In Situ Isotope Geochemistry by Ion Microprobe: Accuracy vs. Precision

John Valley
SIMS Measurement of stable isotope ratios

Accuracy vs. Precision
SIMS vs. other techniques
Spot size vs. precision, FC vs. EM
X-Y effects
Polishing relief
Imaging: correlated analysis, targeting sample spots, pit evaluation
Regular vs. irregular pits
Standards: Bias, IMF
Crystallographic orientation effects
Applications: Otoliths, Tooth enamel, Diagenetic cements, Sulfides, Microfossils

IMS-1280
Conventional (non-SIMS) Analysis of $\delta^{18}$O
Powders & chips
mm- to cm-scale
Gas-source mass spectrometer

$10^{-5}$ g  $10^{-2}$ g  $10^{-3}$-$10^{-4}$ g
In situ analysis
1-10 micrometer spot
$10^{-9} - 10^{-12}$ g
Million to billion times smaller!

Isotope Ratios: H, Li, B, C, N, O, Mg, Si, S, Cl, Ca, Fe
Light & trace elements

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
CAMECA ims1280
Ion Microprobe- Secondary Ion Mass Spectrometer

- Electrostatic Lens
- Electrostatic Deflector
- Aperture or Slit
- Cs-
- ESA
- J.W. Valley, HiRes2015 - High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison

Magnet

10 Detectors
5 FC’s, 5 EM’s
Ion Microprobe/ SIMS
Analytical Precision
30 years of Improvement

Oxygen Isotopes

IMS-1280
IMS-7f
nanoSIMS
SHRIMP II
Laser ablation

Valley & Kita 2009

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Trade-Off

**Precision vs. Spot Size**

Amount of sample sputtered

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

**Secondary Ion Intensity (cps)**

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

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

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

**FC**: Faraday Cup

**EM**: Electron Multiplier

\((^{18}\text{O}/^{16}\text{O})\) Precision (‰)

- **18O/16O Precision (‰)**
  - FC-FC Mode: ≤0.3‰
  - FC-EM Mode: 0.5-1‰

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
FC-FC: $\delta^{18}O$ 10 µm spot

Average Precision < 0.3‰ 2SD, 0.04‰ 2SE

48 hrs, 658 analyses of quartz

Valley & Kita 2009
FC-EM: $\delta^{18}O$ 3 µm spot Calcite

$2SD = 0.7 \%$

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison

Kozdon et al. 2009
$\delta^{18}$O sub 1-µm spot, ~ 1 pg
2 SD = 2 ‰

Page et al. 2007
Bowman et al. 2011

J.W. Valley, HiRes2015 - High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
X-Y effect

Larger holder minimizes X-Y effects

Stable isotope analyses ≤5mm radius from center

Micro-welded tungsten lip (20mm internal diameter and 0.1mm thick)

Sample diameter ≤25.6mm
Preferred thickness <5mm

New larger holder

Larger holder minimizes X-Y effects

Analysis zone:
10 mm diameter
78 mm²

Analysis zone:
16 mm diameter
201 mm²

Peres et al. 2012

J.W. Valley, HiRes2015 - High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
**X-Y effect**

**Flat glass disk**

$\pm 0.10\%$

Radius = 4mm

$\pm 0.13\%$

Radius = 6mm

Peres et al. 2013

$\pm 0.45\%$

Radius = 9mm

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Polishing relief

Rounded or Inclined surface, Edges

Surface Profilometer ~10µm topography

Quartz

UWQ-1 (12.33‰ VSMOW)
A grain with ~12µm relief

Rim: 5.19±1.05‰
Center: 5.49±0.26‰

18O RAW

Distance from rim (µm)

Kita et al. (2009)

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Modification of surface electrostatic field

Request all the users to determine if polishing relief is less than a few µm.

Changes the angle of secondary ions?

Polishing Relief

Zircon

Epoxy resin

21 µm

15 µm

10 µm

0.2 µm

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Polishing relief

KIM-5
Zircon Standard

ZYGO White-light Profilometer

Zircon Standard (KIM5) Relief Test

Reproducibility (%)

Average Relief (μm)

Kita et al. 2009

J.W. Valley, HiRes2015 - High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Well-Polished Sample
Precise & Accurate

Grain boundary
Flat surface
Low relief

No Polishing relief

30.53‰ ±0.09 2SE

30.58‰ ±0.19‰ (2SD)

30.53±0.25‰ (2SD)

Inside: 30.58±0.19‰ (2SD)

Edge: 30.53±0.25‰ (2SD)

(b)

95ADK-6 Diopside
diopside
epoxy

30.53‰ ±0.09 2SE

30.58‰ ±0.08 2SE

Kita et al. 2009

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Foraminifera Calcite

$\delta^{18}O$ 3 µm spot SIMS

Mg/Ca EPMA

Kozdon et al. 2013
Correlated Analysis by SIMS

Carbonates

Imaging –
- Optics,
- SEM (BSE, CL),
- Confocal laser fluorescence

$\delta^{18}O$
$\delta^{13}C$

Major & Trace elements
- Fe/Mg
- Mg/Ca
- Sr/Ca

Sliwinski et al., HiRes2015Poster
Denny et al., HiRes2015Poster
Sample Imaging (CL, BSE, ...)

Nautilus, prismatic aragonite

Plain Light

UV

100 micron

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Regular pits &
Irregular pit (cavity) in
UWC-3 calcite standard

Sample Imaging, Post-analysis
SIMS pits in a planktic foraminiferal shell (Early Paleogene)
3 regular pits
1 irregular pit
SE image of an Au-coated sample, showing a foraminiferal chamber wall with ~3 µm SIMS analysis pits. Some of the pits are crosscutting growth bands that are filled with epoxy and/or organics, compromising the analyses. Thus, data from these pits were not used.

Measurements in these domains should be avoided by careful sample imaging, preselection of suitable targets, and careful pit placement. However, it is essential to image every SIMS pit by SEM as the preselected domain may have been missed by a few µm. Moreover, unwanted features in the pits such as cracks, inclusions, cavities, organics, or epoxy that may compromise the analysis must be identified by post-analysis SEM imaging.
Accuracy vs. Precision

Precision of SIMS measurements
\( \sigma, \text{SD, SE} \)
Standard deviation vs. Standard error

Accuracy of SIMS measurements
Bias (IMF): \( \delta(\text{measured}) \) vs. \( \delta(\text{true}) \)
Reference standards
chemical & structural match to samples
calibrated & homogeneous

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Bias- IMF

IMS-4f- High energy offset, Single EM Detector

Hervig et al. 1992

Eiler et al. 1997

IMS-1280
Multiple FCs
MRP = 2500
Low E-offset

Valley and Kita 2009

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Matrix effect of various minerals with solid solution

Valley and Kita (2009)
Bias - IMF

Carbonate standards -
\(\delta^{18}O\) Instrument bias

Valley & Kita 2009

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
**Bias - Oxygen isotopes**

Sliwinski et al. 2015a, HiRes2015Poster

13 Carbonate Standards

Fe# = Fe / (Mg+Fe)

$\Delta \text{bias}^{18}$O(\text{STD-UW6220}) = \frac{(\Delta \text{bias}_{\text{max}})x^n}{k^n + x^n}$

**Session S12 (10 µm spot-size)**

- Best fit curve
- 95% Confidence band

**Session S14 (3 µm spot-size)**

- Fit using values of 'n' and 'k' from session S12 (10-µm calibration)
- 95% Confidence band

Best fit curve

<table>
<thead>
<tr>
<th>Value</th>
<th>SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>bias max</td>
<td>11.6  0.4</td>
</tr>
<tr>
<td>k</td>
<td>0.10  0.01</td>
</tr>
<tr>
<td>n</td>
<td>1.2   0.1</td>
</tr>
</tbody>
</table>

**Fe# = Fe / (Mg+Fe)**
Bias - IMF

Carbon isotopes

$$ \text{Bias}^*(\text{Std-UW6220}) = -1 \left( \frac{(\text{bias}^*_\text{max.})X^n}{K^n + X^n} \right) $$

$$ X = \text{Fe#} $$

$$ K, n = \text{constants} $$

Sliwinski et al. 2015, HiRes2015 Poster
Biocarbonates

Orland, tutorial lecture, 9 AM, Tuesday

Monitor “water” on unused channel: H$_2$O, OH, Organic matter

$^{16}$O, $^{16}$OH, $^{18}$O  FC, FC, FC
$^{12}$C, $^{13}$C, $^{13}$CH  FC, EM, EM

Wang et al. 2014

Zircons

Radiation damaged
Crystalline

Background corrected $^{16}$OH/$^{16}$O

Wang et al. 2014

CaCO$_3$

$^{\delta^{18}}$O offset [%, acid digestion – SIMS]

Calcite sample
Aragonite sample

Speleothem
Foraminifera
Nautilus

Orland et al. 2015

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Garnet

Fe(II),Mn

Pyrope: \( \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12} \)
Almandine: \( \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} \)
Spessartine: \( \text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12} \)
Grossular: \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \)
Andradite: \( \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} \)

Page et al. (2010)

Bias-IMF

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Bias- IMF

Fe - Mg
Ca - Mg
Mn - Mg

Page et al. (2010)
New standards

Kitajima et al., Poster, Tue.

49 garnet standards

Bias rel. to UWG2 ‰

Fe - Mg
Ca - Mg
Mn - Mg

Grs + Uv

Pyp + Alm + Sps

Bias rel. UWG2 ‰

Bias rel. UWG2 ‰

Ca

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Crystal orientation

Magnetite

5830  M34572-A  5830

Poor reproducibility!

±2.5‰ (2SD)

Quartz ±0.3‰

Magnetite ±2.5‰

Huberty et al. (2010)

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Crystal orientation

Ion Channeling and Focusing

Ion Channeling

Ion Focusing

Deeper Cs$^+$ primary ion implantation

Preferential secondary ion ejection

$\theta=21^\circ$

Huberty et al. (2010)

SIMS Raw $\delta^{18}O$ changes with Crystal Orientation
**Crystal orientation**

Low kV-Analyses of Multiple Grains

**X-axis:** Data obtained at the routine condition +10/-10kV (±3‰)

**Y-axis:**

- **+10/-3kV** 26°
- **+6.5/-6.5kV** 21°
- **+3/-10kV** 14°

*condition less stable*

Quartz: ±1‰

Magnetite: ±2.2‰

Quartz: ±0.4-0.5‰

Magnetite: ±1.8‰

Quartz: ±0.4‰

Magnetite: ±0.8‰

Huberty et al. (2010)
Kita et al. (2011)
Crystal orientation

Morphology of SIMS pit shape vs. S Ion Yield and Isotope Ratio

\[ \delta^{34}S_{RAW} \hspace{1cm} \text{vs.} \hspace{1cm} \text{Secondary }^{32}\text{S}^- \times 10^9 \text{cps/nA} \]

Sphalerite

Grain 7: 2.0x10^9 cps/nA
Grain 8: 2.1x10^9 cps/nA
Grain 16: 2.3x10^9 cps/nA

Kozdon et al. 2010

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Other Minerals, Isotopes?
Rutile: Gordon et al. 2012,
Sulfur isotopes: Sphalerite and Galena: Kozdon et al. (2010)
Fe isotopes: Magnetite: Kita et al. (2011)
C isotopes: graphite: Ushikubo (unpd)
+3kV/-10kV conditions minimize orientation effects.

Most minerals do not show crystal orientation effects!
carbonates, quartz, zircon, olivines, pyroxenes, feldspars, garnets, melilites, sphene, spinel, chromite for oxygen isotopes.
pyrite, chalcopyrite, pyrrhotite for sulfur isotopes.
**Petrology**
- Igneous & Metamorphic minerals,
- Zircons
- Diamonds & inclusions
- Diagenetic cements

**Meteorites**

**Materials Science**
- Thin films, depth profiles
- Trace elements

**Paleoclimate Proxies**
- Foraminifera, Coral, Sponges,
- Mollusks,
- Speleothems
- Fish otoliths
- Tooth enamel
- Finely layered sediments
- Others: Diatoms, Pollen, ……

**Biology**

**Anthropology & Archeology**

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**Ion microprobe = SIMS**

Isotopes, Trace elements, Light elements

δ$^{18}$O ±0.3‰, 10 μm spot, 3 minutes; ±1‰ < 1 μm spots
C, Si, O 3-isotopes, S 4-isotopes, Isotopes of a trace element (C- microfossils, bacteria)

Complements: Electron microprobe (Major and minor elements) & Other techniques

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What are the opportunities for high resolution study of paleoclimate proxies?

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Small, Precious or Zoned

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J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
P. cod Otoliths, Aialik Bay, Alaska

Valley & Kita 2009

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Otoliths – Humpback chub
Little Colorado River, Grand Canyon

<table>
<thead>
<tr>
<th>River</th>
<th>Ba:Ca x 10⁻³</th>
<th>Se:Ca x 10⁻³</th>
<th>Sr:Ca x 10⁻³</th>
<th>δ¹³C, ‰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Little Colorado River</td>
<td>1.38 (0.36)</td>
<td>0.019 (0.002)</td>
<td>9.34 (0.92)</td>
<td>0.59 (1.24)</td>
</tr>
<tr>
<td>Colorado mainstem</td>
<td>1.43 (0.03)</td>
<td>0.024 (0.002)</td>
<td>10.80 (0.88)</td>
<td>-8.87 (0.49)</td>
</tr>
</tbody>
</table>

Limburg et al. 2013

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Tooth enamel, wood rat

Blumenthal et al. 2014
Quartz Overgrowths

Porosity

50 µm

Harwood et al 2013

Detrital Quartz 1

2 µm

Cement

Detrital Quartz 2

12 µm

50 µm

8‰ range in $\delta^{18}O$

$\delta^{18}O_{\text{quartz}} = +10‰$

Distance µm

J.W. Valley, HiRes2015 - High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Mt. Simon sandstone, Wisconsin Arch

Pollington et al. unpbd.

Above P-C unconformity

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Turee Creek Group
2400 Ma
Sulfur Isotope ratios

\[ \Delta^{33}\text{S} (a) = -1.65 \pm 0.09\text{‰ (2 SD)} \]
\[ \delta^{34}\text{S} 3 \mu\text{m} \pm 0.8\text{‰}, 10 \mu\text{m} \pm 0.2\text{‰ (2 SD)} \]

Two analyses sessions
- 10 µm Sulfur 3 isotope (3 FCs)
- 3 µm Sulfur 2 isotope (2FCs)

Large negative \( \delta^{34}\text{S} \) & non-zero \( \Delta^{33}\text{S} \)
- Microbial sulfate reduction
- ± 1 ‰ level resolvable \( \Delta^{33}\text{S} \) MIF

GOE

Williford et al. 2011

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Kerogen bias varies with $^{12}$C, $^{13}$C, $^{13}$CH

Tumbiana Formation (SV1 core, 55.3 m)  

bulk $\delta^{13}$C$_{org} = -49.7\%$

$\delta^{13}$C 2700 Ma  Tumbiana Fm  Williford et al. 2013

J.W. Valley, HiRes2015- High Resolution Proxies of Paleoclimate, June 1-3, 2015, UW-Madison
Leiosphaerida crassa
eukaryote?  
Chichkan Fm, Kazakhstan, 750 Ma

Myxococcoides sp.
cyanobacteria?

Williford et al. 2013

\[ \delta^{13}C \]
There are many opportunities for high resolution study of paleoclimate proxies

Small, Precious or Zoned