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Title: Utility of heavy stable isotope measurements to characterize UOC

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Utility of heavy stable isotope measurements to characterize UOC



Jeremy Inglis, C-NR

10/2/18



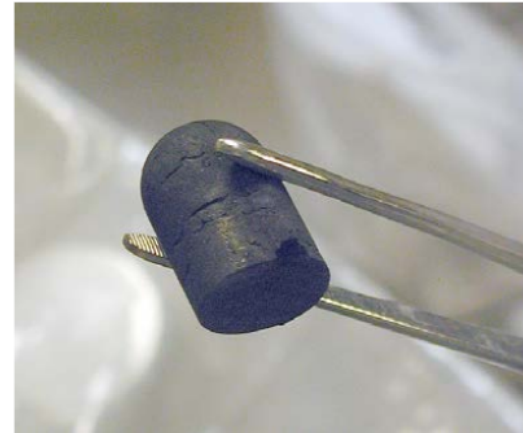
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Agenda

- **Introduction to nuclear forensics**
- **Importance of isotope analysis**
- **Overview of mass spectrometry capabilities at C-NR**
- **Heavy stable isotopes as a tool to characterize UOC's**

Nuclear forensic Science

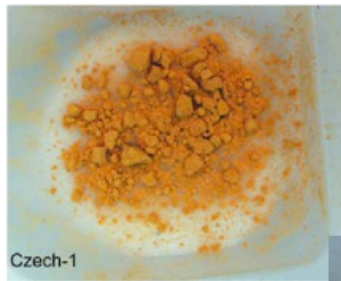
- **Nuclear Forensics – the collection and analysis of nuclear or radiological material to support investigations into the diversion, trafficking or illicit activities involving materials**
- **What is the material**
- **What was its intended use**
- **How was the material made**
- **When was the material produced**
- **Who is associated with the material**



Goal: link nuclear material in question to people, processes, event and/or locations

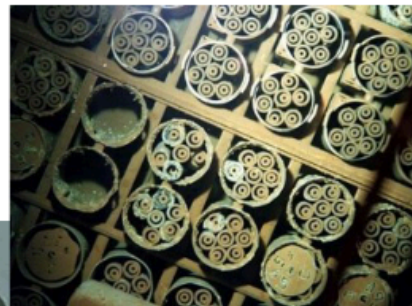
Nuclear materials

- There are nuclear materials involved at every step of the fuel cycle
 - Many different chemical forms
 - Different isotopic compositions



UOC

Fuel



Spent Fuel

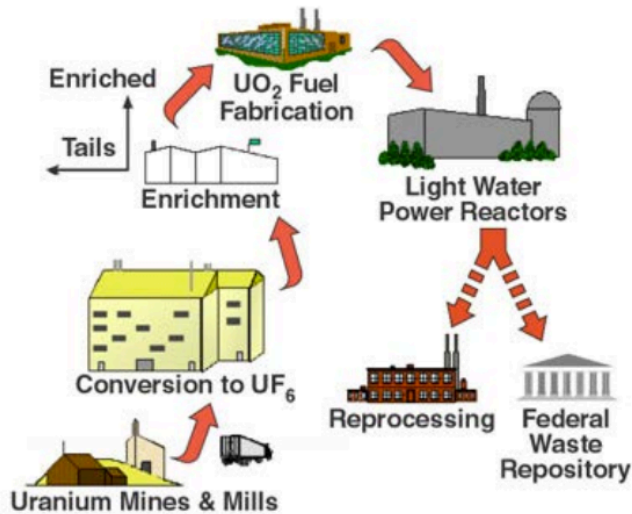
Finished Pu Metal



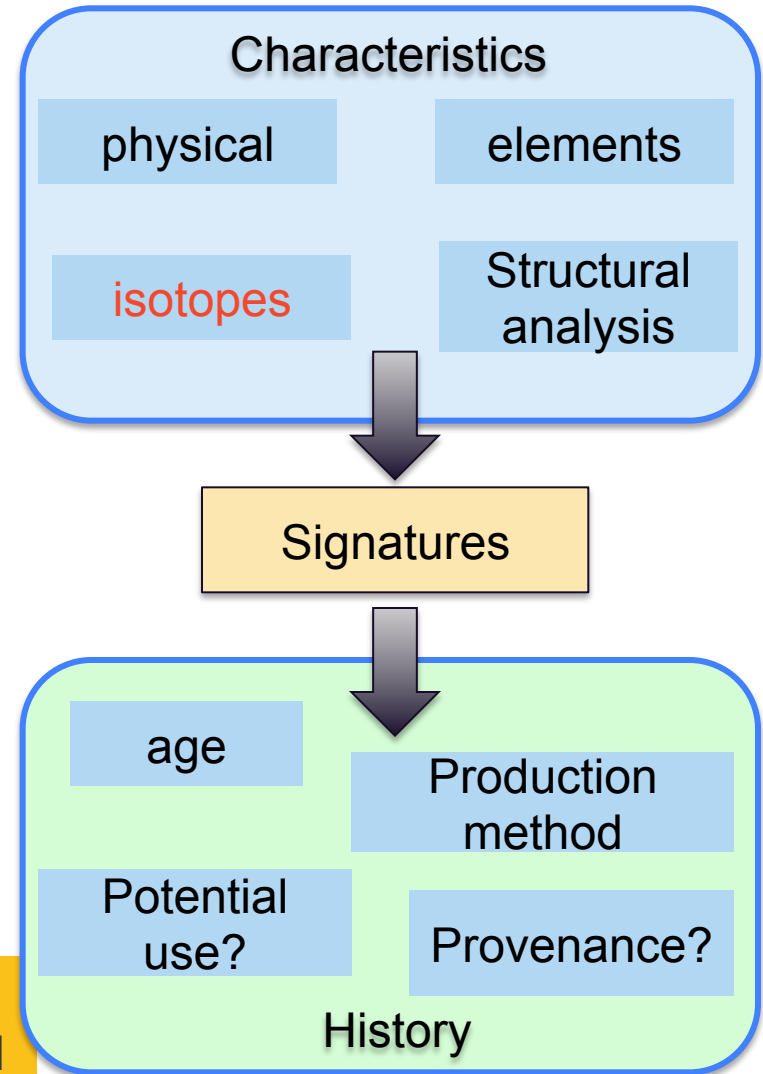
Reprocessed Pu

All of these materials (and many more) have the potential to be the subject of a forensic examination!

Nuclear Forensic - signatures



All nuclear materials have characteristics that are indicative of production history and method



Importance of isotope analysis in forensic characterization

Radio-
chronometry

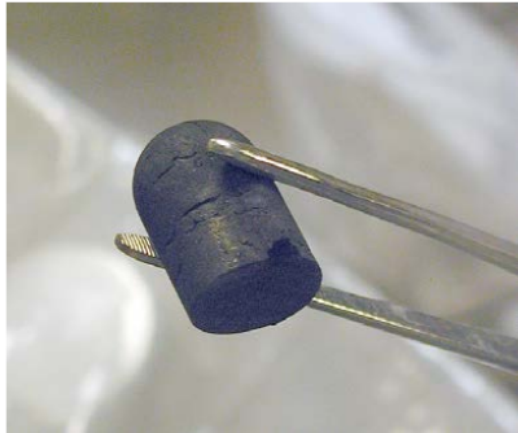
Reactor type

Level of
Enrichment

Reactor
History?

Origin?

**Isotope
Analysis**



Importance of isotope analysis in forensic characterization

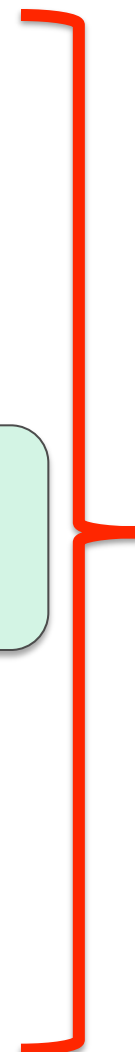


Mine
Type/location

Processing
history?

Milling type/
location?

**Isotope
Analysis**



Facilities to work with materials of all quantities

All facilities house ongoing missions that exercise analytical capabilities routinely

TA-48



Sigma



CMR

TA-55



$< 10^{11}$ atoms Pu-239

$10^9 - 10^{22}$ atoms Pu-239



RC-1, Sigma

Nuclear facilities (CMR, PF-4)



$> 10^{22}$ atoms Pu-239

RC-45 Clean Chemistry and Mass Spectrometry Facility



- Class 10,000 hallways and laboratories
- Class 100 work areas and exhausted laminar flow work cabinets
- Perchloric acid capability
- Ultra low-level sample handling
- Co-located clean radiochemistry and analysis capability
- Isotopic and elemental analysis

CN-R elemental and isotope mass spectrometry

Multi-collector ICP-MS (MC-ICP-MS)

High precision, high accuracy
Isotope ratios (U, Th, Sr, Pb,
Fe, B...)



Sector Field ICP-MS (SF-ICP-MS)

ppq – ppm element
conc. and some
isotope ratios



Multi-collector TIMS

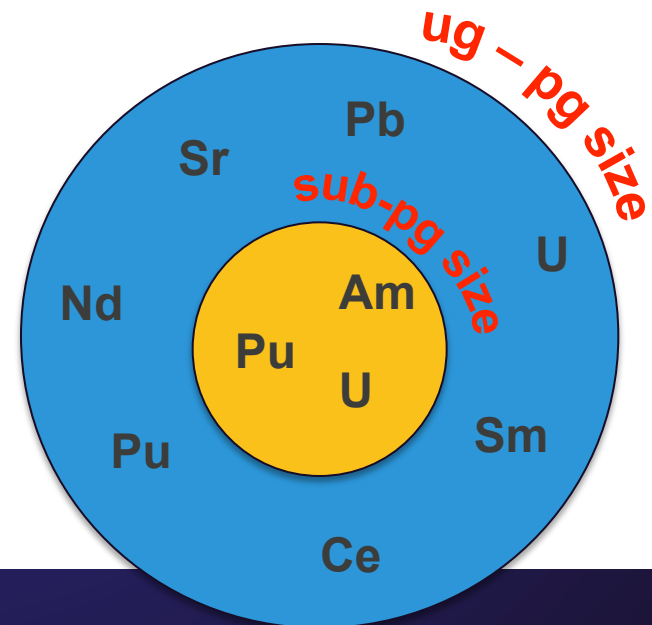
Pu, U, Am, Np,
Sr, Nd, others



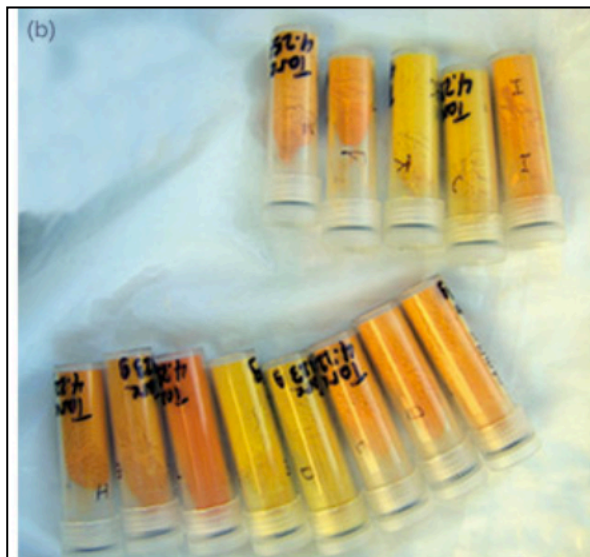
Thermal Ionization Mass Spectrometry - LANL

3 modified Phoenix TIMS, by Isotopx, Manchester UK.

- Large front turbo fitted for improved source pumping
- Rear Turbo fitted for ultra-high vacuum in flight tube and analyzer ($<1e-9$), yields abundance sensitivity of:
 - <0.2 ppm at the focal plane
 - <0.015 ppm behind WARP
- 9 Faraday cups for analysis of large ion beams
- 7 movable multiple ion counters fitted to allow simultaneous detection of isotopes in sub-pg sized samples



Mass spectrometry capabilities

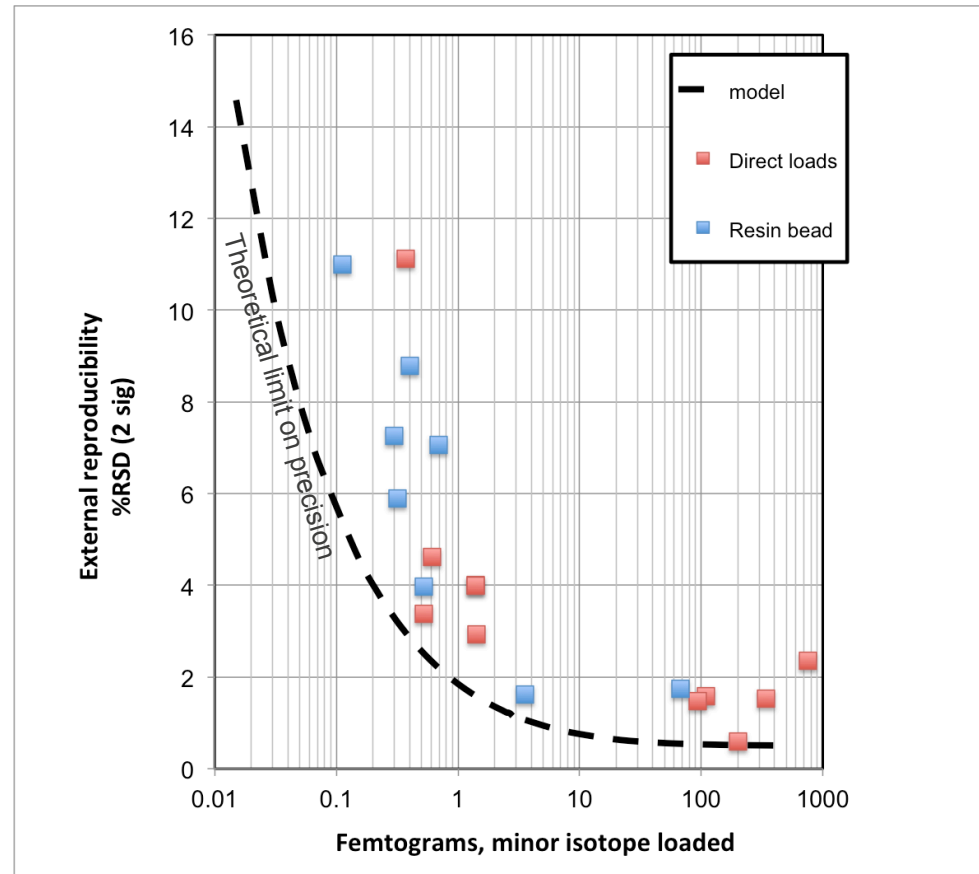


Ultra-low level environmental analysis

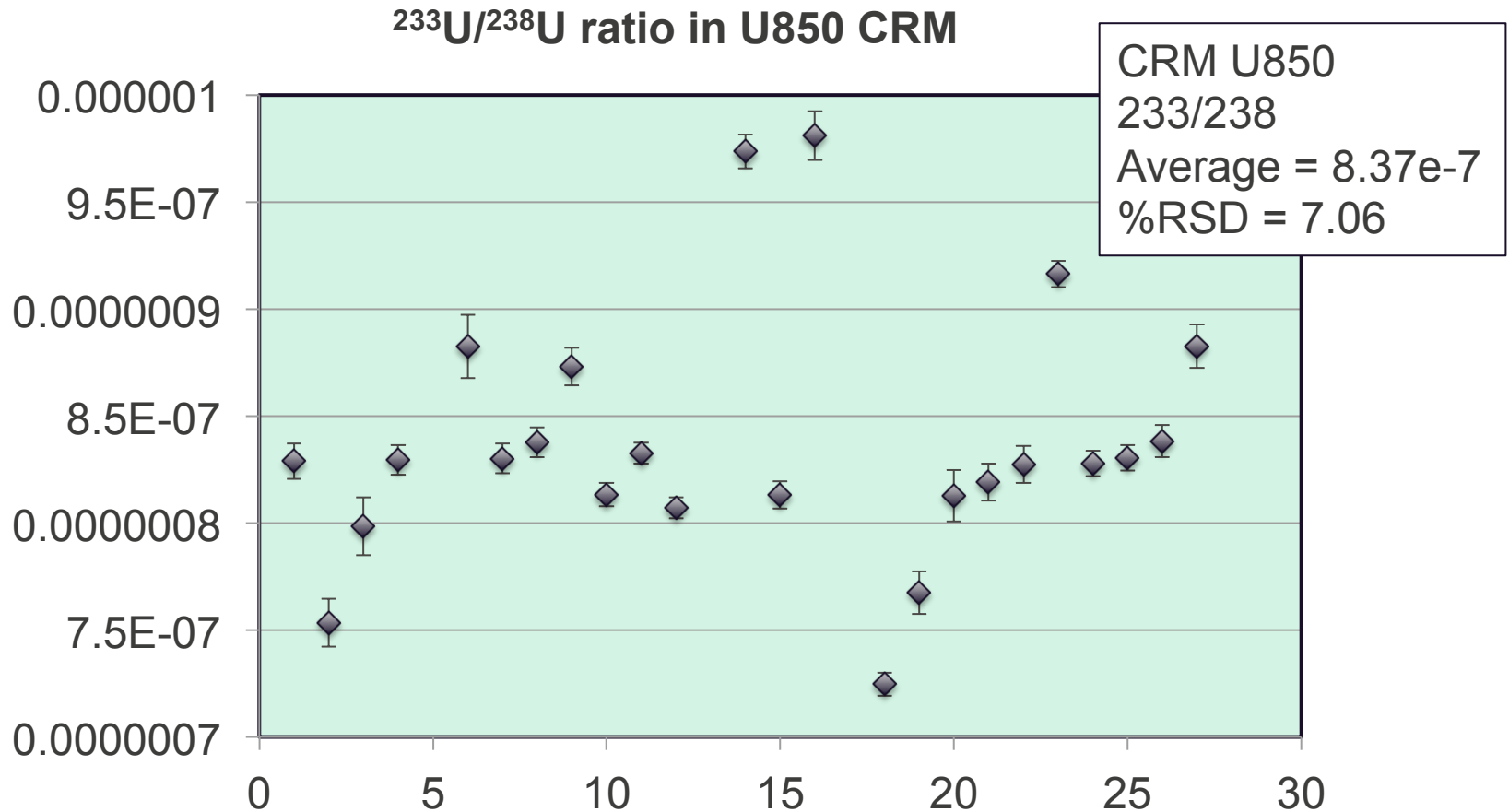
- External precisions of 1.5% RSD (2 σ) achievable on aliquots approaching 100 fg for the minor ^{240}Pu isotope.
- Accurate analysis of less 1 fg of ^{240}Pu , is achievable, with an external reproducibility of better than 10% RSD
- Will allow routine measurement of pg and fg sized NWAL Pu samples by TIMS

Two applicable loading techniques

- Direct loads onto carburized filaments for 'large' samples
- Resin bead loads for ultra-trace analysis (fg range)



High precision analysis of large samples



Heavy Stable isotope analysis at C-NR

Strontium

4 stable isotopes
 ^{84}Sr , ^{86}Sr , ^{87}Sr , ^{88}Sr

$^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$

Neodymium

7 stable isotopes
 ^{142}Nd , ^{143}Nd , ^{144}Nd , ^{145}Nd ,
 ^{146}Nd , ^{148}Nd , ^{150}Nd

$^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$

Samarium

7 stable isotopes
 ^{144}Sm , ^{147}Sm , ^{148}Sm , ^{149}Sm ,
 ^{150}Sm , ^{152}Sm , ^{154}Sm

$^{149}\text{Sm} \rightarrow ^{150}\text{Sm}$

Lead

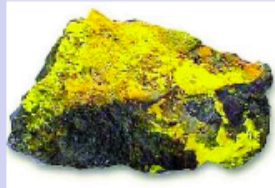
4 stable isotopes
 ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb

$^{235}\text{U} \rightarrow ^{207}\text{Pb}$

Stable Isotope signatures in UOC's

- Can ore signatures survive UOC's process?
- Do milling and conversion methods produce new signatures?
- Can we identify a particular process in a sample?

U Ore



- Typically 0.05 – 2% U by weight
- Commercial viability depends on
 - U content
 - Co-extracted mineral value
- Common mineral forms
 - Urananite / pitchblende
 - Coffinite
 - Carnotite

- U chemically purified by solvent extraction
- Conversion to UF₆ (enrichment feed)
- Common chemical forms at plants

- U₃O₈
- UO₃
- UO₂
- UF₄
- UF₆



Plant

UF₆ Cylinder

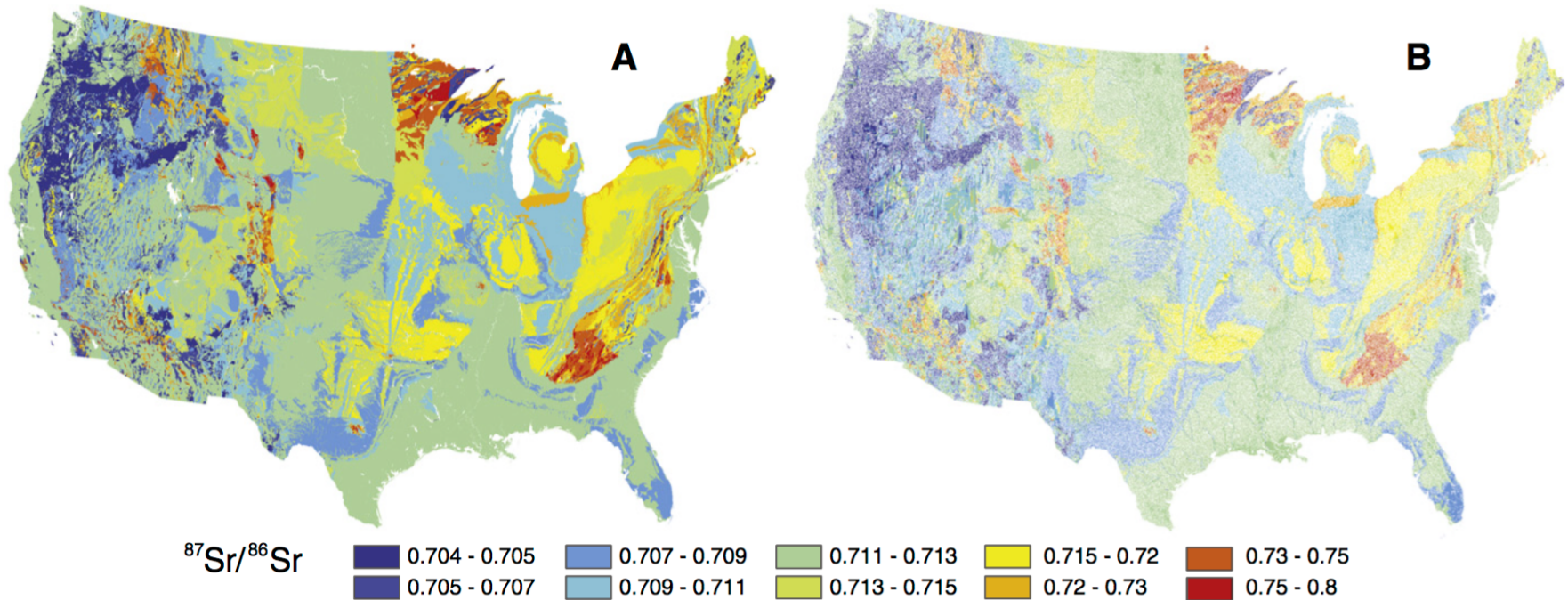


- U physically and chemically separated
- UOC or Yellowcake
 - Minimum 65% U by weight
 - Some very-high purity
- Common chemical forms
 - U₃O₈
 - (NH₄)₂U₂O₇
 - Na₂U₂O₇

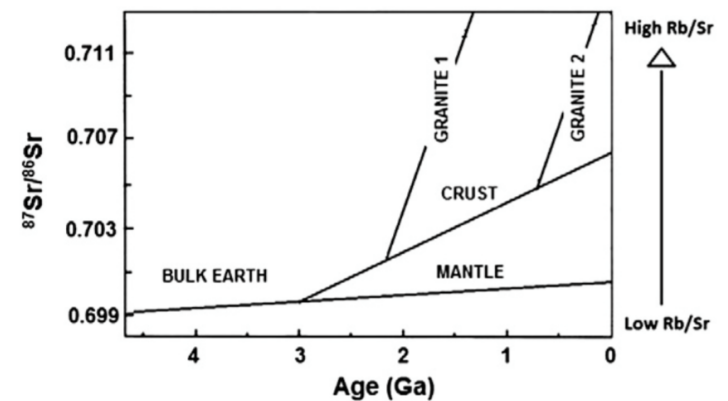
U Mill



Strontium variation in rocks and ores

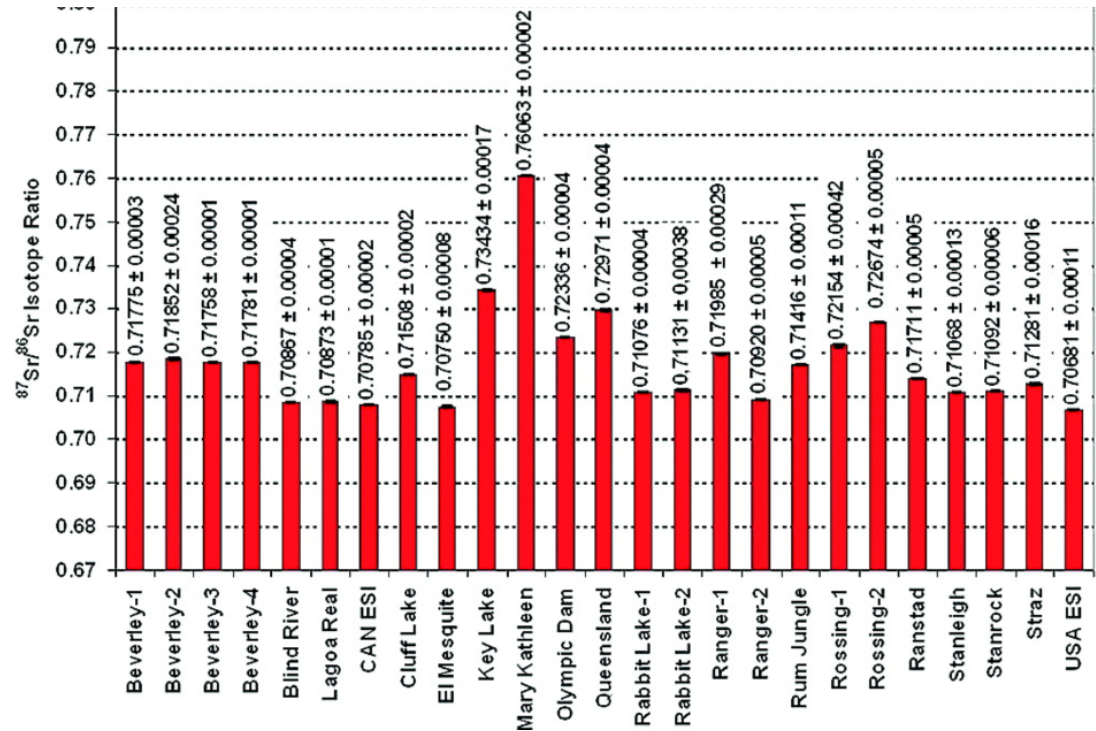


- The $^{87}\text{Sr}/^{86}\text{Sr}$ of a rock determined by
 - The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio
 - The Rb/Sr ratio
 - The age



Strontium

- $^{87}\text{Sr}/^{86}\text{Sr}$ may provide provenance information
- Sr highly mobile element and can be inhomogeneous within an ore body
- Original value can be easily contaminated by other Sr during processing

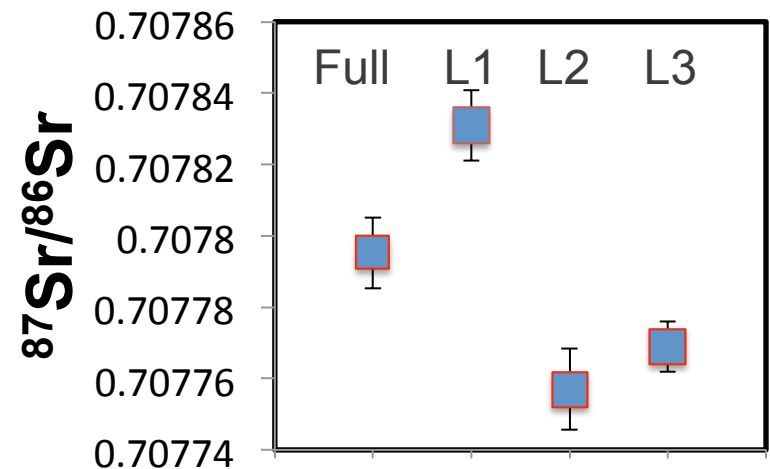
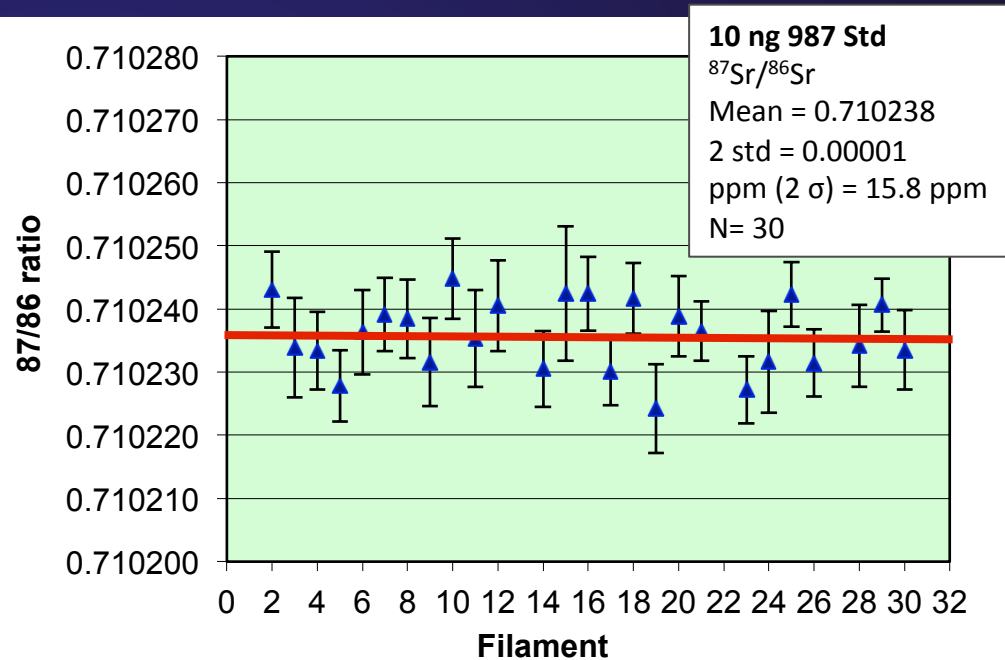


Varga et al. 2009

Sr analysis at LANL:

Specialize in

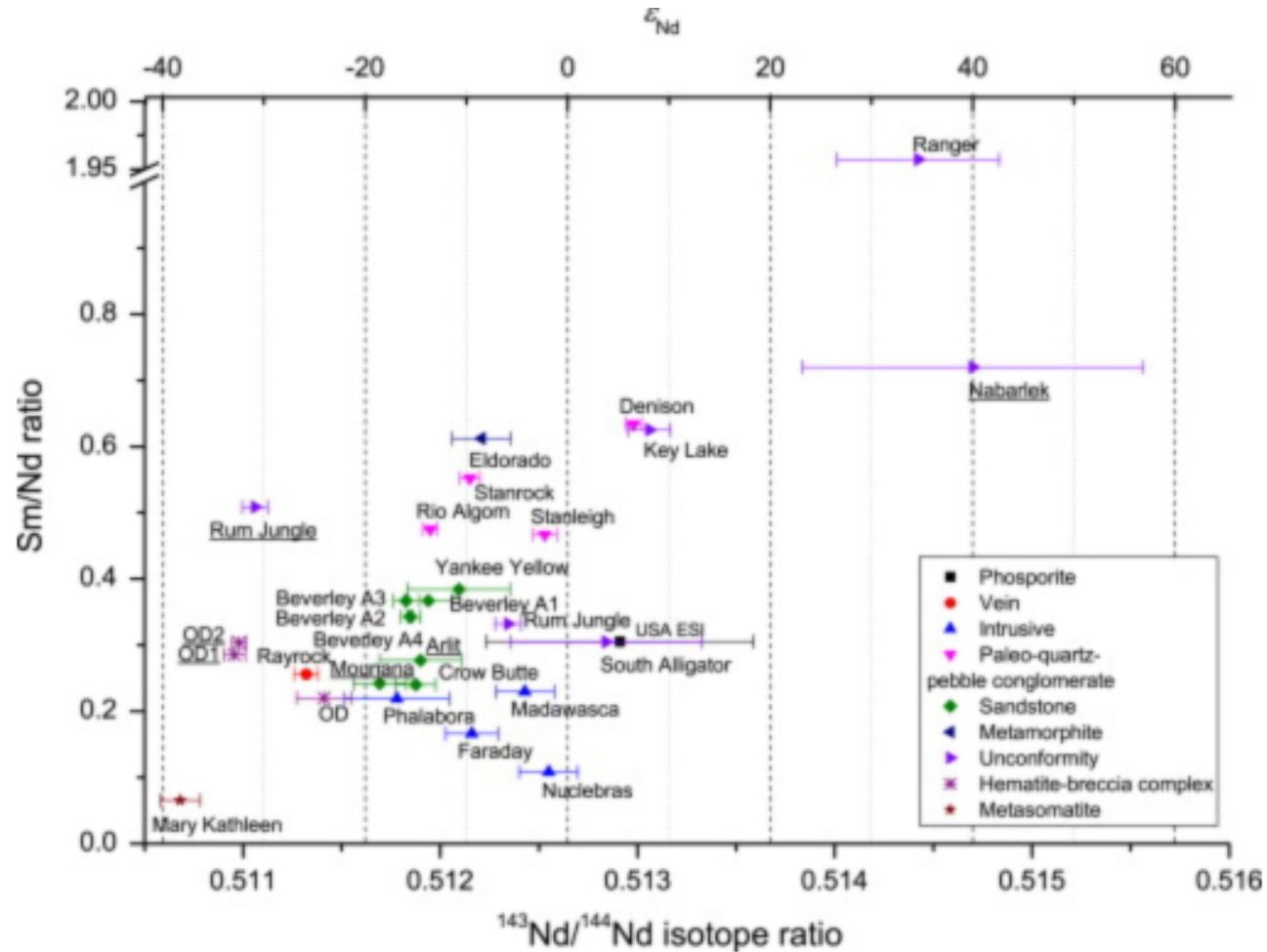
- High precision analysis at low levels (1 - 10 ng total Sr)
- Leachate studies to differentiate separate isotope reservoirs within a sample
- Total evaporation measurements



Neodymium

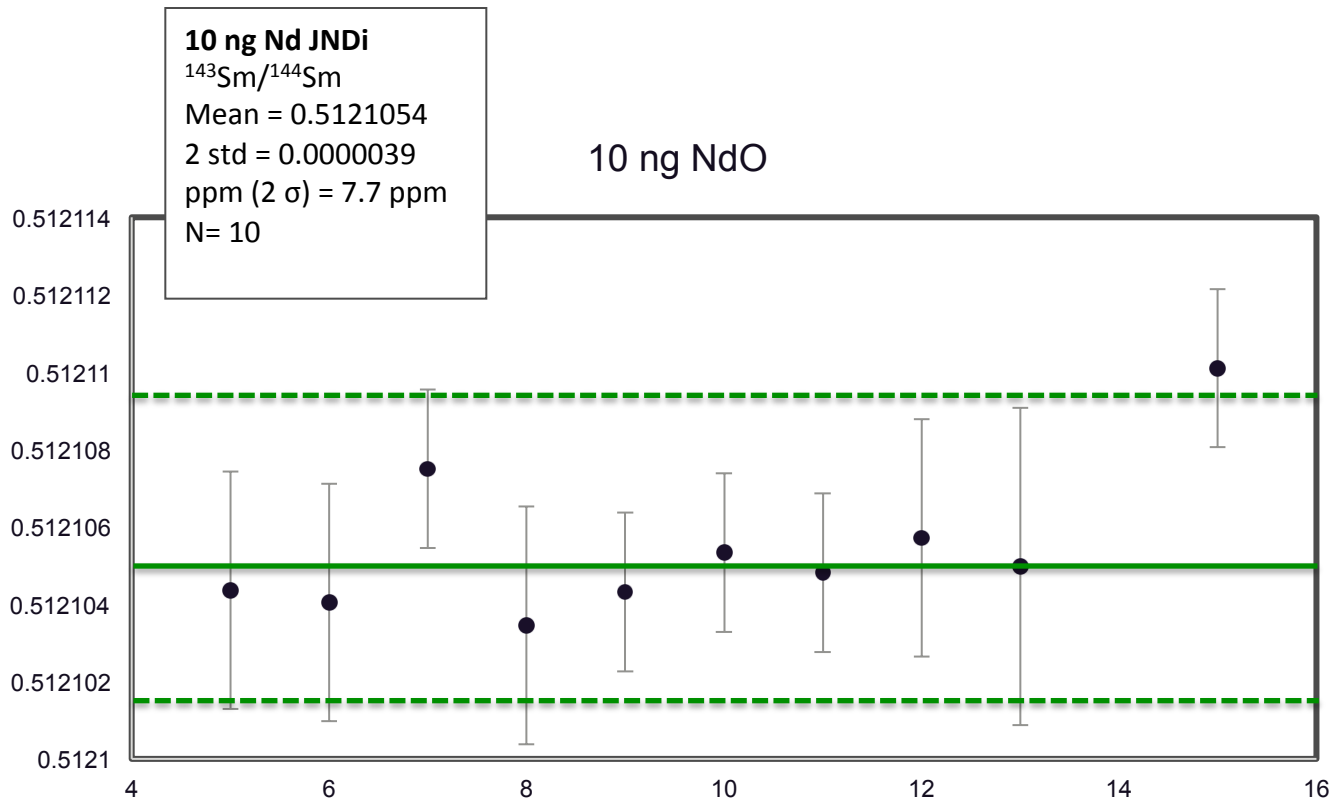
Has the potential to be used as an isotopic UOC fingerprint

High resolution $^{143}\text{Nd}/^{144}\text{Nd}$ measurements vital to differentiate ores



Krajko et al. 2014

Neodymium



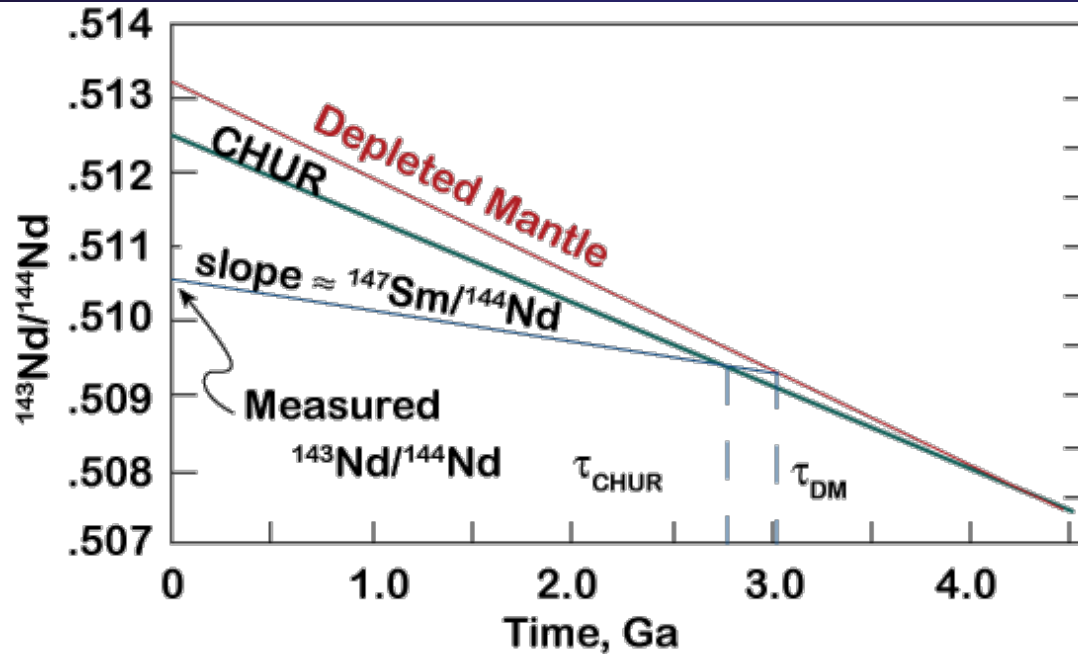
Data from UNC Phoenix, Inglis 2016

Utility of Sm – Nd isotope measurements

¹⁴⁴ Sm 3.07	¹⁴⁵ Sm	¹⁴⁶ Sm	¹⁴⁷ Sm 14.99	¹⁴⁸ Sm 11.24	¹⁴⁹ Sm 13.28	¹⁵⁰ Sm 7.38	¹⁵¹ Sm	¹⁵² Sm 26.75	¹⁵³ Sm	¹⁵⁴ Sm 22.75			
	¹⁴⁴ Pm	¹⁴⁵ Pm	¹⁴⁶ Pm	¹⁴⁷ Pm	¹⁴⁸ Pm	¹⁴⁹ Pm	¹⁵⁰ Pm	¹⁵¹ Pm	¹⁵² Pm	¹⁵³ Pm	¹⁵⁴ Pm		
¹⁴² Nd 27.2	¹⁴³ Nd 12.2	¹⁴⁴ Nd 23.8	¹⁴⁵ Nd 8.3	¹⁴⁶ Nd 17.2	¹⁴⁷ Nd	¹⁴⁸ Nd 5.7	¹⁴⁹ Nd	¹⁵⁰ Nd 5.6	¹⁵¹ Nd	¹⁵² Nd	¹⁵³ Nd	¹⁵⁴ Nd	
			¹⁴⁴ Pr	¹⁴⁵ Pr	¹⁴⁶ Pr	¹⁴⁷ Pr	¹⁴⁸ Pr	¹⁴⁹ Pr	¹⁵⁰ Pr	¹⁵¹ Pr	¹⁵² Pr	¹⁵³ Pr	¹⁵⁴ Pr

- The ¹⁴³Nd/¹⁴⁴Nd composition of Nd increases as a function of time because of the decay of ¹⁴⁷Sm
- The ¹⁴³Nd/¹⁴⁴Nd composition of a rock (or ore) is determined by
 - The initial ¹⁴³Nd/¹⁴⁴Nd ratio
 - The ¹⁴⁷Sm/¹⁴⁴Nd ratio (this is different to the elemental Sm/Nd ratio)
 - The age
- This relationship between the ¹⁴⁷Sm/¹⁴⁴Sm and ¹⁴³Nd/¹⁴⁴Nd can be more useful than the simple elemental ratio

Sm/Nd model ages



In some instances the model age will match age of ore (e.g. juvenile rocks)

Sm/Nd analysis can yield model ages (AKA crustal residence time)

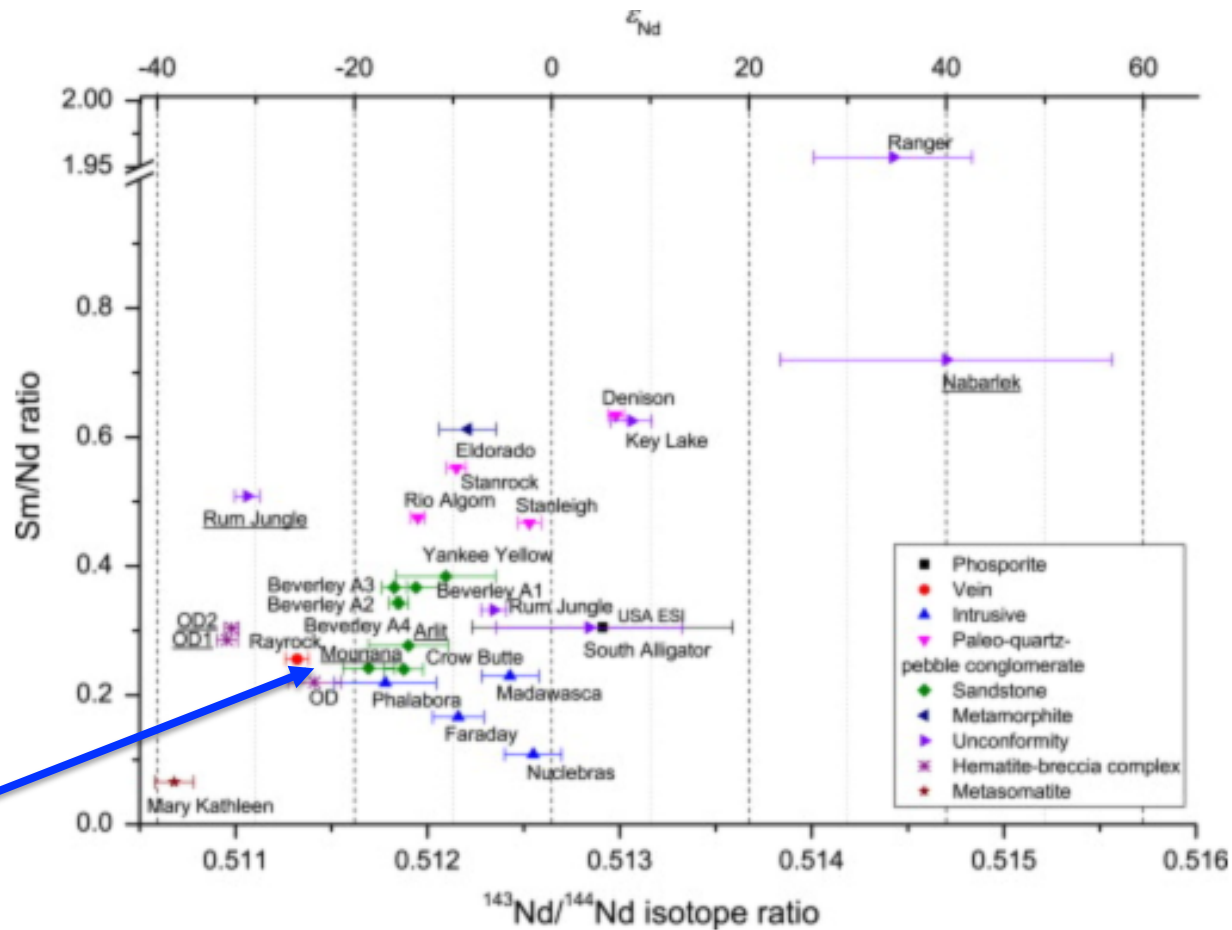
Basic idea is that there is a relatively large fractionation between Sm and Nd during melting to form new additions to crust. Subsequent crustal processing produces little change in Sm/Nd.

We project back along the slope defined by $^{147}\text{Sm}/^{144}\text{Nd}$ to the point of intersection on the mantle evolution curve

Sm/Nd model ages

Ores and UOCs with different $^{147}\text{Sm}/^{144}\text{Nd}$ ratios may yield different model ages for the same $^{143}\text{Nd}/^{144}\text{Nd}$ ratio

May help in analysis of ores that have closely similar modern day Nd isotope ratios

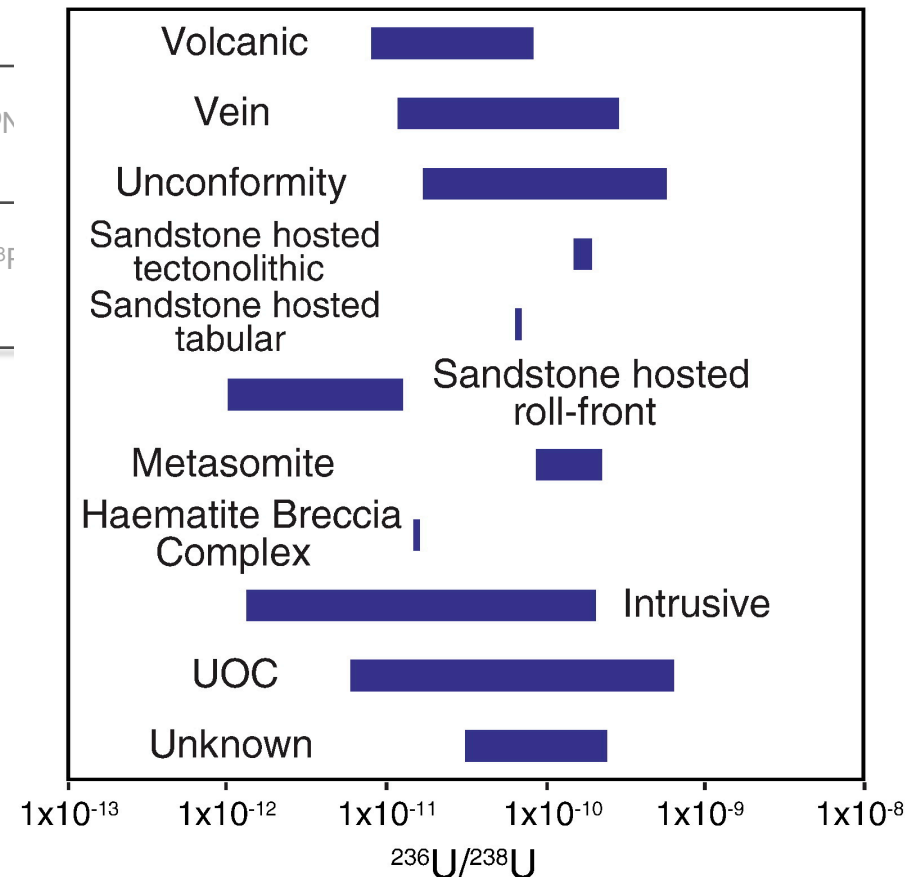


Krajko et al. 2014

Sm isotope analysis

¹⁴⁴ Sm 3.07	¹⁴⁵ Sm	¹⁴⁶ Sm	¹⁴⁷ Sm 14.99	¹⁴⁸ Sm 11.24	¹⁴⁹ Sm 13.28 40E3	¹⁵⁰ Sm 7.38	¹⁵¹ Sm	¹⁵² Sm 26.75	¹⁵³ Sm	¹⁵⁴ Sm 22.75			
	¹⁴⁴ Pm	¹⁴⁵ Pm	¹⁴⁶ Pm	¹⁴⁷ Pm	¹⁴⁸ Pm	¹⁴⁹ Pm	¹⁵⁰ Pm	¹⁵¹ Pm	¹⁵² Pm	¹⁵³ Pm	¹⁵⁴ Pm		
¹⁴² Nd 27.2	¹⁴³ Nd 12.2	¹⁴⁴ Nd 23.8	¹⁴⁵ Nd 8.3	¹⁴⁶ Nd 17.2	¹⁴⁷ Nd	¹⁴⁸ Nd 5.7	¹⁴⁹ Nd						
			¹⁴⁴ Pr	¹⁴⁵ Pr	¹⁴⁶ Pr	¹⁴⁷ Pr	¹⁴⁸ Pr						

- ¹⁴⁹Sm has a large neutron capture section (40,000 barn)
- Orders of magnitude higher than ²³⁵U
- Ores with a discernable ²³⁶U signal may also have Sm isotope perturbation's



Sm isotope analysis

^{144}Sm 3.07	^{145}Sm	^{146}Sm	^{147}Sm 14.99	^{148}Sm 11.24	^{149}Sm 13.28 40E3	^{150}Sm 7.38	^{151}Sm	^{152}Sm 26.75 21E1	^{153}Sm	^{154}Sm 22.75			
	^{144}Pm	^{145}Pm	^{146}Pm	^{147}Pm	^{148}Pm	^{149}Pm	^{150}Pm	^{151}Pm	^{152}Pm	^{153}Pm	^{154}Pm		
^{142}Nd 27.2	^{143}Nd 12.2	^{144}Nd 23.8	^{145}Nd 8.3	^{146}Nd 17.2	^{147}Nd	^{148}Nd 5.7	^{149}Nd	^{150}Nd 5.6	^{151}Nd	^{152}Nd	^{153}Nd	^{154}Nd	
			^{144}Pr	^{145}Pr	^{146}Pr	^{147}Pr	^{148}Pr	^{149}Pr	^{150}Pr	^{151}Pr	^{152}Pr	^{153}Pr	^{154}Pr

- **Not a typical analysis**

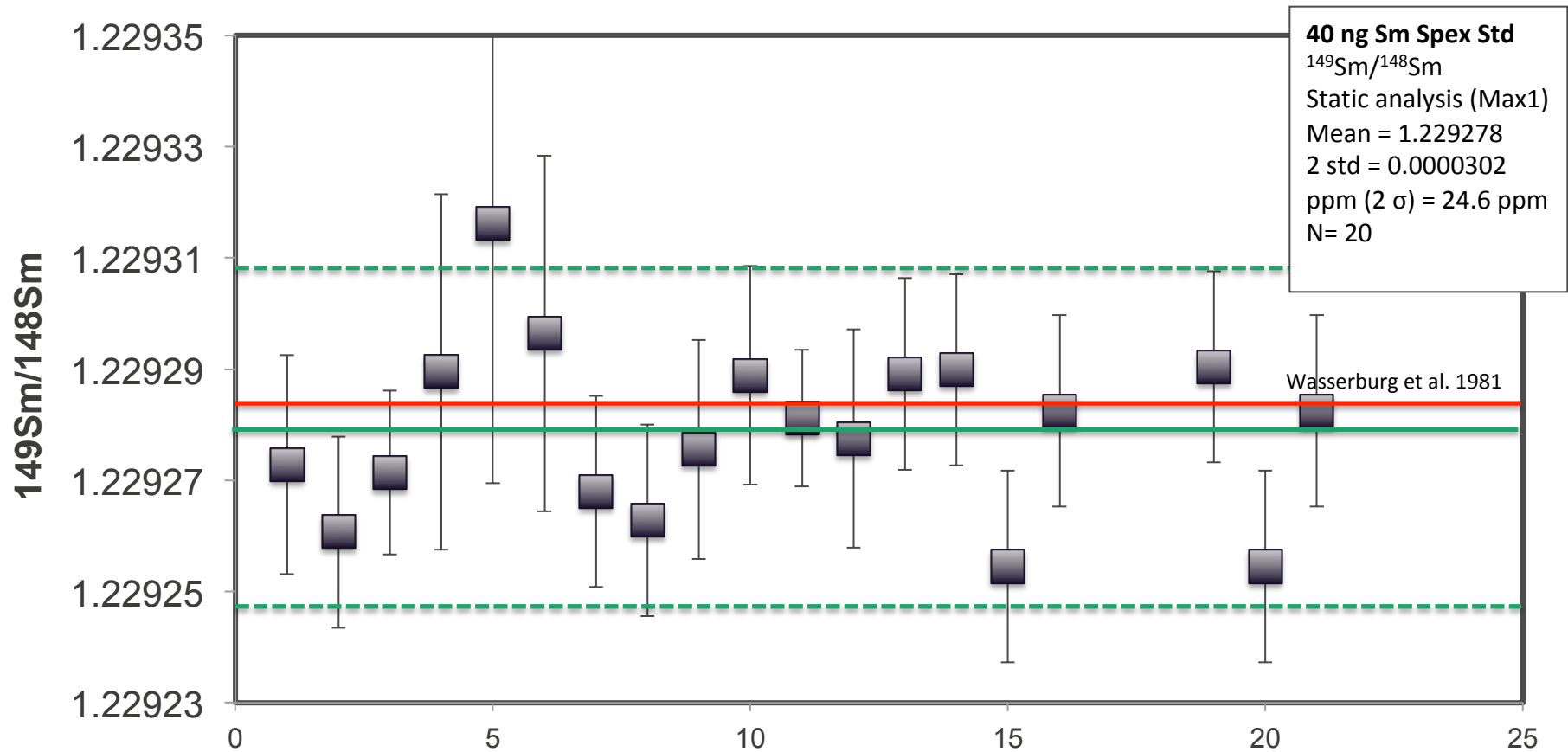
- Convention is to normalize using the $^{149}\text{Sm}/^{152}\text{Sm}$ ratio
- Not possible if fission or capture is suspected

- **Stable Nd isotopes block fission input onto ^{144}Sm and ^{148}Sm**

- **Allows for TIMS analysis using the $^{144}\text{Sm}/^{148}\text{Sm}$ for normalization**

- Difficult due to abundance of ^{144}Sm and ^{148}Sm

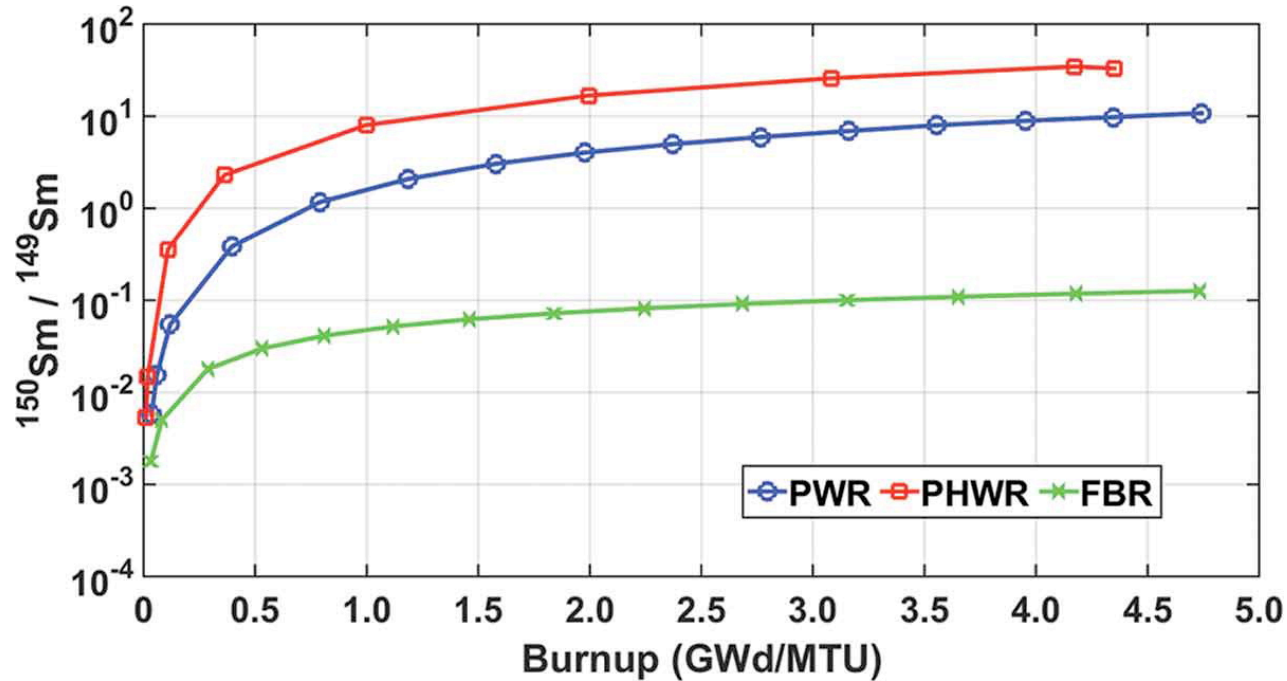
Preliminary Sm isotope data



- External precision using TaF Gel ~20ppm for all isotope ratios
- Accuracy is within 7 ppm of Wasserburg et al. value of 1.229284
- Typical Load sizes range between 4-40ng, measured as little as 2ng

Another use for Sm analysis: Reactor type

Osborn et al. 2018



Osborn et al. 2018 – modeled ^{150}Sm in growth during burnup