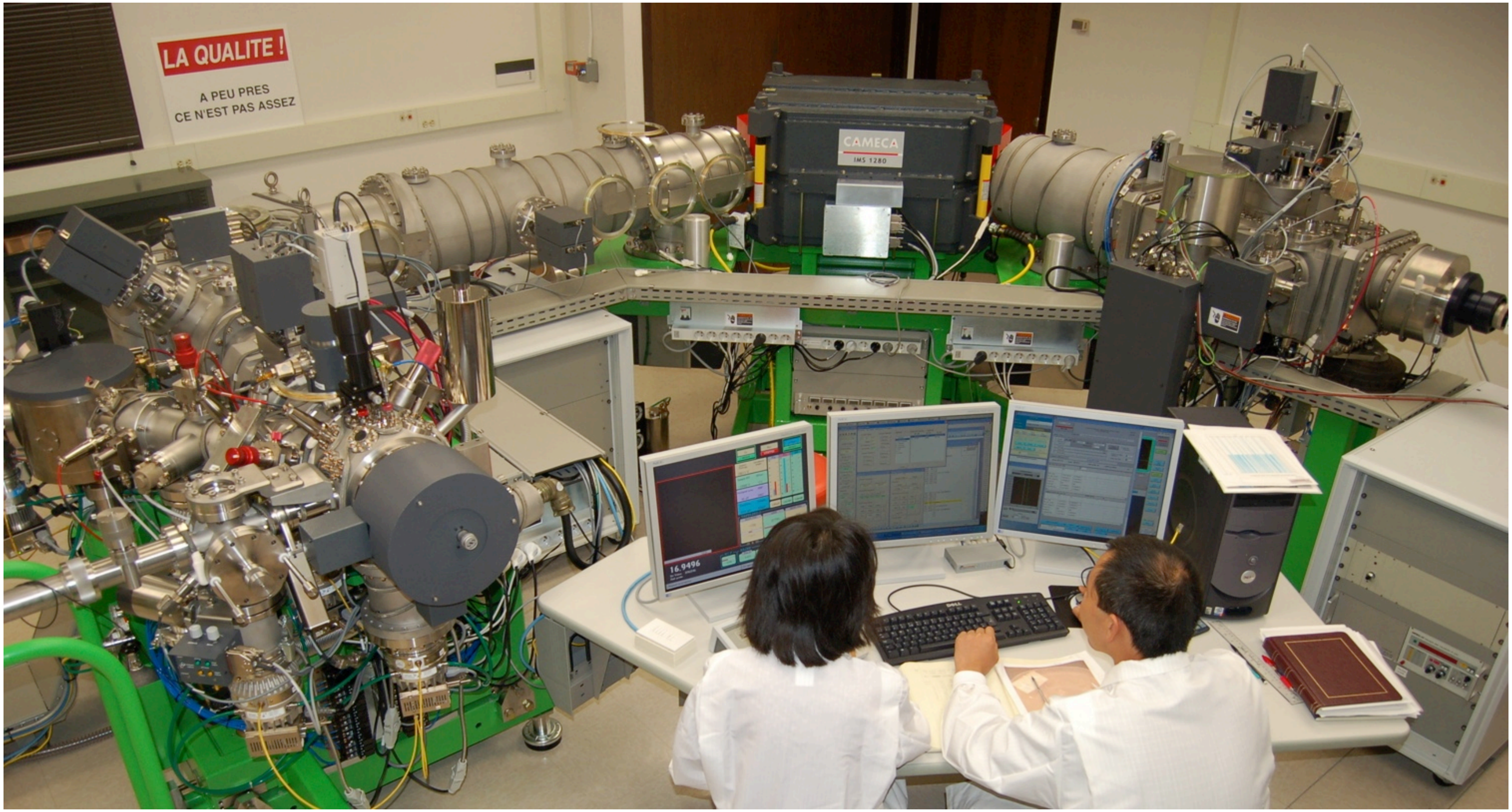
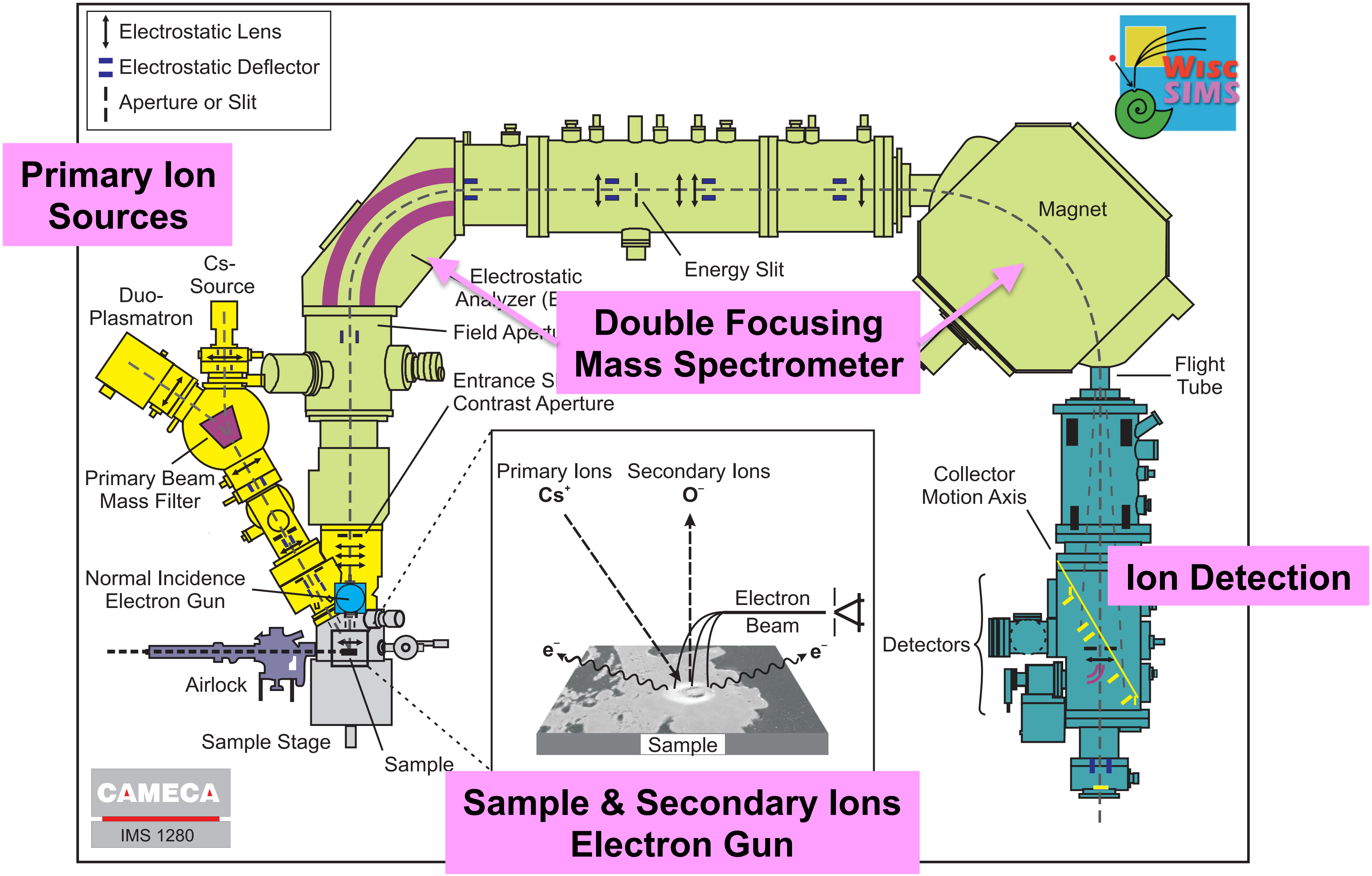
SIMS Basics



Noriko Kita
WiscSIMS, UW-Madison

Secondary Ion Mass Spectrometer: IMS-1280



Secondary Ion Mass Spectrometer

Double Focusing Sector Magnet

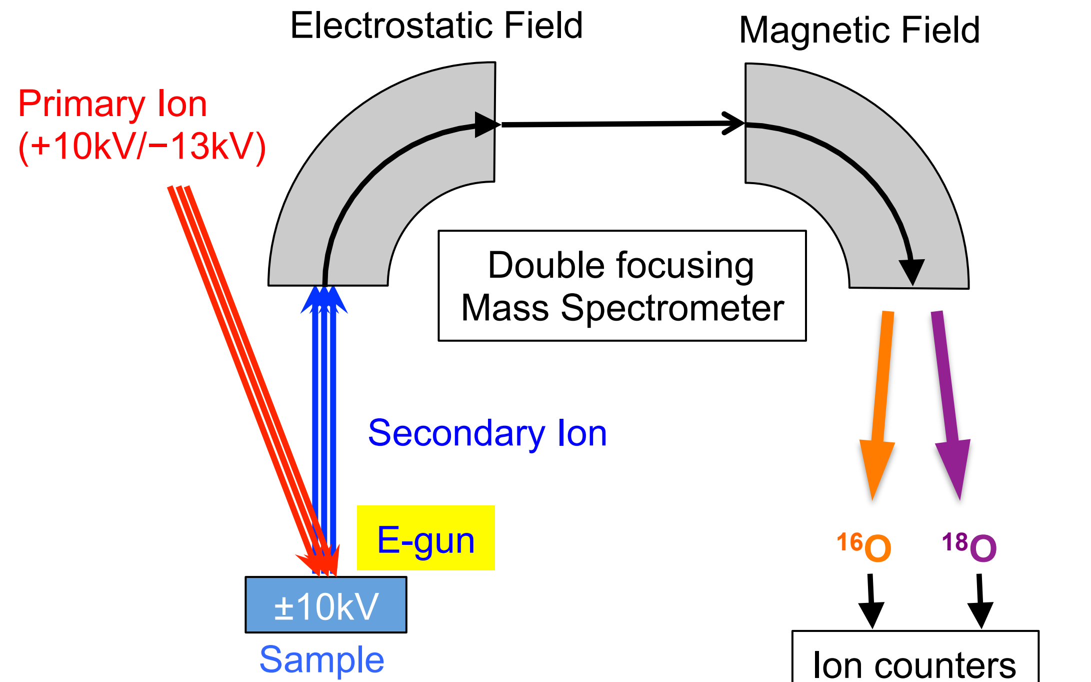
- **IMS1270/1280/1280HR**: Large radius, high mass resolution
  - **Stable isotope**, Geochronology, Nuclear forensic
- NanoSIMS: high spatial resolution (50nm beam), high mass resolution
  - Imaging, biological applications
- SHRIMP: Large radius, high mass resolution
  - Geochronology
- IMF 7f/7fGeo: Conventional SIMS

TOF (Time of flight)

- Shallow depth analysis, thin film

Secondary Ion Mass Spectrometer

Secondary ions are produced by the sputtering of primary ions



Simplified Schematic of SIMS

Surface analysis

- trace element
- elemental mapping
- **isotope ratios**

Analytical volume

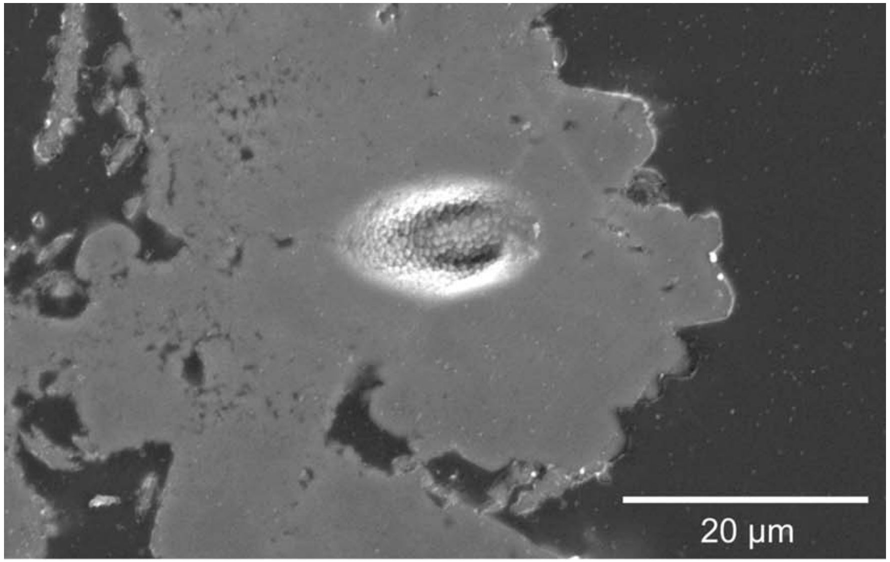
10μm diameter, 1μm depth

1-2 μm

** 0.3 ng to a few pg

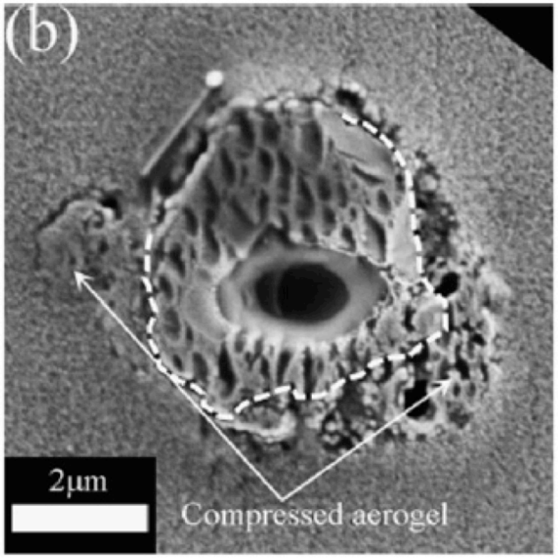
SIMS analysis spots

Cs+ primary beam 10-15 μm spots



Foraminifera; Kozdon et al. (2011)

Cs+ primary beam 1-2 μm spots

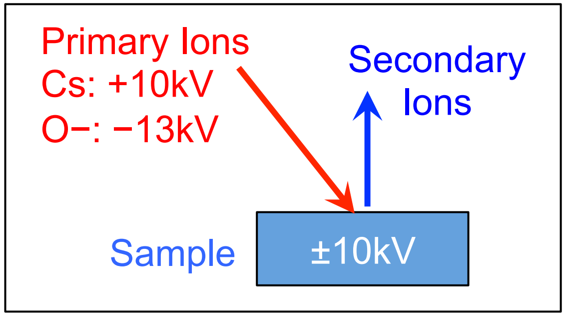


Comet sample return; Nakashima et al. (2012)

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

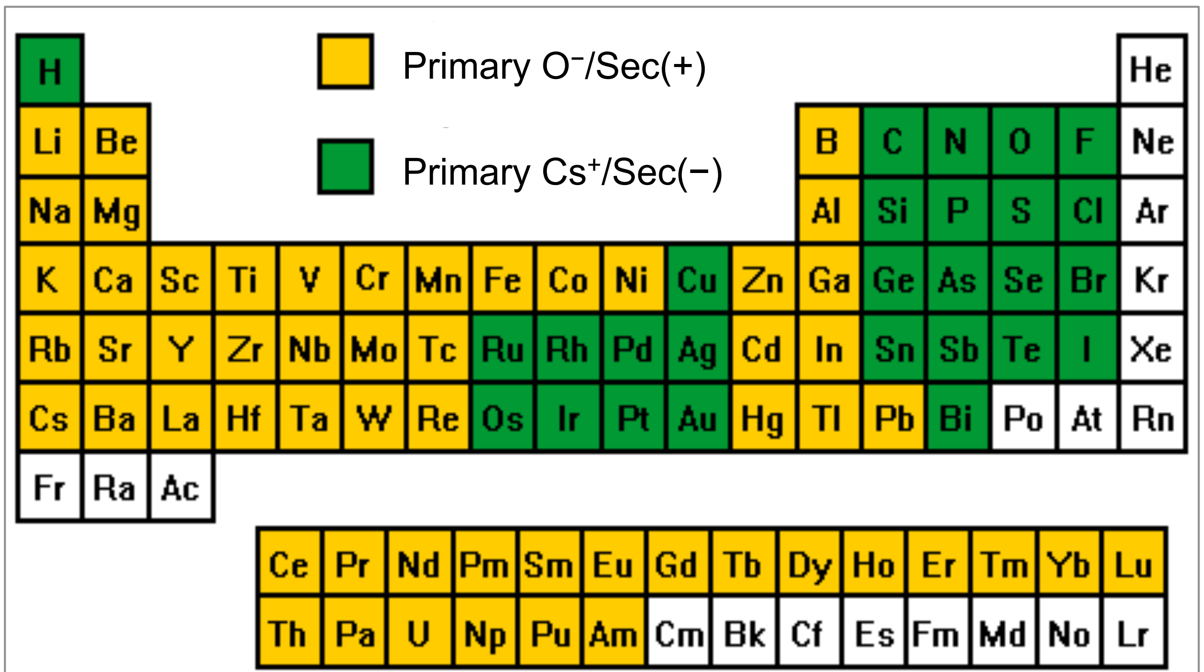
Precisions of oxygen isotope ratios ~ 0.3‰ ------------> 1-2 ‰

Most of elements in periodic table are ionized



Primary Cs+ → Secondary negative ions
Higher electronegativity: O^-, C^-, S^-, Si^-

Primary O^- → Secondary positive ions
Higher ionization tendency: Mg+, Ca+, Pb+



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

- Noble gases do not ionize.
- Nitrogen in carbon bearing phase ionize as CN^-

Ionization efficiency varies significantly from 0.1 to 10%

Secondary Ion Mass Spectrometer: IMS-1280

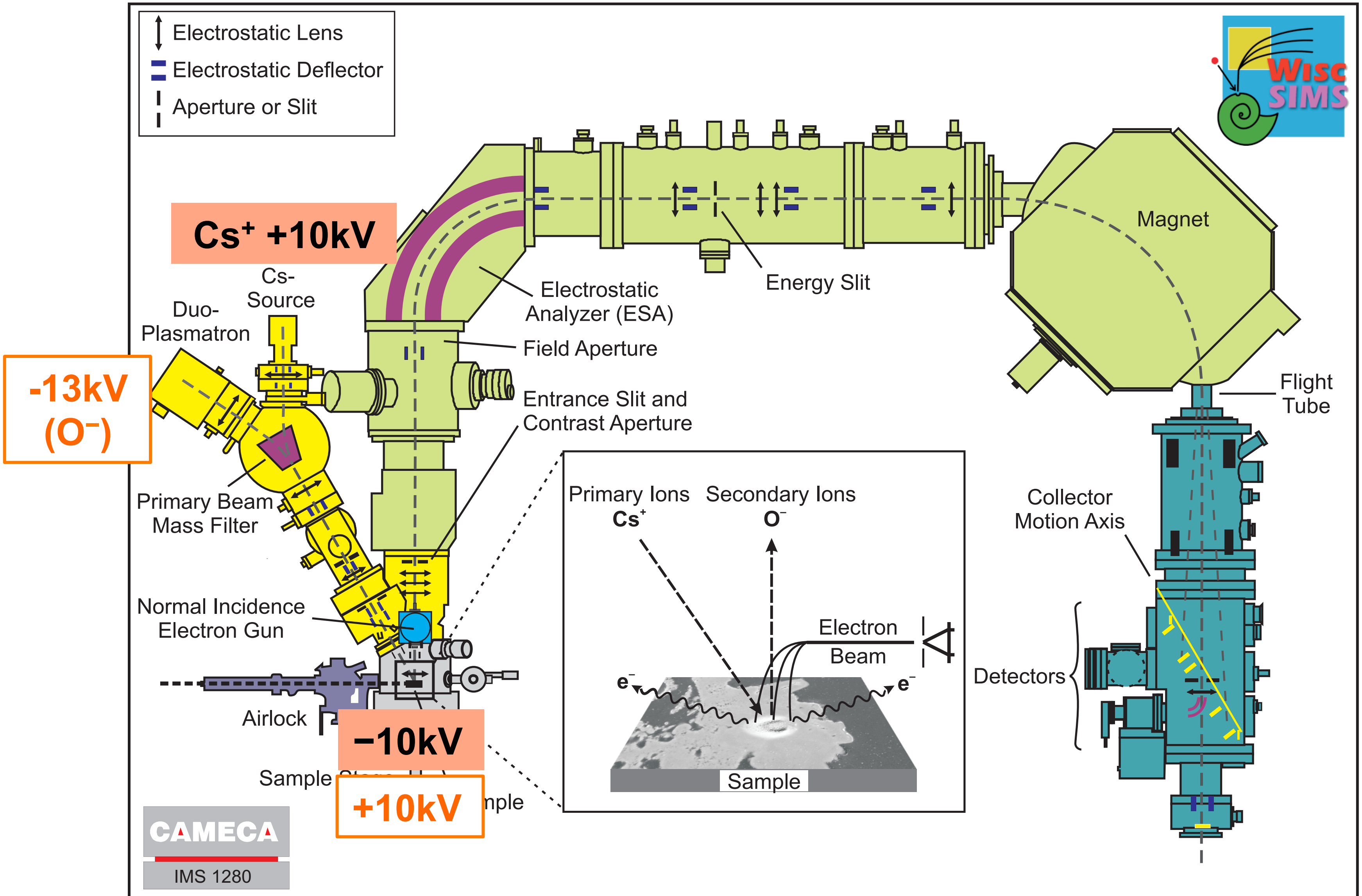
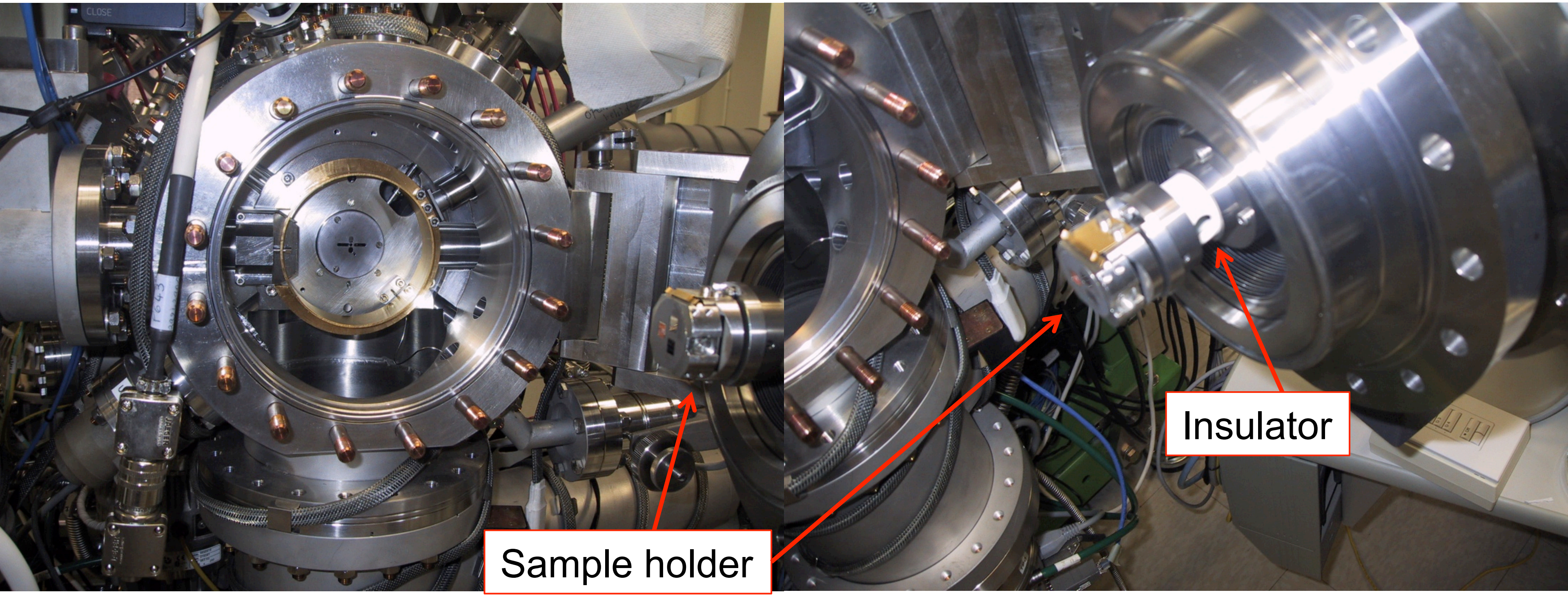
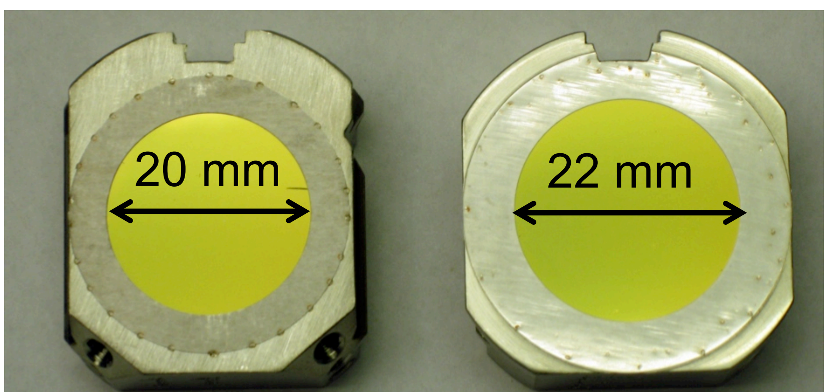


Image after Kozdon et al. 2011

Secondary Ion Mass Spectrometer: IMS-1280

Entrance of secondary optics (Main chamber door is opened)

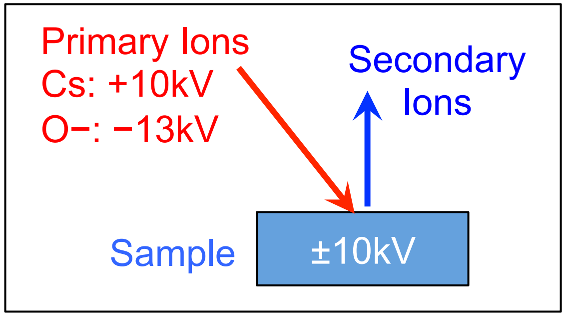




Sample holder is held at ± 10kV

Sample holders
(original 25mm and new 32 mm)

Most of elements in periodic table are ionized



Primary Cs+ → Secondary negative ions
Higher electronegativity: O^-, C^-, S^-, Si^-

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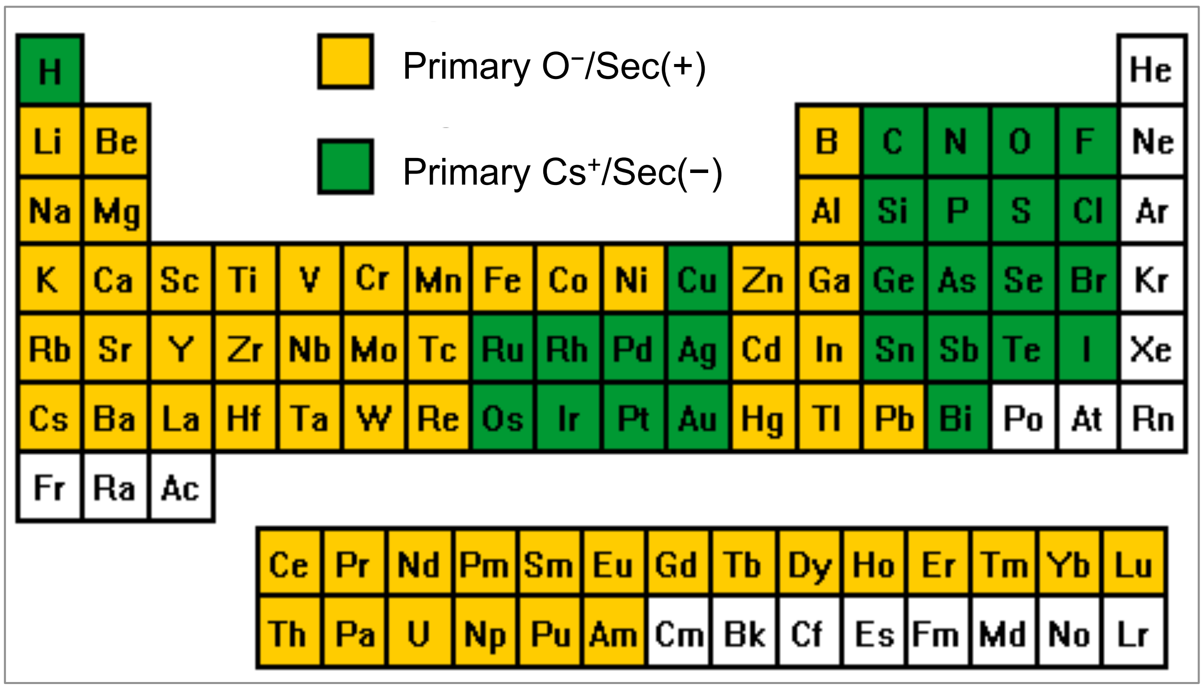
Higher ionization tendency: Mg+, Ca+, Pb+



- Noble gases do not ionize.
- Nitrogen in carbon bearing phase ionize as CN^-

Ionization efficiency varies among elements significantly from 0.1 to 10%

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

Secondary ionization efficiency

Ionization efficiencies = (numbers of secondary ions)/(numbers of atoms sputtered)

O^- in silicate, carbonates, oxide minerals ~10%

C^- in carbonates ≤ 0.3%

Si^- in quartz ~ 1%

Ex. 1) Comparison of secondary ion intensities of calcite ($CaCO_3$) using 10um SIMS spot (Cs^+ ~2nA)

C^- = 2×10^7 cps (=count per second)

O^- = 2×10^9 cps

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

Ex. 2) Comparison of secondary ion intensities of quartz (SiO_2) using 10um SIMS spot (Cs^+ ~2nA)

O^- = 2×10^9 cps

Si^- = 1×10^8 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‰

(These values are from WiscSIMS data)

Detail examination of Sputtering Process

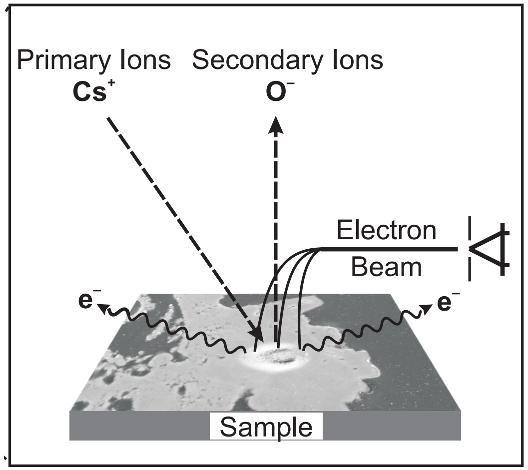
Ejection of electron from sample surface causes charging of sample
--- electron gun

Initial kinetic energy of secondary ions
--- double focusing mass spectrometer

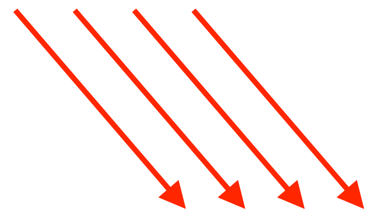
Formation of multiple atomic and molecular ions, divalent ions
--- high mass resolution power by large radius sector magnet

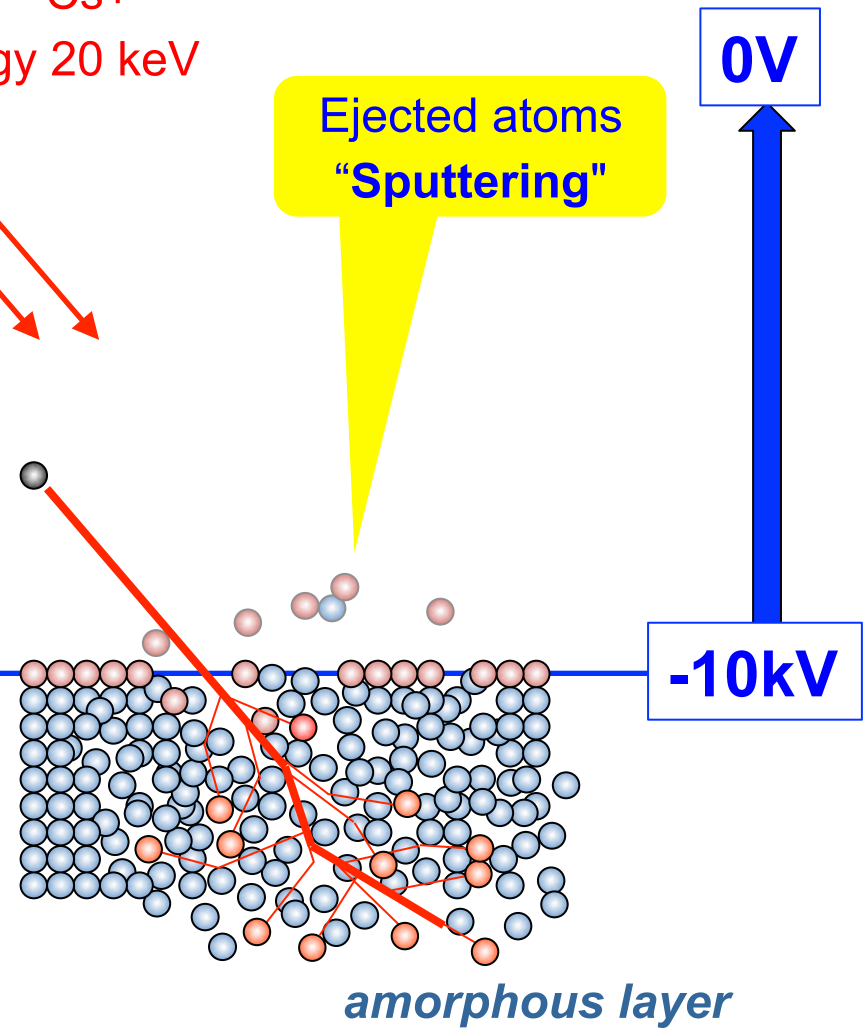
These factors determined the performance of the instrument for high precision stable isotope analyses

Sputtering: Ejection of atoms



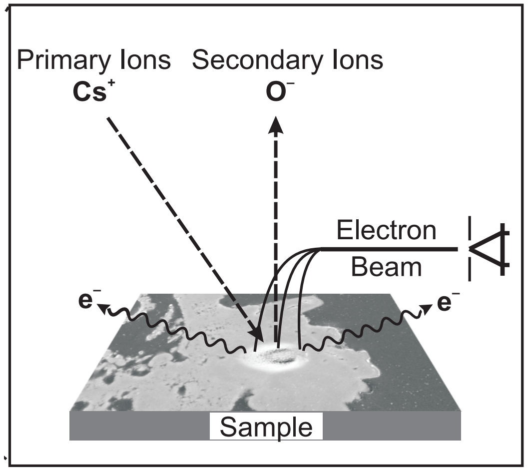
Primary Ion $^{133}Cs^{+}$
Impact energy 20 keV

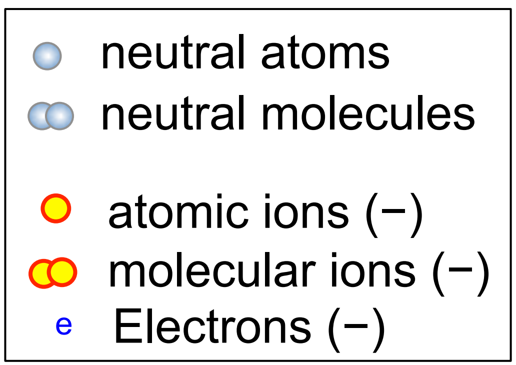




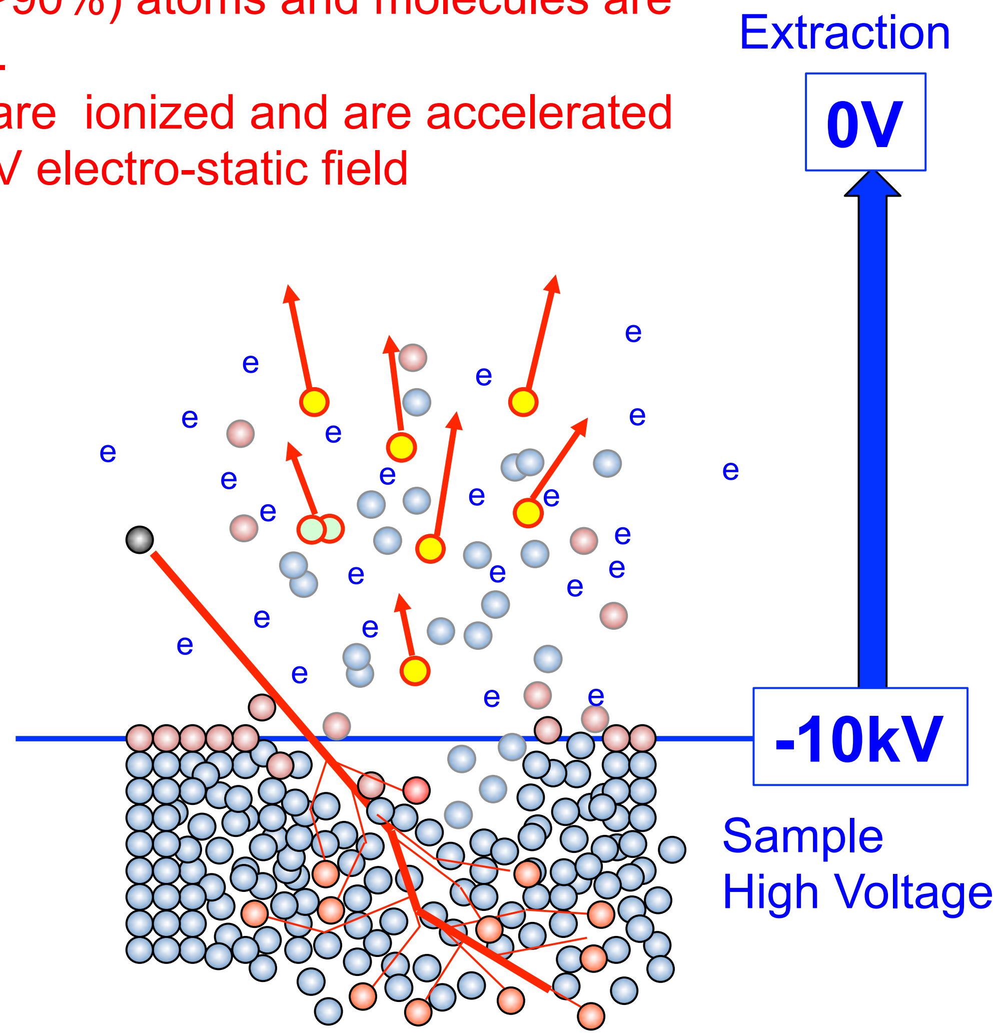
- Primary ions are implanted to the interior of sample.
- Atoms in the sample are displaced by collision cascade. Lattice structures are destroyed and amorphous layer (~30 nm) is formed. Some atoms are ejected from the surface = sputtering

Secondary Ion Generation

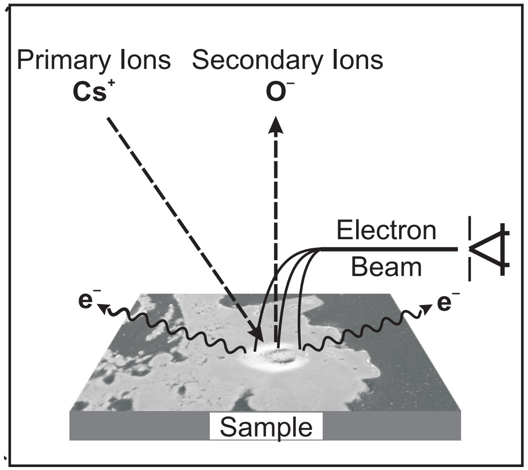




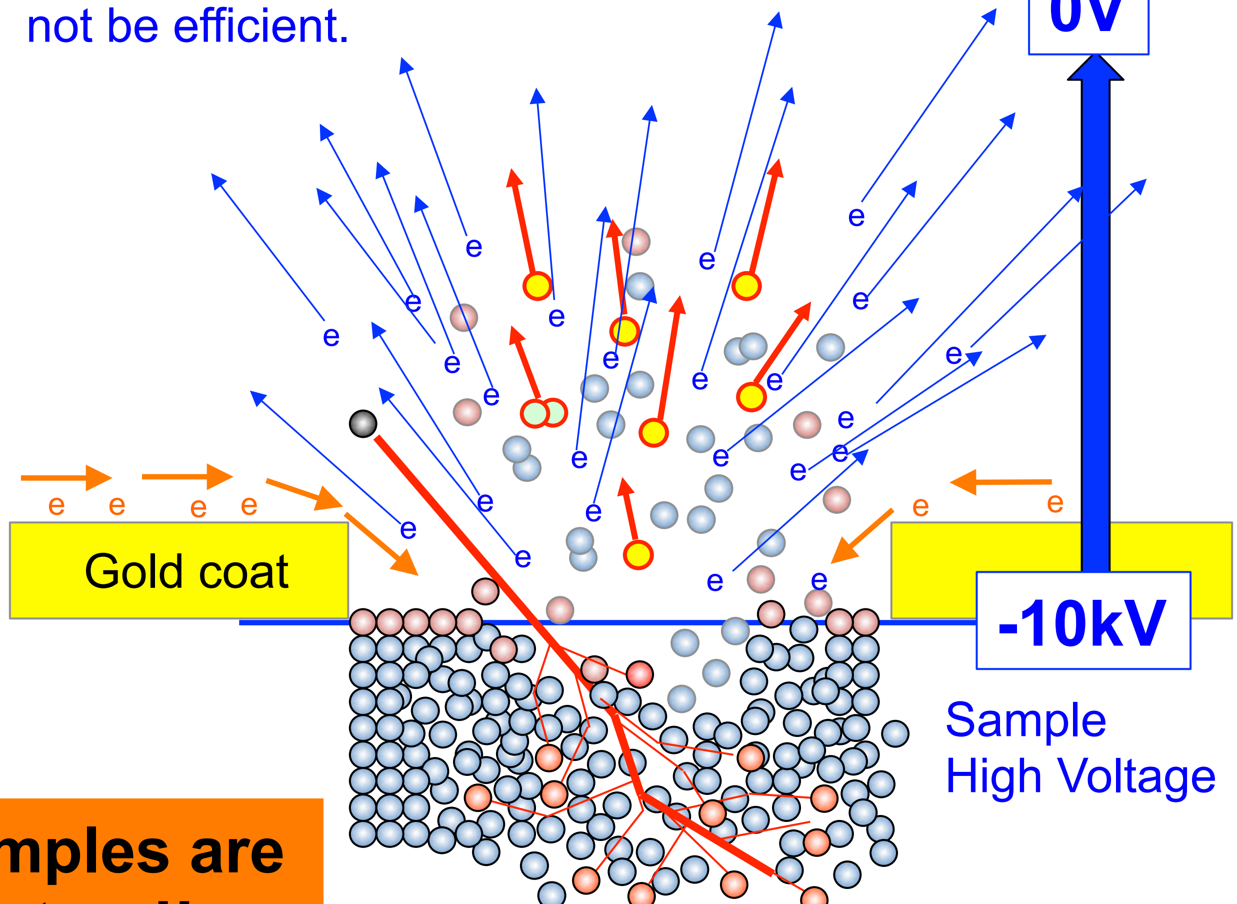
Most (>90%) atoms and molecules are neutral.
Some are ionized and are accelerated by 10kV electro-static field



Sample charging by the loss of electron



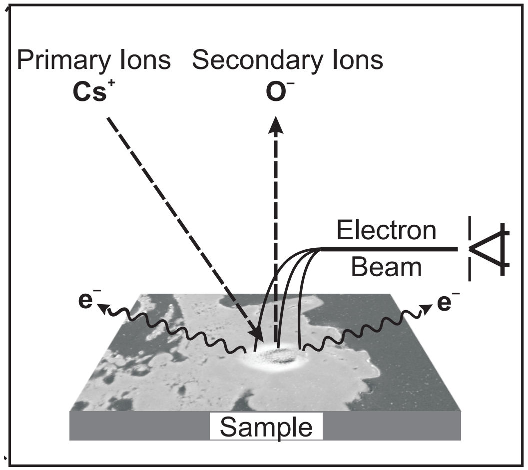
Electron is easily ejected out from the sample by the same -10kV field !
Electron supply through gold coating may not be efficient.



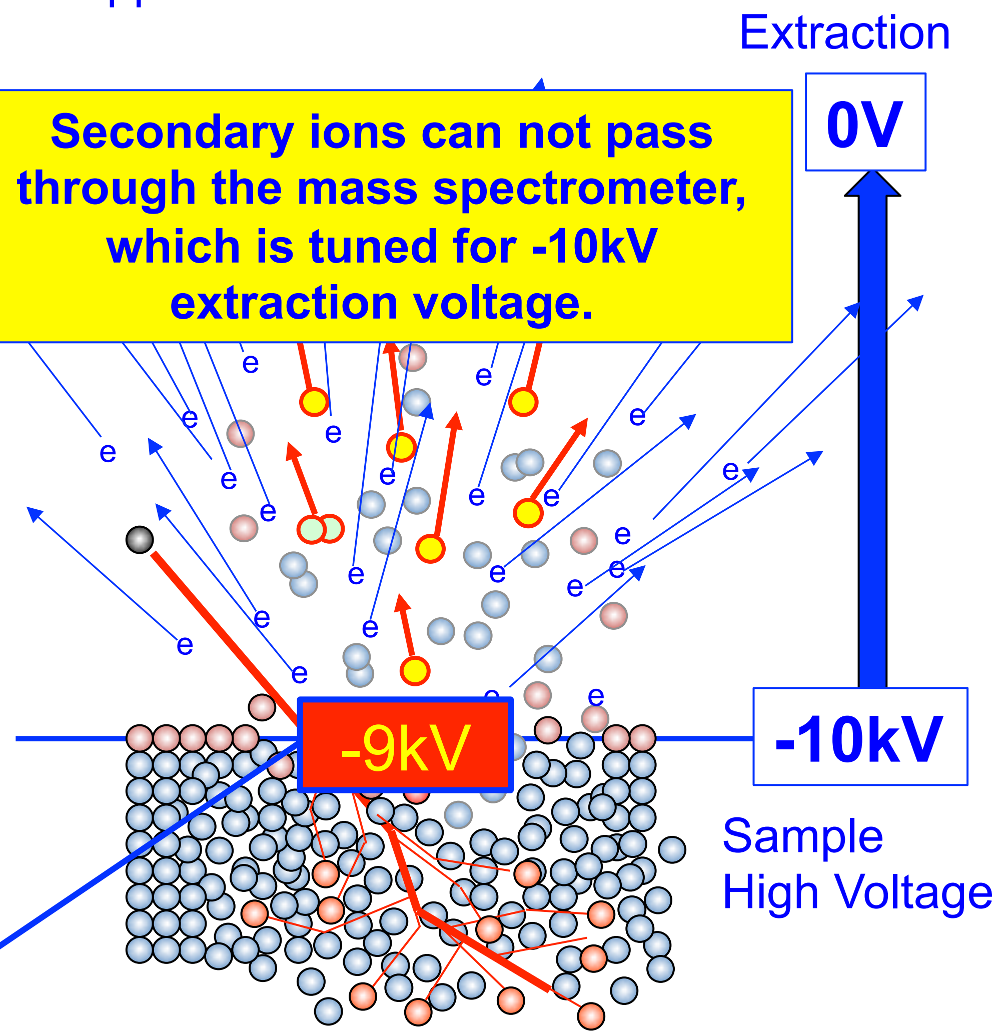
- neutral atoms
- neutral molecules
- atomic ions (−)
- molecular ions (−)
- e Electrons (−)

Your samples are insulators!!

Sample charging by the loss of electron



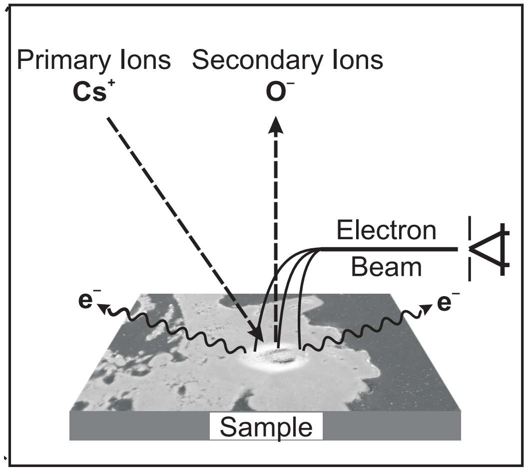
What will happen if electron is lost?



- neutral atoms
- neutral molecules
- atomic ions (−)
- molecular ions (−)
- e Electrons (−)

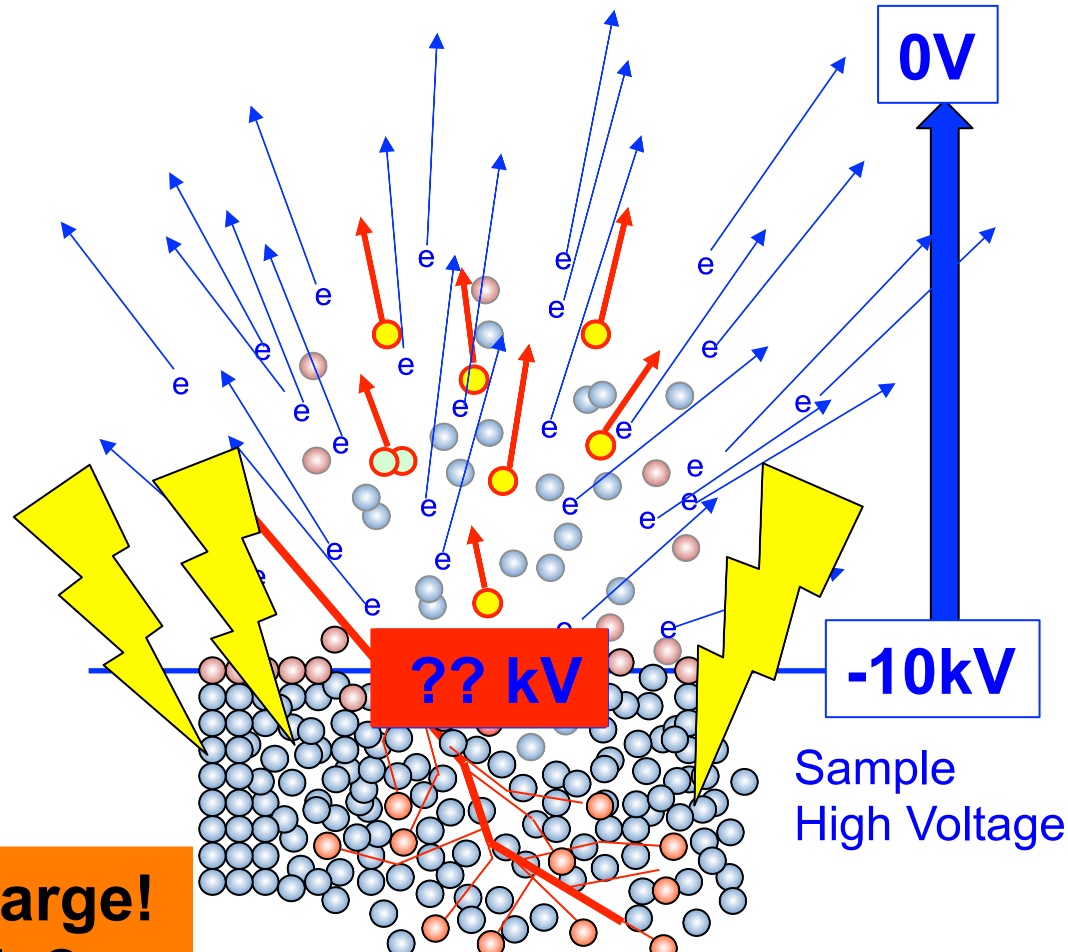
Surface voltage goes up (>-10kV) as it charges up

Sample charging by the loss of electron



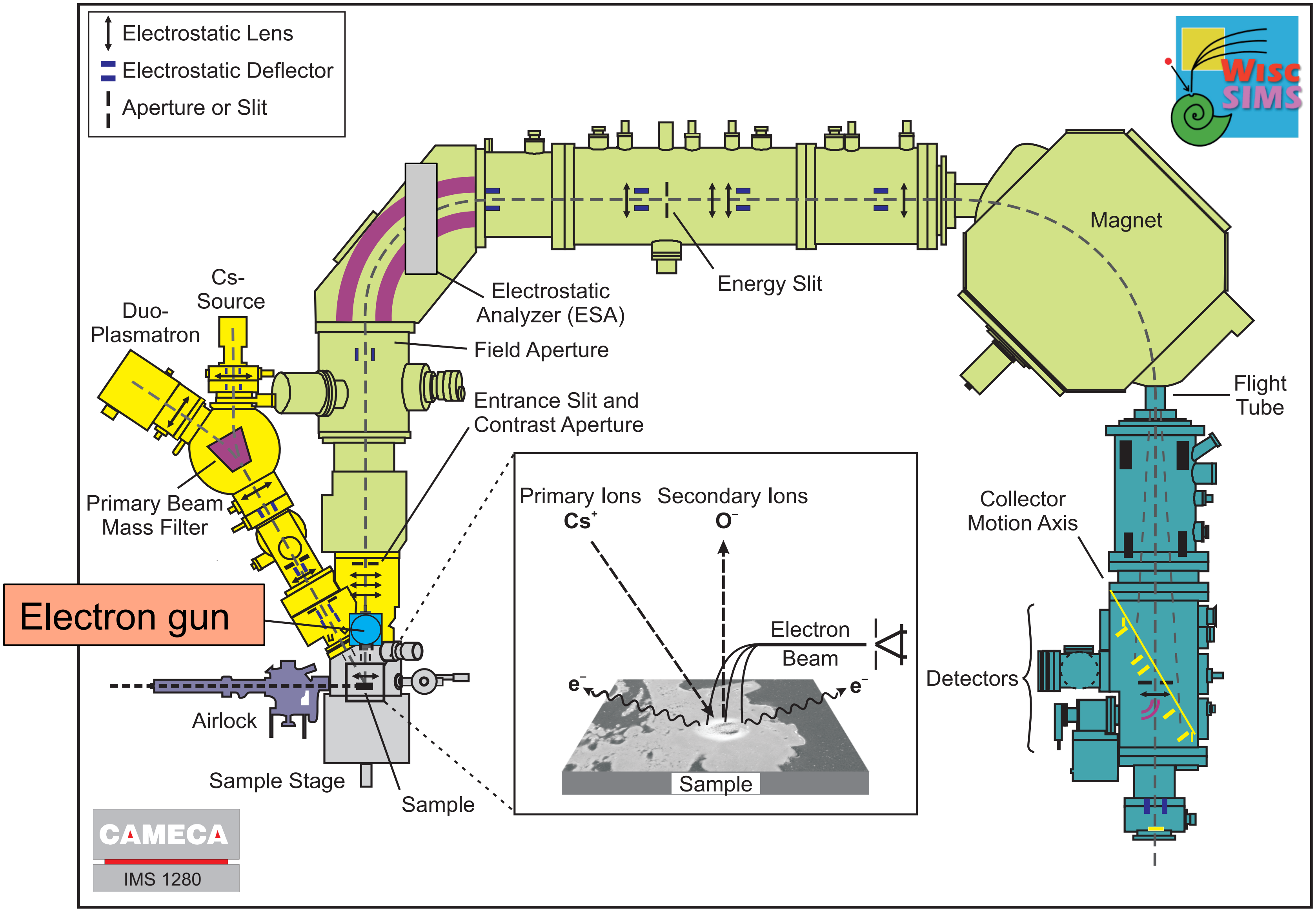
neutral atoms	
neutral molecules	
atomic ions (−)	
molecular ions (−)	
e	Electrons (−)

What would happen if we can not supply enough electrons?

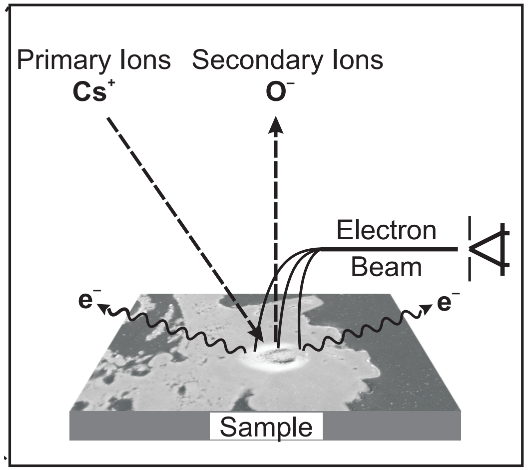


Electrostatic discharge!
…on your sample?

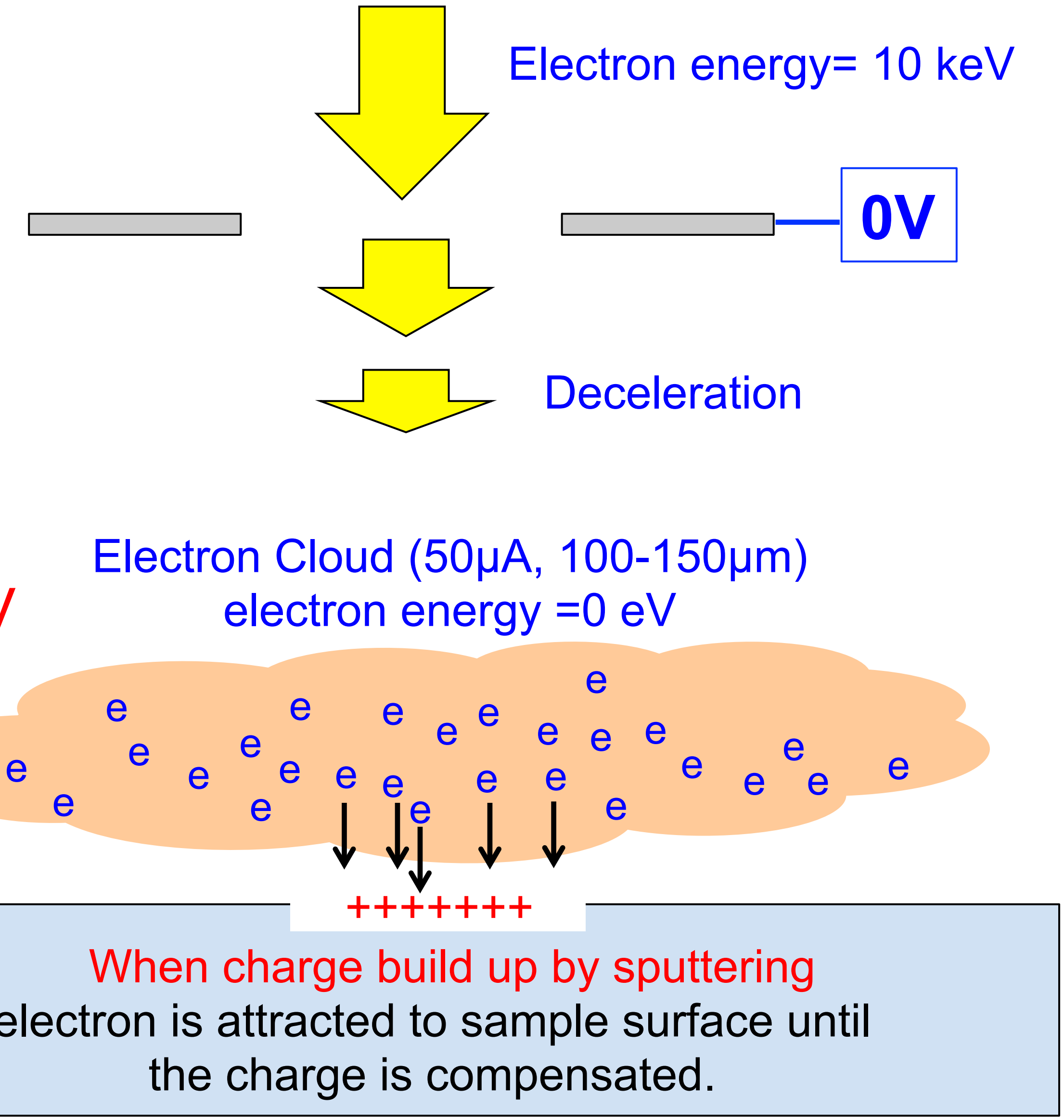
Electron Gun



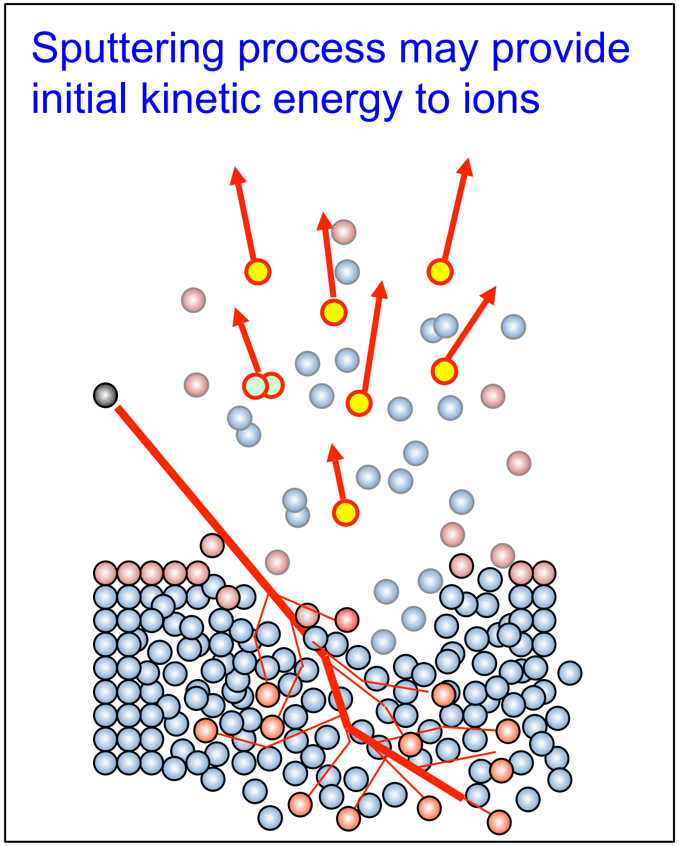
Electron Gun for Charge Compensation

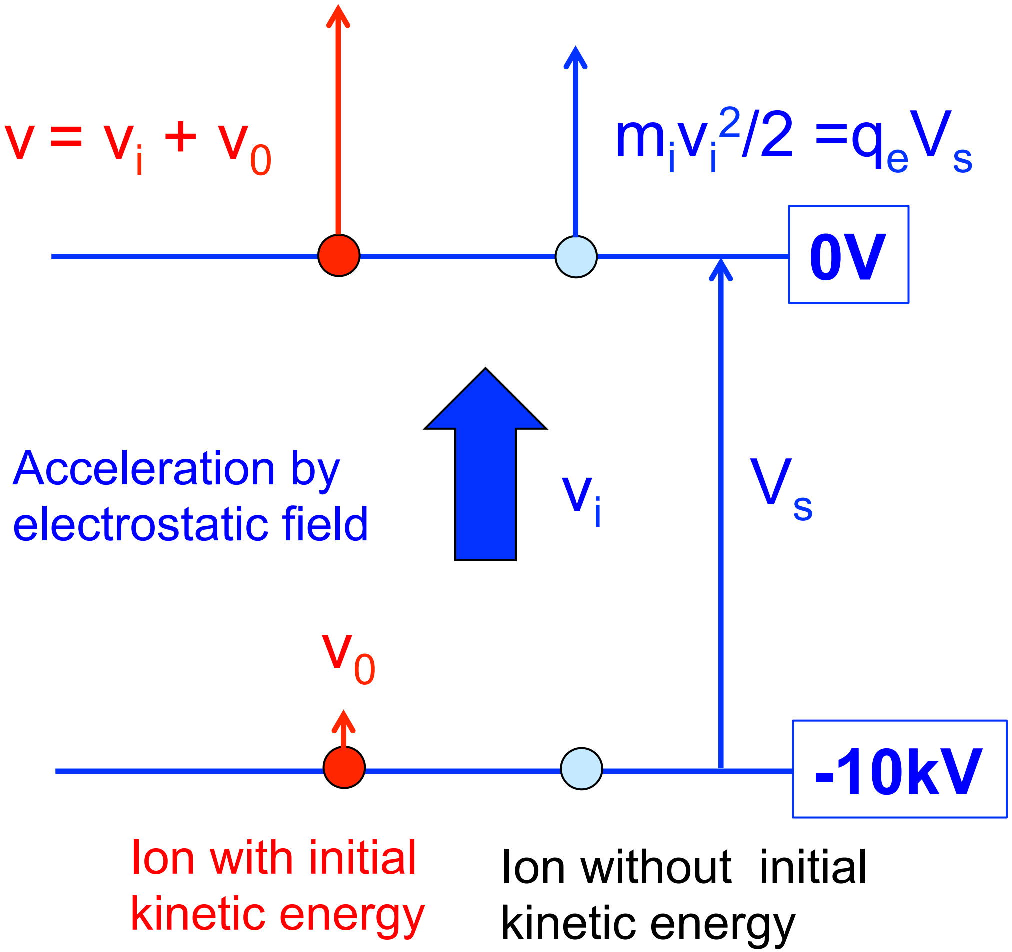


Electron gun: -10 kV
Sample acceleration: -10 kV



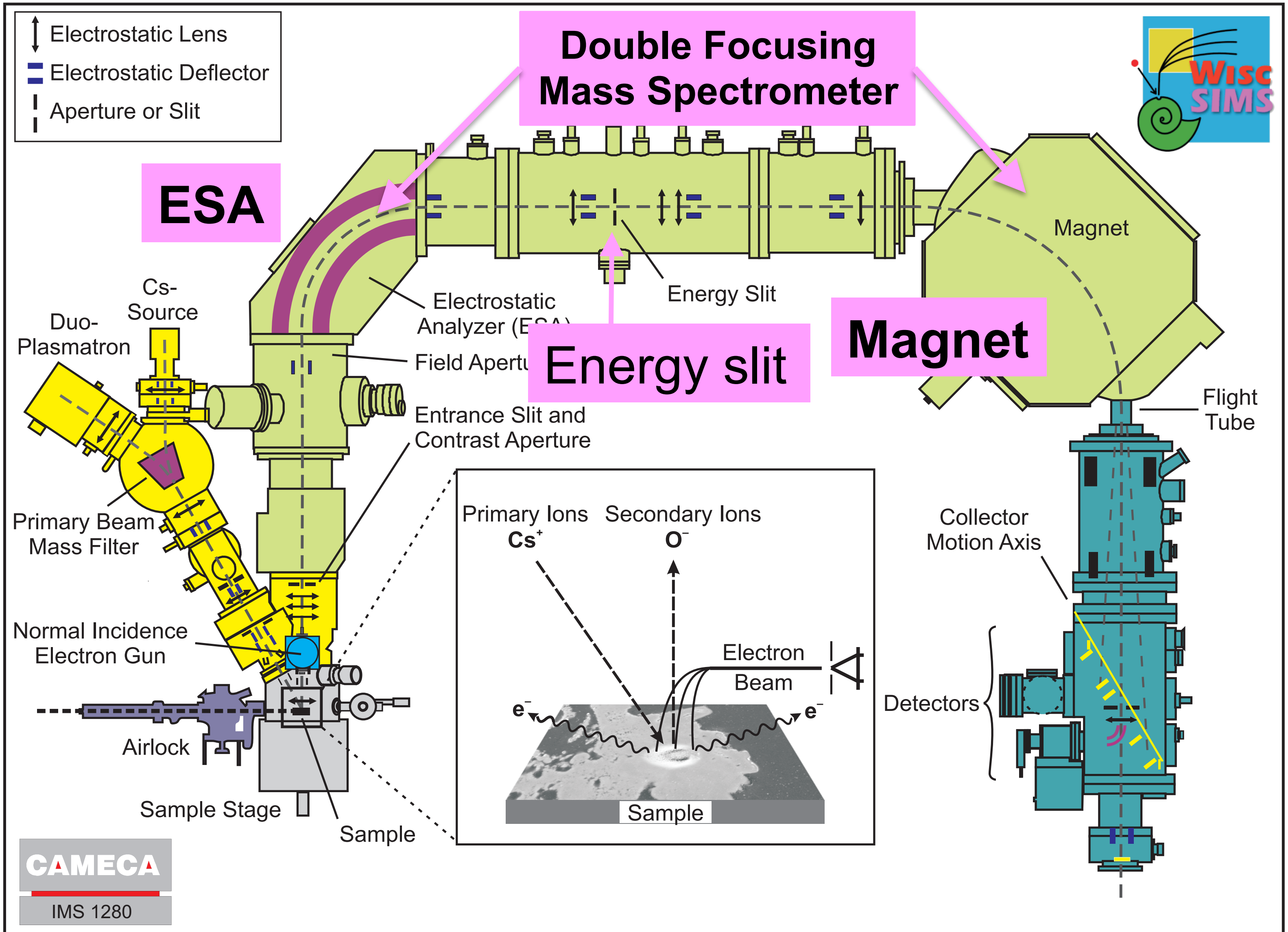
Initial Kinetic Energy of Secondary Ions





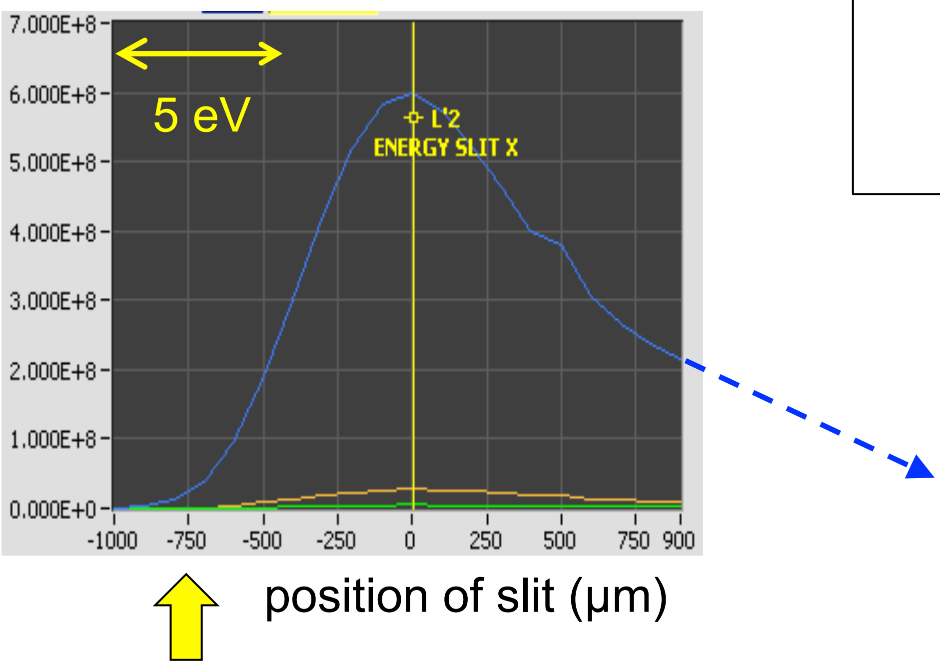
Trajectory of ions with different energies are different

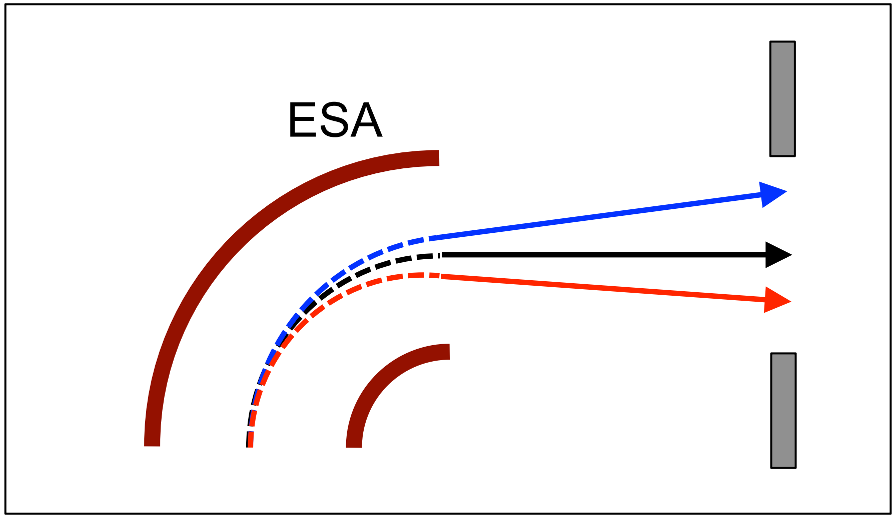
Double Focusing Mass Spectrometer



Initial Kinetic Energy of Secondary Ions

Energy slit scan of $^{16}O^{-}$ ions





position of slit (μm)

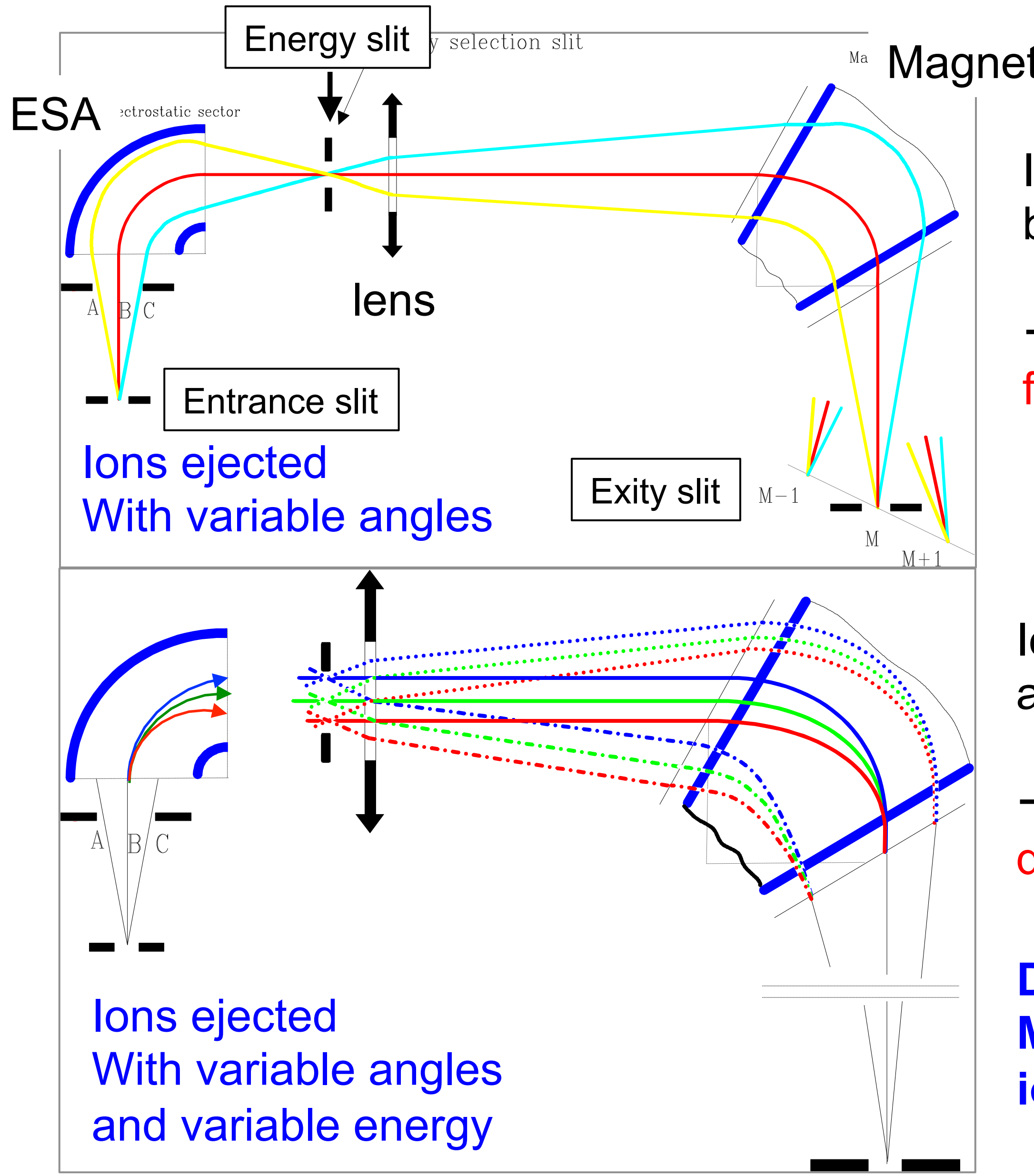
−10 keV (no initial energy)

Main peak is within ~30 eV
(0.3% of total energy)

Some ions show higher energy

Double Focusing Mass Spectrometer

From Cameca IMS manual



Ions without energy dispersion, but variable angles

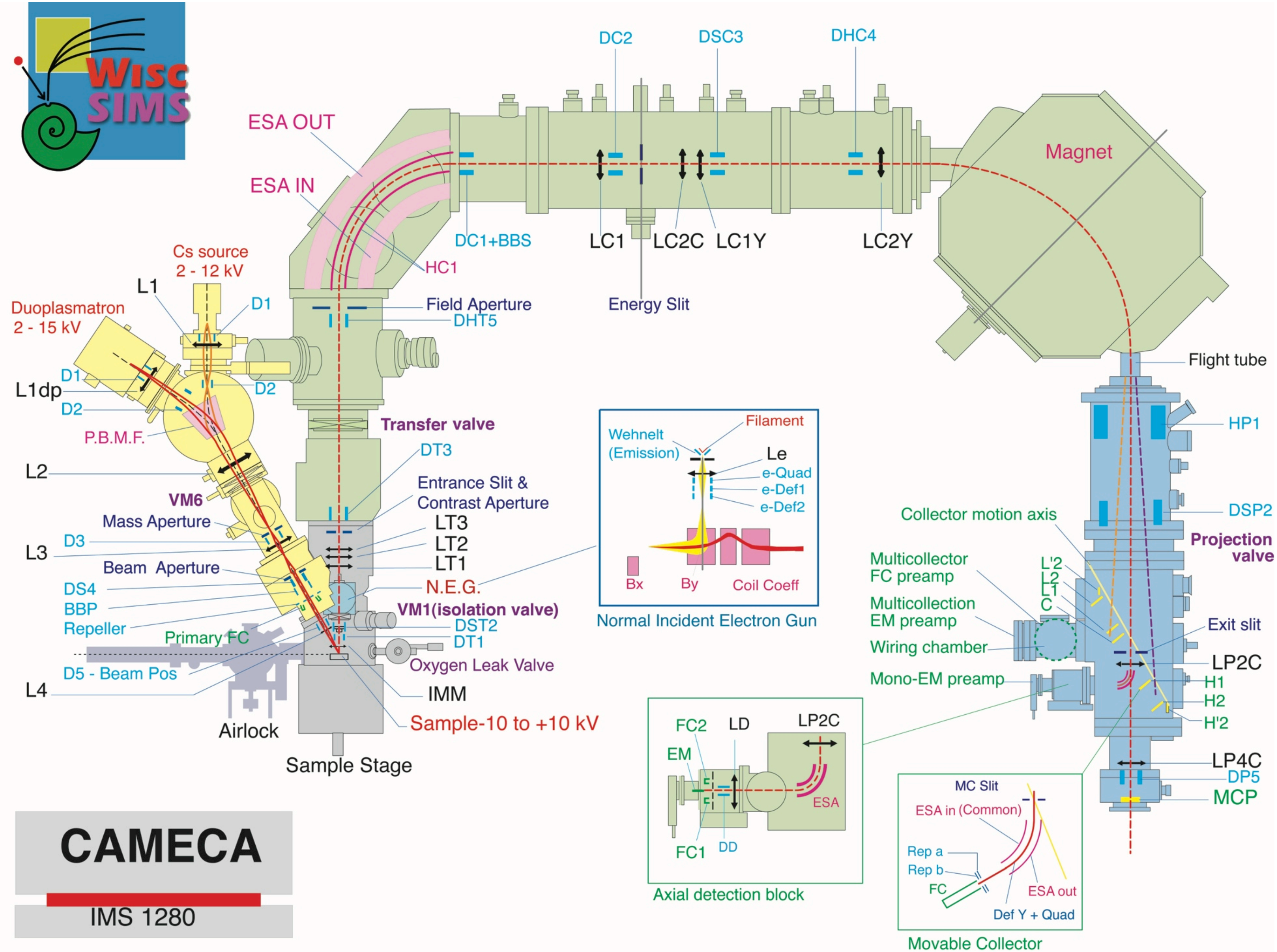
→ Ions with different angles focus by ESA and Magnet.

Ions with energy dispersion and variable angles

→ Ions with different energy disperse by ESA and Magnet

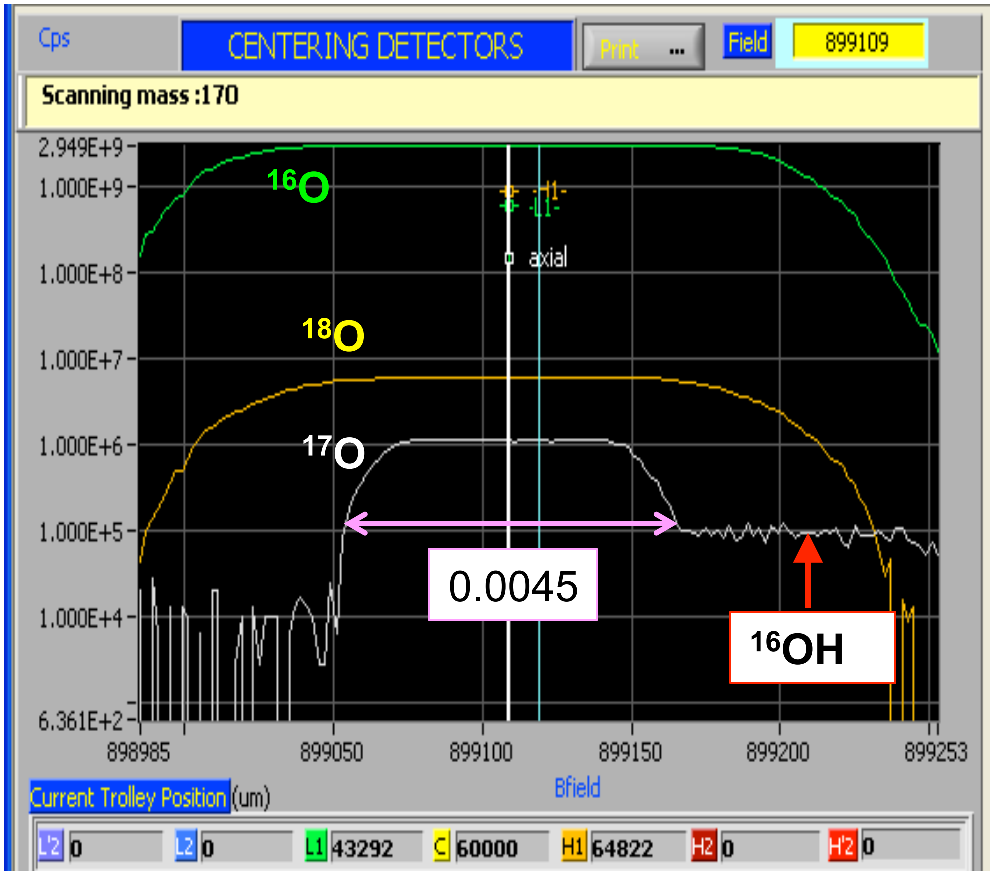
Dispersions made by ESA and Magnet are coupled to focus ions with variable energy.

Detail schematics of IMS-1280



Mass Spectrum (oxygen three isotope)

Mass Resolution Power (MRP) = (Mass of the peak)/(10% width)



^{17}O peak MRP

10% width: 0.0045 amu

MRP = 17/0.0045

~ 4,000

^{16}O, ^{18}O: MRP ~2,200

Magnetic field is regulated by NMR sensor.

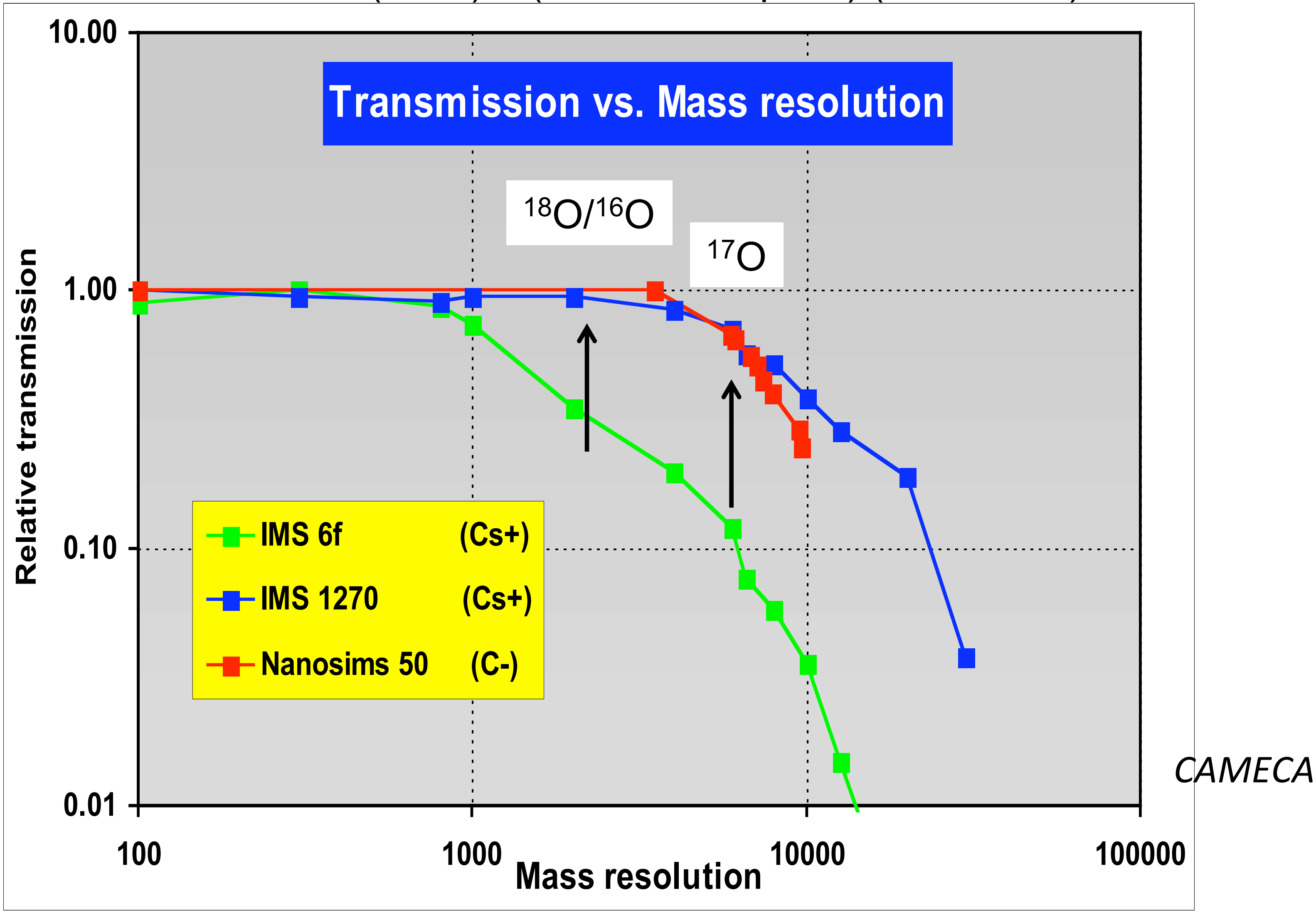
Drift (ΔB) <5 ppm for 12 hours

ΔM (OH-^{17}O) = −0.0036 amu

($M/\Delta M$) ~5,000

Ion Transmission

Mass Resolution Power (MRP) = (Mass of the peak)/(10% width)

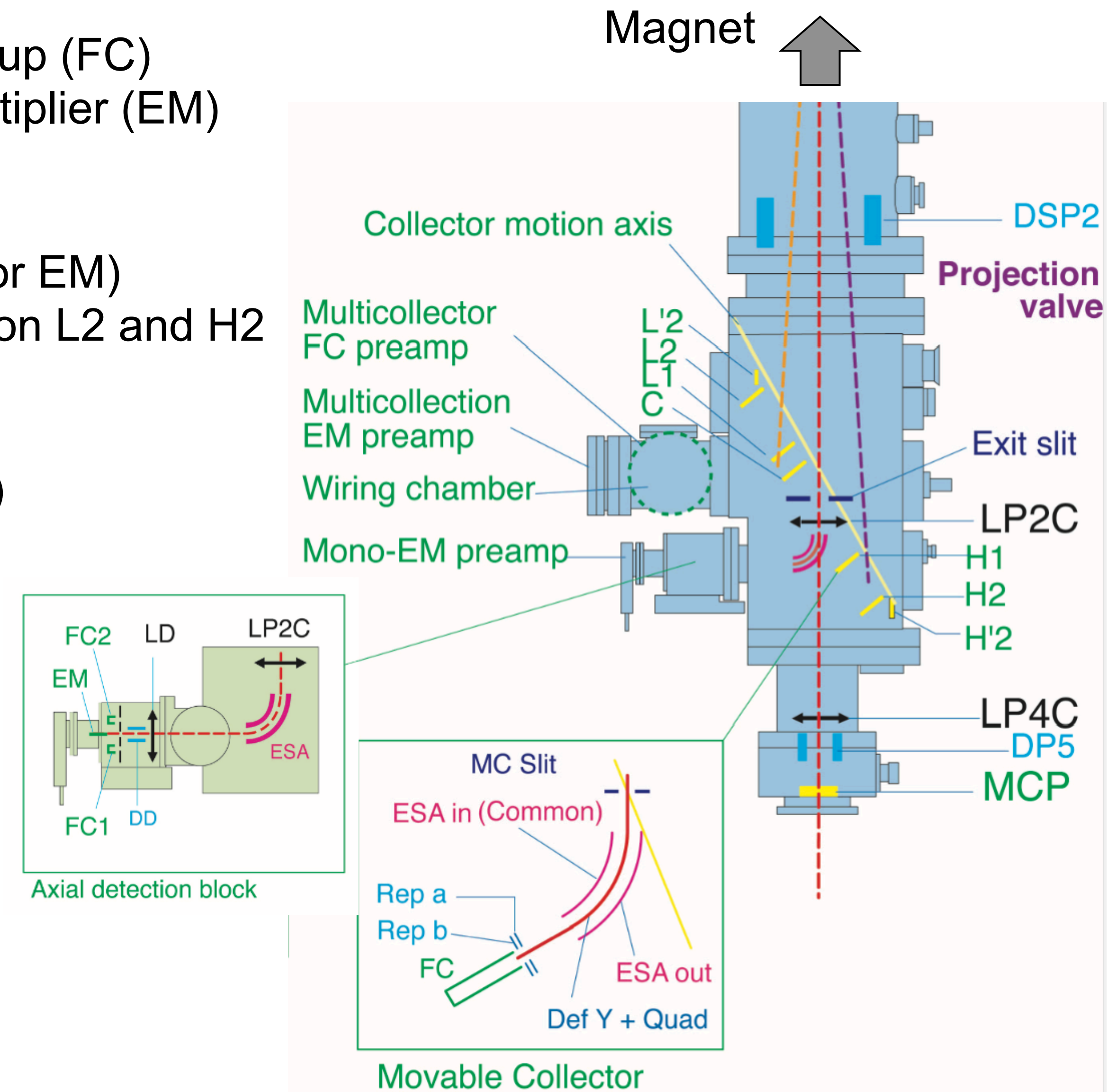


Detectors

Mono-collection: 2 Faraday Cup (FC)
Electron Multiplier (EM)

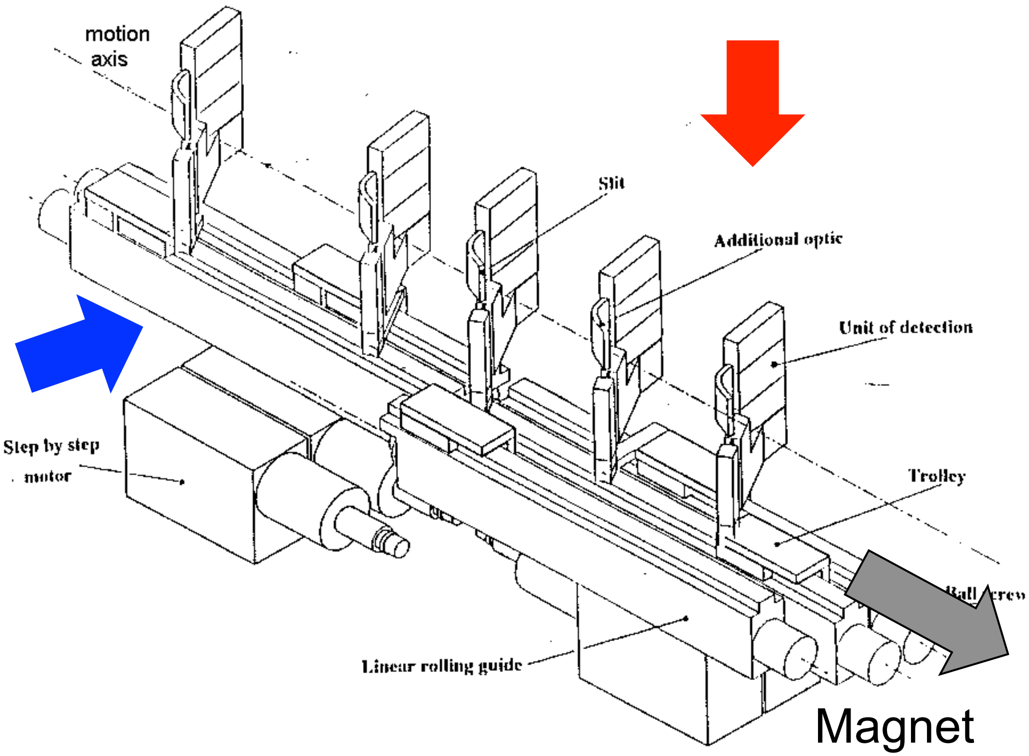
Multi-collection:
- 5 movable detectors (FC or EM)
- 2 additional FC detectors on L2 and H2

Direct image detection
- Multi-channel Plate (MCP)

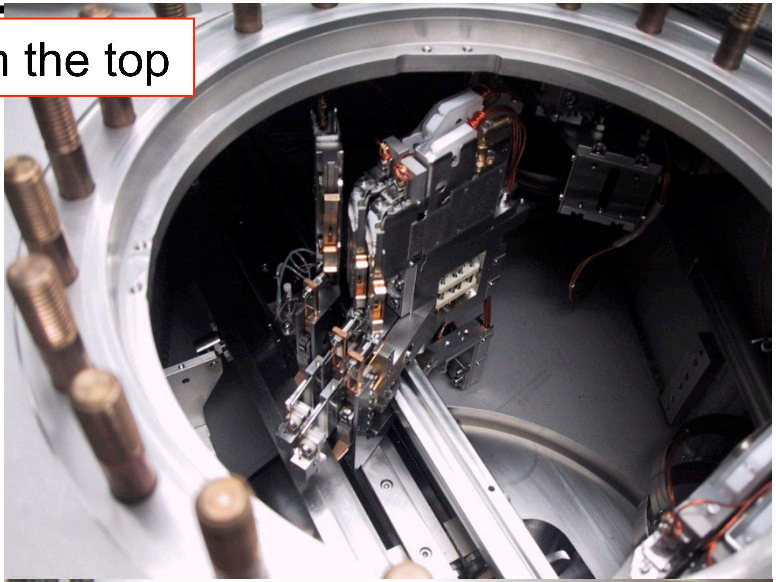


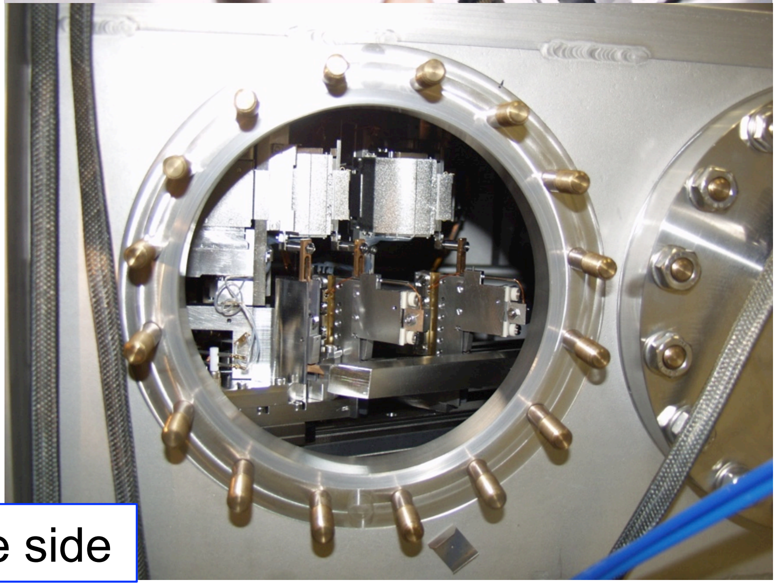
Multi-collection FC system is originally designed by Finnigan MAT.
Very similar to modern ICP-MS and TIMS instruments.

Multi-collection System



Looked from the top





Looked from the the side

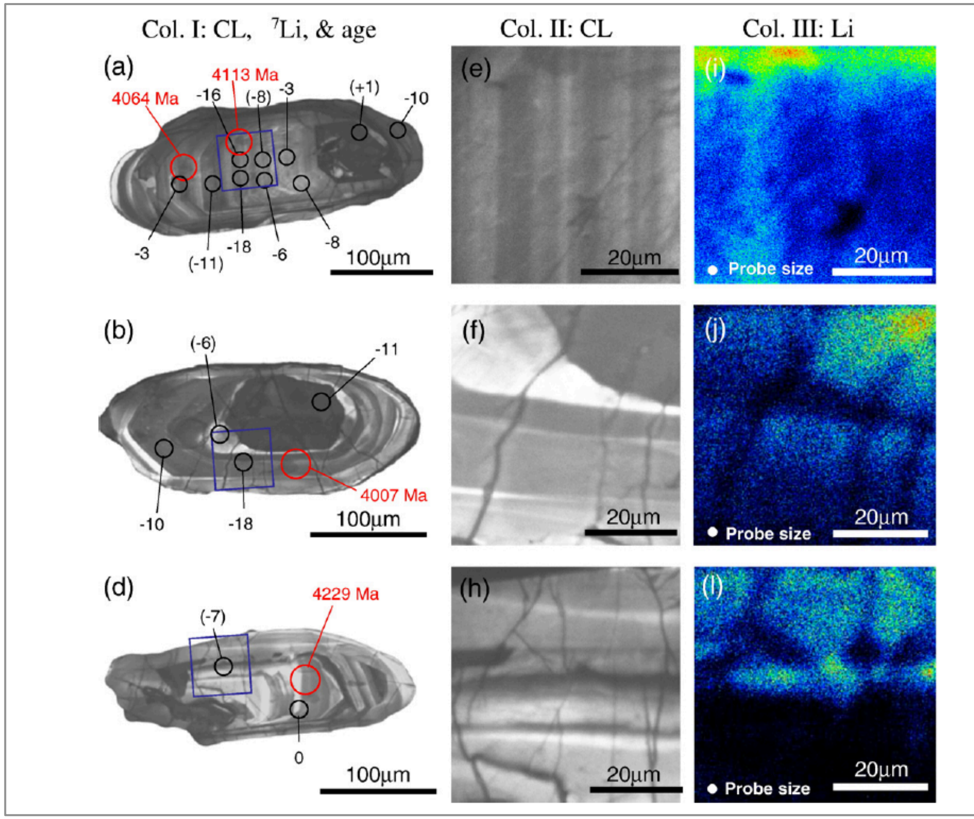
Analysis Types

Spot analysis: **High precision stable isotope analyses.**
Trace element analyses.

Scanning Ion Imaging (SII):
Raster primary ions and synchronize secondary ion detection. Secondary ions are detected by EM (not FC) due to fast response time (<10 ns)

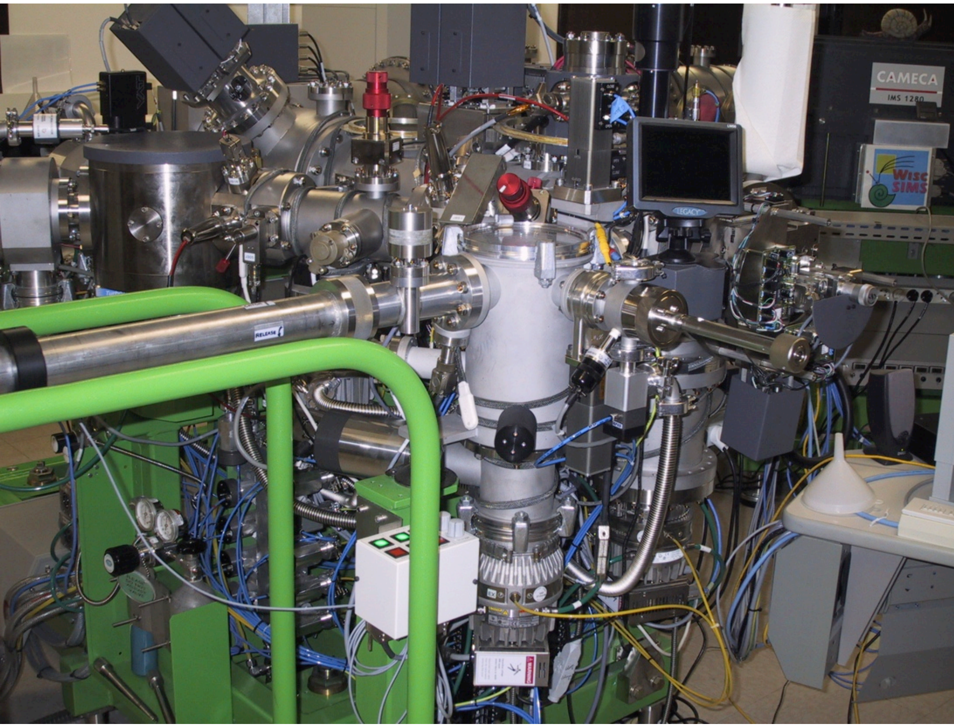
Direct Ion Image:
IMS 1280/7f series works as "ion microscope". Positions of ions produced on the sample surface will be transferred to MCP. SCAPS detector is used in Hokkaido 1270 and Hawaii 1280.

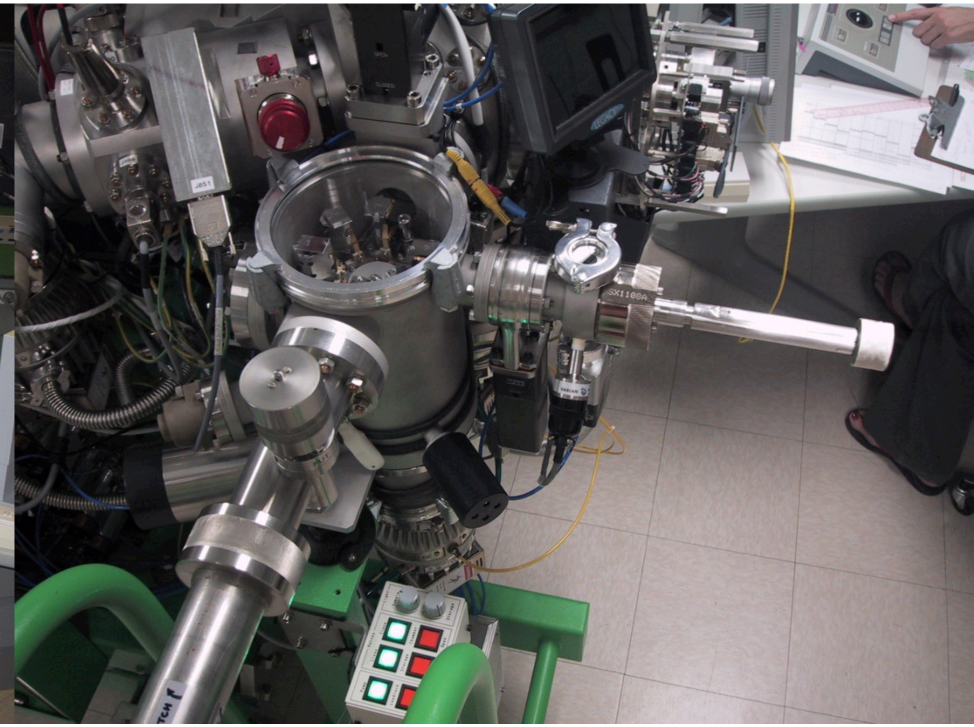
Example of SII (Ushikubo et al. 2008)



Additional Improvement

6 holder airlock system (storage lock)



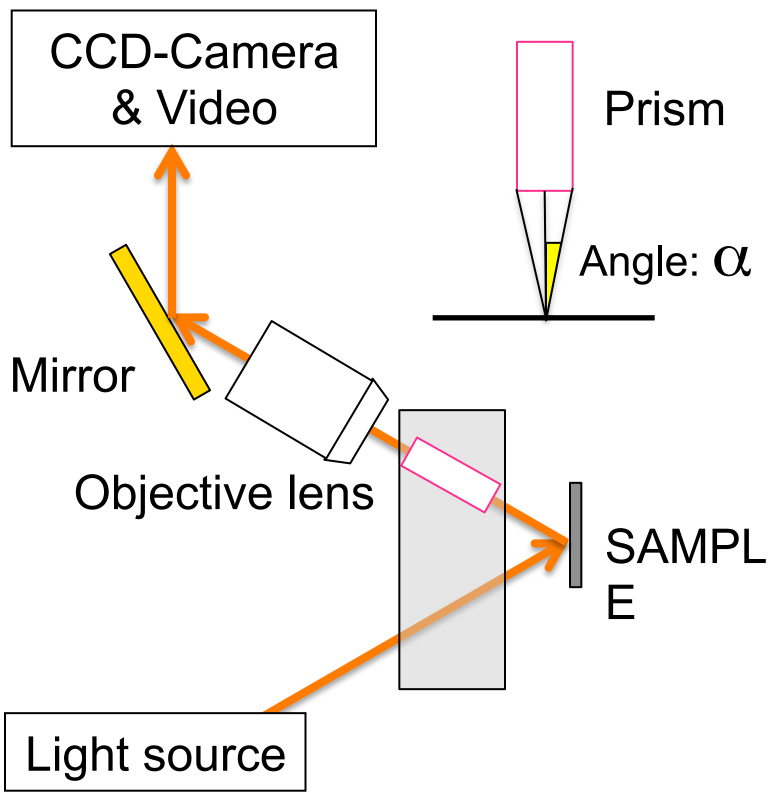


Option from Cameca: Original system only keeps one additional sample.

Reduced time for pumping individual samples

UV compatible optical microscope system

Resolution **d** $= \lambda / (2 \sin(\alpha))$
$= \lambda / 0.24$



We could not see 1-2 µm spots

0. Halogen light (original)

λ~ 0.7 µm → d ~ 3 µm

Actual d~ 3.5 µm & chromatic effect

1. Blue LED

λ ~ 450 nm→ d ~ 1.9 µm

Actual ~ 2.5 µm

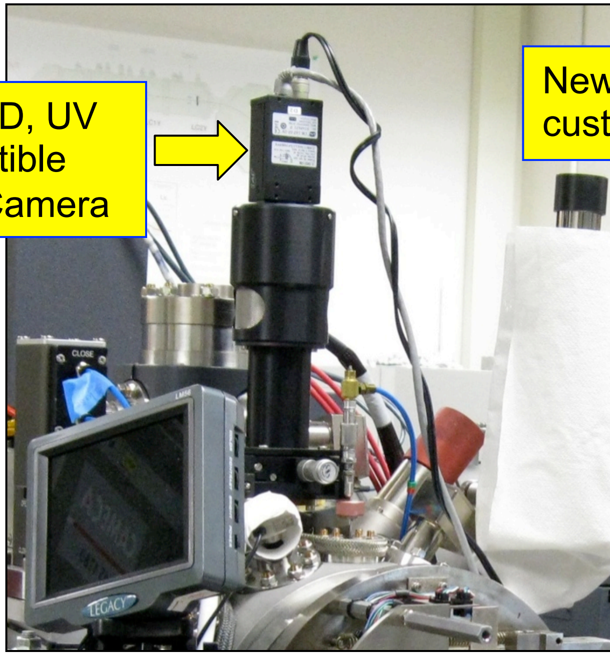
2. UV LED

λ ~ 370 nm→ d ~ 1.5 µm

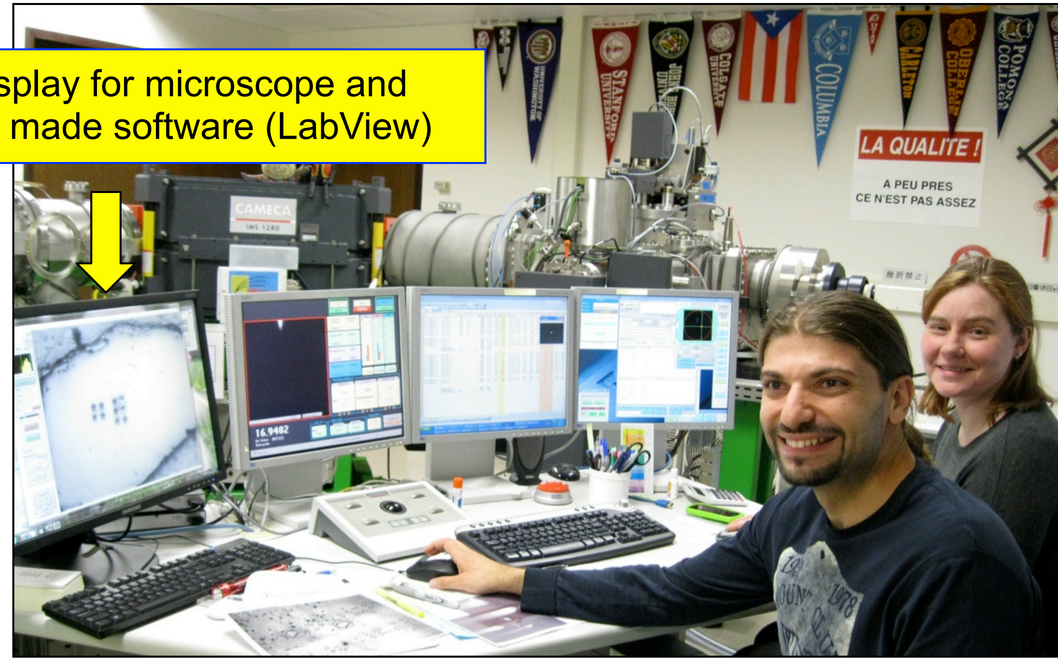
Actual ~ 1.5 µm

* Multiple optical components were replaced to UV compatible.

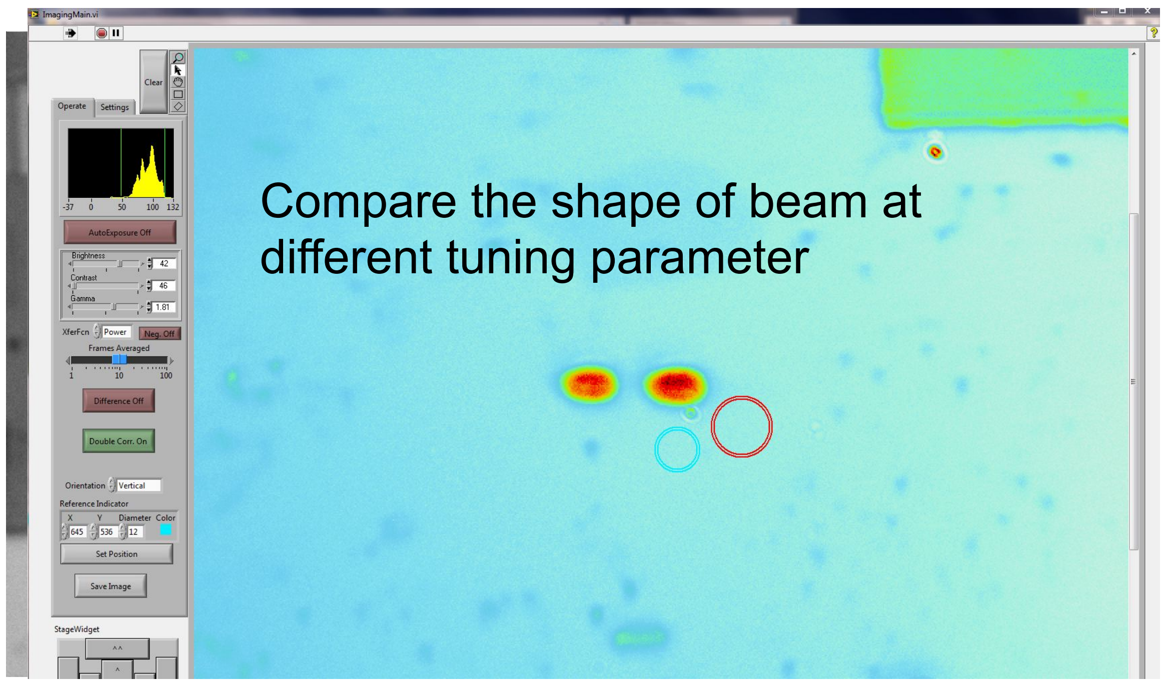
New HD, UV compatible CCD Camera



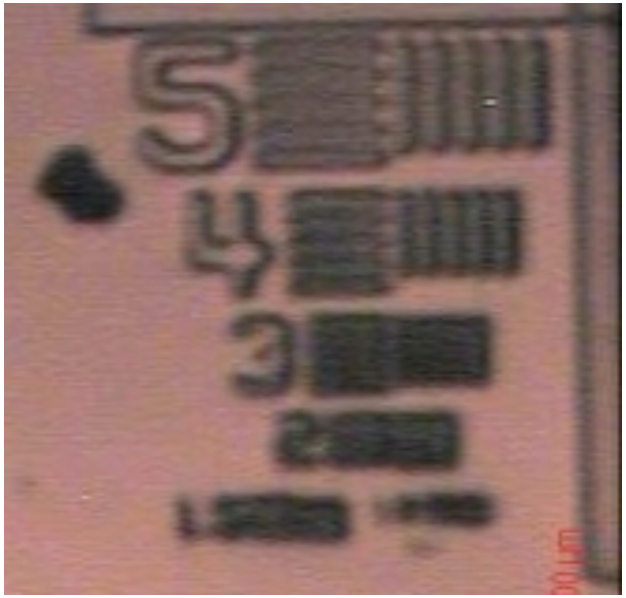
New display for microscope and custom made software (LabView)



New Software
- zoom/unzoom
- pseudocolor

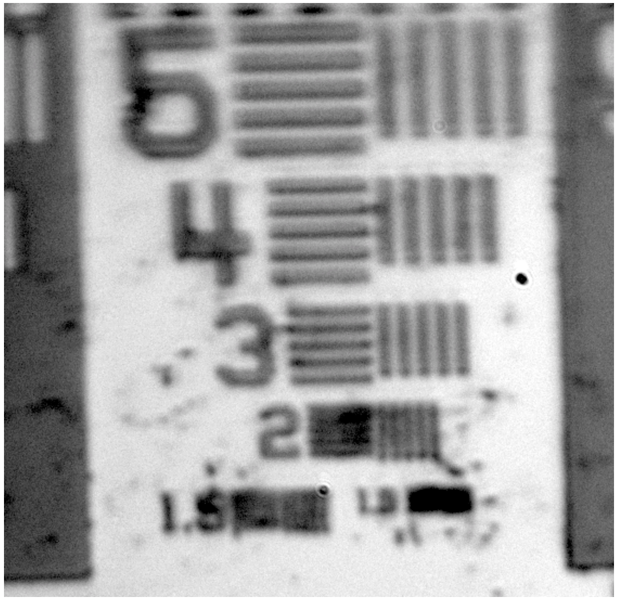


Improved optical resolution



Original
(halogen light)

Blue LED
(450 nm)



UV LED
(370 nm)

It is much easier to aim best position for the analysis

Other improvements that helped better stable isotope analysis

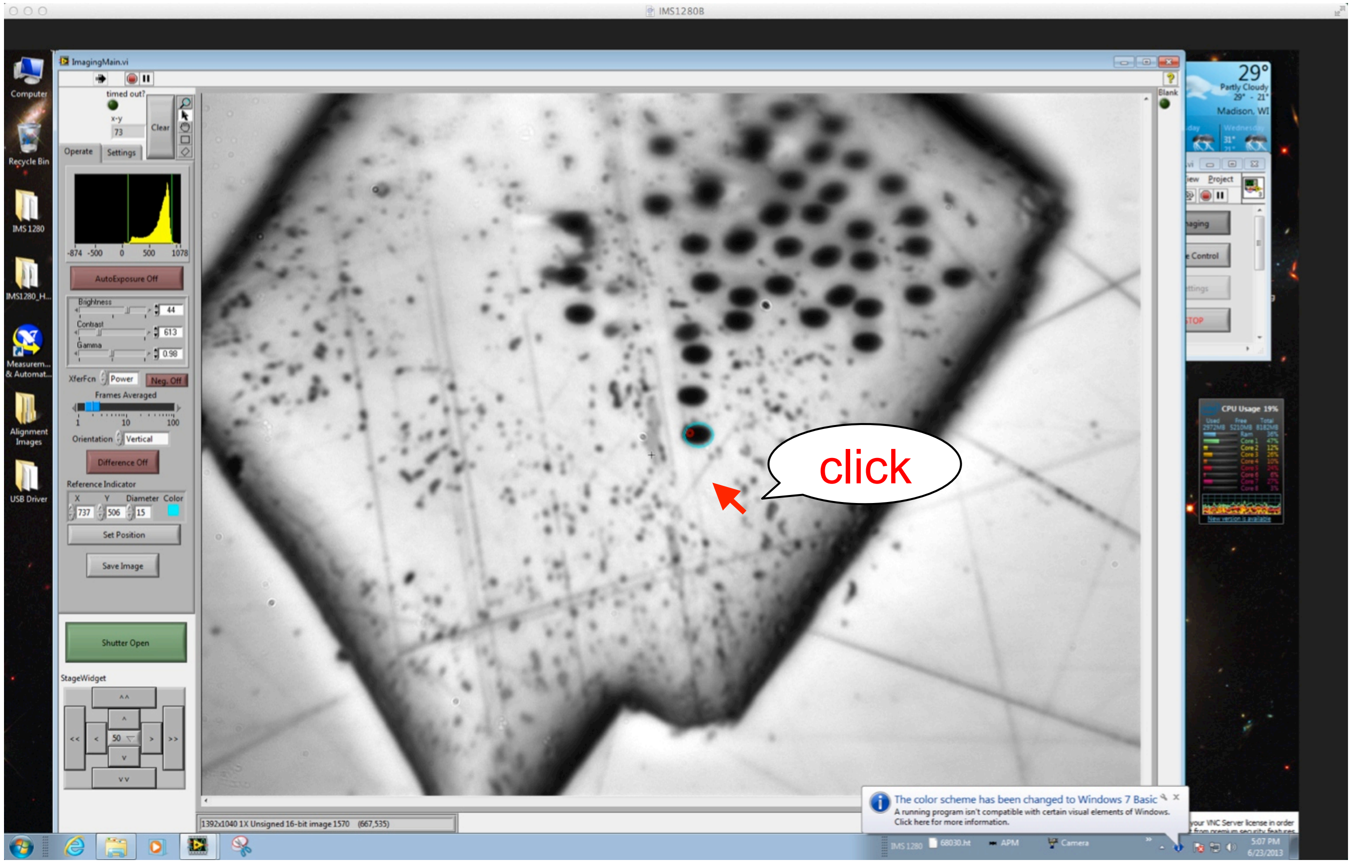
Add dumper to Turbo pumps → ~2 μm level vibration stopped.

Dedicated rough pumping for FC amplifier housing.
Keep constant pressure of ~0.3 torr.

Oxygen isotope analyses

Instrument is fully tuned including detector positions and magnetic field.

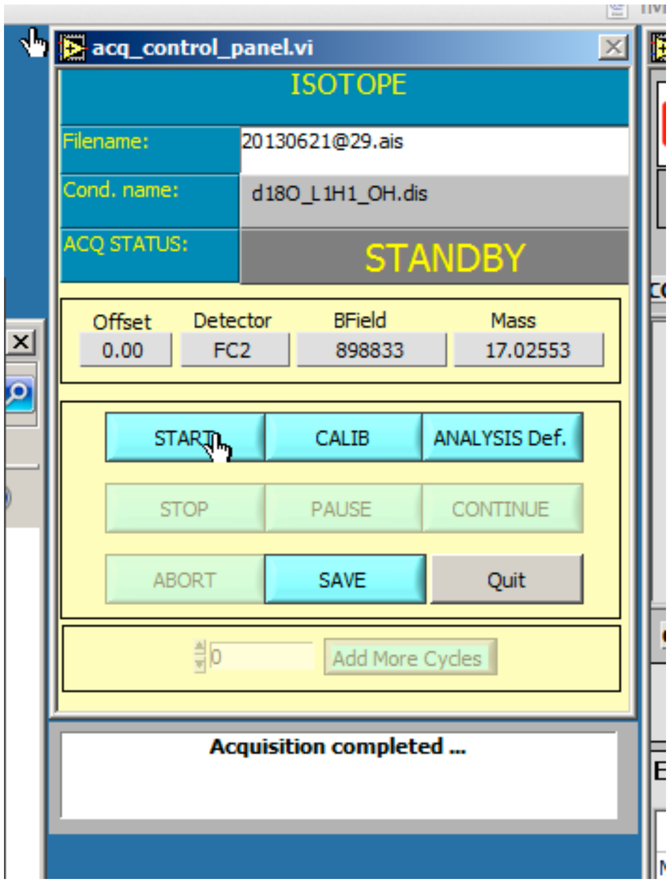
- Move to standard grain in your sample. Move to your analysis position.



Oxygen isotope analyses

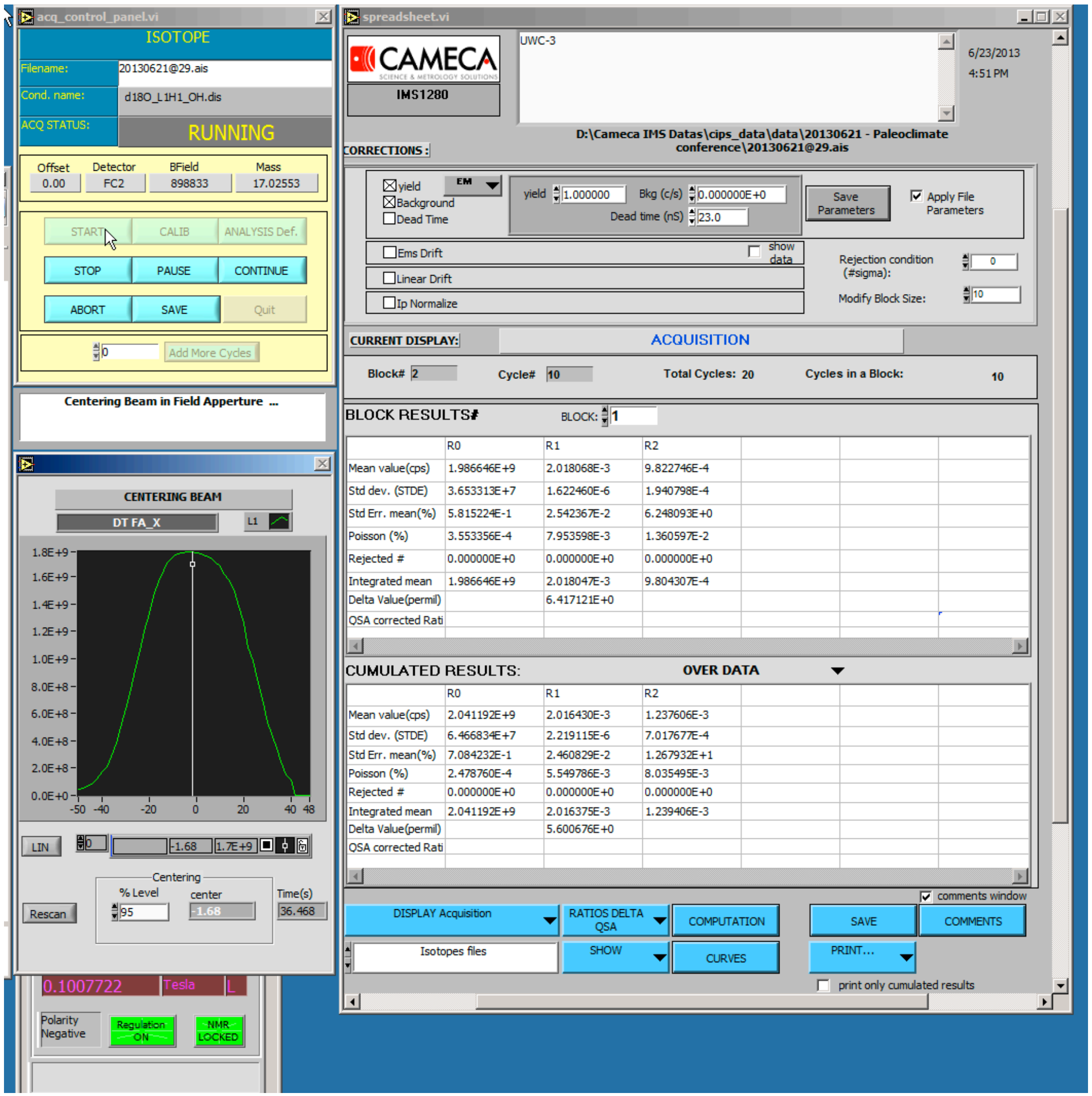
Instrument is fully tuned including detector positions and magnetic field.

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



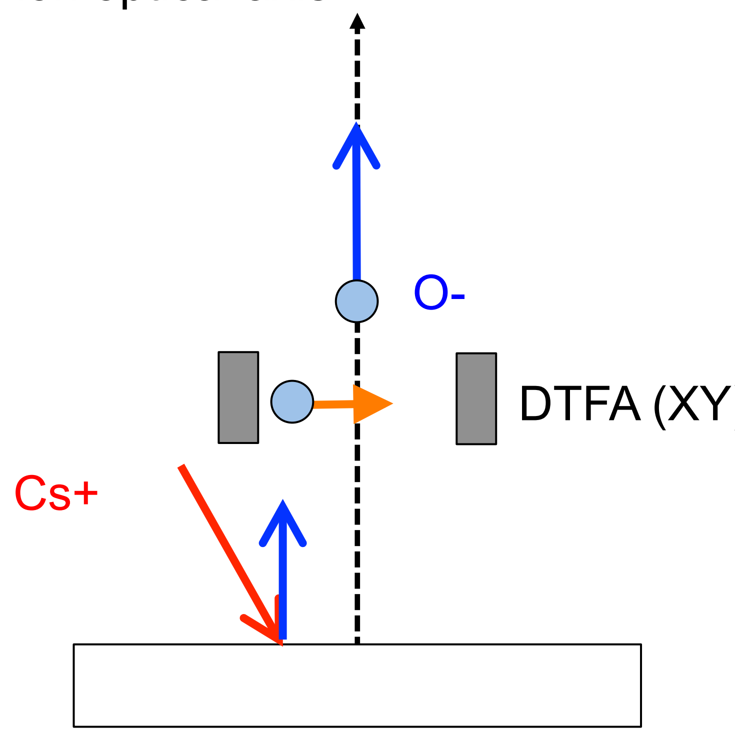
Wait 3 min
until the analysis is done

Oxygen isotope analyses



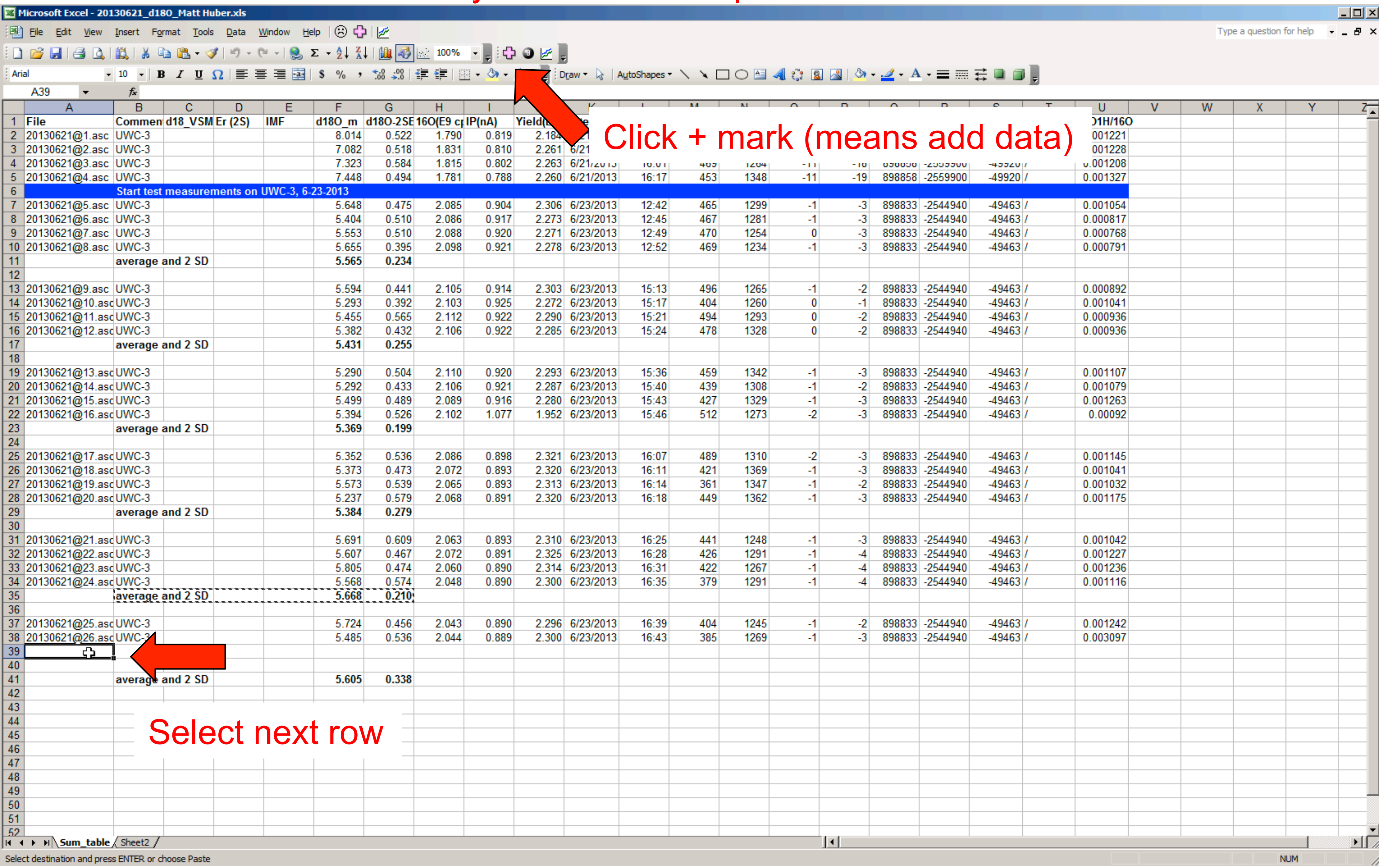
During first 1 min, there will be series of scanning.

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



Oxygen isotope analyses

When Analysis finished – import data to work sheet



	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(											1H/16O
2	20130621@1.asc	UWC-3				8.014	0.522	1.790	0.819	2.184											001221
3	20130621@2.asc	UWC-3				7.082	0.518	1.831	0.810	2.261	6/21										001228
4	20130621@3.asc	UWC-3				7.323	0.584	1.815	0.802	2.263	6/21/2013	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	/	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																					
40																					
41		**average and 2 SD**				**5.605**	**0.338**														

Oxygen isotope analyses

Data is imported

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 cp	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

Sum_table / Sheet2

Oxygen isotope analyses

Move to next position
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