Lecture 8 Spring 2000

GEOCHRONOLOGY IV

THE U-TH-PB SYSTEM

U and Th are, strictly speaking, rare earth elements, though 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 may have a valence of +6. In six-fold coordination, U^{4+} has an ionic radius of 0.89 Å[1]; U^{6+} has an ionic radius of 0.73 Å in 6-fold and 0.86 in 8-fold coordination. Th has an ionic radius of 0.94Å. These radii are not particularly large, but the combination of relatively 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, 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 oxyanion complex, UO_2^{z-}. 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 ($[La,Ce,Th]PO_4$) which concentrations Th more than U. These elements may be also concentrated in other accessory phases such as apatite ($Ca_5(PO_4)_3(OH)$) and sphene ($CaTi(SiO_4)OH$). But zircon is by far and away the most important from a geochronological perspective. Both U and Th are highly refractory elements, and we can therefore expect the Th/U ratio of the Earth to be the same as chondrites. 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 geochemistry of Pb is not 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 much of the Earth's Pb is in the core (we cannot, however, 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 1.19Å in 6-fold coordination and 1.29Å 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 reasonably readily for K (ionic radius 1.33), particularly in potassium feldspar. 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

---

[1]In eight-fold coordination, the effective ionic radius of U^{4+} is 1.00Å. In zircon, a mineral which highly concentrations 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.

chloride and sulfide complexes become somewhat soluble, and Pb is readily transported in hydrothermal solutions.

Though 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 8.1 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:

$$^{207}Pb^{*} = {}^{235}U\left(e^{\lambda_5 t} - 1\right) \qquad 8.1$$

$$^{206}Pb^{*} = {}^{238}U\left(e^{\lambda_8 t} - 1\right) \qquad 8.2$$

where the asterisk designates *radiogenic* ^{206}Pb and ^{207}Pb, and λ_5 and λ_8 are the decay constants for ^{235}U and ^{238}U respectively. If we divide 8.1 by 8.2, we have:

$$\left(\frac{^{207}Pb^{*}}{^{206}Pb^{*}}\right) = \frac{^{235}U\left(e^{\lambda_5 t} - 1\right)}{^{238}U\left(e^{\lambda_8 t} - 1\right)} \qquad 8.3$$

Now if the ratio of the U isotopes is everywhere the same (at the present day), 8.3 can be written as

$$\frac{^{207}Pb^{*}}{^{206}Pb^{*}} = \frac{1\left(e^{\lambda_5 t} - 1\right)}{137.88\left(e^{\lambda_8 t} - 1\right)} \qquad 8.4$$

The nice thing about equation 8.4 is that the only variable on the right hand side is time; in other words the $^{207}Pb^*/^{206}Pb^*$ is a function only of time.

TABLE 8.1. Parameters of the U-Th-Pb System

Parent	Decay Mode	λ	Half-life	Daughter	Ratio
^{232}Th	α,β	$4.948 \times 10^{-11} y^{-1}$	$1.4 \times 10^{10} y$	^{208}Pb, 8 ^{4}He	$^{208}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{235}U	α,β	$9.849 \times 10^{-10} y^{-1}$	$7.07 \times 10^{8} y$	^{207}Pb, 7 ^{4}He	$^{207}Pb/^{204}Pb$, $^{3}He/^{4}He$
^{238}U	α,β	$1.551 \times 10^{-10} y^{-1}$	$4.47 \times 10^{9} y$	^{206}Pb, 6 ^{4}He	$^{206}Pb/^{204}Pb$, $^{3}He/^{4}He$

In practice what this means is that the age is independent of the parent/daughter ratio; i.e., we 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 8.3 using ^{232}Th and ^{208}Pb instead of ^{235}U and ^{207}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}U-^{206}Pb, ^{235}U-^{207}Pb, ^{232}Th-^{208}Pb, and ^{207}Pb-^{206}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}Th-^{208}Pb system, which might prove useful if you could separate only 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 $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ is proportional to age since:

$$\frac{\Delta\left(^{207}Pb/^{204}Pb\right)}{\Delta\left(^{206}Pb/^{204}Pb\right)} = \frac{1\left(e^{\lambda_5 t} - 1\right)}{137.88\left(e^{\lambda_8 t} - 1\right)} \qquad 8.5$$

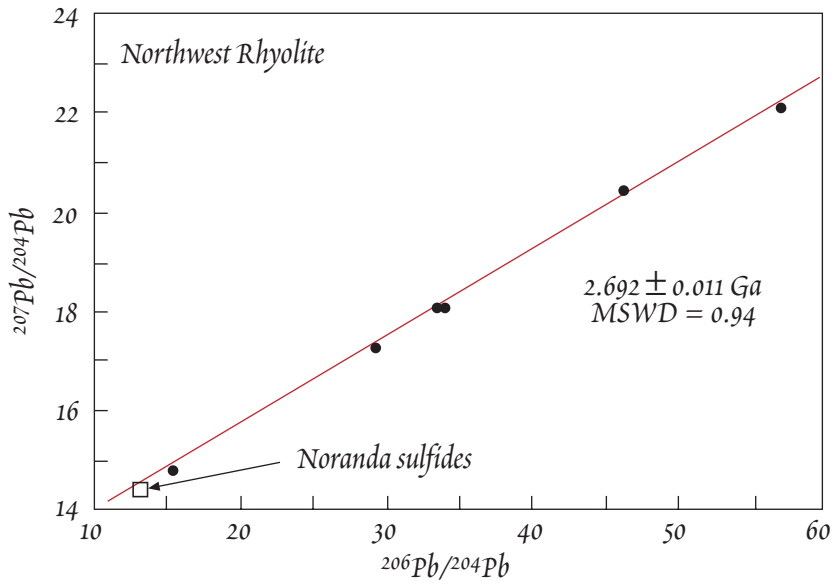


Figure 8.1. A Pb-Pb isochron obtained on volcanic rocks hosting the Noranda (Quebec) Cu-Zn sulfide deposit.

Note that equation 8.5 is very similar to equation 8.4. We would use 8.4 when either 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 8.5 when initial Pb is present in significant quantities and has an unknown composition. Figure 8.1 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 fluid dynamics.

The U-Pb system achieves it 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, though 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 ^{207}Pb and

^{206}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 $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$. The basis of this is as follows. We write the usual growth equations for ^{206}Pb and ^{208}Pb.

$$^{206}Pb/^{204}Pb = \left(^{206}Pb/^{204}Pb\right)_0 + {}^{238}U/^{204}Pb\left(e^{\lambda_8 t} - 1\right) \quad 8.6$$

$$^{208}Pb/^{204}Pb = \left(^{208}Pb/^{204}Pb\right)_0 + {}^{232}Th/^{204}Pb\left(e^{\lambda_2 t} - 1\right) \quad 8.7$$

(remember that μ is used to designate the $^{238}U/^{204}Pb$ ratio). Subtracting the initial ratio from each side of each equation and dividing 8.7 by 8.6 we have

$$\frac{\Delta\left(^{208}Pb/^{204}Pb\right)}{\Delta\left(^{206}Pb/^{204}Pb\right)} = \frac{^{232}Th/^{204}Pb\left(e^{\lambda_2 t} - 1\right)}{^{238}U/^{204}Pb\left(e^{\lambda_8 t} - 1\right)} \quad 8.8$$

or

$$\frac{\Delta\left(^{208}Pb/^{204}Pb\right)}{\Delta\left(^{206}Pb/^{204}Pb\right)} = \frac{\kappa\left(e^{\lambda_2 t} - 1\right)}{\left(e^{\lambda_8 t} - 1\right)} \quad 8.9$$

where κ is used to designate the $^{232}Th/^{238}U$ ratio. (using μ to designate the $^{238}U/^{204}Pb$ ratio. Thus the parent-daughter ratio of the Th-Pb system is the product μκ.

Equation 8.9 tells us that the slope of a line on a plot of $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ is proportional to time and κ, provided that κ does not vary. If we can calculate *t* from the corresponding $^{207}Pb/^{204}Pb$–$^{206}Pb/^{204}Pb$ slope, we can solve 8.9 for κ. If, however, κ varies linearly with μ, a straight line will still result on the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot and our estimate of κ will be incorrect.

References and Suggestions for Further Reading

Dickin, A. 1995. *Radiogenic Isotope Geochemistry*. Cambrige: Cambridge University Press.
DePaolo, D. J. 1988. *Neodymium Isotope Geochemistry, an Introduction*, Berlin: Springer-Verlag.