CHAPTER 3
Radioactive decay equations

3.1 The radioactive decay law

As discussed in Chapter 2, the decay rate of a radioactive substance was found to decrease exponentially with time. Radioactive decay was found to follow a statistical law, that is, it is impossible to predict when any given atom will disintegrate. The rate at which a radioactive substance N_1 decays is given by

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \qquad (3.1)$$

where N is the number of radioactive atoms and λ_1 is called the **decay constant**, which represents the probability per unit time for one atom to decay. The fundamental assumption in the statistical law for radioactive decay is that this probability for decay is constant, that is, it does not depend on time or on the number of radioactive atoms present.

Eq. 3.1 can be integrated with the boundary condition that the initial number of radioactive atoms is $N_1^o = N_1(0)$. This leads to the **exponential law of radioactive decay**:

$$N_1 = N_1^o e^{-\lambda_1 t} \qquad (3.2)$$

Denoting the daughter product of N_1 as N_2, and for the case in which N_2 is a **stable daughter** product, the accumulation of N_2 is simply given by

$$N_2 = N_2^o + N_1^o(1 - e^{-\lambda_1 t})$$
$$N_2 = N_2^o + N_1(e^{\lambda_1 t} - 1) \qquad (3.3)$$

where N_2^o is the initial amount of N_2 prior to the accumulation of radioactive decay products of N_1.

For measurement purposes, it is often convenient to express Eq. 3.2 in terms of the activity A of a radioactive substance, which is defined to be the number of decays per unit time or simply $A = \lambda_1 N_1$. If we multiply both sides of Eq. 3.2 by λ_1, we find that

$$-\frac{dN_1}{dt} = \lambda_1 N_1 = \lambda_1 N_1^o e^{-\lambda_1 t} \qquad (3.4)$$

It follows that

$$A_1 = A_1^o e^{-\lambda t} \qquad (3.5)$$

where A_1^o is the initial activity of the radioactive substance. The unit most commonly used in activity measurements is the **curie** (Ci), which is defined as 3.7×10^{10} decays/s.

The half-life of a radioactive substance is defined as the elapsed time over which the radioactive substance has decreased to half its original abundance. Thus, by letting $N_1 = N_1^o / 2$ in Eq. 3.2, the half-life is given by

$$t_{0.5} = \frac{\ln 2}{\lambda} = \frac{0.69315}{\lambda} \qquad (3.6)$$

The mean life, $\bar{t}$, or the average amount of time a radioactive element lives, is given by

$$\bar{t} = -\frac{1}{N_o}\int_0^\infty t\, dN = \frac{1}{N_o}\int_0^\infty t\lambda_1 N_1 dt = \lambda_1 \int_0^\infty te^{-\lambda_1 t}dt = \frac{1}{\lambda_1} \qquad (3.7)$$

Thus, the mean life is simply the inverse of the decay constant. During the mean life, the abundance of a radioactive substance decreases by a factor of 1/e.

3.2 Branched decay

3.2.1 Basic equations

In some cases, the parent N_1 decays to two different products, a process termed **branched decay**. Calling these two decay modes *a* and *b*, we define the probability of each decay mode as

$$\lambda_a = -\frac{(dN_1/dt)_a}{N_1}$$
$$\qquad \qquad (3.8)$$
$$\lambda_b = -\frac{(dN_1/dt)_b}{N_1}$$

The total decay rate of N_1 is

$$-\left(\frac{dN_1}{dt}\right)_{total} = -\left(\frac{dN_1}{dt}\right)_a -\left(\frac{dN_1}{dt}\right)_b = N_1\left(\lambda_{1,a} + \lambda_{1,b}\right) = N_1\lambda_{1,total} \qquad (3.9)$$

where $\left(\lambda_{1,a} + \lambda_{1,b}\right) = \lambda_{1,total}$ is the total decay constant. It follows that N_1 decays according to the following law

$$\boxed{N_1 = N_1^o e^{-\lambda_{1total}t}} \qquad (3.10)$$

Thus, if we were to measure only the abundance or activity of the radioactive nuclide, N_1, we would have no way of distinguishing between the two decay modes because we can only measure the total decay constant.

However, if we were to monitor the evolution of the abundance or activity of the two daughter products of N_1 as a function of time, we would be able to distinguish between the two decay modes. For example, we know that a fraction $\lambda_{1,a}/\lambda_{1,total}$ of N_1 decays by mode *a* and a fraction $\lambda_{1,b}/\lambda_{1,total}$ decays by mode *b*. Denoting the two types of daughter products as $N_{2,a}$ and $N_{2,b}$, the formulas describing the accumulation of each of the daughter products are

$$N_{2,a} = N_{2,a}^o + \left(\lambda_{1,a}/\lambda_{total}\right)N_1^o (1-e^{-\lambda_{1,total}t})$$
$$\qquad \qquad (3.11)$$
$$N_{2,b} = N_{2,b}^o + \left(\lambda_{1,b}/\lambda_{total}\right)N_1^o (1-e^{-\lambda_{1total}t})$$

where $N_{2,a}^o$ and $N_{2,b}^o$ are the initial amounts of daughter product $N_{2,a}$ and $N_{2,b}$ present before the decay of N_1.

3.2.2 Example: decay of ^{40}K to ^{40}Ar and ^{40}Ca

An example of a branched decay is the decay of naturally occurring ^{40}K to stable ^{40}Ar and ^{40}Ca, the former by electron capture and the latter by β- emission (negatron emission). Electron capture decay to ^{40}Ar is favored by 11.2 % of ^{40}K atoms and beta decay to ^{40}Ca is favored by 88.8 %. Accordingly, the decay constants for each branching decay, $\lambda_{K,Ar}$ and $\lambda_{K,Ca}$, are

$$\lambda_{K,Ar} = 0.581 \times 10^{-10} \; yr^{-1}$$
$$\lambda_{K,Ca} = 4.962 \times 10^{-10} \; yr^{-1}$$

(3.12)

and the total decay constant, $\lambda_{K,total} = \lambda_{K,Ar} + \lambda_{K,Ca}$, is 5.543×10^{-10} y^{-1}, corresponding to a half-life of 1.250 Gy. Referring back to Eq. 3.11, we find that the total number of ^{40}Ar atoms in a system with ^{40}K is given by

$$^{40}Ar = {}^{40}Ar^o + (\lambda_{K,Ar} / \lambda_{K,total})^{40}K(e^{\lambda_{K,total}t} - 1)$$

(3.13)

where ^{40}Ar^o is the initial number of ^{40}Ar atoms present prior to the decay of ^{40}K. Both the ^{40}K-^{40}Ar and ^{40}K-^{40}Ca isotopic systems have geologic applications. The K-Ar system, in particular, has been used extensively as a geochronometer.

3.3 Decay series
3.3.1 $N_1 \rightarrow N_2 \rightarrow N_3$

In Section 3.1, we discussed the decay of a nuclide N_1 to a stable daughter product N_2. We now discuss the case in which N_2 decays to N_3. The decay rates of N_1 and N_2 are given by

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

(3.14)

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

(3.15)

where λ_1 and λ_2 are the decay constants of N_1 and N_2, respectively. Substituting Eq. 3.2 into 3.15 and rearranging yields

$$\frac{dN_2}{dt} + \lambda_2 N_2 - \lambda_1 N_1^o e^{-\lambda_1 t} = 0$$

(3.16)

The solution to Eq. 3.16 is

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^o (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^o e^{-\lambda_2 t}$$

(3.17)

and can be verified by substitution into Eq. 3.16. In Eq. 3.17, the first term on the right reflects the production of N_2 by decay of N_1 and the loss of N_2 by decay. The second term on the right represents the contribution from any initial N_2 in the system. Note that if λ_2 is zero, that is, N_2 is a stable nuclide, then Eq. 3.17 is equivalent to Eq. 3.3.

Secular equilibrium in a decay chain

Figure 1. Secular Equilibrium.
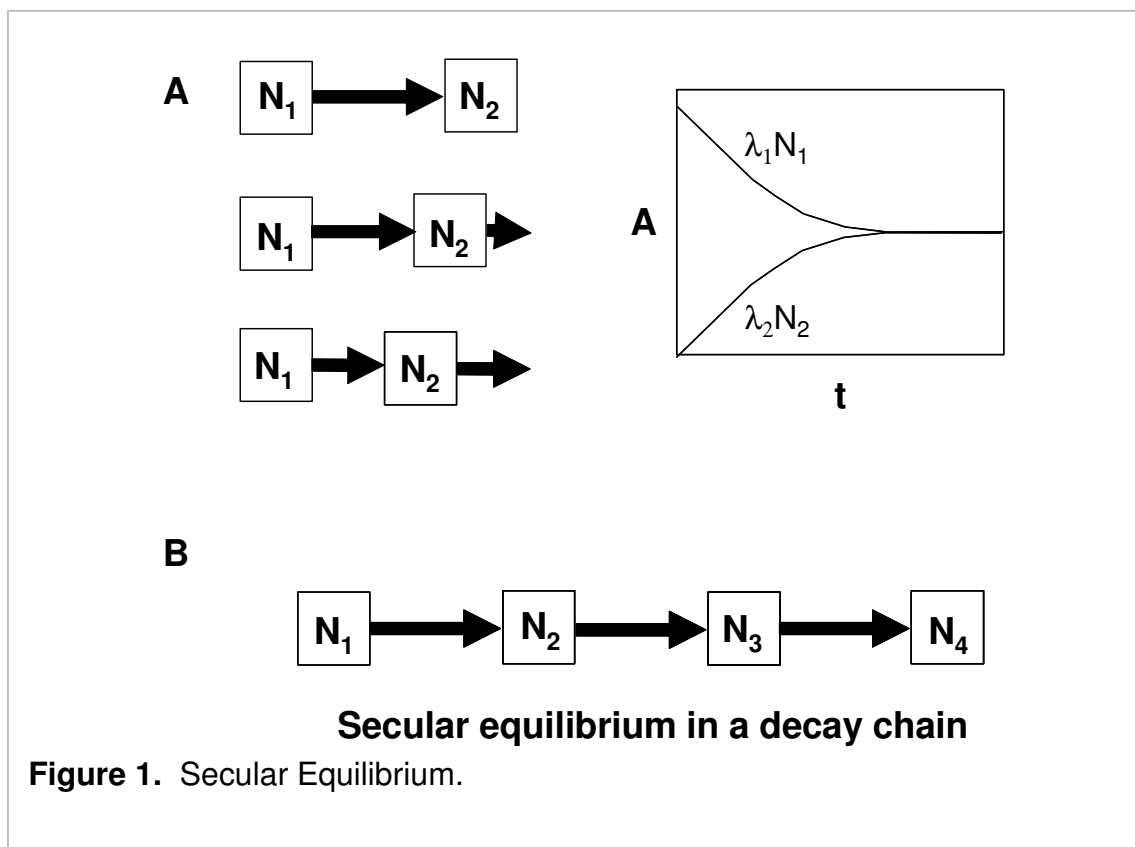
A better understanding of Eq. 3.17 can be had if we look at some examples. For example, let us assume that $\lambda_1 \ll \lambda_2$, that is, N_1 decays much slower than N_2. It follows that for long times the quantity $e^{-\lambda_1 t}$ is much larger than $e^{-\lambda_2 t}$, and therefore Eq. 3.17 simplifies approximately to

$$N_2 \sim \frac{\lambda_1}{\lambda_2} N_1^o e^{-\lambda_1 t} = \lambda_1 N_1 \tag{3.18}$$

or in other words

$$\lambda_1 N_1 = \lambda_2 N_2 \tag{3.19}$$

which essentially means that the activities (or decay rate) of N_1 and N_2 are equal. This asymptotic state is called **secular equilibrium** and is illustrated schematically in Figure X. Secular equilibrium is another way of saying a system has reached steady-state, that is, there is no longer a change in the decay rates of each nuclide. For example, let N_2 represent the number of people in a restaurant. At 5 PM, the restaurant doors open. Initially, there are no people in the restaurant, but immediately after 5 PM, there is a steady stream of people entering the restaurant. Assuming each person finishes eating and leaves the restaurant in about 45 minutes, we would see that initially the number of people in the restaurant would increase, but after a while, a maximum number will be reached as people start to exit. At this point, the amount of people leaving the restaurant equals the amount entering. This situation is called steady state and is a form of secular equilibrium. At *secular equilibrium*, it can be shown that the stable daughter nuclide (in this case, N_3) increases as

$$N_3 = N_1^o \left(1 - e^{-\lambda_1 t}\right) \tag{3.20}$$

from which it can be seen that the growth of N_3 depends only on the decay constant of N_1. We leave the proof of Eq. 3.20 as an exercise for the student.

Another scenario of Eq. 3.16 is when N_1 decays only slightly slower than N_2, e.g. $\lambda_1 < \lambda_2$. In this case, we can combine Eq. 3.2 and Eq. 3.17 for the case in which there is no initial nuclide of N_2. We thus have

$$\frac{\lambda_2 N_2}{\lambda_1 N_1} = \frac{\lambda_2}{\lambda_2 - \lambda_1}(1 - e^{-(\lambda_2 - \lambda_1)t}) \tag{3.21}$$

For long times, the exponential term goes to zero such that the ratio of the activities of N_2 and N_1 approaches a limiting constant, that is,

$$\frac{A_2}{A_1} = \frac{\lambda_2 N_2}{\lambda_1 N_1} \rightarrow \frac{\lambda_2}{\lambda_2 - \lambda_1} \tag{3.22}$$

This situation is known as **transient equilibrium**.

Another situation is when $\lambda_1 > \lambda_2$, where N_1 decays faster than N_2. For long times, the contribution from N_1 becomes insignificant and the abundance of N_2 rises to a maximum and decays with its characteristic decay constant. For the case in which there is no initial N_2, Eq. 3.17 simplifies to

$$N_2 \sim \frac{\lambda_1}{\lambda_1 - \lambda_2} N_1^o e^{-\lambda_2 t} \tag{3.23}$$

3.3.2 Generalized decay series

We now treat the more general case where a decay series is composed of n-chains. For each nuclide i in a decay series, the following general equation must hold

$$\frac{dN_i}{dt} = \lambda_{i-1} N_{i-1} - \lambda_i N_i \tag{3.24}$$

The general solution for the case of N_1^o atoms of N_1 with no other nuclides initially present is given by

$$A_n = \lambda_n N_n = N_1^o \sum_{i=1}^{n} c_i e^{-\lambda_i t}$$

$$= N_1^o \left(c_1 e^{-\lambda_1 t} + c_2 e^{-\lambda_2 t} \ldots + c_n e^{-\lambda_n t} \right) \tag{3.25}$$

where

$$c_m = \frac{\prod_{i=1}^{n} \lambda_i}{\prod_{i=1}^{n}{}'(\lambda_i - \lambda_m)}$$

$$= \frac{\lambda_1 \lambda_2 \cdots \lambda_n}{(\lambda_1 - \lambda_m)(\lambda_2 - \lambda_m)\cdots(\lambda_n - \lambda_m)} \tag{3.26}$$

where the prime on the lower product indicates that the $i=m$ term is omitted. Secular equilibrium in an n-series decay chain is given by $\lambda_1 N_1 = \lambda_n N_n$. Some examples of long decay series include ^{238}U, ^{235}U, and ^{232}Th, which decay to ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively, through a series of intermediary decay products. For example, Fig. 2 shows

Figure 2. The ^{238}U decay chain.
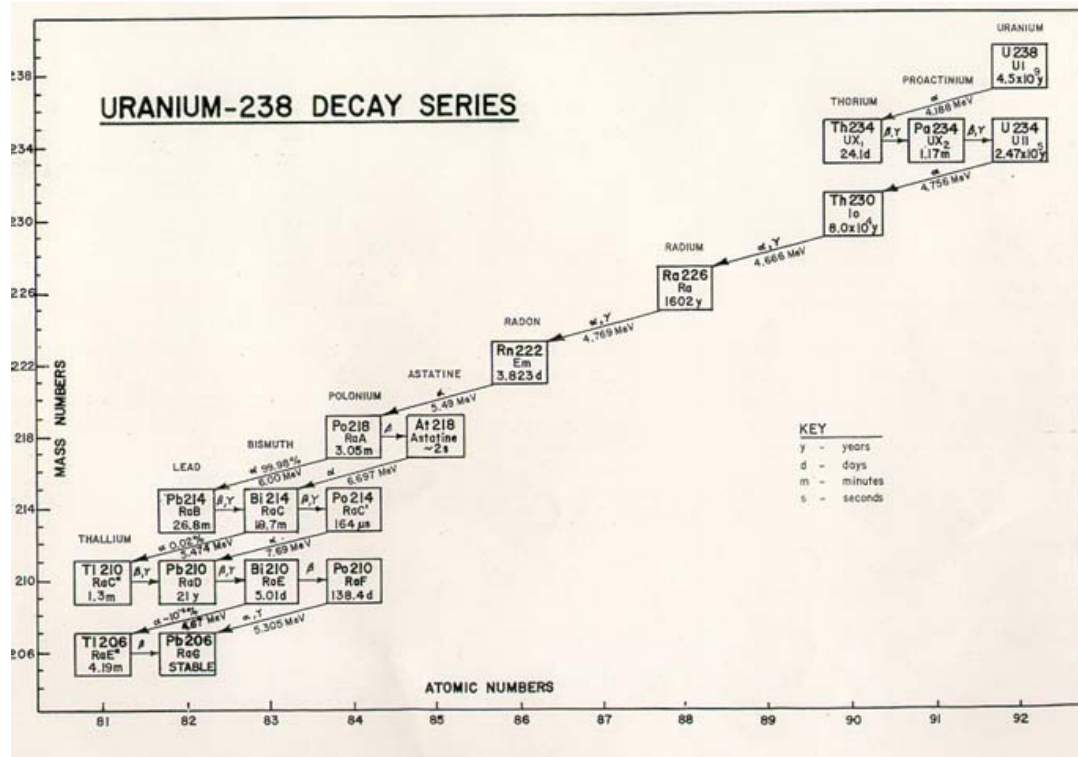
the decay series for ^{238}U. For long times, the entire decay of ^{238}U to ^{206}Pb is controlled by the first alpha decay of ^{238}U to ^{234}Th, which is 4.5 Gy.

3.4 Production of radioactivity

We now treat the situation in which a radioactive nuclide is being externally produced and decaying at the same time. If we denote the rate at which the radionuclide N_1 is being produced as R (atoms per unit time) and if we assume that R is constant, then the rate at which N_1 changes is given by

$$\frac{dN_1}{dt} = R - \lambda_1 N_1 \tag{3.27}$$

The solution to Eq. 3.27 for the case of no initial N_1 is

$$N_1 = \frac{R}{\lambda_1}\left(1 - e^{-\lambda_1 t}\right) \tag{3.28}$$

and the activity of N_1 at any given time is

$$A_1 = \lambda_1 N_1 = R\left(1 - e^{-\lambda_1 t}\right) \tag{3.29}$$

For small times, the exponential can be approximated by its expansion (e.g., $e^x = 1 + x + \frac{1}{2}x^2 + \cdots$) so that Eq. 3.29 simplifies to

$$A_1 = \lambda_1 N_1 = R\lambda_1 t \tag{3.30}$$

which states that the activity of N_1 increases with time at a constant rate. For long times, the exponential term goes to zero, and a state of secular equilibrium is reached:

$$A_1 = \lambda_1 N_1 = R \tag{3.31}$$

Eq. 3.31 essentially states that for long times, the production rate equals the decay rate, and therefore the activity of N_1 becomes constant.

The production of radioactivity occurs in a number of situations. A man-made example is the production of radioactive nuclides by neutron bombardment of target nuclei in a nuclear reactor or in an accelerator. In such a case, the production rate of a radionuclide is

$$R = N_o \sigma I \tag{3.32}$$

where N_o is the number of target nuclei, I is the neutron flux (number of incident neutrons per unit area) and σ is called the cross-section (cm^2), which represents the probability of neutron capture by the target nuclei. Because the number of target nuclei N_o must decrease for every radionuclide N_1 produced, the production rate R must decrease. However, because the probability of neutron capture is so small R can generally be considered constant.

An example from nature is the production of radioactive nuclides by the bombardment of stable nuclides by secondary cosmic ray neutrons. In the Earth's atmosphere, cosmic ray bombardment of oxygen, nitrogen, and argon ("spallation reactions") can lead to the formation of such radionuclides as ^3H, ^{10}Be, ^{14}C, ^{26}Al, ^{32}Si, ^{36}Cl, ^{29}Ar and ^{81}Kr. The example of ^{14}C is discussed below.

3.4.1 Application: Cosmogenic ^{14}C dating

An example of a cosmogenic radionuclide is ^{14}C. Carbon-14 is produced by the reaction of cosmic-ray neutrons with the nucleus of stable ^{14}N

$$^1_0 n + {}^{14}_7 N \rightarrow {}^{14}_6 C + {}^1_1 H \tag{3.32}$$

The neutrons are created by reactions between cosmic rays (dominated by protons) and atmospheric gases. At the same time as ^{14}C is being produced it is also decaying by emission of a negative beta particle ($t_{0.5} = 5730 \pm 40$ y):

$$^{14}_6 C \rightarrow {}^{14}_7 N + \beta^- + \bar{\nu} + 0.156 \; MeV \tag{3.33}$$

An equilibrium abundance of ^{14}C (in the form of $^{14}CO_2$) is therefore attained in the atmosphere due to its simultaneous production and decay.

The search for measurable amounts of ^{14}C in the atmosphere and in living matter was pioneered by W. F. Libby at the University of Chicago. Libby demonstrated that the activity of ^{14}C in the atmosphere was nearly constant throughout all latitudes. He and co-workers then showed that ^{14}C could be used to date the time of death of organic matter, and for this pioneering work, Libby received the Noble Prize for chemistry in 1960. The use of ^{14}C to date organic material is known as "radiocarbon dating" and is based on the following assumptions. Because of the rapid mixing times of the atmosphere, the $^{14}C/^{12}C$ concentration in the atmosphere is nearly homogeneous. The activity of ^{14}C in living plants is maintained at a constant level because plants are constantly exchanging CO_2 with the atmosphere, which itself has attained steady state levels of $^{14}CO_2$. However, when a plant dies, it ceases to exchange with the atmosphere. As a result, the activity of ^{14}C in a dead plant begins to decay because no new ^{14}C is being replenished in the dead

plant. The age of decayed matter, that is, the elapsed time since such matter was alive, is determined by the exponential decay law

$$A = A_o e^{-\lambda t} \tag{3.34}$$

where A is the present activity of ^{14}C and A_o was the original ^{14}C activity when the plant was alive. A very important assumption in Eq. 3.34 is that the current activity of ^{14}C in living matter has been constant through time and does not depend on geography or elevation. While short atmospheric circulation times render the second assumption mostly valid, the assumption that the ^{14}C activity of the atmosphere has not changed in the past is not generally valid. This is because it is likely that the cosmic ray flux to Earth has changed due to changes in the source of cosmic rays and to changes in the magnetic field of the Earth, which ultimately guide the incoming charged particles in cosmic rays. While the source of cosmic rays is not known exactly, it is likely that a large component originates from the sun because variations in the cosmic ray flux appear to correlate with solar flares. In order to account for these variations, geologists have attempted to calibrate the ^{14}C timescale with tree-ring data (which takes us back 6000 years) and with U-Th series data on corals (which takes us back 10,000 years). Radiocarbon ages therefore need to be corrected to account for changes in the ^{14}C content of the atmosphere. We will discuss the assumptions of ^{14}C-dating in more detail later.

3.5 Geochronology

From the above discussions, it is easy to see how Eq. 3.2 or 3.3 can be rearranged so that one can obtain the elapsed time over which a nuclide has decayed. Provided one knows the amount of initial radionuclide, the present amount of radionuclide and the decay constant, calculating the elapsed time is trivial. This concept is illustrated qualitatively by using an hour glass as an example. Assuming we know the rate at which sand falls through the neck of an hour glass, we could always determine the time at which the hourglass clock started ticking if we know the initial amount of sand in the upper vessel and the current amount remaining in the upper vessel. Similarly, if we knew the initial amount of sand in the lower vessel and the current amount in the upper and lower vessels, we could also derive the elapsed time. However, if we want to apply this to the general case of dating geologic materials, knowing the initial amount of radionuclide or daughter product is not trivial.

To see how we can apply Eq. 3.3 to dating rocks, let us explore the Sm-Nd isotopic system (Sm = Samarium; Nd = Neodymium) in which ^{147}Sm alpha decays to ^{143}Nd with a half life of 106 Gy (λ=6.54 x 10^{-12} / yr). Eq. 3.3 is expressed as follows

$$^{147}Sm(e^{\lambda t}-1)+^{143}Nd_o=^{143}Nd \tag{3.35}$$

Eq. 3.35 is not particularly useful to geologists as most geologists measure isotope ratios on mass spectrometers rather than the absolute number of atoms. For this reason, we will modify Eq. 3.35 so that it can be expressed in terms of isotope ratios. Let us use another isotope ^{144}Nd, which is stable and has no radioactive parent (meaning that its total abundance in the solar system has remained constant), to normalize Eq. 3.35. This yields

$$\frac{^{147}Sm}{^{144}Nd}(e^{\lambda t}-1)+\frac{^{143}Nd_o}{^{144}Nd_o}=\frac{^{143}Nd}{^{144}Nd} \tag{3.36}$$
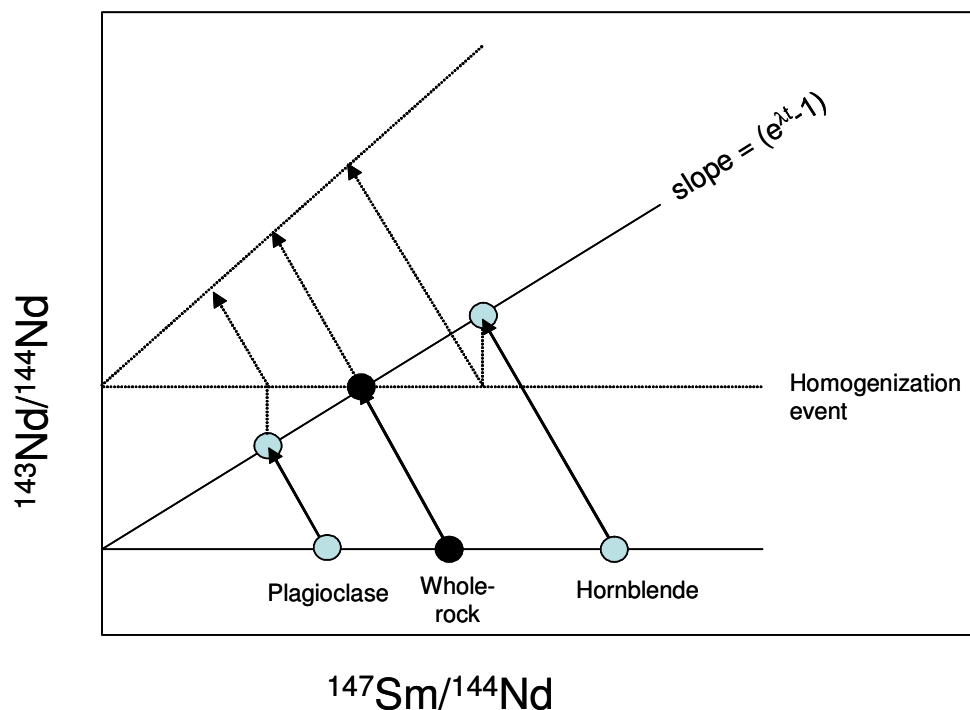
Figure 3. Plot of $^{143}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ that illustrates the concept of an isochron. The concept of homogenization.

The geochemist can measure $\frac{^{147}Sm}{^{144}Nd}$ and $\frac{^{143}Nd}{^{144}Nd}$ ratios very precisely in the laboratory, and the decay constant λ is known from experiments. We are thus left with two unknowns, the age (e.g., the time elapsed since ^{147}Sm started decaying) and the initial Nd isotopic composition, $\frac{^{143}Nd_o}{^{144}Nd_o}$, but we have only one equation!

Before going further, we must define what we mean by the "age of a rock". In most cases, when geologists say, "the age of a rock is 60 My", what they mean is the time at which that rock was last isotopically homogenized amongst its constituent mineral phases. Let's take granite for example. Granite is composed of several minerals: quartz, alkali feldspar, plagioclase, and mica. Each one of these minerals are likely to have different Sm/Nd ratios because the preference for these elements is not identical in every mineral. Thus, if each mineral behaved as a closed system, their time-integrated Nd isotopic compositions would all be different. It turns out, however, that atoms have a tendency to diffuse along concentration or free energy gradients, such that there is a tendency to want to homogenize the Nd isotopes. At low temperatures the diffusion kinetics are extremely sluggish so for all intents and purposes each mineral can be considered separately as a closed system. At high temperatures, however, diffusion kinetics are more rapid and the minerals behave as open systems, thereby homogenizing their isotopic signatures. The temperature window through which minerals pass from open to closed systems is termed the **closure temperature**. The radiometric age of the

granite therefore represents the time at which it passed through its closure temperature, that is, the time at which the granitic pluton crystallized. It is at this point that the "clock" starts ticking. More generally, the age of a rock refers to the time when the constituent minerals were last homogenized. For sedimentary rocks, this could represent the time of diagenesis.

We now return to Eq. 3.36 and apply it to the granite example. Let us pick mineral phases with different parent-daughter ratios, e.g. different $[^{147}Sm/^{144}Nd]$ ratios. Depending on the degree to which Sm and Nd are partitioned into a particular mineral, two different minerals are likely to have different parent daughter ratios. Those with high parent-daughter element ratios will generate, by radioactive decay, more daughter products for a given interval of time than those minerals with low parent-daughter ratios. Those without any parent element will retain the initial daughter isotopic composition indefinitely. Thus, if we assume that all the minerals in a system began with the same initial daughter isotopic composition, e.g. $[^{143}Nd/^{144}Nd]_o$, we will find that with time, every different mineral in a plot of $[^{143}Nd/^{144}Nd]$ versus $[^{147}Sm^{44}Nd]$ will fall on a straight line having a slope of

$$m = (e^{\lambda t} - 1) \tag{3.37}$$

The y-intercept (e.g., where $[^{147}Sm^{44}Nd]=0$) would correspond to the initial Nd isotopic composition $[^{143}Nd/^{144}Nd]_o$ of the system and all the minerals. The structures of Eqs. 3.36 and 3.37 show that the tieline connecting all of the mineral points in such a plot will rotate counter-clockwise with age. At zero age, i.e. the time at which the "clock" started ticking, the tieline has a slope of zero. At any other time, the age of the rock can be trivially obtained from the slope of the line

$$t = \frac{1}{\lambda} \ln(m+1) \tag{3.38}$$

where m is the slope.

Problem Set

1. Calculate the binding energy per nucleon for ^{6}Li, ^{31}P, ^{108}Pd, ^{195}Pt, and ^{238}U from a) the masses given in Appendix Table 1, and b) from the semi-empirical binding-energy equation.

2. Define alpha, beta (negatron and positron) electron capture decay. Without consulting the chart of nuclides, specify Z, N, and A for the daughters of the following radionuclides which decay by positron or electron capture decay: $^{22}_{11}Na$ and $^{88}_{39}Y$. Do the same for $^{14}_{6}C$ and $^{87}_{37}Rb$ which decay by negatron emission, and for $^{147}_{62}Sm$ and $^{234}_{92}U$ which decay by alpha emission.

3. What is fission decay? For ^{238}U, estimate the energy available for a) alpha decay and b) spontaneous fission into equal fragments.

4. Osmium is made up of 7 isotopes (184, 186, 187, 188, 189, 190, and 192). Based on mass spectrometry measurements, a sample of Os is found to have the following isotopic ratios ^{186}Os/^{188}Os = 0.11996, ^{187}Os/^{188}Os = 0.17444, ^{189}Os/^{188}Os = 1.21966, ^{190}Os/^{188}Os = 1.98389, and ^{192}Os/^{188}Os = 3.08261 (assume ^{184}Os/^{188}Os is almost negligible). Calculate the atomic weight of Os. Note that ^{187}Os is the radiogenic daughter product of ^{187}Re by β- decay and ^{186}Os is the daughter product of ^{190}Pt by α decay. The half-life of ^{187}Re is ~43 Gy and therefore the relative abundance of ^{187}Os varies in nature. The half-life of ^{190}Pt is so long (650 Gy) that only under certain circumstances can variations in ^{186}Os be measured.

5. (Faure 11.1) Given that the atomic abundances of Pb isotopes relative to ^{206}Pb are stated as ^{204}Pb = 0.143, ^{206}Pb = 1.00, ^{207}Pb = 12.95, ^{208}Pb = 21.96, recalculate their abundances in terms of atom percent and determine the atomic weight of this sample of Pb. The masses of the isotopes in amu are ^{204}Pb = 203.9730, ^{206}Pb = 205.9744, ^{207}Pb = 206.9759, and ^{208}Pb = 207.9766. Answer (207.55).

6. The rate at which a radioactive nuclide decays is linearly proportional to the amount of radioactive nuclides present, e.g.

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \tag{1}$$

This equation is trivially derived from the following equation

$$\frac{dN_1}{N_1} = -\lambda_1 dt \tag{2}$$

Explain in words what Eq. 2 implies. Do so by first explaining what the left-hand side of Eq. 2 means. Then explain what the decay constant means. Explain why the decay constant does not vary with the number of radioactive nuclides present. Can you think of any other situation in physics, biology, ecology, etc., which can be described by a first-order differential equation.

7. **Pb-Pb isochrons.** U has two radioactive isotopes, ^{238}U and ^{235}U. The natural ^{238}U/^{235}U ratio today is 137.88. The decay of ^{238}U to ^{206}Pb can be expressed as:

$$\left(\frac{^{206}Pb}{^{204}Pb}\right)=\left(\frac{^{206}Pb}{^{204}Pb}\right)_0+\left(\frac{^{238}U}{^{204}Pb}\right)\left[e^{\lambda_{238U}t}-1\right]$$

- Write down what each term means.
- Write down an equivalent expression for the radiogenic ingrowth of ^{207}Pb.
- The decay constants of the U isotopes are: $\lambda_{238U} = 1.55125\times10^{-10}$ /y and $\lambda_{235U} = 9.8485\times10^{-10}$ /y. What are the half-lives of ^{238}U and ^{235}U in Gy?
- On a ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb diagram, plot the growth of radiogenic Pb for the following values of ^{238}U/^{204}Pb = 5, 10, 15. Contour the growth curves according to age (1, 2, 3, 4, and 4.55 Gy); these contours are known as Pb-Pb isochrons. Assume that the initial Pb isotopic composition is ^{206}Pb/^{204}Pb = 9.3066 and ^{207}Pb/^{204}Pb = 10.293.
- Write down a mathematical expression showing how one can determine the age from the slope of the Pb-Pb isochron.
- What is the advantage of dating rocks by the Pb-Pb isochron method compared to a standard single parent-single daughter isochron method? How was the age of the Earth inferred using the Pb-Pb isochron?

8. **Calibration of the Lu-Hf clock.** ^{176}Lu decays to ^{176}Hf by emission of a β- particle. Lu and Hf are fractionated from each other during various magmatic and metamorphic processes that occur in the silicate Earth. The Lu-Hf isotopic system has proven to be a powerful tool in constraining the rates and extent of continental crust extraction from the mantle, and in constraining the source of sediment and wind-blown dust in pelagic sediments. Recently, there have been attempts to date rocks or meteorites by the Lu-Hf isotopic system. Accurate application of a radiometric clock requires that we know the decay constant accurately. Up until recently, there was a 4% error in the decay constant. The first widely used decay constant was $1.94\pm0.07\times10^{-11}$ /y, which was determined from the slope of a Lu-Hf isochron of a meteorite of known age. This number was then updated after the decay constant was determined directly by beta counting ($1.86\pm0.01\times10^{-11}$ /y). In 2001, Scherer et al. (Science 293:683-687) determined the decay constant to much higher precision using the slope of Lu-Hf isochrons in rocks whose ages are well constrained by the U-Pb clock for which the decay constants are known much more precisely and accurately. We will use their data as an exercise in error propagation.

- Express the age of a rock in terms of the slope of the ^{176}Hf/^{177}Hf – ^{176}Lu/^{177}Hf isochron and the ^{176}Lu decay constant. Show that the age can be expressed as t = [ln(m+1)]/λ, where m is the slope.
- Using principles of error propagation in the lecture notes, show that a 4% error on the decay constant is equal to a 4% error on the calculated age assuming that the slope of the isochron has zero error. In other words, show that $\dfrac{dt}{t}=\dfrac{d\lambda}{\lambda}$.

- Scherer et al. report the following measurements on a baddeleyite and apatite grain in the Phalaborwa carbonatite:
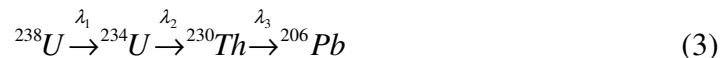
	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$
Baddeleyite	0.00000467(1)	0.281193(14)
Apatite	2.125(4)	0.364150(22)

where the numbers in parentheses represent in the last one ($^{176}Lu/^{177}Hf$) or two digits ($^{176}Hf/^{177}Hf$). Calculate the slope of this two-point isochron. Using error propagation principles and the reported errors on the measurements, estimate the error on the slope. Illustrate the data and your results graphically.

- Rewrite the expression relating the slope of the isochron to the decay constant and age of the isochron. The age of the Phalaborwa carbonatite is 2059.9±3.4 Ma as determined independently from the U-Pb systematics of baddeleyite and apatite grains. Calculate the ^{176}Lu decay constant using this information and the measured slope determined above. Using the estimated error on the above slope and the error on U-Pb age, calculate the error on your decay constant by first writing an expression relating the error on the decay constant to the errors in the slope and U-Pb age. Show that this is within error of the ^{176}Lu decay constant determined directly from beta counting.

- It is clear now that the ^{176}Lu decay constant you calculated above is pinned to the U-Pb age. What is the fundamental assumption involved in this approach? (Hint: think about the concept of closure temperature). Comment on the validity of this assumption.

9. **Short-lived radionuclides**: The ^{238}U decay scheme can be expressed as follows

$$N_1 \xrightarrow{\lambda_1} N_2 \xrightarrow{\lambda_2} N_3 \xrightarrow{\lambda_3} N_4,$$ or explicitly as

$$^{238}U \xrightarrow{\lambda_1} {}^{234}U \xrightarrow{\lambda_2} {}^{230}Th \xrightarrow{\lambda_3} {}^{206}Pb \qquad (3)$$

where the half lives are:

$$^{238}U \quad t_{1/2} = 4.47 \text{ Gy}$$
$$^{234}U \quad t_{1/2} = 245 \text{ ky}$$
$$^{230}Th \quad t_{1/2} = 75.4 \text{ ky}$$

If we denote ^{238}U as N_1, ^{234}U as N_2, and ^{230Th} as N_3, the rates of decay of N_1, N_2, and N_3 are given by

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

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \qquad (4)$$

$$\frac{dN_3}{dt} = \lambda_2 N_2 - \lambda_3 N_3$$

In this problem, we will investigate how the U-Th decay series can be used to put constraints on the timing of magmatic processes that fractionated U from Th. Let's take the case where a magmatic fluid is generated in the mantle. U is preferentially

incorporated into the fluid relative to Th, and the solid residue becomes depleted in U relative to Th.

- We can assume that ^{238}U and ^{234}U are always in secular equilibrium. This means that $dN_2/dt = 0$. Show that the condition of secular equilibrium for ^{238}U and ^{234}U requires that

$$\lambda_1 N_1 = \lambda_2 N_2 \qquad (5)$$

or in other words, the activities of N_1 and N_3 are equal. Explain what the term 'activity' means, and explain why ^{238}U and ^{234}U are always in secular equilibrium for the case of magma genesis.

- At the point of melting, ^{230}Th and ^{238}U cannot be in secular equilibrium because the two elements are fractionated in a very short time compared to their radioactive decay rates.

- Write out an expression for N_1 as a function of N_1^o, λ_1, and t.

- Plug your answer from the preceding bullet into Eq. 4. The solution to Eq. 4 should be of the following form:

$$N_3 = ae^{-\lambda_1 t} + be^{-\lambda_3 t} \qquad (6)$$

where a and b are constants. Show that the constants are

$$a = -b = \frac{\lambda_1 N_1^o}{\lambda_3 - \lambda_1} \qquad (7)$$

In order to do so, assume that $N_3(0) = 0$ and substitute Eq. 6 into Eq. 5.

- Next, show that for the case of no initial N_3, Eq. 6 can be expressed as

$$N_3 = \frac{\lambda_1 N_1^o}{\lambda_3 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_3 t}\right) \qquad (8)$$

- If we also account for the possibility of an initial amount of N_3, show that Eq. 8 becomes

$$N_3 = \frac{\lambda_1 N_1^o}{\lambda_3 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_3 t}\right) + N_3^o e^{-\lambda_3 t} \qquad (9)$$

- Write down the full expressions for the activities of N_1 and N_3. Denoting the activity of N_1 and N_3 as (N_1) and (N_3), verify the following relationship

$$\frac{(N_3)}{(N_1)} = \frac{\lambda_3}{\lambda_3 - \lambda_1} + e^{-(\lambda_3 - \lambda_1)t}\left[\frac{(N_3)^o}{(N_1)^o} - \frac{\lambda_3}{\lambda_3 - \lambda_1}\right] \qquad (10)$$

- The decay constant of ^{238}U is much smaller than that of ^{230}Th. This means that the ^{238}U can be considered to be constant over the lifespan of the decay of ^{230}Th. Assuming, then, that $\lambda_{238U} \ll \lambda_{230Th}$ or $\lambda_1 \ll \lambda_3$, show that Eq. 10 simplifies to the following:

$$\left(^{230}Th\right) = \left(^{230}Th\right)^o e^{-\lambda_{230Th} t} + \left(^{238}U\right)\left[1 - e^{-\lambda_{230Th} t}\right] \qquad (11)$$

where the symbols in parentheses represent activities.

- Since geochemists measure isotope ratios much better than absolute quantities, Eq. 11 can be re-expressed by dividing by the activity of ^{232}Th (^{232}Th), where the half-life of ^{232}Th is 14.1 Gy. Eq. 11 then becomes

$$\frac{\left(^{230}Th\right)}{\left(^{232}Th\right)} = \frac{\left(^{230}Th\right)^o}{\left(^{232}Th\right)^o} e^{-\lambda_{230Th}t} + \frac{\left(^{238}U\right)}{\left(^{232}Th\right)}\left[1 - e^{-\lambda_{230Th}t}\right] \tag{12}$$

What is (^{230}Th/^{232}Th) when $t=0$? When t is infinite? Eq. 12 is essentially an isochron plot in (^{230}Th/^{232}Th) versus (^{238}U/^{232}Th) space, where the slope of the line is given by $[1-e^{-(\lambda 230Th)t}]$.

- Assume that just prior to melting, the magma source region is in secular equilibrium with respect to U and Th. Assume also that the initial (^{230}Th/^{232}Th)^o activity ratio is also equal to 1. At the point of melting, the ^{238}U/^{232}Th ratio is fractionated but not the ^{230}Th/^{232}Th ratio. On a plot of (^{230}Th/^{232}Th) versus (^{238}U/^{232}Th) draw a set of isochrones for t= 20, 80, 150, and 350 kyrs. Compare with Figure 2 of Hawkesworth et al. (U-Th isotopes in arc magmas: implications for element transfer from the subducted crust; Science, v. 276, 551-555, 1997). Explain how we can use the U-Th series isochrones to estimate the time elapsed between magmatic eruption and magma generation. What are the assumptions involved in these calculations?

10. **Isotope mixing**: Write out a mass balance equation for the mixture of two components A and B having different Sr and Nd isotopic compositions: ^{87}Sr$_A$/^{86}Sr$_A$, ^{87}Sr$_B$/^{86}Sr$_B$, ^{143}Nd$_A$/^{144}Nd$_A$, and ^{143}Nd$_B$/^{144}Nd$_B$. Using EXCEL, show a mixing diagram between components A and B by calculating the composition of mixtures at 10% increments of component A. Use the following information:

> Component A (e.g., continental crust)
> ^{87}Sr/^{86}Sr = 0.7110
> Sr = 300 ppm
> ^{143}Nd/^{144}Nd = 0.5124
> Nd = 5 ppm

> Component B (e.g., mid-ocean ridge basalt)
> ^{87}Sr/^{86}Sr = 0.7025
> Sr = 70 ppm
> ^{143}Nd/^{144}Nd = 0.5129
> Nd = 5 ppm

11. **Simple isotope mixing in a box: the ocean**: The Sr concentration in seawater is controlled by the inputs and outputs of Sr from the ocean. Inputs can come from rivers, hydrothermal alteration of oceanic crust and carbonate diagenesis. Outputs can occur through carbonate deposition. A mass balance equation for Sr concentration in the ocean can be written as:

$$\frac{dSr_{SW}}{dt} = \frac{dSr_{in}}{dt} - \frac{dSr_{out}}{dt} = \sum_{i=1} \frac{dSr_{in(i)}}{dt} - \sum_{j} \frac{dSr_{out(j)}}{dt} \tag{13}$$

It follows that the $^{87}Sr/^{86}Sr$ of seawater is also controlled by outputs and inputs. However, it can be shown that the rate of change in $^{87}Sr/^{86}Sr$ of seawater does not directly depend on the output flux of Sr, but depends only on the $^{87}Sr/^{86}Sr$ compositions of the inputs, the magnitude of Sr inputs, and the $^{87}Sr/^{86}Sr$ ratio of seawater. For times significantly less than the half-life of ^{87}Rb decay to ^{87}Sr, show that the rate of change in $^{87}Sr/^{86}Sr$ of seawater can be expressed as follows:

$$\frac{d\left(^{87}Sr/^{86}Sr\right)_{SW}}{dt} = \sum \frac{dSr_{(in)i}}{dt} \frac{\left(^{87}Sr/^{86}Sr_{in(i)} - ^{87}Sr/^{86}Sr_{SW}\right)}{Sr_{SW}} \tag{14}$$