The 70th Scientific Conference of the University of Latvia
Session of Geology
Section “Groundwater in sedimentary Basins”
January 30, 2012

The state of art and new trends in application of isotope –geochemistry for groundwater research

Rein.Vaikmäe

Institute of Geology at Tallinn University of Technology, Estonia

Rein.vaikmae@ttu.ee

Outlines:

- A short look in the history
- Willi Dansgaard
- The role of IAEA
- Tallinn isotope Lab
- New trends- noble gas applications

Willi Dansgaard

- One of the pioneers of isotope hydrology and ice core research Dr. Willi Dansgaard passed away in January 2011 at the age of 88.

The beginning

- 1951 MS Lab in the Copenhagen University O&N isotopes for biological and medical research
- 1952:discovered O18/T correlation in precipitation
- “The O18- abundance in fresh water”,
- Geochim, et Cosmochim Acta 6, 1954
- “Stable isotopes in precipitation” Tellus 16, 1964

Isotopes in precipitation1952/1961

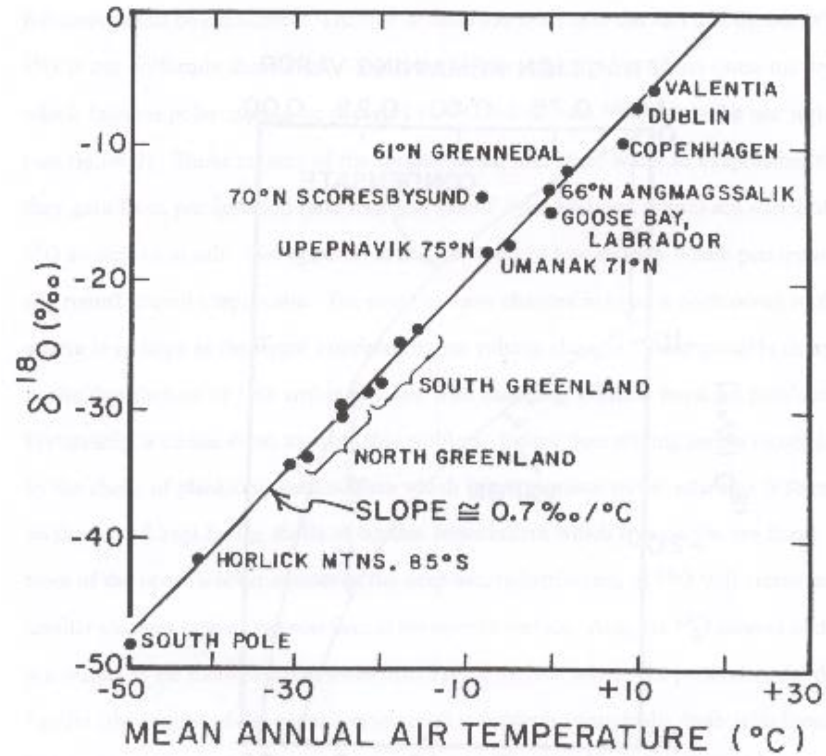


Figure 7. Observed $\delta^{18}O$ in average annual precipitation as a function of mean annual air temperature (Dansgaard, 1964). Note that all the points on this graph are for high latitudes (>45°). The $\delta^{18}O$ values are calculated as follows:

$$\delta^{18}O = \frac{{}^{18}O/{}^{16}O sample - {}^{18}O/{}^{16}O std.}{{}^{18}O/{}^{16}O std.} \times 1000$$

IAEA

- Formally establised in 1957
- Isotope Hydrology Section:
- Radioactive fallout from atmospheric thermonuclear testing (particularly tritium and its impact on human health and the environment

THE GLOBAL NETWORK OF ISOTOPES IN PRECIPITATION GNIP

Pradeep Aggarwal

Luis Araguás

International Atomic Energy Agency

Water Resources Programme

Isotope Hydrology Section

Main objective of the Water Resources Programme of the IAEA

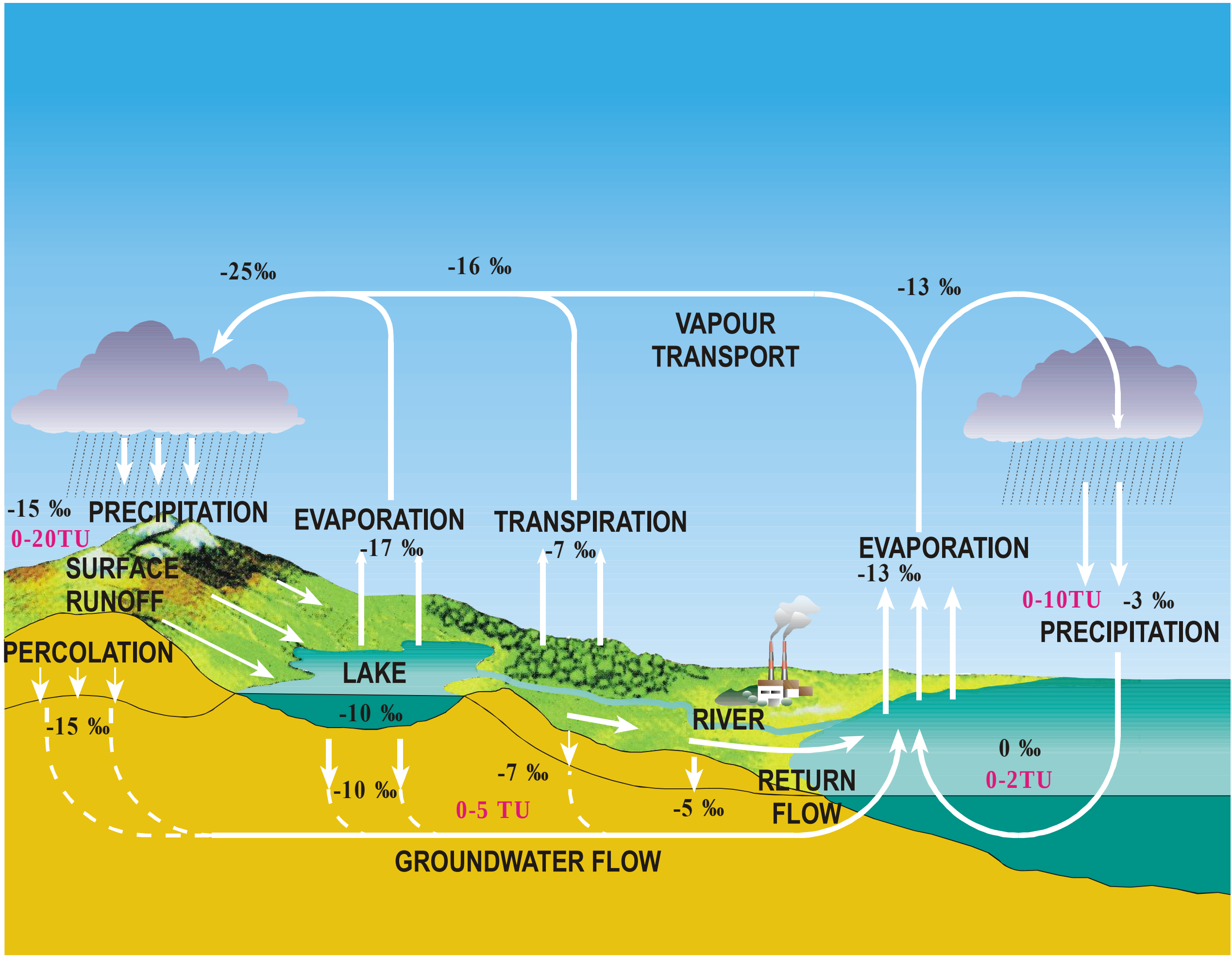
To improve the management of water resources by Member States with the use of isotope technologies

- Improve understanding of the water cycle
- Sustainable exploitation of water resources
- Improved hydrogeological and hydrogeo-chemical data.
- Capacity for monitoring the quantity and quality of water resources

scientific background of isotope hydrology

- Isotope fractionation of ^{18}O and ^{2}H occurs during evaporation, condensation, and vapor transport

- Stable isotopes are fingerprints of water ➔ excellent tracers of the origin of water, and of changes in the hydrological cycle



GNIP

Oxygen and hydrogen isotopes as tracers in the Water cycle and climate

Joint activity IAEA/WMO since 1961

GNIP programme in hydrology, climatology and related fields

Main objective of GNIP

Systematic collection of basic data on isotopic content in precipitation (monthly basis) on a global scale to determine temporal and spatial variations of environmental isotopes in precipitation

1990s

New monitoring needs, besides "classical input function for hydrology"

Global climate modelling requires broader spatial coverage →AGCM

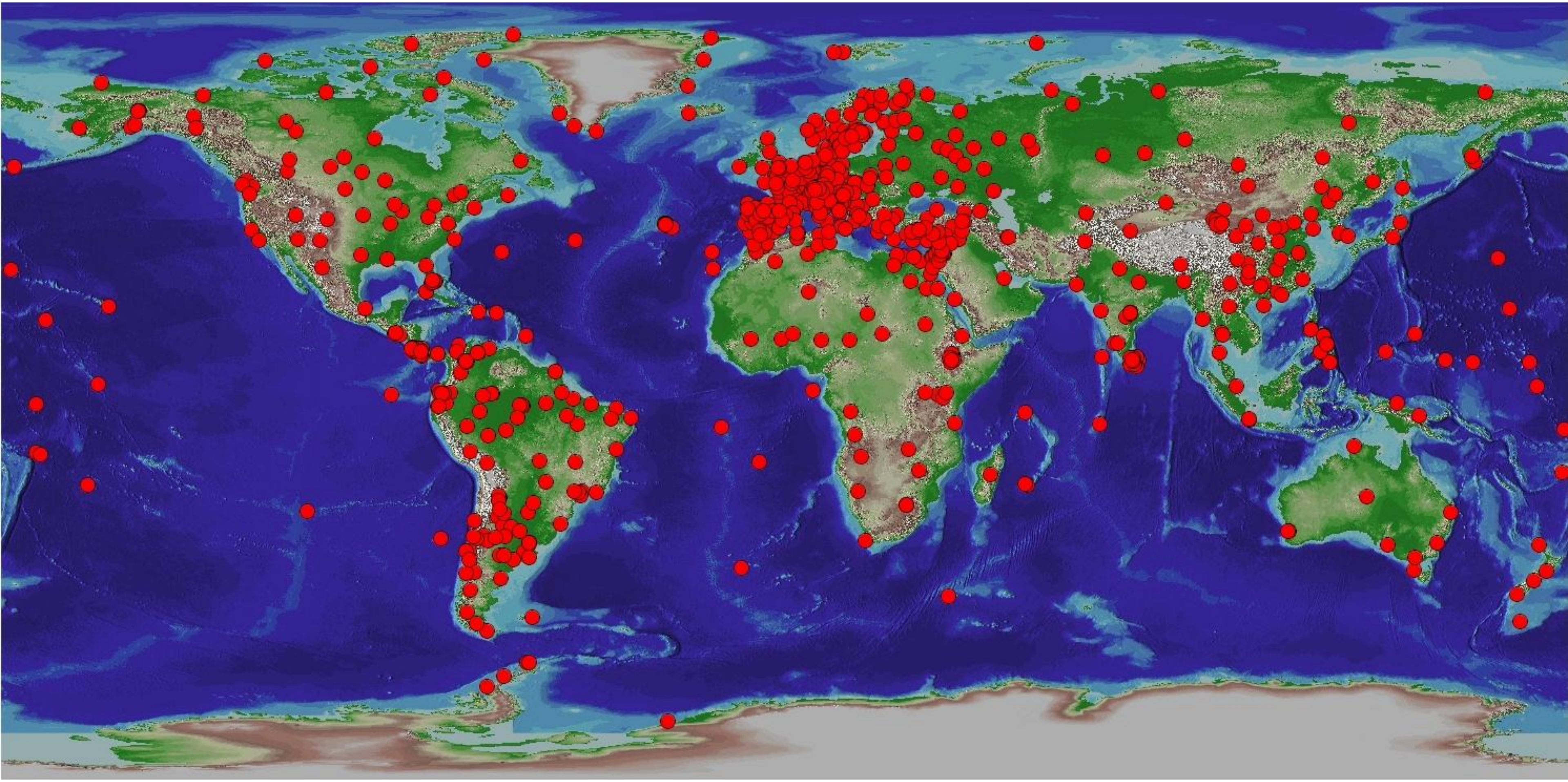
Interest in:

High latitudes and altitude areas

Climate-sensitive areas

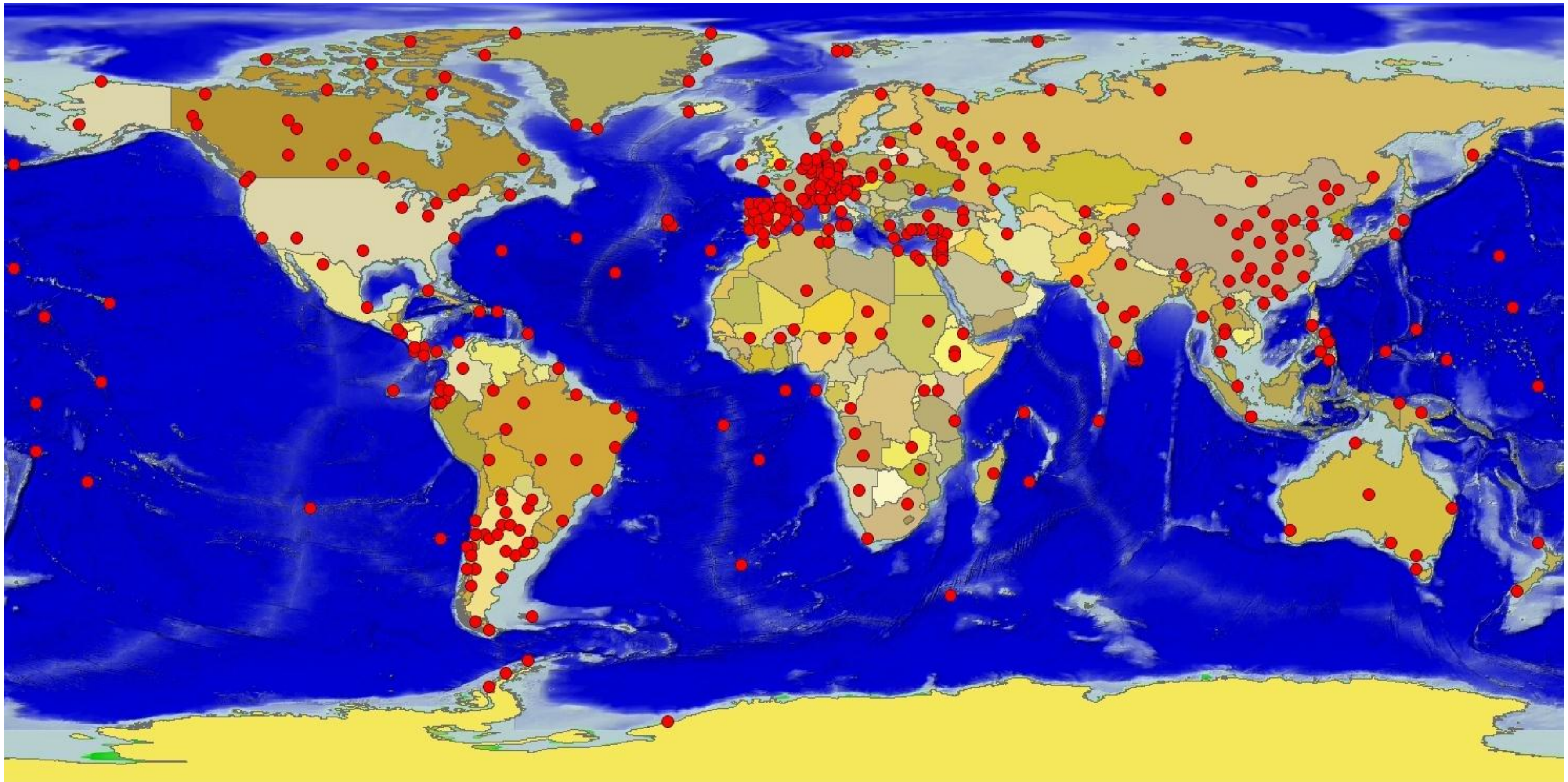
Tropical zones

GNIP STATIONS

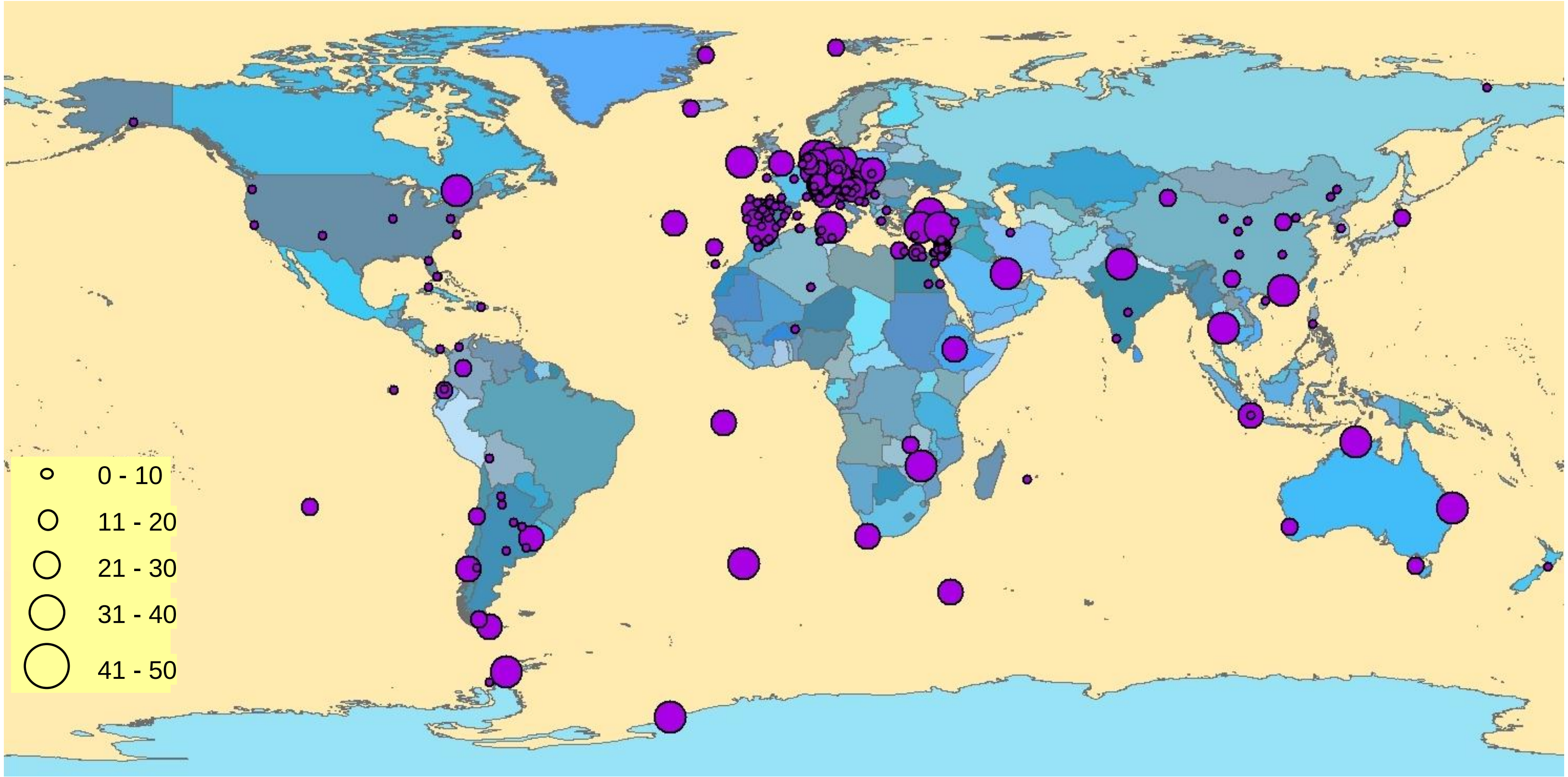


1953-2006, about 830 stations

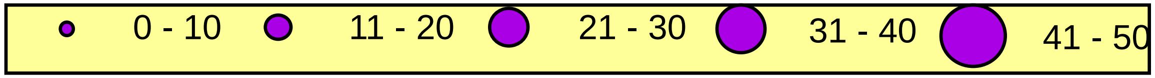
GNIP STATIONS / Record > 2 years



ACTIVE GNIP STATIONS



^{18}O and ^{2}H RECORDS (in years)



Contents of the GNIP database

amount of precipitation (mm)

•Type of precipitation (rain, snow, both)

•Mean air temperature (ºC)

•Mean water vapour pressure (hPa)

Monthly values:

•Total

•Stable Isotope contents (O-18, H-2) (‰)

•Tritium content and uncertainty (TU)

Status of the network

About 210 active stations in 53 countries

The IAEA´s Isotope Hydrology Laboratory is currently performing isotope analyses of about 40 % of the collected precipitation samples

30 other laboratories are analysing GNIP samples

Structure of the GNIP network

The network is composed of:

- IAEA/WMO stations situated in climatically relevant locations

- National Networks composed of stations and labs operated by national authorities

- affiliated stations which are stations resulting from hydrological studies, often of short-term in nature

Operation of GNIP

- International Atomic Energy Agency
  - Isotope Hydrology Section
  - Isotope Hydrology Laboratory
- World Meteorological Organization
  - Link to the stations
  - Meteorological information
- Cooperating institutes and laboratories (voluntary basis)

Latest developments

- GNIP data distributed into 3 categories
  - GNIP- monthly ~100.000 records ~780 st
  - GNIP- event ~25.000 records ~100 st
  - GNIP- vapour ~700 records ~6 st

- Completion of ISOHIS-Map
  - Easier visualization to GNIP, GNIR, IGLASS

Creation of National focal points

- **Link with national institutes coordinating activities related to isotope monitoring**
- **Data compilation and quality control at national level → submission to the GNIP database**

Isotopes help to define groundwater origin, dynamics and flow patterns

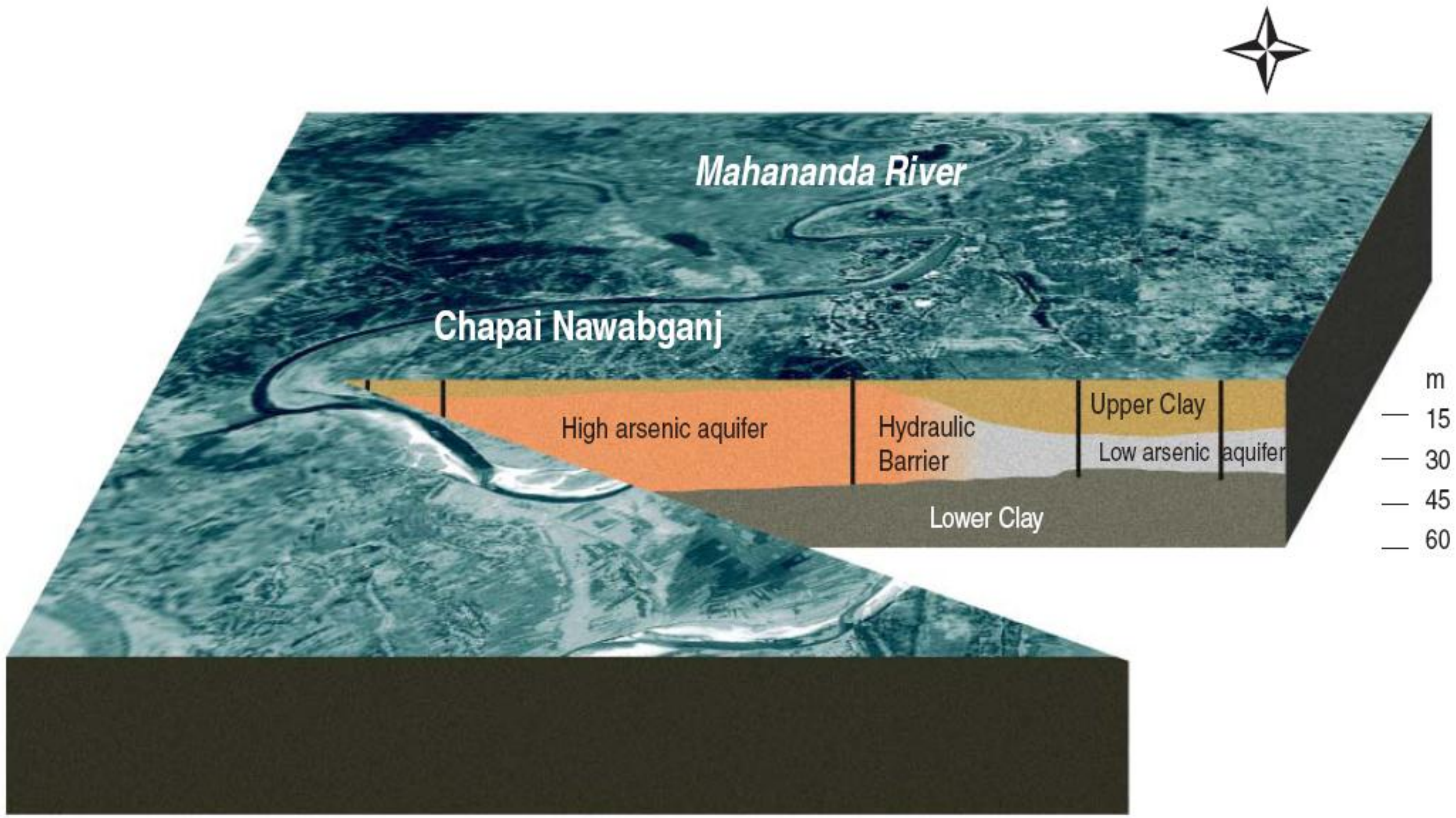
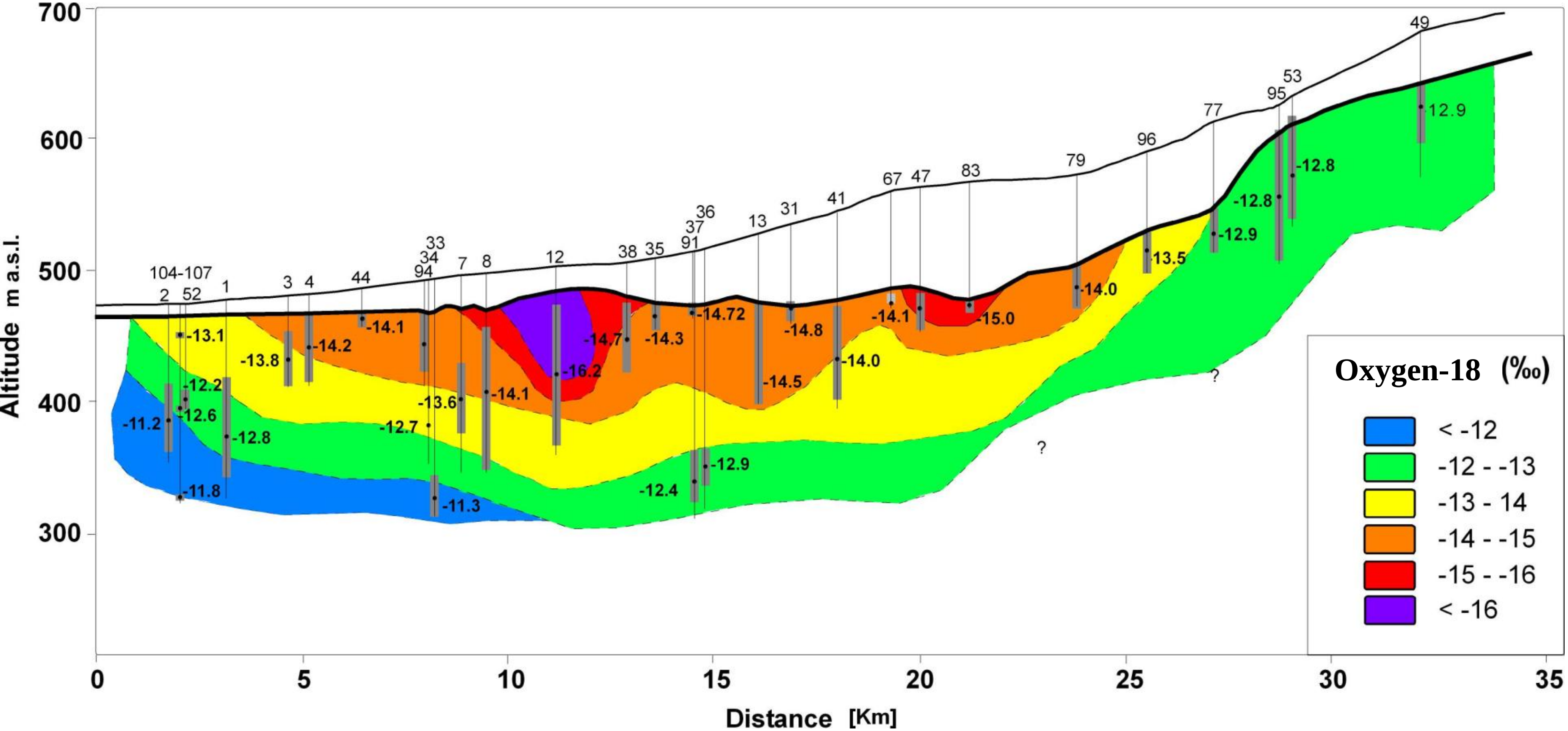
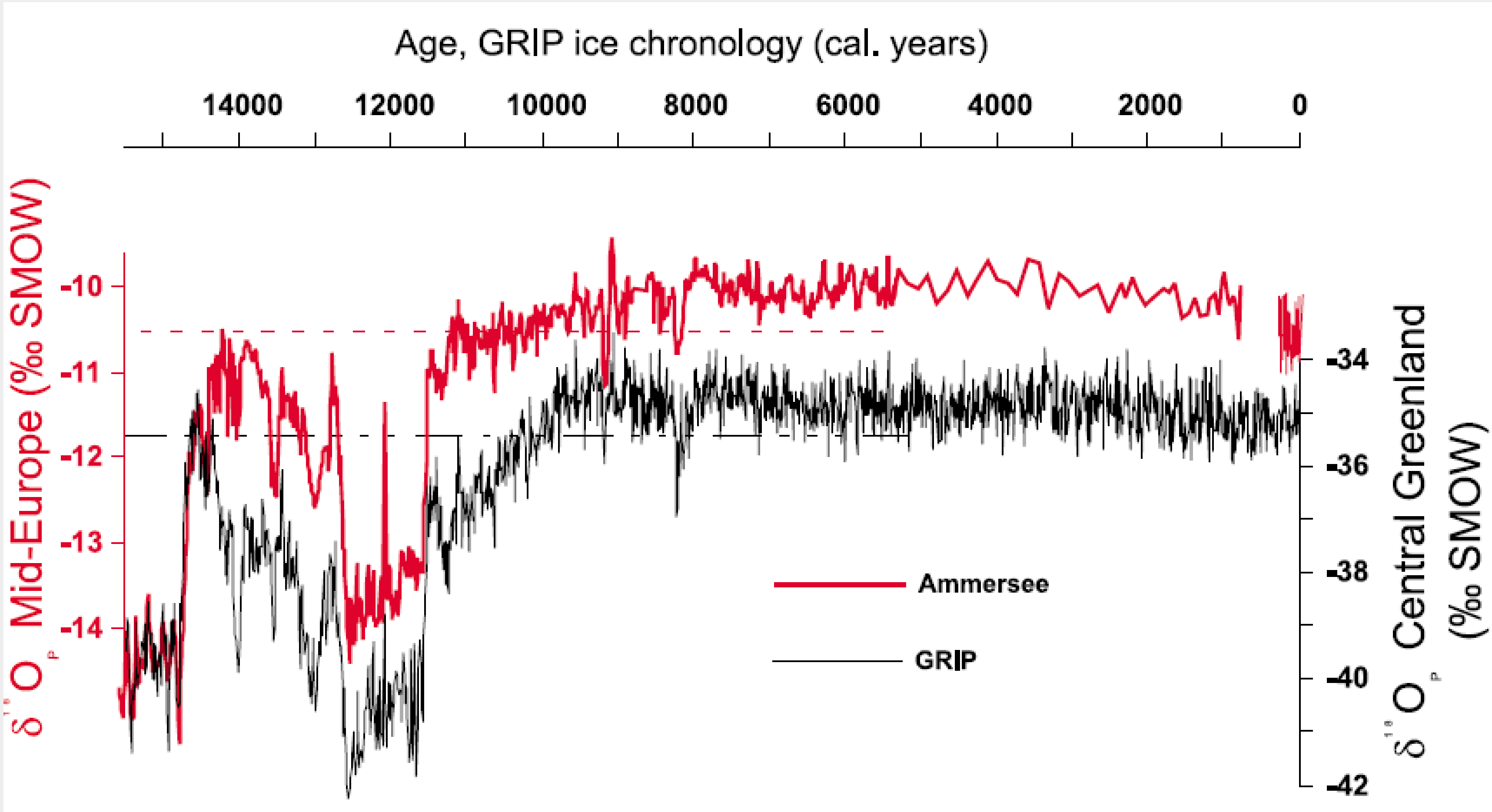


Fig. 1: Hydrogeological setting of Chapai Nawabganj area.

Santiago de Chile: Isotopes help to define sources of recharge, groundwater origin, flow patterns and pollutant transport



ISOTOPE CHANGES IN ICE CORES AND LAKE ARCHIVES



The graph shows examples of isotopic changes in a Greenland ice core (GRIP) and a lake archive (Ammersee, Germany) over the past 16,000 years interpreted mainly as temperature signals. Higher delta values of oxygen-18 reflect warmer climatic conditions.

Source: based on U. v. Grafenstein, H. Erlenkeuser, A. Brauer, J. Jouzel, S. Johnsen (1999): A mid-European decadal isotope-climate record from 15,500 to 5,000 years B.P. - Science 284, 1654-1657.

Modelling isotope contents over the Andes

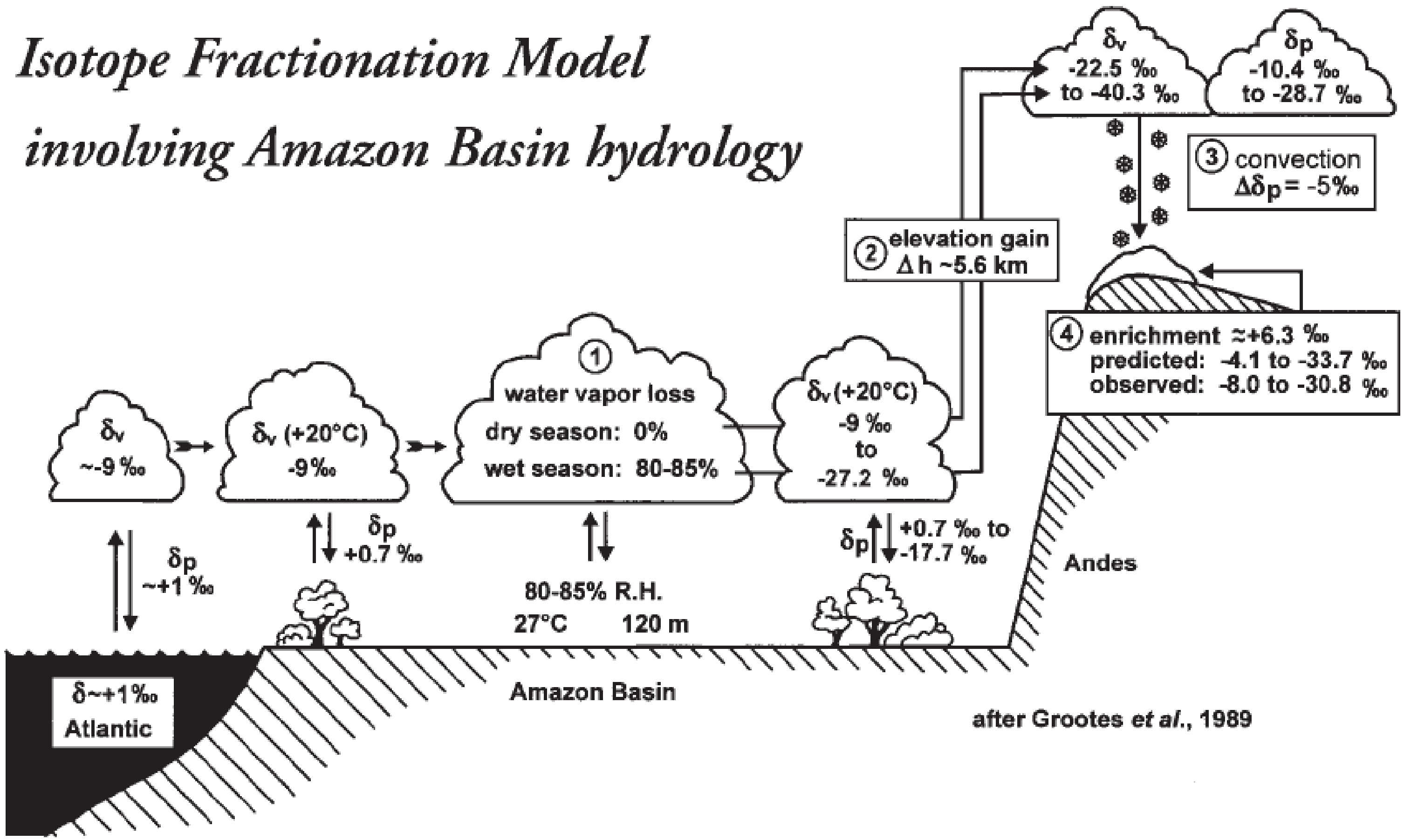


Figure 6 This schematic traces the $\delta^{18}O$ composition of the water vapor and precipitation along a transect from the Atlantic Ocean to the top of the Andes (Quelccaya ice cap). Each of the four steps shown is discussed in the text. This figure was modified from Grootes *et al.* (1989).

Links of GNIP with intern. programs

- GTN-H Global Terrestrial Networks – Hydrology
- GCOS Global Climate Observing System
- UNESCO-IHP
- UNEP-GEMS Global Env Monitoring System
- IGBP-PAGES Past Global Changes
- World Data Centre-A for paleoclimatology
- WMO - WCRP (GEWEX CLIVAR)

GNIP/WMO stations

National networks

Argentina, Australia, Austria, Canada, China, Chile, Croatia, France, Germany, Morocco, Netherlands, Portugal, South Africa, Spain, Switzerland, Turkey, USA

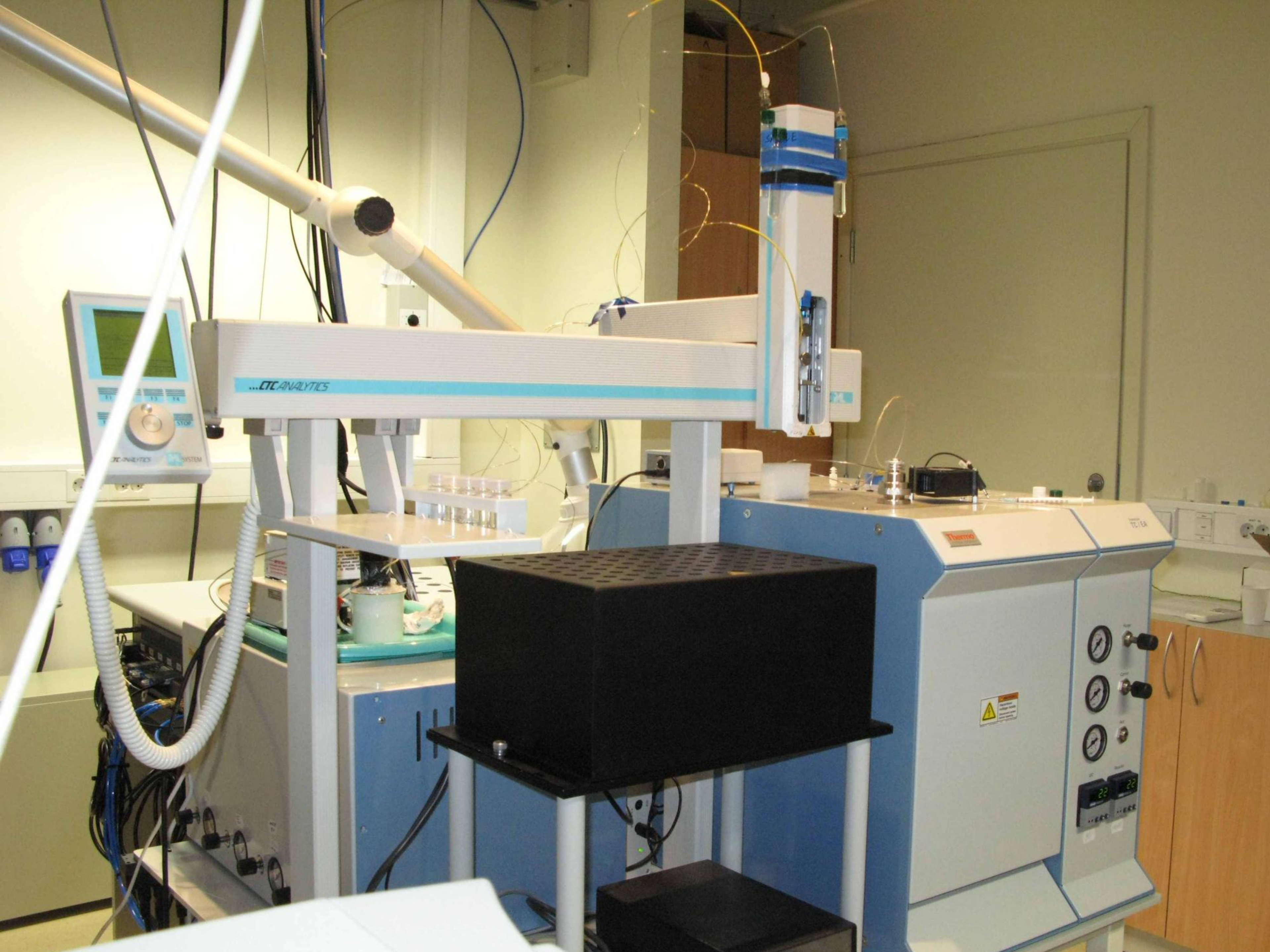
One station maintained in:

Algeria, Egypt, Indonesia, Israel, Jordan, New-Zealand, Poland, Slovenia, U.K.

Tallinn Isotope Lab

- Established in early 70th
- Major research objects
- Ice cores (Svalbard, Antarctica)
- Permafrost & massive ground ice (Siberia& Arctic Canada
- Groundwater


TC/EA with liquid injector
(δD and $\delta^{18}O$)
Delta V Advantage
(Thermo Fisher Scientific)
Thermo
DELTA V ADVANTAGE
Isotope Ratio MS
Linde


...CTC ANALYTICS
STOP
Thermo

TC / EA
90
1331

PICARRO L2120-i

δD and δ^{18}O

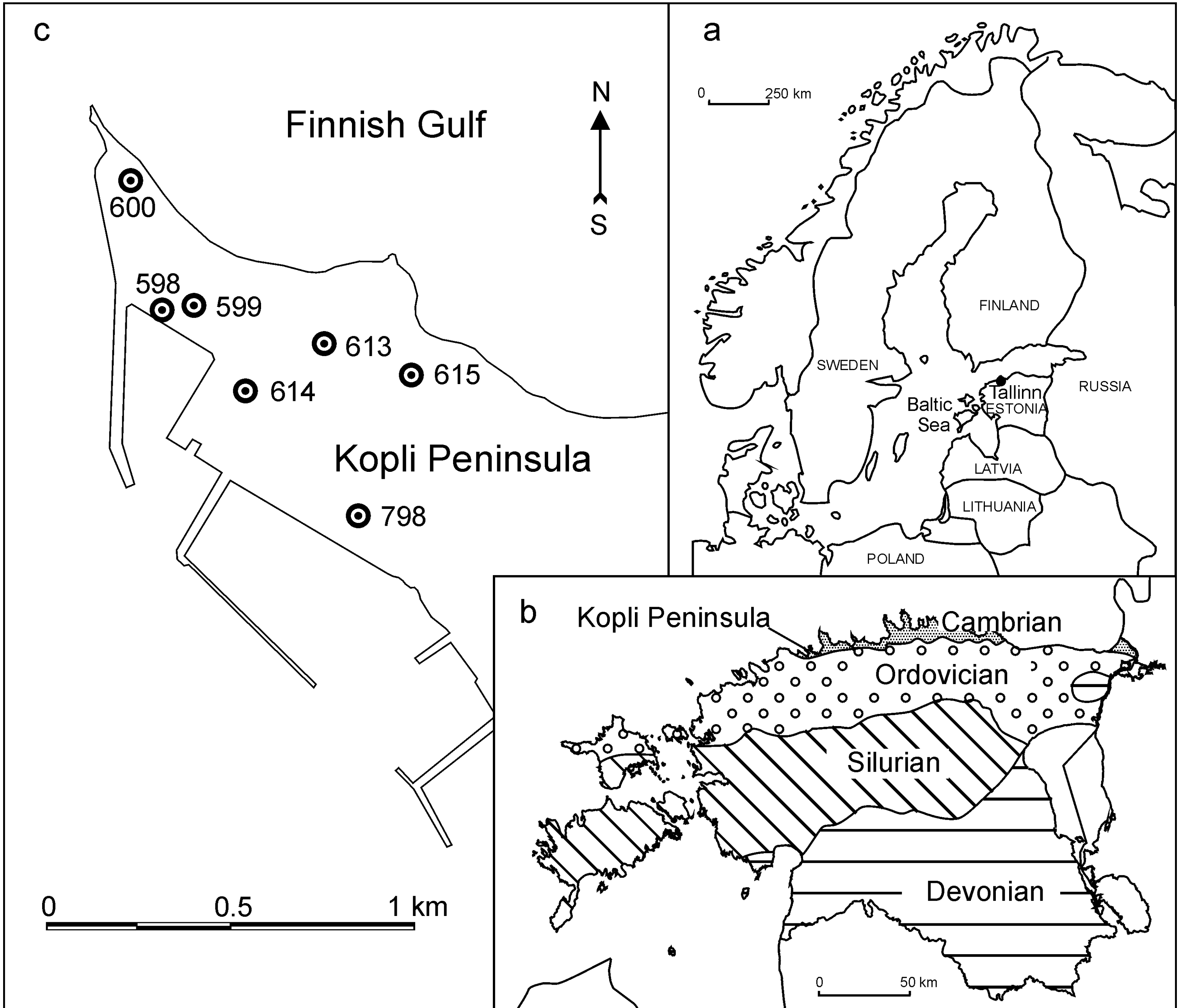
Analyzer

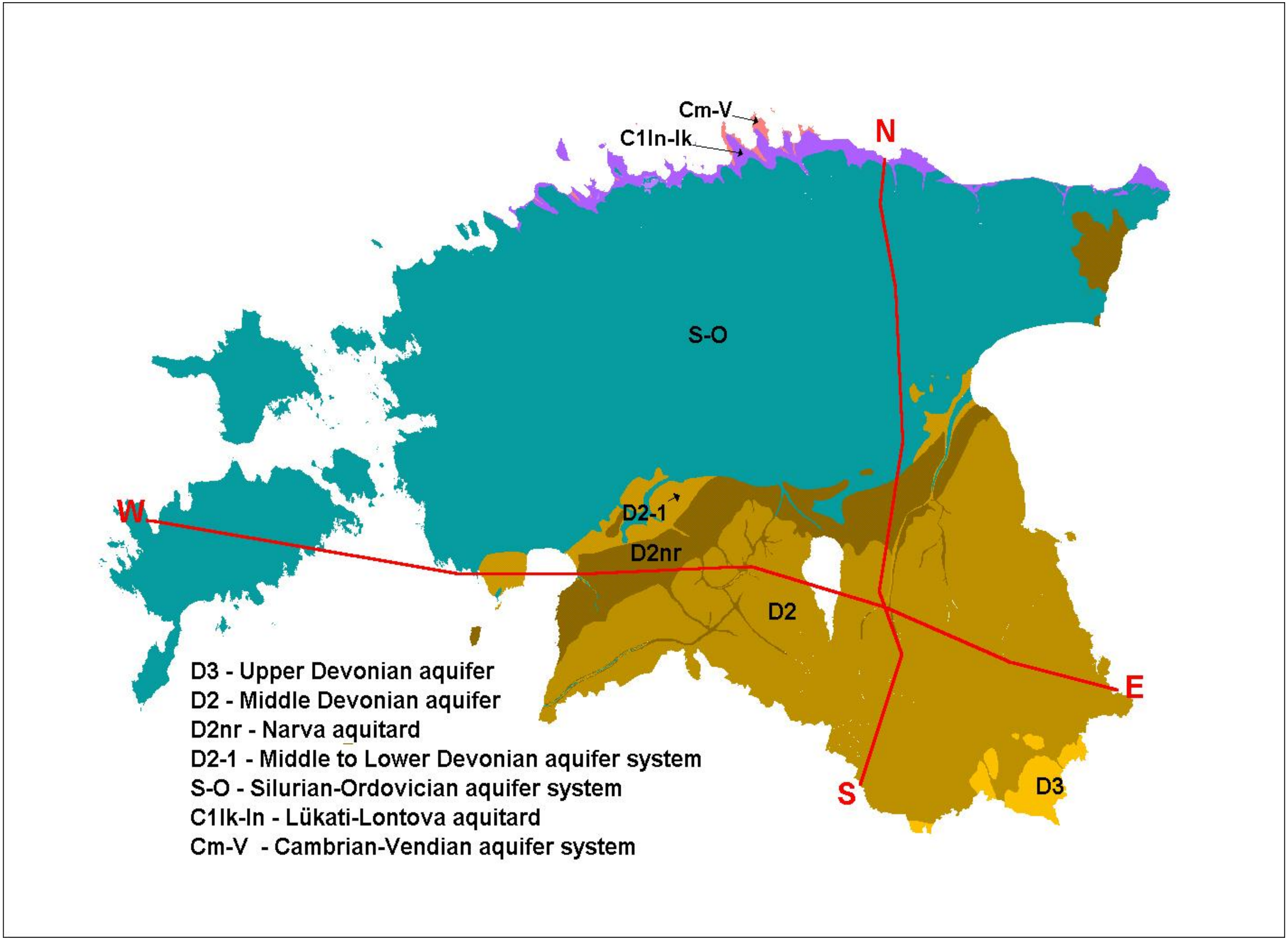
(*L2120-i*

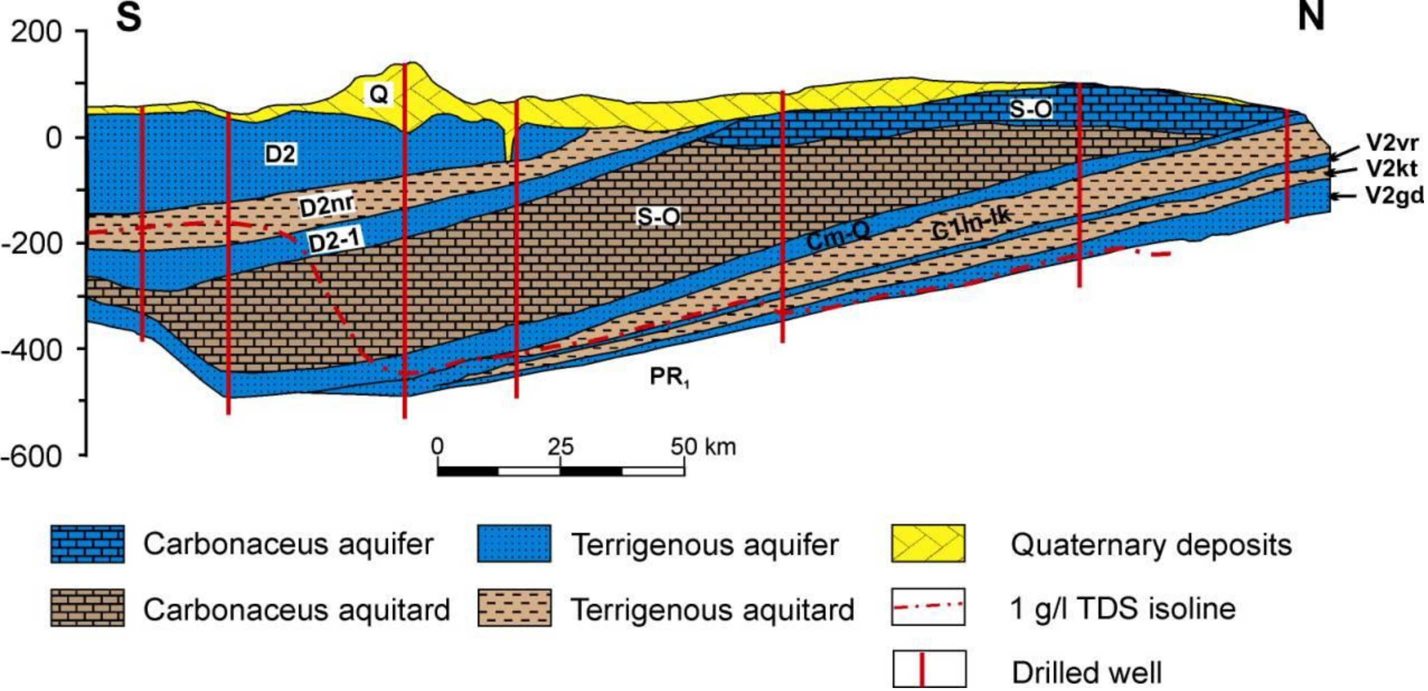
Isotopically light meltwater from Scandinavian ice sheet in the Cambrian-Vendian aquifer system of northern Estonia

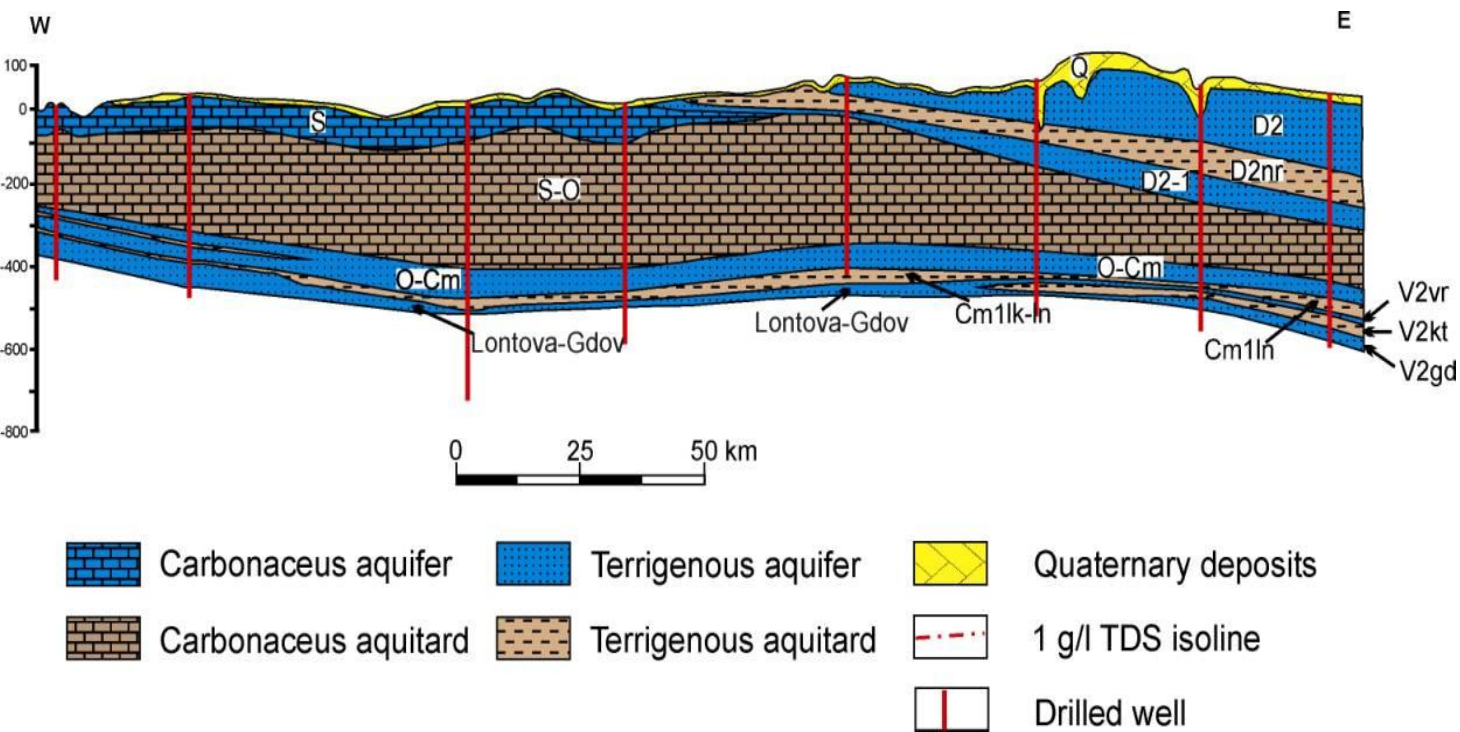
Study landmarks

- **monitoring of $\delta^{18}O$ in Estonian groundwater (in 1980`s)**
- **isotope meetings in Freiberg/Leipzig (in 1980`s)**
- **Miniconference on palaeogroundwaters, Paris, 1993**
- **EU 4th FP project PALEAUX (1996-1999)**
- **EU 5th FP project BASELINE (2000-2003)**

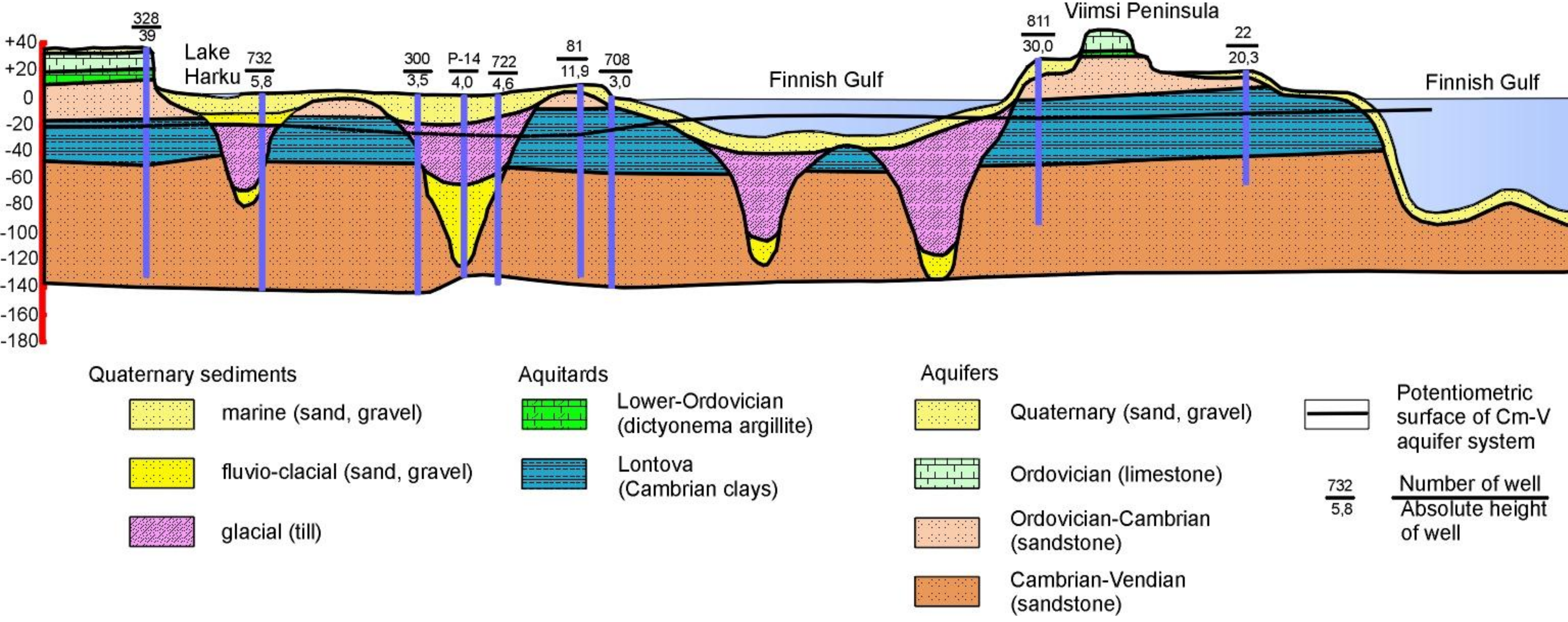

c
Finnish Gulf
N
S
600
598
599
613
615
614
Kopli Peninsula
798
0
0.5
1 km
a
0
250 km
FINLAND
SWEDEN
RUSSIA
Tallinn
Baltic
Sea
ESTONIA
LATVIA
LITHUANIA
POLAND
b
Kopli Peninsula
Cambrian
Ordovician
Silurian
Devonian
0
50 km


Cm-V
C1ln-lk
N
S-O
W
D2-1
D2nr
D2
E
S
D3
D3 - Upper Devonian aquifer
D2 - Middle Devonian aquifer
D2nr - Narva aquitard
D2-1 - Middle to Lower Devonian aquifer system
S-O - Silurian-Ordovician aquifer system
C1lk-ln - Lükati-Lontova aquitard
Cm-V - Cambrian-Vendian aquifer system


S
N
200
0
-200
-400
-600
Q
S-O
D2
D2nr
D2-1
S-O
Cm-O
G1ln-lk
V2vr
V2kt
V2gd
PR1
0
25
50 km
Carbonaceus aquifer
Terrigenous aquifer
Quaternary deposits
Carbonaceus aquitard
Terrigenous aquitard
1 g/l TDS isoline
Drilled well

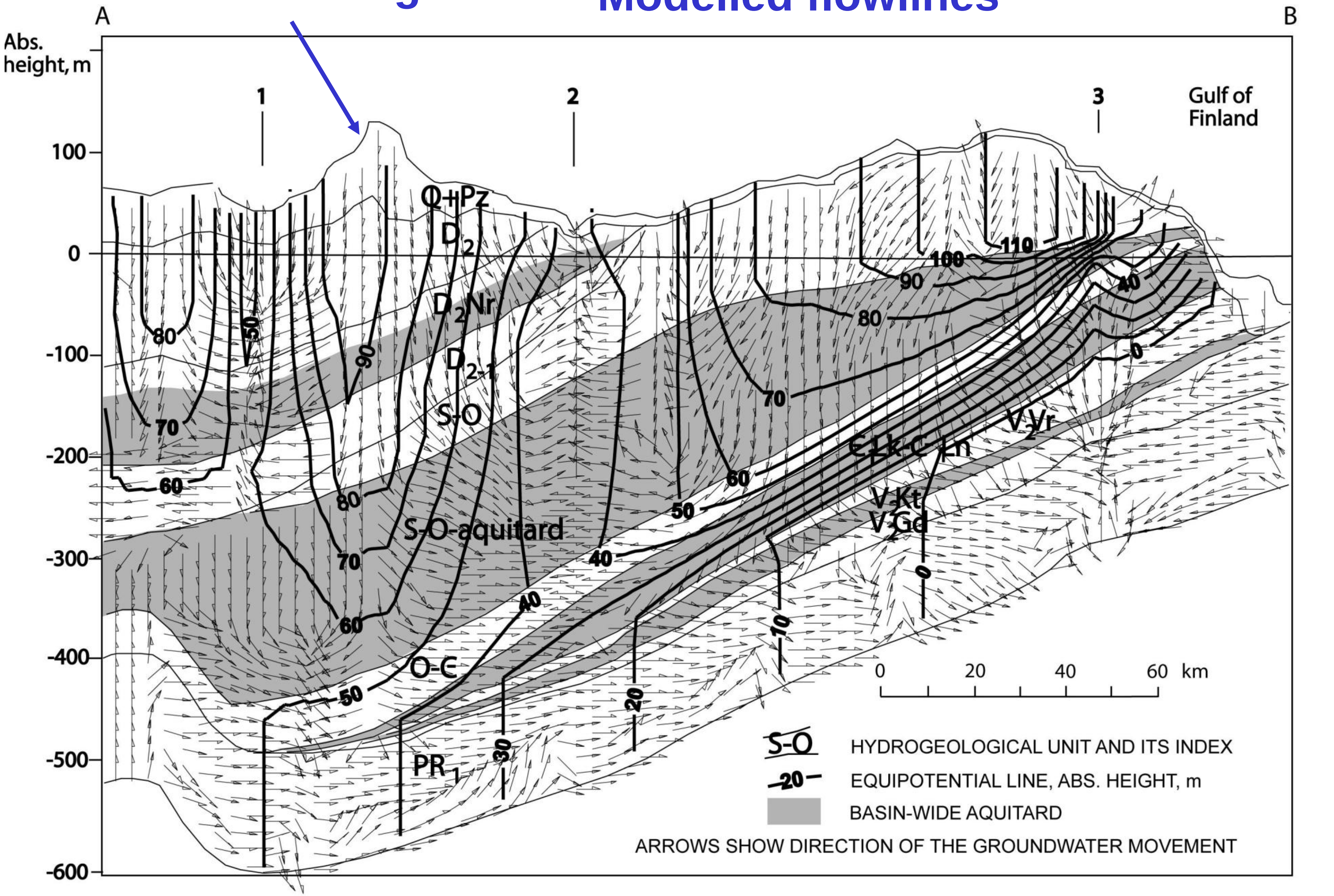

W
E
100
0
-200
-400
-600
-800
Q
S
D2
D2nr
D2-1
S-O
O-Cm
O-Cm
V2vr
V2kt
V2gd
Lontova-Gdov
Lontova-Gdov
Cm1lk-ln
Cm1ln
0
25
50 km
Carbonaceus aquifer
Terrigenous aquifer
Quaternary deposits
Carbonaceus aquitard
Terrigenous aquitard
1 g/l TDS isoline
Drilled well

Buried valleys



Cm-V recharge

Modelled flowlines



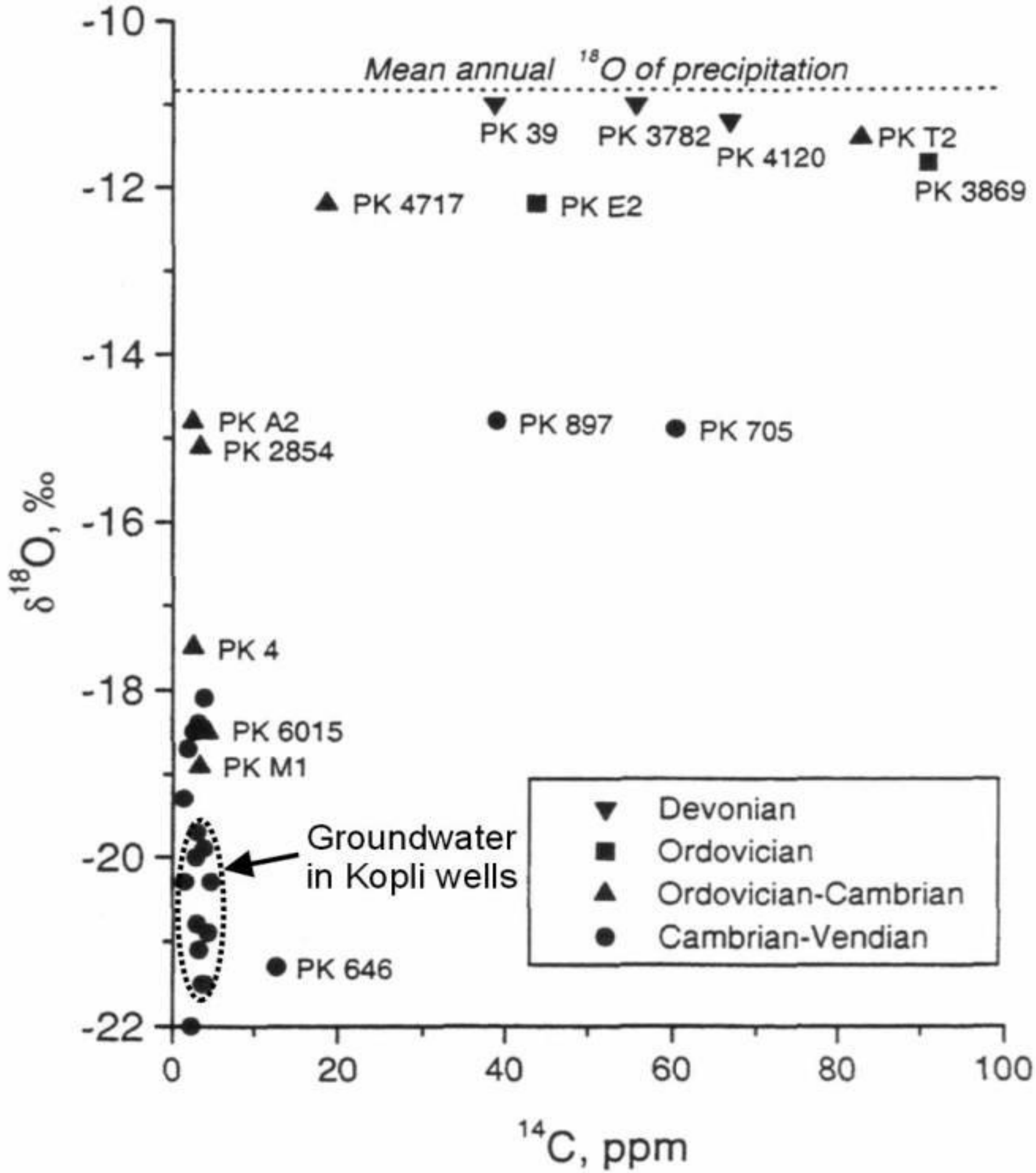
Major chemical types of Cm-V groundwater

1. “Original/relict ” Cm-V water in South Estonia: Cl-Na type; TDS concentration 2 – 20 g/l
2. Freshwater in North Estonia: Ca-Na-HCO_3-Cl type; TDS concentration 300 – 1000 mg/l
3. Mixture of relict and freshwater in NE Estonia: Cl- HCO_3-Na type; TDS about 1 g/l
4. Freshwater around buried valleys: Ca- HCO_3 type; TDS concentration 200 – 500 mg/l

The characteristic isotopic composition of Estonian groundwaters

Aquifer system	Lithology	$\delta^{18}O$, ‰	^{14}C, pmC	^{3}H, TU
Ordovician	limestones, dolomites	-11,7 to -12.2	43.77 to 90.91	13.1 to 21.0
Ordovician -Cambrian	detrial sandstones, sandstones	-11,4 to -18.9	2.40 to 18.60	1.8 to 21.3
Cambrian-Vendian	sandstones	-18.1 to - 22.0	1.40 to 12.76	0.5 to 2.1

Atmospheric precipitation: annual mean $\delta^{18}O$= - 10.4 ‰



Mean annual ^{18}O of precipitation
PK 39
PK 3782
PK 4120
PK T2
PK 3869
PK 4717
PK E2
PK A2
PK 2854
PK 897
PK 705
PK 4
PK 6015
PK M1
Groundwater in Kopli wells
PK 646
Devonian
Ordovician
Ordovician-Cambrian
Cambrian-Vendian
$\delta^{18}O$, ‰
^{14}C, ppm

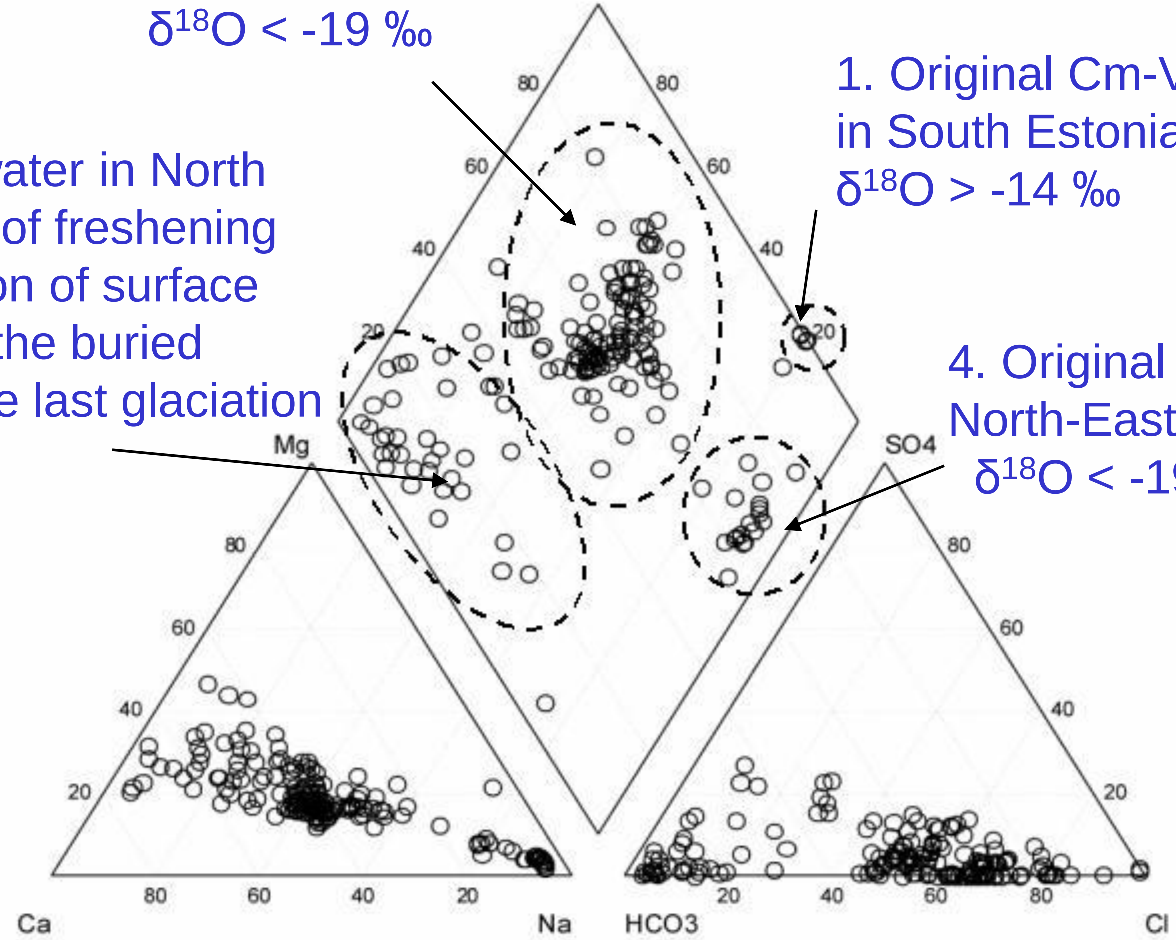
Major chemical types of Cm-V groundwater

2.The Cm-V water in North Estonia : glacial meltwater $\delta^{18}O < -19$ ‰

1. Original Cm-V water in South Estonia $\delta^{18}O > -14$ ‰

3. The Cm-V water in North Estonia: result of freshening doe to infiltration of surface water through the buried valleys after the last glaciation $\delta^{18}O > -14$ ‰

4. Original Cm-V water in North-East Estonia $\delta^{18}O < -19$ ‰



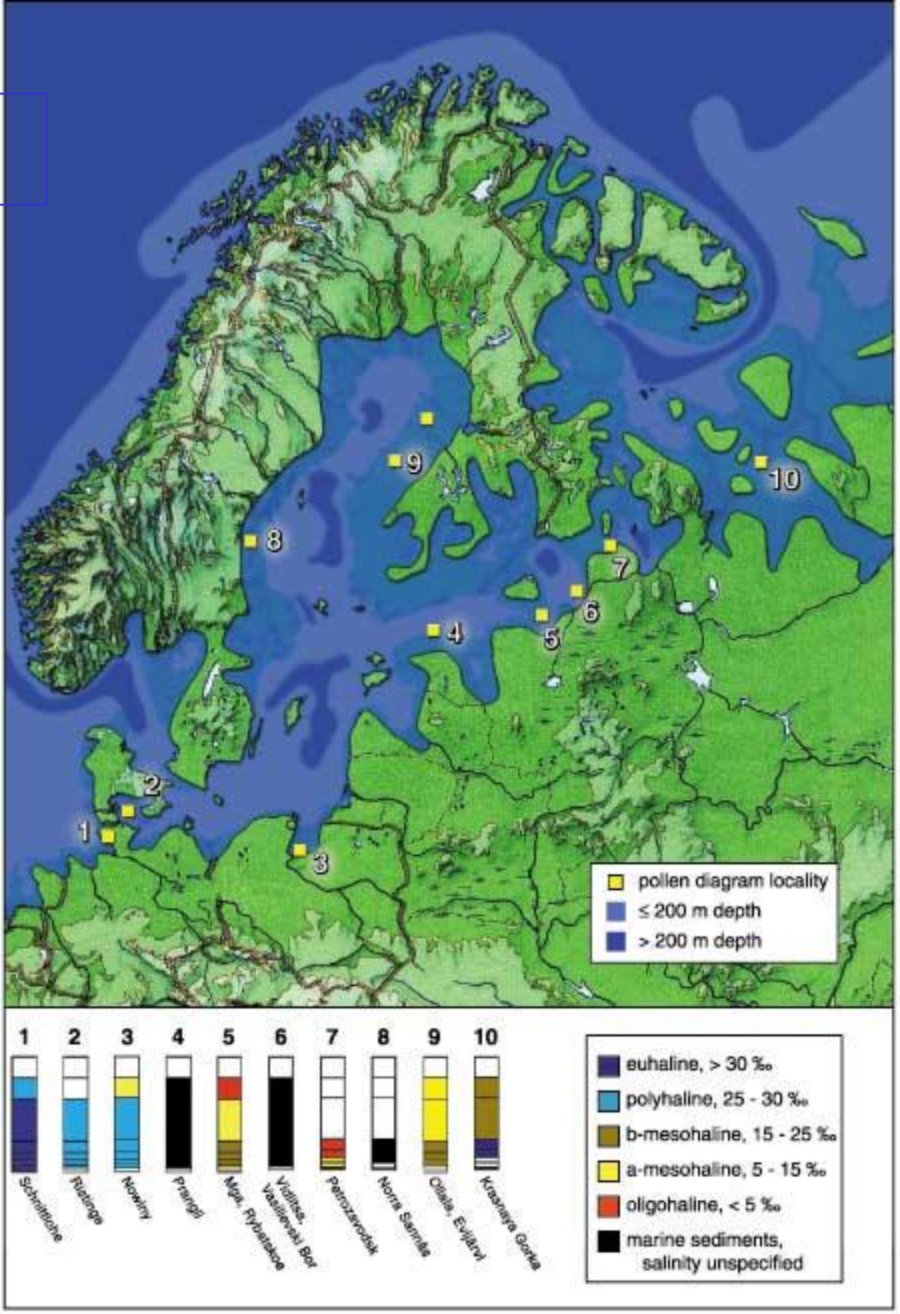
Special features

- $\delta^{13}C$ values between - 8.6 to - 19.3‰
- high gas concentration in several wells (oversaturation by factor 2-5!)
- Methane in some gas samples ($\delta^{13}C$ between -75 to - 78 ‰ :biogenic origin?)
- NGRT and ^{39}Ar analysis

Formation of palaeogroundwater:some hypothesis

- Cryogenic metamorphism?
- Baltic Ice Lake?
- Subglacial drainage through aquifers?

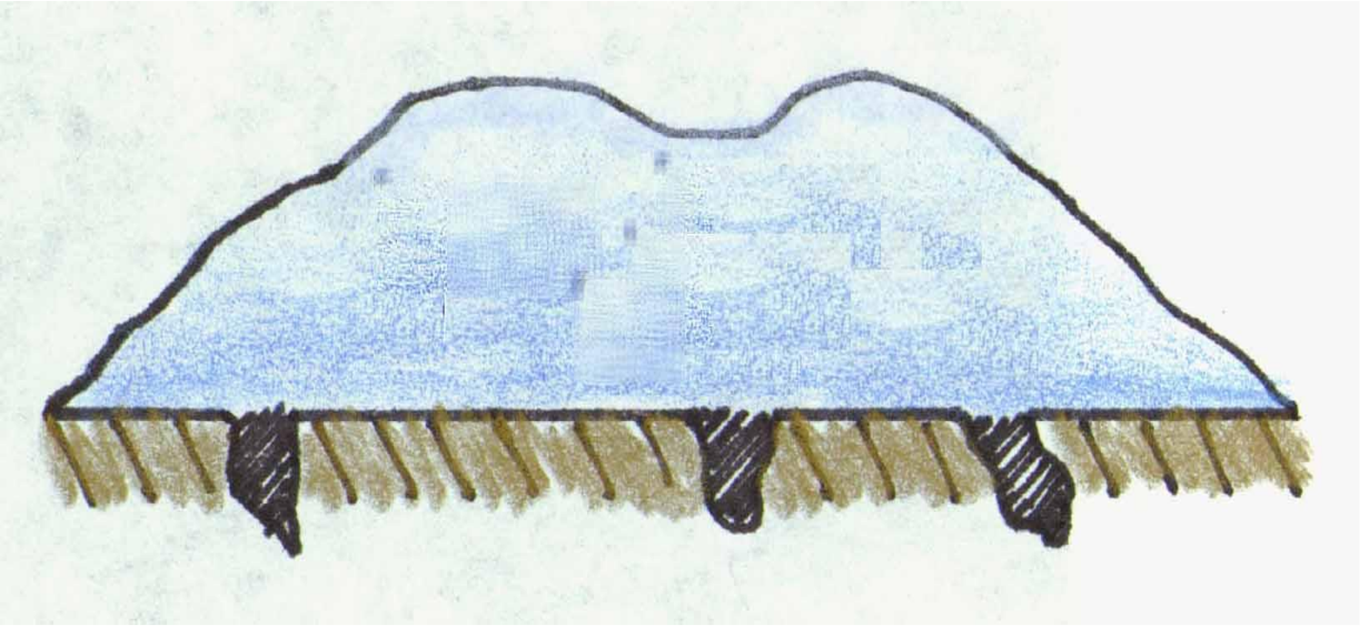
Emian interglacial



LGM

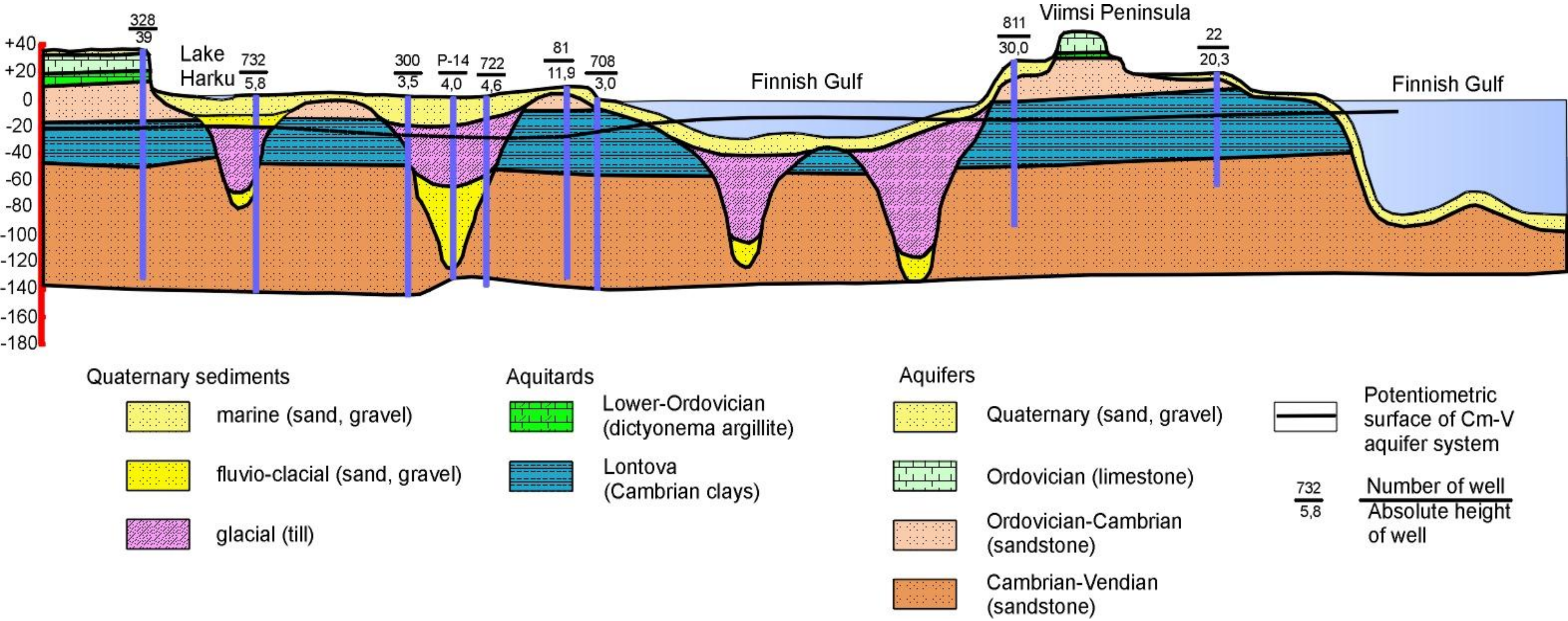
Late Weichselian glacial maximum
-according to various sources
-according to our hypothesis
Early / Middle Weichselian glacial maximum
-according to our hypothesis
Quaternary glaciation limit (asynchronous)
-according to various sources

Nay channels



Valley cut by subglacial meltwater on Bylot Island

Buried valleys in Estonia



Subglacial meltwater flow

Conclusions

- Cm-V groundwater in N-Estonia recharged during the last glaciation
- Most characteristic features: lightest known oxygen isotopic composition in Europe, low ^{14}C concentration and absence of ^{3}H
- Overexploitation has resulted in development of two basin-wide depressions of potentiometric level
- The main sources of dissolved load are the leaching of host rock and leakage from underlying crystalline basement
- Intrusion of seawater is at present time not evident, but should be considered in coming decades

$\delta^{18}O \sim -22‰$

GROUNDWATER DATING AND PAST CLIMATE RECONSTRUCTION

A review with focus on noble gases and recharge conditions in glacial environments

Roland Purtschert
Physics Institute, University of Bern, Switzerland

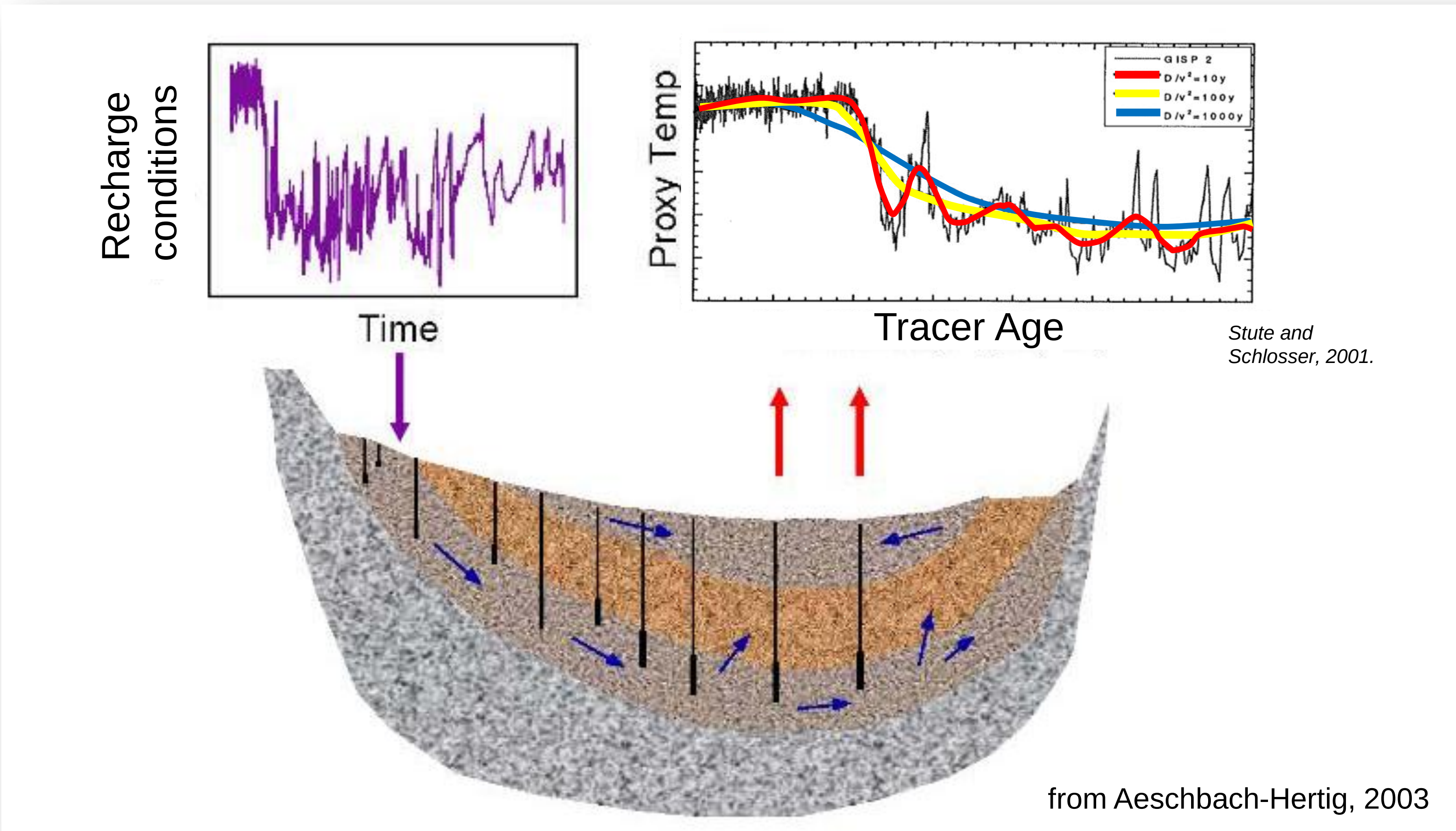
Jose Corcho
Institute of Radiation Physics, University of Lausanne

Rolf Kipfer
Swiss Federal Institute of Aquatic Science and Technology (EAWAG)

Z.-T. Lu
Physics Division, Argonne National Laboratory, USA

Neil Sturchio
Department of Earth and Environmental Sciences, University of Illinois at Chicago

Palaeohydrology: Groundwater as a climate archive



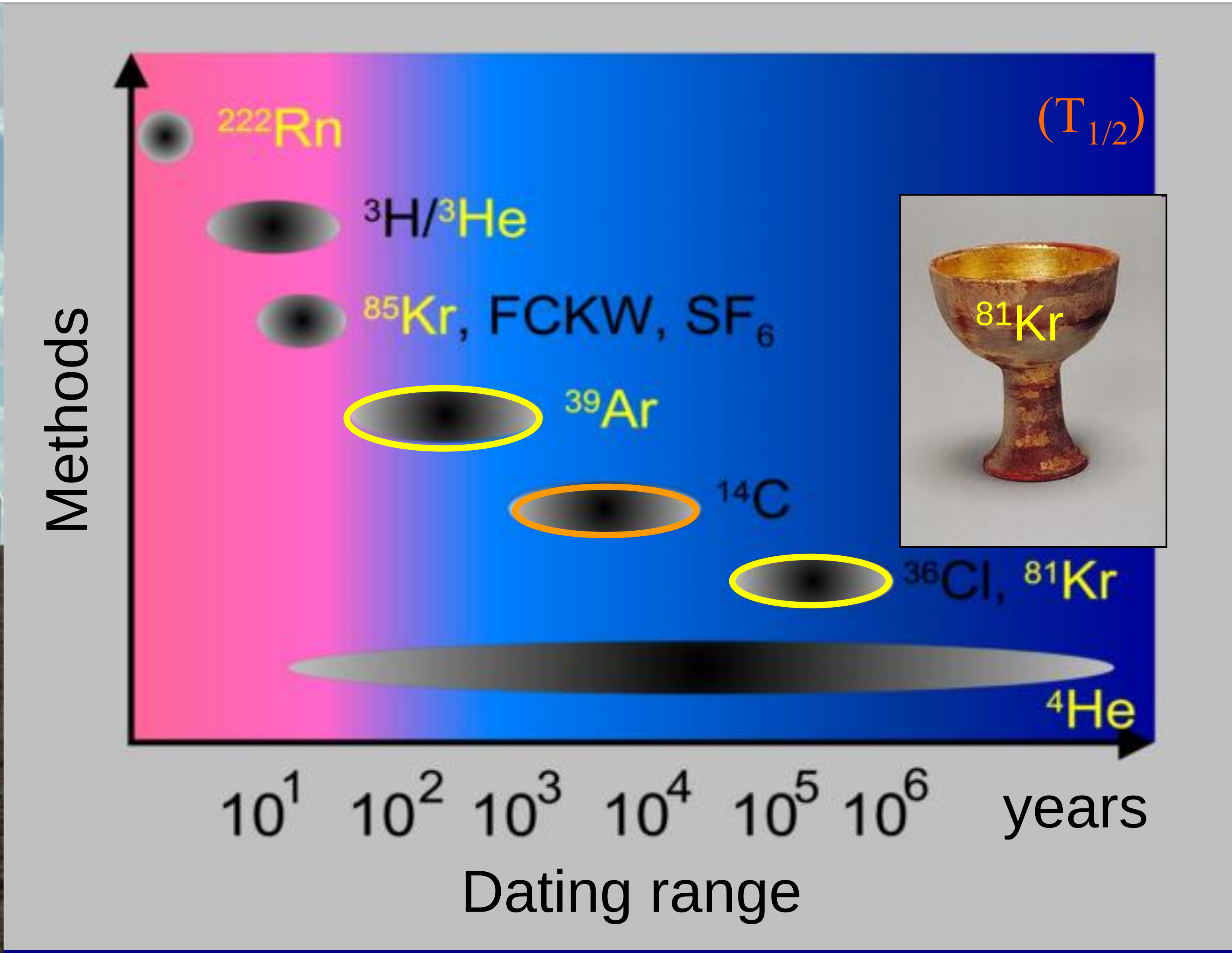
Relations

Past climate reconstruction

Impact of climate change to groundwater recharge dynamics

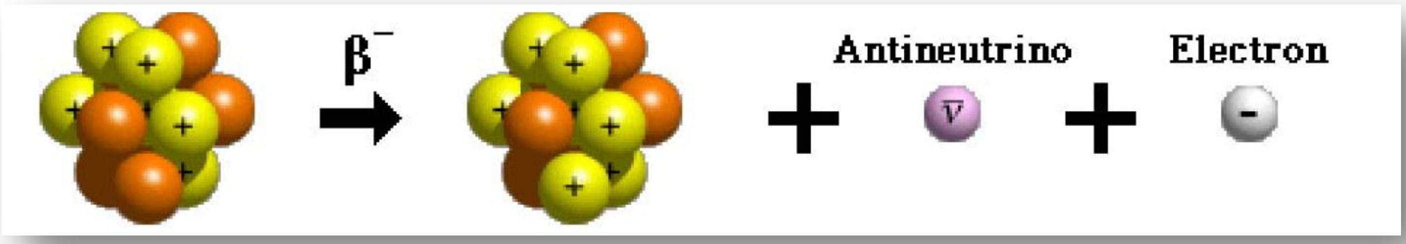
Questions and Topics

Timescales of groundwater dating methods



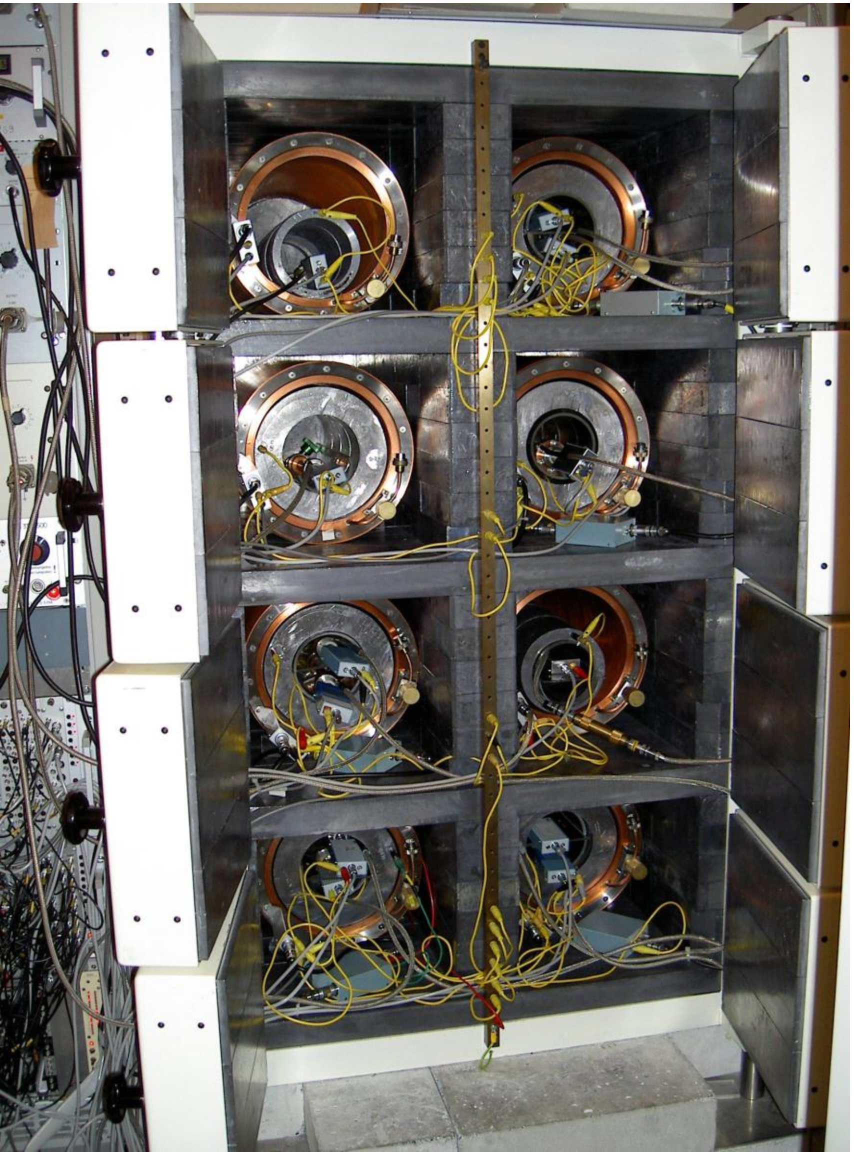
^{39}Ar: Key data

Detection by decay counting



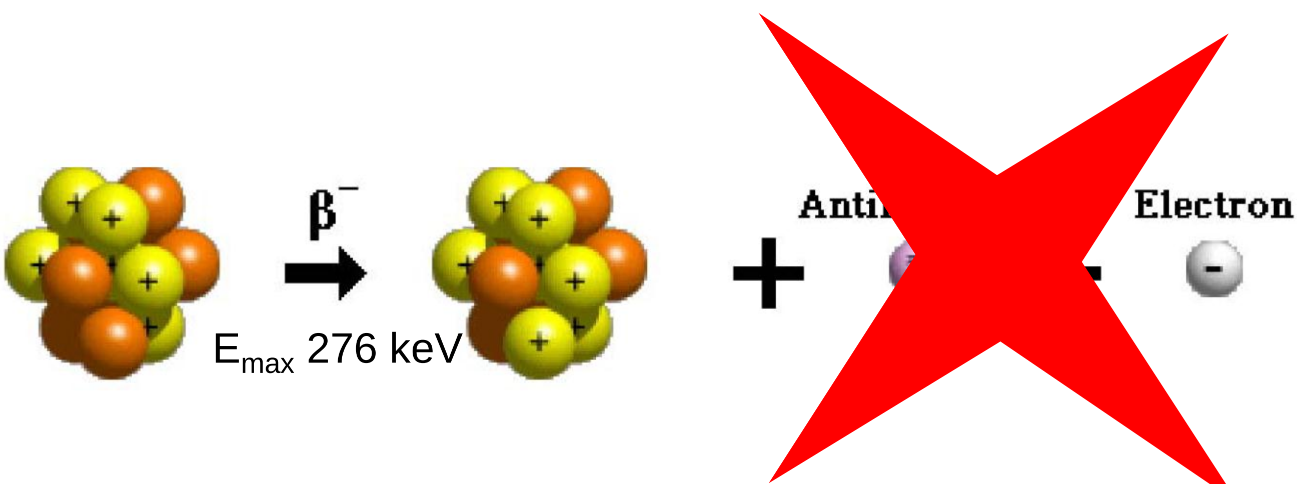
Water sample volume:
1-2 tons!

LLC facility at University of Bern

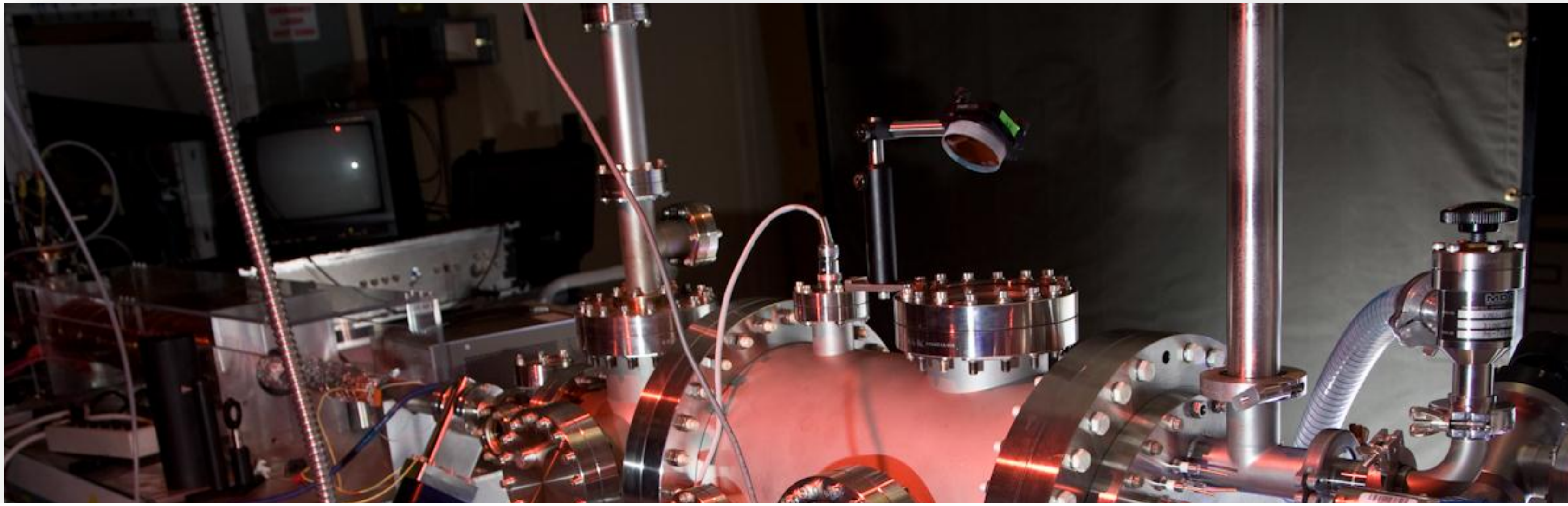


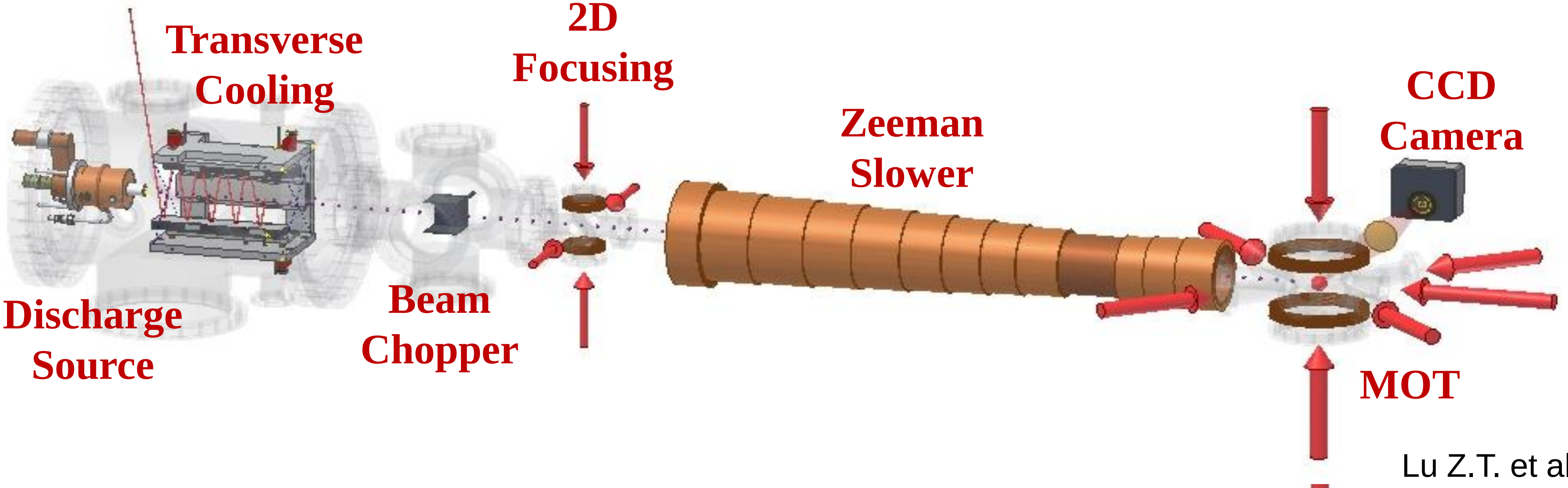
- Deep laboratory (70 m water equivalent) build with low activity concrete
- Passive shielding with old lead
- Active shielding (anti-coincidence arrangement)

^{81}Kr: Key data



AtomTrap Trace Analysis (ATTA): Basic Principle - laser based atom counting

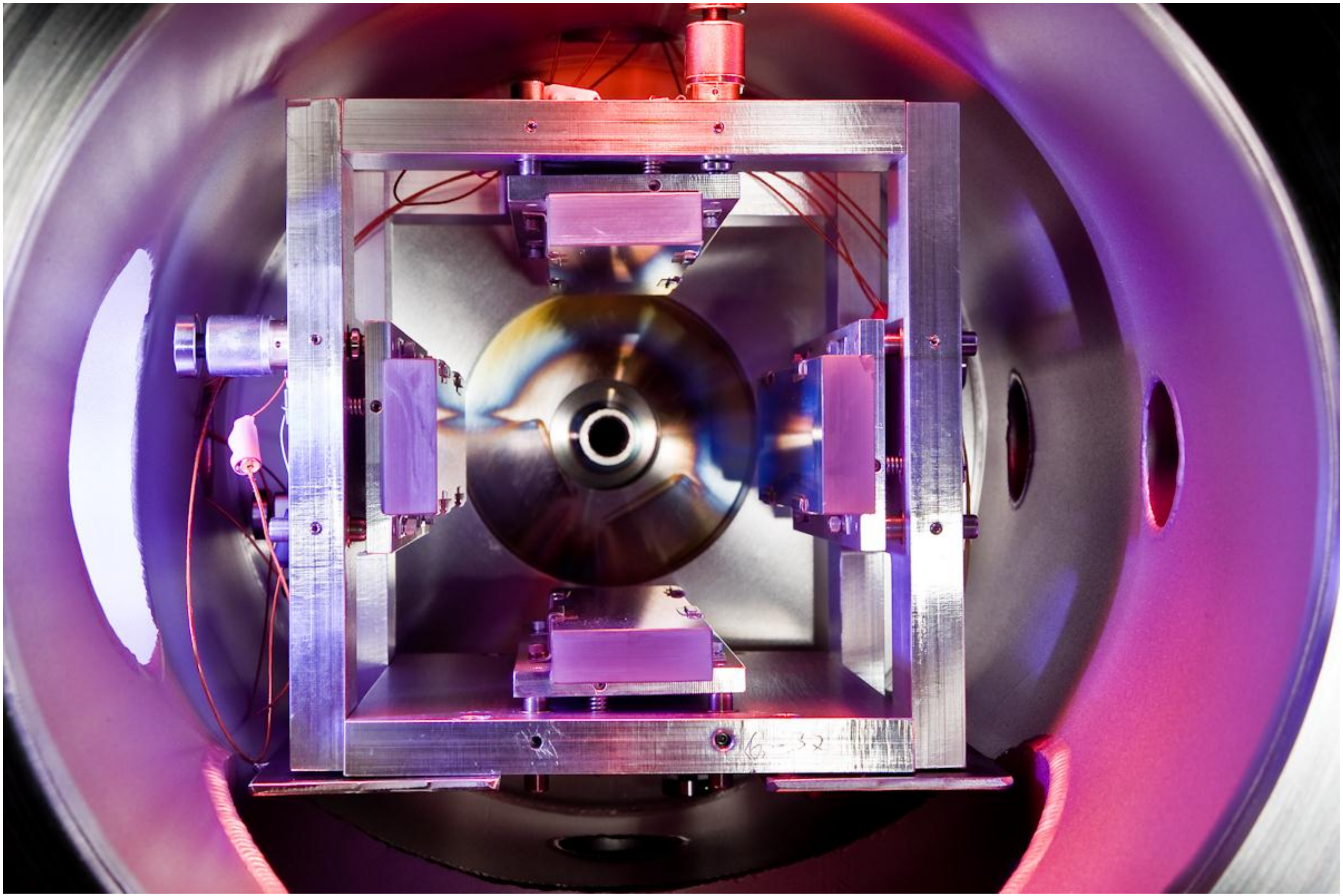




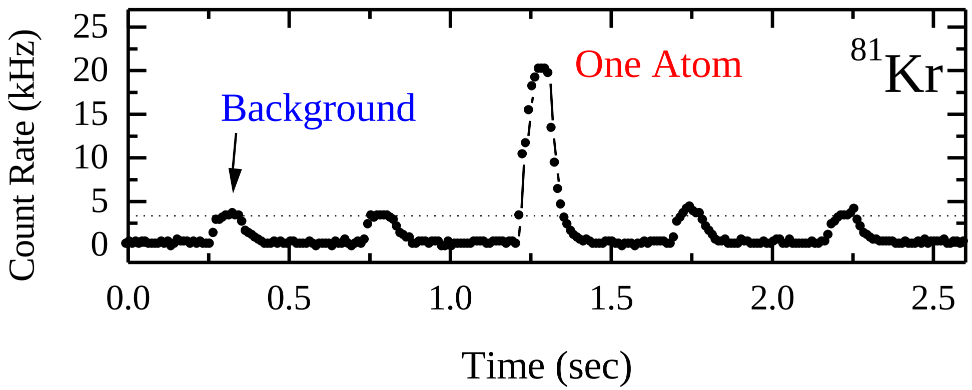
Lu Z.T. et al

Photo © Lu Z.T.

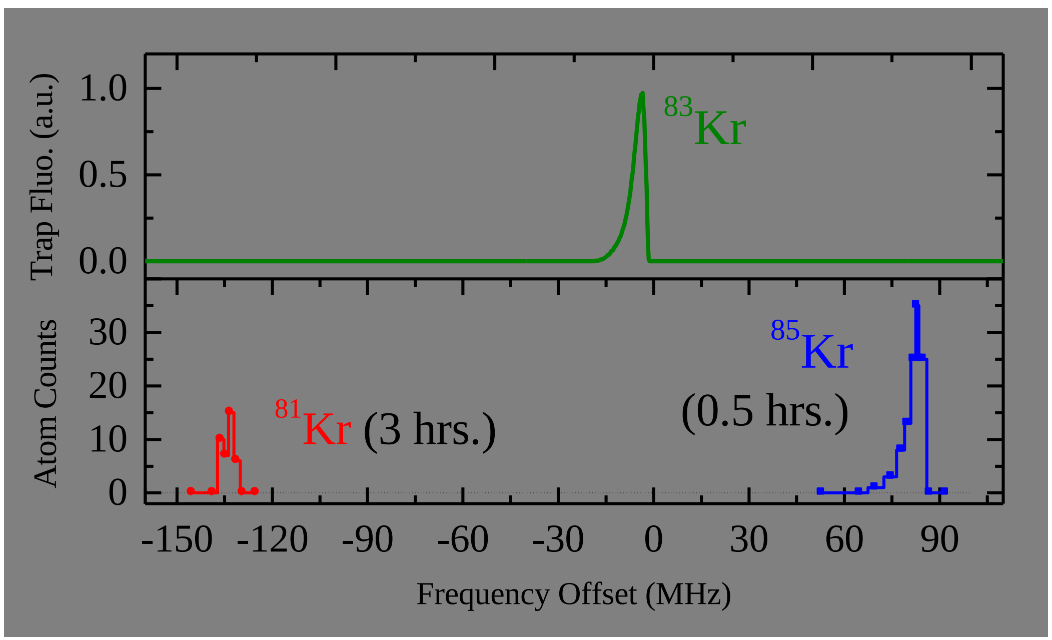
ATTA 3



Advantages ATTA



High Signal/Noise Ratio

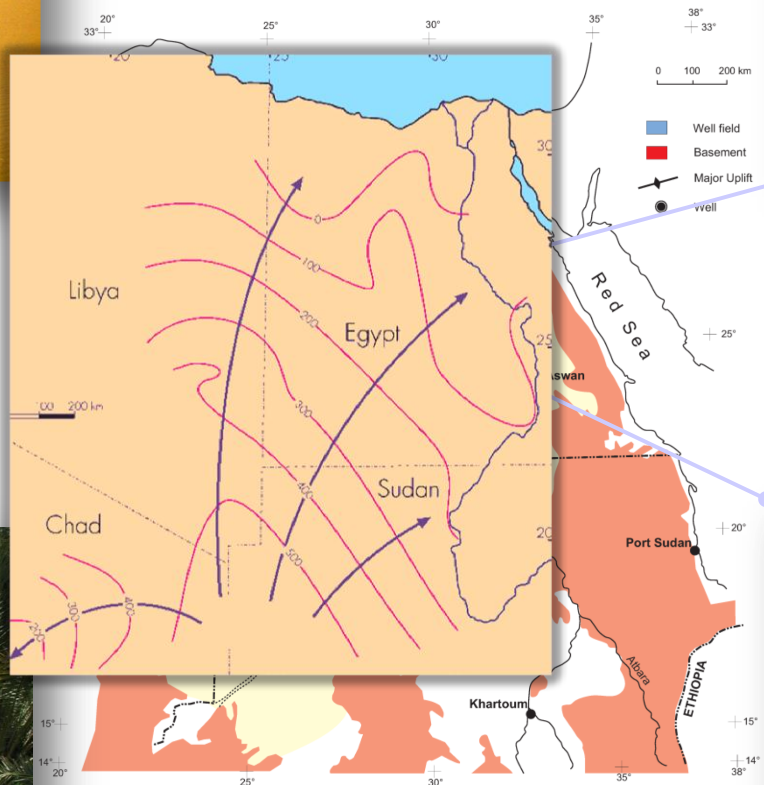


Excellent Isotope selectivity

.

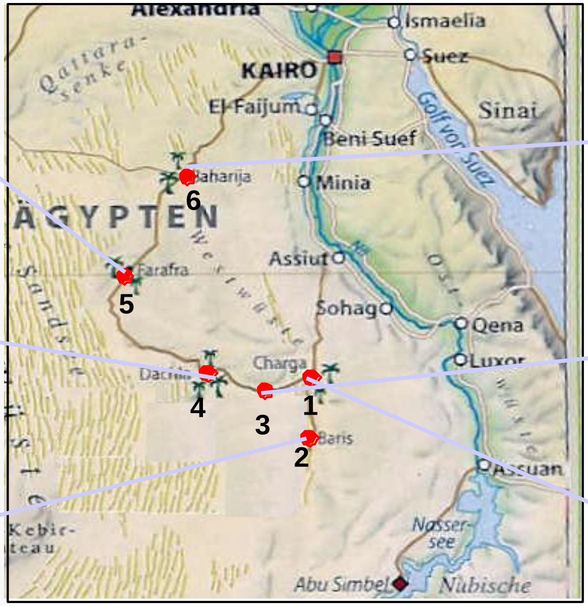
^{81}Kr: Nubian Aquifer Egypt
Area of Investigation

Desert



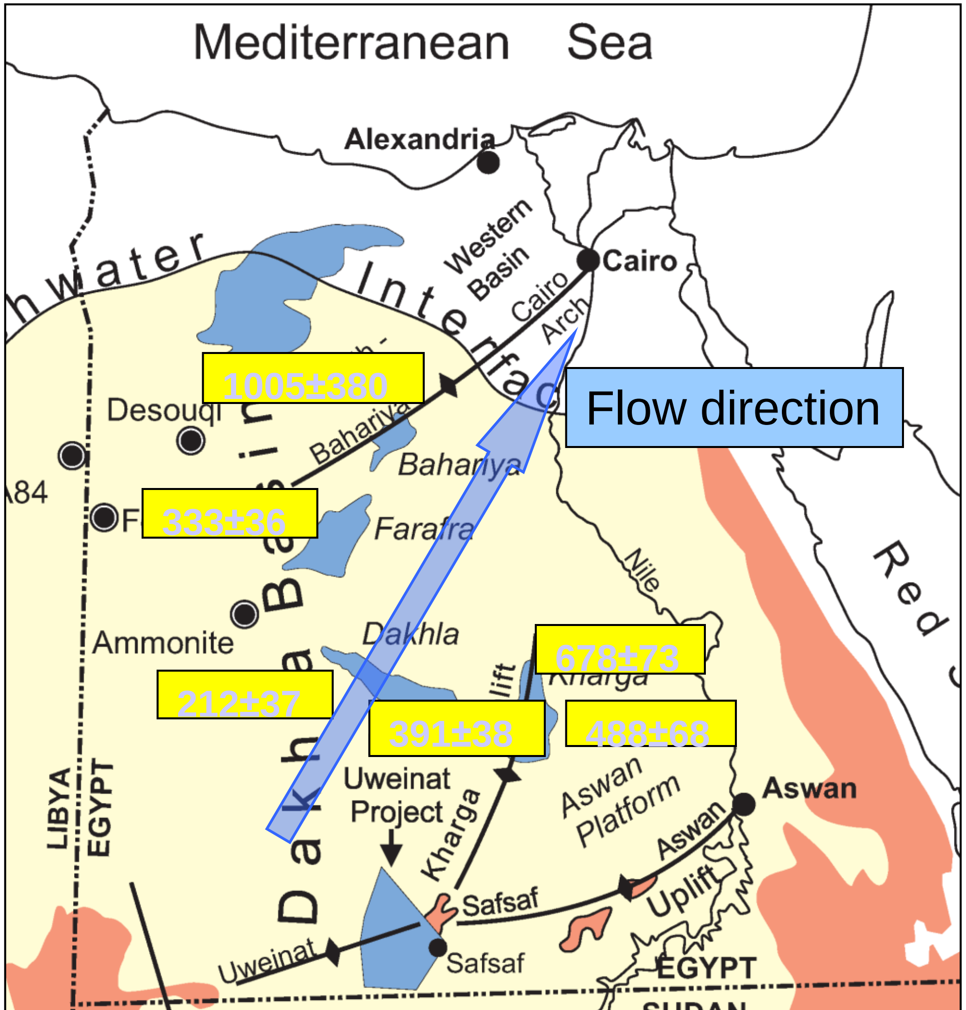
Oasis

Sampling conditions in Egypt(1)



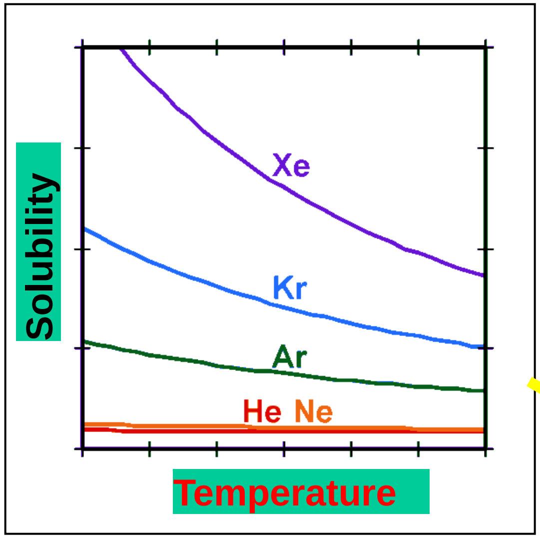
Results

Groundwater ages [kyears]



- **6 samples were dated**
- **Error < 10% with one exception**
- **Age range : 0.2-1 Mio years**

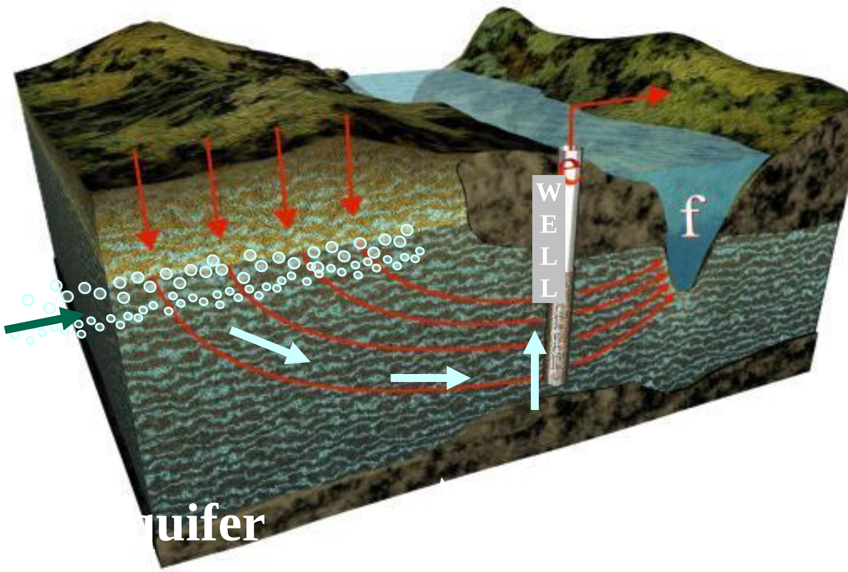
Noble gases (He, Ne, Ar, Kr, Xe)



Dissolution

Quasi-saturated zone

Excess air addition



Water table fluctuations

↓

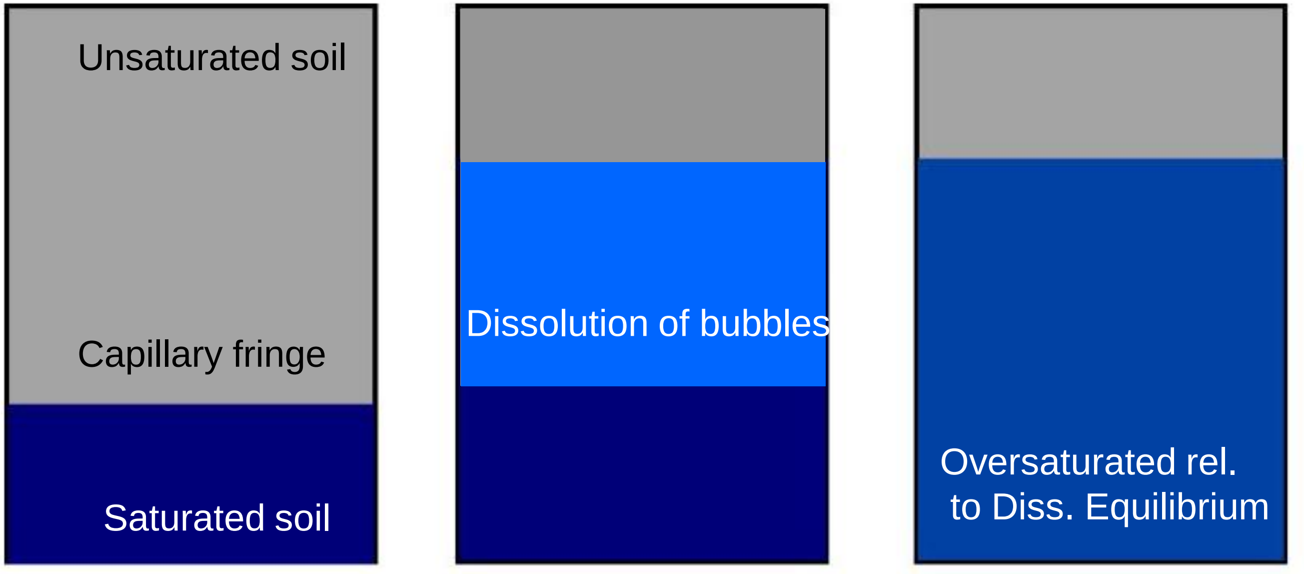
Recharge-Precipit.

↓

Humidity

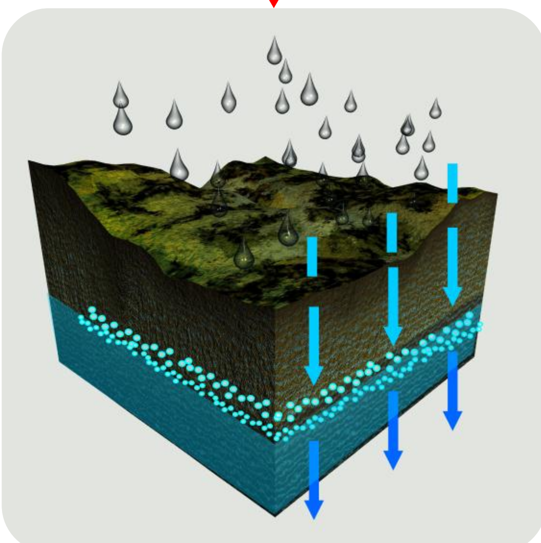
Inverse modeling of the observed noble gas concentrations is used to interpret the data in terms of recharge temperature and excess air.

Excess Air

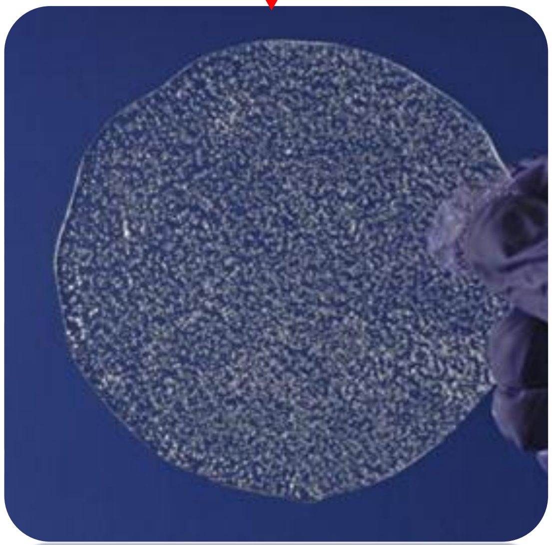


Unsaturated soil
Capillary fringe
Saturated soil
Dissolution of bubbles
Oversaturated rel.
to Diss. Equilibrium

Palaeowaters:
Interpretation of high Excess Air (EA)

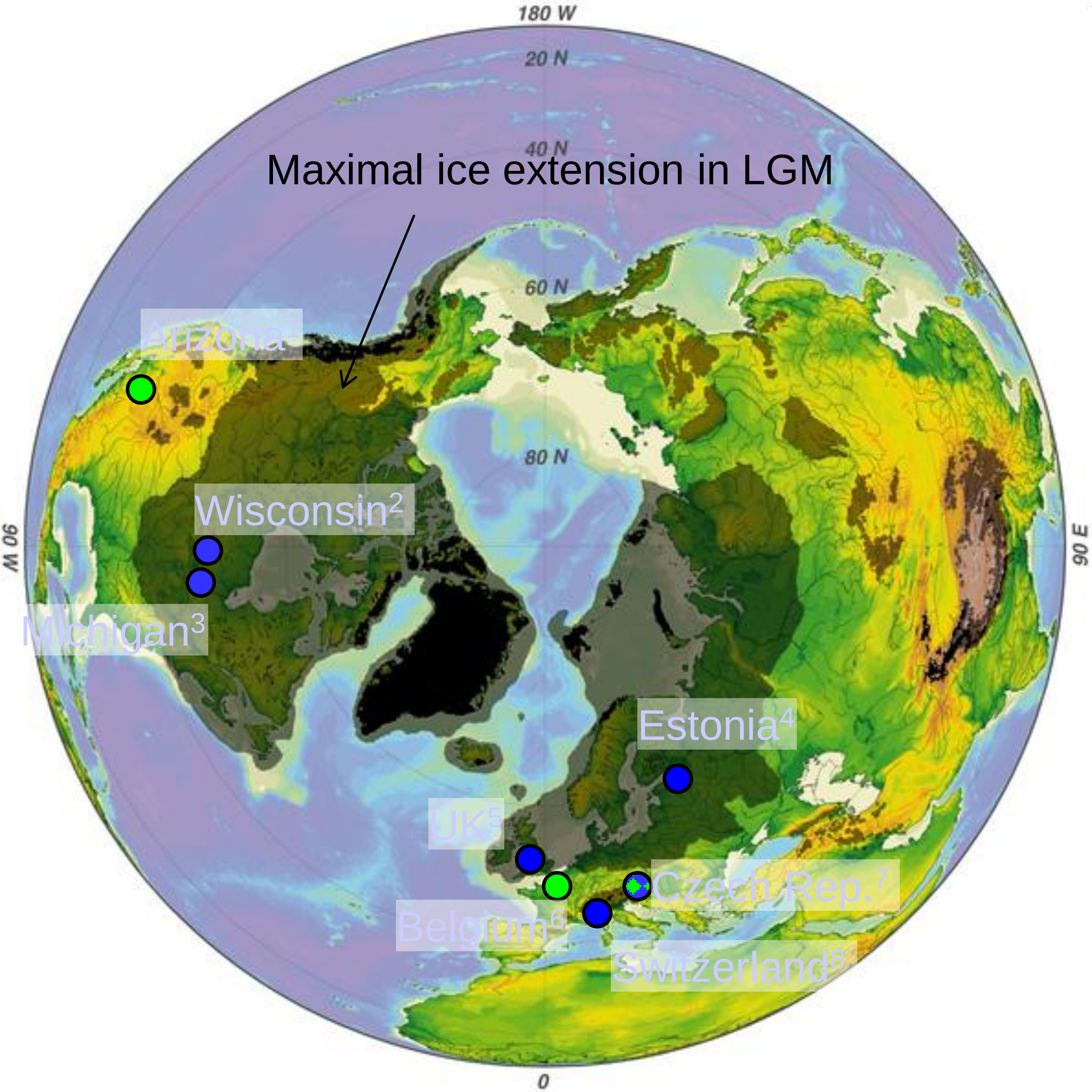


Intensive recharge events



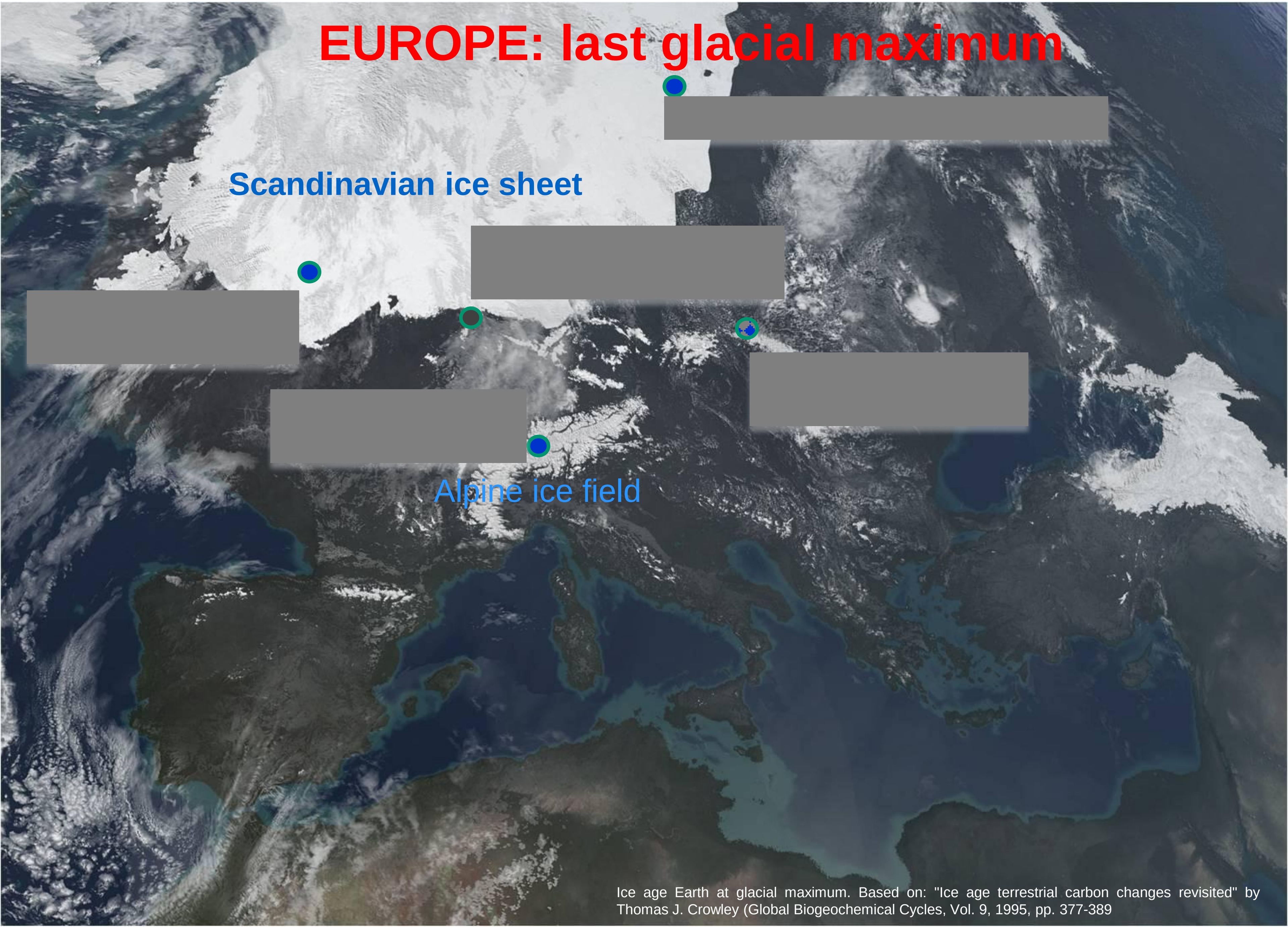
Recharge of glacial meltwater that is oversaturated due to dissolved air bubbles

Case study sites



Zhu & Kipfer, 2010
2: Klump et al., 2008
3: Ma et 1: al., 2004
4: Vaikmäe et al., 2001
5: (Andrews & Lee, 1979
6: Blaser et al., 2010
7: Corcho et al., 2011
8: Beylerle al, 1998
Purtschert et al, 2001

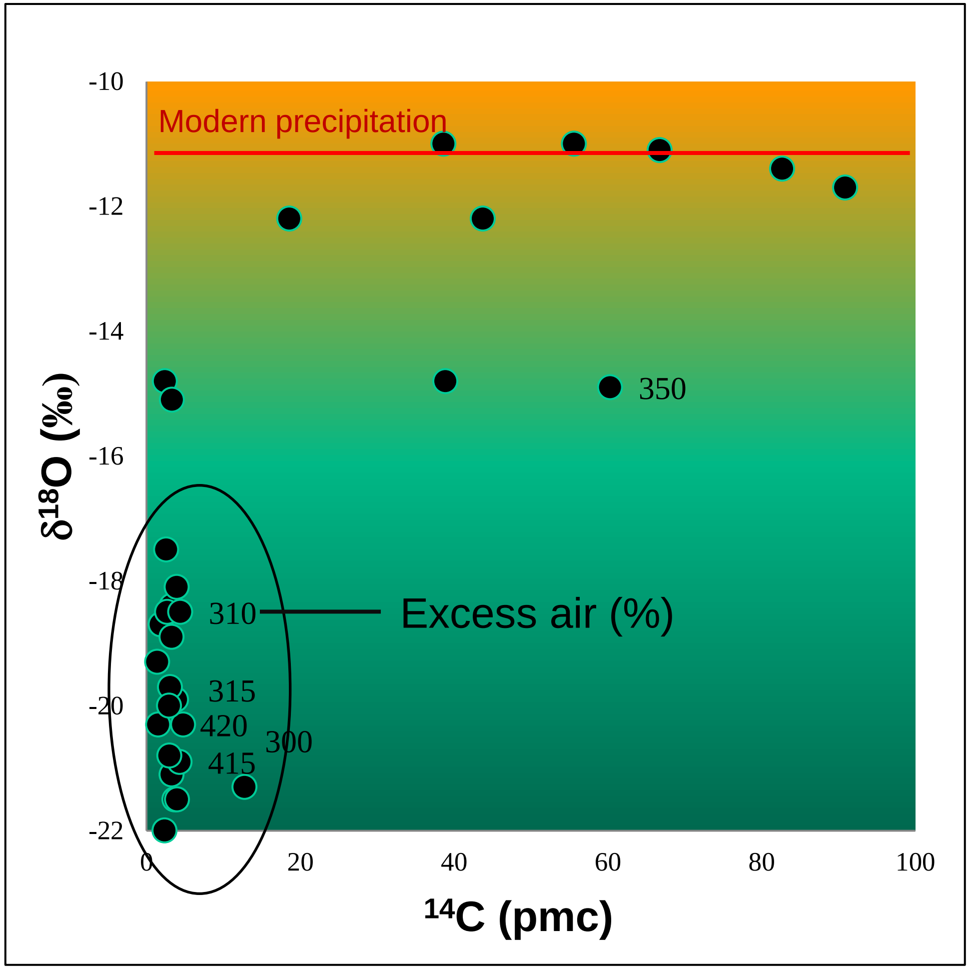
EUROPE: last glacial maximum



Ice age Earth at glacial maximum. Based on: "Ice age terrestrial carbon changes revisited" by Thomas J. Crowley (Global Biogeochemical Cycles, Vol. 9, 1995, pp. 377-389

Cambrian Vendian Aquifer, Estonia

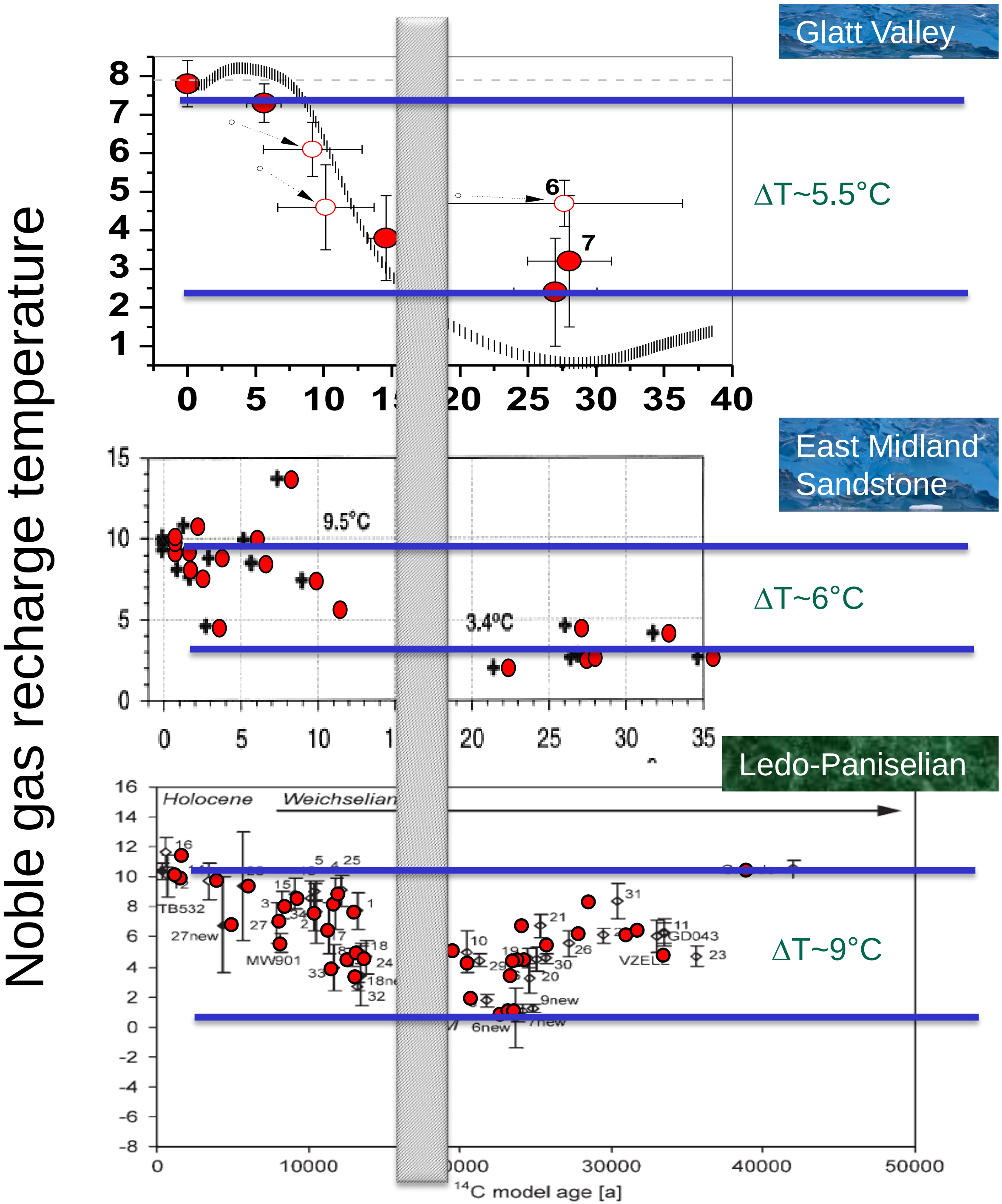
(Vaikmäe et al, 2001)



Pleistocene (^{14}C depleted) waters are characterized by

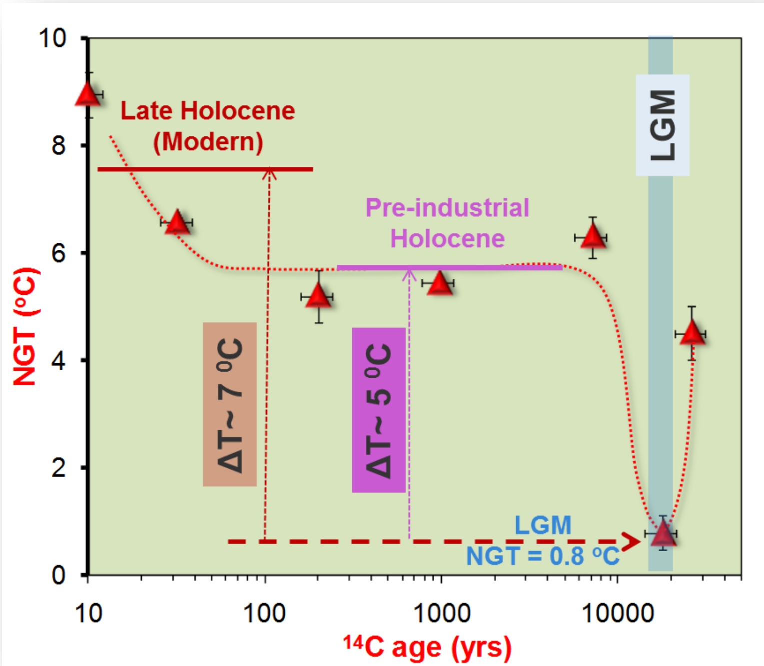
- A strongly depleted $\delta^{18}O$ signature
- Very high excess air contents

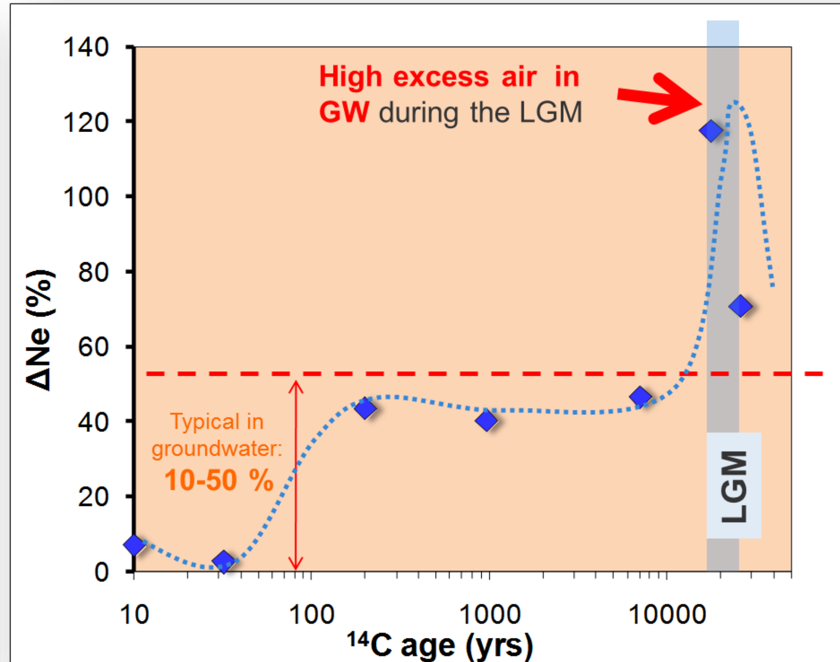
- Recharge under high pressure conditions
- Sub glacial recharge of meltwater


Noble gas recharge temperature
Glatt Valley
ΔT~5.5°C
East Midland Sandstone
9.5°C
3.4°C
ΔT~6°C
Ledo-Paniselian
Holocene
Weichselian
ΔT~9°C
14C model age [a]

Cenomanian Aquifer, Czech Republic

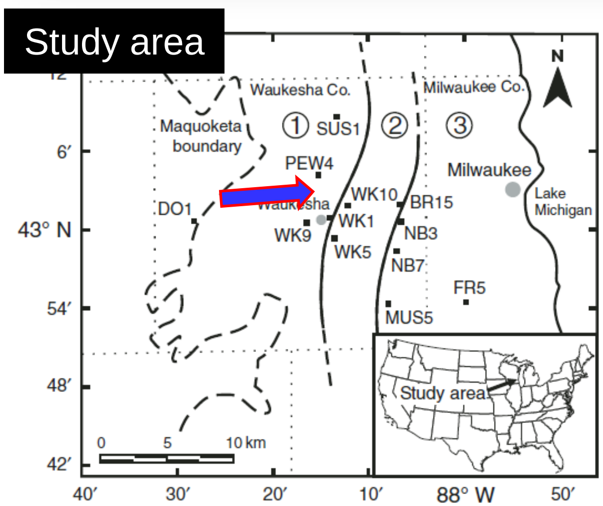
Corcho et al, submitted

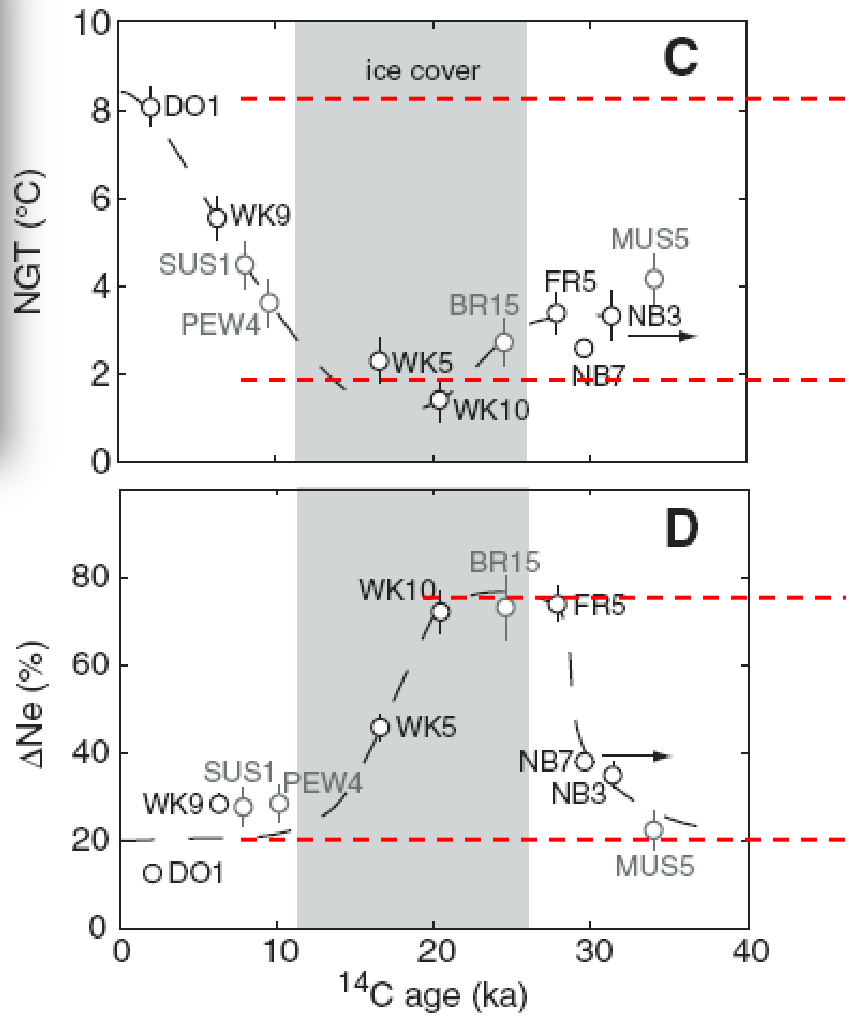




Peak in excess air during LGM

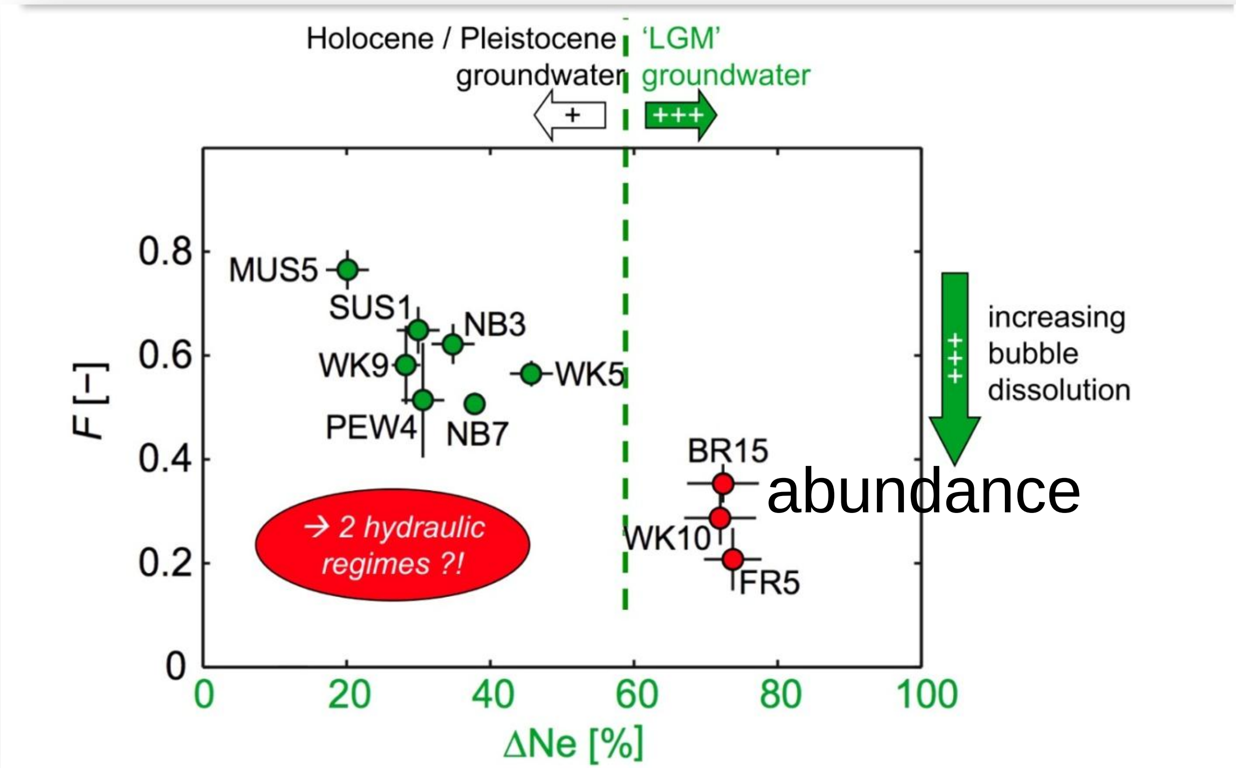
Sandstone Aquifer, Wisconsin
Klump et al, 2008





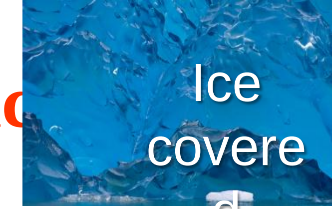
Klump, S., Grundl, T., Purtschert, R. and Kipfer, R. (2008) Pleistocene groundwater dynamics in Wisconsin derived from noble gas, ^{14}C and stable isotope data. Geology 36(5), 395–398.

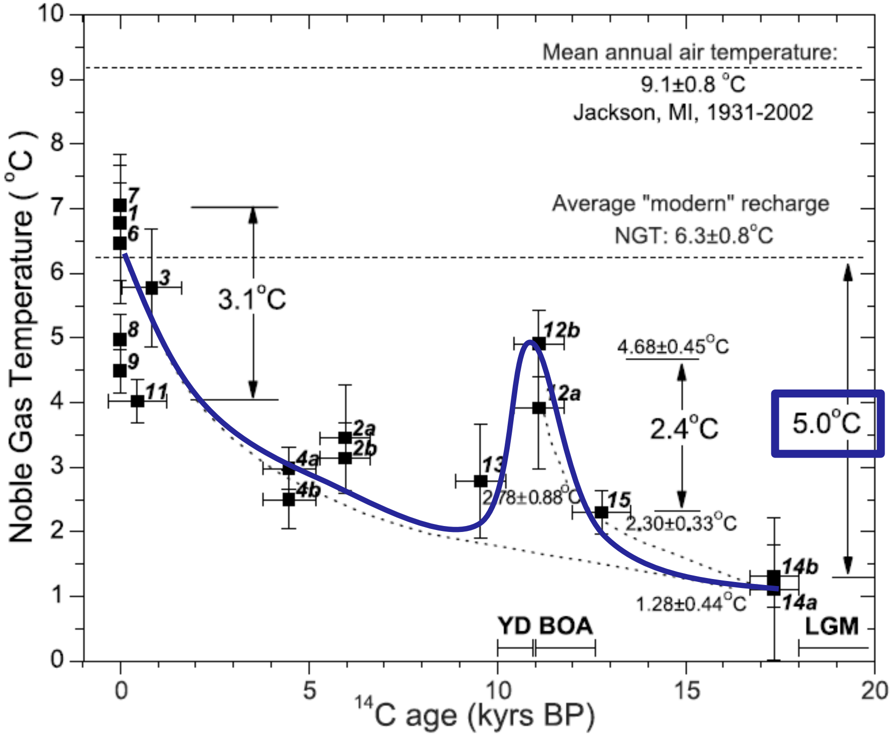
Excess air as hydraulic proxy

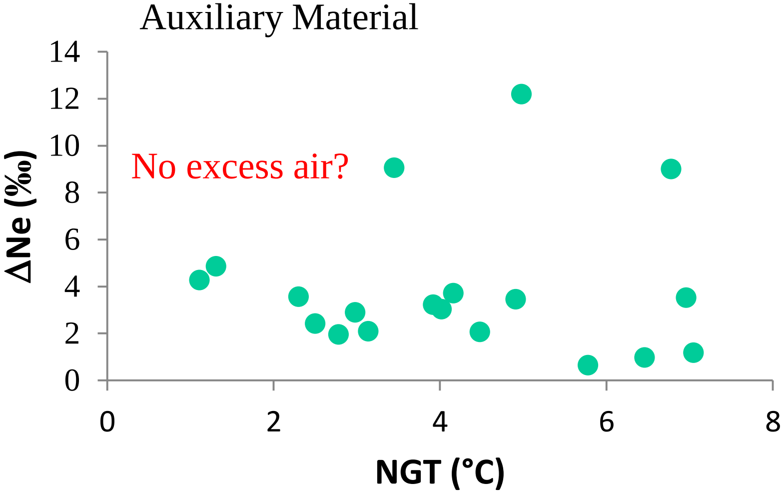


abundance

Marshall aquifer, Southern Mic
Ma et al., 2004







Conclusions

Acknowledgements

- Roland Purtschert and Swiss noble gas team + IAEA IsotopeHydrology Section for summary slides