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Introduction to U-series Geochemistry

**Bernard Bourdon¹, Simon Turner²,
Gideon M. Henderson³ and Craig C. Lundstrom⁴**

*¹Laboratoire de Géochimie et Cosmochimie
IPGP-CNRS UMR 7579*

*4 Place Jussieu
75252 Paris cedex 05, France*

*²Department of Earth Sciences
Wills Memorial Building
University of Bristol
Bristol, BS8 1RJ, United Kingdom*

*³Department of Earth Sciences
University of Oxford
Parks Road
Oxford, OX1 3PR, United Kingdom*

*⁴Department of Geology
University of Illinois at Urbana Champaign
245 NHB, 1301 W. Green St.
Urbana, Illinois, 61801, U.S.A.*

1. NEW DEVELOPMENTS IN U-SERIES GEOCHEMISTRY

During the last century, the Earth Sciences underwent two major revolutions in understanding. The first was the recognition of the great antiquity of the Earth and the second was the development of plate tectonic theory. These leaps in knowledge moved geology from its largely descriptive origins and established the modern, quantitative, Earth sciences. For any science, and particularly for the Earth sciences, time scales are of central importance. Until recently, however, the study of time scales in the Earth Sciences was largely restricted to the unraveling of the ancient history of our planet. For several decades, Earth scientists have used a variety of isotope chronometers to unravel the long-term evolution of the planet. A fuller understanding of the physical and chemical processes driving this evolution often remained elusive because such processes occur on time scales ($1-10^5$ years) which are simply not resolvable by most conventional chronometers. The U-series isotopes, however, do provide tools with sufficient time resolution to study these Earth processes. During the last decade, the Earth sciences have become increasingly focused on fundamental processes and U-series geochemistry has witnessed a renaissance, with widespread application in disciplines as diverse as modern oceanography and igneous petrology.

The uranium and thorium decay-series contain radioactive isotopes of many elements (in particular, U, Th, Pa, Ra and Rn). The varied geochemical properties of these elements cause nuclides within the chain to be fractionated in different geological environments. While the varied half-lives of the nuclides allows investigation of processes occurring on time scales from days to 10^5 years. U-series measurements have therefore revolutionized the Earth Sciences by offering some of the only quantitative constraints on time scales applicable to the physical processes that take place on the Earth.

The application of U-series geochemistry to the Earth Sciences was thoroughly

summarized in 1982 and again in 1992 with the two editions of “Uranium-series disequilibrium, Applications to Earth, Marine and Environmental Sciences,” edited by M. Ivanovich and R.S. Harmon. It is now over a decade since the publication of the second of those volumes, and a great deal of new U-series work has been conducted. Much of this new work has relied on the development of new analytical techniques. These advances began in the late 1980’s with the development of thermal ionization mass spectrometric techniques for the measurement of U, Th, Pa and Ra including the ability to measure isotope ratios greater than 10^5 (see Goldstein and Stirling 2003). More recently, multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has further improved the sensitivity, speed, and possibly precision of U-series measurements. Advances have also been made in the chemical separation techniques for U-series nuclides. The analytical chemistry of these elements has been known since the 1950’s but adapting these techniques to geological samples with a complex matrix occurred more recently. Efficient techniques involving actinide-specific resin have also only been implemented in the last 10 years.

The need to understand the processes operating on Earth, coupled to recent analytical advances, have ensured that the U-series nuclides have seen widespread application since the last Ivanovich and Harmon book (1992). This volume does not set out to repeat material in that book, but is an attempt to bring together the advances in the subject over the last ten years, highlighting the excitement and rapid expansion of U-series research. The scope of the various chapters in this book is laid out at the end of this introduction. The remainder of this chapter introduces some of the basic concepts of U-series geochemistry, the chemical behavior of the elements involved, and the half-lives of the U- and Th-series nuclides. This chapter is not intended to be an exhaustive summary of the nuclear or radio-chemistry of the U-series nuclides and for additional information, the reader is referred to Ivanovich (1992).

2. U AND Th RADIOACTIVE DECAY SERIES

2.1 Basic concepts

There are three naturally occurring radioactive decay chains; each starts with an actinide nuclide (^{238}U , ^{235}U and ^{232}Th) having a long half-life ($t_{1/2} > 0.7$ Gyr) and ends with a stable isotope of lead (Fig. 1). In between is a series of nuclides with half-lives ranging from microseconds to hundreds of thousands of years. U-series disequilibrium refers to any fractionation between different members within a decay chain resulting in a non-steady state condition (steady state is known as secular equilibrium as explained below). The members of the decay chain most commonly studied are ^{234}U ($t_{1/2} = 245$ ka), ^{230}Th ($t_{1/2} = 76$ ka) and ^{226}Ra ($t_{1/2} = 1599$ yr) in the ^{238}U decay chain and ^{231}Pa ($t_{1/2} = 33$ ka) in the ^{235}U decay chain. The relatively long half-lives make these nuclides particularly suited to investigating many geological processes that occur over time scales similar to their decay period. An important characteristic of these decay-chains is that the ultimate parent isotope (e.g., ^{238}U) is radioactive and has a much longer half-life than all the intermediate nuclides.

The equation of decay for a given number of atoms, N , of a given nuclide can be written as follows:

For the parent nuclide:

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \quad (1) \quad \text{📄}$$

For all the intermediate nuclides of interest:

$$\frac{dN_i}{dt} = -\lambda_i N_i + \lambda_{i-1} N_{i-1} \quad (2)$$

where the decay constant, λ is related to the half-life by $\lambda = \ln 2/t_{1/2}$ and subscript $i - 1$ refers to the next nuclide higher up in the decay chain. These equations were first solved by Bateman (1910) and are illustrated here with reference to the first two nuclides of a decay chain. The appendix provides a general solution using a Laplace transform that can also be used in the case of linear box models which track changes in U-series nuclide concentrations.

The concept most commonly used when dealing with radioactive nuclides is activity. By definition, the activity of a number of atoms of a nuclide is the number of decay events per unit of time. The law of radioactivity tells us that this activity is equal to the decay constant times the number of atoms. The units for activities are given in **Table 1**.

If we solve Equations (1) and (2) for the first two nuclides in a decay chain, we obtain (Bateman 1910):

$$N_1 = N_1^0 e^{-\lambda_1 t} \quad (3a)$$

and

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \quad (3b)$$

where N_1^0 and N_2^0 are the number of atoms of nuclides 1 and 2 at $t = 0$. In Equation (3b), the first term represents the ingrowth of N_2 by decay of N_1 and the second term represents the decay of N_2 initially present. In situations where there is no initial N_2 , the second term can be dropped. These equations enable one to estimate the evolution of activity as a function of time starting with an initial activity ratio $\lambda_2 N_2^0 / \lambda_1 N_1^0$.

If we consider this pair of radioactive isotopes for time scales greater than six half-lives of N_2 , Equation (3b) can be simplified. Because each decay series starts with a long-lived parent, it is commonly the case that $\lambda_1 \ll \lambda_2$. In this case, after six half lives, $e^{-\lambda_2 t}$ approaches zero and can be removed from the equation. For time scales such that $6T_2, \ll t \ll T_1$ then



$$N_2 \approx \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t} \approx \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1 \quad (4)$$

With the second simplification reflecting the fact that insignificant decay of N_1 will have occurred because $t \ll T_1$. Because $\lambda_1 \gg \lambda_2$, Equation (4) can be further simplified because $\lambda_2 - \lambda_1 \approx \lambda_2$ so that:

$$N_2 \approx \frac{\lambda_1}{\lambda_2} N_1 \quad (5)$$

This situation, when the activity of the higher atomic number nuclide, the “parent,” is equal to the activity in the next step in the chain, the “daughter,” is known as radioactive equilibrium (also referred to as secular equilibrium). Thus, secular equilibrium between a parent and a daughter implies an activity ratio of 1.

A useful analogy for understanding secular equilibrium is visualizing a decay chain as a series of pools of water (**Fig. 2**). These pools eventually lead to a continuously filling

pool representing a stable isotope of lead (either ^{206}Pb , ^{207}Pb or ^{208}Pb). Over the timescale relevant to U-series disequilibria studies, the parent nuclides ^{238}U , ^{235}U , and ^{232}Th all have half-lives much longer than any of the other isotopes in the chain. Therefore, the flux of radioactive decay (the activity) coming from the top of the chain remains essentially constant over the time relevant to study of the short-lived members. Thus, we can assume the flux of water coming out of the top pipe in Figure 2 is constant. In this schematic model, each tank represents an individual nuclide and has a spout of size proportional to the decay constant of that nuclide. In steady state, the flux of water through each tank in the system will be constant when the hydraulic head within a tank increases to equalize the flux in and out of the tank. Thus, the flux of water through a set of tanks is analogous to the activity (in Bq/g or dpm/g) of all nuclides in the chain in secular equilibrium. In both the decay chain and water analogy, flow occurs only in one direction and the change in any pool's depth (or nuclide concentration) does not affect the pool above it. Because the activity of any nuclide is equal to λN , the amount of water in a given tank is proportional to the number of atoms of a nuclide at secular equilibrium. In other words, a tank with a small spout having a large volume of water is analogous to a long-lived nuclide that has a relatively high concentration of atoms in secular equilibrium. In contrast, a tank with a large spout (which results in small steady-state amount of water) is analogous to a short-lived nuclide that has a lower concentration of atoms in secular equilibrium.

2.2 Disequilibrium between U-series nuclides

Processes that fractionate nuclides within a chain produce parent-daughter disequilibrium; the return to equilibrium then allows quantification of time. Because of the prescribed decay behavior, U-series disequilibria can be used for geochronology or for examining the rates and time scales of any dynamic processes which induces fractionation. In many cases, the direction of disequilibrium (activity ratios above or below one) provides a powerful means of tracing specific processes.

Based on Equation (3), in the case of a system where there is an initial disequilibrium in the chain (namely: $\lambda_1 N_1 \neq \lambda_2 N_2$), it is generally stated that the system returns to secular equilibrium after \approx six half-lives of the daughter. The wide variety of parent-daughter pairs allows disequilibria to provide temporal constraints over a wide range in time scales (Fig. 3).

One of the behaviors of the system not easy to grasp is why the return to equilibrium is mostly controlled by the half-life of the daughter nuclide? This can be investigated by considering the $^{226}\text{Ra}/^{230}\text{Th}$ system (^{230}Th decays to form ^{226}Ra with a half-life of 1599 years). If fractionation by some process results in an activity ratio greater than 1 at time $t = 0$, the equation describing the return to equilibrium, as shown above, is:

$$^{226}\text{Ra} = \frac{\lambda_{\text{Th}}}{\lambda_{\text{Ra}} - \lambda_{\text{Th}}} ^{230}\text{Th}_0 \left(e^{-\lambda_{\text{Th}}t} - e^{-\lambda_{\text{Ra}}t} \right) + ^{226}\text{Ra}_0 e^{-\lambda_{\text{Ra}}t} \quad (6)$$

If we now take into account the fact that since $\lambda_{\text{Ra}} \gg \lambda_{\text{Th}}$, this equation can be rewritten using activity ratios as:

$$\left[\left(\frac{^{226}\text{Ra}}{^{230}\text{Th}} \right) - 1 \right] = \left[\left(\frac{^{226}\text{Ra}}{^{230}\text{Th}} \right)_i - 1 \right] e^{-\lambda_{\text{Ra}}t} \quad (7)$$

The quantity in brackets represents the excess of ^{226}Ra relative to ^{230}Th . It follows that after six half-lives of ^{226}Ra , the term $e^{-\lambda t}$ will be equal to $1/2^6 = 1/64$ which means that $^{226}\text{Ra}/^{230}\text{Th}$ activity ratios will be equal to 1 within approximately 1%. Now consider

the case of a system where there is no initial ^{226}Ra . The same equation applies except that in this case $(^{226}\text{Ra}/^{230}\text{Th})_i = 0$. Since there is no initial ^{226}Ra , how is it possible that the half-life of ^{226}Ra controls the return to secular equilibrium for this system? In fact, the system is also controlled by the half-life of ^{230}Th and the issue boils down to the concept of activity. In the case of a system with no initial ^{226}Ra , there are $\lambda_{\text{Th}}N_{\text{Th}}\Delta t$ atoms of ^{226}Ra produced during Δt . If we assume that ^{226}Ra is not decaying, it will take $\Delta t = 1/\lambda_{\text{Ra}}$ to accumulate enough ^{226}Ra atoms to reach the condition for secular equilibrium $N_{\text{Ra}} = \lambda_{\text{Th}}N_{\text{Th}}/\lambda_{\text{Ra}}$. Because ^{226}Ra is decaying, it effectively takes more time than $1/\lambda_{\text{Ra}}$ to return to secular equilibrium (see Fig. 4). This illustrates that the return to secular equilibrium is limited by the decay of ^{226}Ra .

2.3 Processes creating disequilibria between U- series nuclides

The previous section showed that if the decay chain remains undisturbed for a period of approximately 6 times the longest half-lived intermediate nuclide then the chain will be in a state of secular equilibrium (i.e., equal activities for all the nuclides). The key to the utility of the U-series is that several natural processes are capable of disrupting this state of equilibrium.

Two types of mechanism need to be distinguished here. Firstly, each element has distinct chemical properties and thus, the U-series nuclides can become fractionated during processes that discriminate chemical behavior: phase change, partial melting, crystallization, partitioning, dissolution, adsorption, degassing, oxidation/reduction, complexation. For example, during crystallization of a mineral from a melt, the ($^{230}\text{Th}/^{238}\text{U}$) activity ratio in the mineral will be:

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_{\text{mineral}} = \frac{D_{\text{Th}}}{D_{\text{U}}}\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_{\text{melt}} \quad (8)$$

where D_{Th} and D_{U} are the mineral/melt partition coefficients. Provided that the partition coefficients are different, the ^{230}Th - ^{238}U activity ratio in the mineral will be distinct from that of the melt. This process is generally called fractionation but for the U-series nuclides, the result is transitory disequilibrium.

Secondly, fractionation can also take place as a result of radioactive decay, especially in the low-temperature environment, and these effects are generally described as recoil effects. To illustrate the physics of recoil, we choose for example the decay of ^{238}U :



The resulting particles (^{234}Th and ^4He) are charged and emitted with finite kinetic energy. In order to estimate this energy, it is necessary to undertake an energy balance for decay that is analogous to the energy balance for a chemical reaction. During decay, we assume that both total momentum and kinetic energy are conservative. If we also assume that the nucleus was initially at rest:

$$Q = \Delta Mc^2 = E_c^{\text{Th}} + E_c^{\alpha} \quad (10a)$$

$$M_{\alpha} V_{\alpha} = M_{\text{Th}} V_{\text{Th}} \quad (10b)$$

where E_c , M and V are the kinetic energy, the mass and the velocity of the daughter nuclide and the helium atom. From these equations, the kinetic energy of the daughter nuclide can be shown to be a small fraction of the total energy release Q :

$$E_c^{\text{Th}} = Q \frac{M_\alpha}{M_\alpha + M_{\text{Th}}} \quad (11)$$

The effect of recoil is three-fold: firstly, the recoil atom is displaced from the site where it was located. It can thus be ejected directly into an adjacent phase. The displacement distance is approximately 40 nm, depending on the substrate (Harvey 1962) and is known as the range. It can be estimated using the following equation:

$$\delta = \frac{(M_{\text{Th}} + M_a)(M_a E_c^{\text{Th}} K)(Z_{\text{Th}}^{2/3} + Z_a^{2/3})^{1/2}}{(M_{\text{Th}} Z_{\text{Th}} Z_a \rho)} \quad (12)$$

where Z_{Th} is the atomic number of ^{234}Th , and Z_a and M_a denotes the atomic number and mass of the absorber, K is a constant (6.02) and ρ is the density. E is given here in keV while δ is in nanometers. Secondly, the site is damaged by the α -particle, which makes the daughter more prone to subsequent mobilization. Lastly, the atom is displaced from its original site and can also be more easily removed. It is difficult to determine which of these processes control the extent to which a daughter nuclide is more readily mobilized than its parent. Nevertheless, it is possible to estimate the fraction of daughter nuclides that would be directly ejected by recoil. This calculation was made by Fleischer and Raabe (1975) for plutonium particles and is described below. For a spherical particle with radius r and for a range δ , the fraction of volume that will be affected by recoil into another phase is:

$$f_v = \frac{r^3 - (r - \delta)^3}{r^3} \quad (13)$$

Out of this volume, only half of the particles will be ejected towards the rim of the grain and only a half of those will have trajectories which actually cross the grain boundary (Fig. 5). Thus, for a porous media with porosity ϕ and density ρ_s the number of daughter nuclides ejected per unit of time per unit of mass is:

$$R_N = \rho_s (1 - \phi) \frac{r^3 - (r - \delta)^3}{4r^3} \lambda N \quad (14)$$

where λ and N are the decay constant and number of atoms per unit of mass of the parent nuclide.

Such alpha-recoil plays a fundamental role in fractionating the nuclides from one another in the low-temperature environment. During igneous processes, on the other hand, alpha recoil is probably not important in the generation of disequilibria (^{230}Th , ^{226}Ra , and ^{231}Pa). Beattie (1993) pointed out that the time scale of annealing of alpha decay damage at high temperatures was much shorter than the time scale of decay of these nuclides.

One of the important theoretical advances in the last decade was the development of models of disequilibria generation based on the dynamic process of a fluid moving relative to a solid. McKenzie (1985) was the first to show how radioactive disequilibrium can be created if U-series nuclides have different residence times within a melting column during two-phase flow. This model was developed to simulate mantle melting beneath mid-ocean ridges but in reality applies to any earth process where U-series nuclides move at different velocities due to exchange between the fluid and the solid. In this model, different elements will have different effective velocities based on how they partition between the moving fluid and a solid. This situation could be a magma

exchanging with mantle minerals or could be groundwater exchanging with the surfaces of minerals

Consider a steady-state situation of a parent-daughter pair within a fluid flowing through, and chemically exchanging with, mineral grains in a column of length x . Assume the mineral grains and the fluid are homogenous and in chemical equilibrium with each other and the U-series nuclides in both phases are in secular equilibrium ($A_{\text{parent}} = A_{\text{daughter}}$). If a continuous stream of the fluid is fed into the column, elements that do not partition into the solid ($D^{\text{solid/liquid}} = 0$) will move at the velocity of the fluid whereas elements that partition into the solid, even slightly, will travel more slowly. Thus, if an element favors the fluid phase, it will have a shorter residence time in the column than elements which favor the solid phase. Once it has achieved steady state this system will have no effect on the concentration of non-radioactive elements in the fluid leaving the column and they will equal the inputs to the column. Nevertheless, this situation can have profound effects on short-lived nuclides within a decay chain, even once steady state has been achieved.

If the parent nuclide, for instance, has a greater preference for the solid phase than the daughter it will have a correspondingly greater residence time in the column. The daughter will, therefore, effectively “see” more parent than in a static situation where there is no differential movement of nuclides. For instance the total amount of the parent in the column at a given time will be $A_{\text{parent}}x/w_{\text{eff-parent}}$ where $w_{\text{eff-parent}}$ is the effective velocity of the parent. In contrast, the number of daughter atoms in the column will be $A_{\text{daughter}}x/w_{\text{eff-daughter}}$. If $w_{\text{eff-daughter}} > w_{\text{eff-parent}}$, then $A_{\text{parent}}x/w_{\text{eff-parent}}$ will be greater than $A_{\text{daughter}}x/w_{\text{eff-daughter}}$ and the daughter will be effectively supported by a greater amount of parent than that in secular equilibrium.

3. CHEMISTRY AND GEOCHEMISTRY OF THE U-SERIES NUCLIDES

Knowledge of the chemical properties of the U-series nuclides is essential to any understanding of fractionation within the U-series chains. The nuclides of particular geochemical interest are ^{238}U , ^{234}U , ^{234}Th , ^{230}Th , ^{226}Ra , ^{231}Pa , ^{222}Rn and ^{210}Pb (Table 1). In this section, we review some basic chemical properties of these nuclides. Much of this material can also be found in Ivanovich and Harmon (1992).

Most of the U-series nuclides are metals. Five of them belong to the actinide family corresponding to the filling of the internal orbitals while the orbitals 7s are filled. A sixth, Ra is an alkali earth and shares some chemical properties with other alkali earths, particularly the heavier ones (Sr and Ba), while a seventh, Rn, is a noble gas. The filling of the orbitals prescribes the possible oxidation states of these elements. Their preferred oxidation state is obtained when the electronic configuration is that of the closest rare gas (Rn).

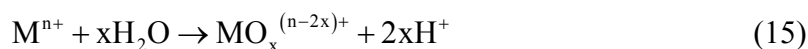
An important chemical property of relevance to geochemistry is the ionic radii in different coordinations. In general, Th has a larger ionic radius than U despite U having the larger atomic number; this is a phenomenon known as the actinide contraction and is similar to the well-known lanthanide contraction. This means that in general the heavier actinide (e.g., U) should be more easily be accommodated in minerals than the lighter ones (e.g., Th) at a given oxidation state. There are exceptions to this as explained by Blundy and Wood (2003).

The diffusion of U and Th within a solid is, in general, very slow due to their large size and charge (Van Orman et al. 1998). Even at mantle temperatures, it is expected that a solid will not fully equilibrate with the surrounding phases (fluid, melt or other solid

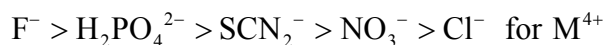
phases) if solid diffusion controls the equilibration. As yet, there have been no direct determinations of diffusion coefficients for any other decay chain element.

From a geochemical viewpoint, U is an incompatible lithophile and refractory element. U exists in three distinct oxidation states in nature (Calas 1978) but the most common are U^{4+} ([Rn] $5f^2$) and U^{6+} ([Rn]). The most reduced form (metal) is never found in natural environments. At the surface of the earth, U is dominantly in the U^{6+} form. However, in a reducing environment, it will be in the U^{4+} state where it is insoluble and therefore generally far less mobile than U(VI). In the mantle, U is thought to occur in the U^{4+} state, except in the subduction zone environment where the oxygen fugacity is thought to be higher (as discussed by Turner et al. 2003).

In aqueous solutions, the chemistry of U and Th is highly dependent on their ability to form complexes with other ions in solution. In non-complexing acid media, they generally exists as M^{n+} . At higher oxidation states (e.g., U^{6+}), the cations will react with water, a reaction known as hydrolysis:



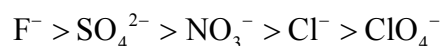
U^{6+} in the aqueous solutions is thus present as the uranyl ion $(UO_2)^{2+}$. As pH increases, the form of these ions evolves to $M(OH)^{(n-1)+}$ or $MO_xOH^{(n-2x-1)+}$. In a non-complexing media, the limitation to solubility is generally the hydroxide form (e.g., $Th(OH)_4$ or $UO_2(OH)_2$). The mobility of U and Th is largely controlled by their ability to form complexes both with inorganic (F^- , Cl^- , PO_4^{3-} , CO_3^{2-}) and organic ligands. This has been described in detail for Th, U, and Pa (Langmuir 1978; Langmuir and Herman 1980; Guillaumont et al. 1968). In natural environments, depending on the ratio of organic acids to inorganic ligands, the dominant species might be variable. For inorganic ligands, the strongest affinity is obtained with those ligands with the highest charge. The order of affinity for single and double -charge species is:



In general, however, organic ligands such as humic acids have the strongest affinities.

Radium has a distinctive chemistry compared with the actinides since it is an alkali earth (already said). Its large ionic radius (Table 1) makes it incompatible in most minerals although minerals which accommodate Ba generally take up large amounts of Ra (e.g., barite, phlogopite or celsiane, a Ba-rich feldspar). In general, Ra is only slightly soluble compared with Ca or Sr and its solubility is controlled by the concentrations of sulfate or carbonate ions. In many cases, its concentration in natural waters is controlled by recoil from the host rock (see above).

Protactinium is an element with complex behavior. It is part of the actinide family with atomic number ($Z = 91$) between those of U and Th. It generally occurs in the +5 oxidation state such that the +5 ion is slightly smaller than U or Th. The +4 oxidation state also exists but is generally thought to be metastable, at least in solutions. The +5 oxidation state of protactinium makes its properties in solutions similar in behavior to high field strength element such as Nb and Ta but its ionic radii is very different. This similarity of properties has mostly been noted in the case of aqueous solutions but their respective behavior in the mantle could be quite different because their ionic radii which controls mineral/melt partitioning are quite different. Pa is insoluble and forms hydroxide complexes or polymers similar to Th (see above). Its affinity for inorganic ligands follows the following order:



Pa has strong affinities for organic complexing ligands and so it is expected that Pa might be more soluble in natural waters where such ligands are present compared with solutions containing only inorganic ligands. For example, it has been shown that the residence time of Pa in seawater is longer than that of Th (Henderson and Anderson 2003). At high pressure and temperature, the behavior of Pa is far less well known than for U and Th because of the difficulties in running experiments. Predictions of its partitioning behavior are given in Blundy and Wood (2003).

Radon is a noble gas and is therefore not readily ionized or chemically reactive. Its properties in terrestrial material will be controlled by its solubility in melt and fluid as well as its diffusion coefficients. Compared with the lighter noble gases, Rn diffuses more slowly and has a lower solubility in water. It will also more readily adsorb onto surface than the lighter rare gases. It can, however be lost by degassing in magmatic systems (Condomines et al. 2003). More information about the behavior of Rn can be found in Ivanovich and Harmon (1992).

Lead is a chalcophile element that is also slightly volatile at high temperature. During mantle melting, in the absence of sulfide phase, it tends to partition into the melt relative to the solid. The solubility of lead in aqueous fluids is very low. However, in the presence of complexing agent such as chloride, sulfide, carbonate or organic ligands, its solubility is enhanced. This is particularly true at higher temperature where lead can be transported in fluids and later precipitate as galena (PbS). With respect to the short-lived ^{210}Pb , The short-lived lead nuclide, ^{210}Pb , is often found in secular equilibrium with ^{226}Ra . Exceptions to this are environments where ^{222}Rn is lost from the system by degassing (e.g., see Condomines et al. 2003), or aqueous systems where the insoluble nature of ^{210}Pb leads to its preferential removal. The speciation of Pb in natural waters is rather complex and heavily depends on the availability of organic complexing agents for which Pb has the highest affinity. In the oceans, Pb has a very short residence (30-150 yrs) and is rapidly scavenged by particles.

4. DETERMINATION OF THE HALF-LIVES OF U-SERIES NUCLIDES

Application of the U-series theory outlined above relies on accurate knowledge of the half-lives of the various nuclides, especially when U-series based chronologies are compared with other chronologies. Considerable analytical effort has gone into careful measurement of the half-lives and most are now known to better than 1%. Recommended half-lives for all U-series nuclides are provided in [Table 2](#). These half-lives have been assessed using one of five techniques as follows:

4.1. Decay of the nuclide itself

The conceptually simplest approach is to take a known quantity of the nuclide of interest, P, and repeatedly measure it over a sufficiently long period. The observed decrease in activity with time provides the half-life to an acceptable precision and it was this technique that was originally used to establish the concept of half-lives (Rutherford 1900). Most early attempts to assess half lives, such as that for ^{234}Th depicted on the front cover of this volume, followed this method (Rutherford and Soddy 1903). This approach may use measurement of either the activity of P, or the number of atoms of P, although the former is more commonly used. Care must be taken that the nuclide is sufficiently pure so that, for instance, no parent of P is admixed allowing continued production of P during the experiment. The technique is obviously limited to those nuclides with sufficiently short half-lives that decay can readily be measured in a realistic timeframe. In

practice, the longest-lived isotopes which can be assessed in this way have half-lives of a few decades (e.g., ^{210}Pb ; Merritt et al. 1957).

4.2. Ingrowth of a daughter nuclide

For longer-lived nuclides where reduction of P itself is not observable, an alternative is to start with a quantity of P which is initially entirely clean of its daughter, D, and to observe the ingrowth of D with time. If D is stable, calculation of the half-life is then straightforward. A stable daughter is not normally the case for U-series nuclides; however α -decay also produces ^4He which is stable. Ingrowth of ^4He has been used, for instance, to assess the half-life ^{226}Ra (Kohman et al. 1949), although care must be taken to allow for additional ^4He production from the decay of ^{222}Rn and subsequent daughters as these start to grow in from ^{226}Ra . Where D is not stable, its ingrowth will be dependent on the product of the mean lives of P and D. If the half-life of D is well known, the ingrowth of D can therefore still be used to assess the half-life of P. This approach was used for most early attempts to assess the half-life of ^{230}Th , via the ingrowth of ^{226}Ra (e.g., Soddy 1931).

4.3. Measurement of specific activity

The half-life of a nuclide can be readily calculated if both the number of atoms and their rate of decay can be measured, i.e., if the activity A and the number of atoms of P can be measured, then λ is known from $A = \lambda P$. As instrumentation for both atom counting and decay counting has improved in recent decades, this approach has become the dominant method of assessing half-lives. Potential problems with this technique include the accurate and precise calibration of decay-counter efficiency; and ensuring sufficient purity of the nuclide of interest. This technique provides the presently used half-lives for many nuclides, including those for the parents of the three decay chains, ^{238}U , ^{235}U (Jaffey et al. 1971), and ^{232}Th .

4.4. Calorimetry


Radioactive decay produces heat and the rate of heat production can be used to calculate half-life. If the heat production from a known quantity of a pure parent, P, is measured by calorimetry, and the energy released by each decay is also known, the half-life can be calculated in a manner similar to that of the specific activity approach. Calorimetry has been widely used to assess half-lives and works particularly well for pure α -emitters (Attree et al. 1962). As with the specific activity approach, calibration of the measurement technique and purity of the nuclide are the two biggest problems to overcome. Calorimetry provides the best estimates of the half lives of several U-series nuclides including ^{231}Pa , ^{226}Ra , ^{227}Ac , and ^{210}Po (Holden 1990).

4.5. Secular equilibrium materials

For materials that have remained a closed system for sufficient time that secular equilibrium has been achieved, the half-lives of nuclides within the decay chain can be calculated from the relationship $\lambda P = \lambda D$. If the atom ratio P/D is measured, and one of the decay constants is well known, then the other can be readily calculated. Limitations on this approach are the ability to measure the atom ratios to sufficient precision, and finding samples that have remained closed systems for a sufficient length of time. This approach has been used to derive the present recommended half lives for ^{230}Th and ^{234}U (Cheng et al. 2000; Ludwig et al. 1992).

In general, the half lives of the U-series nuclides are known with sufficient precision and accuracy that the geological uncertainty in the behavior of the nuclides far outweighs any uncertainty due to poorly known half-lives. The one area where this is not entirely

true is in some applications of absolute chronology where analytical precisions are now sufficiently high (typically at the permil level), and the geochemical system sufficiently well understood, that half-life uncertainty can become a significant fraction of final age uncertainty. The key nuclides presently used for such chronology are ^{234}U , ^{230}Th , and ^{231}Pa and a brief word follows about the recommended half lives for each of these three nuclides:

 **^{234}U .** The history of ^{234}U half-life measurements has recently been summarized by Cheng et al. (2000). For many years a value of $244,500 \pm 1000$ kyr was used, based on the close agreement between two assessments: $244,600 \pm 730$ yrs (De Bievre et al. 1971) and $244,400 \pm 1200$ yrs (Lounsbury and Durham 1971). The Commission on Radiochemistry and Nuclear Techniques assessed the half-lives of several nuclides and, for ^{234}U , reassessed the data of both of these studies together with five other studies and suggested a half-life of $245,500 \pm 1,200$ yrs (Holden 1989). This differs by 4‰ from the commonly used value, a significant difference given present analytical precisions of $\approx 1\%$. Ludwig et al. (1992) used a secular equilibrium approach using a single uraninite material and measured a half-life of $245,290 \pm 140$ yrs. Using a similar approach, but applying it to a wide variety of secular equilibrium materials, Cheng et al. (2000) derived a half-life of $245,250 \pm 490$ yrs, in good agreement with the values of Ludwig et al. (1992) and Holden (1989) This value is therefore the present best estimate of the ^{234}U half live (Table 2). Given the relative ease of measurement of $^{234}\text{U}/^{238}\text{U}$ atom ratios with modern technology, other laboratories have already repeated this secular equilibrium approach (e.g., Bernal et al. 2002) and further refinement of the half-life is possible. Nevertheless, at the time of publication of this volume, the broad agreement between various laboratories suggests that the true value lies within the uncertainty quoted by Cheng et al. (2000)

^{230}Th . The early history of ^{230}Th half-life measurements was summarized by Meadows et al. (1980). These measurements relied on a variety of techniques including daughter ingrowth, calorimetry, and specific activity. The study of Meadows et al. itself used specific activity to derive a value of $75,381 \pm 590$ yrs and a very similar value was recommended by the Commission on Radiochemistry and Nuclear Techniques (Holden, 1989). The uncertainty on this value of some 8‰ is significant given present analytical precisions of $\approx 1\%$. This has led to a recent re-appraisal of the ^{230}Th half-life using a variety of secular equilibrium materials (Cheng et al. 2000). The Cheng et al value of $75,690 \pm 230$ yrs is within error of the Meadows et al. (1980) value but with a two-fold improvement in uncertainty. This value is therefore recommended (Table 2).

^{231}Pa . The most recent measurement of the ^{231}Pa half-life established a value of $32,760 \pm 220$ yrs based on calorimetry (Robert et al. 1969). This value has been accepted as the commonly used value by most laboratories (e.g., Picket et al. 1994; Edwards et al. 1997). The Commission on Radiochemistry and Nuclear Techniques suggest a value of $32,500 \pm 200$ yrs based on a straightforward average of five studies. The difference between these two values, and indeed the uncertainty on either value, is comparable to the best presently achievable measurement precision and so the choice of half-life is not particularly significant. With future improvements of measurement precision, the uncertainty on the ^{231}Pa may become a dominant source of error and a reassessment will be required. Until that time, we recommend a value of $32,760 \pm 220$ (Robert et al., 1969) to enable straightforward comparison with published data.

5. OUTLINE OF THE VOLUME

The chapters of this volume provide detailed reviews of the current understanding in

a range of U-series isotope applications with emphasis on advances made since 1992. Although each chapter has been written to stand alone, cross referencing to other chapters is included where appropriate.

The second chapter (Goldstein and Stirling) gives an overview of developments in analytical techniques over the last decade including, thermal ionization and MC-ICP mass spectrometry. This chapter shows how the development of these new techniques have improved the sensitivity and accuracy of U-series measurements and how new analytical schemes have been developed for measuring Ra and Pa by mass spectrometry. These breakthroughs have greatly aided many of the exciting new advances discussed in subsequent chapters.

In the third chapter, Blundy and Wood discuss the advances made in our understanding of U-series partitioning between minerals and their melts. In the second edition of “Uranium-series disequilibria” (Ivanovich and Harmon 1992), Gascoyne wrote “At present, little information is available on the partitioning of uranium and thorium between crystals and silicate melts.” This picture has radically changed over the past ten years. This has been made possible by both the introduction of ion-microprobe measurements of partition coefficients and by the development of the lattice-strain model allowing prediction of mineral/melt partition coefficients for a wide range of U-series nuclides in the major igneous rock forming minerals.

The next four chapters are concerned with the application of U-series isotopes to magmatic processes within the Earth. Chapter four reviews recent developments in the dating of young volcanic rocks and in the rapidly expanding study of magma residence times and magma chamber processes. These authors emphasize some of the difficulties in interpreting mineral ages but also how these may often provide different, but complimentary, information to groundmass ages. New methods for estimating the rates of degassing have also emerged providing the potential for closer links to volcanology and hazard prediction. Chapters five to seven deal with the study of magmatism at mid-ocean ridges, above hotspots and at convergent margins respectively. Over the last decade many investigations of melting processes have been made and our view of this field has completely changed due to both a greater number of high-quality analyses and to improved theoretical modeling. Thus, it is now possible to build a much more detailed picture of how melt generation, migration and modification occurs within the Earth— aspects fundamental to models for Earth differentiation and dynamics. Central to these advances is the notion that knowledge of time scale constrains the physical mechanism of a process.

From Chapter 8 onwards, the focus of the volume shifts to lower temperature geochemistry, starting with a chapter on the behavior of the U-series nuclides in groundwaters. This subject merited a chapter on its own in the Ivanovich and Harmon (1992) volume and its continued interest has led to significant advances in understanding and in application over the last decade. The next two chapters deal with the dating of carbonates: in ocean and lakes in Chapter 9; and in caves in Chapter 10. The U/Th chronometer is one of the few tools that can be applied to date important climate and sea-level events in the Quaternary and this area has seen some of the more high-profile applications of the U-series in the past decade.

Chapters 11 and 12 focus on the oceans. The first of these describes the use of U-series nuclides in the modern ocean, where they have been particularly useful during the last decade to study the downward flux of carbon. The second ocean chapter looks at the paleoceanographic uses of U-series nuclides, which include assessment of sedimentation rates, ocean circulation rates, and paleoproductivity. Both of these ocean chapters

demonstrate that knowledge of the behavior of the U-series is now sufficiently well developed that their measurement provides useful quantitative information about much more than just the geochemistry of these elements.

The emphasis shifts to the continental domain in Chapter 13 which addresses the fractionation of the U-series nuclides during continental weathering and subsequent riverine transport. This subject area also merited a chapter in the volume by Ivanovich and Harmon (1992) and, to some extent, the community has been slow to capitalize on the understanding of terrestrial fractionation processes during the last decade. Recent studies of soil and riverine U-series chemistry look set to change this omission, however, and these are detailed in this chapter. Having seen how the U-series nuclides are mobilized and transported in surface waters, Chapter 14 summarizes their behavior during transfer to the oceans at estuaries. This is a complicated field, with diverse aspects of the river chemistry and environment controlling the precise behavior. But our developing understanding of the possible range of behavior is providing ever more accurate oceanic budgets for the U-series elements.

Chapter 15 brings the emphasis to the human scale as it describes the use of U-series chronometers to date the history of human evolution. U/Th dating provides one of the few chronometers for a crucial period of such evolution which saw the emergence of modern humans, the extinction of both Neanderthals and *H. erectus*, and a great deal of environmental change. Recently developed tools, described in this chapter, look set to put the time scales for such change onto a much more secure footing.

Finally, Chapter 16 provides information about the handling of U-series data, with a particular focus on the appropriate propagation of errors. Such error propagation can be complex, especially in the multi-dimensional space required for ^{238}U - ^{234}U - ^{230}Th - ^{232}Th chronology. All too often, short cuts are taken during data analysis which are not statistically justified and this chapter sets out some more appropriate ways of handling U-series data.

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**APPENDIX:
GENERAL SOLUTIONS OF U-SERIES DECAY
EQUATION USING LAPLACE TRANSFORMS**

The solution to the general decay equations is often given in textbooks (e.g., Faure 1986). However, this solution is given for initial abundances of the daughter nuclides that are equal to zero. In the most general cases, the initial abundances of the daughter nuclides are not equal to zero. For examples, in many geological examples, we make the assumptions that the decay chain is in secular equilibrium. The solutions of these equations can also be used to solve simple box models of U-series nuclides where a first order kinetics are assumed.

The Laplace transform of a function f is defined as:

$$\tilde{f}(s) = \int_0^{\infty} f(t)e^{-st} dt \quad (\text{A1})$$

By applying the Laplace transform to the U-series decay equation, one obtains simple linear equations that can be solved for the Laplace transforms of N_i (the number of nuclei i in the system). By inverting the Laplace transforms using tables, the time-dependent solutions are directly obtained. The Laplace transform for Equation (1) is:

$$s\tilde{N}_1 - \tilde{N}_1^0 = -\lambda_1\tilde{N}_1 \quad (\text{A2})$$

For Equation (2), the Laplace transform is:

$$s\tilde{N}_i - \tilde{N}_i^0 = -\lambda_i\tilde{N}_i + \lambda_{i-1}\tilde{N}_{i-1} \quad (\text{A3})$$

We now give a solution for the first four nuclides in the chain corresponding for example to ^{238}U - ^{234}U - ^{230}Th - ^{226}Ra which has relevance for application in the study of magmatic processes or weathering.

$$\tilde{N}_1 = \frac{N_1^0}{s + \lambda_1} \quad (\text{A4a})$$

$$\tilde{N}_2 = \frac{N_2^0}{s + \lambda_2} + \frac{\lambda_1 N_1^0}{(s + \lambda_1)(s + \lambda_2)} \quad (\text{A4b})$$

$$\tilde{N}_3 = \frac{N_3^0}{s + \lambda_3} + \frac{\lambda_2 N_2^0}{(s + \lambda_2)(s + \lambda_3)} + \frac{\lambda_1 \lambda_2 N_1^0}{(s + \lambda_1)(s + \lambda_2)(s + \lambda_3)} \quad (\text{A4c})$$

$$\begin{aligned} \tilde{N}_4 = & \frac{N_4^0}{s + \lambda_4} + \frac{\lambda_3 N_3^0}{(s + \lambda_3)(s + \lambda_4)} + \frac{\lambda_2 \lambda_3 N_2^0}{(s + \lambda_2)(s + \lambda_3)(s + \lambda_4)} \\ & + \frac{\lambda_1 \lambda_2 \lambda_3 N_1^0}{(s + \lambda_1)(s + \lambda_2)(s + \lambda_3)(s + \lambda_4)} \end{aligned} \quad (\text{A4d})$$

Each of these equations can then be inverted to time-space once the fractions are decomposed as follows:

$$\frac{1}{(s + \lambda_1)(s + \lambda_2)\dots(s + \lambda_n)} = \sum_{i=1}^n \frac{a_i}{s + \lambda_i} \quad (\text{A5})$$

$$\text{where } a_i = \prod_{j \neq i} \frac{1}{\lambda_j - \lambda_i}$$

By remembering that the inverse of the function $1/(s+\lambda_i)$ is $e^{-\lambda_i t}$, the general solutions can be written in a rather compact form as:

$$N_i = \sum_{j=1}^i \left(\prod_{k=1}^j \lambda_k \right) a_j N_j^0 e^{-\lambda_j t} \quad (\text{A6})$$

where N_j^0 represents the initial abundance of nuclide j .

Figure 1. Schematic drawing of the ^{238}U , ^{235}U and ^{232}Th decay chains.

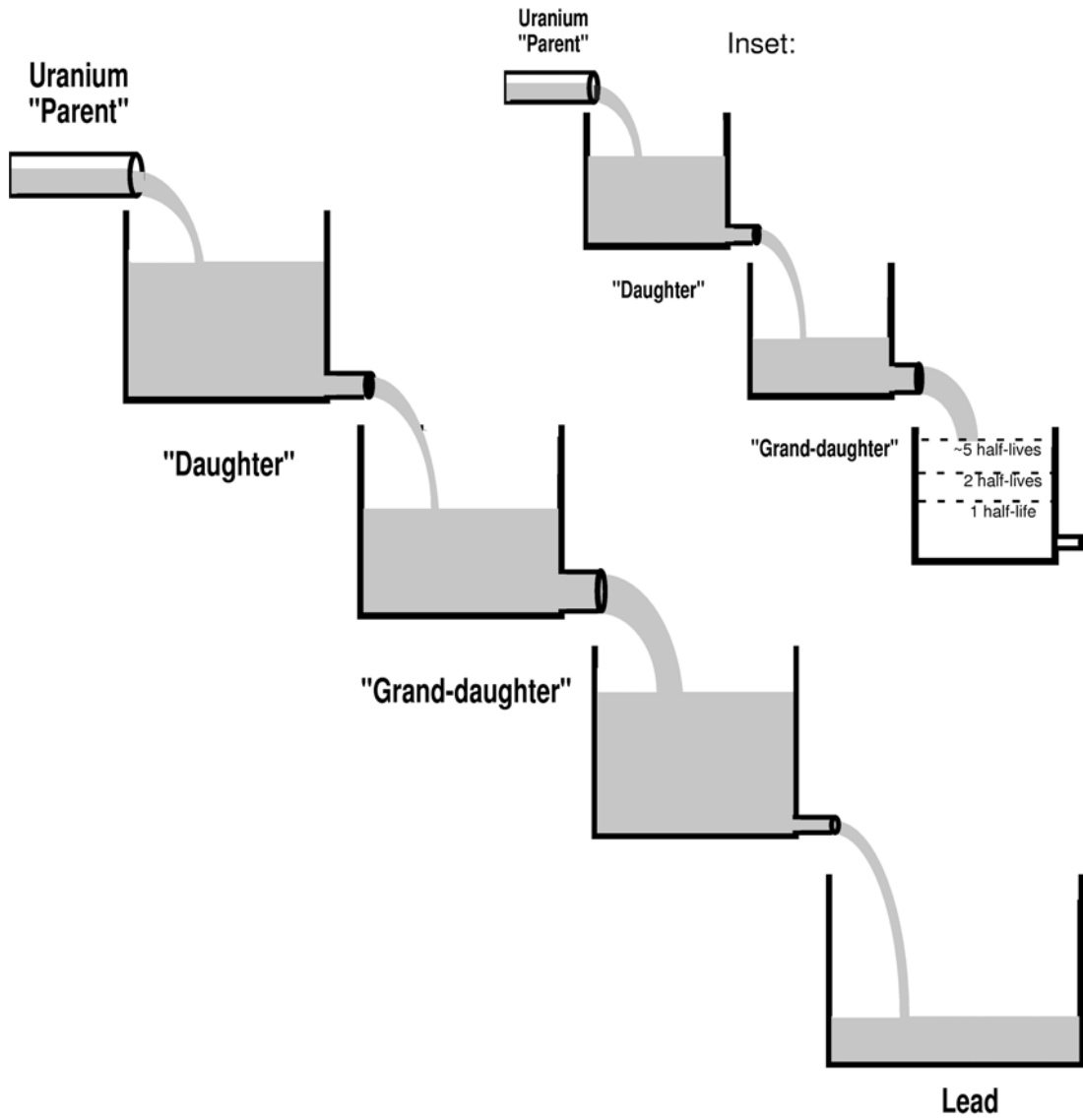


Figure 2. Analogy of U-series decay chain with a series of tanks feeding into each other. See text for description.

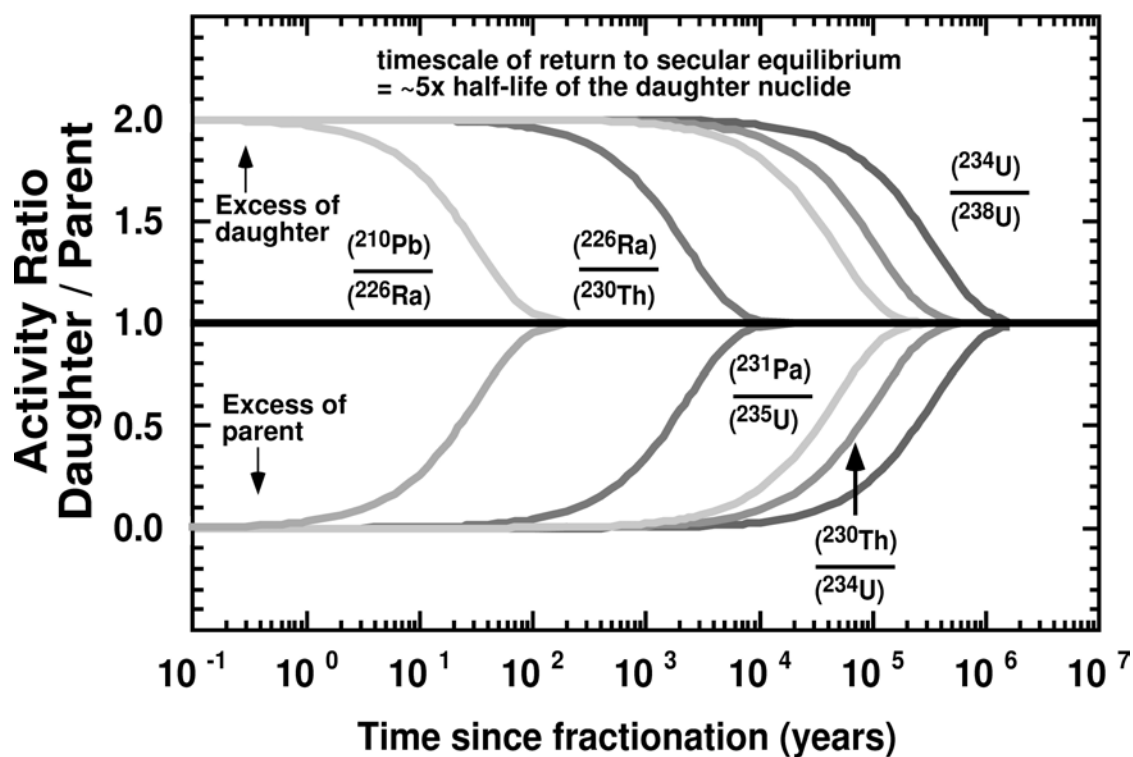


Figure 3. Parent daughter disequilibrium will return to equilibrium over a known time scale related to the half-life of the daughter nuclide. To return to within 5% of an activity ratio of 1 requires a time period equal to five times the half-life of the daughter nuclide. Because of the wide variety of half-lives within the U-decay-series, these systems can be used to constrain the time scales of processes from single years up to 1 Ma.

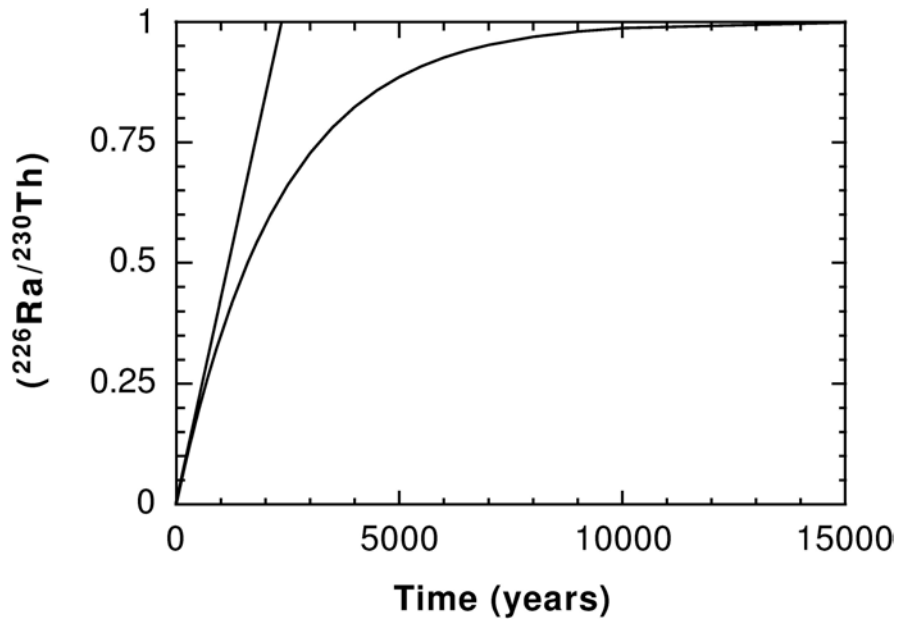


Figure 4. Return to secular equilibrium of $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio with no initial ^{226}Ra . The return to secular equilibrium essentially depends on the half-life of the daughter isotope. If the decay of ^{226}Ra is “turned off,” the return to secular equilibrium takes $1/\lambda_{\text{Ra}}$ years.



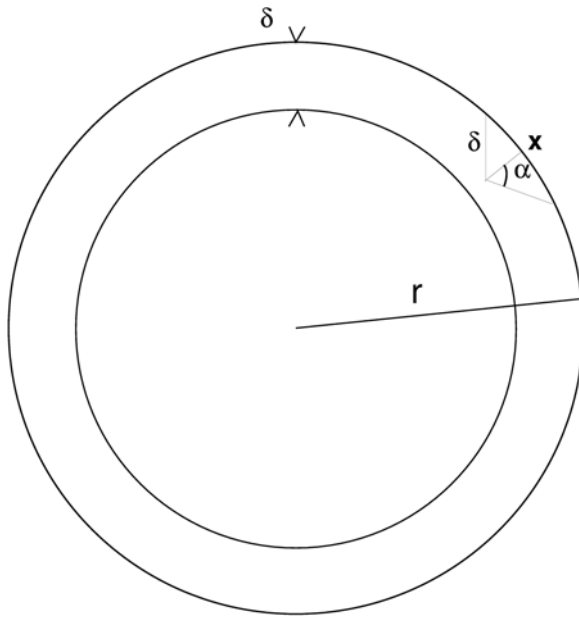


Figure 5. Ejection of daughter nuclide out of a grain due to recoil. Only a fraction of the nuclides located in a cone will be ejected for a given range δ . As shown on the diagram, at a distance x from the surface of the grain, the only nuclide to escape by recoil will be located in a cone with an angle α .

Table 1. Chemical properties of the main U-series nuclides

	<i>Z</i>	<i>Electronic Configuration</i>	<i>Oxidation States*</i>	<i>Geochemical Properties</i>	<i>Ionization Potential (kJ/mol)</i>	<i>Melting point (K)</i>
U	92	[Rn]5f ³ 6d ¹ 7s ²	0, 3, 4, 5, 6	Lithophile Incompatible Soluble (+6) Insoluble (+4)	584	1405.5
Pa	91	[Rn]5f ² 6d ¹ 7s ²	3, 4, 5	Lithophile Incompatible Insoluble	568	2113
Th	90	[Rn]6d ² 7s ²	0, 3, 4	Lithophile Incompatible Insoluble	587	2023
Ra	89	[Rn]7s ²	2	Lithophile Incompatible Sl. soluble	509.3	973
Rn	86	[Rn]	0, 2	Volatile Soluble	1037	202
Po	84	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	-2, +2, + 4 , +6	Volatile	812	527
Pb	82	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	0, 2, 4	Chalcophile Incompatible M. Volatile Insoluble	715.5	600.65

*bold indicates preferred oxidation state in terrestrial material

Source material: Emsley (1989)

Table 2. Half-lives for the U- and Th- decay series nuclides, with decay modes.

²³⁸ U decay chain			²³⁵ U decay chain			²³² Th decay chain		
<i>Nuclide</i>	<i>Half-life</i>	<i>Ref.</i>	<i>Nuclide</i>	<i>Half-life</i>	<i>Ref.</i>	<i>Nuclide</i>	<i>Half-life</i>	<i>Ref.</i>
²³⁸ U _	4.4683 ± 0.0048 Byrs	1	²³⁵ U _	0.70381 ± 0.00096 Byrs	1	²³² Th _	14.0100 Byrs	6
²³⁴ Th _	24.1 days	2	²³¹ Th _	1.063 days	2	²²⁸ Ra _	5.75 ± 0.03 yrs	4
²³⁴ Pa _	6.69 hours	2	²³¹ Pa _	32,760 ± 220 yrs	5	²²⁸ Ac _	6.15 hours	2
²³⁴ U _	245,250 ± 490 yrs	3	²²⁷ Ac _	21.77 ± 0.02 yrs	4	²²⁸ Th _	1.912 ± 0.002 yrs	4
²³⁰ Th _	75,690 ± 230 yrs	3	²²⁷ Th _	18.72 days	2	²²⁴ Ra _	3.66 days	2
²²⁶ Ra _	1599 ± 4 yrs	4	²²³ Fr _	22 min.	2	²²⁰ Rn _	55.6 sec.	2
²²² Rn _	3.823 ± 0.004 days	4	²²³ Ra _	11.435 days	2	²¹⁶ Po _	0.145 sec.	2
²¹⁸ Po _	3.04 min.	2	²¹⁹ At _	50 sec.	2	²¹² Pb _	10.64 hours	2
²¹⁸ At _	1.6 sec.	2	²¹⁹ Rn _	3.96 sec.	2	²¹² Bi _	1.009 hours	2
²¹⁸ Rn _	35 msec.	2	²¹⁵ Bi _	7.7 min.	2	²¹² Po _	0.298 μsec.	2
²¹⁴ Pb _	26.9 min.	2	²¹⁵ Po _	1.78 msec.	2	²⁰⁸ Tl _	3.053 min.	2
²¹⁴ Bi _	19.7 min.	2	²¹⁵ At _	0.1 msec.	2	²⁰⁸ Pb	stable	
²¹⁴ Po _	0.1637 msec.	2	²¹¹ Pb _	36.1 min.	2			
²¹⁰ Tl _	1.3 min.	2	²¹¹ Bi _	2.14 min.	2			
²¹⁰ Pb _	22.6 ± 0.1 yrs	4	²¹¹ Po _	0.516 sec.	2			
²¹⁰ Bi _	5.01 days	2	²⁰⁷ Tl _	4.77 min.	2			
²¹⁰ Po _	138.4 ± 0.1 days	4	²⁰⁷ Pb	stable				
²⁰⁶ Hg _	8.2 min.	2						
²⁰⁶ Tl _	4.2 min.	2						
²⁰⁶ Pb	stable							

*References: 1. Jaffey et al. (1971); 2. Lide (1998); 3. Cheng et al. (2000); 4. Holden (1990); 5. Robert et al. (1969); 6. Le Roux and Glendenin (1963)