Radiochemistry Webinars
Chronometry

In Cooperation with our University Partners

Meet the Presenter…

Dr. Amy Gaffney

Dr. Amy Gaffney is a staff scientist in the Nuclear and Chemical Sciences Division at Lawrence Livermore National Laboratory. Her research focuses on the use of radiochronometry as a signature of the origin and history of nuclear material. Dr. Gaffney is engaged in collaborations on the development of analytical methods for radiochronometry with several international partners. She also mentors graduate student interns through the Glenn T. Seaborg Institute at LLNL. Through her service at LLNL, she has earned a Department of Energy Secretarial Honor Award and a DOE Office of Science Outstanding Mentor Award. Dr. Gaffney's research is presented in over 30 peer-reviewed scientific publications. Dr. Gaffney received her Bachelor's degree in Geology from The Colorado College, and her M.S. and Ph.D. in Geological Sciences from the University of Washington. She held postdoctoral appointments at the University of New Mexico and LLNL prior to joining LLNL as a staff member in 2009.

Contact Information: gaffney1@llnl.gov

Lawrence Livermore National Laboratory

Radiochronometry for Nuclear Forensics

NAMP Webinar
September 22, 2016

Amy Gaffney, Gary Eppich, Theresa Kayzar-Boggs[1], Michael Kristo, Kerri Schorzman, Ross Williams

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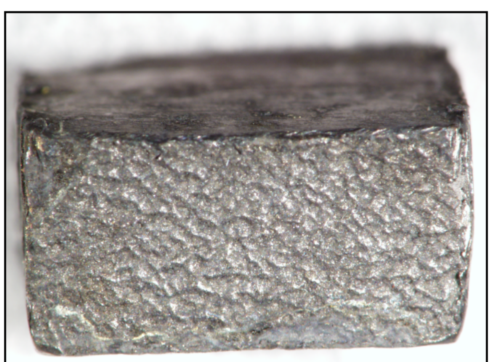
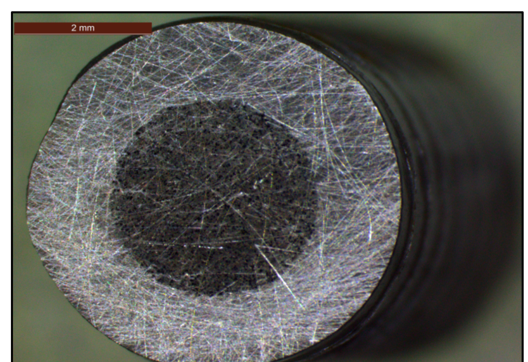
Lawrence Livermore National Laboratory
1: now at Los Alamos National Laboratory

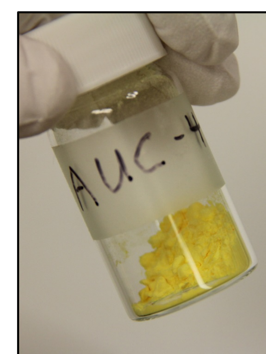
Radiochronometry and signatures

- The model age of nuclear material is a powerful signature for nuclear forensics

- *Comparative signature:* no assumptions are required about sample purification or production history
- *Predictive signature:* model sample history is assumed
  - sample was completely purified from decay products at some time in the past
  - sample has remained a closed system since that time

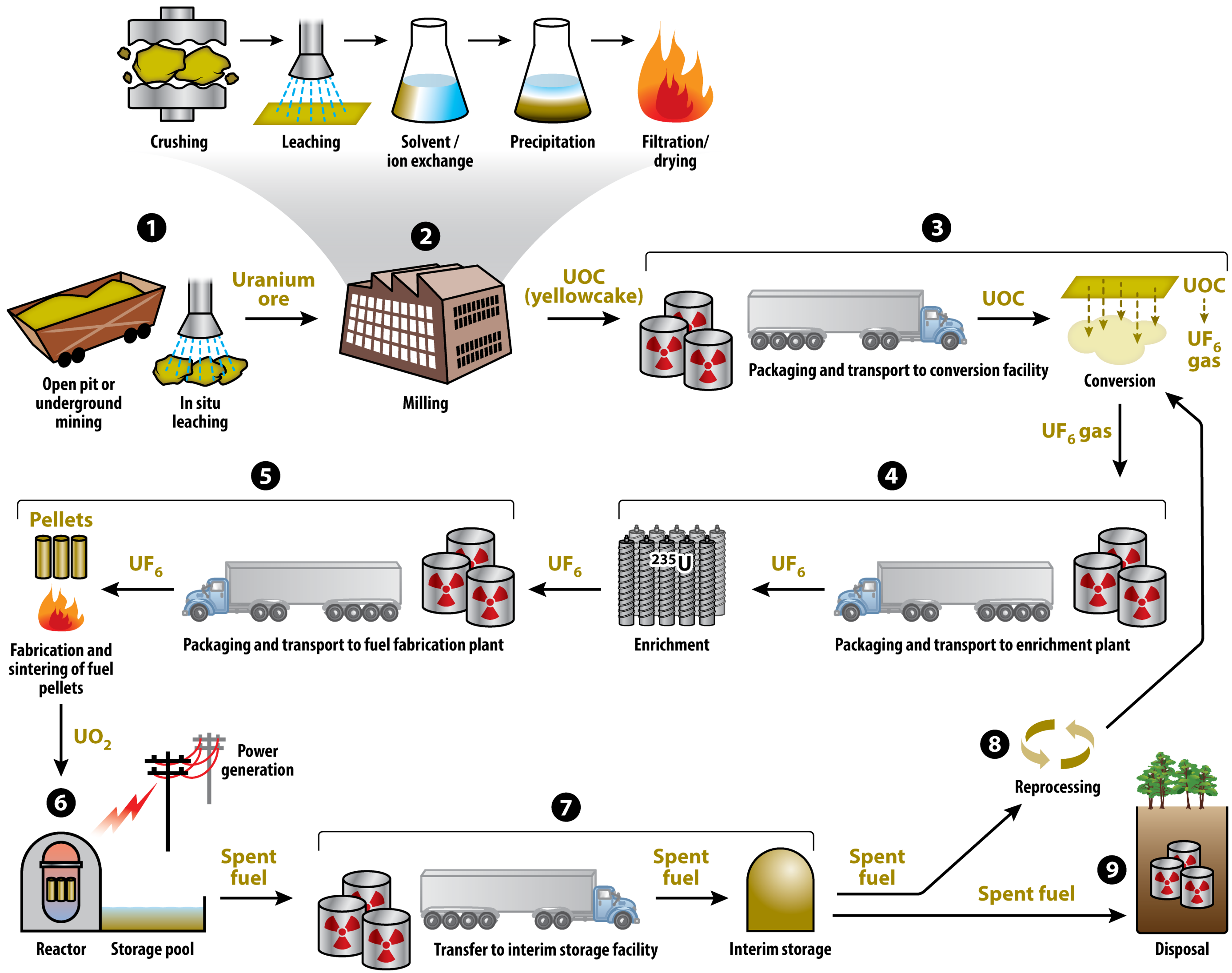






Uranium fuel cycle

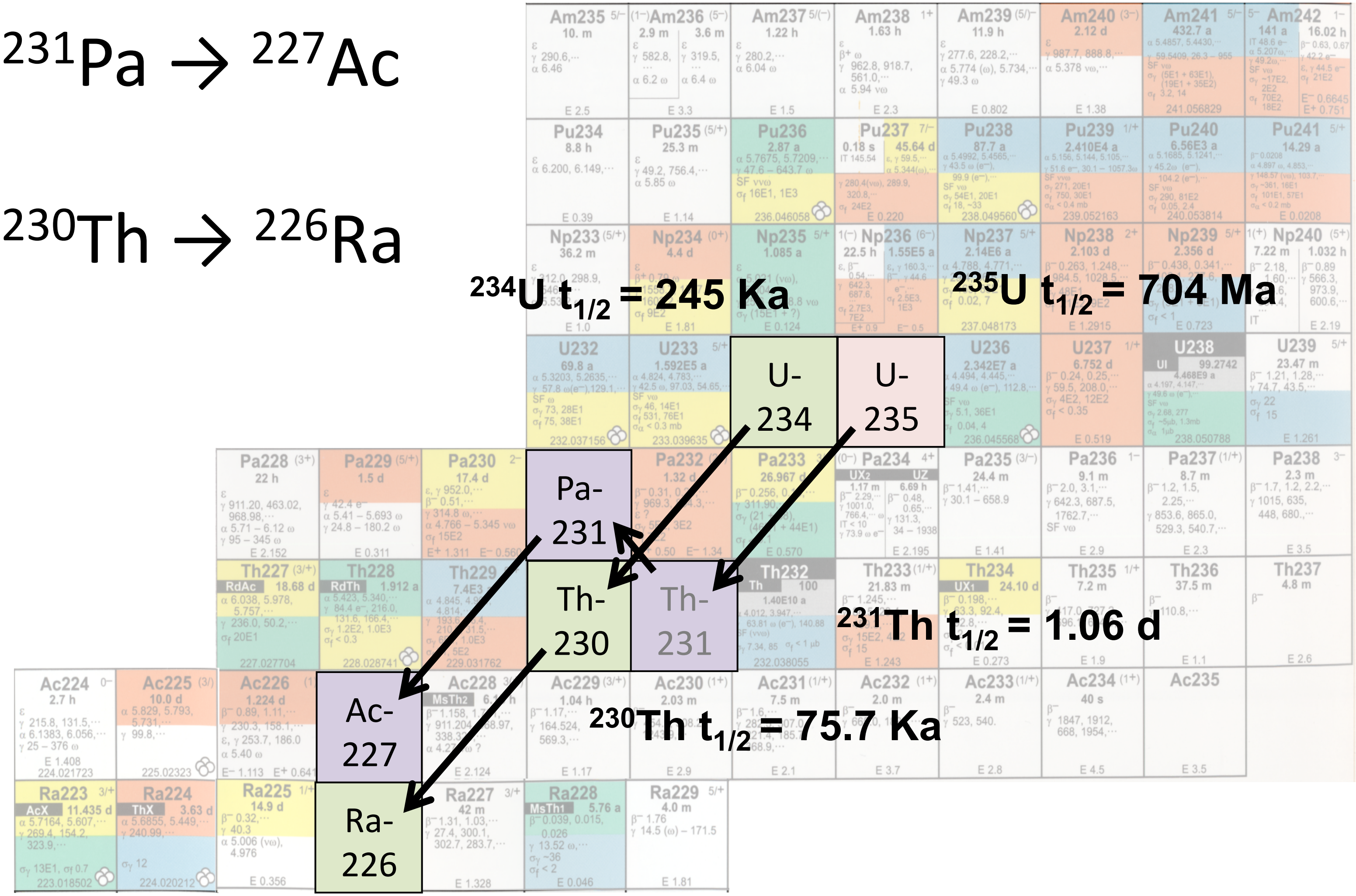
- Uranium processing may purify decay products *or* add contaminants to bulk uranium
- How do decay products behave during uranium production processes?



Kristo et al. (2016) *AREPS* 44:555-79

Uranium-series chronometers

- $^{235}U \rightarrow {}^{231}Pa \rightarrow {}^{227}Ac$
- $^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra$



Radioactive decay equations

- Amount of parent present at time = t

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

- Amount of daughter present at time = t

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

- Definitions
  - Subscripts: 1 = parent, 2 = daughter
  - N = number of atoms
  - λ = decay constant
  - t = time of interest,
    positive value measured from t = 0 in the past

Model age for daughter/parent system

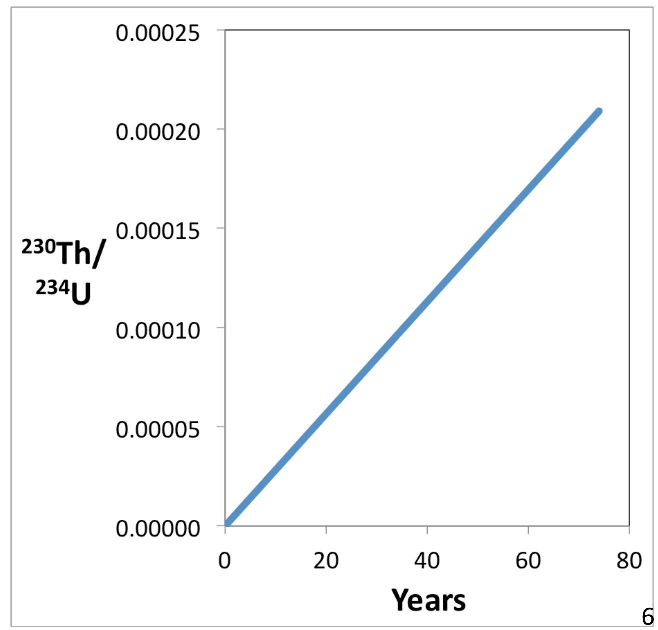
- Model assumption: no daughter present at t=0

$$N_2(t) = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} N_1(t)(1 - e^{(\lambda_1 - \lambda_2)t})$$

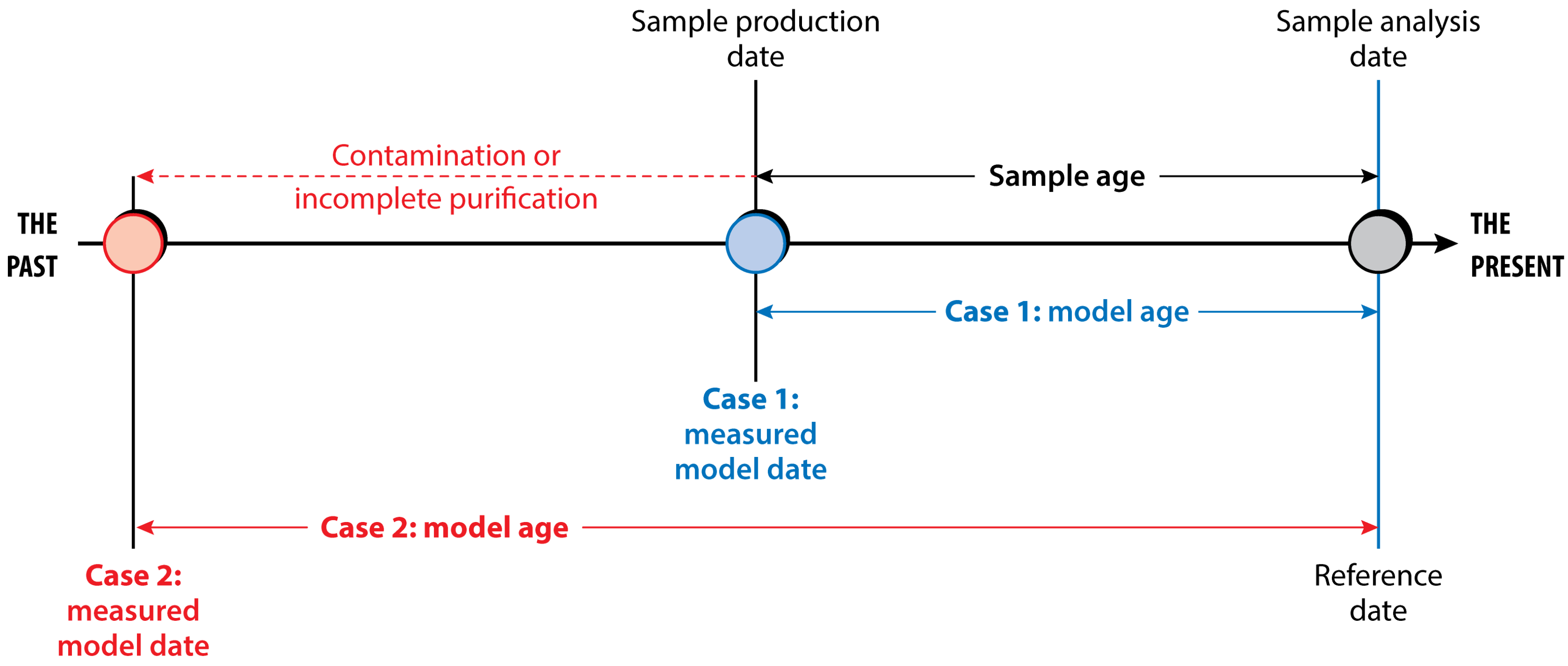
- Expression for t, the age of the material

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

Measured daughter/parent ratio



Model age definitions



- Case 1: material completely purified from decay product at time of production, model age = sample age
- Case 2: material incompletely purified at time of production *or* material contaminated since time of production, model age > sample age

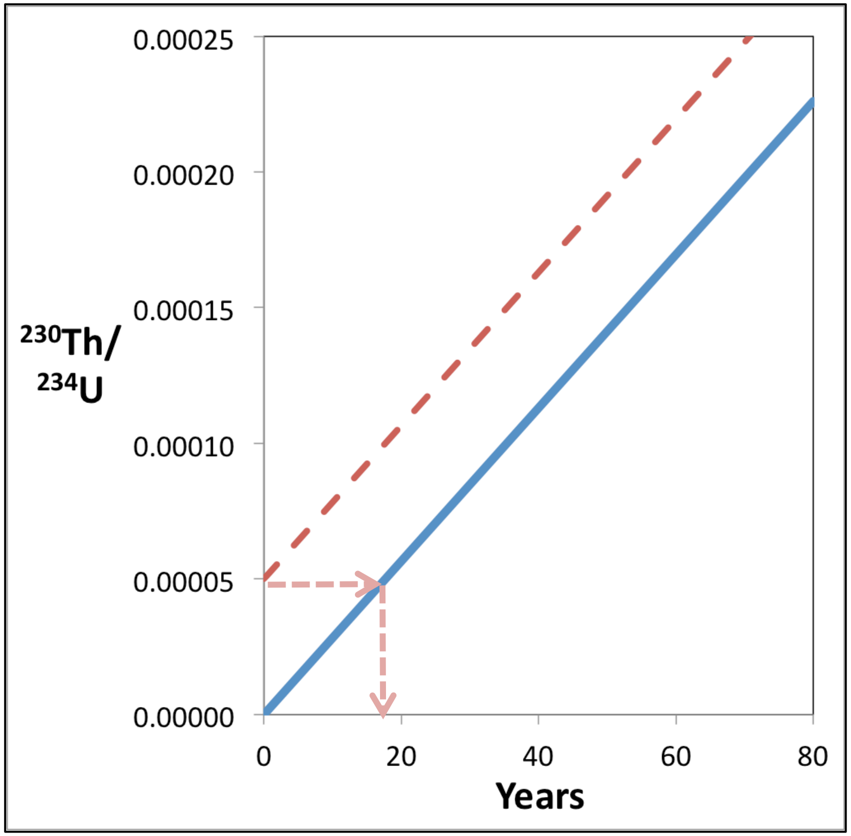
Kristo et al. (2016) *AREPS* 44:555-79

Assumptions for model ages

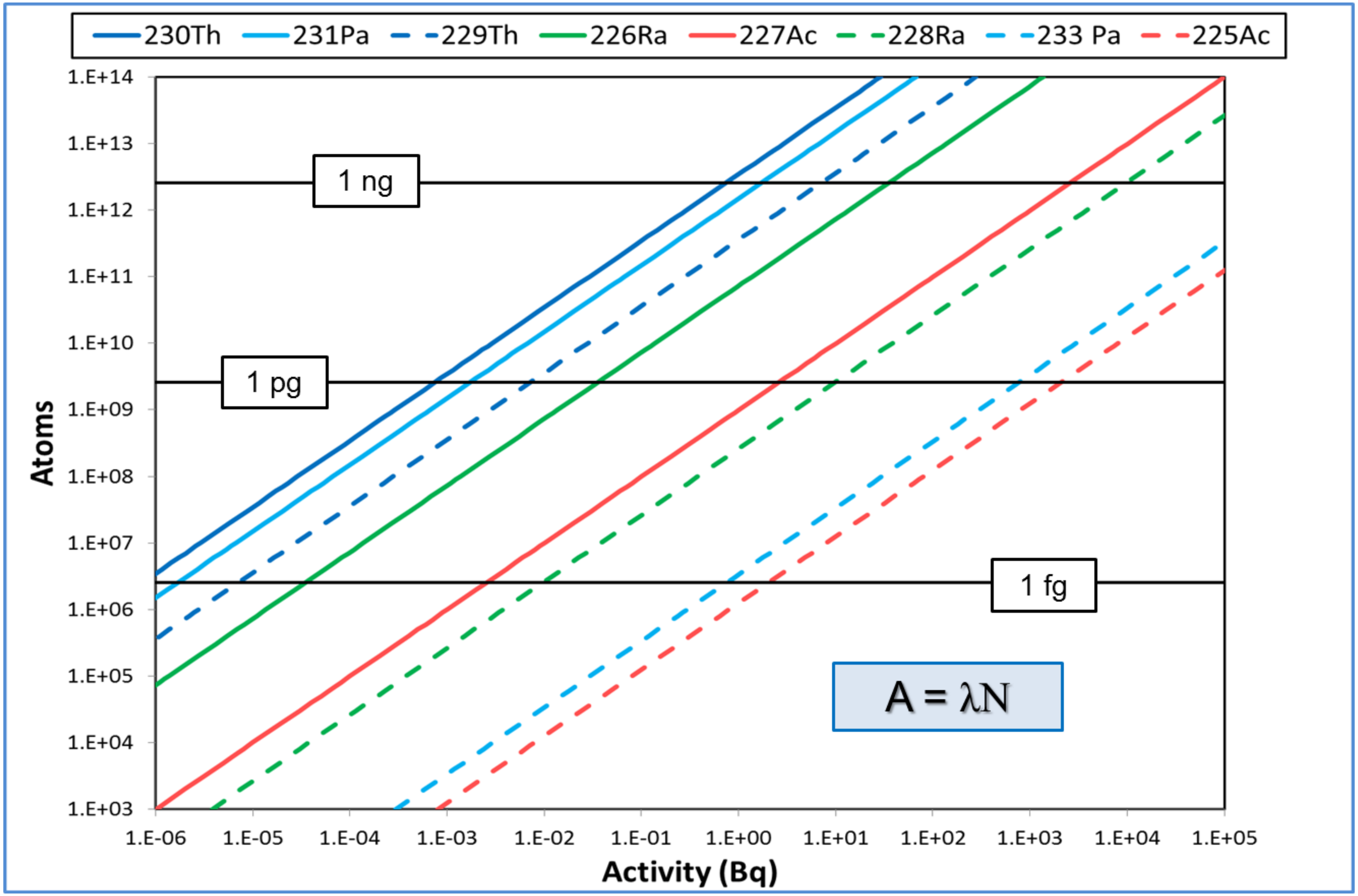
$$t = \frac{1}{\lambda_{234} - \lambda_{230}} \ln\left[1 + \boxed{\frac{^{230}Th}{^{234}U}} \frac{\lambda_{234} - \lambda_{230}}{\lambda_{234}}\right]$$

- The model age is proportional to the measured daughter/parent isotope ratio

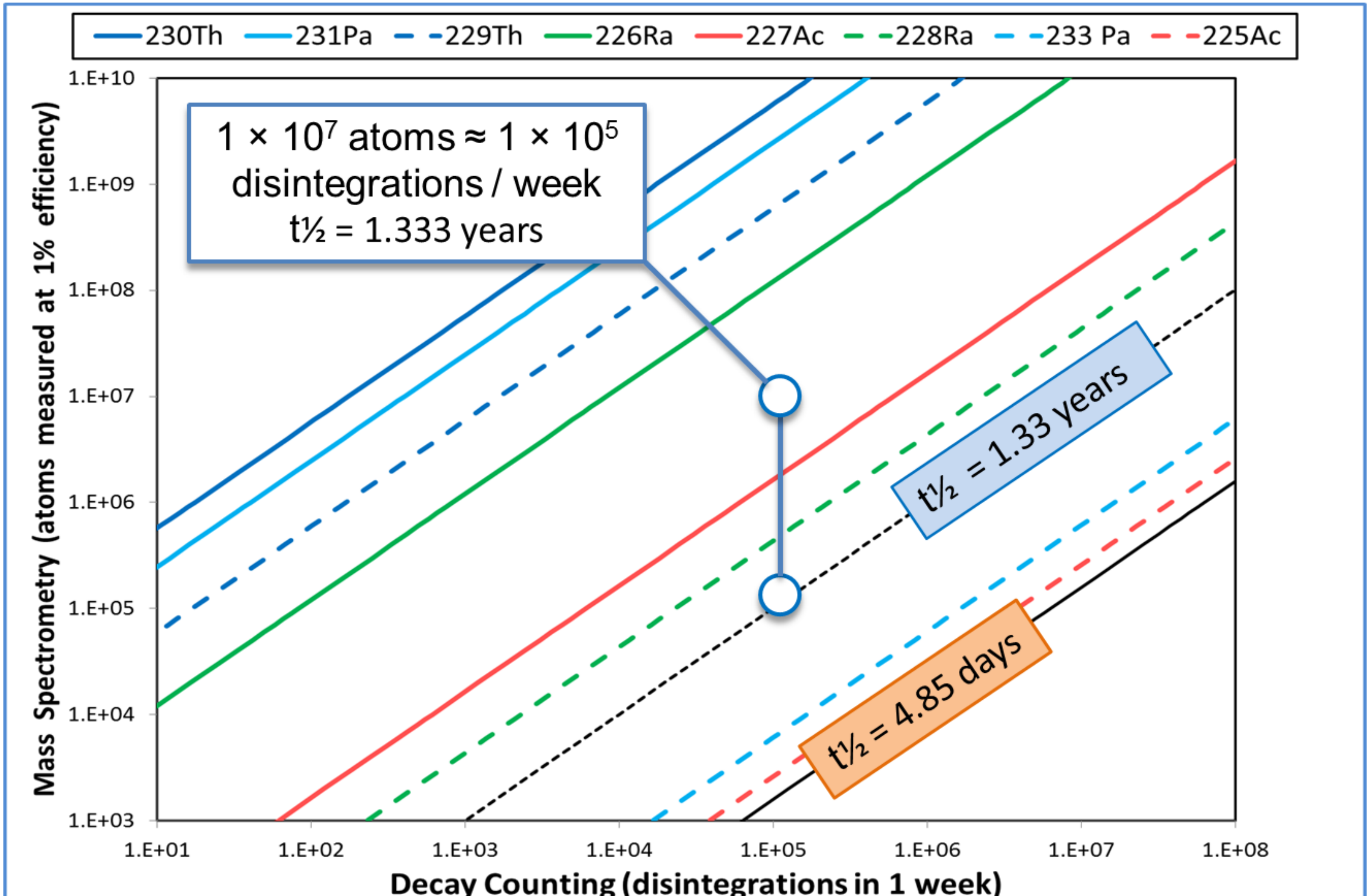
- Contamination or incomplete purification results in sample model age that is older than the sample production age



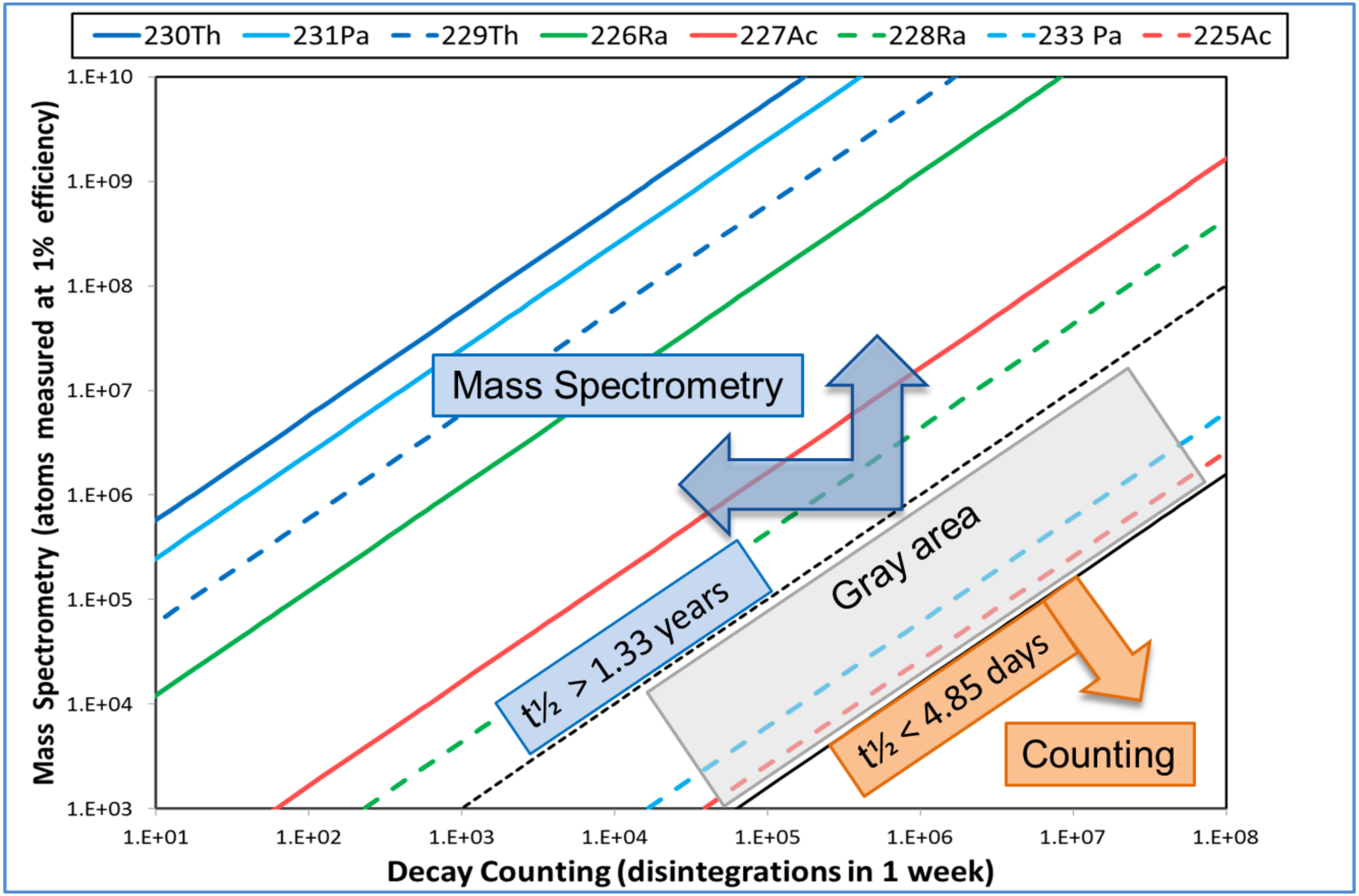
U-series nuclides used for radiochronometry



Mass spectrometry vs. decay counting



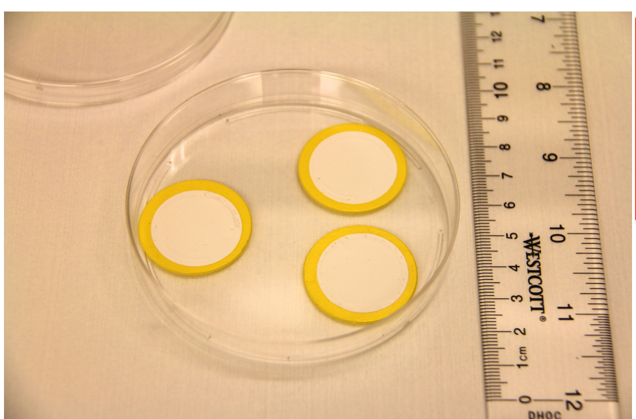
Measurements in practice



Decay-counting methods

High-Resolution HPGE Gamma Spectrometry

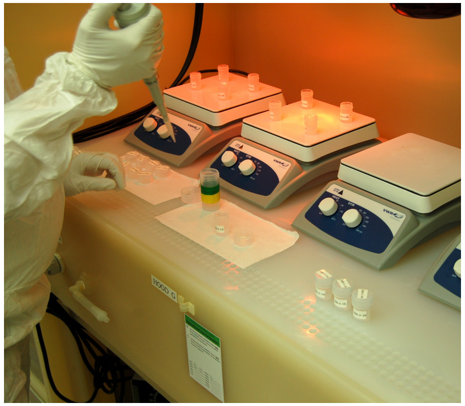
Decay-counting methods can be non-destructive or destructive



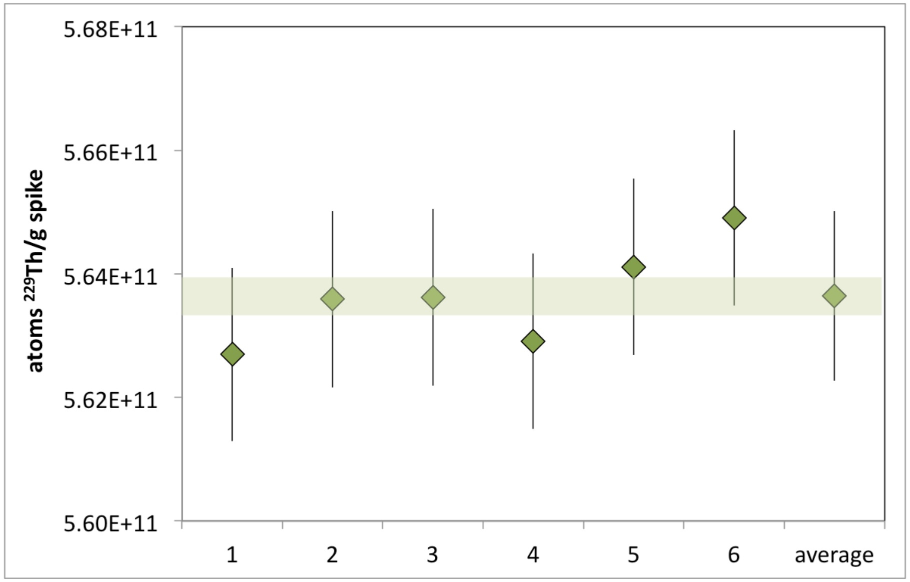
High-Resolution Solid-State and Gas-proportional Alpha Spectrometry

Isotope dilution requires isotope tracers (spikes)

- Purchased from metrology institute (e.g. NIST, IRMM) or calibrated against traceable concentration standard
  - ^{233}U, ^{229}Th, ^{233}Pa
- ^{229}Th calibration example:
  - Calibrated with NIST SRM 4342A ^{230}Th radioactivity standard
  - Requires ^{230}Th half-life to calculate ^{230}Th atoms/g in SRM 4342A

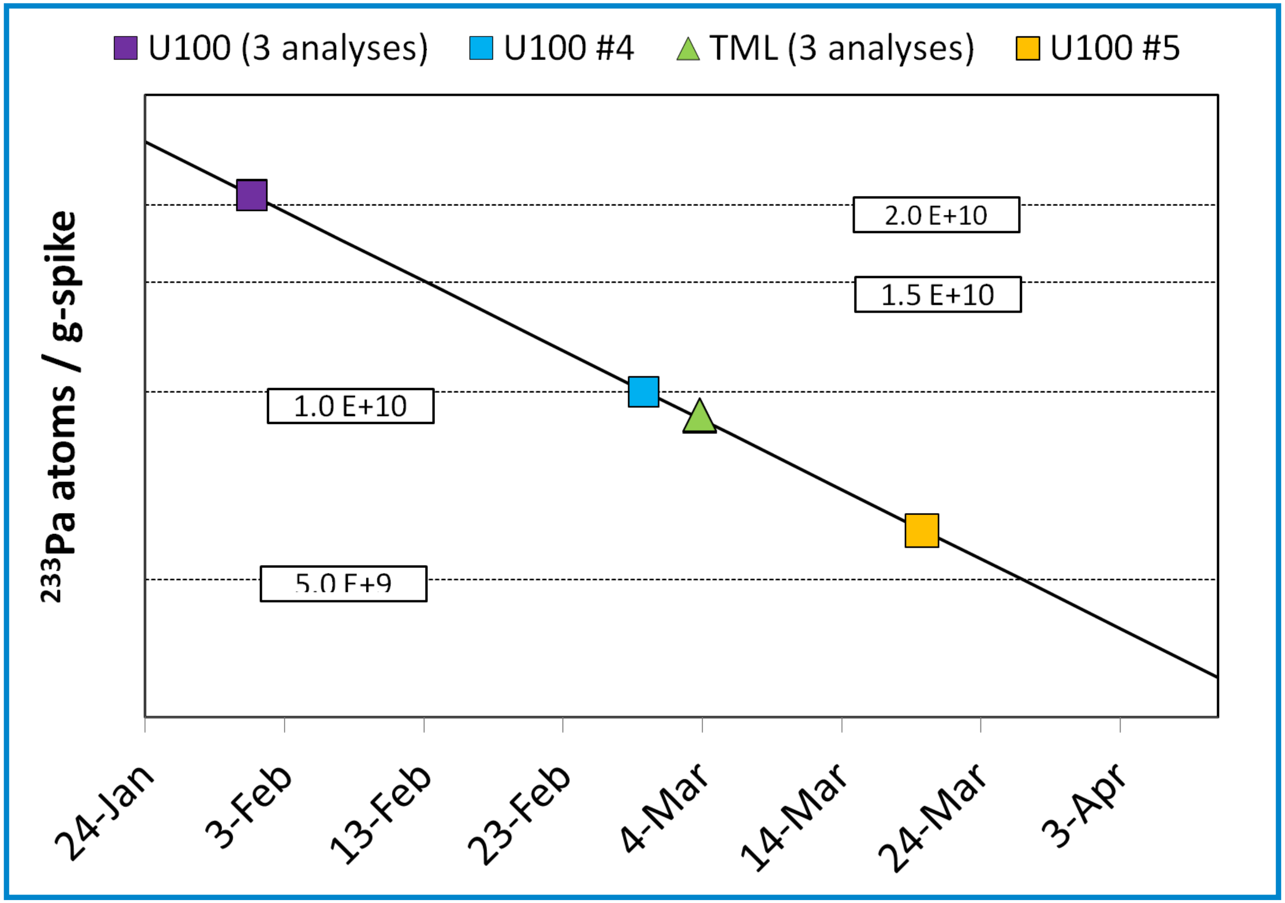


Calibration Uncertainty
- SE (n=6): 0.058%
- NIST 4342A: 0.24%



^{233}Pa spike for ^{231}Pa analyses

- ^{233}Pa ($t_{1/2}$ = 27 days) is milked from ^{237}Np and calibrated using geologic standards, assuming secular equilibrium



Eppich *et al.*, J. Anal. At. Spectrom., 28, 666-674, 2013.

Radiochronometry analyses - standards

New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM 125-A
Uranium (UO_2) Pellet Assay, Isotopic, and Radiochronometric Standard

Amount Content :	0.88129	g U•g^{-1} pellet		
Uncertainty:	0.00014	g U•g^{-1} pellet		
	$n(^{234}U)/n(^{238}U)$	$n(^{235}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$	
Isotope-Amount Ratio:	0.00039130	0.042301	0.0000040754	
Uncertainty:	0.00000038	0.000025	0.0000000047	
	$n(^{234}U)/n(U)$	$n(^{235}U)/n(U)$	$n(^{236}U)/n(U)$	$n(^{238}U)/n(U)$
Isotope-Amount Fraction (•100):	0.037528	4.0569	0.00039085	95.9052
Uncertainty:	0.000037	0.0023	0.00000045	0.0023
	$m(^{234}U)/m(U)$	$m(^{235}U)/m(U)$	$m(^{236}U)/m(U)$	$m(^{238}U)/m(U)$
Isotope Mass Fraction (•100):	0.036915	4.0077	0.00038776	95.9550
Uncertainty:	0.000036	0.0023	0.00000045	0.0023

Molar Mass:	237.927291 g•mol^{-1}		Model Purification Date:	August 18, 1994
Uncertainty:	0.000071 g•mol^{-1}		Uncertainty:	116 days

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements (Geel)

CERTIFIED REFERENCE MATERIAL IRMM–1000a

CERTIFICATE OF ANALYSIS

20 mg URANIUM NITRATE		
	Production date based on the $n(^{230}Th)/n(^{234}U)$ radiochronometer	
	Certified value	Uncertainty [4)] [day]
Production date [1)]	09/07/2012 (UTC) [2)] 2012-07-09Z [3)]	13

1) The production date is the date of the last chemical separation of ^{230}Th from ^{234}U in the uranium reference material.

2) The certified value is expressed as a date dd/mm/yyyy, relative to the universal coordinated time (UTC).

... is expressed as yyyy-mm-ddZ according to ISO 8601.

... expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of ... in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in ...), ISO, 2008. It is based on the confirmation measurements and calculations using the ... traceable to the International System of units (SI).

New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM U630
Uranium (U_3O_8) Isotopic and Radiochronometric Standard

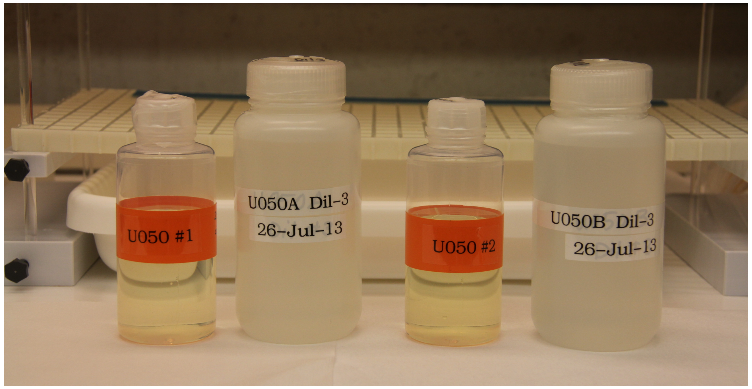
	$n(^{234}U)/n(^{235}U)$	$n(^{236}U)/n(^{235}U)$	$n(^{238}U)/n(^{235}U)$	
Isotope-Amount Ratio:	0.0097698	0.0151895	0.55351	
Uncertainty:	0.0000062	0.0000097	0.00049	
	$n(^{234}U)/n(U)$	$n(^{235}U)/n(U)$	$n(^{236}U)/n(U)$	$n(^{238}U)/n(U)$
Isotope-Amount Fraction (•100):	0.61894	63.353	0.96230	35.066
Uncertainty:	0.00043	0.020	0.00067	0.020
	$m(^{234}U)/m(U)$	$m(^{235}U)/m(U)$	$m(^{236}U)/m(U)$	$m(^{238}U)/m(U)$
Isotope Mass Fraction (•100):	0.61354	63.069	0.96207	35.356
Uncertainty:	0.00043	0.020	0.00067	0.020

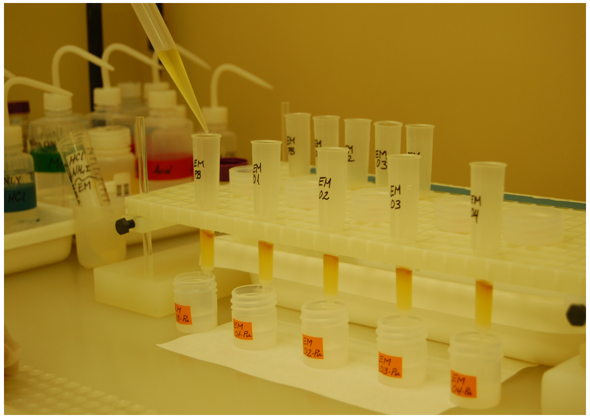
Molar Mass:	236.10175 g•mol^{-1}		Model Purification Date:	June 6, 1989
Uncertainty:	0.00061 g•mol^{-1}		Uncertainty:	190 days

Radiochronometry standards are required for method validation

Sample preparation and analysis methods

- Mass spectrometry is a destructive analytical method
  - element of interest is purified from bulk sample
  - eliminate isobaric interferences, matrix effects
- Sample is dissolved
- Purification utilizes ion exchange, selective extraction and other methods



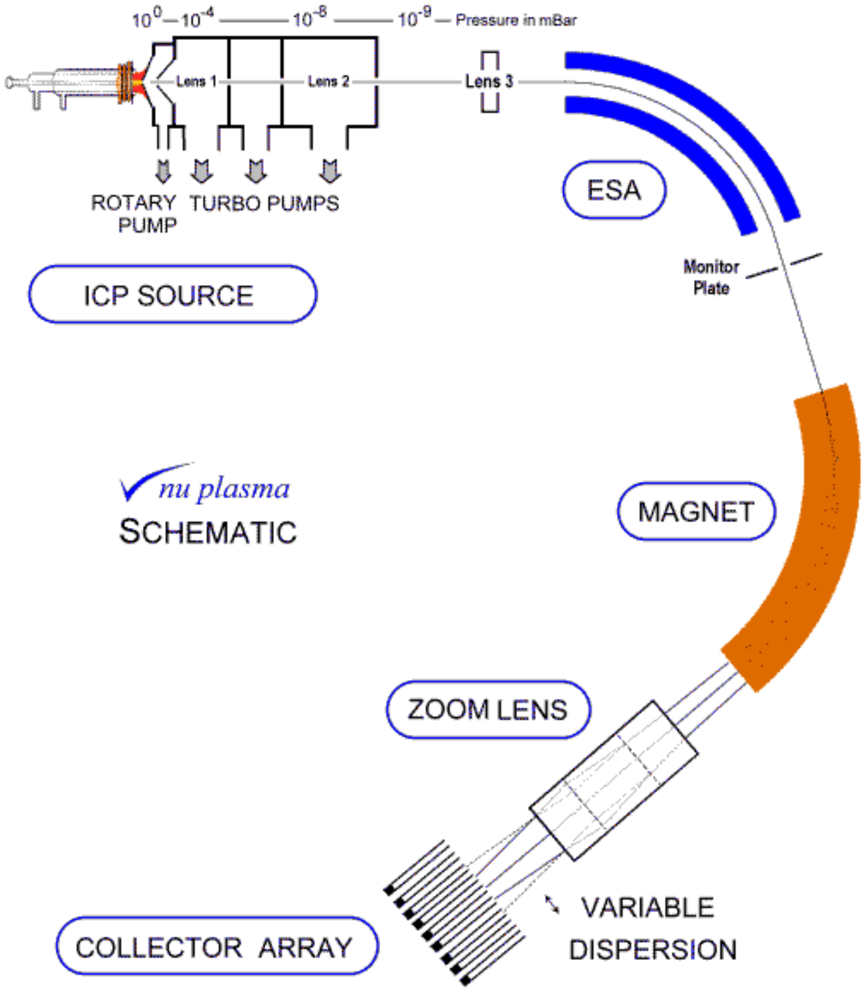


Mass spectrometers

- **High-resolution single-collector ICP-MS**, e.g., Thermo Scientific Element
- **Multi-collector ICP-MS**, e.g., Nu Plasma, Thermo Scientific Neptune
- **Thermal ionization mass spectrometer** (TIMS), e.g., Thermo Scientific Triton, Isotopix Phoenix

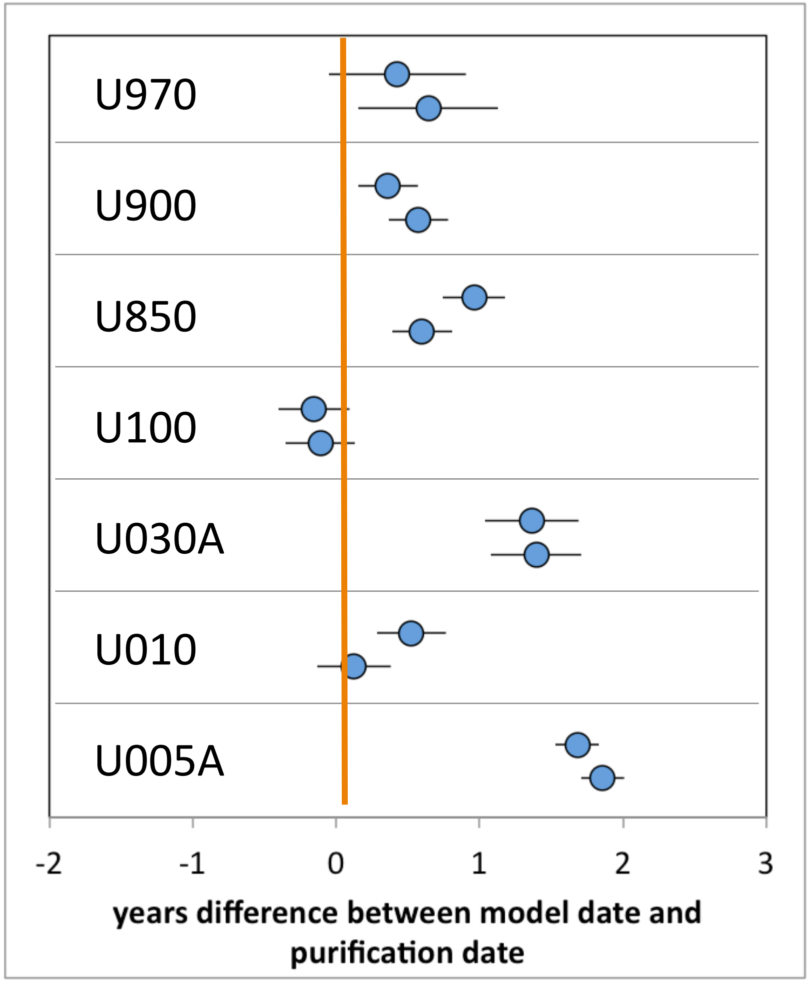
Mass spectrometry

- Ion Source
  - Plasma ionization
  - Thermal ionization
- Magnet
- Focusing, energy filters
- Collectors
  - Faraday cups
  - Ion counters



Example: ^{230}Th-^{234}U model ages of NBL CRMs

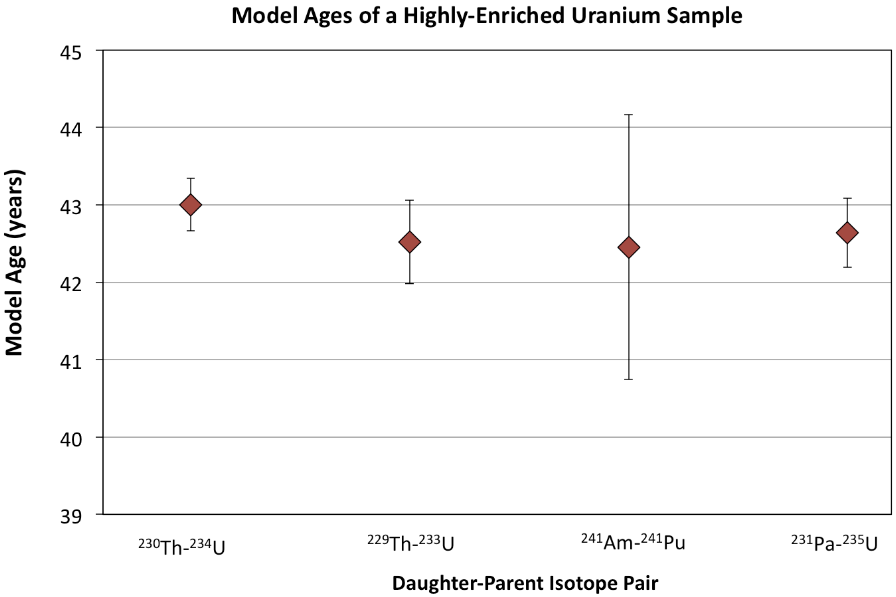
- Most CRMs produced in late-1950's to early-1960's
- U030A and U005A produced in 1981
- In general, model ages are slightly biased old
  - Duplicate analyses are in agreement
- Interpreted to represent incomplete purification of ^{230}Th during material production
- Bias greater in younger CRMs
  - Are more recently produced CRM's less pure?

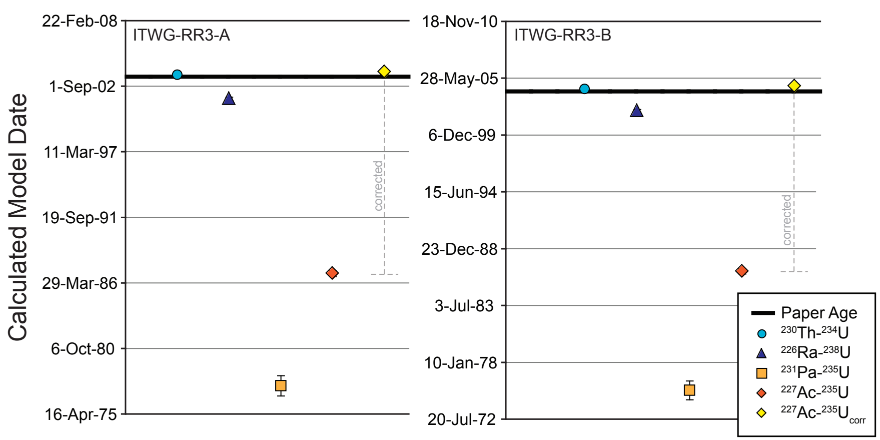


Williams and Gaffney (2011) *Proc. Radiochim. Acta* **1**: 31-35.

Concordant and discordant radiochronometers

- *Concordant model ages* from two or more radiochronometers provides a high degree of confidence that the model age represents the actual purification age of the sample.
- *Discordant model ages* provide information on the relative fractionation between daughter isotopes and parent during sample production.
  - The degree of purification, or contamination, of different daughter isotopes may help to identify the process.
- Regardless of concordance or discordance, if the system remains closed, the model dates are constant, high-value signatures.

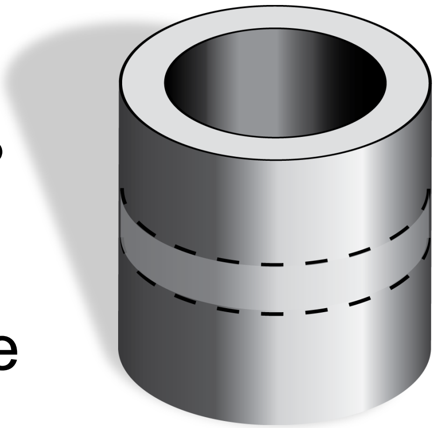


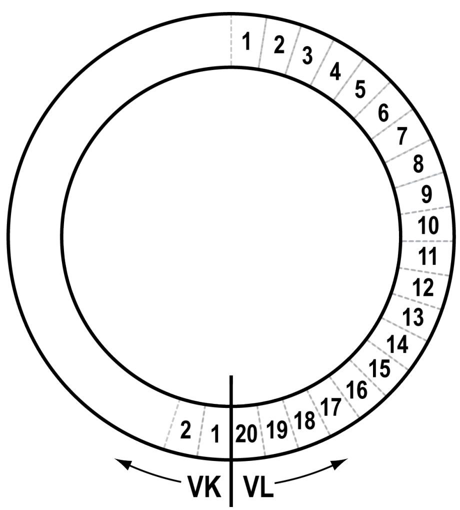


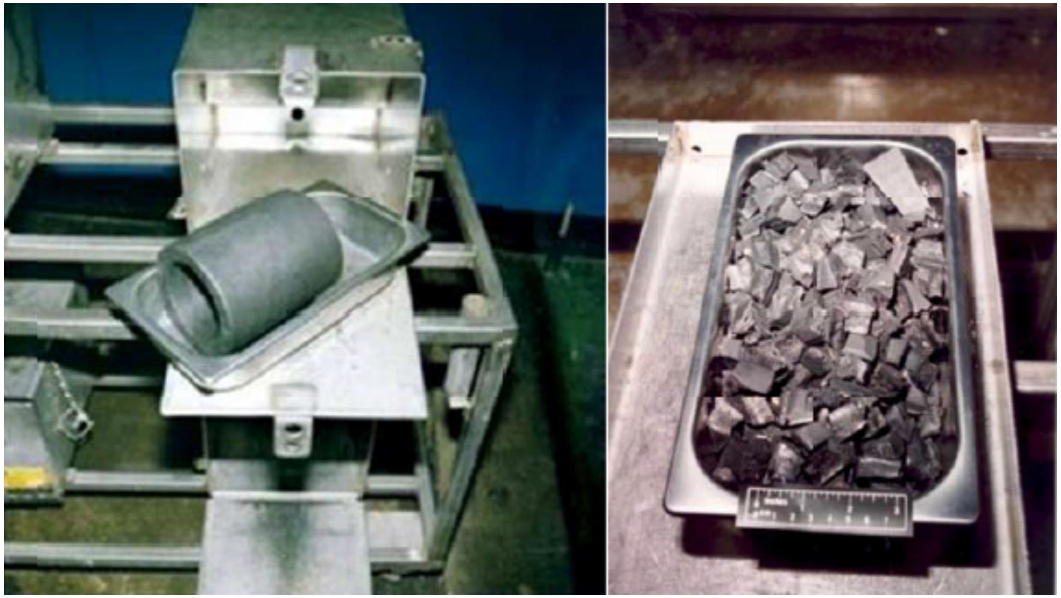
Kayzar and Williams (2016) JRNC 307:2061-2068

Example: ITWG-RR3 (2010)

- Exercise scenario - two pieces of metal seized separately at a border crossing
  – are the two samples related, and if so, how?
- Samples are pieces of two HEU ‘storage logs’
  – Logs consist of scrap uranium, unknown age
  – Casting dates known: May 2003, January 2004

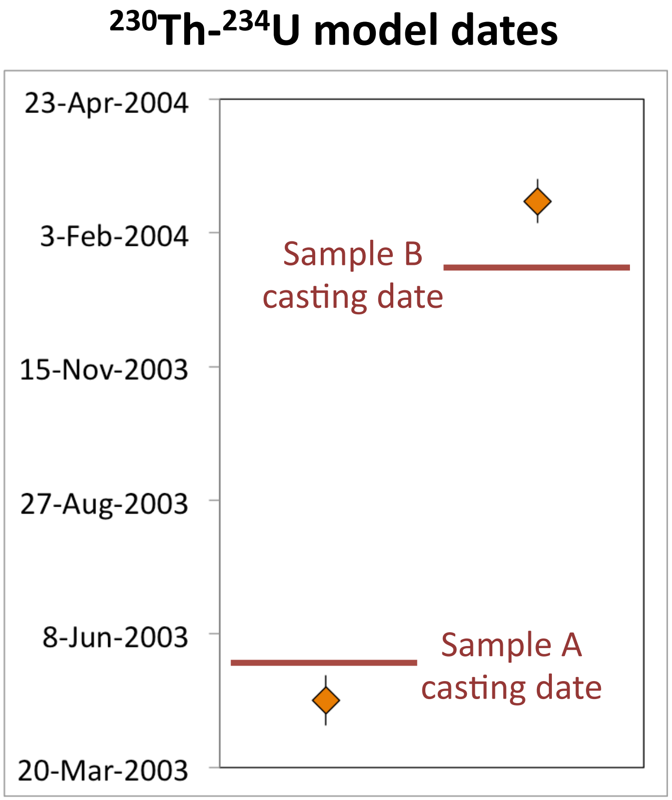






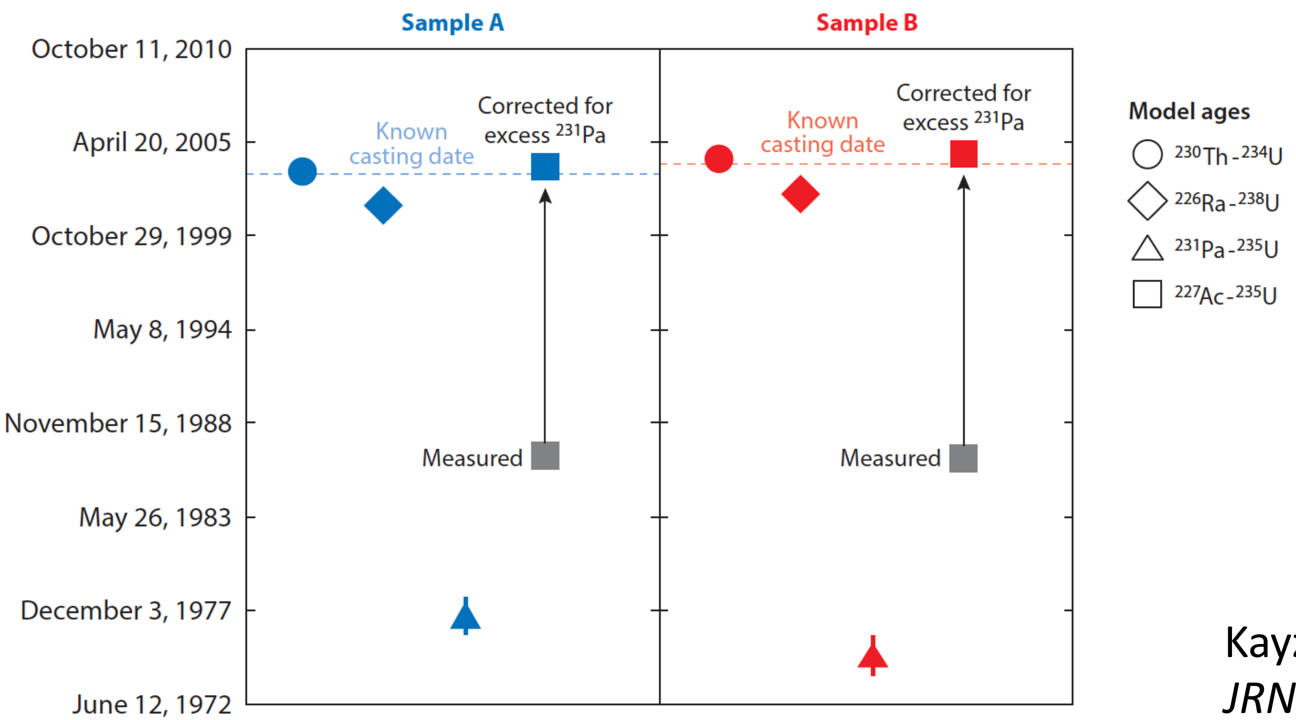
Example: ITWG-RR3

- ^{230}Th-^{234}U model dates are close to known casting dates
  - Th is effectively purified during U metal casting
- ^{231}Pa-^{235}U model dates are 1974-1976
  - Pa is not purified from U during metal casting
- Two samples are *not* from the same batch of material
- Metal casting has different effects on Th/U and Pa/U



Example: ITWG-RR3

- Grand-daughter chronometry reveals additional information on behavior of Ra and Ac during U metal casting
- ^{226}Ra-^{238}U model ages < 2 years older than known casting date
  - Ra not as efficiently purified from U as Th during metal casting
- ^{227}Ac-^{235}U$_{corr}$ model ages nearly concordant with casting date: Ac supported by ^{231}Pa since casting
  - Efficient Ac segregation during metal casting



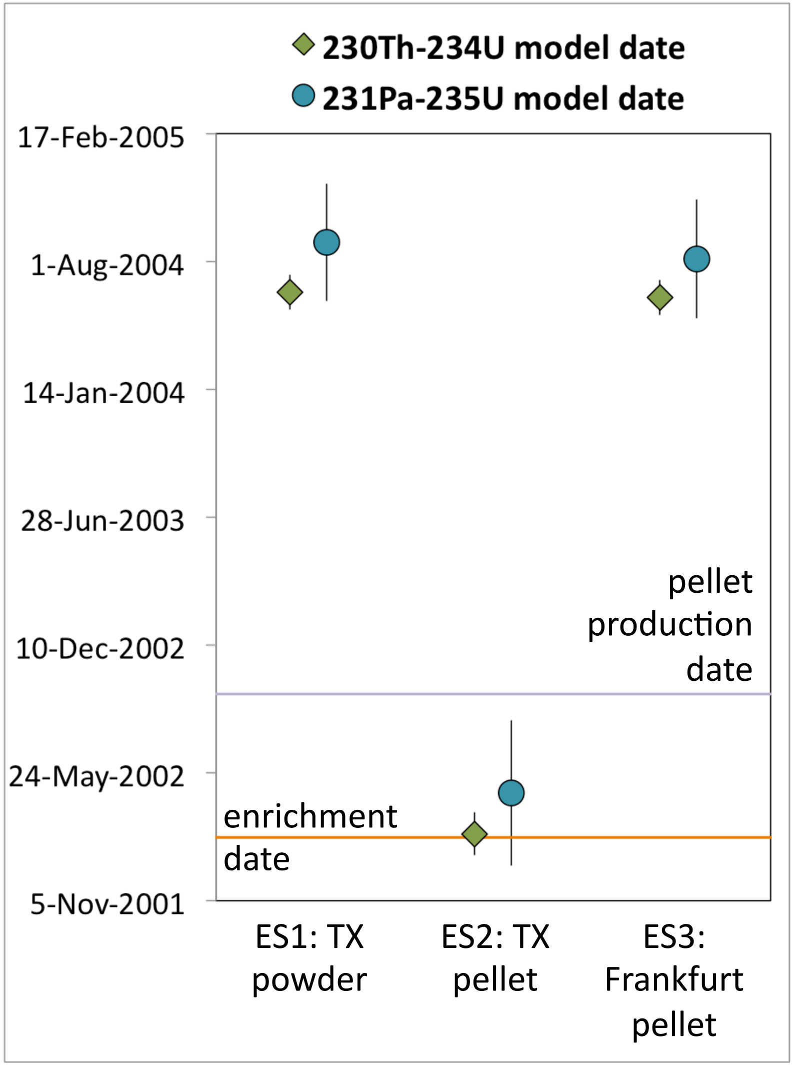
Kayzar and Williams (2016)
JRNC 307: 2061-2068

Example: ITWG-CMX4 (2014)

- Scenario
  - Passenger on Dallas-to-Frankfurt flight found to possess uranium powder
  - Search of passenger's home reveals pellet
  - Similar pellet found previously in Frankfurt warehouse
- Do the materials share an origin?
  - facility
  - process
  - batch

Example: ITWG-CMX4

- ^{230}Th-^{234}U and ^{231}Pa-^{235}U samples are concordant for each sample
- ES2 model ages are concordant with enrichment date, not pellet production date
- ES1 and ES3 are similar in both chronometers, likely from same batch; consistent with known production in 2004



Example: historical plutonium from Hanford

- In 2004, jug containing Pu uncovered in waste trench at Hanford
- ‘Low-burn’ Pu could represent early US production
- Material has unknown history - evaluate model age assumptions

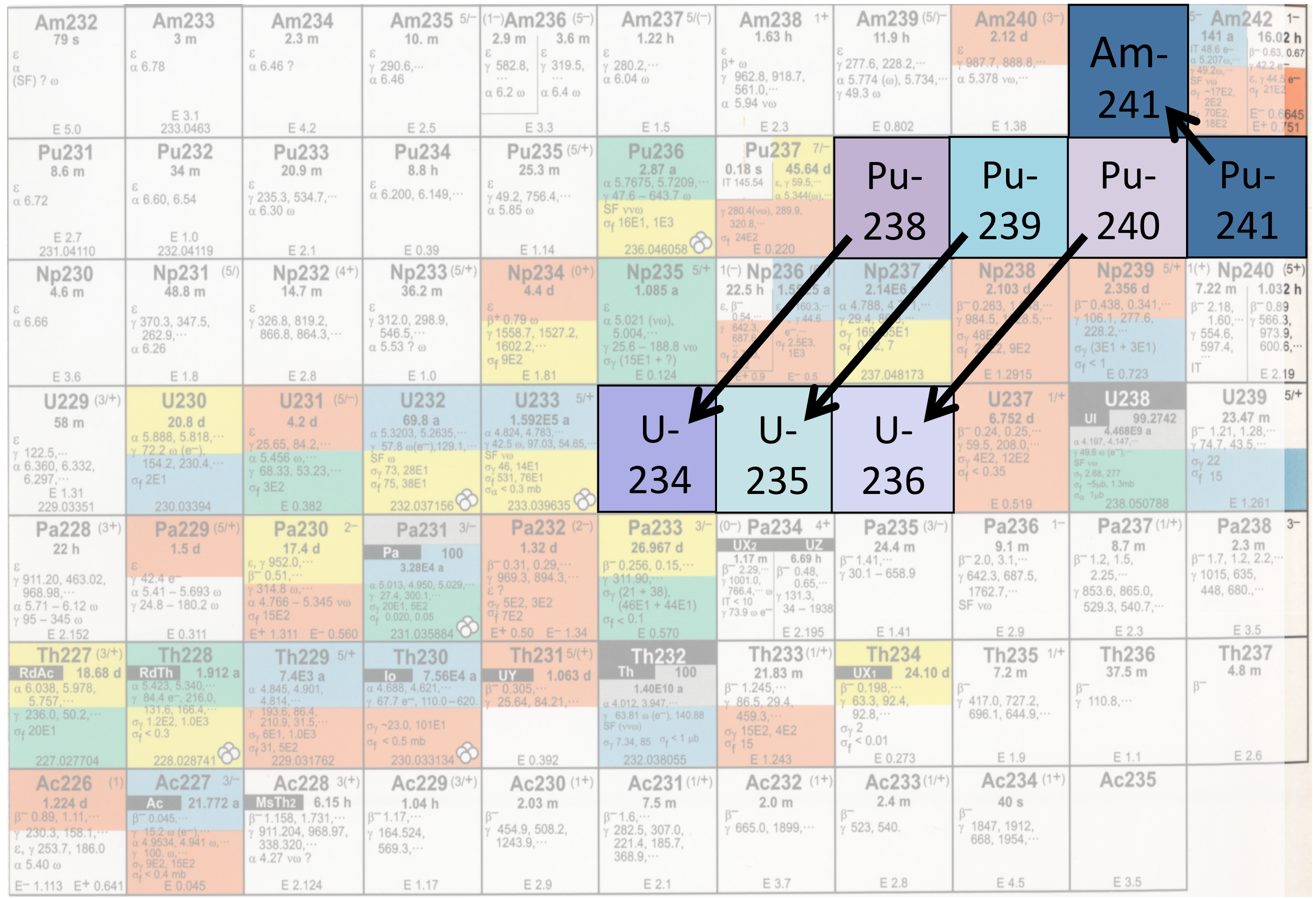
(a.)

(b.)

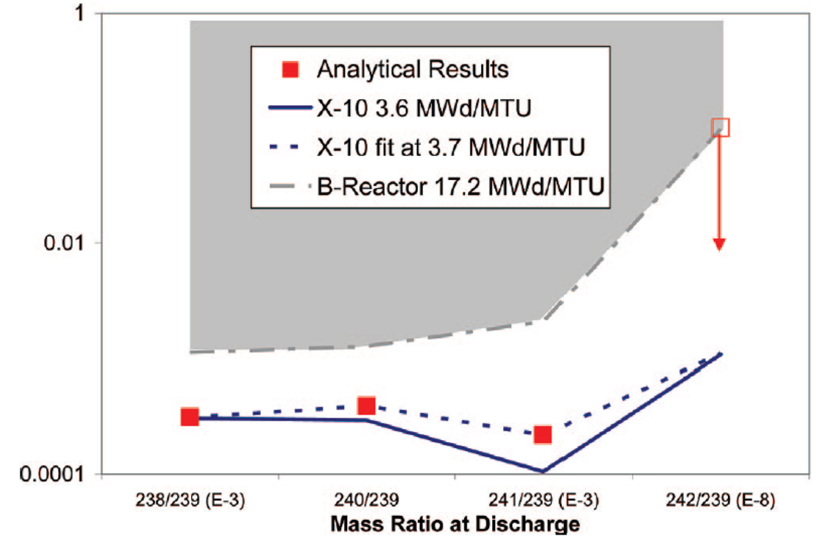
Schwantes (2009) *Anal. Chem.* 81:1297-1306

Plutonium chronometry: daughter-parent

- $^{238}Pu \rightarrow {}^{234}U$
- $^{239}Pu \rightarrow {}^{235}U$
- $^{240}Pu \rightarrow {}^{236}U$
- $^{241}Pu \rightarrow {}^{241}Am$



Example: U-Pu radiochronometry



- Three U-Pu daughter-parent pairs
  - ^{234}U-^{238}Pu
  - ^{235}U-^{239}Pu
  - ^{236}U-^{240}Pu
- Model age: 1946 ± 4.5 years
- Absence of detectable ^{241}Pu (^{241}Pu $t_{1/2}$ = ~14 years) consistent with this model age
- Reactor modeling and historical records suggest that material was produced in X-10 reactor, Oak Ridge
- Material is second-oldest known sample of Pu

Schwantes (2009) *Anal. Chem.* 81:1297-1306

Summary

- Model age is a powerful signature for nuclear forensics
  - comparative: establish or eliminate genetic link
  - predictive: assume sample history
- Model age assumptions
  - material is purified from decay products at time of production
  - material is 'closed system'
- Measuring multiple chronometers for a sample is important for increased confidence in interpretation
  - Concordant ages provide validation for model age assumptions
  - Discordant ages can constrain the processes used in material production or contaminant characteristics

Upcoming Webinars

- Development of Signatures: October 27, 2016
- Statistics in Nuclear Forensics: November 17, 2016
- Source and Route Attribution: December 8, 2016

NAMP website: www.wipp.energy.gov/namp