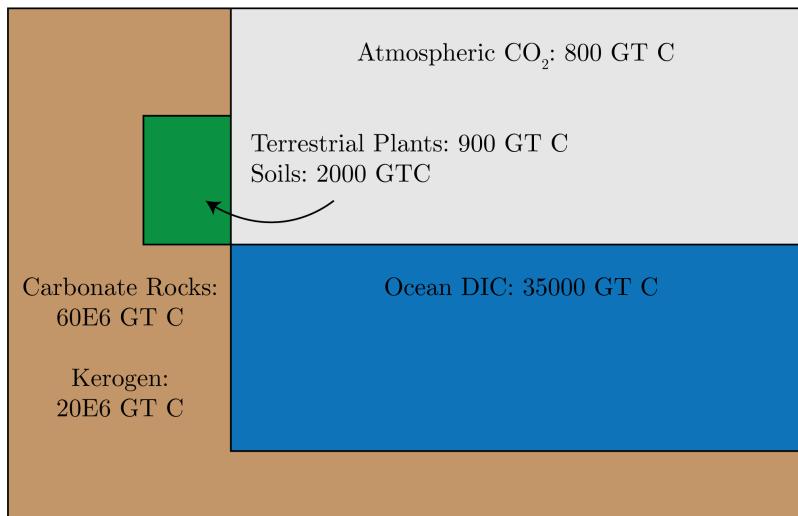


Fig. 4: A schematic of the Earth's carbon cycle and the major carbon reservoirs.

From data, we know that there are only small changes in atmospheric  $\delta^{13}\text{C}$  and therefore the surface ocean, given equilibration time scales. However, we can use deep ocean  $\delta^{13}\text{C}$ , and specifically the ventilation age to describe the natural carbon cycle variations. We can look at the surface reservoir age of  $\Delta^{14}\text{C}$  (exchanged from the atmosphere), which is different from the atmosphere (which has a value of 0), and see that the patterns are almost exactly the same as ocean circulation, specifically inverse relations. So, in the N. Atlantic we get the least anomaly versus in the N. Pacific, which have the largest changes.

## Anthropocene

The Seuss Effect is the increased decrease in  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ , due to the isotope signature of anthropogenic emissions being greatly negative compared to the natural variations in the carbon cycle. We can look at [Problem Set 3](#) for more information on human influence.

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# 12.744: Lecture 17

## Nontraditional, light stable isotopes

### The Basics

We define these as non-CHONS, namely:

- Li
- B
- Mg
- Ca
- K
- Si
- Cl

We discuss the first two. The history of using these is because these do not produce gaseous species, so we needed a new measurement technique. This was traditionally Thermal Ionization Mass Spectrometry, when elements are drawn across a heated filament, for which there is a large fractionation which makes it tricky. The solution was Inductively Coupled Plasma Mass Spectrometry, which makes an EM field that makes a plasma that ionizes the elements, which does not have the same fractionation. It is usually an Ar plasma.

Many of these have interesting properties:

- B has a high concentration in SW
- Li goes into mineral lattices (such as carbonates)
- Mg, Ca are key elements in biogeochemical cycles (such as in carbonates and silicates)
- K is one of the most important nutrients

### Boron

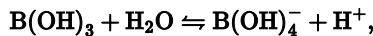
It has two isotopes:

- $^{10}\text{B}$  is 19.9%
- $^{11}\text{B}$  is 80.1%

In seawater, the concentration is quite high and has two species:

- $\text{B}(\text{OH})_3$ : boric acid
- $\text{B}(\text{OH})_4^-$ : borate ion

These are proxy for  $\text{pH}$  and for  $\text{pCO}_2$ . We can write the equilibrium as:



where the equilibrium constant is:

$$K_a = \frac{[\text{B}(\text{OH})_4^-][\text{H}^+]}{[\text{B}(\text{OH})_3]}.$$

The corresponding  $\text{pKa}$  is  $-\log K_a$ , which basically gives us the relative amount of the two species is proportional to the  $\text{pH}$ . Conveniently, the  $\text{pKa} \approx 8.6$ , which is relatively close the seawater  $\text{pH}$  which then means that the small changes in the seawater will affect the relative abundance of these species. We can therefore write the relationship as:

$$\log \frac{[\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]} = \text{pH} - \text{pKa}.$$

Now, we note that the boric acid is trigonal and borate ion is tetrahedral, therefore the isotope fractionation is going to be different. We can write a mass balance equation for  $R_i = {}^{11}\text{B}/{}^{10}\text{B}$  for  $i$  the speciation in hydroxyl ions, we get:

$$[\text{B}]_{sw} R_{sw} = [\text{B}(\text{OH})_3] R_3 + [\text{B}(\text{OH})_4^-] R_4.$$

We also know  $\alpha_{3/4}$  is experimentally constrained. To use this, we take advantage of the fact that the borate ion goes into carbonates, as well as the fact that we know the fractionation as well as the  $\text{pKa}$ . We additionally note that the residence time of B in seawater is 10 to 20 [Myr], which means that over time frames less than this, we have that  $\delta^{11}\text{B}_{sw}$  is constant, i.e. it is equal to modern values over this timeframe. Therefore, if we measure  $\delta^{11}\text{B}_{\text{carbonates}} \approx \delta^{11}\text{B}_{\text{B}(\text{OH})_4^-}$ , which along with the fractionation factor we can get  $\delta^{11}\text{B}_{\text{B}(\text{OH})_3}$ . Thus, we can get from the above equation the

difference of  $pH$  and  $pK_a$ . This all then means that if we know the solubility coefficient, we can get  $pCO_2$  reconstructions from solid carbon records through time, which often serve as a tie breaker against other proxies. This is presented in Fig. 1. 1:

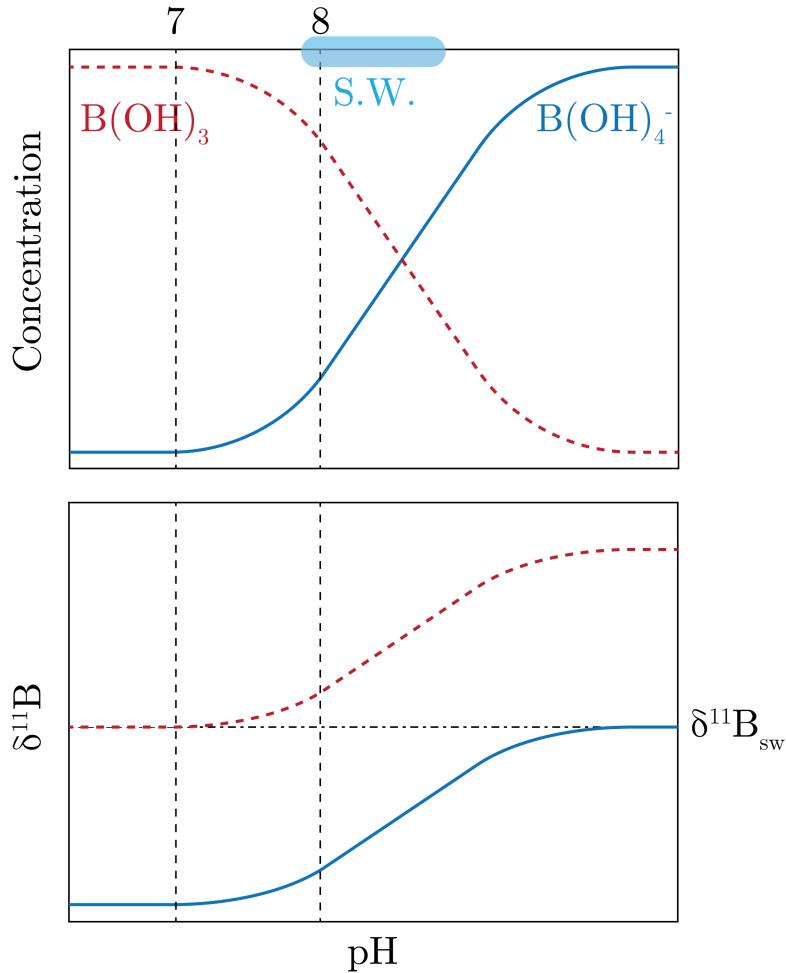


Fig. 1: The boron proxy in play.

## Lithium

There are two isotopes:

- ${}^6Li$  which is 7.5%
- ${}^7Li$  which is 92.5%

and we note that there was a reverse convention to report the light over heavy of the isotope originally. The relative mass difference is large, at about:

$$\frac{\Delta m}{m} \simeq 0.14,$$

which allows for large isotope fractionation to arise. It substitutes for Mg, Fe, and Al in lattices, which means it is a member of minerals. The application has been using it for chemical weathering, despite the fact that there is little to no fractionation during weathering (dissolution). Despite this, it was found that the dissolved load has a much higher and greater spread than the rocks from which they derive.

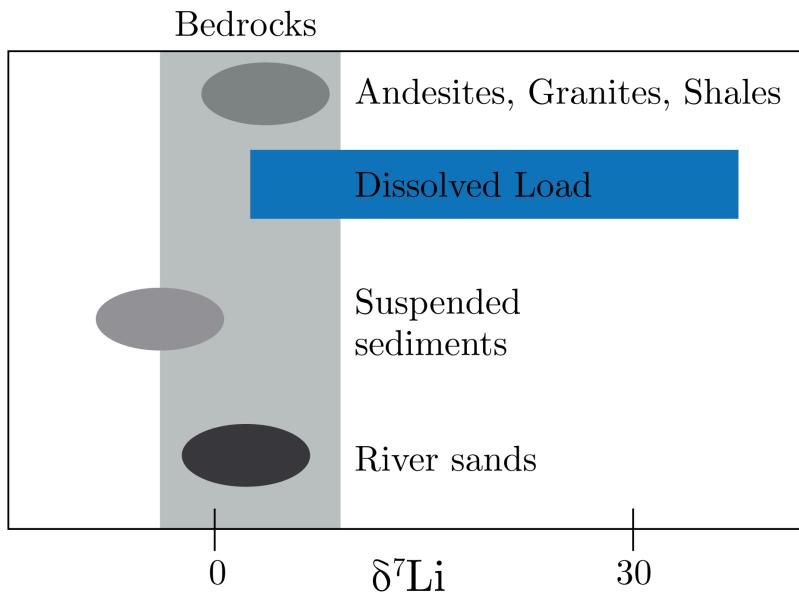
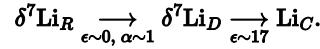


Fig. 2: Dissolved loads have a huge spread of lithium, contrasted against the rocks that it derives from.

This is because Li goes into the mineral lattice during secondary clay formation, which is preferentially included, which fractionates during weathering. Experiments have shown that with increasing temperature, there is a decrease in fractionation, which is expected from the theory. However, at low temperatures there is a large fractionation factor, at which the formation of clays occur.

We can imagine the following model:



However, we also note that there is a branching at the second step, to which lithium can also remain dissolved. This is what we can measure. So, we bring back out fractional remaining, defined as:

$$f = \frac{F_D}{F_C + F_D} = \frac{F_D}{F_0}.$$

We go now into Rayleigh distillation versus the batch model.

### Batch Model

Here we have a closed system, in which the dissolved minerals can reabsorb. We define:

$$F_0 \delta_0 = F_C \delta_C + F_D \delta_D,$$

and also:

$$\Delta_{C/D} = \delta_C - \delta_D \sim 10^3 \log \alpha_{C/D},$$

this is also equivalent to  $\epsilon$  that we have been using. Therefore, we can get:

$$\delta_0 = (1 - f)\delta_C + f\delta_D$$

which leads to:

$$f\delta_D = \delta_0 - (1 - f)(\Delta_{C/D} + \delta_D).$$

Thus, we get:

$$\delta_D = \delta_0 - (1 - f)\Delta_{C/D}.$$

This then means that we can get the difference between the dissolved load and the total lithium as a function of the fractional abundance remaining.

### Rayleigh Model

Now, the difference here is that the dissolved load is taken away from the reaction. The model is then:

$$\delta_D = \delta_0 + \log f \Delta_{C/D}.$$

We can do some asymptotic analysis that as  $f \rightarrow 1$  we get that all Li remains in the solution. We can also see that  $f \rightarrow 0$  that all Li is in the clays. So, for  $\delta_D - \delta_0 \simeq \Delta_{C/D}$  we can use the batch model and for  $\delta_D - \delta_O \gg \Delta_{C/D}$  we would use the Rayleigh model. This then allows us to see what major processes are happening in nature.

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# 12.744: Lecture 18

## Simple Decay – Radiometric Dating

### Theory

A review of important terms:

1. Radioactive: decaying
2. Cosmogenic: from space
3. Anthropogenic: produced by humans
4. Primordial: existing at the beginning of the universe
5. Closed system: a closed box

We start with the decay equation:

$$\frac{N}{N_0} = \exp[-\lambda t].$$

We can reformulate this as:

$$N = N_0 \exp[-\lambda t],$$

or:

$$N_0 = N \exp[\lambda t].$$

This relates the original number of isotopes (at  $t = 0$ ) to the number of isotopes now (at time  $t$ ). In order to apply this, we can measure  $N$  and we can measure  $\lambda$  experimentally. However, there are a few unknowns, such as  $t$  and  $N_0$ . What we can say, though, is that we can note that:

$$D^* = N_0 - N,$$

where  $D^*$  is the number of radiogenic daughter nuclides. So, we can get a new equation:

$$D^* = N \exp[\lambda t] - N = N(\exp[\lambda t] - 1).$$

We can then use:

$$D = D_0 + D^*,$$

where  $D$  is the total daughter and  $D_0$  is the primordial activity. Therefore, we get:

$$D = D_0 + N(\exp[\lambda t] - 1).$$

Now, as MS is really good at measuring ratios, we introduce the following:

$$\frac{D}{D_s} = \frac{D_0}{D_s} + \frac{N}{D_s}(\exp[\lambda t] - 1),$$

where  $D_s$  is the stable isotope of the daughter element. This is the form used in Eq. (1) in the Patterson (1956). We can clearly see that this is essentially:

$$y \sim b + mx,$$

which we use in the isochron method. There is a neat trick for doing the calculations in your head:

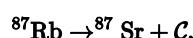
$$\exp[\lambda t] = 1 + (\lambda t) + \frac{(\lambda t)^2}{2!} + \dots,$$

and in special cases for  $t \ll \tau_{1/2}$ , we can forget all terms greater than linear. Thus, we get:

$$\frac{D}{D_s} = \frac{D_0}{D_s} + \frac{N}{D_s} \lambda t.$$

### Application

We start with the:



via  $\beta^-$  decay. So, in order to do this, we want to balance the charges. To do this, we need to balance the following:

1. charge
2. baryons
3. leptons

and then we can balance each based on the decay above and get that:

$$\mathcal{C} = e^- + p + \nu^-.$$

We can look at the relative abundances of the Sr element and want to choose the stable isotope that is of similar magnitude to the radioactive element. This is why we want to choose  $\text{^{86}Sr}$  as the normalization isotope. We can then measure two or more samples and plot the line as discussed previously and get the initial value. There are a few major assumptions with this:

1. System was isotopically homogeneous
2. System was variable in its elemental concentrations,
3. System has to be closed.

As Bernhard Peucker-Ehrenbrink has said: "Without age, we are lost in time".

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# 12.744: Lecture 19

We are interested in understanding why there is a spread in different parent / daughter ratios. Now, there are a few configurations of isotopes we are interested in, and they are often in tetrahedral and octohedral configurations. We can define a few ratio of radius of cations to anions of the isotopes we are interested in:

Trigonal	$\frac{R_c}{R_a} \sim 0.15 - 0.22$
Tetrahedral	$\frac{R_c}{R_a} \sim 0.22 - 0.41$
Octohedral	$\frac{R_c}{R_a} \sim 0.41 - 0.73$
Cubic	$\frac{R_c}{R_a} \sim 0.73 <$

This means there is more space for the larger in decreasing configuration size. If we want to replace one cation with a larger one, i.e. into a space that doesn't quite fit, we move to the "lattice-strain model". This was developed by Bryce (1975) and expanded by Wood and Blundy (1997).

We start with the fact that when applying a stress, we get a strain:

$$\text{stress} \rightarrow \text{strain} \sim [\text{Nm}^{-2}] = [\text{Pa}].$$

We can define the "Young's Modulus" by the ratio:

$$E = \frac{\text{stress}}{\text{strain}}.$$

Next, we define the distribution coefficient,  $D$ , which defines the ability of the material to change phase, i.e.:

$$D = \frac{C_{\text{solid}}}{C_{\text{liquid}}},$$

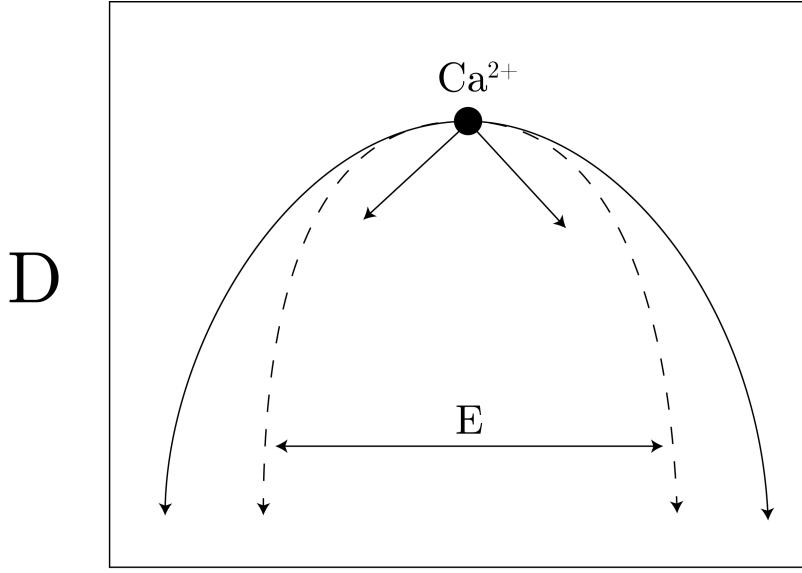
which are experimentally defined. We can next define the dependency of temperature as:

$$D_i = D_0 \exp [\Delta G / (RT)],$$

where the strain energy

$$\Delta G = A \cdot E \cdot B \left[ \frac{R_0}{2(r_i - r_0)^2} + \frac{1}{3(r_i - r_0)^3} \right].$$

This shows us that the strain energy increases if the replacement radius is larger than the ideal radius. This then gives a picture like Fig. 1, presented below.



## Cation Radius

Fig. 1: Strain energy vs. cation radius, related to the Young's Modulus.

Now, we want to determine the concentration from mixing, as given by Fig. 2.

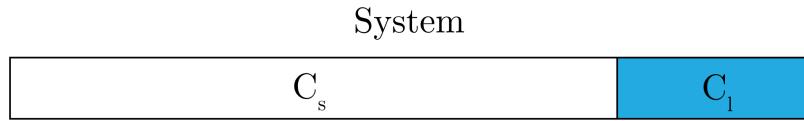


Fig. 2: Our (closed) system of interest for mixing.

Given:

$$D = \frac{C_s}{C_l},$$

we can get:

$$C_0 = C_l F + C_s(1 - F) = \frac{C_s}{D} F + C_s - C_s F.$$

With some rearranging, we get:

$$C_s = \frac{DC_0}{F + D(1 - F)}.$$

By the same algebra, we can also get:

$$C_d = \frac{C_0}{D + F(1 - D)}.$$

Now, from this we can note:

$$\frac{C_l}{C_0} \sim \frac{1}{F} \quad \text{if } D \ll F \quad \text{incompatible}$$

We also get:

$$\frac{C_l}{C_0} \sim \frac{1}{D} \quad \text{if } F \ll D \quad \text{compatible.}$$

Next, we can plot this all out, for the concentration of the earth crust and mantle, in Fig. 3.

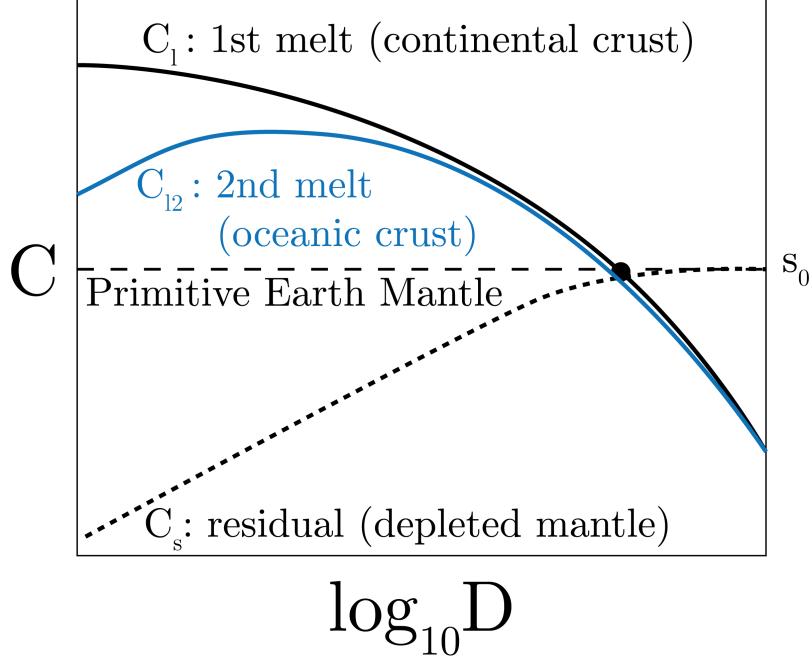


Fig. 3: How concentration  $C$  varies with partition coefficients,  $D$

Specifically, when we refer to the oceanic crust, we are talking about the Mid Ocean Ridge Basalt (MORB). Fig. 3 shows the progression from 1st melt and the residual to the 2nd melt.

We now want to look at the time evolution of continental crust, which we plot in Fig. 4

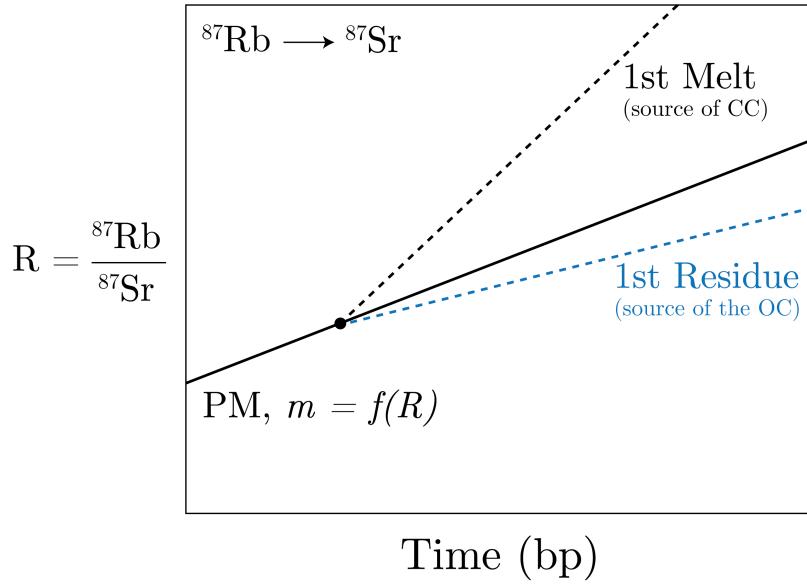


Fig. 4: How the ratio of parent-daughter ratio changes in time for a specific isotope system.

To make this graph, we compare to see which  $D$  is larger (i.e., the element which does not melt). If the daughter is more compatible (larger  $D$ ), then it will take longer to grow in the CC than in the OC and vice versa. We can do a similar analysis for other isotope systems, like  $^{147}\text{Sm}/^{143}\text{Nd}$  system (which is the opposite of the Fig. 4 scenario). The key point here is as follows: the radiogenic isotope ratios are time-integrated parent/daughter element concentration ratios. From data, we have determined the average age of the CC is  $\mathcal{O}(10^9)$  years versus OC at  $\mathcal{O}(10^7)$ . We note that for isochrons we are really interested in systems that are initially that are radiogenically homogeneous but chemically heterogeneous.

# **12.744: Lecture 20**

## **Instrumental Mass Bias**

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This lecture was devoted to solving a problem in isotope geochemistry.

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# 12.744: Lecture 21

## Following up on Deep Time

We remember the iso / geochron methodology in Fig. 1.

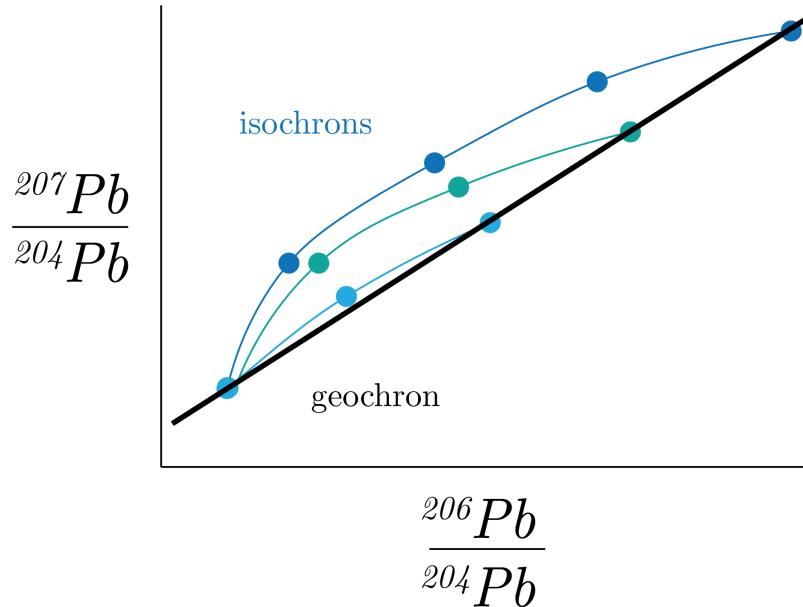


Fig. 1: A cartoon of the iso / geochron method for Pb.

To determine the error statistics, we note the natural abundances of the and see that  $^{204}\text{Pb}$  has the lowest ( $\sim 1.4\%$ ). We plot this error for the Clair Patterson paper in Fig. 2.

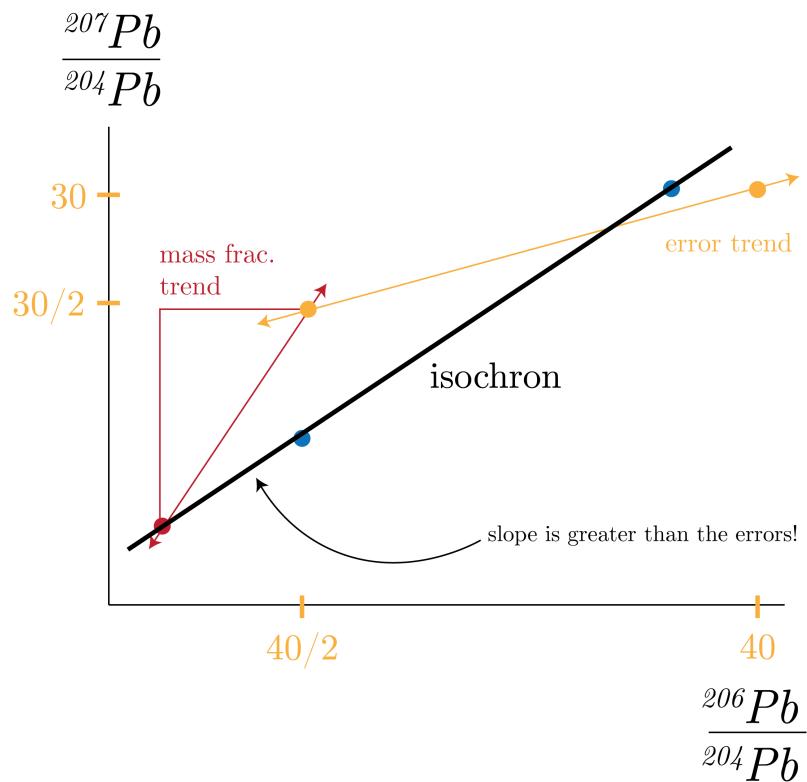


Fig. 2: A cartoon of the isochron in Pb including errors as used in the Patterson (1956) paper.

We can think of the decay as in Fig. 3.

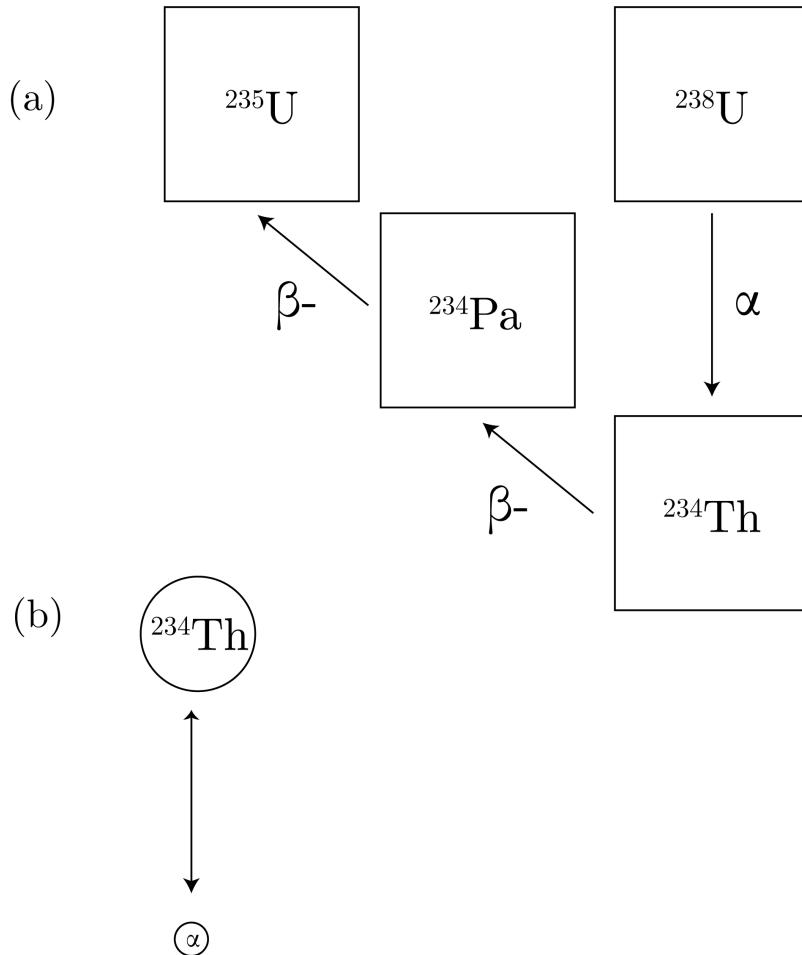


Fig. 3: (a) The top terms of radioactive decay of the  $^{238}\text{U}$  decay chain. (b) The mass conservation of the initial decay in the chain.

We define the activity as:

$$A = \lambda N,$$

for  $N$  the number of atoms. We define secular equilibrium as, for  $A_i$  the activities in a decay chain after some parent:

$$A_1 = A_2 = A_3 = \dots$$

which then means that:

$$\lambda N_1 = \lambda N_2 = \lambda N_3 = \dots$$

Therefore, we can update our decay equation to give:

$$-\frac{dN_1}{dt} = \lambda_1 N_1,$$

for the first, then:

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda N_2 = \lambda_1 N_1(t_0) \exp[-\lambda_1 t] - \lambda_2 N_2,$$

which we can solve, which we call the Bateman Equations, for coupled exponentials. A fun idea: set up these equation solutions for all of the 238 decay chain, so that we can turn cool knobs.

# **12.744: Lecture 22**

## **Instrumental Mass Bias**

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This lecture was devoted to solving a problem in isotope geochemistry.

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# 12.744: Lecture 23

## Radioactive Decay

We can continue our work with the decay series of  $^{238}\text{U}$ , we consider the amount of the daughter left,  $N_2$ , from a parent,  $N_1$ , in which we sum the input and the output from decay:

$$N_2 = \underbrace{\frac{\lambda_1}{\lambda_1 - \lambda_2} N_{1,0} (\exp[-\lambda_1 t] - \exp[-\lambda_2 t])}_{N_2 \text{ atoms produced by the decay of the parent, } N_1, \text{ but not decayed yet}} + \underbrace{N_{2,0} \exp[-\lambda_2 t]}_{N_2 \text{ atoms originally present and not yet decayed}}$$

We introduce the notation  $(^i X)$ , which denotes:

$$(^i X) = \lambda_i N_i.$$

For a specific system, let's consider  ${}^i X = {}^{230}\text{Th}$ , which is described by:

$$({}^{234}\text{Th}) = \underbrace{({}^{230}\text{Th})_x}_{\text{excess}} + \underbrace{({}^{230}\text{Th})_s}_{\text{support}},$$

where we have that the **excess** is from sources outside of our "box" we are modeling/bean-counting in and **support** is produced within the box from its parent,  ${}^{234}\text{U}$ . We can consider depth profiles in sediment of  ${}^{230}\text{Th}$ , given in Fig. 1.

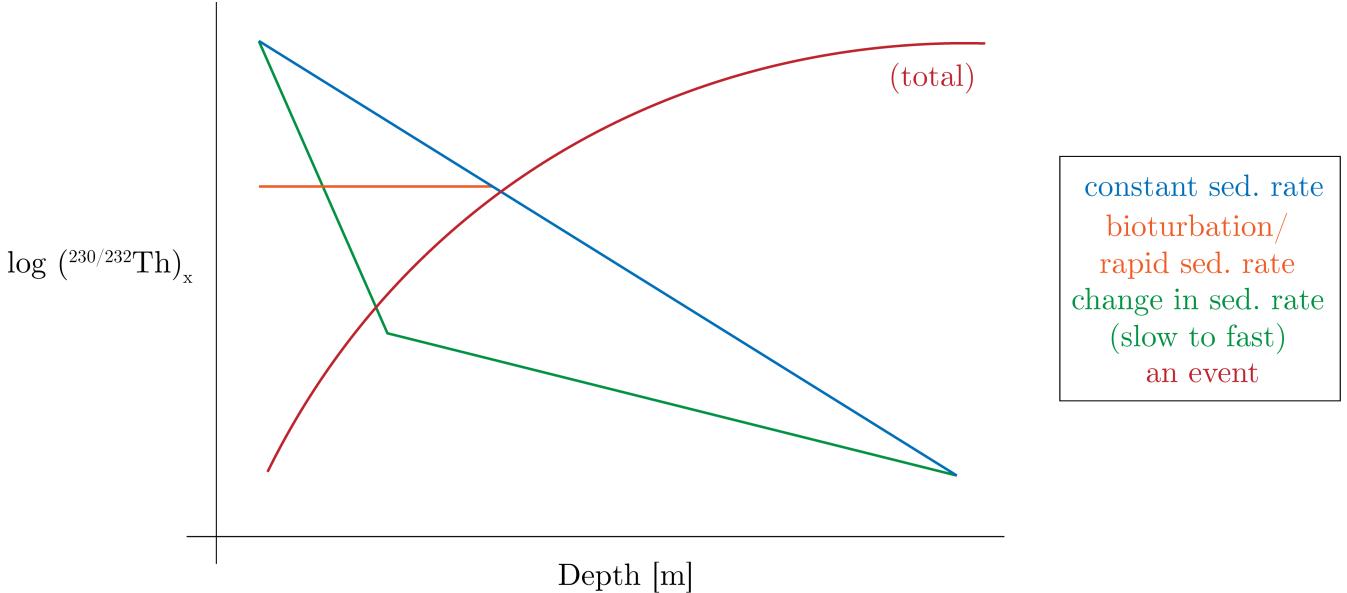


Fig. 1: Different regimes for sedimentation rates.

To understand the red regime (for total activity), we consider the following. We assume that  ${}^{238}\text{U}$  decays to  ${}^{230}\text{Th}$  and normalize to the long-lived Th isotope. So, we have:

$${}^{230}\text{Th} = \frac{\lambda_{234}}{\lambda_{230} - \lambda_{234}} {}^{234}\text{U}_0 (\exp[-\lambda_{234}t] - \exp[-\lambda_{230}t]),$$

then as secular equilibrium we have that:

$$({}^{234}\text{U}) = ({}^{238}\text{U}) = {}^{234}\text{U} \lambda_{234}.$$

We further note that:

$$\lambda_{230} - \lambda_{234} \sim \lambda_{230},$$

which means that:

$$\exp[-\lambda_{234}t] \sim 1.$$

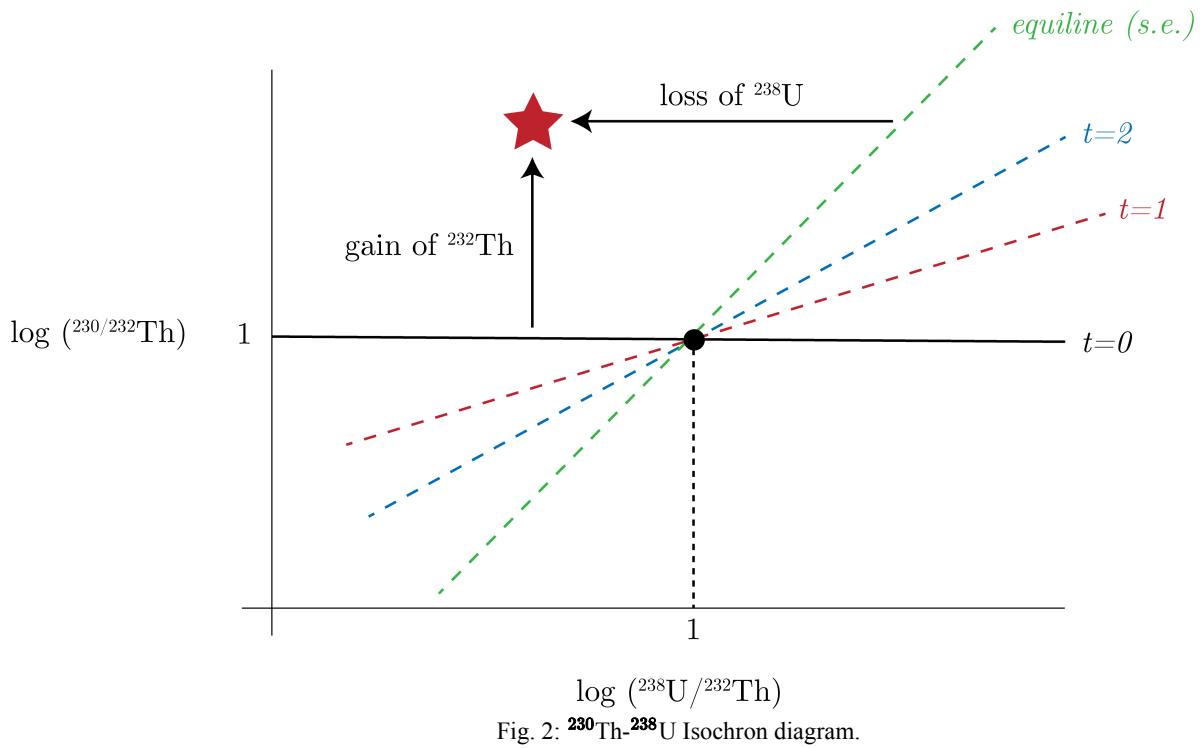
Therefore, we have that:

$$\lambda_{230} \cdot {}^{230}\text{Th} = \lambda_{234} \cdot {}^{234}\text{U}_0 (1 - \exp[-\lambda_{230}t]),$$

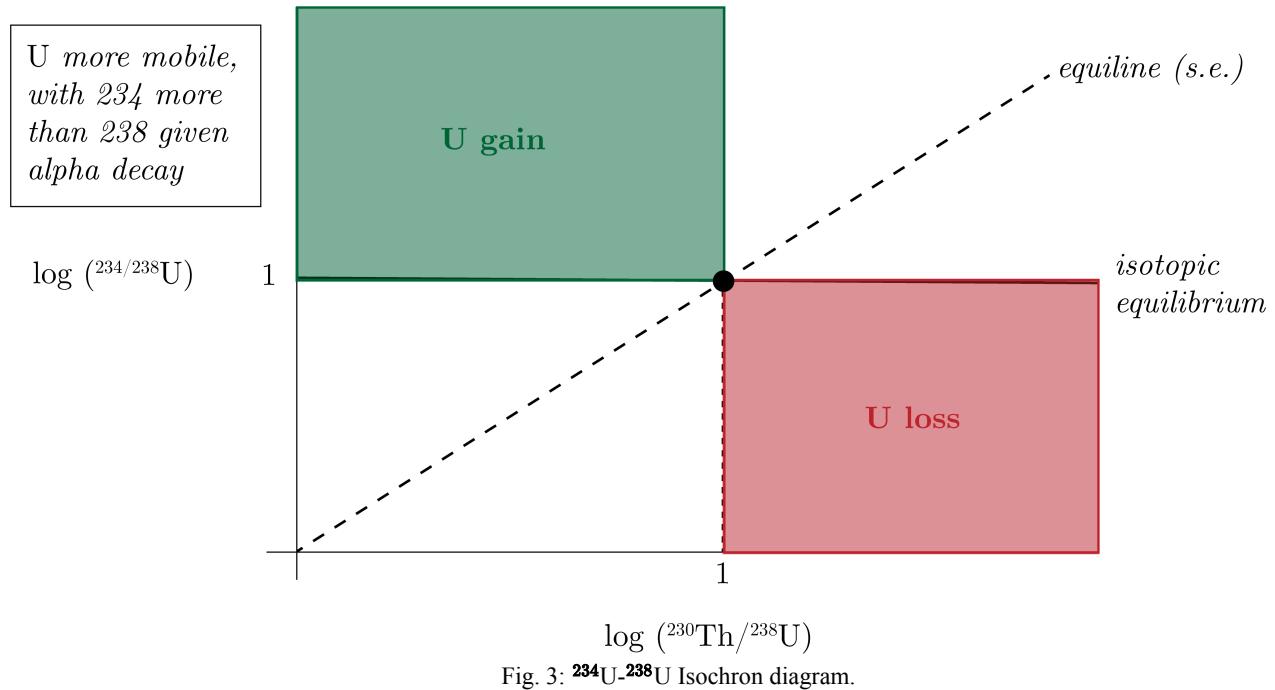
and thus:

$$\left( \frac{^{230}}{^{232}}\text{Th} \right) = \left( \frac{^{230}}{^{232}}\text{Th} \right)_{x,0} \exp [-\lambda_{230}t] + \frac{^{238}\text{U}_0}{^{232}\text{Th}_0} \exp [-\lambda_{238}t].$$

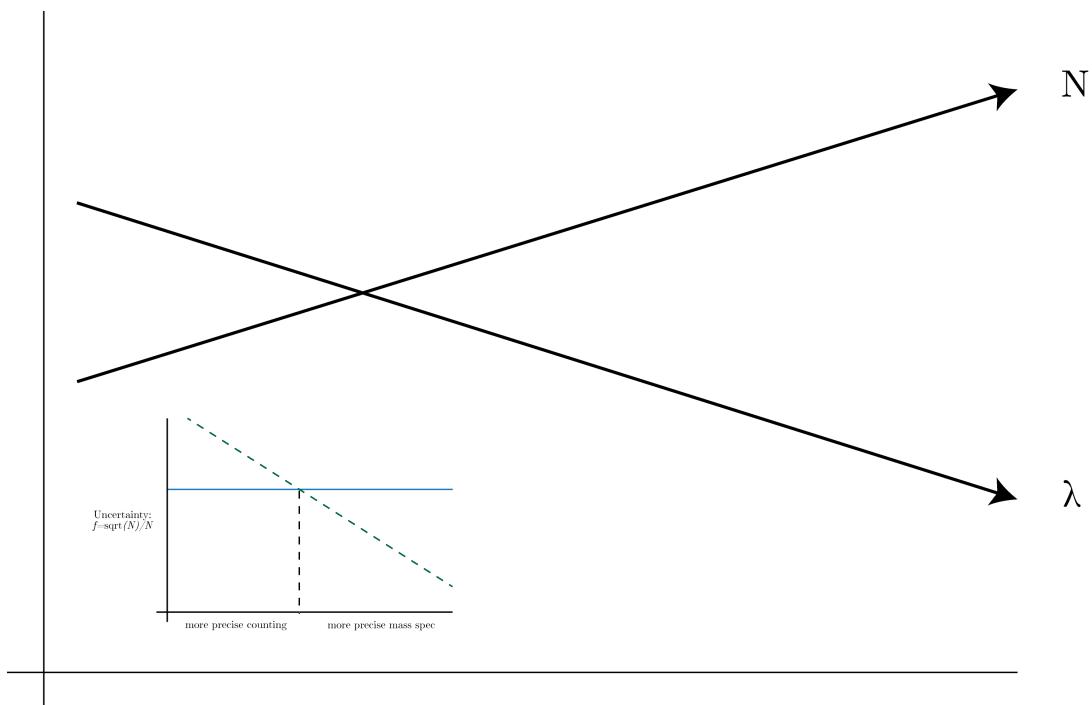
We plot this in Fig. 2.



We can view this as a change in the support of  $^{230}\text{Th}$  over time, at which the equiline is define as the secular equilibrium point. We can also study the  $^{238}\text{U}$ - $^{234}\text{U}$  system in Fig. 3.



The green zone is seawater! We can also consider the counting statistics, as in Fig. 4.



Half-life  $[t^{-1}]$

Fig. 4: Counting statistics, comparing mass spec. precision to counting.

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# 12.744: Lecture 24

## Tackling New Stable Isotope Systems

We have seen, with the development and proliferation of Inductively Coupled Plasma Mass Spectrometry (ICP-MS), massive development in developing these isotope systems. From our Qualitative Rules of Equilibrium Isotope Fractionation, we note that the mass fractionation scales inversely with mass. We now look at an example case.

### Boron – a Return

Boric acid has a lower coordination number, has stronger bonds with O, and therefore has a stronger affinity to fractionate. This is to say that heavy isotopes are concentrated in substances where that element forms the stiffest bonds (i.e., a lower coordination number). We can think of this as a high spring constant, meaning short, strong chemical bonds. We plot this, comparing Boric Acid with Borate, in Fig. 1.

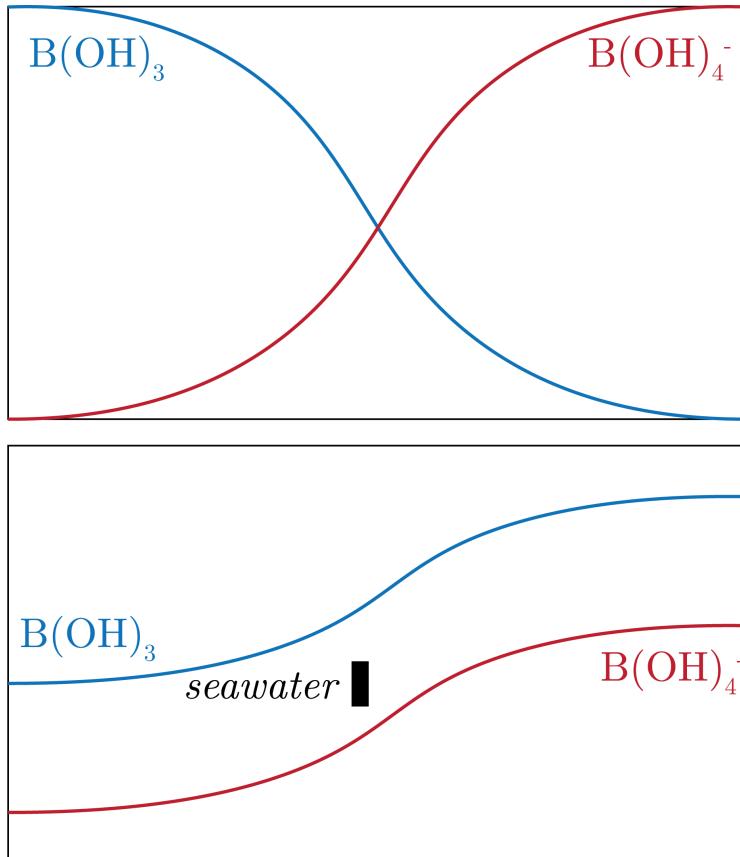


Fig. 1: A comparison of boron ions.

See Valier's lecture on Boron for more information.

### Strontium – another Return

First, we remember that:  $^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$  by  $\beta^-$ . We consider the diagram in Fig. 2.

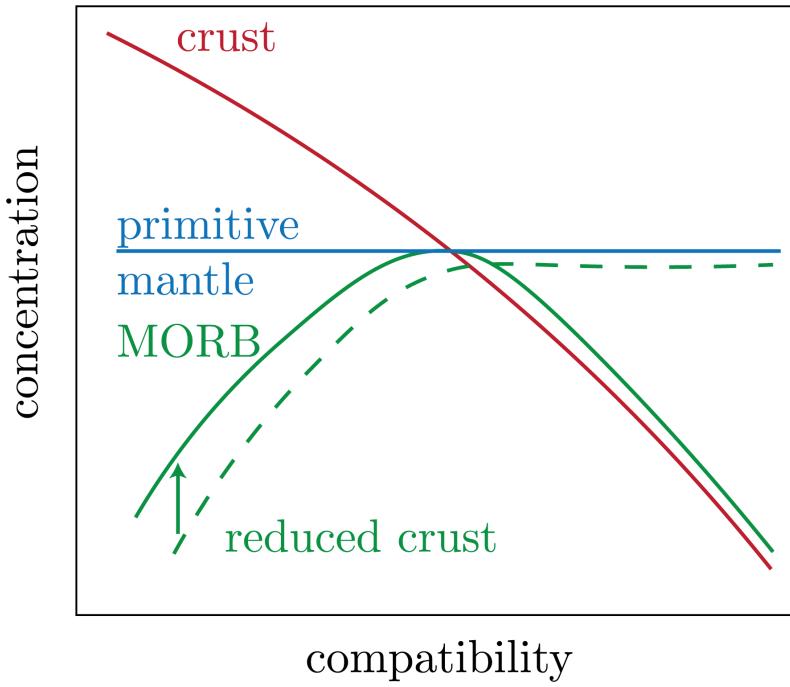


Fig. 2: Reason for Rb being higher in rivers.

We note that the reduced crust is below the MORB, therefore there is less Rb in the oceans than in the rivers, so we have that the ratio of Sr to Rb isotopes that we are interested in will be higher in the rivers than in the ocean. Importantly, Rb has a half life of about 49 billion years. Now, we can use a mixing equation to get the respect mixing for the river  $r$  and the ocean  $o$  for this system:

$$[Sr] = a[Sr]_o + b[Sr]_r.$$

We note that it is linear mixing mixing, as we have the same isotope in the denominator so that it progresses 1:1 and not with some other gradient. However, we find that this is not the case, and we see that there needs to be some isotope fractionation effect that causes the seawater water to be greater than the expected linear mixing. We can see this in Fig. 3, where we note that  $\Delta_x m = 2$  and  $\Delta_y m = 1$ .

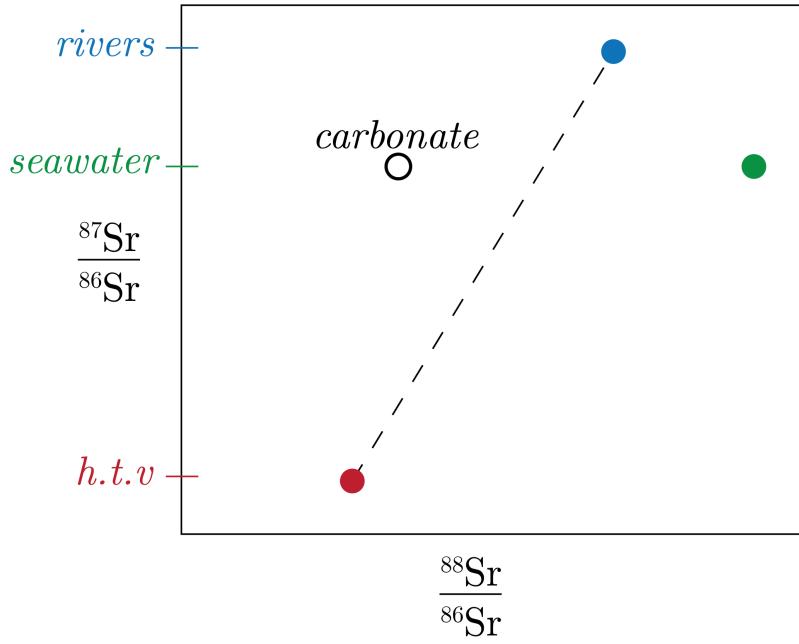


Fig. 3: Sr-Sr system.

So, our mixing equation becomes:

$$[Sr] = a[Sr]_o + b[Sr]_r - c[Sr]_c.$$

### Molybdenum – a New System!

We can view the Mo system as in Fig. 4.

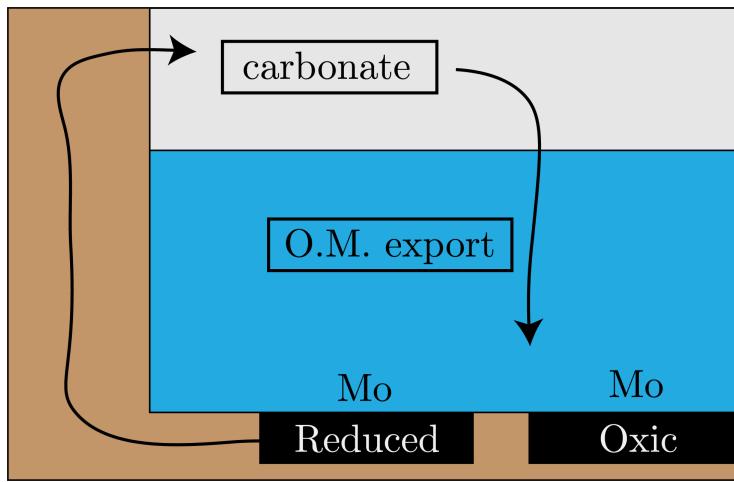


Fig. 4: The Mo system that we are thinking about.

We can think of this as a box model:

$$F_{in}\delta_{in} = F_{oxic}\delta_{oxic} + F_{anoxic}\delta_{anoxic},$$

where we have that the anoxic is heavy, because the removal of Mo from solution is quantitative, meaning that the pore waters in the sediment will be the ultimate source of Mo. Basically, what we see is that there is a step-wise addition of S that replaces the O in the Mo-O compound, which then makes it so that unless we are in a complete euxinic environment, it is harder to get a handle on the actual oxygenation state of seawater. We can see a schematic of this in Fig. 5.

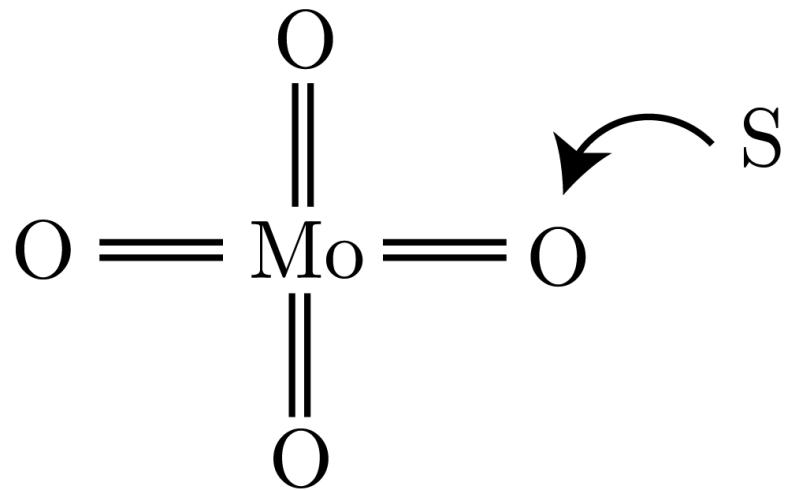


Fig. 5: The formation of thiomolybdates.

What this means then is that the ligands are changing, as O is being replaced with the weak ligand S, and these compounds become more particle reactive. This all happens in the sediments, and we see that with these stepwise actions, we get decreasing effects (intermediate) from isotope fractionation.

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