^{39}Ar ATTA @ Heidelberg – Preparation of Water and Ice Samples

INSTITUTE OF ENVIRONMENTAL PHYSICS
HEIDELBERG UNIVERSITY

GROUNDWATER AND PALEOCLIMATE

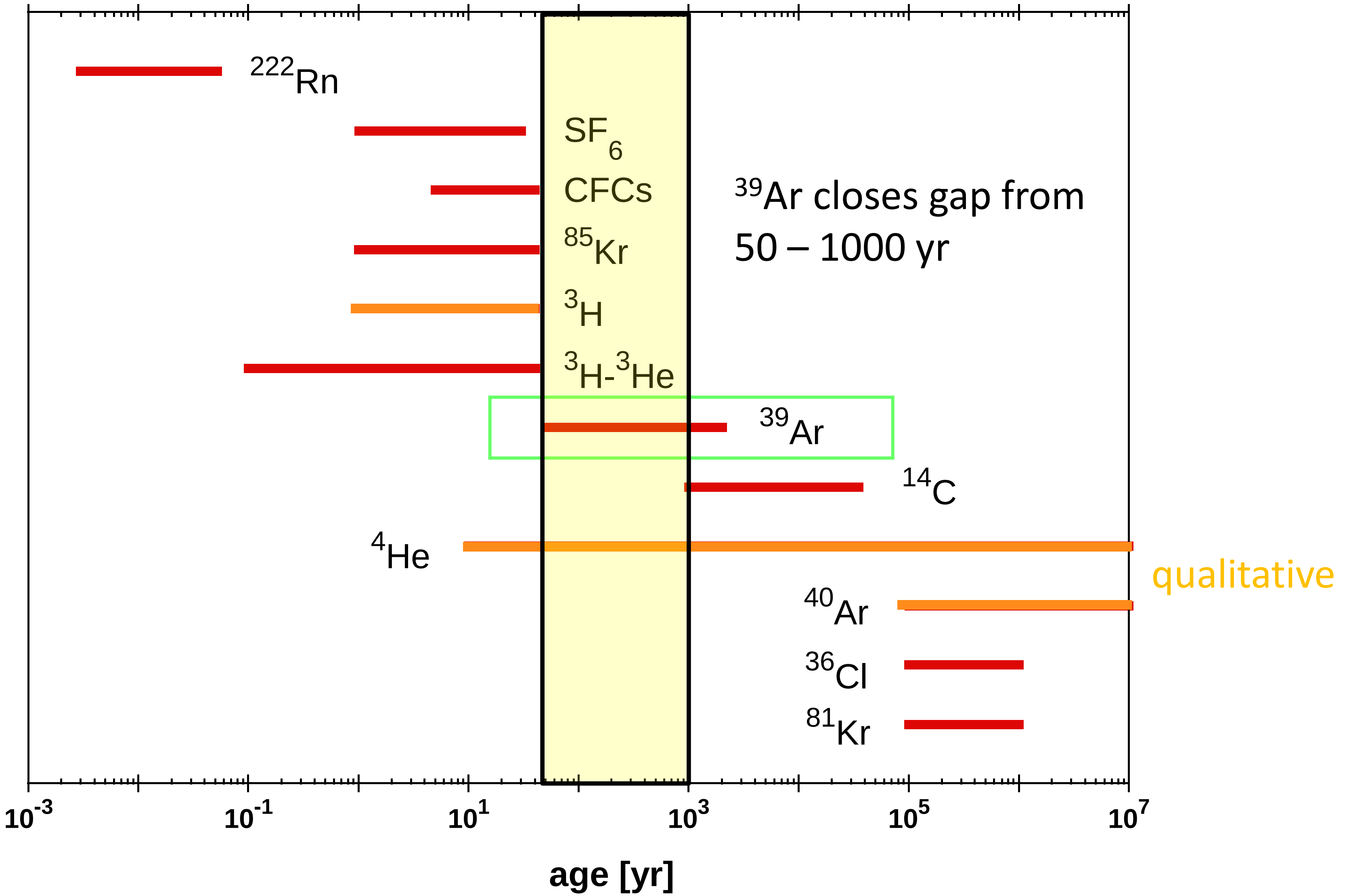
WERNER AESCHBACH-HERTIG, T. REICHEL, R. SCHWEFEL, D. WAGENBACH

TANGR 2012, Chicago

Outline

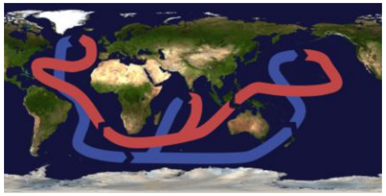
- Why ^{39}Ar?
- The ^{39}Ar ATTA group at Heidelberg
- Preparation of Ar from (large) water samples
  - Degassing by a membrane contactor
  - Ar separation by chromatography on zeolite
- Preparation of Ar from ice samples
  - Ar separation by gettering
- Conclusions

^{39}Ar among Dating Methods for Groundwater



^{39}Ar: Applications

- Water dating:
  - Ocean circulation
  - Groundwater
  - Lakes, pore water?



} ~ 8'000 atoms/l of water

- Ice dating (on trapped air):
  - Alpine glacier ice
  - Ice caps, cave ice?

} ~ 20'000 atoms/l of ice

- Air dating:
  - Archives of old air (fluid incl.)?

} ~ 200'000 atoms/l of air

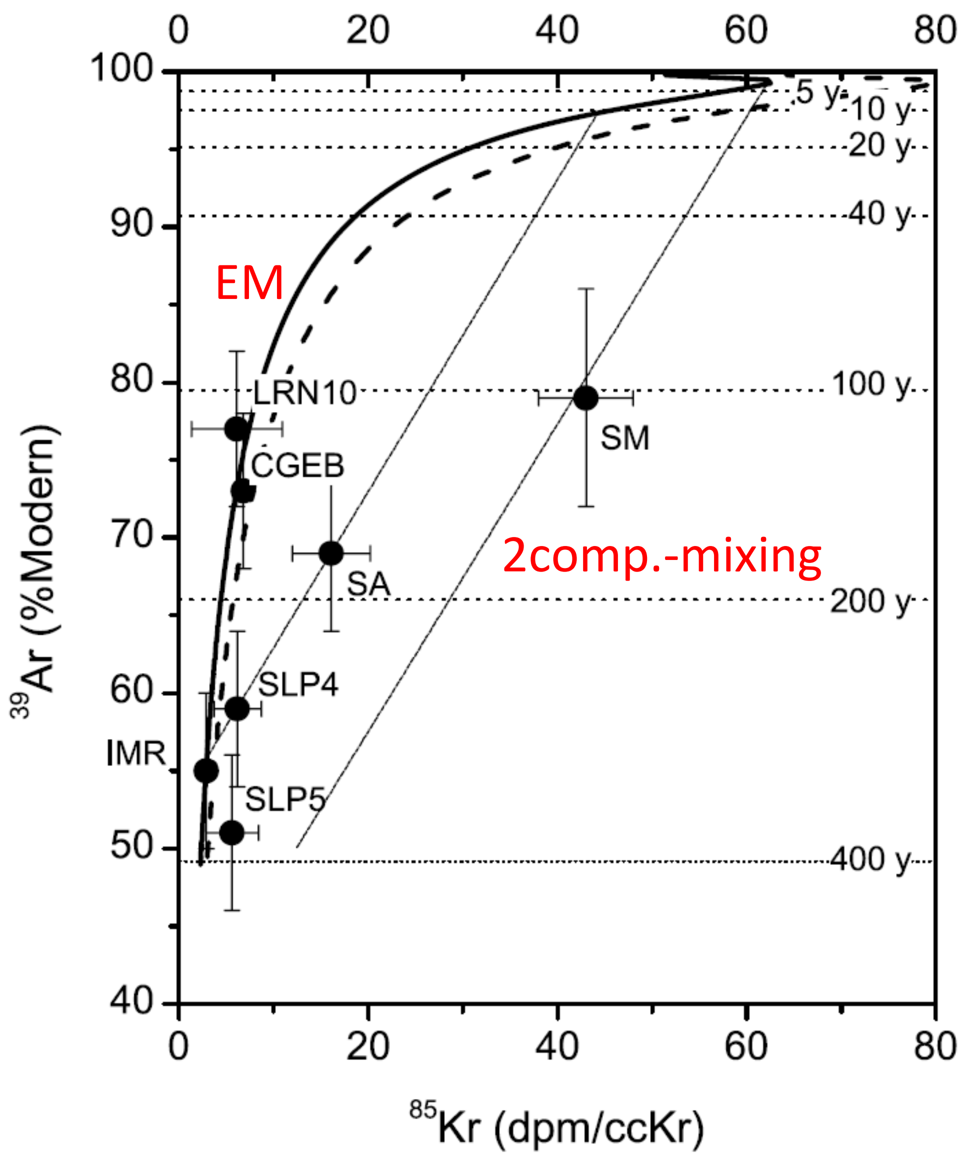
- Fundamental Physics:
  - Ar-detector for WIMPs

} $^{39}Ar/Ar$ as low as possible

Application of ^{39}Ar in Groundwater: TTD

Groundwater samples represent mixtures of components with different ages.

^{39}Ar provides information on the long tail of the transit time distribution.



Corcho Alvarado et al., 2007. Constraining the age distribution of highly mixed groundwater using ^{39}Ar. Water Resour. Res., 43, W03427, doi:10.1029/2006WR005096.

^{39}Ar-ATTA Team Heidelberg

Collaboration of Atom Physics and Environmental Physics

MATTER WAVE OPTICS

Environmental Physics
Groundwater and Paleoclimate

Markus
Oberthaler

Joachim
Welte

Werner
Aeschbach

Thomas
Reichel

Contributions by this team:

- Welte et al., 2009. Rev. Sci. Instrum. 80, 113109, doi:10.1063/1.3257691. "Hyperfine spectroscopy of the $1s_5$−$2p_9$ transition of ^{39}Ar"
- Welte et al., 2010. New J. Phys. 12, doi:10.1088/1367-2630/12/6/065031 "Towards the realization of atom trap trace analysis for ^{39}Ar"

Sample Preparation for ^{39}Ar Analysis

Two main steps:

- Extraction of (atmospheric) gases from water/ice/…
- Separation of pure Ar from other gases (mainly N_2, O_2)

Different sizes of samples:

- 10s-100s of l of air from 1000s of l of water (for LLC analysis)
- < 1 l of air, e.g. from < 10 l of water or ice (for ATTA analysis)

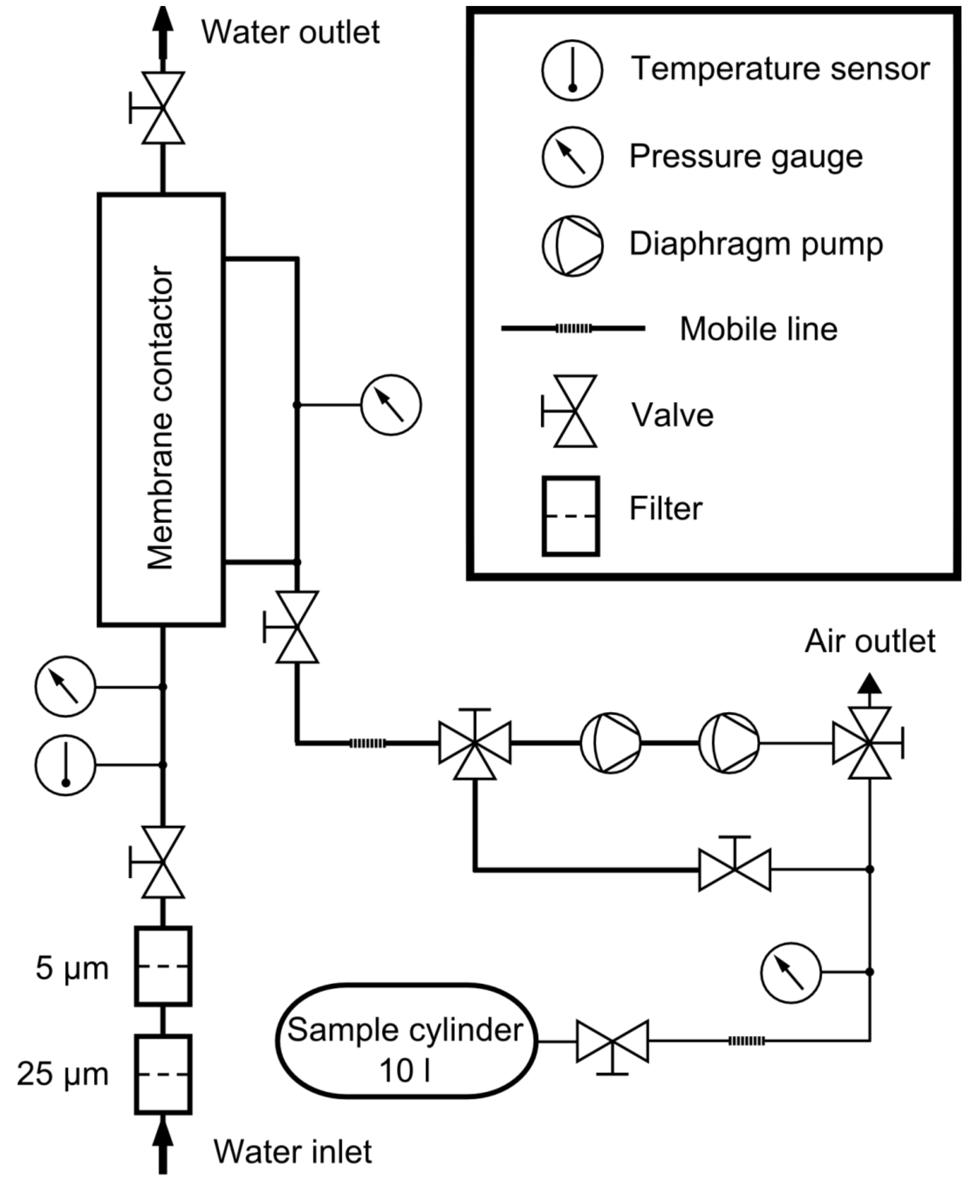
Degassing of Groundwater: Schematic

Gas/water separation by membrane contactor (Liqui-Cel, Membrana).

Degassing efficiency in lab tests at 33 l/min: ~ 88 %.

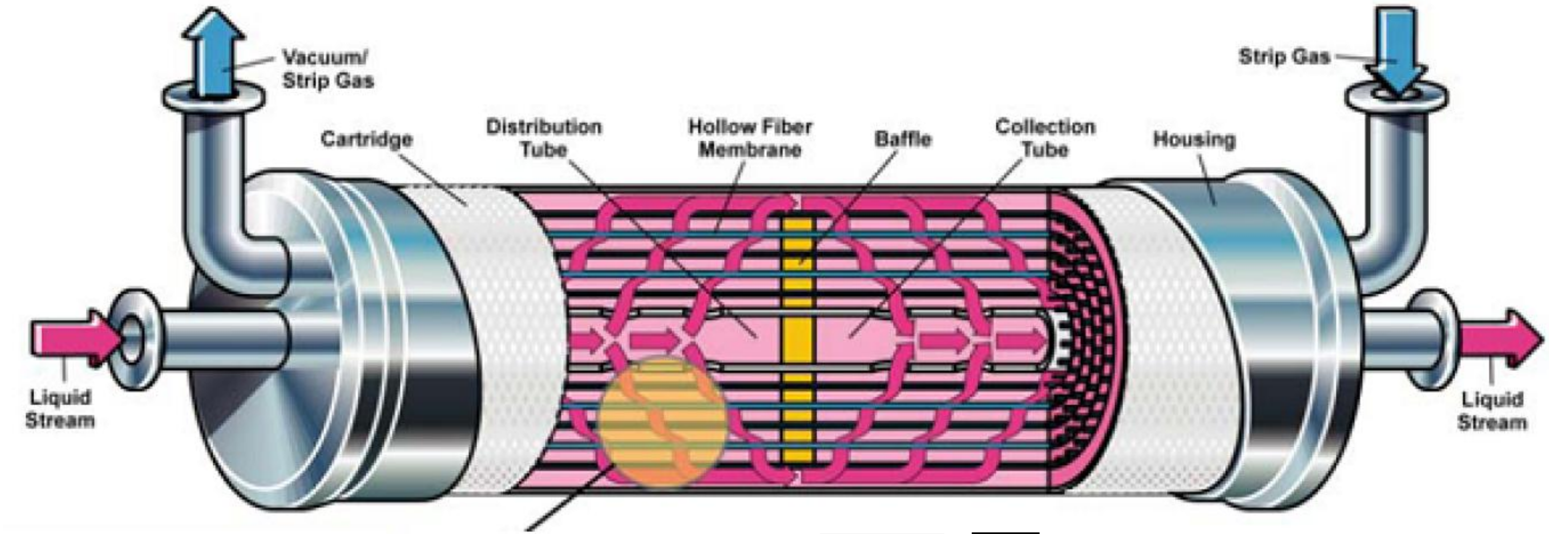
Particle filtering in water cycle before membrane.

Compression of extracted gas into sample cylinder.



The Membrane Contactor

Principle:



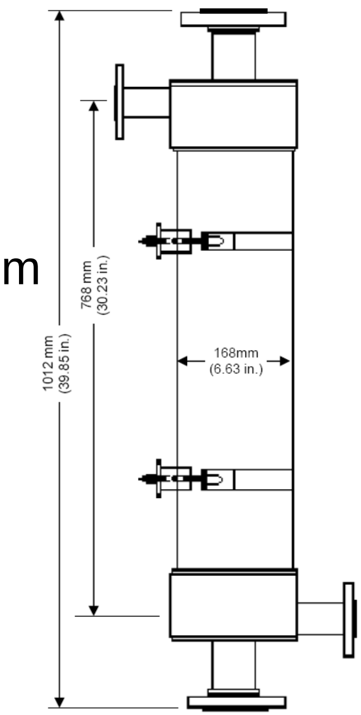
6x28 extra flow Liqui-Cel

Flowrate: 1 – 11 m^3/hr

Membrane area: 42 m^2

Pore size: 200 – 300 µm

1 m



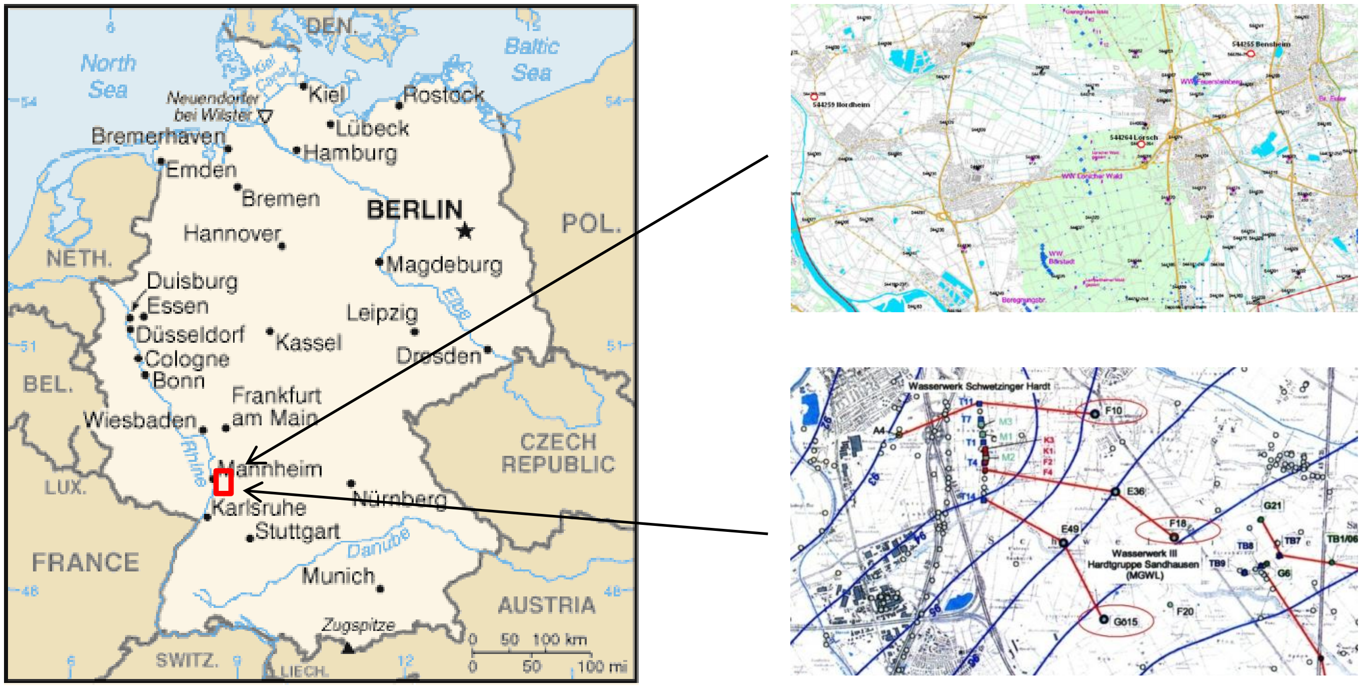
Membrana, 2007. Product data sheet

Degassing of Groundwater in the Field

Large membrane contactor, filters, flow & pressure gauges

Full setup with generator, compressor, sample tank, etc.

Recent Sampling for Groundwater



2 sampling campaigns conducted in sedimentary aquifers of the Upper Rhine Graben (N and S of Heidelberg)

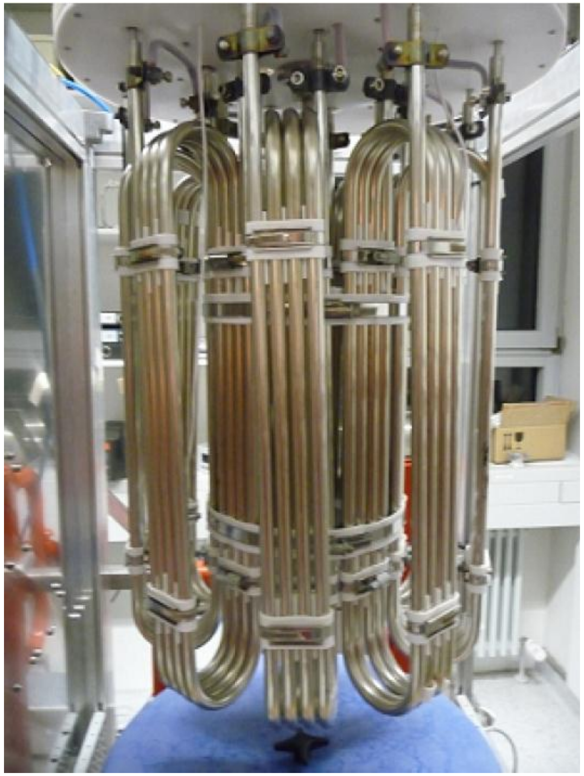
A total of 8 wells sampled, covering wide age spectrum

- Recent (^{3}H active)
- Submodern (no ^{3}H, high ^{14}C)
- Pleistocene (low ^{14}C)

Goal: Comparison of ATTA and LLC measurements

Ar Separation for Groundwater

- Gas chromatographic separation of Ar designed for large gas amounts (current samples: ca. 63 L STP gas)
- System built following developments at Univ. of Bern (PhD thesis Riedmann)



Detail:

9 large GC-columns filled with Li-LSX zeolite, cooled by LN_2 and heated to regulate temperature. Best separation at about -130°C.

Large Sample Ar Separation: Schematic

Separation procedure:

Sample gas dried by cold trap

Helium as carrier gas (recycled)

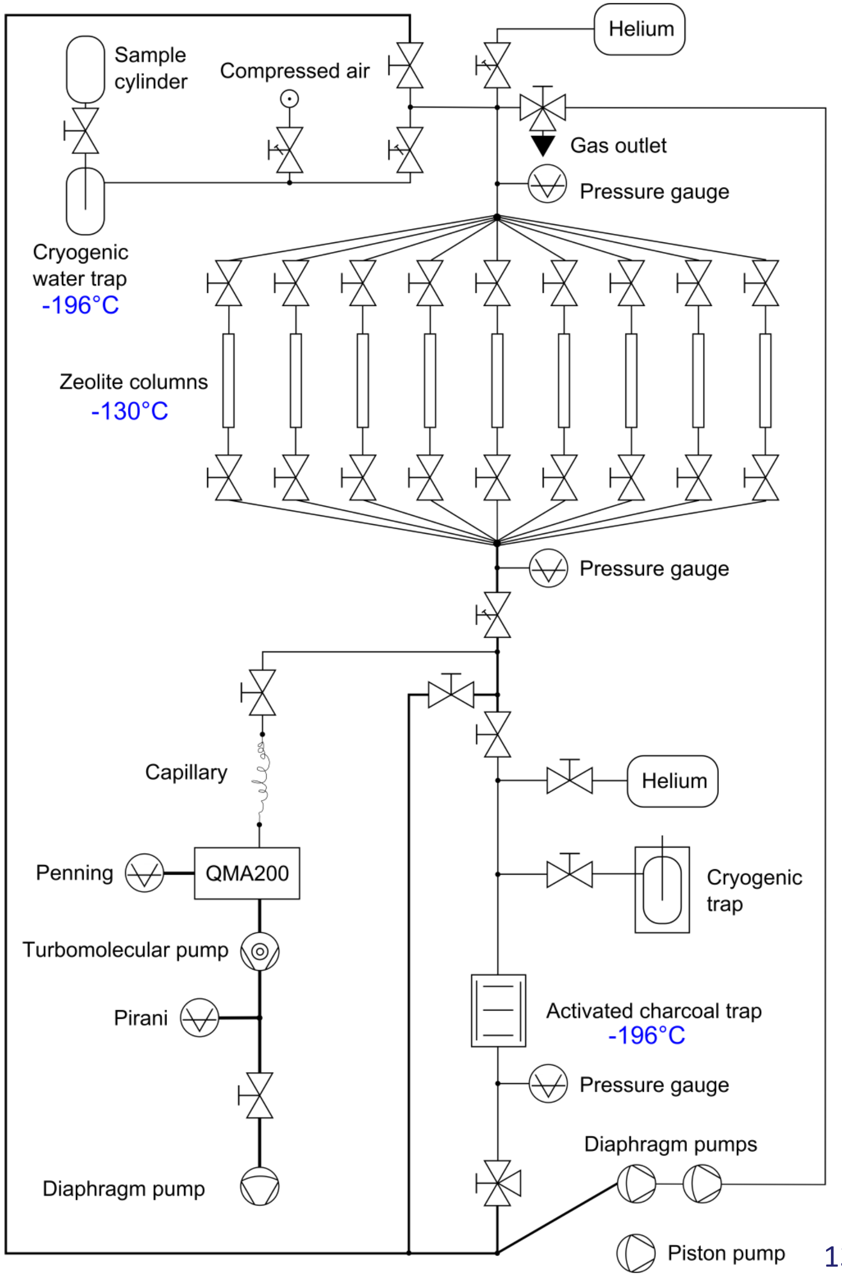
Li-LSX zeolite columns at -130°C

Quadrupole MS to check output

Ar peak trapped on cold charcoal

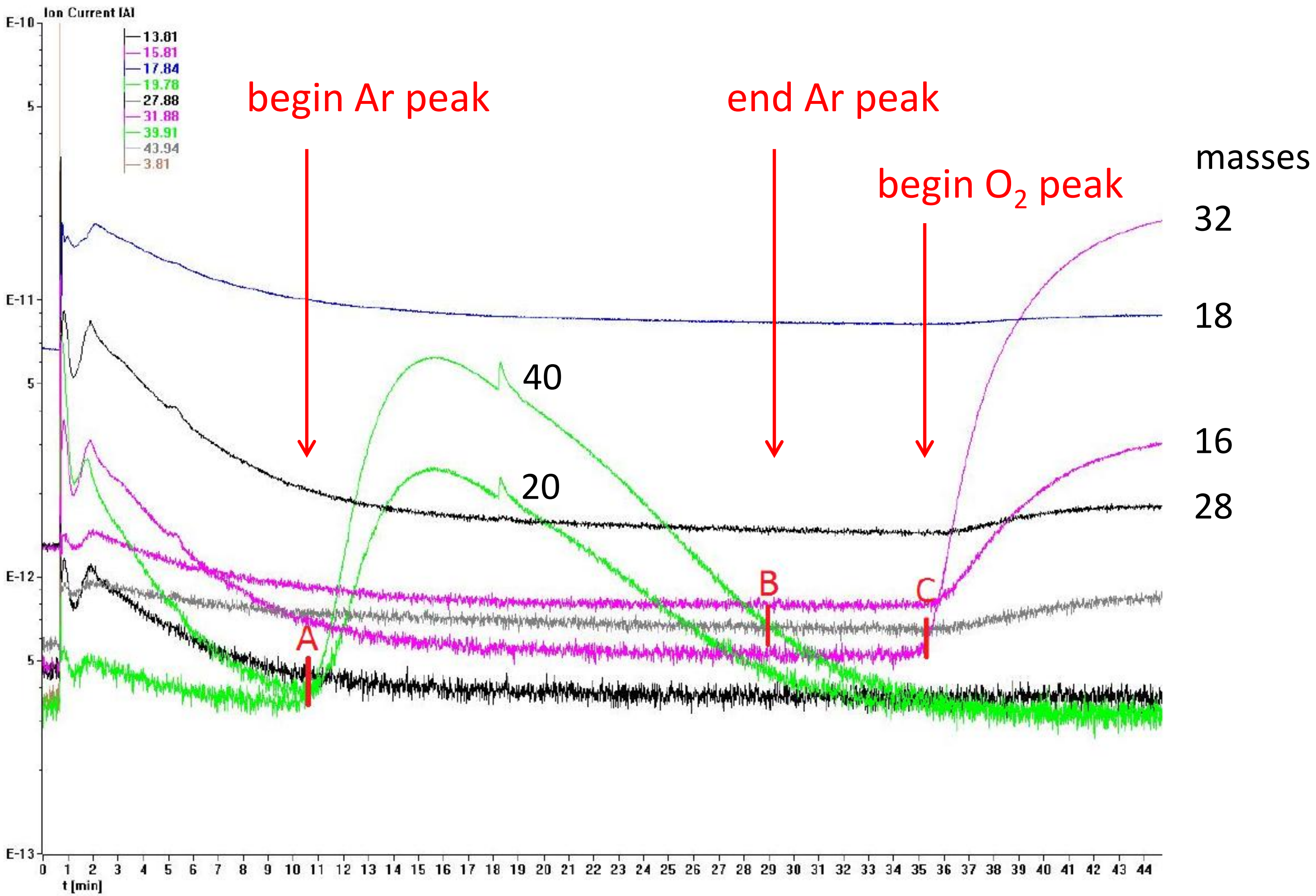
Later peaks (O_2, N_2,..) pumped

Ar transferred to sample container for later analysis



„Chromatogram of an Ar Separation

Quadrupole measurements of gas stream from columns



Summary for Large Volume Samples

Extraction:

Efficiency ~ 88 %

No isotope fractionation detected

High flow rates possible

Duration of sampling: few hours

Ar separation:

Good separation of Ar peak from O_2 and N_2 at -130 °C

Purity of resulting Ar = ~ 98 %

No isotope fractionation detected

Duration of complete separation process ~ 7h

Gas Extraction and Ar Separation for Ice

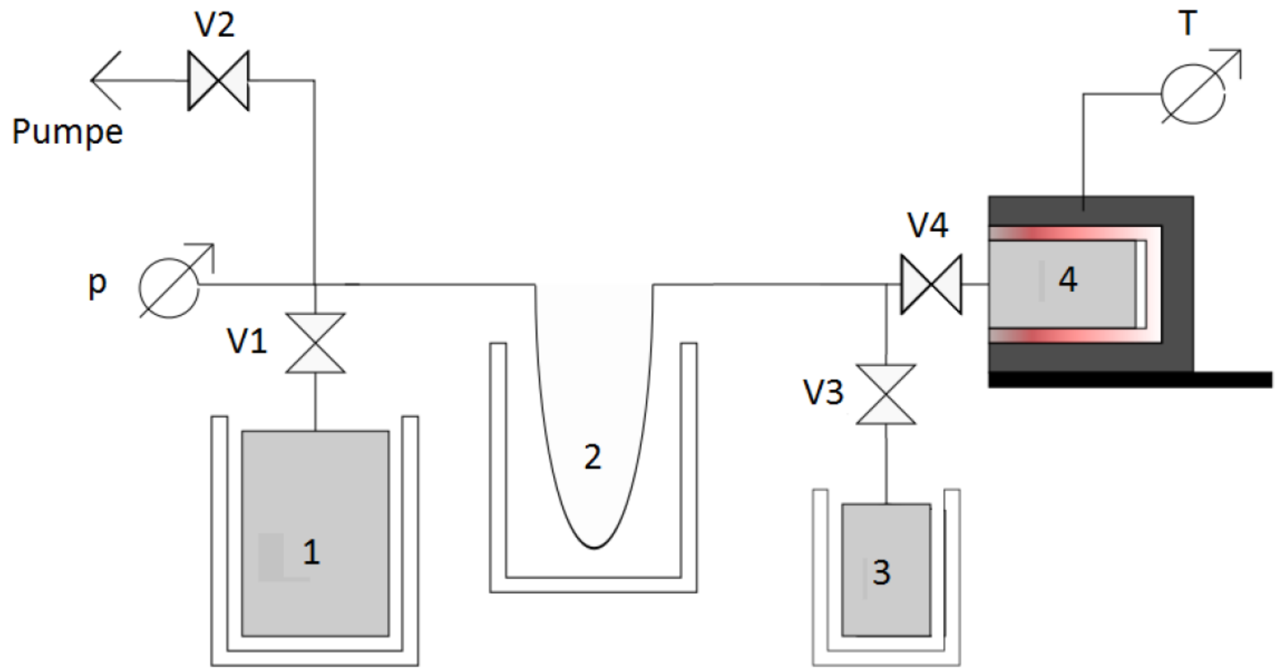
- Glacier ice contains trapped air in about 10 % of its volume
- Higher gas content than water (~ 20 ml / l)
- But: Much smaller samples (< 1 l, thus < 100 ml air, < 1 ml Ar)
- Extraction and separation methods for groundwater are not suitable

- Extraction by melting of ice in evacuated container
- Collection of extracted gas on active charcoal trap
- Separation of Ar by absorption of reactive gases on titanium getter

Extraction and Separation for Ice

Processing of ice samples:

Cutting	**(500 g ice)**
⇩	
Melting	⇩
⇩	
Degassing	**(ca. 50 ml STP gas)**
⇩	⇩
Argon separation	**(0.5 ml Argon)**



1: Sample container

2: Water trap

3: Charcoal trap

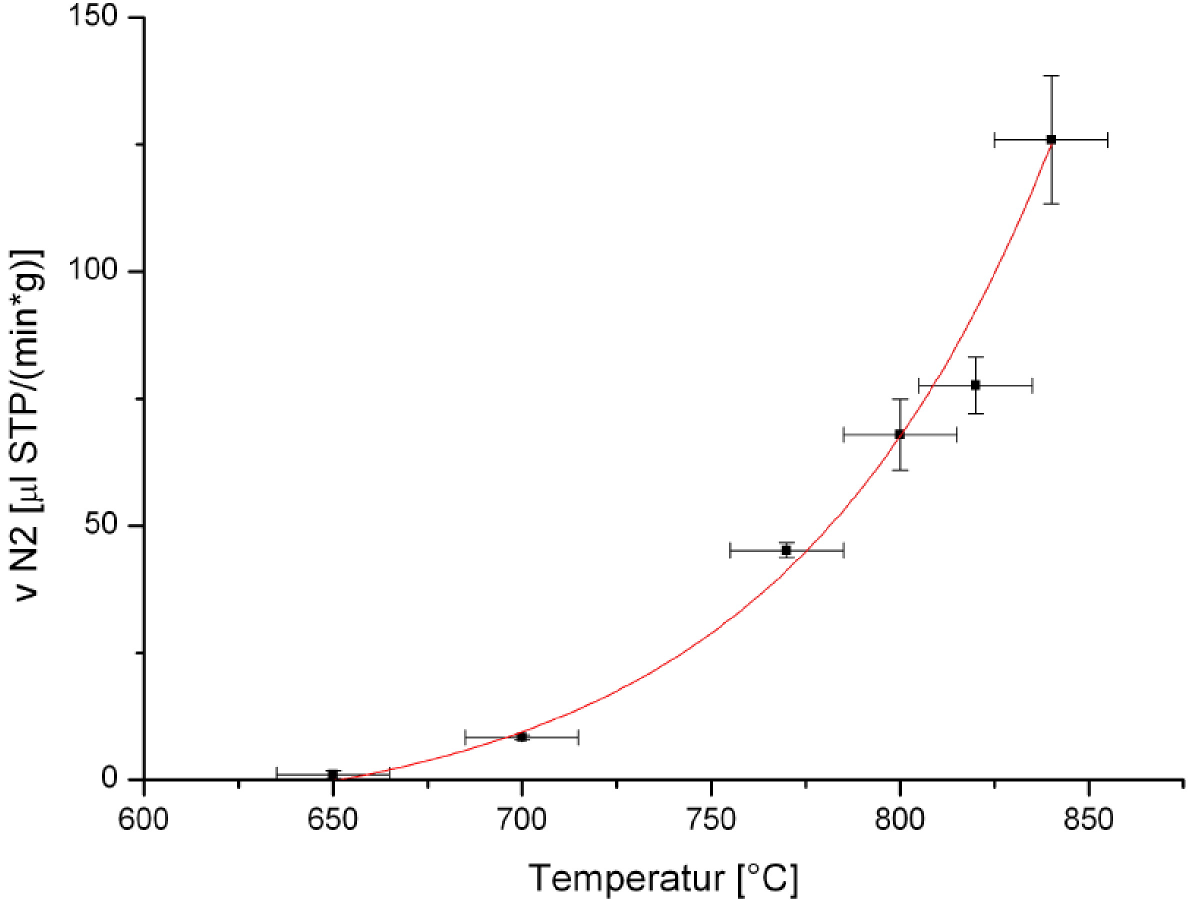
4: Getter

Schwefel, 2012. Diploma thesis, Heidelberg University

Ar Separation by Gettering

Properties of titanium sponge as getter to remove reactive gases

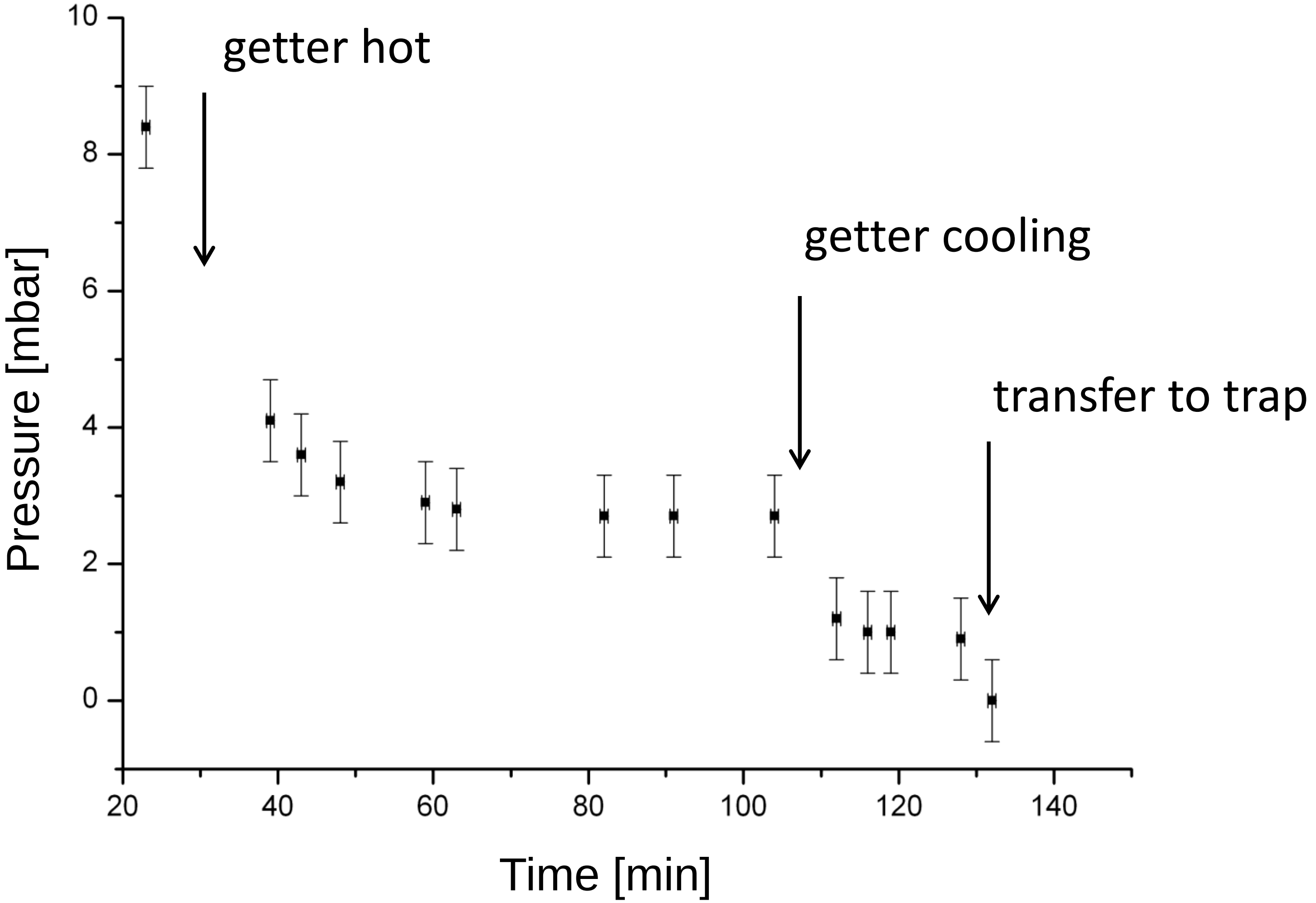
- Capacity: ~ 60 ccSTP of gas per g of getter material
- Speed: ~ 0.1 ccSTP N_2 per min. and g of getter at > 800 °C



Schwefel, 2012. Diploma thesis, Heidelberg University

Ar Separation for Ice

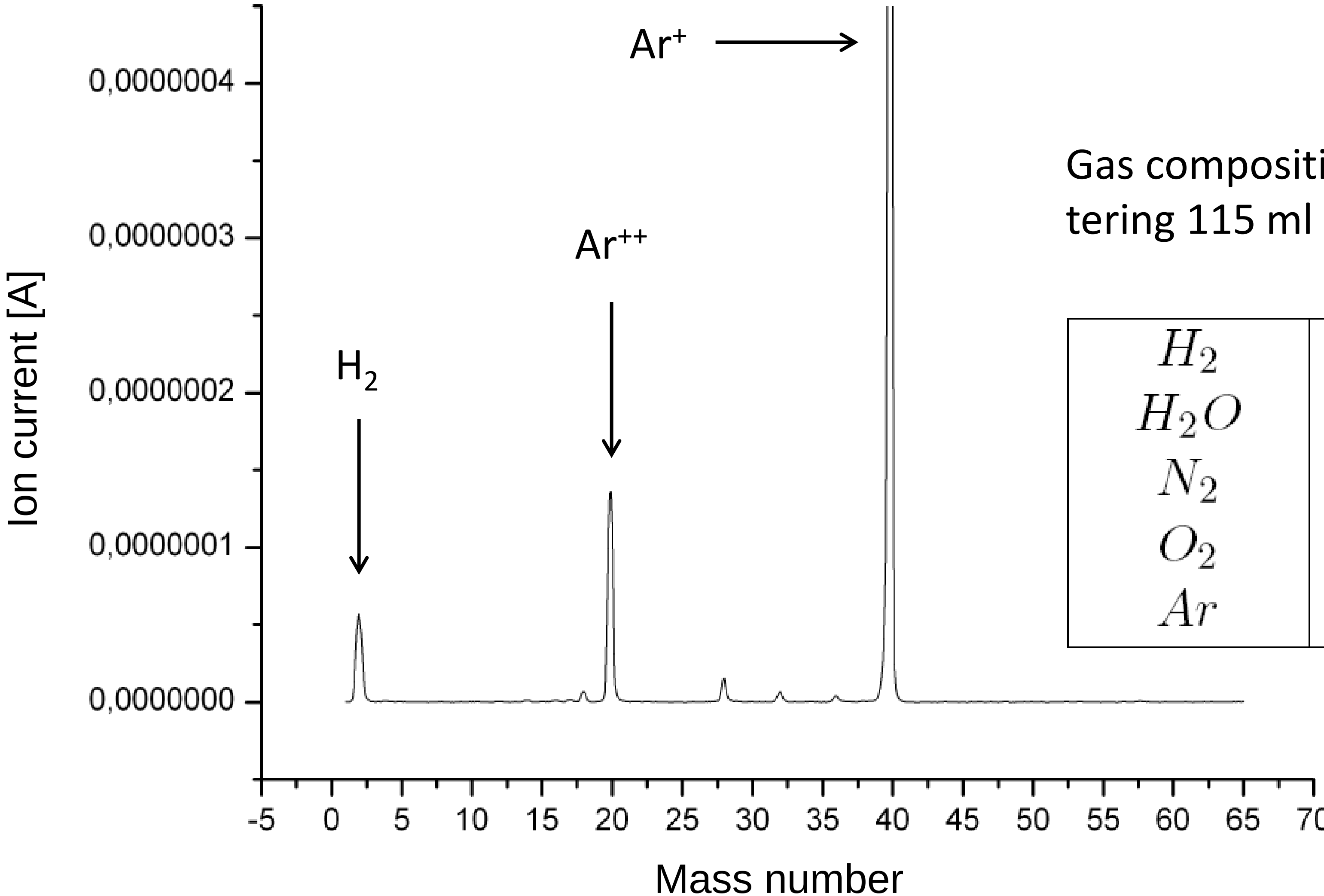
- Fast reduction of reactive gases on hot getter
- Reduction of H_2 background on cold getter



Schwefel, 2012. Diploma thesis, Heidelberg University

Ar Separation by Gettering

Gas composition after gettering measured on QMS



Gas composition after gettering 115 ml air at 800 °C

	fraction (%)
H_2	4,6
H_2O	0,5
N_2	1,2
O_2	0,7
Ar	92,2

Conclusions

ATTA promises to make ^{39}Ar dating more accessible:

- Smaller samples
- Faster analysis

Methods for sample preparation have to be adapted:

- Degassing via membranes and gas chromatographic Ar separation on cold zeolite-filled columns work well for large water samples
- Extraction by melting and Ar separation by gettering works for ice
- Gettering is preferred separation method for small samples


Thanks to:
Thomas Reichel
(water system)
Robert Schwefel
(ice system)

Facts on Separation

Gain (Ar-Separation) = 97 +/- 1%

Duration (Ar-Separation) ~ 7h	[min]
•Cooling the columns to -130°C:	40
•Loading the columns with sample	20
•Separation	30-40
•Regeneration of the columns	60
•Pumping He from active carbon trap (act)	60
•Heating act and freezing Ar to container	60
•Regeneration of next Ar container	60
•Regeneration of act	60

98,5% pure Ar after separation (0,85% He; 0,5%N2; 0,15%O2)

Distance Ar – O2 peak @ -130°C for 8 columns	[min]
•63 l STP ambient air	2-5
•35 l STP ambient air	24-25
•63 l STP gw sample (little O2)	30