Mass spectrometry in radionuclide analyses

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Range of mass spectrometric techniques

- TIMS
- SIMS
- RIMS
- AMS
- ICPMS
  - quadrupole ICPMS
  - HR-ICPMS
  - MC-ICPMS

Advantages of mass spectrometry

- Often rapid analyses
- Improved data quality

  (e.g. ^{238}U:^{235}U ratios)
- Permits analyses that are not possible radiometrically

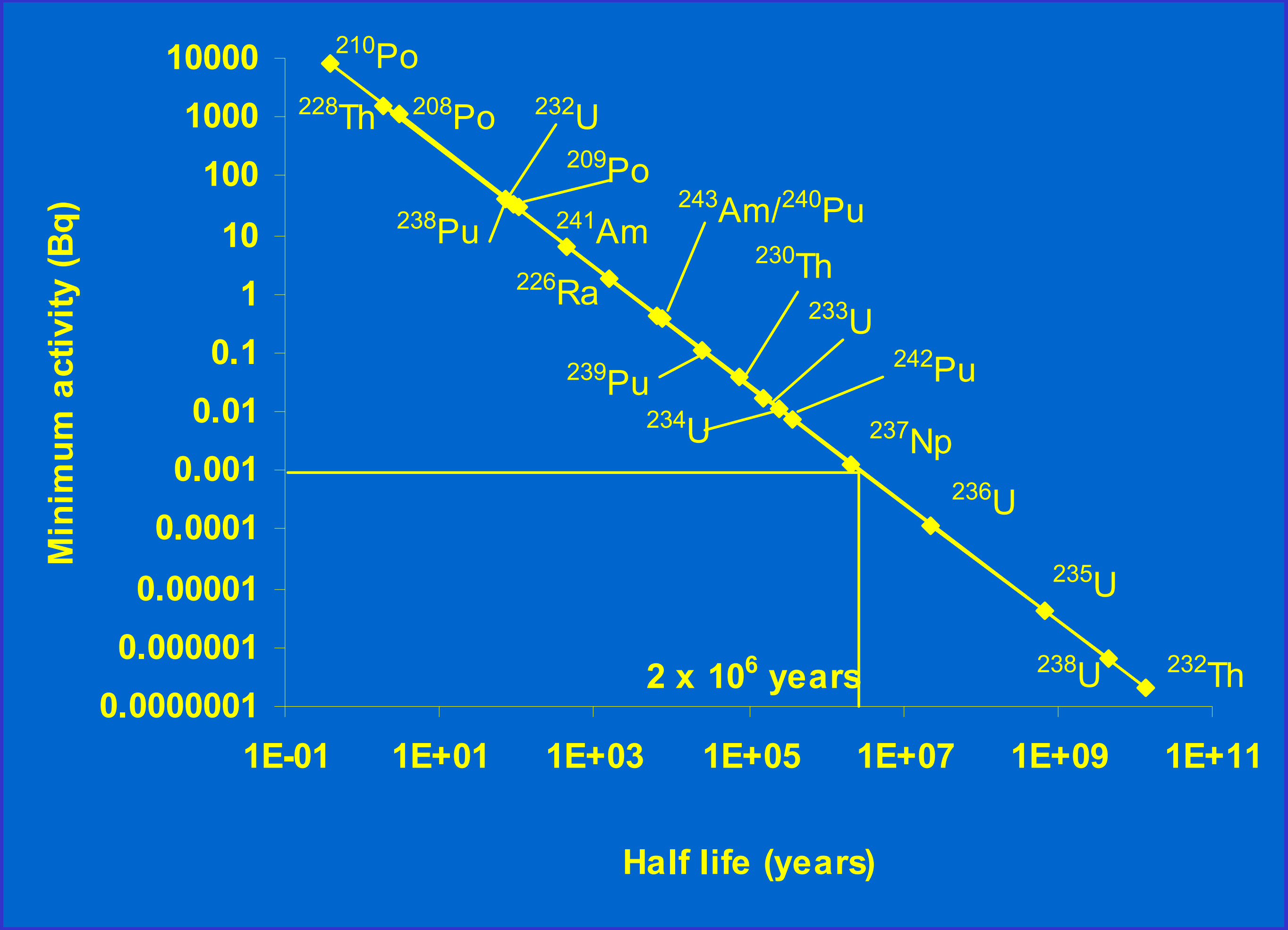
  (e.g. ^{239}Pu and ^{240}Pu separately)
- Improved sensitivity for long lived nuclides

Comparison of mass spectrometric techniques

Method	U required for detection	U required for isotope ratios	Isotopes reported	Typical accuracy	Typical precision (2σ)
HRGS	10 μg	1 mg	^{235}U, ^{238}U	10%	10%
Alpha spec	10 ng	10 μg	^{234}U, ^{238}U	10%	5%
Quad ICPMS	5 pg	1 μ g	^{235}U, ^{236}U, ^{238}U	2%	5%
HRICPMS	50 fg	5 μ g	^{234}U, ^{235}U, ^{236}U, ^{238}U	1 – 8%	0.1 – 1%
TIMS	1 fg	1 ng	^{234}U, ^{235}U, ^{236}U, ^{238}U	0.1 – 2%	0.1 – 0.2%
SIMS	5 pg	5 ng	^{235}U, ^{238}U	1 – 5%	10%
MCICPMS	5-50 fg	1 pg	^{234}U, ^{235}U, ^{236}U, ^{238}U	0.1 – 0.2%	0.1 – 0.2%

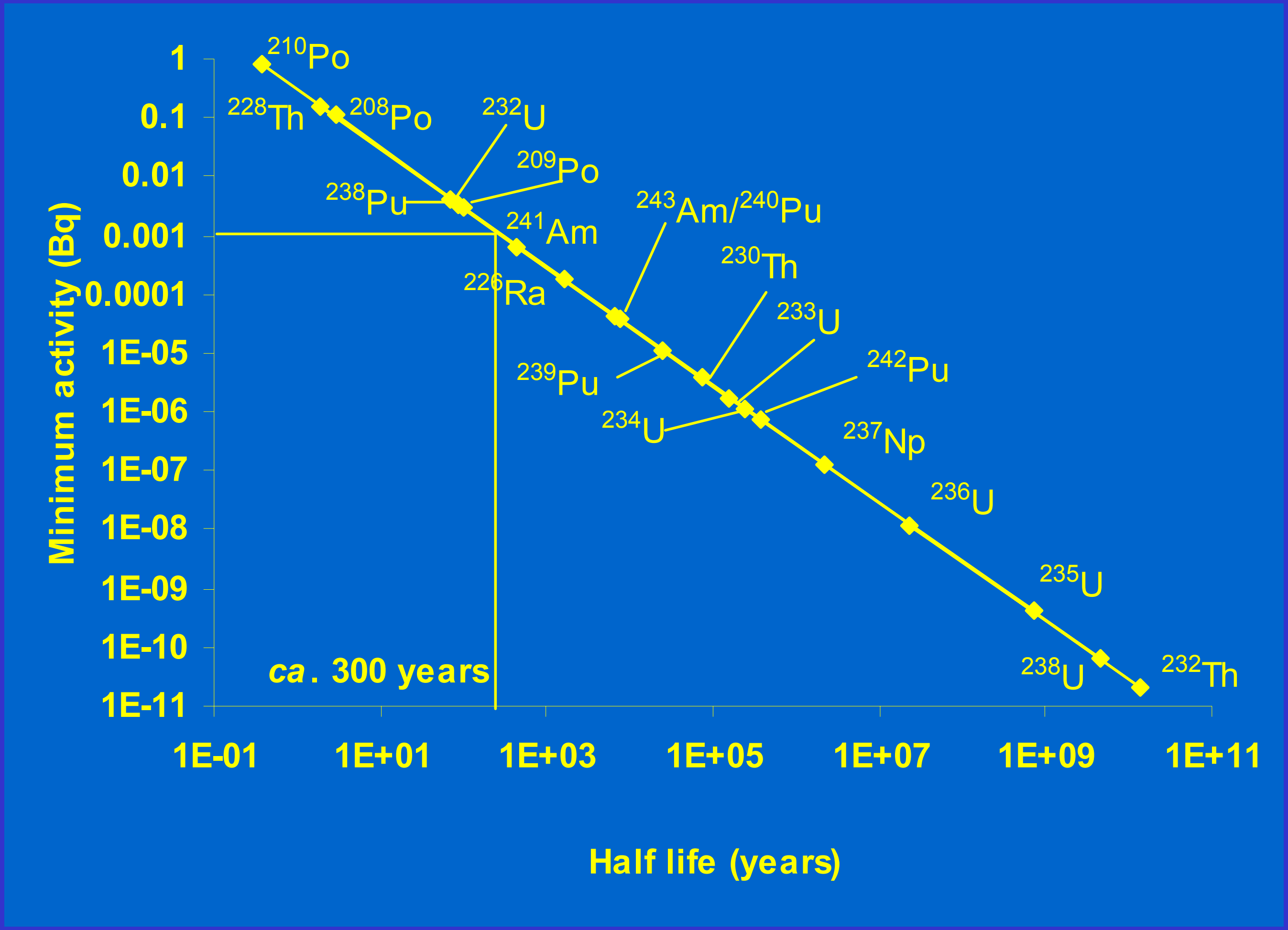
Modified from Toole et al, 1997

Sensitivity of ICPMS versus alpha spectrometry



Assuming 10ppt limit
5ml solution

Sensitivity of MC-ICPMS versus alpha spectrometry



Assuming 5ppq limit
1ml solution

Challenges

- Isobaric interferences (e.g. ^{99}Ru on ^{99}Tc)
- Polyatomic interferences (e.g. $^{197}Au^{40}Ar$ on ^{237}Np)
- Peak tailing
- Isotopic fractionation
- Beam instability
- Matrix effects
- Method blanks

High Precision Pu Isotope Ratio Measurements

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Analytical techniques used for $^{240}Pu/^{239}Pu$

METHOD	ADVANTAGE	DISADVANTAGE	NOMINAL PRECISION 2 sigma ~50 fg
Alpha Spectrometry	Not suitable because alpha energies interfere		
AMS	Can measure ~50fg	High potential cost	~ 18%
ICPMS Quad	High ionisation efficiency	Ion beam instability	> 30%
ICPMS Sector	High ionisation efficiency	Better stability than ICPMS Quad	~ 3%
TIMS	Stable ion beam	• Low ionisation efficiency • No internal interelement fractionation correction	~ 10%
MC-ICPMS	• Unstable ion beam but multicollection negates this effect • Interelement mass fractionation correction capability • Can measure 5 fg	High ionisation efficiency	~ 1%

Some applications for $^{240}Pu/^{239}Pu$ ratios

Source characterisation

Analogous to using $^{238}Pu/^{239,240}Pu$ but is a clearer discriminator

e.g. the $^{240}Pu/^{239}Pu$ in weapon's testing depend on the parameters of each individual test . Therefore the $^{240}Pu/^{239}Pu$ in the fallout varies with time.

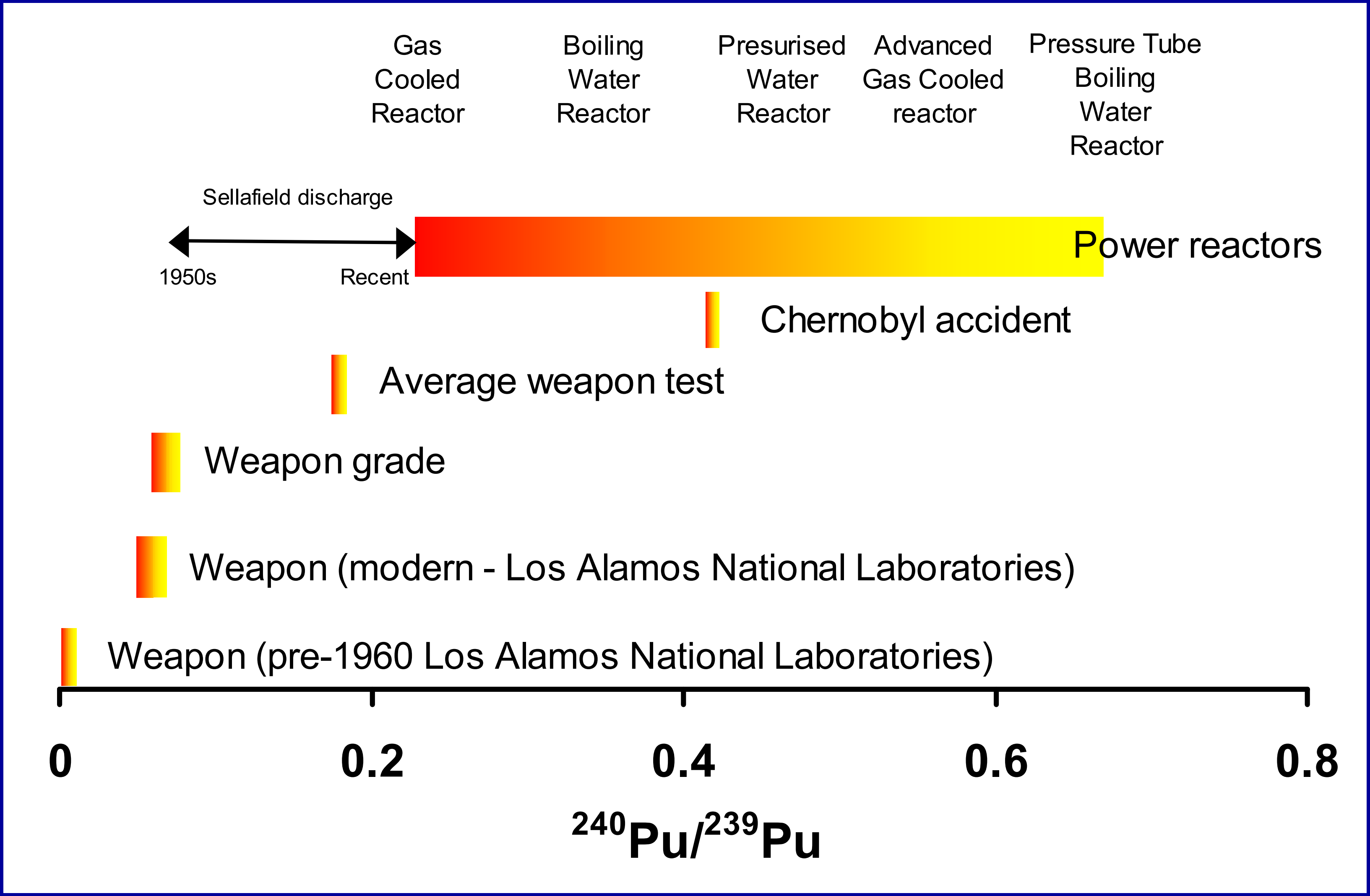
Dating

using impulse and continuous events

Similar to using $^{239,240}Pu$, ^{241}Am or ^{137}Cs

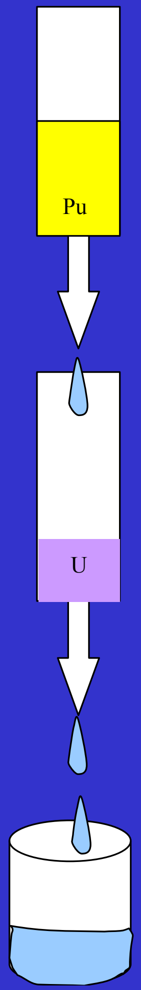
The $^{240}Pu/^{239}Pu$ *versus* time has significant features that can be attributed to certain years.

Range of Pu isotope ratios



Stage 1 piggy-back columns

1. Load sample in 10 ml 8M HNO_3 with 1drop of concentrated HCl
2. Elute 20 ml 8M HNO_3 followed by 30ml of 3M HNO_3



6 x 0.7 cm i.d.
Eichrom 1-X8 ANION RESIN

2 x 0.7 cm i.d.
Eichrom UTEVA™ resin

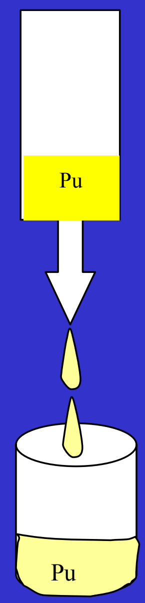
STAGE 2
Separate the columns

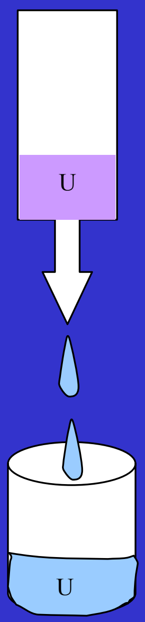
Pu eluted with 50 ml of fresh 1.2M HCl/H_2O_2 (50:1)

30ml 3M HNO_3
25ml 9M HCl to remove Th

U eluted with 10ml 0.02M HCl

Anion





UTEVA

<u>Plus use a small 2nd anion clean-up column</u>

Removal of any U remaining because ^{238}U hydride interferes with ^{239}Pu measurement.

Plutonium isotope ratio measurement

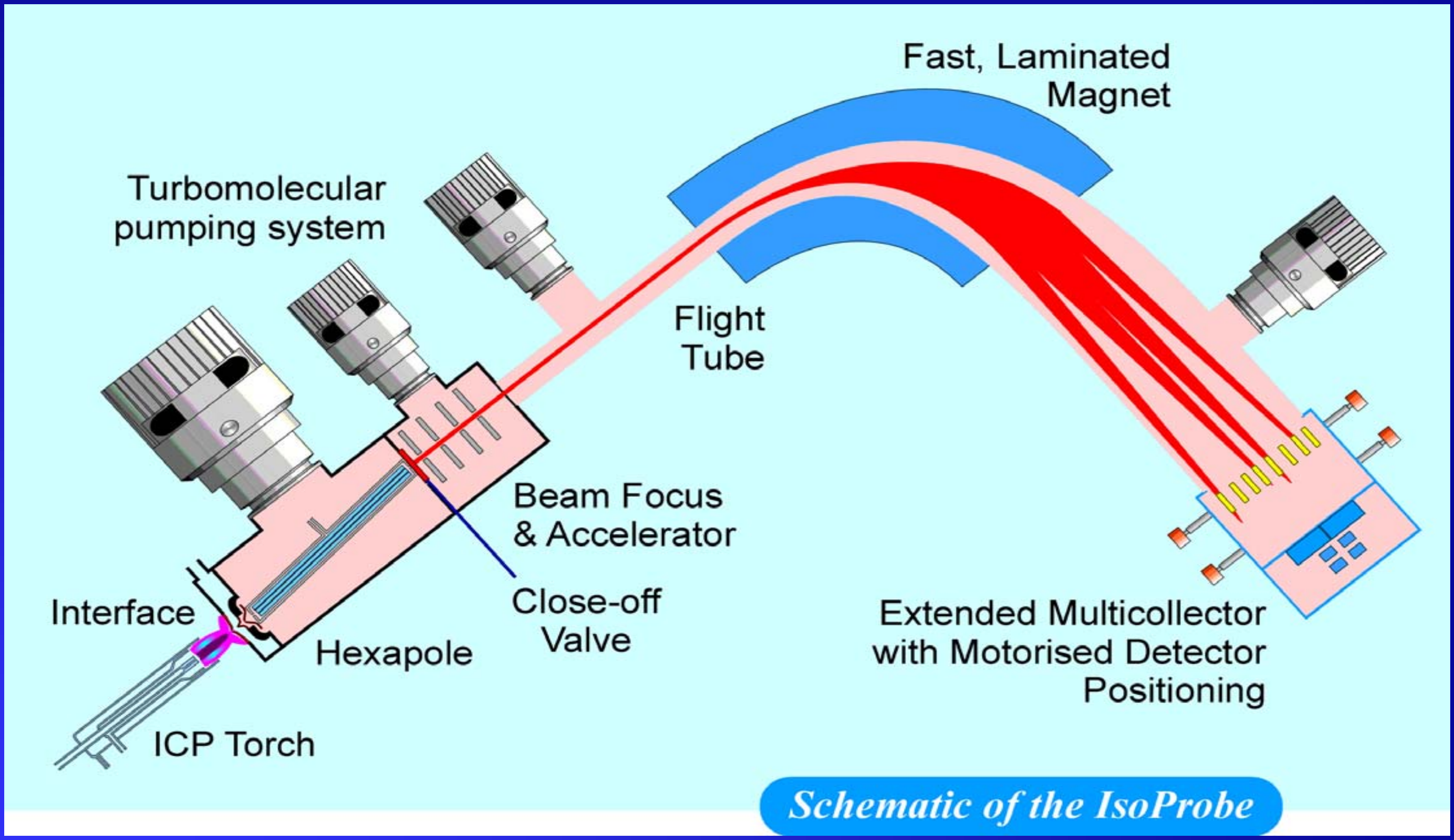
Objective:

To measure $^{240}Pu/^{239}Pu$ with a reproducibility and accuracy <5% 2sd on samples containing <50fg Pu (<150 µBq), to enable the analysis of low-level environmental samples.

Method:

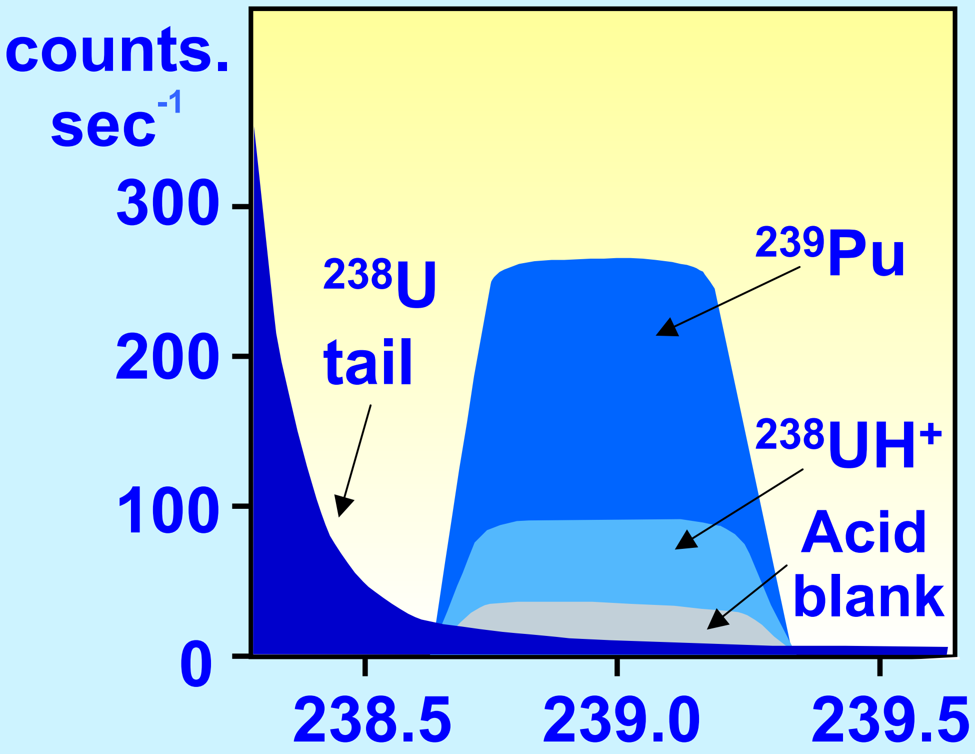
Multicollector ICP-MS (Micromass IsoProbe) using :

Peak jump ion counting through a Daly detector with inter-peak normalisation to ^{236}U.


Fast, Laminated Magnet
Turbomolecular pumping system
Flight Tube
Beam Focus & Accelerator
Close-off Valve
Interface
Hexapole
Extended Multicollector with Motorised Detector Positioning
ICP Torch
Schematic of the IsoProbe

Corrections required:

1. On-peak blank subtraction including detector zero
2. Tail from ^{238}U at +1 a.m.u. (200 ppb)
3. $^{238}UH^+$ interference at m/z 239 (5.5 ppm)
4. Pu addition from $^{236+233}U$ spike (2 ppm)
5. Mass bias of U-Pu (0.6% amu^{-1})



m/z 239 composition using:

25 ppq Pu

30 ppb U

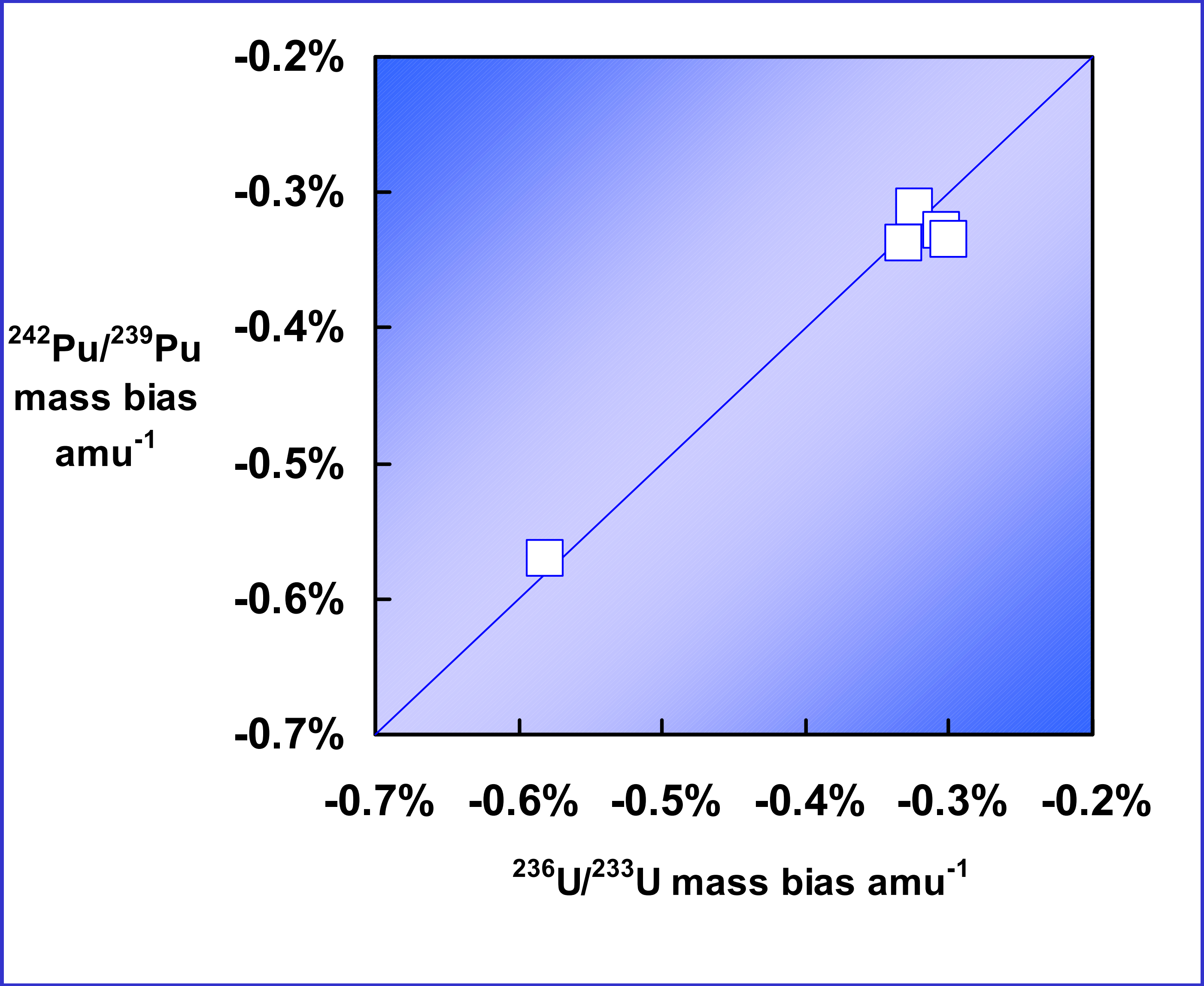
no $^{233+236}U$

	Sequence 1	Sequence 2	Sequence 3
Axial Daly	240	239	242
Low 1 Faraday	(237)	236	(239)
Low 2 Faraday	236	(235)	238
Low 3 Faraday	(234)	233	236

Detector and peak-jump array for Pu isotope ratios using U-double spike

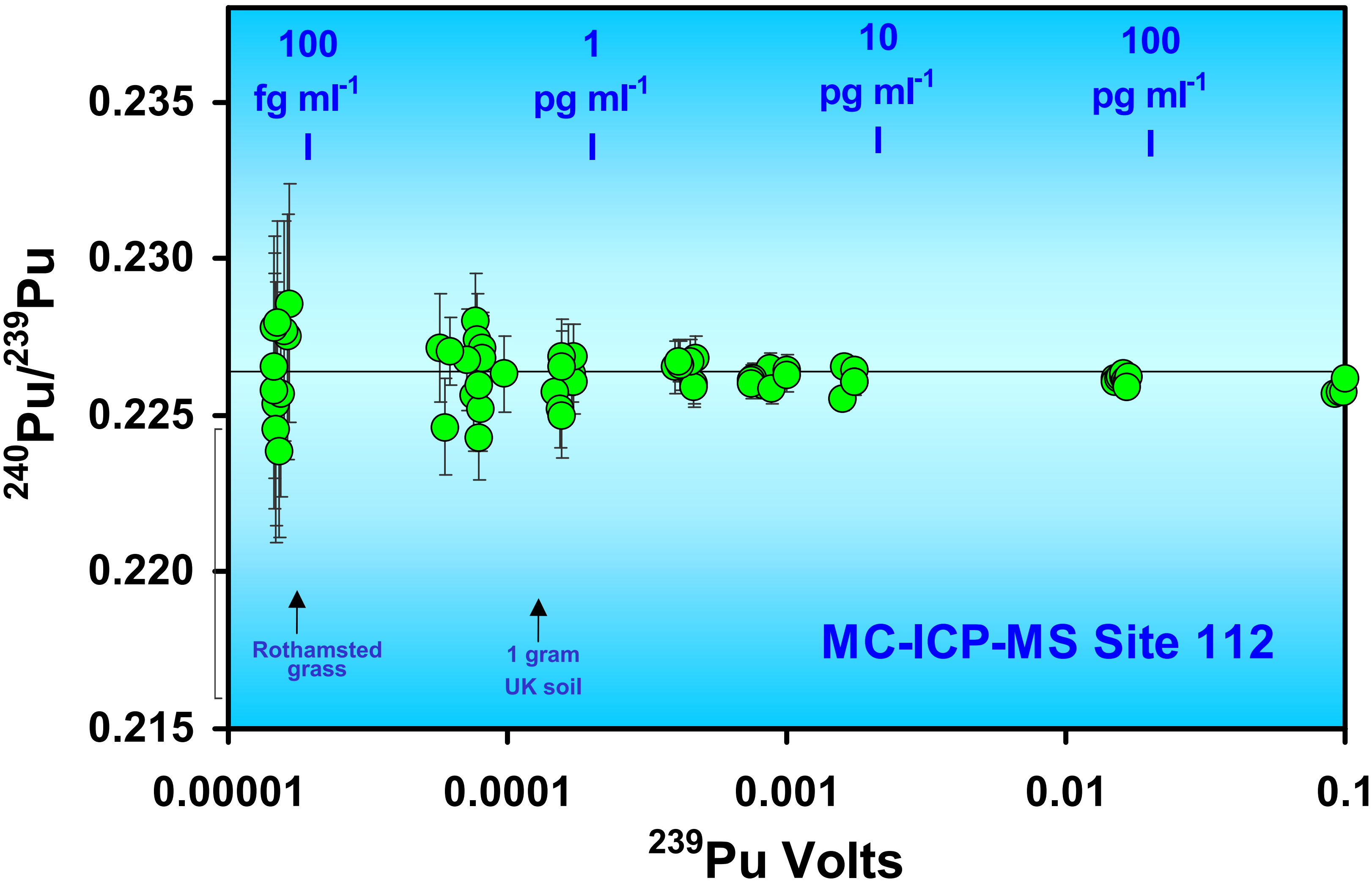
Taylor R.N., Warneke T., Milton J.A., Croudace I.W., Warwick P.E. and Nesbitt R.W. (2001) Plutonium isotope ratio analysis at fg to ng levels by multicollector ICP-MS. J. Anal. At. Spectrom., **16**, 279-284.

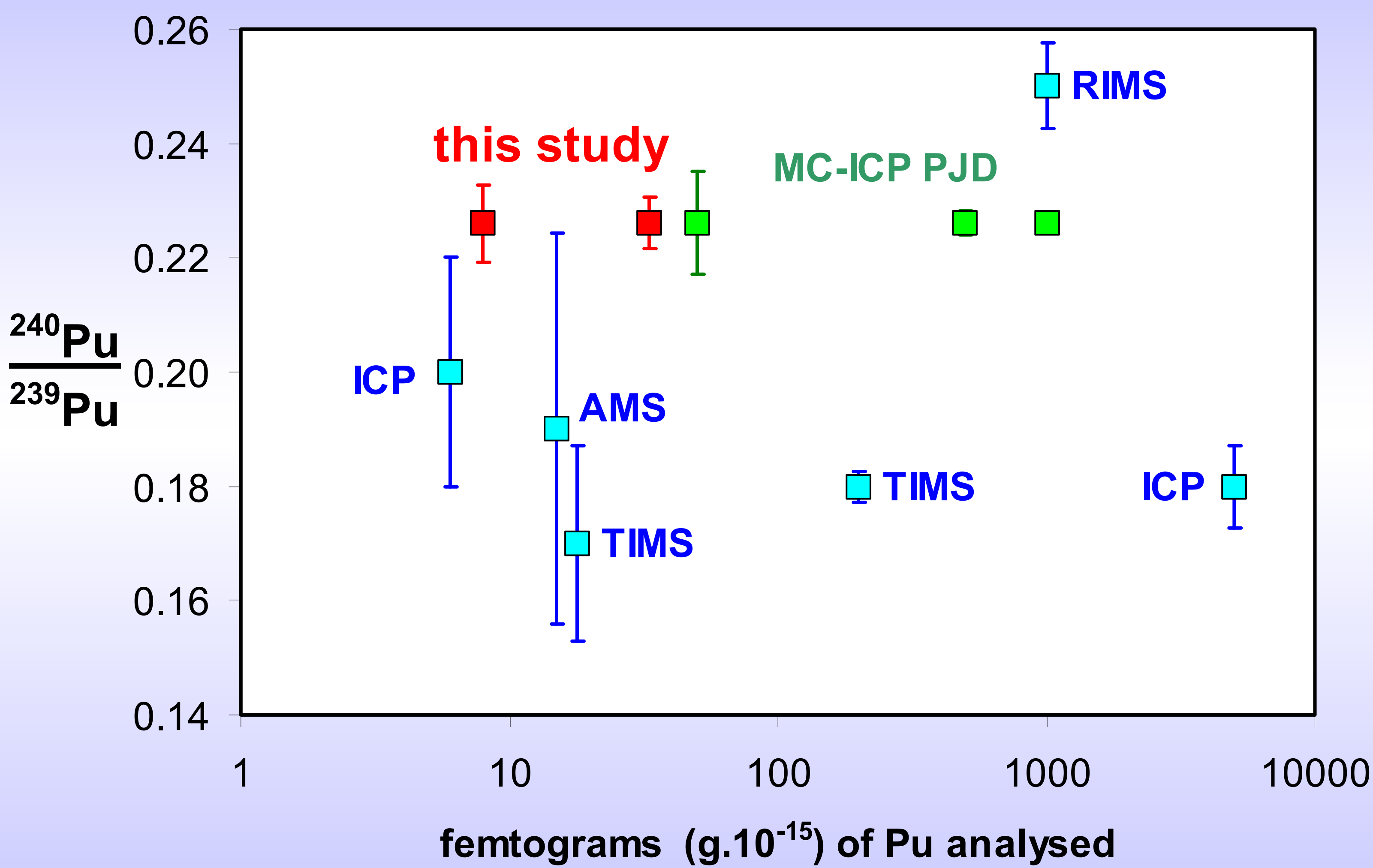
^{236}U-^{233}U (1:1) added to separated Pu solutions to correct for mass bias and instrument drift between Daly peak jumps



1ng ^{239}Pu = 2.3 Bq

Therefore only ~1g of a typical UK soil with fallout Pu of 0.3 Bq/Kg is needed for a precise analysis of the Pu isotope ratio




0.26
0.24
0.22
0.20
0.18
0.16
0.14
240Pu / 239Pu
this study
MC-ICP PJD
RIMS
ICP
AMS
TIMS
TIMS
ICP
1
10
100
1000
10000
femtograms (g.10-15) of Pu analysed

Accuracy for $^{240}Pu/^{239}Pu$ atom ratios

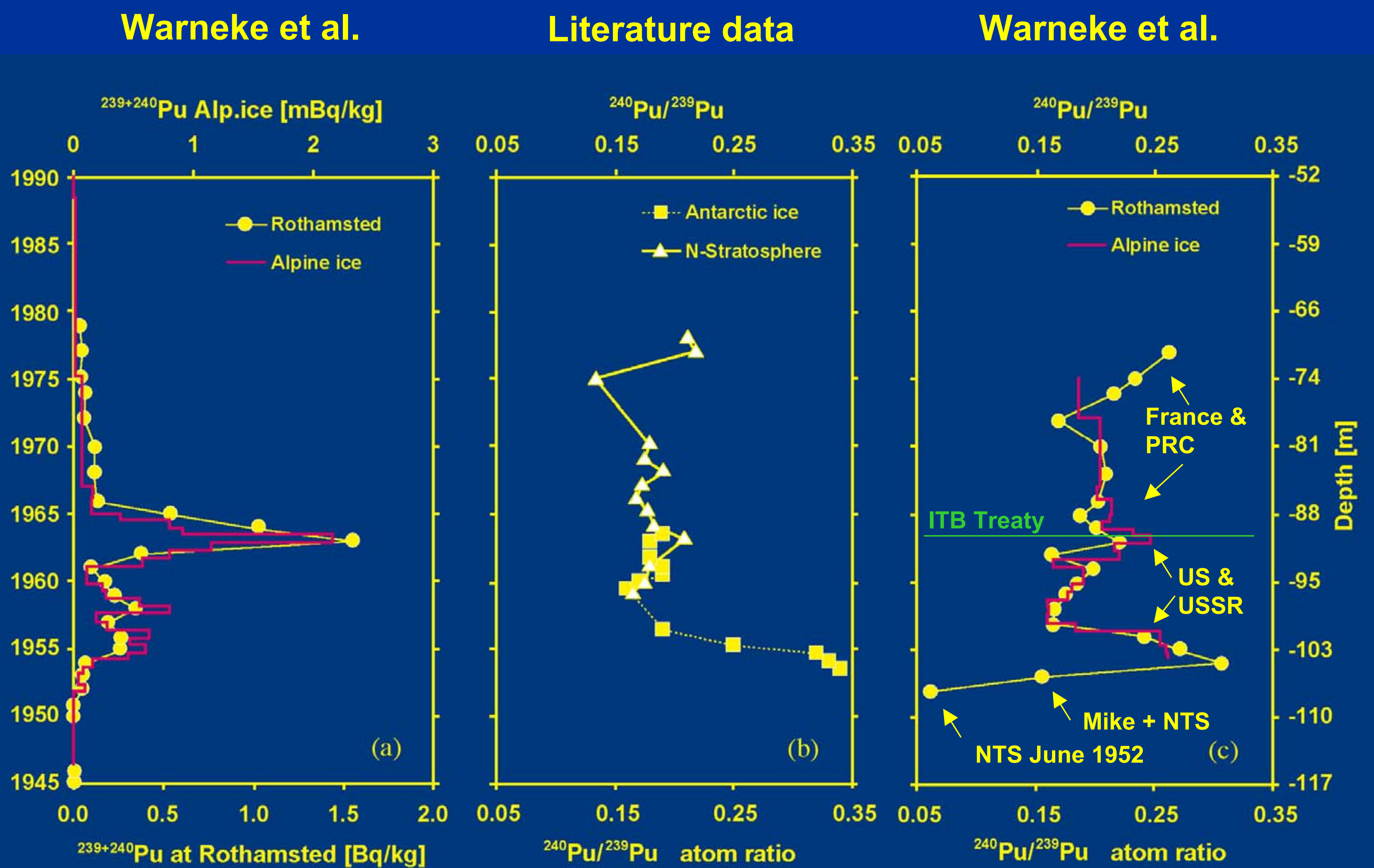
	Certified $^{240}Pu/^{239}Pu$ Atom ratio	Measured $^{240}Pu/^{239}Pu$	
		0.5 ng/ml	5 ng/ml
NBL122	0.1320	0.1318 ± 0.001 (n=4)	0.1321 ± 0.0001 (n=3)
NBL 126	0.0209	0.0211 (n=1)	0.0204 (n=1)
NBL 128	0.0007	-	0.0007 (n=1)
UK-Pu-5	0.9662 ± 0.0011	-	0.9645 ± 0.0013 (n=7)

NBL –US New Brunswick National Laboratory; UK-Pu-5 - AEA Technology

An application of the developed method

Establishing a northern latitude fallout record

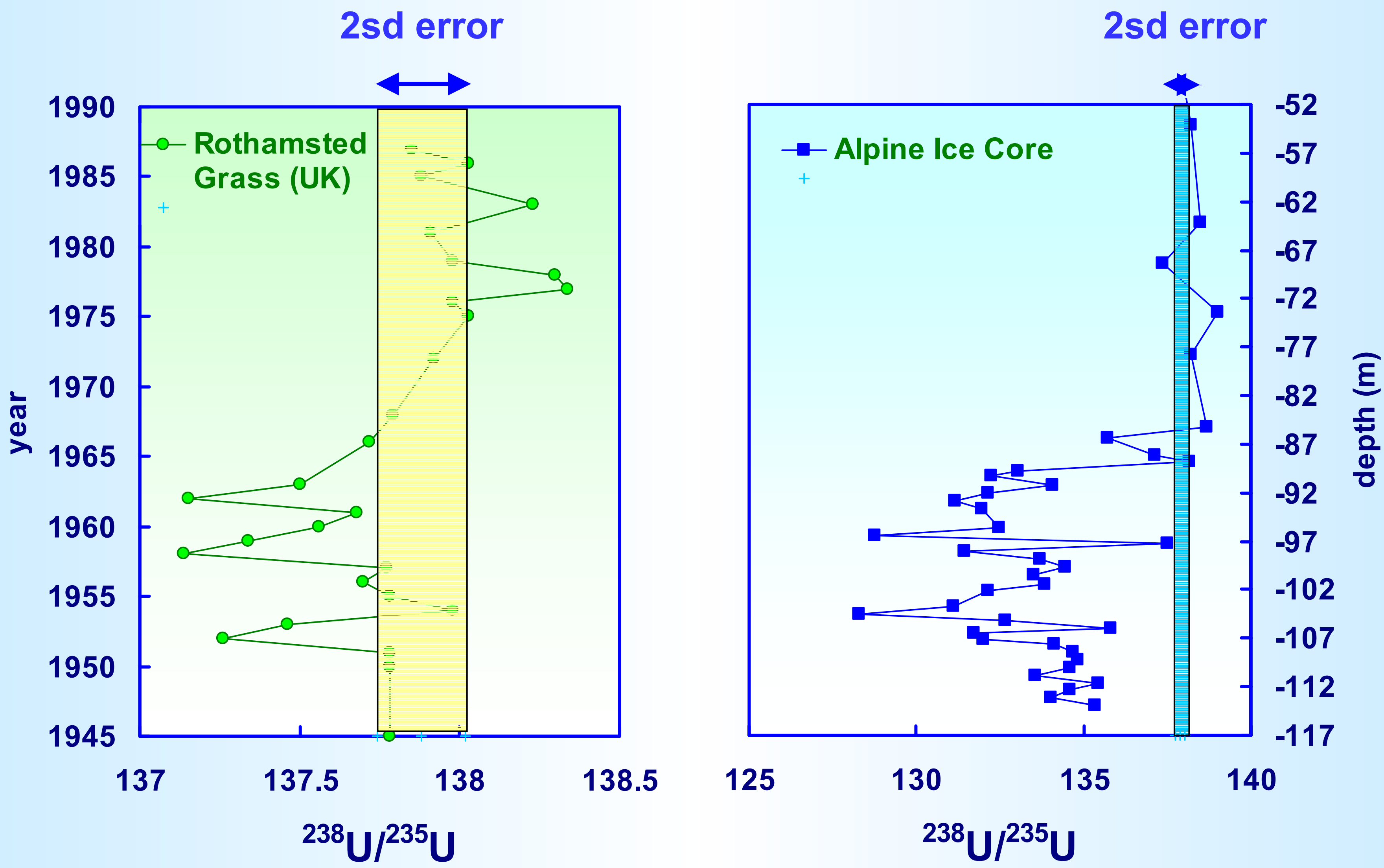
1 Rothamsted Grass Archive (IACR Rothamsted, Harpenden)	Unique collection of herbage and soil since 1843. Samples collected and stored annually or bi-annually Given permission to take 50 grams of dried grass from 1945 until 1990
2 Alpine ice core	116 m ice core, Mont Blanc



Warneke, Croudace, Warwick & Taylor (2002) *Earth Planetary Science Letters*, ***203***, *1047-57*

Warneke, Croudace, Warwick & Taylor (2002) *EPSL*, ***203***, *1047-57*

Uranium isotope - $^{238}U/^{235}U$ fallout record - Europe



Summary

MC-ICP-MS is a highly effective method to measure $^{240}Pu/^{239}Pu$ in environmental and other samples.

Precise measurements are possible at <10 fg Pu (<30 µBq).

Used to investigate fallout history, global and local nuclear events, sediment ages in estuarine environments, source of plutonium contamination.

Other Possible Future Application

Has great potential in plutonium and uranium bioassay

Precise U isotopic analysis using only 50ml of sample

Typically 1-2 litres urine (bulked monthly) are analysed using alpha spectrometry

Clearly MC-ICPMS can greatly enhance these data quality