

Ultra-trace analysis of anthropogenic long-lived radionuclides in the environment with AMS

Karin Hain

The VERA team, A. Sakaguchi, A. Yokoyama, M. Wagnreich

University of Vienna, Faculty of Physics, Austria

University of Tsukuba, Center for Research in Isotopes and Environmental Dynamics, Japan

Kanazawa University, Institute of Science and Engineering, Japan

University of Vienna, Department of Geology, Austria

(karin.hain@univie.ac.at)

INTERNATIONAL CONFERENCE ON

ACCELERATORS FOR RESEARCH AND SUSTAINABLE DEVELOPMENT

From good practices towards socioeconomic impact



23–27 May 2022

IAEA Headquarters, Vienna, Austria

MIGRATION BEHAVIOUR

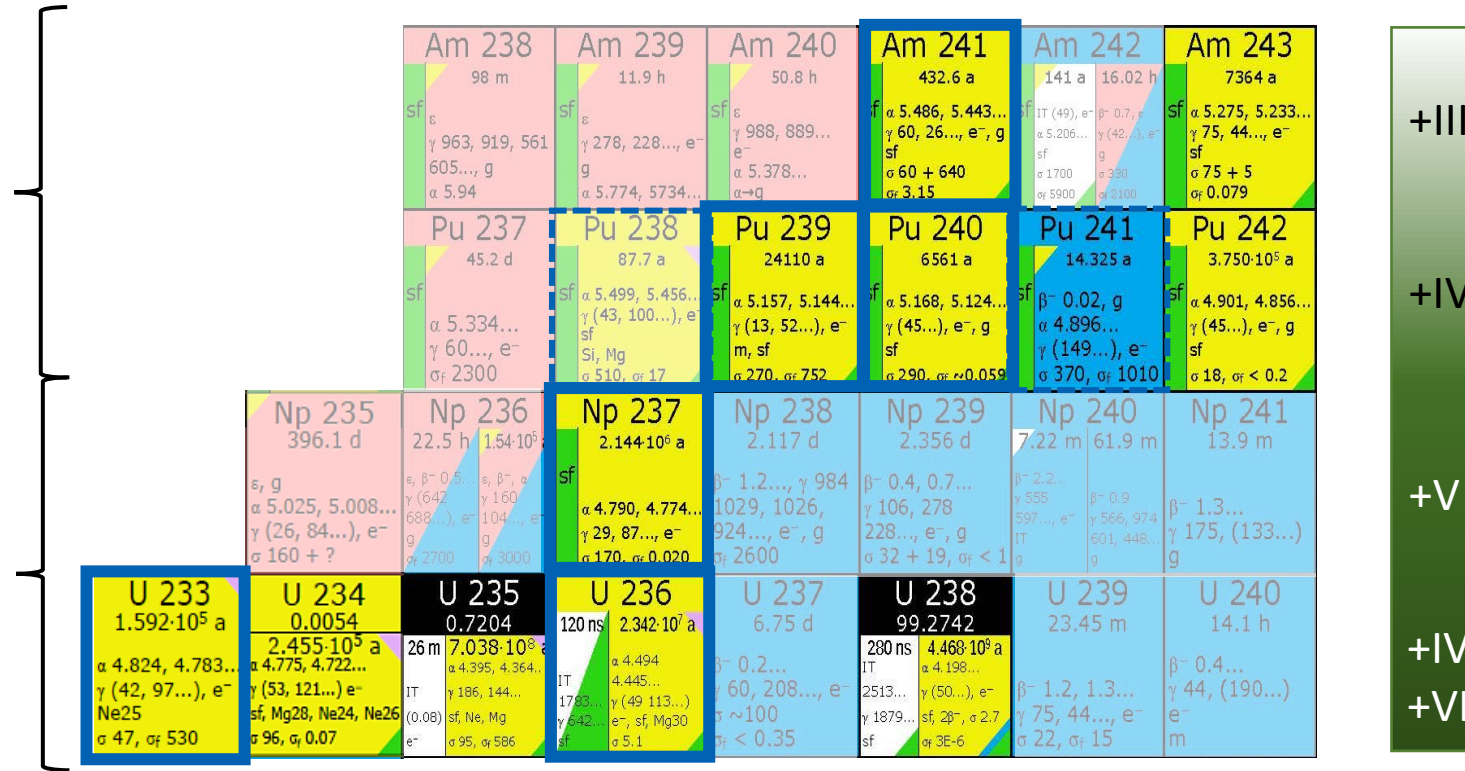
Oxidation state

Particle-reactive

→ Stationary!?

Well soluble

→ Mobile!?



+III
+IV
+V
+IV
+VI



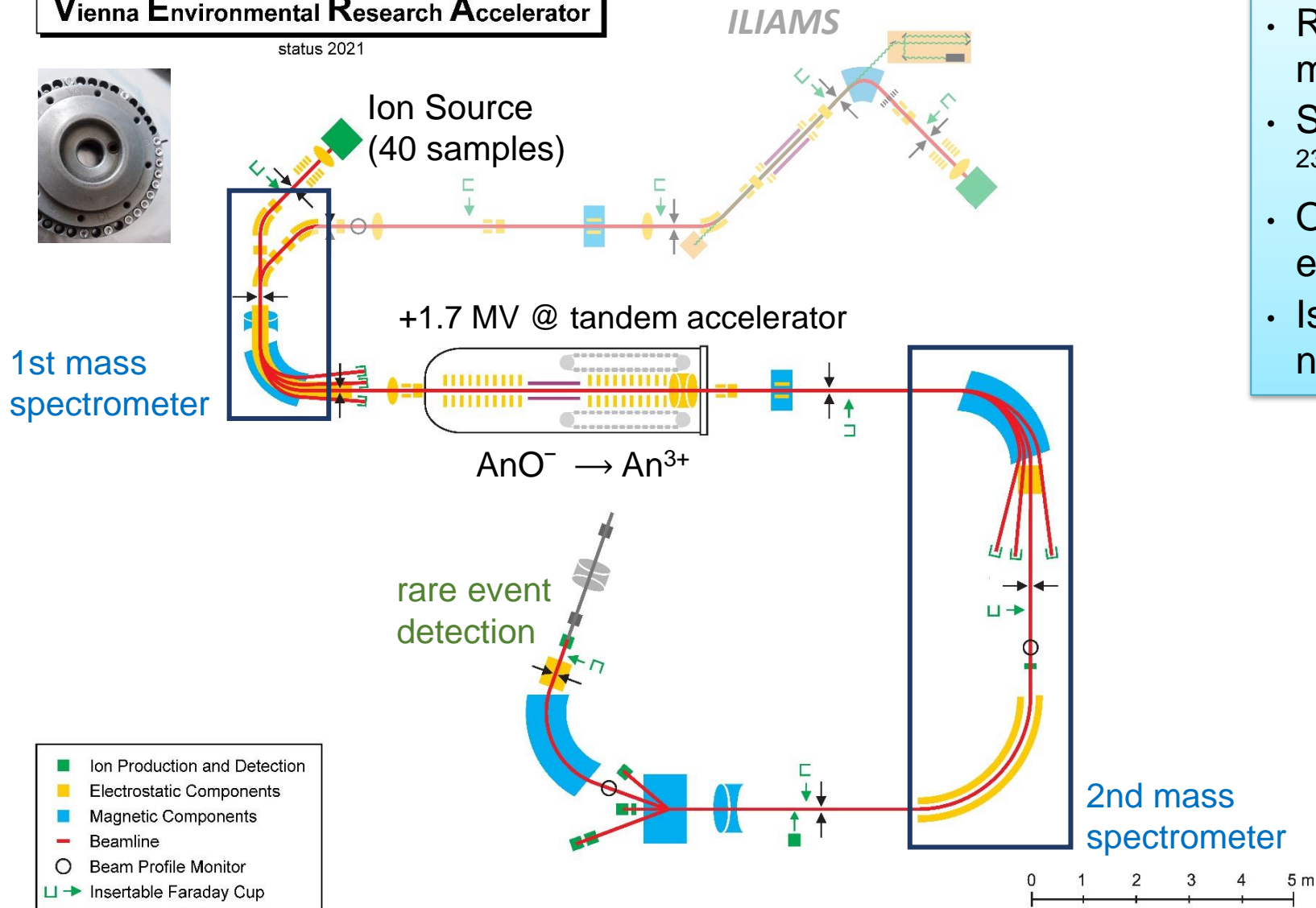
Study migration behaviour in environmental systems at trace level

Radioecology, Nuclear Waste Management, Environmental Sciences (use as tracers)



Vienna Environmental Research Accelerator

status 2021



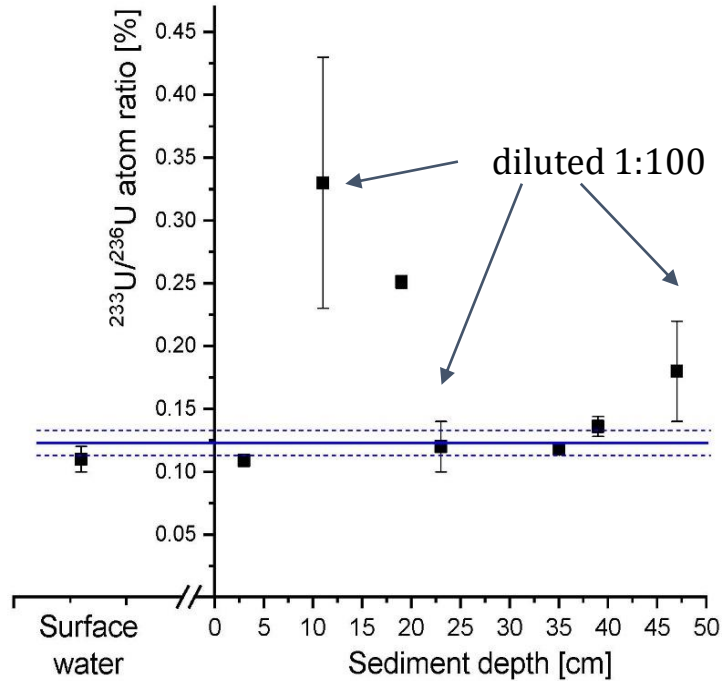
- Ion Production and Detection
- Electrostatic Components
- Magnetic Components
- Beamline
- Beam Profile Monitor
- ↳ Insettable Faraday Cup

- Routine actinide measurement at VERA
- Sensitivity limit: $^{236}\text{U}/^{238}\text{U} < 10^{-12}$
- Overall detection efficiency: $5 \cdot 10^{-4}$
- Isotopic spike for normalisation

Detection Limit:
ag (10^{-18}g)

Irish Sea: nuclear reprocessing

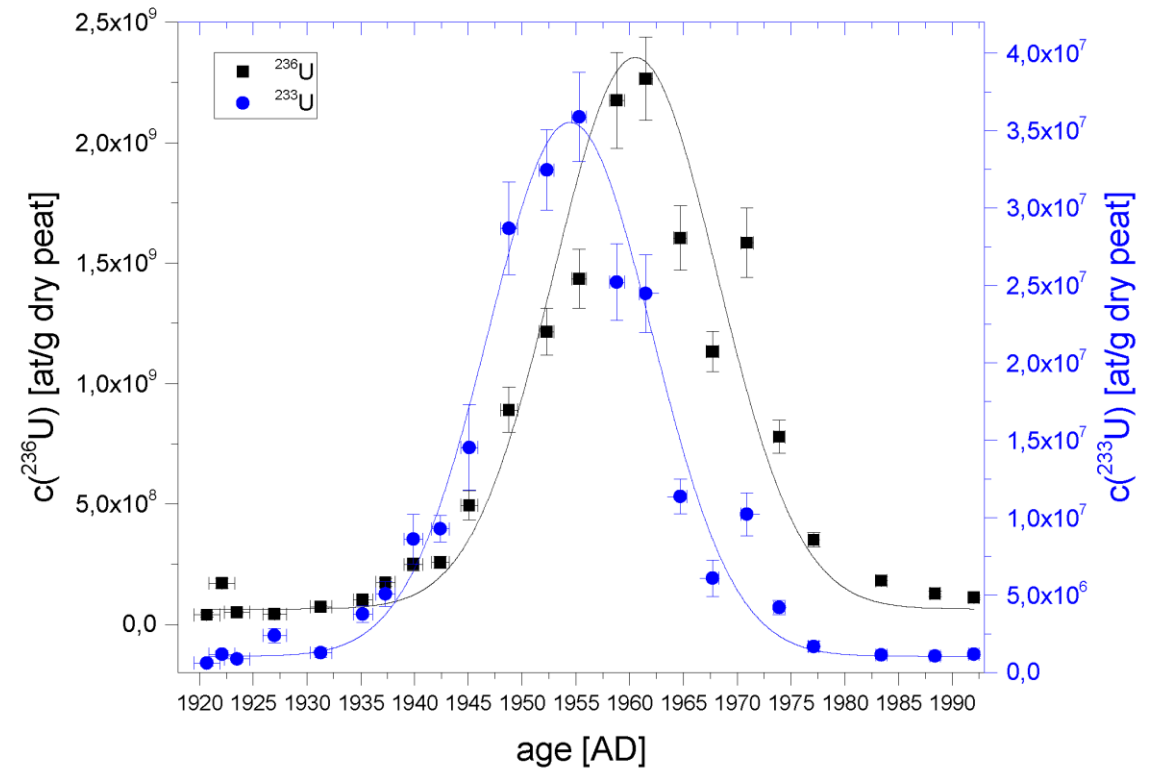
- Dated Sellafield Sediment core
- IAEA-381: Irish Sea Water (1993)



$$^{233}\text{U}/^{236}\text{U} = 0.13 \pm 0.02 \%$$

Peat bog: global fallout

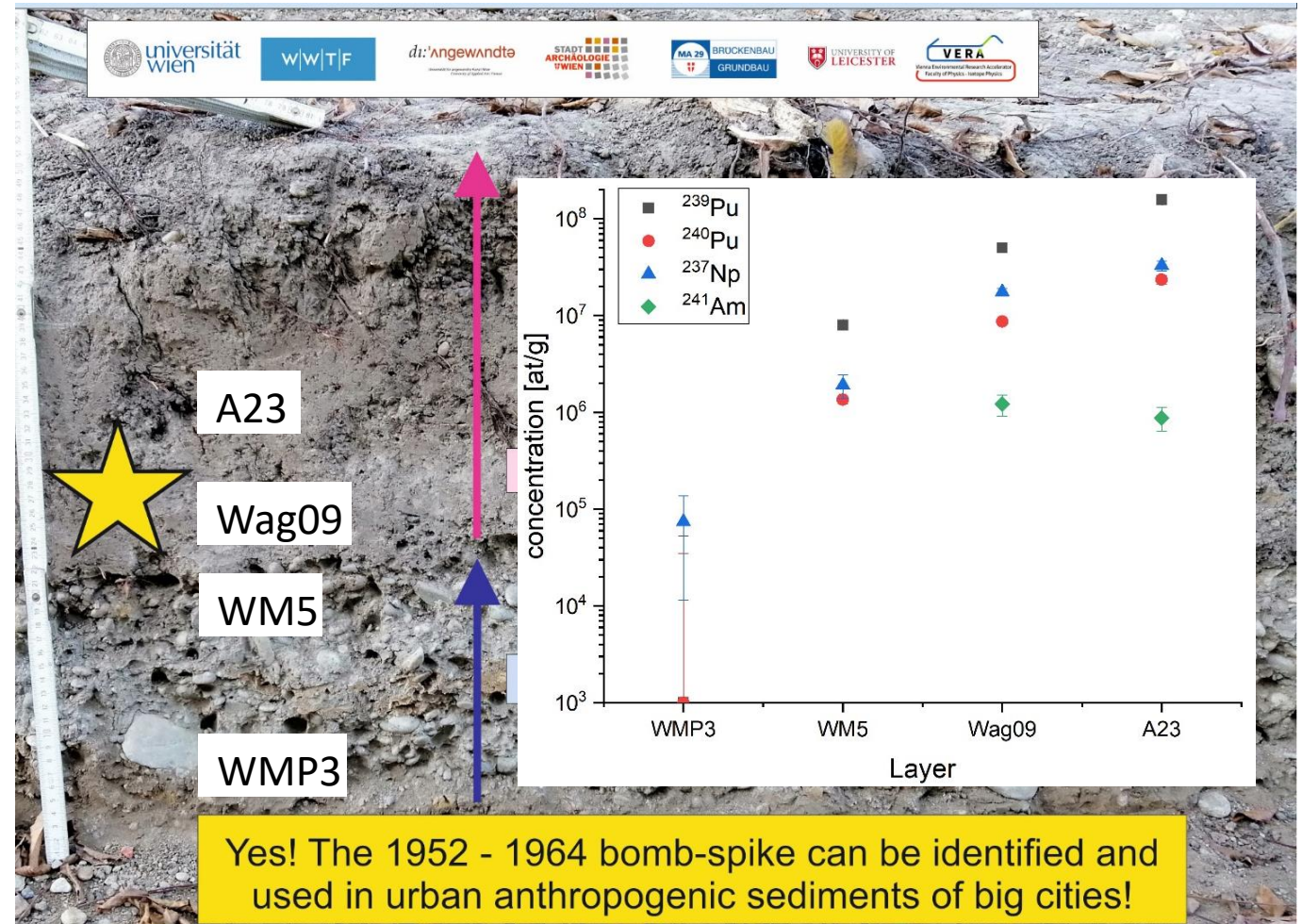
- Core from Black Forest (Germany)



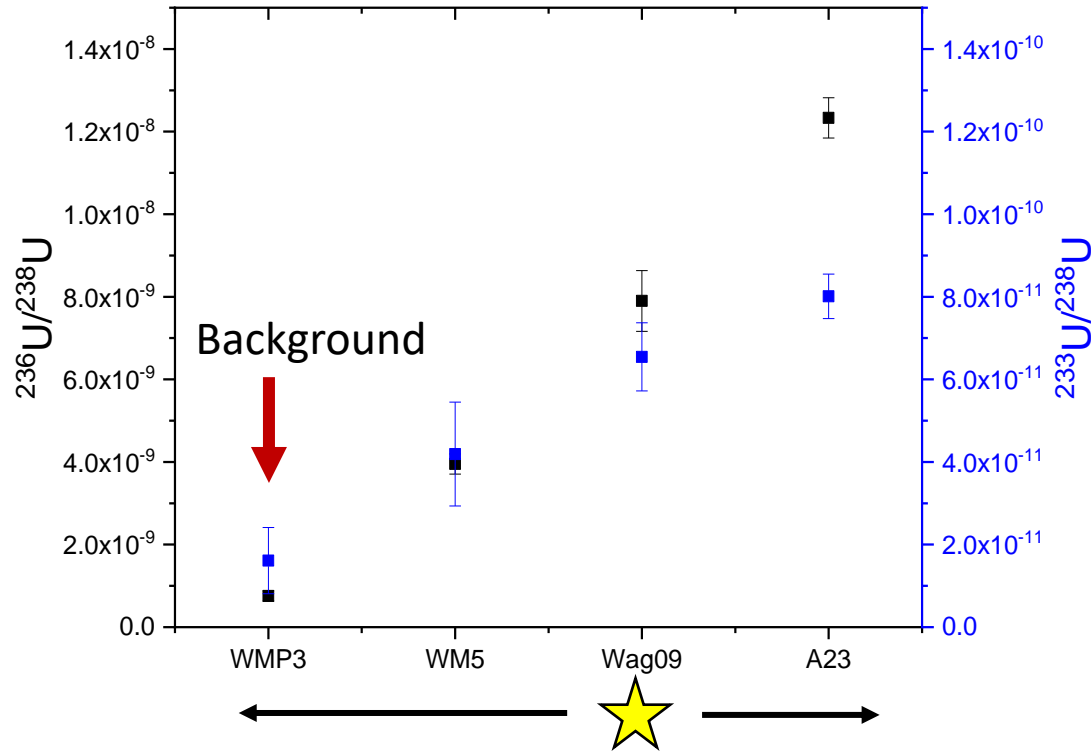
$$^{233}\text{U}/^{236}\text{U} = 1.5 \pm 0.2 \%$$

Karlsplatz, Vienna, Wien Museum

Sample mass: $\approx 10\text{g}$ (sieved and ground)

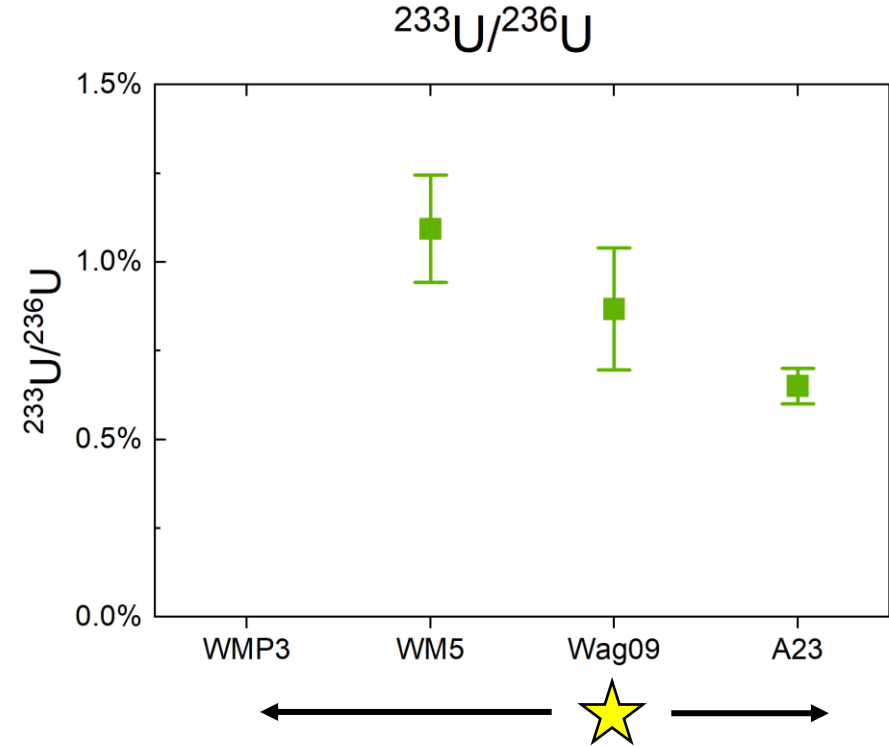


U ratios for source identification



1st half of 20th century
WW2 rubble

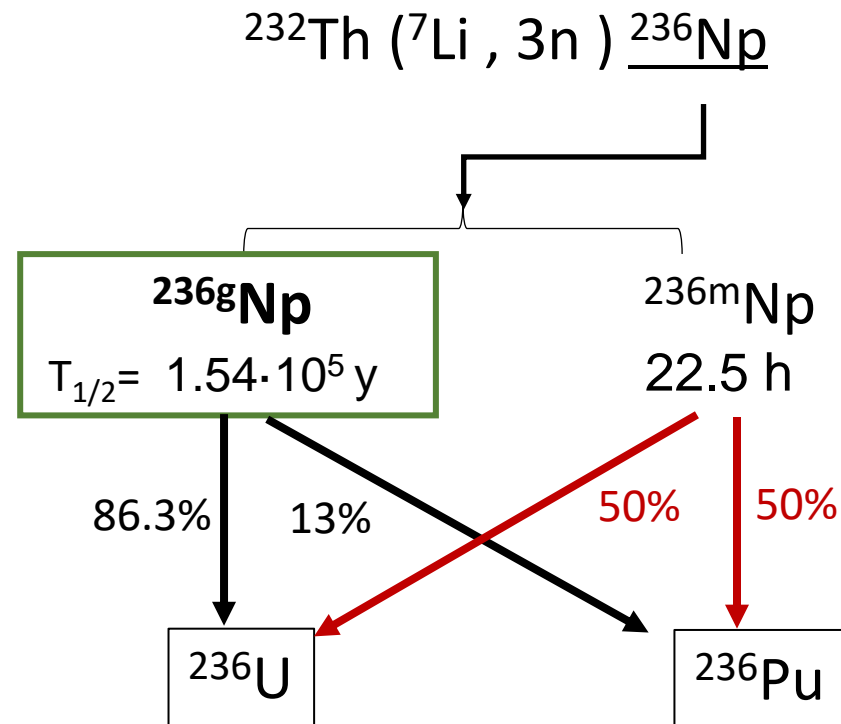
1959 to now



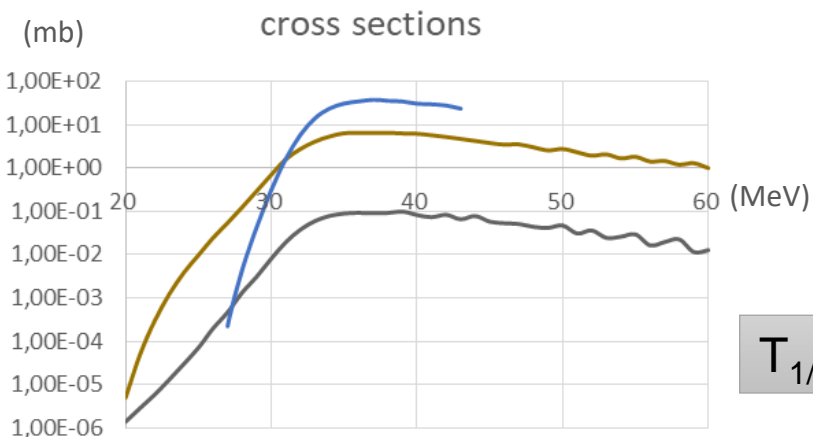
► In contrast to all other anthropogenic radionuclide signals $^{233}\text{U}/^{236}\text{U}$ **decreases!**



Np 235 396.1 d α; 5.07... 5.007... γ(26; 84...); e ⁻ g; σ 160 + ?	Np 236 225 h 1.54 · 10 ⁵ a sf	Np 237 2.144 · 10 ⁶ a sf	Np 238 2.117 d β ⁻ 1.2 γ 984; 1029; 1026; 924...; e ⁻ g; σ 2600	Np 239 2.355 d β ⁻ 0.4; 0.7... γ 555...; 597... 597...; e ⁻ ; g σ 32 + 19; σ 1 < 1	Np 240 7.22 m 65 m β ⁻ 2.2...; β ⁻ 0.9... γ 555...; 597... 597...; e ⁻ ; g σ 32 + 19; σ 1 < 1
U 234 0.0054 2.455 · 10 ⁵ a α 4.775; 4.723...; sf Mg 28; Ne; γ (53; 121...) e ⁻ ; σ 95; σ 0.07	U 235 0.7204 26 m 7.038 · 10 ⁸ a α 4.398...; sf hy (0.07); Ne; γ 186... e ⁻ ; σ 95; σ 58	U 236 120 ns 2.342 · 10 ⁷ a α 4.494...; 4.445... hy 1783; sf; γ (4...) e ⁻ ; σ 27; σ 32-4	^7Li	U 238 99.2742 298 ns 4.468 · 10 ⁹ a α 4.199...; 4.199... hy 254...; 28...; 190... e ⁻ ; σ 27; σ 32-4	U 239 23.5 m β ⁻ 1.2; 1.3... γ 75; 44... σ 22; σ 15
Pa 233 27.0 d β ⁻ 0.3; 0.6... γ 312; 300; 341...; e ⁻ σ 20 + 19; σ 1 < 0.1	Pa 234 1.17 m 6.70 h β ⁻ 2.3... γ (1001); 767... hy (2...); σ 5000	Pa 235 24.2 m β ⁻ 1.4... γ 128 - 659 m	Pa 236 9.1 m β ⁻ 2.0; 3.1... γ 642; 687; 1763...; g βsf ?	Pa 237 8.7 m β ⁻ 1.4; 2.3... γ 854; 865; 529; 541...	Pa 238 2.3 m β ⁻ 1.7; 2.9... γ 1015; 635; 448; 680... g
Th 232 100 1.405 · 10 ¹⁰ a α 4.013; 3.950...; sf γ (64...); e ⁻ σ 7.37; σ 0.000003	Th 233 22.3 m β ⁻ 1.2... γ 87; 29; 459...; e ⁻ σ 1500; σ 15	Th 234 24.10 d β ⁻ 0.2... γ 63; 92; 93... e ⁻ ; m σ 1.8; σ 1 < 0.01	Th 235 7.1 m β ⁻ 1.4... γ 417; 727; 696...	Th 236 37.5 m β ⁻ 1.0... γ 111; (647; 196...)	Th 237 5.0 m β ⁻



No experimental data available!



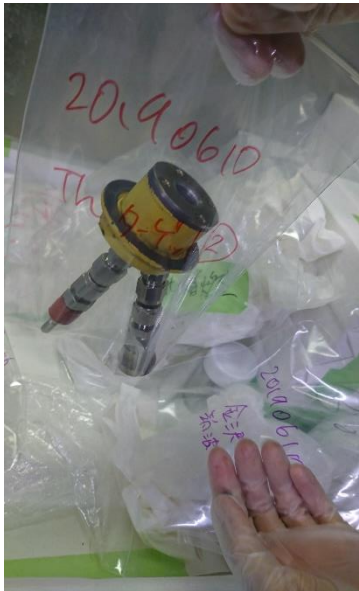
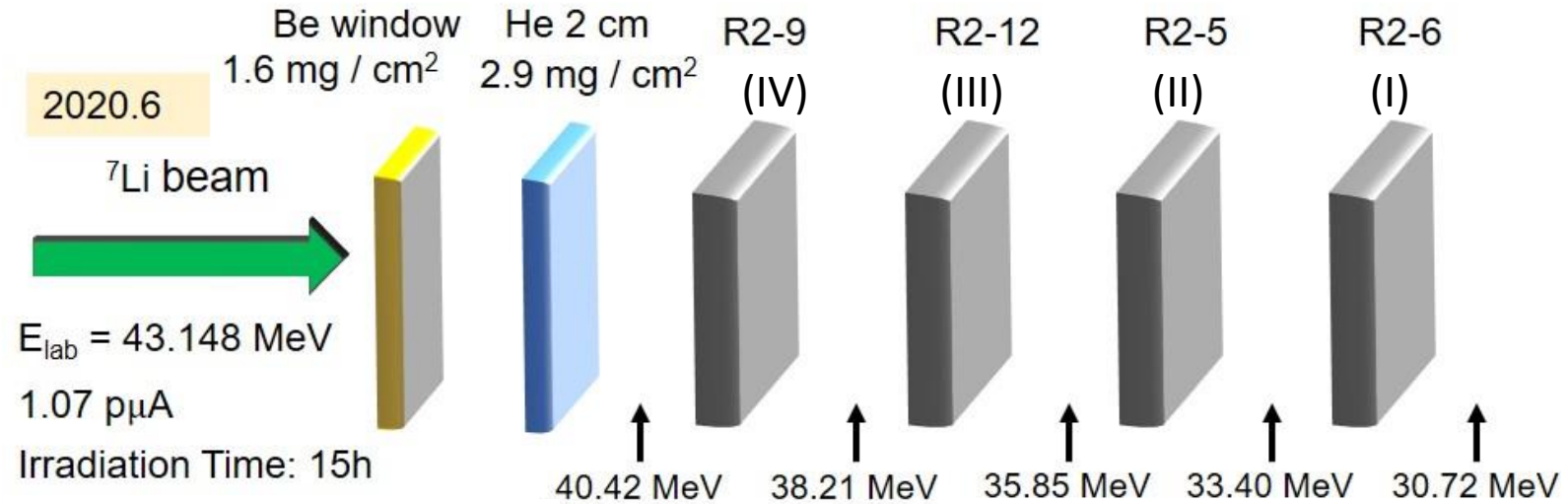
$T_{1/2} (^{235}\text{Np}) = 396\text{d!}$

for $z = ^7\text{Li}$

— Np-237 (z,2n) — Np-236 (z,3n) — Np-235 (z,4n)
Calculated by EMPIREII code

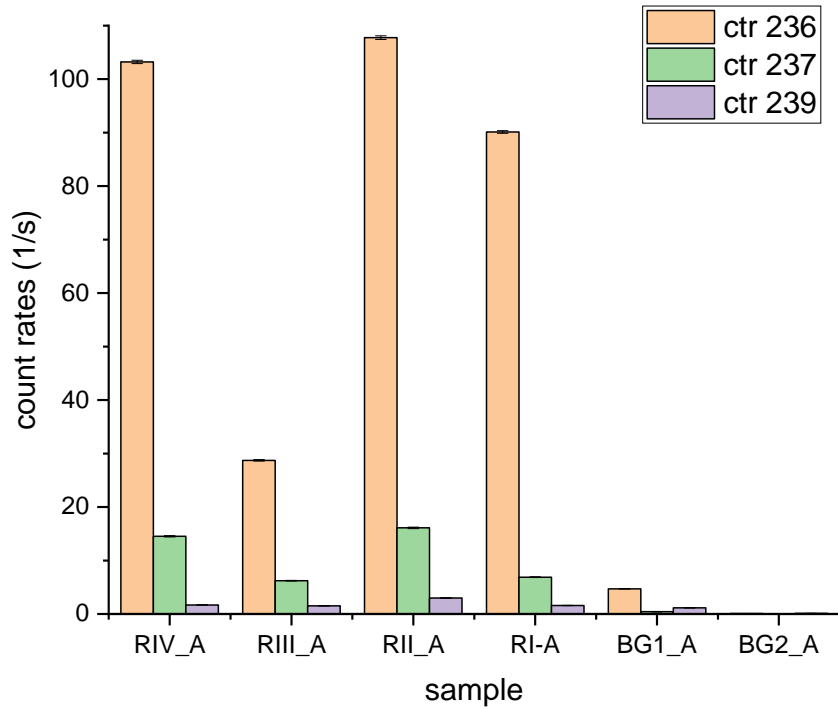
A. Sakaguchi,
University of Tsukuba



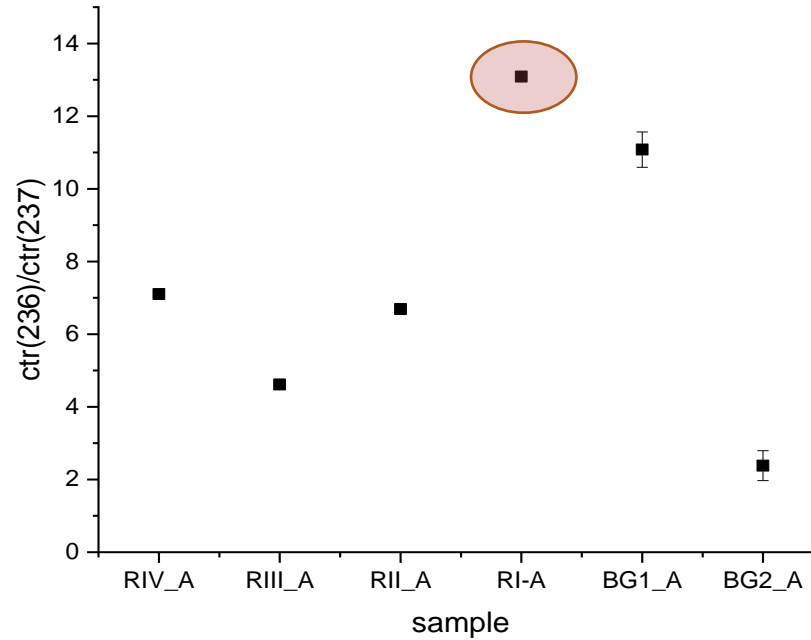
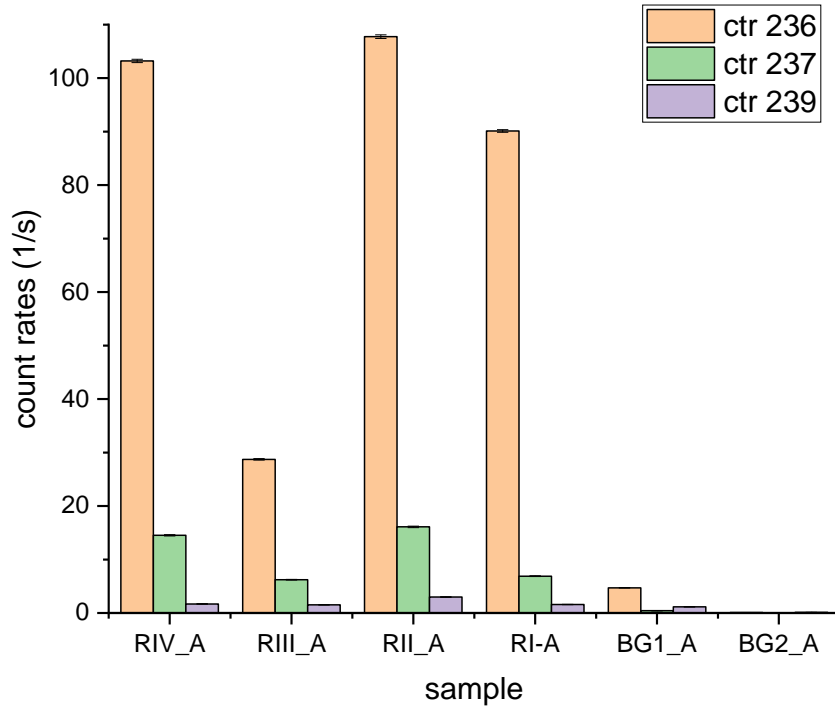


No.	Thickness (mg / cm ²)
R2 - 9	9.75
R2 - 12	10.15
R2 - 5	10.12
R2 - 6	10.58

A. Yokoyama,
 Kanazawa University



- **Mass 236 above BG level produced**
- Only statistical uncertainties included

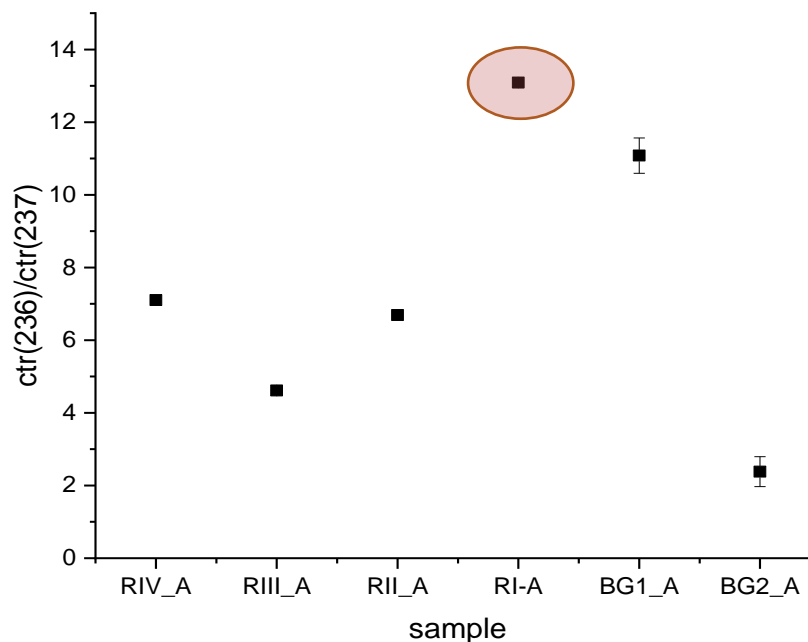
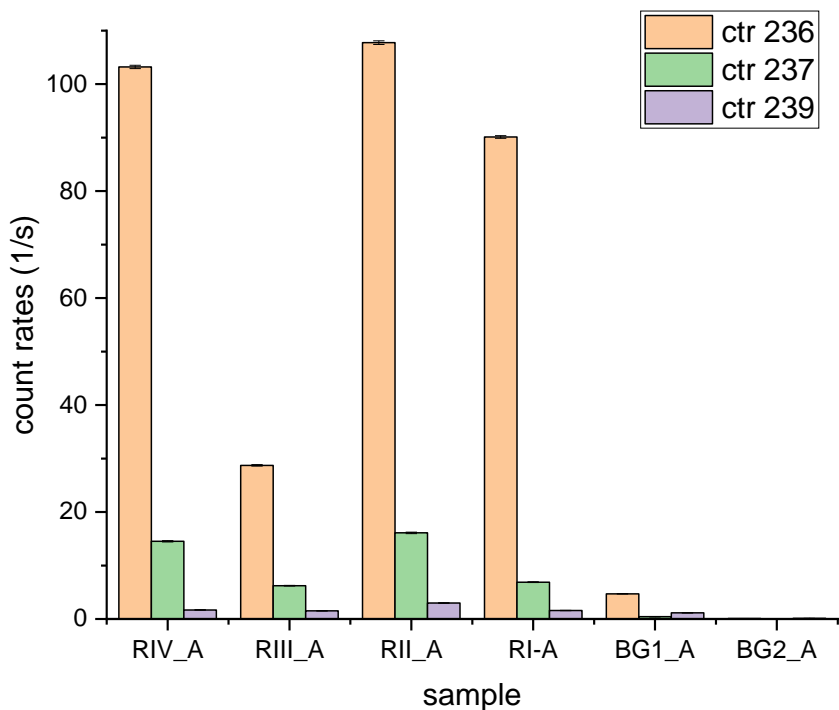


➤ Highest ratio 236/237 ≈ 13

↕

Empire Code: **236/237 ≈ 90**

- **Mass 236 above BG level produced**
- Only statistical uncertainties included



➤ Highest ratio 236/237 \approx 13



Empire Code: 236/237 \approx 90

➤ **Mass 236 above BG level produced**

➤ Only statistical uncertainties included

Problem: considerable ^{233}U production

Measured neutron flux (Au monitor)

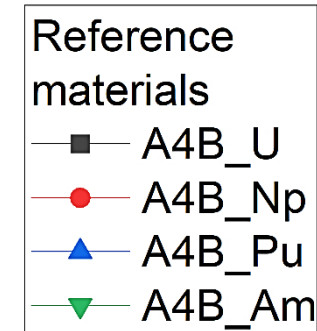
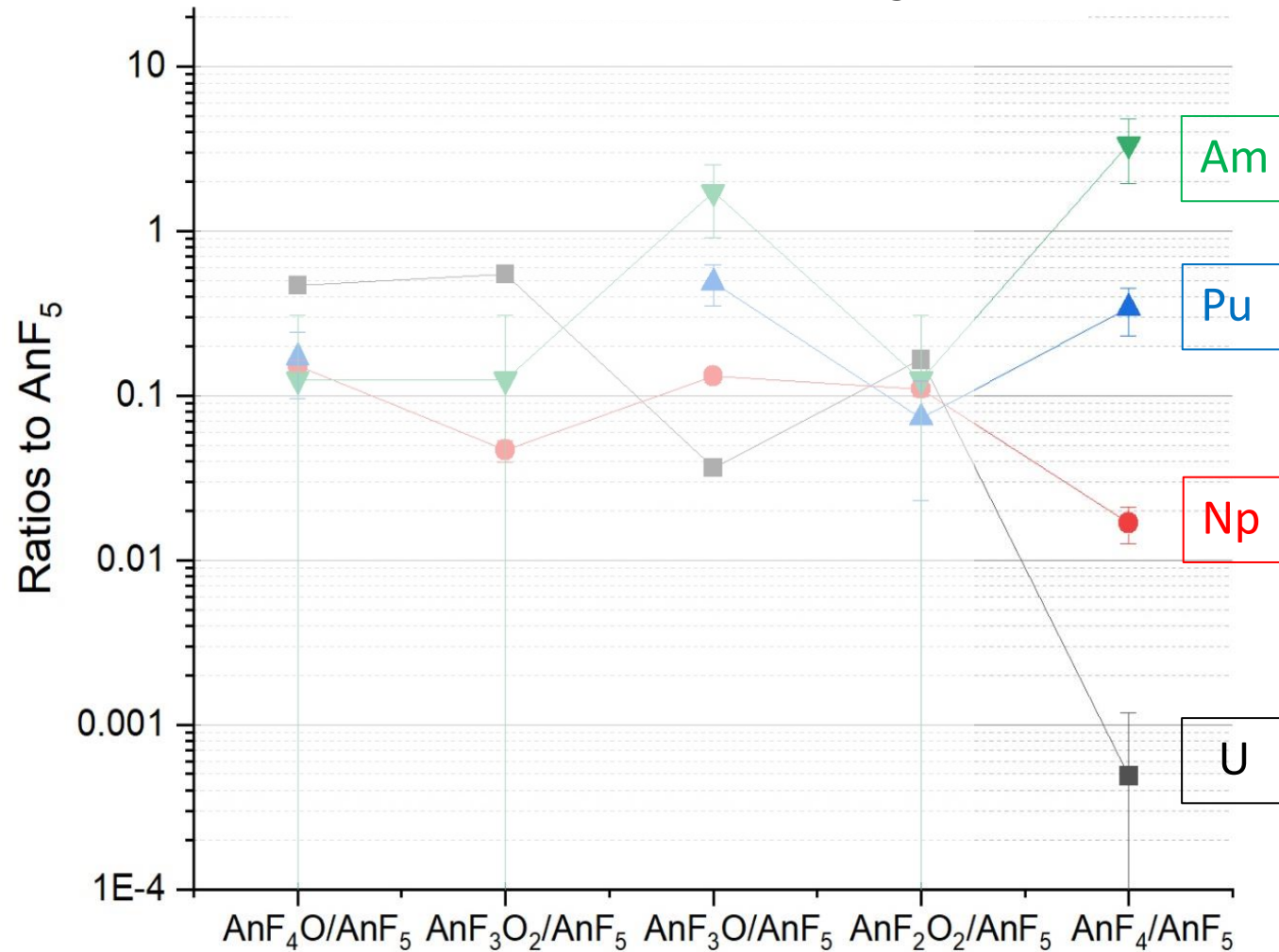
thermal n flux: $6.5 \cdot 10^5 / (\text{scm}^2)$

fast n flux: $2 \cdot 10^7 / (\text{scm}^2)$

M(236) \triangleq ^{236}Np ?

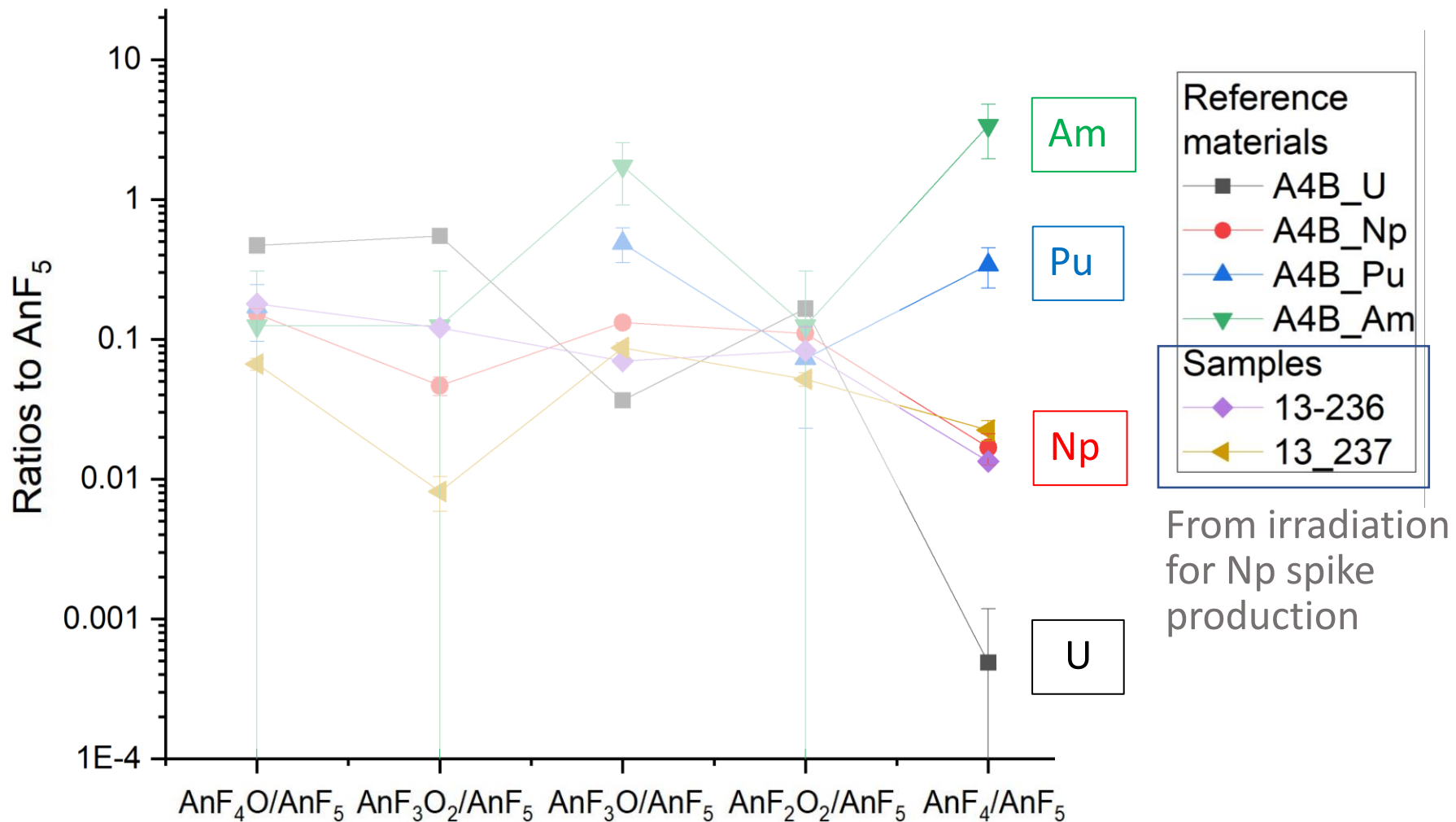


Relative formation of $AnF_mO_n^-$
with respect to AnF_5^-



➤ Higher Actinides prefer the formation of AnF_4^-
(reported in Cornett et al, *NIMB*, 2015)

Relative formation of $AnF_mO_n^-$
with respect to AnF_5^-



Nuclear reprocessing plants



This project



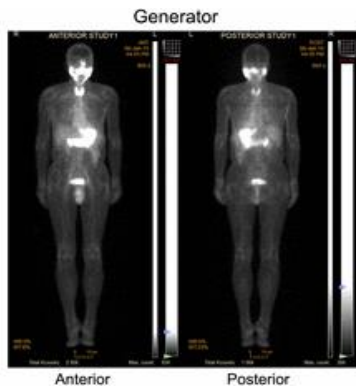
Atmospheric Nuclear Weapons Tests



Estimated total deposition: 140 TBq (220 kg)

Rh 97 44 m 31 m β^+ 2.6... γ 189; 422... γ 259	Rh 98 3.5 m 8.7 m β^+ 2.1... γ 402; 840; 879	Rh 99 4.7 h 16 d β^+ 0.7 γ 341; 1.1... 818; 1261...	Rh 100 4.7 m 20.8 h β^+ 2.8... γ 32; 74 γ 540; 2378; 1503...	Rh 101 4.4 d 3.3 a β^+ 3.07; 545... γ 157	Rh 102 2.9 a 207 d β^+ 4.75; β^+ 1.3 β^+ 1.2 γ 475; γ 142; 626...	Rh 103 56.1 m 100 β^+ 1.1... γ 131
Ru 96 5.54 α 0.23	Ru 97 2.9 d γ 216; 324...	Ru 98 1.87 α < 8	Ru 99 12.76 α 4	Ru 100 12.60 α 5.8	Ru 101 17.06 α 5	Ru 102 31.55 α 1.2
Tc 95 60 d 20 h β^+ 2.04; 562; 835... γ 591	Tc 96 52 m 4.3 d β^+ 3.4 β^+ 0.5 γ 778; 850; 1200...	Tc 97 92.2 d 4.0 · 10 ⁹ a β^+ 0.7 α 0.3	Tc 98 4.2 · 10 ⁶ a β^- 0.4 γ 745; 652 α 0.9 + ?	Tc 99 6.0 h 2.1 · 10 ⁵ a β^- 1.41... β^- 0.3... γ 322; 1 α 23	Tc 100 15.8 s β^- 3.4... γ 540; 591...	Tc 101 14.2 m β^- 1.3... γ 307; 545...
Mo 94 9.23 α 0.02	Mo 95 15.90 α 13.4 α 0.000030	Mo 96 16.68 α 0.5	Mo 97 9.56 α 2.5 α 4E-7	Mo 98 24.19 α 0.14	Mo 99 66.0 h β^- 1.2... γ 740; 182; 778... m; g	Mo 100 9.67 β^- 1.15 · 10 ¹⁹ a α 0.19
Nb 93 16.13 a 100 β^- 0.86 + α 0.29	Nb 94 6.26 m 2 · 10 ⁴ a β^- 0.5 γ 871; 703 β^- 0.6 + γ 871...	Nb 95 86.6 h 34.97 d β^- 2.38 β^- 0.2; α 0.9 β^- 1.0 γ 768... α < 7	Nb 96 23.4 h β^- 0.7... γ 778; 569; 1091...	Nb 97 53 s 74 m β^- 1.3... γ 608...	Nb 98 51 m 2.9 a β^- 2.0... γ 767; 723; 1168...	Nb 99 2.6 m 15 a β^- 3.2... γ 99; 254; 2642; 2854... β^- 3.1 γ 138; γ 305.7 98

(Nuclear Medicine)



- Several proof-of-principle publications by TIMS, RIMS and AMS
- But hardly any studies on environmental concentrations far away from the contamination sources (100L, ICP-MS)

Rh 97 44 m 31 m β^+ 2.6... γ 189; 422... γ 259	Rh 98 3.5 m 8.7 m β^+ 2.1... γ 402; 840; 879	Rh 99 4.7 h 16 d β^+ 0.7; γ 341; 528; 1261	Rh 100 4.7 m 20.8 h β^+ 0.7; γ 33; 74; 540; 607	Rh 101 4.4 d 3.3 a β^+ 2.8... γ 307; 545; γ 157	Rh 102 2.9 a 207 d β^+ 1.3; β^- 1.2; γ 475; 631; 697; γ 475; 826...	Rh 103 56.1 m 100 β^- 1.1... γ 131
Ru 96 5.54 α 0.23	Ru 97 2.9 d α 216; 324...	Ru 98 1.87 α < 8	Ru 99 12.76 α 4	Ru 100 12.60 α 5.8	Ru 101 17.06 α 5	Ru 102 31.55 α 1.2
Tc 95 60 d 20 h β^- 2.6... γ 204; 562; 835; γ (59)	Tc 96 52 m 4.3 d β^- 0.5... γ 778; 778; 1200... 813...	Tc 97 92.2 d 4.0 · 10 ⁹ a β^- 0.4... γ 745; 652 α 0.9 + ?	Tc 98 4.2 · 10 ⁶ a β^- 0.4... γ 745; 652 α 0.9 + ?	Tc 99 6.0 h 2.1 · 10 ⁵ a β^- 0.3... γ 141... γ (22...)	Tc 100 15.8 s β^- 3.4... γ 540; 591...	Tc 101 14.2 m β^- 1.3... γ 307; 545...
Mo 94 9.23 α 0.02	Mo 95 15.90 α 13.4 α n, α 0.000030	Mo 96 16.68 α 0.5	Mo 97 9.56 α 2.5 α n, α 4E-7	Mo 98 24.19 α 0.14	Mo 99 66.0 h β^- 1.2... γ 740; 182; 778... m; g	Mo 100 9.67 1.15 · 10 ¹⁹ a β^- 0.19
Nb 93 16.13 a 100 β^- 0.86... γ (31)	Nb 94 6.26 m 2 · 10 ⁴ a β^- 0.5... γ 871; 703 β^- 0.6... γ (871)	Nb 95 86.6 h 34.97 d β^- 0.2... γ 238 β^- 1.0... γ 768... α < 7	Nb 96 23.4 h β^- 0.7... γ 778; 569; 1091...	Nb 97 53 s 74 m β^- 1.3... γ 608	Nb 98 51 m 2.9 a β^- 2.0... γ 767; 723; 1168...	Nb 99 2.6 m 15 s β^- 3.2... γ 99; 254; 2642; 2854... γ 138; β^- 3.1

interfering
isobar ^{99}Ru

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- But hardly any studies on environmental concentrations far away from the contamination sources (100L, ICP-MS)

no stable isotopes for normalization

Rh 97 44 m 31 m β^+ 2.6... γ 189; 422... γ 259	Rh 98 3.5 m 8.7 m β^+ 2.1... γ 402; 840; 492... 679	Rh 99 4.7 h 16 d β^+ 0.7 γ 341; 1.1... 818; 528; 1261; 353; 90	Rh 100 4.7 m 20.8 h β^+ 32; 74 β^+ 2.8... γ 540; 687... 153	Rh 101 4.4 d 3.3 a β^+ 307; 545... γ 127; 198; 157 325	Rh 102 2.9 a 207 d β^+ 475; 631; 697; β^+ 1.3 β^+ 1.2 γ 475; 626...	Rh 103 56.1 m 100 β^+ 1.1... 131
Ru 96 5.54 α 0.23	Ru 97 2.9 d α 216; 324...	Ru 98 1.87 α < 8	Ru 99 12.76 α 4	Ru 100 12.60 α 5.8	Ru 101 17.06 α 5	Ru 102 31.55 α 1.2
Tc 95 60 d 20 h β^- 204; γ 204; 562; 835; γ (391)	Tc 96 52 m 4.3 d β^- (34) α 778; 778; 1200; 813	Tc 97 92.2 d 4.0 $\cdot 10^9$ a β^- (97) α 20.3	Tc 98 4.2 $\cdot 10^6$ a β^- 0.4 γ 745; 652 α 0.9 + ?	Tc 99 6.0 h 2.1 $\cdot 10^5$ a β^- 141... α 322... β^- 0.3 γ (90)	Tc 100 15.8 s β^- 3.4... α 540; 591...	Tc 101 14.2 m β^- 1.3... γ 307; 545...
Mo 94 9.23 α 0.02	Mo 95 15.90 α 13.4 α n, α 0.000030	Mo 96 16.68 α 0.5	Mo 97 9.56 α 2.5 α n, α 4E-7	Mo 98 24.19 α 0.14	Mo 99 66.0 h β^- 1.2... γ 740; 182; 778... m; g	Mo 100 9.67 1.15 $\cdot 10^{19}$ a β^- 0.19
Nb 93 16.13 a 100 β^- (31) α 0.86 + 0.29	Nb 94 6.26 m 2 $\cdot 10^4$ a β^- 0.5 γ 871; 703 β^- 0.6 + γ (871)	Nb 95 86.6 h 34.97 d β^- 238 β^- 0.2; 0.9 β^- 1.0 γ 768... α < 7	Nb 96 23.4 h β^- 0.7... γ 778; 569; 1091...	Nb 97 53 s 74 m β^- 1.3 γ 608	Nb 98 51 m 2.9 a β^- 2.0... 2.9... γ 787; 723; 1168...	Nb 99 2.6 m 15 s β^- 3.2... γ 99; 254; 2642; 2854... γ 138; β^- 3.1 γ 305.7 98

interfering isobar ^{99}Ru

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no stable isotopes for normalization

Rh 97 44 m 31 m β^+ 2.6... γ 189; 422... γ 259	Rh 98 3.5 m 8.7 m β^+ 2.1... γ 402; 840; 482... γ 679	Rh 99 4.7 h 16 d β^+ 0.7... γ 341; 1.1... γ 528; 1261...	Rh 100 4.7 m 20.8 h β^+ 0.7... γ 32; 74... β^+ 2.8... γ 540; 2378; 687... γ 153	Rh 101 4.4 d 3.3 a β^+ 3.07... γ 307; 545... γ 157	Rh 102 2.9 a 207 d β^+ 4.75... β^+ 1.3... β^+ 1.2... γ 475; 631; 697; 142... γ 626...	Rh 103 56.1 m 100 β^+ 1.1... γ 13
Ru 96 5.54 α 0.23	Ru 97 2.9 d α 216; 324...	Ru 98 1.87 α < 8	Ru 99 12.76 α 4	Ru 100 12.60 α 5.8	Ru 101 17.06 α 5	Ru 102 31.55 α 1.2
Tc 95 60 d 20 h β^- 2.04... γ 204; 562; 835... γ 1074	Tc 96 52 m 4.3 d β^- 34... β^- 778; 1200... β^- 813	Tc 97 92.2 d 4.0 $\cdot 10^5$ a β^- 0.7... γ 97	Tc 98 4.2 $\cdot 10^6$ a β^- 0.4... γ 745; 652... α 0.9 + ?	Tc 99 6.0 h 2.1 $\cdot 10^5$ a β^- 141... β^- 0.3... β^- 1003... β^- 322... α 23	Tc 100 15.8 s β^- 3.4... β^- 540; 591...	Tc 101 14.2 m β^- 1.3... γ 307; 545...
Mo 94 9.23 α 0.02	Mo 95 15.90 α 13.4 α n, α 0.000030	Mo 96 16.68 α 0.5	Mo 97 9.56 α 2.5 α n, α 4E-7	Mo 98 24.19 α 0.14	Mo 99 66.0 h β^- 1.2... γ 740; 182; 778... m; g	Mo 100 9.67 1.15 $\cdot 10^{19}$ a β^- 0.19
Nb 93 16.13 a 100 β^- 31... α 0.86... α 0.29	Nb 94 6.26 m 2 $\cdot 10^4$ a β^- 0.5... β^- 871; 703... β^- 0.6... γ 871...	Nb 95 86.6 h 34.97 d β^- 238... β^- 0.2... β^- 1.0... α < 7	Nb 96 23.4 h β^- 0.7... γ 778; 569; 1091...	Nb 97 53 s 74 m β^- 1.3... β^- 608...	Nb 98 51 m 2.9 a β^- 2.0... β^- 787; 723; 1168... β^- 4.6... β^- 787; 2854... β^- 305.7... β^- 98	Nb 99 2.6 m 15 a β^- 3.2... β^- 98; 254; 2642... β^- 138; 138; 138...

interfering isobar ^{99}Ru

use isotopic spike: ^{97}Tc



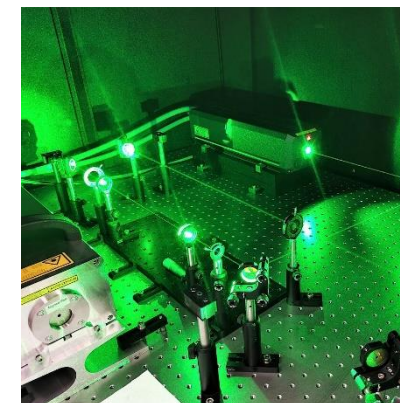
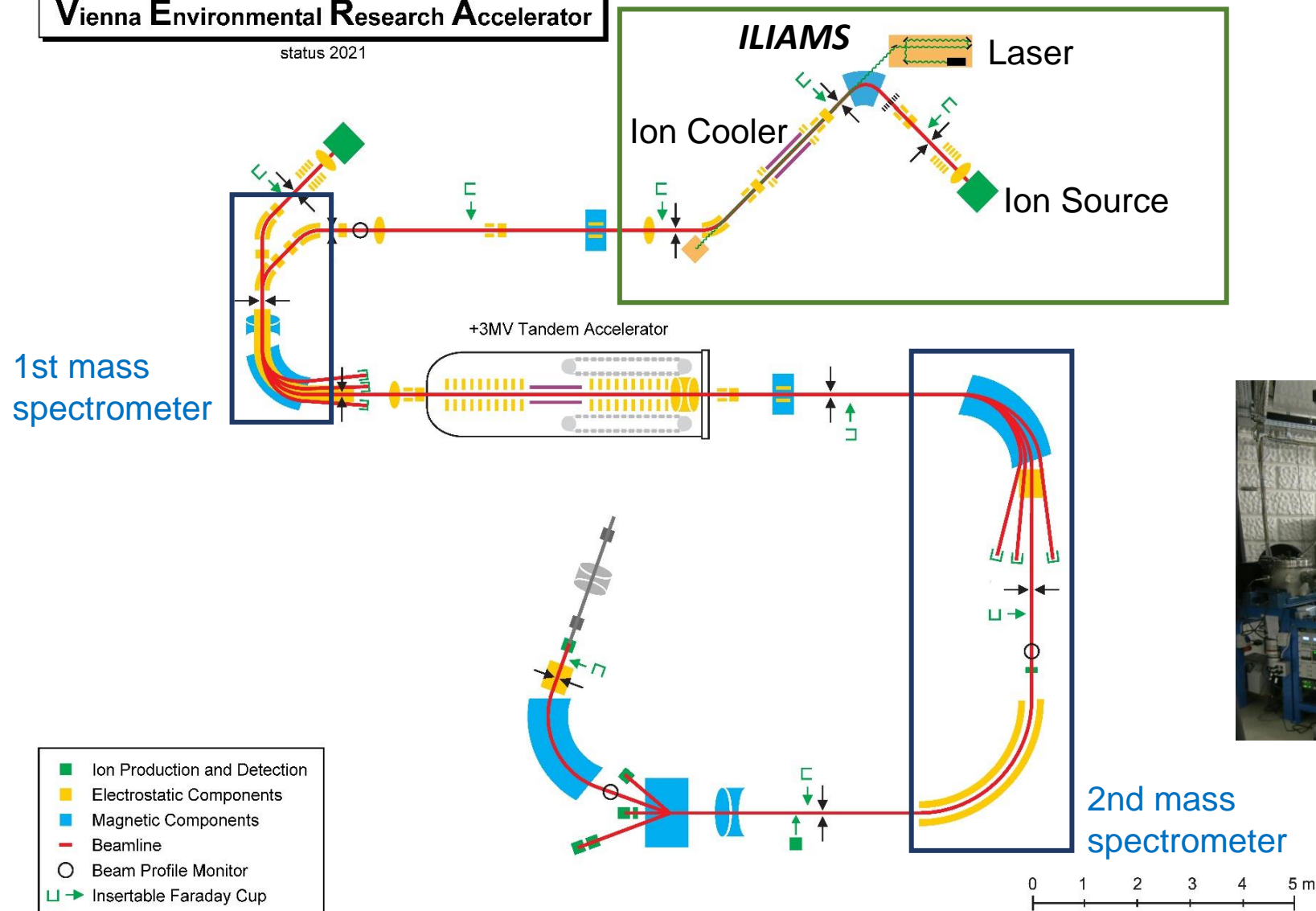
Produced e.g. via $^{93}\text{Nb}(^7\text{Li},3n)^{97}\text{Tc}$

@ 9.5 MV terminal voltage (MLL, Munich)



Vienna Environmental Research Accelerator

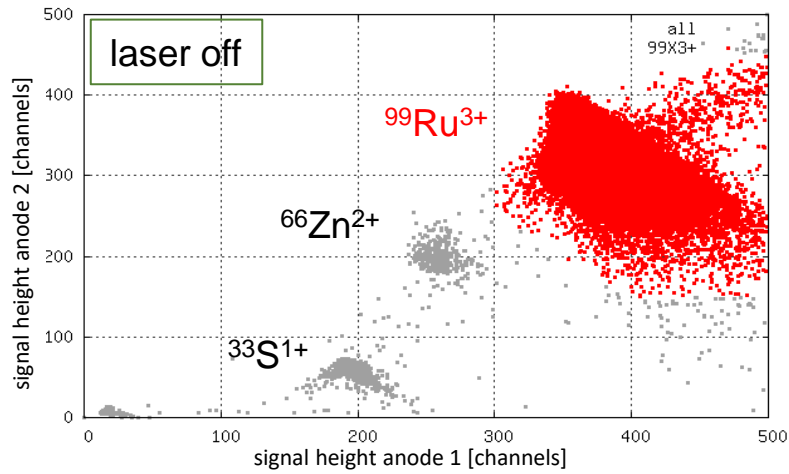
status 2021



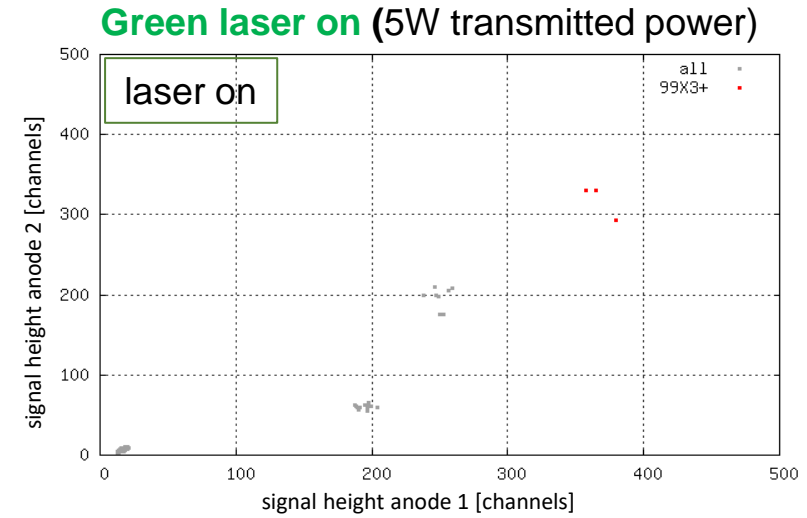
06/03/2017



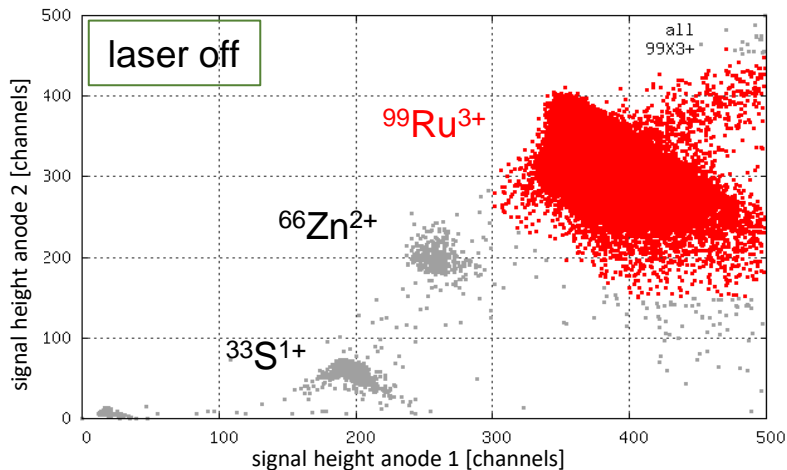
Sample with $7 \cdot 10^{14}$ atoms ^{99}Ru added



Suppression
factor
→
 $\approx 10^4 - 10^5$



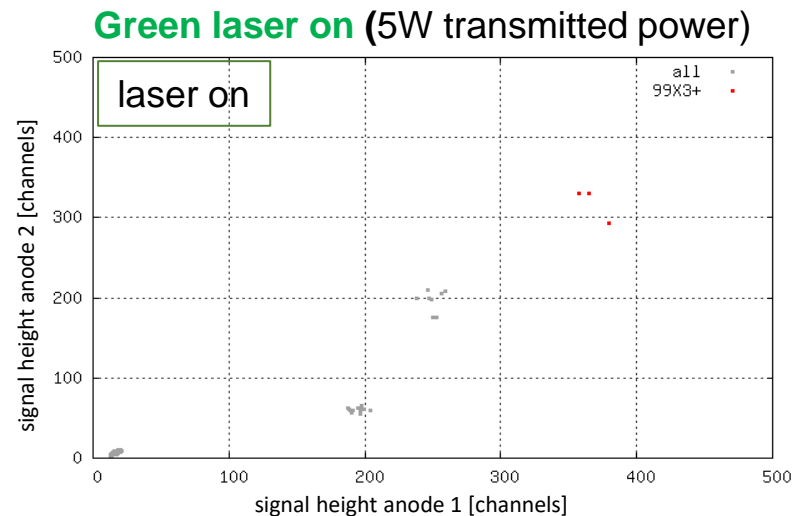
Sample with $7 \cdot 10^{14}$ atoms ^{99}Ru added



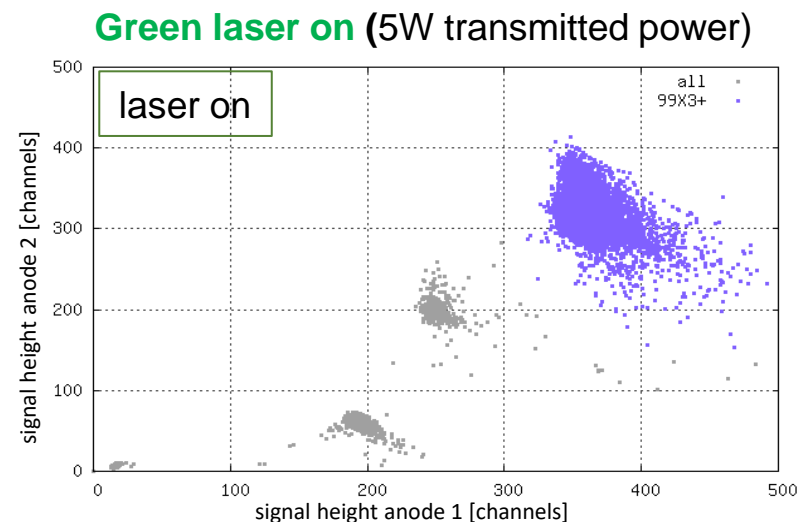
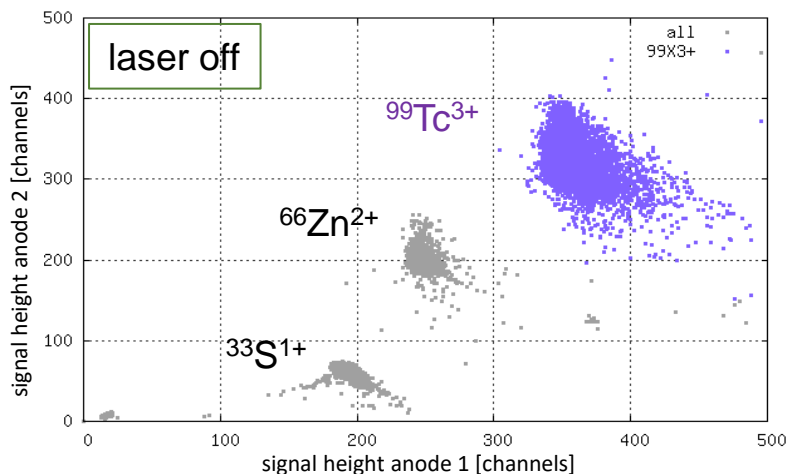
Suppression factor



$\approx 10^4 - 10^5$

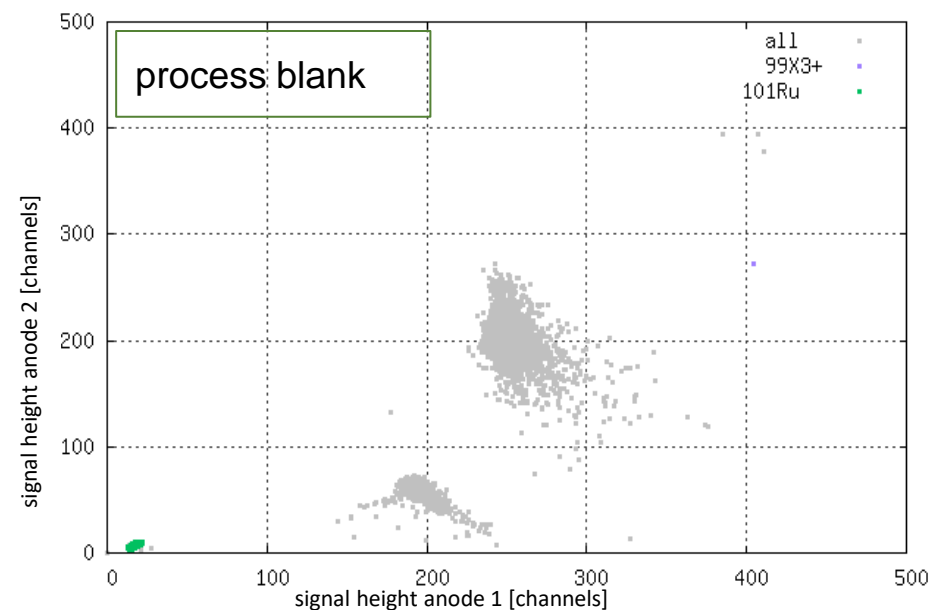
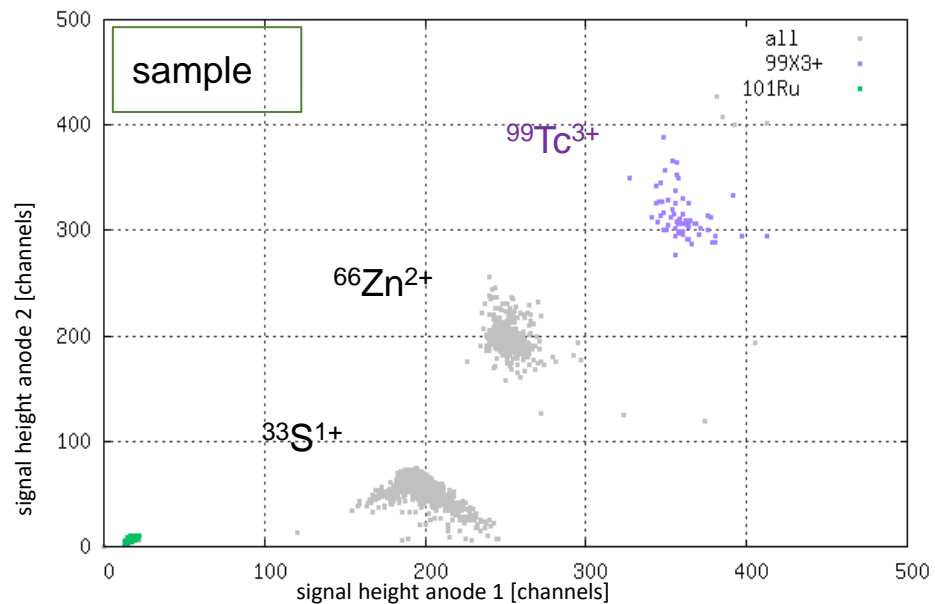


Sample with $4 \cdot 10^{10}$ atoms ^{99}Tc added



**Ombrotrophic peat bog (Austria):
surface water (V = 10L)**

Green laser on (5W transmitted power)



Helium as buffer gas

	Formation ion source	532 nm E = 2.33 eV	355 nm E = 3.40 eV	479 nm E = 2.79 eV
TcF ₅ ⁻		U ≈ 1	U ≈ 150 (?)	1
RuF ₅ ⁻	little	U ≈ 10 ⁵	U > 100*	U ≈ 4·10 ⁴
MoF ₅ ⁻	strong	U ≈ 20	U ≈ 250	U < 2.5
NbF ₅ ⁻	20 nA	U ≈ 1	U ≈ 1.2	1

* Upper limit:
no counts detected

- Normalization on ⁹⁷Tc will be challenging
focus on Mo suppression
(chemistry, other reactive gases, cooler settings)
- ✘ Normalization on Nb adds large uncertainties
temporal behaviour of TcF₅⁻ differs from NbF₅⁻
Nb suppresses formation of TcF₅⁻



Thank you

Acknowledgements

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European Union's Horizon 2020
research and innovation programme:
grant agreement No 824096



INTERNATIONAL CONFERENCE ON

ACCELERATORS FOR RESEARCH AND SUSTAINABLE DEVELOPMENT

From good practices towards socioeconomic impact



23–27 May 2022

IAEA Headquarters, Vienna, Austria