A New Approach to Old Water:
Atom-Trap Trace Analysis of Noble Gas Radionuclides

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Noble gas radionuclides: Ideal tracers of residence time

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (yr)</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{81}$Kr</td>
<td>229,000</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>$^{85}$Kr</td>
<td>10.8</td>
<td>$10^{-11}$</td>
</tr>
<tr>
<td>$^{39}$Ar</td>
<td>296</td>
<td>$10^{-15}$</td>
</tr>
</tbody>
</table>

Well-mixed

Solubility equilibrium

Isotopic Abundance vs. Time (Years)
### Noble Gas Radionuclides vs. Other Tracers

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life</th>
<th>Atmospheric isotopic abundance</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{85}\text{Kr}$</td>
<td>10.8 yr</td>
<td>$2 \times 10^{-11}$</td>
<td>Nuclear fuel reprocessing</td>
</tr>
<tr>
<td>$^{39}\text{Ar}$</td>
<td>269 yr</td>
<td>$8 \times 10^{-16}$</td>
<td>Cosmic-ray induced reaction</td>
</tr>
<tr>
<td>$^{81}\text{Kr}$</td>
<td>229,000 yr</td>
<td>$1 \times 10^{-12}$</td>
<td>Cosmic-ray induced reaction</td>
</tr>
</tbody>
</table>

![Graph showing age range for various isotopes](graph.png)
Analytical Challenge of Noble Gas Radionuclides

How do you find 1 atom in $10^{15}$ atoms which all look very similar?

Example: $^{39}\text{Ar}$

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance</th>
<th>Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>$0.003336$</td>
<td>Stable</td>
</tr>
<tr>
<td>38</td>
<td>$0.000629$</td>
<td>Stable</td>
</tr>
<tr>
<td>39</td>
<td>$8.1 \times 10^{-16}$</td>
<td>269 y</td>
</tr>
<tr>
<td>40</td>
<td>$0.996$</td>
<td>Stable</td>
</tr>
</tbody>
</table>
The Three Methods: LLC, AMS, and ATTA

Low Level Counting (LLC)

Underground laboratory in Bern, Switzerland
35 meters below ground

Detection Limit: $\sim 4 \times 10^{-17}$
Sample Size: $\sim 0.3-1$L STP Ar (1-3 Tons H$_2$O)
Time: 8-60 days
Limiting Factors: Variation of environmental background
The Three Methods: LLC, AMS, and ATTA

Accelerator Mass Spectrometry (AMS)

Detection Limit: $\sim 4.3 \times 10^{-17}$
Sample Size: $\sim 2$ mL STP Ar (2 L H$_2$O)
Time: $\sim 8$ hours
Limiting Factors:
Accelerator based
Background from $^{39}$K

The Three Methods: LLC, AMS, and ATTA

Atom Trap Trace Analysis (ATTA)

- Based on Selectivity of Magneto-Optical Trap (MOT)
  - Long observation time -- 100 ms
  - High loading rates -- $10^9$-$10^{12}$ s$^{-1}$ for $^{38}$Ar
  - Narrow linewidth
  - Spatial confinement -- trap size < 1 mm
  - Extremely high selectivity → statistics limited
  - Background from scattered laser light

Atom-Trap Trace Analysis (ATTA-2) @ 2003

Only 1000 liters for $^{81}$Kr in groundwater!

ATTA-1: Chen et al., Science (1999)
Kr atom excitation and trapping scheme (Chen et al., SCIENCE, 1999)

Ground-level Kr atom

5p[5/2]_3

5s[3/2]_2

Metastable \( \tau \approx 40 \text{ sec} \)

10 eV electron collision

811 nm

4p^6

Anti-Helmholtz Coils

Discharge

Kr Inlet

Transverse Cooling

Trapping Laser Beams

Zeeman Slower

Trapping Region

Camera/Detector
Counting $^{81}\text{Kr}$ and $^{85}\text{Kr}$ with ATTA

[Graph showing the counting of $^{81}\text{Kr}$ and $^{85}\text{Kr}$ with ATTA, with peaks at various frequency offsets.]
Single Atom Detection!
First application of ATTA in hydrology: Nubian Aquifer, Egypt (2003)
First application of ATTA in hydrology:
Nubian Aquifer, Egypt (2003)

(Sturchio et al., GRL, 2004; Patterson et al., G³, 2005)
What’s new? ATTA-3!!!

We’re there!!!

What’s new?
ATTA-3!!!

1000
100
10
1

85Kr measured (dpm/cc Kr)

85Kr Mixed (dpm/cc Kr)

10-8 10-7 10-6 10-5 10-4 10-3 10-2 10-1 1

85Kr Mixed (dpm/cc Kr)

for 81Kr:

Groundwater

Polar Ice

Efficiency

Water or Ice
Sample Size (L)

10^7 10^6 10^5 10^4 10^3 10^2 10 1

10^-8 10^-7 10^-6 10^-5 10^-4 10^-3 10^-2 10^-1 1

LLC 1969 1999
AMS 1997 2003
ATTA-1 ATTA-2 ATTA-3
2008 (projected)

85 Kr measured (dpm/cc Kr)

85 Kr Mixed (dpm/cc Kr)

for 81 Kr:

Water or Ice
Sample Size (L)

10^7 10^6 10^5 10^4 10^3 10^2 10 1

10^-8 10^-7 10^-6 10^-5 10^-4 10^-3 10^-2 10^-1 1

LLC 1969 1999
AMS 1997 2003
ATTA-1 ATTA-2 ATTA-3
2008 (projected)
Loading Rate Improvements in ATTA-3

<table>
<thead>
<tr>
<th>Atomic Beam Stage</th>
<th>ATTA II</th>
<th>ATTA III</th>
<th>Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>LN₂ pre-cooling</td>
<td>N.A.</td>
<td>x 2</td>
<td>x 2</td>
</tr>
<tr>
<td>Transverse Cooling</td>
<td>70</td>
<td>x 140</td>
<td>x 2</td>
</tr>
<tr>
<td>Sidebands in T.C.</td>
<td>N.A.</td>
<td>x 3</td>
<td>x 3</td>
</tr>
<tr>
<td>2D-MOT</td>
<td>N.A.</td>
<td>x 3</td>
<td>x 3</td>
</tr>
<tr>
<td>New Zeeman Slower</td>
<td>x1000</td>
<td>x 3000</td>
<td>x 3</td>
</tr>
<tr>
<td>More Trapping Power</td>
<td>N.A.</td>
<td>x 1.5</td>
<td>x 1.5</td>
</tr>
</tbody>
</table>

x 160
What else is new? \(^{39}\text{Ar}\) atom counting!!!
Single Atom Counting of $^{39}\text{Ar}$

I.A. = 0.064\%
Experiment 1: Frequency Switching Results

<table>
<thead>
<tr>
<th>Laser Detuning</th>
<th>Expect to See $^{39}$Ar?</th>
<th>Measured (in 57 hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20 MHz</td>
<td>No</td>
<td>0</td>
</tr>
<tr>
<td>-6 MHz</td>
<td>Yes</td>
<td>12</td>
</tr>
<tr>
<td>+10 MHz</td>
<td>No</td>
<td>0</td>
</tr>
</tbody>
</table>
Experiment 2: $^{39}$Ar in air and groundwater

Jiang et al., PRL 106, 103001 (2011)
Summary

- ATTA-3: enhancement of efficiency by a factor of 160
  - Reduced sample size requirement (10-100 L of H₂O)
  - Faster counting times
  - Improved precision (better than +/- 5%)
- First $^{39}$Ar measurement of Ar from groundwater
- The next generation ATTA is here, opening opportunities for new and exciting applications (to be presented in future talks)