Fluid Inclusions of speleothems I

Stable isotopes & noble gas temperatures

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Review on isotopes in (fluid inclusions of) speleothems


Recent reviews on noble gas temperatures


Fluid Inclusions in Speleothems
Some Pictures of Fluid Inclusions

Dennis et al. (2001), GCA 65: 871-874
Some Pictures of Fluid Inclusions

Some Pictures of Fluid Inclusions

Some Pictures of Fluid Inclusions

Empirical Findings on Fluid Inclusions

• Abundance
  – Water/Calcite ratio of 0.01 to 0.5 % by weight (typical $\leq 1 \, \%$ or 1 mg/g)
  – Non-uniform distribution (layered, high abundance: milky)

• Size
  – Typically 1 to 100 µm (but up to mm in rare cases)

• Shape
  – Often elongated or „thorn shape“, oriented parallel to C axis

• Content
  – Water or air or both (air bubbles in water-filled inclusion)
  – Air to water volume ratio about 1, but highly variable from < 0.1 to > 10
Fluid Inclusions as Paleowater Archive: Link to Groundwater
Subsurface Water Archives

- Precipitation
- Meteoric water
- Modification in soil
- Drip water
- Speleothem fluid inclusions
- Recharge water
- Groundwater

Picture from Wackerbarth 2012, modified from Spötl et al. (2007) and Fairchild et al. (2006)
Groundwater as an Archive

Proxies:
- Stable isotopes
- Noble gases

Dispersion leads to smoothing of climate signals
† low time resolution
Stable Isotopes in Palaeogroundwaters

From: Clark and Fritz, 1997. Environmental Isotopes in Hydrogeology
Stable Isotopes in Palaeogroundwaters

From Clark & Fritz, 1997
Noble Gases: Conservative Tracers

- noble $\rightarrow$ inert $\rightarrow$ conservative
- rare $\rightarrow$ tracers
- $\rightarrow$ ideal physical tracers

Sources of noble gases in water

- Atmosphere (Ne, Ar, Kr, Xe)
  ‡ Temperature
- Nuclear processes (He, Rn)
  ‡ Age
Dissolved noble gas concentrations in equilibrium with air:

\[ C_{i,eq} = \beta_i (T, S) \rho_i \]
Noble Gas Components

- tritiogenic
- radiogenic
- excess air
- equilibrium

Solubility vs. Temperature

Concentration relative to equilibrium:

- $^3$He
- $^4$He
- Ne
- Ar
- Kr
- Xe
Noble Gas Components

- tritiogenic
- radiogenic
- excess air
- equilibrium

Concentration relative to equilibrium

\[ {^3\text{He}} \quad {^4\text{He}} \quad \text{Ne} \quad \text{Ar} \quad \text{Kr} \quad \text{Xe} \]

\[ \beta^- \]

\[ {^3\text{H}} \rightarrow {^3\text{He}} \]

\[ {^\alpha} \text{U, Th} \rightarrow X + {^4\text{He}} \]

Time
Noble Gas Components

- tritiogenic
- radiogenic
- excess air
- equilibrium

Concentration relative to equilibrium

3He 4He Ne Ar Kr Xe

2 1.5 1.0 0.5 0
Excess Air from Inclusion of Air Bubbles

Classical model: Complete dissolution of entrapped air bubbles
⇒ composition of excess air = composition of atmospheric air

\[ c_i = c_i^{eq}(T) + Ac_i^a \]

\[ A = \frac{V_a}{V_w} \]

\[ c_i^a = H_i c_i^{eq} \Rightarrow c_i^{UA} = c_i^{eq}(T) \cdot \left(1 + AH_i(T)\right) \quad \text{UA: Unfractionated Air} \]
Inverse Determination of Parameters

Problem: Determine T and A from

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

Model: \( C_i^{\text{mod}} = C_i^{\text{eq}}(T) + C_i^{\text{ex}}(A) \)

2 free parameters, 4 constraints: overdetermined

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

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

Example: Serra Grande & Cabeças, Brazil

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

Example: Glatt Valley, Switzerland

ΔT Holocene – LGM ≈ 5°C
Recharge gap in LGM

PALAEAUX: $\delta^{18}$O-NGT Relation in Europe

China: $\delta^{18}O$ – Temperature Relation

Kreuzer et al., 2009. Chem. Geol. 259: 168-180
Stable isotopes in fluid inclusions
Stable Isotopes: From Rain to Carbonate

- **Atmosphere**
  - Climate input
  - Temperature
  - Precipitation
  - $\delta^{18}O_{\text{prec}}$

- **Biosphere / Pedosphere**
  - Evapotranspiration
  - Enrichment due to Evapotranspiration
  - Temperature
  - Humidity
  - Type of vegetation
  - Ratio infiltration/precipitation
  - Ratio evaporation/transpiration

- **Lithosphere**
  - Mixing of water parcels
  - Calcite dissolution
  - Residence time
  - $pCO_2$ of soil air
  - Temperature

- **Cave**
  - Fractionation
  - $\delta^{18}O_{\text{drip}} \rightarrow \delta^{18}O_{\text{calcite}}$
  - Temperature
  - $pCO_2$ of cave air
  - Drip interval

Similar to groundwater, but higher resolution and better dating

$\delta^2H$, $\delta^{18}O$ of drip water

Additional information in $H_2O \leftrightarrow CO_3$ fractionation

$\delta^{18}O$ of carbonate

From Wackerbarth 2012
Precipitation of carbonates from water in isotopic equilibrium induces a T-dependent fractionation:

$$\varepsilon_{eq}(T) = \Delta^{18}O_{CO_3} - \Delta^{18}O_{H_2O}$$

This thermometer is accessible with calcite plus fluid inclusions!

Problems:
- Precipitation in equilibrium?
- Which $\varepsilon(T)$ curve is correct?
- Low t-resolution of inclusions
- Possible O-isotope exchange
First Fluid Inclusion Studies


- **Goal:** Paleotemperature through water-calcite-fractionation

- **Assumptions:**
  - Equilibrium conditions can be ascertained by a Hendy-Test
  - $^{18}\text{O}$ of fluid inclusion water exchanges with calcite
  - $\delta^2\text{H}$ is not altered and used to reconstruct $\delta^{18}\text{O}$ via GMWL

Harmon, Schwarcz, and O'Neil, 1979. EPSL 42, 254-266.

- **Goal:** Reconstruction of isotopic composition of precipitation

- **Result:** $\delta^2\text{H}$ of glacial water depleted relative to modern precip.

Methods for Water Extraction

Crushing by Squeezing a Tube

Not very efficient crushing mechanism (coarse grains, low yield)
Needs very large samples (up to 20 g) ‡ bad age resolution
Possible bias due to incomplete transfer of water (adsorption)

Harmon et al., 1979
Methods for Water Extraction

Thermal decrepitation

Heating of sample to between about 700 and 900 °C.

Better yield, smaller samples, but offset in $\delta^2 H$ of extracted water from original water: $\Delta_{ex}$ between $-22 \%$ (Yonge, 1982, PhD thesis) to $-30 \%$ (Matthews et al., 2000, Chem. Geol. 166, 183-191).

Production of CO$_2$ at high temperatures, definitely leads to oxygen isotope exchange $\not\Delta$ not applicable for $^{18}O$. 

Vennemann & O'Neil, 1993, Chem. Geol. 103, 227-234
Methods for Water Extraction

Crushing and mild heating in vacuum cell

Heating to 150 °C avoids adsorption of water on calcite surfaces, which otherwise leads to water loss and isotope fractionation.

Produces reliable $\delta^2$H-values. Used e.g. by Fleitmann et al., 2003 (Quat. Res. 60, 223-232) to reconstruct changing sources of drip water (precipitation) in Oman.

Dennis et al., 2001, GCA 65, 874-881
Methods for Water Extraction

Crusher linked to continuous flow IRMS

Also see Vonhof et al., 2006, Rapid Commun. Mass Spectrom. 20, 2553-2558
First FI-Paleotemperature Record

Vancouver Island: Absolute temperature from $\delta^2H_w - \delta^{18}O_c$

Methods for Water Extraction

Optimisation of thermal decrepitation

• No offset in $\delta^2$H for heating up to 550 °C.

• Optimal conditions: Pre-crushing and heating to 300-400 °C.

• Sample size of 20 mg with heating to 350 °C and continuous flow.

Crushing combined with cavity ring-down spectroscopy

Noble gases in fluid inclusions
Noble gases in caves

Expectation: Drip water in solubility equilibrium with cave air

NGT measures cave T, which is close to mean annual air T

Adapted from J. Fohlmeister
Noble gases in caves

Reality: Air-filled inclusions

Scheidegger et al., 2010, Chemical Geology

Water inclusions contain T-information in dissolved noble gas concentrations

Air inclusions add air-derived noble gases and mask the information

Analogous to „excess air“ in groundwater, but much higher air contribution

Air-Excess Parameter: \( A = \frac{V_{\text{air}}}{V_{\text{water}}} \)

Groundwater: Typically \( A < 0.01 \)

Speleothems: Typically \( A \sim 1 \)

Maximum tolerable value of \( A \) is \( \sim 0.1 \)
Air/Water Ratio A in Speleothems

Stalagmites from Bunker Cave, Germany

Niggemann et al., 2003
QSR 22

BU-1
BU-Uwe
NG Temperatures from Bunker Cave

First speleothem NGTs

Temperature difference is ok
Absolute temperature too low?
(Modern MAAT ~ 9.5 °C)
Due to water adsorption during crushing: Resolved by heating crusher to 150 °C


Pollen data

Davis et al., QSR 22, 2003
Methods for Noble Gas Extraction

Mechanical crushing in vacuo to extract gases and water
Reduction of the Air/Water Ratio

Stepwise crushing (or heating): Opens air inclusions first

Separation of air and water during extraction is needed.

Air inclusions tend to sit at grain boundaries (B1).

Scheidegger et al. 2008, PAGES News 16/3: 10-12
Pre-Crushing and Sieving

Crushing and Sieving under Vacuum

Vogel et al., in press. Geochem., Geophys., Geosystems, DOI 10.1002/ggge.20164
Crushing and Sieving under Vacuum

Vogel et al., in press. Geochem., Geophys., Geosystems, DOI 10.1002/ggge.20164
Crushing and Sieving under Vacuum

Vogel et al., in press. Geochem., Geophys., Geosystems, DOI 10.1002/ggge.20164
Some stalagmites have more Ne than expected.

Possible reason for Ne excess: Lattice-trapped He and Ne

Scheidegger et al., 2010, Chem. Geol. 272, 31-39.
Ne Excess under Stepwise Crushing

Example: H12 (Hoti Cave, Oman)

Neon excess visible from the first extraction step on!
Test with Air-Equilibrated Water (AEW)

µL-size samples of air-equilibrated water

Temperature known

‡ expected equilibrium concentration known

Sander et al., in preparation
Summary

- Stable isotopes of meteoric water and atmospheric noble gases are established climate proxies in groundwater
- Fluid inclusions in speleothems are a promising new archive for both proxies, with many benefits
- Extraction and analysis are challenging, but much progress is being made
- Reliable absolute temperatures from the NG thermometer plus drip water isotopes should help to understand $\delta^{18}O_c$
Error Analysis for T Depending on A

The goal \( \Delta T < 1 \, ^\circ \text{C} \) requires

\( A < 0.3, \sigma < 1 \% \)

or

\( A < 0.1, \sigma < 2 \% \)