

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

GEOCHRONOLOGY VI

U-DECAY SERIES DATING

Up to now, we have been discussing decay schemes that are based on measuring the amount of a stable daughter nuclide relative to the amount of the radioactive parent. Since the decay of the parent takes place at an invariant rate, this ratio of daughter to parent is proportional to time (in a closed system). In this lecture, we will discuss a method of dating in which both parent and daughter are radioactive. U-decay series dating differs in a very fundamental way from the conventional techniques we have been discussing. It does, however, share two features. First, the time we are measuring is the time since the system closed, and second, an accurate date requires the system to have remained closed.

Basic Principles

The fundamental principle involved in U decay series dating is that, in a closed system, the ratio of parent to daughter will tend toward an equilibrium state in which the rate of decay of the parent is equal to the rate of decay of the daughter. A closed system will approach this equilibrium state at a predictable rate with the ratio of the parent to daughter being proportional to time, provided equilibrium has not been reached. Once equilibrium has been achieved, the ratio of parent to daughter no longer depends on the time elapsed, and we can calculate only a minimum age*.

U and Th do not decay directly to Pb; rather the transition from U to Pb passes through many intermediate radioactive daughters (Figure 10.1). Most of these daughters have very short half-lives,

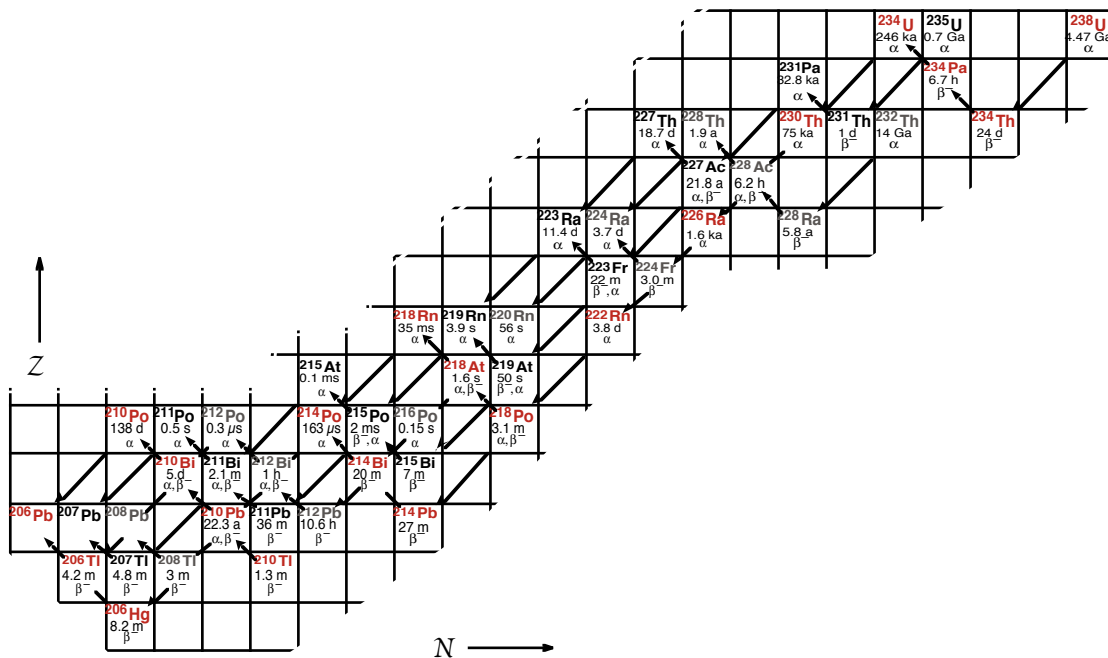


Figure 10.1. Part of the chart of the nuclides showing the series of decays that occur as ^{238}U , ^{235}U , and ^{232}Th are transformed to ^{206}Pb , ^{207}Pb , and ^{208}Pb respectively.

* In principle anyway, a system will approach equilibrium asymptotically, and will only achieve equilibrium after an infinite amount of time. In practice, an effective equilibrium is achieved when the difference between the measured ratio of parent to daughter is less than the analytical uncertainty of the measurement. This typically will occur after a

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

TABLE 10.1. Half-lives and decay constants of long-lived U and Th daughters

Nuclide	Half-life, yrs	Decay constant, yr ⁻¹	Parent
²³⁴ U	246,000	2.794 × 10 ⁻⁶	²³⁸ U
²³¹ Pa	32,480	2.134 × 10 ⁻⁵	²³⁵ U
²³⁰ Th	75,200	9.217 × 10 ⁻⁶	²³⁸ U
²²⁶ Ra	1,622	4.272 × 10 ⁻⁴	²³⁸ U
²²⁸ Ra	6.7	1.06 × 10 ⁻¹	²³² Th
²¹⁰ Pb	22.26	3.11 × 10 ⁻²	²³⁸ U

ranging from milliseconds to hours, and are of little use in study of the Earth. However, a number of these intermediate daughters have half-lives ranging from days to hundreds of thousands of years and do provide useful information about geological processes. Table 10.1 lists half-lives and decay constants of some of the most useful of these isotopes. As one might guess from the short half-lives, U-decay series isotopes are used to date

relatively recent events.

The half-lives of all of these daughters isotopes are short enough so that any atoms present when the Earth formed have long since decayed (to Pb). They exist in the Earth (and in all other bodies of the solar system) only because they are continually produced by the decay of U and Th. The abundance of such isotopes depends on the balance between its own radioactive decay and the rate at which it is produced by the decay of its parent:

$$\frac{dN_D}{dt} = \lambda_P N_P - \lambda_D N_D \quad 10.01$$

where subscripts P and D refer to parent and daughter respectively. This equation says simply that the rate of change of the abundance of the daughter isotope is equal to the rate of production less the rate of decay. This can be integrated to give:

$$N_D = \frac{\lambda_P}{\lambda_D - \lambda_P} N_P^o (e^{-\lambda_P t} - e^{-\lambda_D t}) + N_D^o e^{-\lambda_D t} \quad 10.02$$

Scientists dealing with the intermediate daughters of U and Th (it is the daughters of ²³⁸U that are of the most interest), generally work with *activities* rather than atomic abundances. By activity, we mean rate of decay, dN/dt , measured in disintegrations per unit time[†]. One reason for this is that the abundance of these isotopes was traditionally determined by detecting their decay. Today, abundances of the longer-lived nuclides can be measured by mass spectrometry, but the shorter-lived ones are so rare that they are still most readily detected by their decay. The other reason we work with activities will become apparent shortly. We will follow the standard convention of denoting activities by enclosing the isotope or isotope ratio in parentheses. Thus (²³⁰Th) denotes the activity of ²³⁰Th, and (²³⁰Th/²³⁸U) denotes the ratio of activities of ²³⁰Th and ²³⁸U. Activities are related to atomic (or molar) abundances by the basic equation of radioactive decay:

$$\frac{dN}{dt} = -\lambda N \quad (2.01)$$

Hence if we know the activity, the molar abundance can be calculated and visa versa.

The *radioactive equilibrium* state of the daughter and the parent is the condition where their *activities* are equal, i.e.:

maximum of 7-10 half-lives of the nuclide with the shortest half-life.

[†] The SI, and therefore official, unit of radioactivity is the *Becquerel* (abbreviated Beq), and is equal to 1 disintegration per second. An older and still used unit is the *Curie* (abbreviated Ci) equal to 3.7 × 10¹⁰ disintegrations per second. Because concentrations of these elements in nature are generally low, activity is often expressed in disintegrations per minute (dpm).

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

$$\frac{dN_D}{dt} = \frac{dN_P}{dt} \quad 10.03$$

This is the state that will be eventually achieved by any system if it is not perturbed (remains closed).

We can demonstrate that this is so in two ways. The first is a simple mathematical demonstration. The equilibrium state is the steady state where the abundance of the daughter does not change, i.e. where the left hand side of 10.1 is zero:

$$0 = \lambda_P N_P - \lambda_D N_D \quad 10.04$$

We substitute the dN/dt for the λN terms in 10.4, rearrange and we obtain 10.03; *QED*.

The second demonstration is a thought experiment. Imagine a hopper, a grain hopper for example, with an open top and a door in the bottom. The door is spring-loaded such that the more weight placed on the door, the wider it opens. Suppose we start dropping marbles into the hopper at a constant rate. The weight of marbles accumulating in the hopper will force the door open slightly and marbles will start falling out at a slow rate. Because the marbles are falling out more slowly than they are falling in, the number and weight of marbles in the hopper will continue to increase. As a result, the door will continue to open. At some point, the door will be open so wide that marbles are falling out as fast as they are falling in. This is the steady, or equilibrium, state. Marbles no longer accumulate in the hopper and hence the door is not forced to open any wider. The marbles falling into the door are like the decay of the parent isotope. The marbles in the hopper represent the population of daughter isotopes. Their decay is represented by their passing through the bottom door. Just as the number of marbles passing through the door depends on the number of marbles in the hopper, the activity (number of decays per unit time) of an isotope depends on the number of atoms present.

If the rate of marbles dropping into the hopper decreases for some reason, marbles will fall out of the hopper faster than they fall in. The number of marbles in the hopper will decrease, as a result the weight on the door decreases and it starts to close. It continues to close (as the number of marbles decreases) until the rate at which marbles fall out equals the rate at which marbles fall in. At that point, there is no longer a change in the number of marbles in the hopper and the position of the door stabilizes. Again equilibrium has been achieved, this time with fewer marbles in the hopper, but nevertheless at the point where the rate of marbles going in equals the rate of marbles going out. The analogy to radioactive decay is exact.

Thus when a system is disturbed by addition or loss of parent or daughter, it will ultimately return to equilibrium. The rate at which it returns to equilibrium is determined by the decay constants of the parent and daughter. If we know how far out of equilibrium the system was when it was disturbed, we can determine the amount of time which has passed since it was disturbed by measuring the present rate of decay of the parent and daughter.

²³⁴U-²³⁸U dating

An example of this is ²³⁴U-²³⁸U dating of sediments. As it turns out, (²³⁴U) and (²³⁸U) in seawater are not in equilibrium, i.e., the (²³⁴U/²³⁸U) ratio is not 1. It is uniform[†], however, with a ratio of about 1.14±0.03. The reason the ratio is higher than 1 is that ²³⁴U is preferentially leached from rocks because ²³⁴U is located in crystals of rocks in damaged lattice sites. It occupies the site of a ²³⁸U atom that has undergone α -decay. The α -particle and the recoil of the nucleus damage this site. Since it occupies a damaged site, it is more easily removed from the crystal by weathering than ²³⁸U. The oceans collect this 'leachate', hence they are enriched in ²³⁴U. When U precipitates from seawater into, for example, the calcium carbonate in a coral skeleton, it will initially have the same (²³⁴U/²³⁸U) as seawater, but ²³⁴U

[†] The ratio is uniform in space, but there is evidence to suggest it has varied slightly with time, particularly between glacial and interglacial periods.

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

will decay faster than it is created by decay of ^{238}U , so $(^{234}\text{U}/^{238}\text{U})$ will slowly return to the equilibrium condition where $(^{234}\text{U}/^{238}\text{U}) = 1$.

Let's see how we can take advantage of this to determine geologic time. We can divide the activity of ^{234}U in a sample into that which is supported by ^{238}U , i.e. that amount in radioactive equilibrium with ^{238}U and that amount which is excess, i.e. unsupported by ^{238}U :

$$(^{234}\text{U}) = (^{234}\text{U})_s + (^{234}\text{U})_u \quad 10.05$$

where we are using parentheses to denote activity and subscripts s and u denote *supported* and *unsupported* abundances respectively. The activity of the excess ^{234}U decreases with time according to equation 2.01, which we can rewrite as:

$$(^{234}\text{U})_u = (^{234}\text{U})_u^0 e^{-\lambda_{234}t} \quad 10.06$$

where the superscript naught denotes the initial activity (at time $t = 0$). We can also write:

$$(^{234}\text{U})_u^0 = (^{234}\text{U})^0 - (^{234}\text{U})_s \quad 10.07$$

which just says that the initial unsupported activity of ^{234}U is equal to the total initial activity of ^{234}U less the (initial) supported activity of ^{234}U . Since to a very good approximation the activity of the parent, ^{238}U , does not change over times on the order of the half-life of ^{234}U or even ten half-lives of ^{234}U , the present ^{238}U activity is equal to the activity at $t = 0$ (we make the usual assumption that the system is closed). And by definition the supported activity of ^{234}U is equal to the activity of ^{238}U , both now and at $t = 0$. Hence, 10.05 can be expressed as:

$$(^{234}\text{U}) = (^{238}\text{U}) + (^{234}\text{U})_u \quad 10.08$$

and 10.07 becomes

$$(^{234}\text{U})_u^0 = (^{234}\text{U})^0 - (^{238}\text{U}) \quad 10.09$$

Substituting 10.09 into 10.06 yields:

$$(^{234}\text{U})_u = [(^{234}\text{U})^0 - (^{238}\text{U})] e^{-\lambda_{234}t} \quad 10.10$$

Substituting 10.10 into 10.08, we have:

$$(^{234}\text{U}) = (^{238}\text{U}) + [(^{234}\text{U})^0 - (^{238}\text{U})] e^{-\lambda_{234}t} \quad 10.11$$

Just as for other isotope systems, it is generally most convenient to deal with ratios rather than absolute activities (among other things, this allows us to ignore detector efficiency provided the detector is equally efficient at all energies of interest[‡]), hence we divide by the activity of ^{238}U :

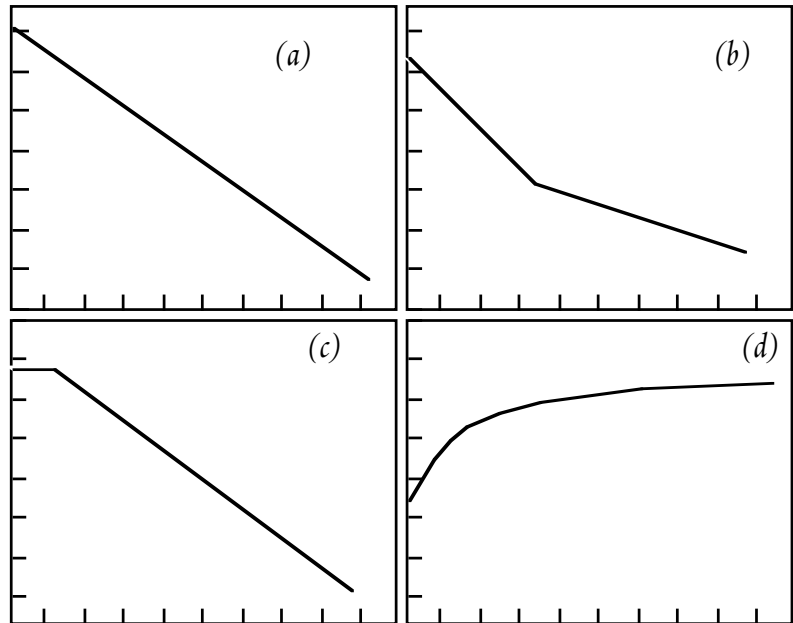


Figure 10.2. Hypothetical $(^{230}\text{Th}/^{232}\text{Th})$ as a function of depth in a core. (a) is normal, constant sedimentation rate, (b) reflects a change in sedimentation rate, (c) reflects bioturbation mixing the sediment at the top of the core, (d) is a case of dominance by U-supported ^{230}Th . From Faure (1986).

[‡] In the case of ^{238}U and ^{234}U the α energies are quite similar (4.2 and 4.7 MeV). Interestingly, the energies of α

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) = 1 + \left\{ \frac{(^{234}\text{U})^o - (^{238}\text{U})}{(^{238}\text{U})} \right\} e^{-\lambda_{234}t} \quad 10.12$$

or since $^{238}\text{U} = ^{238}\text{U}^o$:

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) = 1 + \left\{ \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)^o - 1 \right\} e^{-\lambda_{234}t} \quad 10.13$$

Thus the present activity ratio can be expressed in term of the initial activity ratio, the decay constant of ^{234}U , and time. For material such as a coral, in (isotopic) equilibrium with seawater at some time $t = 0$, we know the initial activity ratio was 1.14. Carbonates, for example, concentrate U. If we measure the $(^{234}\text{U}/^{238}\text{U})$ ratio of an ancient coral, and assume that the seawater in which that coral grew had a $(^{234}\text{U}/^{238}\text{U})$ the same as modern seawater (1.14), the age of the coral can be obtained by solving equation 10.13 for t . The age determined is the time since the material last reached isotopic equilibrium with seawater.

The application of $^{234}\text{U}/^{238}\text{U}$ has been largely restricted to corals. It is not generally useful for freshwater carbonates because of uncertainty in the initial activity ratio. Mollusk shells and pelagic biogenic carbonate (e.g., foraminiferal ooze) often take up U after initial deposition of the carbonate and death of the organism, thus violating our closed system assumption. The technique is typically useful up to about 4 times the half-life of ^{234}U when alpha spectrometry is the analytical method, but can be applied to longer times with mass spectrometry because of higher precision.

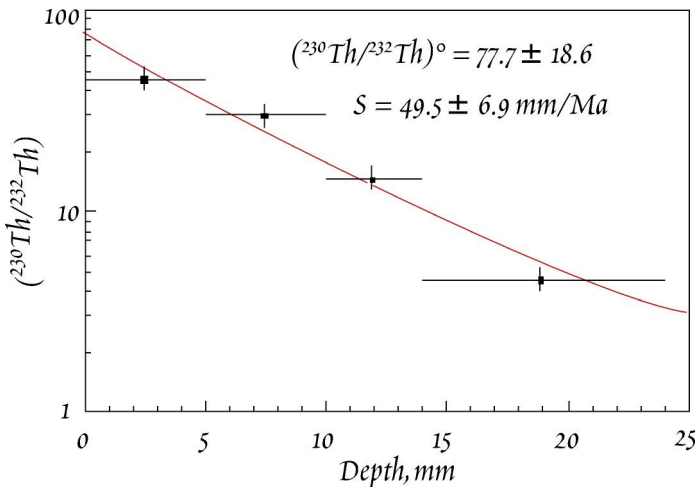


Figure 10.4. $^{230}\text{Th}/^{232}\text{Th}$ as a function in depth in a manganese nodule from MANOP Site H. After Huh and Ku (1984).

^{230}Th - ^{238}U Dating

The ^{244}U - ^{238}U technique does not have high temperature applications, because at high temperature, ^{234}U and ^{238}U do not fractionate as they do at low temperature. The reason is that radiation damage, which is the reason ^{234}U is removed in weathering more easily than ^{238}U , anneals quite rapidly at high temperature. Disequilibrium between ^{230}Th (the daughter of ^{234}U) and its U parents can, however, provide useful geochronological and geochemical information in both high- and low-temperature systems. We start with an equation analogous to equation 10.06:

$$(^{230}\text{Th})_u = (^{230}\text{Th})_u^o e^{-\lambda_{230}t} \quad 10.14$$

As is the usual practice, we normalize to a non-radiogenic isotope:

$$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)_u = \left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)_u^o e^{-\lambda_{230}t} \quad 10.15$$

(^{232}Th , although non-radiogenic, is radioactive, of course. However, with a half-life of 14Ga, its abundance will not change on time scales comparable to the half-life of ^{230}Th .)

particles are approximately inversely proportional to half-life. From our discussion of α decay, you should be able to surmise why.

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

In seawater, and in its oxidized state generally, U is quite soluble. Th, however, is quite insoluble: its seawater residence time is 300 years or less compared to about 500,000 year for U. (It should be noted here that solubility in seawater does not control concentrations or residence times. Nevertheless solubility is a good guide to both of these.) Once a ^{234}U atom decays to ^{230}Th , it is quickly absorbed onto particles that in turn are quickly incorporated into sediment. As a result, relatively high concentrations of unsupported ^{230}Th can be removed (by leaching) from some sediments (mainly relatively slowly accumulating ones). In cases where the amount of leached ^{234}U is negligible and where the $(^{230}\text{Th}/^{232}\text{Th})$ is known (from, for example, zero-age sediment at the seawater-sediment interface), equation 10.14 can be used to determine the age of the sediment. If we can't neglect ^{234}U then we can still determine the age by taking this into account, though the mathematics becomes more complex (see Dickin, 1995). The point is that by determining $^{230}\text{Th}/^{232}\text{Th}$ ratios in a series of sediments down a core, sedimentation rate can be determined. Various curves of $(^{230}\text{Th}/^{232}\text{Th})$ vs. depth suggest various processes, as is illustrated in Fig. 10.2.

In systems where we can assume $(^{234}\text{U}) = (^{238}\text{U})$, high-temperatures systems for example, the mathematics simplifies somewhat. With this assumption, we can treat the production of ^{230}Th as if it were the direct decay product of ^{238}U . We write an equation analogous to 10.5 and from it derive:

$$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right) = \left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)^0 e^{-\lambda_{230}t} + \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right)(1 - e^{-\lambda_{230}t}) \quad 10.16$$

(the tricks to this derivation are to make the approximations $\lambda_{230} - \lambda_{238} = \lambda_{230}$ and $e^{-\lambda_{238}t} = 1$; i.e., assume $\lambda_{238} \approx 0$; this is the mathematical equivalent of assuming the activity of ^{238}U does not change with time). The first term on the right describes the decay of unsupported ^{230}Th while the second term describes the growth of supported ^{230}Th . Note that this equation has the form of a straight line in $(^{230}\text{Th}/^{232}\text{Th}) - (^{238}\text{U}/^{232}\text{Th})$ space, where the first term is the intercept and $(1 - e^{-\lambda_{230}t})$ is the slope. This is illustrated in Figure 10.3.

Let's consider an example of a low-temperature application of U-Th dating. The tops of manganese nodules grow by precipitation of Mn-Fe oxides and hydroxides from seawater. They are known to grow very slowly, but how slowly? If we assume the rate of growth is constant then depth in the nod-

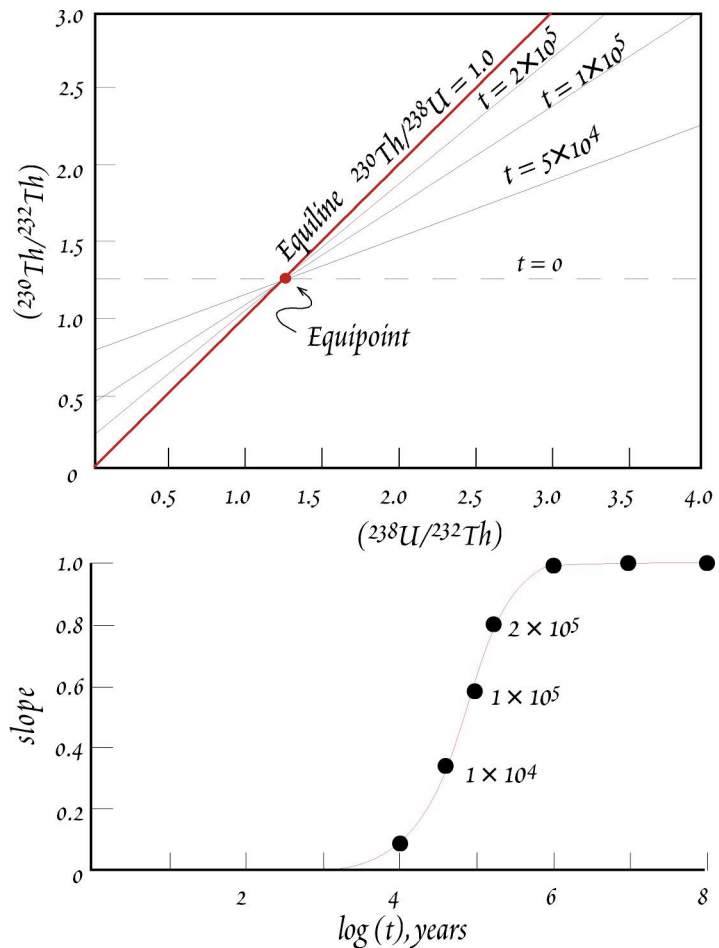


Figure 10.3. (a) ^{230}Th — ^{238}U isochron diagram. The $(^{238}\text{U}/^{232}\text{Th})$ of the source is given by the intersection of the isochron with the equipoint. (b) shows how the slope changes as a function of time. After Faure (1986).

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

ule should be proportional to time. If z is the depth in the nodule, and s is the growth (sedimentation) rate, then:

$$t = z/s \quad 10.17$$

and 10.16 becomes:

$$\left(\frac{{}^{230}\text{Th}}{{}^{232}\text{Th}}\right) = \left(\frac{{}^{230}\text{Th}}{{}^{232}\text{Th}}\right)^0 e^{-\lambda_{230}z/s} + \left(\frac{{}^{238}\text{U}}{{}^{232}\text{Th}}\right) (1 - e^{-\lambda_{230}z/s}) \quad 10.18$$

At the surface of the nodule, $z = 0$, so the exponential terms both go to 1 and the measured activity ratio is initial activity ratio. Having a value for $({}^{230}\text{Th}/{}^{232}\text{Th})^0$, equ. 10.18 can then be solved for s , the growth rate if measurements are made at some other depth.

In practice, however, it is difficult to obtain a sample exactly at the surface: a finite amount of material is required for analysis, and this often translates into a layer of several mm thickness. Equation 10.18 is solved in that instance by less direct means. For example, consider the data shown in Figure 10.4 on a Pacific manganese nodule reported by Huh and Ku (1984). In this plot of $({}^{230}\text{Th}/{}^{232}\text{Th})$ vs. depth, the initial ratio is the intercept of the best-fit line through the data. A growth rate was obtained by obtaining an initial guess of the initial $({}^{230}\text{Th}/{}^{232}\text{Th})$, then iteratively refining the solution to 10.18 by minimizing the difference between computed and observed activity ratios. A growth rate of 49.5 mm/Ma and a $({}^{230}\text{Th}/{}^{232}\text{Th})$ of 77.7 was found to best fit the observations.

Some of the most successful applications of ${}^{230}\text{Th}$ dating has been in determining the age of corals. As we noted, carbonates, including corals, concentrate U and exclude Th. This leads to $({}^{230}\text{Th}/{}^{238}\text{U})$ ratios much smaller than 1 (the equilibrium value); indeed, ${}^{230}\text{Th}/{}^{238}\text{U}$ in modern corals approaches 0. However, the problem of determining ages, specifically the mathematics, is complicated by the disequilibrium that will generally exist between ${}^{234}\text{U}$ and ${}^{238}\text{U}$. The relevant equation is:

$$\left(\frac{{}^{230}\text{Th}}{{}^{234}\text{U}}\right) = \frac{1 - e^{-\lambda_{230}t}}{({}^{234}\text{U}/{}^{238}\text{U})} + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left[1 - \frac{1}{({}^{234}\text{U}/{}^{238}\text{U})}\right] (1 - e^{-(\lambda_{230} - \lambda_{234})t}) \quad 10.19$$

The derivation is given in Dickin (1995). Note that because Th is essentially absent in corals, it is no longer useful to divide by the activity of ${}^{232}\text{Th}$. ${}^{230}\text{Th}$ dating of fossil coral reefs has been extremely useful in determining the rise and fall of sea level over the last glacial cycle (140 ka).

Now let's consider an example of a high temperature application. Imagine a crystallizing magma with homogeneous $({}^{230}\text{Th}/{}^{232}\text{Th})$ and $({}^{238}\text{U}/{}^{232}\text{Th})$ ratios. Th and U will partition into different minerals to different degrees. The minerals will have homogeneous $({}^{230}\text{Th}/{}^{232}\text{Th})$, (assuming crystallization occurs quickly compared to the half-life of Th) since these two isotopes are chemically identical, but variable $({}^{238}\text{U}/{}^{232}\text{Th})$ ratios. Thus the minerals will plot on a horizontal line in Figure 10.3. After the system closes, ${}^{238}\text{U}$ and ${}^{230}\text{Th}$ will begin to come to radioactive equilibrium (either ${}^{230}\text{Th}$ will decay faster than it is produced or visa versa, depending on whether $({}^{230}\text{Th}/{}^{238}\text{U})$ is greater than or less than 1, the equilibrium value). Thus the original horizontal line will rotate, as in a conventional isochron diagram. The rotation occurs about the point where $({}^{230}\text{Th}/{}^{232}\text{Th}) = ({}^{238}\text{U}/{}^{232}\text{Th})$ known as the *equipoint*. As t approaches infinity, the exponential term approaches 1 and:

$$\lim_{t \rightarrow \infty} \left(\frac{{}^{230}\text{Th}}{{}^{232}\text{Th}}\right) = \left(\frac{{}^{238}\text{U}}{{}^{232}\text{Th}}\right) \quad 10.20$$

Thus the *equilibrium* situation, the situation at $t = \infty$, is $({}^{230}\text{Th}/{}^{232}\text{Th}) = ({}^{238}\text{U}/{}^{232}\text{Th})$. In this case, all the minerals will fall on a line, having a slope of 1. This line is known as the *equiline*.

In the past, activities were measured by alpha-counting and fairly large quantities of material were necessary. But improvements in mass spectrometry have made it possible to measure the ${}^{230}\text{Th}/{}^{232}\text{Th}$ ratio (which is of the order of 10^{-6} in igneous rocks) on relatively small quantities of material (and with better precision than α counting). The geochronological work done so far is mainly on cogenetic lavas, where the fractionation of U and Th presumably results from partial melting. Some interesting work

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

on Mount Etna has been done this way. There is some hope that when these more sensitive analytical techniques are fully worked out, Th disequilibrium dating may provide a geochronological tool which will provide insights into volcanic and tectonic processes on relatively short (<100,000 yrs) time scales, for example, processes at mid-ocean ridges.

More interesting, perhaps, are the inferences that can be made from ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{232}\text{Th}$) ratios of zero-age rocks. A series of zero-age comagmatic lavas will plot on a horizontal line. Assuming instantaneous bulk melting, the mantle source should also plot on this line — at its intersection with the equiline, since the source is presumably in radioactive equilibrium. Thus the intersection of the array formed by the data ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{232}\text{Th}$) ratios of zero age comagmatic rocks) and the equiline give the ($^{238}\text{U}/^{232}\text{Th}$) of the source, which is, of course, directly proportional to $^{238}\text{U}/^{232}\text{Th}$. This ability to determine a trace element ratio of mantle sources is unique and has led to some interesting thoughts on magma genesis. The present day source $^{238}\text{U}/^{232}\text{Th}$ can be compared to a time averaged one, which can be deduced from ^{206}Pb and ^{208}Pb data (for example, equation 8.9 suggests one method of determining κ , $^{238}\text{U}/^{232}\text{Th}$). Doing so has led to some very interesting insights into mantle evolution. In actuality, the melting process is complex and the ($^{230}\text{Th}/^{232}\text{Th}$) ratio of a melt will depend on the rate and manner of melting. We'll examine this in detail in Lecture 25.

^{226}Ra Dating

^{226}Ra is another relatively long-lived nuclide ($\tau_{1/2} = 1600$ yr) that has proved useful in dating igneous rocks. The fundamentals are precisely analogous to those we have discussed for ^{234}U and ^{230}Th , with one exception. Unfortunately, Ra has no stable isotope to which one can ratio ^{226}Ra , so the assumption is made that Ra behaves as Ba, and the abundance of Ba is to form a ratio.

Figure 10.5 shows ^{230}Th - ^{238}U and ^{226}Ra - ^{230}Th isochrons obtained on mineral separates, ground-mass, and a whole rock sample from the Castle Creek andesite of Mt. St. Helens. Conventional dating techniques (^{14}C) indicate this lava is only about 2000 years old, but both the ^{230}Th - ^{238}U and ^{226}Ra - ^{230}Th give much older ages. The $^{230}\text{Th}/^{232}\text{Th}$ - $^{238}\text{U}/^{232}\text{Th}$ data define a 27 ± 12 ka isochron, which is clearly much older than the eruption age. This suggests the crystals in the magma may have crystallized as much as 20,000 years or more before eruption. The age ^{226}Ra - ^{230}Th is less precise because the slope is only slightly less than 1, and all samples seem to contain excess ^{226}Ra . Nevertheless, the slope of the data is clearly greater than that of a 2 ka isochron, but significantly less than 1, so these data also suggest the crystallization significantly predated eruption. According to Volpe and Hammond (1991) the difference in the ^{230}Th - ^{238}U and ^{226}Ra - ^{230}Th ages may reflect changes in melt composition, perhaps due to assimilation of country rock or addition of a Ra-rich gas or fluid

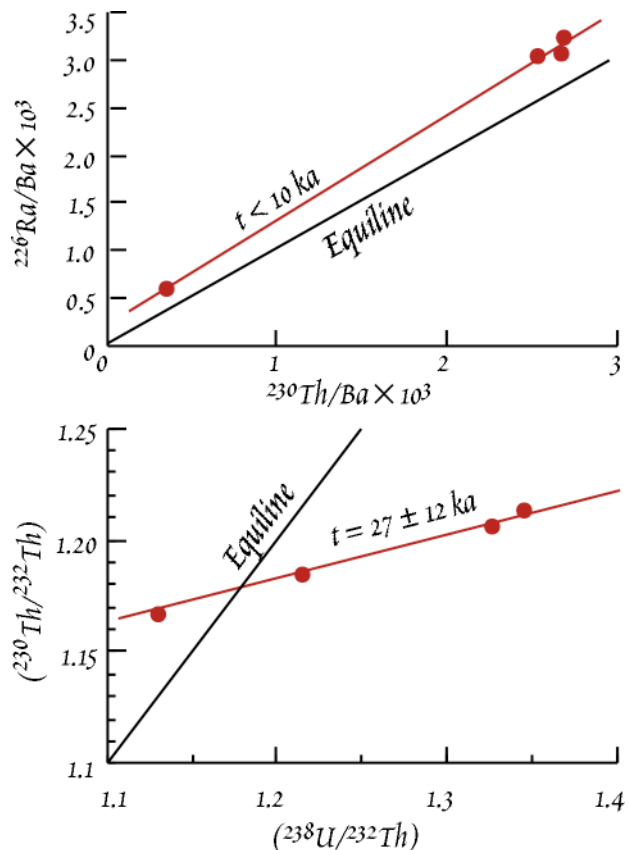


Figure 10.5. ^{230}Th - ^{238}U and ^{226}Ra - ^{230}Th mineral isochrons for the Castle Creek andesite of Mt. St. Helens. ^{14}C and tree ring chronology indicates this lava was erupted 1700-2200 years ago. After Volpe and Hammond (1991).

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

phase to the magma. ^{230}Th - ^{238}U and ^{226}Ra - ^{230}Th ages of the more recent eruptive products of Mt. St. Helens, including the 1980-1986 eruptive phase, were closer to the eruption ages. For example, Volpe and Hammond (1991) obtained a ^{230}Th - ^{238}U age of 6 ± 4 ka on the 1982 dacite. One possible interpretation of this is that when the most recent eruptive phase of Mt. St. Helens began about 4000 years ago, there was significant volume of older magma still present in the magma chamber, and that this older magma has been progressively replaced by fresh magma over the past 4000 years.

^{210}Pb Dating

^{210}Pb has a much shorter half-life (22.3 yrs) than the nuclides we have discussed thus far, so it is useful for much shorter time intervals. It has been applied to dating rapidly accumulating lake sediments and glacial ice. Like Th, Pb is only weakly soluble and very particle active and is scavenged by clay and other particles settling through lake water. Lake sediments thus often have significant unsupported ^{210}Pb in their upper intervals.

We can write an equation analogous to the one equation we wrote for unsupported ^{230}Th (10.14):

$$(^{210}\text{Pb})_u = (^{210}\text{Pb})_u^o e^{-\lambda_{210}t} \quad 10.21$$

Again letting $t = z/s$, we have:

$$(^{210}\text{Pb})_u = (^{210}\text{Pb})_u^o e^{-\lambda_{210}z/s} \quad 10.22$$

Thus we would expect the unsupported ^{210}Pb to decay exponentially with depth.

It is generally not useful to ratio ^{210}Pb to one of the stable isotopes of Pb for several reasons. First, a decaying ^{238}U will pass through a stage as ^{222}Rn , a gas, before decaying to ^{210}Pb . Some of this gas will escape into the atmosphere. However, its half-life is only 4 days and the nuclides between ^{222}Rn and ^{210}Pb are all very short-lived, so this Rn will quickly decay to Pb. The Pb will be adsorbed on particles and washed out of the atmosphere by rain. Thus the pathway of some ^{210}Pb to sediment will be different than that of normal Pb. Second, there has been a very substantial input of anthropogenic (stable) Pb to lakes and streams from leaded gasoline over the 20th century. For both these reasons, the variation of stable Pb with depth in a core will likely be quite different than that of ^{210}Pb .

The first step in determining sediment ages using ^{210}Pb is to estimate the supported ^{210}Pb so it can be subtracted that from the total ^{210}Pb activity to determine unsupported activity. One easy solution results from the fact that ^{210}Pb should reach equilibrium in 5 to 10 half-lives. Thus sediment deposited more than 100-200 years ago should be in equilibrium, so that the total activity is the supported activity. This requires the assumption that the flux of ^{210}Pb has been constant over the last 100-200 years. Alternatively, the activity of supported Pb can be determined by determining the activity of ^{226}Ra . Once the unsupported activity is calculated, we can solve equation 10.22 for s , the sedimentation rate.

This can be done as follows. By taking the log of equation 10.22, we have

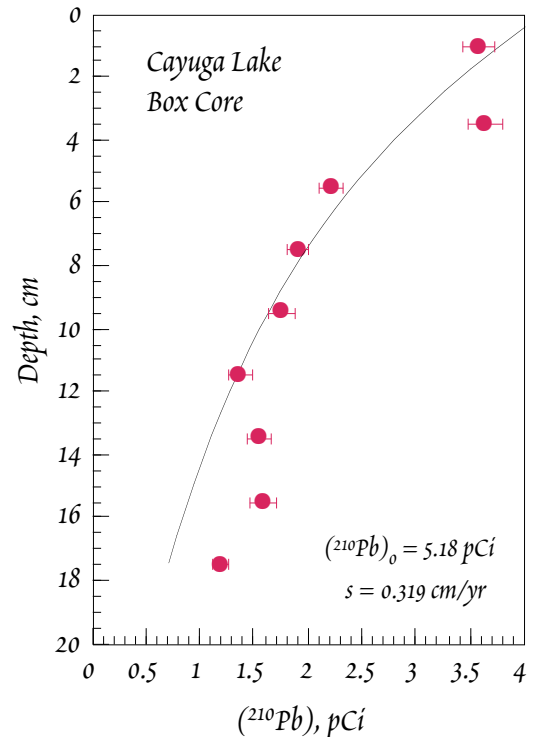


Figure 10.6. Unsupported ^{210}Pb activity measured on sediment samples from a box core taken from Cayuga Lake. The upper 4-5 cm are probably disturbed, either by bioturbation or in the coring process. The line shows the calculated decay of unsupported ^{210}Pb assuming $(^{210}\text{Pb})^0 = 5.19$ pCi and $s = 0.319$ cm/yr. This was calculated by averaging the first 2 points and discarding the last 3. Unpublished data of D. Engstrom.

Geol. 655 Isotope Geochemistry

Lecture 10

Spring 2007

$$\ln(^{210}\text{Pb})_u = \ln(^{210}\text{Pb})_u^o + \frac{-\lambda_{210}}{s} z \quad 10.23$$

Equation 10.23 is the equation of a straight line on a plot of $\ln(^{210}\text{Pb})$ vs depth, where $\ln(^{210}\text{Pb})^o$ is the intercept and $-\lambda_{210}/s$ is the slope. Applying linear regression to the data in this form, we can determine both the slope and the intercept. From the slope, we can easily solve for s . Figure 10.6 illustrates an example calculated in this manner.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

- Dickin, A. 1995. *Radiogenic Isotope Geochemistry*. Cambridge: Cambridge University Press.
- Faure, G., 1986. *Principles of Isotope Geology*, 2nd ed., Wiley & Sons, New York, 589 p.
- Huh, C.-A. and T.-L. Ku, 1984. Radiochemical observations on manganese nodules from three sedimentary environments in the north Pacific, *Geochim. Cosmochim. Acta*, 48, 951-964.
- Volpe, A. M. and P. E. Hammond, 1991. ^{238}U - ^{230}Th - ^{226}Ra disequilibria in young Mount St. Helens rocks: time constraint for magma formation and crystallization, *Earth Planet. Sci. Lett.*, 107, 475-486.