

Determination of the isotopic ratio $^{236}\text{U}/^{238}\text{U}$ in environmental samples

M. Srncik¹, P. Steier², R. Eigl¹, G. Wallner¹

¹ *Institute of Inorganic Chemistry, University of Vienna, Währingerstr. 42,
A-1090 Vienna*

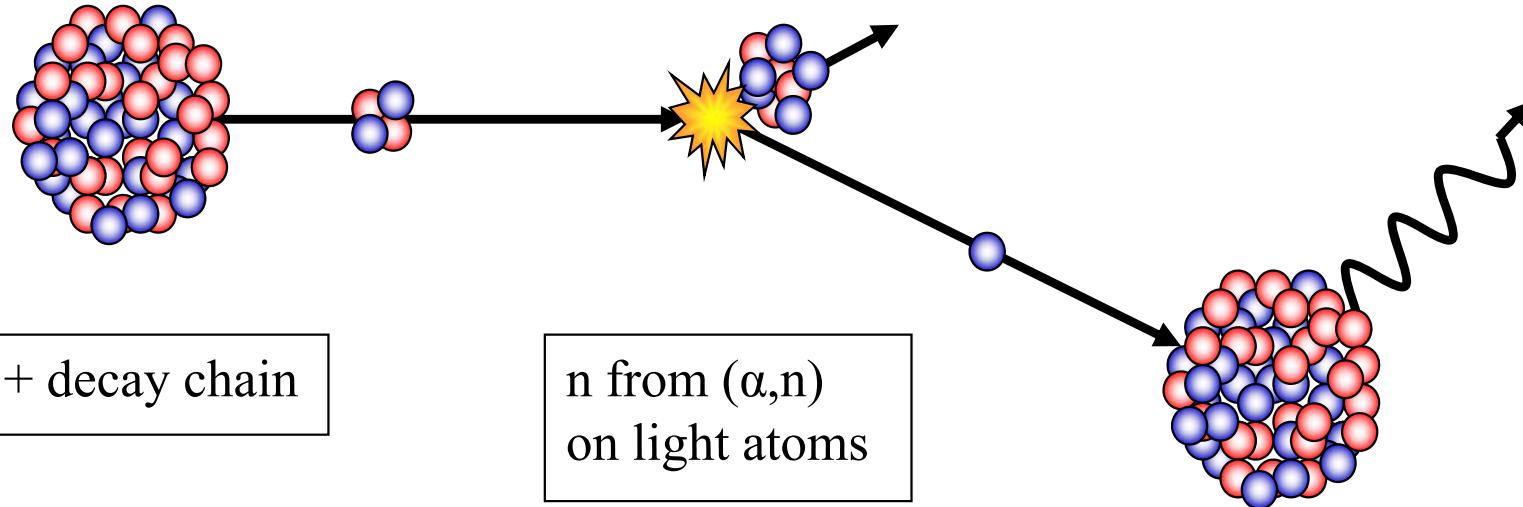
² *Faculty of Physics – Isotope Research, University of Vienna,
Währingerstr. 17, A-1090 Vienna, Austria*



Contents

- production of ^{236}U
- estimated ^{236}U inventory – natural and anthropogenic
- sample preparation and measurement
- results from investigated samples:
 - sediments
 - water and soils
 - sea water
 - antlers
 - ores
 - historical samples
- what we want to do in the future

Production of natural ^{236}U ($t_{1/2} = 23$ Myr)



$^{238}\text{U} + \text{decay chain}$

n from (α, n)
on light atoms

n from fission of
heavy atoms

n from cosmic
rays

$^{235}\text{U}(n,\gamma)^{236}\text{U}$

$\sigma(n,\gamma) = 98$ barn
 $\sigma(n,f) = 583$ barn

Estimated ^{236}U inventory (Steier et al., 2008)

Natural

- uranium ore: typ. $^{236}\text{U}/\text{U} = 5 \times 10^{-11}$, estimated ore reserves: 2.9×10^{10} kg U
 $\Rightarrow 1.5 \text{ kg } ^{236}\text{U}$
- deep lithosphere: equilibrium $^{236}\text{U}/\text{U} = 2 \dots 5 \times 10^{-14}$
 \Rightarrow topmost 1000 m: **22 kg ^{236}U**
- cosmic radiation: ~ 0.5 at $^{236}\text{U} \text{ cm}^{-2} \text{ yr}^{-1}$ (half in top 1 m)
 \Rightarrow equilibrium **10 kg ^{236}U**
- ocean: well mixed river water + cosmogenic,
up to 1×10^{-13}
 \Rightarrow **0.2 kg ^{236}U**

Our in-house standard "Vienna-KkU"



- Uranyl Nitrate prepared before 1918 in the "K.k. Uranfabrik Joachimsthal".
- Separated from uranium ore mined in Joachimsthal (now Jáchymov, Czech Republic).
- Stored in sealed glass bottles in the basement since then.
- About 90 kg still available.
- The ore grade mined at that time was typically 60% U_3O_8 .
- Normalized to REIMEP-18 A certified value

$$\text{Vienna-KkU } {}^{236}\text{U}/{}^{238}\text{U} = (6.98 \pm 0.32) \times 10^{-11}$$

Estimated ^{236}U inventory

(Steier et al., 2008)

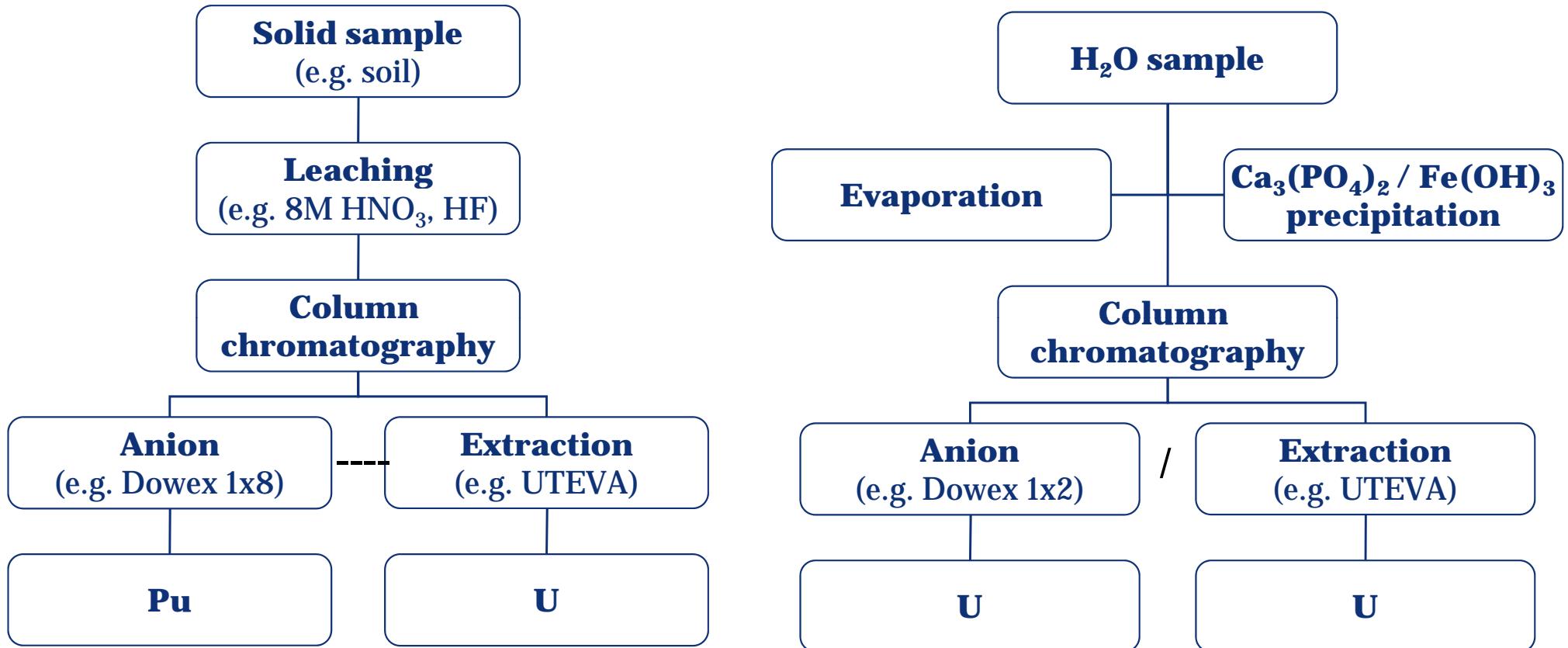
Anthropogenic

- U mined (until 2003): 2.2×10^9 kg, 50 % fissioned
=> 10^6 kg ^{236}U (!)
- (probably) second most abundant anthropogenic isotope

Anthropogenic

- U processing factories: $^{236}\text{U}/\text{U} = 10^{-6} - 10^{-4}$
- reactors, e.g. after the Chernobyl accident: $10^{-6} - 10^{-3}$
- reprocessing plants, e.g. Sellafield:
 $10^{-6} - 10^{-5}$
- fallout from nuclear weapons tests

Sample preparation: overview



micro-precipitation

^{238}U

$^{239(40)}\text{Pu}$



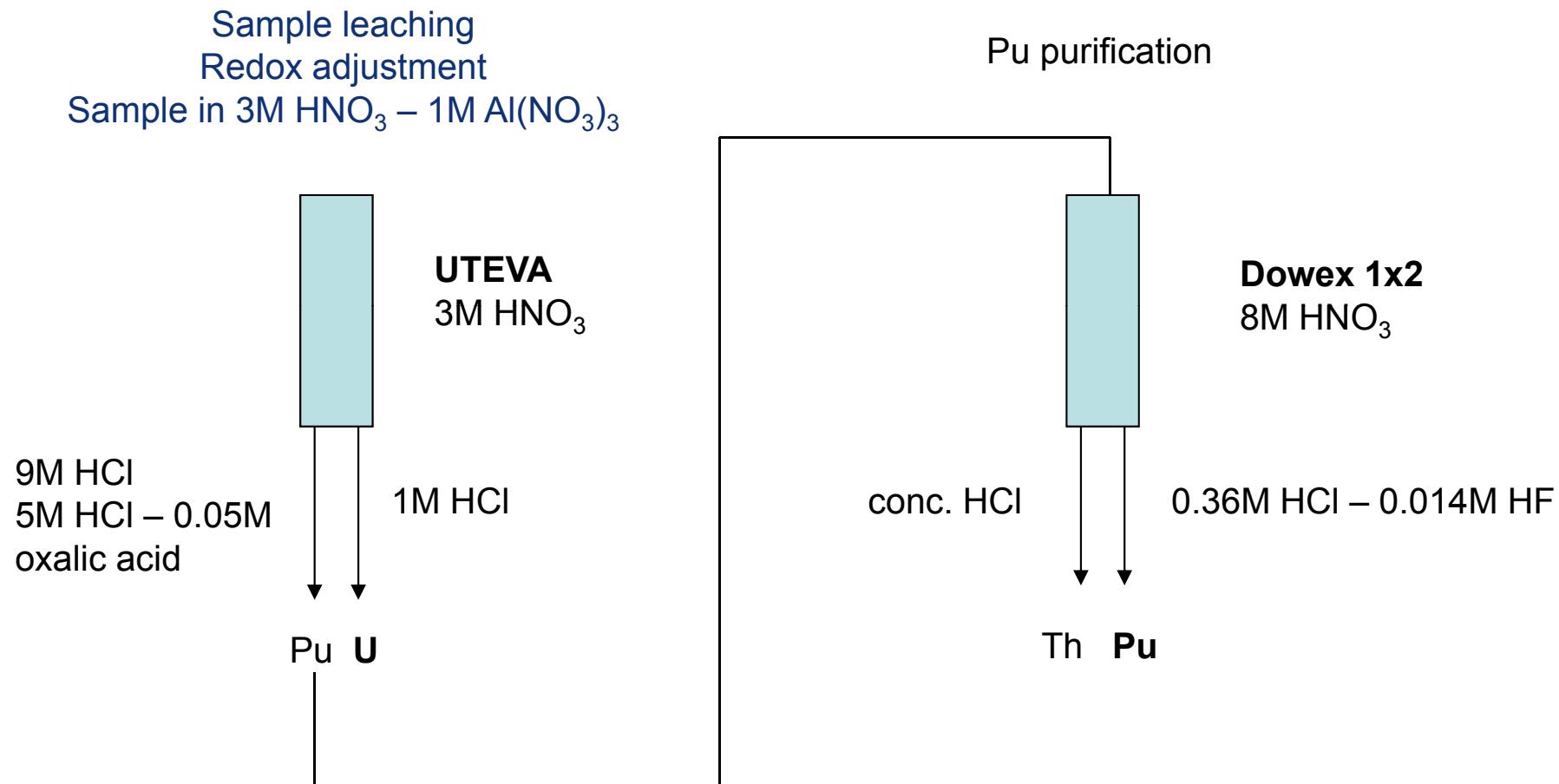
AMS

$^{236}\text{U}/^{238}\text{U}$

$^{240}\text{Pu}/^{239}\text{Pu}$

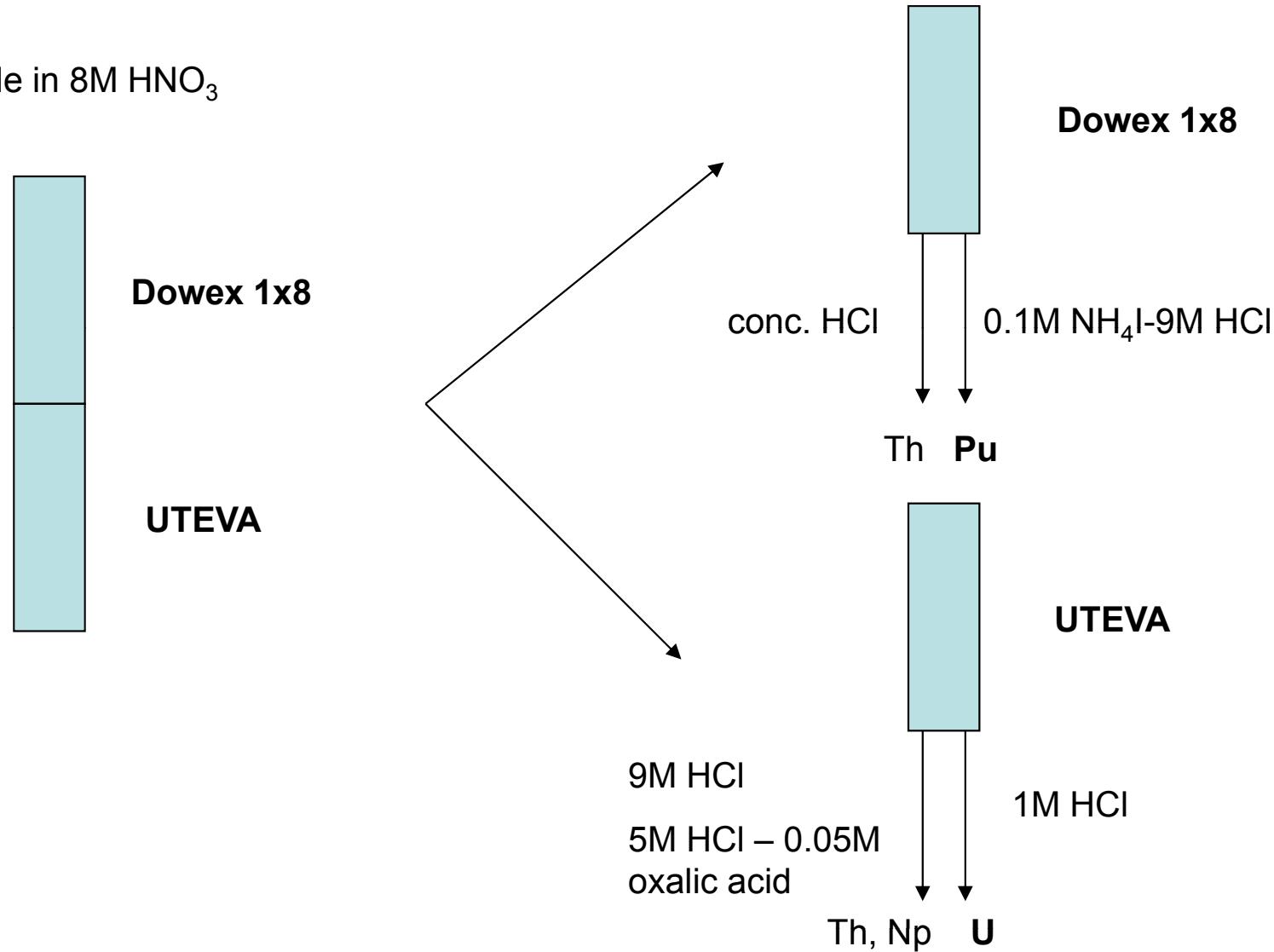


Determination of U and Pu – method A



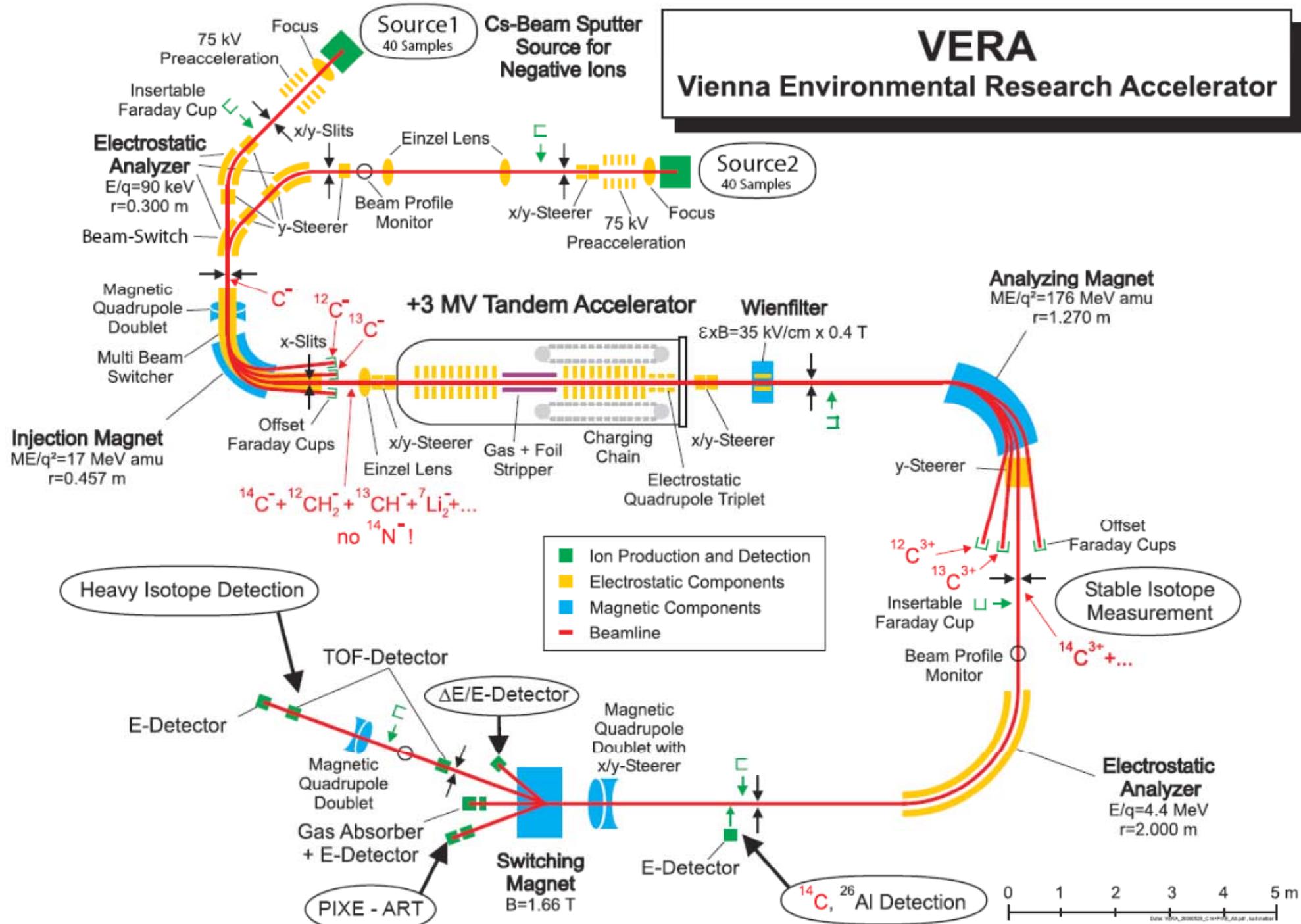
Determination of U and Pu – method B

Sample in 8M HNO₃



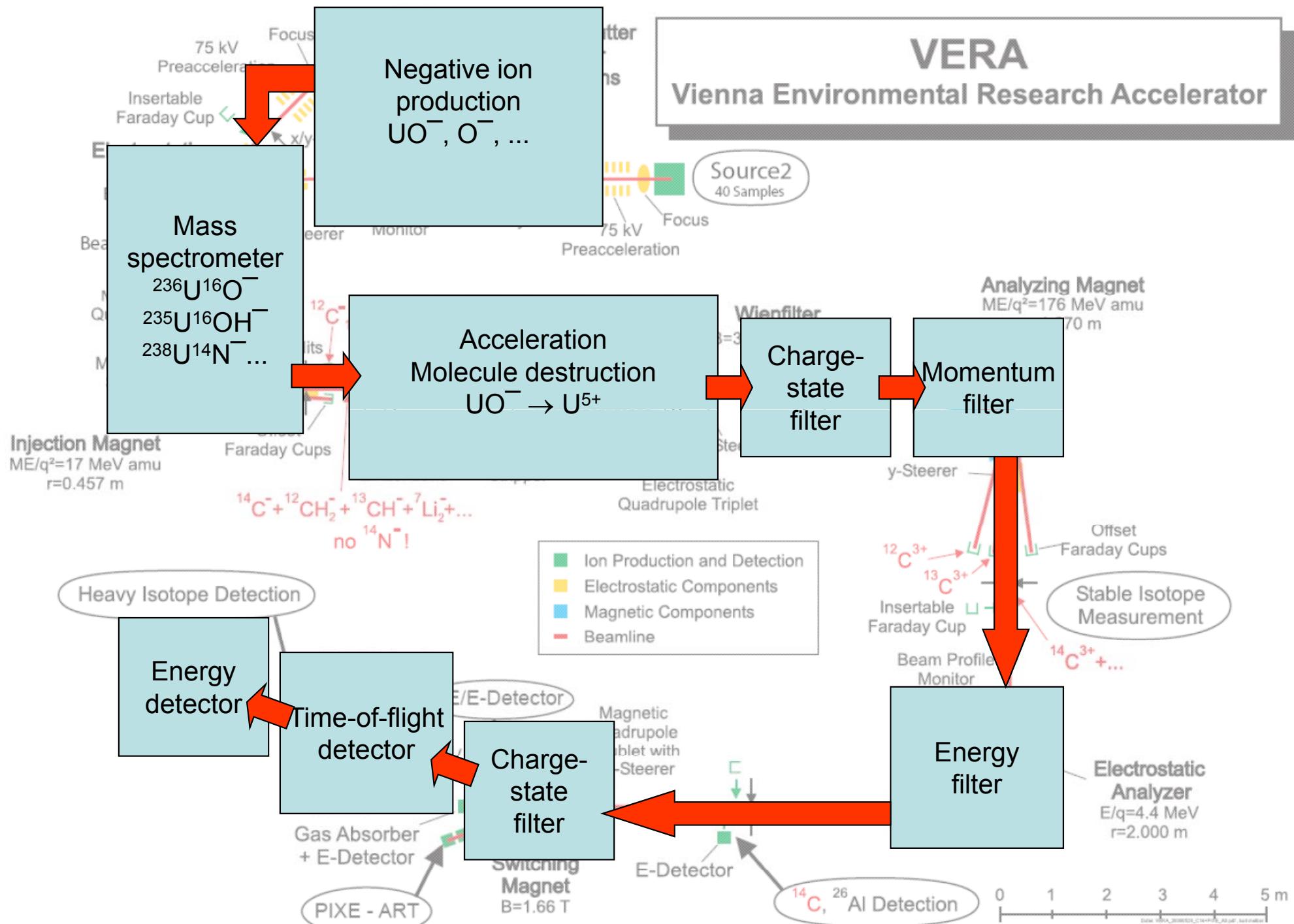
VERA

Vienna Environmental Research Accelerator

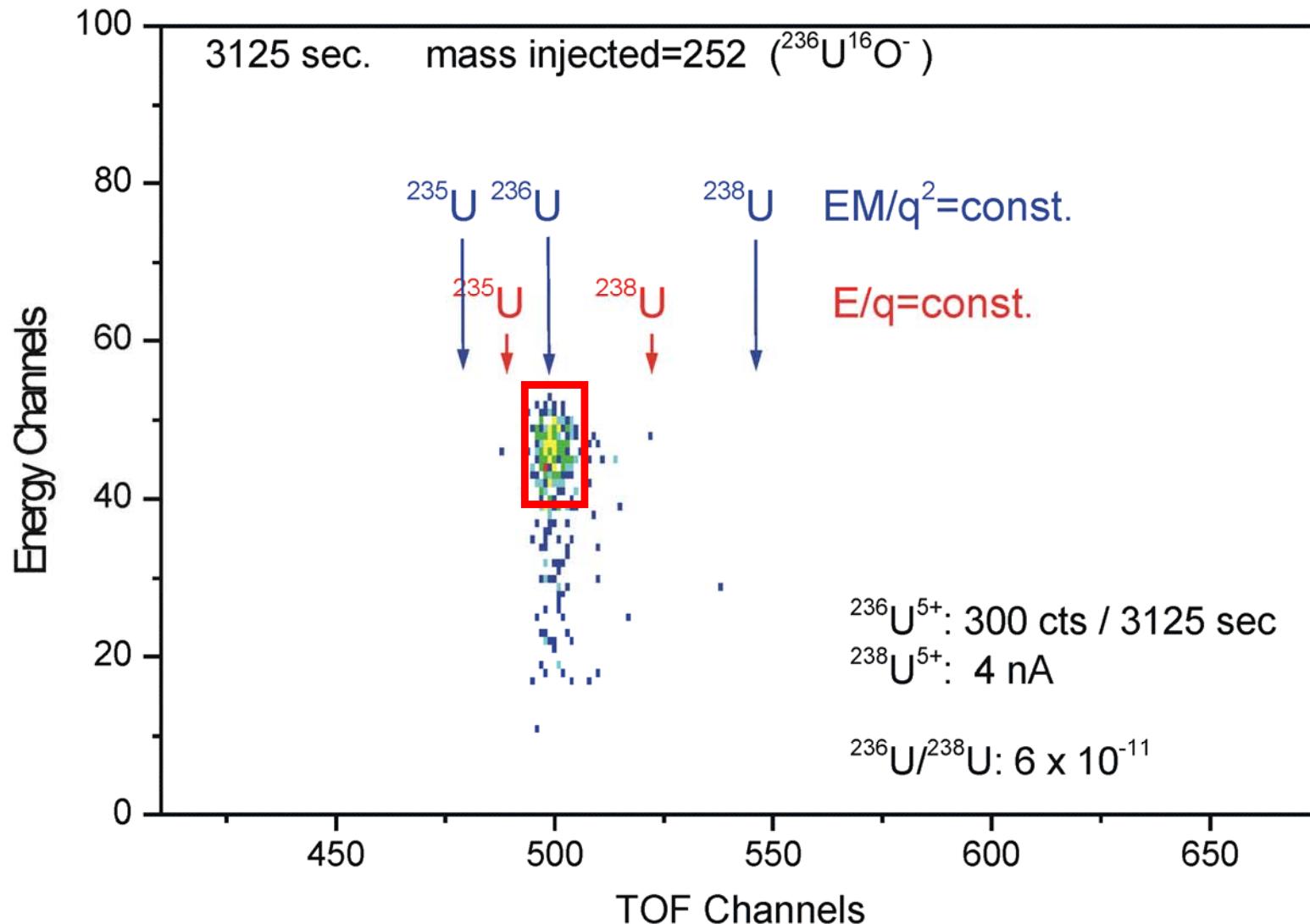


VERA

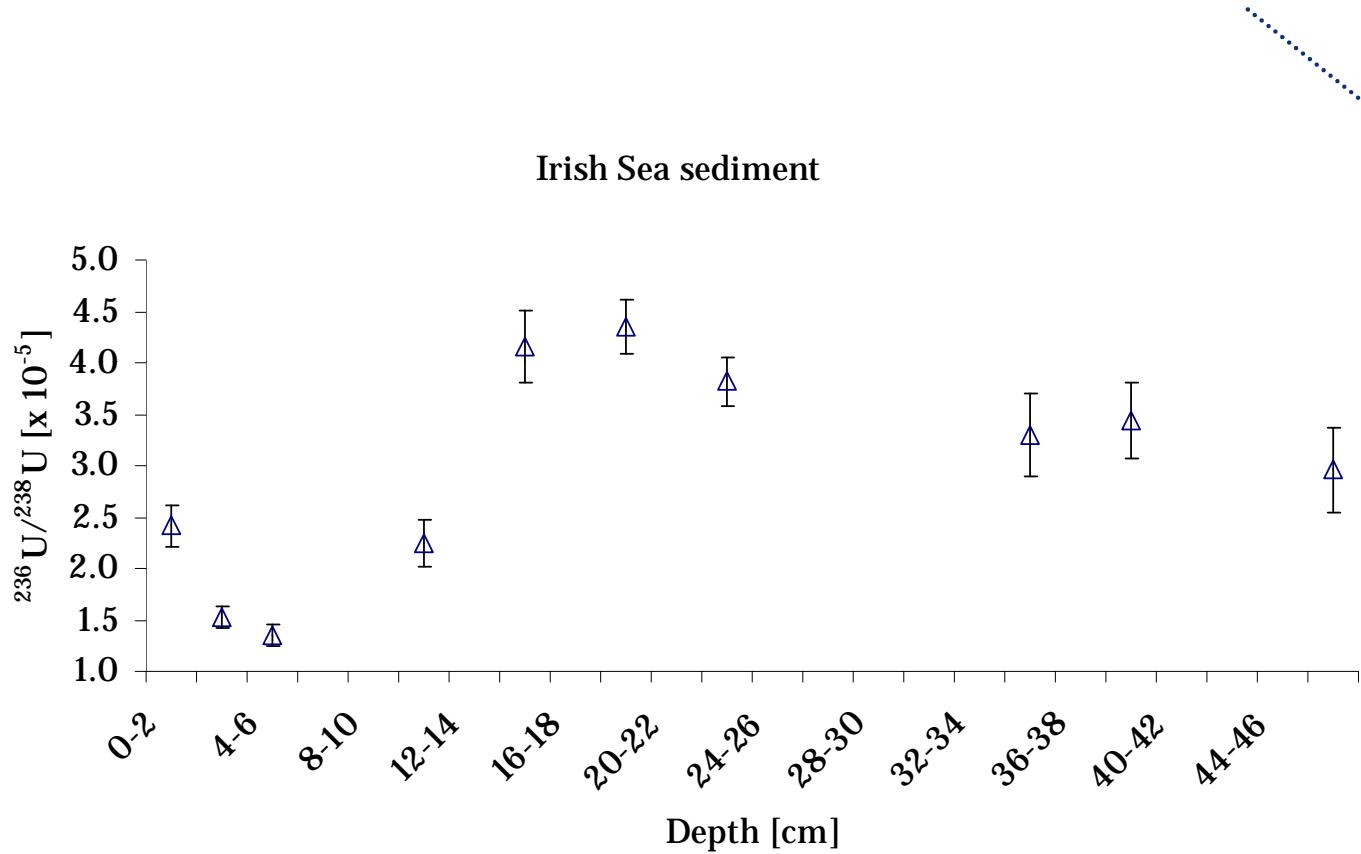
Vienna Environmental Research Accelerator



Spectrum with all filters



Sediment core near Sellafield collected in 1993 (Srncik et al., 2011)



Isotopic ratio 10^{-5} : clearly anthropogenic

^{236}U from nuclear weapons tests

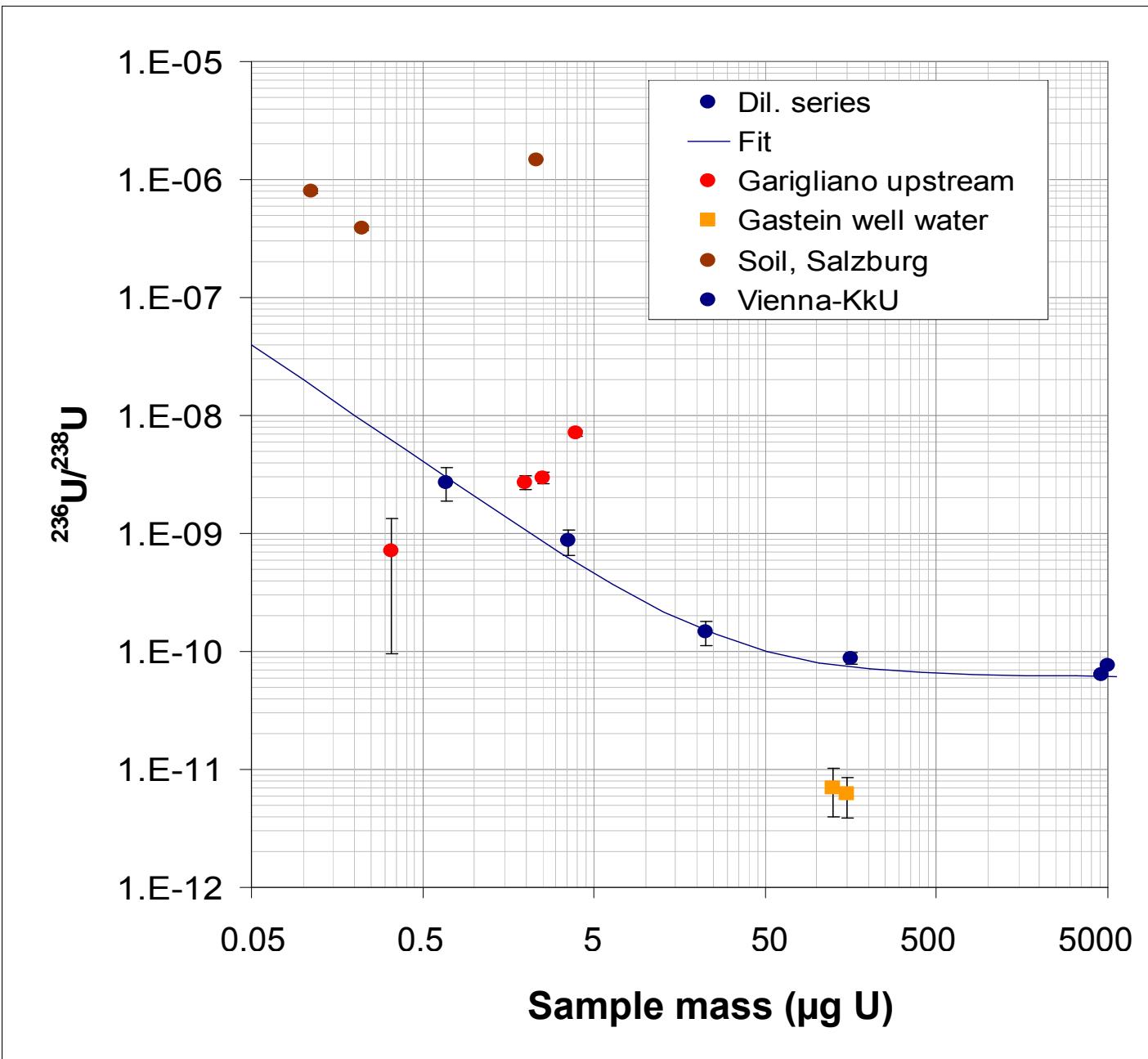
- ^{238}U in fusion devices
- $^{238}\text{U}(\text{n},3\text{n})^{236}\text{U}$ ($E > 10 \text{ MeV}$)
- estimated production: $^{236}\text{U}/^{239}\text{Pu} = 0.2$
- 900 kg ^{236}U globally distributed

Ketterer 2007, Abstract to Goldschmidt conference 2007,
<http://www.the-conference.com/conferences/2007/gold2007/abstracts/K.pdf>:

Global fallout: isotopic ratio $^{236}\text{U}/^{239}\text{Pu} = 0.05$ to 0.50

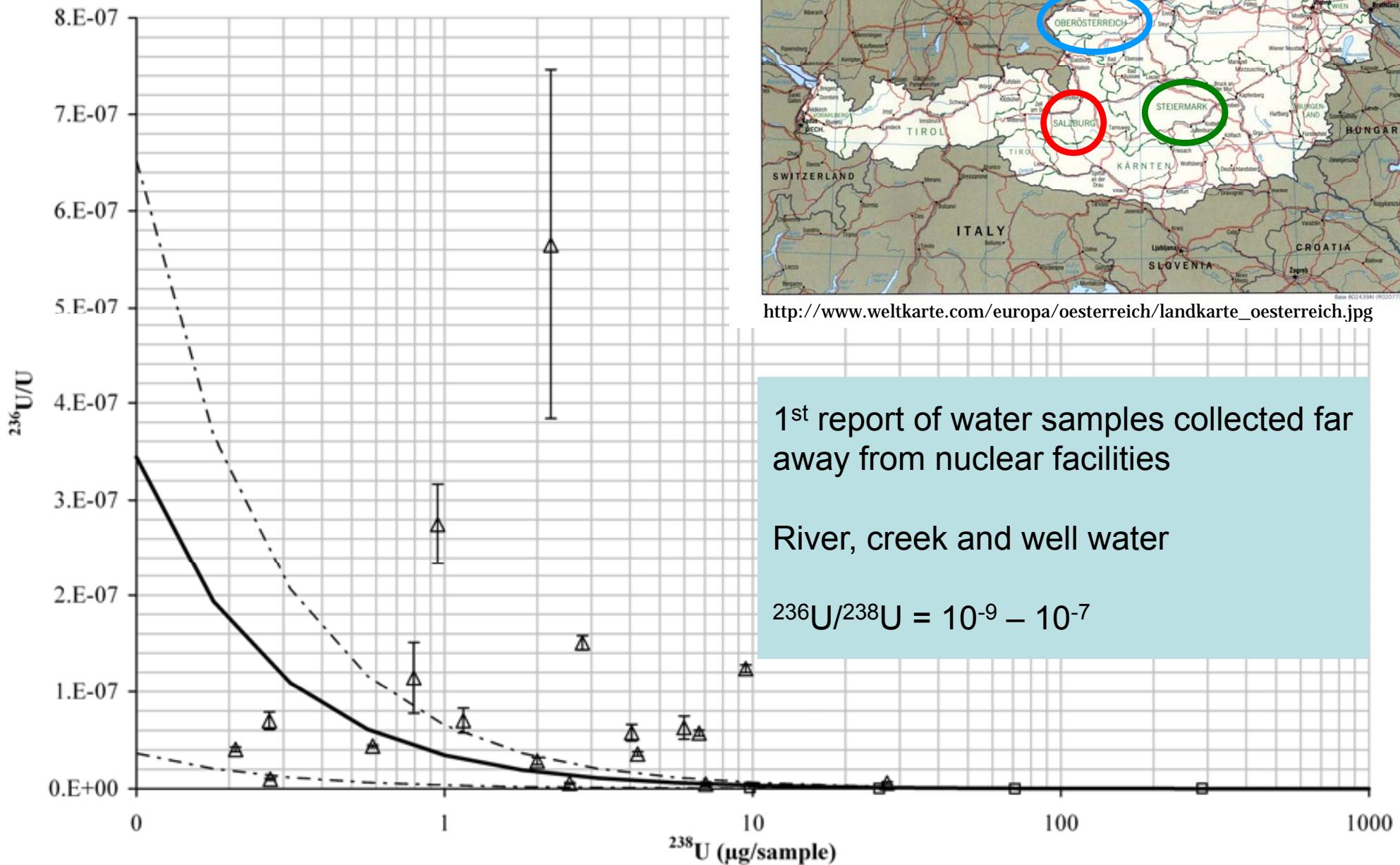
Soils far from contaminated sites

(prepared by F. Quinto)



Water samples from Austria

(Srncik et al., 2010)



Soil samples from La Palma Island, Spain (Srncik et al. 2011)



Core	Depth [cm]	$^{236}\text{U}/^{238}\text{U}$	^{236}U [atoms/g]
LP_B1	0 - 5	$(2.43 \pm 0.04) \cdot 10^{-8}$	$(3.39 \pm 0.39) \cdot 10^8$
LP_B2	15 - 40	$(4.05 \pm 1.15) \cdot 10^{-9}$	$(2.13 \pm 0.64) \cdot 10^8$
LP_A	0 - 5	$(2.98 \pm 0.23) \cdot 10^{-8}$	$(2.40 \pm 0.26) \cdot 10^9$

water samples from all around the globe

(R. Eigm et al., 2012)

Sea water:

- La Palma
- Hawaii
- Black Sea
- Irish Sea

La Palma	$(1.87 \pm 0.56) \cdot 10^{-9}$
Hawaii	$(5.74 \pm 0.31) \cdot 10^{-9}$
Black Sea	$(3.63 \pm 0.49) \cdot 10^{-9}$
Irish Sea	$(2.04 \pm 0.02) \cdot 10^{-6}$
IAEA-381(443)	$(2.45 \pm 0.09) \cdot 10^{-6}$

River water:

- Danube (Romania)
- Rio Negro

Danube (Romania)	$(1.08 \pm 0.26) \cdot 10^{-8}$
Rio Negro	$(2.73 \pm 0.32) \cdot 10^{-8}$

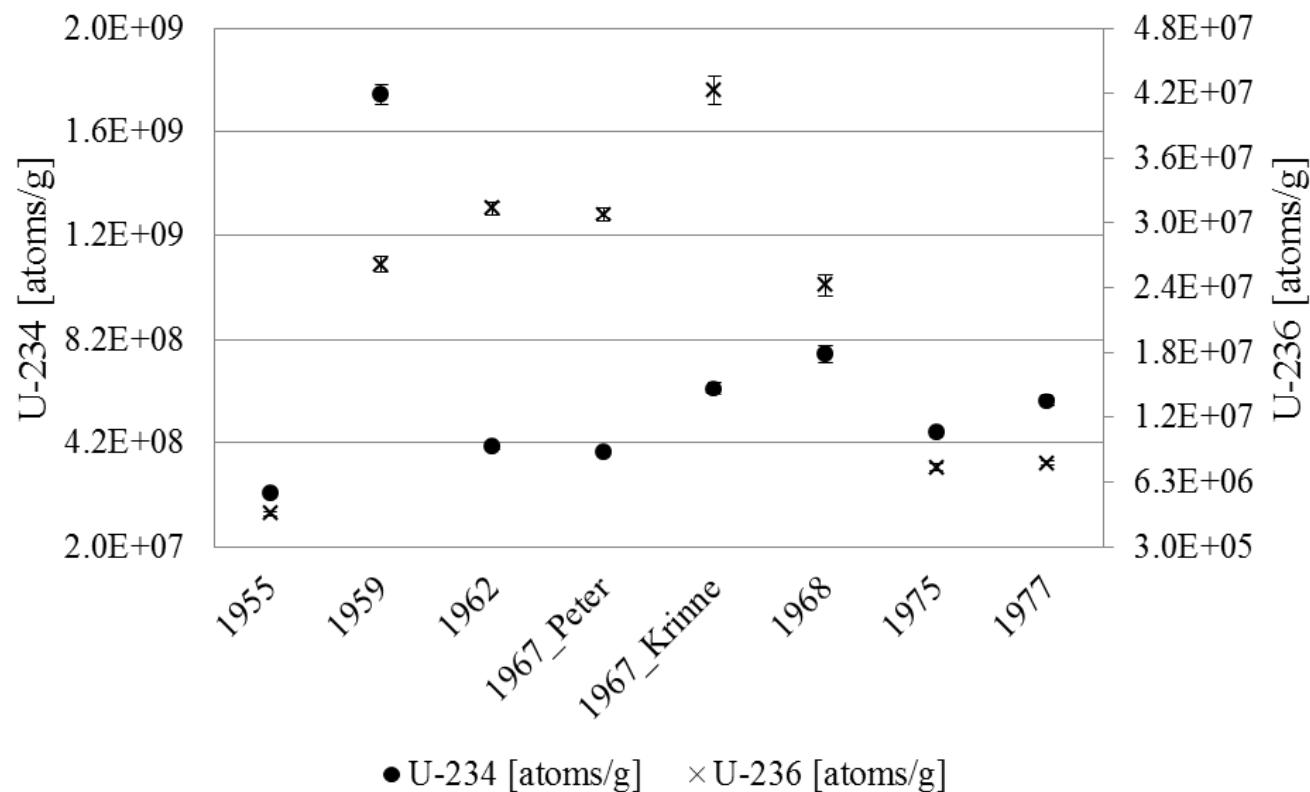
Antlers of roe-deer (Srncik et al., 2012)

- U (Pu) uptake by feed
 - U (Pu) are bone-seekers
 - Histology of antlers similar to bones
 - Antlers are re-grown yearly
 - Trophies from 1955 to 1977
- **sensitive retrospective bio-monitor**

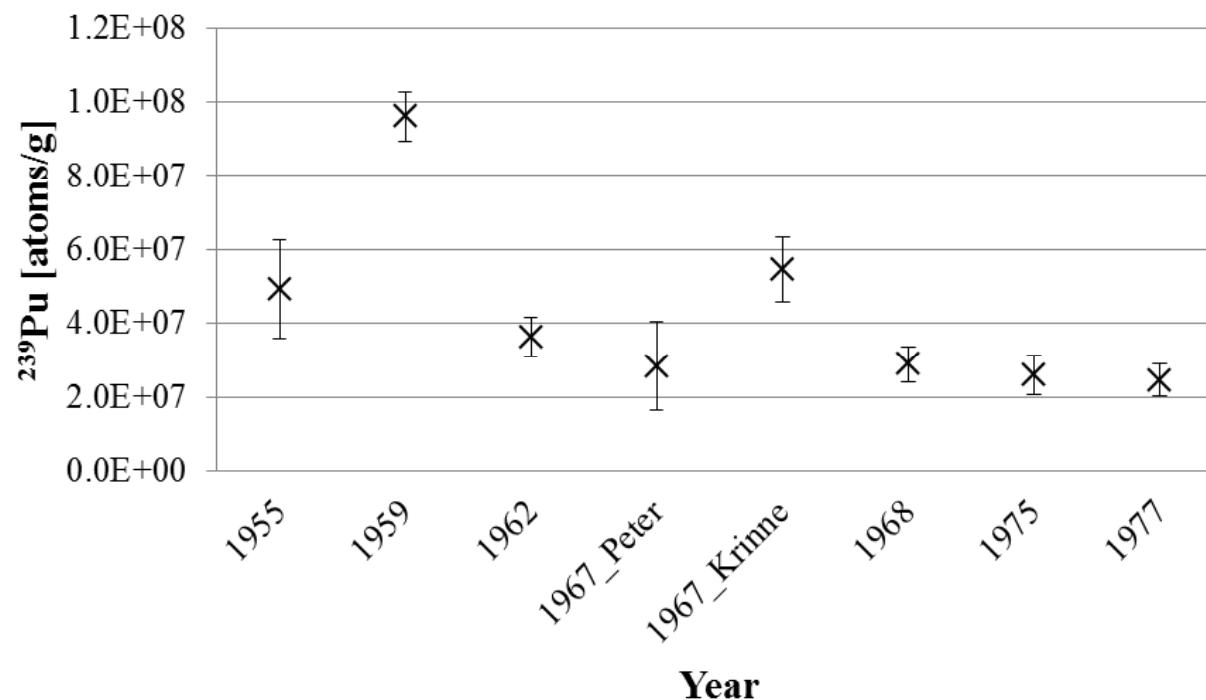


Cleaned antlers are ashed, 30 g of ash used for analysis
Pu separated on Dowex
U separated on UTEVA with very low drop rate

The chronological sequence of ^{234}U [atoms/g] (\bullet ; left axis) and of ^{236}U [atoms/g] (\times ; right axis) between 1955 and 1977



Variation of the ^{239}Pu concentration in the time between 1955 and 1977.



mean $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio 0.17 ± 0.02
→ **global fallout as contamination source**

Natural ^{236}U

- Is $^{236}\text{U}/\text{U}$ a fingerprint for the deposit?
- Isotopic signal $^{236}\text{U}/\text{U}$ in well water as probe for ore deposits ?
- Did fission occur in a certain piece of U? – history
- What's the lowest value we are able to measure?

Uranium ores from ITU Karlsruhe

(Srncik et al., 2011)

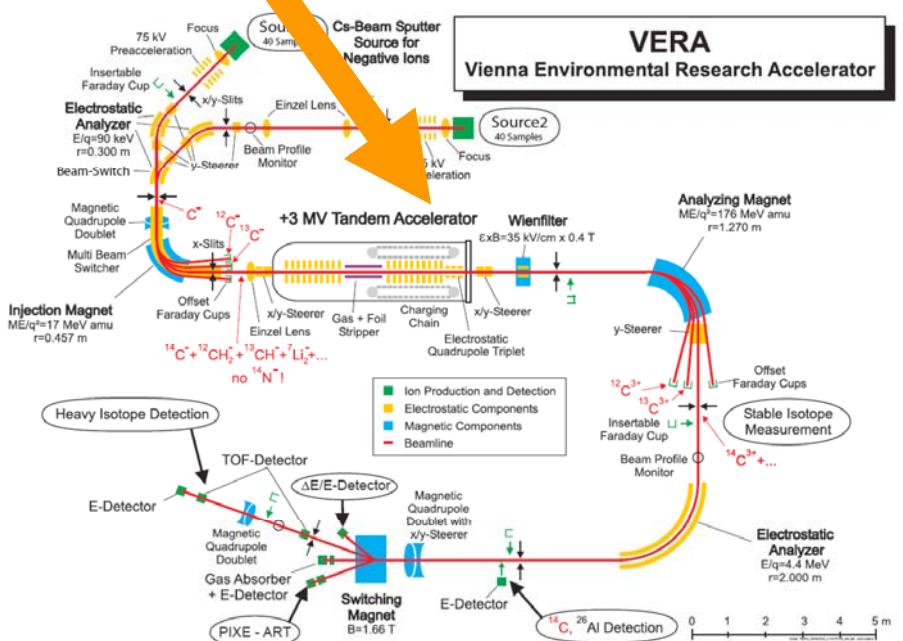
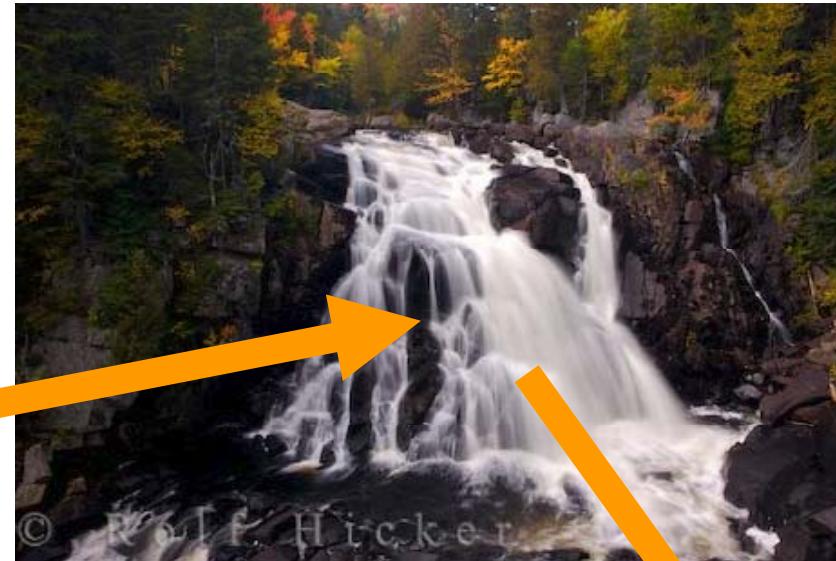
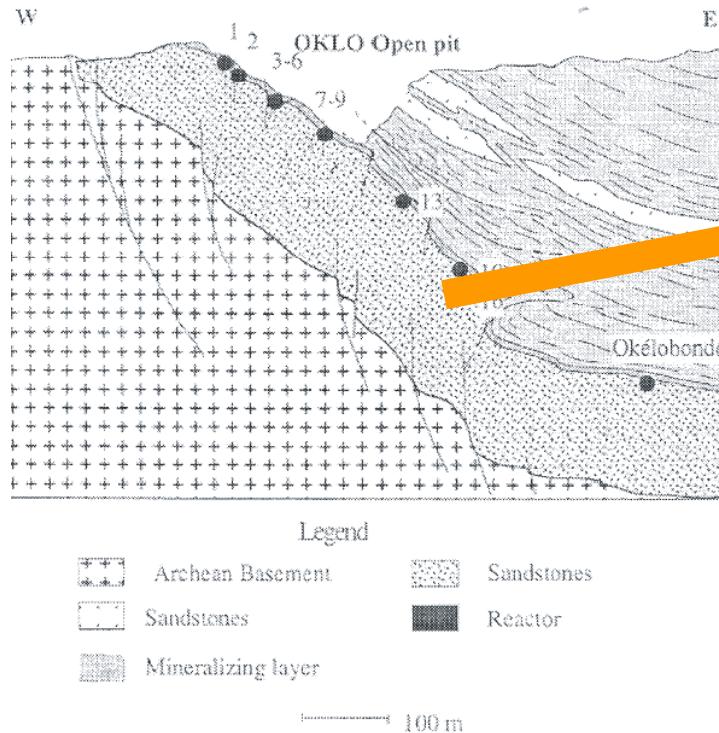
Ores

Sample No.	Mine	Country	$^{236}\text{U}/^{238}\text{U}$	$^{236}\text{U}/^{238}\text{U}$	Ref.
73971	Olympic Dam_4	Australia	$(1.51 \pm 0.44) \cdot 10^{-11}$	$< 1.45 \cdot 10^{-8}$	[1]
73951	Ranger_4	Australia	$(1.92 \pm 0.28) \cdot 10^{-11}$	$< 1.45 \cdot 10^{-8}$	[1]
73950	Ranger_3	Australia	$(1.73 \pm 0.30) \cdot 10^{-11}$		
73947	Ranger_2	Australia	$(1.76 \pm 0.30) \cdot 10^{-11}$		
BR11	Lagoa Real	Brazil	$(4.12 \pm 0.04) \cdot 10^{-9}$		
1425	Rabbit Lake	Canada	$(1.12 \pm 0.06) \cdot 10^{-10}$	$(2.8 \pm 1.7) \cdot 10^{-10}$	[2]

Yellowcakes

Sample No.	Mine	Country	$^{236}\text{U}/^{238}\text{U}$
28	Olympic Dam	Australia	$(4.46 \pm 0.48) \cdot 10^{-11}$
24	Ranger	Australia	$(1.48 \pm 0.26) \cdot 10^{-11}$
15	Lagoa Real	Brazil	$(3.09 \pm 0.38) \cdot 10^{-11}$
51	Rabbit Lake	Canada	$(5.17 \pm 0.48) \cdot 10^{-11}$

Isotopic signal $^{236}\text{U}/\text{U}$ in well water as probe for ore deposits ?



Germany's World War II Program

Pre-nuclear materials



Figure 4: Heisenberg cube

from INMM 2009; Mayer et al. Analysis of Uranium Metal Samples from Germany's World War II Program

Figure 5: Wirtz plate

Sample	$^{236}\text{U}/^{238}\text{U}$ 1st meas.	$^{236}\text{U}/^{238}\text{U}$ 2nd meas.
Heisenberg cube	$(1.06 \pm 0.04) \cdot 10^{-10}$	$(1.00 \pm 0.04) \cdot 10^{-10}$
Wirtz plate	$(1.12 \pm 0.04) \cdot 10^{-10}$	$(1.03 \pm 0.07) \cdot 10^{-10}$
Yellow cake (O. Hahn)	$(1.14 \pm 0.04) \cdot 10^{-10}$	$(0.96 \pm 0.10) \cdot 10^{-10}$
U-disk from Radiuminstitut	$(1.22 \pm 0.07) \cdot 10^{-10}$	$(1.02 \pm 0.07) \cdot 10^{-10}$

Ambient uranium: Bad Gastein healing gallery subsurface well

(Kraft et al., 2004; Steier et al., 2008)



Copyright: Gasteiner Heilstollen.

Water from a subsurface well from within
the "Heilstollen" in Bad Gastein, Austria:

$$^{236}\text{U}/^{238}\text{U} = (6 \pm 2) \times 10^{-12}$$

What we want to do in the future



AMS measurement in
uranium ores:
 $^{236}\text{U}/\text{U} = 7 \times 10^{-11}$ (typ.)



General crust:
 $^{236}\text{U}/\text{U} = 2 \times 10^{-14}$ (est.)



- Thanks to  Der Wissenschaftsfonds.
for funding our research
- JRC-ITU Karlsruhe for hospitality and samples
- Thank you for your attention!