# 单原子灵敏检测
# 用于探索古老的冰与水

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中国科学技术大学 物理学院
中科院量子信息与量子科技创新研究院

物理学院 11月16日

创寰宇学府 育天下英才
严济慈 一九八八年五月题

中国科学技术大学
University of Science and Technology of China

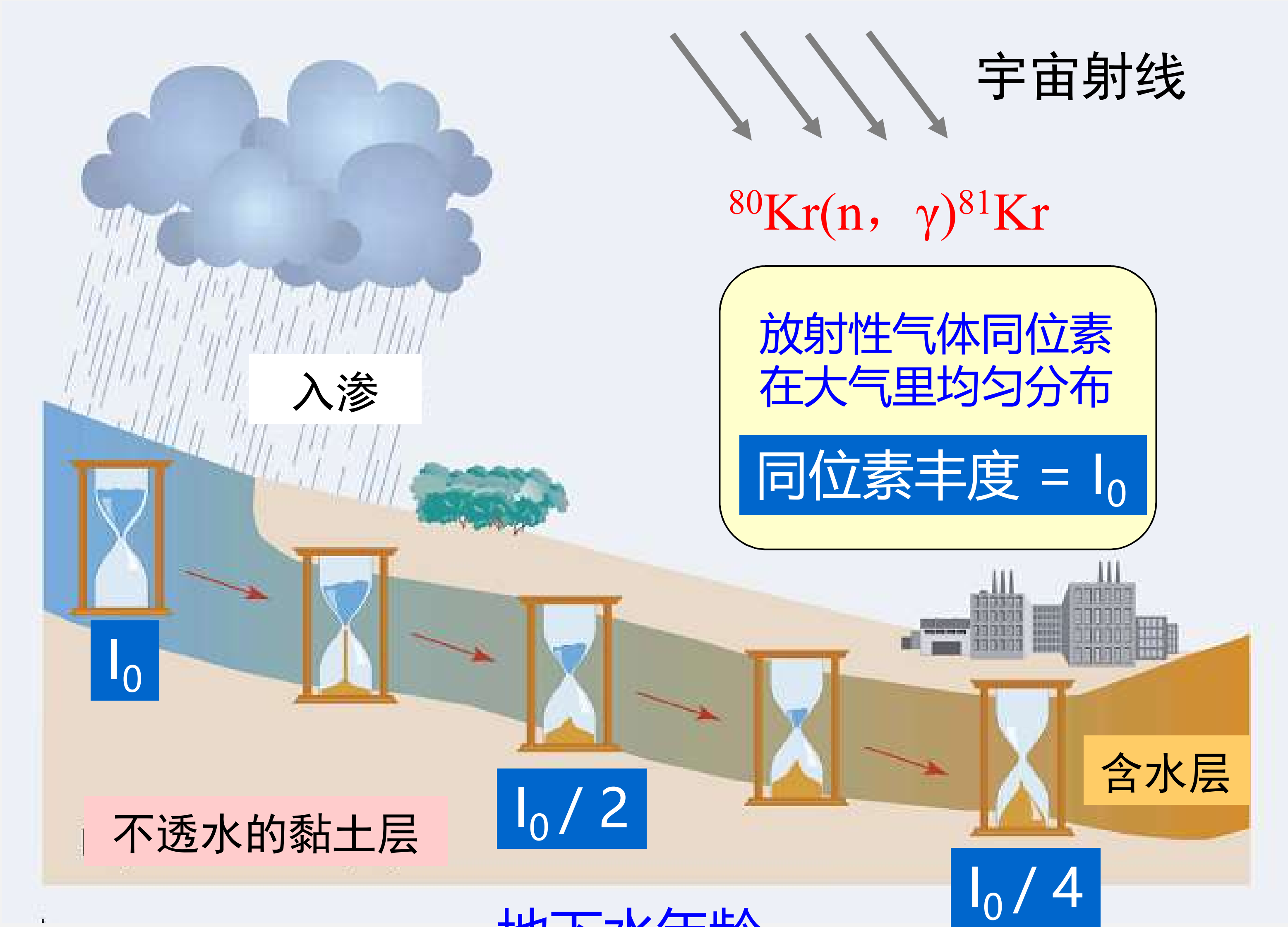
# 中科大激光痕量探测与精密测量实验室

atta.ustc.edu.cn

Z.-T. Lu, Y.-Q. Chu, X.-Z. Dong, J.-Q. Gu, S.-M. Hu, W. Jiang
F. Ritterbusch, A-M. Tong, W.-H. Wang, G.-M. Yang and L. Zhao

感谢支持：基金委、科技部、中科院 Supported by NSFC, MOST, CAS

# 放射性气体同位素定年原理



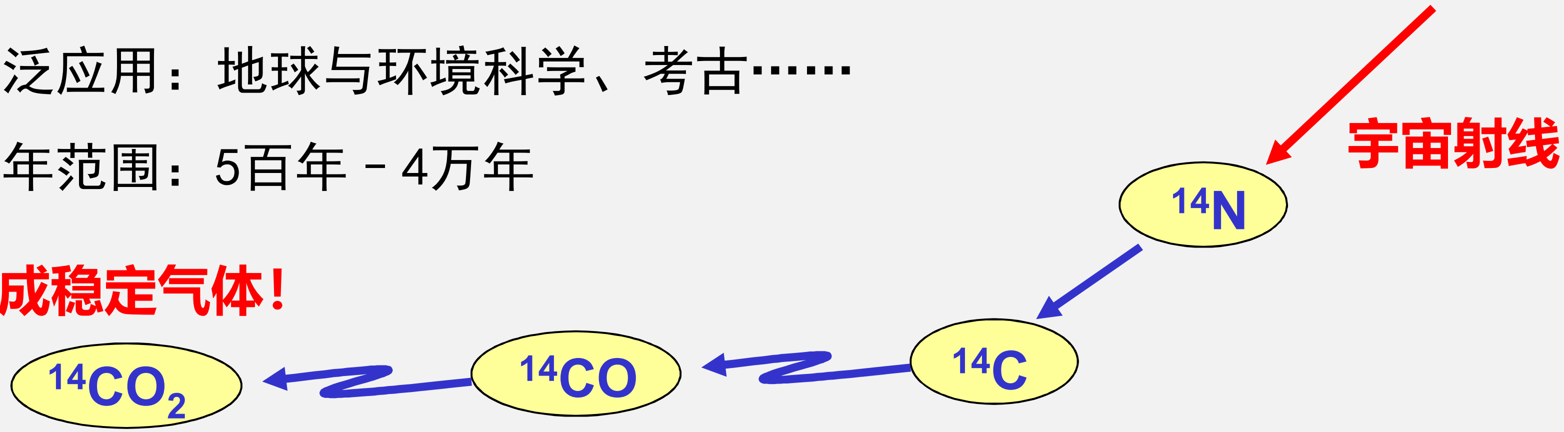

地下水年龄

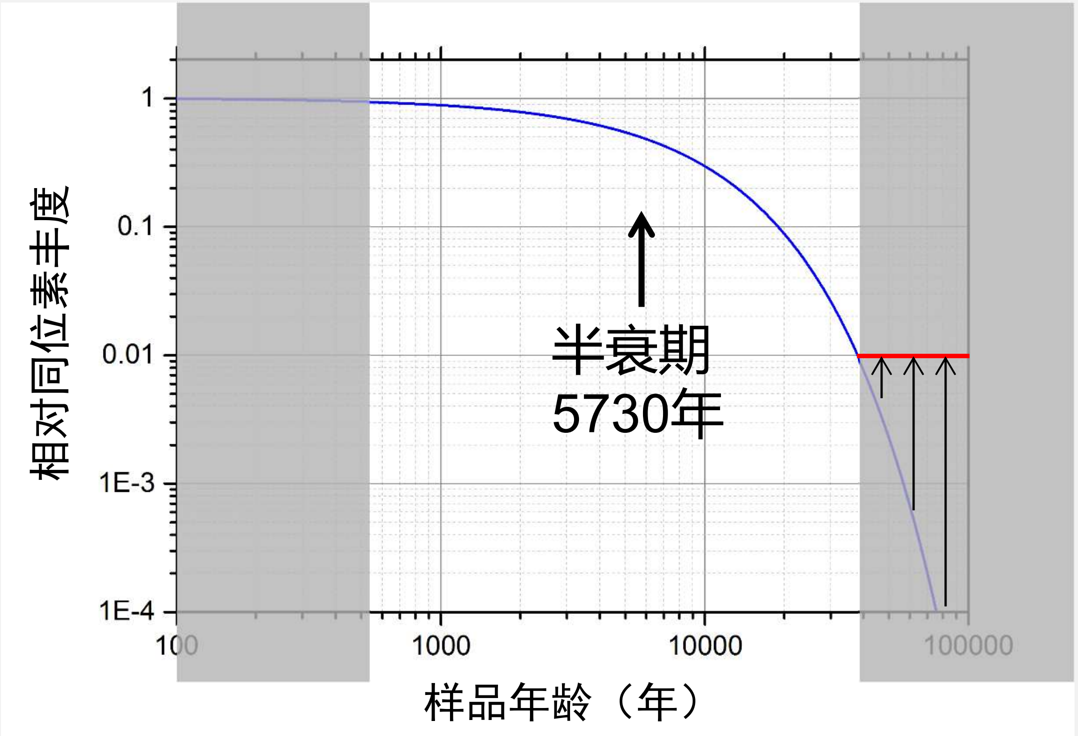
年轻 → 古老

# 碳-14 ($^{14}C$) 定年、示踪

- 广泛应用：地球与环境科学、考古……
- 定年范围：5百年 – 4万年

形成稳定气体！

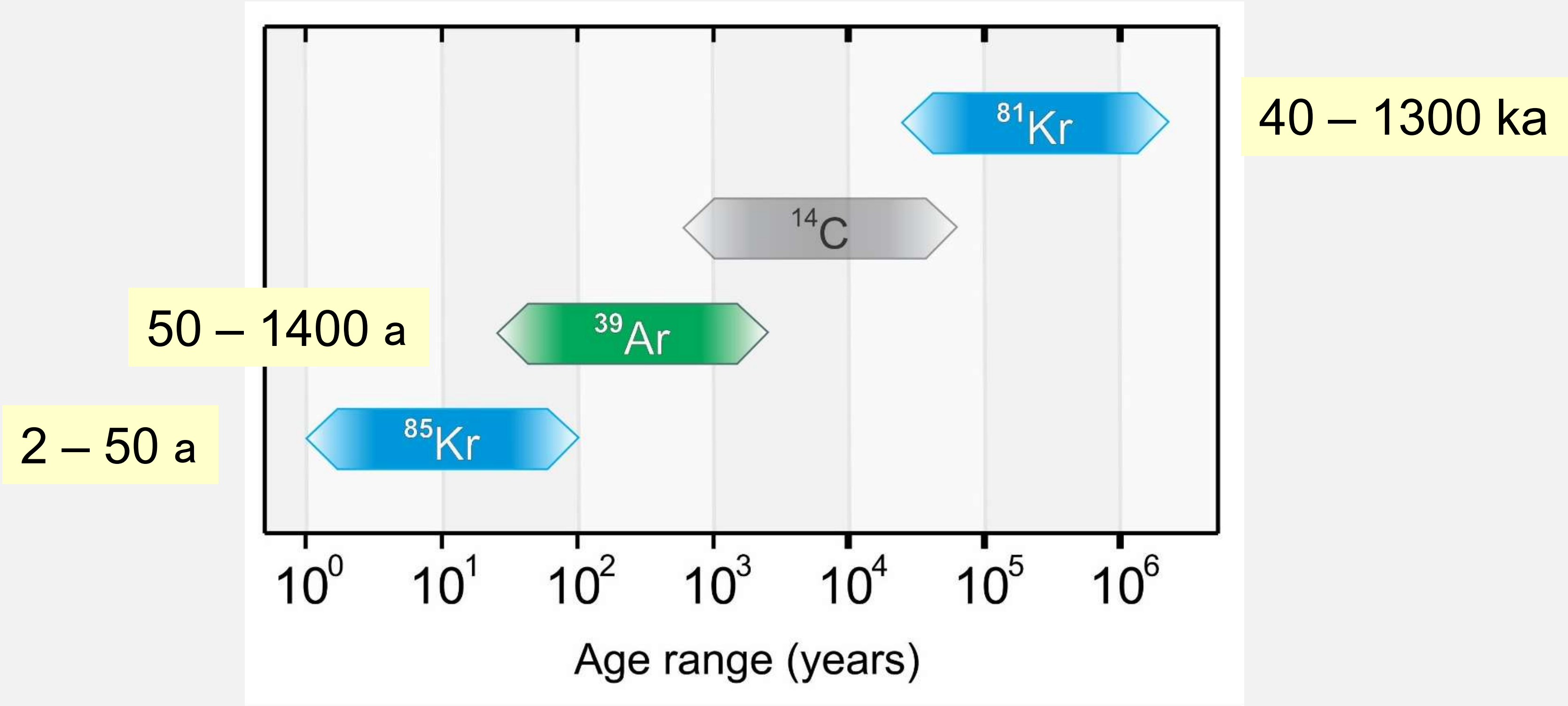



Willard Libby (1908-1980)
芝加哥大学
1960 诺贝尔化学奖

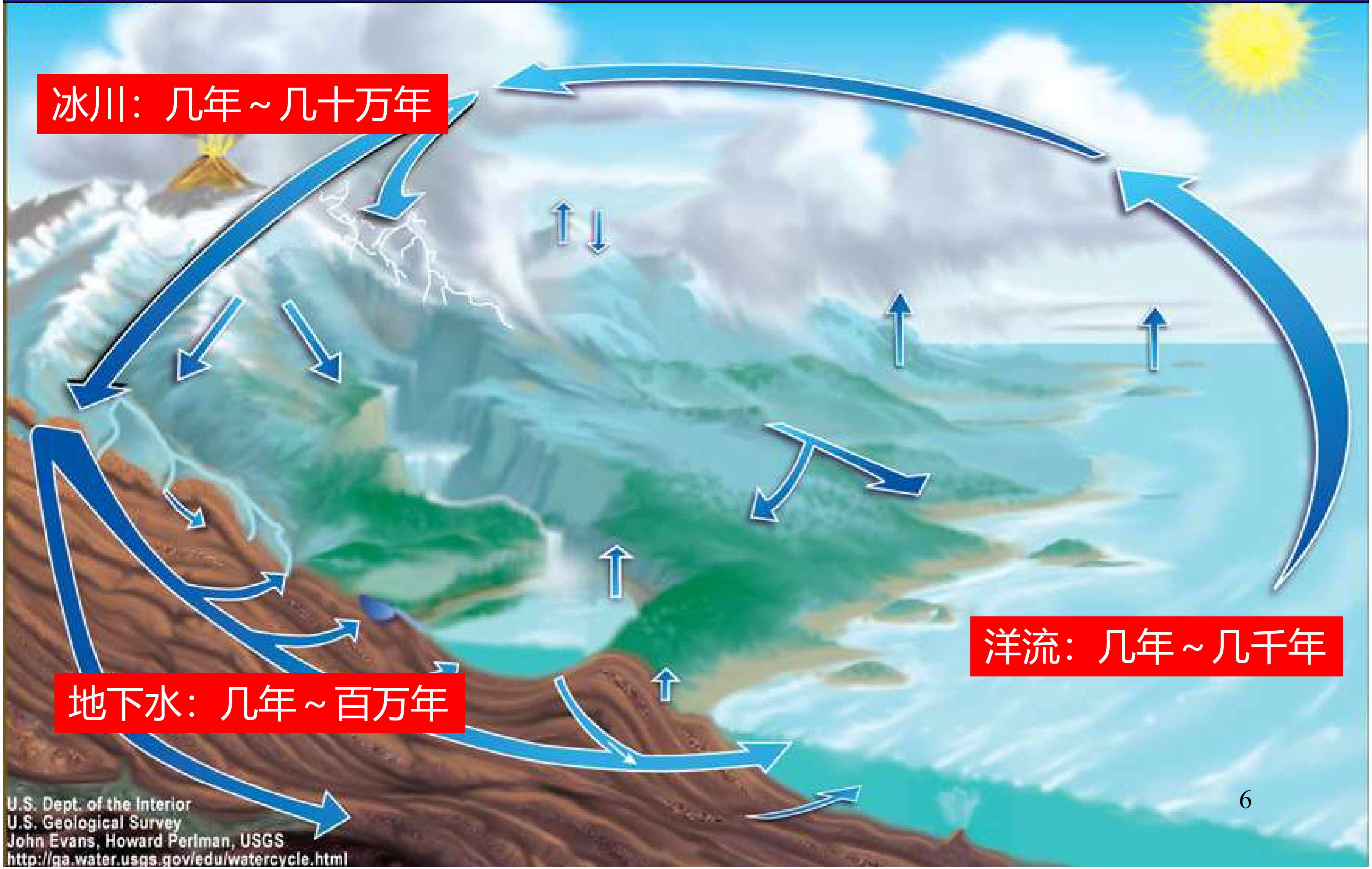
# 放射性气体同位素定年、示踪

- 气体：在大气中分布均匀、稳定。
- 惰性：无化学反应，输运机制简单。
- 与$^{14}C$一起，覆盖了从几年到140万年的范围。

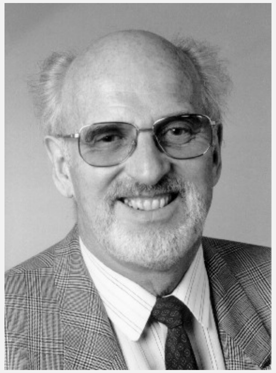



**$^{85}Kr$、$^{39}Ar$、$^{81}Kr$是理想的定年同位素**

# 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



# 科学意义和技术要求



Hans Oeschger
1927 – 1998

Hugo Loosli
1936 - 2021

- $^{81}Kr$、$^{39}Ar$等是环境水的理想测年同位素
  --Loosli & Oeschger, Earth Planet Sci. Lett. (1969)
- 测量极为困难：同位素丰度极低！

| | 产生机制 | 半衰期 | 同位素丰度 | 原子数 / 公斤水 |
|---|---|---|---|---|
| $^{85}Kr$ | 人工核裂变 | 11年 | $2 \times 10^{-11}$ | 30,000 |
| $^{81}Kr$ | 宇宙射线 | 23 万年 | $6 \times 10^{-13}$ | 1,000 |
| $^{39}Ar$ | 宇宙射线 | 269 年 | $8 \times 10^{-16}$ | 8,000 |

**技术要求**

- 高效率：数样品所含的原子
- 高选择：特定同位素分辨，抗干扰

# 物理方法的突破推动了定年与示踪技术的跳跃式发展

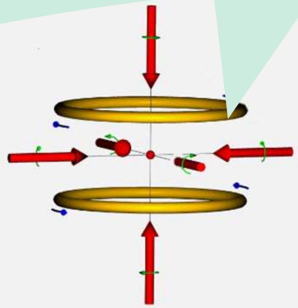
激光原子阱

$^{85}$Kr $^{39}$Ar $^{81}$Kr

同位素定年
与示踪技术

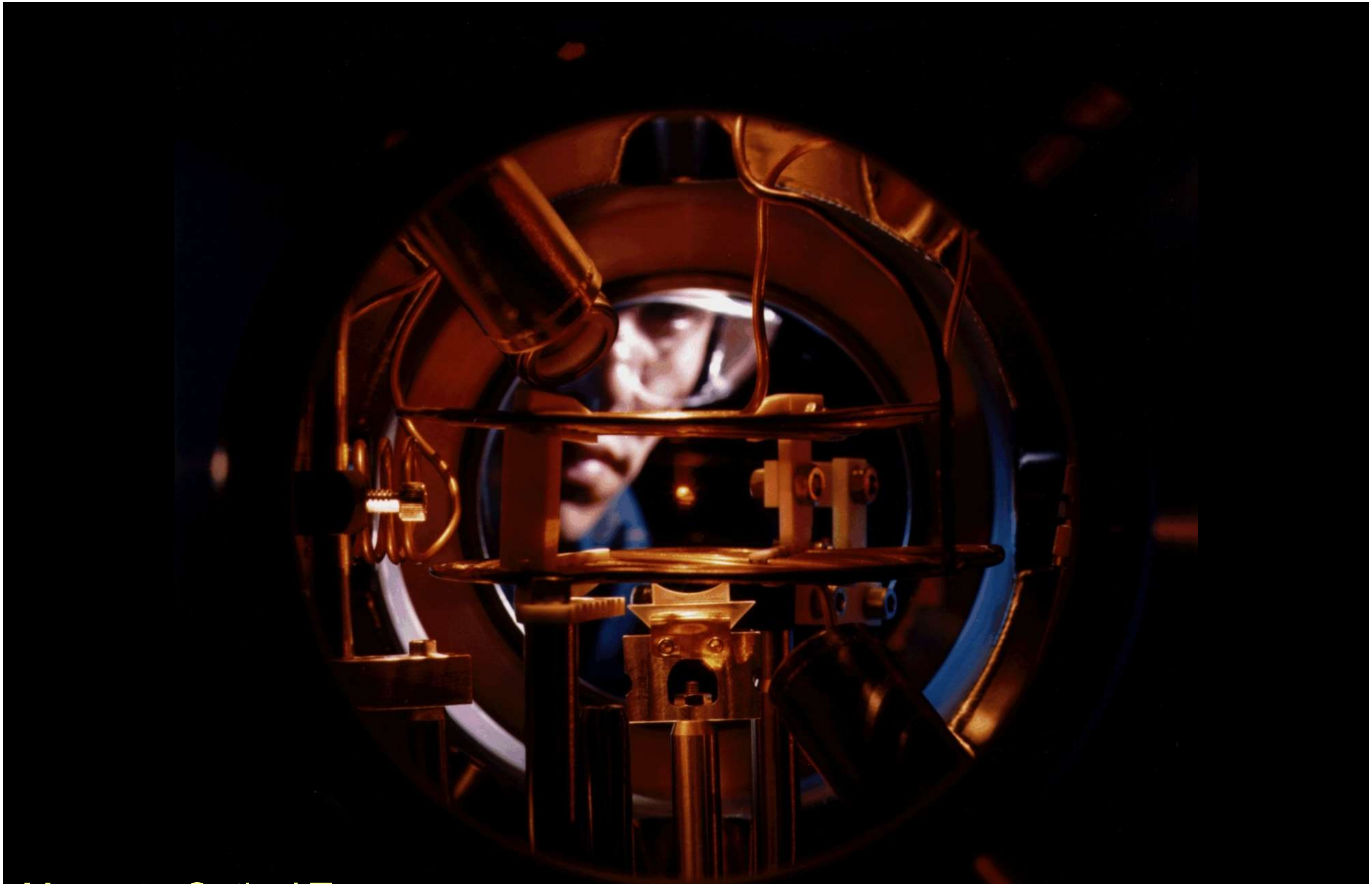
1970s 加速器质谱

$^{14}$C $^{10}$Be $^{36}$Cl



1920s 质谱

稳定同位素

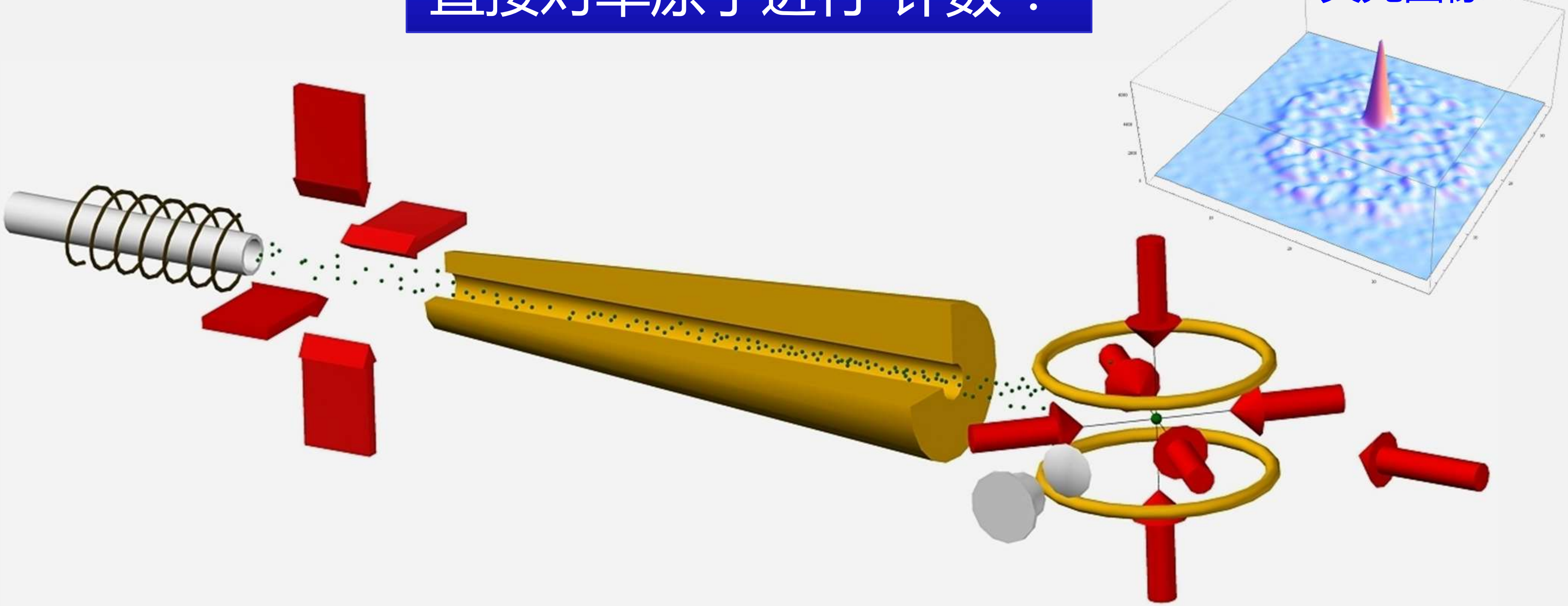


Magneto-Optical Trap
Sodium, NIST, ~ 1990
Nobel Physics Prize, 1997

Photo credit: Mark Helfer, NIST

# 原子阱痕量分析方法
## Atom Trap Trace Analysis (ATTA)

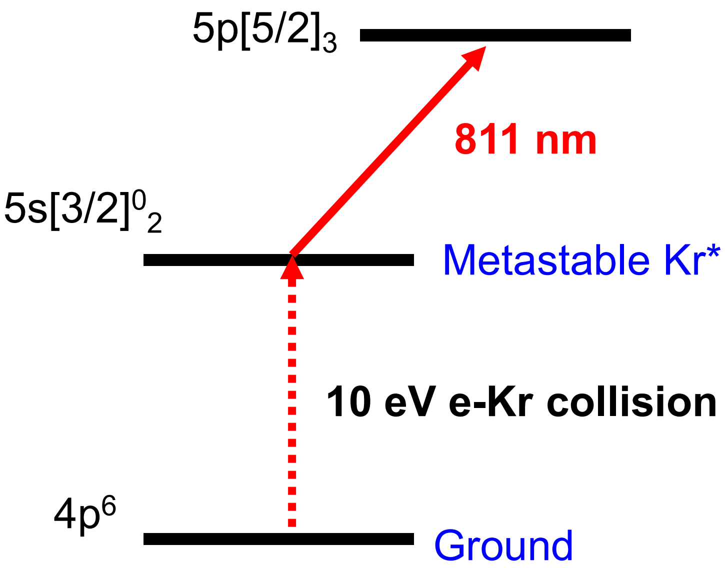
直接对单原子进行“计数”!



单个$^{81}$Kr原子
CCD 荧光图像

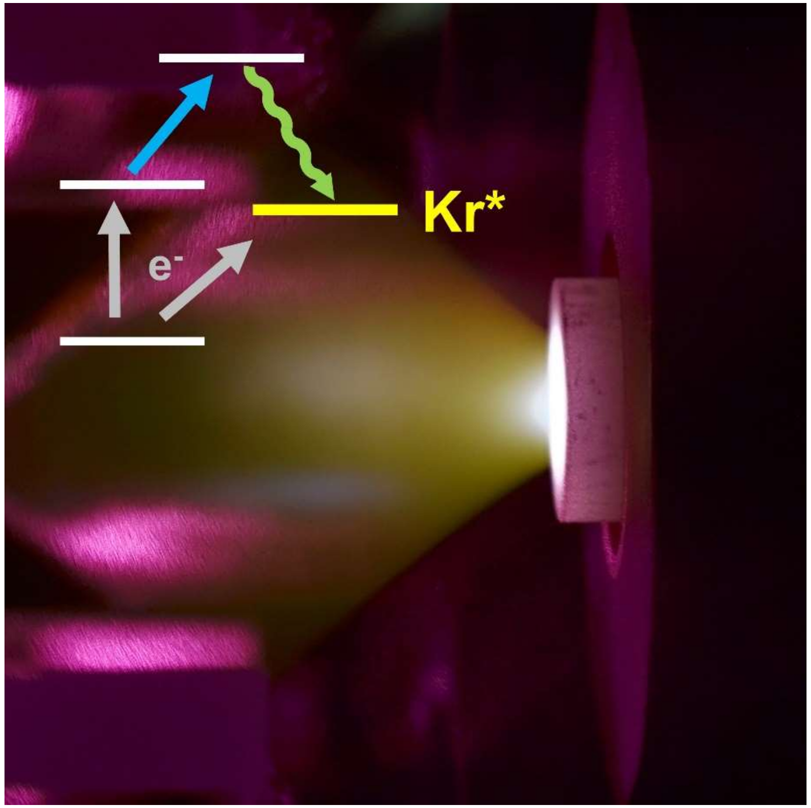
Ultrasensitive isotope trace analyses with a magneto-optical trap
C.Y. Chen, Y.M. Li, K. Bailey, T.P. O'Connor, L. Young, Z.-T. Lu*
*Science* 286, 1139 (1999)

# Discharge Source of Metastable Kr*

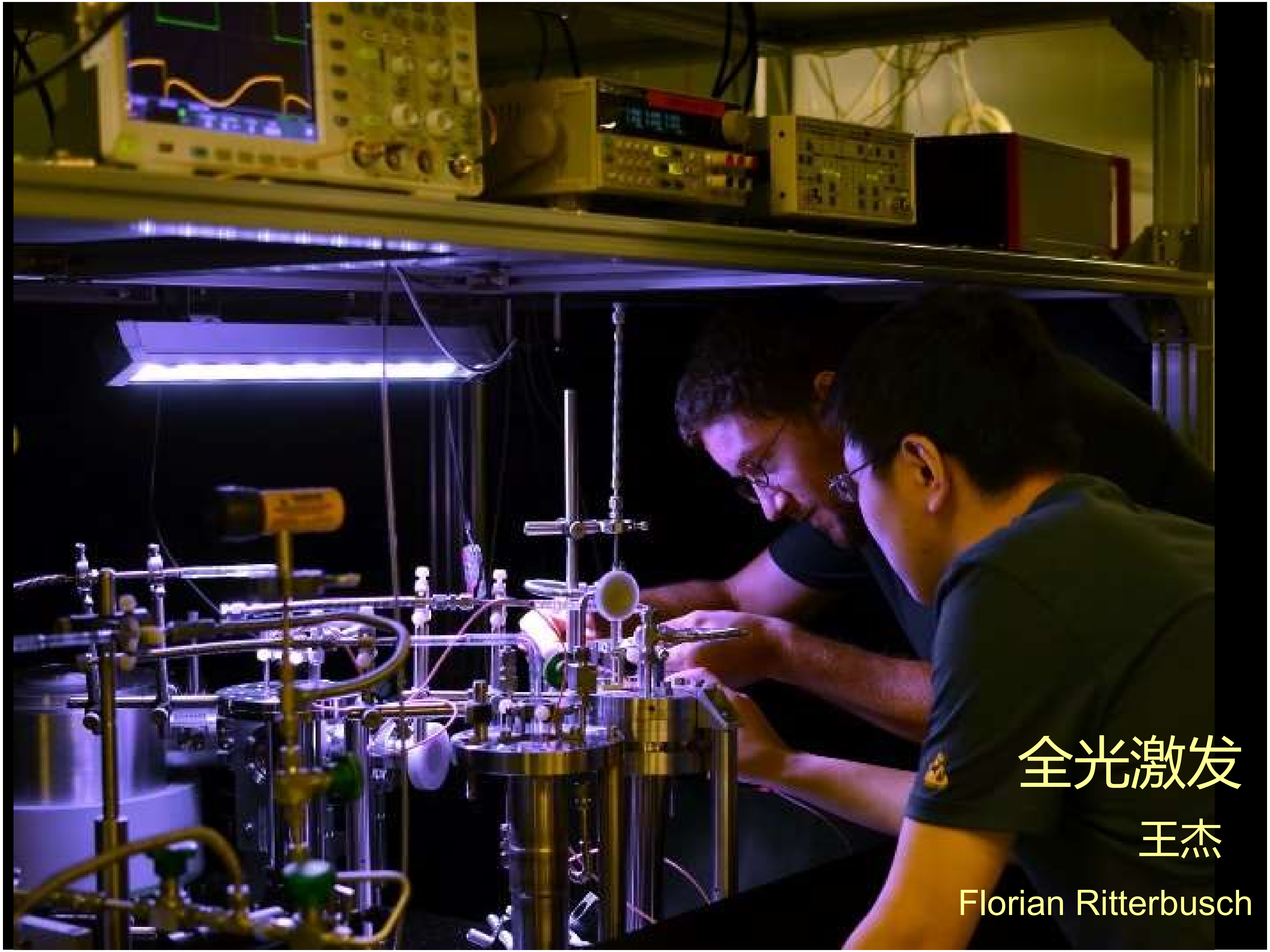



Electron impact excitation

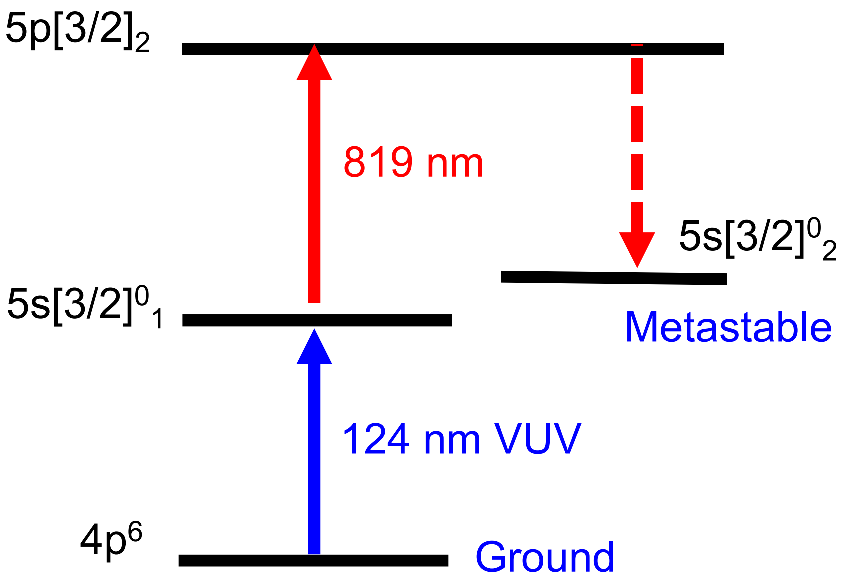
- Efficiency limited $10^{-3}$
- Memory effect

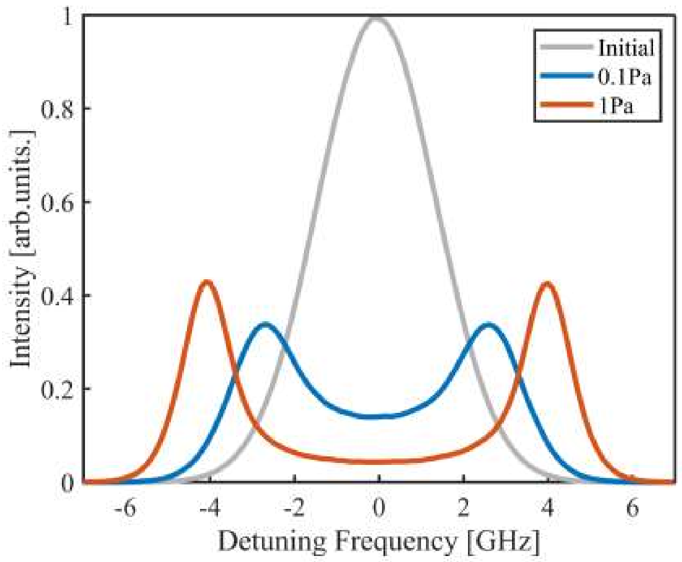



张泽远 Z.-Y. Zhang *et al.*, PRA (2020)


全光激发
王杰
Florian Ritterbusch

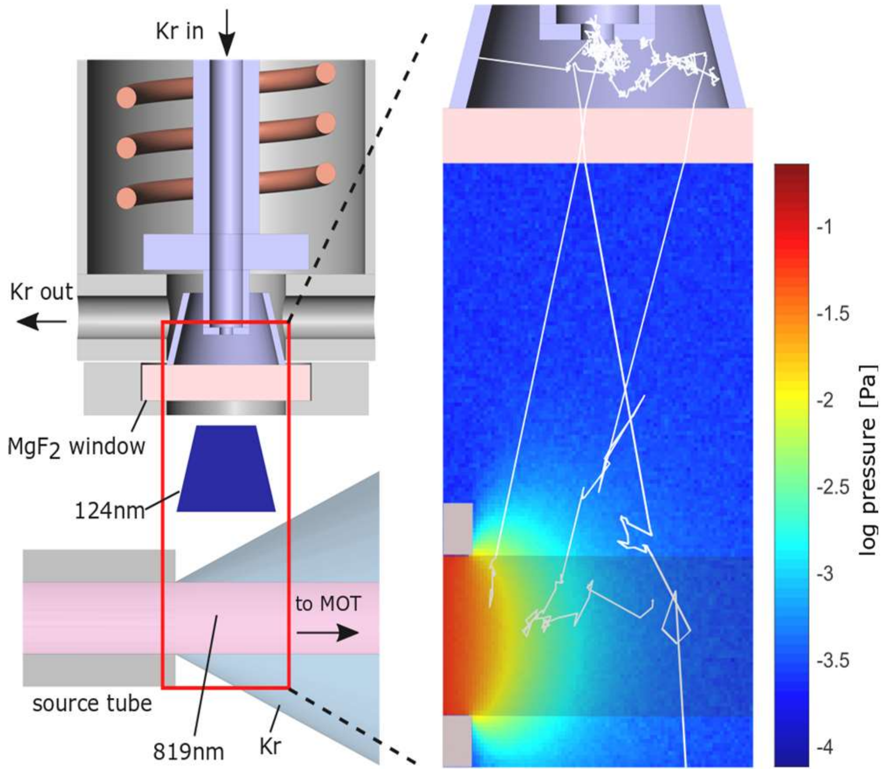
# All-Optical Production of Kr*




## VUV + IR optical excitation

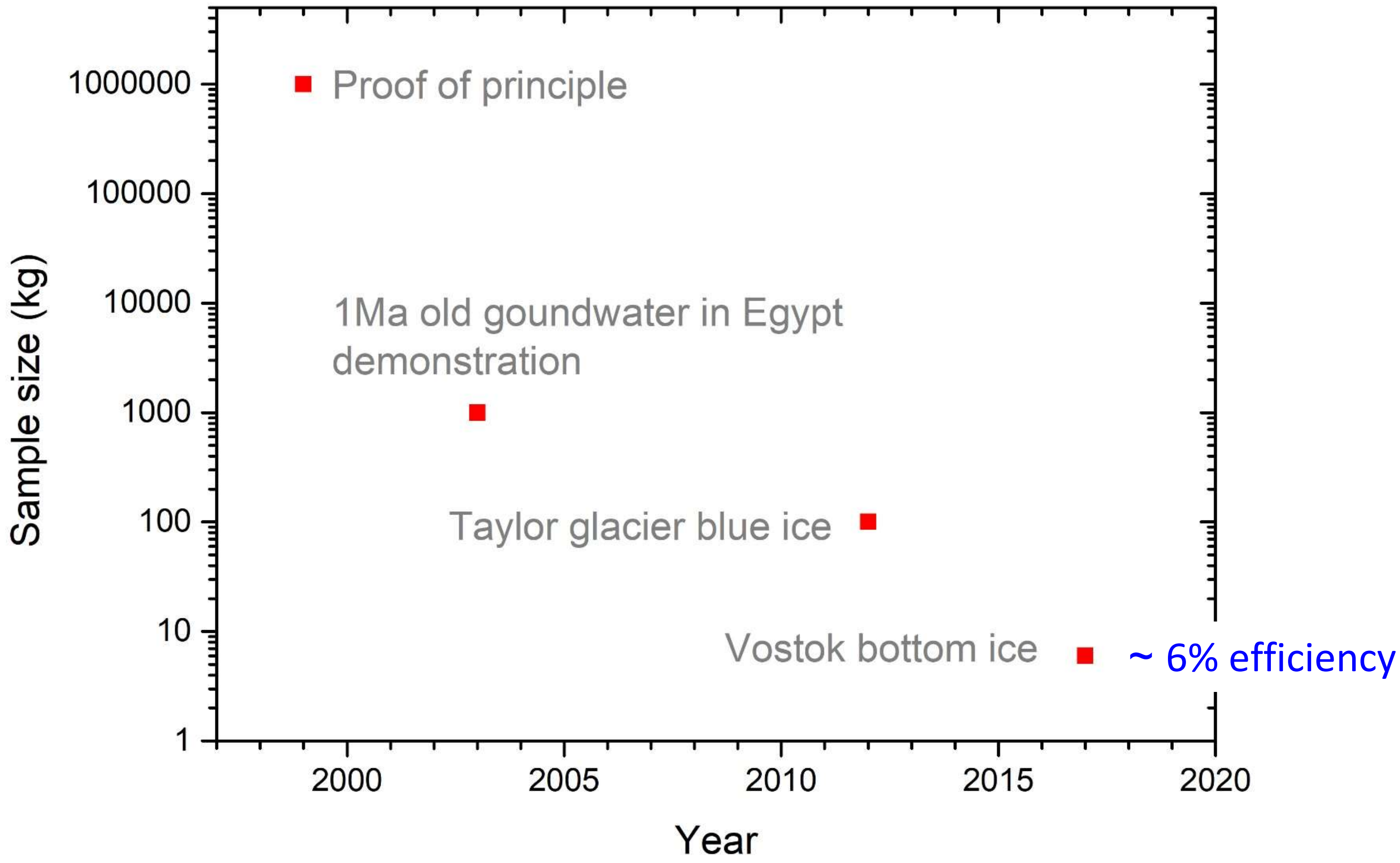
- Develop VUV lamp, laser, FEL
- Brightness: 1 mW in 1 GHz



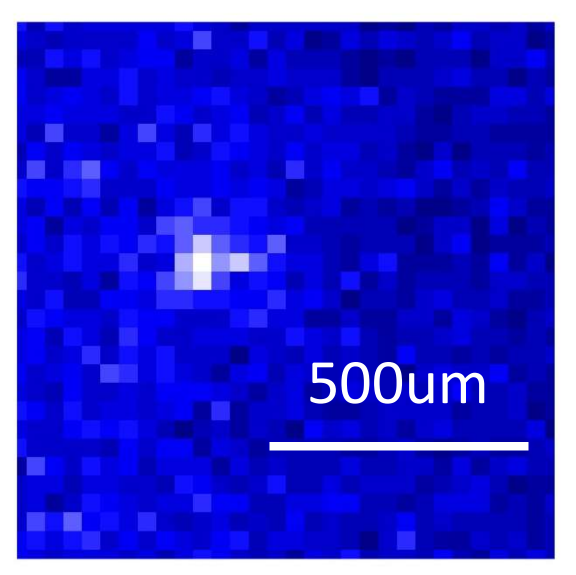

Optical Excitation and Trapping of $^{81}$Kr

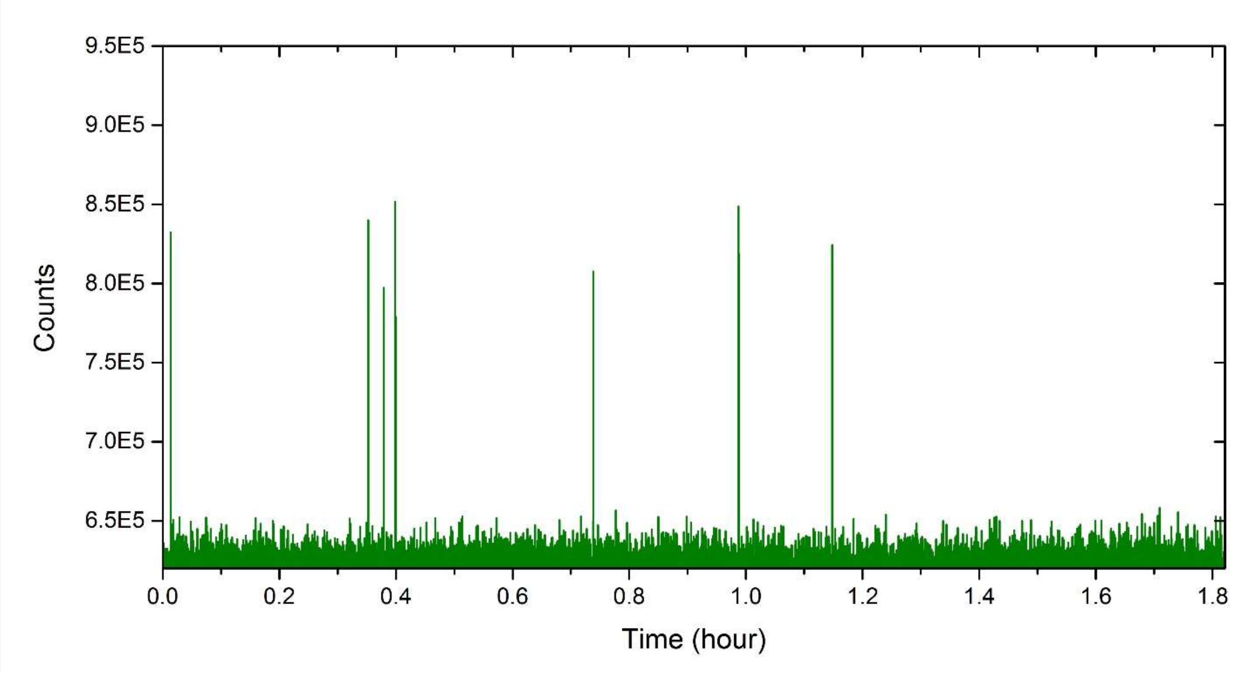
王杰 J.-S. Wang *et al.*, PRL (2021)

# Water/Ice sample size needed over the years



# Ar-39 Detection at $10^{-16}$ Level

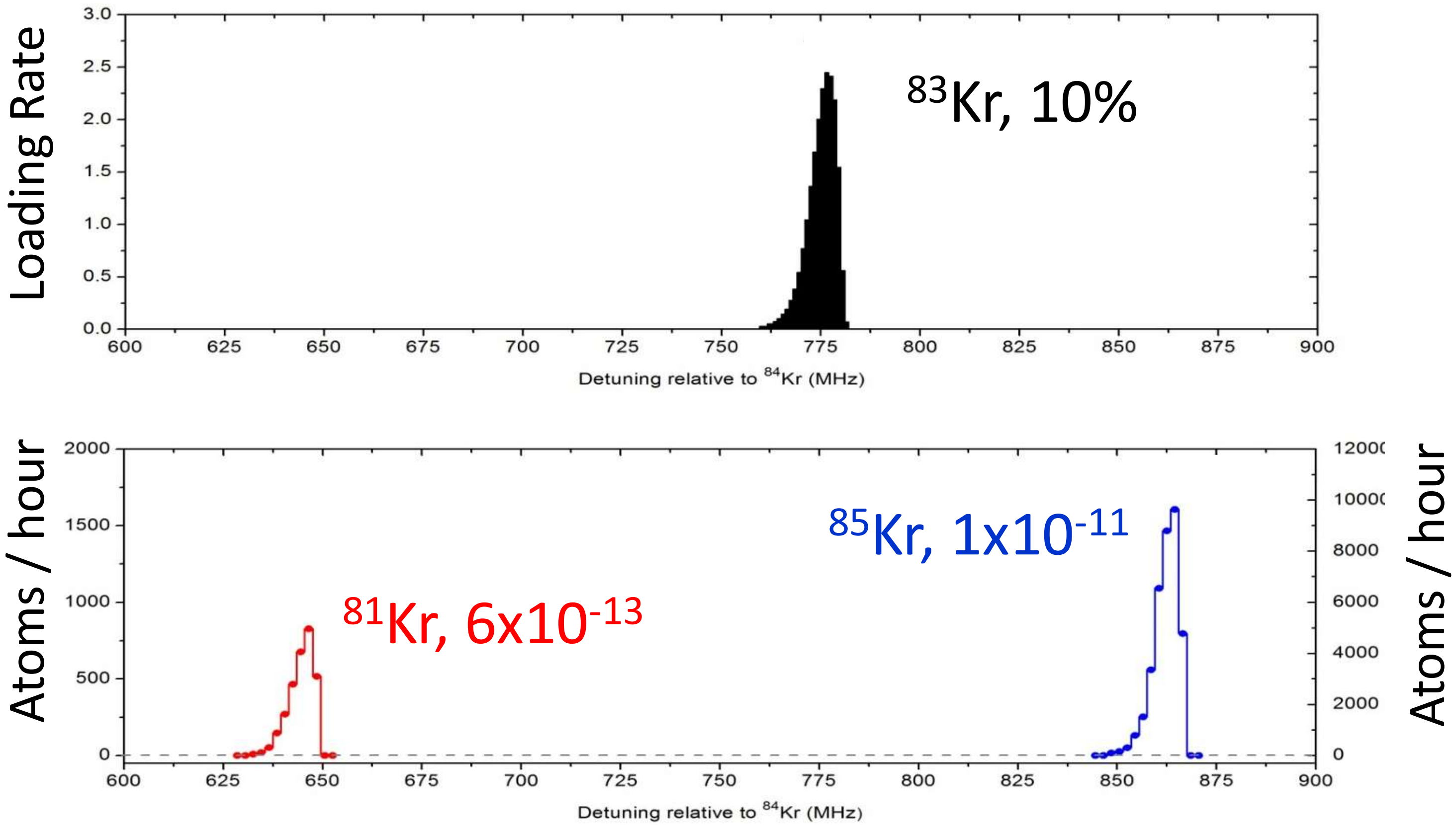



SNR ~ 14;     Counting rate ~ 10 atoms/hr

USTC：阿民 A.L. Tong *et al*., RSI (2021)
Heidelberg: F. Ritterbusch *et al*., GRL (2014)
Chicago: 蒋蔚 W. Jiang *et al*., PRL (2011)

# 超高选择性：多次、共振激发




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

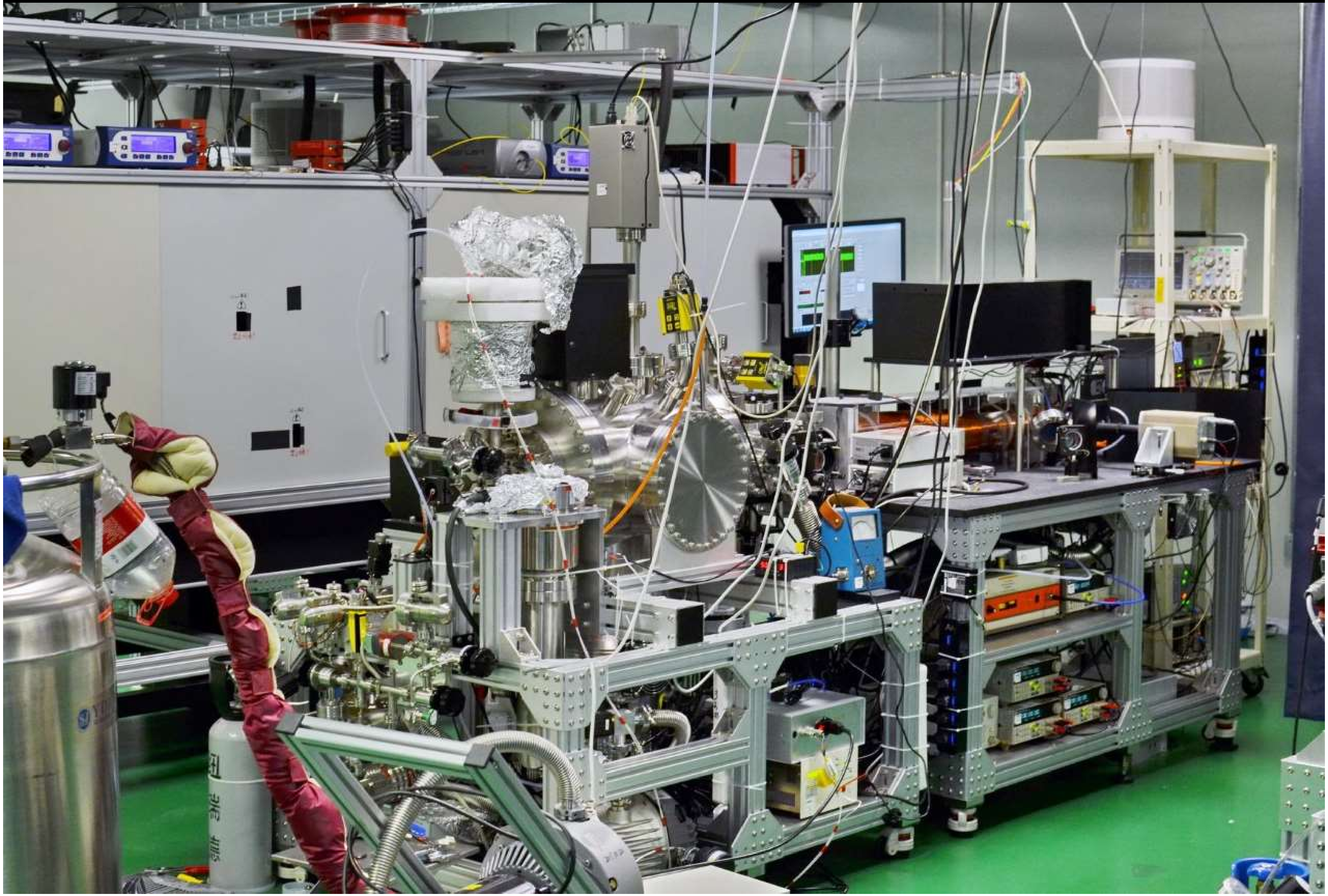
宇宙射线与大气作用产生

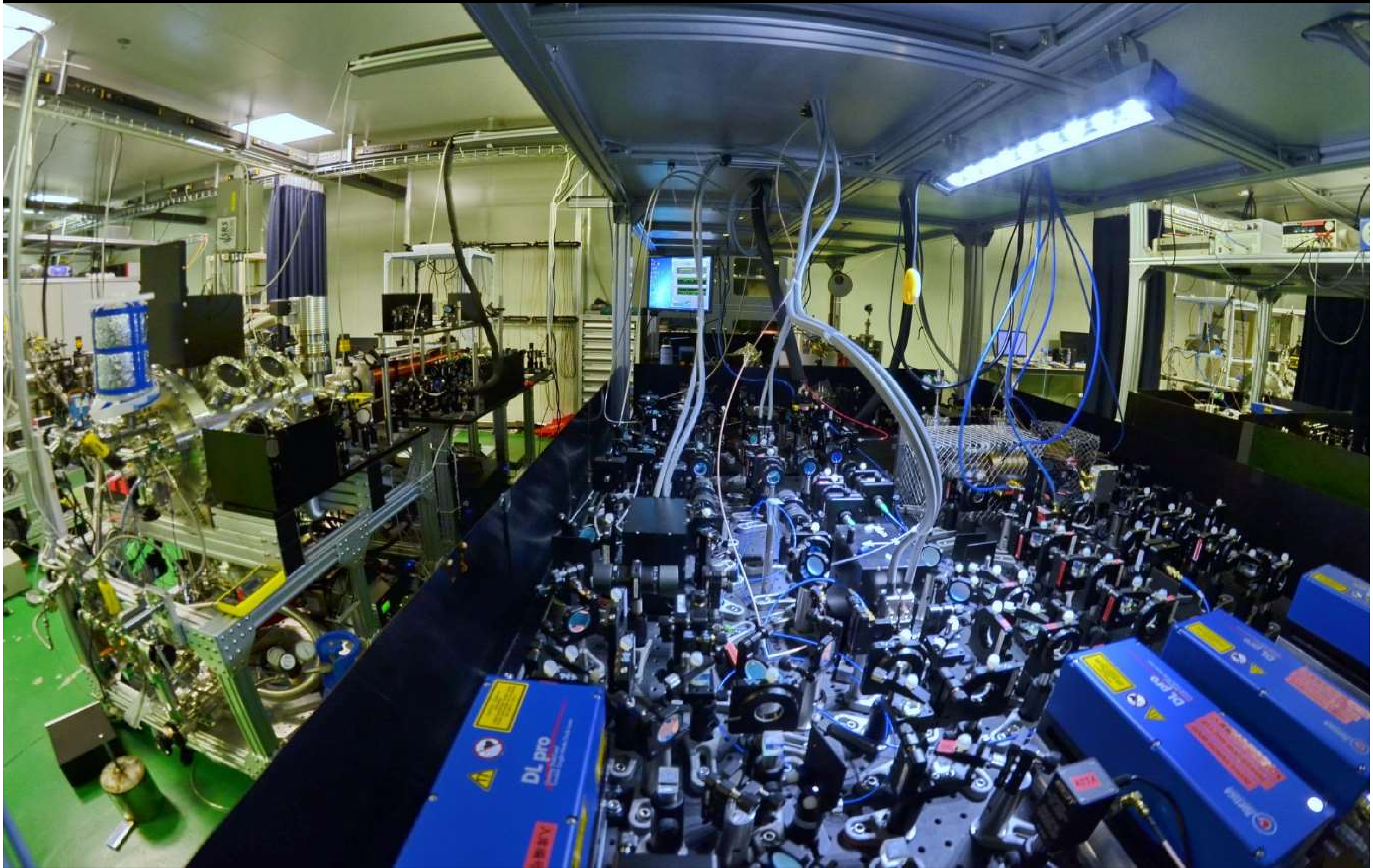
$^{85}Kr/Kr = 2 \times 10^{-11}$

人工核裂变产物

蒋蔚 W. Jiang *et al*., GCA (2012)

# ATTA-Kr for Kr-81 at USTC




DL pro

## 自我检查

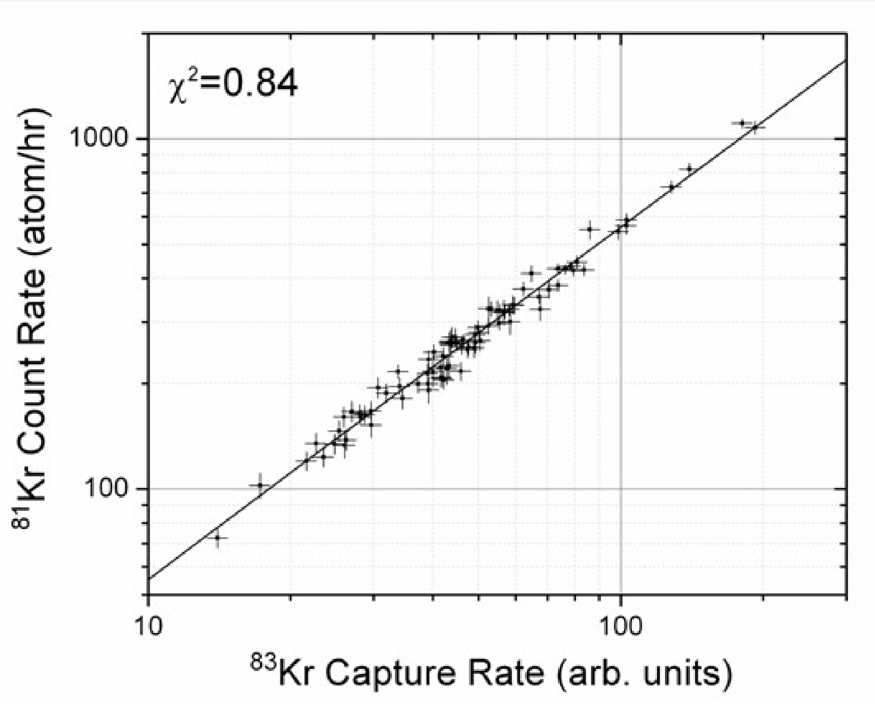
在不同实验条件下测量：

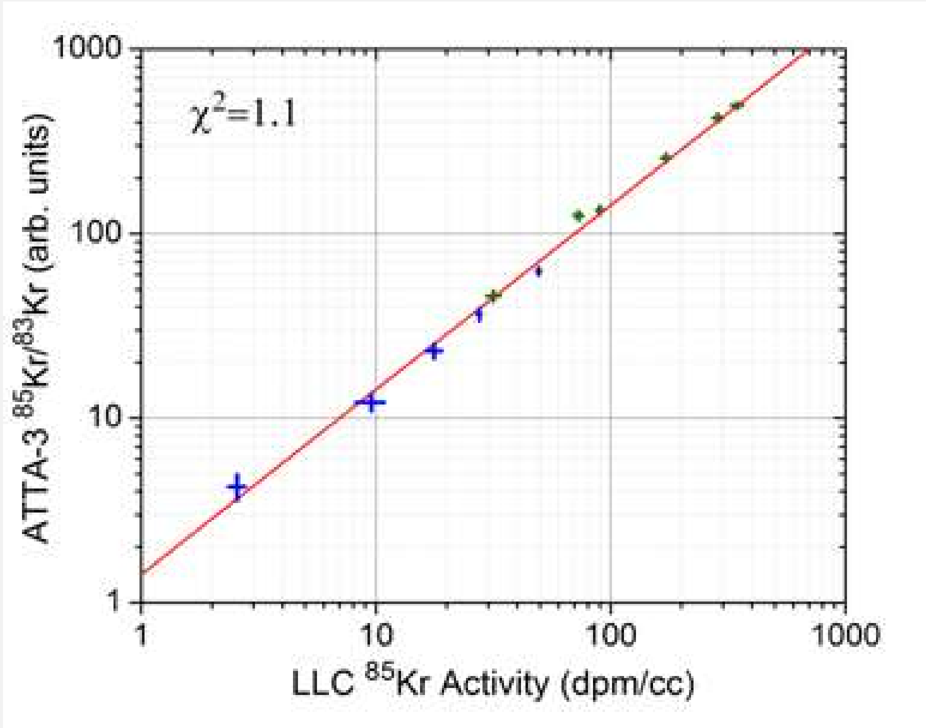
- 激光功率
- 光路重调
- 放电强度
- 气压

## 实验室之间的比对

- 头一批, 6个样品, unblind
- 第二批, 6个样品, blind

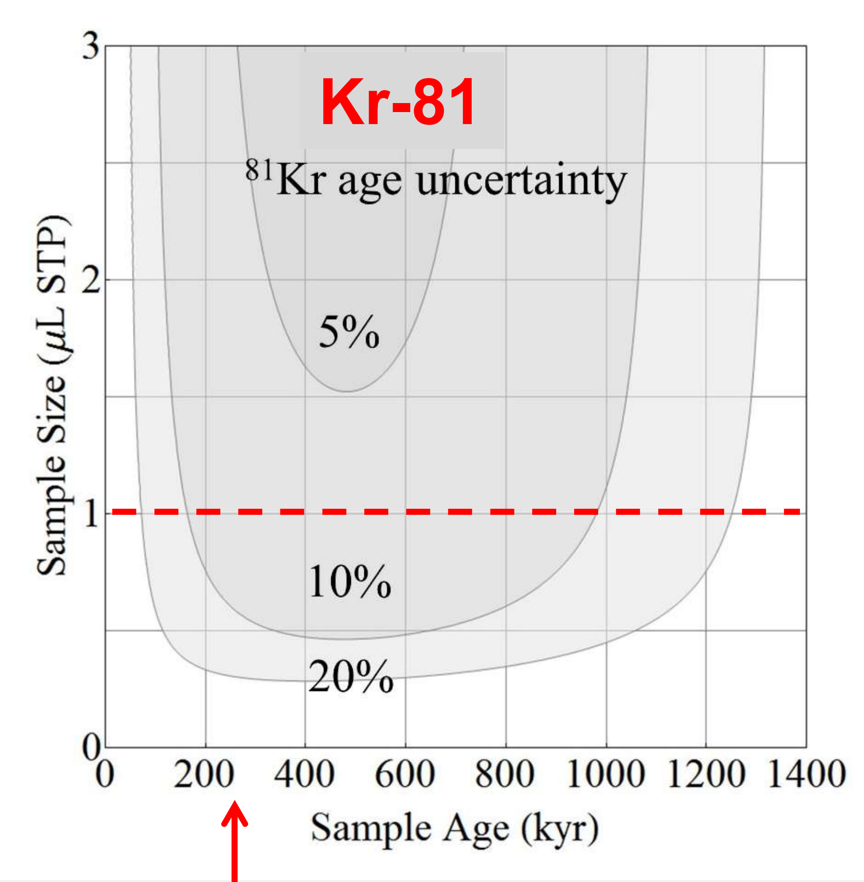
Roland Purtschert
University of Bern



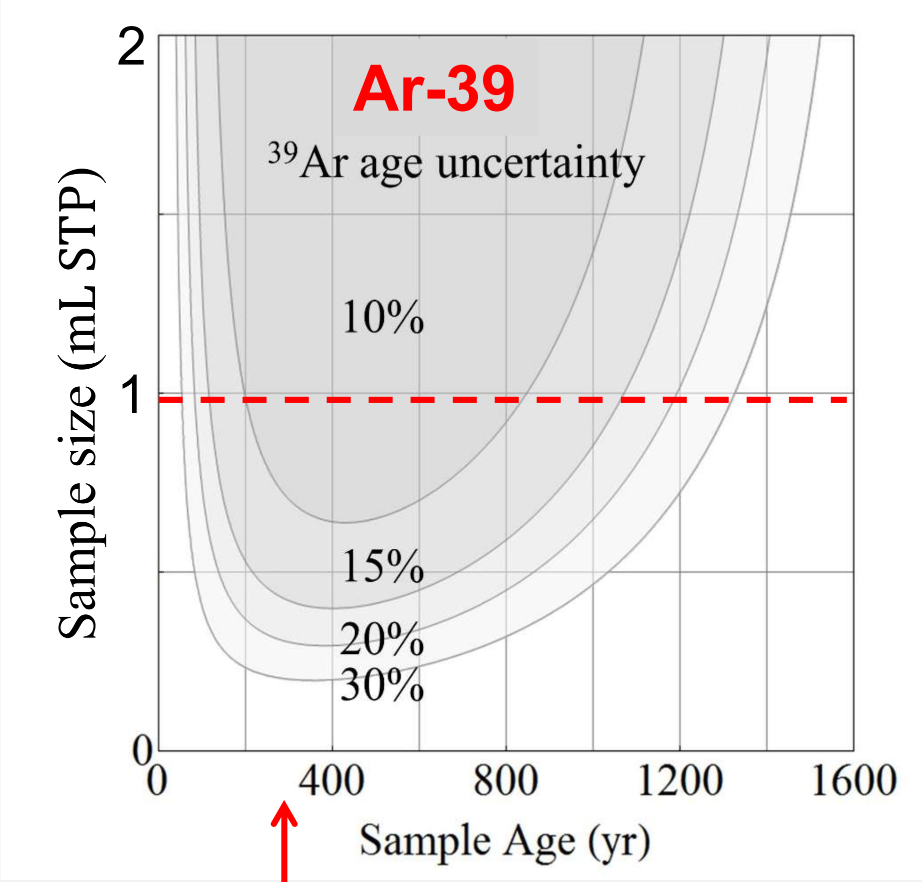




Jiang *et al.*, GCA (2012); Jiang et al., Opt. Lett. (2014)

# Sample Size and Measurement Precision




Half-life 230 kyr




Half-life 269 yr

1 μL STP Kr
20 kg water

1 mL STP Ar
2 kg water

# 放射性氪、氩同位素定年流程

水/冰样品中提取
溶解气/包裹气

→ **野外脱气装置、融冰取气装置**
疏水性脱气膜

气体样品（含$N_2$、$CO_2$、$H_2O$、$CH_4$、Ar、Kr等）

溶解气/包裹气中提取氪、氩气样品

→ **氪、氩气体分离提纯装置**
低温蒸馏、高温钛炉、气相色谱

氪、氩样品

原子阱测量$^{81}$Kr、$^{81}$Kr、$^{39}$Ar相对丰度

→ **原子阱氪、氩同位素定年装置**
单原子计数测量

同位素丰度值

计算得到样品年代

$$\frac{[^{81}Kr/Kr]_{样品}}{[^{81}Kr/Kr]_{大气}} = 2^{-\left(\frac{年龄}{半衰期}\right)}$$

# 放射性氪、氩同位素定年流程

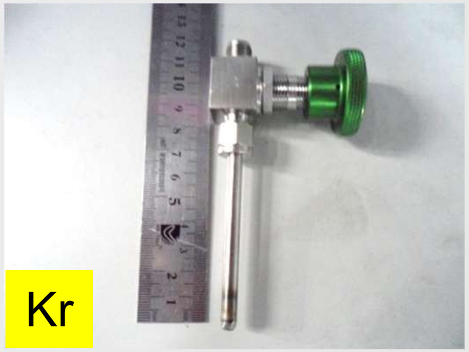
- 1000 $^{81}$Kr atoms in 1kg of ice


20-40kg

**Gas extraction**

1-2L STP

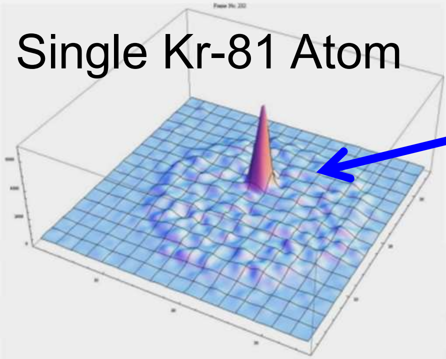
**Kr purification**

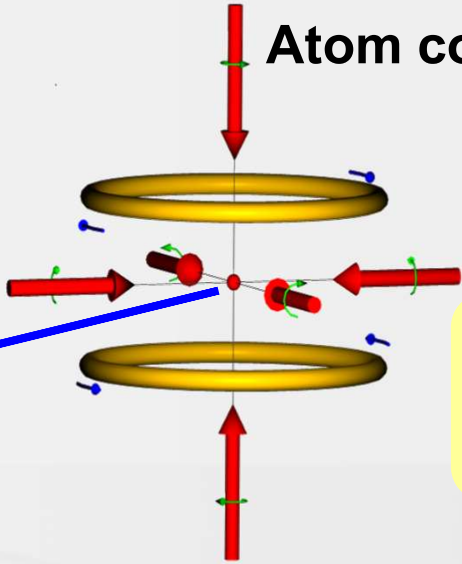



1-2μL STP

**Atom counting**

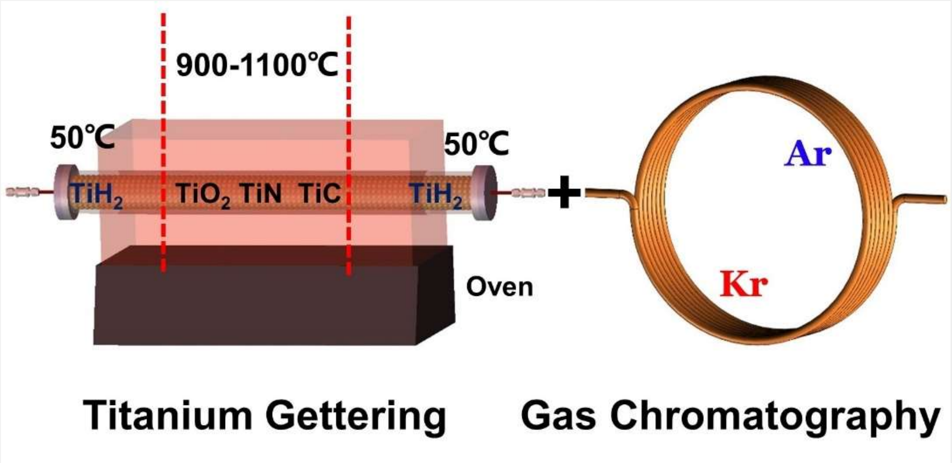
Atom Trap Trace Analysis (ATTA)

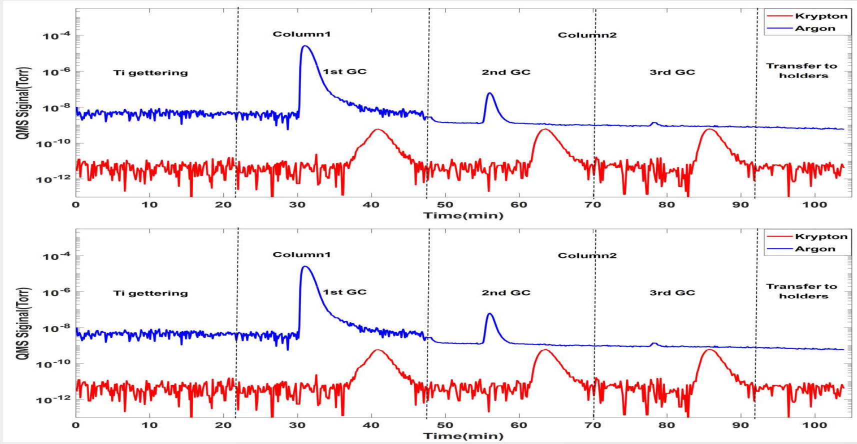


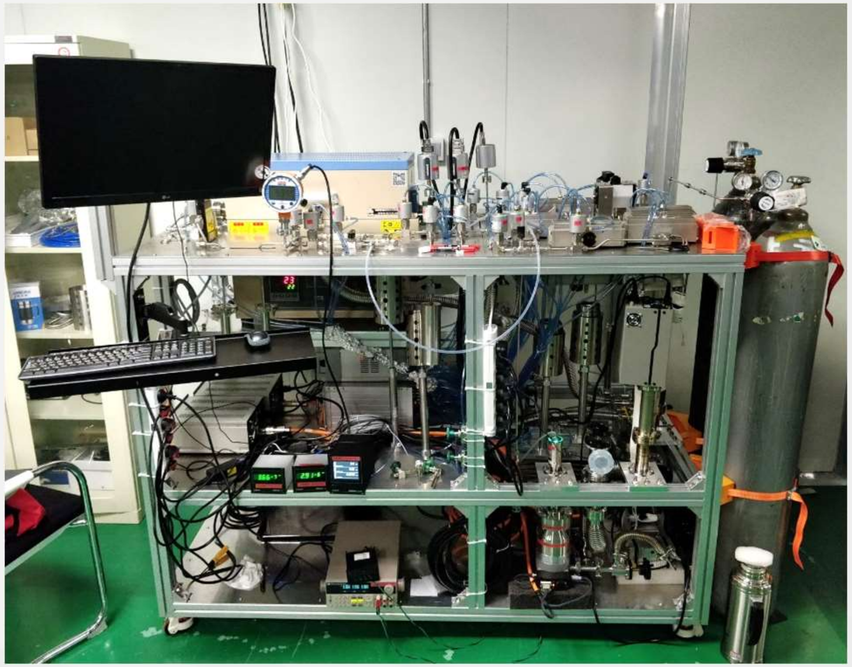



$$\frac{\left[{}^{81}Kr/Kr\right]_{sample}}{\left[{}^{81}Kr/Kr\right]_{air}} = 2^{-\left(\frac{\text{Age}}{\text{Half-life}}\right)}$$

# Dual Kr and Ar Separation and Purification



空气占比：Ar 1%，Kr 1 ppm

- Sample size: 0.5-10 L air
- Time: Less than 2 hours
- Ar： Eff. ~ 99%，purity > 99%
- Kr：Eff. > 90%，purity > 90%

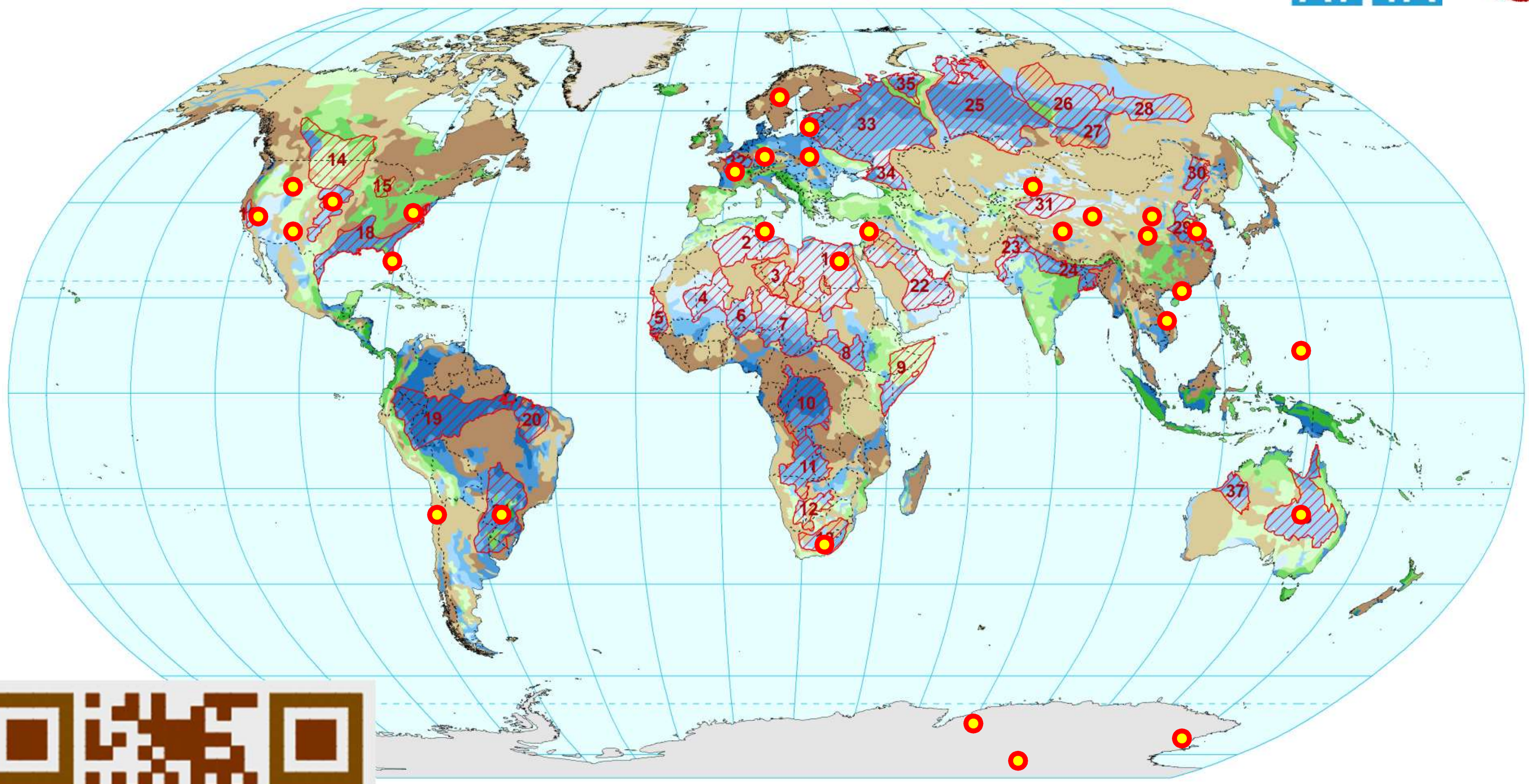
董希泽 X.-Z. Dong *et al.*, Analytical Chemistry (2019)

IAEA Water Resources Programme

ATTA

# Groundwater Resources of the World

## - Large Aquifer Systems -



Large

1. Nu
2. No
3. M
4. Ta
5. Se
6. Iu
7. Cl
8. Su
9. Ogaden-Juba Basin
10. Congo Intracratonic Basin

Basin
ri Basin

ains / Interior Plains Aquifer
n Aquifer System
Valley Aquifer System
ala Aquifer
s Aquifer System
19. Amazonas Basin
20. Maranhao Basin

21. Guarani Aquifer System
22. Arabian Aquifer System
23. Indus Basin
24. Ganges-Brahmaputra Basin
25. West Siberian Artesian Basin
26. Tunguss Basin
27. Angara-Lena Artesian Basin
28. Yakut Basin
29. North China Plain Aquifer System
30. Songliao Basin

31. Tarim Basin
32. Parisian Basin
33. East European Aquifer System
34. North Caucasus Basin
35. Pechora Basin
36. Great Artesian Basin
37. Canning Basin

**Groundwater resources**

groundwater recharge (mm/a)

very high | high | medium | low | very low

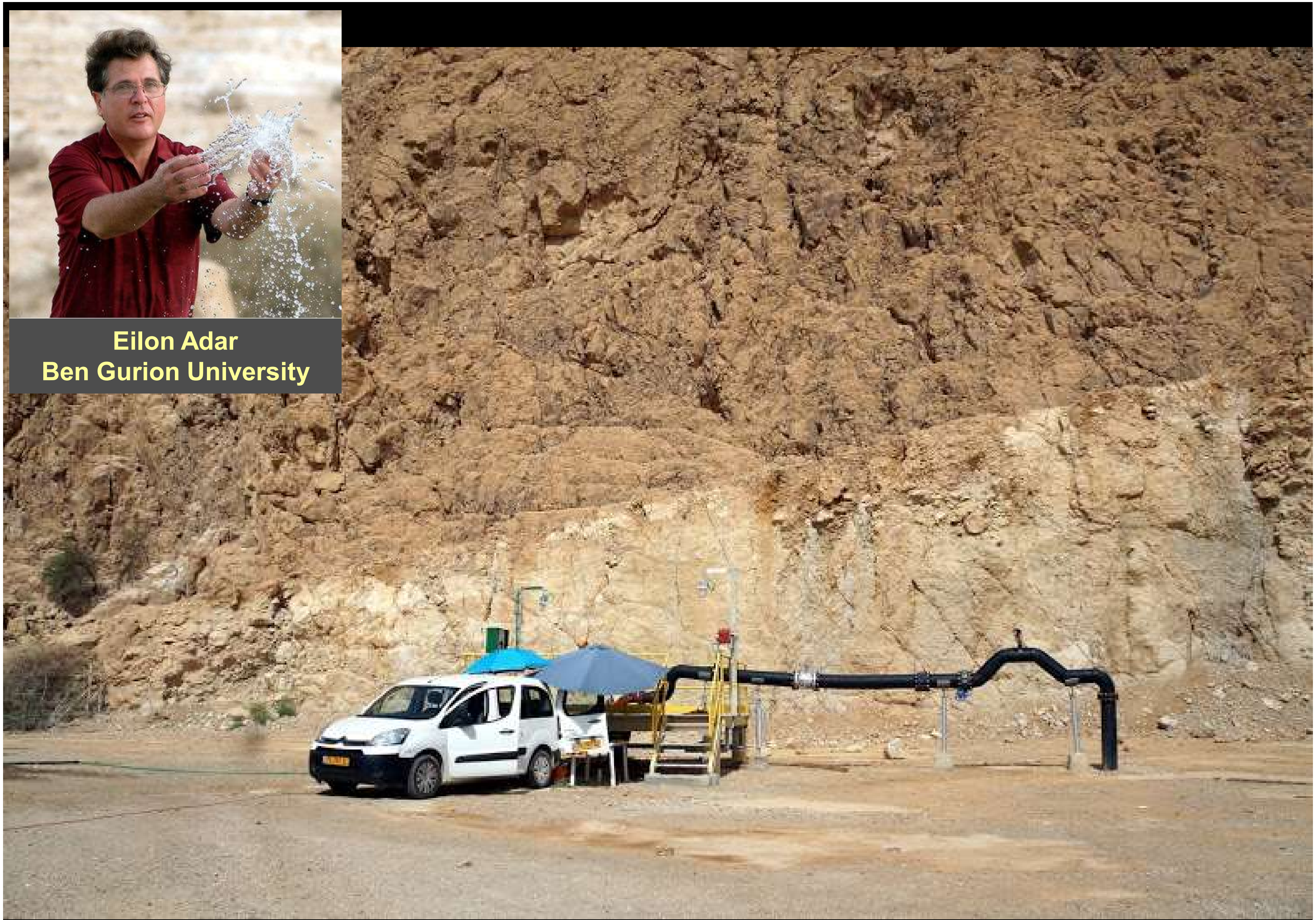
300 | 100 | 20 | 2 | 0

in major groundwater basins

in areas with complex hydrogeological structure

in areas with local and shallow aquifers


Andy Love
Flinders University
Outback, Australia



Eilon Adar
Ben Gurion University

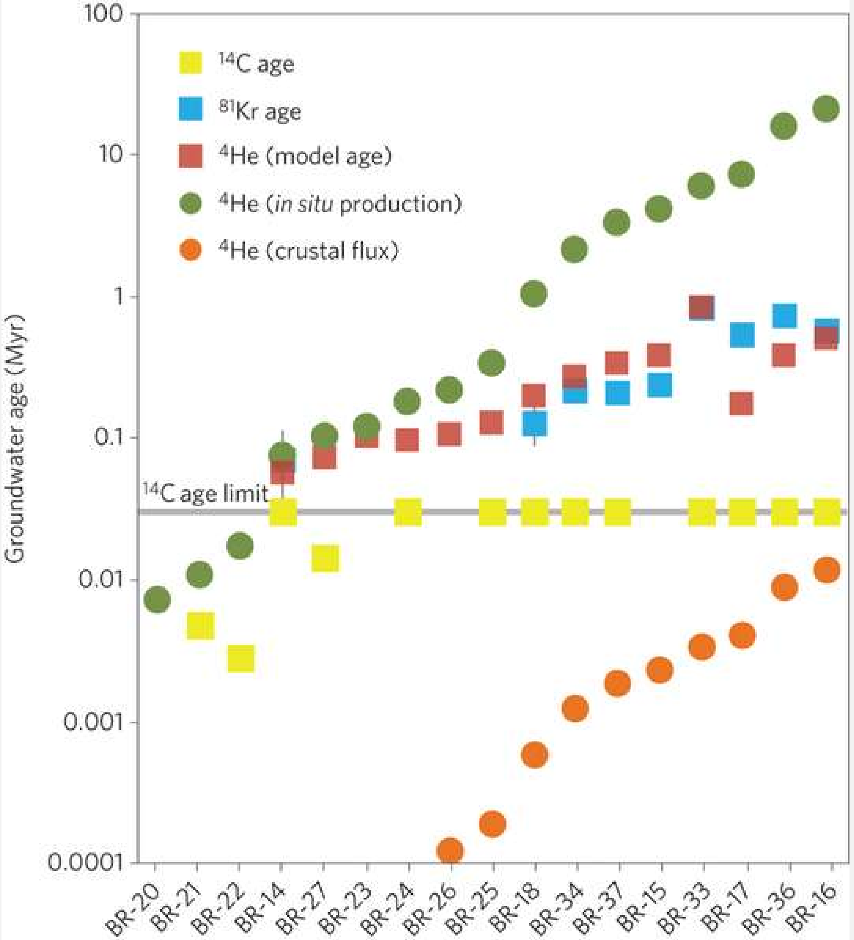
Negev Desert, Israel

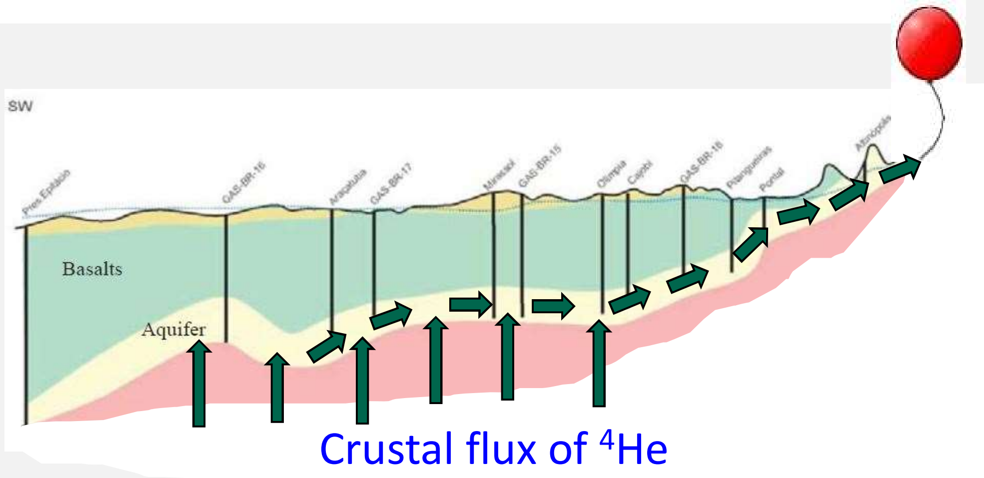

Daniel Emilio Martinez
CONICET
Pampas Plain, Argentina

# Continental degassing of $^4He$ by surficial discharge of deep groundwater

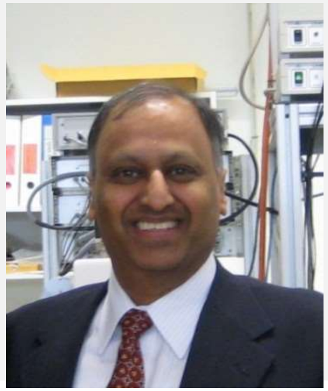
P.K. Aggarwal *et al.*, Nature Geoscience **8**, 35 (2015)

- $^4He$ in the Guarani aquifer accumulates over half- to one-million year timescale.
- $^4He$ degassing from continents is regulated by groundwater discharge, rather than episodic tectonic events.

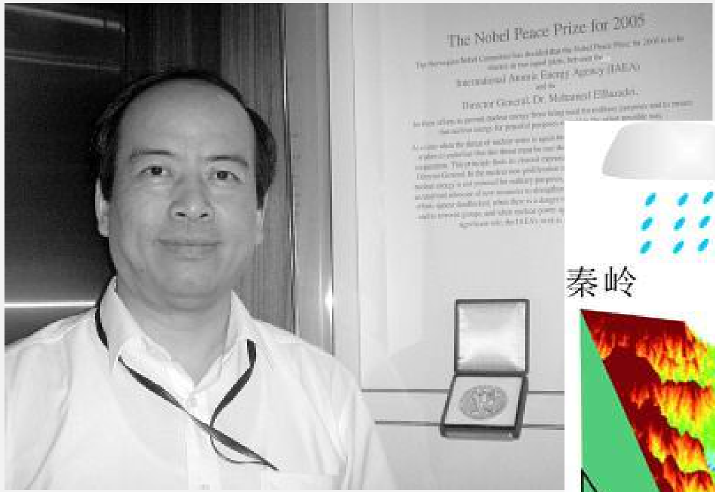


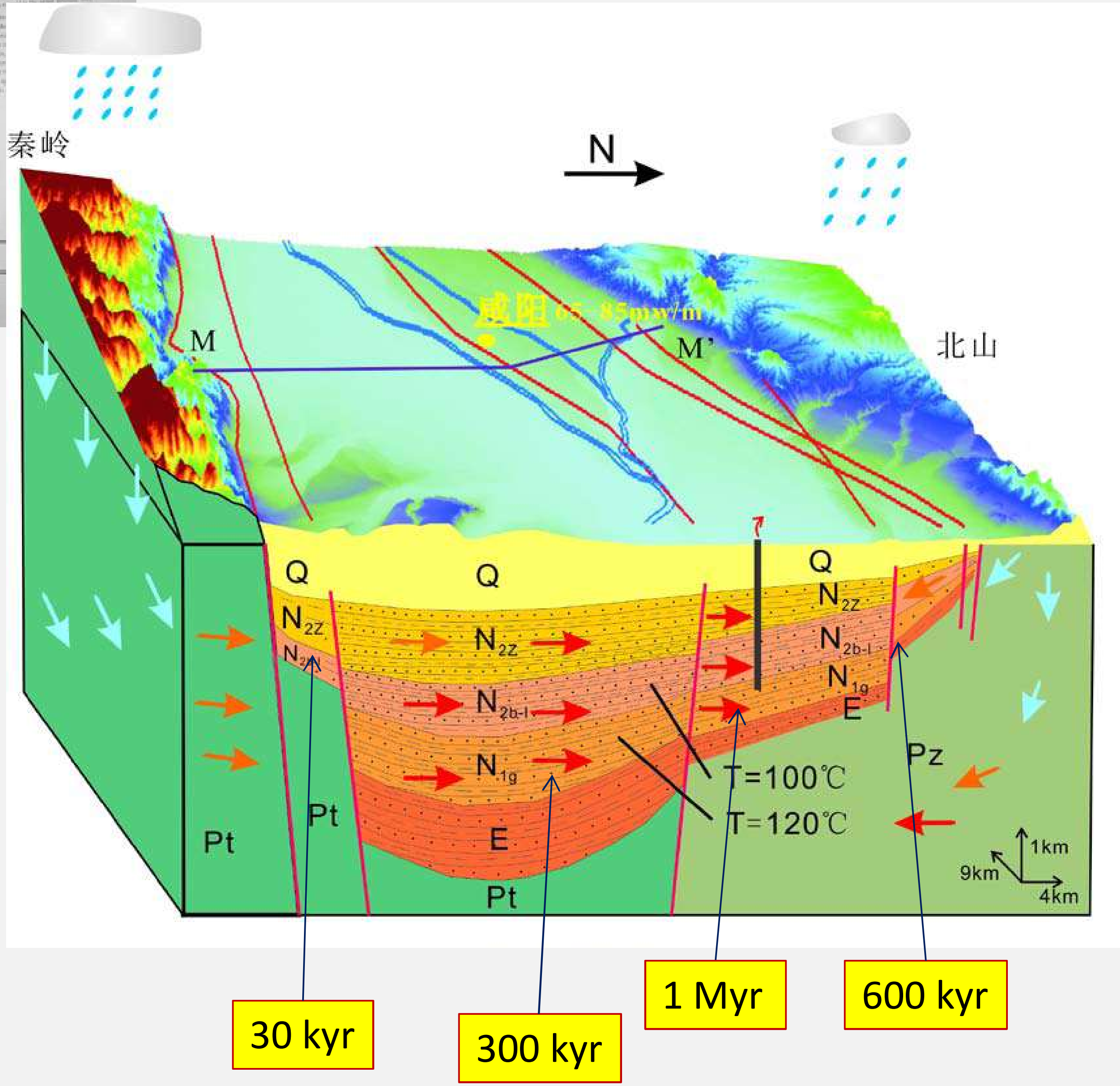

由联合国国际
原子能组织牵头



Pradeep Aggarwal
Water Resources, IAEA

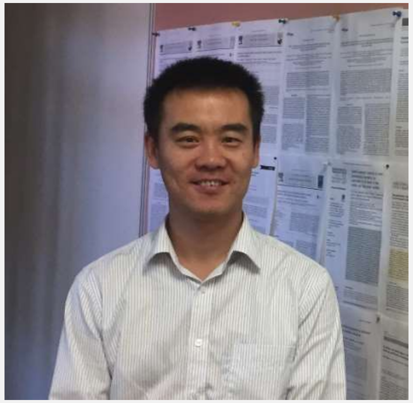



# Model of Guanzhong Basin




**Zhonghe Pang**
**CAS Geology & Geophysics**
**中科院地质地球所**
**庞忠和**

Million-year-old groundwater revealed by krypton-81 dating in Guanzhong Basin, China
J. Li, Z. Pang *et al.*,
Sci. Bulletin 62, 1181 (2017)



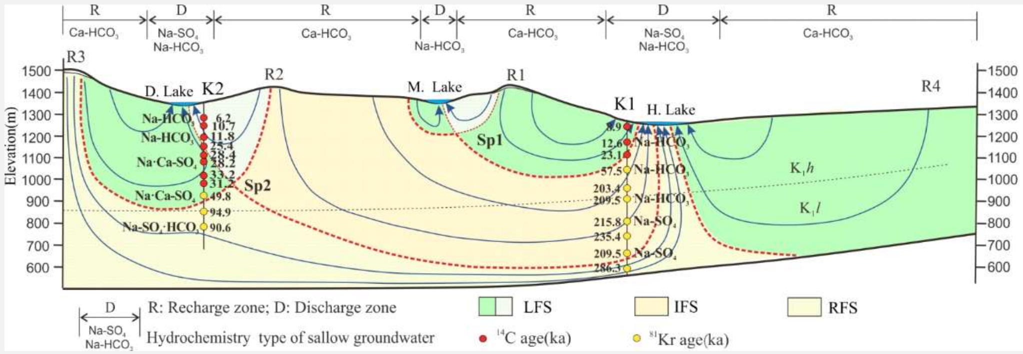
# 利用 $^{81}$Kr 定年，在鄂尔多斯盆地发现古地下水，找到多级嵌套地下水循环系统的“转折点”

张俊 西安地调中心

合作单位：地调局西安地调中心、中科院地质地球所等

Zhang *et al.*, Geophys. Res. Lett. (2021)

- Groundwater age and geochemical profiles were obtained to investigate groundwater flow systems.
- Inflection points on profiles are used to infer interfaces or stagnation points among different groundwater flow systems.
- Groundwater flow models constrained by inflection points greatly reduce the uncertainty of flow system characterization.





中国科学报
CHINA SCIENCE DAILY

总第 7841 期

把看不到的地下水流“画”出来

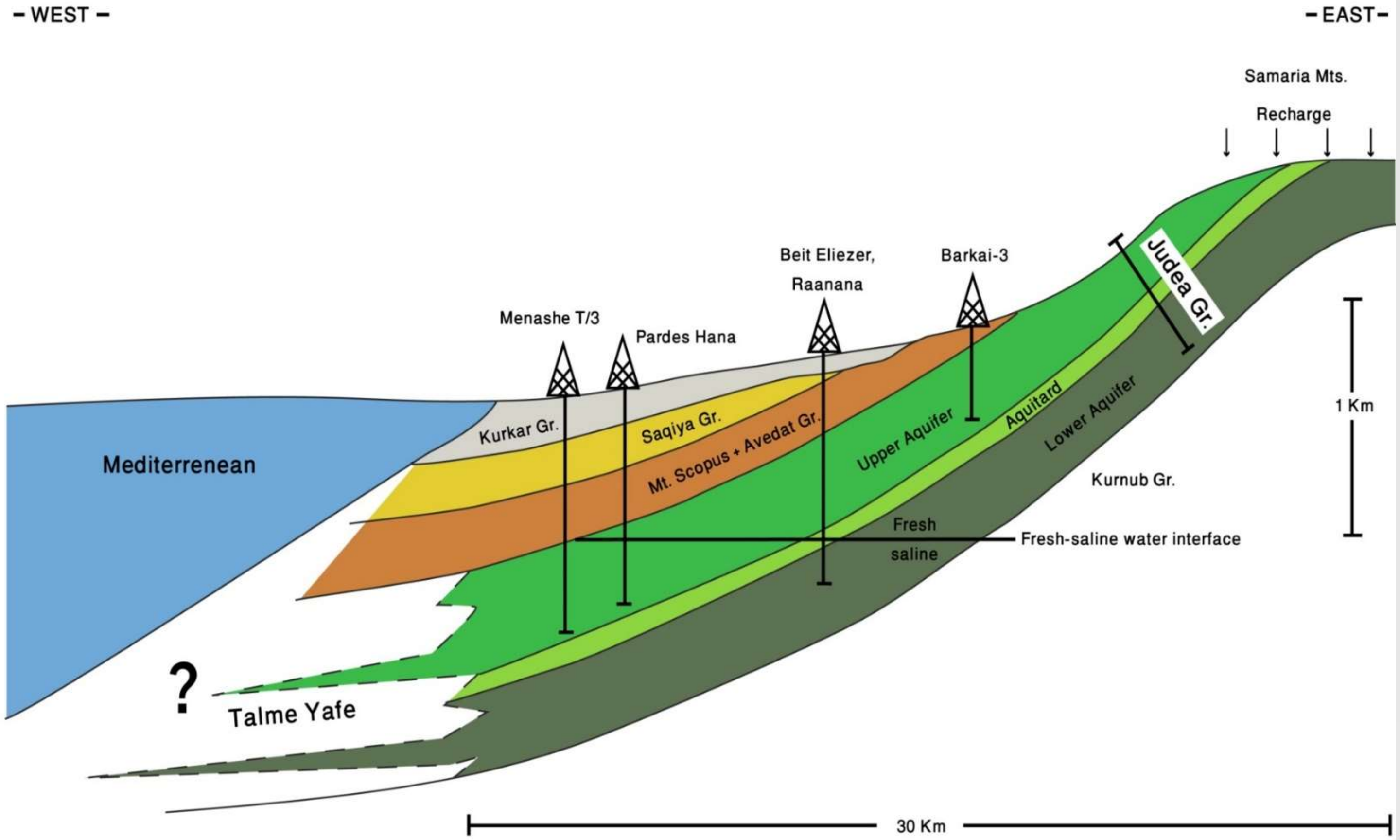
为气候变化大背景下的“深地”开发解锁密码

# Seawater intrusion into deep aquifer

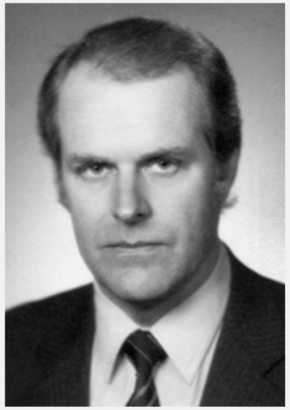
Yoseph Yechieli *et al*., Earth Planetary Sci. Lett. 507, 21-29 (2019)

- Distance from well to connection with the sea: 20 – 30 km
- Ages of saline water: 10 – 26 ka
- Rate of average seawater intrusion: 1 – 3 m/yr

**Yossi Yechieli**
**Israel Geological Survey**
以色列地调局 局长



# Characterize and Date Baltic Artesian Basin

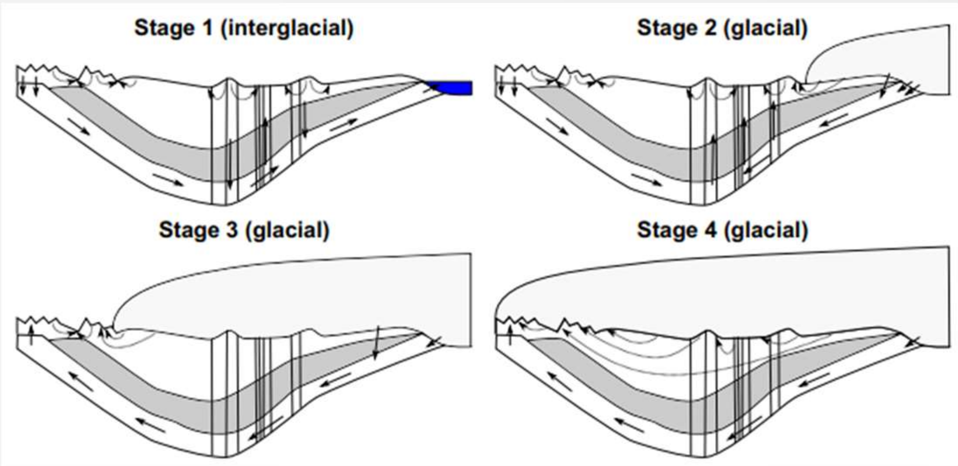


Rein Vaikmae
Tallinn, Estonia

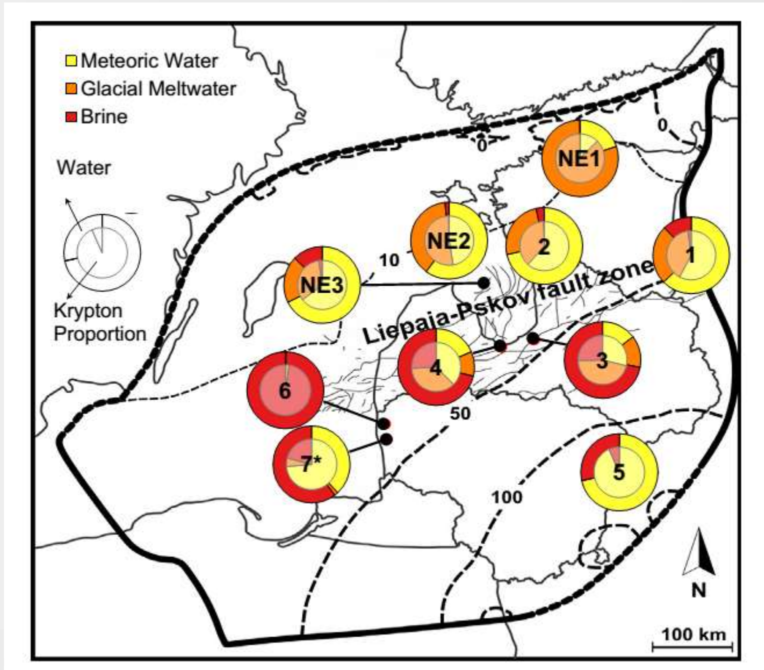
Three components:

- Interglacial meteoric water ($\delta^{18}O \approx -10.4‰$) : 300 ka – 1.3 Ma
- Glacial meltwater ($\delta^{18}O \leq -18‰$): 300 ka – 1.3 Ma
- High-salinity brine ($\delta^{18}O \geq -4.5‰$): > 1.3 Ma

Gerber *et al*., Geochim. Cosmochim. Acta 205, 187-210 (2017)



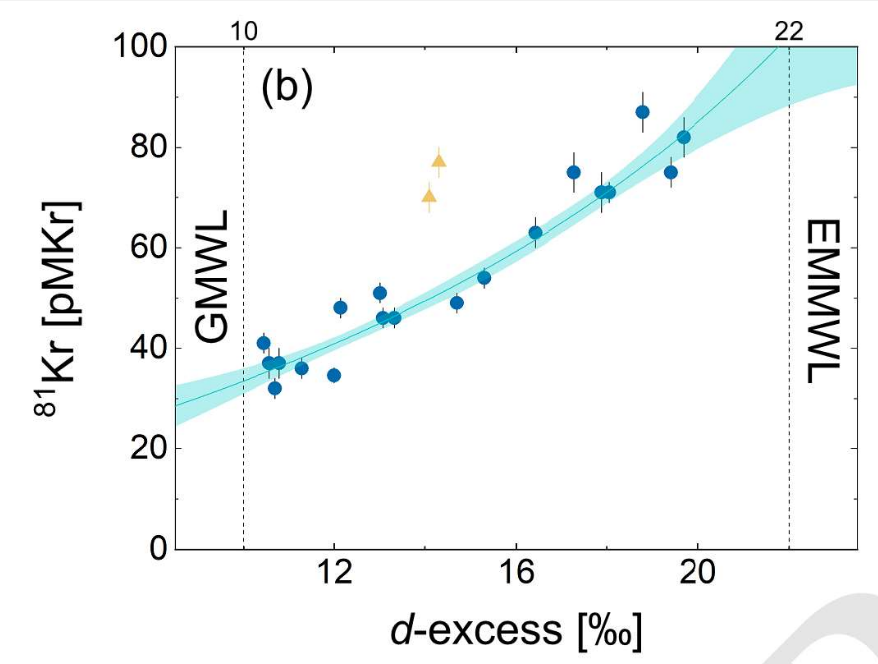

**Presumed flow patterns in interglacial and glacial periods**



# Radiokrypton unveils dual moisture sources of a deep desert aquifer

Yokochi *et al*., PNAS 116, 16222 (2019)

Reika Yokochi
U Chicago




- Investigated the paleo-hydroclimate properties of the Nubian Sandstone Aquifer in the Negev Desert, Israel.
- Resolved subsurface mixing and identified two distinct moisture sources of recharge.
- Reveals that tectonically active terrain can store groundwater.

Atlantic ocean
361±30 ka

Mediterranean
< 38 ka


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


China National Nuclear Corp

## $^{81}Kr$ characterize old (isolated) groundwater environment for sites of nuclear waste repository

- Waste Isolation Pilot Plant (WIPP), New Mexico, USA
- China National Nuclear Corp., Beishan, China
- Central Res. Inst. of Electric Power Industry (CRIEPI), Japan

Beishan, China

# 国际原子能组织 CRP F33023 项目 -- 用$^{81}Kr$给古水定年

亚洲：中国、日本、印度；　　澳洲：澳大利亚；
非洲：摩洛哥、阿尔及利亚、突尼西亚；　欧洲：爱沙尼亚、匈牙利；
北美：加拿大；　南美：巴西、阿根廷

Radiometric $^{81}$Kr dating identifies 120,000-year-old ice at Taylor Glacier, Antarctica

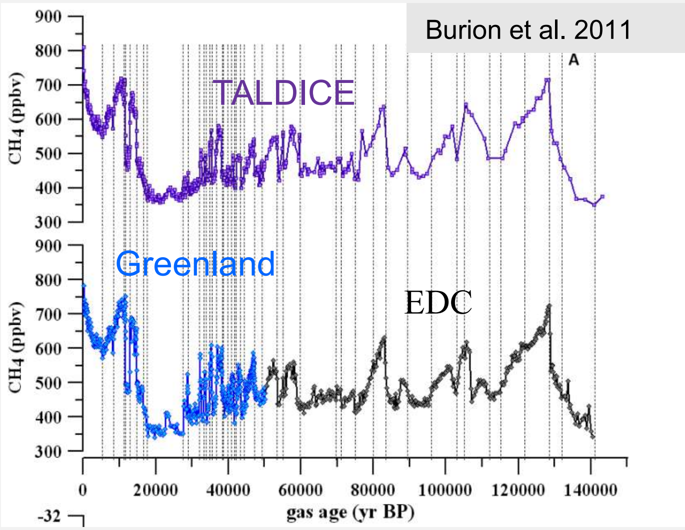
C. Buizert *et al*., Proc. Nat. Acad. Sci. 111, 6876(2014)

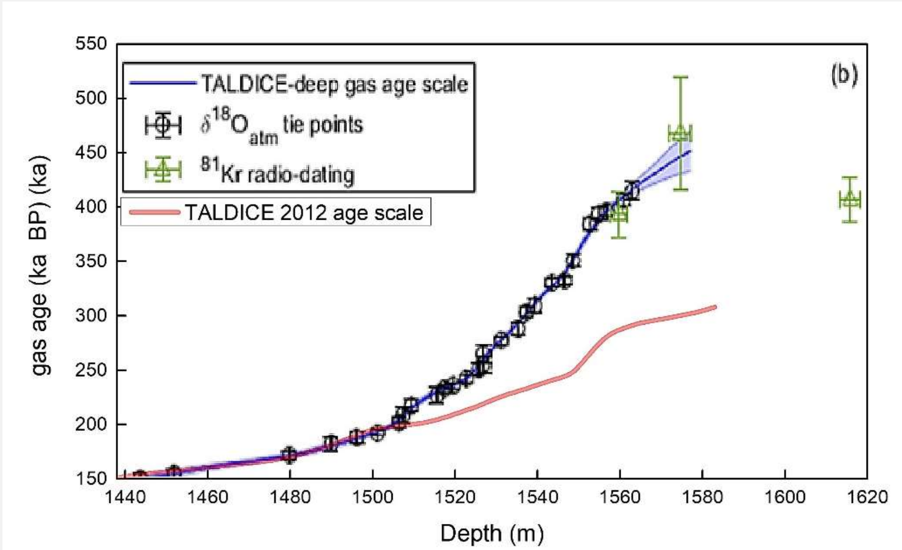
# An extension of the TALDICE ice core age scale reaching back to MIS 10.1

Ilaria Crotti
Venice & LSCE

Crotti *et al.*, QSR 266, 107078 (2021)

- A new δD, $\delta^{18}$Oatm, $\delta^{15}$N and $^{81}$Kr data set for TALDICE
- Definition of the **TALDICE-deep1 chronology** at 1438 - 1548 m depth and ~ 343 ka BP
- **$^{81}$Kr-dated layers** indicate the presence of **ice up to 470 ka** BP and **mixing/folding processes** below 1550 m depth down to the bottom (1620 m)



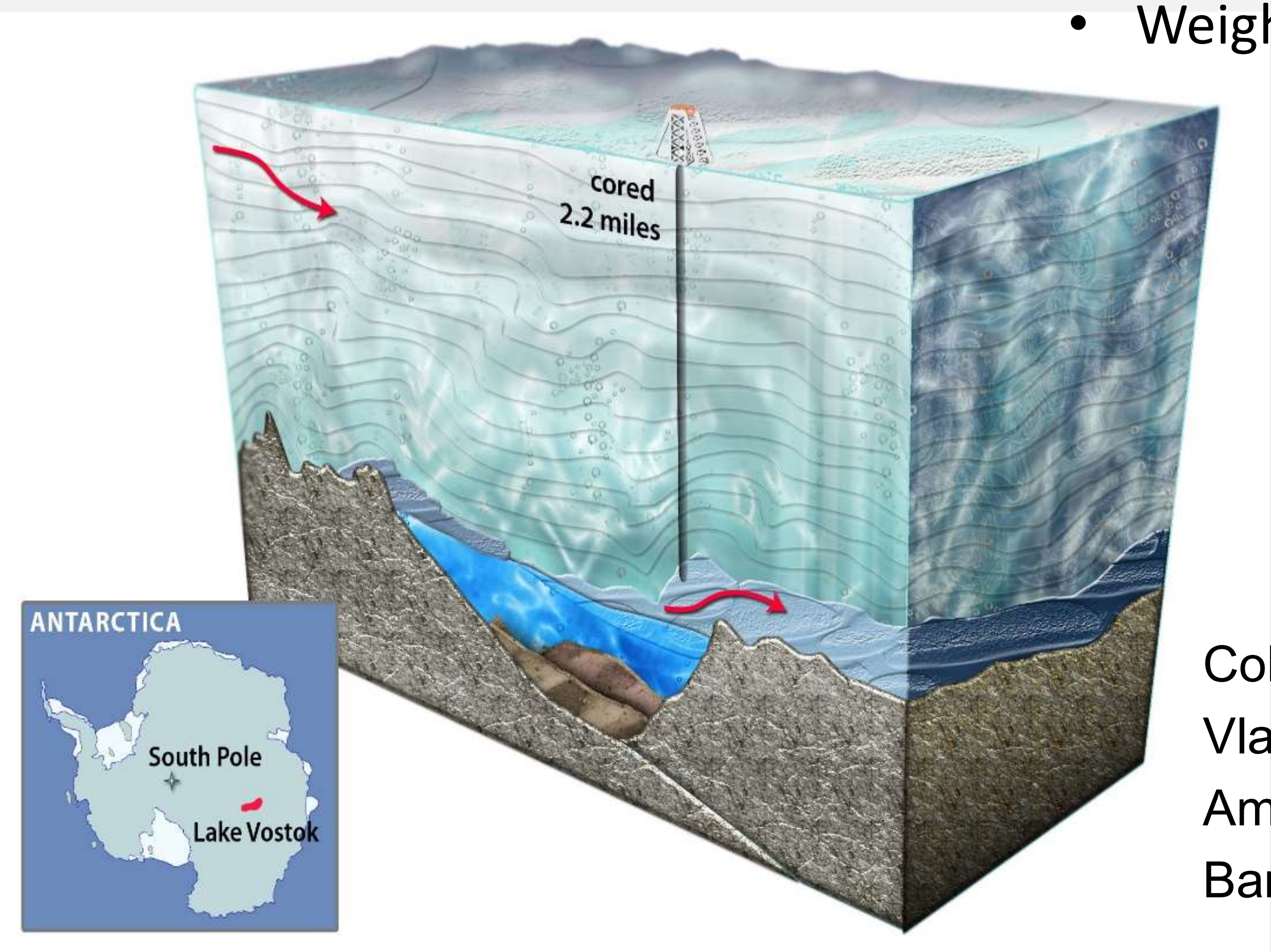




2021

2012

# Vostok Ice Core

- Depth : Below 3500m
- 3 Consecutive samples
- Weight : ~ 6 kg!




Collaborators:
Vladimir Lipenkov, AARI
Amaelle Landais, LSCE
Barbara Stenni, Venice

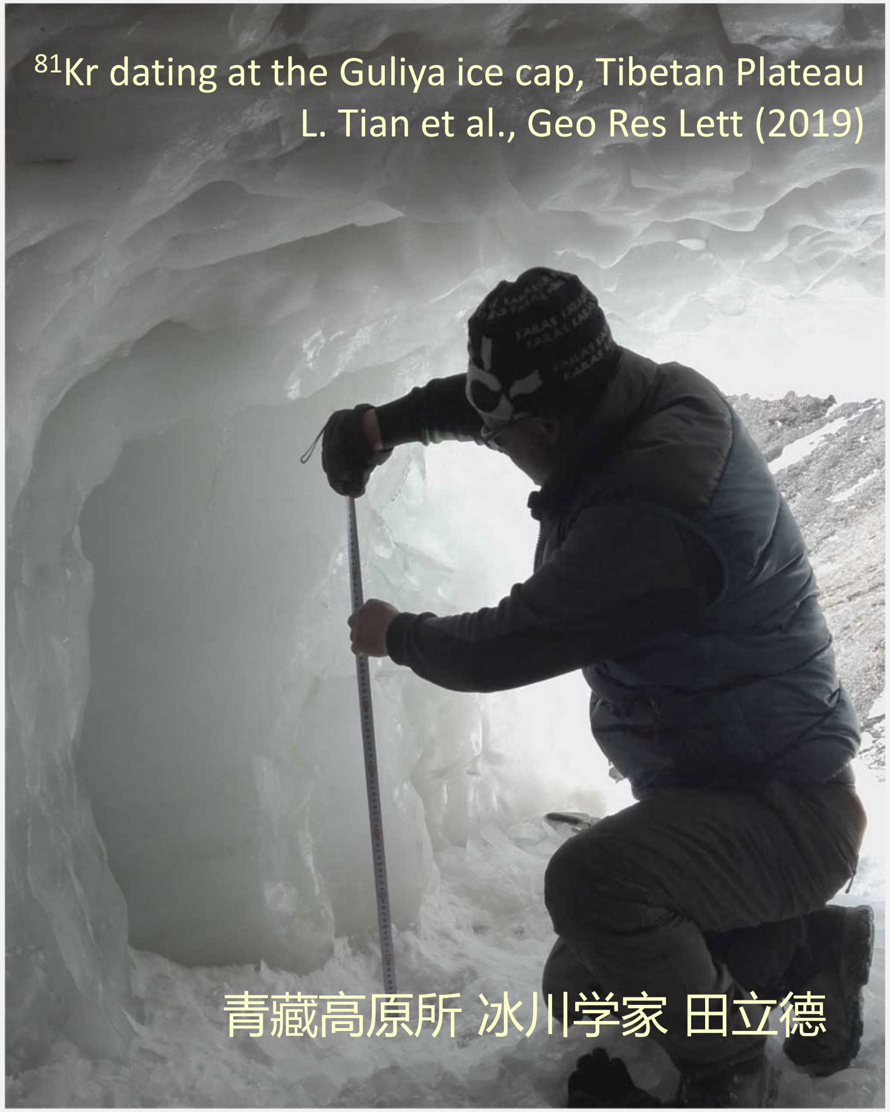
With Laboratory for Sciences of Climate and Environment （LSCE）
Arctic and Antarctic Research Institute（AARI）

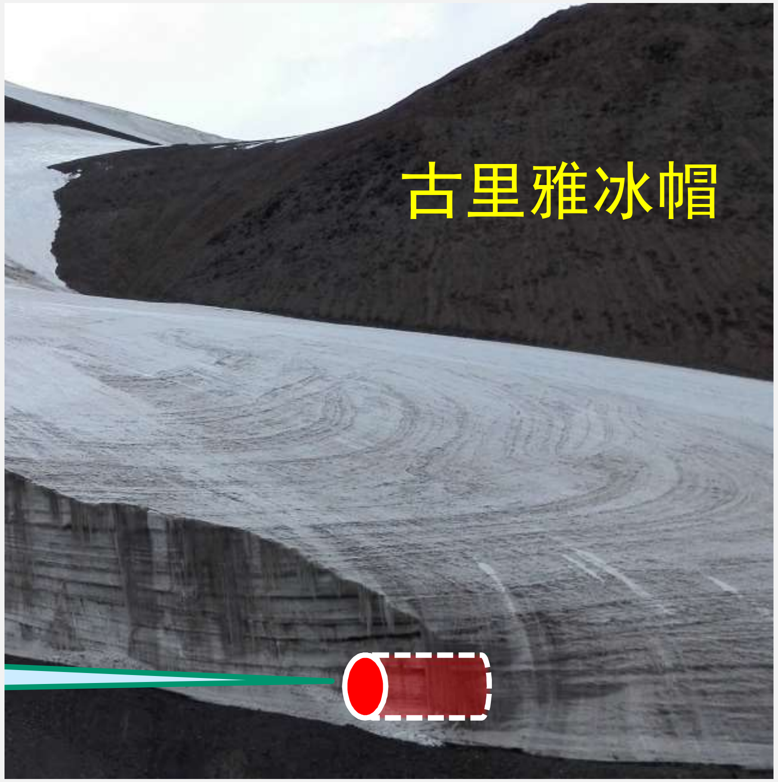
Greenland's Oldest Ice and Sediment
University of Vermont
October 22-25, 2019

丹麦波尔研究所冰库
Dorthe Darl-Jesen教授

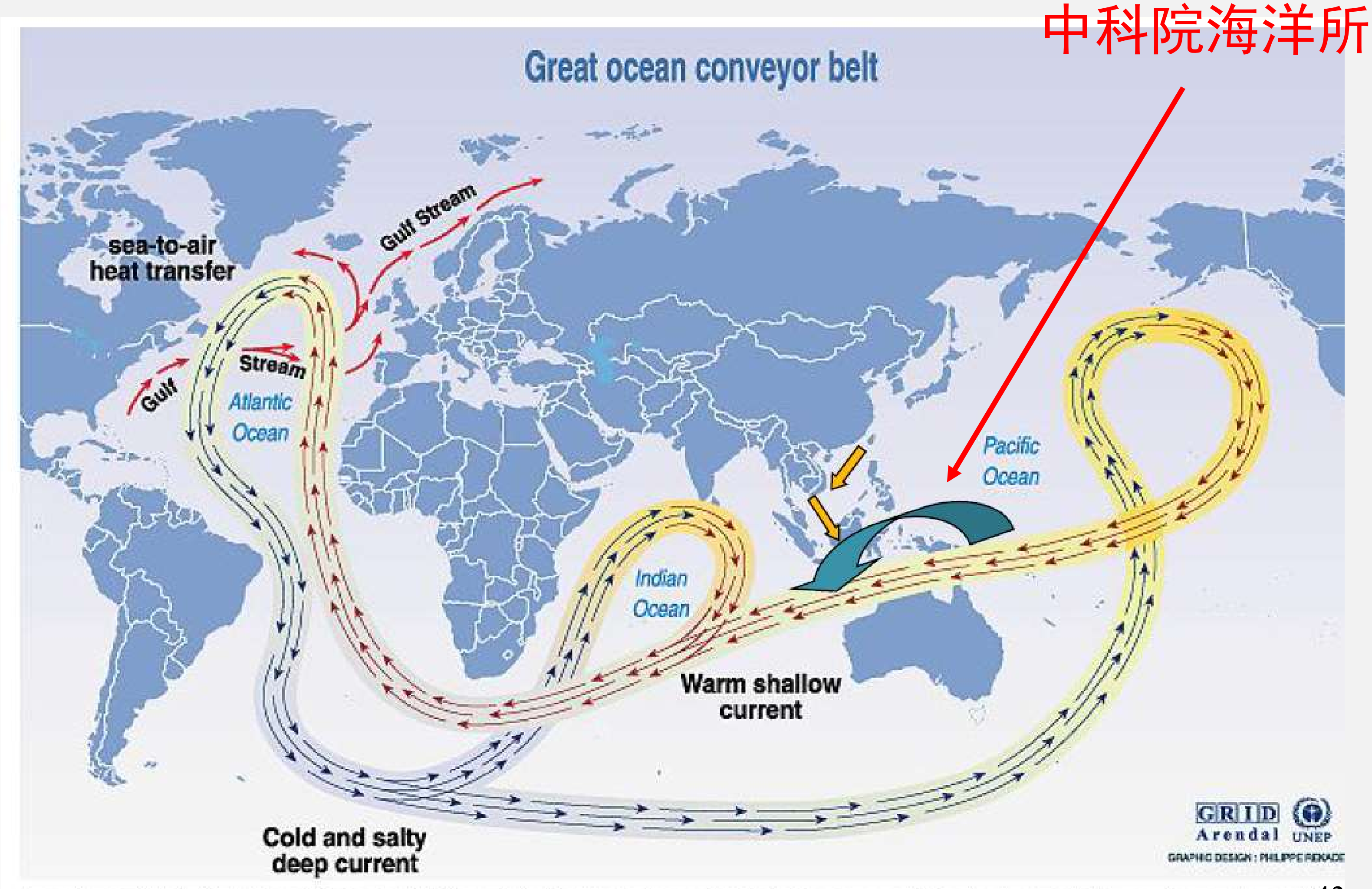
# 科学目标：寻找青藏高原最老的冰

中科院青藏高原研究所



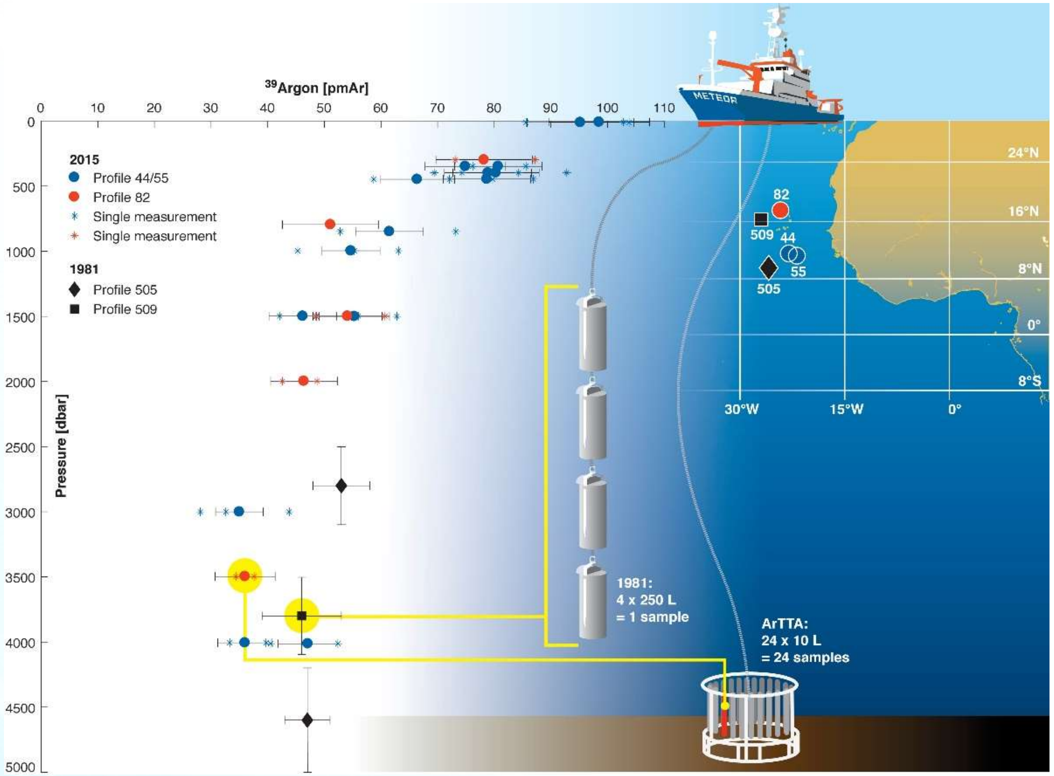
# 科学目标：研究洋流垂向结构、水体来源与去向




Source: Broecker, 1991, in Climate change 1995, Impacts, adaptations and mitigation of climate change: scientific-technical analyses, contribution of working group 2 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

# First $^{39}$Ar-dating of small ocean samples

Heidelberg University (Markus Oberthaler and Werner Aeschbach)
GEOMAR Kiel (Toste Tanhua)




Ebser, S. et al., *Nat. Commun.* **9**, 5046 (2018)

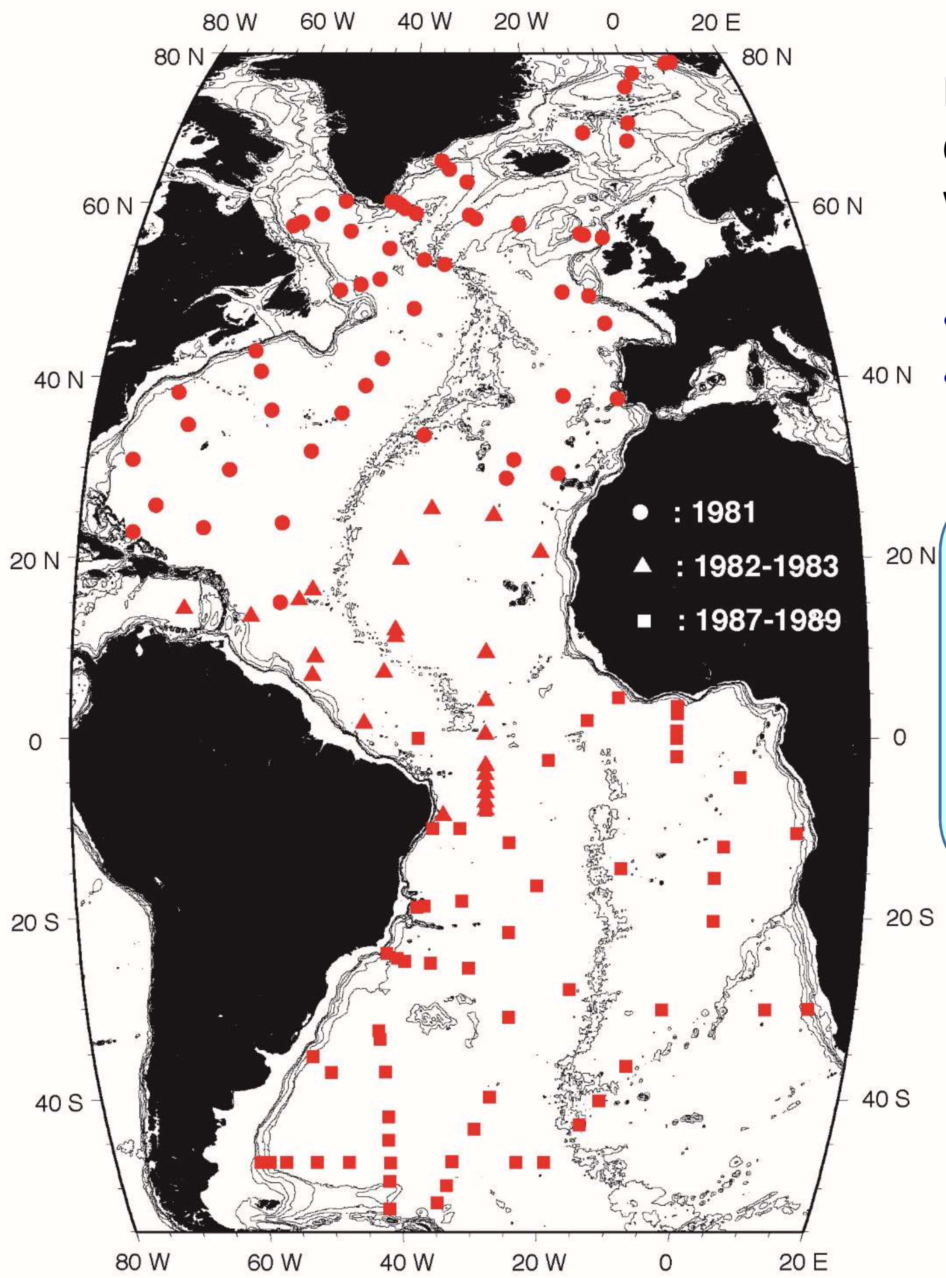
Sampling:

- Three depth profiles from the North Atlantic
  (Eastern tropical North Atlantic Oxygen Minimum Zone)
- 5 liters of water per data point
- Sampling with standard Niskin bottles

Main results:

- $^{39}$Ar & CFC constrain transit time distributions
- Mean ages of up to 800 years
- Reveal ocean ventilation patterns
- Advection in intermediate depths much more important than previously assumed

PPT by Sven Ebser

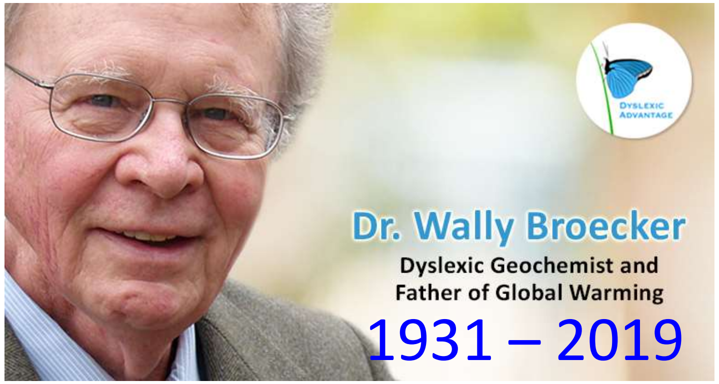



Z.-T. Lu *et al.*, Earth-Sci. Rev. (2014)

Lamont-Doherty Earth Observatory
Columbia University
William Smethie Jr., Martin Stute *et al*.

- 900 Atlantic samples collected in the 80's
- $^{39}$Ar dating by USTC and Heidelberg

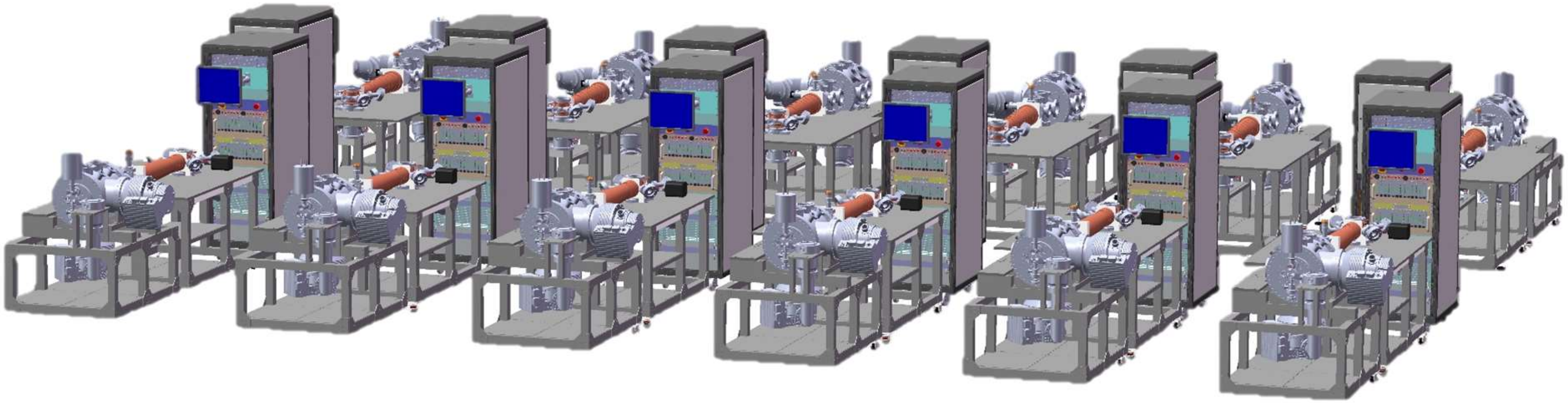
*"a more dense survey of $^{39}$Ar with higher accuracy measurements would prove of great value in constraining ocean general circulation models."*
--- Broecker and Peng (2000)



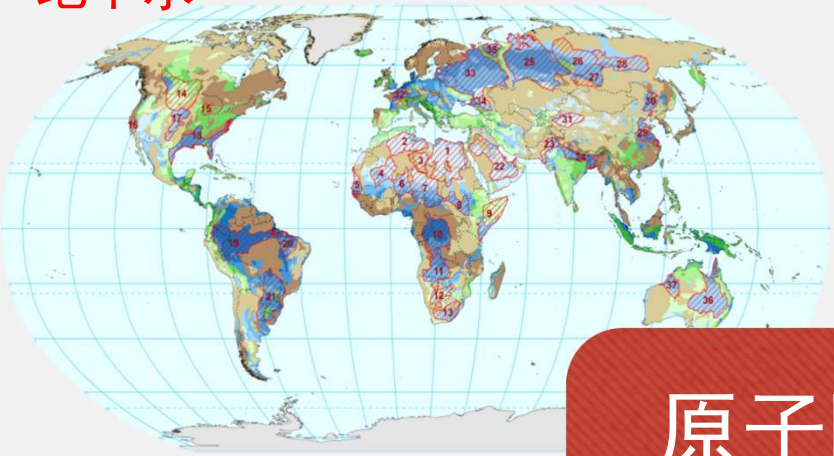
# 十四五规划：空地一体量子精密测量实验设施

## – 单原子探测平台

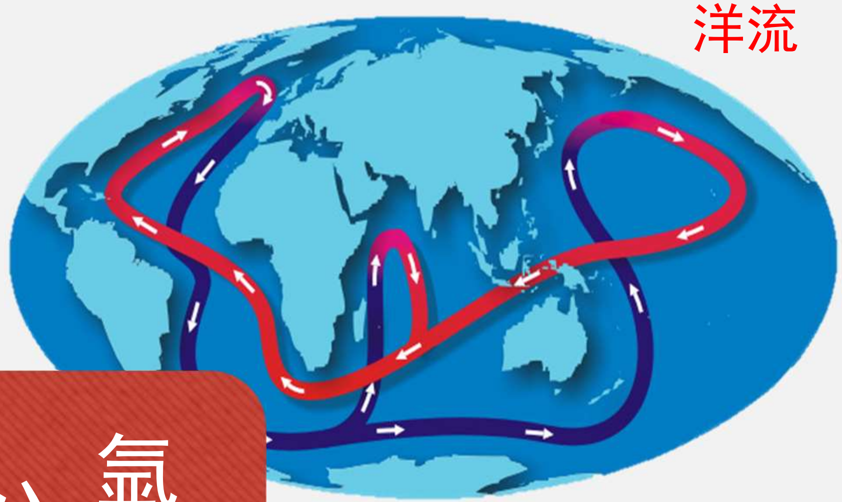
- 地下水研究、水资源管理
- 极地、山地冰川
- 大洋环流
- 环境监测与核安全



地下水

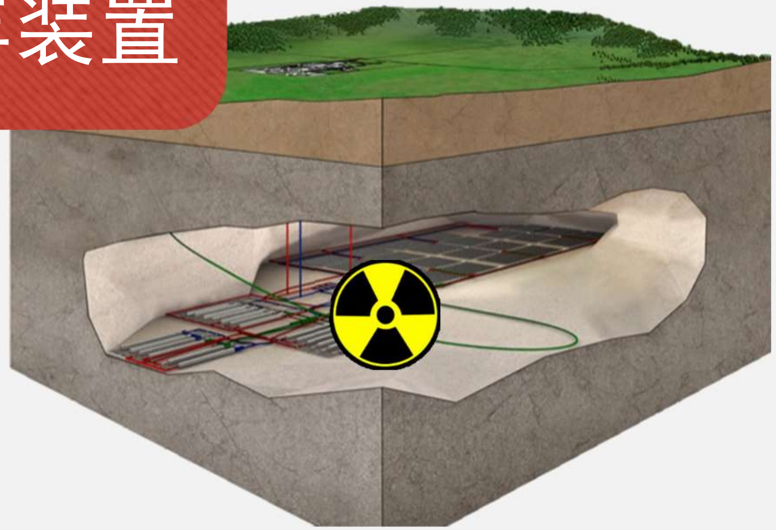


洋流



# 原子阱氪、氩同位素定年装置

冰川



环境监测与核安全