U and Th are, strictly speaking, rare earth elements, although they belong to the actinide series instead of the lanthanide series. The other rare earths we have met so far, Nd and Sm, are lanthanides. As in the lanthanide rare earths, an inner electron shell is being filled as atomic number increases in the actinides. Both U and Th generally have a valence of +4, but under oxidizing conditions, such as at the surface of the Earth, U has a valence of +6. In six-fold coordination, U\(^{4+}\) has an ionic radius of 89 pm\(^1\) (100 pico meters = 1 Å); U\(^{6+}\) has an ionic radius of 73 pm in 6-fold and 86 pm in 8-fold coordination. Th\(^{4+}\) has an ionic radius of 94 pm. These radii are not particularly large, but the combination of somewhat large radius and high-charge is not readily accommodated in crystal lattices of most common rock-forming minerals, so both U and Th are highly incompatible elements. Th is relatively immobile under most circumstances. In its reduced form, U\(^{4+}\) is insoluble and therefore fairly immobile, but in the U\(^{6+}\) form, which is stable under a wide range of conditions at the surface of the Earth, U forms the soluble oxynion complex, UO\(^2+\). As a result, U can be quite mobile. U and Th can form their own phases in sedimentary rocks, uranite and thorite, but they are quite rare. In igneous and metamorphic rocks, U and Th are either dispersed as trace elements in major phases, or concentrated in accessory minerals (when they are present) such as zircon (ZrSiO\(_4\)), which concentrates U more than Th, and monazite ([La\(_i\),Ce,Th]\(PO_4\)) which concentrates Th more than U. These elements may be also concentrated in other accessory phases such as apatite (Ca\(_i\)(PO\(_4\))\(_i\)(OH)) and sphene (CaTi(SiO\(_4\))\(_i\)(OH)). However, zircon is by far and away the most important from a geochronological perspective.

U and Th are refractory elements, and we can therefore expect the Th/U ratio of the Earth to be the same as chondrites or nearly so. There is, however, some debate about the exact terrestrial Th/U ratio, and we can be no more precise than to say it is 4±0.2\(^2\). This ratio is 3.8 in the CI chondrite Orgueil, but may be low due to mobility of U in hydrous fluid in the CI parent body.

The geochemical behavior of Pb is more complex than that of the elements we have discussed so far and consequently, less well understood. It is a relatively volatile element, so its concentration in the Earth is certainly much lower than in chondrites. It is also a chalcophile element. If the core contains, as some believe, S as the light element, it is possible that some of the Earth's Pb is in the core (it is, however, difficult to distinguish loss of Pb from the Earth due to its volatility from loss of Pb from the silicate portion of the Earth due to extraction into the core). Pb can exist in two valence states, Pb\(^{2+}\) and Pb\(^{4+}\). Pb\(^{2+}\) is by far the most common state; the Pb\(^{4+}\) state is rare and restricted to highly alkaline or oxidizing solutions. The ionic radius of Pb\(^{2+}\) is 119 pm in 6-fold coordination and 129 pm in 8-fold coordination. As a result of its large ionic size, Pb is an incompatible element, though not as incompatible as U and Th (incompatibility seems to be comparable to the light rare earths). The most common Pb mineral is galena (PbS). In silicates, Pb substitutes readily for K (ionic radius 133 pm) particularly in potassium feldspar, but less so in other K minerals such as biotite. Most naturally occurring compounds of Pb are highly insoluble under most conditions. As a result, Pb is usually reasonably immobile. However, under conditions of low pH and high temperature, Pb forms stable and somewhat soluble chloride and sulfide complexes, so that Pb can sometimes be readily transported in hydrothermal solutions.

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\(^1\)In eight-fold coordination, the effective ionic radius of U\(^{4+}\) is 1.00Å. In zircon, a mineral which highly concentrates U, U is in 8-fold coordination. This is probably a pretty good indication that 8-fold coordination is the preferred configuration. The figure for 6-fold coordination is given for comparison to other radii, which have been for 6-fold coordination. Th has a radius of 1.05Å in 8-fold coordination.

\(^2\) The uncertainty results from the mobility of U. The CI carbonaceous chondrites experienced mild alteration in hydrous conditions on the parent body. U was mobilized under these conditions and thus the U/Th ratio varies in these meteorites. For this reason, they cannot be used to precisely determine the U/Th ratio of the Solar System and the Earth.
Although Pb is clearly less incompatible that U and Th, these 3 elements have been extracted from the mantle and concentrated in the crust to approximately the same degree. The reason for this is not yet completely understood, and we will discuss the problem later in the course.

The U-Th-Pb system is certainly the most powerful tool in the geochronologist's tool chest. Table 6.1 summarizes this decay system. The reason for the power is simply that there are three parents decaying to 3 isotopes of Pb, and in particular, there are two isotopes of U which decay to Pb with very different half lives. This is important because chemical processes will not change the ratio of the two U isotopes to each other and will not change the ratio of the two Pb daughter isotopes to each other. The point is best illustrated as follows. First we write the decay equation for each of the two U decay systems:

\[
{^{207}}\text{Pb} = {^{235}}\text{U}(e^{\lambda t} - 1)
\]

\[
{^{206}}\text{Pb} = {^{238}}\text{U}(e^{\lambda t} - 1)
\]

where the asterisk designates radiogenic \(206\text{Pb}\) and \(207\text{Pb}\), and \(\lambda_5\) and \(\lambda_8\) are the decay constants for \(235\text{U}\) and \(238\text{U}\) respectively. If we divide 3.01 by 3.02, we have:

\[
\frac{207\text{Pb}^*}{206\text{Pb}^*} = \frac{235\text{U}(e^{\lambda_5 t} - 1)}{238\text{U}(e^{\lambda_8 t} - 1)}
\]

where the asterisk designates radiogenic \(206\text{Pb}\) and \(207\text{Pb}\), and \(\lambda_5\) and \(\lambda_8\) are the decay constants for \(235\text{U}\) and \(238\text{U}\) respectively. If we divide 3.01 by 3.02, we have:

\[
\frac{207\text{Pb}^*}{206\text{Pb}^*} = \frac{235\text{U}(e^{\lambda_5 t} - 1)}{238\text{U}(e^{\lambda_8 t} - 1)}
\]

Now if the ratio of the U isotopes is everywhere the same (as it is at the present day), 3.03 can be written as

\[
\frac{207\text{Pb}^*}{206\text{Pb}^*} = \frac{(e^{\lambda_5 t} - 1)}{137.88(e^{\lambda_8 t} - 1)}
\]

The nice thing about equation 3.04 is that the only variable on the right hand side is time; in other words the \(207\text{Pb}^*/206\text{Pb}^*\) is a function only of time.

**TABLE 3.1. Parameters of the U-Th-Pb System**

<table>
<thead>
<tr>
<th>Parent</th>
<th>Decay Mode</th>
<th>(\lambda)</th>
<th>Half-life</th>
<th>Daughter</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(232\text{Th})</td>
<td>(\alpha\beta)</td>
<td>(4.948 \times 10^{11}\text{y}^{-1})</td>
<td>(1.4 \times 10^{10}\text{y})</td>
<td>(208\text{Pb}, 8\text{He})</td>
<td>(208\text{Pb} / 204\text{Pb}, 3\text{He} / 4\text{He})</td>
</tr>
<tr>
<td>(235\text{U})</td>
<td>(\alpha\beta)</td>
<td>(9.849 \times 10^{10}\text{y}^{-1})</td>
<td>(7.07 \times 10^{9}\text{y})</td>
<td>(207\text{Pb}, 7\text{He})</td>
<td>(207\text{Pb} / 204\text{Pb}, 3\text{He} / 4\text{He})</td>
</tr>
<tr>
<td>(238\text{U})</td>
<td>(\alpha\beta)</td>
<td>(1.551 \times 10^{10}\text{y}^{-1})</td>
<td>(4.47 \times 10^{9}\text{y})</td>
<td>(206\text{Pb}, 6\text{He})</td>
<td>(206\text{Pb} / 204\text{Pb}, 3\text{He} / 4\text{He})</td>
</tr>
</tbody>
</table>

In practice this means is that the age is independent of the parent/daughter ratio; i.e., we do not need to measure the parent/daughter ratio. We shall see that this property actually allows us to somewhat relax our requirement that the system remain closed. We can also see that although we could write an equation similar to 80.3 using \(232\text{Th}\) and \(208\text{Pb}\) instead of \(235\text{U}\) and \(207\text{Pb}\), there would be little advantage to doing so because Th and U are different elements and could well be lost or gained in different proportions.

If Madison Avenue were given the task of selling the U-Th-Pb system, they would probably say that you get 4 dating methods for the price of one: \(238\text{U}, 206\text{Pb}, 235\text{U}, 207\text{Pb}, 232\text{Th}, 208\text{Pb}, 238\text{Pb}, 207\text{Pb}, 208\text{Pb}\). In a certain sense, this is true. However, if you bought the package, you would probably quickly discover that the first three above, applied independently, were not particularly powerful, at least in comparison to either the Pb-Pb technique or simultaneous use of a combination of several techniques (an exception might be the \(232\text{Th}, 208\text{Pb}\) system, which might prove useful on separated Th-bearing minerals). The Pb-Pb method, as it is called, can be quite useful when applied independently, particularly where there is reason to believe that there has been some recent change in the parent/daughter ratio. We have mentioned in an earlier lecture that the slope on a plot of \(208\text{Pb} / 204\text{Pb}\) vs. \(206\text{Pb} / 204\text{Pb}\) is proportional to age since:
Equation 3.05 is very similar to equation 3.04. We would use 3.04 when there is no significant initial Pb, or the amount of initial Pb is sufficiently small that we can make a reasonable estimate of its isotopic composition and make a correction for it. We would use 3.05 when initial Pb is present in significant quantities and has an unknown composition. Figure 3.1 shows an example of a Pb-Pb isochron that yielded a reasonably precise age. Unlike a conventional isochron, the intercept in the Pb-Pb isochron has no significance, and the initial isotopic composition cannot be determined without some additional information about parent/daughter ratios.

There are a couple of reasons why we might suspect parent/daughter ratios have changed, and hence might prefer the Pb-Pb approach to one involving parent-daughter ratios. First, the solubility of U under oxidizing conditions often leads to mobility (open-system behavior) in the zone of weathering. It has often been found that U-Pb ages are spurious, yet Pb-Pb ages seem correct. This circumstance appears to result from recent U mobility as erosion brings a rock into the weathering zone. A second situation where parent/daughter ratios would have experienced recent change is in magma generation. When melting occurs, the U and Pb isotope ratios in the magma will be identical to those in the source (because the isotopes of an element are chemically identical), but the U/Pb ratio (and Th/Pb) ratio will change, as the chemical behaviors of U and Pb differ. So conventional dating schemes cannot generally provide useful geochronological information about sources of magmas. However, the Pb-Pb dating method can, at least in principle, provide useful information, because the Pb isotope ratios of a magma are representative of the source and the method does not depend on parent/daughter ratios. Essentially, what we are doing is allowing volcanism to ‘sample’ the source, generally the mantle, but sometimes the lower continental crust. The sample is representative of the isotopic composition of the source, but not representative of the elemental chemistry of the source. The relationship between Pb isotope ratios in mantle-derived magmas has lead to the conclusion that heterogeneities in the mantle must have existed for times on the order of 1-2 Ga. This is an extremely important constraint not only on the chemical evolution of the mantle, but also on its dynamics.

The U-Pb system achieves its greatest power when we use the $^{238}$U-$^{206}$Pb, $^{235}$U-$^{207}$Pb, and $^{207}$Pb-$^{206}$Pb methods in combination. In many instances, it can actually be used to ‘see through’ open system behavior and obtain an age of initial crystallization. We shall examine this in the next lecture.

**Th/U Ratios**

Provided Th/U ratios are constant and known in a set of samples we wish to date, we can calculate ages from $^{208}$Pb/$^{204}$Pb-$^{206}$Pb/$^{204}$Pb isochrons just as we can using $^{207}$Pb and $^{206}$Pb. However, although U and Th are geochemically similar and the Th/U ratio is not likely to vary much, it would not be
prudent to assume the ratio is actually constant for geochronological purposes. Furthermore, there is little reason to do so, since we can already compute the age using $^{206}\text{Pb}$ and $^{208}\text{Pb}$. But it may be useful in some circumstances to turn the problem around and compute the Th/U ratio from the age and the slope of the data on a plot of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. The basis of this is as follows. We write the usual growth equations for $^{206}\text{Pb}$ and $^{208}\text{Pb}$:

\[
\begin{align*}
^{206}\text{Pb} / \text{Pb}^{204} & = \left( \begin{array}{c}
^{206}\text{Pb} / \text{Pb}^{204} \\
0
\end{array} \right) + \frac{^{238}\text{U}}{^{204}\text{Pb}} (e^{\lambda_{t}} - 1) \\
^{208}\text{Pb} / \text{Pb}^{204} & = \left( \begin{array}{c}
^{208}\text{Pb} / \text{Pb}^{204} \\
0
\end{array} \right) + \frac{^{232}\text{Th}}{^{204}\text{Pb}} (e^{\lambda_{t}} - 1)
\end{align*}
\]

Subtracting the initial ratio from each side of each equation and dividing 3.7 by 3.6 we have

\[
\frac{\Delta \left( ^{208}\text{Pb} / \text{Pb}^{204} \right)}{\Delta \left( ^{206}\text{Pb} / \text{Pb}^{204} \right)} = \frac{^{232}\text{Th} / \text{Pb}^{204} (e^{\lambda_{t}} - 1)}{^{238}\text{U} / \text{Pb}^{204} (e^{\lambda_{t}} - 1)}
\]

or

\[
\frac{\Delta \left( ^{208}\text{Pb} / \text{Pb}^{204} \right)}{\Delta \left( ^{206}\text{Pb} / \text{Pb}^{204} \right)} = \frac{\kappa (e^{\lambda_{t}} - 1)}{(e^{\lambda_{t}} - 1)}
\]

where $\kappa$ is used to designate the $^{232}\text{Th} / ^{238}\text{U}$ ratio. Using $\mu$ to designate the $^{238}\text{U} / ^{204}\text{Pb}$ ratio, the parent-daughter ratio of the Th-Pb system is the product $\mu \kappa$.

Equation 3.09 tells us that the slope of a line on a plot of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ is proportional to time and $\kappa$, provided that $\kappa$ does not vary. If we can calculate $t$ from the corresponding $^{208}\text{Pb}/^{204}\text{Pb}$–$^{206}\text{Pb}/^{204}\text{Pb}$ slope, we can solve 3.09 for $\kappa$. If, however, $\kappa$ varies linearly with $\mu$, a straight line will still result on the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot and our estimate of $\kappa$ will be incorrect.

**THE U-TH-PB SYSTEM: ZIRCON DATING**

Zircon (ZrSiO$_4$) is a mineral with a number of properties that make it extremely useful for geochronologists (Figure 3.02). First of all, it is very hard (hardness 7½/2), which means it extremely resistant to mechanical weathering. Second, it is extremely resistant to chemical weathering and metamorphism. For geochronological purposes, these properties mean it is likely to remain a closed system. Third, it concentrates U (and Th to a lesser extent) and excludes Pb, resulting in typically very high $^{238}\text{U} / ^{204}\text{Pb}$ ratios. It is quite possibly nature’s best clock. Finally, it is reasonably common as an accessory phase in a variety of igneous and metamorphic rocks.

The very high $^{238}\text{U} / ^{204}\text{Pb}$ ratios in zircon (and similar high $\mu$ minerals such as sphere and apatite) provide some special geochronological opportunities and a special diagram, the concordia diagram, has been developed to take advantage of them. The discussion that follows can be applied to any other system with extremely high $^{238}\text{U} / ^{204}\text{Pb}$ ratios, but in practice, zircons constitute the principle target for Pb geochronologists.

A concordia diagram is simply a plot of $^{206}\text{Pb} / ^{238}\text{U}$ vs. $^{207}\text{Pb} / ^{235}\text{U}$. You should satisfy yourself that both of these ratios are proportional to time. In essence, the concordia diagram is a plot of the $^{238}\text{U} - ^{206}\text{Pb}$ age against the $^{235}\text{U} - ^{207}\text{Pb}$ age. The ‘concordia’ curve on such a diagram that is the locus of points where the $^{238}\text{U} - ^{206}\text{Pb}$ age equals the $^{235}\text{U} - ^{207}\text{Pb}$ age. Such ages are said to be concordant. Figure 3.3 is an example of a concordia diagram.

The best way to think about evolution of Pb/U ratios is to imagine that the diagram itself evolves with time, along with its axes, while the actual data point stays fixed. Let’s take a 4.0 Ga old zircon as an example. When it first formed, or “closed”, it would have plotted at the origin, because had anyone been around to analyze it, they would have found the $^{207}\text{Pb} / ^{235}\text{U}$ and $^{208}\text{Pb} / ^{238}\text{U}$ ratios to be 0. Initially, $^{207}\text{Pb} / ^{235}\text{U}$ would have increased rapidly, while the $^{208}\text{Pb} / ^{238}\text{U}$ would have been increasing only slowly. This is because 4.0 Ga ago there was a lot of $^{235}\text{U}$ around (recall that $^{235}\text{U}$ has a short half-life). As time passed, the increase in $^{207}\text{Pb} / ^{235}\text{U}$ would have slowed as the $^{235}\text{U}$ was ‘used up’. So imagine
that the diagram initially ‘grows’ or ‘expands’ to the left, expanding downward only slowly. Had someone been around 3.0 Ga ago to determine ‘zircon’ ages, he would have drawn it as it appears in Figure 3.04 (of course, he would have labeled the 3.0 Ga point as 0, the 4.0 Ga point as 1.0, etc.).

Any zircon that has remained as a completely closed system since its crystallization must plot on the concordia line. What happens when a zircon gains or loses U or Pb? Let’s take the case of Pb loss, since that is the most common type of open-system behavior in zircons. The zircon must lose $^{207}$Pb and $^{206}$Pb in exactly the proportions they exist in the zircon because the two are chemically identical. In other words, a zircon will not lose $^{206}$Pb in preference to $^{207}$Pb or visa versa.

Let’s take the specific case of a 4.0 Ga zircon that experienced some Pb loss during a metamorphic event at 3.0 Ga. If the loss was complete, the zircon would have been reset and would have plotted at the origin in Figure 3.04. We could not distinguish it from one that formed 3.0 Ga. Suppose now that that zircon had lost only half its Pb at 3.0 Ga. During the Pb loss, the $^{206}$Pb/$^{238}$U and $^{207}$Pb/$^{235}$U would have both decreased by half. Consequently, the point would have migrated half way to the origin. At 3.0 Ga, therefore, it would have plotted on a ‘cord’, i.e., a straight line, between its initial position on the concordia curve, the 4.0 Ga point, and the origin (Figure 3.5a) at 3.0 Ga. Had it lost some other amount of Pb, say 30% or 80%, it would have plotted on the same cord, but further or nearer the origin. The line is straight because the loss of $^{207}$Pb is always directly proportional to the loss of $^{206}$Pb. The origin in Figure 9.3a corresponds to the 3.0 Ga point.

Figure 3.02. Upper. Separated Zircon crystals. Notice the zoning. Lower. Strongly zoned zircon showing differing ages of spots analyzed by ion probe.
on the concordia in Figure 3.05b. So, in Figure 3.05b, the zircon would lie on a cord between the 4.0 Ga and the 3.0 Ga point. We would say this is a 'discordant' zircon.

The intercepts of this cord with the concordia give the ages of initial crystallization (4.0 Ga) and metamorphism (3.0 Ga). So if we can determine the cord on which this discordant zircon lies, we can determine the ages of both events from the intercepts of that cord with the concordia. Unfortunately, if our only data point is this single zircon, we can draw an infinite number of cords passing through this point, so the ages of crystallization and metamorphism are indeterminate. However, we can draw only 1 line through 2 points. So by measuring two zircons (or populations of zircons) that have the same crystallization ages and metamorphism ages, but have lost different amounts of Pb, and hence plot on different points on the same cord, the cord can be determined. The closure age and partial resetting ages can then be determined from the intercepts. (as usual in geochronology, however, we are reluctant to draw a line through only two points since any two points define some line; so at least three measurements are generally made).

In practice, different zircon populations are selected based on size, appearance, magnetic properties, color, etc. While zircon is generally a trace mineral, only very small quantities, a few milligrams, are needed for a measurement. Indeed, it is possible to analyze single zircons and even parts of zircons. U gain would affect the position of zircons on the

---

Figure 3.03. The concordia diagram.

Figure 3.04. A concordia diagram as it would have been drawn at 3.0 Ga.
concordia diagram in the same manner as Pb loss; the two processes are essentially indistinguishable on the concordia diagram. U loss, on the other hand, moves the points away from the origin at the time of the loss (Figure 3.6). In this case, the zircons lie on an extension of a cord above the concordia. As is the case for Pb loss, the upper intercept of the cord gives the initial age and the lower intercept gives the age of U loss. U loss in less common than Pb loss. This is true for two reasons. First, U is happy in the zircon, Pb is not. Second, Pb will occupy a site damaged by the alpha decay process, particularly the recoil of the atom as it undergoes alpha decay, making diffusion out of this site easier. Radiation damage to the crystal lattice is a significant problem in zircon geochronology, and one of the main reasons ages can be imprecise. U-rich zircons are particularly subject to radiation damage. Heavily damaged crystals are easily recognized under the microscope and are termed metamict.

Pb gain in zircons is not predictable because the isotopic composition of the Pb gained need not be the same as the composition of the Pb in the zircon. Thus Pb gain would destroy any age relationships. However, Pb gain is much less likely than other open system behaviors.

Zircons that have suffered multiple episodes of open system behavior will have U-Pb systematics that are difficult to interpret and could be incorrectly interpreted. For example, zircons lying on a cord be-

Figure 3.05. (a) Concordia diagram as it would have appeared at 3.0 Ga. Three zircons that experience variable amounts of Pb loss move from the 4.0 Ga point on the concordia curve (their crystallization age) toward the origin. (b) The same three zircons as they would plot at present. The three define a cord between 3.0 Ga and 4.0 Ga. A possible interpretation of this result would be that 4.0 Ga is the crystallization age and 3.0 Ga is the metamorphic age.

Figure 3.06. A concordia plot showing hypothetical zircons that crystallized at 4.0 Ga and lost U during metamorphism at 3.0 Ga.
between 4.0 and 3.0 Ga that subsequently lose Pb and move on a second cord toward the 2.0 Ga could be interpreted as having a metamorphic age of 2.0 Ga and a crystallization age of between 4.0 and 3.0 Ga.

Continuous Pb loss from zircons can also complicate the task of interpretation. The reason is that in continuous Pb loss, zircons do not define a straight-line cord, but rather a slightly curved one. Again imagining that the concordia diagram grows with time, a zircon loosing Pb will always move toward the origin. However, the position of the origin relative to the position of the zircon moves with time in a non-linear fashion. The result is a non-linear evolution of the isotopic composition of the zircon.

Thus although it is possible to “see through” partial resetting of the zircon “clock”, this process nevertheless limits the accuracy with which initial crystallization ages can be determined. Several techniques have been developed to get around this problem. Quite often, zircons are zoned with the outermost layers being the richest in U. This can be a result of increasing U concentration during fractional crystallization of a magma or overgrowth of U-rich layers during metamorphism. Regardless, the outermost zones are most likely to be subject to radiation damage and consequent U-loss. Krogh (1982) showed that these out zones could be removed by abrasion using small air abrasion chambers designed and built expressly for this purpose. He demonstrated that abraded zircons were typically much more concordant than unabraded ones. Consequently, age uncertainties were considerably reduced. In addition to physical abrasion, numerous attempts have been made to chemically abrade, or leach, zircons, the idea being to remove the radiation damaged regions of the crystal. The most successful of these methods has been that of Mattinson (2005), which involves first annealing the crystals at 800-1000°C for 48 hours before step-wise partial dissolution in acid at progressively higher temperatures. This step-wise dissolution allows for an approach similar to step-wise heating in $^{40}\text{Ar} - ^{39}\text{Ar}$ dating, as illustrated in Figure 3.07. The uncertainty in this age is less than 0.1%, a level of accuracy otherwise unattainable. Figure 3.08 shows another example of how this technique improves accurate determination of crystallization ages. Three different fractionations of untreated zircons from a Finnish tonalite are discordant, but define a cord with an upper concordia intercept of about 1870 Ma. The chemically abraded zircon fraction is nearly concordant at this age, allowing a much more precise determination. In this diagram, the analyses are plotted

Figure 3.07. a. Ages calculated from step-wise dissolution of zircons from the Sierra Nevada batholith that had been abraded, then annealed at 850°C for 48 hours. Corresponding U concentrations in the step-wise dissolution. The outer zones of the zircons are the most U-rich and consequently the most radiation-damaged and discordant.
by ellipses in order to represent analytical errors. The analytical errors in on the $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios are highly correlated, hence the elliptical shape.

U-Pb dating has now improved to the point where uncertainty in decay constants now constitutes a major part of the uncertainty in zircon ages. Because it is far less abundant, the decay constant for $^{235}\text{U}$ is the most uncertain. Based on highly concordant zircon analyses obtained through the chemical abrasion technique, Mattinson (2010) has recently proposed that the $^{235}\text{U}$ decay constant should be revised from the conventionally accepted value of $0.98485 \pm 0.00135 \times 10^{-9}$ yr$^{-1}$ to $0.98571 \pm 0.00012 \times 10^{-9}$ yr$^{-1}$.

Given the mechanical and chemical stability of zircon, it should not be surprising that the oldest terrestrial material yet identified is zircon. Until a decade ago, the oldest dated terrestrial rocks were the Isua gneisses in Greenland. These are roughly 3850 Ma old. Work published in 1989, revealed that the Acasta gneisses of the Slave Province (Northwest Territories, Canada) are 3.96 Ga old (Bowring et al, 1989). These ages were determined using an ion probe to date the cores of zircon crystals extracted from these gneisses.

Zircons having ages in the range of 4100-4260 Ma have been identified in quartzites at Mt. Narryer and the Jack Hills in western Australia (e.g., Compston and Pidgeon, 1986). The quartzites themselves are metamorphosed sandstones that were probably deposited about 3100-3300 Ma. They contain zircons derived from a number of sources. A small fraction of these zircons has cores that are in the range of 4100-4200 Ma. The zircons were analyzed by a specially built high-resolution ion probe at the Australian National University nicknamed ‘SHRIMP’. Subsequently, this instrument and similar instruments has been commercially available from several companies. The great advantage of these instruments over conventional analysis of zircons is not only that individual zircons can be analyzed, but individual parts of the zircons can be analyzed. As can be seen in Figure 3.02, zoning in zircon is not uncommon and this zoning often reflects multiple episodes of growth. This was the case with the Mt. Narryer zircons, which had complex histories suffering multiple metamorphic events between 4260 and 2600 Ma. The principal effect was the growth of rims of new material on the older cores around 3500 Ma. Conventional analysis of these zircons would not have recognized the older ages. The cores of these zircons, however, proved to be nearly concordant at the older ages. These ages determined by ion probe were initially highly controversial. By and large, however, the community has come to accept them as reliable, when performed carefully.
Subsequently even older zircons (would be more correct to say parts of zircons) were discovered in the Jack Hills of Australia (Wilde, et al., 2001). An ion probe date on one part of one of these zircons (Figure 3.09) is shown 4.404 Ga ±8 Ma. Thus the oldest known terrestrial materials are approaching the oldest ages from other planetary bodies, including the Moon, Mars, and asteroids (as represented by meteorites). They remain, however, significantly younger than the age of the Solar System, which is 4.556 Ga. Nevertheless, these very old ages seem to demonstrate that it is zircons, not diamonds, that “are forever”.

**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 principal 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 3.10). Most of these daughters have very short half-lives, 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 3.01 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.

* In principle, 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 maximum of 7-10 half-lives of the nuclide with the shortest half-life.
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:

$$\frac{dN_D}{dt} = \lambda_p N_p - \lambda_D N_D$$  \hspace{1cm} (3.10)

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:

$$N_D = \frac{\lambda_p}{\lambda_D - \lambda_p} N_p^0 \left( e^{-\lambda_p t} - e^{-\lambda_D t} \right) + N_D^0 e^{-\lambda_D t}.$$  \hspace{1cm} (3.11)

Scientists dealing with the intermediate daughters of U and Th (it is the daughters of $^{238}$U 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 ($^{230}$Th) denotes the activity of $^{230}$Th, and ($^{230}$Th/$^{238}$U) denotes the ratio of activities of $^{230}$Th and $^{238}$U. Activities are related to atomic (or molar) abundances by the basic equation of radioactive decay:

$$\frac{dN}{dt} = -\lambda N$$  \hspace{1cm} (1.12)

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.:

$$\frac{dN_D}{dt} = \frac{dN_p}{dt}$$  \hspace{1cm} (3.12)

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 3.10 is zero:

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-life, yrs</th>
<th>Decay constant, yr$^{-1}$</th>
<th>Parent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U</td>
<td>246,000</td>
<td>$2.794 \times 10^6$</td>
<td>$^{238}$U</td>
</tr>
<tr>
<td>$^{233}$Pa</td>
<td>32,480</td>
<td>$2.134 \times 10^5$</td>
<td>$^{235}$U</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>75,200</td>
<td>$9.217 \times 10^6$</td>
<td>$^{238}$U</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>1,622</td>
<td>$4.272 \times 10^4$</td>
<td>$^{233}$U</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>6.7</td>
<td>$1.06 \times 10^1$</td>
<td>$^{232}$Th</td>
</tr>
<tr>
<td>$^{210}$Pb</td>
<td>22.26</td>
<td>$3.11 \times 10^{-2}$</td>
<td>$^{238}$U</td>
</tr>
</tbody>
</table>

† 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 it the Curie (abbreviated Ci) equal to $3.7 \times 10^8$ disintegrations per second. Because concentrations of these elements in nature are generally low, activity is often expressed in disintegrations per minute (dpm).
We substitute the \( \frac{dN}{dt} \) for the \( \lambda N \) terms in (7.04), rearrange and we obtain 3.12; 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 the 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.

\( ^{234}\text{U} - ^{238}\text{U} \) dating

An example of this is \(^{234}\text{U} - ^{238}\text{U} \) dating of sediments. As it turns out, \(^{234}\text{U} \) and \(^{238}\text{U} \) in seawater are not in equilibrium, i.e., the \(^{234}\text{U} / ^{238}\text{U} \) ratio is not 1. It is uniform\(^\dagger\), however, with a ratio of about 1.14±0.03. The reason the ratio is higher than 1 is that \(^{234}\text{U} \) is preferentially leached from rocks because \(^{234}\text{U} \) is located in crystals of rocks in damaged lattice sites. It occupies the site of a \(^{238}\text{U} \) atom that has undergone \( \alpha \)-decay. The \( \alpha \)-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 \(^{238}\text{U} \). The oceans collect this ‘leachate’, hence they are enriched in \(^{234}\text{U} \). When U precipitates from seawater into, for example, the calcium carbonate in a coral skeleton, it will initially have the same \(^{234}\text{U} / ^{238}\text{U} \) as seawater, but \(^{234}\text{U} \) will decay faster than it is created by decay of \(^{238}\text{U} \), 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 \(^{234}\text{U} \) in a sample into that which is supported by \(^{238}\text{U} \), i.e. that amount in radioactive equilibrium with \(^{238}\text{U} \) and that amount which is excess, i.e. unsupported by \(^{238}\text{U} \):

\[
\left( ^{234}\text{U} \right) = \left( ^{234}\text{U} \right)_s + \left( ^{234}\text{U} \right)_u
\]

\(^\dagger\) The ratio is uniform in space, but there is evidence to suggest it has varied slightly with time, particularly between glacial and interglacial periods.
where we are using parentheses to denote activity and subscripts $s$ and $u$ denote supported and unsupported abundances respectively. The activity of the excess $^{234}\text{U}$ decreases with time according to equation 2.04, which we can rewrite as:

\[ (^{234}\text{U})_{u} = (^{234}\text{U})_{u}^{0} e^{-\lambda_{234}t} \]

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

\[ (^{234}\text{U})_{u}^{0} = (^{234}\text{U})^{0} - (^{238}\text{U})_{s} \]

which just says that the initial unsupported activity of $^{234}\text{U}$ is equal to the total initial activity of $^{234}\text{U}$ less the (initial) supported activity of $^{234}\text{U}$. Since to a very good approximation the activity of the parent, $^{238}\text{U}$, does not change over times on the order of the half-life of $^{234}\text{U}$ or even ten half-lives of $^{234}\text{U}$, the present $^{238}\text{U}$ 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 $^{234}\text{U}$ is equal to the activity of $^{238}\text{U}$, both now and at $t = 0$. Hence, 3.14 can be expressed as:

\[ (^{234}\text{U}) = (^{238}\text{U}) + (^{234}\text{U})_{u} \]

and 3.16 becomes

\[ (^{234}\text{U})_{u}^{0} = (^{234}\text{U})^{0} - (^{238}\text{U}) \]

Substituting 3.18 into 3.15 yields:

\[ (^{234}\text{U})_{u} = [(^{234}\text{U})^{0} - (^{238}\text{U})] e^{-\lambda_{234}t} \]

Substituting 3.19 into 3.17, we have:

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

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$^\dagger$), hence we divide by the activity of $^{238}\text{U}$:

\[ \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) = 1 + \left(\frac{(^{234}\text{U})^{0} - (^{238}\text{U})}{^{238}\text{U}}\right) e^{-\lambda_{234}t} \]

\[ \dagger \text{In the case of } ^{238}\text{U and } ^{234}\text{U the } \alpha \text{ energies are quite similar (4.2 and 4.7 MeV). Interestingly, the energies of } \alpha \text{ particles are approximately inversely proportional to half-life. From our discussion of } \alpha \text{ decay, you should be able to surmise why.} \]
or since $^{238}U = ^{238}U^o$:

$$\left(\frac{^{234}U}{^{238}U}\right) = 1 + \left\{\left(\frac{^{234}U}{^{238}U}\right)^o - 1\right\} e^{-\lambda_{234}t} \quad 3.22$$

Thus the present activity ratio can be expressed in terms 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 $\left(\frac{^{234}U}{^{238}U}\right)$ ratio of an ancient coral, and assume that the seawater in which that coral grew had $\left(\frac{^{234}U}{^{238}U}\right)$ the same as modern seawater (1.14), the age of the coral can be obtained by solving equation 3.22 for $t$. The age determined is the time since the material last reached isotopic equilibrium with seawater.

The application of $^{234}U/^{238}U$ 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.

$^{230}Th-^{238}U$ 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 7.06:

$$\left(\frac{^{230}Th}{^{238}U}\right) = \left(\frac{^{230}Th}{^{238}U}\right)^o e^{-\lambda_{230}t} \quad 3.23$$

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

Figure 3.12. (a) $^{230}Th-^{238}U$ isochron diagram. The $\left(\frac{^{238}U}{^{232}Th}\right)$ of the source is given by the intersection of the isochron with the equiline. (b) shows how the slope changes as a function of time. After Faure (1986).
(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.)

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 (232-Th/230-Th) is known (from, for example, zero-age sediment at the seawater-sediment interface), equation 7.14 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-Th/232-Th ratios in a series of sediments down a core, sedimentation rate can be determined. Various curves of (230-Th/232-Th) vs. depth suggest various processes, as is illustrated in Fig. 3.11.

In systems where we can assume (234-U) = (238-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 7.05 and from it derive:

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

(3.25)

(the tricks to this derivation are to make the approximations \( \lambda_{230} = \lambda_{238} = \lambda_{230} = \lambda_{238} = 1 \); i.e., assume \( \lambda_{238} = 0 \); 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 3.12.

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

\[ t = \frac{z}{s} \]

and 3.25 becomes:

\[
\left( \frac{230}{232}Th \right) = \left( \frac{230}{232}Th \right) e^{-\lambda_{230}z/s} + \left( \frac{238}{232}Th \right) \left( 1 - e^{-\lambda_{230}z/s} \right)
\]

(3.27)

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. 3.27 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 3.27 is solved in that instance by less direct means. For example, consider the data shown in Figure 3.13 on a Pacific manganese nodule reported by Huh and Ku (1984). In this plot of log \((230\text{Th} / 232\text{Th})\) 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 3.27 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 have 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 \(230\text{Th}\). The relevant equation is:

![Image](https://example.com/image.png)

### Figure 3.13. \(230\text{Th}/232\text{Th}\) as a function in depth in a manganese nodule from MANOP Site H. After Huh and Ku (1984).

\[
\frac{230\text{Th}}{234\text{U}} = \frac{1 - e^{-\lambda_{230}t}}{\lambda_{230} - \lambda_{234}} \left[ \frac{1}{\lambda_{230} - \lambda_{234}} \right] \left( 1 - e^{-(\lambda_{230} - \lambda_{234})t} \right)
\]

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 3.12. After the system closes, \(238\text{U}\) and \(230\text{Th}\) will begin to come to radioactive equilibrium (either \(238\text{U}\) 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 *equi-point*. As \(t\) approaches infinity, the exponential term approaches 1 and:

\[
\lim_{t \to \infty} \frac{230\text{Th}}{232\text{Th}} = \frac{238\text{U}}{232\text{Th}}
\]

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 \(\alpha\) 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 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 \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \) and \( \frac{^{238}\text{U}}{^{232}\text{Th}} \) ratios of zero-age rocks. Measurement of \( \frac{^{230}\text{Th}}{^{232}\text{Th}} \) ratios together with \( \frac{^{231}\text{Pa}}{^{235}\text{U}} \) in young volcanic rocks, such as those of mid-ocean ridges and oceanic islands such as Hawaii, allows inferences to be made about rate and extent of melting in the mantle. We’ll examine this in detail in a later lecture.

\( ^{226}\text{Ra} \) Dating

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

Figure 3.14 shows \( ^{230}\text{Th}–^{238}\text{U} \) and \( ^{226}\text{Ra}–^{230}\text{Th} \) mineral isochrons obtained on mineral separates, groundmass, and a whole rock sample from the Castle Creek andesite of Mt. St. Helens. Conventional dating techniques (\(^{14}\text{C}\)) indicate this lava is only about 2000 years old, but both the \( ^{230}\text{Th}–^{238}\text{U} \) and \( ^{226}\text{Ra}–^{230}\text{Th} \) give much older ages. The \( ^{230}\text{Th}/^{238}\text{U}/^{232}\text{Th} \) 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 \( ^{226}\text{Ra}–^{230}\text{Th} \) is less precise because the slope is only slightly less than 1, and all samples seem to contain excess \( ^{226}\text{Ra} \). 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 \( ^{230}\text{Th}–^{238}\text{U} \) and \( ^{226}\text{Ra}–^{230}\text{Th} \) ages may reflect changes in melt composition, perhaps due to assimilation of country rock or addition of a Ra-rich gas or fluid phase to the magma. \( ^{230}\text{Th}–^{238}\text{U} \) and \( ^{226}\text{Ra}–^{230}\text{Th} \) 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 \( ^{230}\text{Th}–^{238}\text{U} \) age of 6±4 ka on the 1982 dacite. One possible interpretation of this is that when the most recent eruptive stage 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.

\( ^{210}\text{Pb} \) Dating

\( ^{210}\text{Pb} \) 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 \( ^{210}\text{Pb} \) in their upper intervals.

Figure 3.14. \( ^{230}\text{Th}–^{238}\text{U} \) and \( ^{226}\text{Ra}–^{230}\text{Th} \) mineral isochrons for the Castle Creek andesite of Mt. St. Helens. \(^{14}\text{C}\) and tree ring chronology indicates this lava was erupted 1700-2200 years ago. After Volpe and Hammond (1991).
We can write an equation analogous to the one equation we wrote for unsupported $^{230}$Th (3.23):

$$(^{210}Pb)_u = (^{210}Pb)_u^o e^{-\lambda_{210}t}$$  \hspace{1cm} 3.30

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

$$ (^{210}Pb)_u = (^{210}Pb)_u^o e^{-\lambda_{210}z/s}$$  \hspace{1cm} 3.31

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 that 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 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 3.31 for $s$, the sedimentation rate.

This can be done as follows. By taking the log of equation 3.31, we have

$$\ln(^{210}Pb)_u = \ln(^{210}Pb)_u^o + \frac{-\lambda_{210}z}{s}$$  \hspace{1cm} 3.32

Equation 3.32 is the equation of a straight line on a plot of $\ln(^{210}Pb)$ vs depth, where $\ln(^{210}Pb)^o$ 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 3.156 illustrates an example calculated in this manner.
REFERENCES AND SUGGESTIONS FOR FURTHER READING