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

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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”,
- “Stable isotopes in precipitation” Tellus 16, 1964
Isotopes in precipitation 1952/1961
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:

$$\delta^{18}O = \frac{^{18}O_{\text{sample}} - ^{18}O_{\text{std.}}}{^{18}O_{\text{std.}}} \times 1000$$
IAEA

• Formally established 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 hydrogeochemical data.
• Capacity for monitoring the quantity and quality of water resources
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.
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

18O and 2H RECORDS (in years)
Contents of the GNIP database

- Amount of precipitation (mm)
  - Type of precipitation (rain, snow, both)
  - Mean air temperature (°C)
  - 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.
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.

Modelling isotope contents over the Andes

Isotope Fractionation Model involving Amazon Basin hydrology

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
($\delta D$ and $\delta^{18}O$)

Delta V Advantage
(Thermo Fisher Scientific)
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)
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
C1Ik-In - Lükati-Lontova aquitard
Cm-V - Cambrian-Vendian aquifer system
Buried valleys

Quaternary sediments
- marine (sand, gravel)
- fluvio-clacial (sand, gravel)
- glacial (till)

Aquitards
- Lower-Ordovician (dictyonema argillite)
- Lontova (Cambrian clays)

Aquifers
- Quaternary (sand, gravel)
- Ordovician (limestone)
- Ordovician-Cambrian (sandstone)
- Cambrian-Vendian (sandstone)

Potentiometric surface of Cm-V aquifer system

Number of well
Absolute height of well
Cm-V recharge

Modelled flowlines

Abs. height, m

Gulf of Finland

0 20 40 60 km

HYDROGEOLOGICAL UNIT AND ITS INDEX

EQUIPOTENTIAL LINE, ABS. HEIGHT, m

BASIN-WIDE AQUIFER

ARROWS SHOW DIRECTION OF THE GROUNDWATER MOVEMENT
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-HCO₃-Cl type; TDS concentration 300 – 1000 mg/l
3. Mixture of relict and freshwater in NE Estonia: Cl- HCO₃-Na type; TDS about 1 g/l
4. Freshwater around buried valleys: Ca- HCO₃ type; TDS concentration 200 – 500 mg/l
The characteristic isotopic composition of Estonian groundwaters

<table>
<thead>
<tr>
<th>Aquifer system</th>
<th>Lithology</th>
<th>$\delta^{18}$O, ‰</th>
<th>$^{14}$C, pmC</th>
<th>$^3$H, TU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordovician</td>
<td>limestones, dolomites</td>
<td>-11.7 to -12.2</td>
<td>43.77 to 90.91</td>
<td>13.1 to 21.0</td>
</tr>
<tr>
<td>Ordovician-Cambrian</td>
<td>detrital sandstones, sandstones</td>
<td>-11.4 to -18.9</td>
<td>2.40 to 18.60</td>
<td>1.8 to 21.3</td>
</tr>
<tr>
<td>Cambrian-Vendian</td>
<td>sandstones</td>
<td>-18.1 to -22.0</td>
<td>1.40 to 12.76</td>
<td>0.5 to 2.1</td>
</tr>
</tbody>
</table>

Atmospheric precipitation: annual mean $\delta^{18}$O= - 10.4 ‰
Major chemical types of Cm-V groundwater

1. Original Cm-V water in South Estonia
   \( \delta^{18}O > -14 \% \)

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

3. The Cm-V water in North Estonia: result of freshening due 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?
Nay channels
Valley cut by subglacial meltwater on Bylot Island
Buried valleys in Estonia

Quaternary sediments
- marine (sand, gravel)
- fluvio-clacial (sand, gravel)
- glacial (till)

Aquitards
- Lower-Ordovician (dictyonema argillite)
- Lontova (Cambrian clays)

Aquifers
- Quaternary (sand, gravel)
- Ordovician (limestone)
- Ordovician-Cambrian (sandstone)
- Cambrian-Vendian (sandstone)

Potentiometric surface of Cm-V aquifer system

Number of well
Absolute height of well

Finnish Gulf
Viimsi Peninsula
Lake Harku

328
39
732
5.8
300
3.5
P-I4
4.0
722
4.6
81
11.9
708
3.0
811
30.0
22
20.3
732
5.8

+40
+20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
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
δ^{18}O ~ -22‰
GROUNDWATER DATING AND PAST CLIMATE RECONSTRUCTION

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

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Palaeohydrology: Groundwater as a climate archive

Flow velocity ~1 m/yr → 20 kyr of record within ~20 km of flow distance


from Aeschbach-Hertig, 2003
Relations

Past climate reconstruction

Impact of climate change to groundwater recharge dynamics
How are climate conditions that prevailed during groundwater recharge encoded in groundwater?

How can the corresponding time of recharge be determined?
Timescales of groundwater dating methods

- **Dating range**
- **Methods**
  - $^{222}\text{Rn}$
  - $^3\text{H}/^3\text{He}$
  - $^{85}\text{Kr}$, FCKW, SF$_6$
  - $^{39}\text{Ar}$
  - $^{14}\text{C}$
  - $^{36}\text{Cl}$, $^{81}\text{Kr}$
  - $^4\text{He}$

Sampling in GAB, Australia
$^{39}\text{Ar}$: Key data

- Half-life: 269 years
- Decay mode: $b$ decay
- $^{39}\text{Ar}/\text{Ar}$ ratio (100% modern): $8.1 \times 10^{-16}$

1 Liter water contains ~ 8700 $^{39}\text{Ar}$ atoms

How do you find 1 atom in $10^{15}$ atoms which all look very similar?
Detection by decay counting

\[
\text{Activity: } 7.1 \times 10^{-7} \text{ Bq/L water} \rightarrow 22 \text{ decays/L/year}
\]

\[39\text{Ar}\]

\[39\text{K}\]

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)
$^{81}\text{Kr}$: Key data

- Half-life: 229,000 years
- Decay mode: $\beta^-$ decay (EC)
- $^{81}\text{Kr}/^{81}\text{Br}$ ratio (100% modern): $5.2 \times 10^{-13}$
- 1 Liter water contains $\sim 1300$ $^{81}\text{Kr}$ atoms
- Activity: $1.3 \times 10^{-10}$ Bq/L water → 4 decays/m$^3$ H$_2$O/year

Detection

- $^{81}\text{Kr}$ → $^{81}\text{Br}$

$E_{max} = 276$ keV

Correlation diagram:

Antineutrino + Electron → $^{81}\text{Kr}$
Atom Trap Trace Analysis (ATTA): Basic Principle - laser based atom counting
ATTA 3
Advantages ATTA

High Signal/Noise Ratio

Excellent Isotope selectivity

$^{81}$Kr: Nubian Aquifer Egypt
Area of Investigation
Sampling conditions in Egypt(1)
Results

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

Groundwater ages [kyears]

Flow direction

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 relative to Diss. Equilibrium

Qualitatively we state:

- Excess air (EA) is produced by the complete or partial dissolution of air bubbles due to increased hydrostatic pressure relative to the atmospheric pressure.
- Amount and composition of the EA is related to the frequency and intensity of recharge events:
  - High frequency → more EA
  - High intensity → more complete dissolution → less fractionation
- Low intense recharge tends to produce EA that is depleted in Ne relatively to the heavier noble gases Xe, Kr.
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

Maximal ice extension in LGM

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

Scandinavian ice sheet

Alpine ice field

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

RT (°C)

C age [kyr BP]

Glatt Valley

East Midland Sandstone

Ledo-Paniselian

Holocene
Weichselian

ΔT~5.5°C

ΔT~6°C

ΔT~9°C

Subglacial recharge seems to be inhibited due to ice cover and/or permafrost in all cases.
Partly ice covered

Peak in excess air during LGM

High excess air in GW during the LGM

Stable isotopes: not significantly depleted

Cenomanian Aquifer, Czech Republic
Corcho et al, submitted
Sandstone Aquifer, Wisconsin
Klump et al, 2008
Excess air as hydraulic proxy

The fractionation factor $F$ is correlated with the hydrostatic pressure ($D_{Ne}$) because high pressure leads to a more complete dissolution of the trapped gas phase.

Changes of amount and fractionation can be interpreted in terms of changes in hydraulic conditions.
Marshall aquifer, Southern Michigan
Ma et al., 2004

Our NGT record provides important direct support for the existence of subglacial recharge in Michigan and indicates a temperature underneath glaciers at 1°C. It further suggests a ground temperature at the late stages of the LGM 5°C cooler than that of "modern" recharge.

Mean annual air temperature:
9.1±0.8 °C
Jackson, MI, 1931-2002

Average "modern" recharge
NGT: 6.3±0.8°C

No excess air?
Conclusions

- Radio noble gases (\(^{85}\)Kr, \(^{81}\)Kr, \(^{39}\)Ar) have high potential to extend and complete the \(^{14}\)C dating range.
- Half-lives and corresponding dating times range from weeks up to 1 million years.
- Low abundances and isotope ratios make them relatively difficult to measure.
- The new ATTA technique is the most promising method for a future routine use of radio-noble-gas dating.
- Stable noble gases dissolved in groundwater have a high potential to reconstruct palaeoenvironmental conditions and to constrain glacier-aquifer interactions.
- However, more research is needed to understand the link between e.g. high \(^{2}^{18}\)Ne and recharge dynamics in particular for paleowaters.
Acknowledgements

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