Tutorial: SIMS Basics

- Overview of SIMS
- Sputtering process
- Electron-gun
- Mass spectrum
- Detectors
- WiscSIMS modification
- Isotope Analyses

Please stop me anytime for questions!

Noriko Kita (WiscSIMS, UW-Madison)
Secondary Ion Mass Spectrometer (SIMS)

- Surface chemical and isotope analyses
- High sensitivity (≤ppb)
- Medium lateral resolution (50 nm-20 µm)
- Depth resolution 2-30 nm
- Destructive Analysis

Geoscience applications:
- Isotope ratios
- Trace elements
- Volatile elements
Principle of Secondary Ion Mass Spectrometer

**Primary Ions:**
- $Cs^+$, $O^-/O^{2-}$: higher sensitivity
- $O_2^+$, $Ar^+$
- $Ga^+$: nm-scale spot sizes
- Cluster ions ($Ar_n^+$, $C_{60}^+$): less sample damage

**Mass Spectrometer:**
- Magnetic Sector: High precisions
- Time of Flight (TOF): pulsed beam, surface analysis
- Fourier Transform Ion Cyclotron Resonance (FT-ICR)
- Ion Trap (Orbitrap)

**Analysis types:**
- Spot isotope/chemical analysis
- Ion imaging (scanning/direct)
- Depth profile
- 3D imaging
Ion Sputtering Process and Secondary Ionization

1. Primary ions are implanted to the interior of sample.
2. Atoms are displaced by collision cascade.
3. Atoms, molecules, ions, electrons are ejected from sample surface.

Mass Spectrometer should
- Separate molecular isobaric interference by high mass resolving power \( (M/\Delta M) \geq 2000 \)
- Compensation of surface charging
- Focus ions with variable initial kinetic energy

Secondary Ions (<10%)
- Mostly neutral atoms and molecules
- Atomic and molecular ions (+/-)
- Secondary electrons (-)
IMS 1280: Magnetic Sector Double-focusing MS

Mass Spectrometer should
- Separate molecular isobaric interference by high mass resolving power \( (M/\Delta M) \geq 2000 \)
  - Large radius sector magnet
- Compensation of surface charging
  - electron gun
- Focus ions with variable initial kinetic energy
  - Double-focusing MS
SIMS used for Geoscience

Double Focusing Mass Spectrometers

- Large radius (high mass resolution: \( M/\Delta M \geq 5,000 \))
- Sector Magnet radius
  - **IMS 1270/1280/1280-HR/1300-HR²**: \( R = 585 \text{ mm} \)
    - **Stable isotope**, Geochronology, Nuclear forensic
  - **SHRIMP**: Geochronology (zircon U-Pb ages) \( R = 1,000 \text{ mm} \)
  - **NanoSIMS**: High spatial resolution (50nm beam)
    - Imaging, biological applications
  - **Conventional SIMS** (low mass resolution): IMF 7f/7fGeo: \( R = 120 \text{ mm} \)

**TOF (Time of flight)**: Shallow depth analysis, thin film
SIMS Analysis Spots

<table>
<thead>
<tr>
<th>Datum</th>
<th>Biozone</th>
<th>Sample ID</th>
<th>Age (Ma)</th>
<th>Sedimentation Rate, Linear (m/Myr)</th>
<th>Depth, 865B (mbsf)</th>
<th>Depth, 865C (mbsf)</th>
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</thead>
<tbody>
<tr>
<td>FO D. sublodoensis</td>
<td>NP14</td>
<td>865B 9H</td>
<td>-410</td>
<td>49.70</td>
<td>79.60</td>
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<td>LO D. orthostylus</td>
<td>NP13</td>
<td>865B 9H</td>
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<td>865B 10H</td>
<td>-460</td>
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<td>89.60</td>
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<td>FO T. contortus</td>
<td>NP11 865B 10H</td>
<td>-511</td>
<td>53.61</td>
<td>2.64/5.6</td>
<td>91.61</td>
<td>91.74</td>
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<tr>
<td>FO D. diastypus</td>
<td>NP10 865B 11H</td>
<td>-670/865C 12H</td>
<td>-313</td>
<td>55.00</td>
<td>102.20</td>
<td>102.68</td>
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<tr>
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<td>865C 13H</td>
<td>-580</td>
<td>56.20</td>
<td>114.60</td>
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</tr>
</tbody>
</table>

Core depths [Bralower and Mutterlose, 1995] and ages [Berggren et al., 1995] assigned to various nannofossil biostratigraphic datums for calculating linear sedimentation rates that were used to construct a chronostratigraphic framework for the late Paleocene–early Eocene section from Site 865.

FO, first occurrence; LO, last occurrence.

Figure 1. (a) Scanning electron microscope (SEM) image of a test of Morozovella velascoensis (ODP Site 865) in edge view. (b) Enlargement of the chamber wall and muricae. Several mural pores are highlighted by arrows. Blade-like diagenetic crystallites are cemented on top of the biogenic muricae. (c, d) High contrast SEM backscattered electron images of a polished morozovellid test. Figure 1c is a cross section taken perpendicular to the coiling axis of a M. velascoensis test from the 300–355 m sieve fraction, with a width of 450 µm (Hole 865C, 103.10 mbsf). Figure 1d is an enlargement of a cross section of the same test, showing muricae fused into a keel-like structure at the test periphery. (e) SEM image of the gold-coated sample displaying a ∼10 µm ion microprobe pit for δ¹⁸O analysis. Textures in the pit are etched by the Cs⁺ beam.

Foraminifera; Kozdon et al. (2011)

Primary Ion intensity ~ 2 nA
Precisions of oxygen isotope ratios ~ 0.3‰

Comet sample return; Nakashima et al. (2012)

Cs⁺ primary beam 10-15 µm spots
“Large” Spot

Cs⁺ primary beam 1-2 µm spots
“Small” Spot

Primary Ion intensity ~ 3 pA
Precisions of oxygen isotope ratios ~ 1-2 ‰
Most of elements in periodic table are ionized

Ionization efficiency varies significantly from 0.1 to 10%

O⁻/Sec(+)

Higher ionization tendency: Mg⁺, Ca⁺, Pb⁺

Sample ±10kV

Primary Ions
Cs⁺: +10kV
O⁻: −13kV

Secondary Ions

Cs+/Sec(−)

Higher electronegativity:
O⁻, C⁻, S⁻, Si⁻

- Noble gases do not ionize.
- Nitrogen in carbon bearing phase: CN⁻

Secondary Ions: Ionization Efficiency

**Ionization efficiencies**

= (N of secondary ions)/ (N of atoms sputtered)

O⁻ in silicate, carbonates, oxide minerals ~10%

C⁻ in carbonates ≤ 0.3%

Si⁻ in quartz ~ 1%

**Instrumental bias on isotope ratio**

= \left( \frac{^{18}O^-/^{16}O^-}{^{18}O/^{16}O} \right)_{\text{SIMS}} / \left( \frac{^{18}O/^{16}O}{} \right)_{\text{True}}

oxygen isotope \( ^{18}O/^{16}O \) in silicate, carbonates, oxide minerals: ±10‰

carbon isotope \( ^{13}C/^{12}C \) in calcite: −40‰

silicon isotope \( ^{30}Si/^{28}Si \) in quartz: −30‰

**Secondary Ion intensities**

**Calcite (CaCO₃)**

C⁻ = 2×10⁷ cps

O⁻ = 2×10⁹ cps

Ca⁻ ~0 (ionized as CaO⁻)

**Quartz (SiO₂)**

O⁻ = 2×10⁹ cps

Si⁻ = 1×10⁸ cps
Ion sputtering and electron gun
Sputtering of samples

**Ion Sources**
- Cs\(^+\) +10kV
- O\(^-\) −13kV

**Impact Energy**
- 20-23 keV

**Sample**
- −10kV
- +10kV
Entrance of secondary optics (Main chamber door is opened)

Sample holder is held at ± 10kV
Sample holders (original 25mm and new 32 mm)
Analysis of insulator: secondary electrons

Secondary electrons ejection

Primary Ion

Secondary Ions

Ion Extraction Field

±10kV

0V

+10kV

M+

Electrons returns to sample surface

0V

-10kV

M−

Electrons escape from sample surface

Secondary electrons ejection

neutral atoms, molecules (>90%)
atomic and molecular ions (+/−)
secondary electrons (−)
Electrostatic discharge! ...on your sample?

Analysis of insulator: secondary electrons

Minimum charging

Electrons return to sample surface

Positive secondary ion

Electrons escape from sample surface

Negative secondary ion

Charge built up

+10kV

-10kV

0V

-9.9kV
Electron Gun for Charge Compensation

Electrostatic Lens
Electrostatic Deflector
Aperture or Slit

Duo-Plasmatron
Primary Beam
Mass Filter

Cs-Source
Electrostatic Analyzer (ESA)
Field Aperture

Entrance Slit and Contrast Aperture

Primary Ions
Secondary Ions

O'

Electron Beam

Sample

Collector
Motion Axis

Flight Tube

Detectors

Electron Gun
Electron Gun for Charge Compensation

Acceleration voltage: -10kV
Current: 50 µA

Deceleration

Electron Cloud (100-150µm): electron energy =0 eV

When charge build up by sputtering electron is attracted to sample surface until the charge is compensated.

Sample

Electron gun: -10 kV
Sample acceleration: -10 kV

0V

-10kV
Double Focusing Mass Spectrometer
Double Focusing Mass Spectrometer

- Electrostatic Lens
- Electrostatic Deflector
- Aperture or Slit

- Electrostatic Analyzer (ESA)
- Entrance Slit and Contrast Aperture
- Energy Slit
- Flight Tube
- Magnet
- Collector Motion Axis
- Detectors
IMS 1280: Magnetic Sector Double-focusing MS

\[ qE = \frac{mv^2}{RE} \]

\[ qV = \frac{mv^2}{2} \]

\[ q = \text{electron charge} \]

\[ V = \pm 10 \text{ kV} \]

\[ m = \text{mass of ion} \]

\[ v = \text{velocity of ion} \]
Initial Kinetic Energy of Secondary Ions

Trajectory of ions with variable energies and angles will be different

Sputtering process may provide initial kinetic energy to ions

\[ v = v_i + v_0 \]

\[ m_i v_i^2 / 2 = q_e V_s \]

Acceleration by electrostatic field

Ion with initial kinetic energy and angles

Ion without initial kinetic energy

Sample
Electrostatic Analyzer (ESA)

Ions with variable angles: Focus
Ions with variable energy: Dispersion

ESA

Focus
Energy Slit

ESA

dispersion
Energy Slit

greater energy
slower ions

ESA

fast ions
Energy Slit
Ions with variable energy
Sector Magnet: Ions with different masses

Magnet separate ions with different mass
Sector Magnet: Ions with the same mass

Ions with different angles: Focus
Ions with different energy: Dispersion

Similar to ESA

**different energy**
**different angles**
Double focusing mass spectrometer

Dispersions made by ESA and Magnet are coupled to focus ions with variable energy.

From Cameca IMS manual

Focus ions with variable angles

Focus ions with variable initial energy
Detailed schematics of IMS 1280

**Primary Column**
- Magnet (PBMF)
- Lens: 5
- Deflector: 7
- Stigmator: 2
- Aperture: 2

**Secondary optics**
- Magnet
- ESA
- Lens: 10
- Deflector: 6
- Stigmator: 3
- Hexapole: 3
- Slit: 3
- Aperture: 2

**Electron Gun**
- Coil: 2
- Lens: 1
- Deflector: 2
- Quadrupole: 1

**Detectors**
- FC: 6
- EM: 4
- MCP
- ESA: 6
Mass Spectrum and Ion Detection
Mass Spectrum and Stability (NMR)

MRP=(M/ΔM): mass resolving power

\(^{17}\text{O}\): MRP ~ 4,000; \(^{16}\text{O}, \:^{18}\text{O}\): MRP ~2,200

Magnetic field is regulated by NMR sensor. Drift (ΔB) < 5 ppm for 12 hours

*Hall Probe stability: ~30 ppm for 1 hour

NMR (Nuclear Magnetic Resonance) sensors between electro-magnets

Multi-collectors
Ion Transmission

Transmission vs. Mass resolution

WiscSIMS IMS 1280
- Oxygen 2 isotope >90%
- C isotope >90%
- Oxygen 3 isotope >70%

Large radius SIMS
Small radius SIMS

CAMECA
Ion Detectors

- **FC (Faraday cup):** Direct ion current measurements $>10^6$ cps

  - Ion current: $2 \times 10^9$ cps
    - $= 3 \times 10^{-11}$ A
  - $R = 10^{11}$ ohm
  - $V = I \times R$
  - $3V$
  - Stable Gain
  - Slower response (sec)
  - Thermal noise (~1000 cps)

- **EM (electron multiplier):** Pulse counting $<10^6$ cps

  - Series of dynodes (N~20): each ejects 2-3 electrons
  - $10^8$ electrons produced per single ion – detected as an electronic pulse
  - Low noise $<0.01$ cps
  - Fast response (20-70 ns)
  - Gain drift
Ion detection system

- Single collector: 2 FC, 1EM (switch by deflectors)
- Multi-collectors: 4 FC, 3 EM
  - Multi-collection FC system is originally designed by Finnigan MAT.
  - Very similar to modern ICP-MS and TIMS instruments.
- Multi-channel plate (MCP)
  - Direct image, tuning
Types of analyses using SIMS

Spot analysis:
  High precision stable isotope analyses
  Trace element analyses

Scanning Ion Imaging (SII): NanoSIMS
  Trace element, isotope mapping
  Resolution = Primary beam size (0.5μm - 3 μm)

Direct Ion Image:
  IMS 1280/7f series works as “ion microscope”.
  MCP detection
  SCAPS detector (Hokkaido 1270 and Hawaii 1280)
  Resolution = Optical resolution (~0.5 μm)

Example of SII (Ushikubo et al. 2008)
Modification and upgrade
## Modifications and upgrade of WiscSIMS IMS 1280

WiscSIMS IMS 1280 performs as good as newer instruments; IMS 1280-HR and 1300-HR³

<table>
<thead>
<tr>
<th><strong>Analytical improvement</strong></th>
<th><strong>Efficiency and easy operations</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>• FC amplifier pump (2010)</td>
<td>• Sample chamber camera (2008)</td>
</tr>
<tr>
<td>• Exit slit modifications (2010, 2016)</td>
<td>• Six sample airlock (2009, Cameca)</td>
</tr>
<tr>
<td>• Large sample holder (2012)</td>
<td></td>
</tr>
<tr>
<td>• FC amplifier upgrade (2016, Cameca)</td>
<td></td>
</tr>
<tr>
<td>• RF Plasma Source (2017, Cameca)</td>
<td></td>
</tr>
</tbody>
</table>

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<tr>
<th><strong>Small spot (≤ 2 µm) analyses</strong></th>
<th><strong>Sample navigation and imaging</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Turbo pump dampers (2011)</td>
<td>• Blue light illumination (2009)</td>
</tr>
<tr>
<td>• NanoDeflector (2014)</td>
<td>• UV light illumination (2011)</td>
</tr>
<tr>
<td></td>
<td>• Software “Badgerscope©“ (2012)</td>
</tr>
</tbody>
</table>

Mostly in-house modifications

Adapted to newest IMS 1300-HR³
Modification of WiscSIMS IMS 1280 (UV light microscope, 2011)

IMS 1280
Optical microscope

Kita et al. (2015, JAAS)

Original: White halogen lump
Resolution ~3.5 μm
Chromatic aberration

UV light optics
356 nm LED
HD camera
Resolution ~1.3 μm

* Replaced multiple optical components.
New sample viewing software “Badgerscope©” (2012)

New software to view HD-camera

Image processing

Kita et al. (2015, JAAS)
NanoDeflector (2014)

**Accuracy of aiming ≥1 µm**
- Stage minimum step =1 µm
- Primary beam deflection minimum = 1µm

Apply additional voltage to beam deflector

**Resolution: 0.1 µm**

Comet particle analyses (Defouilloy et al. 2017; EPSL)

(a) SEM image of comet particle with FIB mark
(b) before adjustment
(c) after displacement of the stage
(d) after adjustment with the NanoDeflector
(e) SEM image of comet particle after SIMS analysis

In-house microprocessor board attached to Cameca original deflector board
RF Plasma Source for O$^-$/O$_2^-$ ions (coming soon!)

Mg isotope analyses of extraterrestrial materials

- x10 increase in intensity
- Mg isotope analysis (MgO~0.5%)
  - Oxygen isotope analysis
    - Cs$^+$: 1-2 µm, 3pA
    - 30 min /spot
  - Mg isotope analysis
    - O$^-$: 2-3 µm, 3pA
    - 11 h /spot

Mg isotope analyses of comet particle (Nakashima et al. 2015)

- Smaller spots ≤ 2 µm
- Faster analyses ≤ 1h
RF Plasma Source for O\(^{-}/\)O\(_2^{-}\) ions (coming soon!)

- **Cosmochemistry**
  - \(^{26}\)Al-\(^{26}\)Mg extinct nuclide chronology
  - Mg isotope fractionation by evaporation

- **U-Pb geochronology (zircon)**

- **Trace element analyses**

Other isotope system in carbonates?
- Mg isotope fractionation
- Ca isotope fractionation
- Sr isotope (\(^{87}\)Sr/\(^{86}\)Sr)
Finally, ..... SIMS analysis is easy
Oxygen isotope analyses

Instrument is fully tuned including detector positions and magnetic field.

- Move to standard grain in your sample.
- Move to your analysis position.
Oxygen isotope analyses

Instrument is fully tuned including detector positions and magnetic field.

- Move to standard grain in your sample.
- Move to your analysis position.
- Press START

Acquisition takes 3 min
Oxygen isotope analyses

During first 1 min, there will be series of scanning.

This is called “DTFA Scan” that adjustment of primary beam misalignment against secondary ion optical axis.
After the analysis: import new data to excel sheet

Click Macro-button

Select next row
After the analysis: import new data to excel sheet
Oxygen isotope analyses

Instrument is fully tuned including detector positions and magnetic field.

- Move to standard grain in your sample.
- Move to your analysis position.
- Move to next position

Repeat this 12 hours