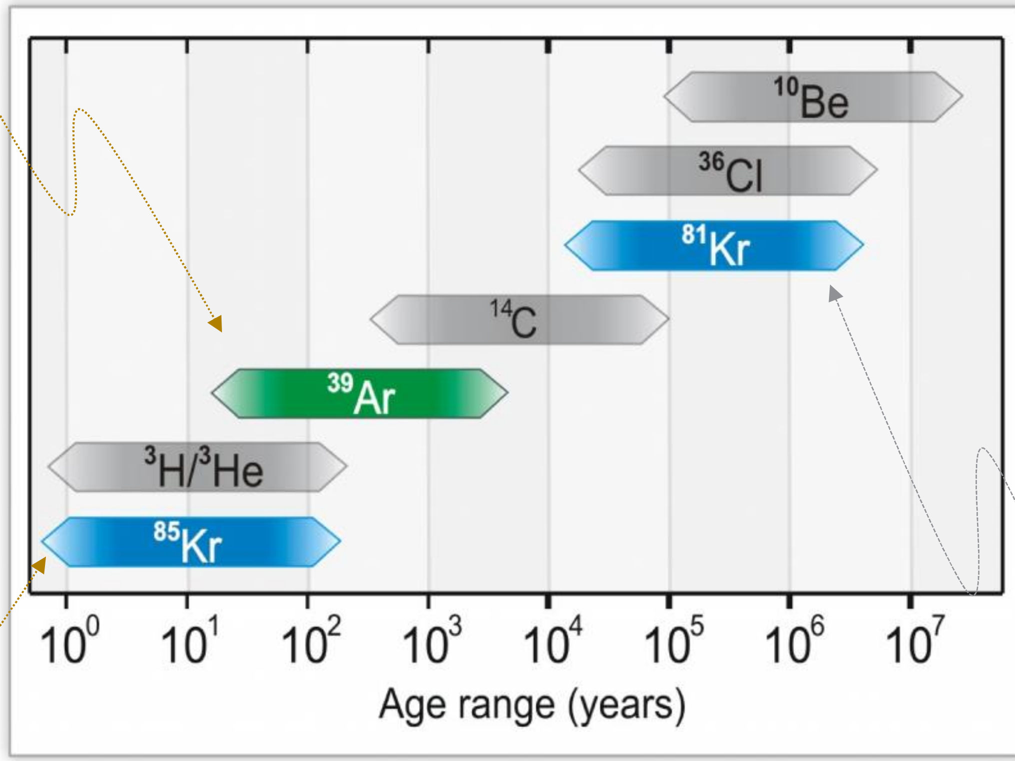
ATOM TRAP TRACE ANALYSIS OF RARE NOBLE GAS ISOTOPES

PETER MUELLER

Noble Gas Tracers for Radio-Isotope Dating

$^{39}Ar/Ar = 8 \times 10^{-16}$

Cosmic-ray induced reaction



$^{85}Kr/Kr = 2 \times 10^{-11}$

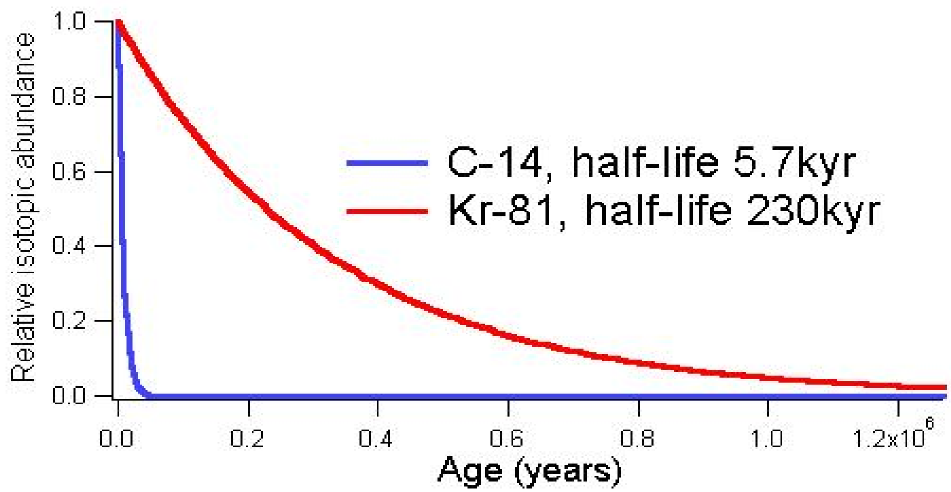
Nuclear fuel reprocessing

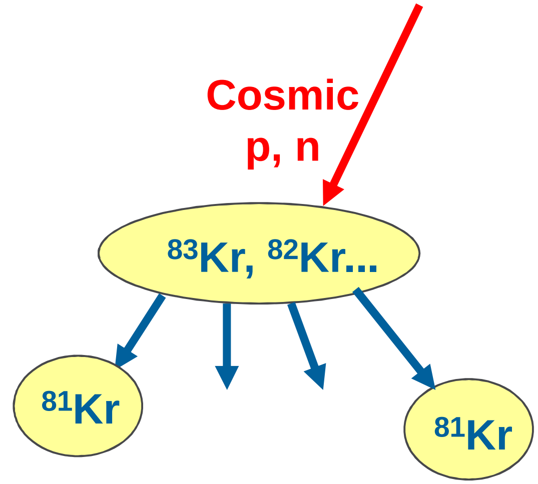
$^{81}Kr/Kr = 6 \times 10^{-13}$

Cosmic-ray induced reaction

KR-81

$t_{1/2}$ = 230 kyr, I.A.= 6×10^{-13}



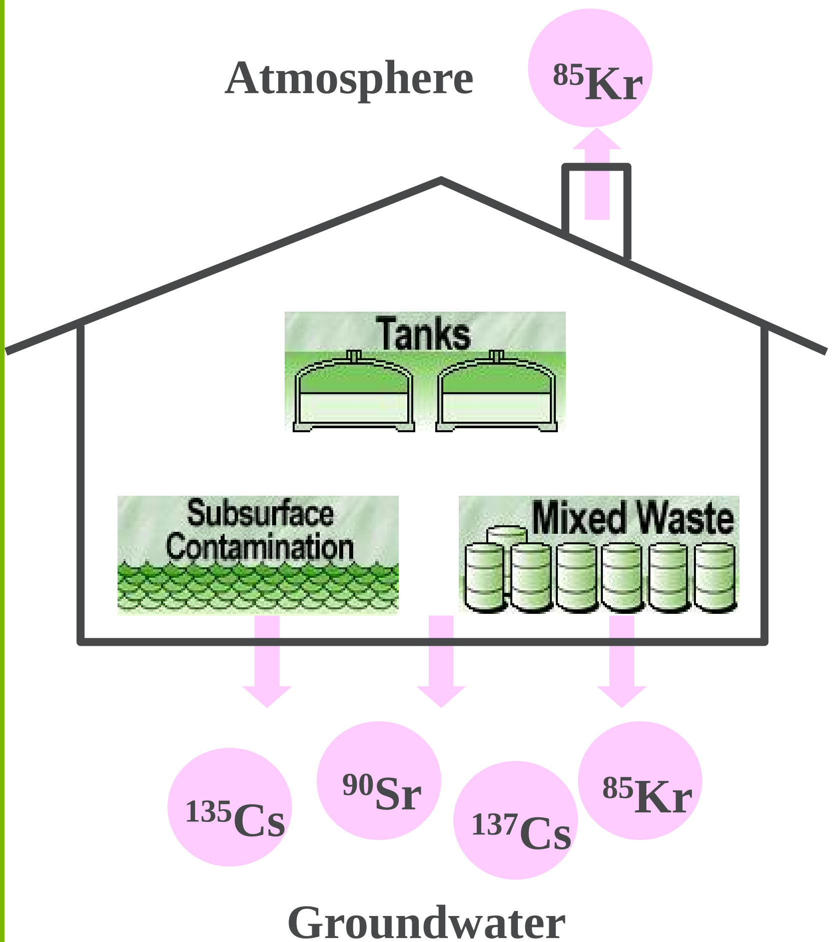


- Ideal for dating ancient groundwater
- Polar ice as a natural climate archive
- Number of ^{81}Kr atoms in 1 liter of

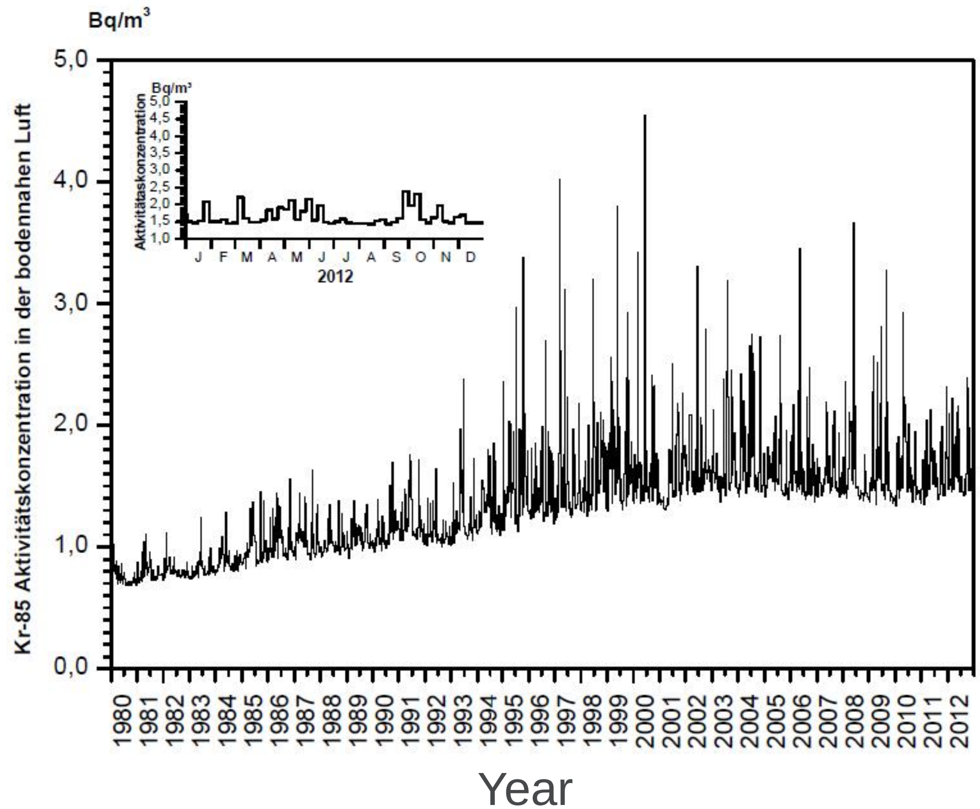
Air	~ 20,000
Water, Ice	~ 1,000

KR-85

^{85}Kr: $t_{1/2}$ = 10.8 yr, I.A.~ 2×10^{-11}



Kr-85 activity in air near Freiburg, Germany



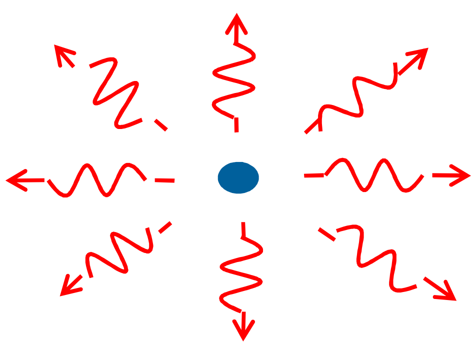
Bundesamt fuer Strahlenschutz Jahresbericht 2012

ATOM TRAP TRACE ANALYSIS - METHOD

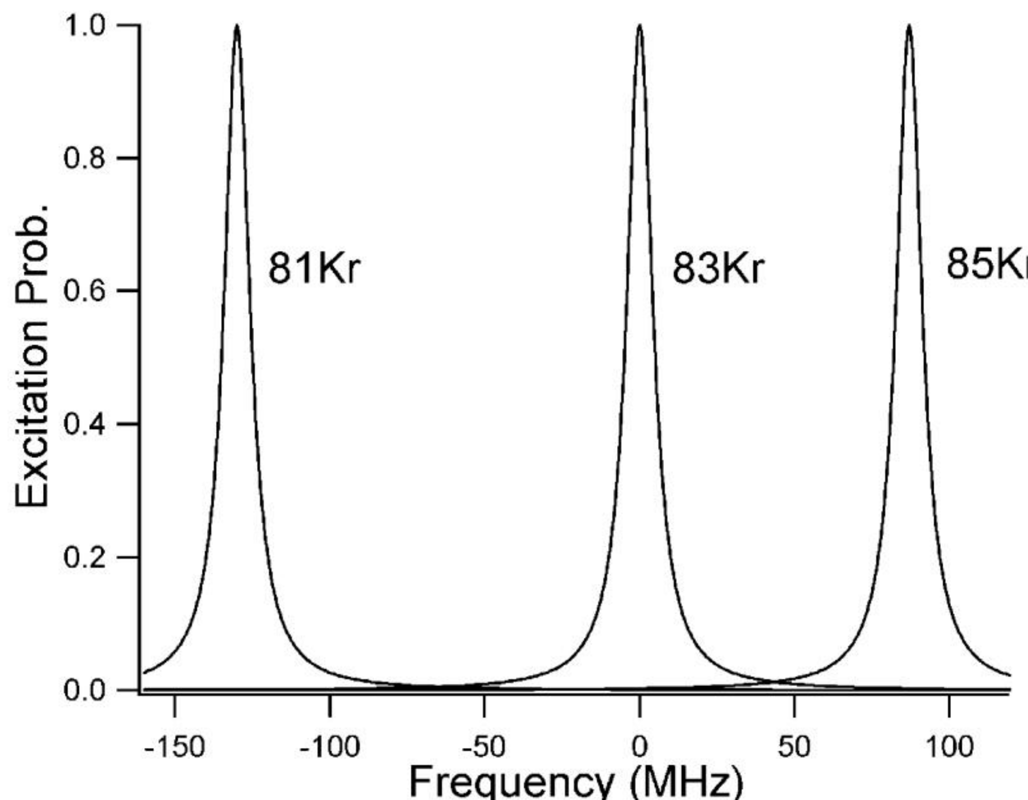
LASER METHODS BASED ON ISOTOPE SHIFTS

Isotope shift due to the change in nuclear mass, charge radii and moments

$1s_5$--$2p_9$ 811nm Laser Frequency (MHz)



Transition rate: 10^7 /sec

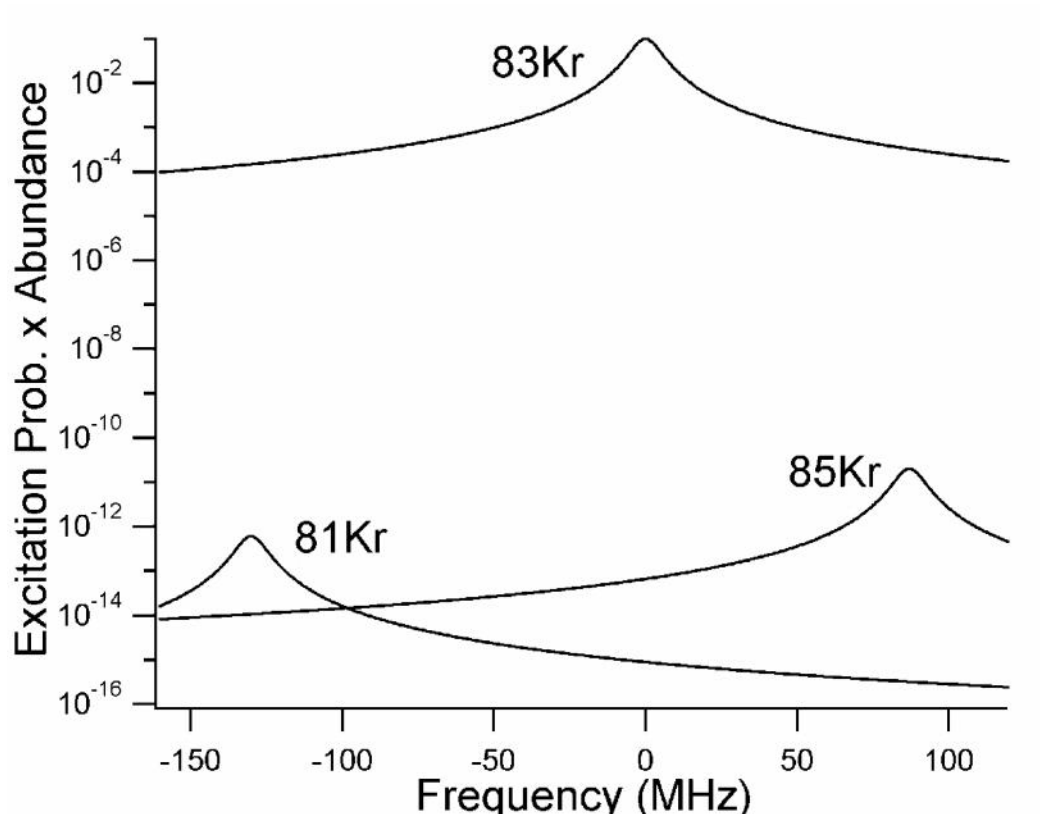


LASER METHODS BASED ON ISOTOPE SHIFTS

Isotope shift due to the change in nuclear mass, charge radii and moments

$1s_5$--$2p_9$ 811nm Laser Frequency (MHz)

Prob x I.A.



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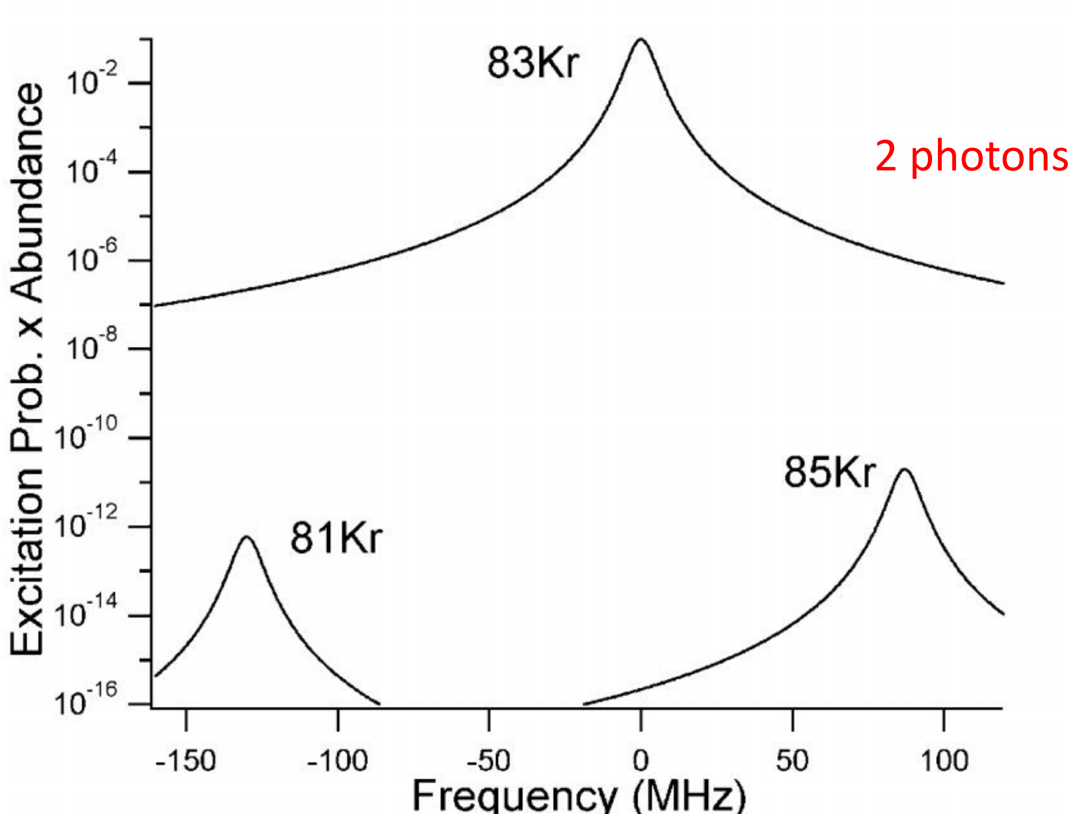
LASER METHODS BASED ON ISOTOPE SHIFTS

Isotope shift due to the change in nuclear mass, charge radii and moments

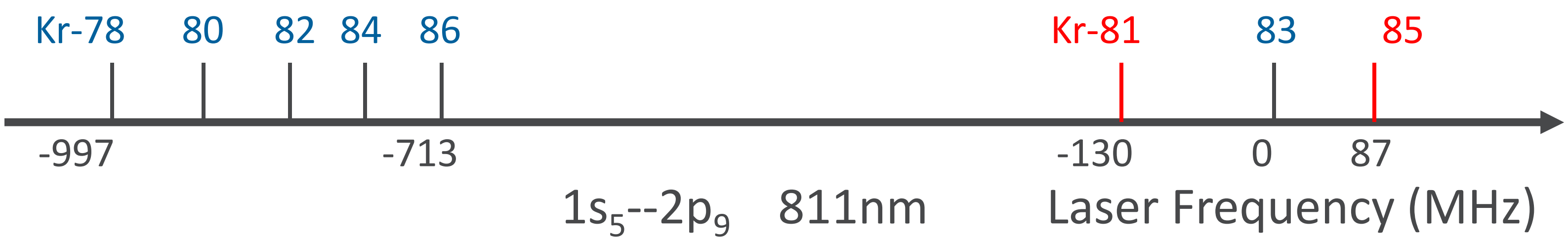
$1s_5$--$2p_9$ 811nm Laser Frequency (MHz)

(Prob)^2 x I.A.

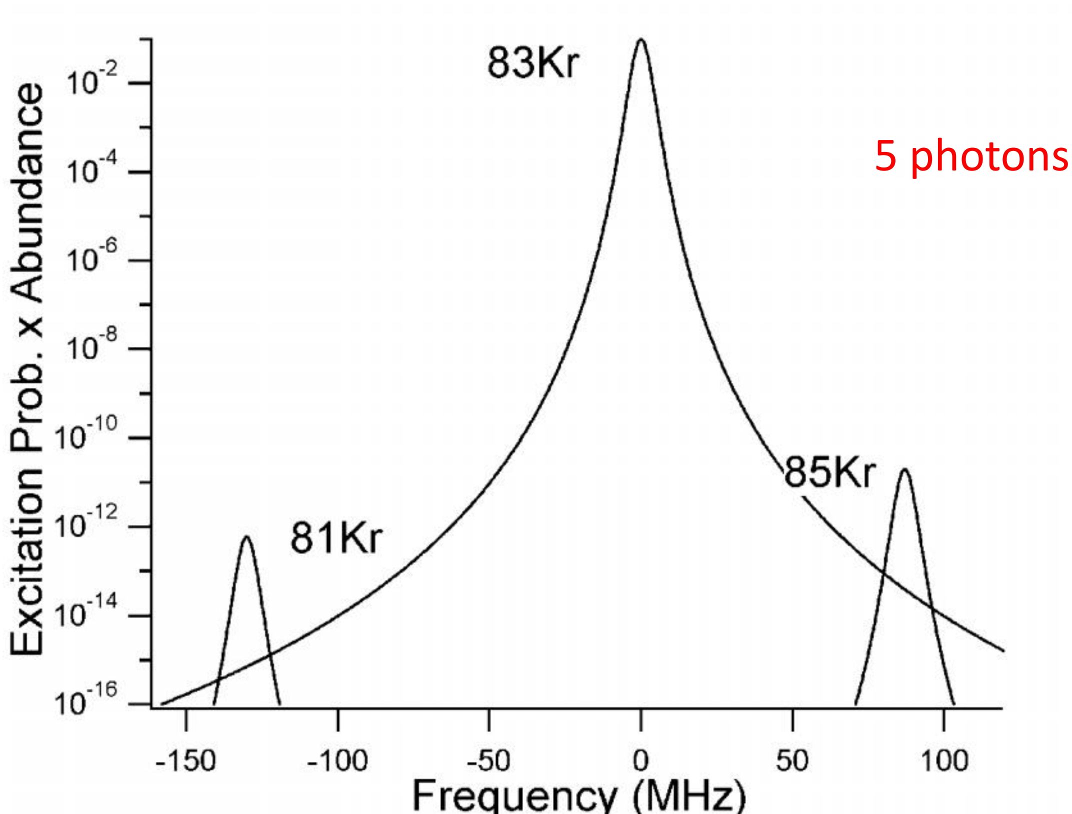


LASER METHODS BASED ON ISOTOPE SHIFTS

Isotope shift due to the change in nuclear mass, charge radii and moments

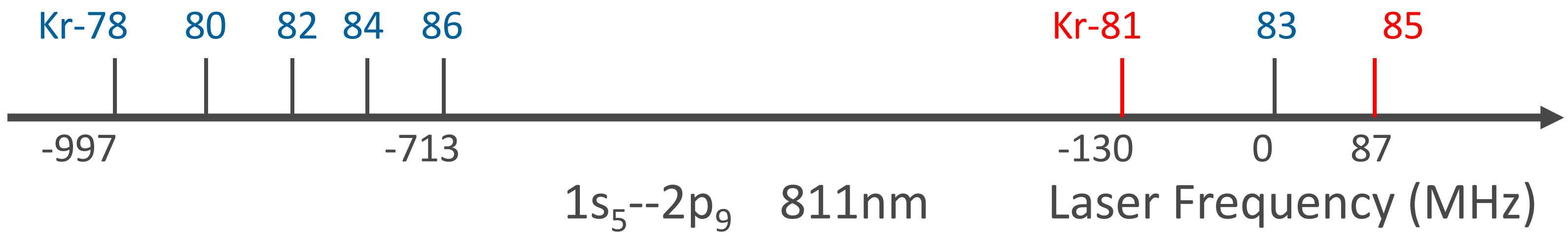


$(Prob)^5$ x I.A.



LASER METHODS BASED ON ISOTOPE SHIFTS

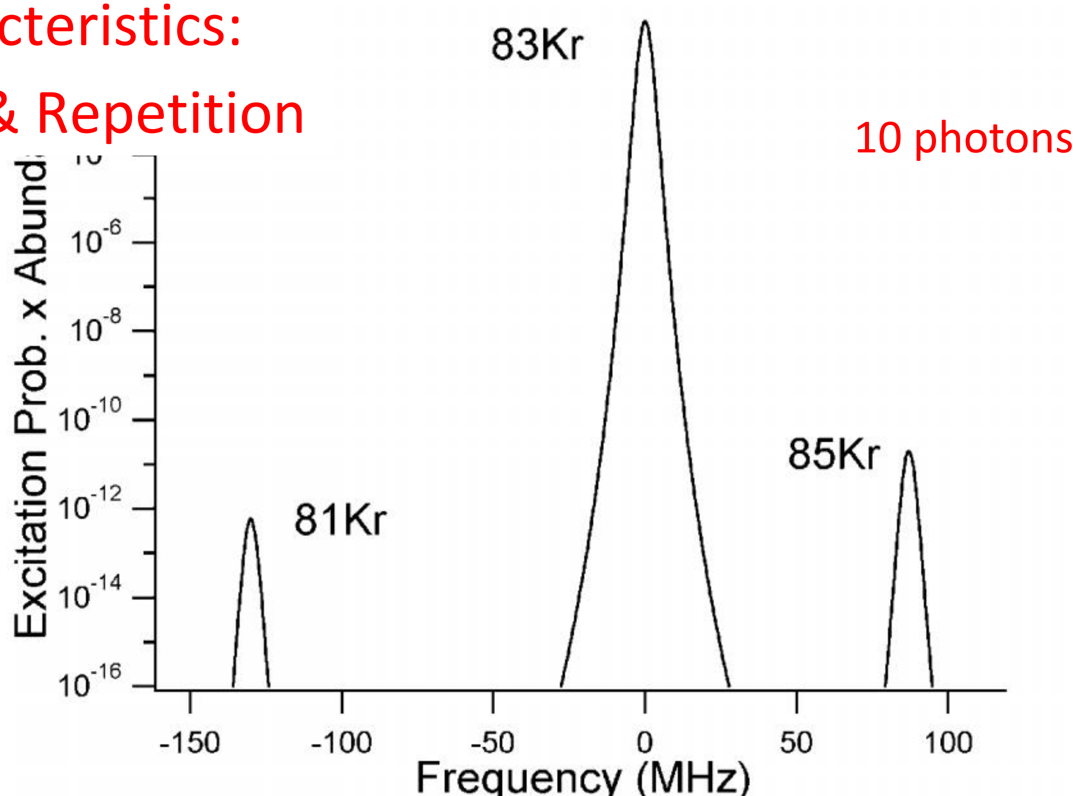
Isotope shift due to the change in nuclear mass, charge radii and moments



Key characteristics:

Resonance & Repetition

Zheng-Tian Lu



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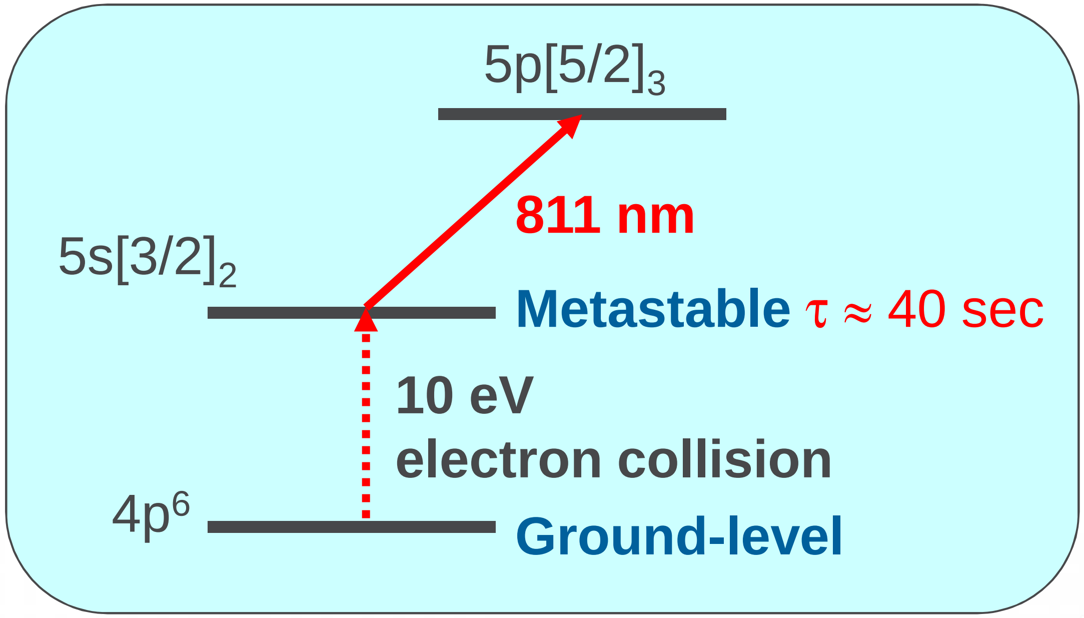
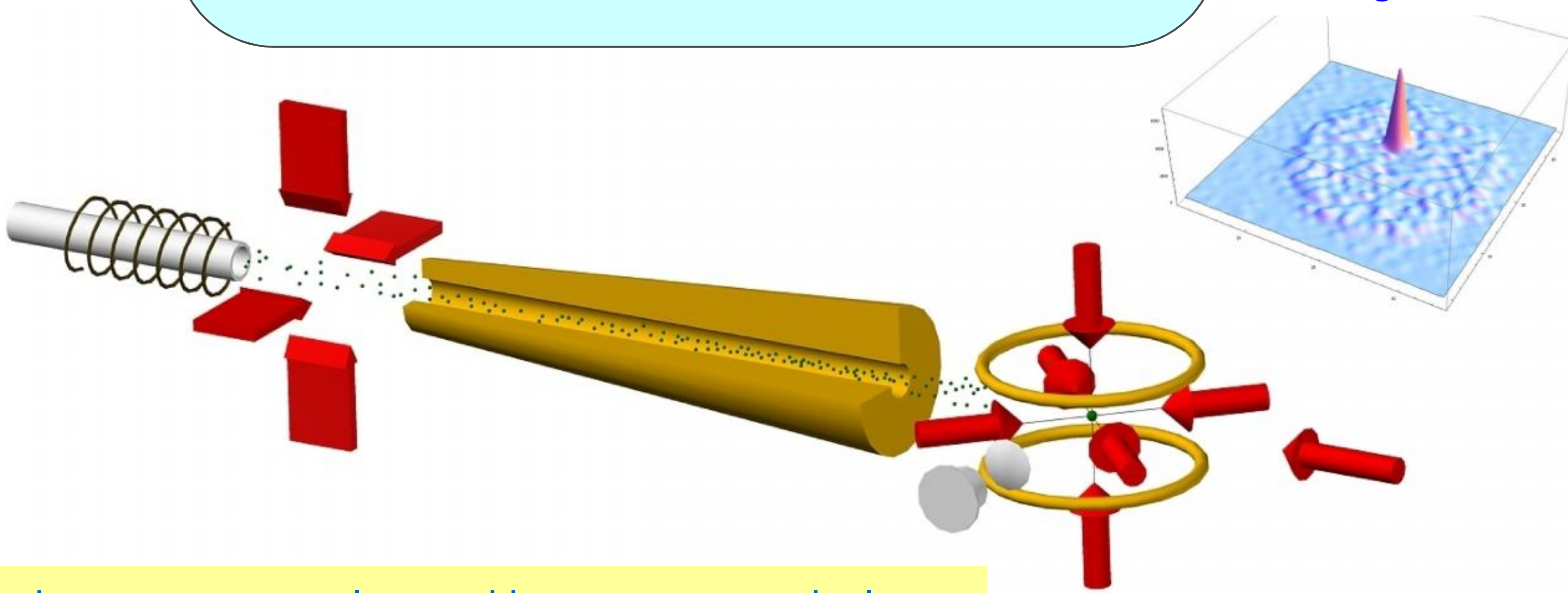
Magneto-Optical Trap
Sodium, NIST, ~ 1990
Nobel Prize in Physics, 1997

Photo credit: Mark Helfer, NIST

ATOM TRAP TRACE ANALYSIS (ATTA) – KRYPTON





Ultrasensitive isotope trace analyses with a magneto-optical trap

Chen *et al.*, Science (1999)

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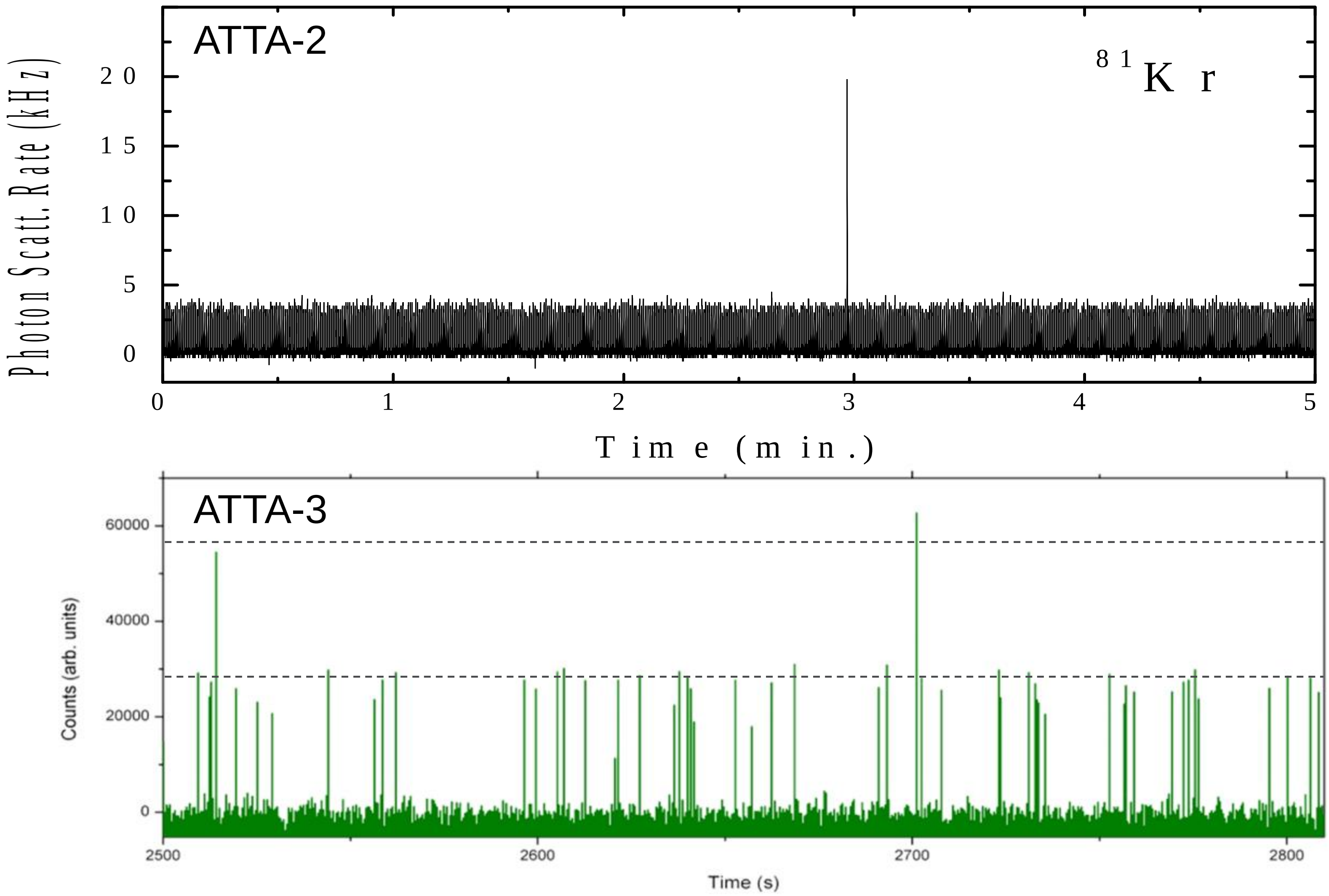
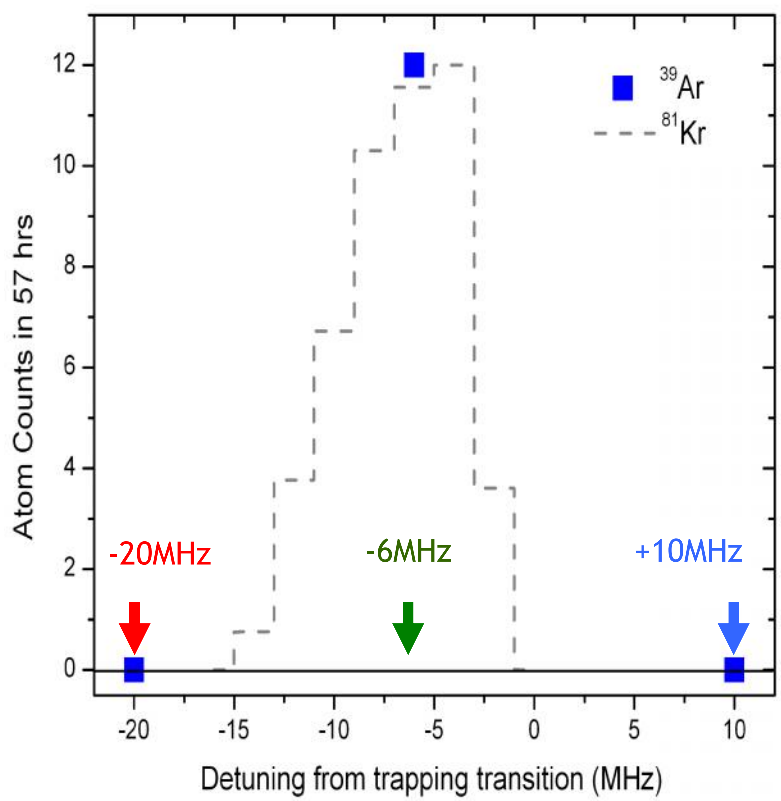
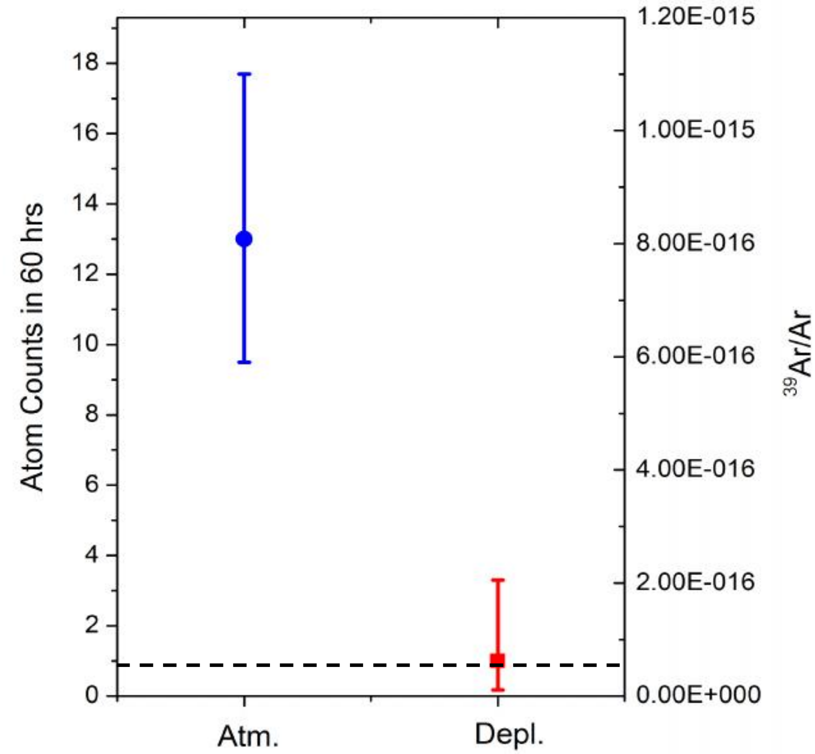
$^{81}Kr / Kr = 6 \times 10^{-13} = 0.5$ ppt



Great Selectivity: Detection of ^{39}Ar at 10^{-16} level

W. Jiang *et al.*, PRL **106**, 103001 (2011)





- Demonstrated isotope detection at the **1×10^{-16}** level
- Need to increase counting rate by a factor of ~ 100 for ocean applications.

How to Measure Loading Rate of ^{83}Kr – The Ion Collection Method

$$\frac{dN}{dt} = L - ¥N - \quad N^2$$

Penning ionization, associative ionization

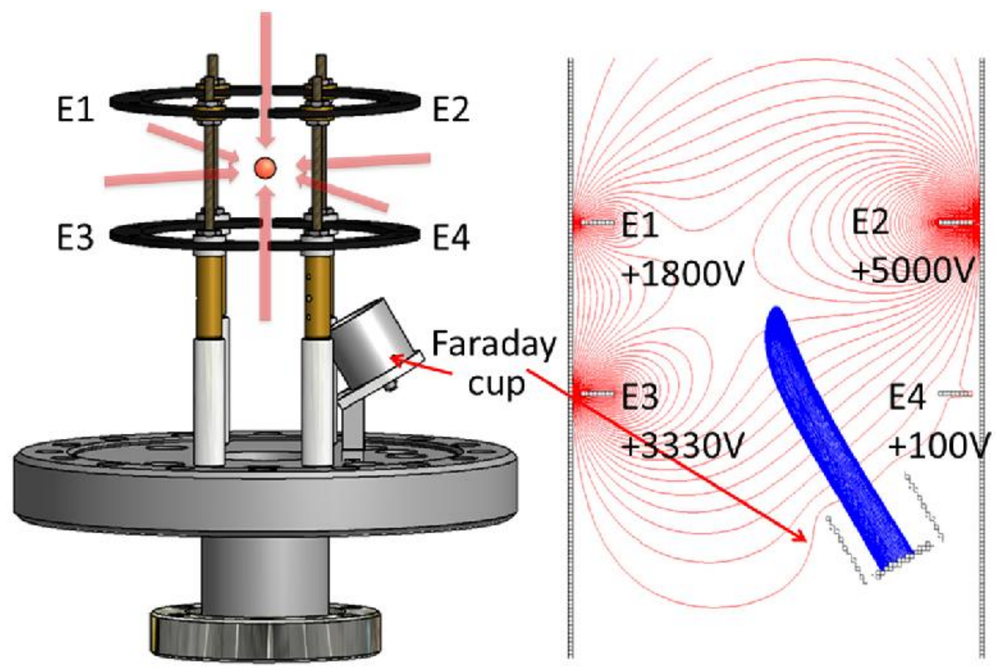
$$Kr(1s_5) + Kr(1s_5) \rightarrow Kr(^1S_0) + Kr^+ + e,$$

$$Kr(1s_5) + Kr(1s_5) \rightarrow Kr_2{}^+ + e.$$

Steady state $\quad L \approx \quad N^2 \longrightarrow$ Ions

$$N >> ¥$$

1) Insensitive to MOT alignment
2) High Signal-to-Noise-Ratio

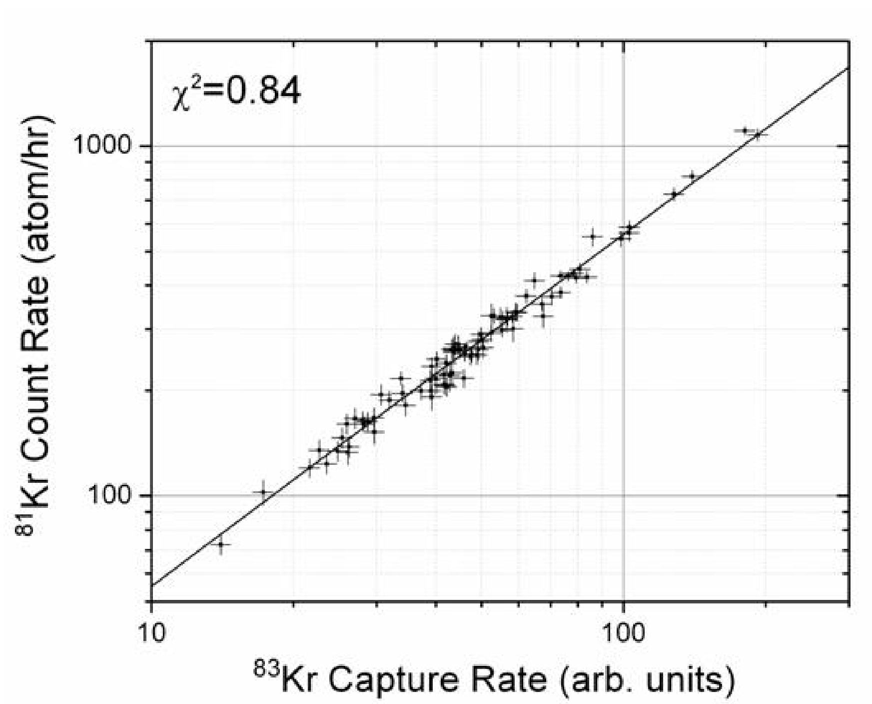


(a) (b)

ATTA-3
Self – Consistency Check

Sample measured under different conditions:

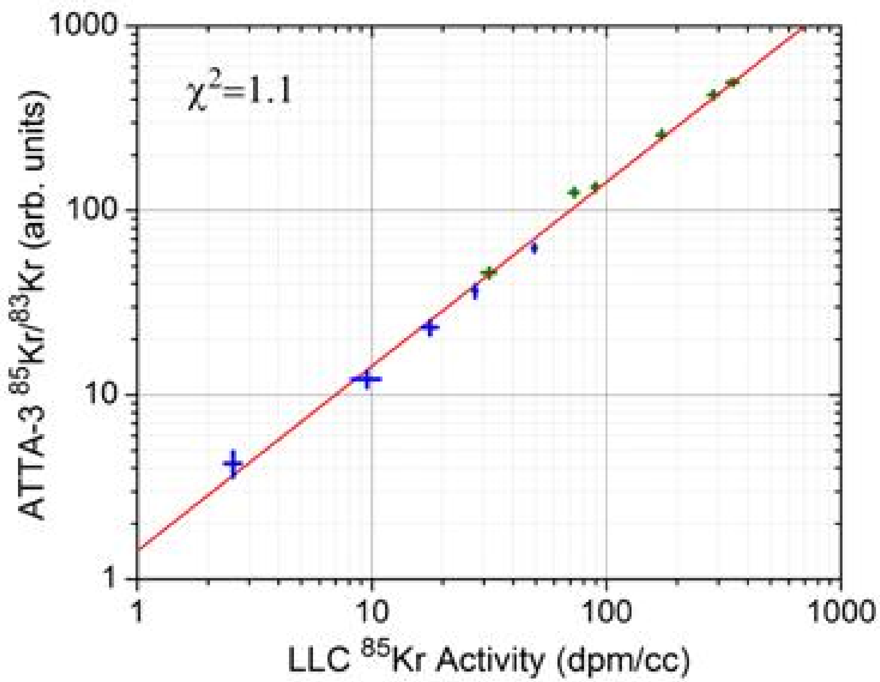
- Laser power
- Alignment
- Discharge
- Pressure
- ……



ATTA-3 at Argonne vs. Decay Counting at Bern

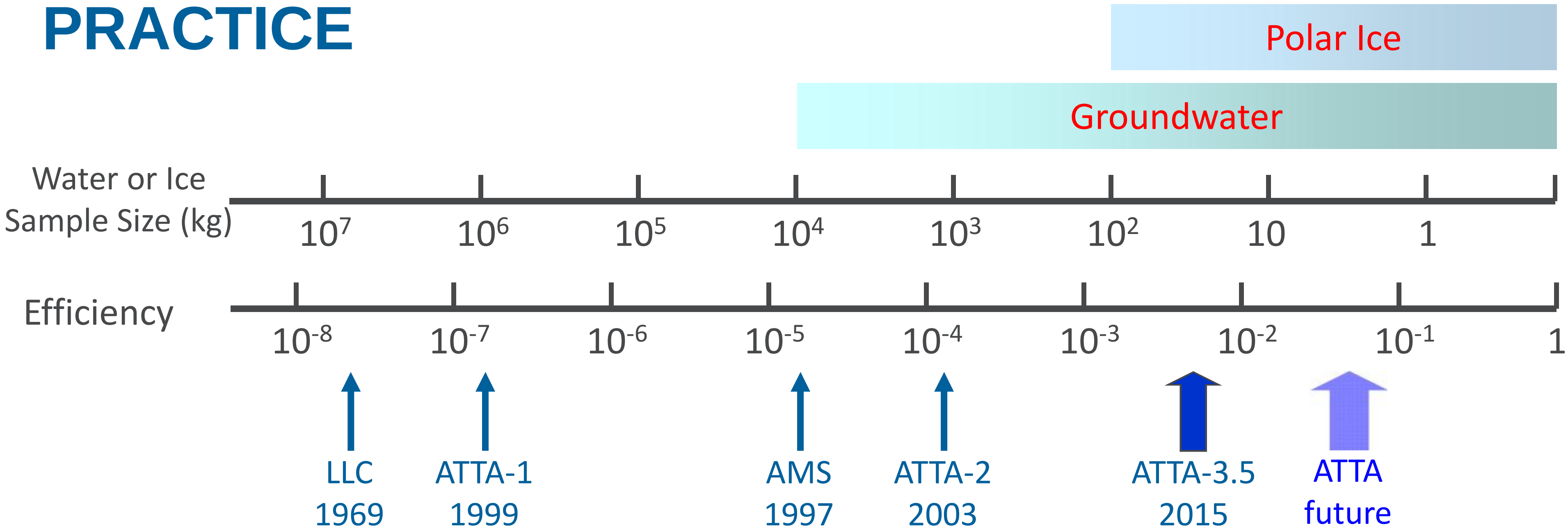
Roland Purtschert
University of Bern

- First batch, 6 samples, unblind
- Second batch, 6 samples, blind



ATTA-3: Jiang *et al.,* Geochim. Cosmochim. Acta (2012)

^{81}KR DATING: FROM DREAM TO PRACTICE



- Sample size: 2~10 μL STP of Kr;
- Degassing in the field.

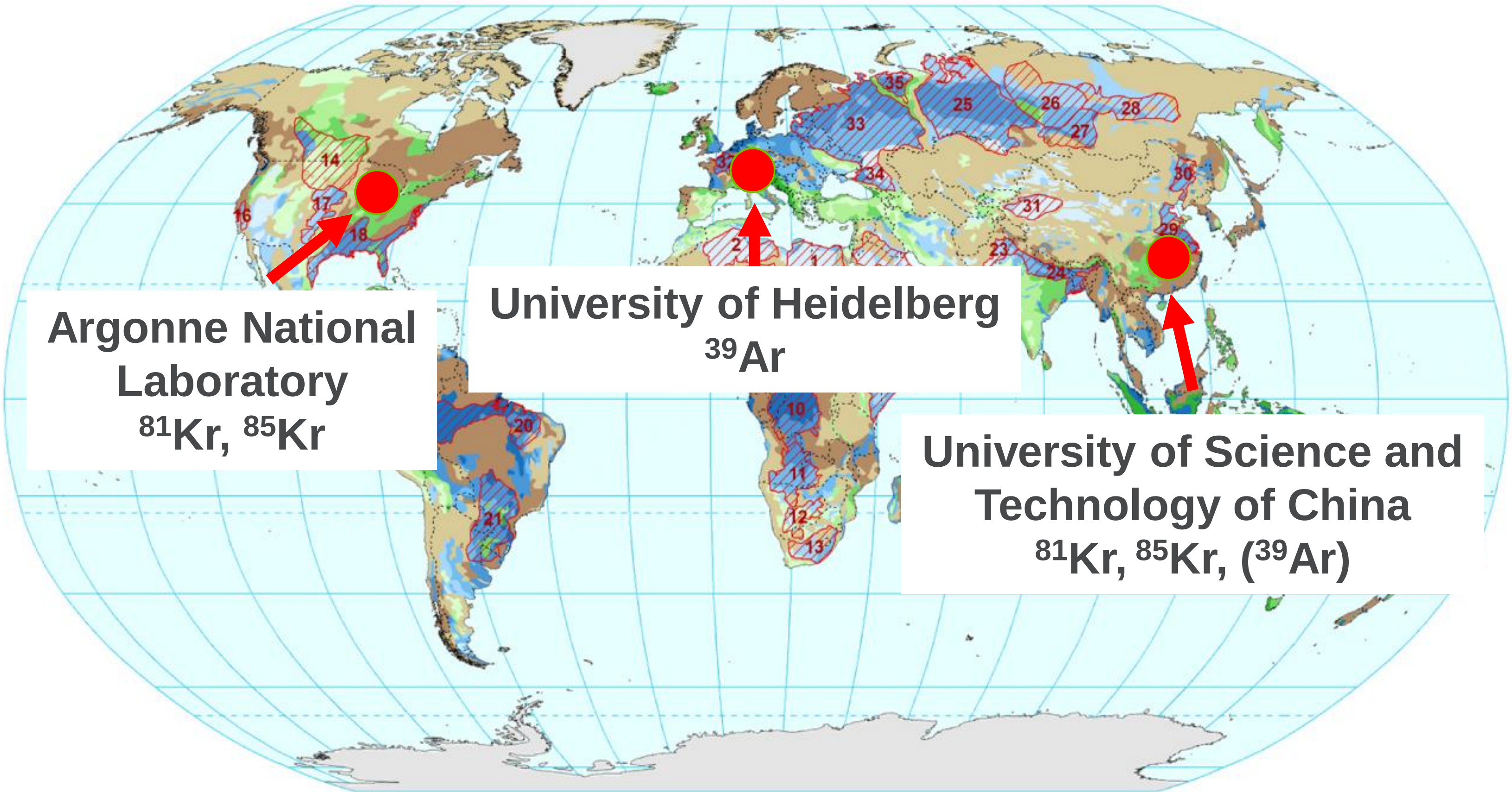
- Next goal: ~1 μL;
- Sample water/ice in the field.

Present Status of ATTA-3.5:

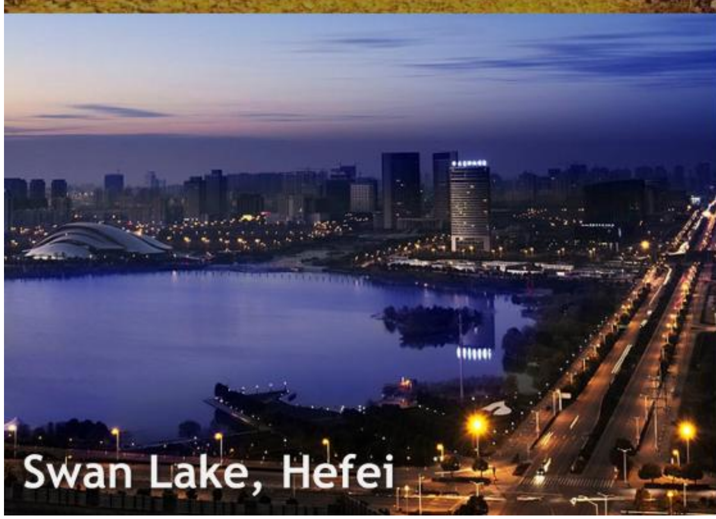
- Detection sensitivity: Done;
- Selectivity requirement: Done;
- Efficiency requirements: Ready for large-scale studies.

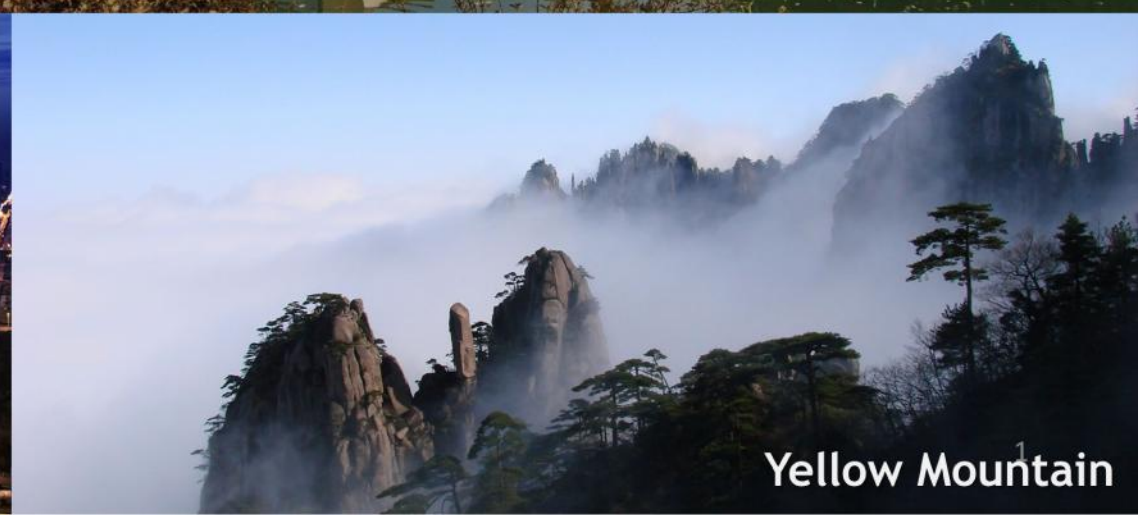
ATTA-1: *Chen et al., Science (1999)*
ATTA-2: *Du et al., Geophys. Res. Lett. (2003)*
ATTA-3: *Jiang et al., Geochim. Cosmochim. Acta (2012)*

ATTA WORLDWIDE




The 3rd International Workshop on
Tracer Applications of Noble Gas Radionuclides (TANGR2018)
University of Science and Technology of China, Hefei, China
September 5-7, 2018


Swan Lake, Hefei


Yellow Mountain

ATOM TRAP TRACE ANALYSIS –
RADIO-KRYPTON DATING APPLICATIONS

Membrane Gas Extractor

Reika Yokochi, University of Chicago

Water flow:
10 L / min

Gas / water:
50 cc / L

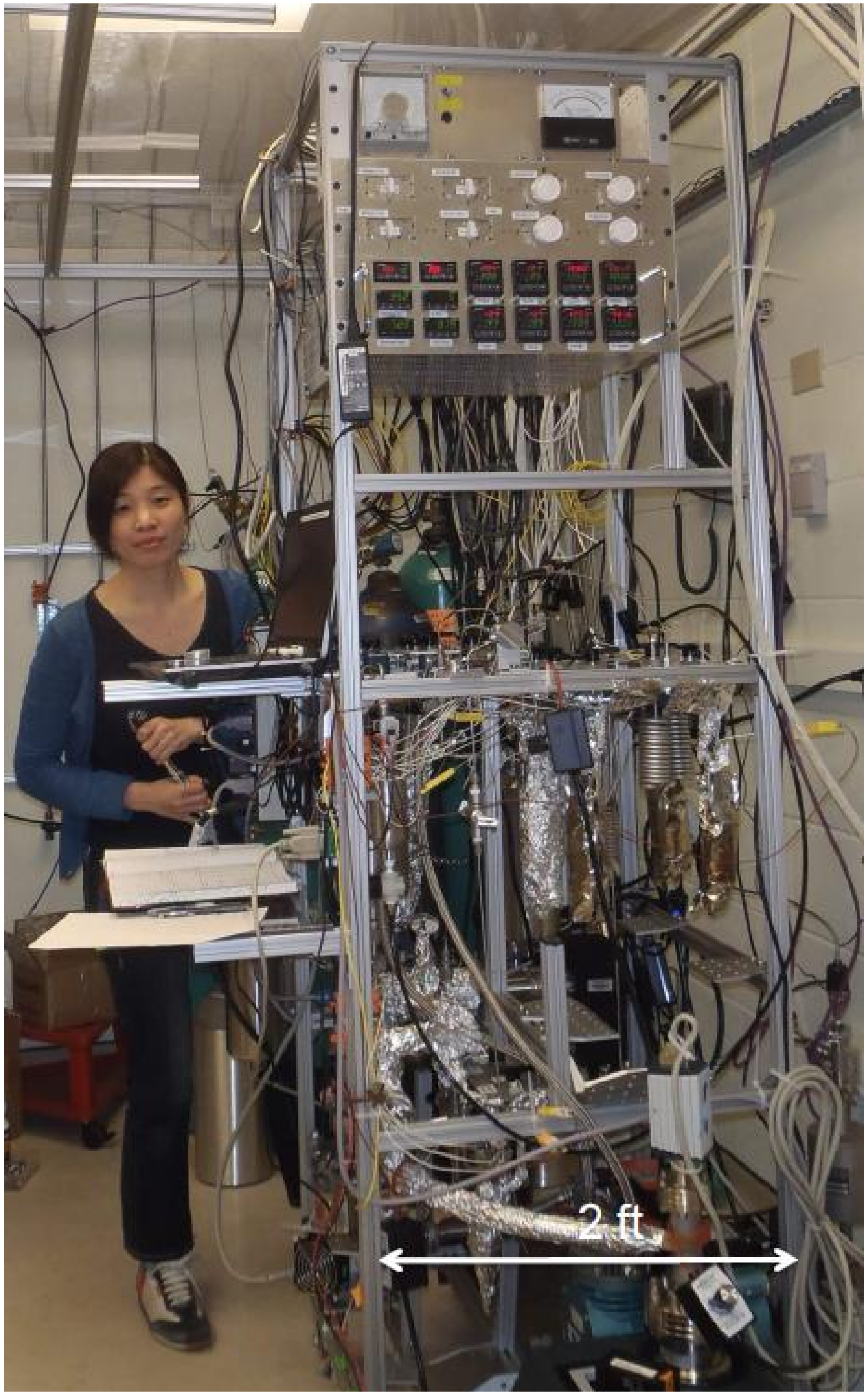
Sample time:
1 hour

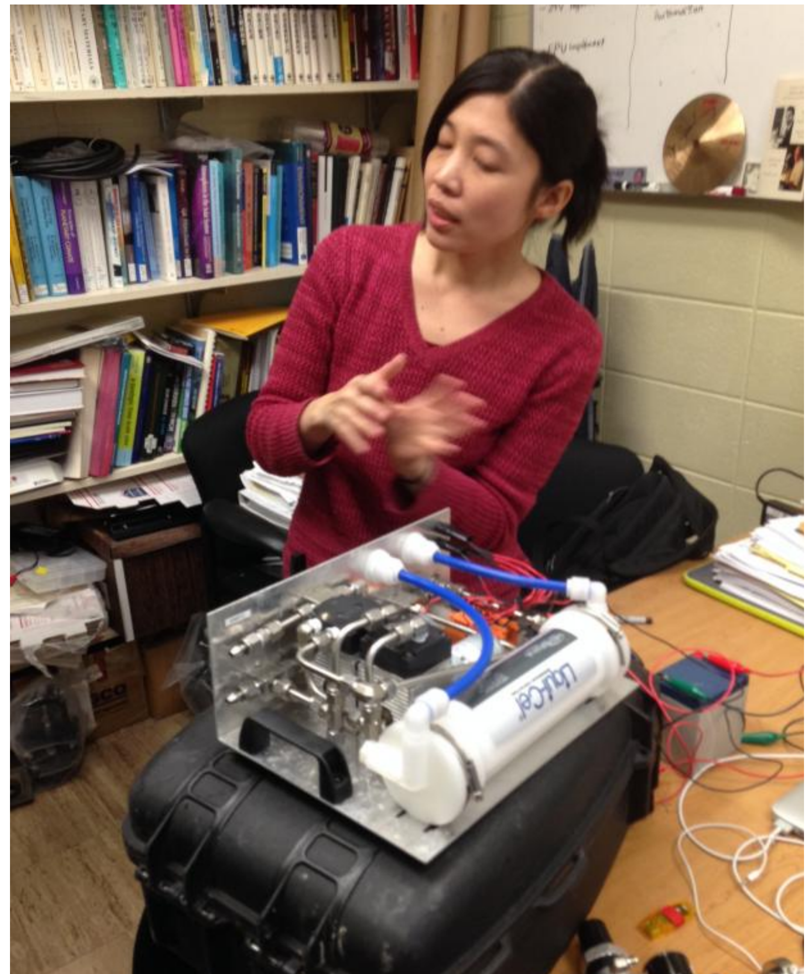
Gas sample:
4 bars x 4 L

Kr Gas Purification System

Reika Yokochi, University of Chicago

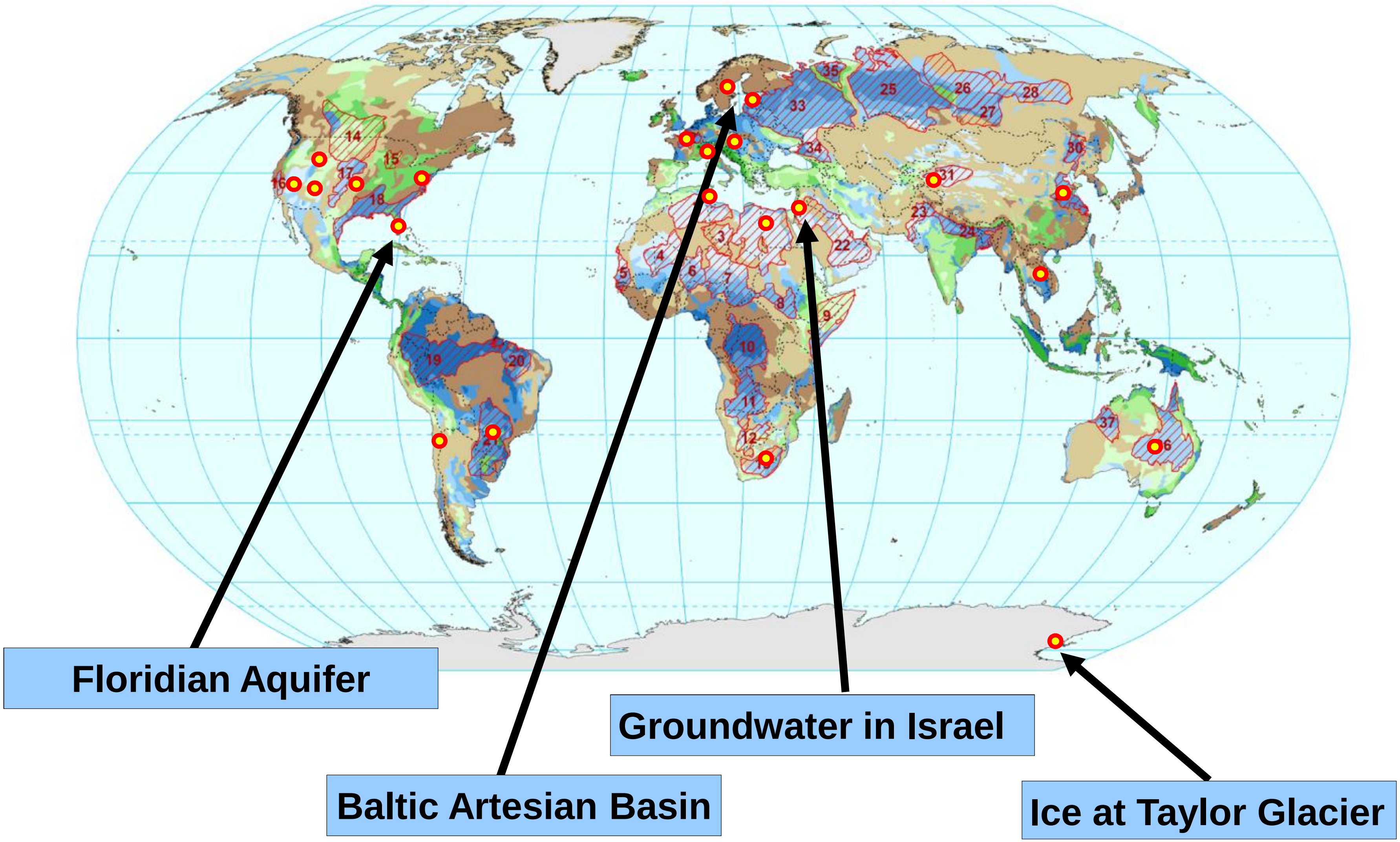
“Pure krypton in 60 minutes”
within a 2’ x 2’ footprint





Portable Membrane Gas Extractor

Radio-Krypton Dating Applications Worldwide

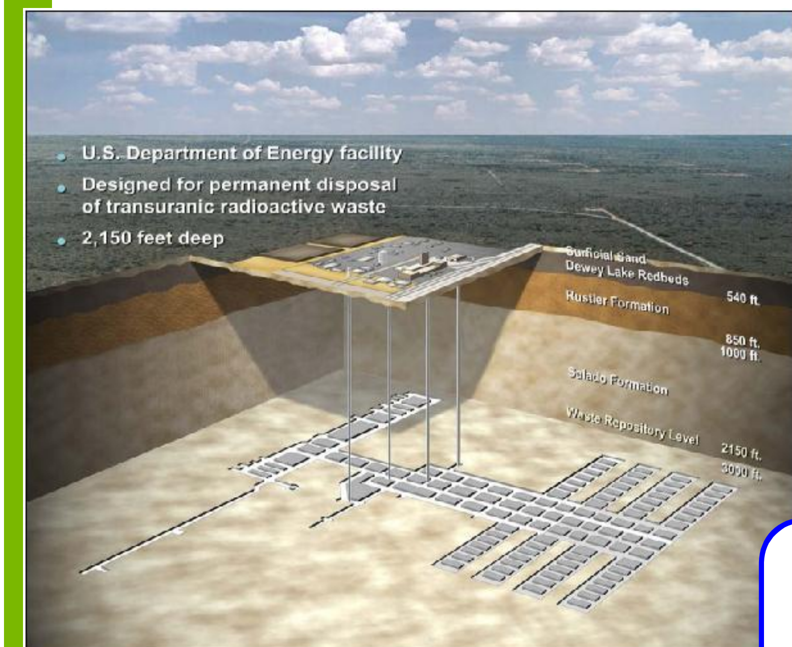


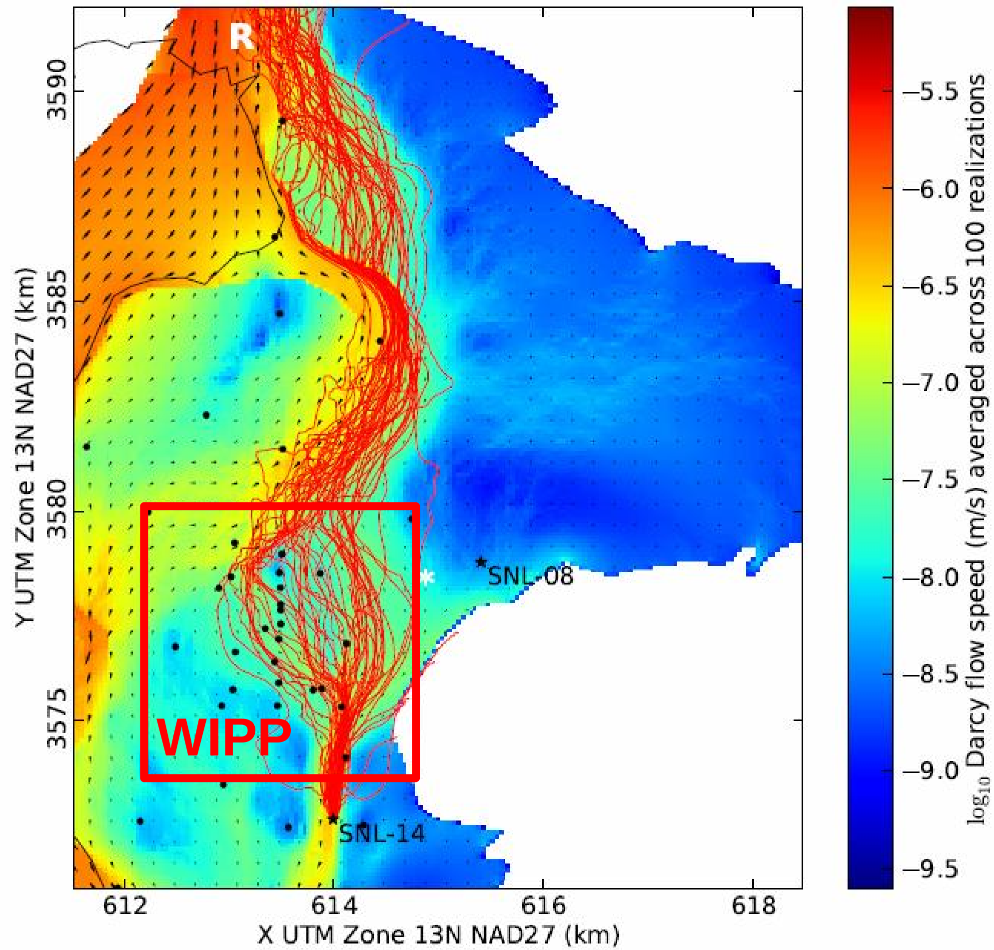
>200 samples from >20 collaborative projects

^{81}Kr Transport in Groundwater of the Culebra Dolomite Aquifer Near the Waste Isolation Pilot Plant (WIPP), New Mexico

Neil Sturchio
Earth and Environ.
Univ. of Delaware

Kris Kuhlman
Repository Performance
Sandia National Lab



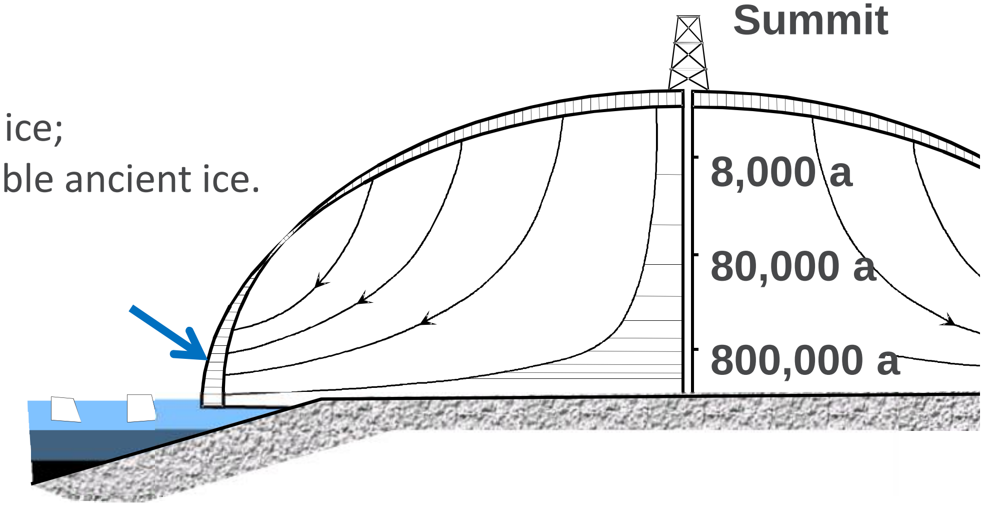


- First campaign: ***J. Contaminant Hydrology* 160, 12 (2014)**
  - SNL-8: 330 ($^{+40}/_{-30}$) × 10^3 yr
  - SNL-14: 130 ($^{+30}/_{-20}$) × 10^3 yr
- Second campaign: samples analyzed in FY2016

^{81}KR-DATING OF ICE CORE AND ICE MARGIN

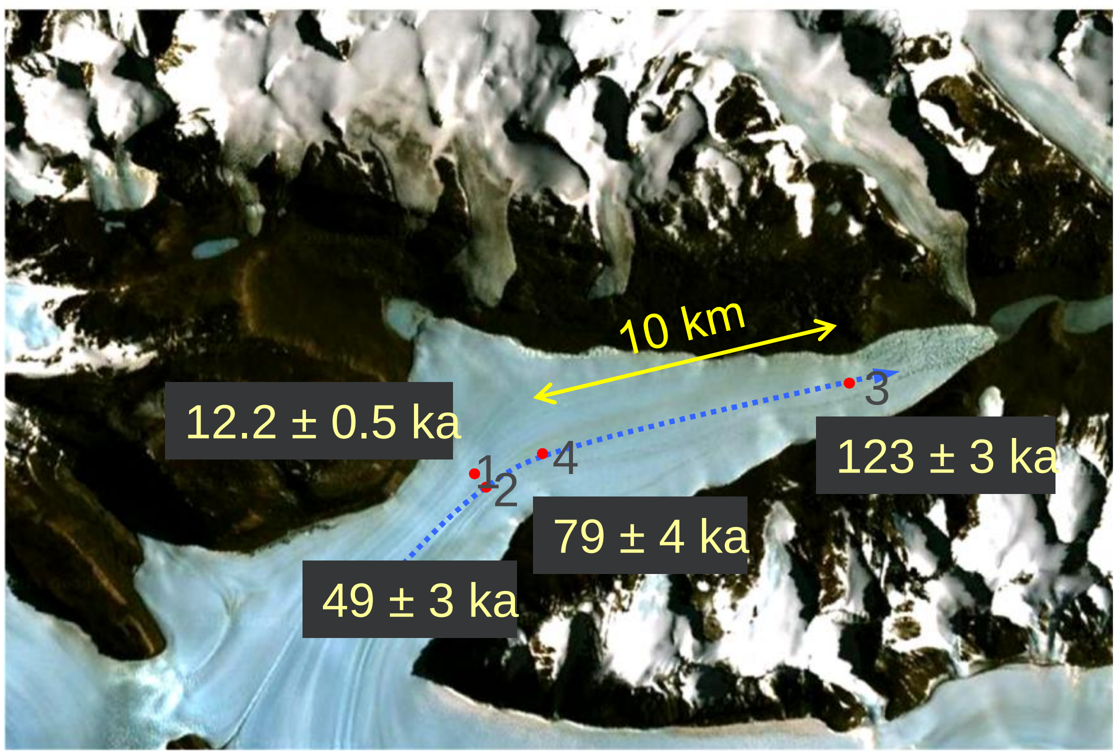
Radiometric dating of old ice:

- ^{81}Kr is a promising technique for dating ancient ice;
- Blue Ice Areas provide large amounts of accessible ancient ice.



This pilot study:

- We sampled Taylor Glacier blue ice;
- Four samples have been dated with ^{81}Kr;
- C. Buizert, *et al*., PNAS **111**, 6876 (2014)



GROUNDWATER SAMPLING IN ISRAEL

- Collaboration with
  Eilon Adar, Ben-Gurion University

- Water resource management

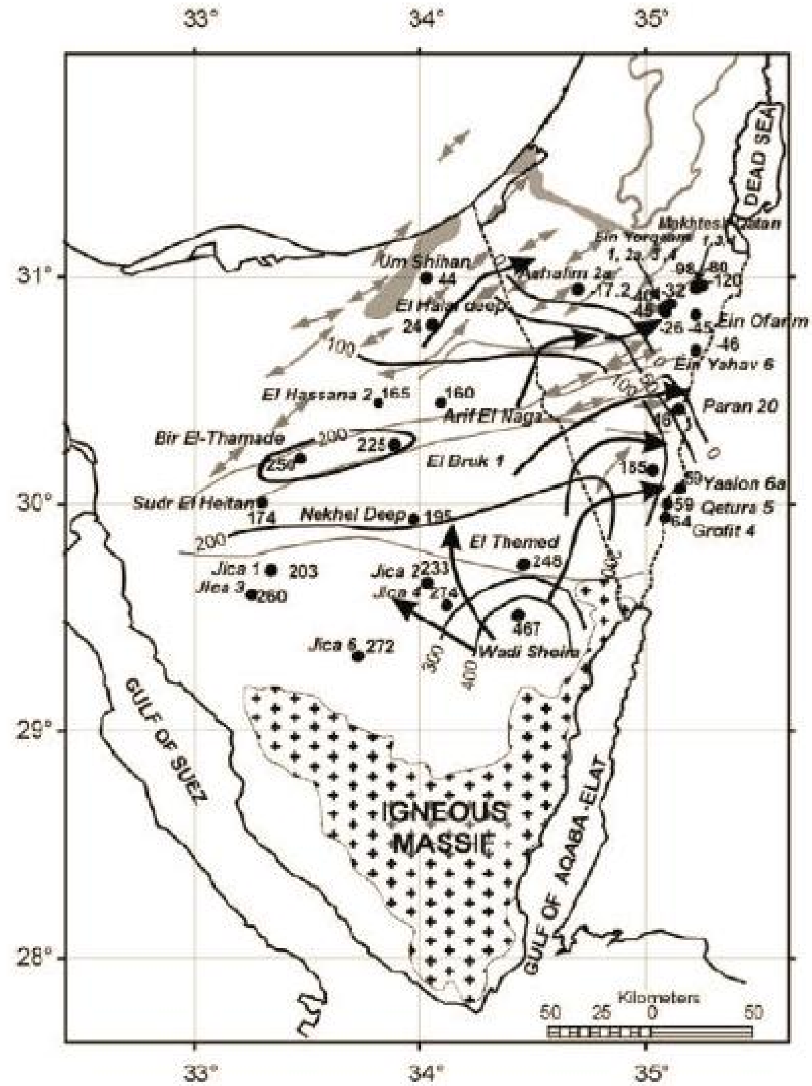
- 1st sampling campaign 2014
  - 29 samples

- 2nd sampling campaign 2015
  - 42 samples

Binational Science Foundation & LDRD

WATER RESEARCH INITIATIVE

waterresearchinitiative.org



THE UNIVERSITY OF CHICAGO

THE INSTITUTE FOR MOLECULAR ENGINEERING THE UNIVERSITY OF CHICAGO

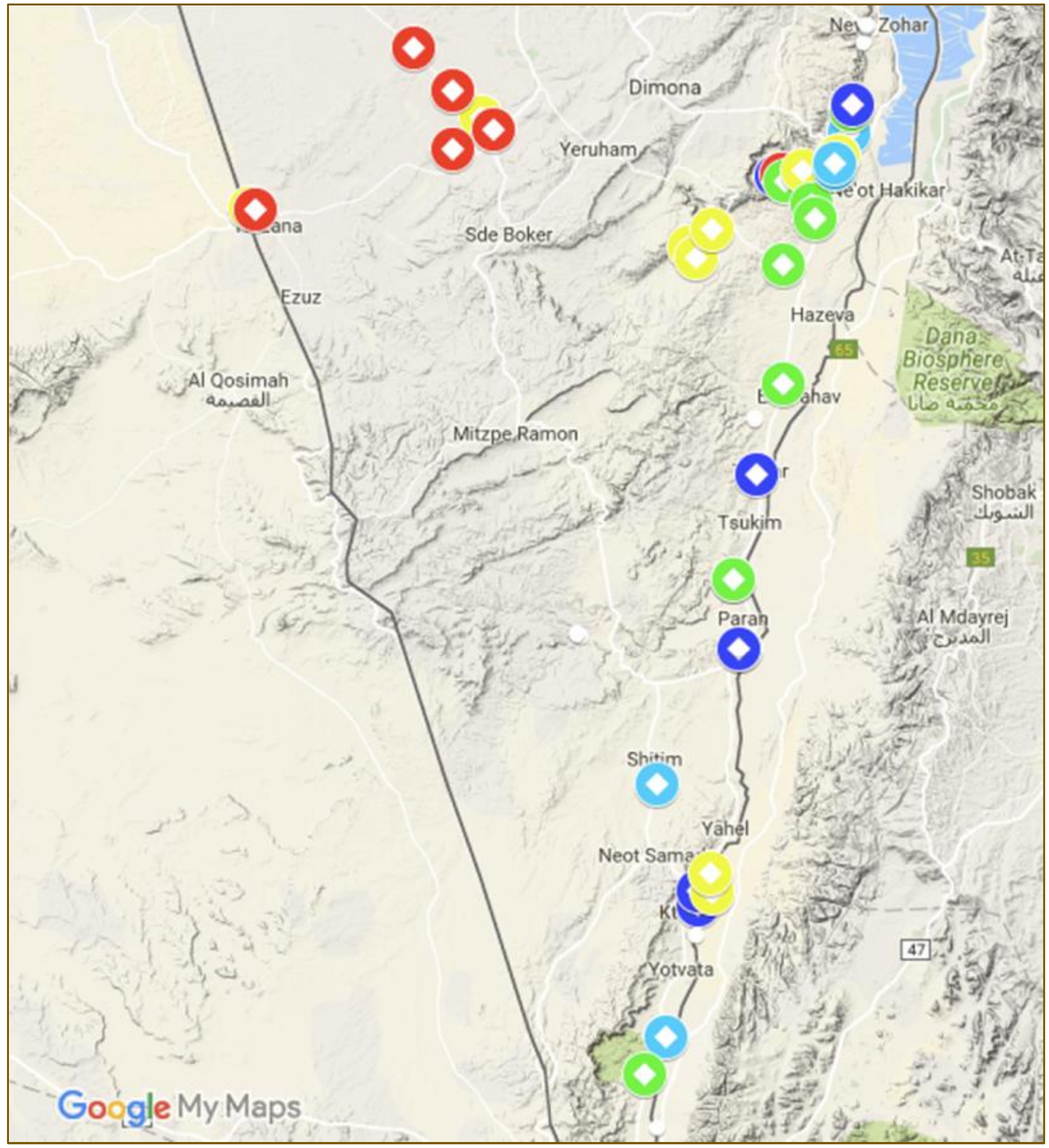
Argonne NATIONAL LABORATORY

Ben-Gurion University of the Negev

GROUNDWATER SAMPLING IN ISRAEL

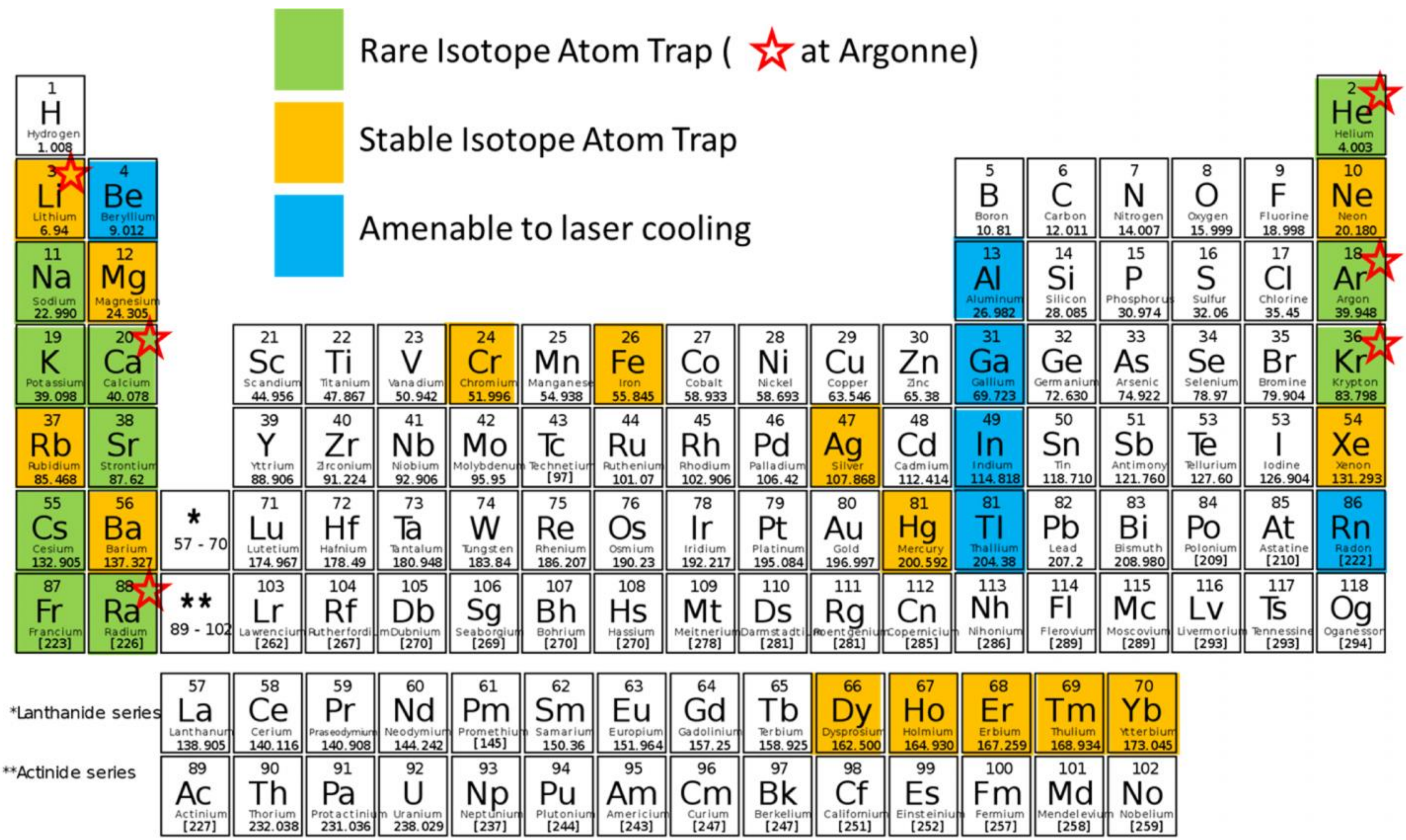
^{81}Kr-dating results

- 30 kyrs and younger
- 30 – 120 krys
- 120 – 220 krys
- 220 – 320 krys
- 320 krys and older (up to 620 kyrs)



ATOM TRAP TRACE ANALYSIS – THOUGHTS

TRAPPABLE ELEMENTS



ATTA – CAPABILITIES AND LIMITS

- Free of background from other isotopes, elements, molecules, …
- Atom counting (not decay counting), independent of radioactive lifetime
- Works for rare stable isotopes, element mixtures, e.g. ^{3}He, Kr in Xe
- High detection efficiency: > 1% (with recirculation)
- Small sample size requirements: ~ micro-L to m-L gas (STP)
- Samples can have high levels of impurities

But …

- Limited to “Trappable” Elements
- Element specific setup
- Counting rate limitations due to vacuum requirements
- Instrumental memory effect, e.g. due to discharge sources

CONCLUSIONS

Atom Trap Trace Analysis

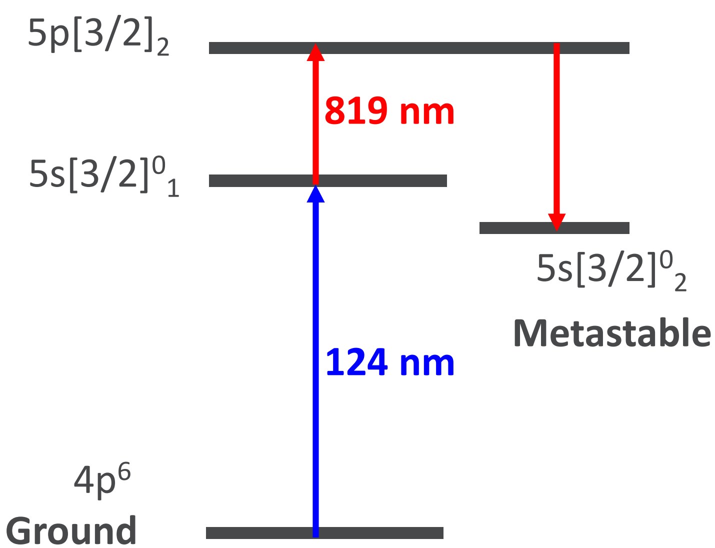
- Atom counting method with ultimate isotope selectivity
- Applicable to noble gases and other “trappable” elements
- Mature technology ready for large scale applications
- ATTA user facilities are coming on-line

THANK YOU!

www.anl.gov

ATTA-4 in Need of Another Breakthrough: Optical Excitation of Kr*

- no memory effect
- faster throughput
- reduced sample size
- increased efficiency



A thermal beam of metastable krypton atoms produced by optical excitation, Y. Ding *et al.*, RSI **78**, 023103 (2007).

Jake's lamp