Go Small or Go Home

How Small is Too Small for Isotope Ratio Analysis?

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Atom Probe Tomography
Secondary Ion Mass Spectrometry

Detection Range

Resolvable Features

Valley et al. 2016, GSA, Denver
Bulk Stable Isotope analysis

Valley et al. 2016, GSA, Denver
In situ Stable Isotope Analysis

**SIMS**

**Oxygen Isotopes**

Ion Microprobe
Analytical Precision & Spot size
30 years of Improvement

**δ^{18}O** ± 1 SD

- 1 standard deviation: 10‰, 1‰, 0.3‰, 0.1‰

Valley et al. 2016, GSA, Denver
CAMECA
IMS- 3f, -7f
* IMS- 1270, -1300
NanoSIMS
SHRIMP

Transmission vs. Mass resolution

Valley et al. 2016, GSA, Denver
Volume = 75 μm²

Useful ion yield
~7% for δ¹⁸O
IMS-1280
at WiscSIMS

Valley et al. 2016, GSA, Denver
Theoretical Limit: Precision vs. Pit Volume

1σ = √N
7% yield
δ^{18}O
Zircon

Valley et al. 2016, GSA, Denver
SIMS Uncertainty $^{18}\text{O}/^{16}\text{O}$

<table>
<thead>
<tr>
<th>Spot Size</th>
<th>Secondary Intensity $^{18}\text{O}$ (cps)</th>
<th>Uncertainty (2SE) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;μm spot</td>
<td>1200 s EM-EM</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>1 μm spot FC-EM</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>3 μm spot FC-EM</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10-15 μm spot FC-FC</td>
<td>10</td>
</tr>
</tbody>
</table>

- FC = Faraday Cup
- EM = Electron Multiplier

Additional factors: Deadtime, QSA, IMF

Valley et al. 2016, GSA, Denver
Precision of Analyses vs. Primary Beam Current

Secondary Ion Intensity (cps) vs. Primary (nA)

- **3 pg 1µm**
- **30 pg 3µm**
- **0.5 ng 7-15µm**

Amount of samples sputtered
Spot diameter

- **16O**
- **18O**

**FC-EM Mode:**
- 1-3 µm (2pA -30pA)
- 0.5-1‰ 10-30 min

**FC-FC Mode:**
- 10-15 µm (2-3nA)
- ≤0.3‰ 3 min

**18O/16O Precision**
- 2 SD ‰

Kita 2011 BGSW

Valley et al. 2016, GSA, Denver
Comet Wild 2

BSE/SEM 2008

Reflected Light Microscope 2007

Valley et al. 2016, GSA, Denver

Nakamura et al. 2008, Science
White Light
\( \lambda = 400-700 \text{ nm} \)
3.5 \( \mu \text{m} \)

Blue LED
\( \lambda = 455 \text{ nm} \)
2.2 \( \mu \text{m} \)

UV LED
\( \lambda = 365 \text{ nm} \)
1.3 \( \mu \text{m} \)

Nakashima et al. 2015

1 & 2 \( \mu \text{m} \) spots, 2015

Badgerscope software
Kita et al. 2015

Nakashima et al. 2015

Valley et al. 2016, GSA, Denver
Oxygen diffusion in Zircon

Sub-micron spot - $\delta^{18}O$

Page et al. 2007
Bowman et al. 2011

Valley et al. 2016, GSA, Denver
Atom Probe Tomography
Quantitative
Spatially resolved, sub-nm
Single-atom scale
Mass-spectrometry

Nano-Geochronology
Evaluate Pb mobility in zircon

LEAP 3000
LEAP 4000
LEAP 5000

LEAP 5000
Local Electrode Atom Probe

Valley et al. 2016, GSA, Denver

CAMECA Instruments
Factory, Madison, WI
Valley et al. 2016, GSA, Denver

APT Specimen

$10^5$-$10^6$ smaller than SIMS
Atom Probe Tomography (APT)

Sample zircon

Needle-shaped Specimen
20-100 nm radius at apex
Specimen T=20-100K

Laser or voltage pulse initiates evaporation

High Voltage ~10 kV

Vacuum @ 10^-8 Pa (10^-10 mbar)

Valley et al. 2015 Am Min

Valley et al. 2016, GSA, Denver
APT spectra on zircon

Valley et al. 2015 Am. Min.

Valley et al. 2016, GSA, Denver
Inside Y-rich clusters

\[ ^{206}\text{Pb}^{2+} \]

\[ ^{207}\text{Pb}^{2+} \]

\[ ^{208}\text{Pb}^{2+} \]

\[ \text{Si}_2\text{O}_3^+ \]

Outside clusters

No Pb

\[ ^{28}\text{Si}_{2}^{16}\text{O}_3 \]

\[ ^{28}\text{Si}_{2}^{29}\text{Si}^{16}\text{O}_3 \]

APT spectra on zircon AMU

Valley et al. 2015 Am Min

Valley et al. 2016, GSA, Denver
Clusters, 4.4 Ga

Y & Pb

Valley et al. 2014 Nat. Geosci.
Valley et al. 2015 Am. Min.
Valley et al. 2016, GSA, Denver
Clusters, 4.4 Ga

391 clusters, 5,287 Pb atoms
$^{207}\text{Pb}/^{206}\text{Pb} = 1.2 \pm 0.05$

1 cluster, 25 Pb atoms
$^{207}\text{Pb}/^{206}\text{Pb} = 1.1 \ (13/12)$

Valley et al. 2014 Nat. Geosci.
Valley et al. 2015 Am. Min.
Valley et al. 2016, GSA, Denver
Small is always better...... until it isn’t.

How Small is Too Small for Isotope Ratio Analysis?

Depends on the application:

\[ \leq 0.5 \, \mu m \] for \( \delta^{18}O \) at natural abundance

\[ \leq 10 \, \text{nm} \] for \( ^{207}\text{Pb}/^{206}\text{Pb} \) in Archean clusters

**Zircons**

- \( ^{207}\text{Pb}/^{206}\text{Pb} \)
- \( ^{208}\text{Pb}, \text{O} \& \text{Li isotopes} \)

**SIMS**

- Smiley face

**APT**

- Smiley face
- Sad face

Valley et al. 2016, GSA, Denver