Determination of Radionuclides using Accelerator Mass Spectrometry
-
analysis of the rarest atom species for earth and environmental science

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ACCELERATOR MASS SPECTROMETRY

Several MeV

Extreme abundance sensitivity typ. $10^{-12}$ to $10^{-16}$

All stable isotopes present in practically every material

Molecules are MUCH more abundant
TANDEM ACCELERATOR

- starts with negative ions and
- provides sufficient energy [MeV]
  - to break up incoming molecular ions in the stripping process,
  - and to identify outgoing atomic ions, e.g. by M, E and dE/dx(Z).

14UD Tandem Accelerator at the Australian National University, Canberra, Australia
Radioisotopes with $T_{1/2} > 1$ year

Kutschera, W. 1990. NIM B 50:252
Radioisotopes with more than 1 year half life

Peter Steier and Kutschera, W. 1990. NIM B 50:252

Decay counting
Radioisotopes with more than 1 year half life

Primordially abundant (conventional MS)

Decay counting

Kutschera, W. 1990. NIM B 50:252
Radioisotopes with more than 1 year half life

Primordially abundant (conventional MS)

AMS now

Decay counting

Kutschera, W. 1990. NIM B 50:252
VERA
Vienna Environmental Research Accelerator

Negative ion production
$UO^-$, $O^-$, ...

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

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

Charge-state filter
Momentum filter

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

Ion Production and Detection
Electrostatic Components
Magnetic Components
Beamline

Stable Isotope Measurement
$^{14}C, ^{13}C, ^{3}C, ^{3}He, ^{7}Li, ^{11}B, ^{19}F, ^{25}Mg, ^{35}Cl, ^{41}Ca, ^{55}Mn, ^{55}Fe, ^{57}Fe, ^{65}Zn, ^{129}Xe$
Facilities used for AMS

- **Big**
  - 15 MV Tandem
  - TU and LMU München
  - Germany

- **Small**
  - 3 MV Tandem VERA
  - Universität Wien
  - Austria
  - 0.5 MV Tandem
  - ETH Zürich
  - Switzerland

ICP-MS, TIMS
Sample requirements

- Small abundance of rare isotope
- Large amount of stable isotope needed (µg, mg)
- Very high (negative) ion currents (10 nA – 100 µA)
- Cesium sputter ion source
- Solid sample material needed
Sophisticated machines, rudimentary chemistry

Facilities are run by physics departments

High motivation to improve instrumentation

Students from physics, geology, ... use legacy recipes for sample preparation without deeper understanding
The $^{14}$C bomb peak

Long-term observations of $^{14}$C in atmospheric CO$_2$ in the northern and in the southern hemisphere (Figure from Levin and Hesshaimer (2000)).
The $^{14}$C bomb peak

Long-term observations of $^{14}$C in atmospheric CO$_2$ in the northern and in the southern hemisphere (Figure from Levin and Hesshaimer (2000)).
$^{14}$C bomb peak dating of human DNA

Example: DNA from the olfactory bulb
Very small carbon samples ($\sim \mu g$)
Are new neurons formed in the adult human brain?

(Cells must be sorted by species!)

Kirsty L. Spalding et al., Cell, Vol. 122 (15 July 2005) 133-143

No!
Chemistry

- combustion in flame sealed quartz vial to CO$_2$
- reduction to graphite with H$_2$ on iron catalyst

recently:
- “elemental analyzer” for combustion
- “online” graphitization of CO$_2$ on titanium surface inside Cs sputter source
Four possible limitations for ultrasmall $^{14}$C samples (<10 µg C)

- Poisson statistics of $^{14}$C atoms in sample
- Handling, quantification, processing
- Detection efficiency
- Background (contamination with carbon during processing)
Small $^{14}$C samples: compound specific analysis

The HPLC (High-Performance Liquid Chromatograph) at the Japan Agency for Marine-Earth Science and Technology (courtesy of Nao Ohkouchi)

Institute of Particle Physics, ETH Zürich, Switzerland

- Extraction of compounds by HPLC or PCGC
- Direct coupling to gas ion source
- Radiocarbon dating

Druffel et al., RADIOCARBON 52 (2010) 1215–1223
The "standard" AMS isotopes

$^{10}$Be, $^{26}$Al, $^{36}$Cl, $^{41}$Ca, $^{129}$I

- VERA at the University of Vienna is the first 3 MV tandem where all these isotopes can be measured competitively
- Method development is a central goal at VERA
(New) 5 to 6 MV facilities for Earth Sciences

$^{10}\text{Be}, \ ^{26}\text{Al}, \ ^{36}\text{Cl}, \ ^{41}\text{Ca}, \ ^{129}\text{I}$
The "standard" AMS isotopes

$^{10}\text{Be}$, $^{26}\text{Al}$, $^{36}\text{Cl}$, $^{41}\text{Ca}$, $^{129}\text{I}$

Applications:
- exposure dating
- proxy in climate research
- environmental tracer

Trends:
- New dedicated facilities affiliated at earth and environmental science
- Routine service (including sample chemistry)
- Intercomparison exercises
- Establishing of suitable standard materials
Geological exposure and burial dating

\[ ^{16}\text{O}(n,4p3n)^{10}\text{Be} \]
\[ ^{16}\text{O}(\mu-,3p3n)^{10}\text{Be} \]
\[ ^{28}\text{Si}(n,p2n)^{26}\text{Al} \]
\[ ^{28}\text{Si}(\mu-,2n)^{26}\text{Al} \]
\[ ^{39}\text{K}(n,2n2p)^{36}\text{Cl} \]
\[ ^{40}\text{Ca}(n,2n3p)^{36}\text{Cl} \]
\[ ^{35}\text{Cl}(n,\gamma)^{36}\text{Cl} \]

From: J. Fabryka-Martin, 1988
Chemistry $^{10}$Be exposure dating

1. Extract quartz phase of rock (grounding, acid leaching, density separation)
2. Complete dissolution (HF, microwave)
3. Ion exchange to separate e.g. Al
4. Removal of isobar boron-10 with HF
5. Hydroxide precipitation
6. Combustion to BeO
4 fold increase in global erosion during last 5 Myr?

Ocean sediment volumes suggest YES

$^{10}\text{Be}/^{9}\text{Be}$ says NO
$^{10}\text{Be}$ input from cosmic rays is constant
$^{9}\text{Be}$ is from erosion
Actinide AMS
Anthropogenic Pu isotopes as tracer for sediment transport

e.g. Pan et al., $^{137}$Cs, $^{239+240}$Pu concentrations and the $^{240}$Pu/$^{239}$Pu atom ratio in a sediment core from the sub-aqueous delta of Yangtze River estuary. Journal of Environmental Radioactivity 102 (2011) 930-936

- Globally distributed from weapons tests
- Pu binds to particles
- AMS is often more sensitive than other mass spectrometric techniques
Production of $^{236}\text{U}$ ($t_{1/2} = 23$ Myr)

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

$(\alpha,n)$ on light target

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

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.)

Spent reactor fuel: $^{236}\text{U}/\text{U} = 10^{-2}$ (typ.)
"... severe contamination of fresh surface water and sea water with radio-Cs has been confirmed. [...] concentration and isotopic compositions of U and Pu isotopes in the waters were consistent with minimal dispersal of these elements."
Estimated $^{236}\text{U}$ inventory
(Steier et al., 2008 and Sakaguchi et al., 2010)

**Natural**

- Topmost 1000 m of lithosphere: **30 kg $^{236}\text{U}$**.
- Ocean: **0.2 kg $^{236}\text{U}$**

**Anthropogenic**

- Reactors => **$10^6$ kg $^{236}\text{U}$ (!)**
- **900 kg** nuclear weapons tests
Forest soil – vicinity of LLRL
Ishikawa Pref., Japan

$^{236}\text{U}/\text{U} \sim 10^{-7} – 10^{-8}$

$^{236}\text{U}$ in global fallout
(Sakaguchi et al., 2009)

~900 kg of $^{236}\text{U}$ released by weapons tests
Chemistry for Actinides in soil

1. Leaching with acid
2. Ion exchange (TEVA, UTEVA)
3. Co-precipitation with iron hydroxide
Anthropogenic $^{236}\text{U}$ as an oceanographic tracer

Requirements for an oceanographic tracer:

• well defined temporally resolved source function
  -> bomb tests

• conservative behavior in seawater (i.e. long residence time)
  -> 500000 a

• sufficiently long half-life allowing its measurement over at least one decade
  -> 23 Ma
Dissolved vs. particle bound

$^{236}$U ($\times 10^7$ atom/kg)

- dissolved
- in suspended solid

Depth (m)

Sample $^{236}$U (atom/m$^2$)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$^{236}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR14</td>
<td>$1.5 \times 10^{10}$</td>
</tr>
</tbody>
</table>

- $^{236}$U exists as dissolved phase
- Negligible deposition in bottom sediment
Comparison with $^{137}\text{Cs}$ (CR 47)

$^{236}\text{U}/^{137}\text{Cs} = 7.2 \pm 0.5 \text{ (at/at)}$

But:

Chemistry for uranium in sea water

Co-precipitation with iron hydroxide

Ion exchange (TEVA, UTEVA)

Co-precipitation with iron hydroxide
$^{236}\text{U}$ in Corals

- Corals build uranium into their aragonite skeletons (~3ppm)
- This uranium represents the uranium in seawater at the time of growth
- Some corals display well-defined yearly banding
- Core HMF-1 collected January 2007, Turneffe Atoll, 19ft below surface

The HMF-1 $^{236}$U and $^{14}$C record

- We have obtained the year-by-year $^{236}$U bomb-pulse in ocean waters
- $^{236}$U in corals provide a temporally resolved archive
Chemistry for prenuclear $^{236}$U

- Distillation of HNO$_3$
- “Modern” uranium is contaminated with $^{236}$U (especially “ambient” background uranium)
- Cleaning of HCl with UTEVA resin
- Dust-free workplace
- Single use plastic tools
- Avoid samples and reagents of unsure origin
- Use of pre-nuclear iron reagent
- Avoid samples and reagents of unsure origin
AMS Isotopes: $T_{1/2} = 10^4 \ldots 10^8$ a

Now possible at VERA

Very large AMS required

(some more actinides not shown)
AMS Isotopes: $T_{1/2} = 10^4 \ldots 10^8 \text{ a}$

Now possible at VERA

Very large AMS required

Isobar separation presently impossible

Many are present in the environment as fission products
A chemical reaction cell for isobar separation

Kieser at al., EPJ Web of Conferences 24, 07007 (2012)
Separation of $^{41}\text{CaF}_3^-$ from $^{41}\text{KF}_3^-$
Summary: Trends in AMS

- more facilities
  - $^{14}$C
    - smaller machines
    - bomb peak dating
    - smaller samples (< 10 µg)
    - compound specific analysis
- Standard AMS isotopes ($^{10}$Be, $^{26}$Al, $^{36}$Cl, $^{41}$Ca, $^{129}$I)
  - New larger (5 to 6 MV) systems affiliated at earth and environmental sciences
  - 3 MV machines become competitive
  - increase in professionalism
- Anthropogenic actinides as environmental tracers
- Isobar separation before injection (reaction cell, photo detachment)
Detection Limit for $^{236}\text{U}$

Peter Steier, Universität Wien
Water samples from Austria (Srncik et al., 2010)

1st report of water samples collected far away from nuclear facilities

River, creek and well water:

$\frac{^{236}U}{^{238}U} = 10^{-9} - 10^{-7}$
The Garigliano nuclear power plant
(Quinto et al., 2009)

- in operation in 1964 - 1976
- Presently decommissioning
- Sample from sediment in cooling water drain channel

Negligible $^{236}$U in drain channel found.

- boiling water
- enriched uranium
- Thermal Power: 150 MW
$^{236}\text{U}$ in Garigliano Drain Channel and River Sediment

Peter Steier
Soil samples from La Palma Island, Spain (Srnčik et al. 2011)

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth [cm]</th>
<th>(^{236}\text{U}/^{238}\text{U})</th>
<th>(^{236}\text{U}) [atoms/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP_B1</td>
<td>0 - 5</td>
<td>((2.43 \pm 0.04)\times10^{-8})</td>
<td>((3.39 \pm 0.39)\times10^{8})</td>
</tr>
<tr>
<td>LP_B2</td>
<td>15 - 40</td>
<td>((4.05 \pm 1.15)\times10^{-9})</td>
<td>((2.13 \pm 0.64)\times10^{8})</td>
</tr>
<tr>
<td>LP_A</td>
<td>0 - 5</td>
<td>((2.98 \pm 0.23)\times10^{-8})</td>
<td>((2.40 \pm 0.26)\times10^{9})</td>
</tr>
</tbody>
</table>
Soil and water samples from all around the globe
(Eigl et al., 201?)

Soils:
• La Palma
• New Zealand
• Hawaii
• Nußdorf (Vienna)

River water:
• Danube (Romania)
• Rio Negro (Brasil)

Sea water:
• La Palma (Canary Islands, Spain)
• Hawaii
• Black Sea
• Irish Sea

Anthropogenic $^{236}$U is everywhere
Depth profiles of $^{236}\text{U}$

Depth profiles for different locations:
- CR34
- CR41
- CR47
- CR2
- CR17
- CR58
- CR66

Depth profiles show the distribution of $^{236}\text{U}$ concentration with depth.
$^{14}$C from nuclear weapon tests

Tsar H-bomb test, 50 Megaton (~3500 Hiroshima bombs)
Novaya Zemlya, 30 Oct 1961
$^{14}$C Bomb peak dating

Yearly yield of all nuclear weapons tests in the atmosphere and underground during 1945 – 2000 (Figure from UNSCEAR (2000)).
**The "standard" AMS isotopes**

- $^{10}\text{Be}$ - cosmogenic: meteoric or in situ
- $^{26}\text{Al}$ - cosmogenic: meteoric and in situ;
- $^{36}\text{Cl}$ - cosmogenic: meteoric and in situ
  - radiogenic
  - anthropogenic: bomb peak
- $^{41}\text{Ca}$ - cosmogenic: in situ
  - radiogenic
  - tracer in biomed
- $^{129}\text{I}$ - anthropogenic, radiogenic, cosmogenic
Our initial assumption:
Little $^{236}$U in global fallout since
- no $^{235}$U in fusion bombs
- mainly fast neutrons

=> is wrong!

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


Global fallout: $^{236}$U/$^{239}$Pu = 0.05 to 0.50
Why $^{236}\text{U}$ as ocean tracer?

• Why several radio-nuclides?
  • Resolve mixing and dilution of water masses
    • dilution: e.g. conc. $[^{137}\text{Cs}]$ and $[^{238}\text{U}]$ decreases, but $^{137}\text{Cs}/^{236}\text{U}$ stays the same

• Advantage of $^{236}\text{U}$ over $^{137}\text{Cs}$
  • $^{137}\text{Cs}$ min. sample size: 10 L (Povinec 2010) in underground laboratory
  • AMS: surface: $10^7$ atoms $^{236}\text{U}/\text{kg}$, det. eff. $\sim 10^{-4}$) $\Rightarrow \leq 1$ L

• Advantage of $^{236}\text{U}$ over $^{129}\text{I}$
  • $^{236}\text{U}$ is "globally available", $^{129}\text{I}$ originates almost exclusively from a few reprocessing plants
  • Environmental behavior is better understood ($^{129}\text{I}$ also migrates in gaseous form)