SpeleoSIMS

Developments and challenges in ion microprobe studies of speleothems at WiscSIMS

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Developments and challenges in ion microprobe studies of speleothems at WiscSIMS

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Outline:

Introduction, case study

Methodological accomplishments

Issue

Developments

Challenges

Conclusions

time

Scale

space
Records of Past Climate

different strengths

courtesy: R. Kozdon

Speleothems

Carlsbad Caverns stalagmite

Soreq Cave stalactite

H₂O + CO₂ + CaCO₃ = Ca²⁺ + 2HCO₃⁻
Case study: Soreq Cave

Ayalon et al., 1998

Long-term record

from Bar-Matthews et al., 2003; Petit et al., 1999

Is there a measurable signal of seasonality in Israel (& Soreq Cave speleothems)?
Modern observations: rainfall

Modern observations: dripwater

~1-2‰

Orland et al., 2009; Avner Ayalon

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Outline:

I. Introduction, case study
II. Developments
III. Challenges
IV. Methodological accomplishments

Issues:
- WiscSIMS capabilities
- Imaging of fluorescent banding
- Sample preparation, registration
- Standardization, analytical output
- Comparison to conventional $\delta^{18}O$
- Trace element analyses

Method development

Objective is to obtain sub-annual resolution.

1) High-precision, high-spatial-resolution $\delta^{18}$O analyses
   [ Ion Microprobe ]

2) Imaging of annual bands
   [ Confocal Laser Fluorescent Microscope ]
Sample pit:

~7 x 10 µm
1 µm deep
1 ng sample

δ^{18}O: ± 0.3‰ 2SD
Organic molecules re-emit light with characteristic $\lambda$.
Confocal Fluorescent Microscope


courtesy: C. Alexander, Univ. of Minnesota
Confocal Fluorescent Microscope

Orland et al., 2009

$\Delta^{18}O = \delta^{18}O_{\text{dark}} - \delta^{18}O_{\text{bright}}$

- Dark zone: high $\delta^{18}O$
  - organic poor
  - dry season
- Bright zone: low $\delta^{18}O$
  - organic rich
  - wet season

Orland et al., 2009
Modern Samples:

- $\Delta^{18}O$ is a rain gauge
- mini-Hendy test ($2SD = 0.31\%$)

Orland et al., in review

1) Compare seasonality across broad time scales
2) Investigate rapid climate events at high resolution

Sample preparation

1. Determine the working traverse and grind this surface flat.

2. Cut working traverse into ~10 mm lengths.

3. Arrange two sample pieces in each mount with the working traverse nearest the center. Place 3-5 grains of calcite standard between the pieces.
Sample registration

3 issues:

1. Sample preparation and alignment

2. Image registration
   - for analysis
   - for mapping

3. Session registration

Sample registration

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1. Sample preparation and alignment

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   - for analysis
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Orland et al., 2012
Standardization, rate of analysis

40 hours continuous analysis

Sample 2-6, 427 analyses

Avg. $\delta^{18}$O bracket ±0.17‰ (1 s.d.)

UWC-3 standard, 158 analyses

SIMS vs. conventional $\delta^{18}O$ data

Spring Valley Cavern, MN, USA

$\delta^{18}O$ offset: 0.57‰
Tests to evaluate $\delta^{18}O$ offset

Roasting to remove organics

Test influence of sample porosity

Analysis of SIMS pit depths in sample vs. standard

Minor element composition of sample vs. standard

Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples
Influence of sample porosity

Typical spot porosity

Porosity ~1-5%

Multiple analyses along single porous bands

Average 2SD of along-band analyses = 0.71%
Tests to evaluate $\delta^{18}O$ offset

- Roasting to remove organics
- Test influence of sample porosity
- Analysis of SIMS pit depths in sample vs. standard
- Minor element composition of sample vs. standard
- Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples
Pit depth comparison

Sample

Standard

average pit depth = 1.5 \( \mu \)m

average pit depth = 1.5 \( \mu \)m
Tests to evaluate $\delta^{18}O$ offset

Roasting to remove organics

Test influence of sample porosity

Analysis of SIMS pit depths in sample vs. standard

Minor element composition of sample vs. standard

Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples
Minor element composition

Influence of Mg content on instrumental bias?

\[ y = -5.3776x^2 - 8.2613x - 0.0655 \]

\[ R^2 = 0.99976 \]

Bias relative to UWC-1 calcite std

Bias (‰) vs. Mg/(Ca+Fe+Mg)

Tests to evaluate $\delta^{18}O$ offset

- Roasting to remove organics
- Test influence of sample porosity
- Analysis of SIMS pit depths in sample vs. standard
- Minor element composition of sample vs. standard
- Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples
OH/O peak height

Tests to evaluate $\delta^{18}O$ offset

Roasting to remove organics

Test influence of sample porosity

Analysis of SIMS pit depths in sample vs. standard

Minor element composition of sample vs. standard

Measure $^{16}O^{1}H/^{16}O$ peak in all carbonate samples

Way forward:
Lack of $\delta^{13}C$ offset points to $H_2O$ as the source of $\delta^{18}O$ offset in SIMS vs. conventional analyses
$\delta^{18}O$ offset in this same section is 0.9‰
Trace elements: SIMS & LA-ICP-MS


Orland et al., in review
Trace elements: SIMS & LA-ICP-MS

Orland et al., in review

Trace elements: SIMS & µ-XRF

100 µm resolution
Slit size = 2.0 x 0.1 mm

Conclusions

Promising progress so far, with room for more.

Jump in, the ball pit’s fine!