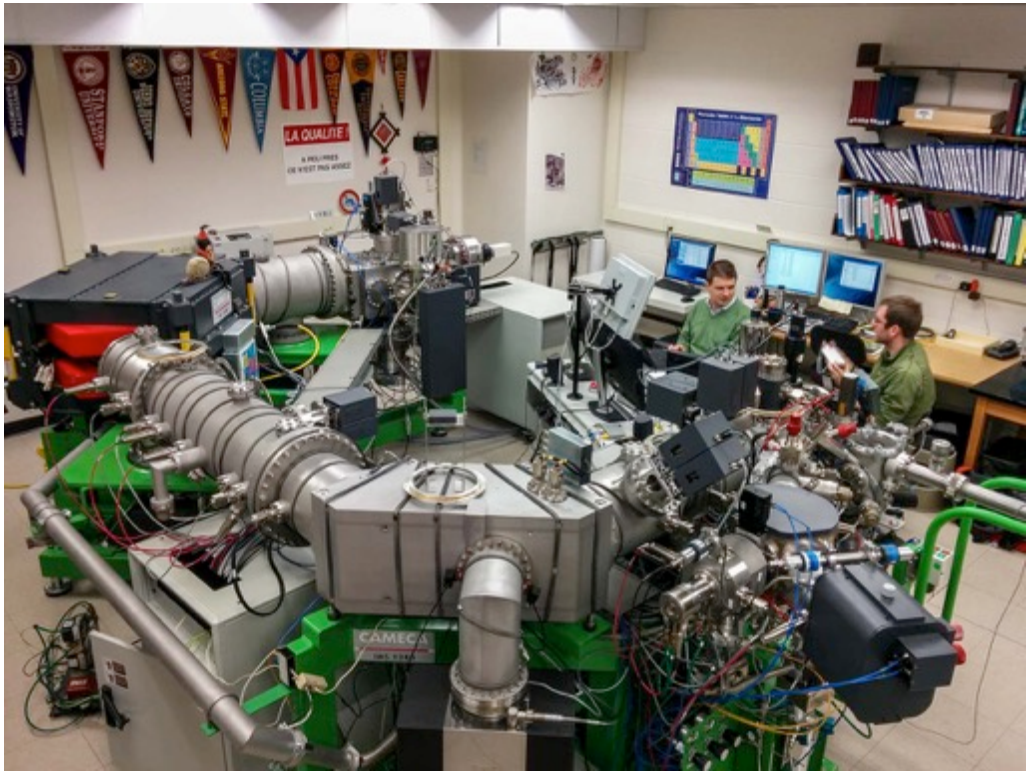
# Tutorial: SIMS Basics

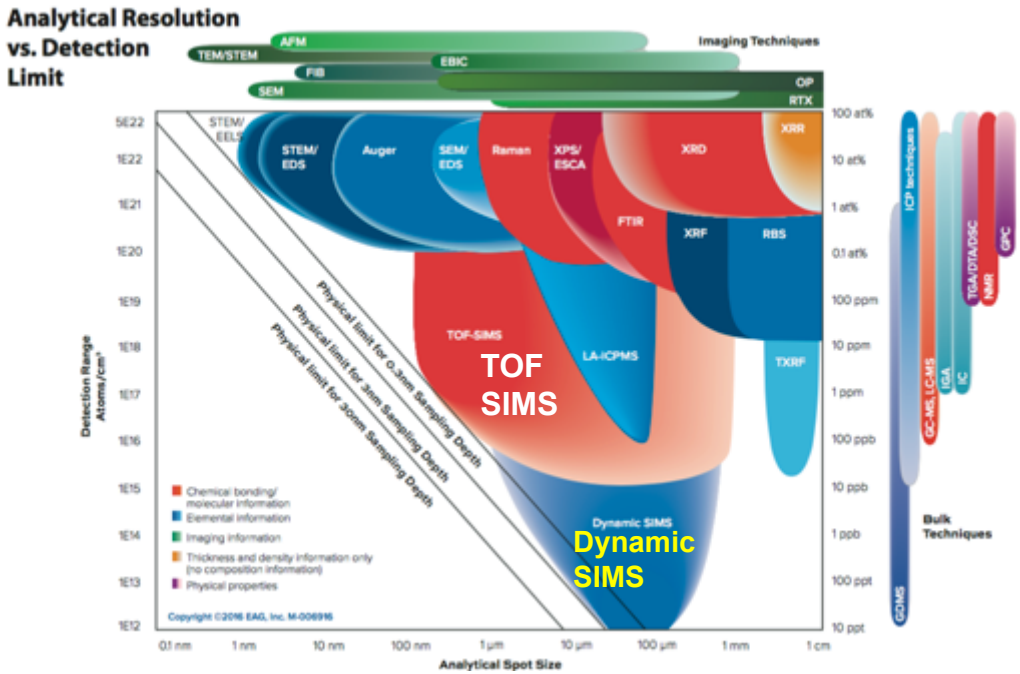



- Overview of SIMS
- Sputtering process
- Electron-gun
- Mass spectrum
- Detectors
- WiscSIMS modification
- Isotope Analyses

**Please stop me anytime for questions!**

Noriko Kita (WiscSIMS, UW-Madison)

# Secondary Ion Mass Spectrometer (SIMS)




IMS 1280: 2µm -20µm

NanoSIMS: 50 nm

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

- **Destructive Analysis**

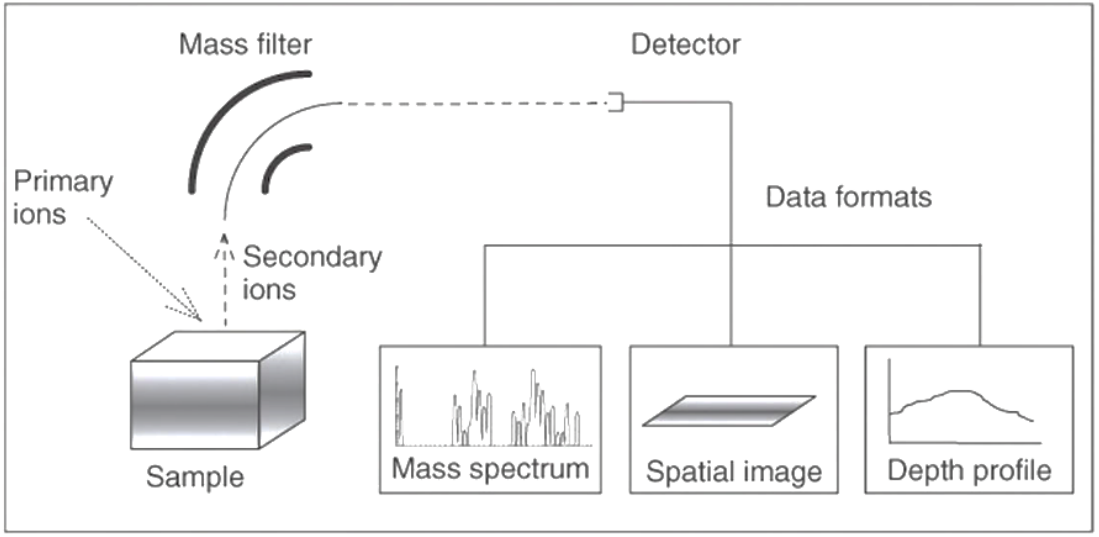
Geoscience applications:

- 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:**

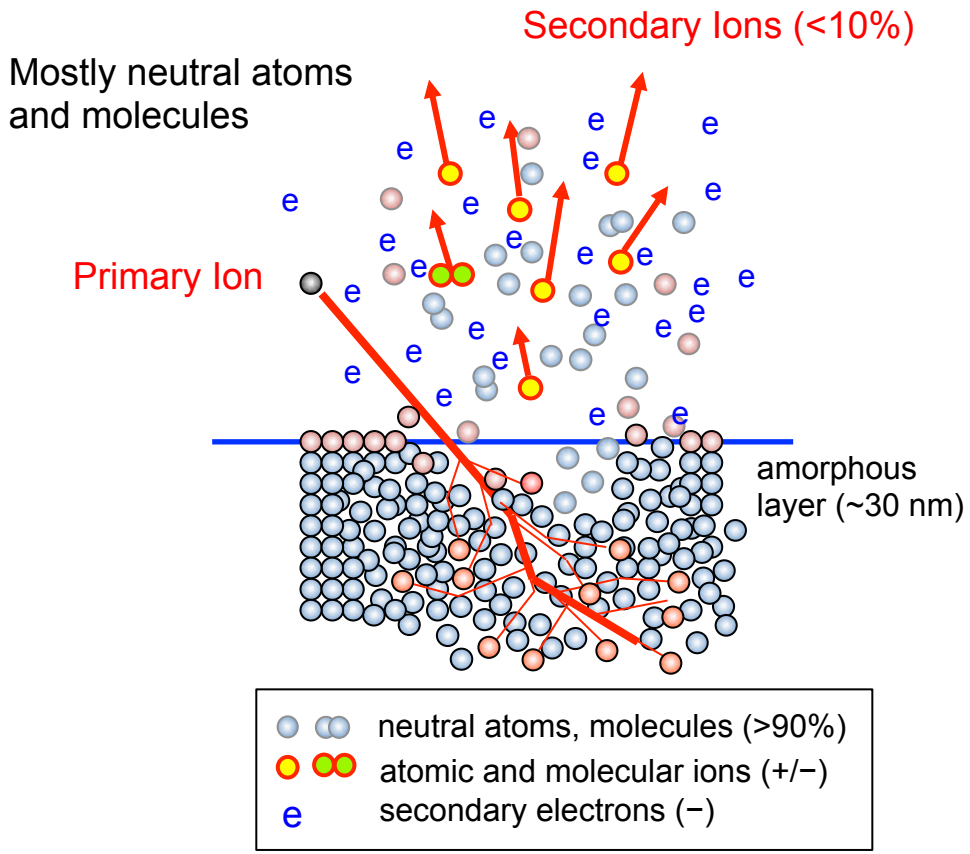
- Spot isotope/chemical analysis
- Ion imaging (scanning/ direct)
- Depth profile
- 3D imaging

# Ion Sputtering Process and Secondary Ionization

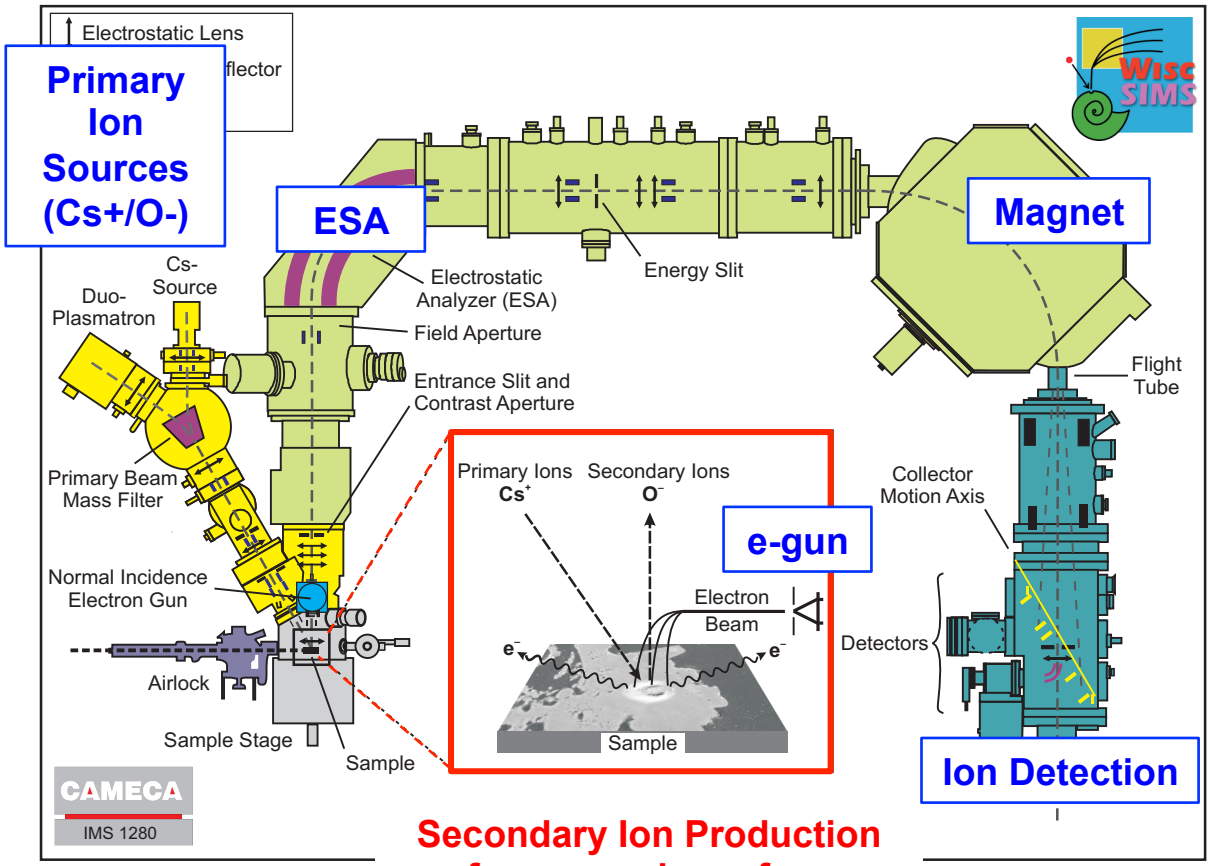
1. Primary ions are implanted to the interior of sample.
2. Atoms are displaced by collision cascade.
3. Atoms, molecules, ions, electrons are ejected from sample surface.

**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



# IMS 1280: Magnetic Sector Double-focusing MS




**Secondary Ion Production from sample surface**

**Mass Spectrometer should**

- Separate molecular isobaric interference by high mass resolving power ($M/\Delta M$) ≥ 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

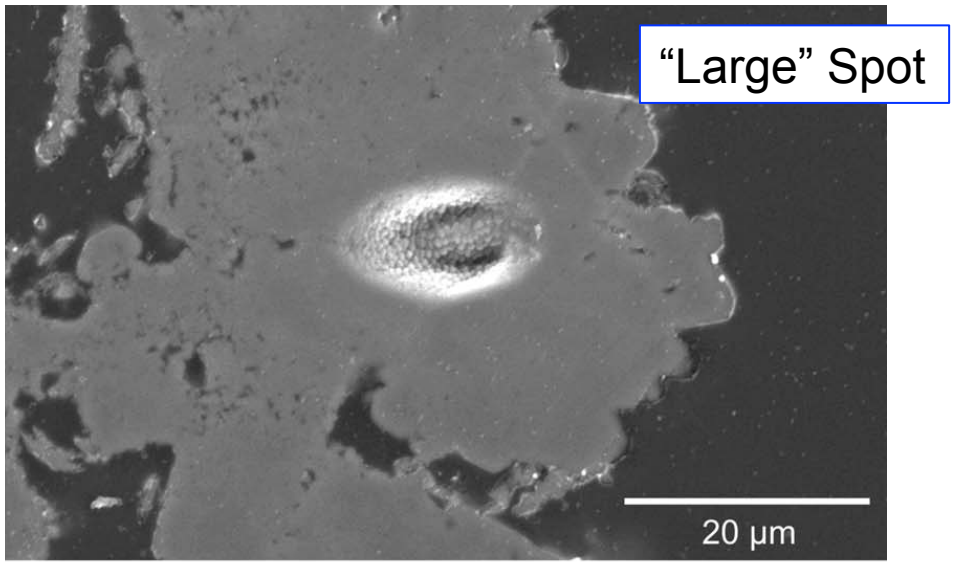
## Double Focusing Mass Spectrometers

- Large radius (high mass resolution: M/ΔM ≥ 5,000) Sector Magnet radius
  - **IMS 1270/1280/1280-HR/1300-HR[3]:** ---------- R = 585 mm
    **Stable isotope**, Geochronology, Nuclear forensic
  - SHRIMP: Geochronology (zircon U-Pb ages) ---------- R = 1,000 mm
  - NanoSIMS: High spatial resolution (50nm beam)
    Imaging, biological applications
- Conventional SIMS (low mass resolution): IMF 7f/ 7fGeo: ------- R = 120 mm

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

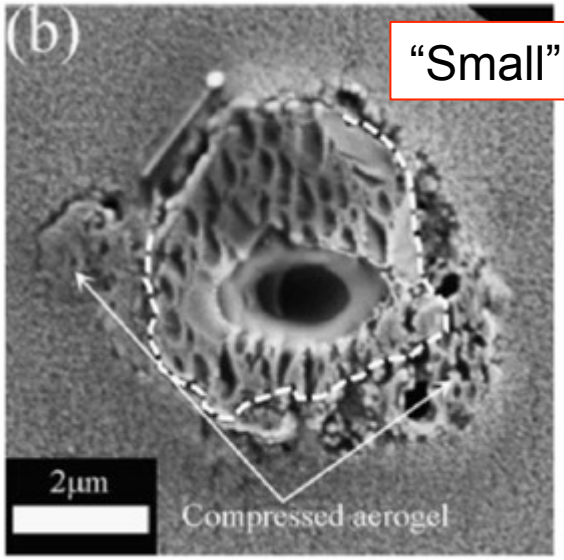
# SIMS Analysis Spots

Cs+ primary beam 10-15 µm spots




*Foraminifera; Kozdon et al. (2011)*

Cs+ primary beam 1-2 µm spots




*Comet sample return; Nakashima et al. (2012)*

Primary Ion intensity ~ 2 nA ----------→ 3 pA

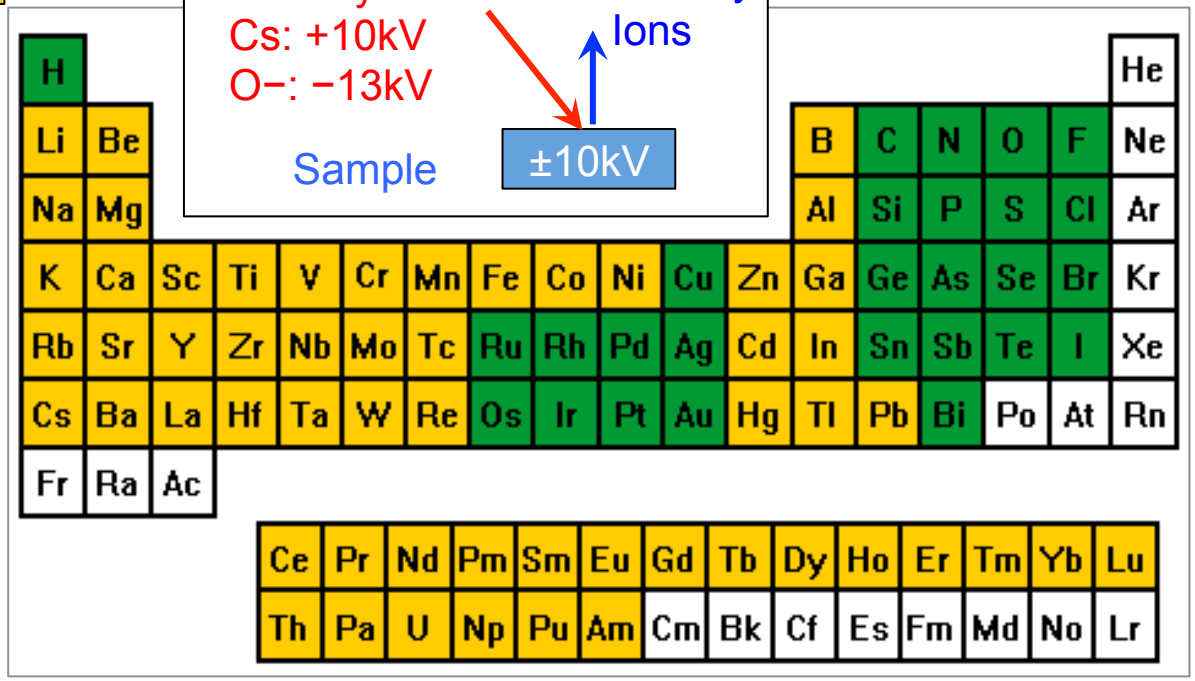
Precisions of oxygen isotope ratios ~ 0.3‰ ----------→ 1-2 ‰

# 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+




Modified from Evans Analytical Group: http://www.eaglabs.com/mc/sims-theory.html

**Cs+/Sec(−)**

Higher electro-negativity: $O^-$, $C^-$, $S^-$, $Si^-$

- 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%

**Secondary Ion intensities**

Calcite ($CaCO_3$)

$C^-$ = $2\times10^7$ cps

$O^-$ = $2\times10^9$ cps

$Ca^-$ ~0 (ionized as $CaO^-$)

Quartz ($SiO_2$)

$O^-$ = $2\times10^9$ cps

$Si^-$ = $1\times10^8$ cps

**Instrumental bias on isotope ratio**

= $(^{18}O^-/^{16}O^-)_{SIMS}$ /$(^{18}O/^{16}O)_{True}$

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‰

Ion sputtering and electron gun

# Sputtering of samples

**Ion Sources**

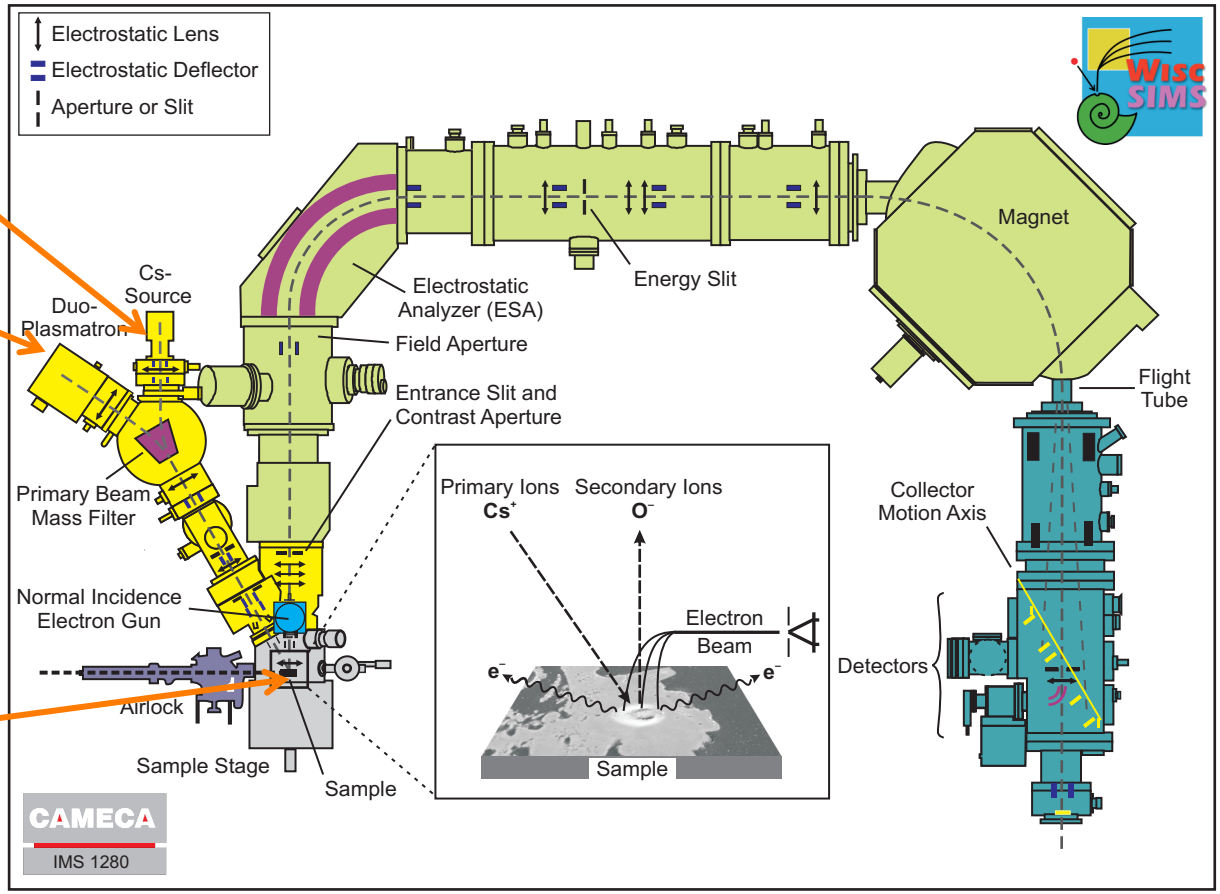
**$Cs^+$ +10kV**

**$O^-$ −13kV**

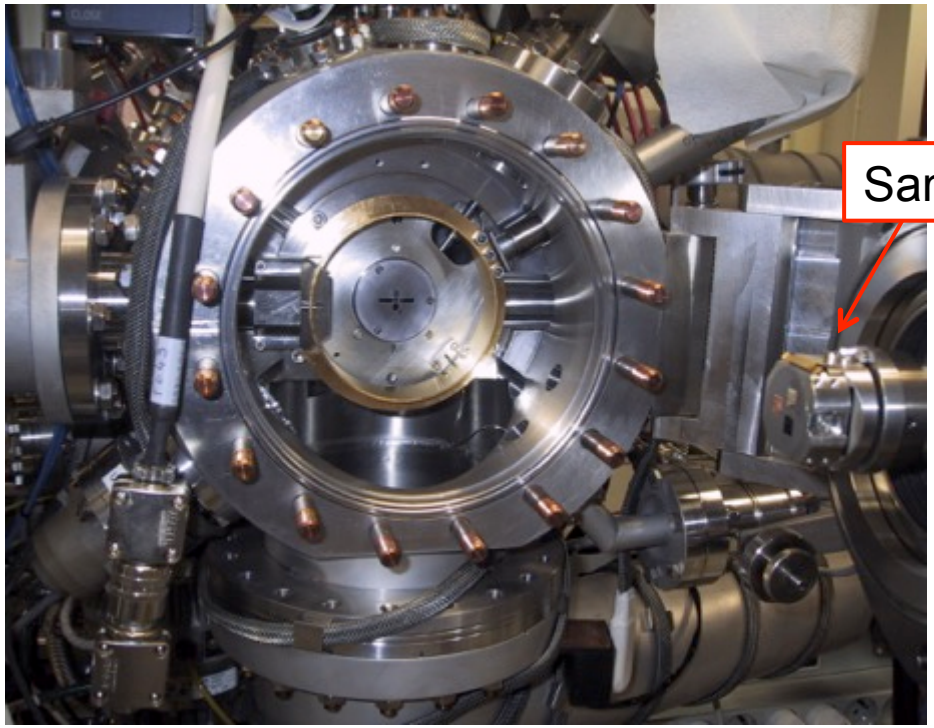
**Impact Energy 20-23 keV**

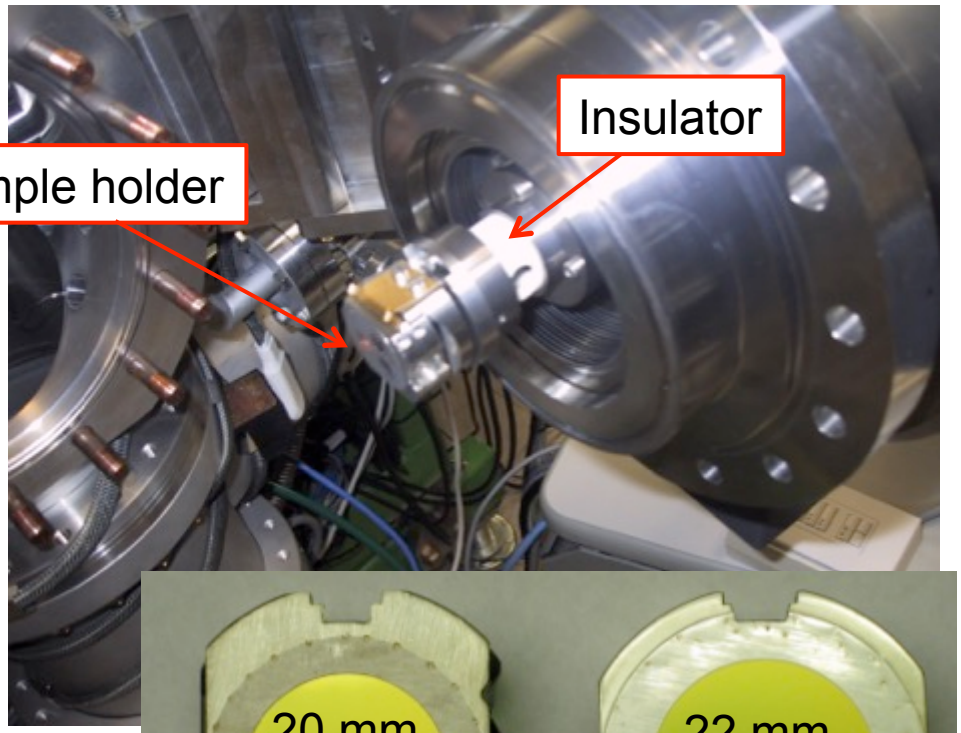
**−10kV**

**Sample** **+10kV**



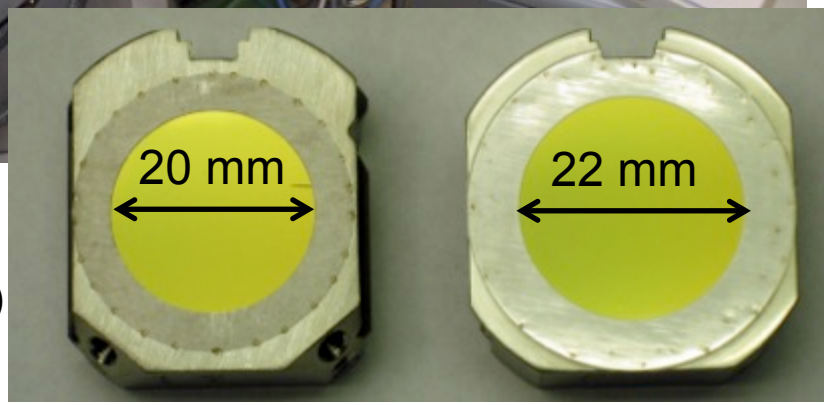
Entrance of secondary optics (Main chamber door is opened)



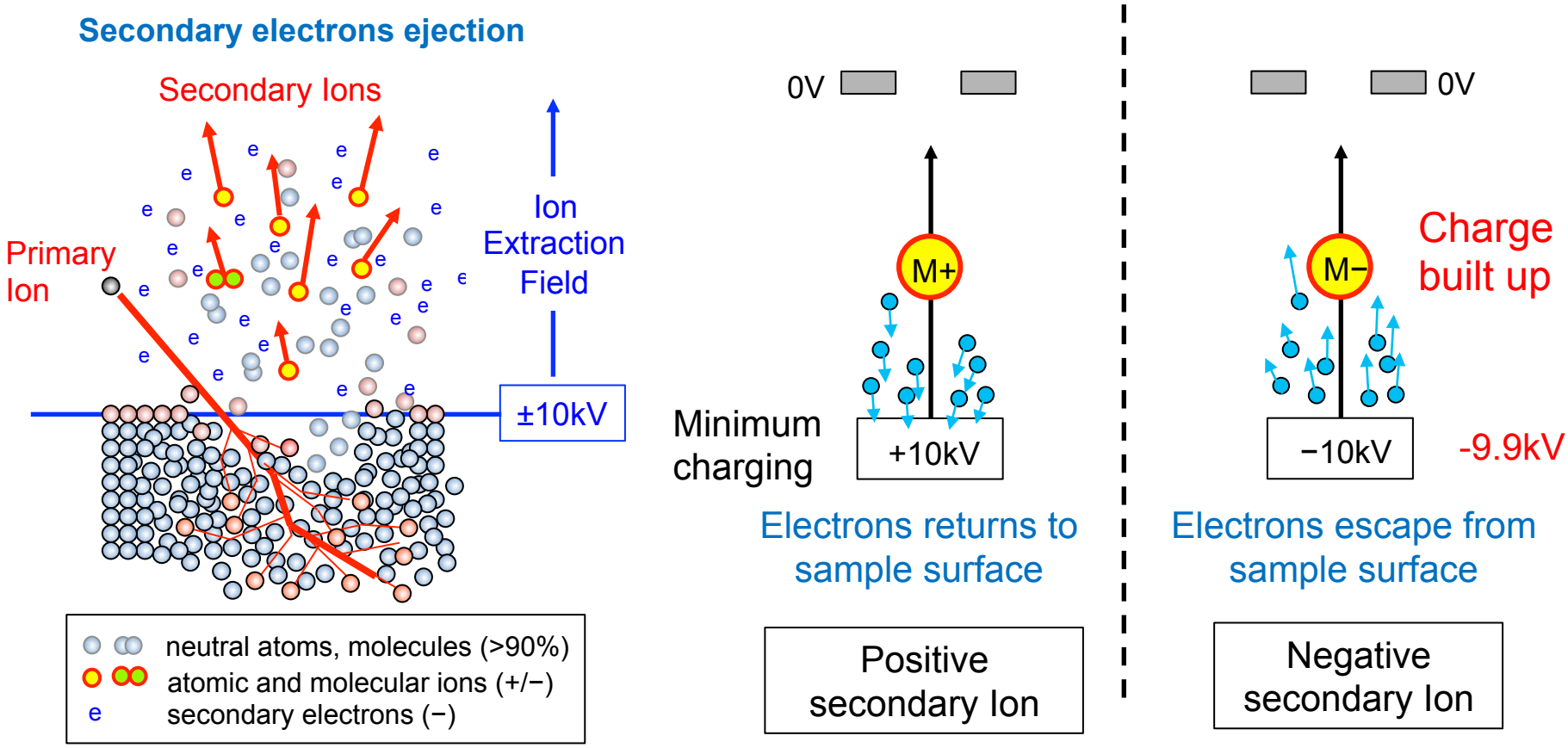




Sample holder is held at ± 10kV

Sample holders (original 25mm and new 32 mm)



# Analysis of insulator: secondary electrons



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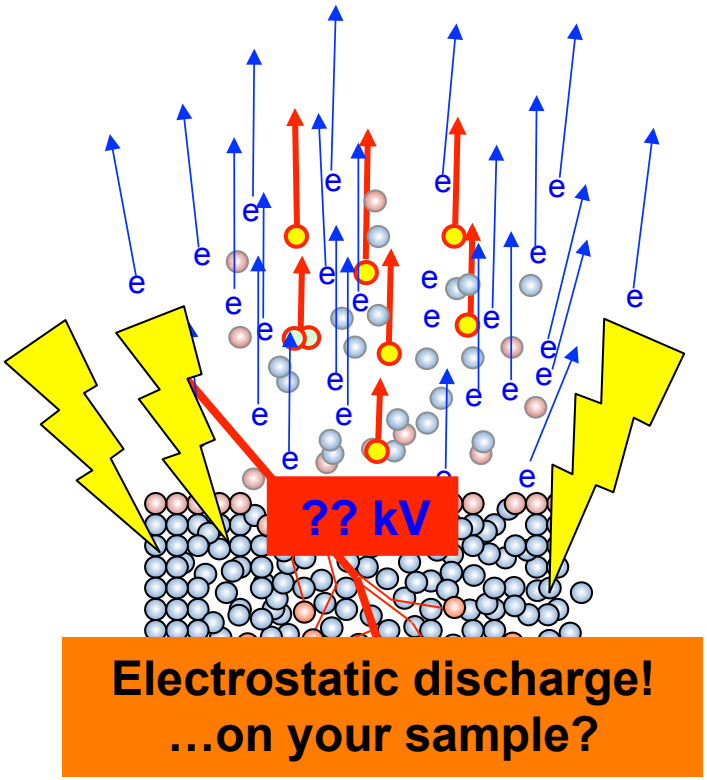
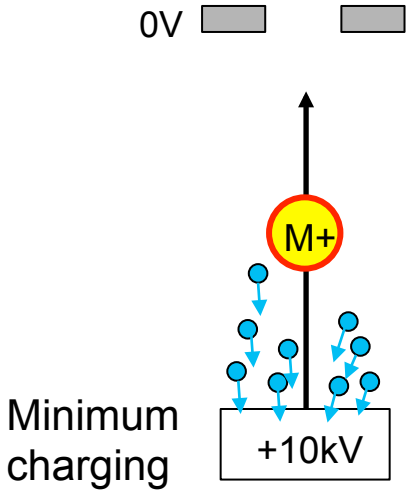
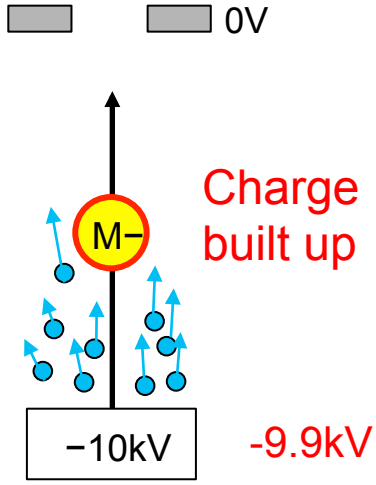



Electrons returns to sample surface

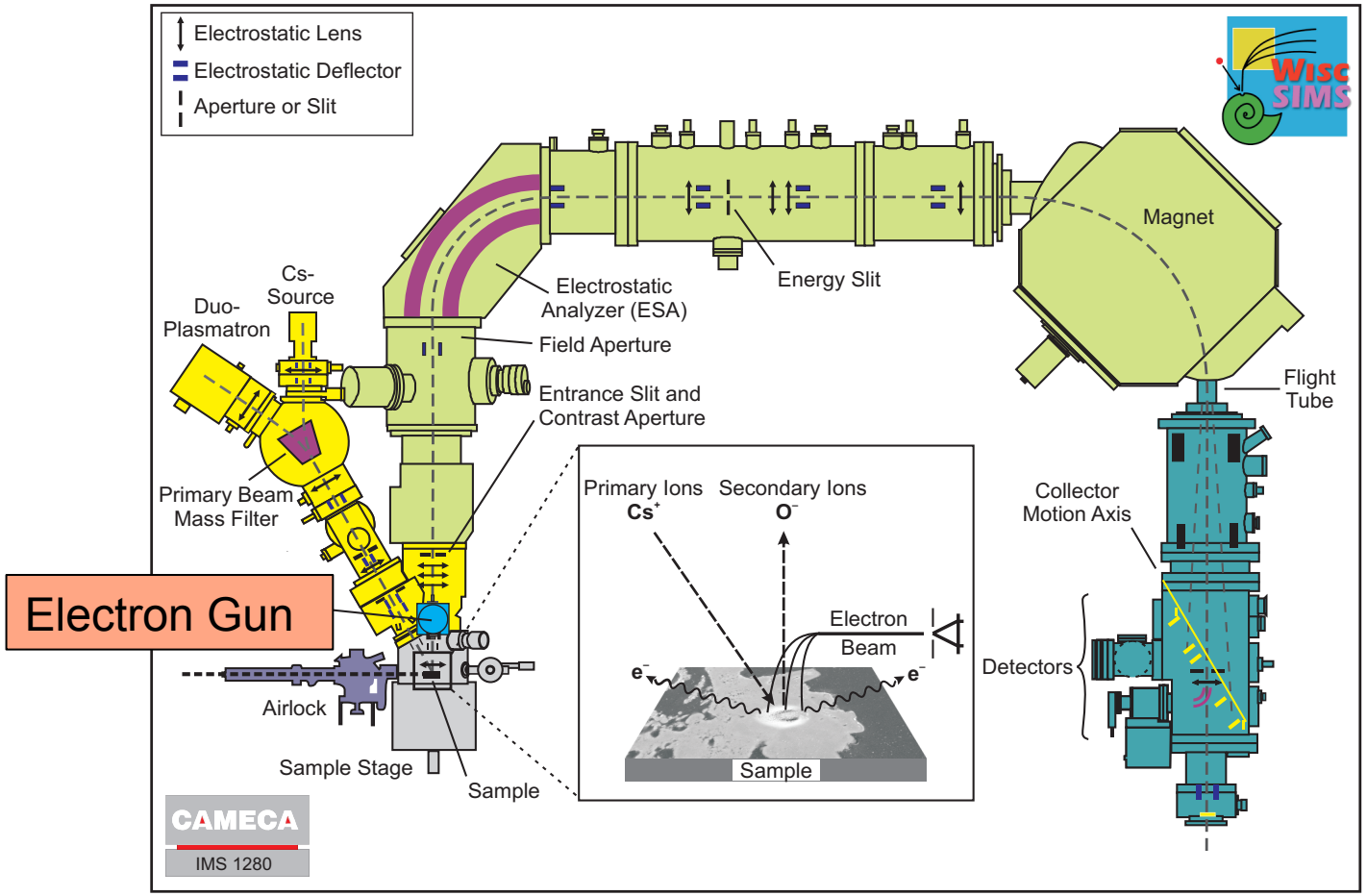
Positive secondary Ion



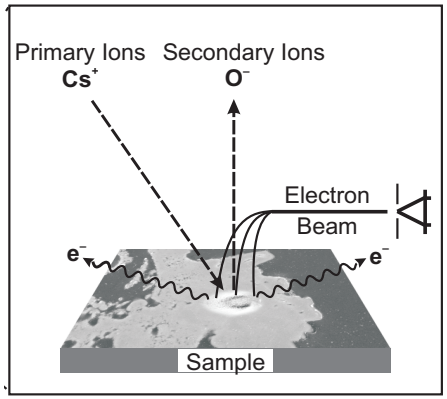

Electrons escape from sample surface

Negative secondary Ion

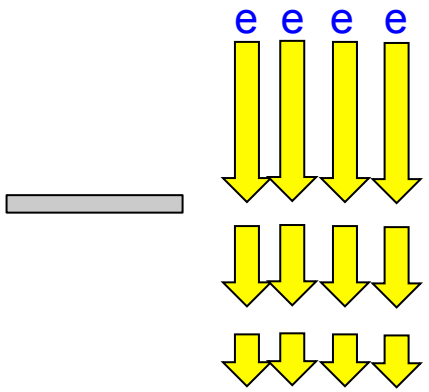
# Electron Gun for Charge Compensation



# Electron Gun for Charge Compensation




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

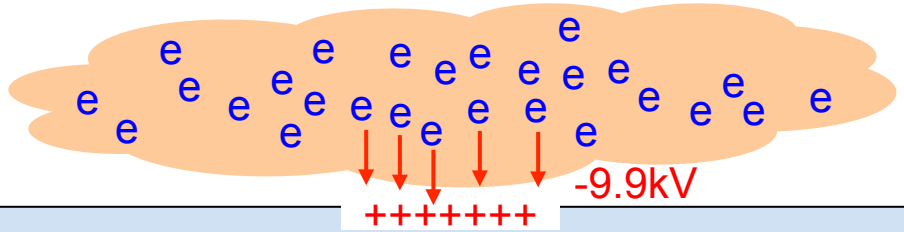



**Acceleration voltage: -10kV**
**Current: 50 µA**

**0V**

Deceleration

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



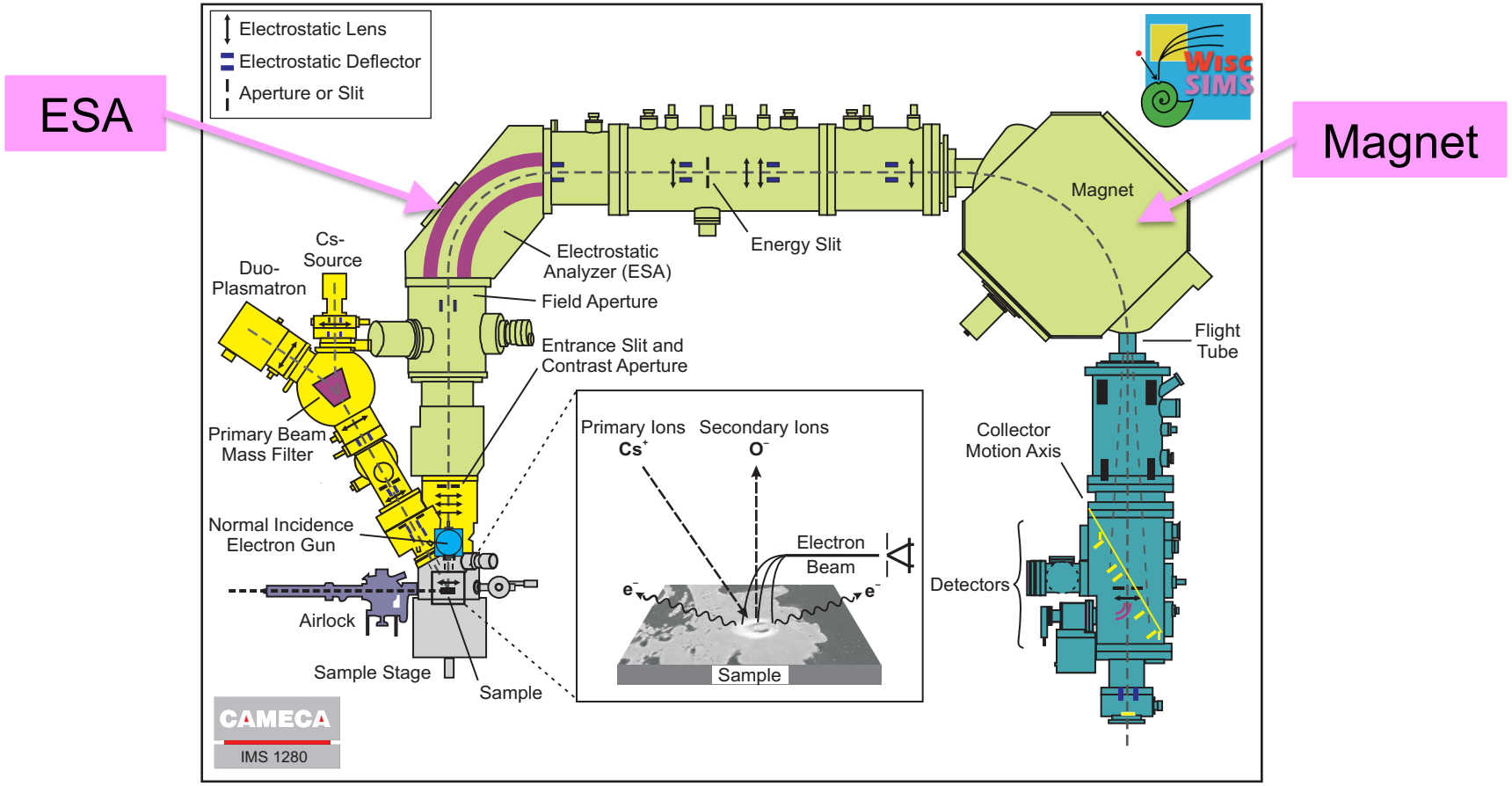

Sample

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

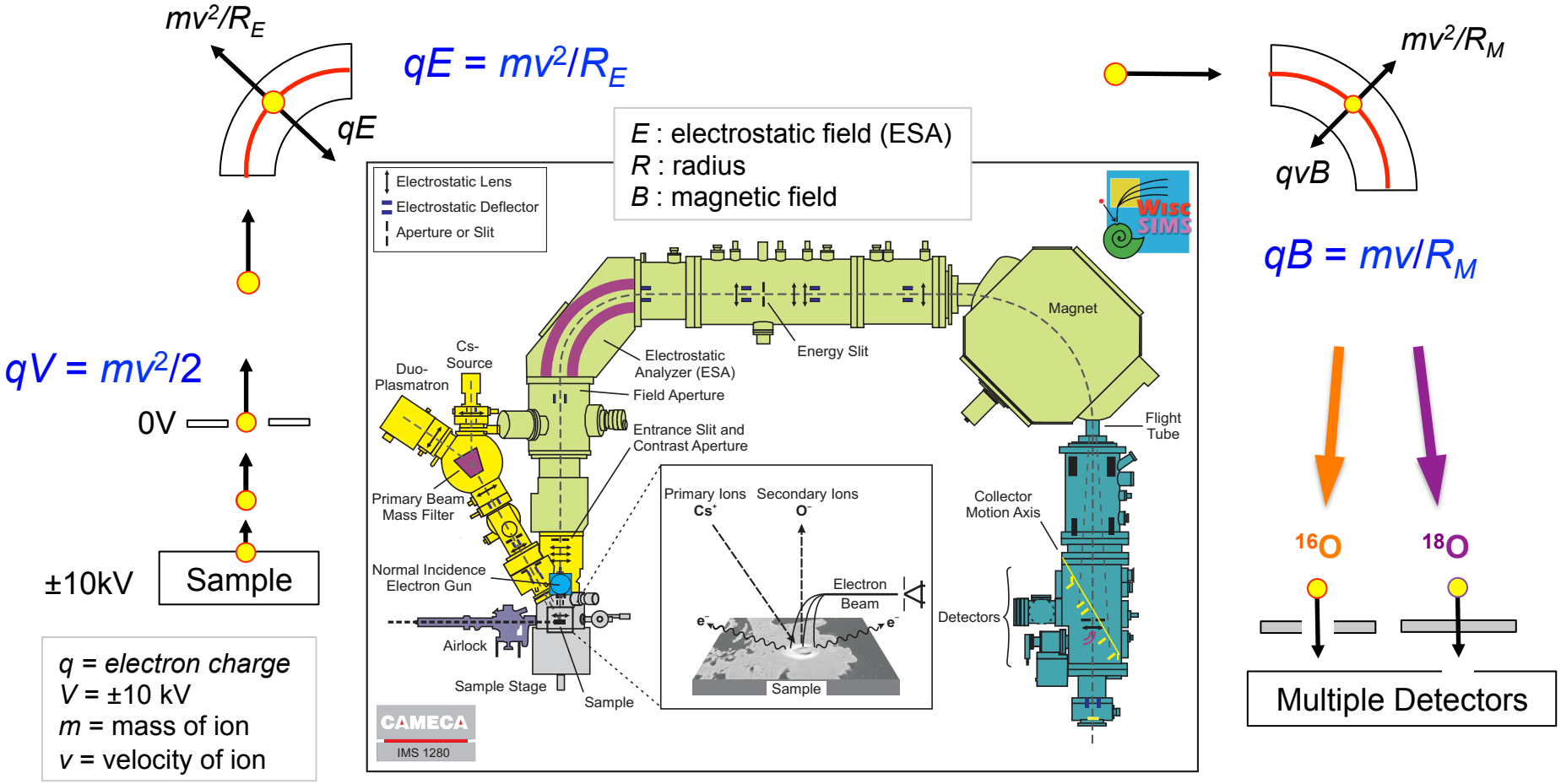
**-10kV**

# Double Focusing Mass Spectrometer

# Double Focusing Mass Spectrometer



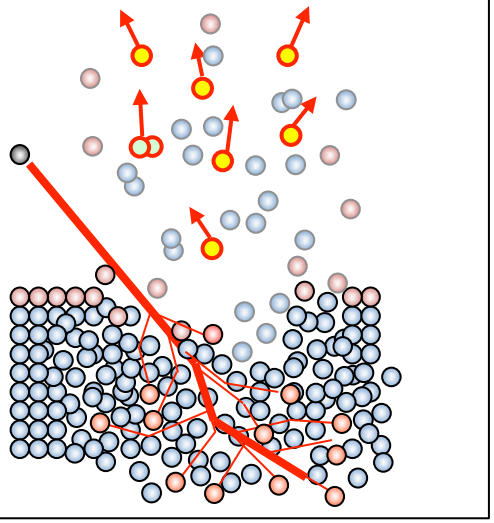
# IMS 1280: Magnetic Sector Double-focusing MS

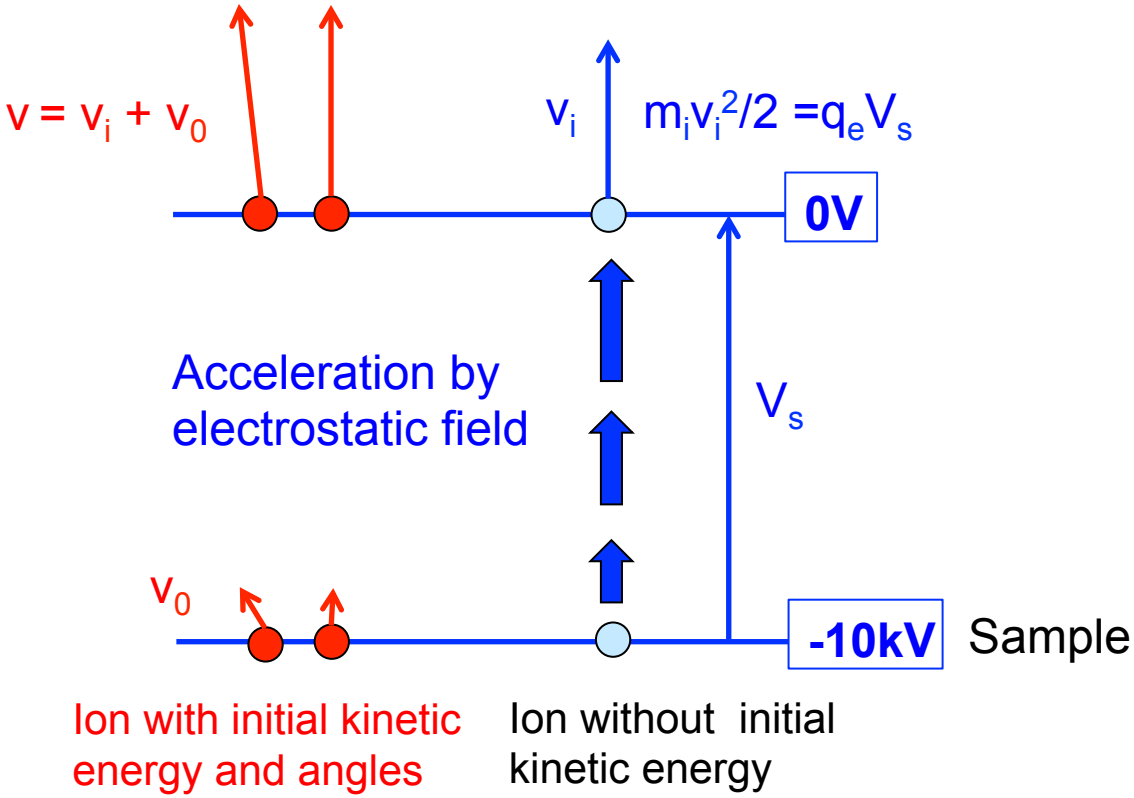


# Initial Kinetic Energy of Secondary Ions

**Trajectory of ions with variable energies and angles will be different**

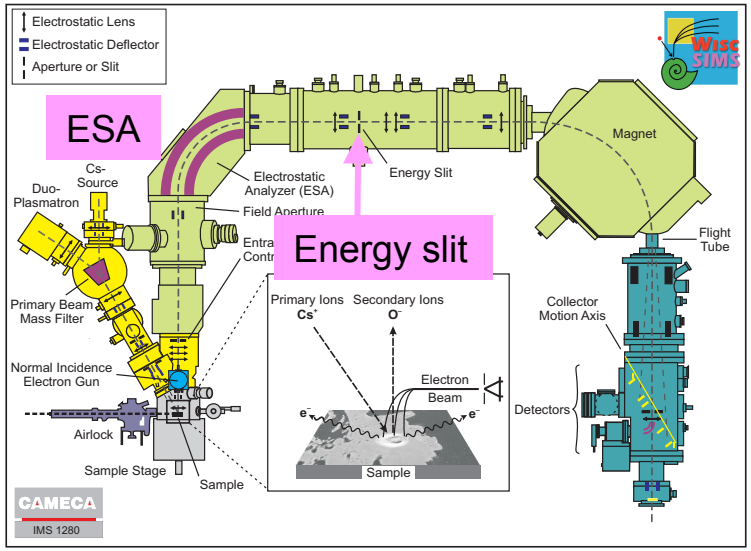
Sputtering process may provide initial kinetic energy to ions

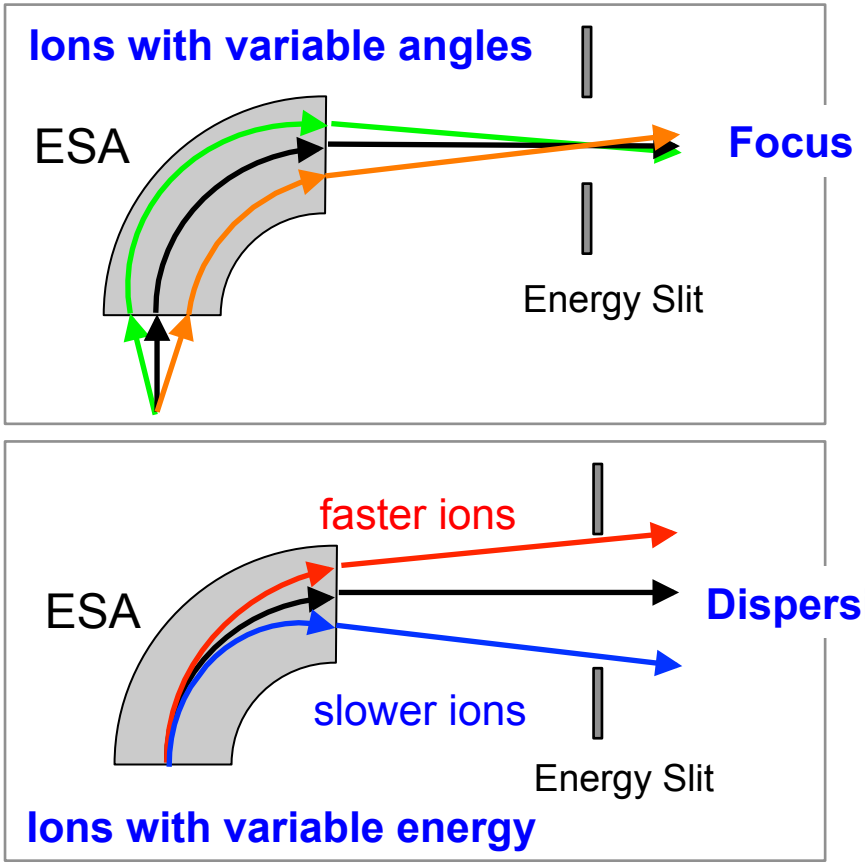




# Electrostatic Analyzer (ESA)

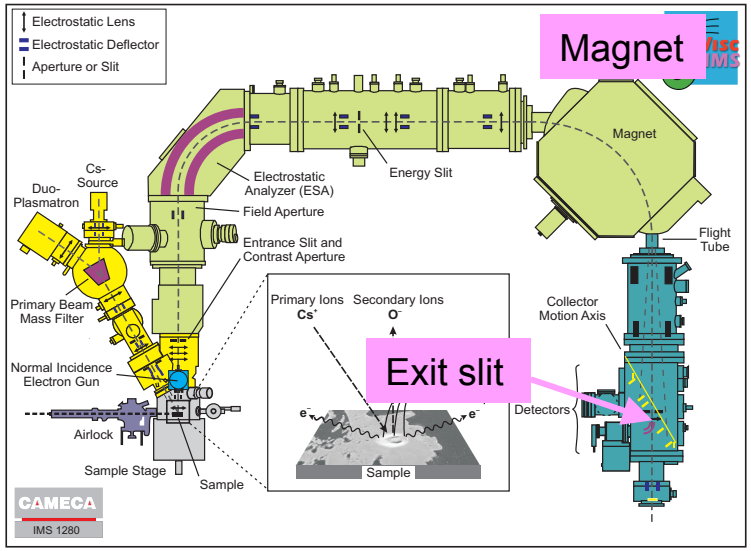
Ions with variable angles: Focus
Ions with variable energy: Dispersion

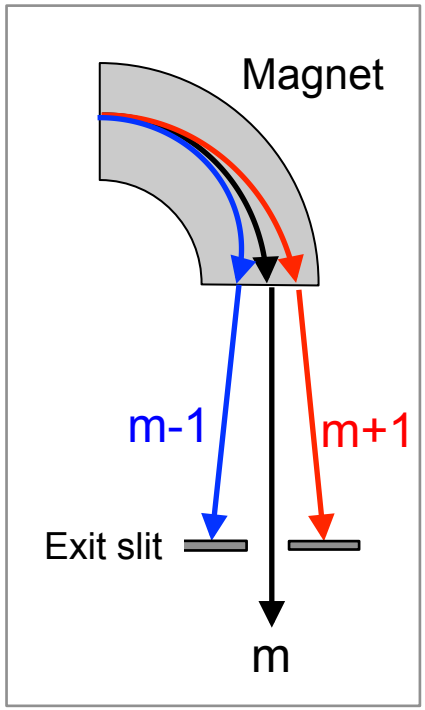


# Sector Magnet: Ions with different masses

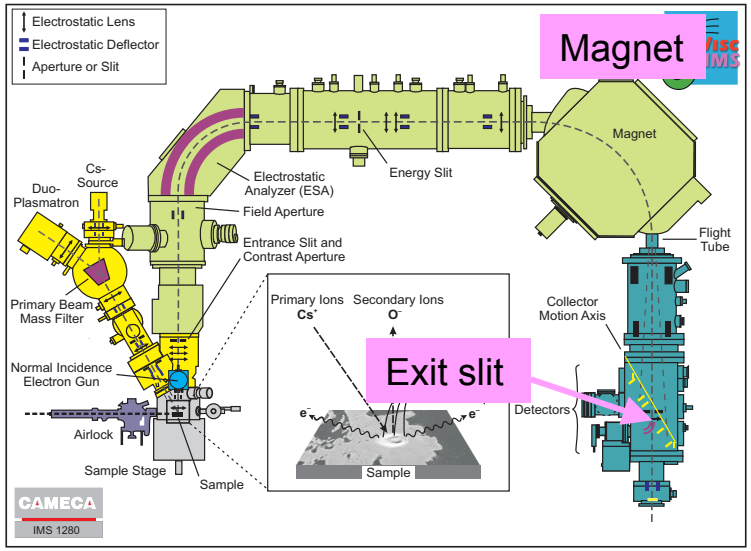
Magnet separate ions with different mass



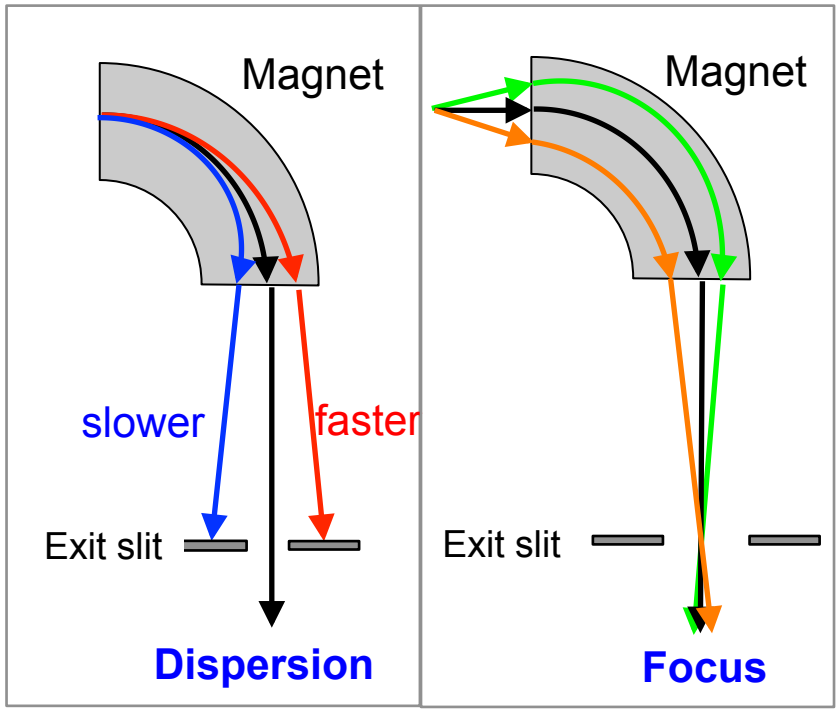
# Sector Magnet: Ions with the same mass

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



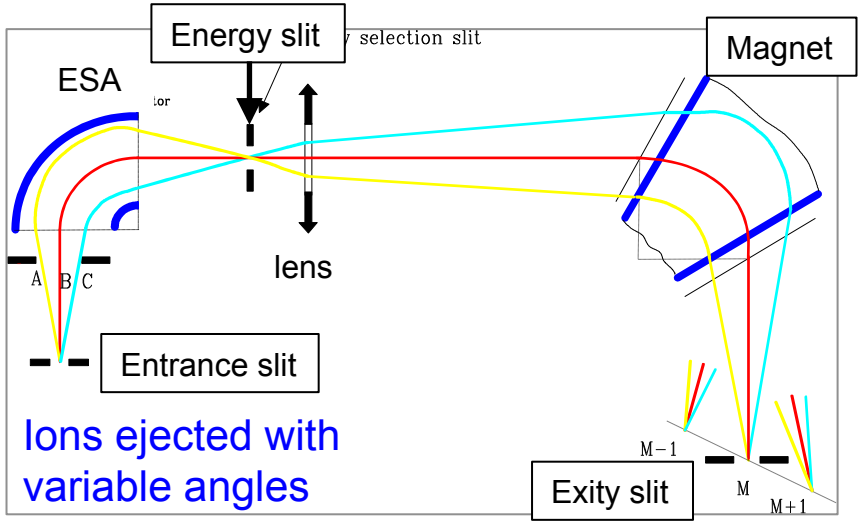

Similar to ESA

**different energy** **different angles**

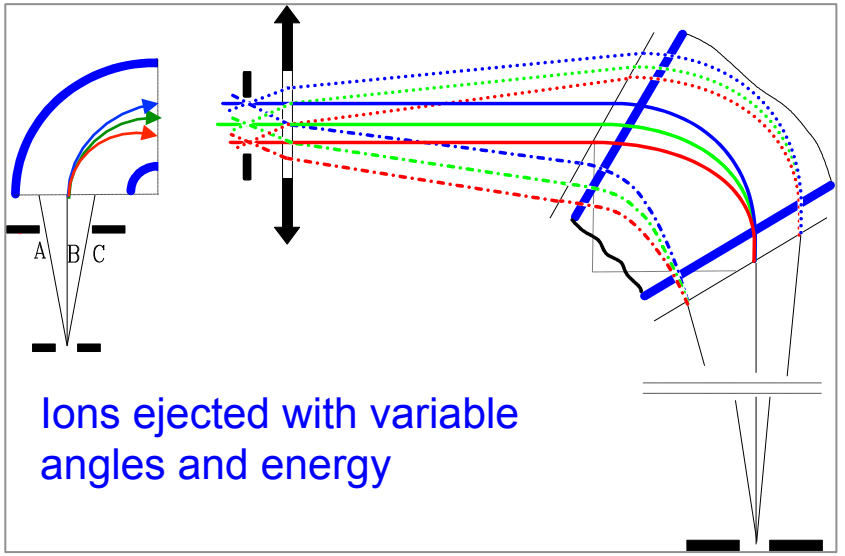


# Double focusing mass spectrometer

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

<u>Primary Column</u>

Magnet (PBMF)

Lens: 5

Deflector: 7

Stigmator: 2

Aperture: 2

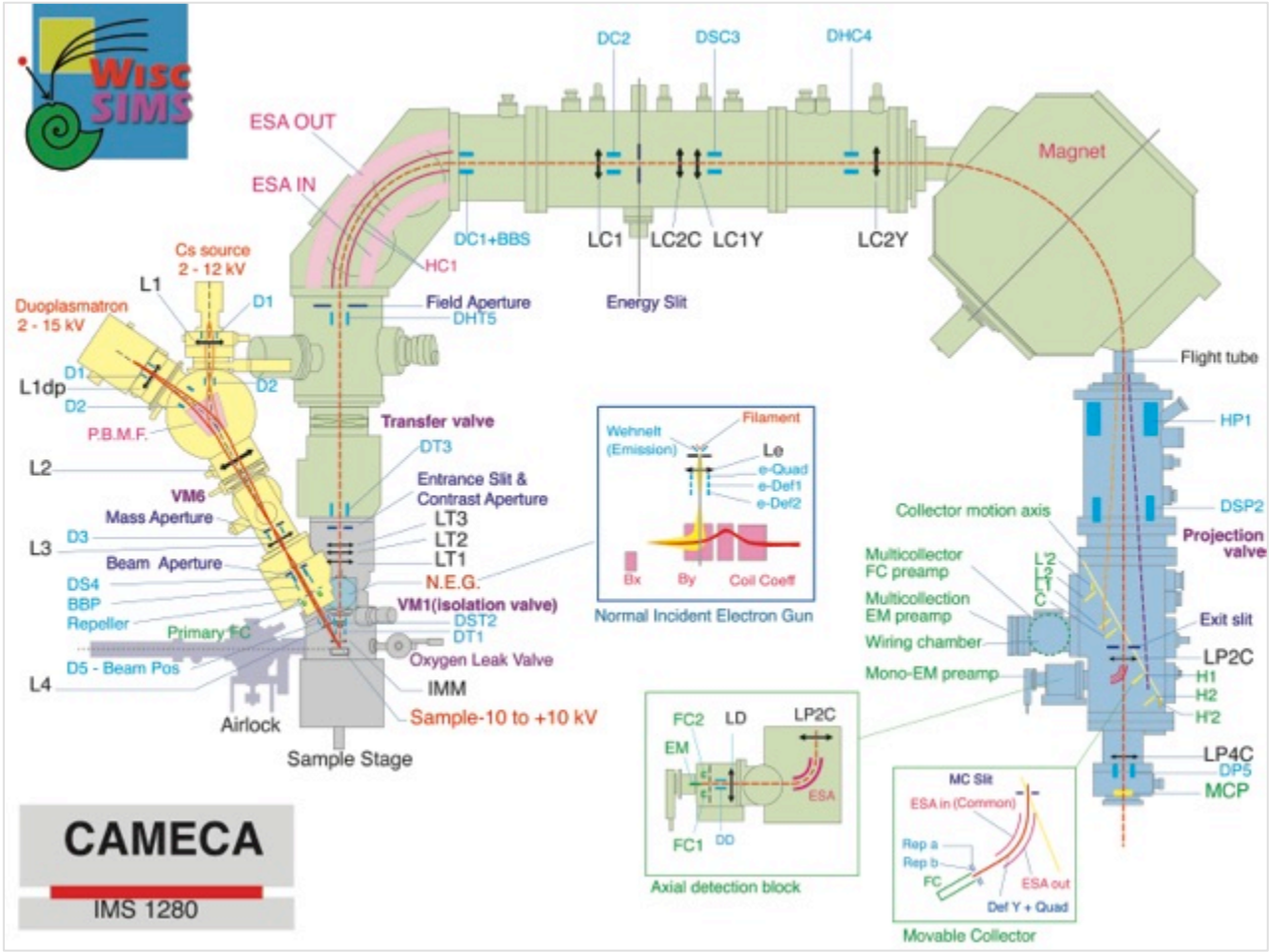
<u>Electron Gun</u>

Coil: 2

Lens: 1

Deflector: 2

Quadrapole: 1




<u>Secondary optics</u>

Magnet

ESA

Lens: 10

Deflector: 6

Stigmator: 3

Hexapole: 3

Slit: 3

Aperture: 2

<u>Detectors</u>

FC: 6

EM: 4

MCP

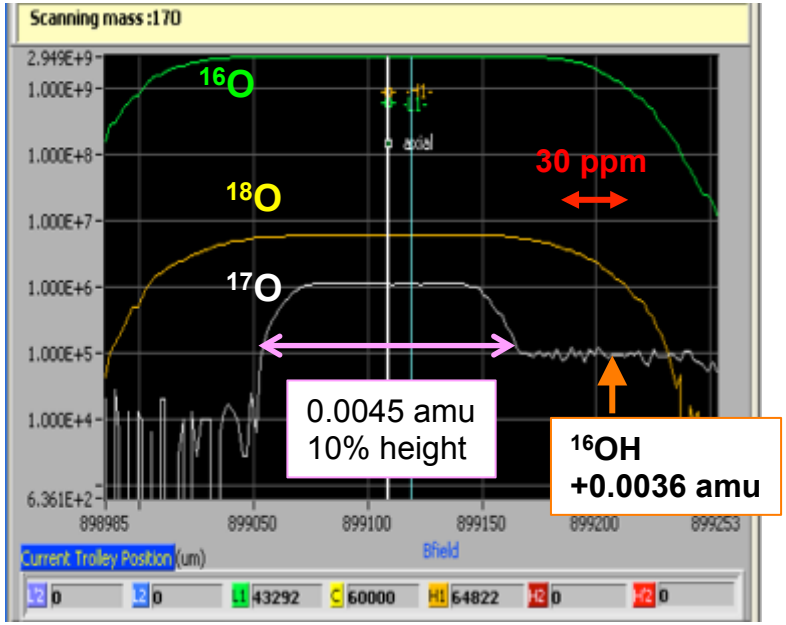
ESA: 6

# Mass Spectrum and Ion Detection

# Mass Spectrum and Stability (NMR)

MRP=(M/ΔM): mass resolving power

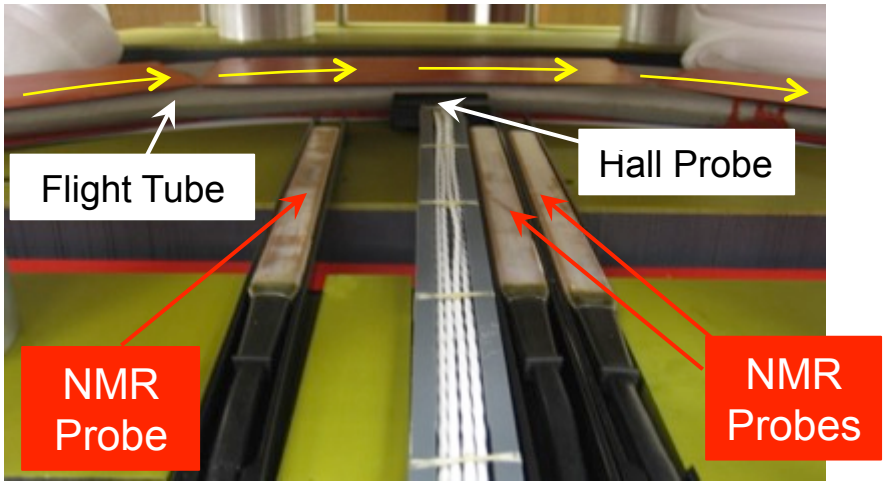
$^{17}O$: MRP ~ 4,000; $^{16}O$, $^{18}O$: MRP ~2,200




Multi-collectors

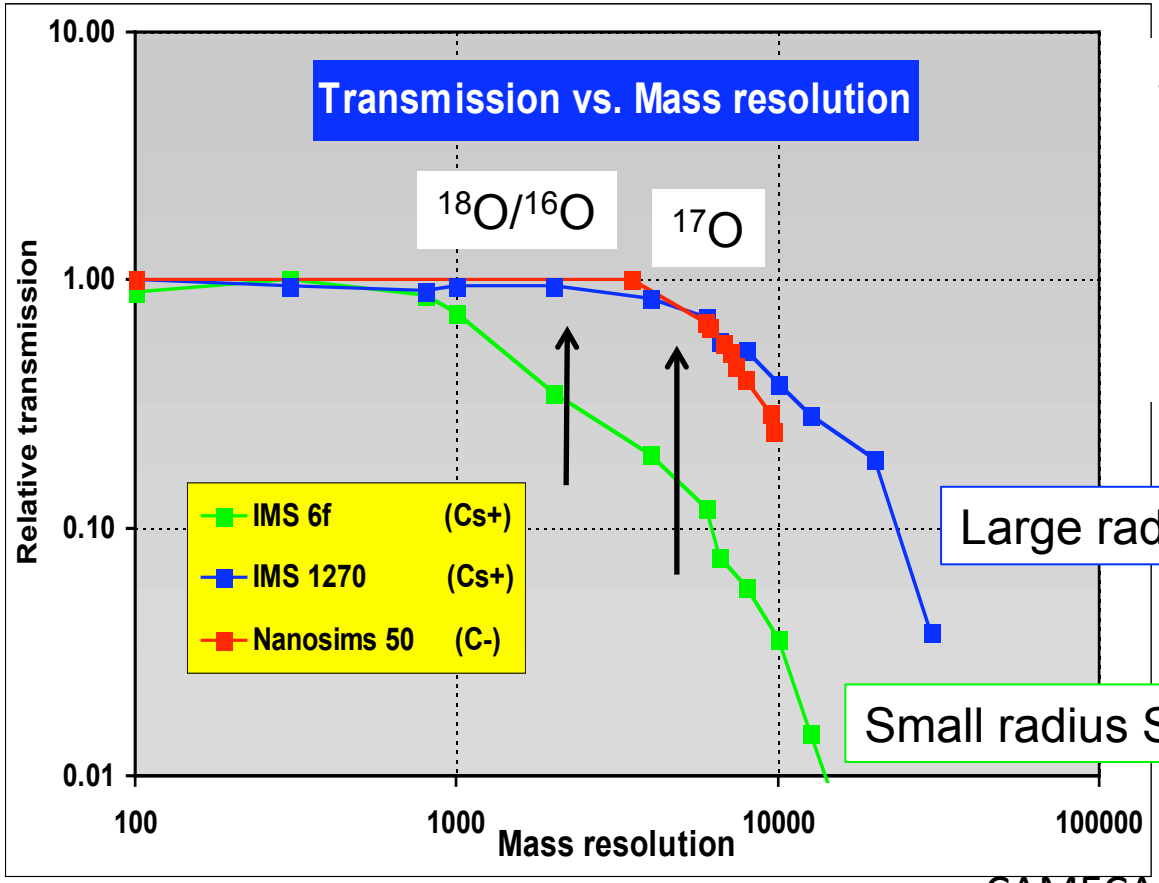
Magnetic field is regulated by NMR sensor.
Drift (ΔB) <5 ppm for 12 hours

*Hall Probe stability: ~30 ppm for 1 hour




NMR (Nuclear Magnetic Resonance) sensors between electro-magnets

# Ion Transmission




WiscSIMS IMS 1280

- Oxygen 2 isotope >90%
- C isotope >90%
- Oxygen 3 isotope >70%

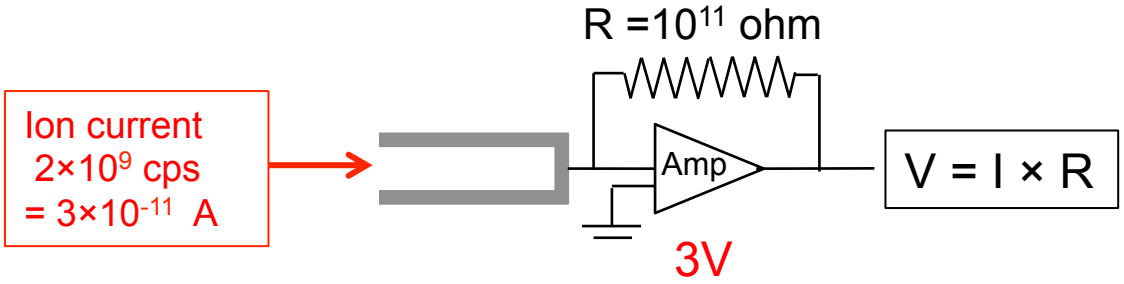
Large radius SIMS

Small radius SIMS

CAMECA

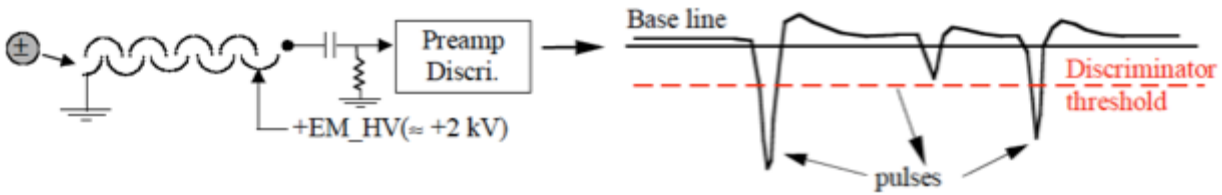
# Ion Detectors

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




Stable Gain
Slower response (sec)
Thermal noise (~1000 cps)

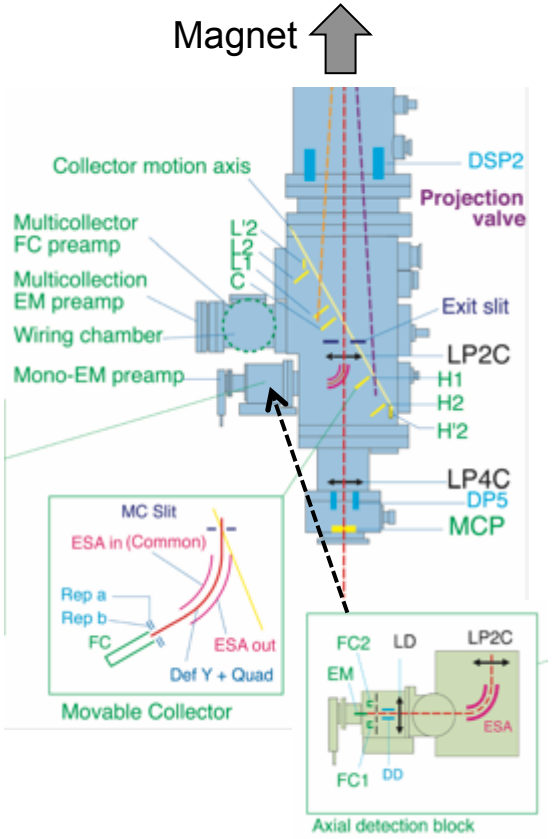
- EM (electron multiplier): Pulse counting <$10^6$ cps



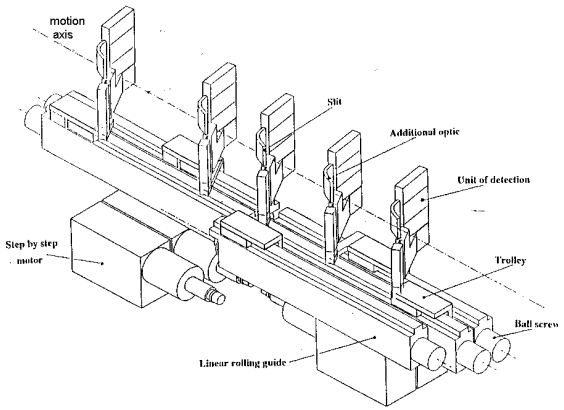

Low noise <0.01 cps
Fast response (20-70 ns)
Gain drift

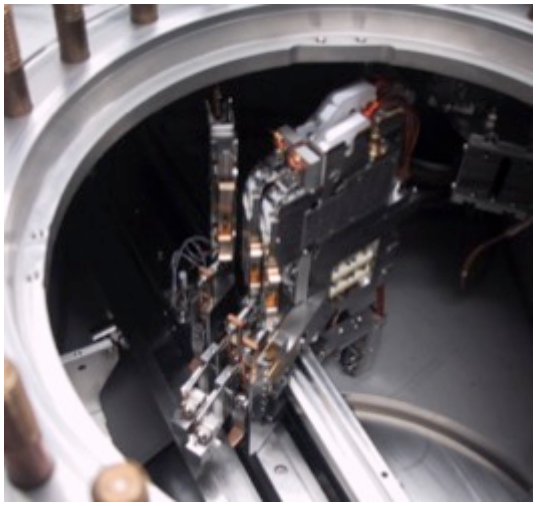
Series of dynodes (N~20): each ejects 2-3 electrons
$10^8$ electrons produced per single ion – detected as an electronic pulse

# 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)

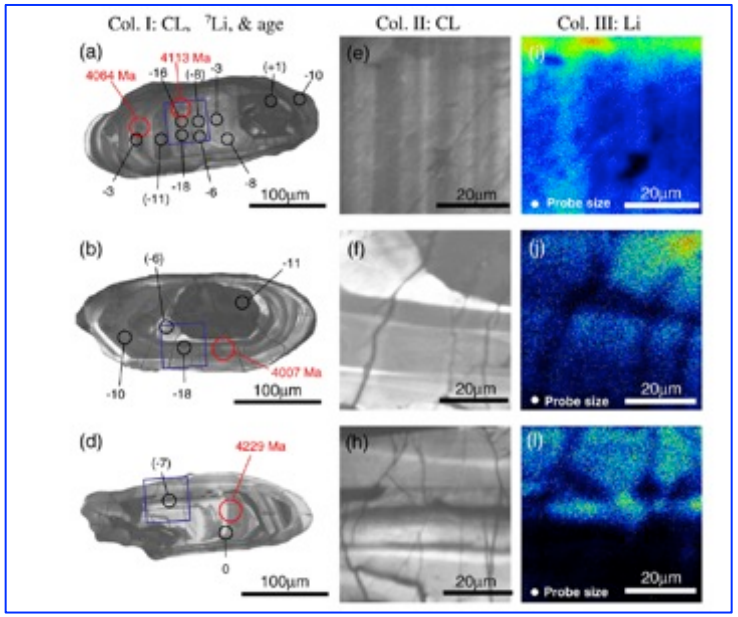
Direct Ion Image:

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-HR$^3$

**Analytical improvement**

- FC amplifier pump (2010)
- Exit slit modifications (2010, 2016)
- Large sample holder (2012)
- FC amplifier upgrade (2016, Cameca)
- RF Plasma Source (2017, Cameca)

**Small spot (≤ 2 µm) analyses**

- Turbo pump dampers (2011)
- NanoDeflector (2014)

**Efficiency and easy operations**

- Sample chamber camera (2008)
- Six sample airlock (2009, Cameca

**Sample navigation and imaging**

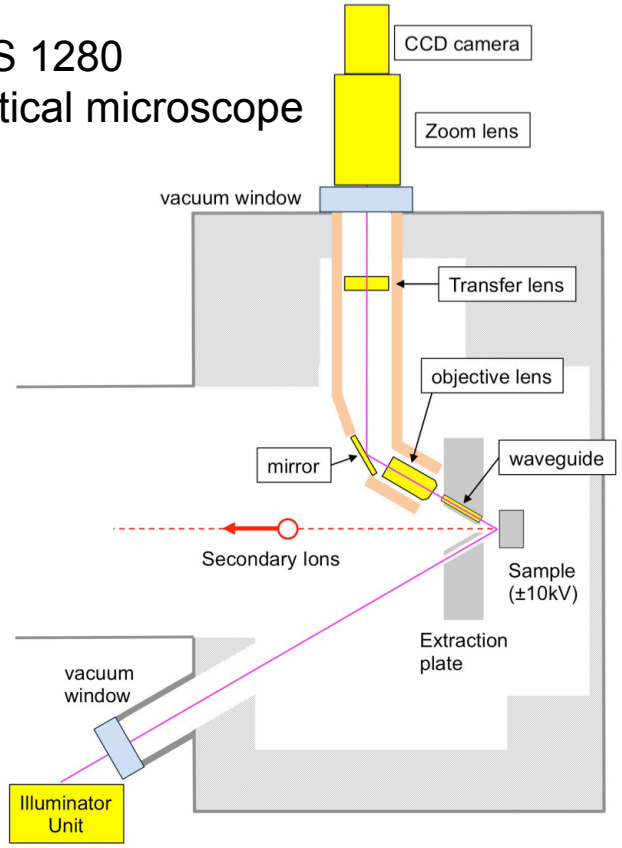
- Blue light illumination (2009)
- UV light illumination (2011)
- Software "Badgerscope©" (2012)

Adapted to newest IMS 1300-HR$^3$

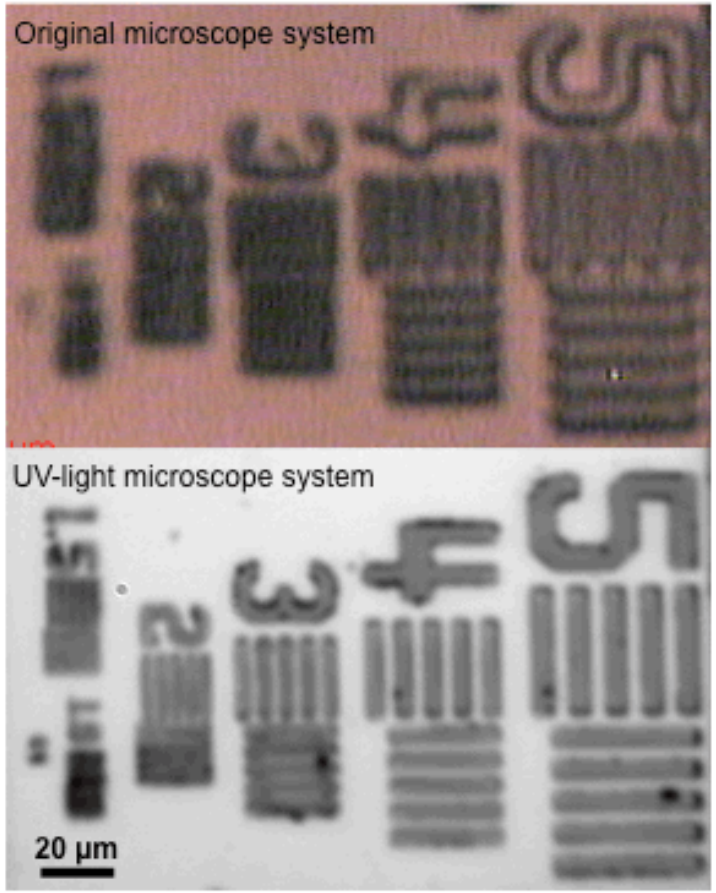
*Mostly in-house modifications*

# Modification of WiscSIMS IMS 1280 (UV light microscope, 2011)

IMS 1280
Optical microscope




Kita et al. (2015, JAAS)



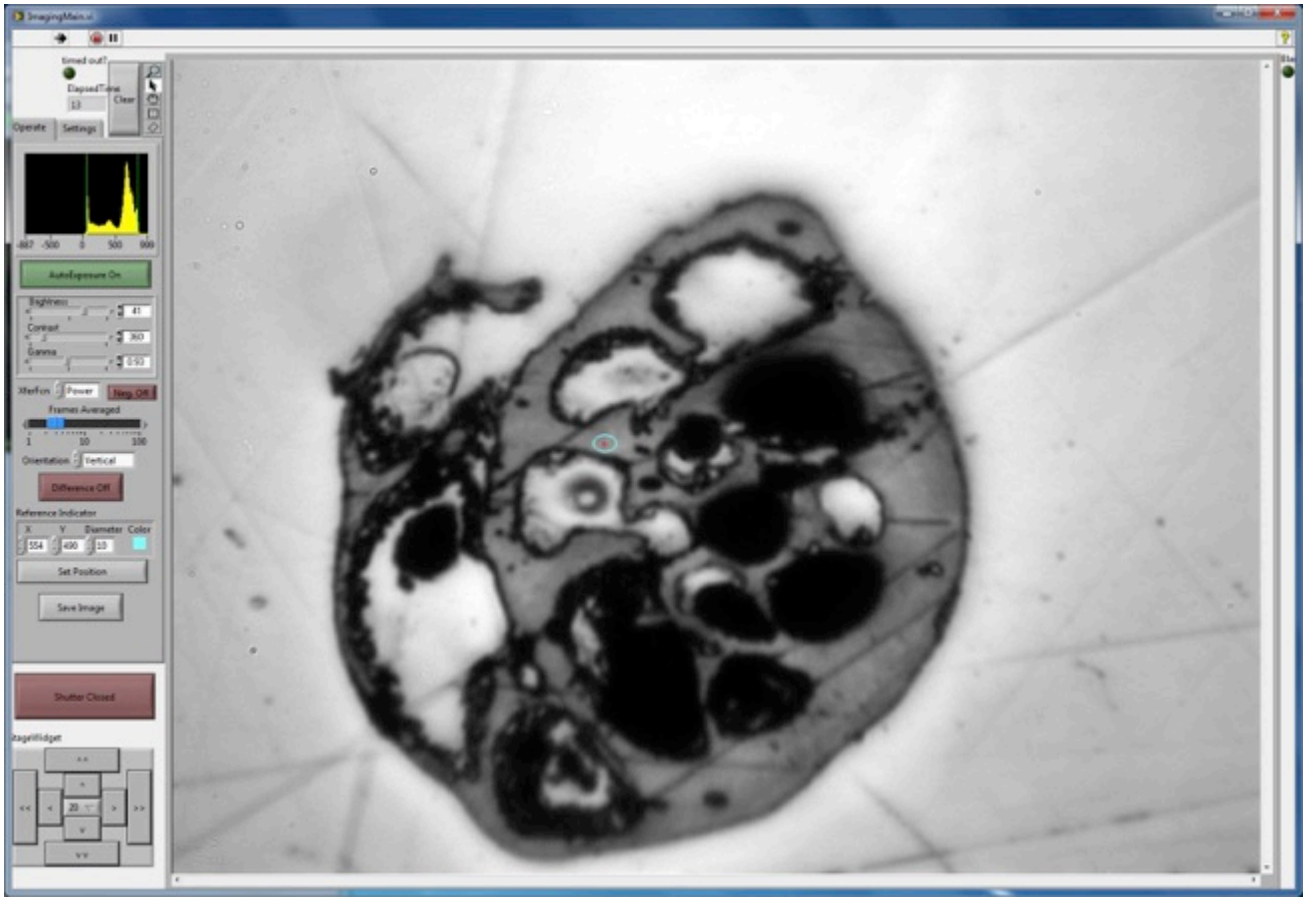

Original:
White halogen lump

Resolution ~3.5 µm
Chromatic abberation

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

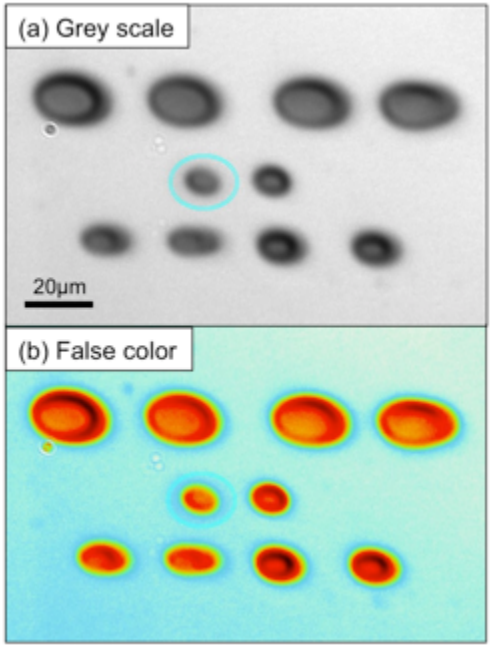
* Replaced multiple optical components.

# New sample viewing software “Badgerscope©” (2012)



**New software to view HD-camera**

Image processing



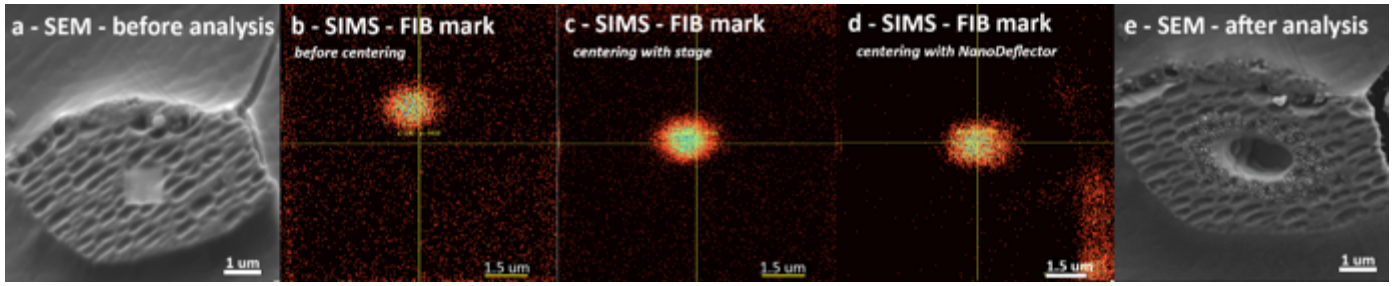

Kita et al. (2015, JAAS)

# 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

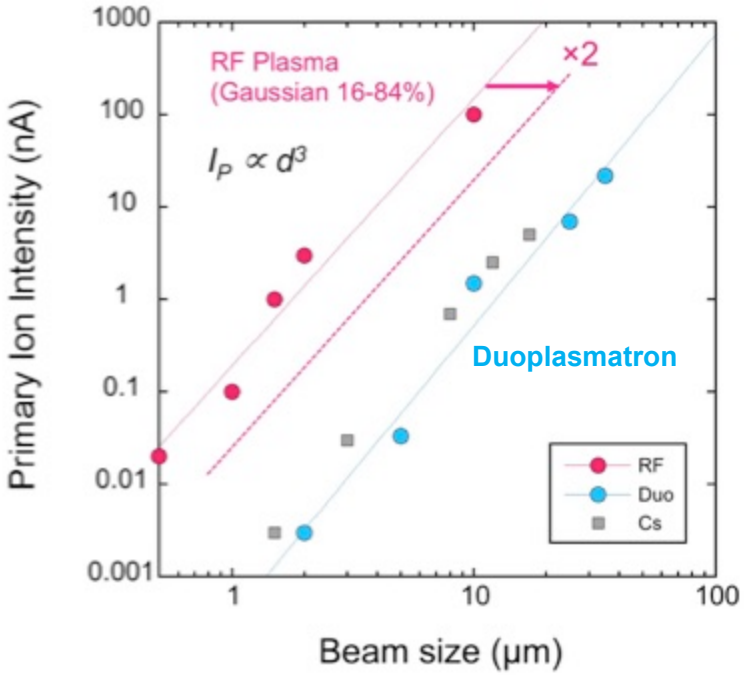
SIMS $^{16}O^-$ ion images of the FIB mark with 10 µm rastering.
(b) before adjustment
(c) after displacement of the stage
(d) after adjustment with the NanoDeflector

(e) SEM image of comet particle after SIMS analysis

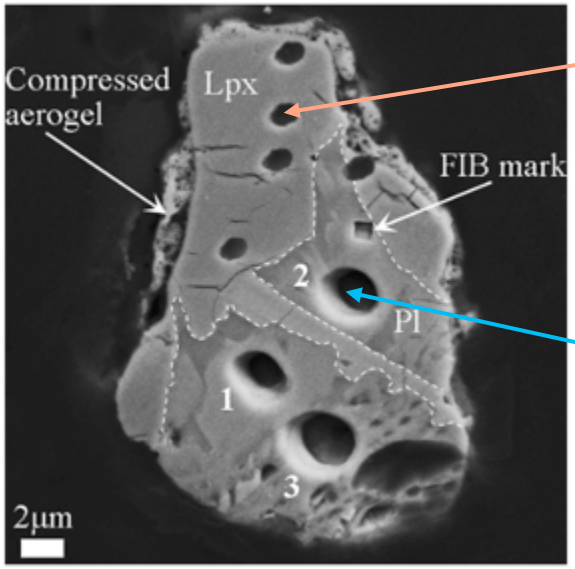
*In-house microprocessor board attached to Cameca original deflector board*

# RF Plasma Source for $O^-/O_2^-$ ions (coming soon!)

x10 increase in intensity




Mg isotope analyses of extraterrestrial materials




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

Oxygen isotope analysis
$Cs^+$: 1-2 μm, 3pA

30 min /spot

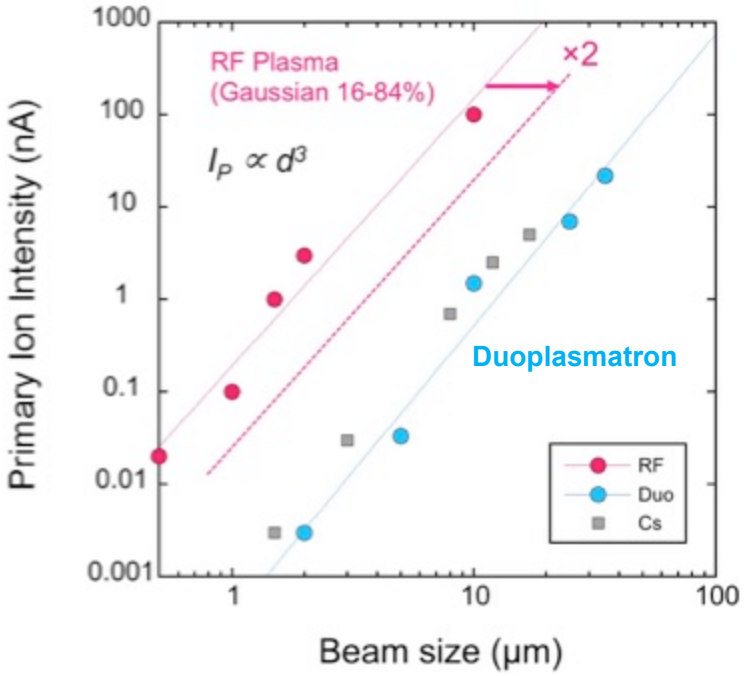
Mg isotope analysis
(MgO~0.5%)
$O^-$: 2-3 μm, 3pA

11 h /spot

Smaller spots ≤ 2 μm
Faster analyses ≤ 1h

# RF Plasma Source for $O^-/O_2^-$ ions (coming soon!)

x10 increase in intensity



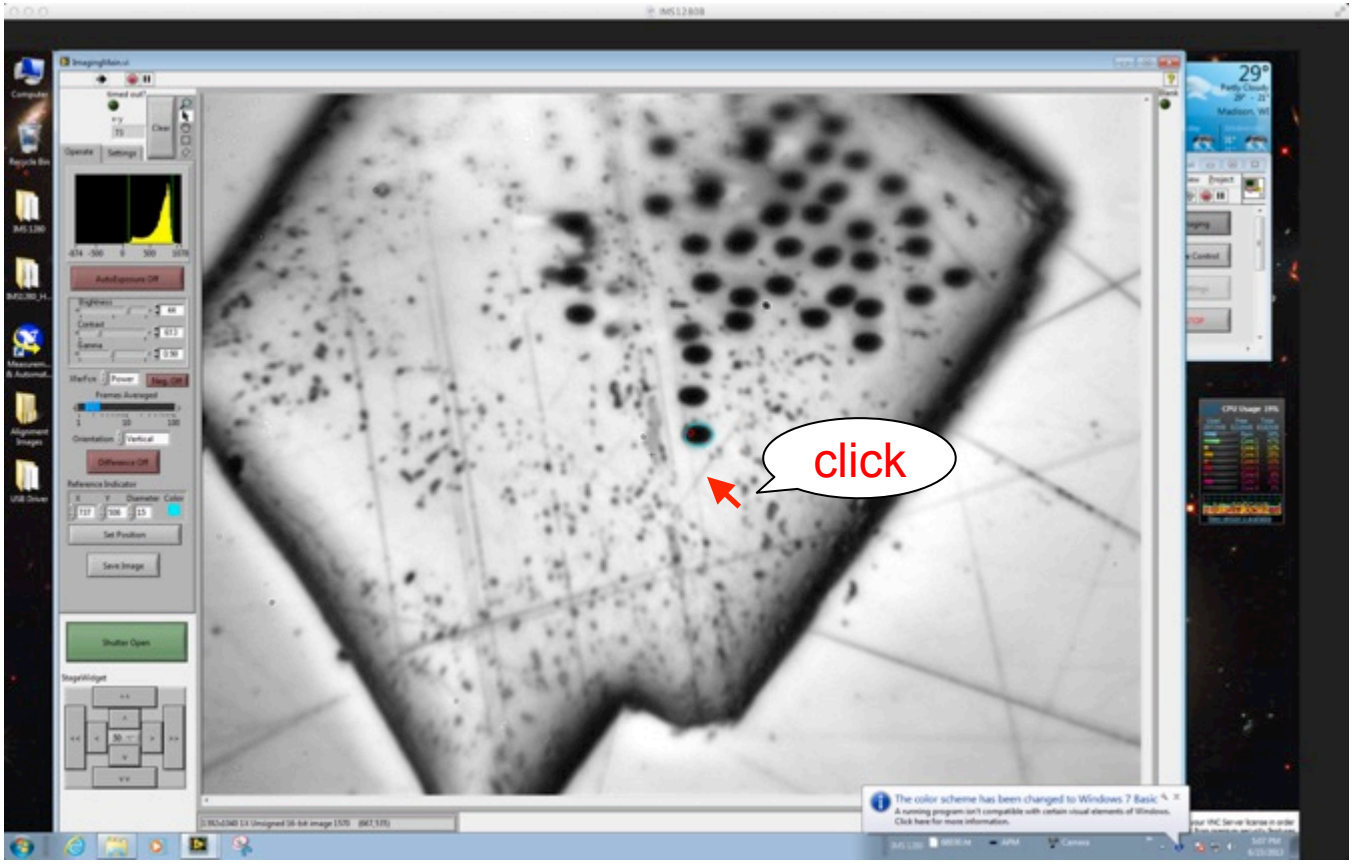

- Cosmochemistry
  - $^{26}Al$-$^{26}Mg$ exitinct nuclide chronology
  - Mg isotope fractionation by evaporation
- U-Pb geochronology (zircon)
- Trace element analyses

Other isotope system in carbonates?

- Mg isotope fractionation
- Ca isotope fractionation
- Sr isotope ($^{87}Sr/^{86}Sr$)

Finally, ….. SIMS analysis is easy

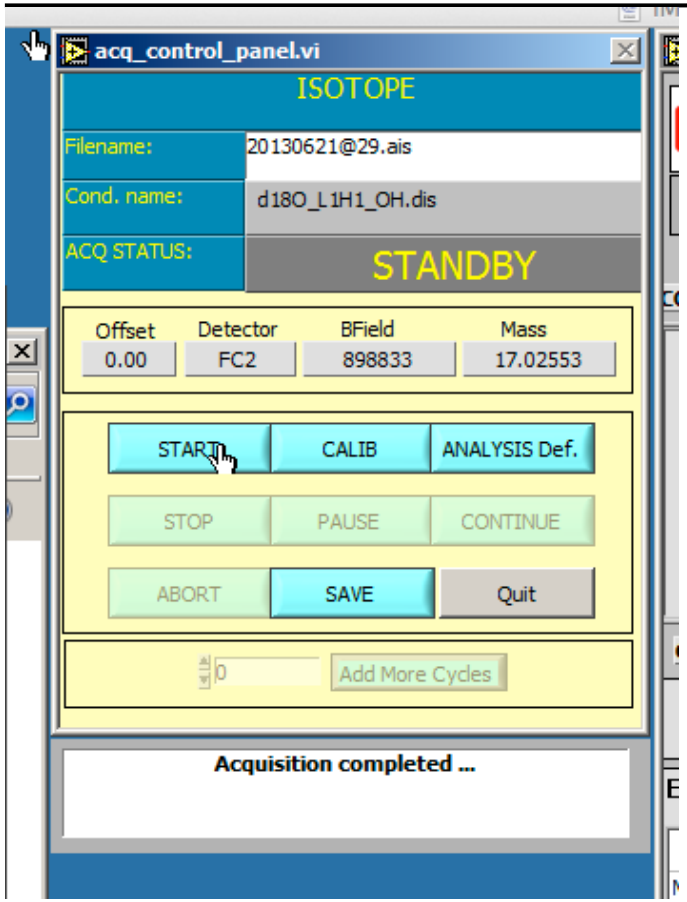
# Oxygen isotope analyses




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




Acquisition takes 3min

Instrument is fully tuned including detector positions and magnetic field.

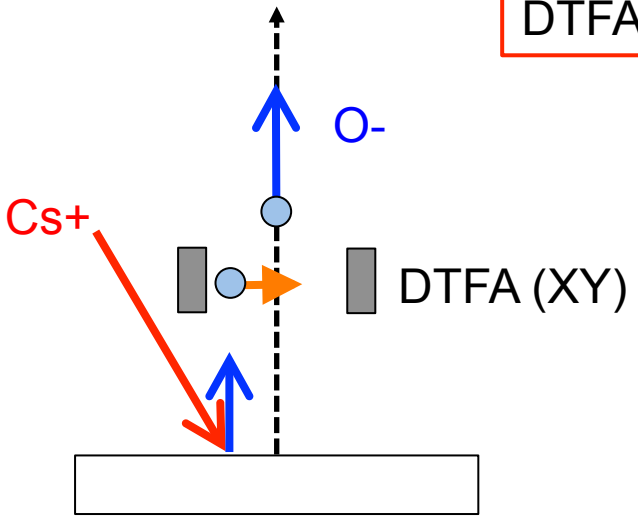
- Move to standard grain in your sample.
- Move to your analysis position.

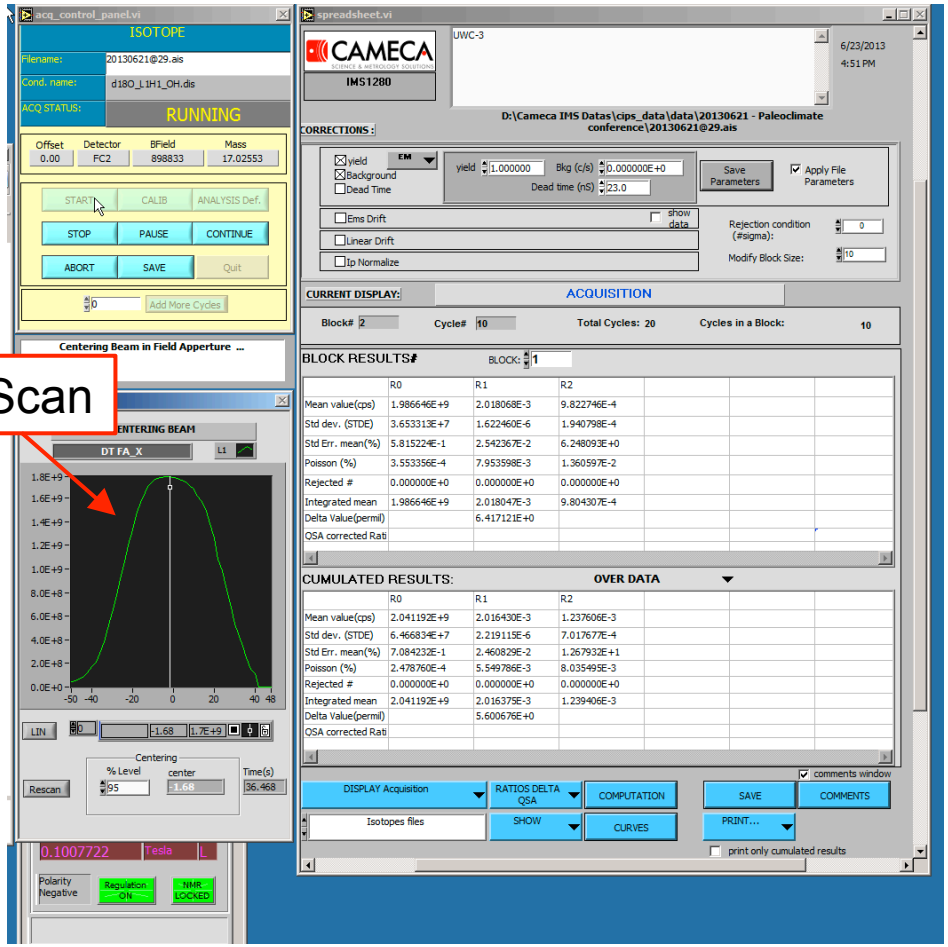
- **Press START**

# Oxygen isotope analyses

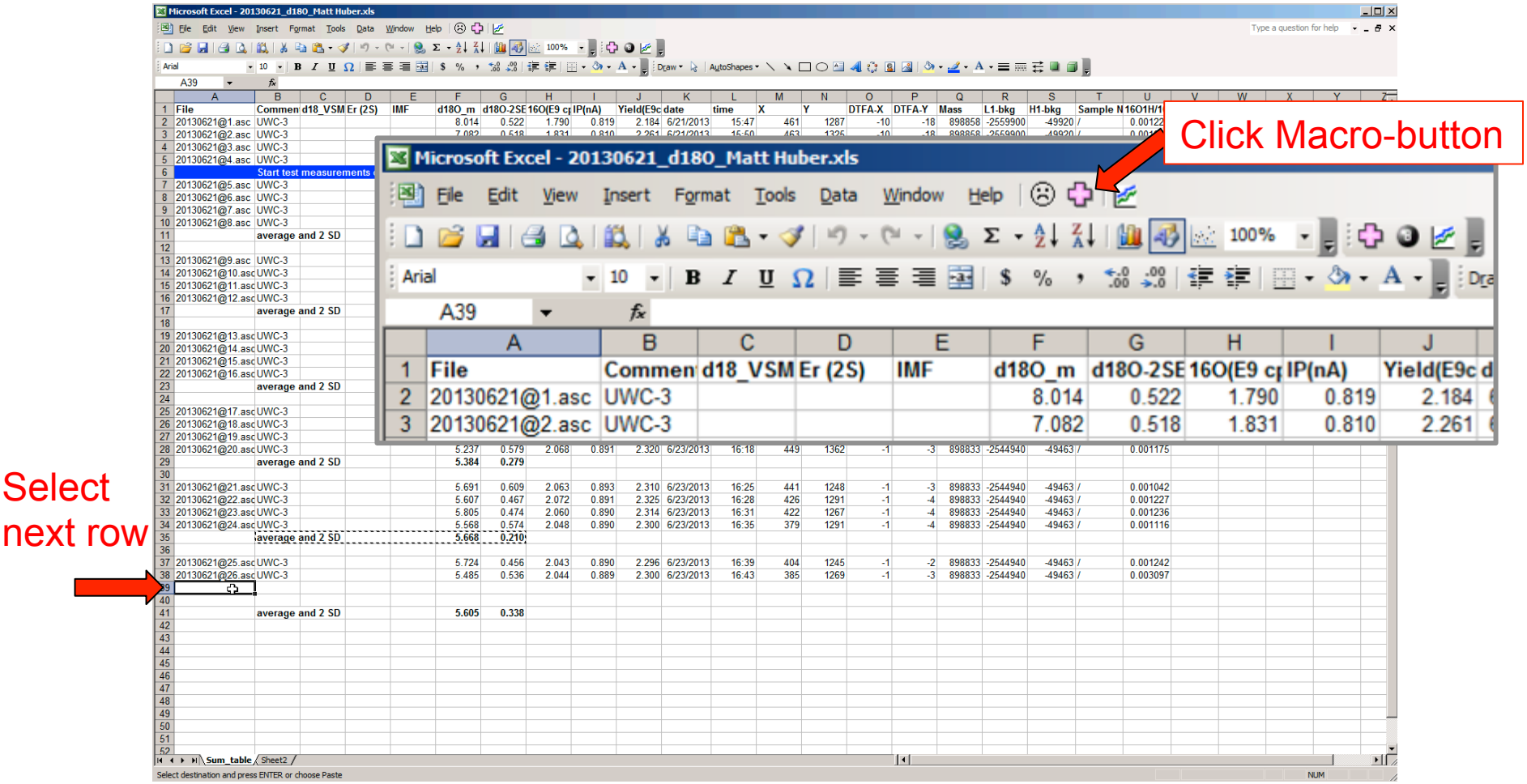
During first 1 min, there will be series of scanning.

This is called “DTFA Scan” that adjustment of primary beam misalignment against secondary ion optical axis.

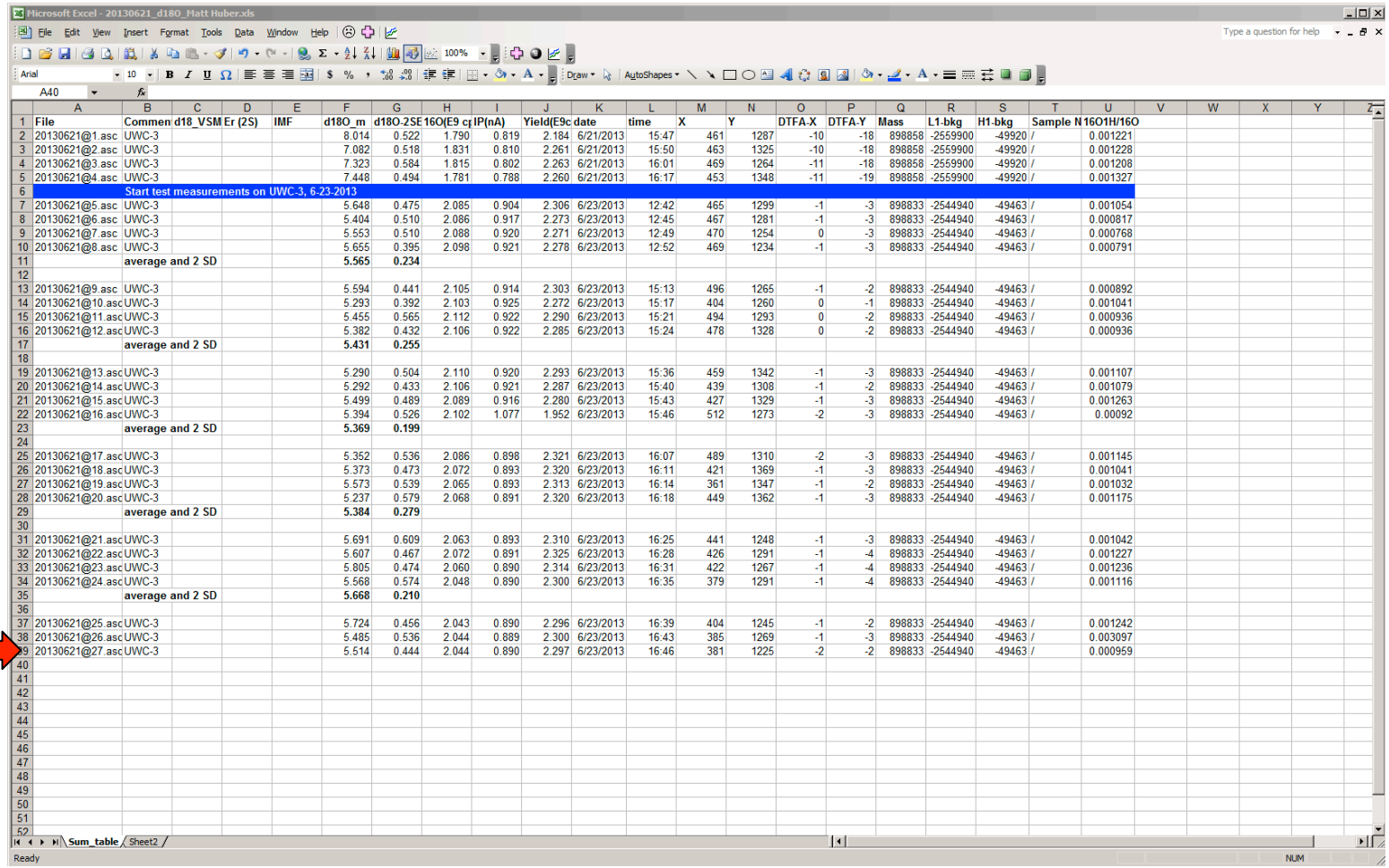


# After the analysis: import new data to excel sheet



# After the analysis: import new data to excel sheet



Microsoft Excel - 20130621_d18O_Matt Huber.xls

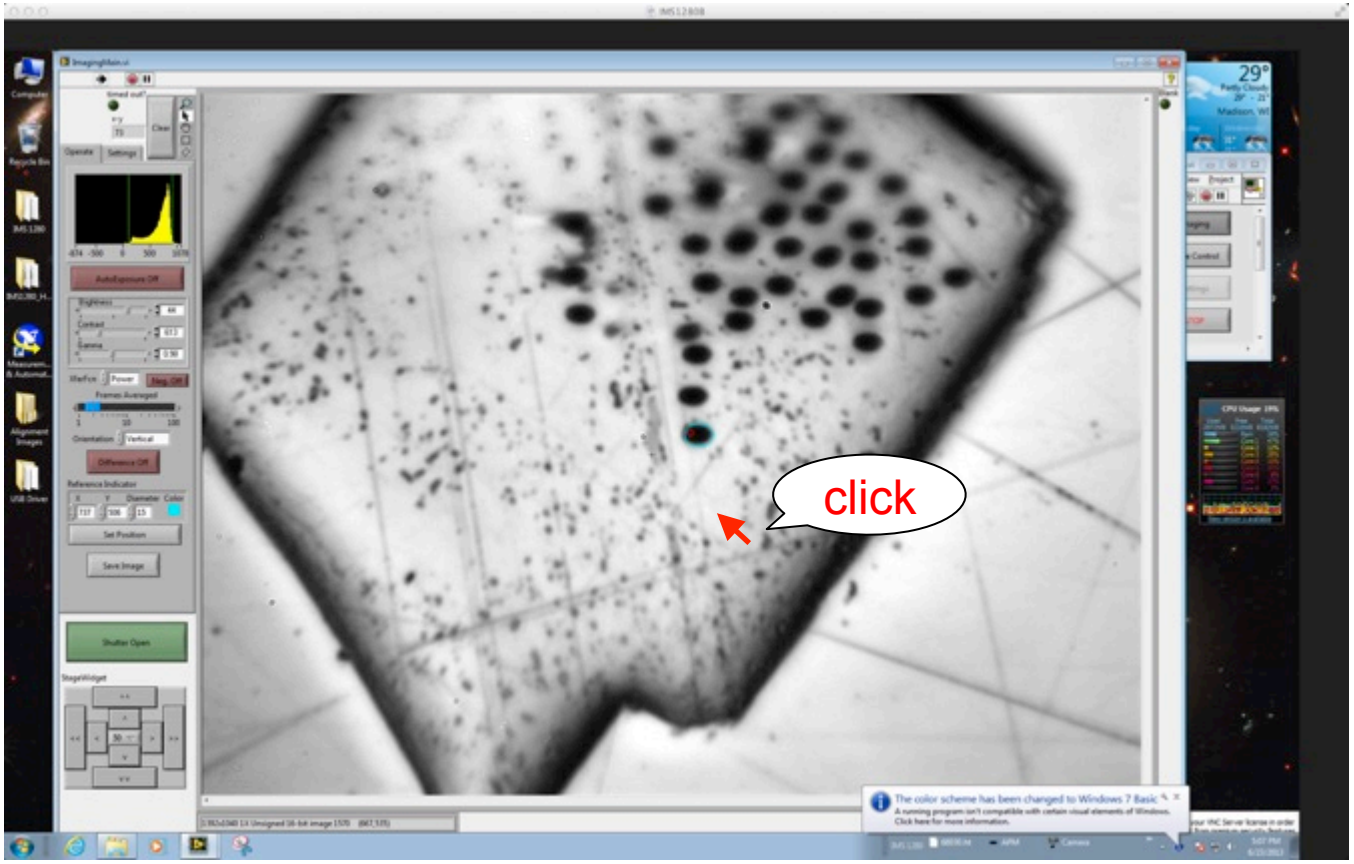
| | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | File | Commen | d18_VSM | Er (2S) | IMF | d18O_m | d18O-2SE | 16O(E9 c | IP(nA) | Yield(E9c | date | time | X | Y | DTFA-X | DTFA-Y | Mass | L1-bkg | H1-bkg | Sample N | 16O1H/16O |
| 2 | 20130621@1.asc | UWC-3 | | | | 8.014 | 0.522 | 1.790 | 0.819 | 2.184 | 6/21/2013 | 15:47 | 461 | 1287 | -10 | -18 | 898858 | -2559900 | -49920 | / | 0.001221 |
| 3 | 20130621@2.asc | UWC-3 | | | | 7.082 | 0.518 | 1.831 | 0.810 | 2.261 | 6/21/2013 | 15:50 | 463 | 1325 | -10 | -18 | 898858 | -2559900 | -49920 | / | 0.001228 |
| 4 | 20130621@3.asc | UWC-3 | | | | 7.323 | 0.584 | 1.815 | 0.802 | 2.263 | 6/21/2013 | 16:01 | 469 | 1264 | -11 | -18 | 898858 | -2559900 | -49920 | / | 0.001208 |
| 5 | 20130621@4.asc | UWC-3 | | | | 7.448 | 0.494 | 1.781 | 0.788 | 2.260 | 6/21/2013 | 16:17 | 453 | 1348 | -11 | -19 | 898858 | -2559900 | -49920 | / | 0.001327 |
| 6 | Start test measurements on UWC-3, 6-23-2013 | | | | | | | | | | | | | | | | | | | | |
| 7 | 20130621@5.asc | UWC-3 | | | | 5.648 | 0.475 | 2.085 | 0.904 | 2.306 | 6/23/2013 | 12:42 | 465 | 1299 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.001054 |
| 8 | 20130621@6.asc | UWC-3 | | | | 5.404 | 0.510 | 2.086 | 0.917 | 2.273 | 6/23/2013 | 12:45 | 467 | 1281 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.000817 |
| 9 | 20130621@7.asc | UWC-3 | | | | 5.553 | 0.510 | 2.088 | 0.920 | 2.271 | 6/23/2013 | 12:49 | 470 | 1254 | 0 | -3 | 898833 | -2544940 | -49463 | / | 0.000768 |
| 10 | 20130621@8.asc | UWC-3 | | | | 5.655 | 0.395 | 2.098 | 0.921 | 2.278 | 6/23/2013 | 12:52 | 469 | 1234 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.000791 |
| 11 | | average and 2 SD | | | | **5.565** | **0.234** | | | | | | | | | | | | | | |
| 12 | | | | | | | | | | | | | | | | | | | | | |
| 13 | 20130621@9.asc | UWC-3 | | | | 5.594 | 0.441 | 2.105 | 0.914 | 2.303 | 6/23/2013 | 15:13 | 496 | 1265 | -1 | -2 | 898833 | -2544940 | -49463 | / | 0.000892 |
| 14 | 20130621@10.asc | UWC-3 | | | | 5.293 | 0.392 | 2.103 | 0.925 | 2.272 | 6/23/2013 | 15:17 | 404 | 1260 | 0 | -1 | 898833 | -2544940 | -49463 | / | 0.001041 |
| 15 | 20130621@11.asc | UWC-3 | | | | 5.455 | 0.565 | 2.112 | 0.922 | 2.290 | 6/23/2013 | 15:21 | 494 | 1293 | 0 | -2 | 898833 | -2544940 | -49463 | / | 0.000936 |
| 16 | 20130621@12.asc | UWC-3 | | | | 5.382 | 0.432 | 2.106 | 0.922 | 2.285 | 6/23/2013 | 15:24 | 478 | 1328 | 0 | -2 | 898833 | -2544940 | -49463 | / | 0.000936 |
| 17 | | average and 2 SD | | | | **5.431** | **0.255** | | | | | | | | | | | | | | |
| 18 | | | | | | | | | | | | | | | | | | | | | |
| 19 | 20130621@13.asc | UWC-3 | | | | 5.290 | 0.504 | 2.110 | 0.920 | 2.293 | 6/23/2013 | 15:36 | 459 | 1342 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.001107 |
| 20 | 20130621@14.asc | UWC-3 | | | | 5.292 | 0.433 | 2.106 | 0.921 | 2.287 | 6/23/2013 | 15:40 | 439 | 1308 | -1 | -2 | 898833 | -2544940 | -49463 | / | 0.001079 |
| 21 | 20130621@15.asc | UWC-3 | | | | 5.499 | 0.489 | 2.089 | 0.916 | 2.280 | 6/23/2013 | 15:43 | 427 | 1329 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.001263 |
| 22 | 20130621@16.asc | UWC-3 | | | | 5.394 | 0.526 | 2.102 | 1.077 | 1.952 | 6/23/2013 | 15:46 | 512 | 1273 | -2 | -3 | 898833 | -2544940 | -49463 | / | 0.00092 |
| 23 | | average and 2 SD | | | | **5.369** | **0.199** | | | | | | | | | | | | | | |
| 24 | | | | | | | | | | | | | | | | | | | | | |
| 25 | 20130621@17.asc | UWC-3 | | | | 5.352 | 0.536 | 2.086 | 0.898 | 2.321 | 6/23/2013 | 16:07 | 489 | 1310 | -2 | -3 | 898833 | -2544940 | -49463 | / | 0.001145 |
| 26 | 20130621@18.asc | UWC-3 | | | | 5.373 | 0.473 | 2.072 | 0.893 | 2.320 | 6/23/2013 | 16:11 | 421 | 1369 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.001041 |
| 27 | 20130621@19.asc | UWC-3 | | | | 5.573 | 0.539 | 2.065 | 0.893 | 2.313 | 6/23/2013 | 16:14 | 361 | 1347 | -1 | -2 | 898833 | -2544940 | -49463 | / | 0.001032 |
| 28 | 20130621@20.asc | UWC-3 | | | | 5.237 | 0.579 | 2.068 | 0.891 | 2.320 | 6/23/2013 | 16:18 | 449 | 1362 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.001175 |
| 29 | | average and 2 SD | | | | **5.384** | **0.279** | | | | | | | | | | | | | | |
| 30 | | | | | | | | | | | | | | | | | | | | | |
| 31 | 20130621@21.asc | UWC-3 | | | | 5.691 | 0.609 | 2.063 | 0.893 | 2.310 | 6/23/2013 | 16:25 | 441 | 1248 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.001042 |
| 32 | 20130621@22.asc | UWC-3 | | | | 5.607 | 0.467 | 2.072 | 0.891 | 2.325 | 6/23/2013 | 16:28 | 426 | 1291 | -1 | -4 | 898833 | -2544940 | -49463 | / | 0.001227 |
| 33 | 20130621@23.asc | UWC-3 | | | | 5.805 | 0.474 | 2.060 | 0.890 | 2.314 | 6/23/2013 | 16:31 | 422 | 1267 | -1 | -4 | 898833 | -2544940 | -49463 | / | 0.001236 |
| 34 | 20130621@24.asc | UWC-3 | | | | 5.568 | 0.574 | 2.048 | 0.890 | 2.300 | 6/23/2013 | 16:35 | 379 | 1291 | -1 | -4 | 898833 | -2544940 | -49463 | / | 0.001116 |
| 35 | | average and 2 SD | | | | **5.668** | **0.210** | | | | | | | | | | | | | | |
| 36 | | | | | | | | | | | | | | | | | | | | | |
| 37 | 20130621@25.asc | UWC-3 | | | | 5.724 | 0.456 | 2.043 | 0.890 | 2.296 | 6/23/2013 | 16:39 | 404 | 1245 | -1 | -2 | 898833 | -2544940 | -49463 | / | 0.001242 |
| 38 | 20130621@26.asc | UWC-3 | | | | 5.485 | 0.536 | 2.044 | 0.889 | 2.300 | 6/23/2013 | 16:43 | 385 | 1269 | -1 | -3 | 898833 | -2544940 | -49463 | / | 0.003097 |
| 39 | 20130621@27.asc | UWC-3 | | | | 5.514 | 0.444 | 2.044 | 0.890 | 2.297 | 6/23/2013 | 16:46 | 381 | 1225 | -2 | -2 | 898833 | -2544940 | -49463 | / | 0.000959 |
| 40 | | | | | | | | | | | | | | | | | | | | | |
| 41 | | | | | | | | | | | | | | | | | | | | | |
| 42 | | | | | | | | | | | | | | | | | | | | | |
| 43 | | | | | | | | | | | | | | | | | | | | | |
| 44 | | | | | | | | | | | | | | | | | | | | | |
| 45 | | | | | | | | | | | | | | | | | | | | | |
| 46 | | | | | | | | | | | | | | | | | | | | | |
| 47 | | | | | | | | | | | | | | | | | | | | | |
| 48 | | | | | | | | | | | | | | | | | | | | | |
| 49 | | | | | | | | | | | | | | | | | | | | | |
| 50 | | | | | | | | | | | | | | | | | | | | | |
| 51 | | | | | | | | | | | | | | | | | | | | | |
| 52 | | | | | | | | | | | | | | | | | | | | | |

Sum_table | Sheet2

Ready

NUM

# 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