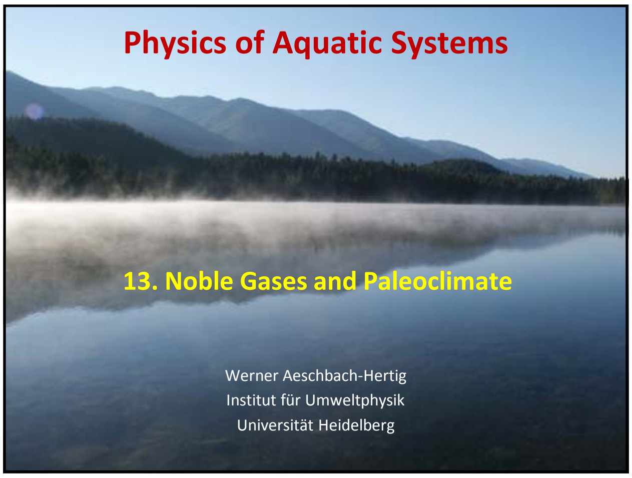

Physics of Aquatic Systems

13. Noble Gases and Paleoclimate

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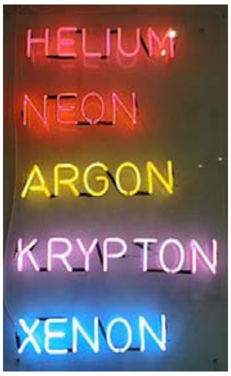
Contents of Session 13

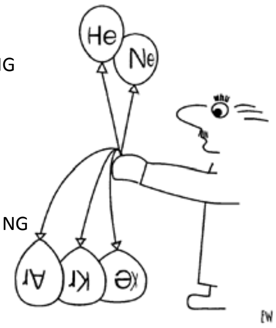
- Literature:
  - Mook Vol. 1, ch. 12 (NG radioisotopes)
  - Cook & Herczeg, 2000, ch. 11 & 12

Noble Gases



light NG

heavy NG



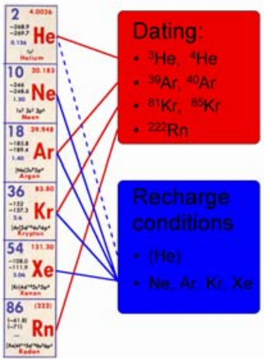
13.1 Noble Gases in Hydrology and Paleoclimate

- noble → inert → conservative
- rare → tracers

→ ideal physical tracers

Sources of noble gases in water

- Atmosphere
- Nuclear processes



Composition of the Atmosphere

Volume mixing ratios x_i in dry air and NG istopic abundances

Gas	Mixing ratio	Selected isotopic abundances		
		stable		unstable
N_2	0.781			
O_2	0.209			
Ar	$9.34 \cdot 10^{-3}$	^{40}Ar: 0.996	^{36}Ar: $3.4 \cdot 10^{-2}$	^{39}Ar: $8.1 \cdot 10^{-16}$
CO_2	$\approx 370 \cdot 10^{-6}$			
Ne	$18.18 \cdot 10^{-6}$	^{20}Ne: 0.905	^{22}Ne: 0.0925	
He	$5.24 \cdot 10^{-6}$	^{4}He: 0.99999	^{3}He: $1.4 \cdot 10^{-6}$	
CH_4	$\approx 1.8 \cdot 10^{-6}$			
Kr	$1.14 \cdot 10^{-6}$	^{84}Kr: 0.57	^{86}Kr: 0.17	^{81}Kr: $5.2 \cdot 10^{-13}$
Xe	$0.087 \cdot 10^{-6}$	^{132}Xe: 0.269	^{129}Xe: 0.264	

Solubility of (Noble) Gases in Water

Henry's law: $c_i^{gas} = H_i \cdot c_i^{water}$ or $p_i = K_{H,i} \cdot c_i$

The Henry coefficient H_i (or $K_{H,i}$) is specific for each gas i and depends on temperature and composition (salinity) of the water

Henry coefficients K_H in [atm·g·cm^{3}STP^{-1}]							
Temp	He	Ne	Ar	Kr	Xe	N_2	O_2
0 °C	106.2	80.3	18.6	9.1	4.5	42.1	20.4
30 °C	115.2	101.0	34.4	19.8	11.6	74.0	37.9

$$K_{H,i} = \frac{p_i\,[atm]}{c_i\,[cc \cdot g^{-1}]}$$

"dimensionless" Henry coefficients H [$L_{water} \cdot L_{gas}^{-1}$]							
Temp	He	Ne	Ar	Kr	Xe	N_2	O_2
0 °C	106.2	80.3	18.6	9.1	4.5	42.1	20.4
30 °C	104.3	91.4	31.2	17.9	10.5	67.0	34.3

$$H_i = \frac{c_i^{gas}\,[mol \cdot L_g^{-1}]}{c_i^{water}\,[mol \cdot L_w^{-1}]}$$

Interpretation: High Henry coefficient ⇔ low solubility

Equal volumes (STP) of air and water at equilibrium: <1 % of He, > 10 % of Xe in water

(Where are the noble gases on Earth? V_{atm} (STP) = $4.0 \cdot 10^{18}$ m^3, V_{ocean} = $1.6 \cdot 10^{18}$ m^3)

Atmospheric Equilibrium Concentrations

C_i^{eq} is the dissolved concentration of gas i in water at equilibrium with **moist** (vapour saturated) air at a total air pressure P

$$C_i^{eq} = \frac{c_i^{atm}}{H_i} = \frac{p_i^{atm}\big|_P}{K_{H,i}} = \frac{(P-e)x_i}{K_{H,i}}$$

e: saturation vapour pressure
x_i: volume fractions in **dry** air

P depends on altitude z (m a.s.l.) via the barometric formula:

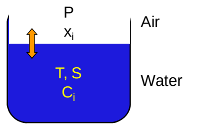
$$P(z) = P_0 \cdot e^{-\frac{z}{z_S}}$$

Using the scale height z_S = 8300 m provides a very good approximation for z < 1800 m.

C_i^{eq} depends on pressure/altitude, but the solubilities H_i do not!
C_i^{eq} depends on temperature T and salinity S, via H_i(T,S) and e(T)

$$C_i^{eq}(P,T,S) = \frac{(P-e(T))x_i}{K_{H,i}(T,S)}$$

The Noble Gas Thermometer

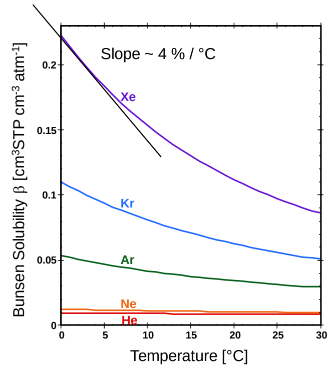


Dissolved noble gas concentrations in equilibrium with air:

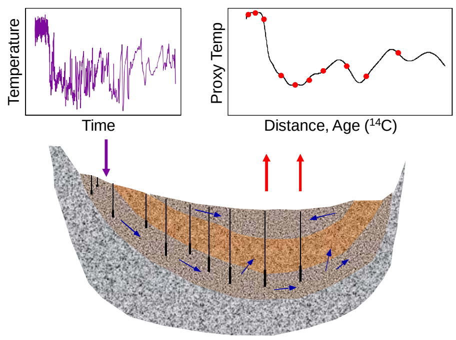
$$C_{i,eq} = \beta_i(T,S)p_i$$

Bunsen solubility for concentration in [cm^3STP_g/cm^3_w]:

$$\beta_i = \frac{\rho_w}{K_{H,i}} = \frac{T_0}{P_0 T}\frac{1}{H_i}$$

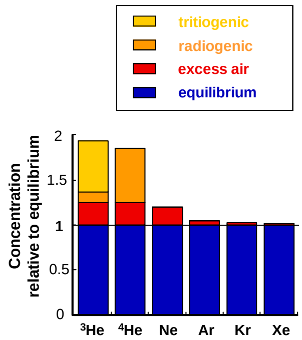


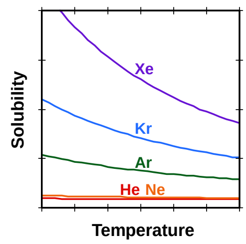
Groundwater as an Archive



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

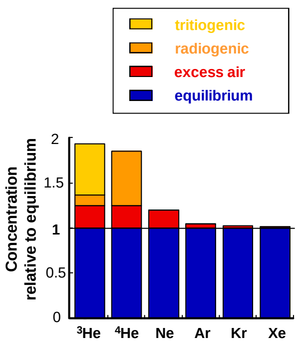
13.2 Noble Gas Components in Groundwater

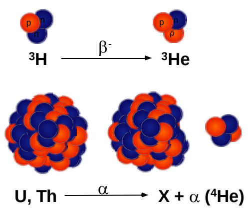




temperature

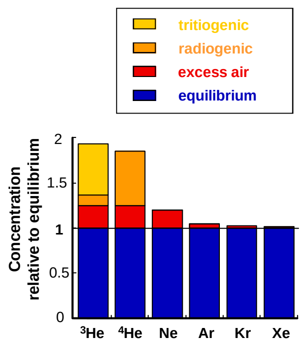
Noble Gas Components in Groundwater

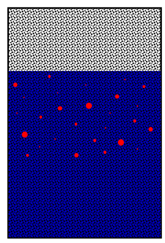




time

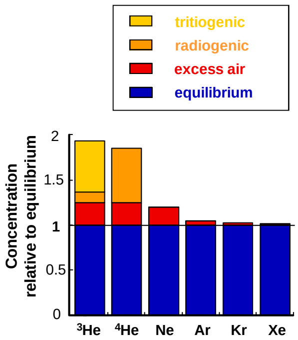
Noble Gas Components in Groundwater





???

13.3 Excess Air Models and Component Separation



How can we separate the components?

Use the differences in their elemental composition!

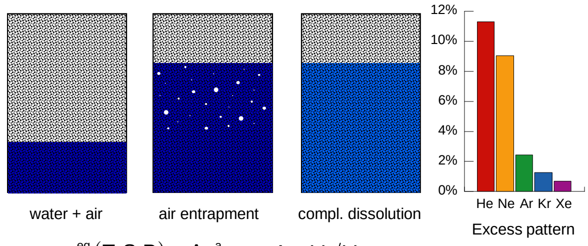
Focus on Ne, Ar, Kr, Xe:
4 gases, 2 components

Equilibrium component:
Depends on 1 parameter: T

Develop models for excess air component with 1 or 2 new unknown parameters

Excess Air Model 1: Complete Dissolution of Air

Classical model: Complete dissolution of entrapped air bubbles
$\Rightarrow$ composition of excess air = composition of atmospheric air



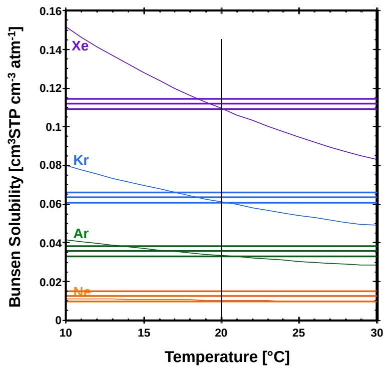
$c_i = c_i^{eq}(T,S,P) + A c_i^a$ $\quad A = V_a/V_w$

$c_i^a = H_i c_i^{eq} \Rightarrow c_i^{UA} = c_i^{eq}(1 + AH_i)$ UA: **U**nfractionated **A**ir

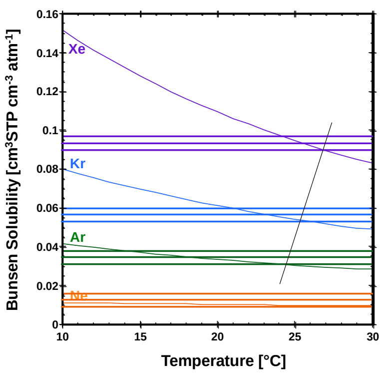
Iterative Determination of the Temperature

- Idea: Equilibration temperatures of all noble gases should be equal
- Raw data: $T_{Xe} > T_{Kr} > T_{Ar} > T_{Ne}$
- Due to excess air, assumed to be atmospheric air
- Correct concentrations by subtracting air, until the different temperatures agree as well as possible (minimise deviations between temperatures)
- T_{NG} = mean(T_{Ne}, T_{Ar}, T_{Kr}, T_{Xe})

Excess Air Correction: Hypothetical Sample

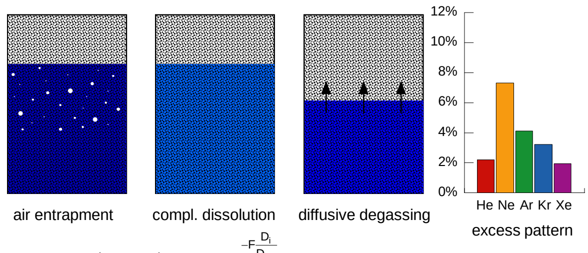


Excess Air Correction: Real Sample



EA Model 2: Dissolution and Diffusive Degassing

PR: **P**artial **R**e-Equilibration

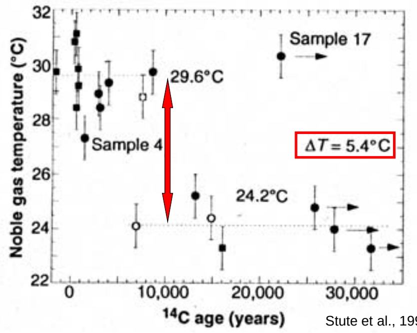


$c_i = c_i^{eq}(T,S,P) + A c_i^a \cdot e^{-F\frac{D_i}{D_{Ne}}}$ F: "Fractionation" rel. to air

$c_i^a = H_i c_i^{eq} \Rightarrow c_i^{PR} = c_i^{eq}\left(1 + AH_i \cdot e^{-F\frac{D_i}{D_{Ne}}}\right)$

Brazil: A "classical" Noble Gas Temperature Study

Cooling of tropical Brazil (5 °C) during the Last Glacial Maximum.



Stute et al., 1995. Science **269**: 379-383

Excess air fractionation:

How reliable is this result?

Inverse Determination of Parameters

Problem: Determine T (or other parameters) from

Data: C_i^{meas} (i = Ne, Ar, Kr, Xe)

Model: $C_i^{mod} = C_i^{eq}(T,S,P) + C_i^{ex}(A,F)$

5 parameters, 4 measured concentrations: underdetermined

The parameters *S* (≈ 0) and *P* (altitude) are usually known!

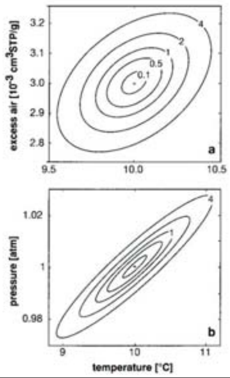
3 free parameters, 4 measured concentrations: overdetermined

Inversion: Find values of *T*, *A*, and *F*, which minimise the weighted deviation between model and data:

$$\chi^2 = \sum_i \frac{\left(C_i^{meas} - C_i^{mod}\right)^2}{\sigma_i^2}$$

Inverse Modeling: Parameter Estimation by Fitting

- Error-weighted non-linear least squares fitting
- Very general approach
- Standard numerical technique
- Flexible choice of free parameters
- Error estimation from χ^2-surface
- Correlations of parameters
- Goodness of fit: χ^2-test
- Objective model selection

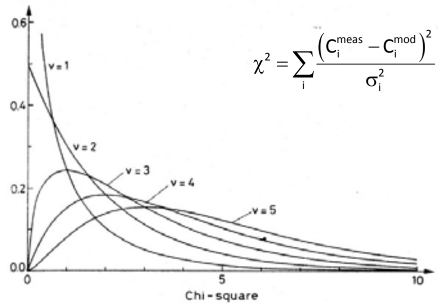


Aeschbach-Hertig et al., 1999
Water Resour. Res., 35: 2779-2792

χ^2-Distribution

Probability distribution of sum of squares of normally distributed variable (errors)

Expectation value of χ^2: number of degrees of freedom n = n – m,
where n = no. of data points, m = no. of parameters



$$\chi^2 = \sum_i \frac{\left(C_i^{meas} - C_i^{mod}\right)^2}{\sigma_i^2}$$

Model Selection: χ^2-Test

Basic idea: If the model provides a perfect description of reality, all deviations between model and data (summarised in χ^2) are due to random experimental errors: statistical assessment possible.

Area beneath tail of χ^2-distribution gives the probability p for a given or higher χ^2-value only due to experimental errors.

Very low probability (e.g. p < 0.01) indicates that the model is not a valid description of the data.

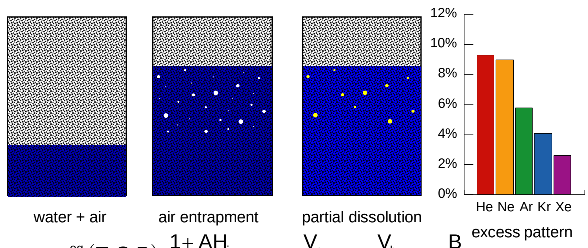
Ballentine & Hall (1999)* showed that neither unfractionated excess air nor partial re-equilibration could explain the data set from Brazil.

Better model needed!

* Ballentine, C. J., and C. M. Hall (1999), *Geochim. Cosmochim. Acta 63*: 2315-2336

EA Model 3: Partial Dissolution and Equilibration

CE: **C**losed-System **E**quilibration

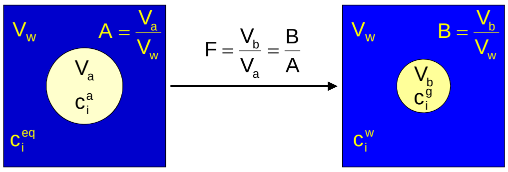


$$C_i = C_i^{eq}(T,S,P) \cdot \frac{1 + AH_i}{1 + BH_i} \qquad A = \frac{V_a}{V_w},\ B = \frac{V_b}{V_w},\ F = \frac{B}{A}$$

$$C_i^{CE} = C_i^{eq}\left(1 + \frac{(1-F)AH_i}{1 + FAH_i}\right)$$

Derivation of the CE-Model

Initial state — Final state

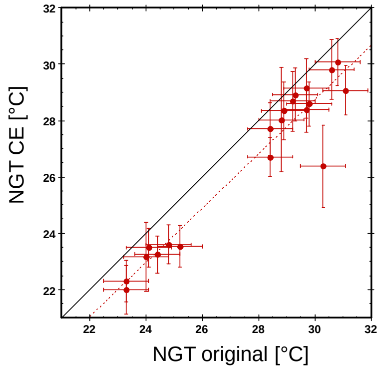


$c_i^a = H_i c_i^{eq}$ equilibrium conditions $c_i^g = H_i c_i^w$

$$\frac{n_i^0}{V_w} = c_i^{eq} + A c_i^a = c_i^{eq}(1+AH_i) \qquad \frac{n_i}{V_w} = c_i^w + B c_i^g = c_i^w(1+BH_i)$$

mass balance: $\frac{n_i^0}{V_w} = \frac{n_i}{V_w} \Rightarrow c_{iw} = c_i^{eq}\frac{1+AH_i}{1+BH_i} = c_i^{eq}\left(1+\frac{(1-F)AH_i}{1+AFH_i}\right)$

Review of the Brazil Data 1: Excess Air Model

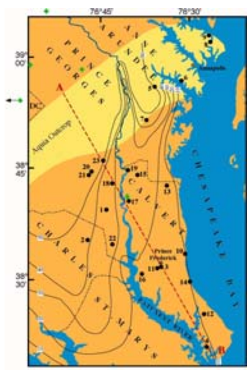


≈ uniform shift of T

ΔT Holocene - LGM remains ≈ 5°C

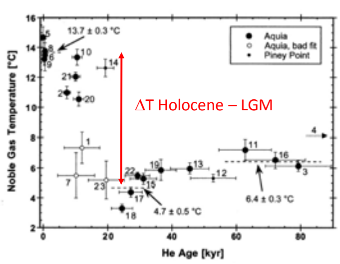
(LGM = Last Glacial Maximum)

13.4 Applications of Noble Gas Paleothermometry

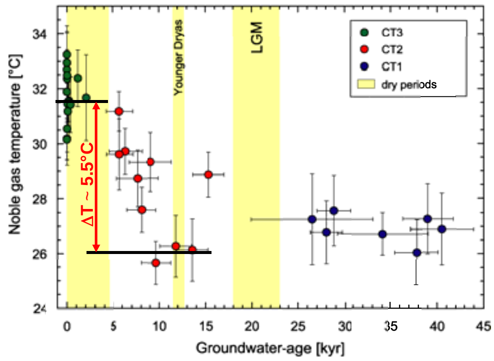


Aquia Aquifer, Maryland, USA

ΔT Holocene – LGM = 9°C

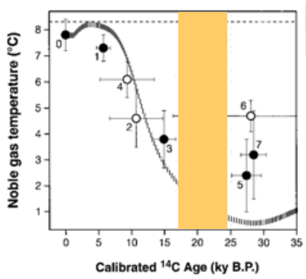


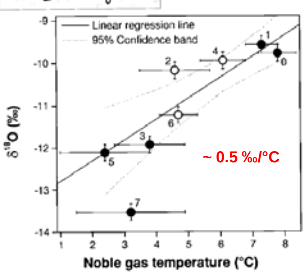
Applications: Continental Terminal, Niger



Beyerle et al., Geophys. Res. Lett. 30 (2003)

Applications: Glatt Valley, Switzerland



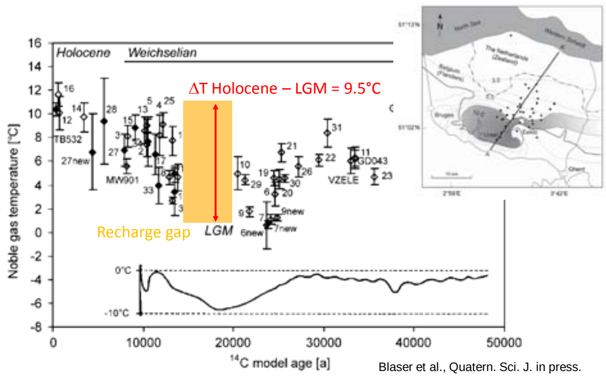


ΔT Holocene – LGM ≈ 5°C

Recharge gap in LGM

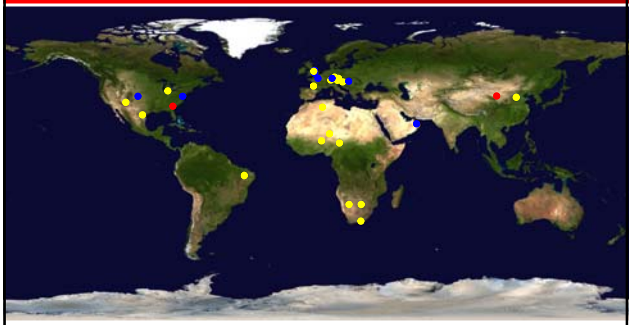
Beyerle et al., 1998. Science 282, 731-734.

Applications: Ledo-Paniselian, Belgium



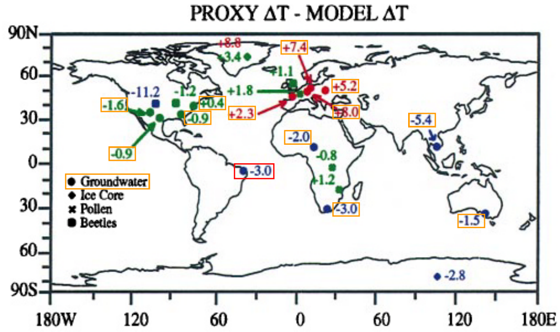
Blaser et al., Quatern. Sci. J. in press.

Noble Gas Temperature Records Worldwide



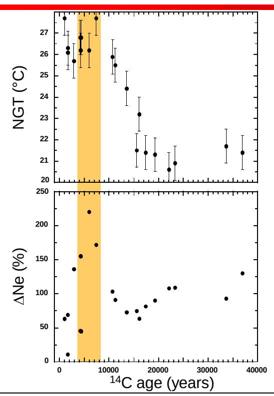
- ΔT Holocene – LGM < 5 °C
- ΔT Holocene – LGM ≈ 5 °C
- ΔT Holocene – LGM > 5 °C

Noble Gas Temperatures and Climate Models



From: Crowley, Climate Dynamics 16 (2000): 241-255

Namibia: Climate Signal in Excess Air?



ΔT Holocene – LGM ≈ 5°C

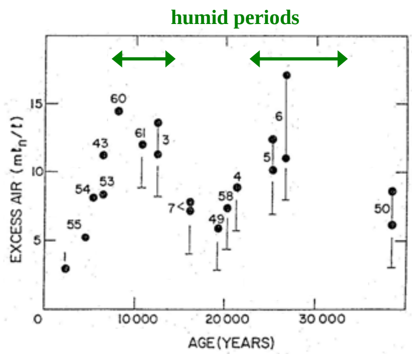
$$\Delta Ne(\%) = \frac{C_{Ne} - C_{Ne}^{eq}}{C_{Ne}^{eq}} \cdot 100\%$$

Peak in ΔNe

Due to change in humidity, rise of water levels?

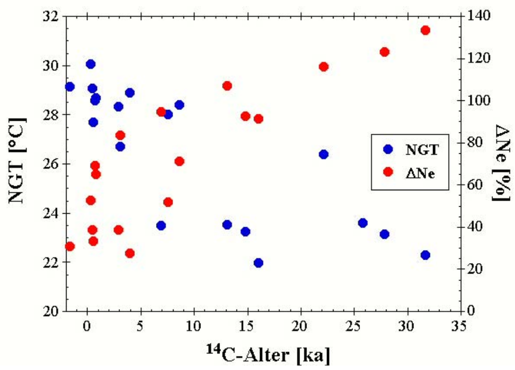
adapted from: Stute and Talma, 1998, IAEA-SM 349/53

Heaton et al. 1983: Stampriet Aquifer, Namibia

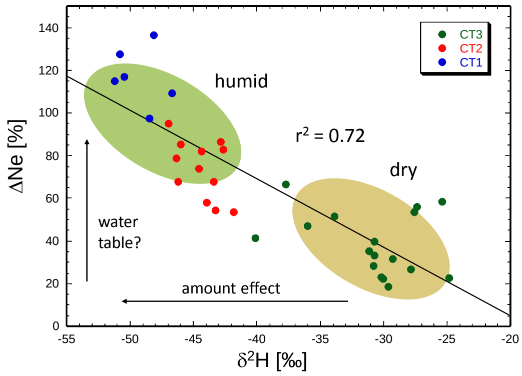


Heaton et al., 1983, J. Hydrol. 62: 243-262.

Review of the Brazil data (2): ΔNe



Niger: Excess Air and Stable Isotopes



13.5 Noble Gas Temperatures from Speleothems?

Goal

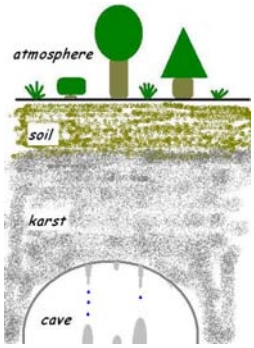
- New proxy-archive combination:
  - accurate noble gas paleothermometer
  - high-resolution speleothem archive

Basic Idea

- Use water in microscopic fluid inclusions
  - 0.1 mg of water (~ 0.1 g of calcite) should be sufficient

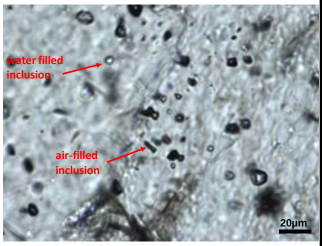
Noble Gases in Stalagmites

Carbonates		Noble gases
CO_2 dissolution		equilibration in soil
$CaCO_3$ dissolution		excess air formation
CO_2 degassing $CaCO_3$ precipitation stalagmite formation		equilibration in cave incorporation in fluid inclusions



Modified from J. Fohlmeister

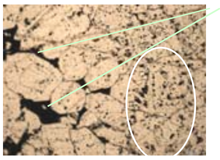
Fluid Inclusions in Speleothems



Use water in fluid inclusions

Problem: Air-filled inclusions

Main Problem: Air-filled Inclusions



Air-filled inclusions
(at grain boundaries)

Water-filled inclusions
(contain T-information)

Leads to "Excess air" as in groundwater:

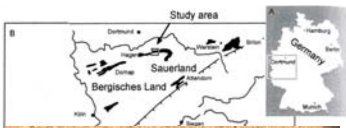
$c_i^{tot} = c_i^{eq}(1 + AH_i)$ $A = V_{air}/V_{water}$ Air/water volume ratio

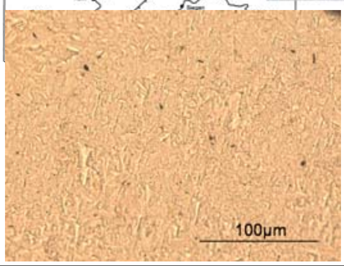
Groundwater: Typically $A < 0.01$

Speleothems: Typically $A \sim 1$, reduction is possible

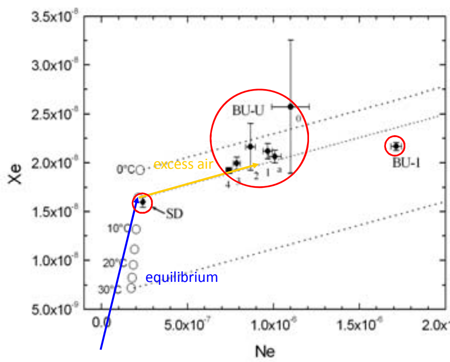
The maximum tolerable value of A for small T-errors is around 0.1

Stalagmites from Bunker Cave, Germany





Noble Gas Data from Bunker Cave



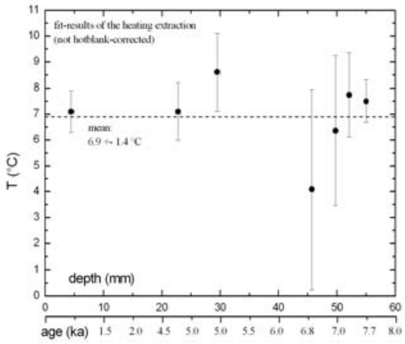
BU-U:
6 samples
T = 2.9 ± 0.7 °C
age: ≈ 11'000 yr

BU-1:
T = 7.1 ± 0.8 °C
age: ≈ 1'300 yr

Soda straw:
T = 6.4 ± 0.4 °C
age: unknown
very little air!

Results from Bunker Cave

BU-1: approximately constant T (~ 7 °C) throughout Holocene



Summary

- Noble gases are almost ideal physical tracers
- Temperature dependence of solubilities: Thermometer
- Aquifers as archives of old water: Paleotemperatures
- Complication: Excess air
- Inverse determination of T and other parameters:
  - General, flexible approach
  - Estimation of errors, assessment of models (χ^2-test)
- Applications: glacial cooling ≈ 5°C in tropics, higher elsewhere
- Climatic signal in ΔNe: humidity, water table fluctuations
- Fluid Inclusions in speleothems as promising new archive