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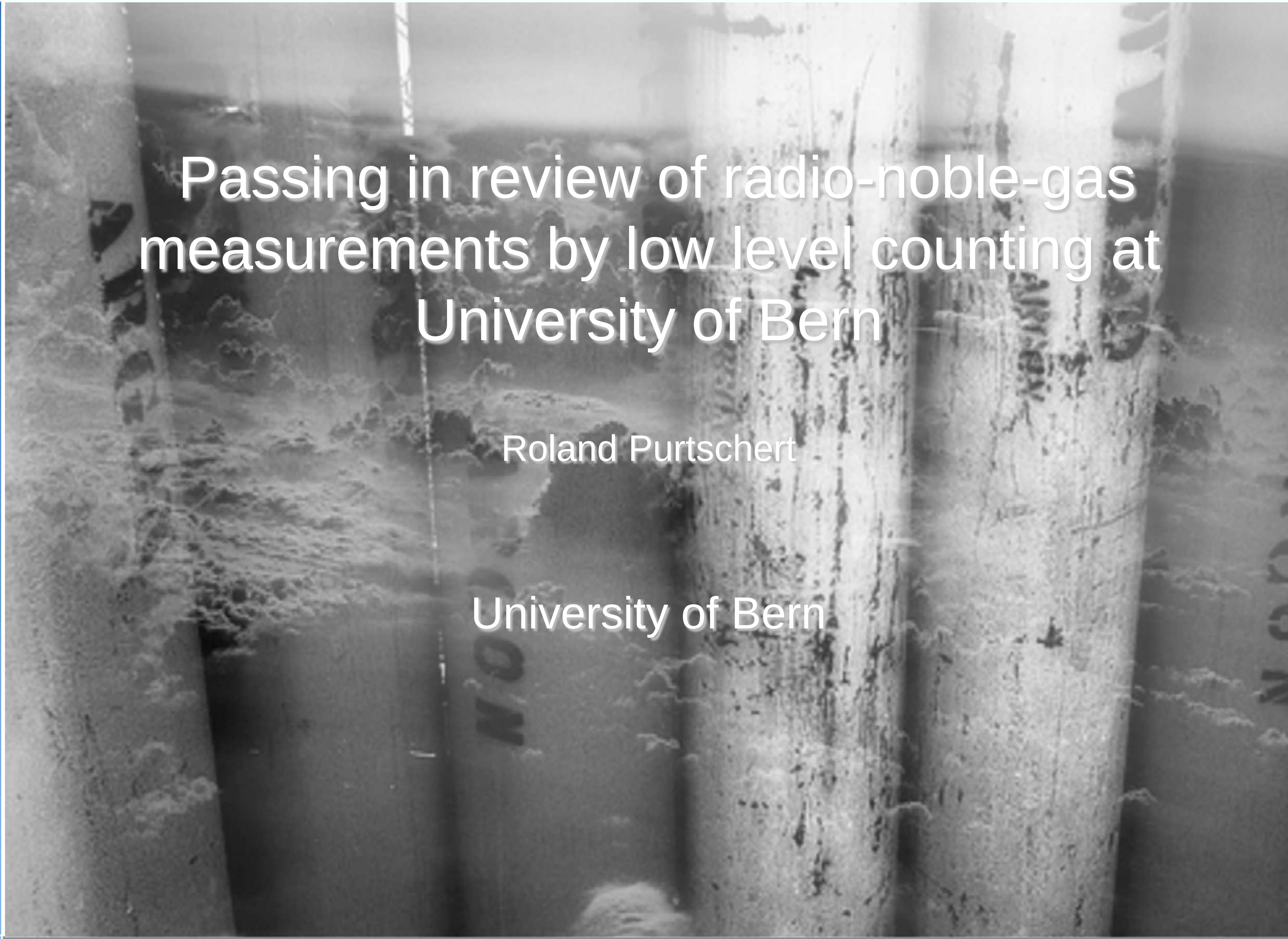
OESCHGER CENTRE CLIMATE CHANGE RESEARCH



Passing in review of radio-noble-gas measurements by low level counting at University of Bern

Roland Purtschert

University of Bern

Climate and Environmental Physics University of Bern

Topics

i. Introduction

Persons, Isotopes and timescales

ii. Activity measurements

Low Level Counting at Climate & Environmental Physics Institute Bern

iii. Sample preparation

Status and outlook

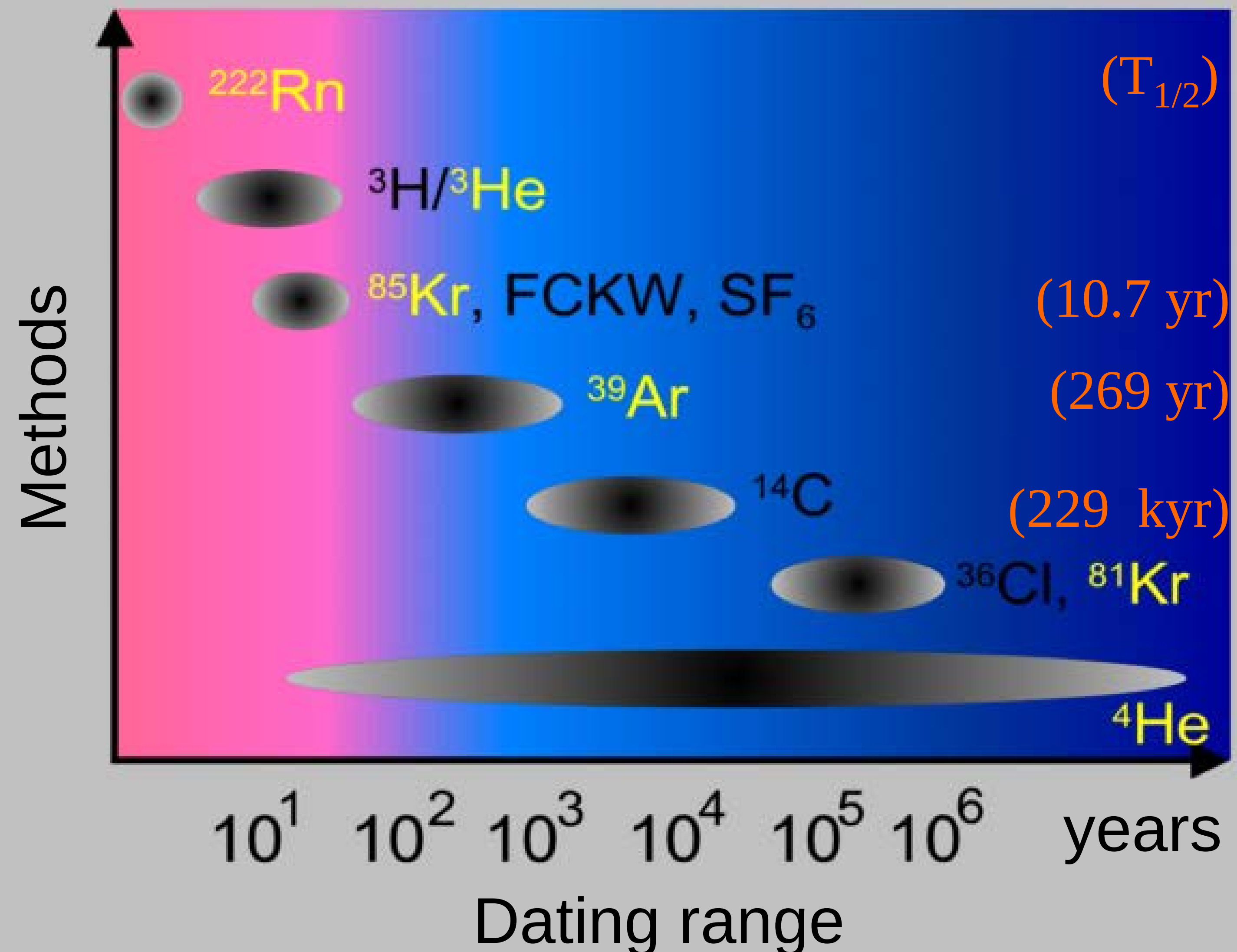
iv. Gas extraction in the field

Requirements and examples under specific conditions

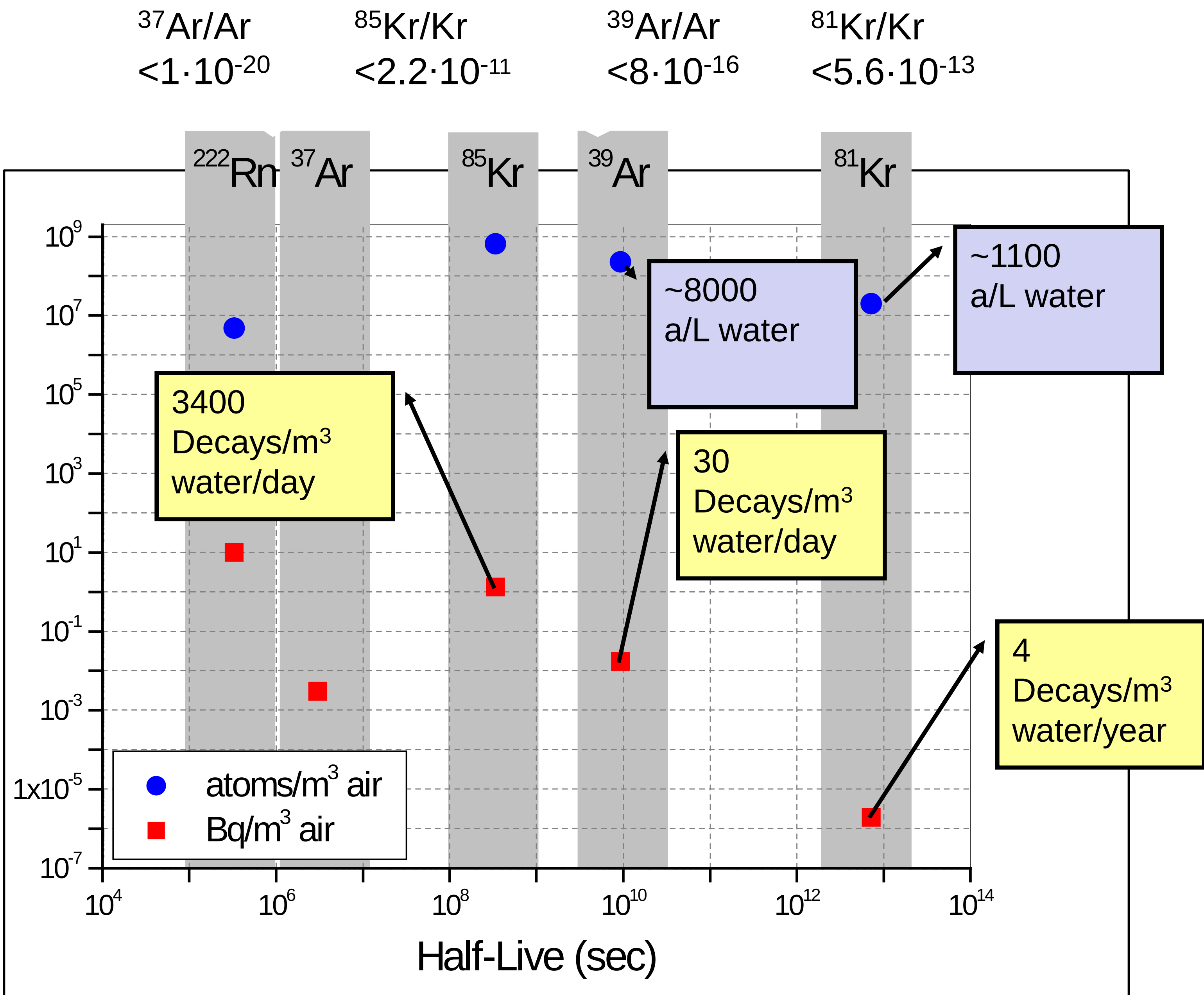
v. Applications

Few snapshots

Timescales and Tracers



Concentrations und Activities



$8 \cdot 10^{-16}$??

$\sim 10^{-10}$

(range of NG MS)

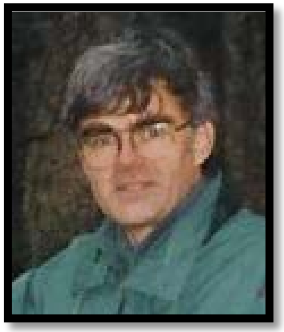
$\sim 10^{-16}$

The pioneers at Physics Institute Bern

Hans Oeschger († 1998)

Heinz Hugo Loosli

Bernhard Lehmann († 2005)



ELSEVIER

Applied Geochemistry

Volume 6, Issue 4, 1991, Pages 419–423

Dating Very Old Groundwater, Milk River Aquifer

^{81}Kr and ^{85}Kr in groundwater, Milk River aquifer, Alberta, Canada

B.E. Lehmann, H.H. Loosli, D. Rauber

Physics Institute, University of Bern, Bern, Switzerland

N. Thonnard, R.D. Willis

Atom Sciences Inc., Oak Ridge, TN 37830, U.S.A.

Received 28 September 1989. Accepted 6 June 1990. Available online 15 April 2003.

http://dx.doi.org/10.1016/0883-2927(91)90041-M, How to Cite or Link Using DOI

Abstract

The ^{85}Kr activity of well No. 9 is (2.1 ± 0.3) mBq/cm^3 STP ofKr or ≈0.3% of the modern atmospheric activity indicating that no young water component is present in this groundwater and that no contamination occurred in extracting a Kr gas sample for ^{81}Kr analysis.

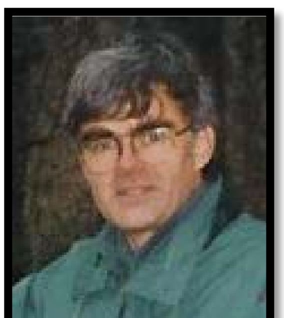
The ^{81}Kr concentration was measured by laser resonance ionization spectroscopy to be 82 ± 18% of the modern atmospheric concentration. Only 5000 atoms of ^{81}Kr were used in the final analytical step which represent ≈7% of the initial number present in a water sample of 50 1. An upper limit of 140 ka is calculated for the age of the water from a simple ^{81}Kr decay model. Of key importance for the future use of a ^{81}Kr dating technique is the conclusion that subsurface production of ^{81}Kr appears to be unimportant.

The pioneers at Physics Institute Bern

Hans Oeschger († 1998)

Heinz Hugo Loosli

Bernhard Lehmann († 2005)



Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms
Volume 17, Issues 5–6, 2 November 1986, Pages 402–405

Ten years low-level counting in the underground laboratoryin in Bern, Switzerland

H.H. Loosli, M. Möll, H. Oeschger, U. Schotterer
Physics Institute, University of Bern, 3012 Bern, Switzerland

Available online 29 October 2002.
http://dx.doi.org/10.1016/0168-583X(86)90172-2, How to Cite or Link Using DOI   Cited by in Scopus (10)
Permissions & Reprints

Abstract

Although new techniques of direct atom counting have been developed, which are also discussed at this conference, the good old low-level counting technique is still important. Looking back to the first decade of measurements in our underground laboratory, we realize that many interesting results have been obtained. The following examples are discussed:

^{39}Ar is up to now only measured in Bern. This isotope has been used for ice and groundwater dating and ...

... and 40 standard, background or blank samples are measured per year. As an example, the ^{14}C results measured in tree leaves at reference stations in Switzerland, unaffected by man-made contributions, are presented.

Although new techniques of direct atom counting have been developed, which are also discussed at this conference, the good old low-level counting technique is still important.

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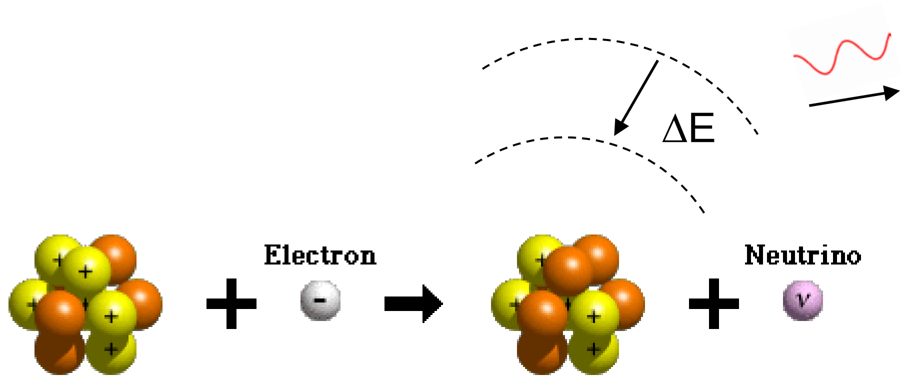
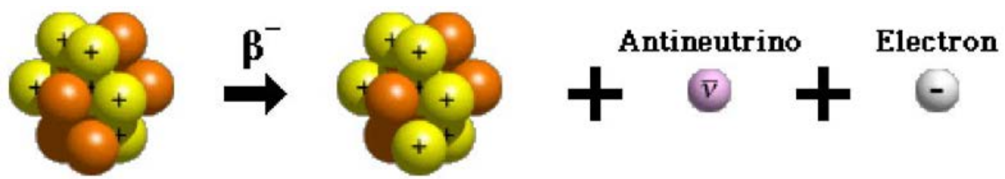
β-Decay modes

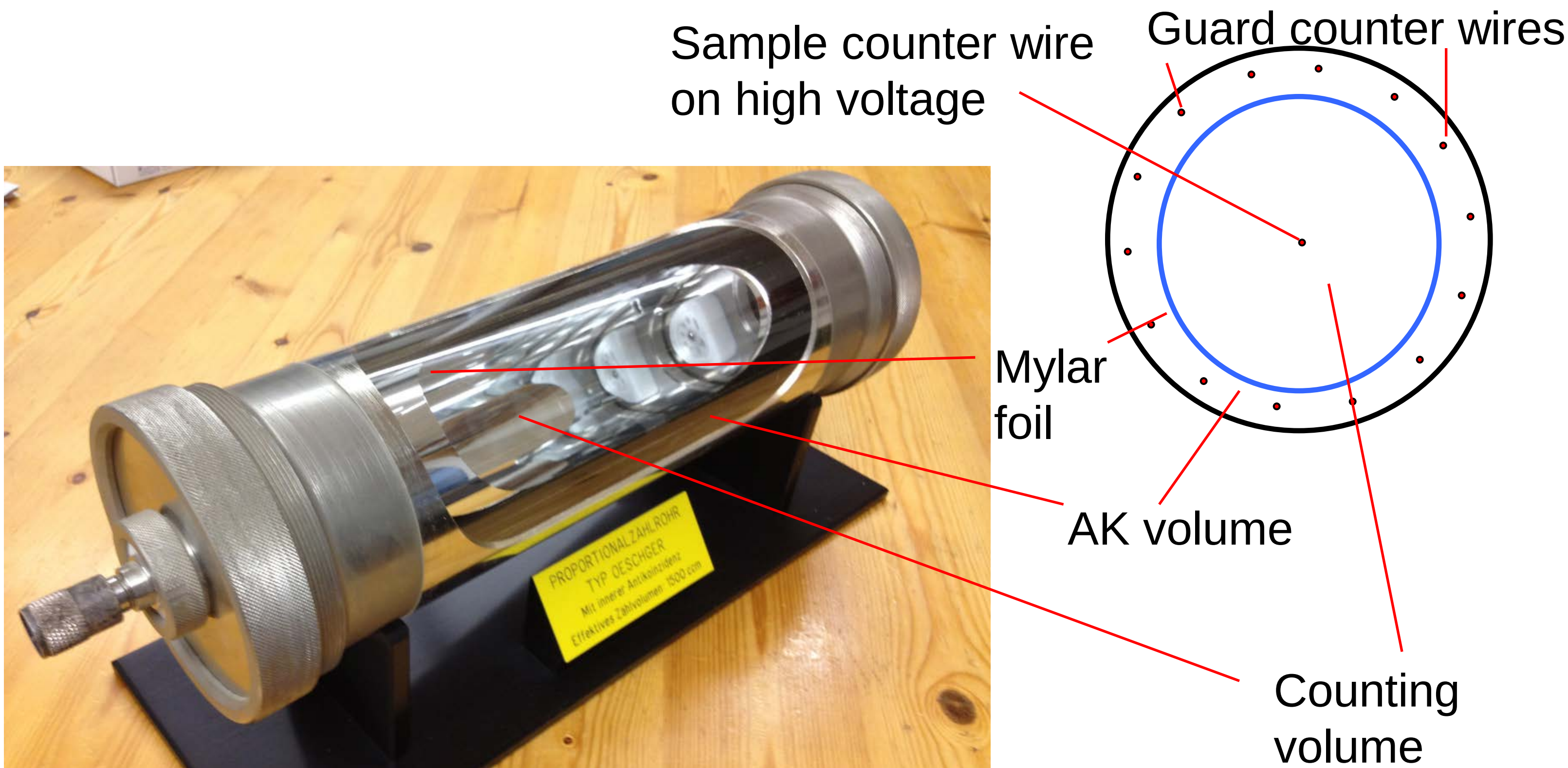


^{37}Ar	^{37}Cl	$\Delta E_{k\alpha}$ 2.8 keV
^{81}Kr	^{81}Br	$\Delta E_{k\alpha}$ 13.5 keV



^{39}Ar	^{39}K	E_{max} 560 keV
^{85}Kr	^{85}Rb	E_{max} 675 keV

Oeschger counter: Principle



Oeschger et al, 1975

- The Oeschger counter allowed finally to measure ^{14}C at natural activity levels.
- It was the leading instrument for many years, which enabled e.g the first time to date the "age" of Pacific deep water

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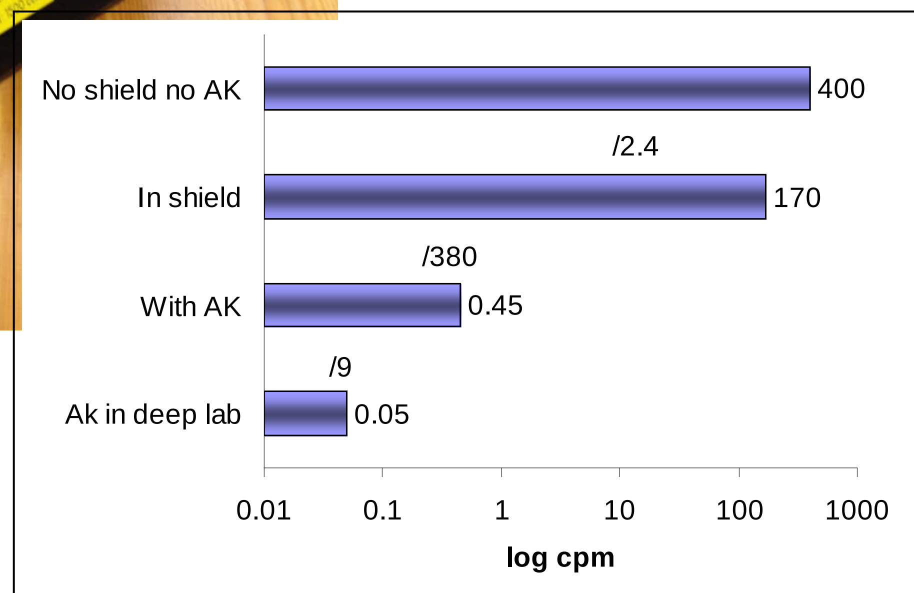
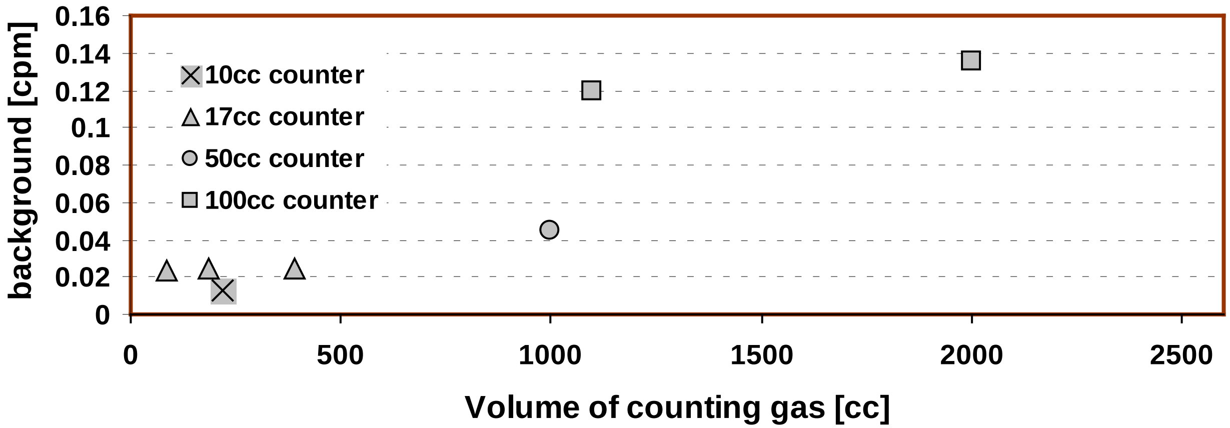
Oeschger counter: Background



Oeschger et al, 1975

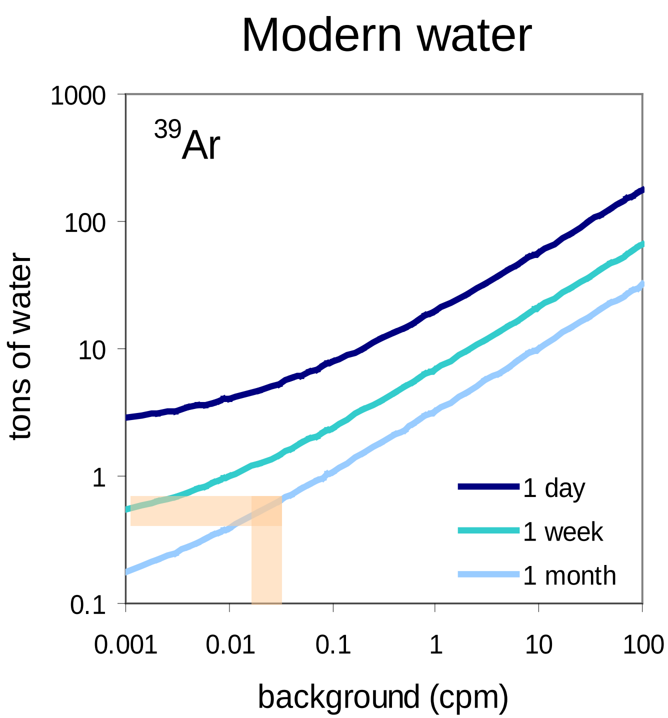
High pressure proportional counters

16 cc counter

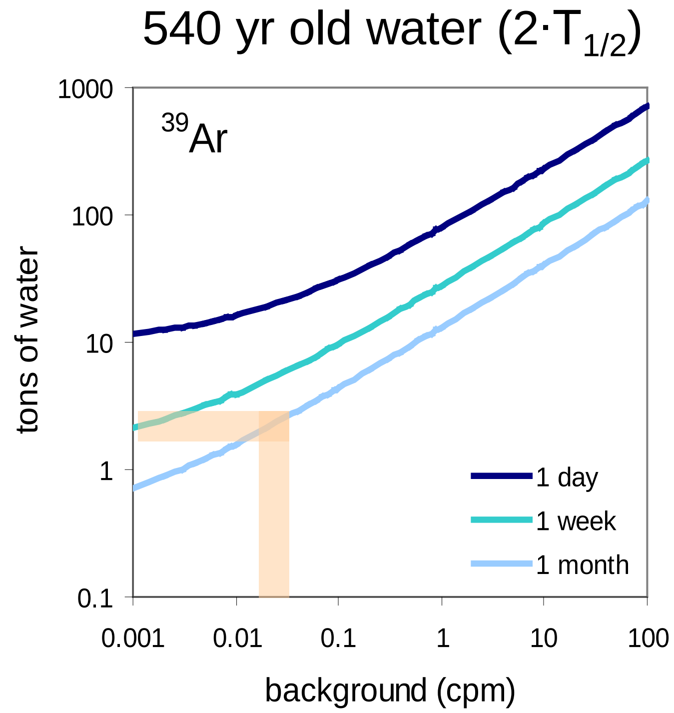


LLC-^{39}Ar: Minimal water volume for a precision of 0.1

Air equilibrated water at 10˚C and 1 atm, counting and extraction yield 0.7



Background 16-cc counter: 0.02 cpm
Counting time: 1 month
Water volume: 0.5 ton

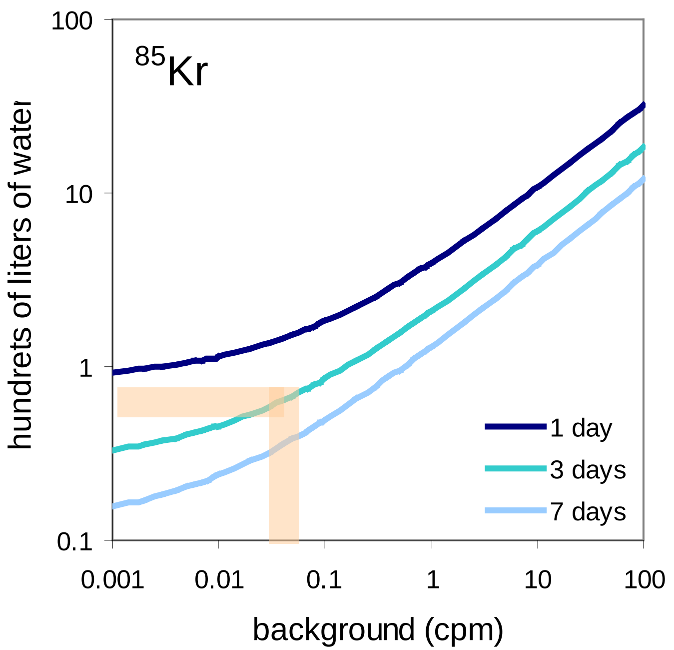


Counting time: 1 month
Water volume: 1.5-2 tons

LLC-^{85}Kr: Minimal water volume for a precision of 0.05

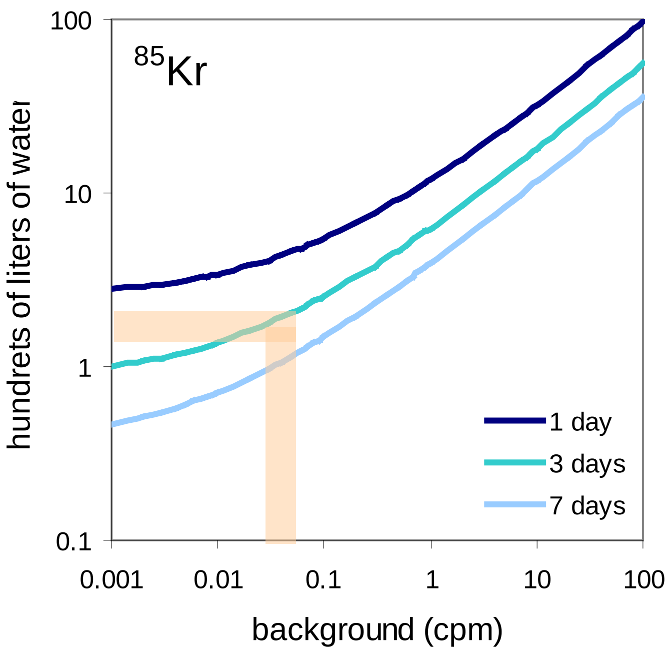
Air equilibrated water at 10˚C and 1 atm, counting and extraction yield 0.7

50 dpm/ccKr
(τ~10 years)



Background 16-cc counter: 0.02 cpm
Counting time: 3 days
Water volume: ~90 Liters

17 dpm/ccKr
(t~22 years)

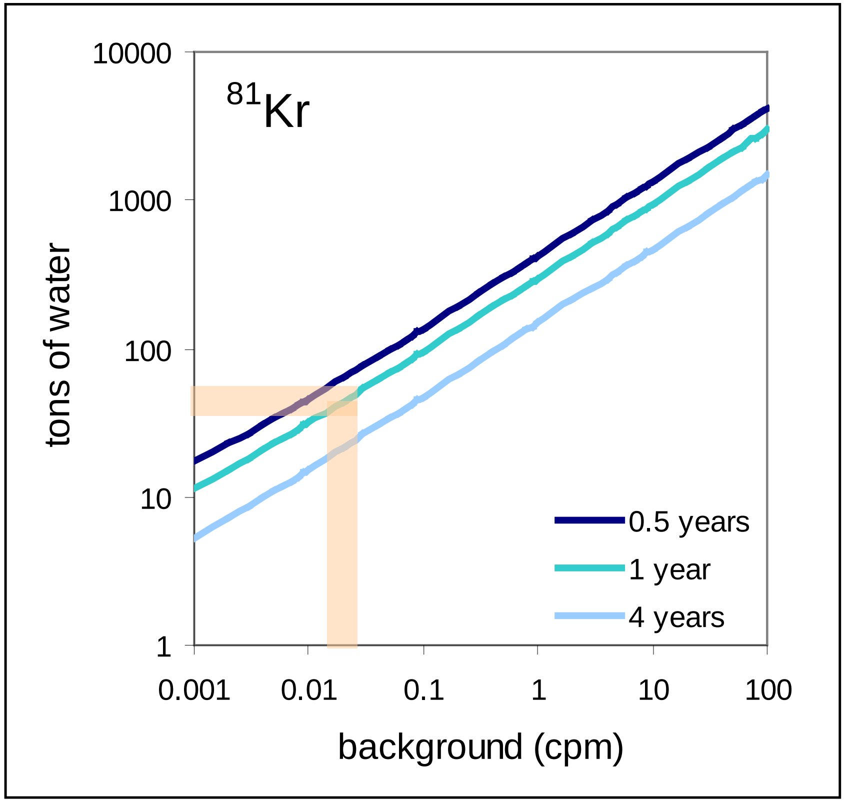


Counting time: 3 days
Water volume: 200 Liters

LLC-^{81}Kr: Minimal water volume for a precision of 0.1

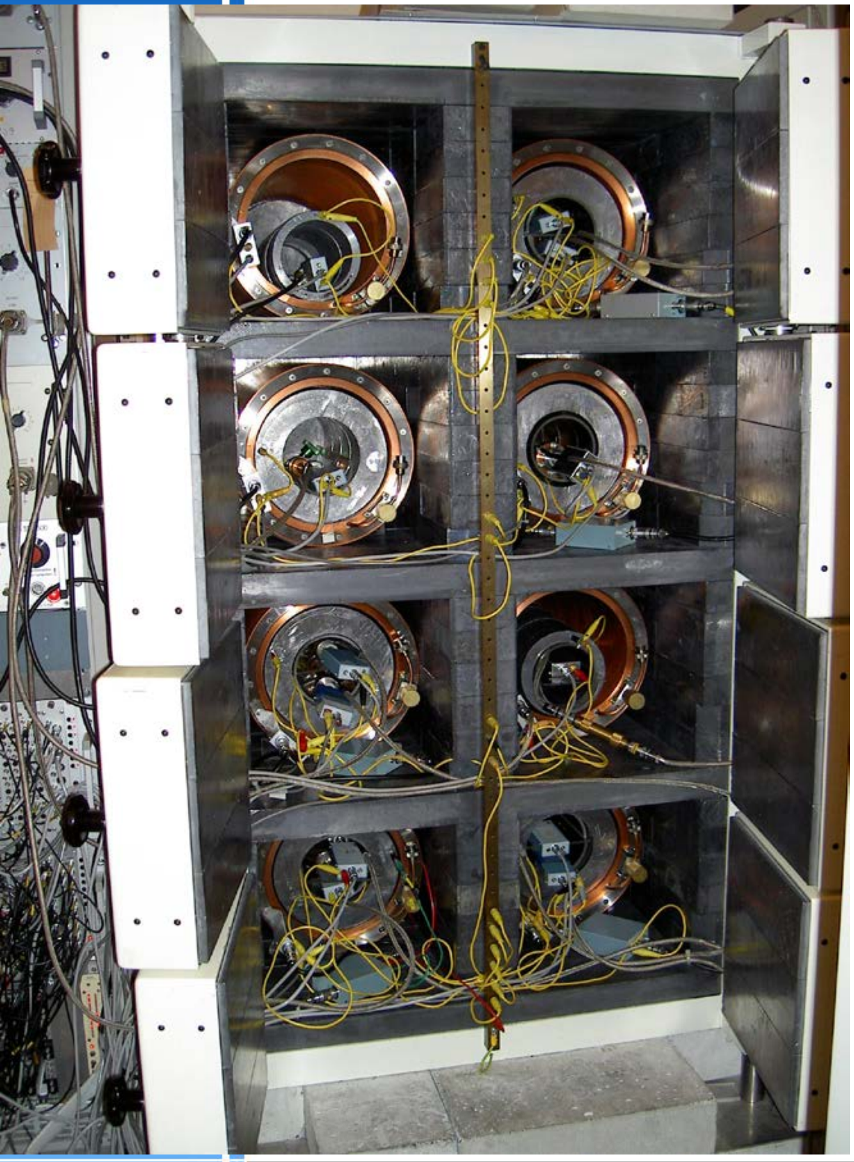
Air equilibrated water at 10˚C and 1 atm, counting and extraction yield 0.7

Modern sample

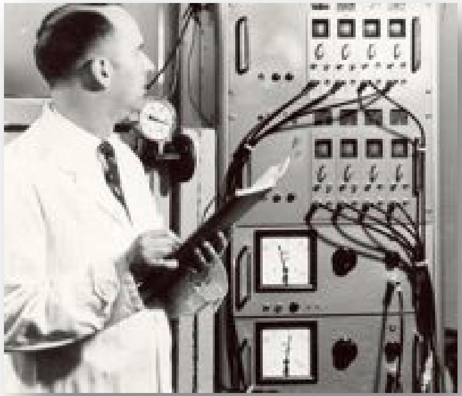


60 tons for counting time 1 year!!

LLC facility at University of Bern

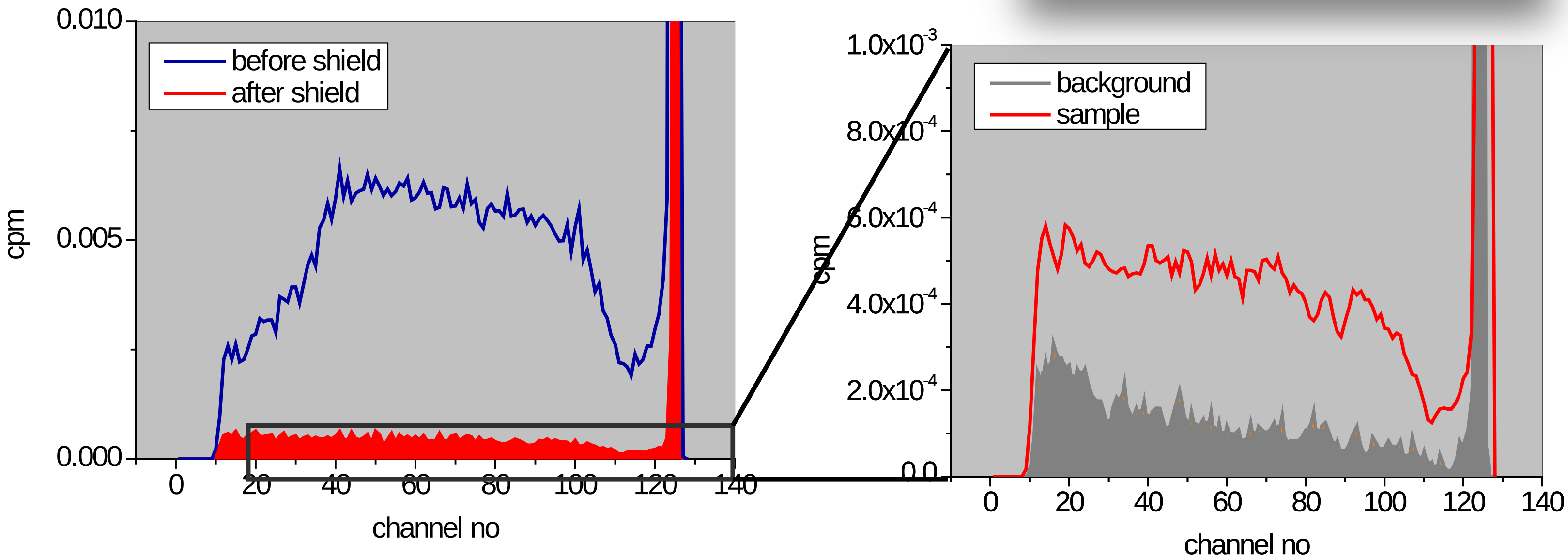


- Deep laboratory (35 m.b.s. :70 m water equivalent) build with low activity concrete
- Passive shielding with old lead (^{210}Pb free)
- Active shielding (external guard counters)



^{39}Ar β-spectra in 16 cc counter

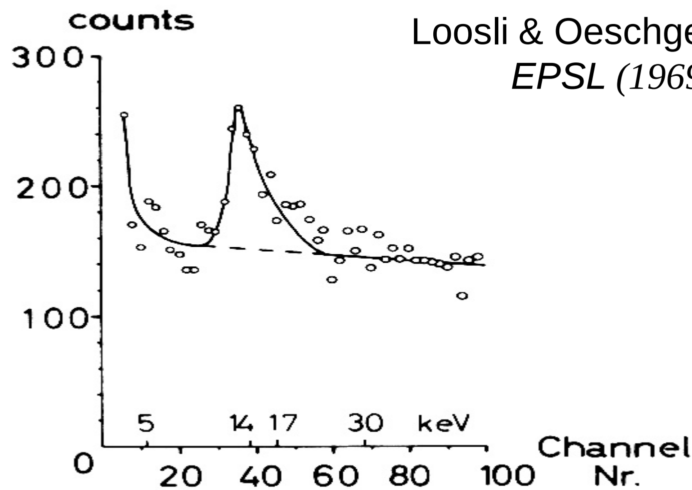
Groundwater sample (100%modern)



Background-reduction
Active shielding
Factor ~10

Modern sample: 0.039 cpm (2.2 cph)
Background : 0.024 cpm (1.5 cph)
(signal/noise: 1.6)

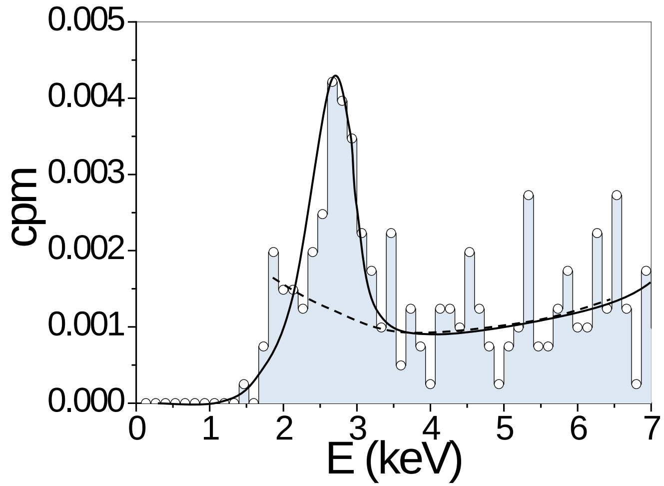
Sample Spectra ^{81}Kr and ^{37}Ar



Loosli & Oeschger
EPSL (1969)

^{81}Kr activity in tropospheric air:

0.1 dpm/l Kr
($^{81}Kr/Kr$: $5.9 \cdot 10^{-13}$)



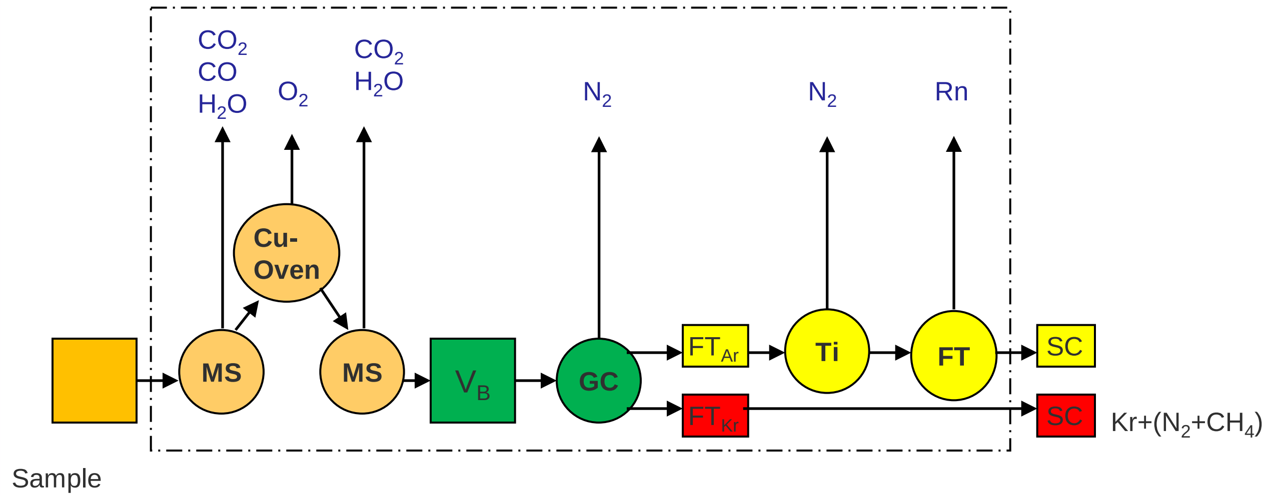
^{37}Ar in tropospheric air in Bern from 25.3.11

7±2 mBq/m^3_{air}

CTBTO, 2011

Large Volume Noble Gas Purifikation

Former Ar-Kr Separation System in Bern



MS: Molecular sieve 5 Å
GC: Activated charcoal and MS 5 Å
FT: Freezing trap
SC: Sample container

- Helium carrier
- Injections of 2-litre aliquots into GC
- Preparation time ~3 days

i.Introduction
ii.LLC
iii.Preparation
iv.Gas extraction
v.Applications

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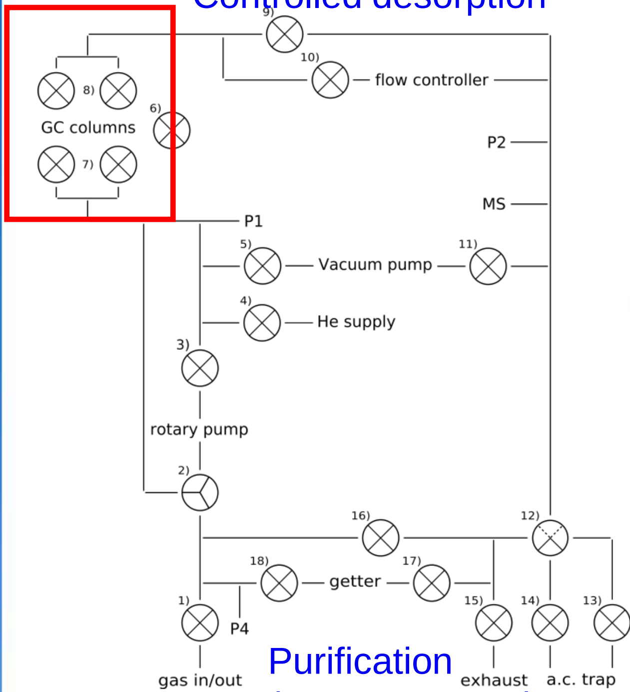
Current Ar separation system

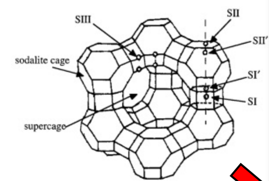
Riedmann, 2011

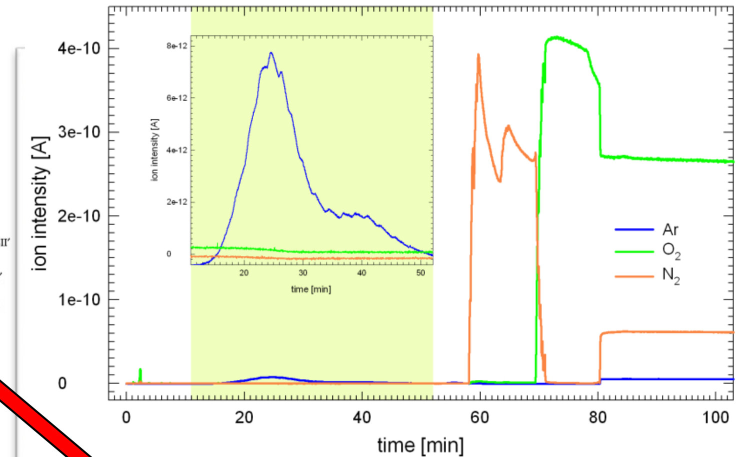
Controlled desorption



Purification (99.99996 % Ar)

Ar trap





- Lithium-cation exchanged faujasite zeolite (Li-LSX)
- High adsorption strength for N_2
- Best O_2/Ar separation at 153K
  → Temperature control is crucial

i.Introduction
ii.LLC
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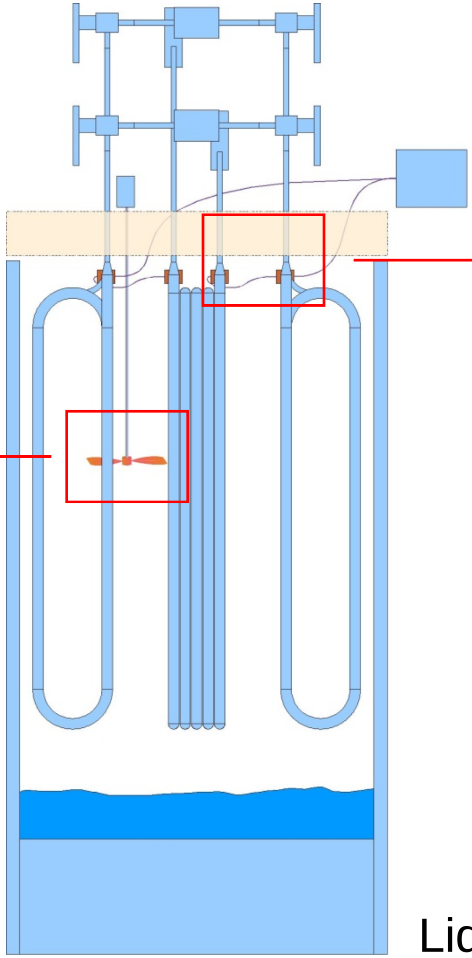
Temperature control

Rotor for T homogenization

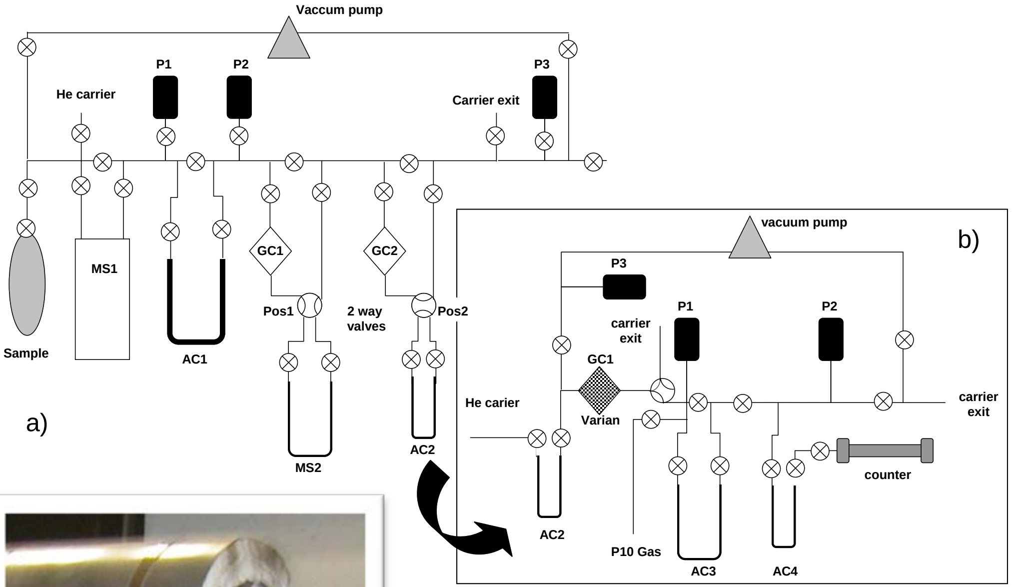


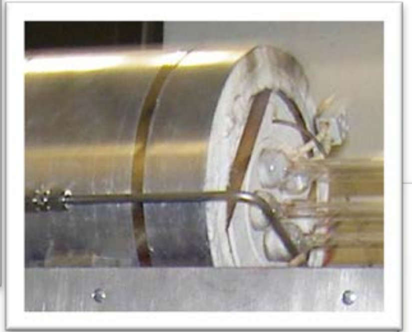
Liquid N_2 (77K)

Direct heating of GC colums (60 A)

83K  473K

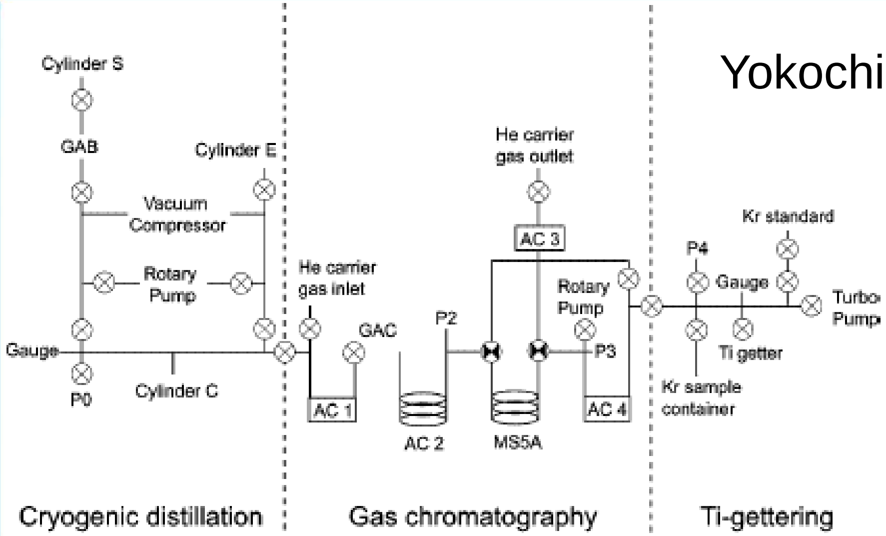
Kr Separation in Bern





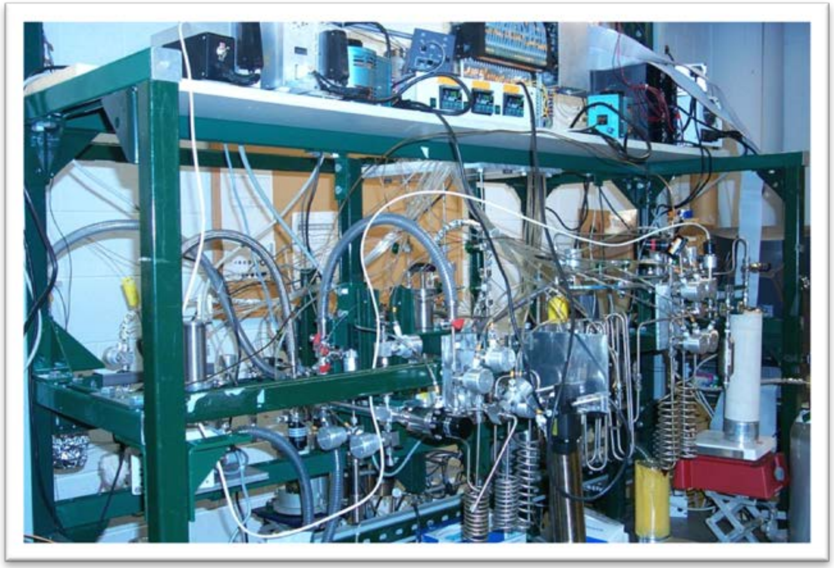
- Helium carrier
- Kr purification by 3 GC steps using MS 5˚A and AC
- Large volume CH_4 separation over Cu oven
- Separation efficiency 70-90% f([CH_4])
- Separation time ~4 hours/sample

Kr seaparation at UIC



Yokochi et al, 2008

See lab tour



Distillation:

- N_2-Ar-O_2 depletion by a factor
- of 50-100 in 3-4 hours

Gas chromatography:

- Kr+CH_4 separation by AC
- Kr separation by MS 5Å
- ~ 300 cc separation in 1 hour

Requirements for gas sampling

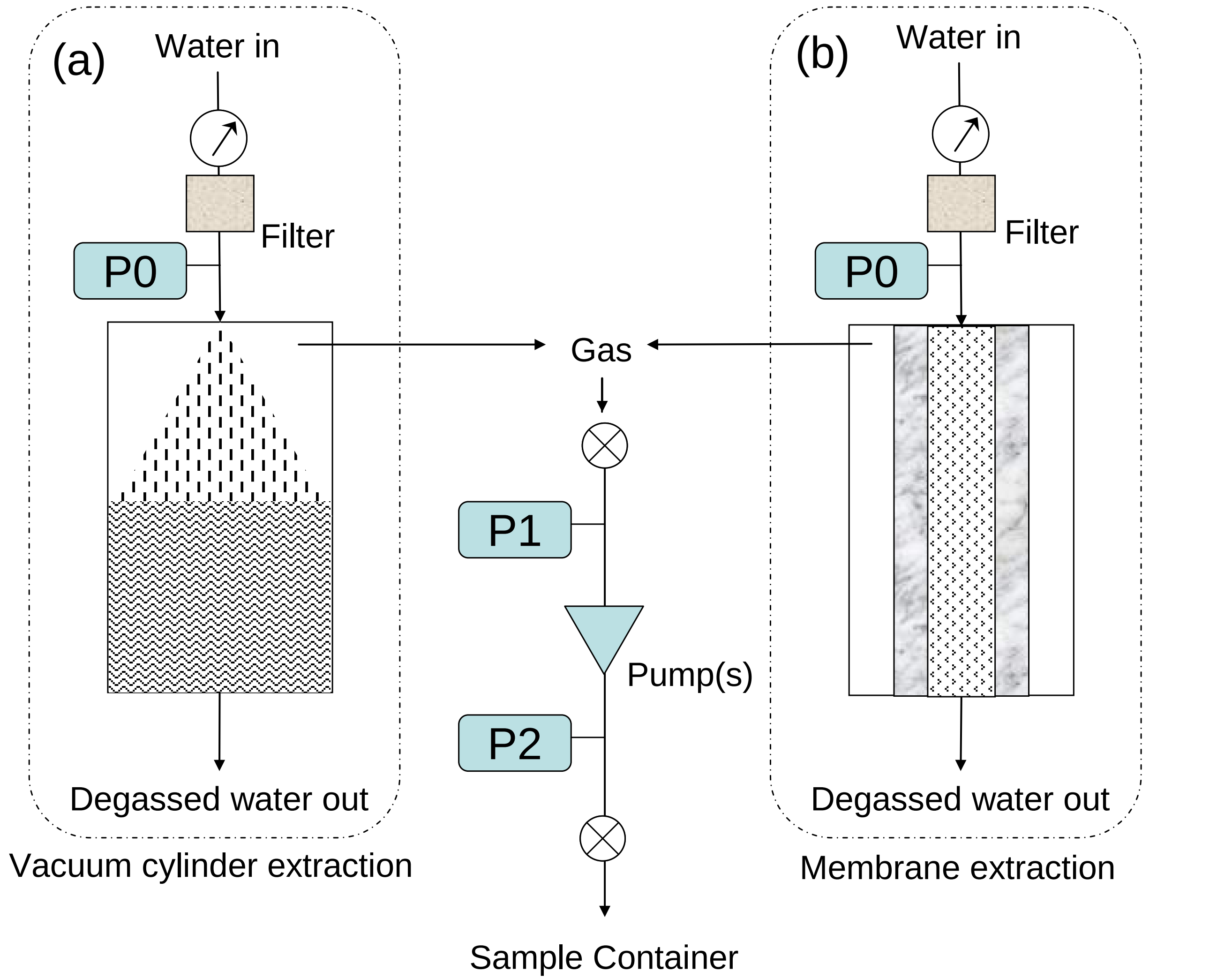
Denmark, 2008

- No contact with atmospheric air
- (Still) relatively large sample volumes must be extracted under controlled and constant conditions
- Degassing in the field with a robust and mobile device with high extraction yield

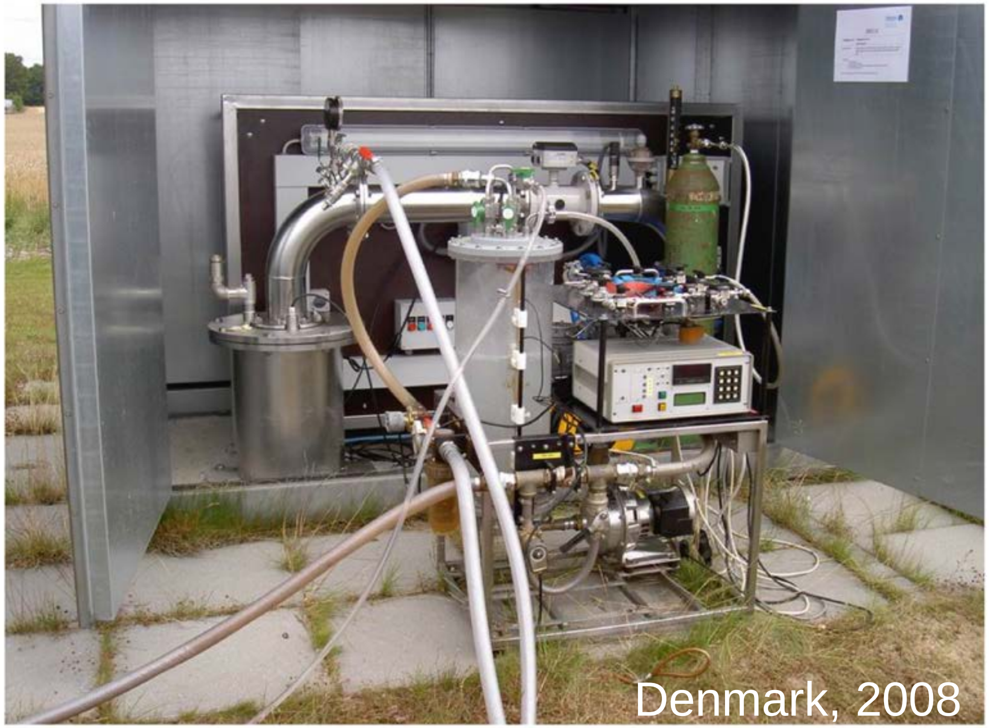
Note Because we measure isotope ratios ($^{39}Ar/Ar$, $^{81}Kr/Kr$ etc) these methods are (rather) insensitive to

- Details of recharge conditions (the addition of excess air, recharge temperature)
- Degree of degassing (both in nature and during sampling)

Gas extraction systems



Vacuum cylinder extraction

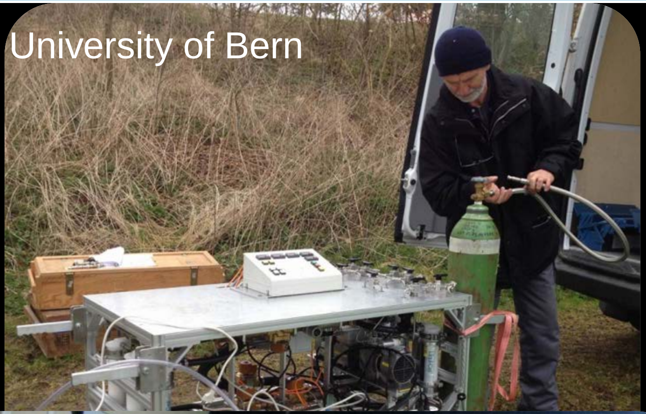



Australia, 2009


Vietnam, 2012


Egypt, 2002

Gasextraction with membranes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University of Heidelberg

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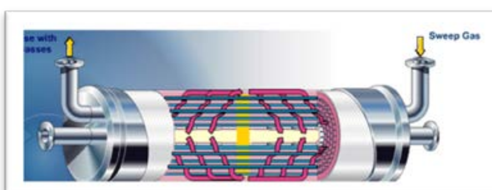
Pros and Contras

+	-
Extraction chamber	
Insensitive to the chemical and physical water composition (pH, Temperature, hydrocarbons, suspended matter etc)	Requires a low extraction pressure and is therefore more sensitive to leaks
Easy to repair in case of breakdown by experienced personnel (importan in remote areas)	Leak testing and setup requires experienced personnel
Operational for a large range of wate fluxes	Relatively high flow resistance may limit water flow rate
Allows a low extraction pressure thu higher extraction efficiency	Not commercially available and therefor lavish to construct



+	-
Membrane contactors	
Commercially available membrane contactors, relatively inexpensive	Sensitive to the chemical and physical water composition:
Modular: several contactors can be combined in parallel (increased water flux) and/or in series (increased extraction efficiency)	- Not suitable in the presence of substances which reduce the surface tension of water.
Compact and relatively easy to operate in the field	- Not suitable for a high-temperature environment (i.e., >70 °C) - Suspended or precipitated matter may clog the pores
Low inlet water pressure facilitates high water flux; operational over larg flux range	A damaged membrane requires a relatively complex regenerating processes

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Varying conditions: untapped water

Nubian aquifer, Egypt, 2003

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Varying conditions: untapped water



Sampling under varying conditions: little water pressure

Italy, Venetian plain, 2008


GAB, Australia, 2009

Even more exotic problems

Yellowstone, USA, 2007

→Talk Reika

Large volume ice sampling

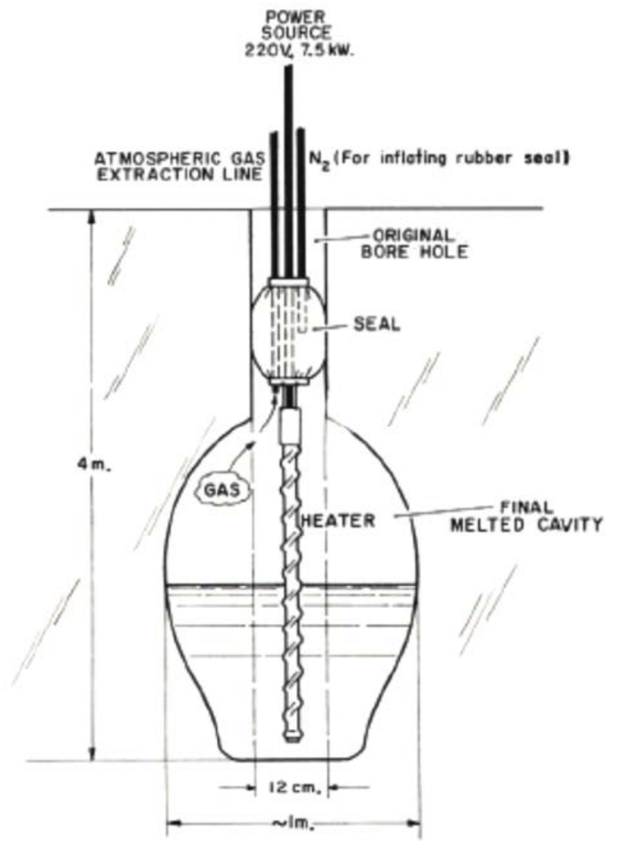
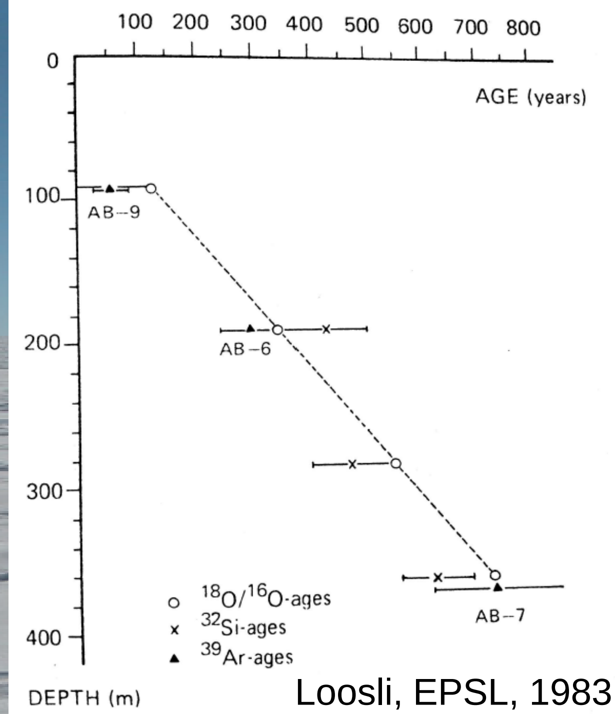


Fig. 1. Schematic diagram of a portable down bore-hole gas-extraction system

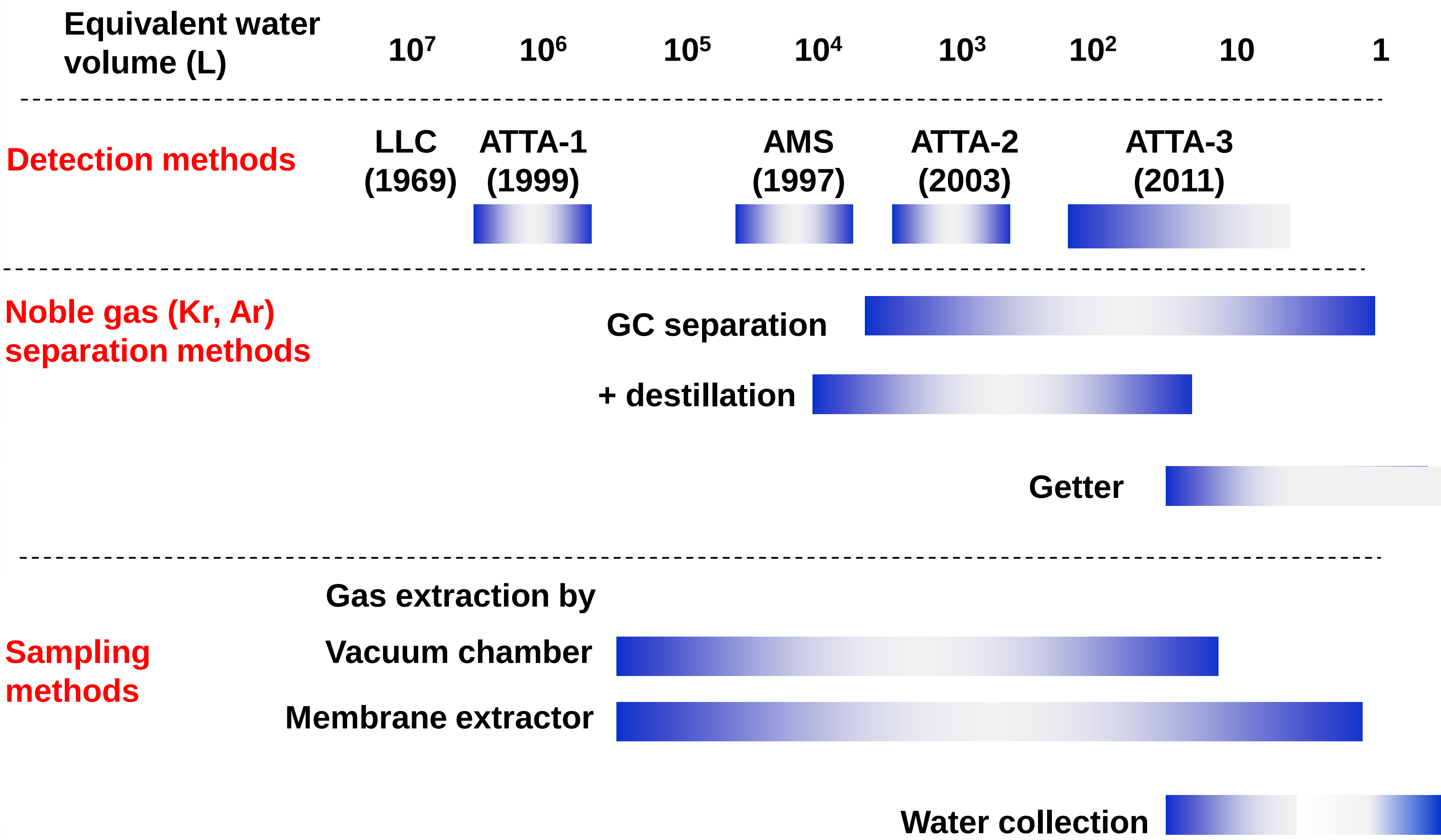
Oeschger et al, 1976



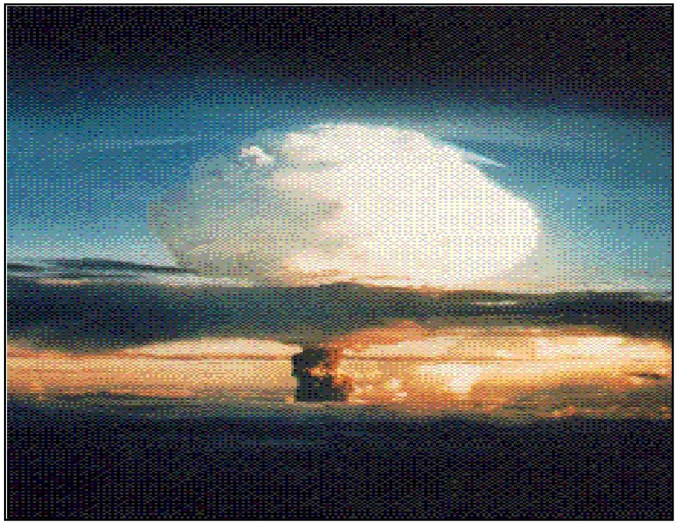
Loosli, EPSL, 1983

→Talk Christo

^{81}Kr: water volume



^{37}Ar as a monitor for clandestine nuclear explosions



Atmosphere

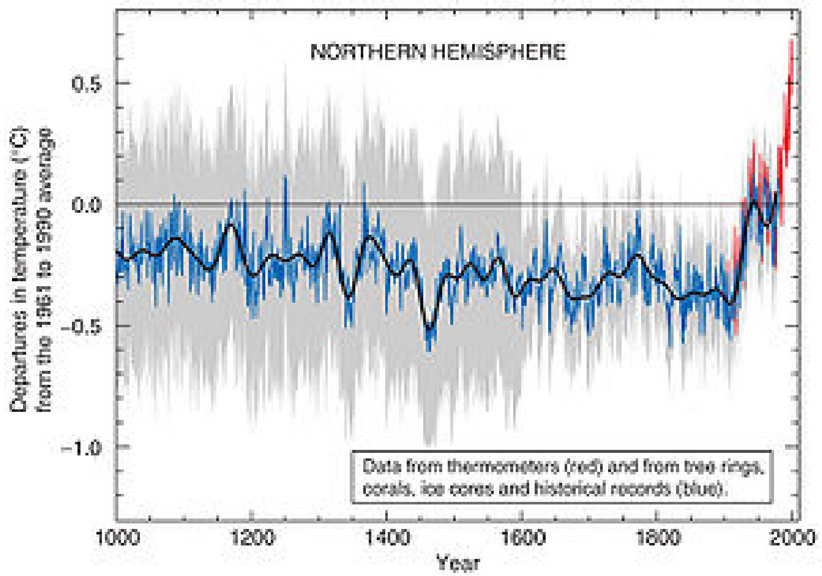
$^{40}Ar + n \rightarrow {}^{37}Ar + 4n$

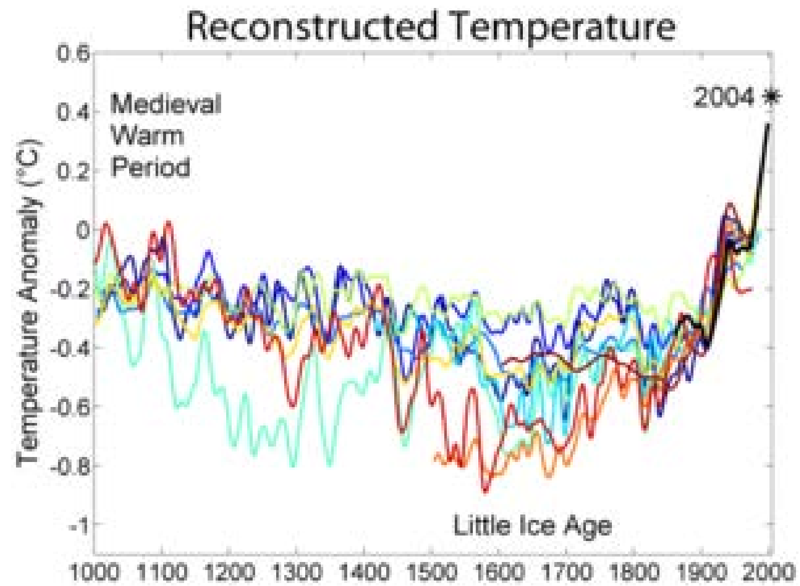
Natural or Artificial

Underground

$^{40}Ca + n \rightarrow {}^{37}Ar + \alpha$

Climate variations over the past millennium (The hockey stick controversery)



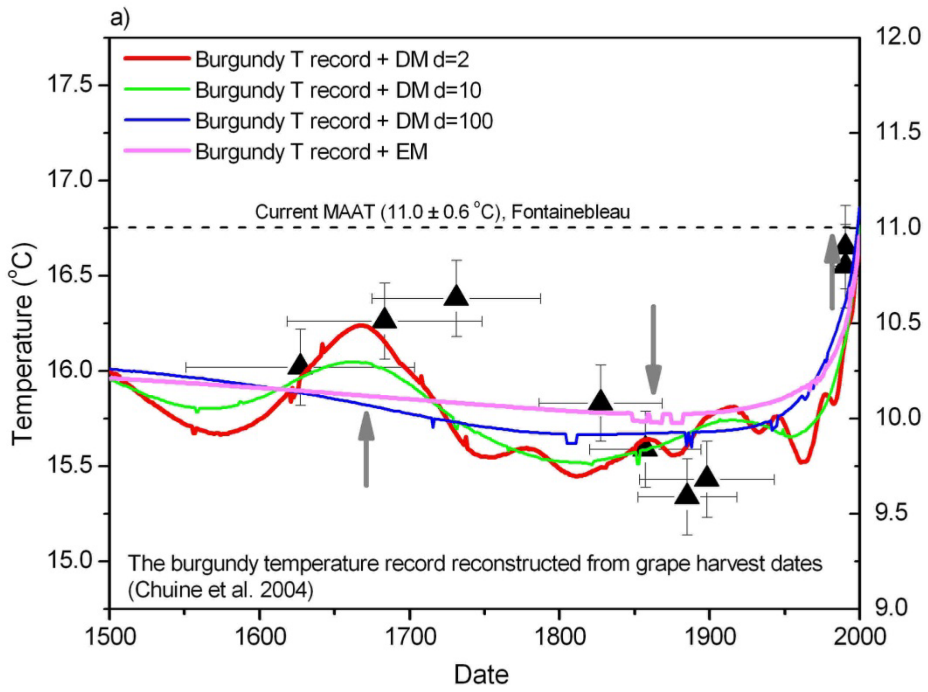


IPCC 2001 (Mann et al, 1999)

How well can past temperatures be reconstructed from the data we have?

- Was the late 20th century the warmest period during the last 1,000 years?
- Are tree rings valid temperature proxies?
- Without using the Bristlecone and Foxtail proxies in the reconstruction, does a hockey stick even exist?

Groundwater as an climate archive



(Corcho et al, 2009)

- NGT's offer an independent and physically based reconstruction of MAT that may not be captured by high resolution data sets (if an appropriate dating tool is available)

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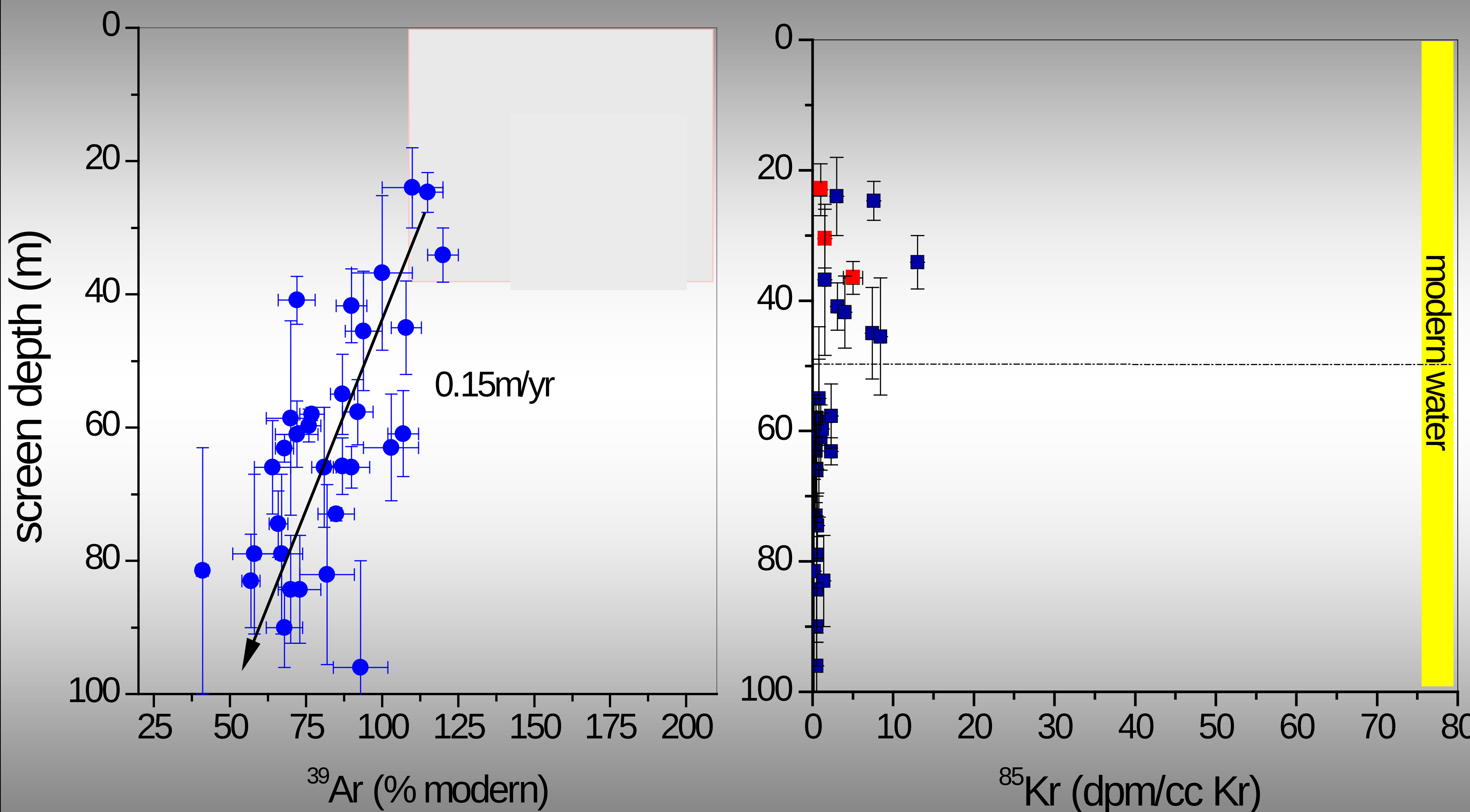
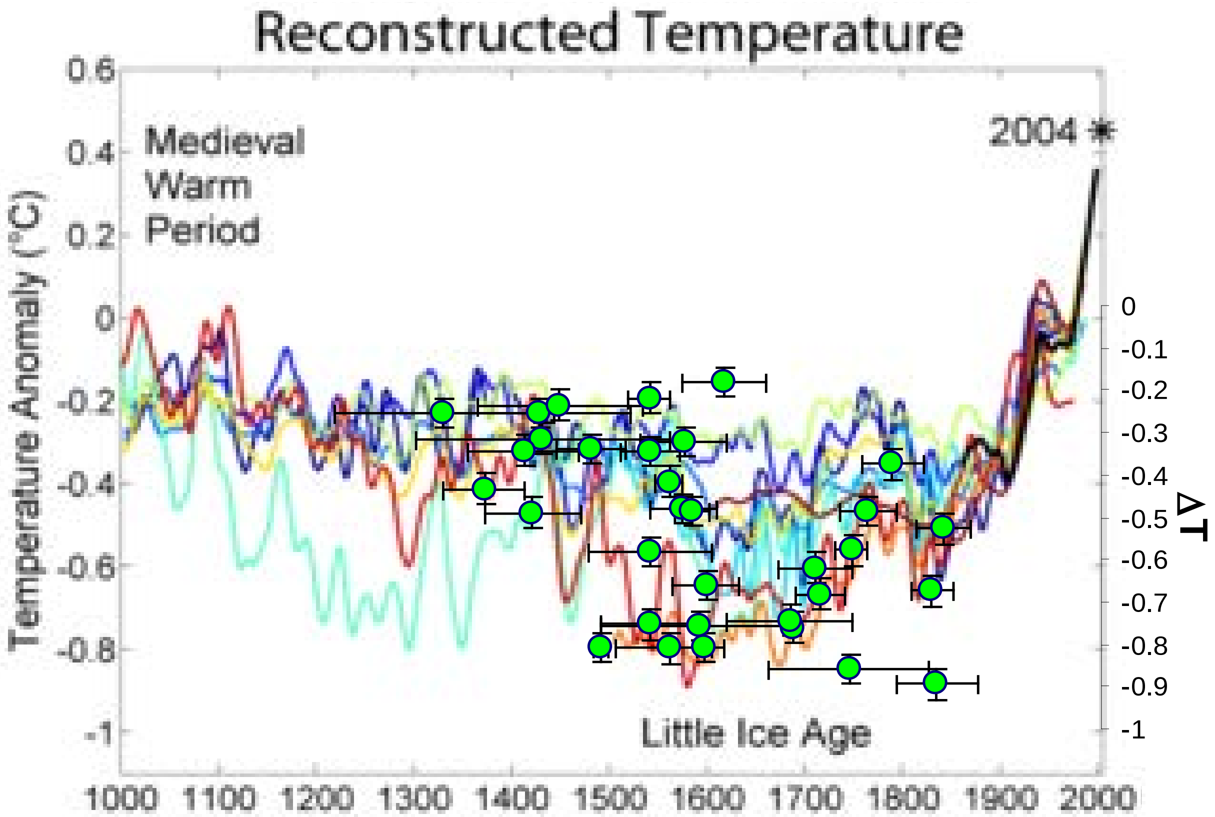
Age chronology with depth





$$\frac{d\,^{18}O}{d^{\circ}C} \approx 0.56‰ / ^{\circ}C \rightarrow \Delta T \approx 0.8^{\circ}C$$

(Schrag, 1996)

GAB, Australia, 2009

(Photo: Paul Shand)

Nubian Aqifer Egypt, 2002