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

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Contents

▪ production of $^{236}\text{U}$

▪ estimated $^{236}\text{U}$ 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 $^{236}\text{U}$ ($t_{1/2} = 23$ Myr)

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

$n$ from $(\alpha, n)$ on light atoms

$n$ from fission of heavy atoms

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

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

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

$n$ from cosmic rays
Estimated $^{236}\text{U}$ inventory
(Steier et al., 2008)

Natural

- uranium ore: typ. $^{236}\text{U}/\text{U} = 5 \times 10^{-11}$, estimated ore reserves: $2.9 \times 10^{10}$ kg U
  \[ \Rightarrow 1.5 \text{ kg } ^{236}\text{U} \]

- deep lithosphere: equilibrium $^{236}\text{U}/\text{U} = 2 \ldots 5 \times 10^{-14}$
  \[ \Rightarrow \text{topmost } 1000 \text{ m: } 22 \text{ kg } ^{236}\text{U} \]

- cosmic radiation: $\sim 0.5$ at $^{236}\text{U} \text{ cm}^{-2} \text{ yr}^{-1}$ (half in top 1 m)
  \[ \Rightarrow \text{equilibrium } 10 \text{ kg } ^{236}\text{U} \]

- ocean: well mixed river water + cosmogenic, up to $1 \times 10^{-13}$
  \[ \Rightarrow 0.2 \text{ kg } ^{236}\text{U} \]
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 Jachimov, 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% U₃O₈.
- Normalized to REIMEP-18 A certified value

Vienna-KkU \frac{^{236}U}{^{238}U} = (6.98 \pm 0.32) \times 10^{-11}
Estimated $^{236}$U inventory
(Steier et al., 2008)

**Anthropogenic**

- U mined (until 2003): $2.2 \times 10^9$ kg, 50 % fissioned
  $\Rightarrow 10^6$ 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

**Solid sample** (e.g. soil)
- **Leaching** (e.g. 8M HNO₃, HF)
  - Column chromatography
    - Anion (e.g. Dowex 1x8)
      - Pu
    - Extraction (e.g. UTEVA)
      - U

**H₂O sample**
- **Evaporation**
  - Ca₃(PO₄)₂ / Fe(OH)₃ precipitation

**Column chromatography**
- Anion (e.g. Dowex 1x2)
  - Extraction (e.g. UTEVA)
  - U

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**micro-precipitation** → AMS

- $^{238}\text{U}$
- $^{239(40)}\text{Pu}$
- $^{236}\text{U}/^{238}\text{U}$
- $^{240}\text{Pu}/^{239}\text{Pu}$
Determination of U and Pu – method A

Sample leaching
Redox adjustment
Sample in 3M HNO₃ – 1M Al(NO₃)₃

Dowex 1x2
8M HNO₃

Pu purification
conc. HCl
0.36M HCl – 0.014M HF

UTEVA
3M HNO₃

Pu

U

9M HCl
5M HCl – 0.05M oxalic acid

Pu

Th

1M HCl
Determination of U and Pu – method B

Sample in 8M HNO₃

Dowex 1x8

conc. HCl

0.1M NH₄I-9M HCl

Th, Pu

UTEVA

9M HCl

5M HCl – 0.05M oxalic acid

1M HCl

Th, Np

UTEVA

U
Sample preparation: overview

Solid sample (e.g. soil)

Solid sample

Liquid (e.g. 8M HNO₃, HF)

Column chromatography

Evaporation

Precipitation

Anion extraction (e.g. Dowex 1x8)

Anion extraction (e.g. UTEVA)

Micro-precipitation AMS

VERA
Vienna Environmental Research Accelerator

Injection Magnet

ME/q²=17 MeV amu
r=0.457 m

+3 MV Tandem Accelerator

EₓB=35 kV/cm x 0.4 T

y-Steerer

Gas + Foil Stripper

Charging Chain

Electrostatic Quadrupole Triplet

Analyzing Magnet

ME/q²=176 MeV amu
r=1.270 m

Offset Faraday Cups

Insertable Faraday Cup

Beam Profile Monitor

Heavy Isotope Detection

TOF-Detector

E-Detector

ΔE/E-Detector

Magnetic Quadrupole Doublet

Gas Absorber + E-Detector

Switching Magnet

B=1.66 T

PIXE - ART

14C, 26Al Detection

12C³⁺

14C⁺

12CH⁺

13CH⁺

7Li₂⁺...

no 14N⁺!

239(40)Pu/239Pu

238U/235U
Negative ion production $\text{UO}^-$, $\text{O}^-$, ...

Mass spectrometer $^{236}\text{U}^{16}\text{O}^-$, $^{235}\text{U}^{16}\text{OH}^-$, $^{238}\text{U}^{14}\text{N}^-$...

Acceleration
Molecule destruction $\text{UO}^- \rightarrow \text{U}^{5+}$

Charge-state filter
Momentum filter

Charge-state detector
Time-of-flight detector
Energy filter

Energy detector

VERA
Vienna Environmental Research Accelerator

Ion Production and Detection
Electrostatic Components
Magnetic Components
Beamline

Stable Isotope Measurement
Electrostatic Analyzer $E/q=4.4$ MeV $r=2.000$ m

$^{14}\text{C}, ^{26}\text{Al}$ Detection

Injection Magnet $\text{ME}/q^2=17$ MeV amu $r=0.457$ m

Source 2
40 Samples

75 kV
Preacceleration
Insertable Faraday Cup

Focus

Beams

$^{12}\text{C} + ^{13}\text{CH}_3 + ^{13}\text{CH}_2^+ + \text{Li}_2^+ + $...

$^{14}\text{C}^++^{12}\text{CH}_3^+ + ^{13}\text{CH}_2^+ +$... no $^{14}\text{N}^-$!
Spectrum with all filters

3125 sec. mass injected=252 \(^{236}\text{U}^{16}\text{O}^-\)

\(^{235}\text{U} / ^{236}\text{U} / ^{238}\text{U}\)

EM/q\(^2\) = const.

E/q = const.

\(^{236}\text{U}^{5+}\): 300 cts / 3125 sec
\(^{238}\text{U}^{5+}\): 4 nA

\(^{236}\text{U} / ^{238}\text{U}\): 6 \times 10^{-11}

Vockenhuber et al., 2002
Sediment core near Sellafield collected in 1993 (Srncik et al., 2011)

Irish Sea sediment

Isotopic ratio $10^{-5}$: clearly anthropogenic
$^{236}\text{U}$ from nuclear weapons tests

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


Global fallout: isotopic ratio $^{236}\text{U}/^{239}\text{Pu} = 0.05$ to 0.50
Soils far from contaminated sites
(prepared by F. Quinto)

![Graph showing the relationship between sample mass (µg U) and uranium isotope ratios. The graph includes data points for different locations such as Garigliano upstream, Gastein well water, Soil, Salzburg, and Vienna-KkU.]
Water samples from Austria (Srsncik et al., 2010)

$^{236}\text{U}/^{238}\text{U} = 10^{-9} - 10^{-7}$
Soil samples from La Palma Island, Spain
(Srnčík et al. 2011)

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth [cm]</th>
<th>$^{236}$U/$^{238}$U</th>
<th>$^{236}$U [atoms/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP_B1</td>
<td>0 - 5</td>
<td>$(2.43 \pm 0.04) \times 10^{-8}$</td>
<td>$(3.39 \pm 0.39) \times 10^8$</td>
</tr>
<tr>
<td>LP_B2</td>
<td>15 - 40</td>
<td>$(4.05 \pm 1.15) \times 10^{-9}$</td>
<td>$(2.13 \pm 0.64) \times 10^8$</td>
</tr>
<tr>
<td>LP_A</td>
<td>0 - 5</td>
<td>$(2.98 \pm 0.23) \times 10^{-8}$</td>
<td>$(2.40 \pm 0.26) \times 10^9$</td>
</tr>
</tbody>
</table>
### Water Samples from All Around the Globe

(R. Eigl et al., 2012)

#### Sea Water:
- La Palma: \((1.87 \pm 0.56) \times 10^{-9}\)
- Hawaii: \((5.74 \pm 0.31) \times 10^{-9}\)
- Black Sea: \((3.63 \pm 0.49) \times 10^{-9}\)
- Irish Sea: \((2.04 \pm 0.02) \times 10^{-6}\)

#### River Water:
- Danube (Romania): \((1.08 \pm 0.26) \times 10^{-8}\)
- Rio Negro: \((2.73 \pm 0.32) \times 10^{-8}\)
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 $^{234}\text{U}$ [atoms/g] (●; left axis) and of $^{236}\text{U}$ [atoms/g] (x; right axis) between 1955 and 1977.
Variation of the $^{239}\text{Pu}$ 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 $^{236}\text{U}$

- 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

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mine</th>
<th>Country</th>
<th>$^{236}\text{U}/^{238}\text{U}$</th>
<th>$^{236}\text{U}/^{238}\text{U}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>73971</td>
<td>Olympic Dam_4</td>
<td>Australia</td>
<td>$(1.51 \pm 0.44)\cdot10^{-11}$</td>
<td>$&lt; 1.45\cdot10^{-8}$</td>
<td>[1]</td>
</tr>
<tr>
<td>73951</td>
<td>Ranger_4</td>
<td>Australia</td>
<td>$(1.92 \pm 0.28)\cdot10^{-11}$</td>
<td>$&lt; 1.45\cdot10^{-8}$</td>
<td>[1]</td>
</tr>
<tr>
<td>73950</td>
<td>Ranger_3</td>
<td>Australia</td>
<td>$(1.73 \pm 0.30)\cdot10^{-11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73947</td>
<td>Ranger_2</td>
<td>Australia</td>
<td>$(1.76 \pm 0.30)\cdot10^{-11}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BR11</td>
<td>Lagoa Real</td>
<td>Brazil</td>
<td>$(4.12 \pm 0.04)\cdot10^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1425</td>
<td>Rabbit Lake</td>
<td>Canada</td>
<td>$(1.12 \pm 0.06)\cdot10^{-10}$</td>
<td>$(2.8 \pm 1.7)\cdot10^{-10}$</td>
<td>[2]</td>
</tr>
</tbody>
</table>

### Yellowcakes

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mine</th>
<th>Country</th>
<th>$^{236}\text{U}/^{238}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>Olympic Dam</td>
<td>Australia</td>
<td>$(4.46 \pm 0.48)\cdot10^{-11}$</td>
</tr>
<tr>
<td>24</td>
<td>Ranger</td>
<td>Australia</td>
<td>$(1.48 \pm 0.26)\cdot10^{-11}$</td>
</tr>
<tr>
<td>15</td>
<td>Lagoa Real</td>
<td>Brazil</td>
<td>$(3.09 \pm 0.38)\cdot10^{-11}$</td>
</tr>
<tr>
<td>51</td>
<td>Rabbit Lake</td>
<td>Canada</td>
<td>$(5.17 \pm 0.48)\cdot10^{-11}$</td>
</tr>
</tbody>
</table>
Isotopic signal $^{236}\text{U}/\text{U}$ in well water as probe for ore deposits?
### Germany’s World War II Program

**Pre-nuclear materials**

- **Heisenberg cube**
- **Wirtz plate**
- **Yellow cake (O. Hahn)**

**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**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{236}\text{U}/^{238}\text{U}) 1st meas.</th>
<th>(^{236}\text{U}/^{238}\text{U}) 2nd meas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heisenberg cube</td>
<td>((1.06 \pm 0.04) \cdot 10^{-10})</td>
<td>((1.00 \pm 0.04) \cdot 10^{-10})</td>
</tr>
<tr>
<td>Wirtz plate</td>
<td>((1.12 \pm 0.04) \cdot 10^{-10})</td>
<td>((1.03 \pm 0.07) \cdot 10^{-10})</td>
</tr>
<tr>
<td>Yellow cake (O. Hahn)</td>
<td>((1.14 \pm 0.04) \cdot 10^{-10})</td>
<td>((0.96 \pm 0.10) \cdot 10^{-10})</td>
</tr>
<tr>
<td>U-disk from Radiuminstitut</td>
<td>((1.22 \pm 0.07) \cdot 10^{-10})</td>
<td>((1.02 \pm 0.07) \cdot 10^{-10})</td>
</tr>
</tbody>
</table>
Ambient uranium: Bad Gastein healing gallery subsurface well
(Kraft et al., 2004; Steier et al., 2008)

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

\[ \frac{^{236}U}{^{238}U} = (6 \pm 2) \times 10^{-12} \]
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 FWF Der Wissenschaftsfonds for funding our research

• JRC-ITU Karlsruhe for hospitality and samples

• Thank you for your attention!