

Radiochronometry Guidance

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Guidance on Radiochronometry

1. Introduction

Radiochronometry is the measurement of radioactive materials and their decay products to determine the “age” of the material. It differs from the practice of geochronology in that the materials (samples) are man-made, and in that the timespan of interest is confined to the nuclear era, *i.e.*, since the discovery of fission in 1939. In radiochronometry, the “age” of the material ideally records the time when the sample was manufactured, or produced in the final form that is analyzed in the laboratory. It is an important predictive signature in a nuclear forensic investigation which can help in the attribution to a source. The calculation of this “age” can only be made if a model is invoked that allows simplification of the parent radionuclide to daughter isotope decay equation. The simplification required for this model is that the parent was purified completely from all traces of its daughter product at the time of sample preparation. Then, this “age” should be described as the “model age” from which a “model date” in the past can then be calculated. For this model date to represent the date of sample preparation, two other assumptions are required to be true. The first is that the material has remained a closed system since that time (*i.e.*, that there has been no loss or gain of either parent or daughter), and the second is that the analyses are accurate.

Measurement accuracy is constrained through quality control practices whereby a confidence value can be assigned to the result. Accuracy of the model is assessed by validation using appropriate materials of known age and composition. Several radiochronometry methods and models have been validated and used in nuclear forensic investigations. Relevant studies can be found in the peer-reviewed scientific literature. [1-10]

Model dates for a nuclear material that are impossibly old and pre-date the nuclear era indicate either that the daughter product was not completely removed at the time of sample production, or that some post-production contamination of the sample has occurred. Model dates that are impossibly young, as could be determined if the material is known to have been in existence in a closed-system for a given time, indicate problems with the measurements.

Regardless of whether the assumptions are true or not, the model date of a radioactive material is an essentially invariant characteristic, or signature, that can be used for attribution (with appropriate caution), and used with other signatures to establish genetic relationships between different samples. For example, an agreement of model dates gives increased confidence in the consanguinity of separate seizures of illicitly trafficked materials.

For many radioactive materials it is possible to measure more than one radiochronometer (parent-daughter pair, or even parent-daughter-granddaughter decay series), and such measurements should be performed when practical. This is common practice in geochronology. Agreement between multiple radiochronometers increases the confidence that the model age gives the date of a historical processing event or sample preparation, but disagreement does not negate the inherent value of the signatures.

Instead, disagreement may provide clues about the process, or processes, used to purify and manufacture the material.

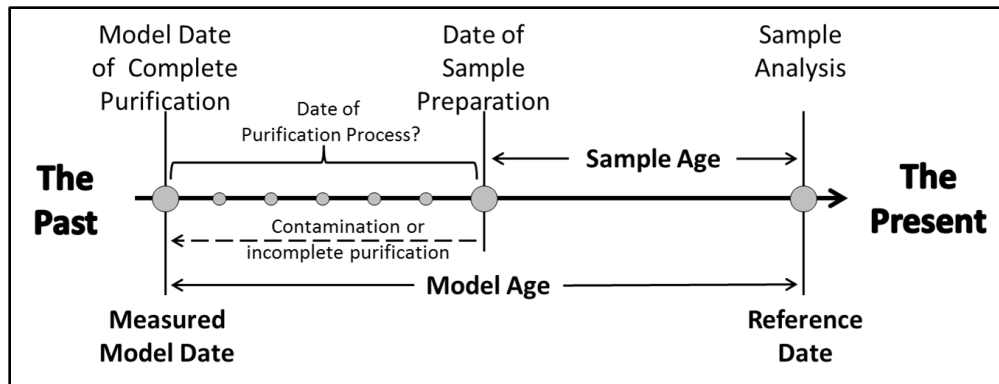
This guidance document applies specifically to radiochronometry of nuclear materials bearing uranium, plutonium and neptunium. It discusses the applicable radiochronometers, provides the mathematical foundation for the calculation of model dates and their uncertainties, and discusses the analytical methods and their precision.

2. Radiochronometry and the Model Age

The mathematical foundation of radiochronometry lies in the solution to the differential equations describing the decay of a radioactive parent isotope to a radioactive daughter, and the daughter to granddaughter, etc. This discussion of radiochronometry is limited to a three-member decay-chain, and the complete equations expressed in terms of number of atoms are given in Appendix 1. These solutions are often referred to as the Bateman equations, named after Harry Bateman who first solved the decay-chain series of differential equations in 1910 [11]. See also Keegan and Gehrke [3] for nicely typeset equations, and the solution for the fourth member of a decay-series.

The “sample age” of a nuclear material is defined as the difference between the present and the date it was manufactured into the form subject to analysis. The concentrations of the parent, daughter and granddaughter isotopes are fully described by equations 1, 2 and 3 in Appendix 1 only when there has been no loss or gain of any isotope from the material. This is a primary assumption of radiochronometry: the material has remained a closed-system since the date of manufacture. The sample age can only be determined if the number of daughter and granddaughter atoms present on the date of sample preparation are known. However, this is unknowable, and therefore further assumptions are necessary for radiochronometry. By invoking a “model” that assumes that no daughter or granddaughter decay product was present in the sample at some time in the past, an explicit “model age” can then be calculated, which corresponds to the time at which the sample was free of daughter or granddaughter decay product.

This is the second assumption of radiochronometry: the parent isotope was purified completely from its decay products at some time. An “age” calculated using this assumption should always be referred to as a “model age.” The calculation of a model age is linked to a reference date, which is the date when the daughter product was separated from its parent for measurement. The “model date” is determined by subtracting the model age from this reference date. These relationships are shown schematically in the following figure.



No purification technique is 100% efficient. There will always be a few atoms of daughter remaining, although perhaps below detection limits. So, the question occurs: “Will the amount of daughter remaining make a significant difference in the model age of the sample?” If “a significant difference” is defined as one which would increase the model age in excess of its uncertainty, then a critical limit for the daughter remaining can be defined. This critical limit of daughter impurity depends on the model age. It can be calculated and evaluated for a specific sample. See Appendix 1 for further discussion of this limit.

An analogous question might be: “How close is the model age to the sample age?” The model age can be the same as the sample age, but it cannot be younger (as long as the closed-system assumption holds). This is because the daughter product is growing-in for some period of time (however short) between the purification time and the time of sample preparation. Following the purification of the material, there may be further processing steps that produce the final form of the manufactured sample that is analyzed in the laboratory. For example, uranium that is chemically purified, such as that coming out of a UF_6 cascade, might be hydrolyzed and calcined to make an oxide, or reduced by sintering to make UO_2 fuel, or even further reduced to U metal, and perhaps alloyed and cast. Each of these steps may re-introduce daughter products by contamination and push the model date further into the past. Or, they may act as another purification process and re-set the model date.

Any interpretation of model dates should bear these considerations in mind. For a sample of unknown origin, the uncertainties that are associated with the production process (the degree of purification, or contamination, and its timing) do not negate the usefulness of radiochronometry and the model date. The amount of daughter present will be only from decay of the parent and from the amount that was present at the time of sample preparation, and thus, the model date gives the maximum age of the material. Accurate radiochronometry results can only give a maximum age, not a minimum.

3. Multiple Radiochronometers

It is common practice in geochronology to use multiple isotopic systems to determine the age of geologic and planetary samples. If the ages determined by different parent-daughter systems are concordant then confidence is increased that the results are “accurate”, and that the model ages determined are meaningful. On the other hand, the lack of concordance can point to a disturbance in one system or the other, or other deviations from the assumptions used to calculate the model ages. Such discordance in itself is useful information that can help unravel the history of sample. The same is true for radiochronometry.

Analyzing different radiochronometers, suitable to a given sample, can lend confidence to the interpretation of model ages and also provide information about the underlying assumptions. Following are several examples.

3.1 Multiple Daughters of Uranium

3.1.1 $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$

For uranium-rich materials, a concordance of model ages returned by these radiochronometers gives high confidence in the veracity of one primary assumption, that the analytical results are accurate, and allows the conclusion that the model date represents the true date of some purification or sample preparation process. This is because it is unlikely that concordant model ages would result from two independent inaccurate analyses, and equally unlikely that the same proportion of ^{230}Th and ^{231}Pa relative to their U parents would be found were it not related to some chemical/physical process. By Occam's razor, a uranium purification process by which both daughters are removed to quantities below their respective critical limits is the simplest interpretation of this concordance.

In the case of discordance between these radiochronometers, the one that gives the most recent model date indicates the daughter that was purified most efficiently from uranium. The contaminant level of the daughter that gives the older model age may be calculated. The following paragraph gives an example of the kind of information that can be extracted from discordancy.

Assume there is a sample for which the $^{230}\text{Th}/^{234}\text{U}$ model date is 13-April-2003, and the $^{231}\text{Pa}/^{235}\text{U}$ model date is 3-October-1941. From this, we know that the sample was not manufactured before April 2003, and that it contained significant excess ^{231}Pa at that time. The amount of excess ^{231}Pa on 13-April-2003 may be calculated from A-1, Eqn. 4 using a value for t equal to the time difference between the model dates. For this example, the delta- t is 61.527 years, and gives $^{231}\text{Pa}/^{235}\text{U} = 6.0556 \times 10^{-8}$. So, on the $^{230}\text{Th}/^{234}\text{U}$ model date, the sample contained an excess of about 60.56 ppb ^{231}Pa relative to ^{235}U .

3.1.2 $^{230}\text{Th}/^{234}\text{U}$, $^{229}\text{Th}/^{233}\text{U}$, and $^{228}\text{Th}/^{232}\text{U}$

Here, the daughters are the same element, and should behave identically in any chemical or physical process that fractionates daughter from parent. Mass-dependent fractionation of the daughter isotopes, while possible, is not considered here, because if it exists, the effects are probably too small to measure. The $^{229}\text{Th}/^{233}\text{U}$ and $^{228}\text{Th}/^{232}\text{U}$ radiochronometers are applicable to uranium-rich samples that have some previous history of irradiation, and consequently a measurable ^{233}U and/or ^{232}U content. (While it is possible to also consider the $^{232}\text{Th}/^{236}\text{U}$ radiochronometer in this section, the likelihood of intrinsic ^{232}Th in most samples of uranium limits its usefulness. Laboratory blank and potential environmental contamination makes low-level ^{232}Th analyses extremely challenging analytically). Concordance between model dates from multiple daughter/parent radiochronometers of this kind can provide additional confidence that the model dates are accurate.

Discordant model dates are more difficult to interpret. They may be the result of inaccurate measurements, or they may be the result of contamination, or reflect the mixing of multiple materials. For example, a blend of old, natural uranium that is mixed with more recently produced irradiated U with appreciable ^{233}U content would probably have highly discordant $^{230}\text{Th}/^{234}\text{U}$ and $^{229}\text{Th}/^{233}\text{U}$ model dates.

Only when U is purified would the model dates converge, becoming theoretically identical if the daughters were completely removed. If these model dates are concordant, this is compelling evidence that such purification occurred on the model date, because any contaminant that would produce concordant dates requires a highly specific Th isotopic composition.

Note that of these Th daughters, ^{228}Th has the shortest half-life ($t_{1/2} = 1.912$ years) and reaches transient equilibrium with ^{232}U ($t_{1/2} = 68.9$ years) in approximately 15 years; shown graphically in Figure 1. As a sample ages and the $^{228}\text{Th}/^{232}\text{U}$ in-growth curve flattens, the uncertainty on the age determined using this system increases dramatically (Figure 2). For the conditions plotted in Figure 2, the uncertainty on the age reaches 100% at 18.4 years. Therefore, if transient equilibrium is measured for this system, the age of the sample must be greater than about 18 years, which could be useful information for a particular sample. The actual “greater than” age will depend on the precision of the measurement.

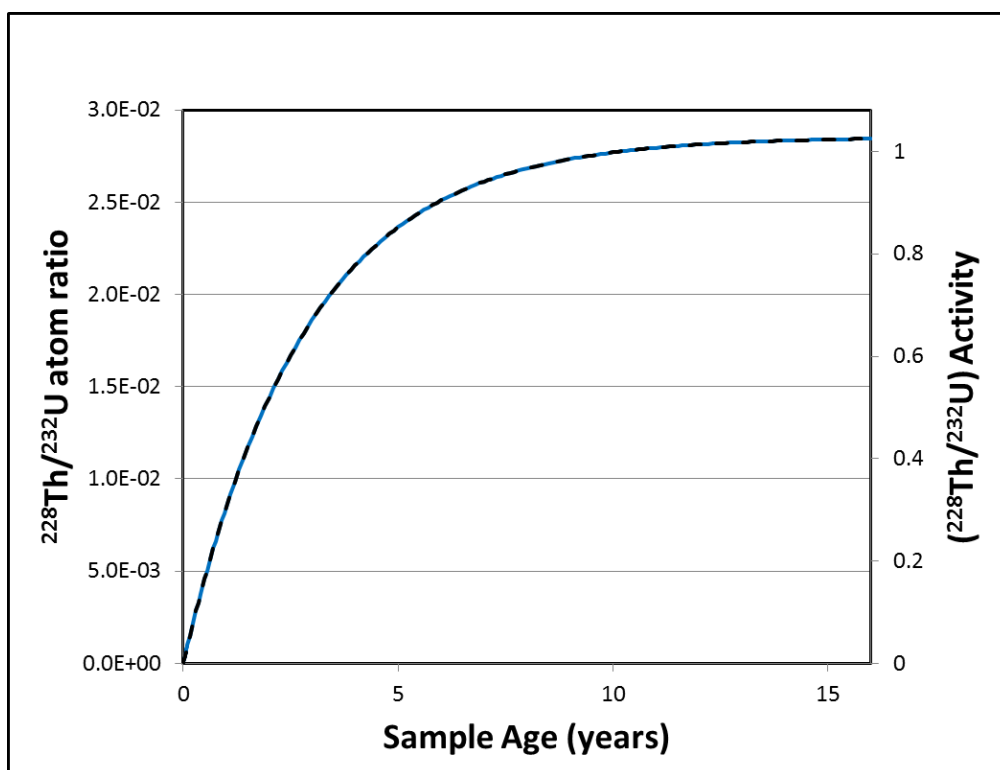


Fig. 1. Ingrowth of ^{228}Th from zero to transient equilibrium with its parent ^{232}U

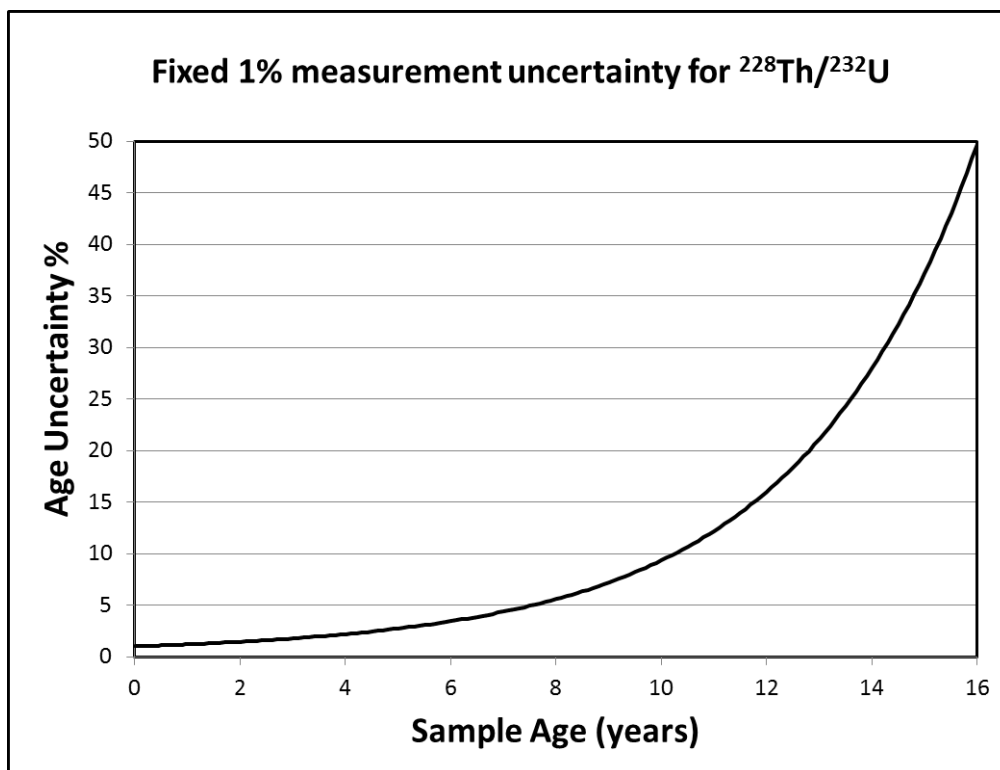


Fig. 2. The relative uncertainty on the age determined from measurements of the $^{228}\text{Th}/^{232}\text{U}$ radiochronometer assuming the daughter/parent ratio is measured with a precision of 1%.

Croatto [12] has shown that the $^{230}\text{Th}/^{234}\text{U}$ and $^{228}\text{Th}/^{232}\text{U}$ radiochronometers can be used in parallel for certain materials, and that analyses of the $^{230}\text{Th}/^{228}\text{Th}$ and $^{234}\text{U}/^{232}\text{U}$ activity ratios by alpha spectrometry can be used to determine the age of such samples. Alpha sources are prepared from purified Th and U. One advantage of this activity ratio approach is that yield tracers do not need to be added to the sample. Also, it can be applied to older samples, because it does not depend on detection of $^{228}\text{Th}/^{232}\text{U}$ different from transient equilibrium. However, it does require the presence of measureable ^{232}U .

An additional caveat related to the use of ^{228}Th for radiochronometry is that it is a member of the ^{232}Th decay chain, and is the daughter of ^{228}Ra (via ^{228}Ac) as well as ^{232}U . The presence of significant natural Th in a sample of uranium will perturb the in-growth systematics, and potentially lead to erroneous age determination. This possibility should be investigated whenever ^{228}Th is utilized.

3.2 Multiple Uranium Daughters of Plutonium:

$^{234}\text{U}/^{238}\text{Pu}$, $^{235}\text{U}/^{239}\text{Pu}$, $^{236}\text{U}/^{240}\text{Pu}$, and $^{238}\text{U}/^{242}\text{Pu}$

These U/Pu radiochronometers are applicable to a Pu-rich sample. As discussed for Th/U above, the concordance between model dates from multiple radiochronometers can provide additional confidence that the model dates are accurate, and concordant model dates for the U/Pu radiochronometers is strong evidence that the Pu was highly purified from the U daughters at this time. For impure Pu with

significant uranium content, discordant radiochronometry results for these systems might be expected. The paper by Sturm *et al.* [13] presents analytical results and discusses the modelling of these radiochronometers for Pu age-dating. The treatment of this subject here augments this discussion.

Because the U daughters have significantly longer half-lives than the Pu parents, with some simplifying assumptions, it is possible to calculate the isotopic composition of the contaminating U. The following equation (1) is derived from Appendix-1, Eqn. 2, by division, and simplified assuming that the decay constants for ^{235}U and ^{236}U are zero. Inaccuracy due to this assumption is less than 1 ppm at $t = 50$ years.

$$\frac{^{236}\text{U}(t) - ^{236}\text{U}(0)}{^{235}\text{U}(t) - ^{235}\text{U}(0)} = \left(\frac{^{240}\text{Pu}}{^{239}\text{Pu}} \right)_t \left[\frac{(1 - e^{\lambda_{240}t})}{(1 - e^{\lambda_{239}t})} \right] \quad (1)$$

The right-hand side of this expression is the production ratio of $^{236}\text{U}/^{235}\text{U}$. For a given Pu isotopic composition, it is essentially constant over the timespan of the nuclear era and is defined as $K_{0/9}$.

$$K_{0/9} = \left(\frac{^{240}\text{Pu}}{^{239}\text{Pu}} \right)_t \left[\frac{(1 - e^{\lambda_{240}t})}{(1 - e^{\lambda_{239}t})} \right] \quad (2)$$

For a given $^{240}\text{Pu}/^{239}\text{Pu}$ ratio, $K_{0/9}$ only varies by 0.2% as t changes from 0.005 years to 50 years.

Equation (1) is transformed into equation (3) by dividing the numerator and denominator of the left-hand side by $^{235}\text{U}(t)$, and separating terms.

$$\left(\frac{^{236}\text{U}}{^{235}\text{U}} \right)_t = K_{0/9} \left(1 - \frac{^{235}\text{U}(0)}{^{235}\text{U}(t)} \right) + \frac{^{236}\text{U}(0)}{^{235}\text{U}(t)} \quad (3)$$

Equation (3) is a relatively simple expression for the measured $^{236}\text{U}/^{235}\text{U}$ ratio, from which the amount of initial ^{235}U or ^{236}U contaminants in the Pu can be determined. If both these contaminants were zero, then the $^{236}\text{U}/^{235}\text{U}$ is simply equal to $K_{0/9}$, the production ratio.

As a numerical example, assume there is a sample of Pu that has a measured $^{235}\text{U}/^{239}\text{Pu} = 0.0005$, which gives a model age of 17.387 years, and has a measured $^{236}\text{U}/^{240}\text{Pu} = 0.001$, which gives a model age of 9.464 years. For the purpose of evaluation, the younger model age must be assumed to be correct, so the older model age given by the $^{235}\text{U}/^{239}\text{Pu}$ radiochronometer must reflect contamination with ^{235}U . The amount of this contamination can be calculated from equation (3). If the $^{240}\text{Pu}/^{239}\text{Pu} = 0.1$, the measured $^{236}\text{U}/^{235}\text{U} = 2.0$, and $K_{0/9} = 0.3675$. By assuming $^{236}\text{U}(0) = 0$, equation (3) can be solved for $\frac{^{235}\text{U}(0)}{^{235}\text{U}(t)}$, which equals 0.4558. So, at least 45.58% of the ^{235}U in this sample was present as a contaminant on the model date given by the $^{236}\text{U}/^{240}\text{Pu}$ radiochronometer. This limit may be useful in attribution.

The Sturm *et al.* [13] paper points out the usefulness of the $^{234}\text{U}/^{238}\text{Pu}$ radiochronometer in conjunction with $^{235}\text{U}/^{239}\text{Pu}$ and $^{236}\text{U}/^{240}\text{Pu}$, and also the sensitivity of the $^{238}\text{U}/^{242}\text{Pu}$ chronometer to uranium contamination. Concordance between all four U/Pu radiochronometers is unlikely. Due to the low abundance of ^{242}Pu in most Pu and its long half-life, the $^{238}\text{U}/^{242}\text{Pu}$ radiochronometer will be the least precise of the four, but the measurement provides information about the residual ^{238}U in the material. This, coupled with the ^{235}U information, that may be derived as described above, will give an estimate of the initial $^{235}\text{U}/^{238}\text{U}$ isotopic composition.

3.3 $^{241}\text{Am}/^{241}\text{Pu}$

This daughter/parent pair deserves its own heading under multiple radiochronometers because it can often be paired with $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ in uranium-rich materials that contain trace levels of plutonium, and also paired with the U/Pu radiochronometers for Pu. Concordant model dates between this radiochronometer and those from other daughter/parent pairs provide strong evidence that the model date represents the actual date of the purification process.

For Pu samples, this is the primary radiochronometer and will give the maximum model age of the material. Generally, the model ages given by the U daughters of Pu discussed in section 3.2, will be greater than the $^{241}\text{Am}/^{241}\text{Pu}$ model age because U is not purified as efficiently as Am during Pu production.

3.4 Three-Member Decay Chains: Granddaughter/Daughter/Parent Radiochronometers

$^{226}\text{Ra}/^{230}\text{Th}/^{234}\text{U}$, $^{227}\text{Ac}/^{231}\text{Pa}/^{235}\text{U}$, $^{228}\text{Th}/^{228}\text{Ra}/^{232}\text{Th}$, $^{229}\text{Th}/^{233}\text{U}/^{237}\text{Np}$, $^{233}\text{U}/^{237}\text{Np}/^{241}\text{Am}$
and $^{237}\text{Np}/^{241}\text{Am}/^{241}\text{Pu}$

For some materials it may be possible to determine the concentration of the third member of a decay-series: the granddaughter. This will depend on the sensitivity of the analytical method used, on the type of material, and on its age.

The simplest assumption for determination of the model age using the granddaughter is the same as for the daughter/parent pairs, but in this case, complete purification of *both* the granddaughter and daughter from the parent must be assumed (see Appendix 1, Eqn. 14). Examples of the ingrowth curves of the granddaughter nuclides for three of these decay-series are shown graphically in Appendix 1. Each curve is calculated for this simplest assumption.

Ages from the granddaughter ingrowth for more complicated models can be calculated. For example, the daughter is assumed to be some fixed value at the time when the granddaughter was removed. Ages from such models are probably best called “model-squared” ages and need rigorous empirical constraints, *i.e.*, additional data, to support the model assumptions.

4. Analytical Methods

4.1 Mass Spectrometry

Better precision and accuracy for most granddaughter, daughter and parent radionuclide measurements is obtained by mass spectrometry, specifically, by measurement using the isotope dilution method. The best isotope dilution mass spectrometry (IDMS) measurements are made using a spike that is a pure isotope of the element which does not exist in the sample. This ideal case is often true in many nuclear materials. For example, samples of uranium that have never been in a reactor will contain no ^{233}U , ^{229}Th or ^{233}Pa (the daughter of ^{237}Np) and high-purity spikes of these isotopes are commonly used to make IDMS analyses of U, Th and Pa. Similarly, samples of plutonium usually contain no ^{244}Pu , which is the preferred spike isotope for IDMS analyses of Pu.

Further, if the granddaughters of ^{234}U and ^{235}U , ^{226}Ra and ^{227}Ac , are to be measured by IDMS, one can assume the sample contains no ^{228}Ra or ^{225}Ac which can be used as spikes for IDMS. Independent of

assumptions, the isotopic composition of an un-spiked sample can be measured and the IDMS calculations can be made accurately.

The following figures show why mass spectrometry analyses are more precise than counting methods.

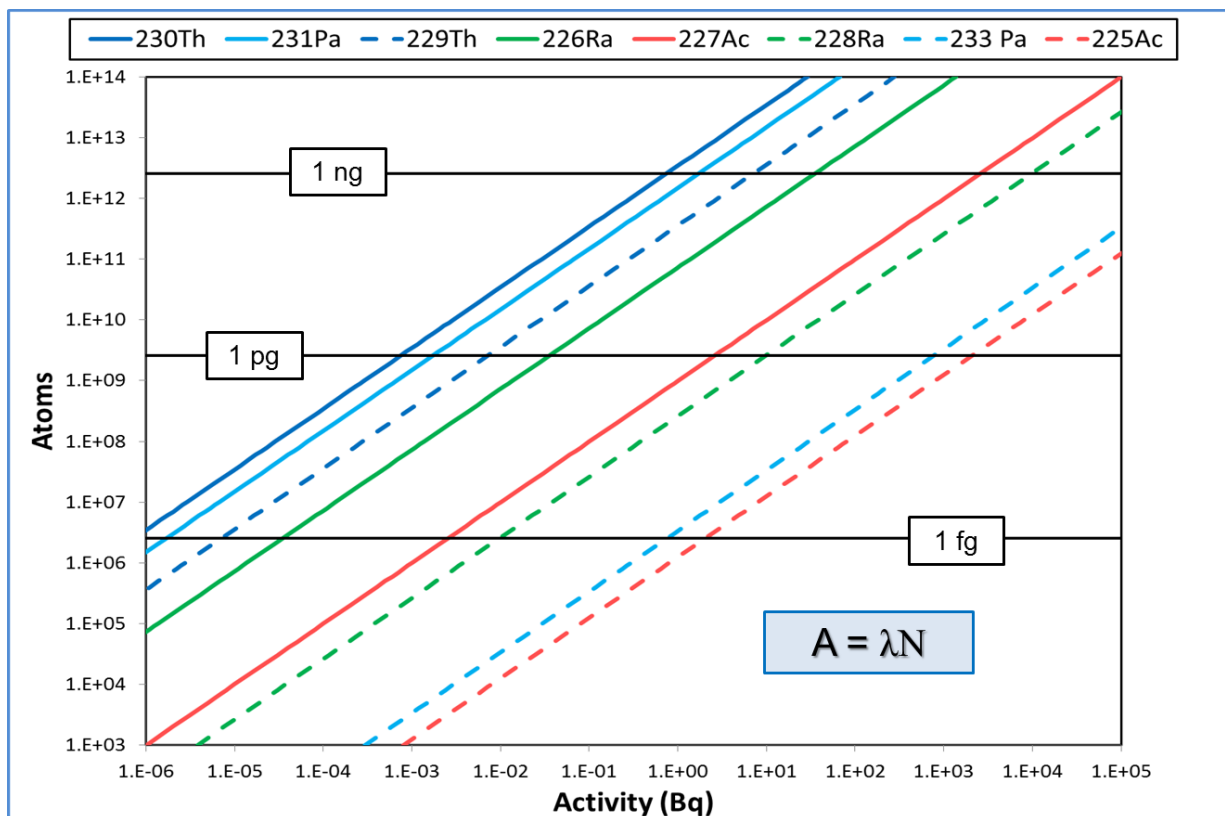


Figure 3. A graph of the law of radioactivity ($A = \lambda N$) with the daughter and granddaughter isotopes of ^{234}U and ^{235}U shown by the solid lines. The spike isotopes used for IDMS analyses are shown by the dashed lines of the same color. Horizontal lines give the approximate mass scale for these isotopes.

Figure 3 is transformed into Figure 4 using the following assumptions: first, that 1% of the atoms available can be measured by mass spectrometry, and second, that the disintegrations in one week from all of the atoms available are detected with 100% efficiency (a best case counting model). The assumption of 1% efficiency represents that seen for most elements by modern multi-collector inductively coupled plasma mass spectrometers. Some elements are ionized and transmitted more efficiently by thermal ionization mass spectrometers.

As an example, take ^{227}Ac (the red curve in Fig. 4) and assume that 10^5 atoms (ions) are measured by mass spectrometry. With the assumption of 1% efficiency, this represents a sample containing 10^7 atoms. In one week, approximately 6100 atoms of these 10^7 atoms of ^{227}Ac will decay, so mass spectrometry will clearly give a more precise measurement ($10^5 > 6100$). From Fig. 4, more ions can be detected by mass spectrometry for any nuclide with a half-life greater than 1.333 years ($\lambda < 0.01$ per week) than disintegrations could be counted in one week.

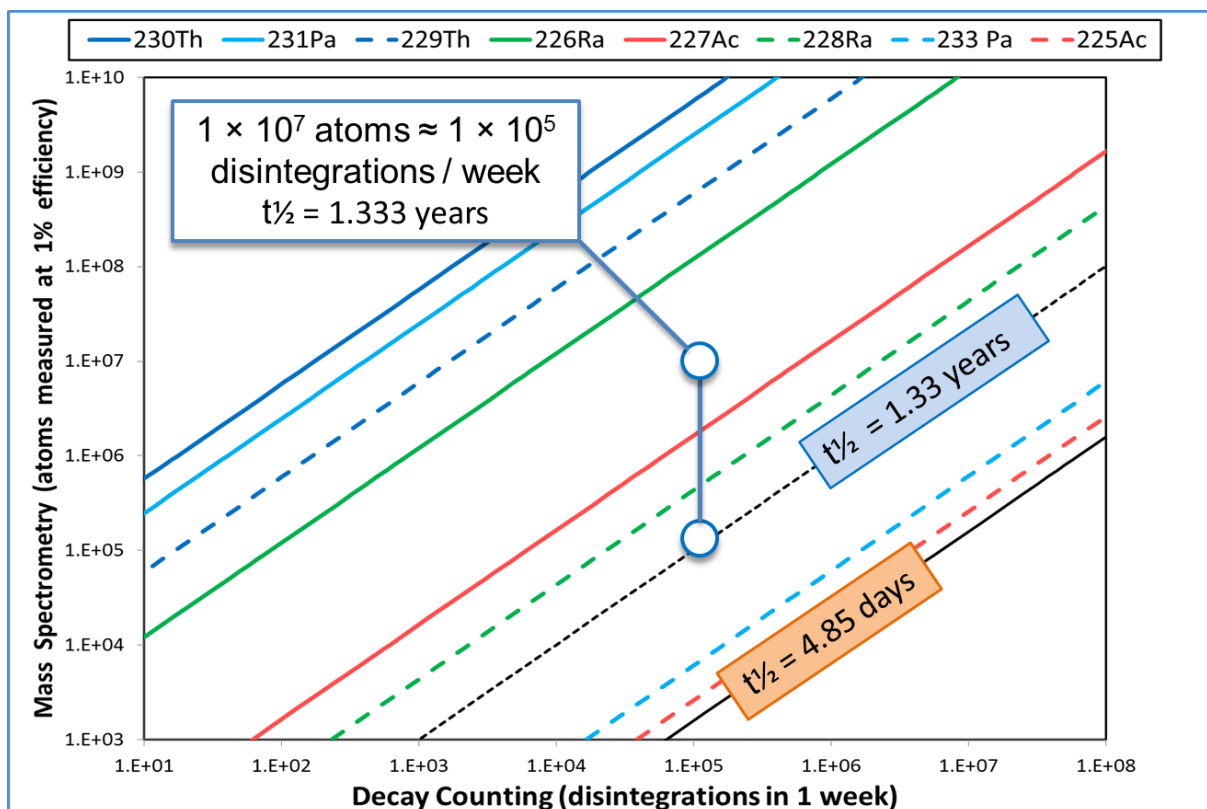


Figure 4. Transformation of Figure 3 using the assumptions given above.

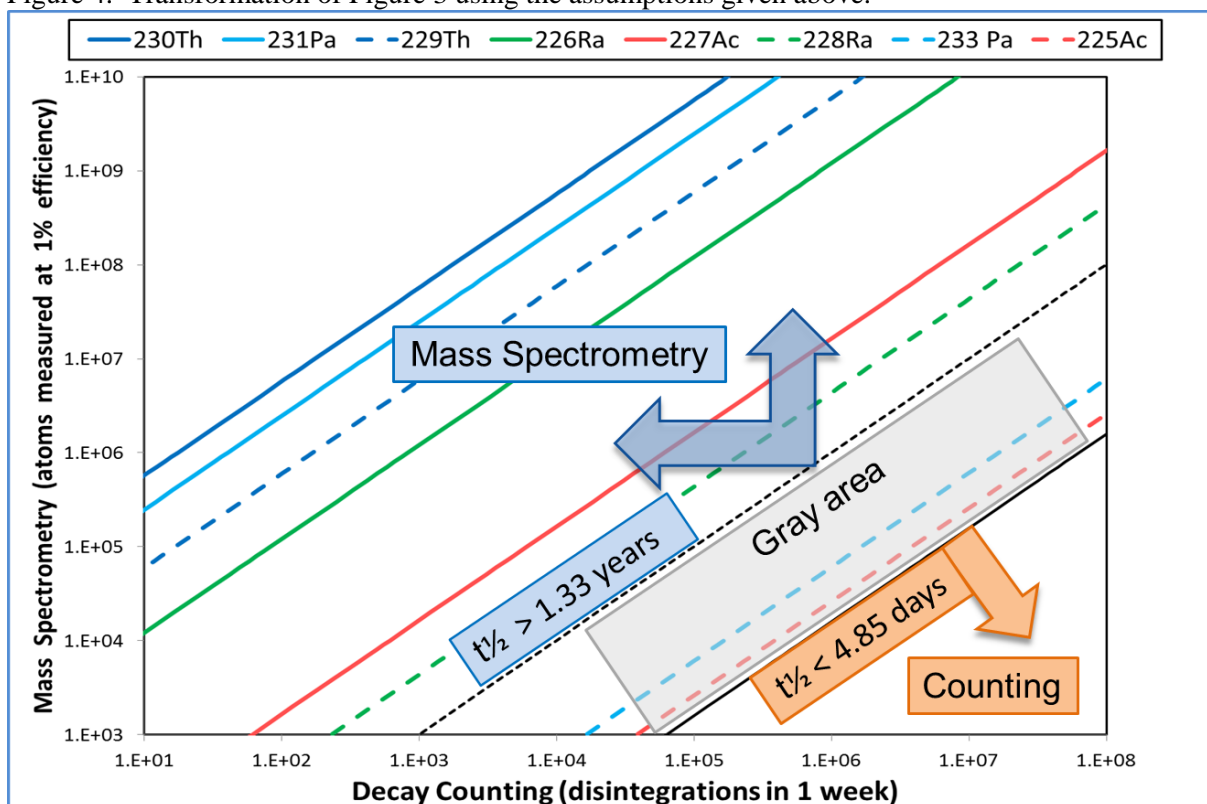


Figure 5. An assessment of the domain of mass spectrometry and that of decay counting methods.

4.2 Alpha spectrometry

The highest theoretical precision is not the only consideration in the choice of analytical methods. While ^{232}U and ^{238}Pu , with half-lives of 68.9 and 87.74 years, respectively, clearly fall in the mass spectrometry domain of Fig. 5, alpha spectrometry is the better choice for measurement of these radionuclides. This is because of the abundant and ubiquitous isobaric interferences from ^{232}Th and ^{238}U which limit the ability of mass spectrometry to measure low-levels of these isotopes. This does not mean that with a sufficiently pure sample and a sufficiently clean instrument that these isotopes could not be measured by mass spectrometry, only that alpha spectrometry is more reliable method.

As mentioned in section 3.1, for samples of uranium having significant ^{232}U content, an alpha spectrometry method where $^{228}\text{Th}/^{230}\text{Th}$ and $^{232}\text{U}/^{234}\text{U}$ are measured on un-spiked purified Th and U fractions can be used for radiochronometry [12].

5. Reporting

Reporting of radiochronometry results should include all of the following information: Sample ID, Daughter/Parent atomic ratio, Reference Date, Model Age, and Model Date, with expanded uncertainties and coverage factors and units, as appropriate. It should also include the decay constants, or the half-lives, used for the calculation. In conversions, the value 365.24 should be used for the number of days/year. For example:

Sample ID	$^{230}\text{Th}/^{234}\text{U}$ (atomic ratio)	U (k=2)	Reference Date	Model Age (years)	U (k=2) (years)	Model Date	U (k=2) (days)
REIMEP-22 A	4.3458E-06	3.33E-08	22-Jan-14	1.538	0.012	9-Jul-12	4.5
$t_{1/2} \text{ } ^{230}\text{Th} = 75,690 \pm 330 \text{ years}$				$t_{1/2} \text{ } ^{234}\text{U} = 245,250 \pm 490 \text{ years}$			

Inclusion of the measured atomic ratio and the reference date in the report allows independent calculation of the model date, or re-calculation at some time in the future if the decay constants of the parent or daughter are updated.

Reports should also specify the analytical method and instrumentation used, and the assumptions of the model for the calculation of the Model Age, and the classification level.

Appendix 1

In the following, N is the number of atoms, λ is the decay constant (*i.e.*, $\ln(2)$ divided by the half-life), and the subscripts 1, 2, and 3, refer to the parent, daughter, and granddaughter, respectively. Time (t) is positive, measured from a time-zero in the past. For example, reading Eqn. 1: the number of atoms of parent isotope at time t (*e.g.*, the present), $N_1(t)$, is equal to the number of atoms of the parent at time-zero (*e.g.*, a time in the past, the purification time), $N_1(0)$, times e to the negative decay constant of the parent times t (the elapsed time between time-zero and the present, *i.e.*, the age).

Parent:

$$N_1(t) = N_1(0)e^{-\lambda_1 t} \quad (\text{Eqn. 1})$$

Daughter:

$$N_2(t) = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} N_1(0)(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2(0)e^{-\lambda_2 t} \quad (\text{Eqn. 2})$$

Granddaughter:

$$N_3(t) = \frac{\lambda_2 \lambda_1}{(\lambda_2 - \lambda_1)} N_1(0) \left[\frac{(e^{-\lambda_1 t} - e^{-\lambda_3 t})}{(\lambda_3 - \lambda_1)} - \frac{(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{(\lambda_3 - \lambda_2)} \right] + \frac{\lambda_2 N_2(0)(e^{-\lambda_2 t} - e^{-\lambda_3 t})}{(\lambda_3 - \lambda_2)} + N_3(0)e^{-\lambda_3 t} \quad (\text{Eqn. 3})$$

These equations are expressed with as few terms as possible to allow relatively simple calculation using Excel or other mathematical calculator. Note that the last terms of Eqns. 2 and 3 express the decay of any radioactive daughter and granddaughter, respectively, that may be present at time-zero. And further, that the middle term of Eqn. 3 expresses the production (and decay) of the granddaughter from any daughter that may be present at time-zero.

Time (t), the age, cannot be algebraically separated from Eqns. 2 and 3. That is, a unique solution for t does not exist using these full expressions, hence the requirement for simplifying assumptions. If we assume that the parent radionuclide was purified completely from its daughter product, then $N_2(0) = 0$, and replacing $N_1(0)$ with $N_1(t)e^{\lambda_1 t}$, Eqn. 2 can be re-written as

$$N_2(t) = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} N_1(t)(1 - e^{(\lambda_1 - \lambda_2)t}) \quad (\text{Eqn. 4})$$

Now t , the age of the material, can be separated.

$$t = \frac{1}{(\lambda_1 - \lambda_2)} \ln \left[1 + \frac{N_2(t)}{N_1(t)} \frac{(\lambda_1 - \lambda_2)}{\lambda_1} \right] \quad (\text{Eqn. 5})$$

Eqn. 5, is the model age equation. If R is defined as the daughter/parent atom ratio at time(t), the time of purification of the daughter for analysis, *i.e.*, $\frac{N_2(t)}{N_1(t)}$, then

$$t = \frac{1}{(\lambda_1 - \lambda_2)} \ln \left[1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1} \right] \quad (\text{Eqn. 5a})$$

In practice, for daughters with half-lives that are long relative to the time between purification for analysis and the analysis itself, no correction of R is necessary for the daughter's decay during this time, and the purification date can be used to calculate the model date. The model date is the purification date minus the model age.

The combined standard uncertainty on t (the age) may be calculated according to GUM [2] using standard methods. First, calculate the partial derivatives, or sensitivity coefficients, for the variables in Eqn. 5a. There are three variables, λ_1 , λ_2 and R .

These sensitivity coefficients are:

$$\frac{\partial t}{\partial \lambda_1} = \left(\frac{1}{\lambda_1 - \lambda_2} \right) \left(\frac{1}{1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1}} \right) \left(\frac{\lambda_2 R}{\lambda_1^2} \right) - \frac{1}{(\lambda_1 - \lambda_2)^2} \ln \left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1} \right) \quad (\text{Eqn. 6})$$

$$\frac{\partial t}{\partial \lambda_2} = \frac{1}{(\lambda_1 - \lambda_2)^2} \ln \left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1} \right) - \frac{R}{\lambda_1 (\lambda_1 - \lambda_2) \left(1 + \frac{R(\lambda_1 - \lambda_2)}{\lambda_1} \right)} \quad (\text{Eqn. 7})$$

$$\frac{\partial t}{\partial R} = \frac{1}{\lambda_1 + R(\lambda_1 - \lambda_2)} \quad (\text{Eqn. 8})$$

Then, multiply these coefficients by the standard uncertainties assigned to the variables, square them, sum the three terms and take the square-root.

The combined standard uncertainty on t equals:

$$u(t) = \sqrt{\left(u(\lambda_1) \frac{\partial t}{\partial \lambda_1} \right)^2 + \left(u(\lambda_2) \frac{\partial t}{\partial \lambda_2} \right)^2 + \left(u(R) \frac{\partial t}{\partial R} \right)^2} \quad (\text{Eqn. 9})$$

Calculation in this manner allows the relative contributions of the uncertainties on the variables to be determined for preparation of the uncertainty budget. These relative contributions, as fractions of the total are:

$$\frac{\left(u(\lambda_1) \frac{\partial t}{\partial \lambda_1} \right)^2}{\left(u(\lambda_1) \frac{\partial t}{\partial \lambda_1} \right)^2 + \left(u(\lambda_2) \frac{\partial t}{\partial \lambda_2} \right)^2 + \left(u(R) \frac{\partial t}{\partial R} \right)^2} \quad (\text{Eqn. 10})$$

$$\frac{\left(u(\lambda_2) \frac{\partial t}{\partial \lambda_2} \right)^2}{\left(u(\lambda_1) \frac{\partial t}{\partial \lambda_1} \right)^2 + \left(u(\lambda_2) \frac{\partial t}{\partial \lambda_2} \right)^2 + \left(u(R) \frac{\partial t}{\partial R} \right)^2} \quad (\text{Eqn. 11})$$

$$\frac{\left(u(R) \frac{\partial t}{\partial R} \right)^2}{\left(u(\lambda_1) \frac{\partial t}{\partial \lambda_1} \right)^2 + \left(u(\lambda_2) \frac{\partial t}{\partial \lambda_2} \right)^2 + \left(u(R) \frac{\partial t}{\partial R} \right)^2} \quad (\text{Eqn. 12})$$

The uncertainty on t may also be calculated using equation 5 in Pomme *et al.* [17], and the definition given in equation 6 of this reference. Note that this equation Pomme *et al.* gives the relative uncertainty,

and not the actual value, which is given here by Eqn.9. Uncertainty on t and the uncertainty budgets may also be calculated using the commercial software GUM Workbench.

To create a complete uncertainty budget, the contribution from the uncertainty on R must be partitioned into the contributions from the measurement of the daughter ($N_2(t)$) and the parent ($N_1(t)$). These contributions should be further partitioned into the uncertainty contributions from the parameters used to calculate these atom amounts, which will depend on the method used for analysis.

For example, if the analyses are done by isotope dilution mass spectrometry, an uncertainty budget for age-dating uranium using the ^{230}Th - ^{234}U radiochronometer, might look like this:

Variable	Percent Contribution	Sub-component 1	Percent Contribution	Sub-Component 2	Percent Contribution
^{230}Th half-life	negligible				
^{234}U half-life	8.13				
R ($^{230}\text{Th} / ^{234}\text{U}$) atomic ratio	91.87	^{230}Th measurement	85.49		
				^{229}Th spike calibration	12.3
				$^{230}\text{Th} / ^{229}\text{Th}$ measurement	85.6
				Bias correction	2.1
		^{234}U measurement	14.51		
				^{233}U spike calibration	8.7
				$^{234}\text{U} / ^{233}\text{U}$ measurement	89.9
				Bias correction	1.4

Further levels of complexity within the uncertainty budgets are possible. For example, the bias corrections have uncertainty components from the measurement of the standard reference material and from the uncertainty on the standard reference material itself. Similarly, the spike calibrations have uncertainty components due to measurement (there are further sub-components here also) and due to the standard used for calibration.

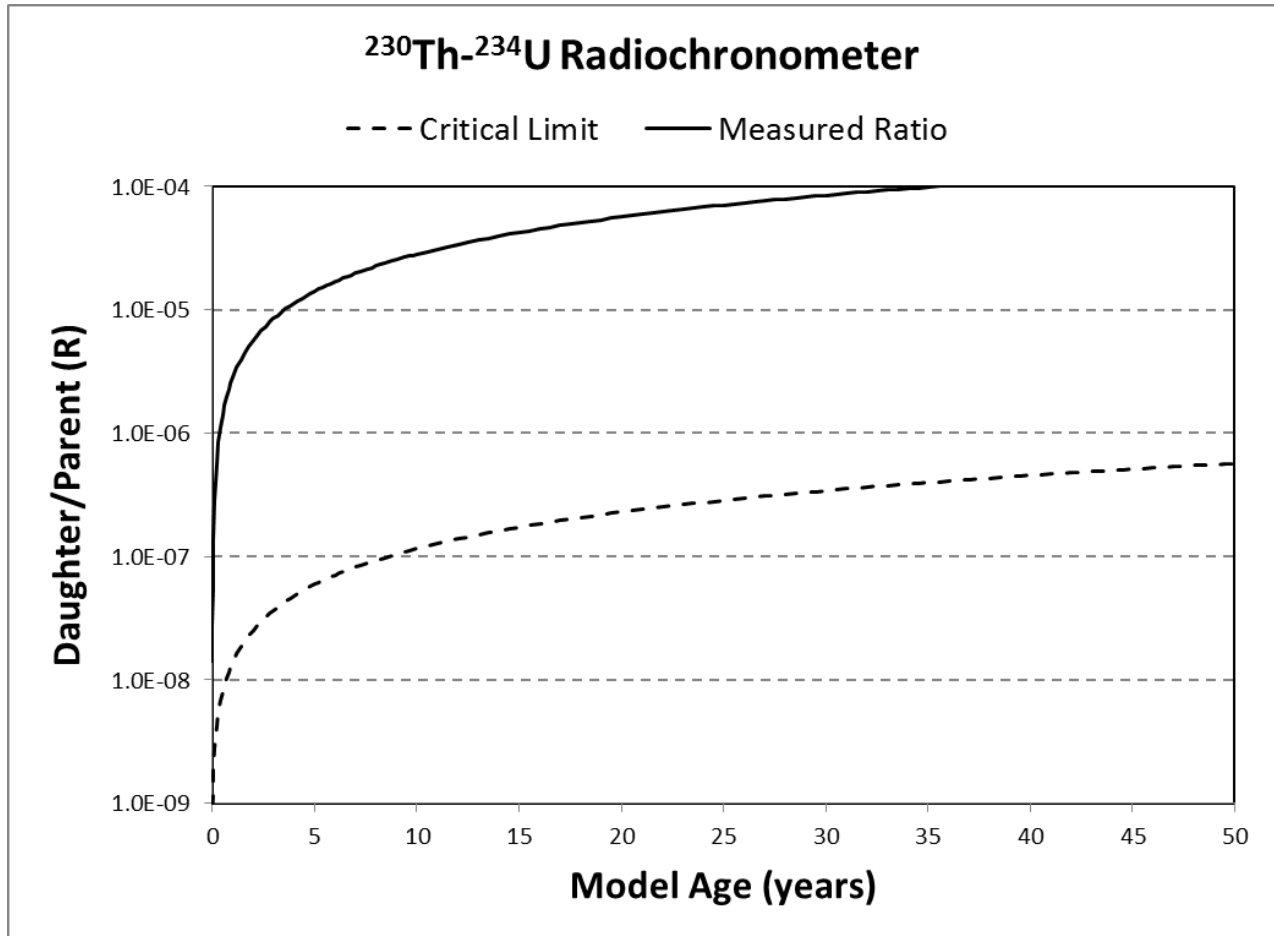
The Critical Limit

The critical limit for a radiochronometry measurement can be defined as the difference in the daughter/parent ratio which would increase the model age in excess of its uncertainty. For a given result, this can be calculated from Eqn. 4 by replacing t with the calculated uncertainty on the model age (call this $U(t)$).

$$\frac{N_2(t)}{N_1(t)} = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} (1 - e^{(\lambda_1 - \lambda_2)U(t)}) \quad (\text{Eqn. 13})$$

The critical limit (Eqn. 13) may be used to determine the effect of contamination with extraneous daughter product, or evaluate the concentration of initial daughter that the model age is not sensitive to.

An example of how this limit might vary with model age is given in the following figure.



The values chosen for $U(t)$ to create the figure above are arbitrary, but realistic. The critical limit maps the uncertainty on the model age to a change in R . For example, consider a sample with a calculated model age of 0.70000 ± 0.00369 years (a relative uncertainty of 0.527 %). This is approximately where the critical limit shown above crosses $R = 1.0E-08$. The interpretation of this is that this sample could not have contained more than 10 ppb ^{230}Th relative to ^{234}U at the time of purification. If it did, then the model age would not be as measured. It would be older, and outside the uncertainty on the model age.

As another example, consider a sample with a model age of 20.000 ± 0.081 years (a relative uncertainty of 0.405%). The critical limit of R for this sample is $2.29\text{E-}07$. This sample could not have contained more than 0.229 ppm ^{230}Th relative to ^{234}U at the time of purification. Again, if it did, then the model age would be older.

The first example illustrates a point that is intuitively obvious: samples with young model ages cannot be contaminated with significant daughter product. That is, the parent purification was highly efficient, resulting in a daughter/parent ratio at most $1\text{ E-}08$. Also, because the critical limit increases with model age, the sensitivity to initial contamination decreases. But this does not mean that older model ages are more accurate, such samples may just be more contaminated. In fact, younger model ages could be considered to be more accurate than older ones, because as noted above, radiochronometry model ages are the maximum age of the sample.

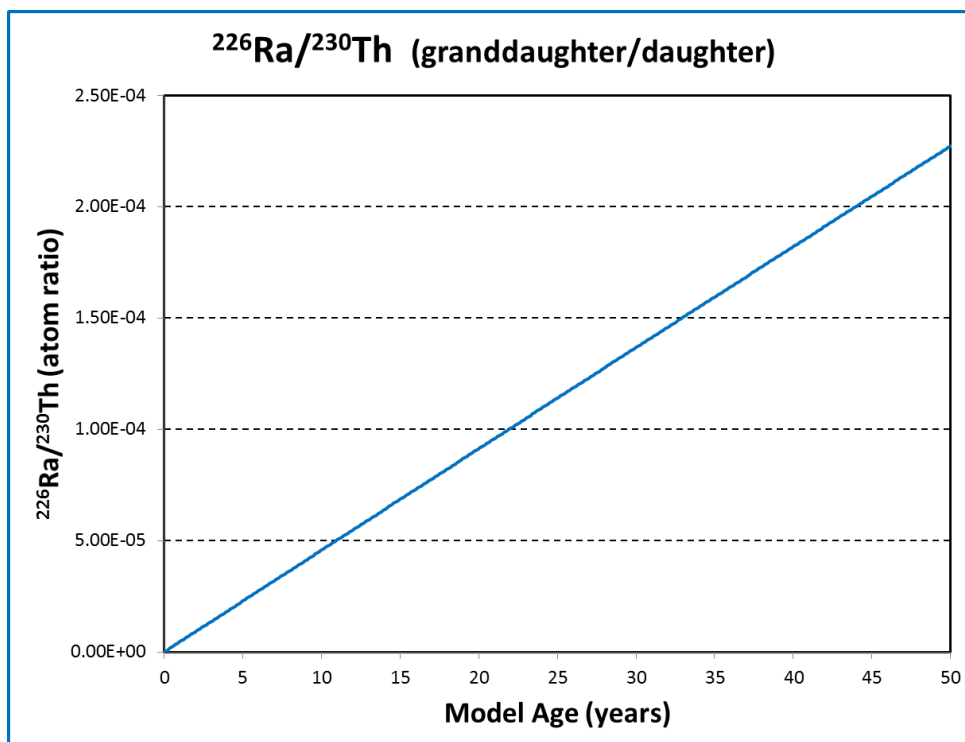
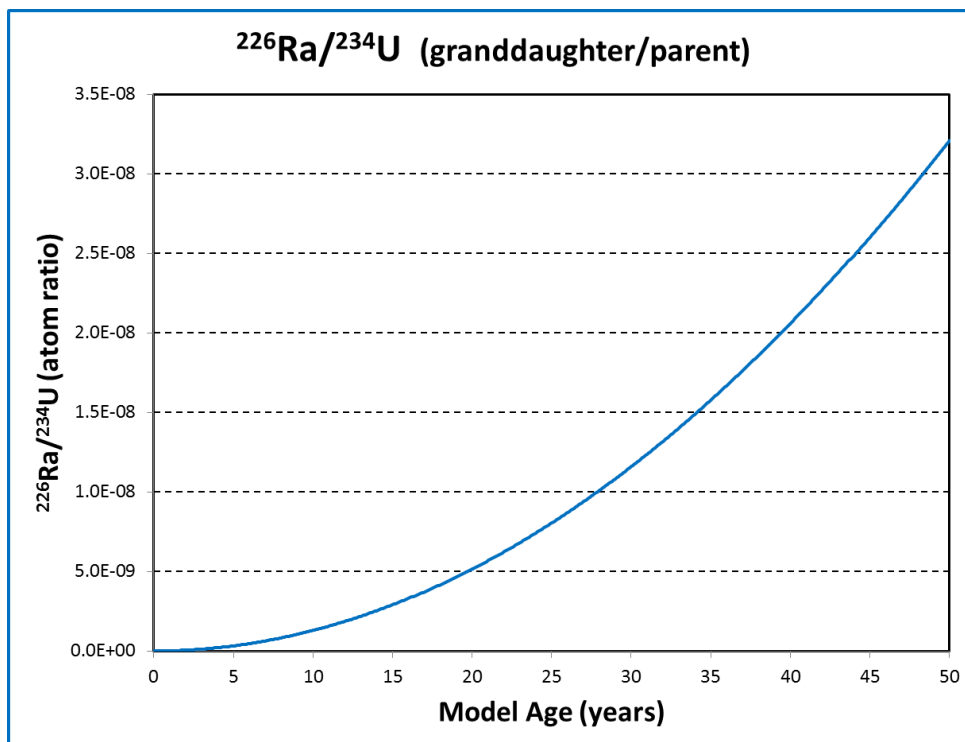
Three member decay-chains: Parent-Granddaughter Radiochronometry

Applying the simplifying assumption that only the parent isotope was present at the time of manufacture, Eqn. 3 can be simplified somewhat (again $N_I(0)$ is replaced with $N_1(t)e^{\lambda_1 t}$).

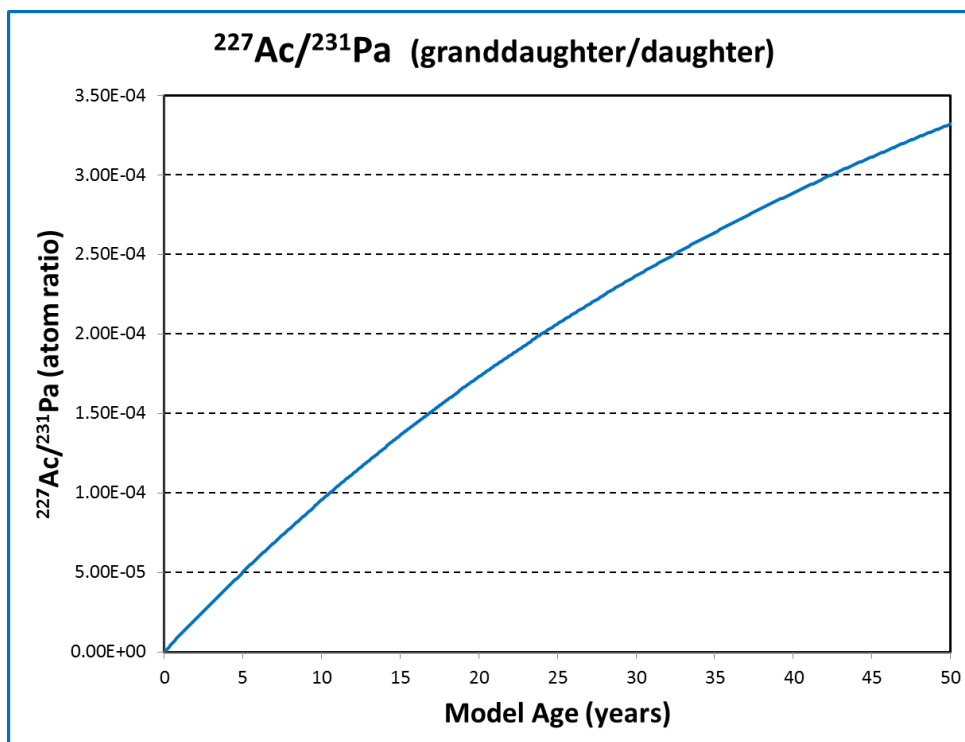
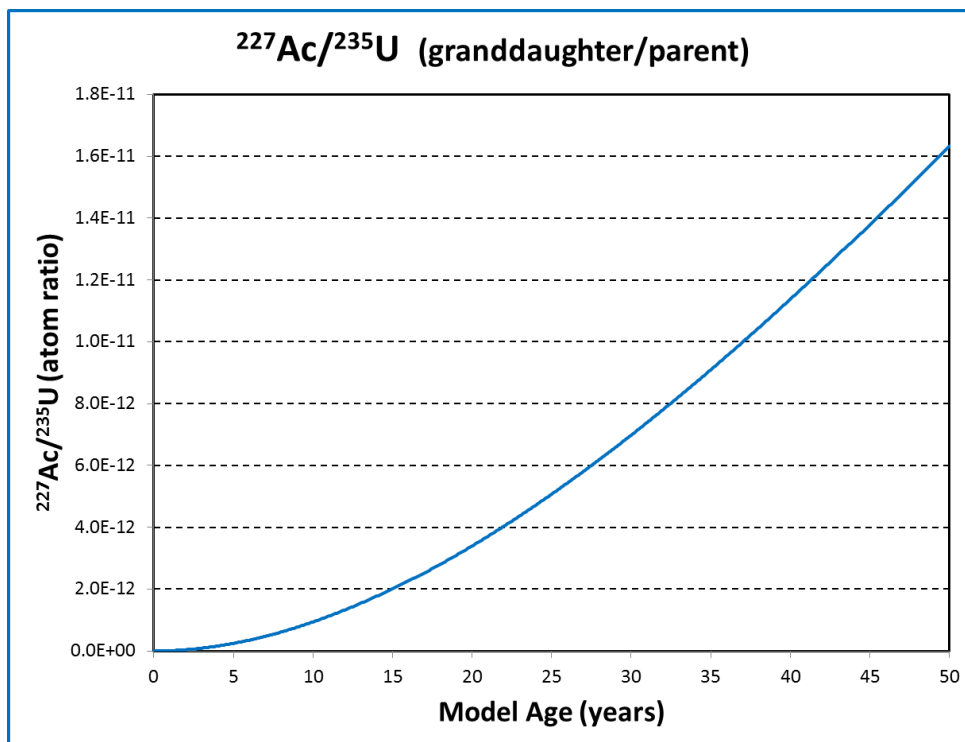
$$\frac{N_3(t)}{N_1(t)} = \frac{\lambda_2 \lambda_1}{(\lambda_2 - \lambda_1)} \left[\frac{(1 - e^{(\lambda_1 - \lambda_3)t})}{(\lambda_3 - \lambda_1)} - \frac{(e^{(\lambda_1 - \lambda_2)t} - e^{(\lambda_1 - \lambda_3)t})}{(\lambda_3 - \lambda_2)} \right] \quad (\text{Eqn. 14})$$

In this case however, t , the model age of the sample, cannot be separated. For a measured granddaughter/parent ratio, the model age must be determined by an iterative approach, substituting different values of t until a match to the measured ratio is found. Using Excel for example, this is not as tedious as it appears, once the right hand side of Eqn. 14 is entered as a formula. In practice, a table of values can be calculated for different values of t , which is how the following set of figures (Fig. A-1, through A-6) were produced. Then, calculating an uncertainty on the model age is done by finding the maximum and minimum values of t that correspond to the uncertainty assigned to the granddaughter/parent ratio.

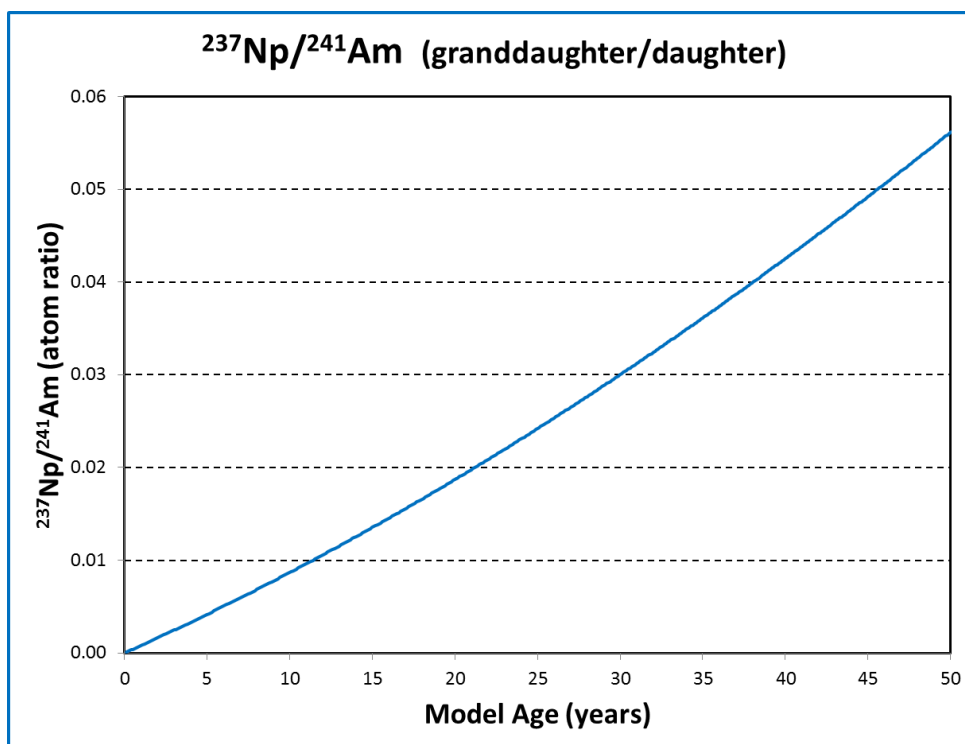
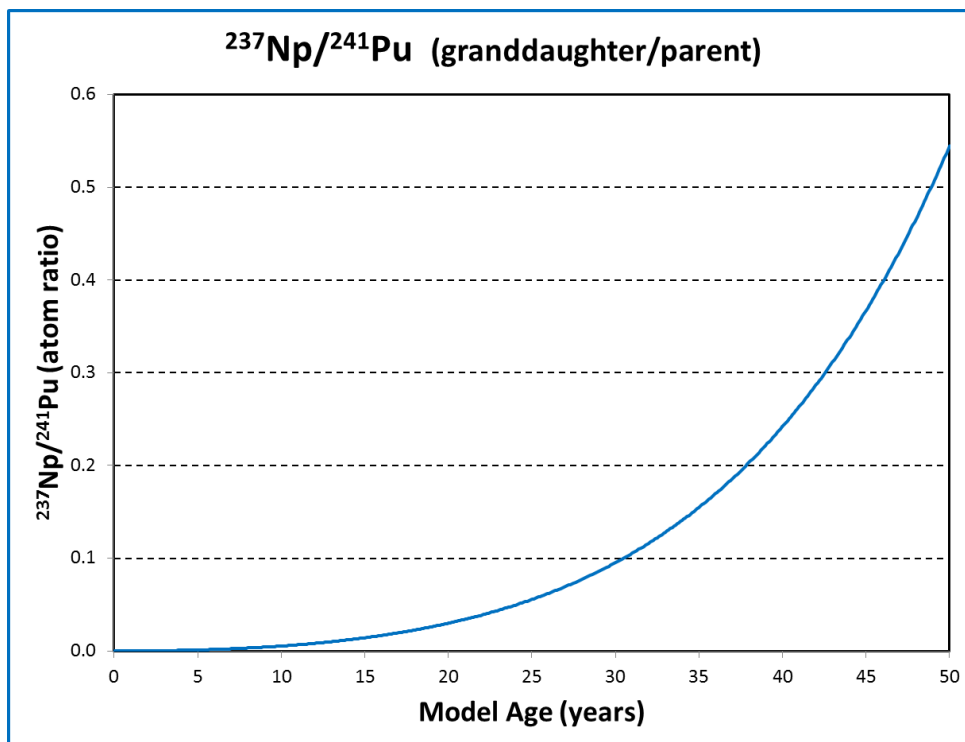
More rigorously, calculation of an uncertainty on a granddaughter model age would require computation using a Monte Carlo algorithm. To a first order, the uncertainty will be dominated by the uncertainty on the measured granddaughter/parent ratio, so that using the approach described above will only slightly underestimate the uncertainty. It will be underestimated because the uncertainties on the decay constants are not included. Development of a Monte Carlo algorithm is the only approach that would allow an uncertainty budget to be calculated that includes these decay constants.



Figures A-1 and A-2. Note the curvature of the $^{226}\text{Ra}/^{234}\text{U}$ ratio with time, indicating greater sensitivity of this radiochronometer at older ages, as would be expected: more time elapsed – more ^{226}Ra ingrown – greater precision on the measurement – and greater precision on the model age.



Figures A-3 and A-4. The curvature of the $^{227}\text{Ac}/^{231}\text{Pa}$ ratio with time is due to the relatively short half-life of ^{227}Ac . This ratio approaches a “quasi”-secular equilibrium value of about $6.6\text{E-}04$ on the several thousand year time-frame, even though the $^{231}\text{Pa}/^{235}\text{U}$ ratio continues to increase.



Figures A-5 and A-6. Note the magnitude of these ratios for the ^{241}Pu decay series relative to the two previous systems, which is the result of this short-lived parent decaying to long-lived daughters.

Appendix 2

Table of half-lives and some constants.

Nuclide	Atomic Weight	Half-life (a)	Uncertainty	References
226Ra	226.025402	1600	7	1, 2
227Ac	227.027746	21.772	0.003	1, 2
228Th	228.028731	1.9126	0.0009	1 #
229Th	229.031755	7932	28	2, 6*
230Th	230.033126	75584	110	3
232Th	232.038050	1.402E+10	6E+07	5
231Pa	231.035878	32670	260	1 #
232U	232.037146	68.9	0.4	2 #
233U	233.039628	159200	200	2, 5
234U	234.040945	245620	260	3
235U	235.043923	7.0381E+08	3.0E+05	4, 7
236U	236.045561	2.343E+07	6E+04	1 #
238U	238.050782	4.4683E+09	2.4E+06	4, 7
237Np	237.048173	2.144E+06	7E+03	1, 2
236Pu	236.046048	2.858	0.008	2
238Pu	238.049553	87.74	0.03	1 #
239Pu	239.052156	24100	11	1 #
240Pu	240.053807	6561	7	1, 2
241Pu	241.056845	14.325	0.006	2 #
242Pu	242.058736	373000	3000	1 #
244Pu	244.064197	8.00E+07	9E+05	2, 5
241Am	241.056822	432.6	0.6	1, 2

Uncertainties on the half-lives are the 95% confidence limits.

Half-life References

- 1: Decay Data Evaluation Project, <http://www.nucleide.org/DDEP.htm>
- 2: NNDC, NuDat 2.6, <http://www.nndc.bnl.gov/nudat2>
- 3: Cheng et al.(2013), Earth and Planetary Science Letters, 371–372, pp. 82–91.
- 4: Mattinson (2010), Chemical Geology, v. 275, pp. 186–198.
- 5: IUPAC (1989), Pure & Appl.Chem., v. 61, No. 8, pp. 1483-1504.
- 6: Kikunaga et al.(2011), Physical Review C, v. 84, 014316
- 7: Jaffey et al. (1971), Physical Review C, v. 4, No. 5, pp. 1889-1906.

* indicates that more recent, and possibly better, measurements have been made

indicates that D.D.E.P. and NNDC values are different

Some Constants:

A =	6.02214129E+23
seconds/year =	3.1556925E+07
days/year =	365.242

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