用单原子探测方法识别古老的冰与水

报告人：卢征天
中国科学技术大学
合肥国家实验室

創寰宇學府
育天下英才
嚴濟慈 一九八八年五月 題

0.5 升空气含 3 × 10^{22} 个原子

包括 1 × 10^{15} 个氪-83原子 (^{83}Kr)

包括 1 × 10^{4} 个氪-81原子 (^{81}Kr)

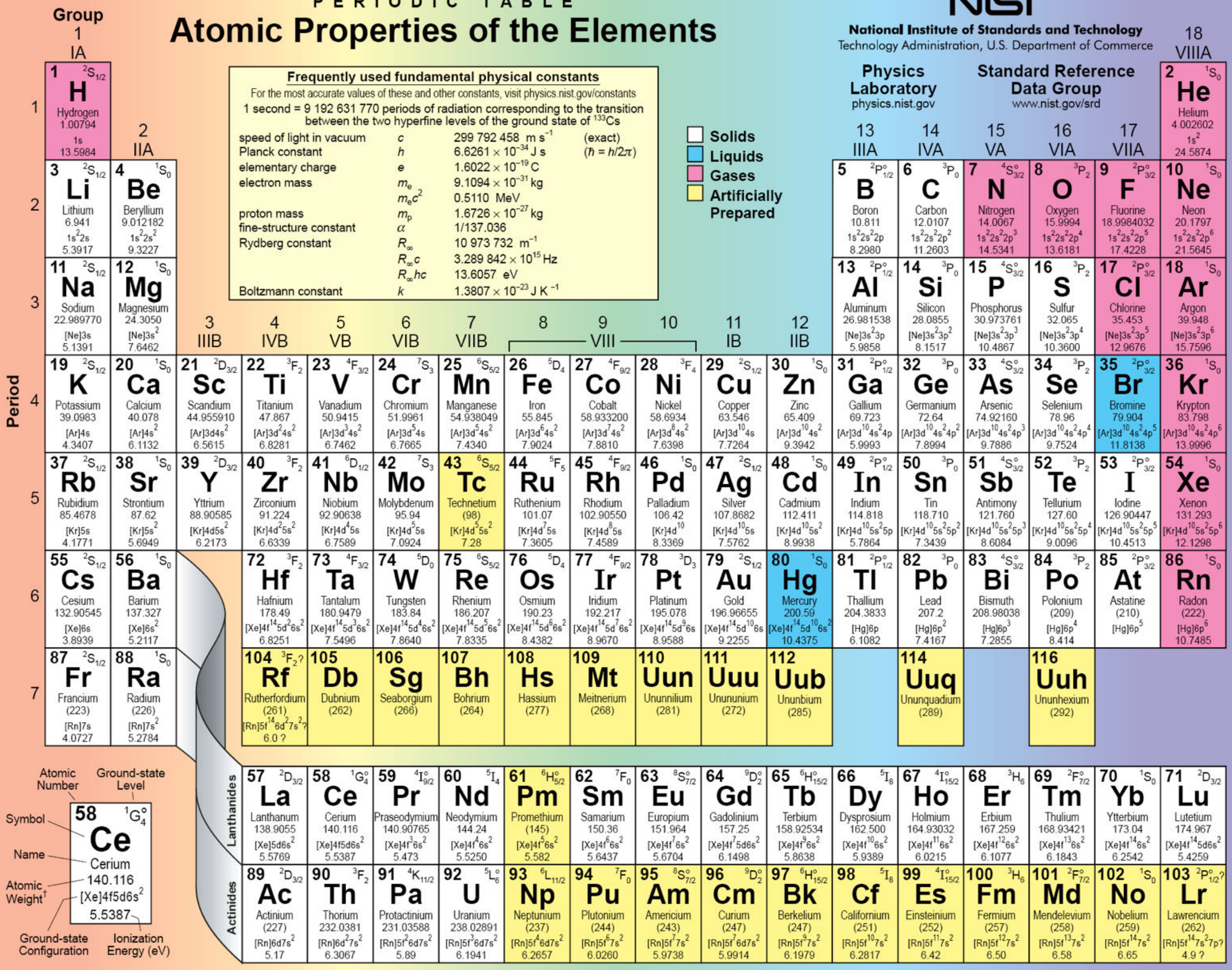
PERIODIC TABLE

Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Physics Laboratory
physics.nist.gov

Standard Reference Data Group
www.nist.gov/srd



Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	6.6261×10^{-34} J s	($\hbar = h/2\pi$)
elementary charge	e	1.6022×10^{-19} C	
electron mass	m_e	9.1094×10^{-31} kg	
	m_ec^2	0.5110 MeV	
proton mass	m_p	1.6726×10^{-27} kg	
fine-structure constant	α	1/137.036	
Rydberg constant	R_∞	10 973 732 m^{-1}	
	$R_\infty c$	$3.289\,842 \times 10^{15}$ Hz	
	$R_\infty hc$	13.6057 eV	
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	

⬜ **Solids**
🟦 **Liquids**
🟪 **Gases**
🟨 **Artificially Prepared**

Group

Period	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 $^2S_{1/2}$ **H** Hydrogen 1.00794 $1s$ 13.5984																	2 $^1S_0$ **He** Helium 4.002602 $1s^2$ 24.5874
2	3 $^2S_{1/2}$ **Li** Lithium 6.941 $1s^22s$ 5.3917	4 $^1S_0$ **Be** Beryllium 9.012182 $1s^22s^2$ 9.3227											5 $^2P^{\circ}_{1/2}$ **B** Boron 10.811 $1s^22s^22p$ 8.2980	6 $^3P_0$ **C** Carbon 12.0107 $1s^22s^22p^2$ 11.2603	7 $^4S^{\circ}_{3/2}$ **N** Nitrogen 14.0067 $1s^22s^22p^3$ 14.5341	8 $^3P_2$ **O** Oxygen 15.9994 $1s^22s^22p^4$ 13.6181	9 $^2P^{\circ}_{3/2}$ **F** Fluorine 18.9984032 $1s^22s^22p^5$ 17.4228	10 $^1S_0$ **Ne** Neon 20.1797 $1s^22s^22p^6$ 21.5645
3	11 $^2S_{1/2}$ **Na** Sodium 22.989770 $[Ne]3s$ 5.1391	12 $^1S_0$ **Mg** Magnesium 24.3050 $[Ne]3s^2$ 7.6462											13 $^2P^{\circ}_{1/2}$ **Al** Aluminum 26.981538 $[Ne]3s^23p$ 5.9858	14 $^3P_0$ **Si** Silicon 28.0855 $[Ne]3s^23p^2$ 8.1517	15 $^4S^{\circ}_{3/2}$ **P** Phosphorus 30.973761 $[Ne]3s^23p^3$ 10.4867	16 $^3P_2$ **S** Sulfur 32.065 $[Ne]3s^23p^4$ 10.3600	17 $^2P^{\circ}_{3/2}$ **Cl** Chlorine 35.453 $[Ne]3s^23p^5$ 12.9676	18 $^1S_0$ **Ar** Argon 39.948 $[Ne]3s^23p^6$ 15.7596
4	19 $^2S_{1/2}$ **K** Potassium 39.0983 $[Ar]4s$ 4.3407	20 $^1S_0$ **Ca** Calcium 40.078 $[Ar]4s^2$ 6.1132	21 $^2D_{3/2}$ **Sc** Scandium 44.955910 $[Ar]3d4s^2$ 6.5615	22 $^3F_2$ **Ti** Titanium 47.867 $[Ar]3d^24s^2$ 6.8281	23 $^4F_{3/2}$ **V** Vanadium 50.9415 $[Ar]3d^34s^2$ 6.7462	24 $^7S_3$ **Cr** Chromium 51.9961 $[Ar]3d^54s$ 6.7665	25 $^6S_{5/2}$ **Mn** Manganese 54.938049 $[Ar]3d^54s^2$ 7.4340	26 $^5D_4$ **Fe** Iron 55.845 $[Ar]3d^64s^2$ 7.9024	27 $^4F_{9/2}$ **Co** Cobalt 58.933200 $[Ar]3d^74s^2$ 7.8810	28 $^3F_4$ **Ni** Nickel 58.6934 $[Ar]3d^84s^2$ 7.6398	29 $^2S_{1/2}$ **Cu** Copper 63.546 $[Ar]3d^{10}4s$ 7.7264	30 $^1S_0$ **Zn** Zinc 65.409 $[Ar]3d^{10}4s^2$ 9.3942	31 $^2P^{\circ}_{1/2}$ **Ga** Gallium 69.723 $[Ar]3d^{10}4s^24p$ 5.9993	32 $^3P_0$ **Ge** Germanium 72.64 $[Ar]3d^{10}4s^24p^2$ 7.8994	33 $^4S^{\circ}_{3/2}$ **As** Arsenic 74.92160 $[Ar]3d^{10}4s^24p^3$ 9.7886	34 $^3P_2$ **Se** Selenium 78.96 $[Ar]3d^{10}4s^24p^4$ 9.7524	35 $^2P^{\circ}_{3/2}$ **Br** Bromine 79.904 $[Ar]3d^{10}4s^24p^5$ 11.8138	36 $^1S_0$ **Kr** Krypton 83.798 $[Ar]3d^{10}4s^24p^6$ 13.9996
5	37 $^2S_{1/2}$ **Rb** Rubidium 85.4678 $[Kr]5s$ 4.1771	38 $^1S_0$ **Sr** Strontium 87.62 $[Kr]5s^2$ 5.6949	39 $^2D_{3/2}$ **Y** Yttrium 88.90585 $[Kr]4d5s^2$ 6.2173	40 $^3F_2$ **Zr** Zirconium 91.224 $[Kr]4d^25s^2$ 6.6339	41 $^6D_{1/2}$ **Nb** Niobium 92.90638 $[Kr]4d^45s$ 6.7589	42 $^7S_3$ **Mo** Molybdenum 95.94 $[Kr]4d^55s$ 7.0924	43 $^6S_{5/2}$ **Tc** Technetium (98) $[Kr]4d^55s^2$ 7.28	44 $^5F_5$ **Ru** Ruthenium 101.07 $[Kr]4d^75s$ 7.3605	45 $^4F_{9/2}$ **Rh** Rhodium 102.90550 $[Kr]4d^85s$ 7.4589	46 $^1S_0$ **Pd** Palladium 106.42 $[Kr]4d^{10}$ 8.3369	47 $^2S_{1/2}$ **Ag** Silver 107.8682 $[Kr]4d^{10}5s$ 7.5762	48 $^1S_0$ **Cd** Cadmium 112.411 $[Kr]4d^{10}5s^2$ 8.9938	49 $^2P^{\circ}_{1/2}$ **In** Indium 114.818 $[Kr]4d^{10}5s^25p$ 5.7864	50 $^3P_0$ **Sn** Tin 118.710 $[Kr]4d^{10}5s^25p^2$ 7.3439	51 $^4S^{\circ}_{3/2}$ **Sb** Antimony 121.760 $[Kr]4d^{10}5s^25p^3$ 8.6084	52 $^3P_2$ **Te** Tellurium 127.60 $[Kr]4d^{10}5s^25p^4$ 9.0096	53 $^2P^{\circ}_{3/2}$ **I** Iodine 126.90447 $[Kr]4d^{10}5s^25p^5$ 10.4513	54 $^1S_0$ **Xe** Xenon 131.293 $[Kr]4d^{10}5s^25p^6$ 12.1298
6	55 $^2S_{1/2}$ **Cs** Cesium 132.90545 $[Xe]6s$ 3.8939	56 $^1S_0$ **Ba** Barium 137.327 $[Xe]6s^2$ 5.2117		72 $^3F_2$ **Hf** Hafnium 178.49 $[Xe]4f^{14}5d^26s^2$ 6.8251	73 $^4F_{3/2}$ **Ta** Tantalum 180.9479 $[Xe]4f^{14}5d^36s^2$ 7.5496	74 $^5D_0$ **W** Tungsten 183.84 $[Xe]4f^{14}5d^46s^2$ 7.8640	75 $^6S_{5/2}$ **Re** Rhenium 186.207 $[Xe]4f^{14}5d^56s^2$ 7.8335	76 $^5D_4$ **Os** Osmium 190.23 $[Xe]4f^{14}5d^66s^2$ 8.4382	77 $^4F_{9/2}$ **Ir** Iridium 192.217 $[Xe]4f^{14}5d^76s^2$ 8.9670	78 $^3D_3$ **Pt** Platinum 195.078 $[Xe]4f^{14}5d^96s$ 8.9588	79 $^2S_{1/2}$ **Au** Gold 196.96655 $[Xe]4f^{14}5d^{10}6s$ 9.2255	80 $^1S_0$ **Hg** Mercury 200.59 $[Xe]4f^{14}5d^{10}6s^2$ 10.4375	81 $^2P^{\circ}_{1/2}$ **Tl** Thallium 204.3833 $[Hg]6p$ 6.1082	82 $^3P_0$ **Pb** Lead 207.2 $[Hg]6p^2$ 7.4167	83 $^4S^{\circ}_{3/2}$ **Bi** Bismuth 208.98038 $[Hg]6p^3$ 7.2855	84 $^3P_2$ **Po** Polonium (209) $[Hg]6p^4$ 8.414	85 $^2P^{\circ}_{3/2}$ **At** Astatine (210) $[Hg]6p^5$	86 $^1S_0$ **Rn** Radon (222) $[Hg]6p^6$ 10.7485
7	87 $^2S_{1/2}$ **Fr** Francium (223) $[Rn]7s$ 4.0727	88 $^1S_0$ **Ra** Radium (226) $[Rn]7s^2$ 5.2784		104 $^3F_2$? **Rf** Rutherfordium (261) $[Rn]5f^{14}6d^27s^2$? 6.0 ?	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (277)	109 **Mt** Meitnerium (268)	110 **Uun** Ununnilium (281)	111 **Uuu** Unununium (272)	112 **Uub** Ununbium (285)		114 **Uuq** Ununquadium (289)		116 **Uuh** Ununhexium (292)		

Lanthanides	57 $^2D_{3/2}$ **La** Lanthanum 138.9055 $[Xe]5d6s^2$ 5.5769	58 $^1G^{\circ}_4$ **Ce** Cerium 140.116 $[Xe]4f5d6s^2$ 5.5387	59 $^4I^{\circ}_{9/2}$ **Pr** Praseodymium 140.90765 $[Xe]4f^36s^2$ 5.473	60 $^5I_4$ **Nd** Neodymium 144.24 $[Xe]4f^46s^2$ 5.5250	61 $^6H^{\circ}_{5/2}$ **Pm** Promethium (145) $[Xe]4f^56s^2$ 5.582	62 $^7F_0$ **Sm** Samarium 150.36 $[Xe]4f^66s^2$ 5.6437	63 $^8S^{\circ}_{7/2}$ **Eu** Europium 151.964 $[Xe]4f^76s^2$ 5.6704	64 $^9D^{\circ}_2$ **Gd** Gadolinium 157.25 $[Xe]4f^75d6s^2$ 6.1498	65 $^6H^{\circ}_{15/2}$ **Tb** Terbium 158.92534 $[Xe]4f^96s^2$ 5.8638	66 $^5I_8$ **Dy** Dysprosium 162.500 $[Xe]4f^{10}6s^2$ 5.9389	67 $^4I^{\circ}_{15/2}$ **Ho** Holmium 164.93032 $[Xe]4f^{11}6s^2$ 6.0215	68 $^3H_6$ **Er** Erbium 167.259 $[Xe]4f^{12}6s^2$ 6.1077	69 $^2F^{\circ}_{7/2}$ **Tm** Thulium 168.93421 $[Xe]4f^{13}6s^2$ 6.1843	70 $^1S_0$ **Yb** Ytterbium 173.04 $[Xe]4f^{14}6s^2$ 6.2542	71 $^2D_{3/2}$ **Lu** Lutetium 174.967 $[Xe]4f^{14}5d6s^2$ 5.4259
Actinides	89 $^2D_{3/2}$ **Ac** Actinium (227) $[Rn]6d7s^2$ 5.17	90 $^3F_2$ **Th** Thorium 232.0381 $[Rn]6d^27s^2$ 6.3067	91 $^4K_{11/2}$ **Pa** Protactinium 231.03588 $[Rn]5f^26d7s^2$ 5.89	92 $^5L^{\circ}_6$ **U** Uranium 238.02891 $[Rn]5f^36d7s^2$ 6.1941	93 $^6L_{11/2}$ **Np** Neptunium (237) $[Rn]5f^46d7s^2$ 6.2657	94 $^7F_0$ **Pu** Plutonium (244) $[Rn]5f^67s^2$ 6.0260	95 $^8S^{\circ}_{7/2}$ **Am** Americium (243) $[Rn]5f^77s^2$ 5.9738	96 $^9D^{\circ}_2$ **Cm** Curium (247) $[Rn]5f^76d7s^2$ 5.9914	97 $^6H^{\circ}_{15/2}$ **Bk** Berkelium (247) $[Rn]5f^97s^2$ 6.1979	98 $^5I_8$ **Cf** Californium (251) $[Rn]5f^{10}7s^2$ 6.2817	99 $^4I^{\circ}_{15/2}$ **Es** Einsteinium (252) $[Rn]5f^{11}7s^2$ 6.42	100 $^3H_6$ **Fm** Fermium (257) $[Rn]5f^{12}7s^2$ 6.50	101 $^2F^{\circ}_{7/2}$ **Md** Mendelevium (258) $[Rn]5f^{13}7s^2$ 6.58	102 $^1S_0$ **No** Nobelium (259) $[Rn]5f^{14}7s^2$ 6.65	103 $^2P^{\circ}_{1/2}$? **Lr** Lawrencium (262) $[Rn]5f^{14}7s^27p$? 4.9 ?

Atomic Number: 58
Ground-state Level: $^1G^{\circ}_4$
Symbol: **Ce**
Name: Cerium
Atomic Weight†: 140.116
Ground-state Configuration: $[Xe]4f5d6s^2$
Ionization Energy (eV): 5.5387

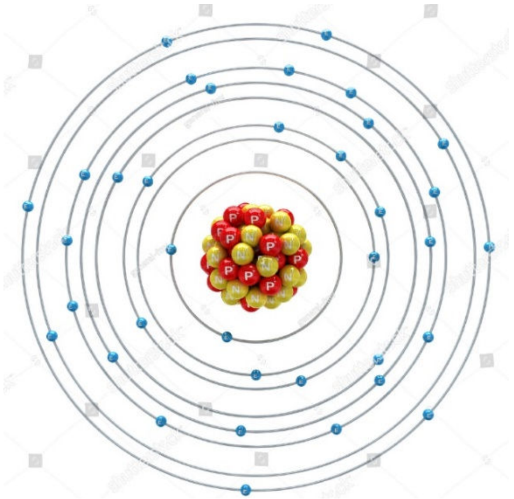
†Based upon ^{12}C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

氪-83同位素

核稳定



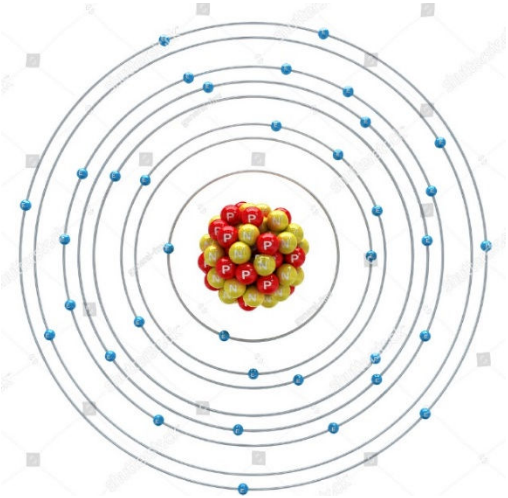
36个电子

核：36 质子，47 中子

重量：83个氢原子

氪-81同位素

核衰变，半衰期 23万年



36个电子

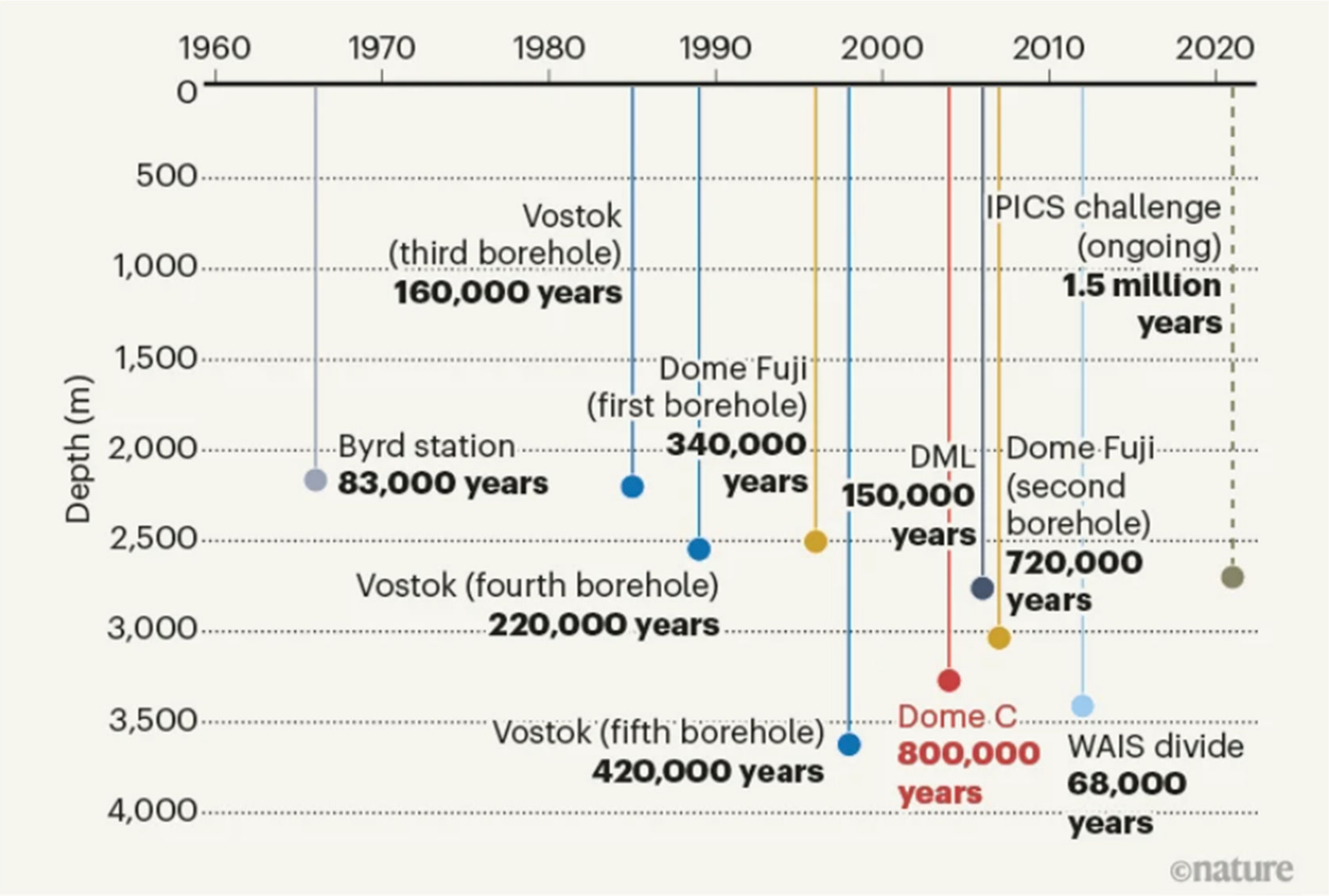
核：36 质子，45 中子

重量：81个氢原子

$$\text{氪-81同位素丰度} = \frac{\text{氪-81原子数目}}{\text{氪-83原子数目}}$$

Nature, News and Views | 10 June 2024
Kawamura & Oyabu

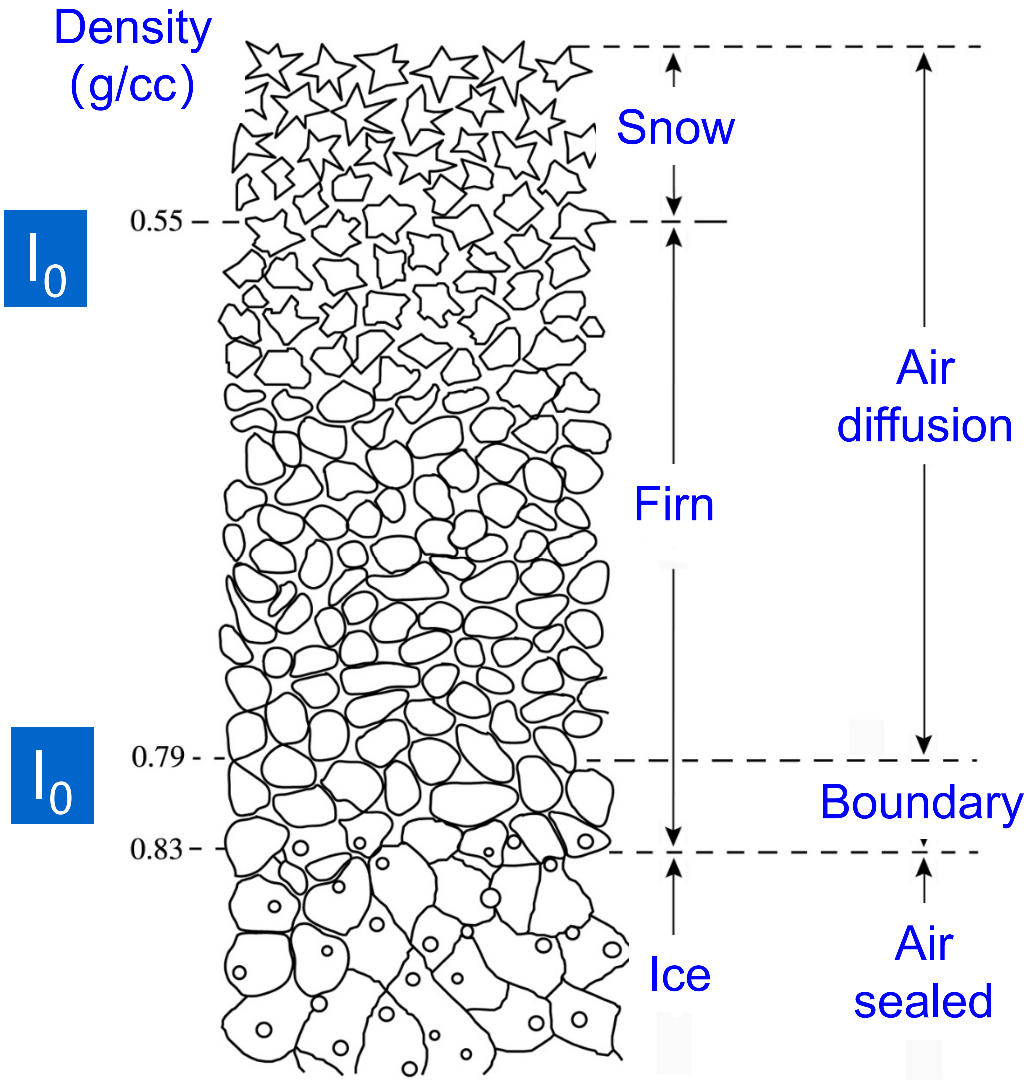
Two decades of deep ice cores from Antarctica



BEYOND
EPICA
OLDEST ICE

Jan. 2025
2800 m
1.2 million years and beyond

Radioactive Gas Isotopes for Dating



I_0

I_0

$I_{sample} < I_0$

Raynaud D and Chappellaz J. (1993)

Cosmic Ray

$^{80}\mathrm{Kr}(\mathrm{n}，\ \gamma)^{81}\mathrm{Kr}$

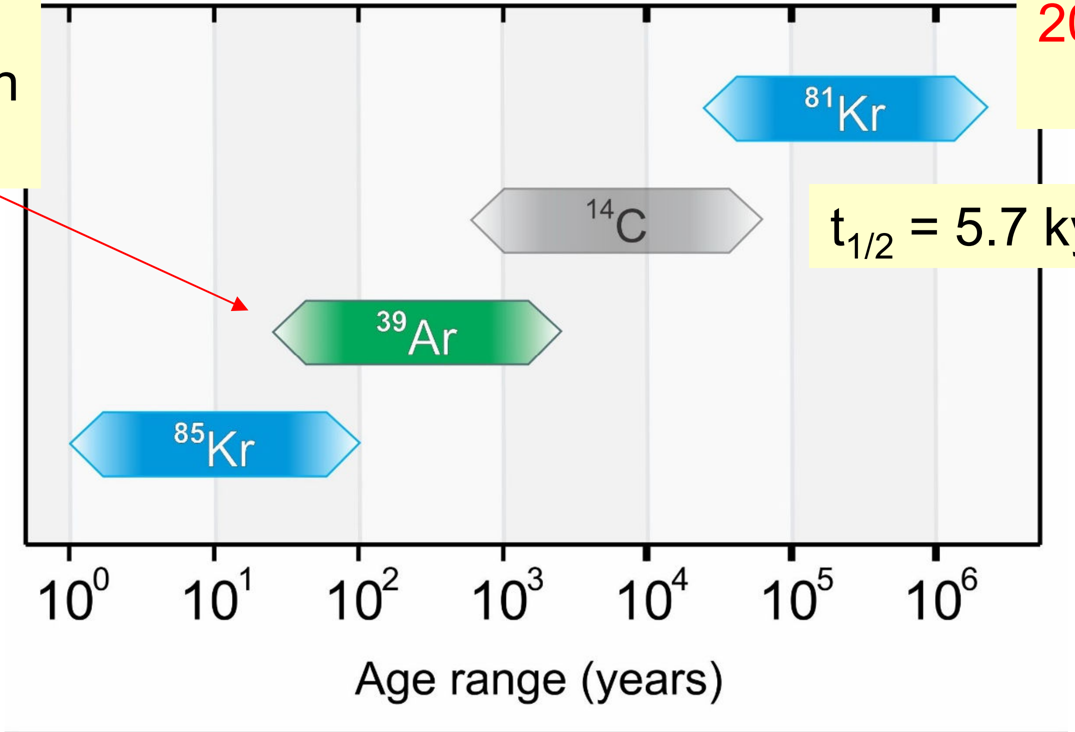
Gas → Uniform distribution in the atmosphere

Isotopic abundance I_0

$$\frac{I_{sample}}{I_0} = 2^{-\left(\frac{\mathrm{Age}}{\mathrm{Half-life}}\right)}$$

Radioactive gas isotopes for tracing / dating

- Gas: Even distribution around the world
- Inert: Simple production, transport and deposition process



Alpine ice
Ocean circulation
$t_{1/2}$ = 302 yr

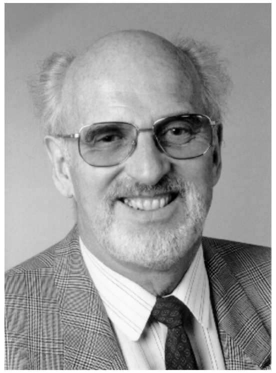
Leak check
$t_{1/2}$ = 11 yr

20 kyr – 1.5 Myr
$t_{1/2}$ = 230 kyr

$t_{1/2}$ = 5.7 kyr

^{85}Kr, ^{39}Ar, ^{81}Kr: Ideal isotopes for dating / tracing

Motivation and Challenges



Hans Oeschger
1927 – 1998

Hugo Loosli
1936 – 2021

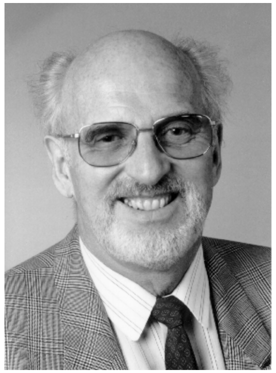
- ^{81}Kr and ^{39}Ar are ideal dating isotopes

  -- Loosli & Oeschger, Earth Planet Sci. Lett. (1969)

- Analyses difficult due to extremely low isotopic abundances

	Half-life	Isotopic abundance	Atoms per liter of water
^{85}Kr	11 yr	2 x 10^{-11}	30,000
^{81}Kr	230 kyr	6 x 10^{-13}	1,000
^{39}Ar	302 yr	8 x 10^{-16}	8,000

Motivation and Challenges


Hans Oeschger
1927 – 1998


Hugo Loosli
1936 – 2021

- ➢ ^{81}Kr and ^{39}Ar are ideal dating isotopes

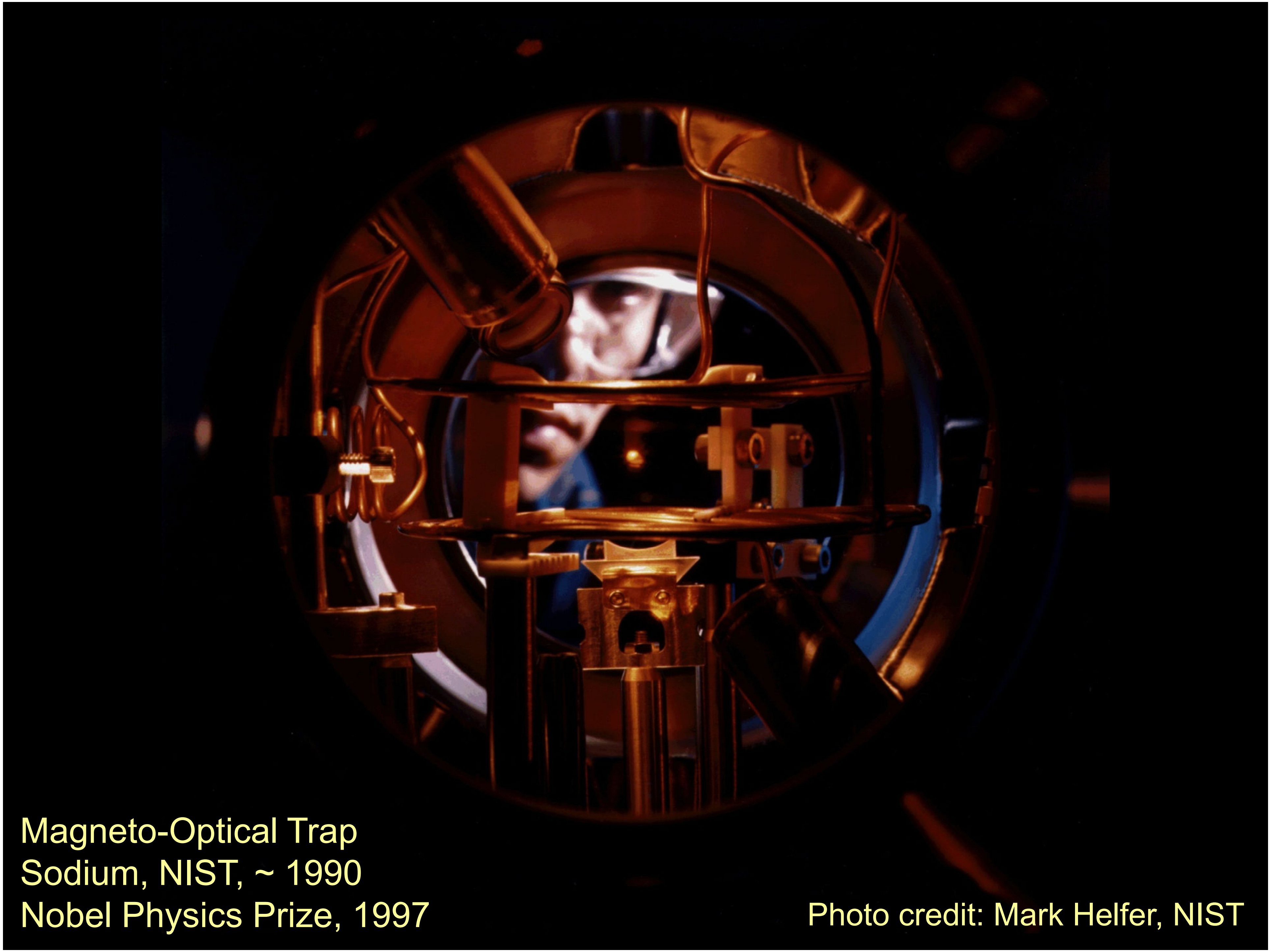
  -- Loosli & Oeschger, Earth Planet Sci. Lett. (1969)

- ➢ Analyses difficult due to extremely low isotopic abundances

1）会有重大影响

2）原理上没问题，不违反任何基本物理定律

3）实践上不可能



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

Photo credit: Mark Helfer, NIST

"for development of methods to cool and trap atoms with laser light"

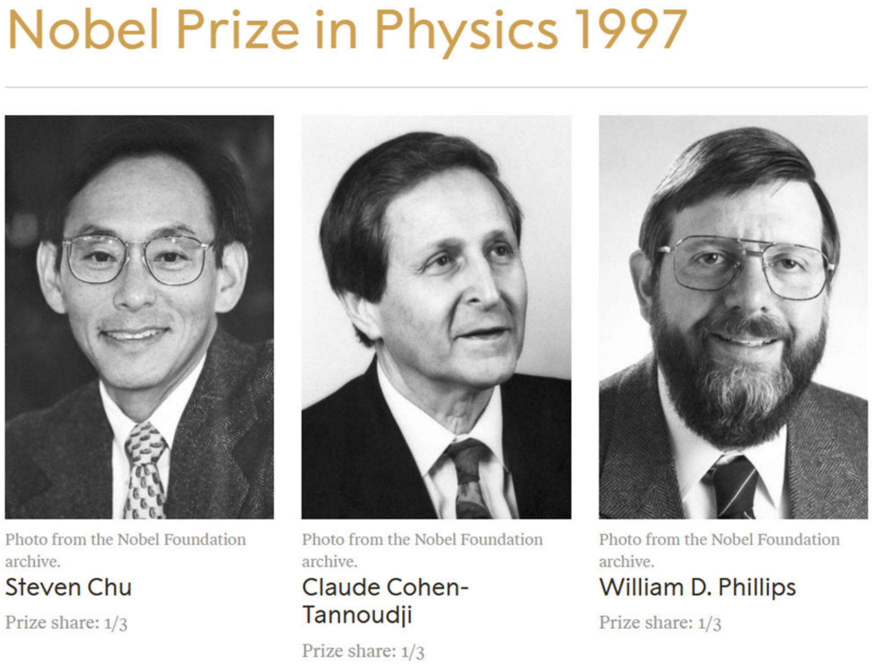

Nobel Prize in Physics 1997

Photo from the Nobel Foundation archive.
Steven Chu
Prize share: 1/3

Photo from the Nobel Foundation archive.
Claude Cohen-Tannoudji
Prize share: 1/3

Photo from the Nobel Foundation archive.
William D. Phillips
Prize share: 1/3

Laser force on a neutral Kr atom

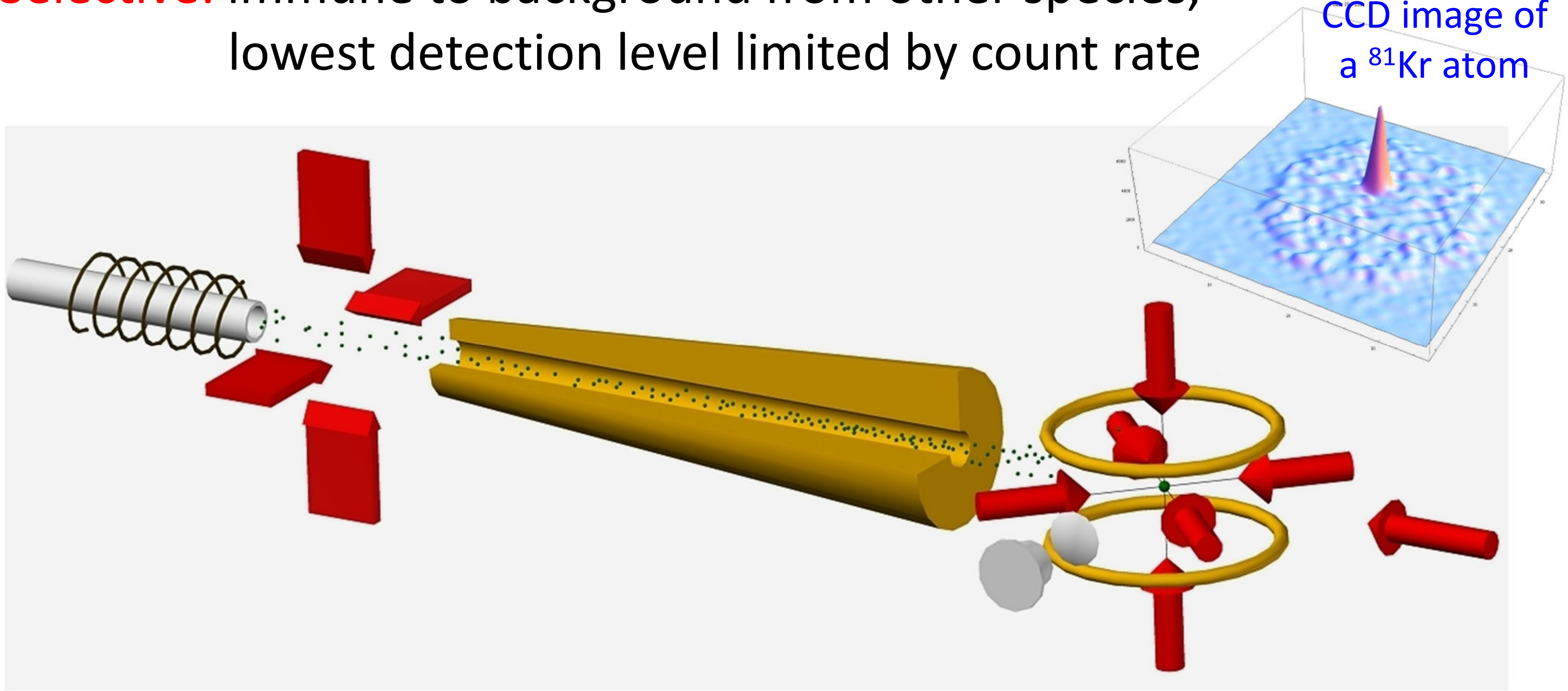
Photon momentum: $p = \dfrac{h}{\lambda}$

- Planck's constant:
  6×10^{-34} J·s
- Wavelength: 811 nm
- Single-photon recoil:
  dv = 6 mm/s
- Transition rate: 10^7 /s
- Acceleration:
  6 x 10^4 m/s^2
- Stopping distance: 1 m

Atom Trap Trace Analysis (ATTA)

Sensitive: single-atom detection

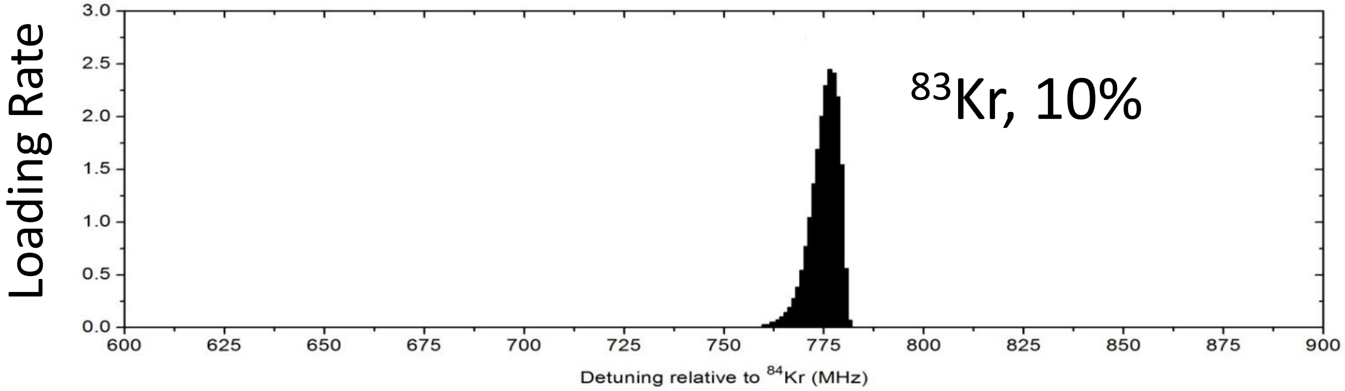
Selective: immune to background from other species,
lowest detection level limited by count rate

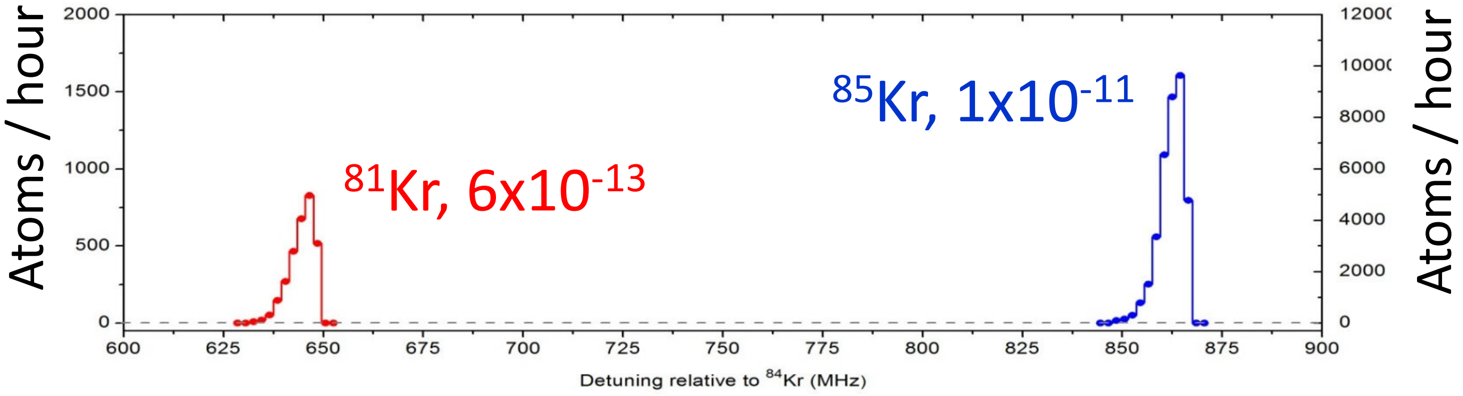


CCD image of
a ^{81}Kr atom

Ultrasensitive isotope trace analyses with a magneto-optical trap
C.Y. Chen, Y.M. Li, K. Bailey, T.P. O’Connor, L. Young, Z.-T. Lu. *Science* **286**, 1139 (1999)
Argonne National Laboratory, U.S.

Superb Selectivity: Repeated, Resonant Excitations





^{81}Kr/Kr = 6 x 10^{-13}

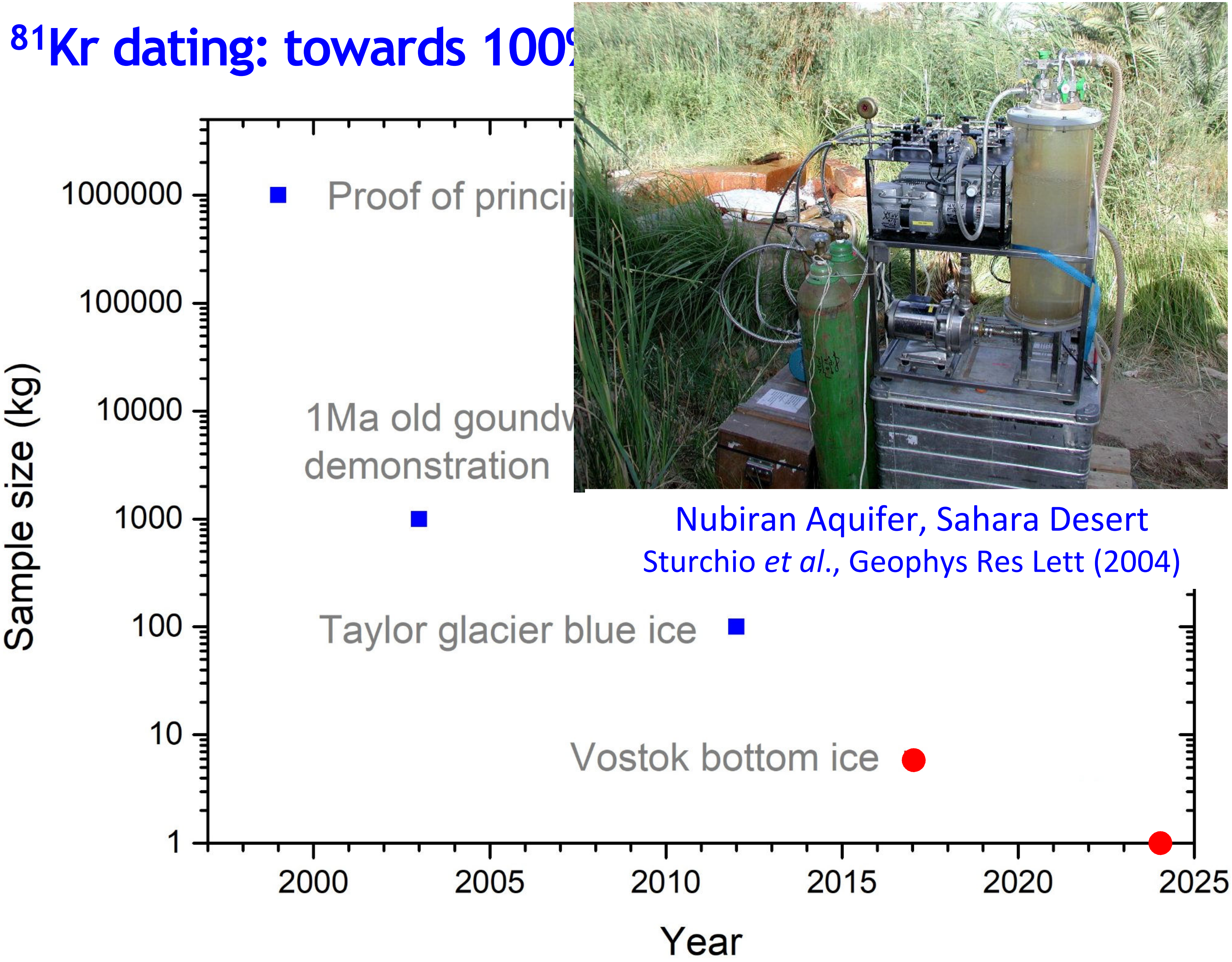
Cosmogenic

^{85}Kr/Kr = 2 x 10^{-11}

Nuclear industry

W. Jiang *et al.*, Geochim. Cosmochim. Acta **91**, 1 (2012)

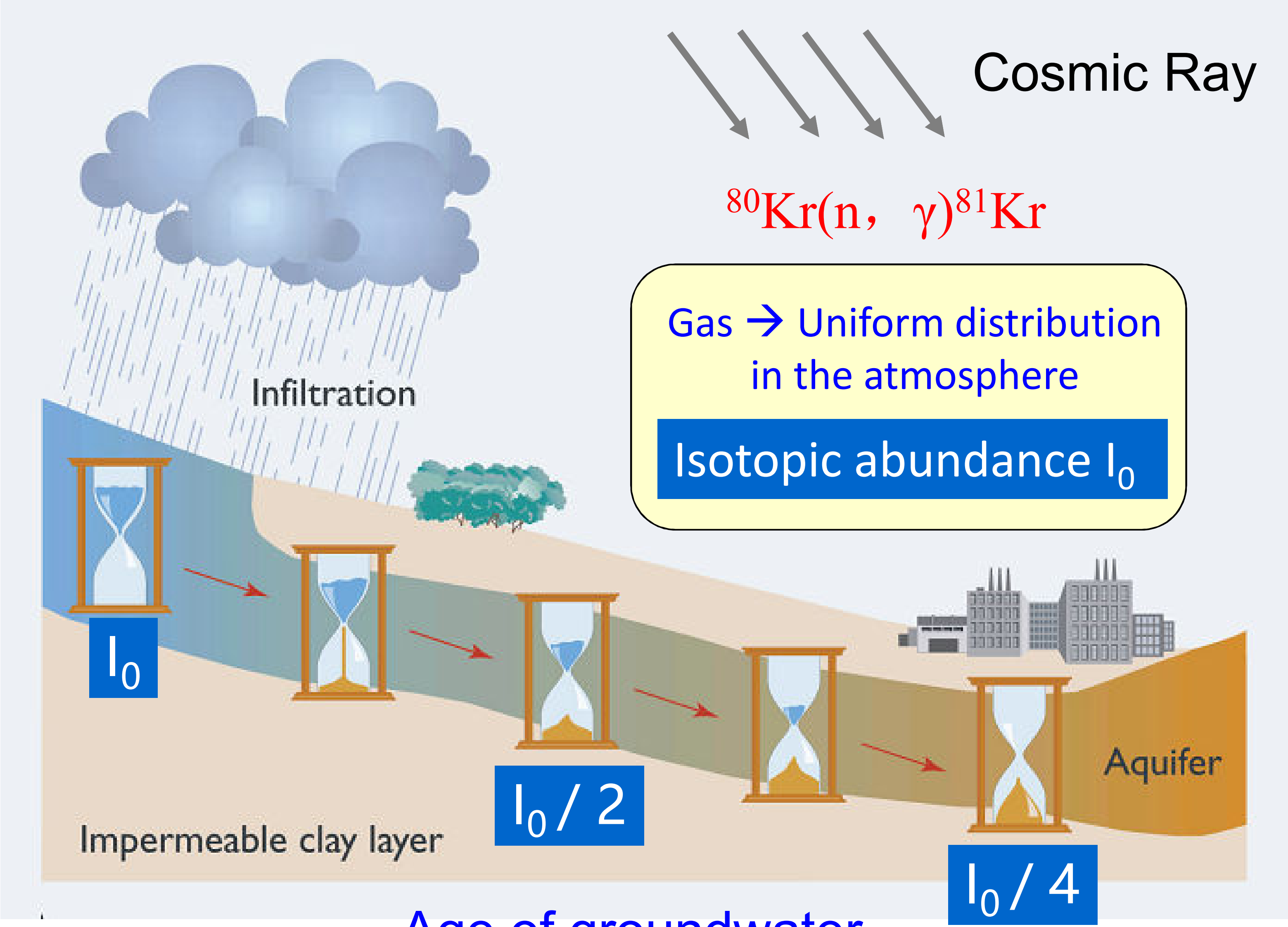
^{81}Kr dating: towards 100



Nubiran Aquifer, Sahara Desert

Sturchio *et al*., Geophys Res Lett (2004)

Radioactive Gas Isotopes for Dating / Tracing



$^{80}\mathrm{Kr}(n，\gamma)^{81}\mathrm{Kr}$

Gas → Uniform distribution in the atmosphere

Isotopic abundance I_0

Age of groundwater

Young → Old

In collaboration with earth and environmental scientists

Google: ATTA Primer

August 13, 2019 | vol. 116 | no. 33 | pp. 16153–16656

PNAS

Proceedings of the National Academy of Sciences of the United States of America

www.pnas.org

Groundwater source tracing using radiokrypton

High-pressure methane hydrate phase

Injected fluid diffusion and induced seismicity

Social genetic effects on adolescent smoking

Yeast antiviral pathway and apoptosis

Yokochi *et al.*, PNAS (2019)

Reika Yokochi
1975 – 2024

2005 PhD, Lorraine, with B. Marty
2008 – 2024 Univ. Chicago

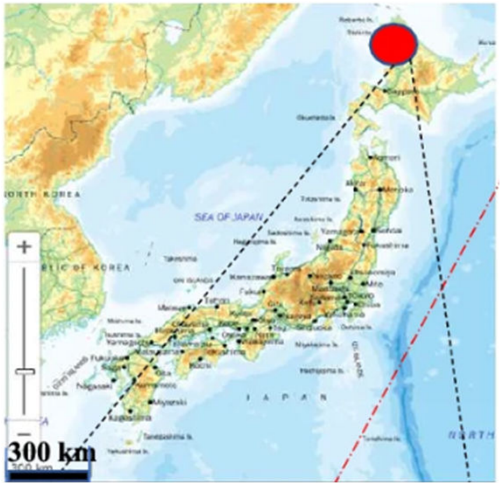
Radiokrypton unveils dual moisture sources of a deep desert aquifer

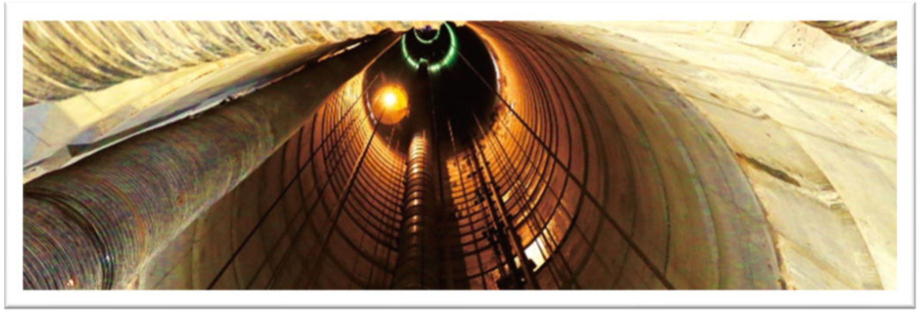
- Paleo-hydroclimate of Nubian Sandstone Aquifer in Negev Desert
- Resolved subsurface mixing and identified two distinct moisture sources of recharge:
    - Modern (< 38 ka)
    - 360 ± 30 ka

^{81}Kr dating of groundwater for assessment of deep geological repository in Japan

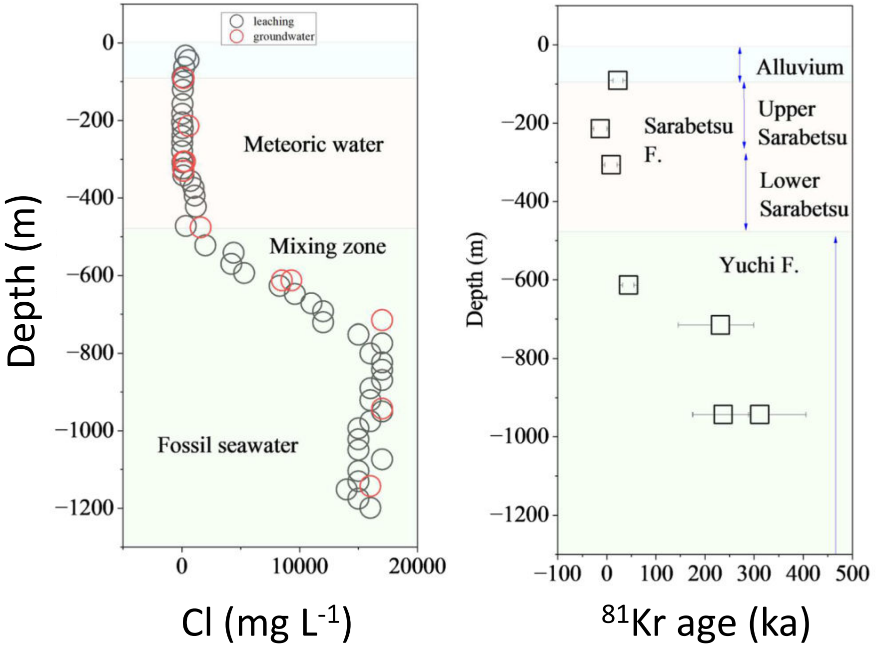
Ohta *et al.*, Sci. Rep. **14**, 15688 (2024)

- Groundwater ages 200 ~ 300 ka found under 700 m
- Two groundwater components identified
- Discrepancy among traditional dating methods resolved





Horonobe Underground
Research Center



Collaborations led by
International Atomic Energy Agency (IAEA) 国际原子能机构

CRP F33023: 2016 – 2023
--13 nations participated

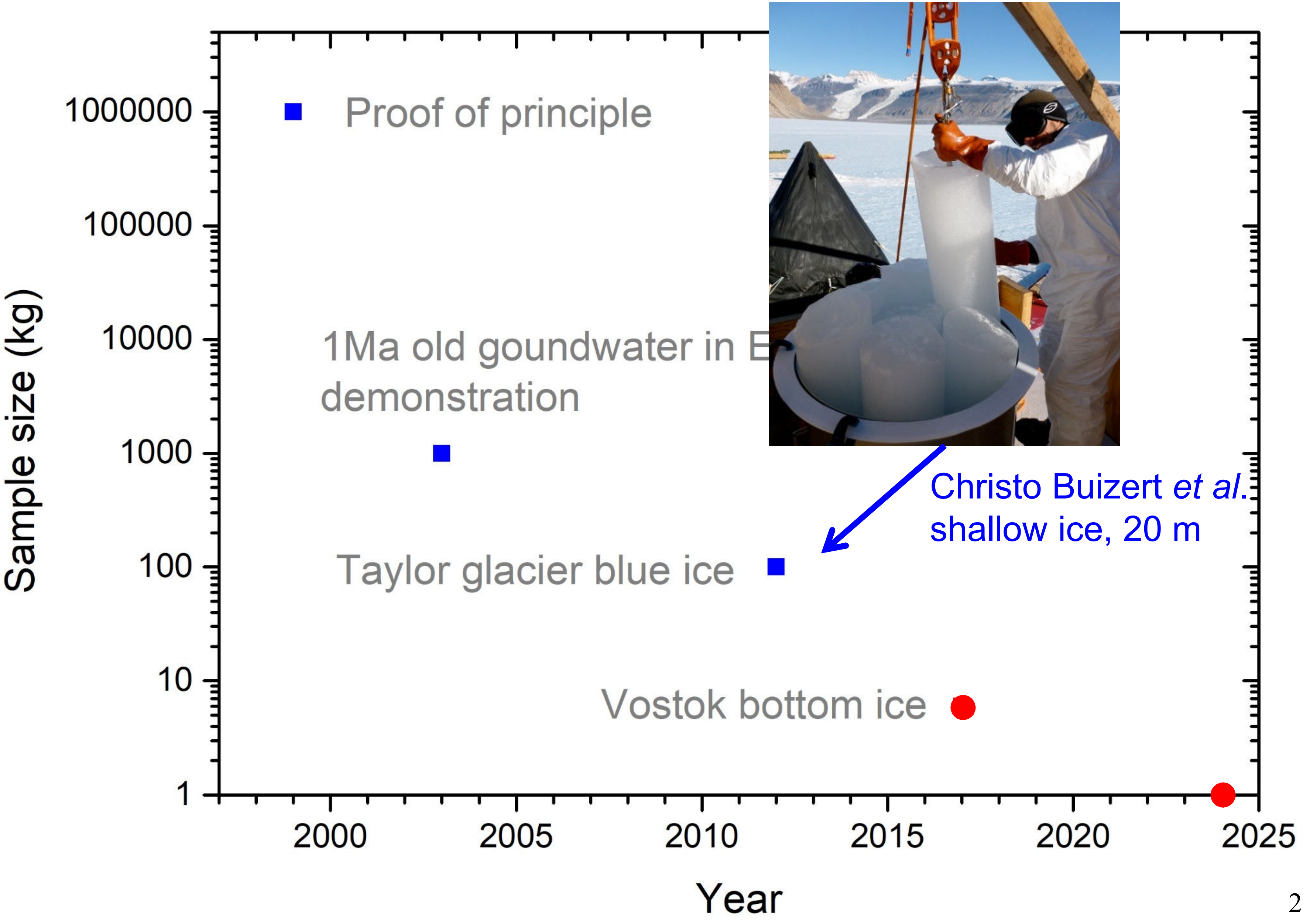
CRP F33028: 2024 – 2027
--15 nations participating

Asia: Cambodia, China
Australia: Australia
Africa: Algeria, Ethiopia, Morocco, Tunisia
Europe: Germany, Hungary, Switzerland, Turkiye
N. Am: Canada, USA
S. Am: Brazil, Argentina

IAEA
International Atomic Energy Agency
(/)

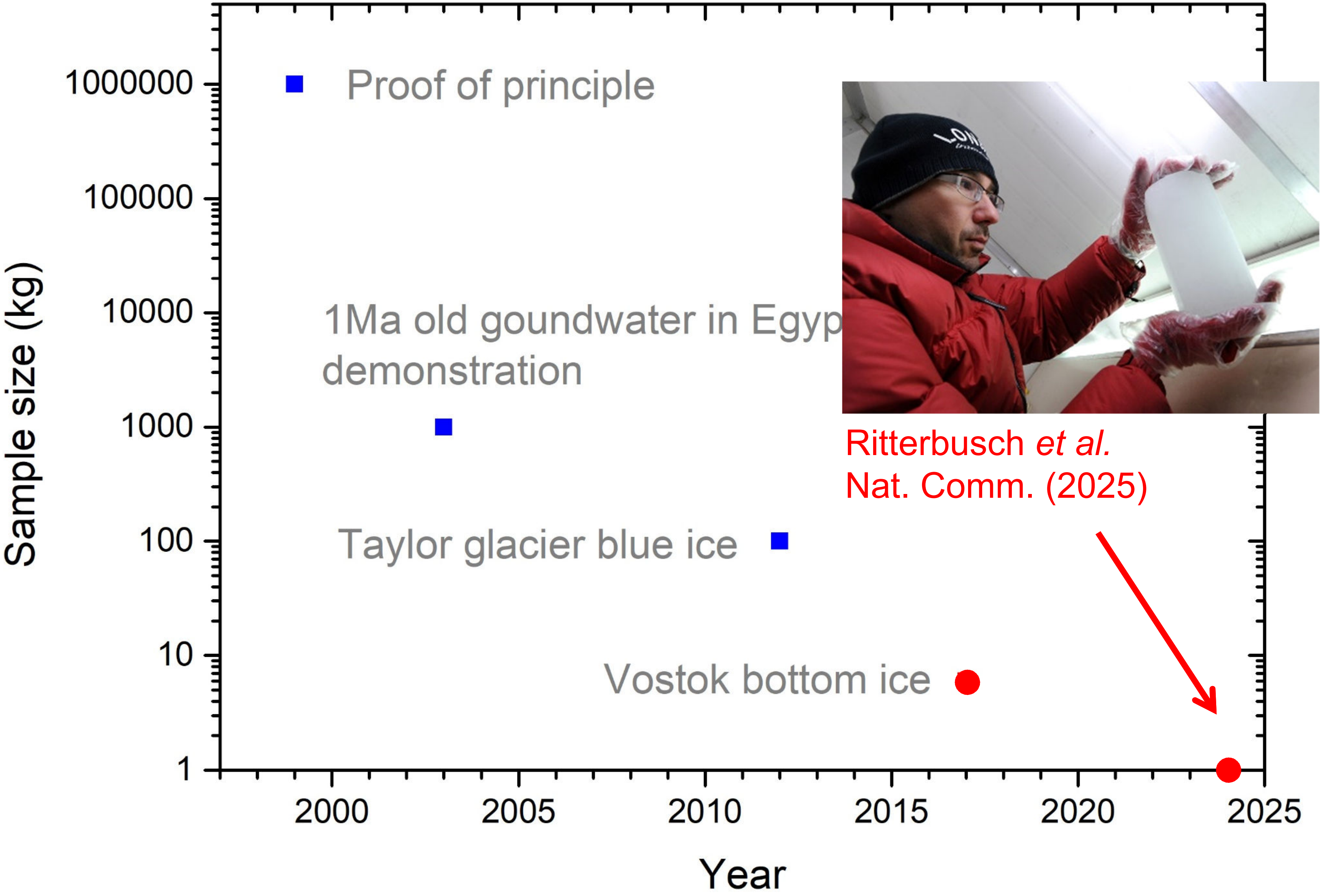
Use of Long-lived Radionuclides for Dating Very Old Groundwaters

^{81}Kr dating: towards 100% efficiency and < 1 kg of ice



Christo Buizert *et al.*
shallow ice, 20 m

^{81}Kr dating: towards 100% efficiency and < 1 kg of ice



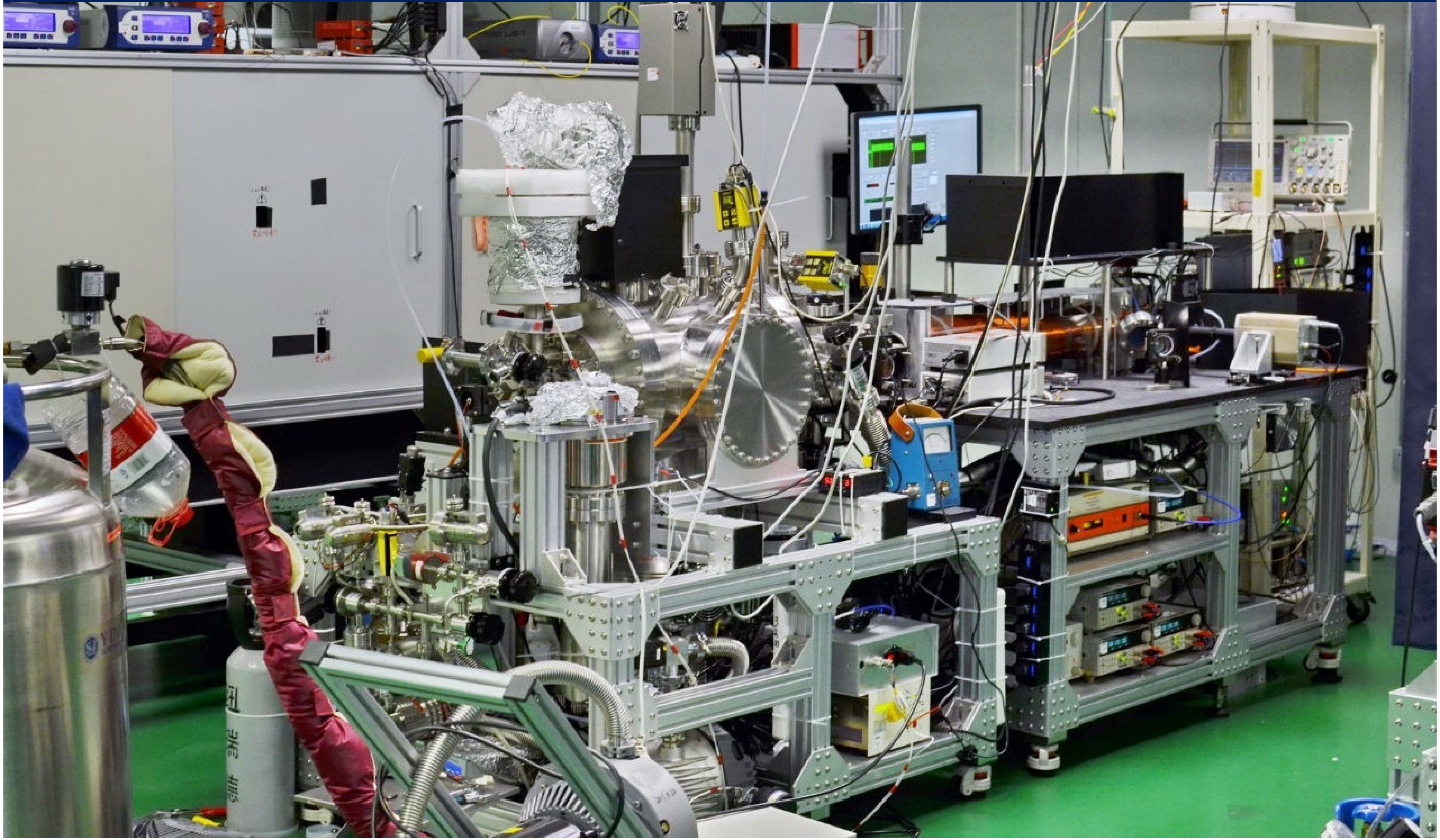
Ritterbusch *et al.*
Nat. Comm. (2025)

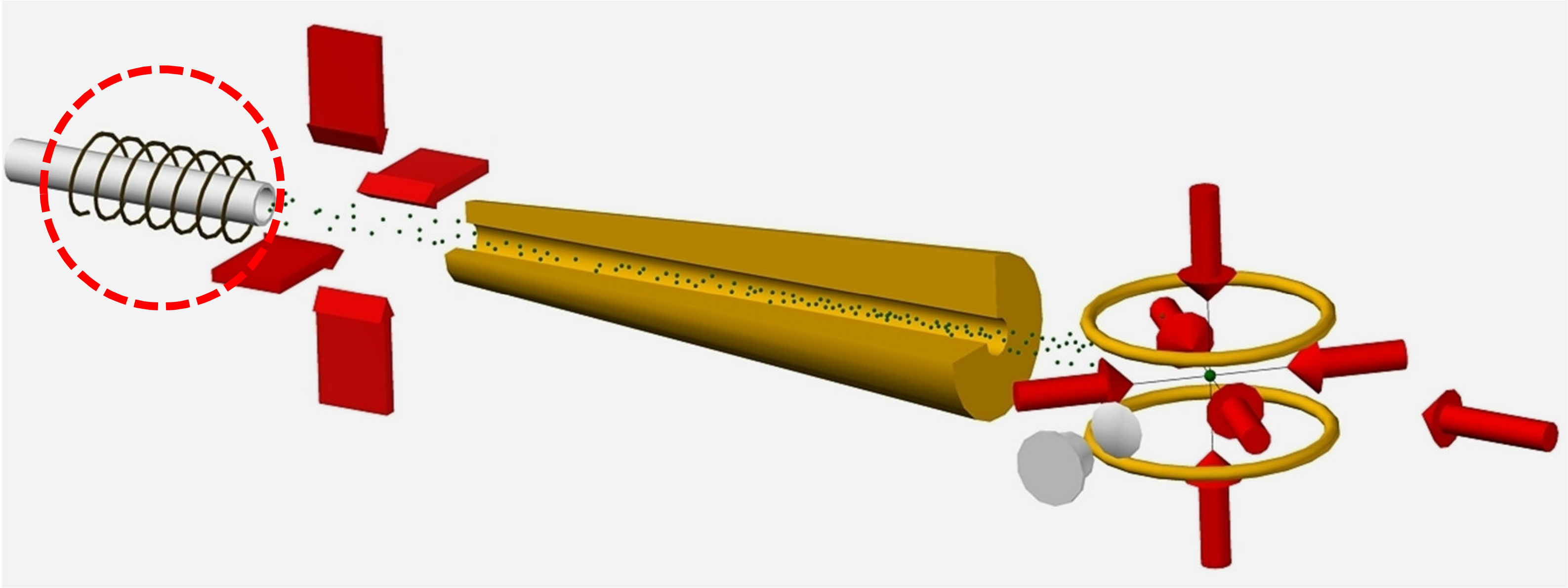
短期预测过于乐观

长期预测过于悲观

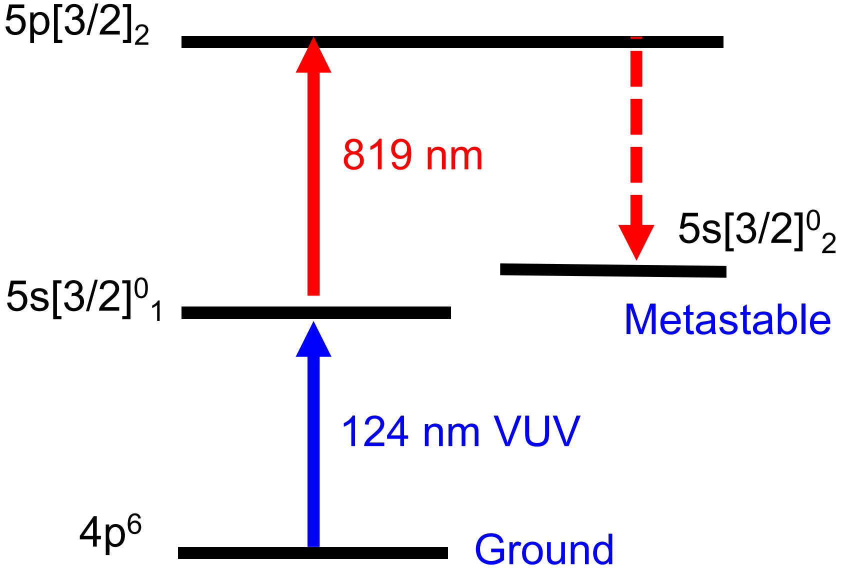
ATTA Instrument at USTC

- **Sensitive:** for rare isotope, single-atom detection
- **Fast:** for primary isotope, trap loading rate ~ 10^{13} s^{-1}
- **Efficient:** ~ 20%





All-Optical Production of Kr*



$5p[3/2]_2$

819 nm

$5s[3/2]^0_2$

$5s[3/2]^0_1$

Metastable

124 nm VUV

$4p^6$

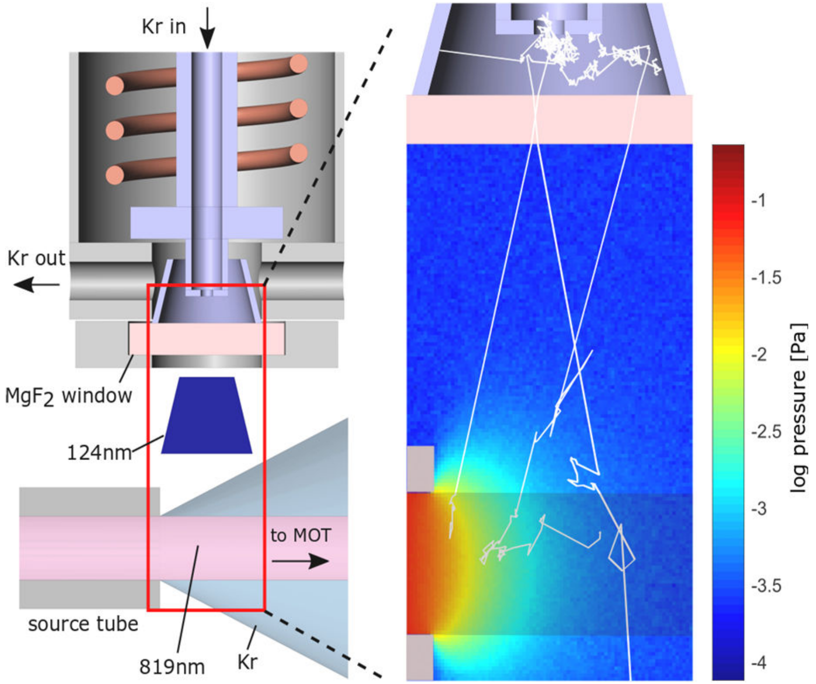
Ground

VUV + IR optical excitation

- Develop VUV lamp, FEL
- Brightness: 1 mW in 1 GHz

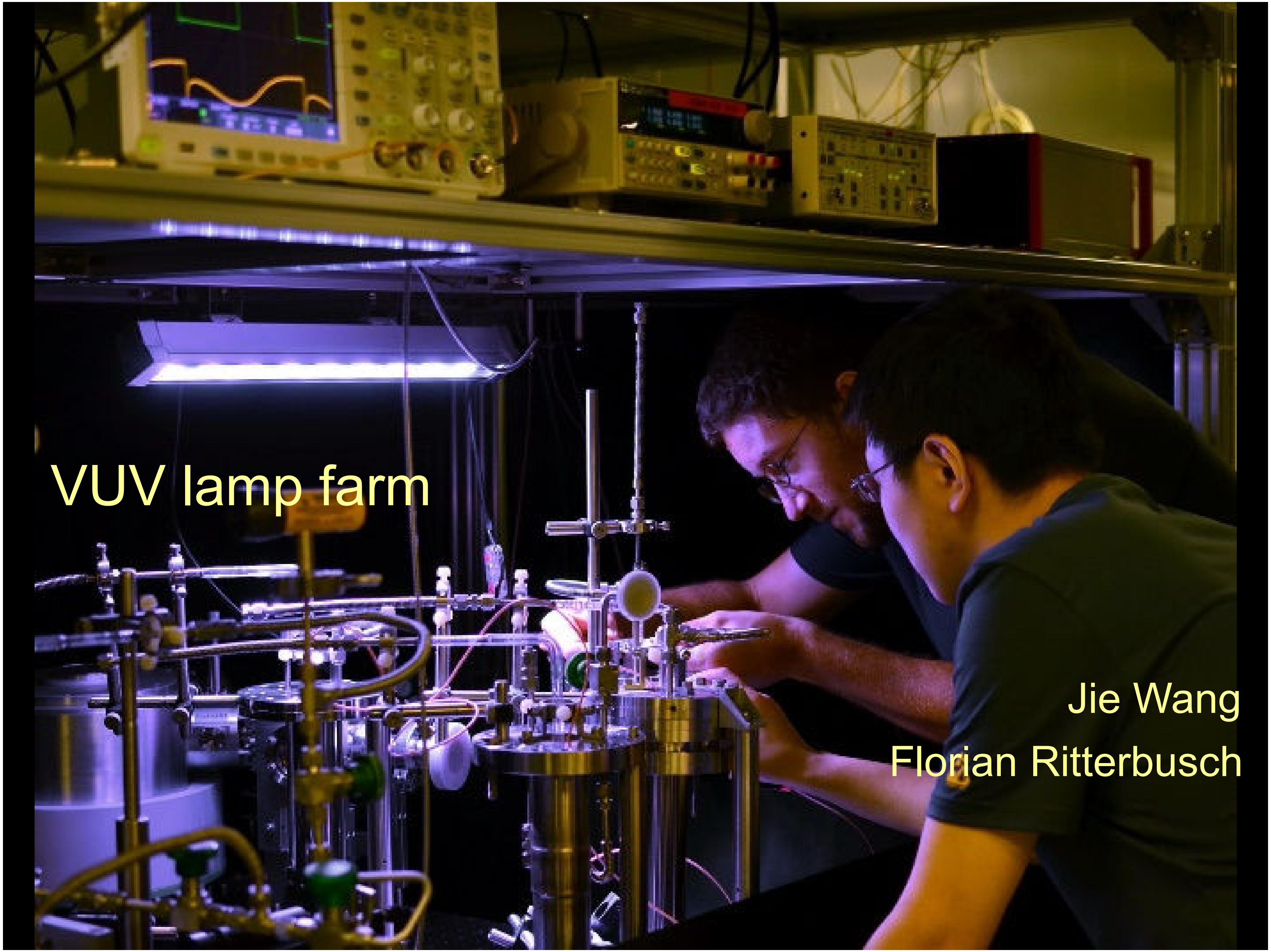
Memory effect eliminated

- Kr outgassing reduced to 20 pL / hr



Optical excitation and trapping of ^{81}Kr

Wang *et al.*, PRL **127**, 023201 (2021)

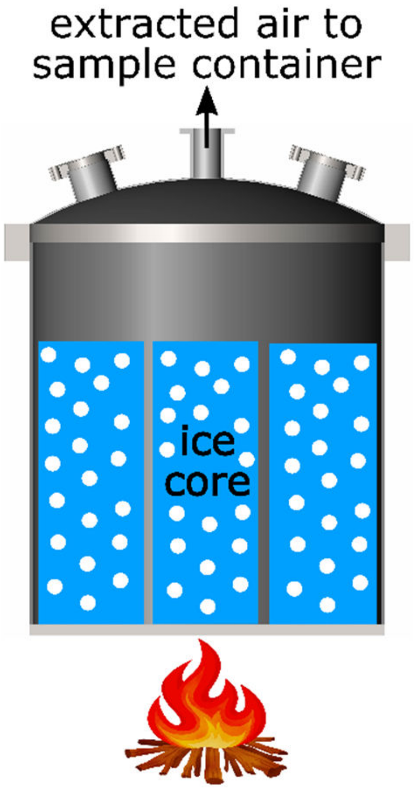


VUV lamp farm

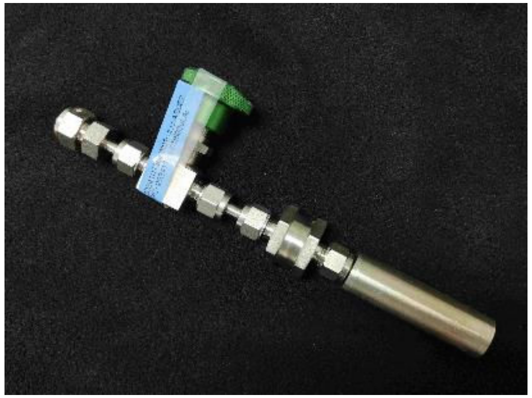
Jie Wang

Florian Ritterbusch

Radio-krypton Dating Procedure

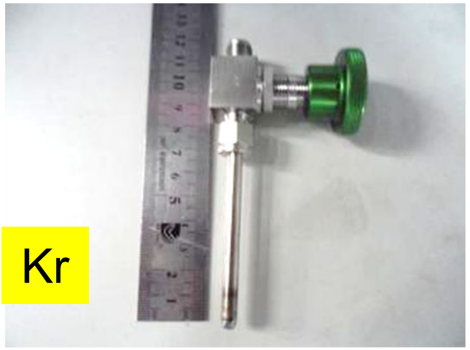


Gas extraction

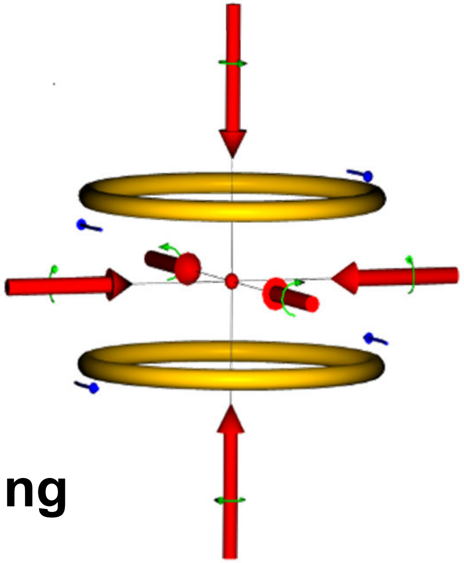


100 mL STP

Kr purification



100 nL STP



Atom counting

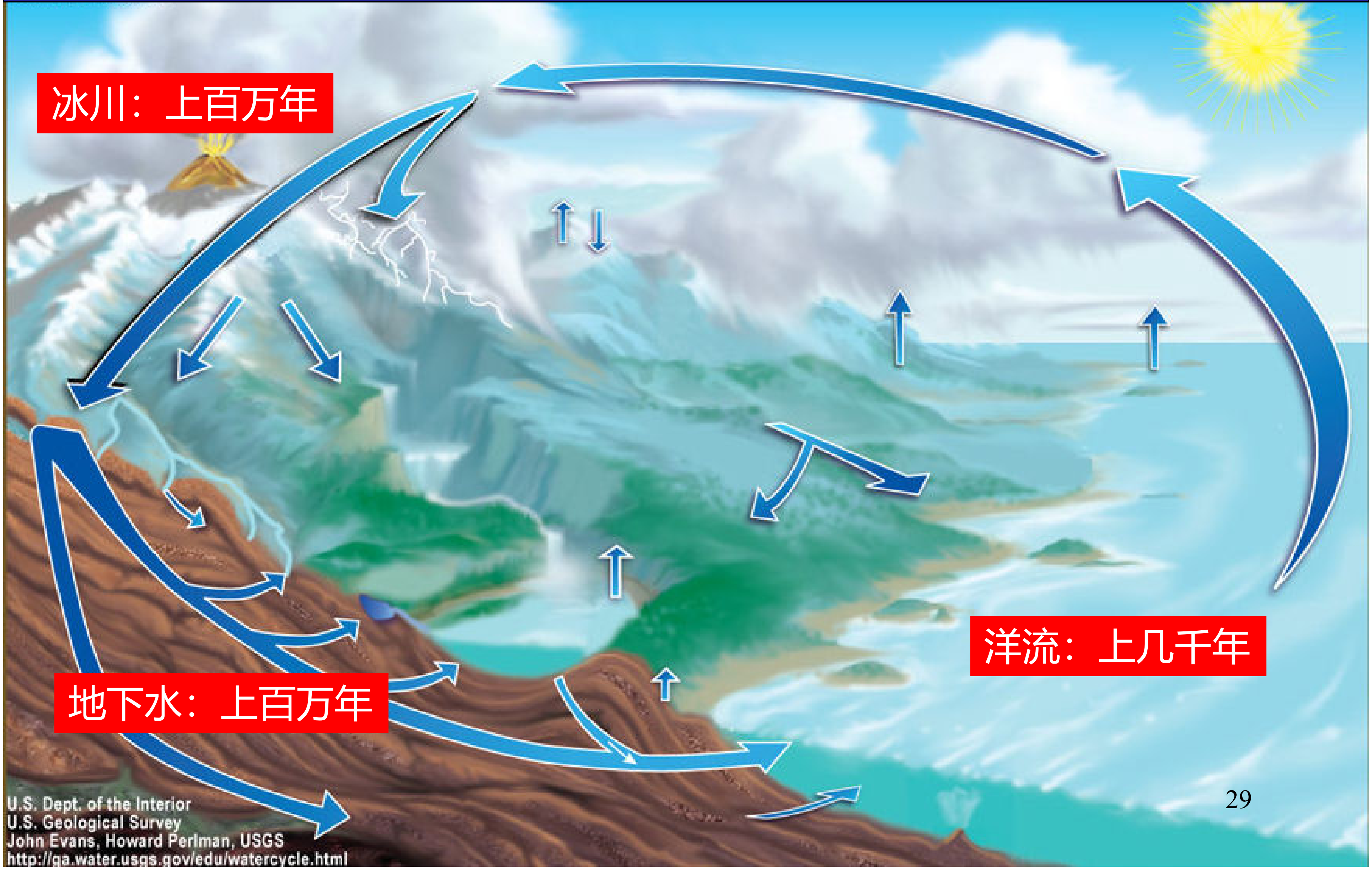
$$\frac{[{}^{81}\boldsymbol{Kr}/{}^{83}\boldsymbol{Kr}]_{sample}}{[{}^{81}\boldsymbol{Kr}/{}^{83}\boldsymbol{Kr}]_{air}} = 2^{-\left(\frac{\text{Age}}{\text{Half−life}}\right)}$$

When was Greenland Green?

- ERC Synergy Grant Project: When was Greenland green? – Perspectives from basal ice and sediments from ice cores (Green2Ice)
- ^{81}Kr dating of basal ice:
    - GISP2, Camp Century, NEEM, NGRIP, Dye-3, GRIP

Lead Scientist:
Dorthe Darl-Jesen
Niels Bohr Institute

核心科学目标:
为研究全球和区域水循环提供关键时间信息



冰川：上百万年

地下水：上百万年

洋流：上几千年

U.S. Dept. of the Interior
U.S. Geological Survey
John Evans, Howard Perlman, USGS
http://ga.water.usgs.gov/edu/watercycle.html