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Experiments with low voltage FE-EPMA: toward achieving improved spatial resolution

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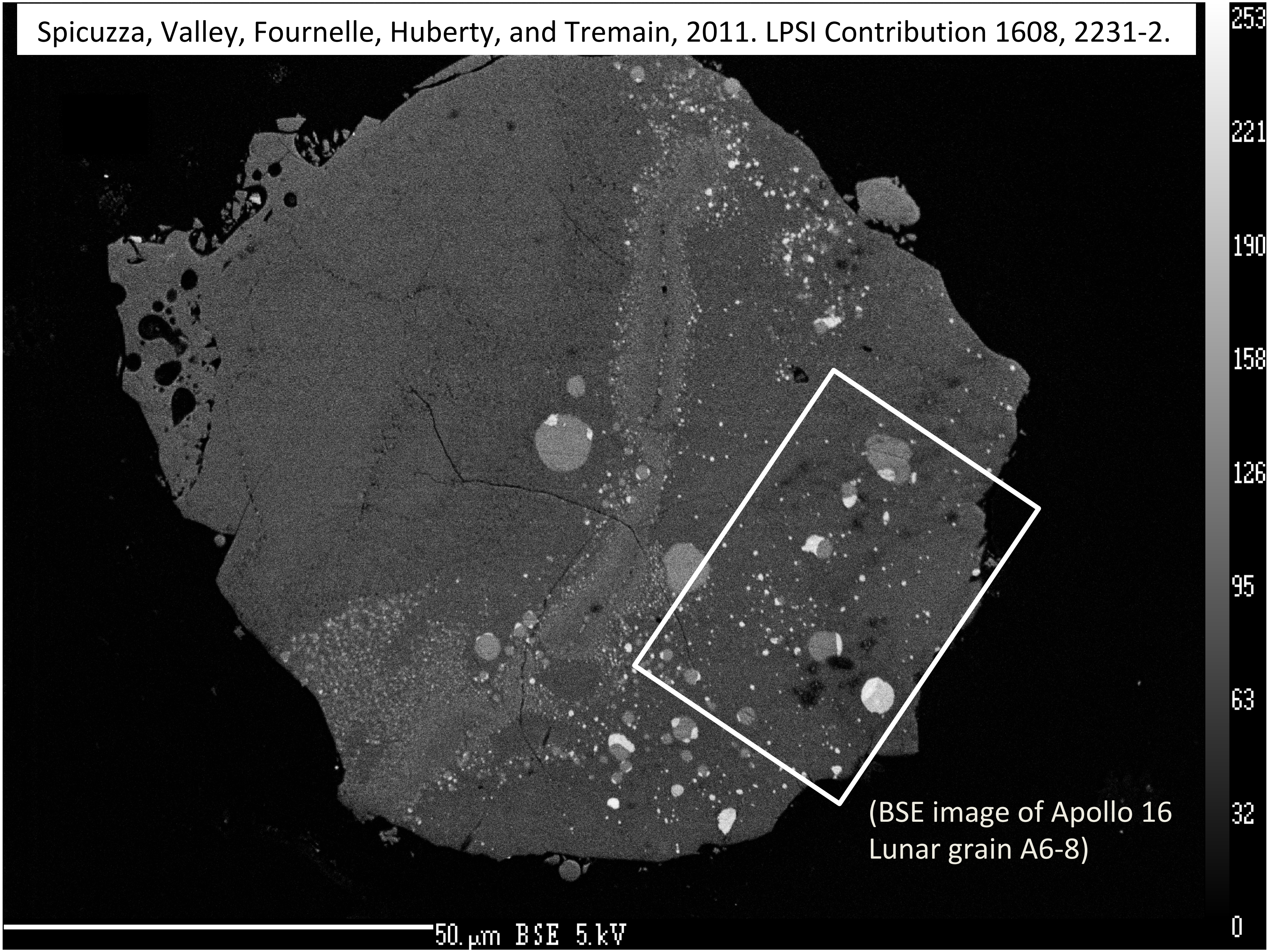


Spicuzza, Valley, Fournelle, Huberty, and Tremain, 2011. LPSI Contribution 1608, 2231-2.

(BSE image of Apollo 16 Lunar grain A6-8)

Dark host = plagioclase; Grey = Si metal; White = Fe silicides

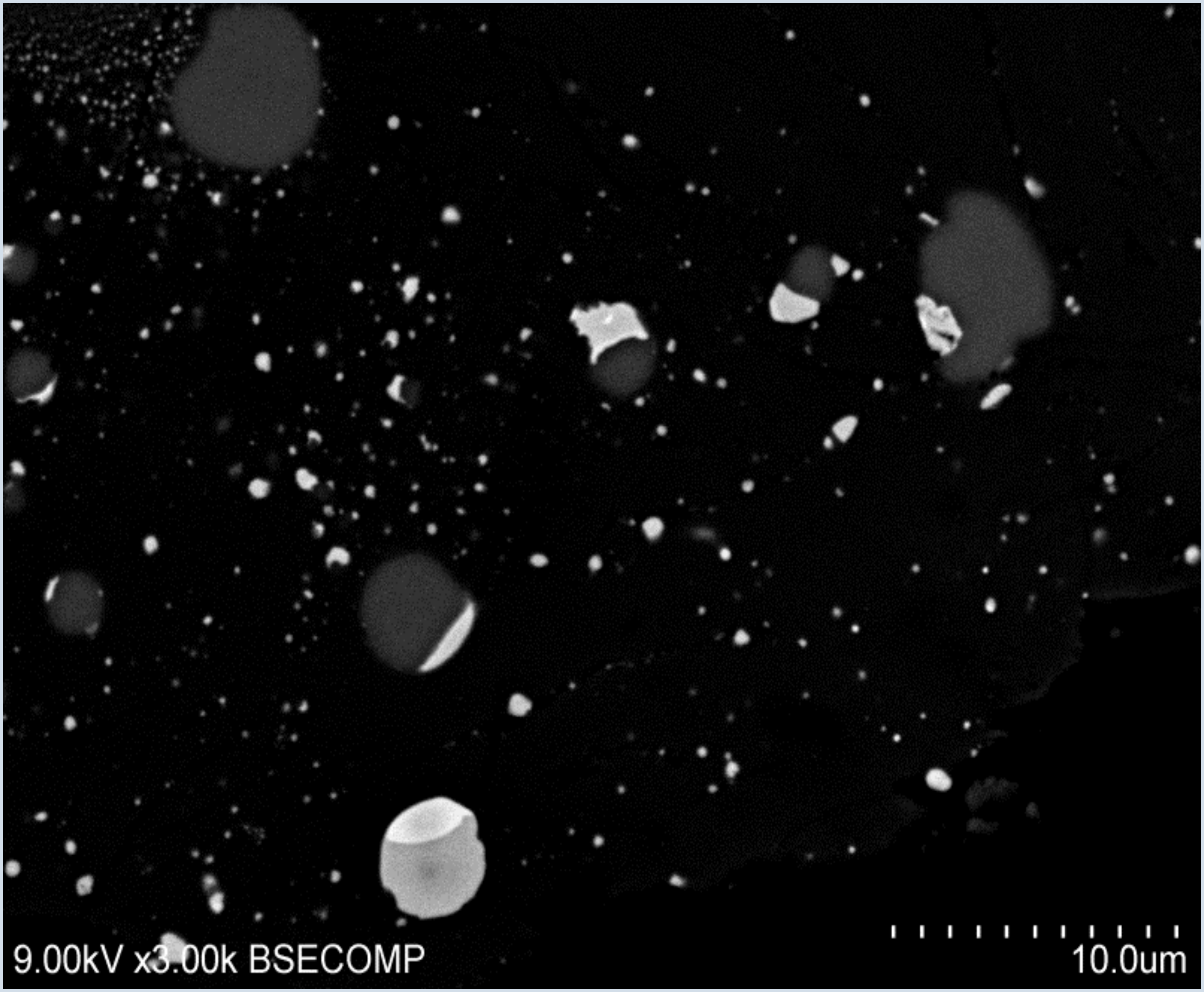
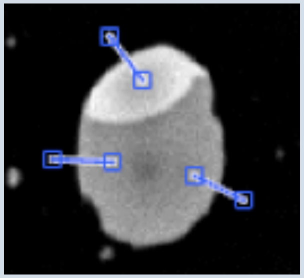
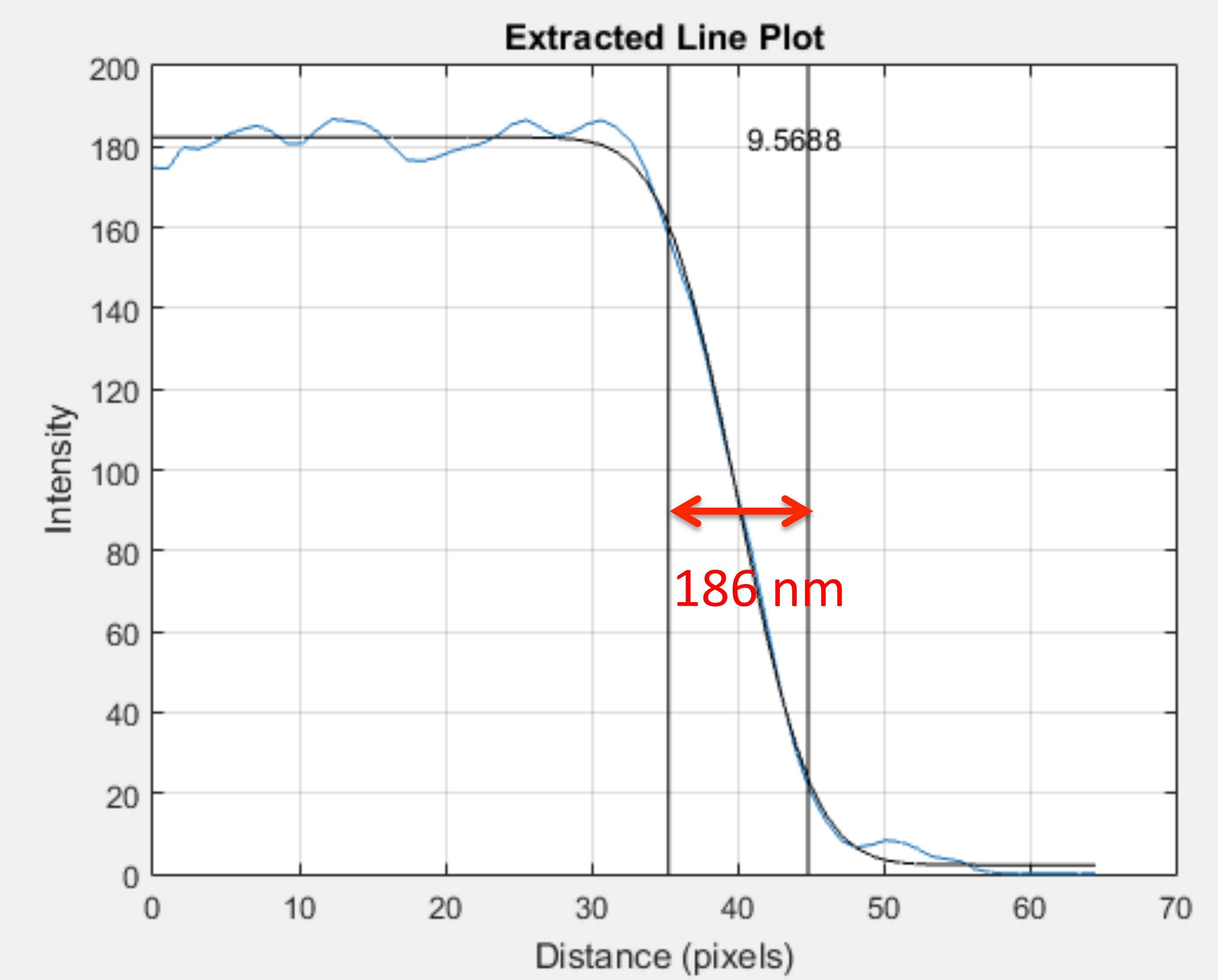


Image Edge Resolution of BSE Image (W source)

Here defined as
12-88% change from
min to max intensity

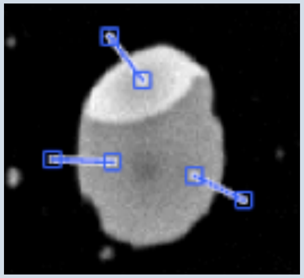


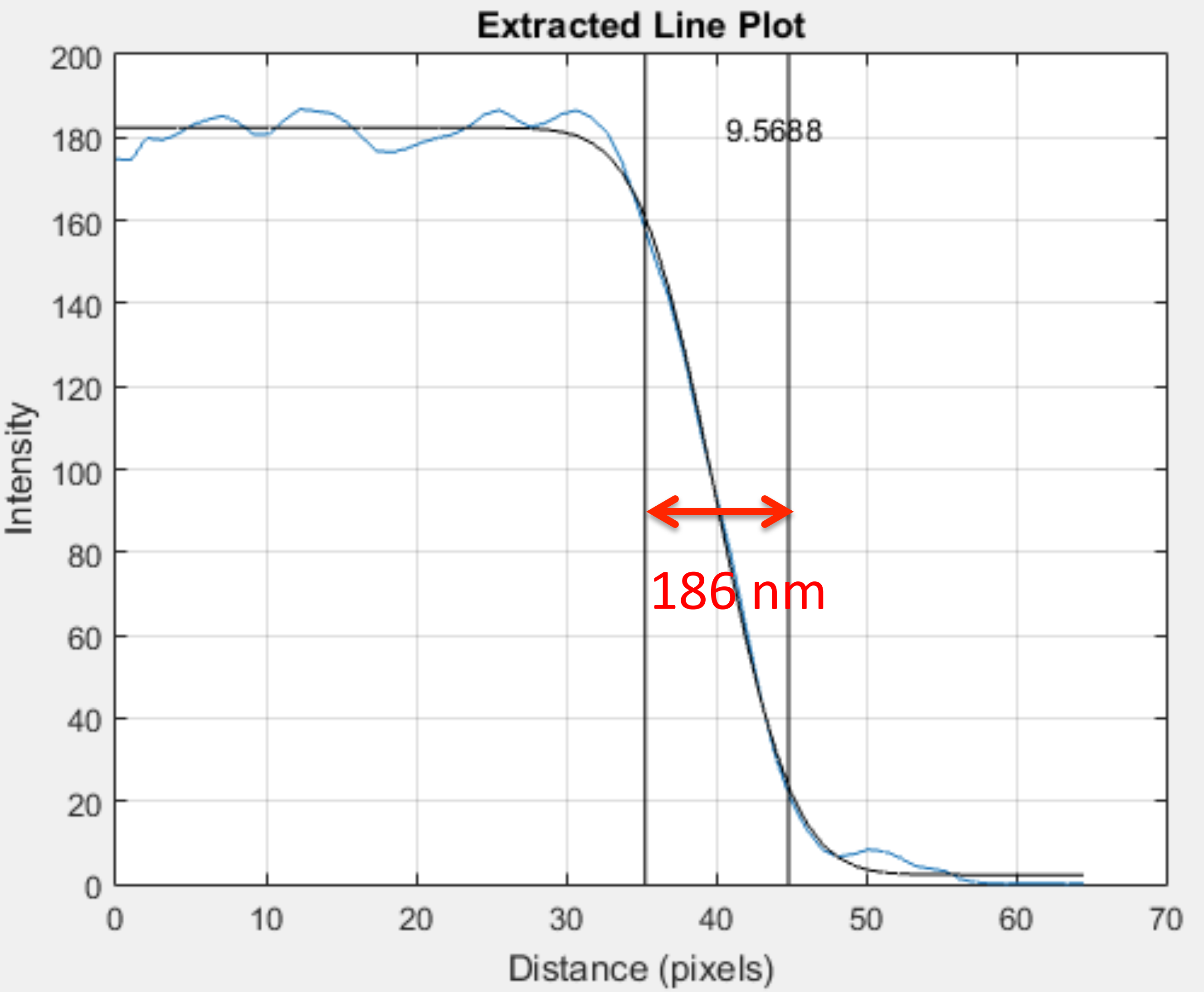


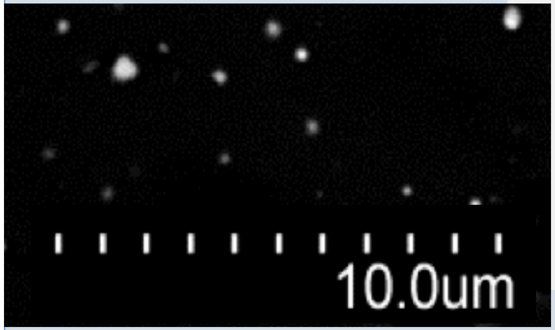
Free application from Peter Sobol at UW-Madison Geoscience

Image Edge Resolution of BSE Image

Here defined as 12-88% change from min to max intensity







Free application from Peter Sobol at UW-Madison Geoscience

Image Edge Resolution

$\neq$

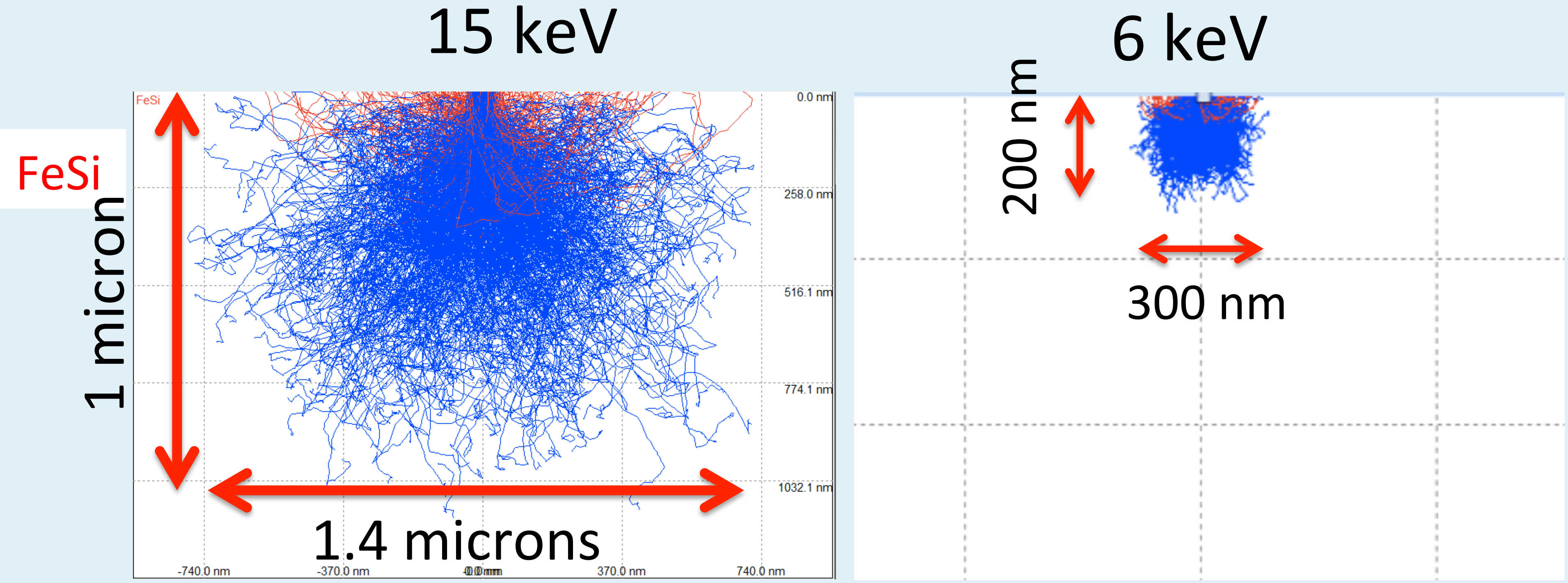
Analytical Spatial Resolution !

Barksdale et al. (2000):

… instead of simply being able to resolve the feature in an image, the entire X-ray information volume must be contained within the feature; lateral resolution is diameter which includes some fraction of total X-ray intensity, e.g. 99%

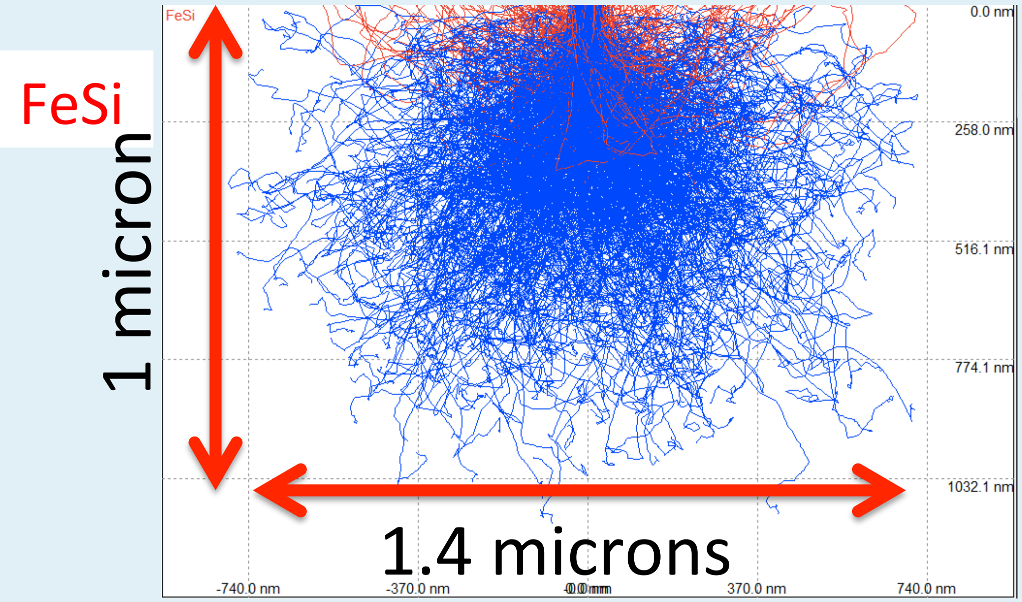
Barkshire I, Karduck P, Rehbach W P and Richter S 2000 *Mikrochim. Acta* **132** 112

Turn down the electron beam voltage....

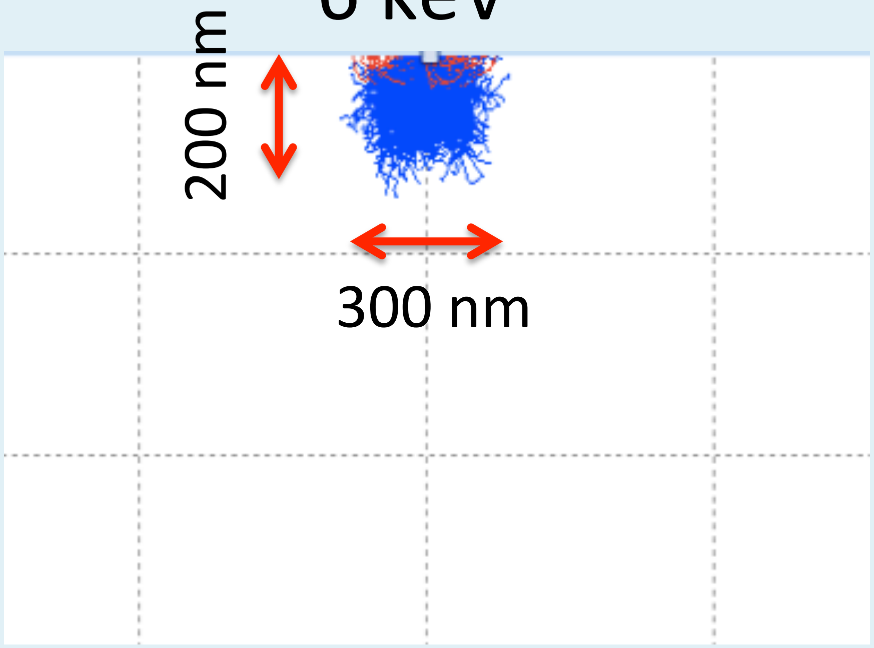


To reduce the interaction volume....

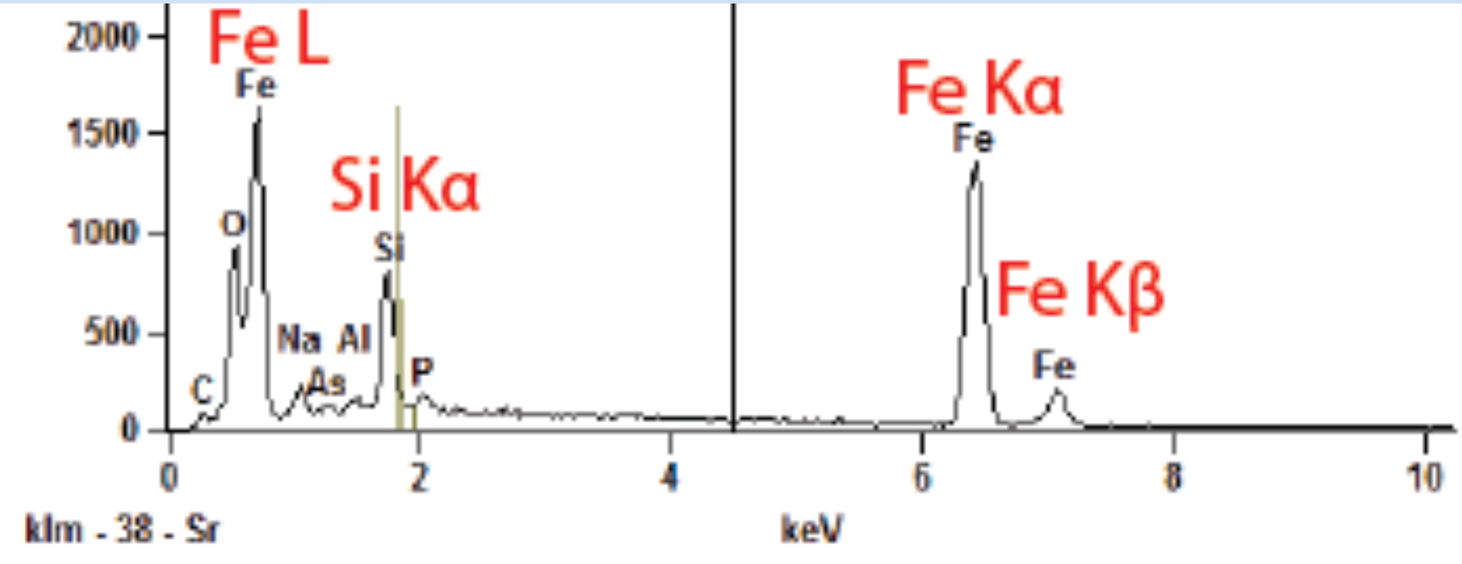
15 keV



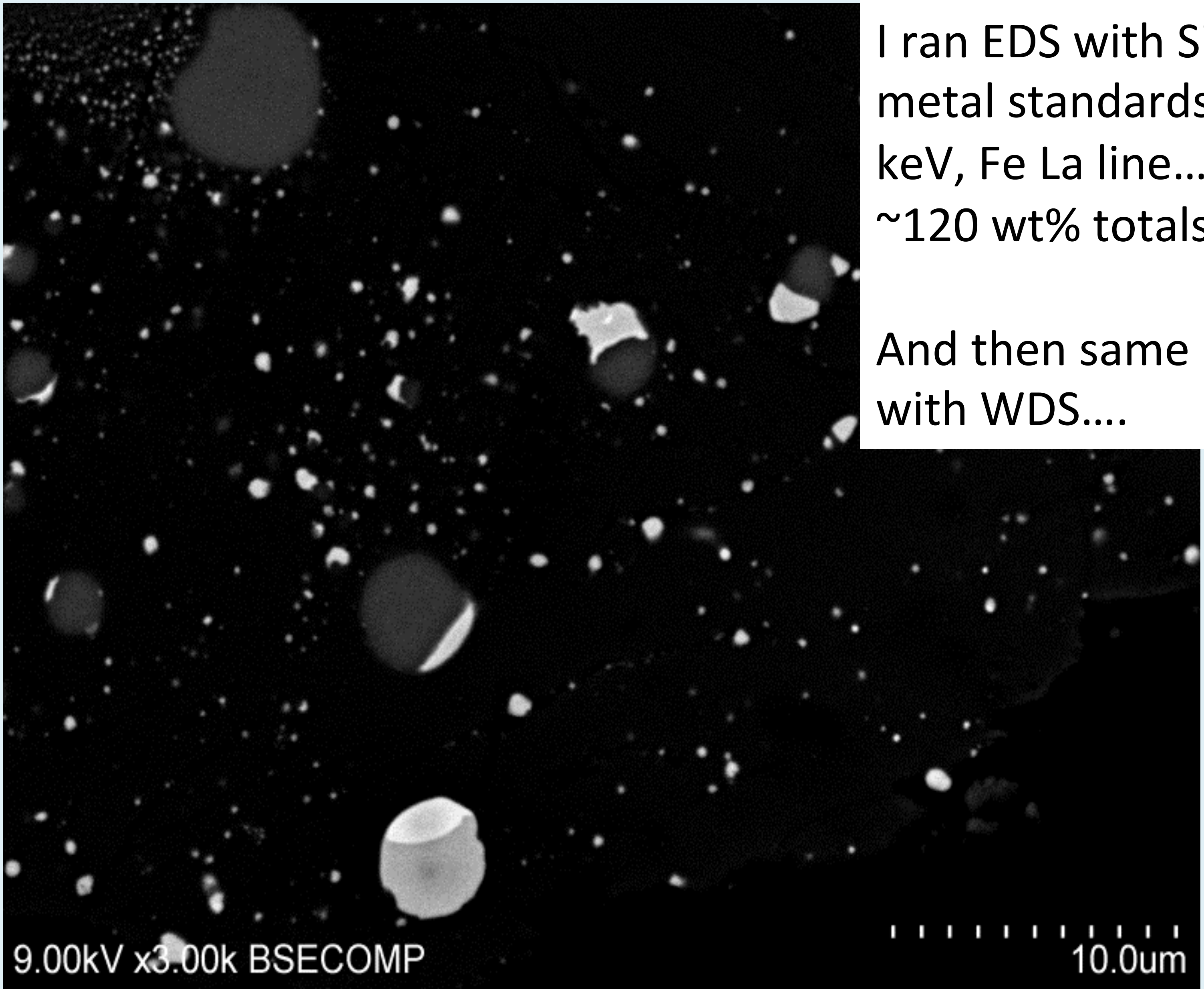
6 keV



But then Fe Ka no longer available below 7.1 keV…



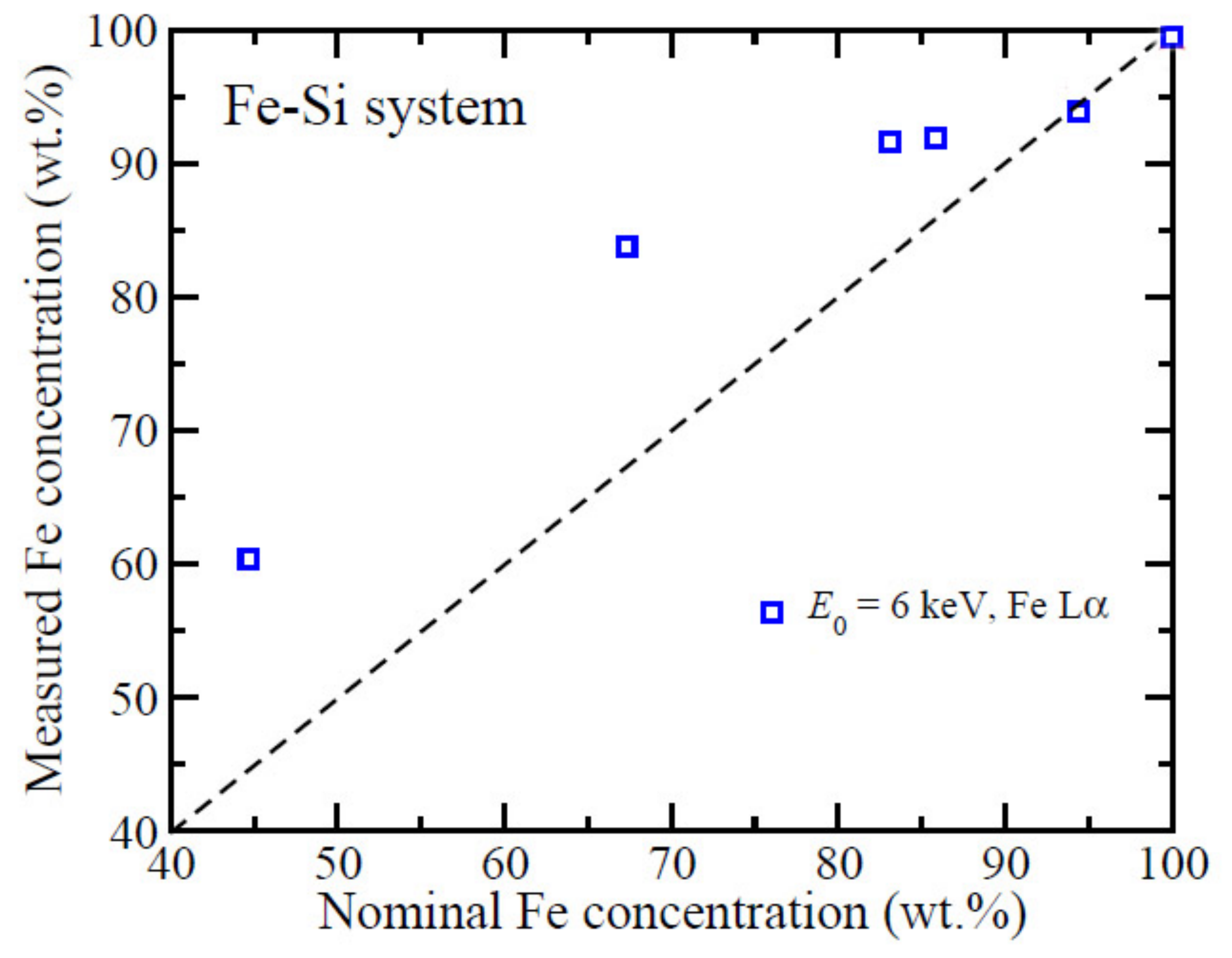
Sub micron low keV analysis



I ran EDS with Si and Fe metal standards, low keV, Fe La line…. And got ~120 wt% totals…

And then same results with WDS….

Acquired (+synthesized) 5 large Fe-Si alloys



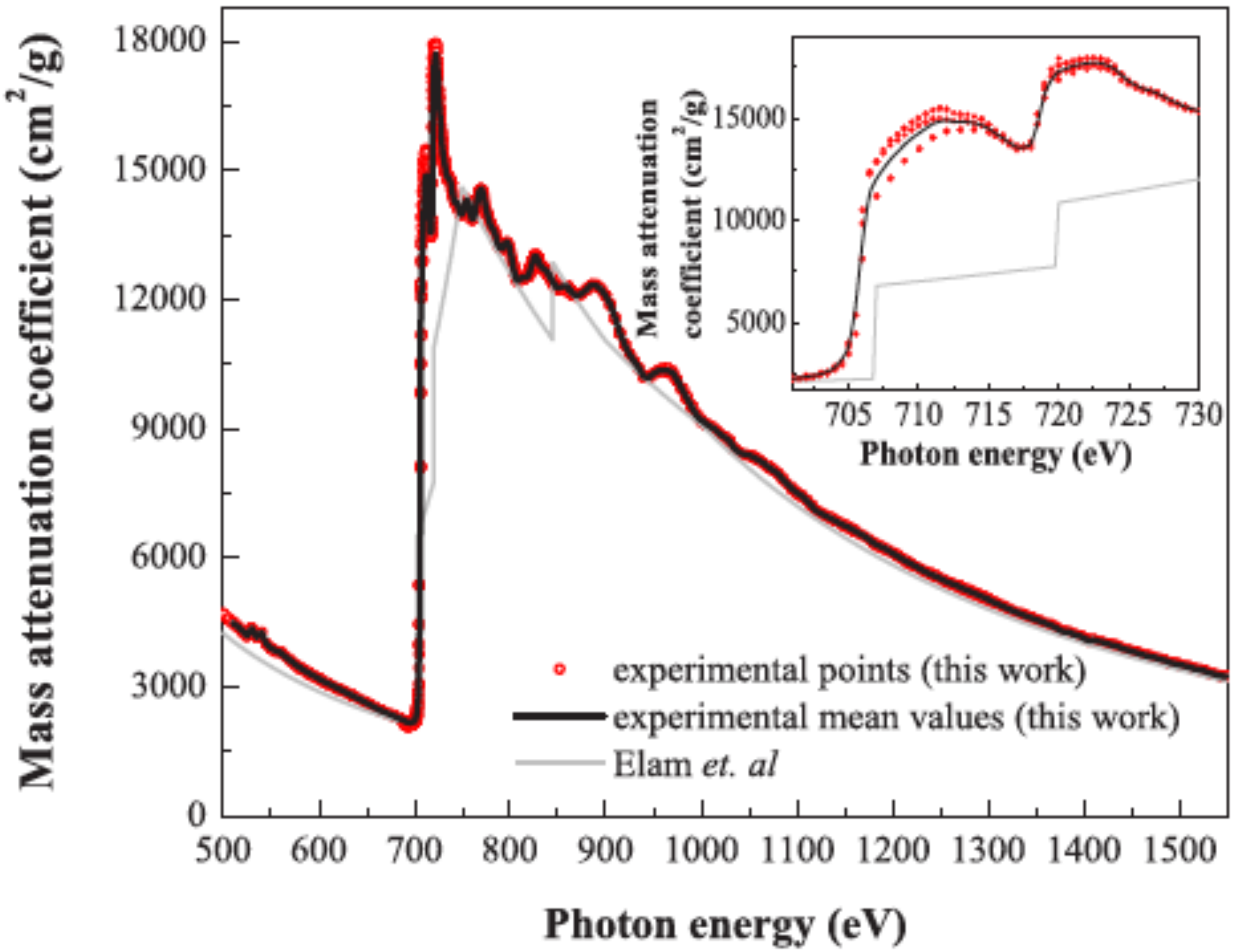
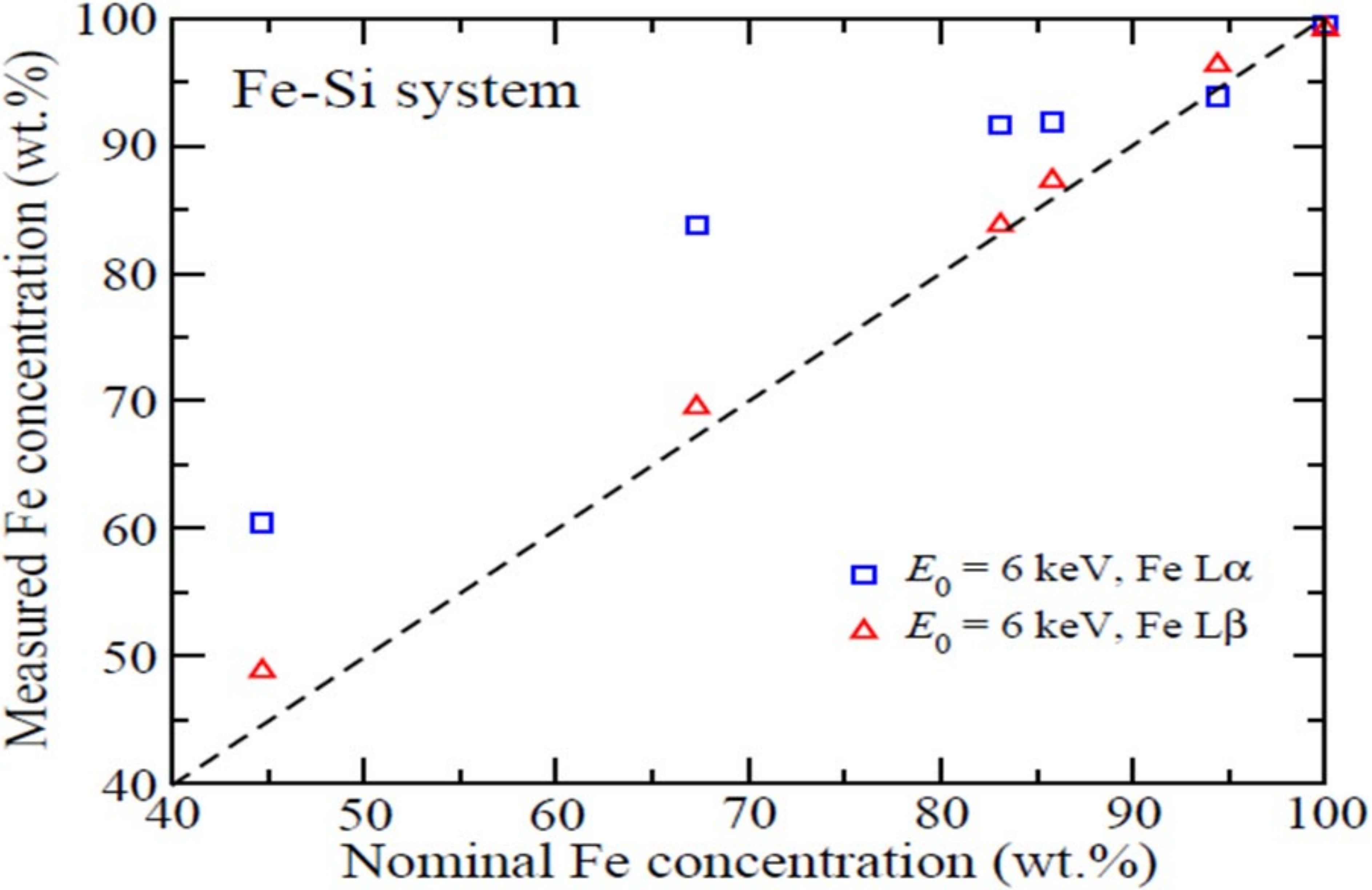


FIG. 3. (Color online) Experimental (this work) and theoretical [34] mass attenuation coefficients for metallic Fe in the energy region 500–1550 eV. The solid line represents the smoothed mean experimental values obtained by multiple transmittance energy scans.

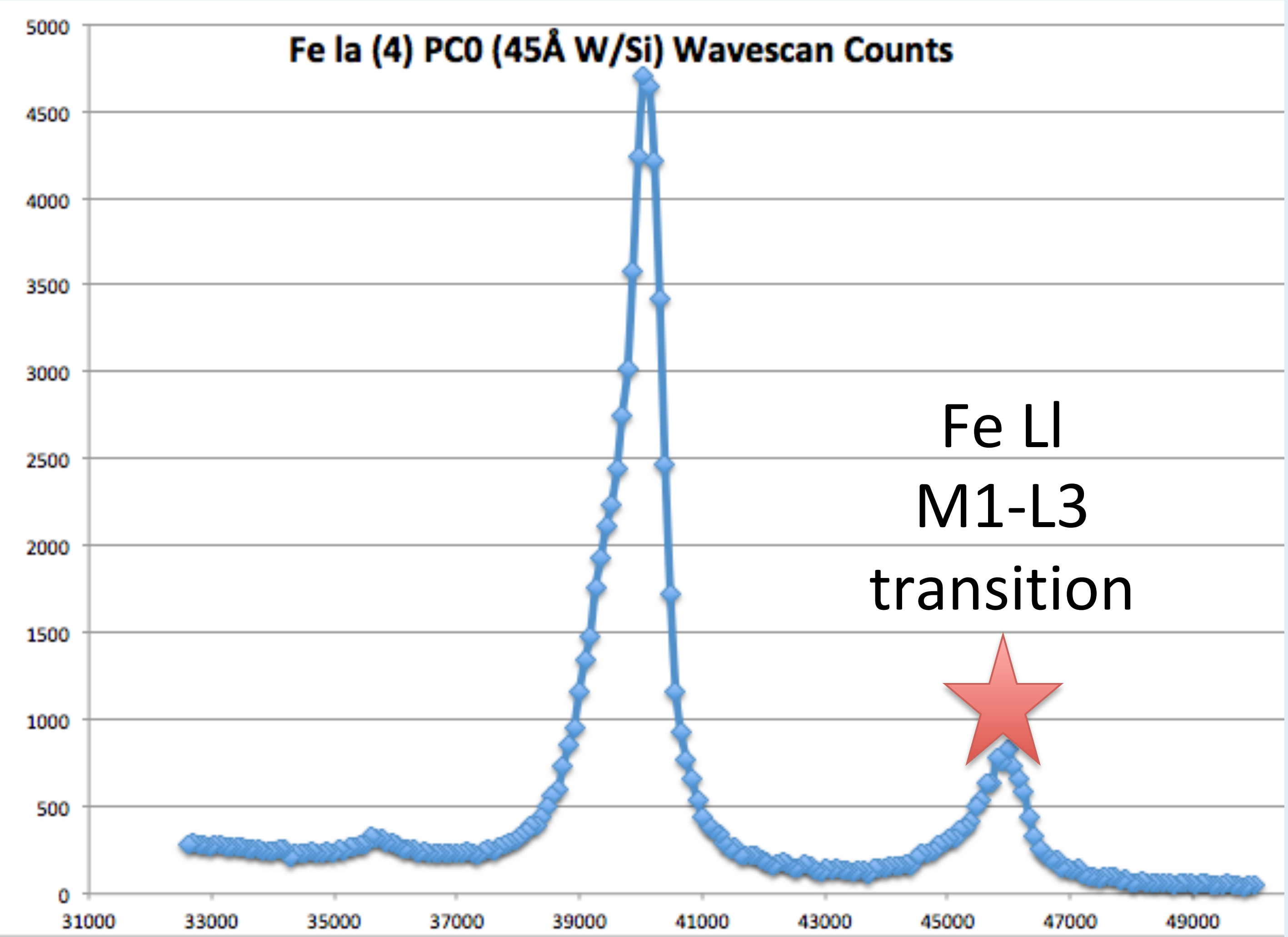
Fe L3 “707 eV”
Fe La “705 eV”

Fe L2 “720 eV”
Fe Lb “719 eV”

Sokaris’et al paper (2011 Phys Rev A 83, 052511): experiment with Fe metal absorption (includes Fe L3 and L2 edges)


Fe-Si system
Measured Fe concentration (wt.%)
Nominal Fe concentration (wt.%)
40
50
60
70
80
90
100
□ E_0 = 6 keV, Fe Lα
△ E_0 = 6 keV, Fe Lβ

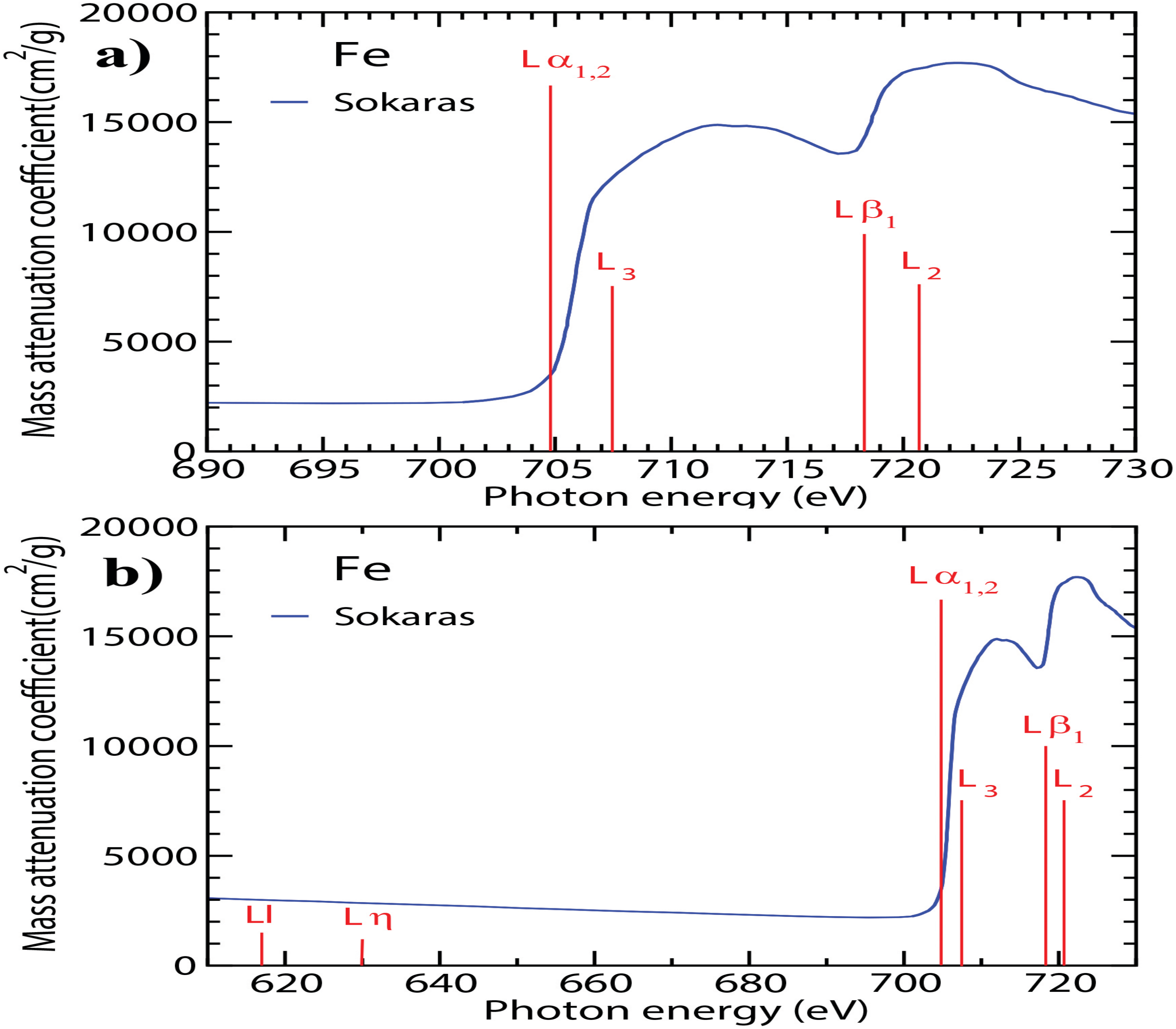
Ah ha moment…



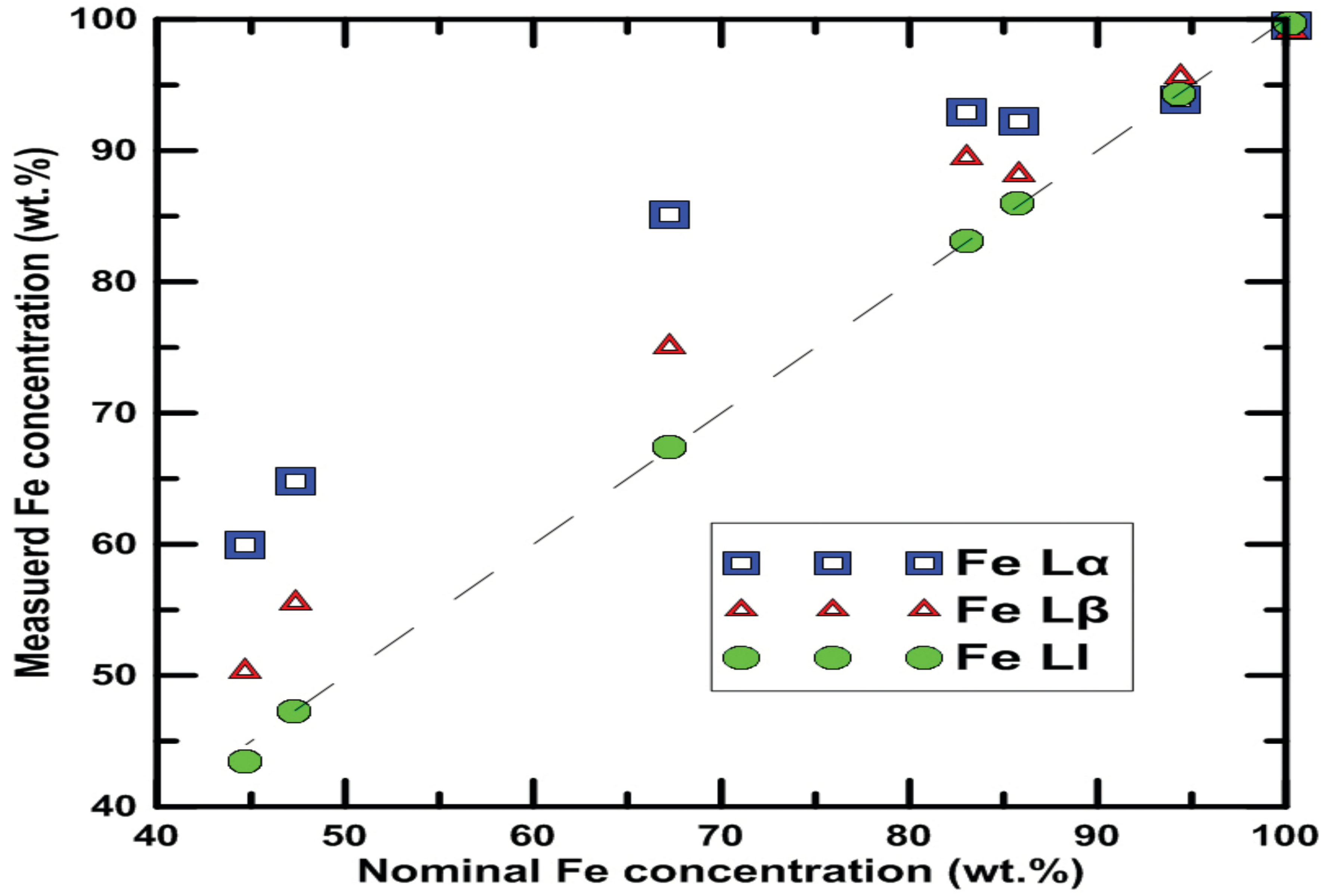
Fe Ll
M1-L3
transition

Why not use the Fe Ll line for Analysis?

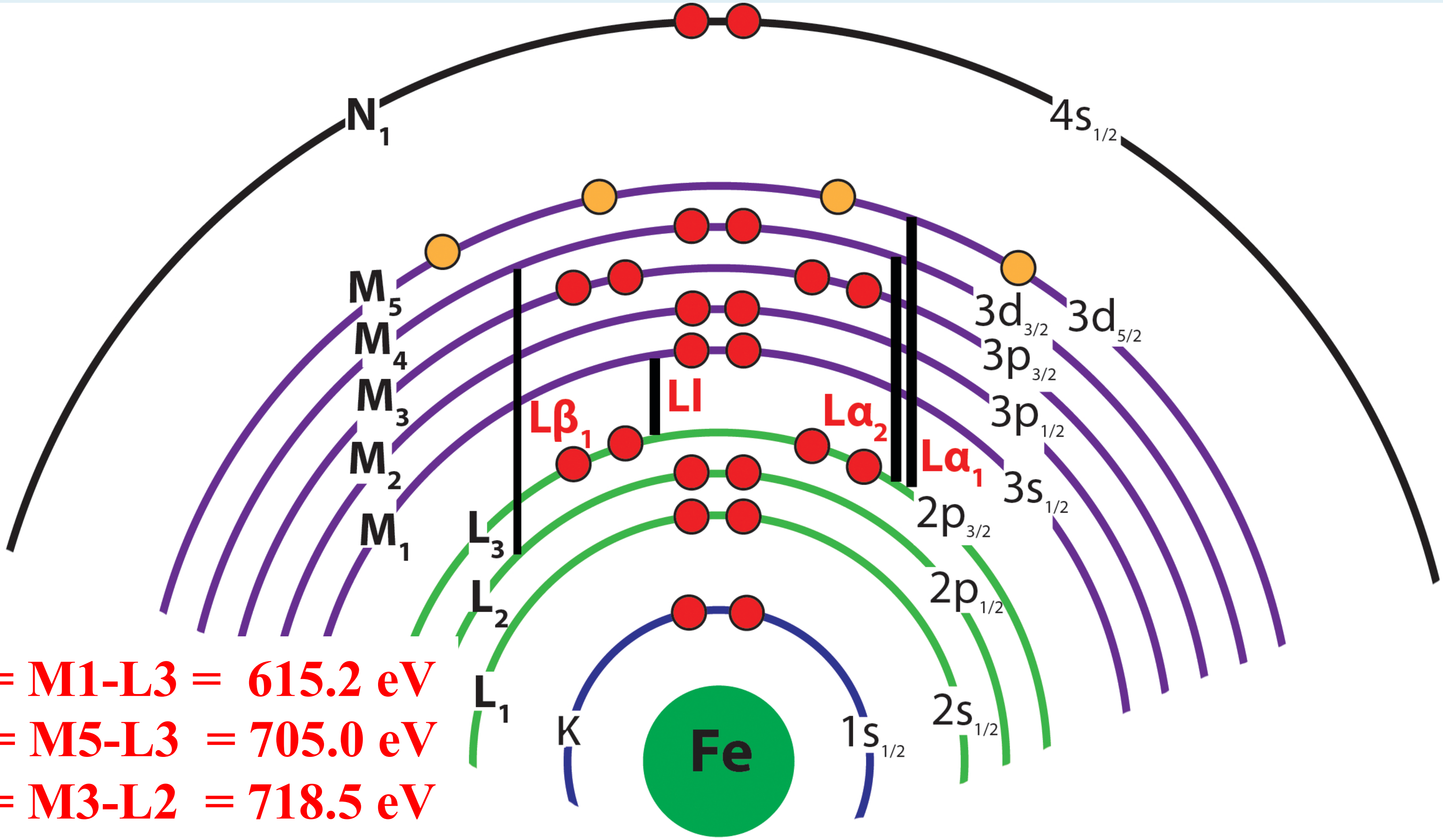
Fe Ll =
M1-L3
transition



Gopon, Fournelle, Sobol and Llovet, 2013, Microscopy & Microanalysis, 19, 1698-1708



Use the Fe Ll line for Low keV Analysis



Ll = M1-L3 = 615.2 eV
Lα= M5-L3 = 705.0 eV
Lβ= M3-L2 = 718.5 eV

However, while Fe Ll offers some opportunities, for many materials the intensity is weak.

Therefore, we are currently working on full Fe L spectral deconvolutions to see if it might be possible to utilize the La/Lb lines, particularly for silicate EPMA.

No time here to discuss other important issues pertinent to low keV EPMA:

- Possible issues due to adventitious carbon contamination, particularly on low energy X-rays
- For fully focused FE-beams on many materials, sample alteration/damage very likely

Exactly how small can we resolve features with low voltage FE EPMA?

= Accurate quantitative analysis

Calculations of X-ray Range

"average path length that electrons travel before slowing down equal to an energy equal to the excitation energy of the considered electron shell" (Merlet and Llovet, 2012)

Castaing (1952)

$$R_X = \frac{33A(E_0^{1.7} - E_{Cr}^{1.7})}{\rho * Z}$$

Range in nm

Various researchers have modified this x-ray range formulation:

- Anderson and Hasler (1966)
- Reed (1966)
- Hovington et al (1997)

→ All with similar form

Calculations of ANALYTICAL RESOLUTION

- Duncumb (1960) suggested need to multiply X-ray Range by 1.6 **for analytical resolution**
- Reed (1975) suggested need to multiply X-ray Range by ~3 **for analytical resolution**.

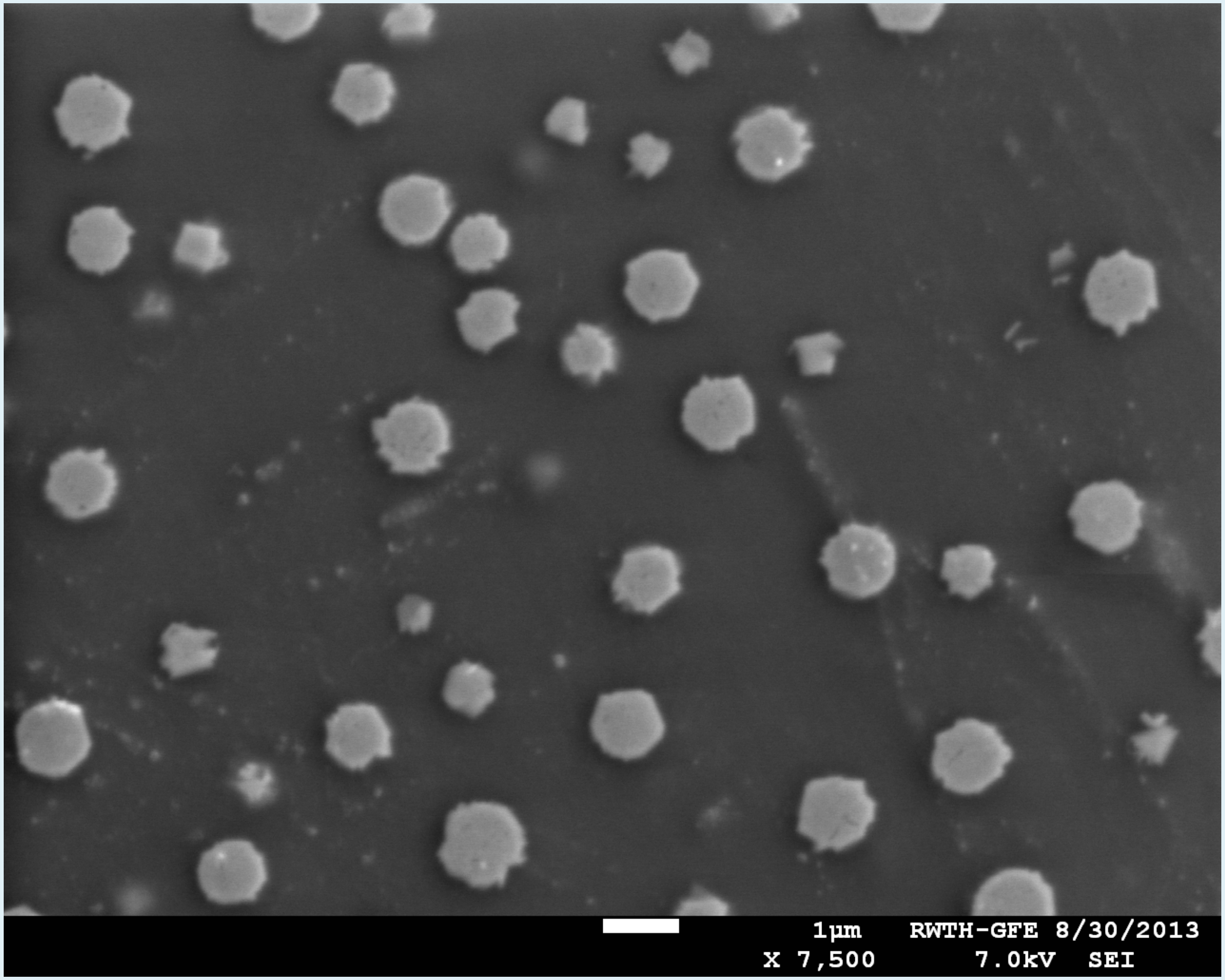
- Merlet and Llovet (2012) suggested explicit inclusion of beam diameter:

$$R_S = \sqrt{4(R_x - Z_m)^2 + d_0^2}$$

- Monte Carlo programs such as PENEPMA provide possible simulations with less simplification and averaging used in range approximations

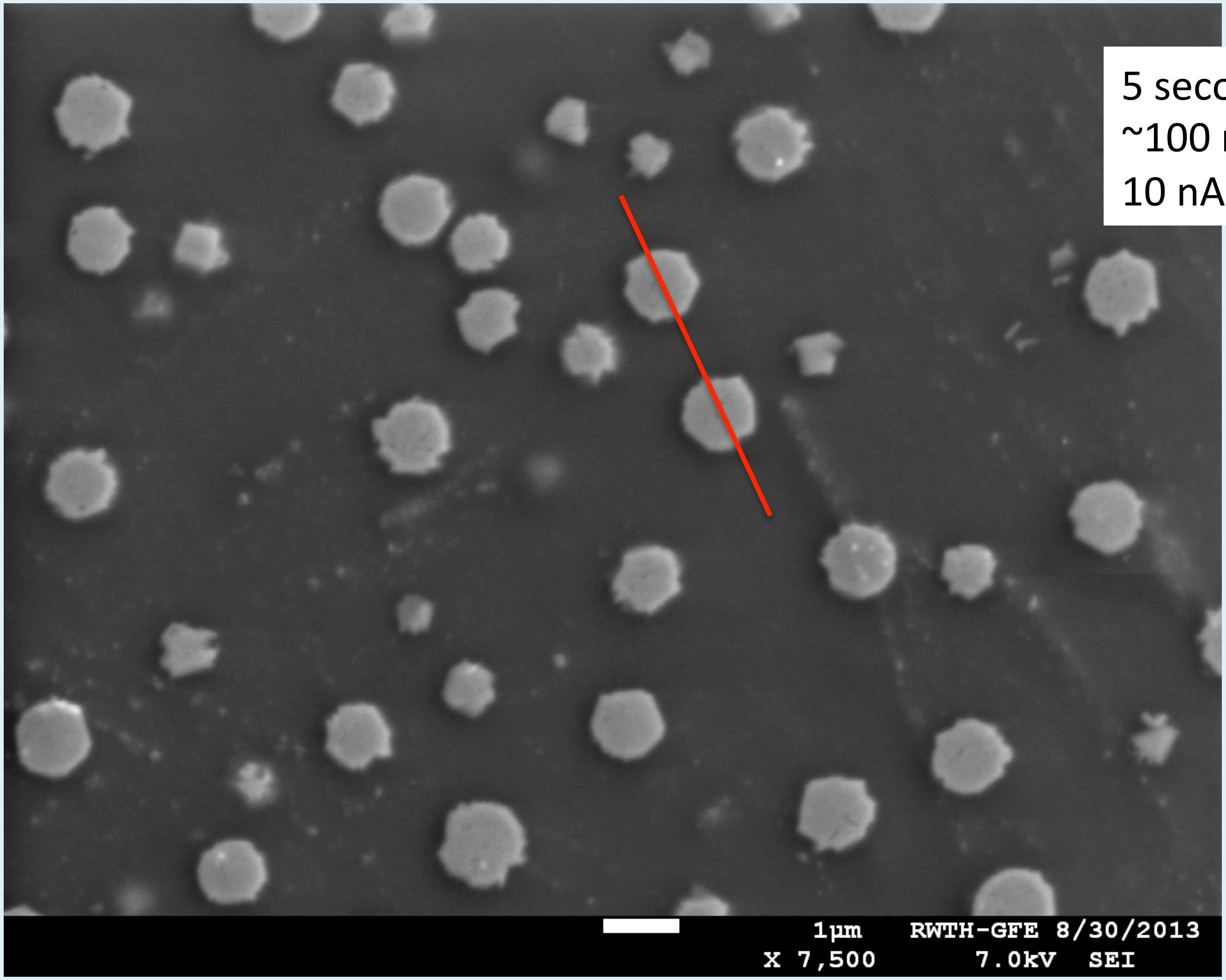
These are all theoretical estimates of “X-ray Range”: can they be evaluated experimentally as far as “lateral analytical spatial resolution?

NBS/NIST K409, a ‘failed experiment’



(I have some fragments I can distribute here at the AMAS meeting)

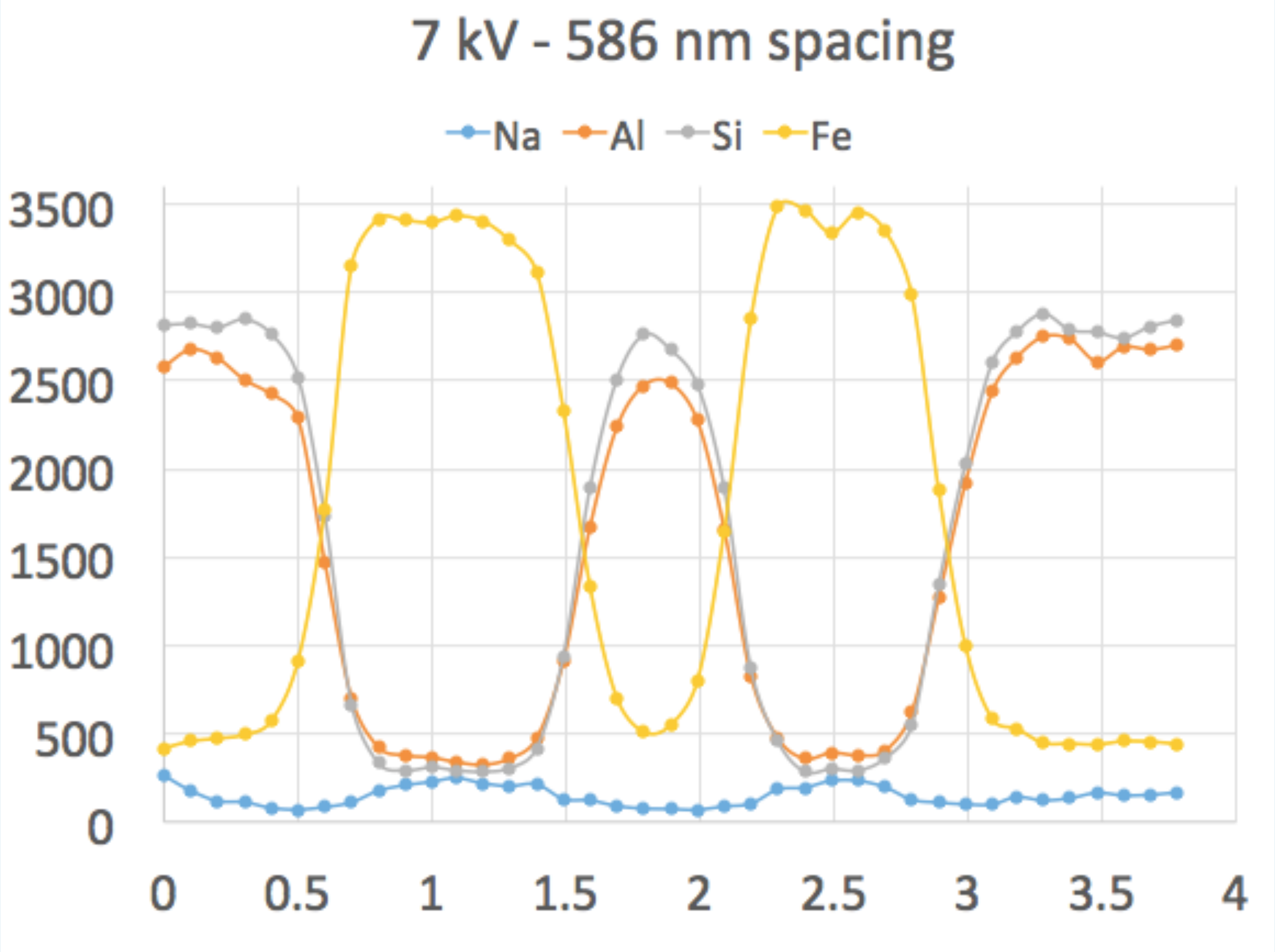
K409 …. Line Traverses – SXFive FE



5 seconds/spot
~100 nm step
10 nA

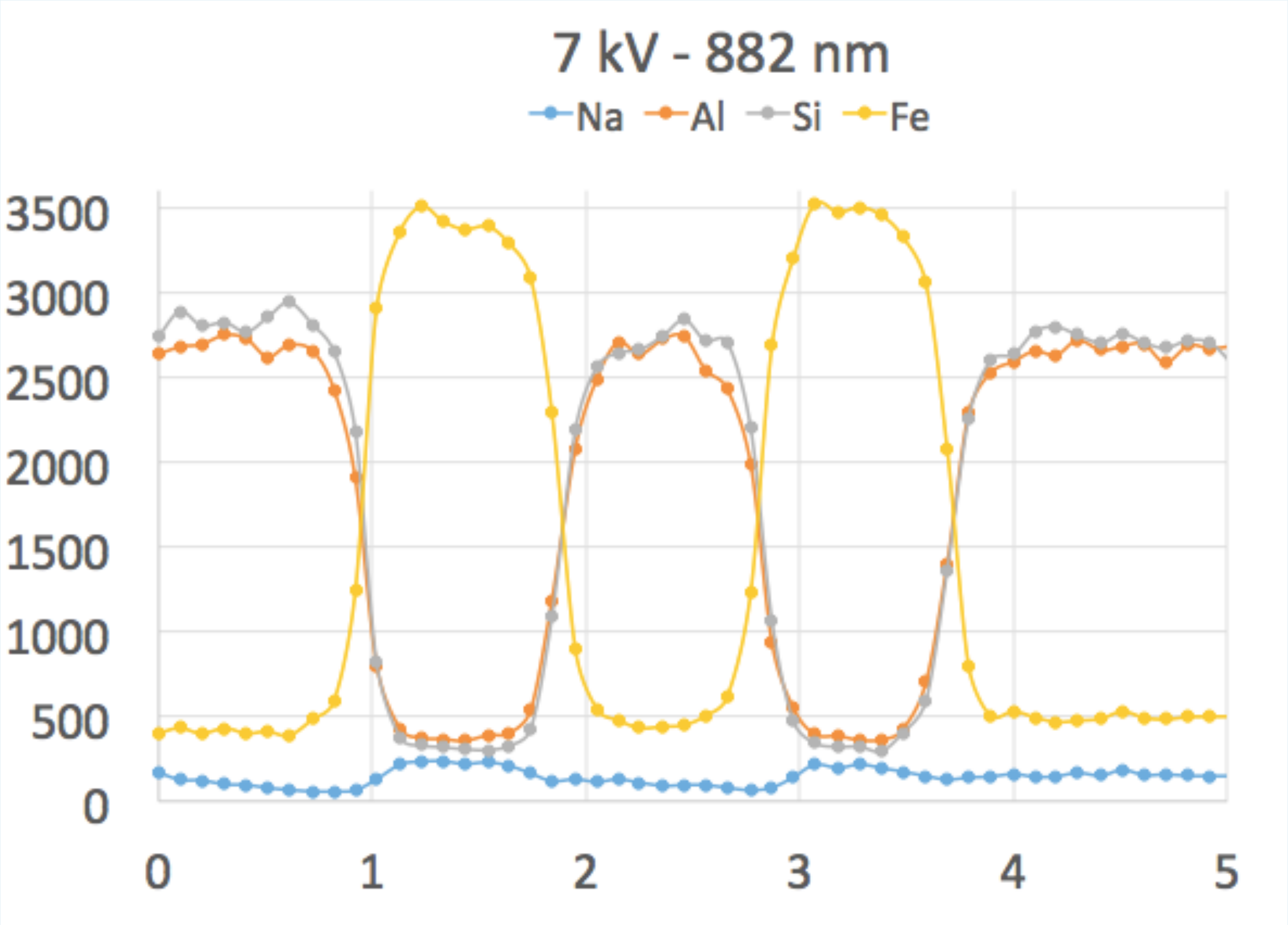
Using K409 to model low keV X-ray spatial resolution

Si 0.91
Al 0.96
Fe 01.02



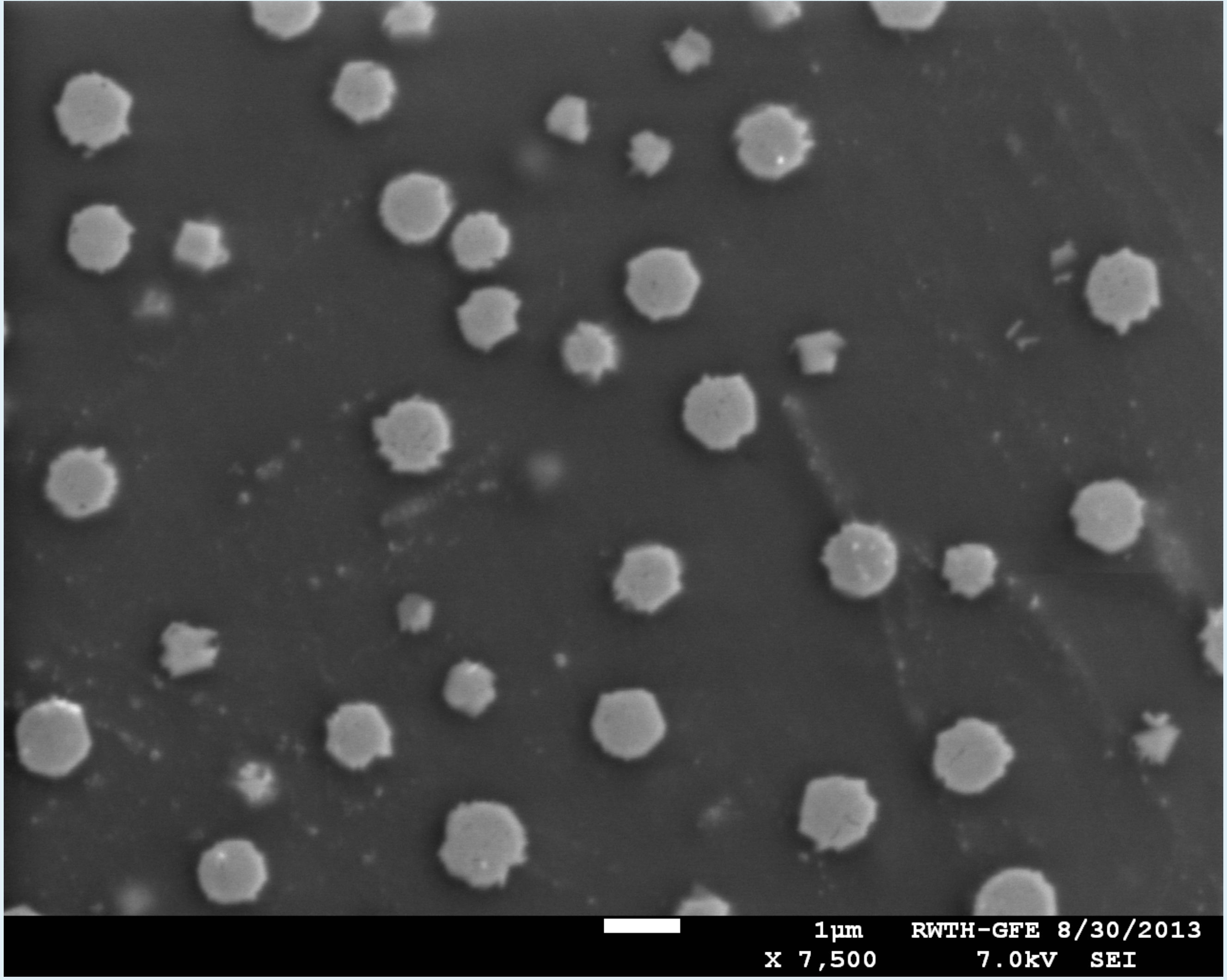
Lateral distance in microns between two K409 Fe-oxide grains = how close can they be to still achieve the same X-ray intensity as ‘far away from Fe-oxide’?

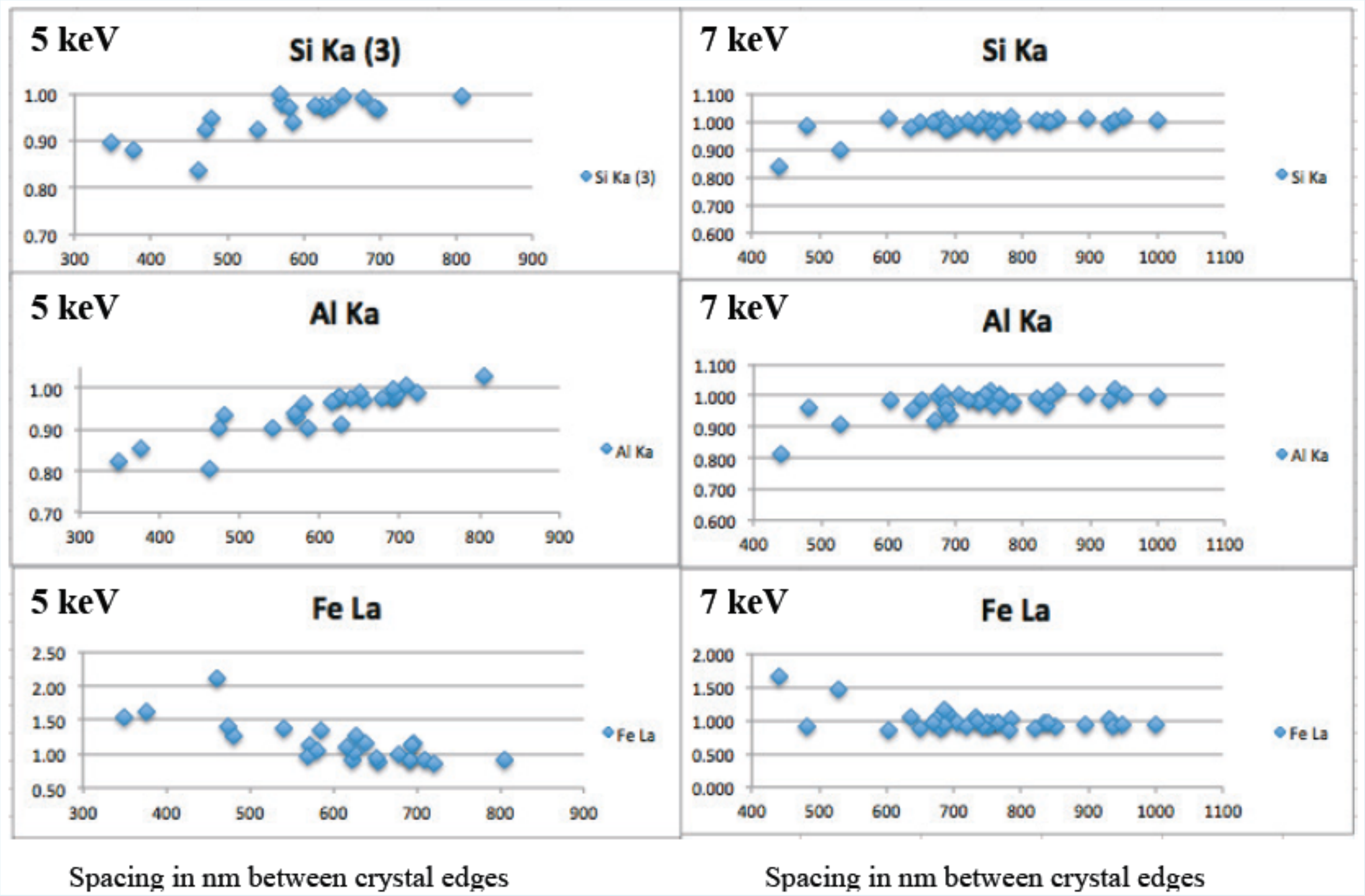
Si 1.01
Al 0.99
Fe 0.96



Note: Na Ka X-rays are immediately “lost” under the focused FE beam (there is 10.8 wt% Na_2O in the glass)

Revised experiment: 50 second measurement in middle between 2 crystals (10 nA)





There does not appear to be any significant benefit in dropping from 7 to 5 keV, as both reach the ‘far’ glass value at 600-700 nm

Table 4. Comparison of experiments at 5 and 7 keV with various estimations of analytical X-ray lateral resolution, for Si-Kα, Al-Kα and Fe-Lα in K409 glass, using various published formulations and results from Monte Carlo simulations. For Merlet-Llovet formula, (a) uses phi-rho-Z max from CASINO, (b) uses phi-rho-Z max from Merlet (pers. comm.). PENEPMA for Fe-Lα not included due to poor statistics.

X-ray ranges	5 keV Al-Kα	5 keV Si-Kα	5 keV Fe-Lα	7 keV Al-Kα	7 keV Si-Kα	7 keV Fe-Lα
Castaing 1952	351	321	405	664	625	730
Anderson-Hasler '66	322	311	352	602	590	632
Reed '66	273	257	314	491	475	531
Hovington et al '97	297	281	333	558	543	1065
Analytical resolution						
Duncumb (x1.6)	437	411	502	785	759	849
Reed (x3)	820	772	940	1472	1424	1593
Merlet-Llovet '12 (a)	578	512	619	989	909	1065
Merlet-Llovet '12 (b)	515	465	607	974	900	1091
PENEPMA (100 %)	500	500	*	700	700	*
CASINO (99.9 %)	360	360	436	674	674	755
K409 point experiments	575-650	575-650	575-650	600-700	600-700	600-700

Can we create an EPMA “app” to estimate analytical lateral spatial resolution for <u>small inclusions in a matrix</u>, that uses the definition of Barksdale et al (2001), such that it achieves at least 99% of the total X-ray intensity?

→Use PENEPMA (PENELOPE) for Monte Carlo model

→Provide several geometries (currently half sphere and rectangular box)

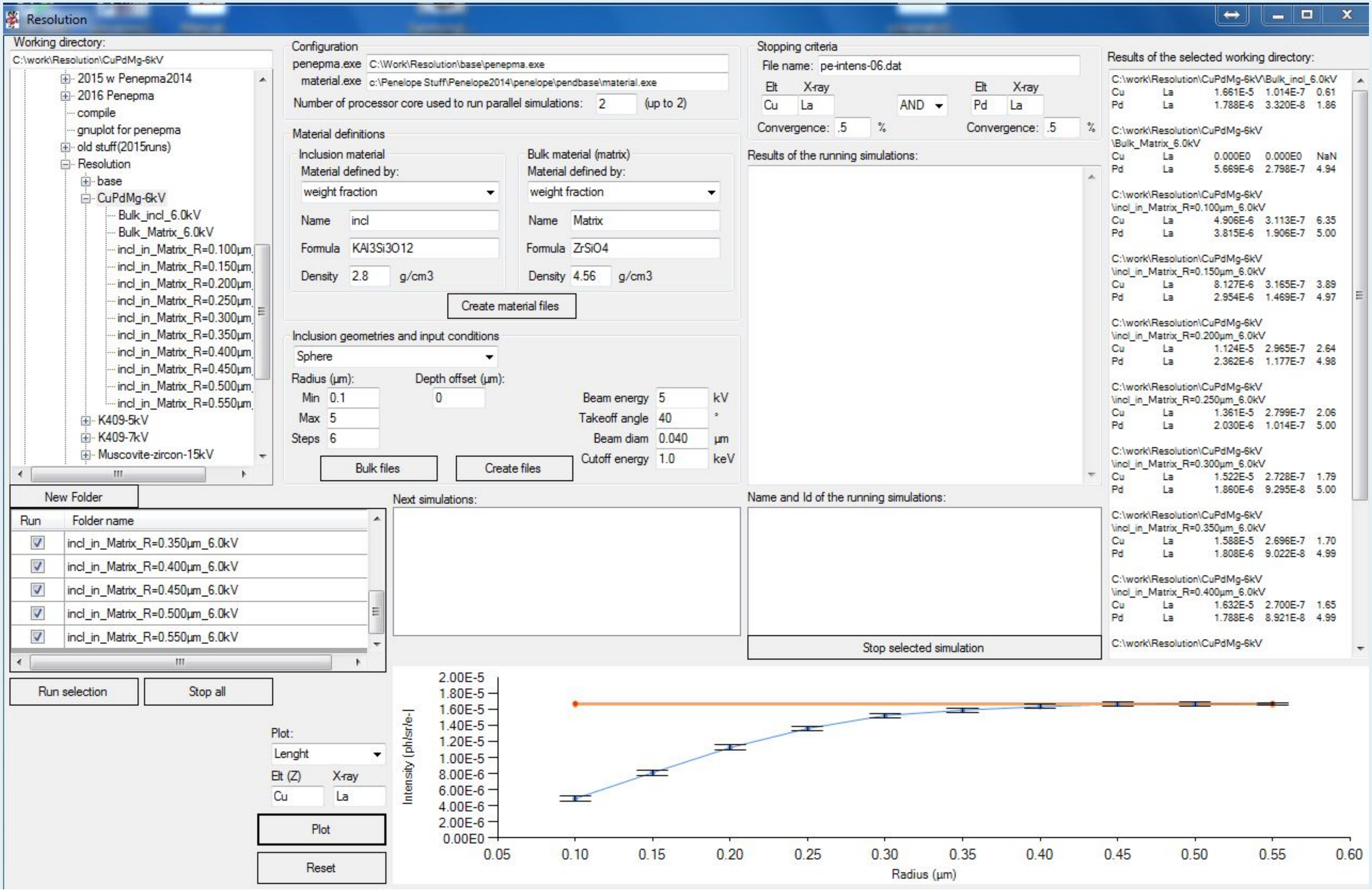
→Easy-to-use GUI

→Use as many processors simultaneously as available on computer

→Raw data immediately displayed (though tighter error bars may take 30+ minutes, depending upon problem)

“WISC-Resolution”

Aurelien Moy has created this interface to PENEPMA which provides estimates of analytical spatial resolution for two inclusion shapes (half sphere; rectangle)



Working directory: C:\work\Resolution\CuPdMg-6kV

- 2015 w Penepma2014
- 2016 Penepma
- compile
- gnuplot for penepma
- old stuff(2015runs)
- Resolution
  - base
  - CuPdMg-6kV
    - Bulk_incl_6.0kV
    - Bulk_Matrix_6.0kV
    - incl_in_Matrix_R=0.100µm
    - incl_in_Matrix_R=0.150µm
    - incl_in_Matrix_R=0.200µm
    - incl_in_Matrix_R=0.250µm
    - incl_in_Matrix_R=0.300µm
    - incl_in_Matrix_R=0.350µm
    - incl_in_Matrix_R=0.400µm
    - incl_in_Matrix_R=0.450µm
    - incl_in_Matrix_R=0.500µm
    - incl_in_Matrix_R=0.550µm
  - K409-5kV
  - K409-7kV
  - Muscovite-zircon-15kV

Run	Folder name
☑	incl_in_Matrix_R=0.350µm_6.0kV
☑	incl_in_Matrix_R=0.400µm_6.0kV
☑	incl_in_Matrix_R=0.450µm_6.0kV
☑	incl_in_Matrix_R=0.500µm_6.0kV
☑	incl_in_Matrix_R=0.550µm_6.0kV

Configuration
penepma.exe: C:\Work\Resolution\base\penepma.exe
material.exe: c:\Penelope Stuff\Penelope2014\penelope\pendbase\material.exe
Number of processor core used to run parallel simulations: 2 (up to 2)

Material definitions

	Inclusion material	Bulk material (matrix)
Material defined by:	weight fraction	weight fraction
Name	incl	Matrix
Formula	KAl3Si3O12	ZrSiO4
Density	2.8 g/cm3	4.56 g/cm3

Inclusion geometries and input conditions
Sphere
Radius (µm): Min 0.1, Max 5, Steps 6
Depth offset (µm): 0
Beam energy: 5 kV
Takeoff angle: 40 °
Beam diam: 0.040 µm
Cutoff energy: 1.0 keV

Stopping criteria
File name: pe-intens-06.dat
Elt: Cu, X-ray: La, Convergence: .5 %
AND
Elt: Pd, X-ray: La, Convergence: .5 %

Results of the running simulations:

Next simulations:

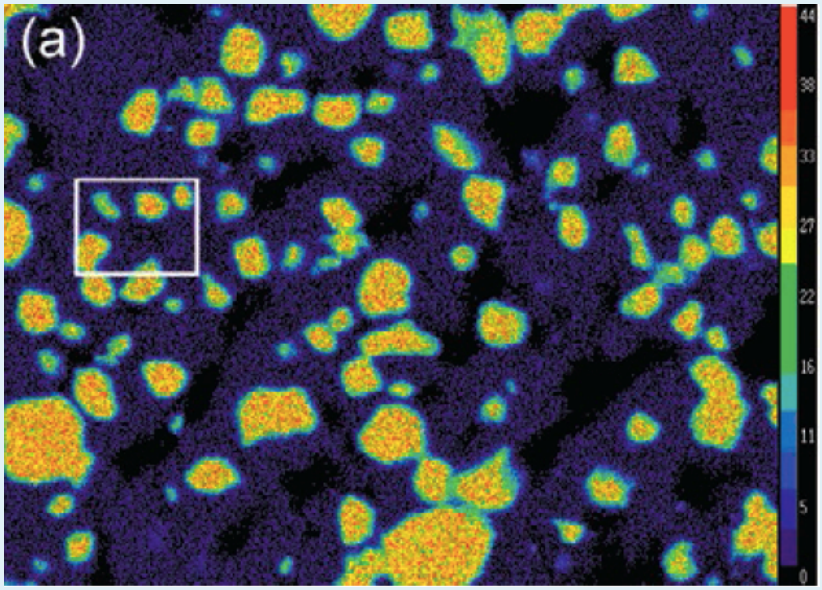
Name and Id of the running simulations:

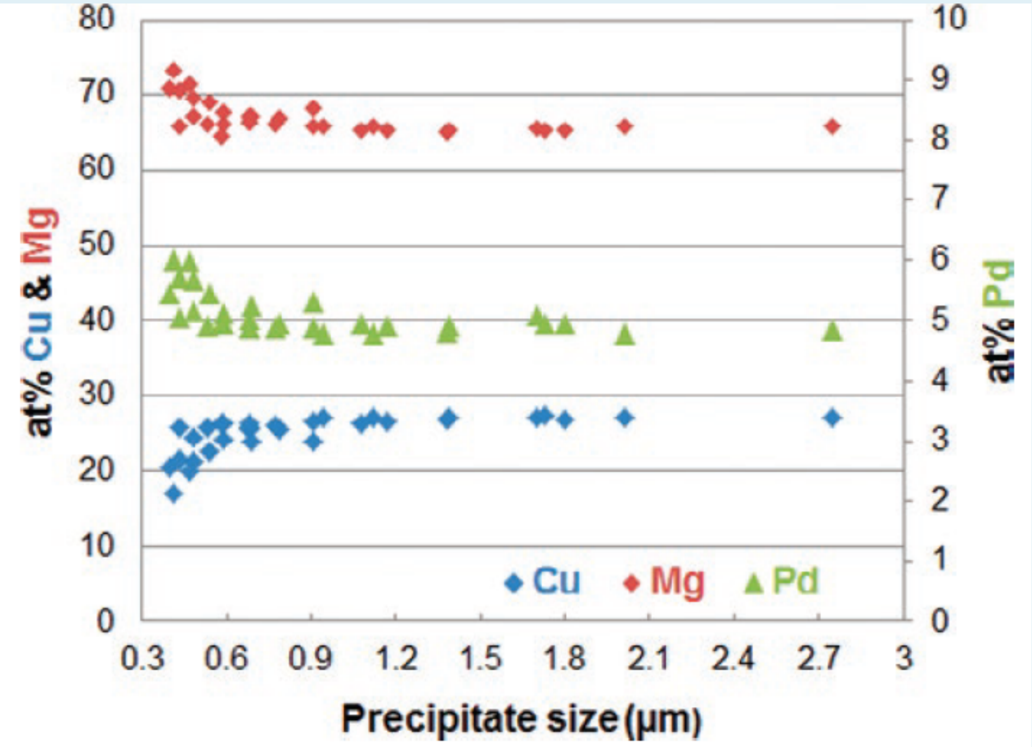
Plot: Lenght
Elt (Z): Cu, X-ray: La

Results of the selected working directory:

```
C:\work\Resolution\CuPdMg-6kV\Bulk_incl_6.0kV
Cu      La      1.661E-5   1.014E-7   0.61
Pd      La      1.788E-6   3.320E-8   1.86

C:\work\Resolution\CuPdMg-6kV
\Bulk_Matrix_6.0kV
Cu      La      0.000E0    0.000E0    NaN
Pd      La      5.669E-6   2.798E-7   4.94

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.100µm_6.0kV
Cu      La      4.906E-6   3.113E-7   6.35
Pd      La      3.815E-6   1.906E-7   5.00

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.150µm_6.0kV
Cu      La      8.127E-6   3.165E-7   3.89
Pd      La      2.954E-6   1.469E-7   4.97

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.200µm_6.0kV
Cu      La      1.124E-5   2.965E-7   2.64
Pd      La      2.362E-6   1.177E-7   4.98

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.250µm_6.0kV
Cu      La      1.361E-5   2.799E-7   2.06
Pd      La      2.030E-6   1.014E-7   5.00

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.300µm_6.0kV
Cu      La      1.522E-5   2.728E-7   1.79
Pd      La      1.860E-6   9.295E-8   5.00

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.350µm_6.0kV
Cu      La      1.588E-5   2.696E-7   1.70
Pd      La      1.808E-6   9.022E-8   4.99

C:\work\Resolution\CuPdMg-6kV
\incl_in_Matrix_R=0.400µm_6.0kV
Cu      La      1.632E-5   2.700E-7   1.65
Pd      La      1.788E-6   8.921E-8   4.99

C:\work\Resolution\CuPdMg-6kV
```

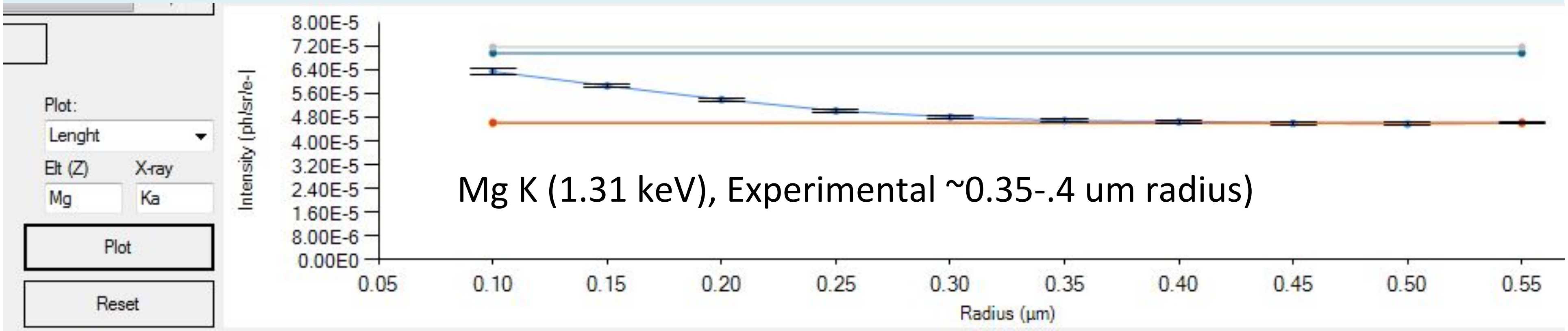
Experimental data





FE EPMA of various sizes of Cu-Mg-Pd phases in a Mg-Pd host (6 keV, 20 nA) from Hombourger & Outrequin, 2013

WISC-Resolution Results for Mg-Pd-Cu (6 keV)

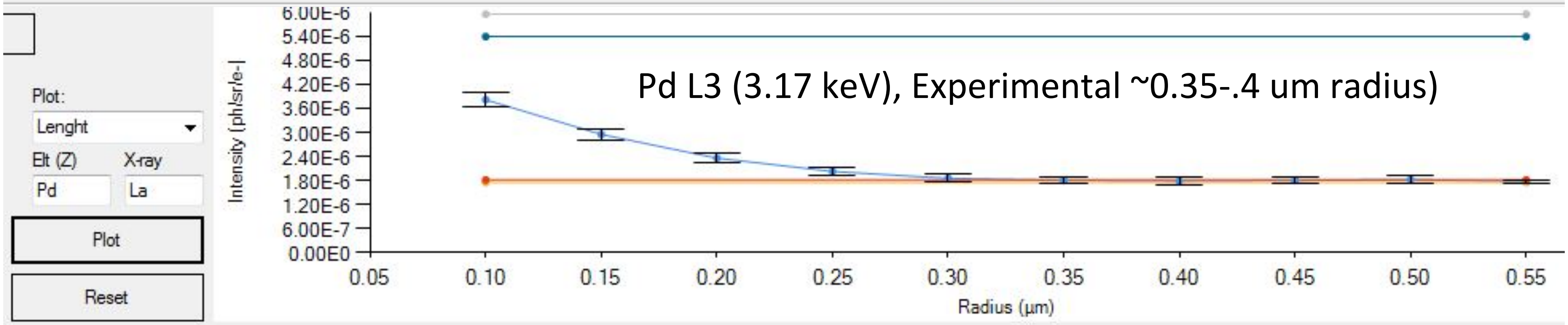


Plot: Lenght

Elt (Z): Mg

X-ray: Ka

Mg K (1.31 keV), Experimental ~0.35-.4 um radius)

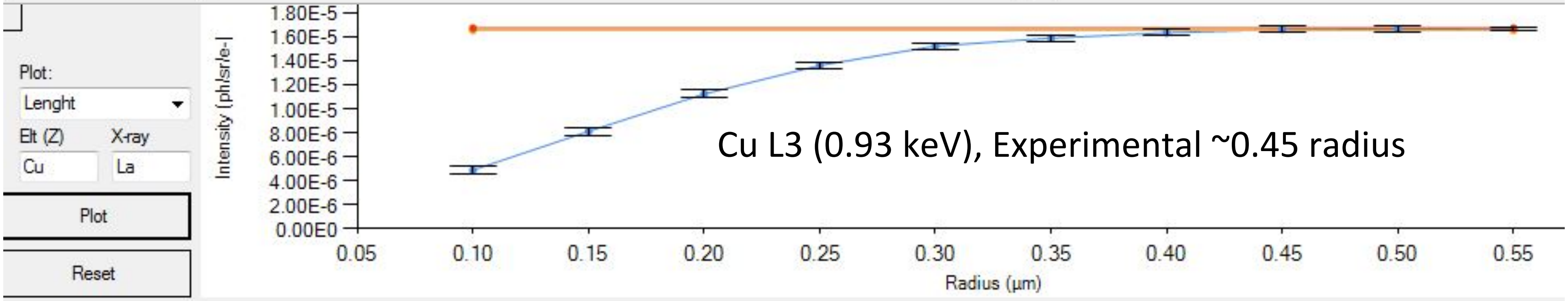


Plot: Lenght

Elt (Z): Pd

X-ray: La

Pd L3 (3.17 keV), Experimental ~0.35-.4 um radius)



Plot: Lenght

Elt (Z): Cu

X-ray: La

Cu L3 (0.93 keV), Experimental ~0.45 radius

Summary

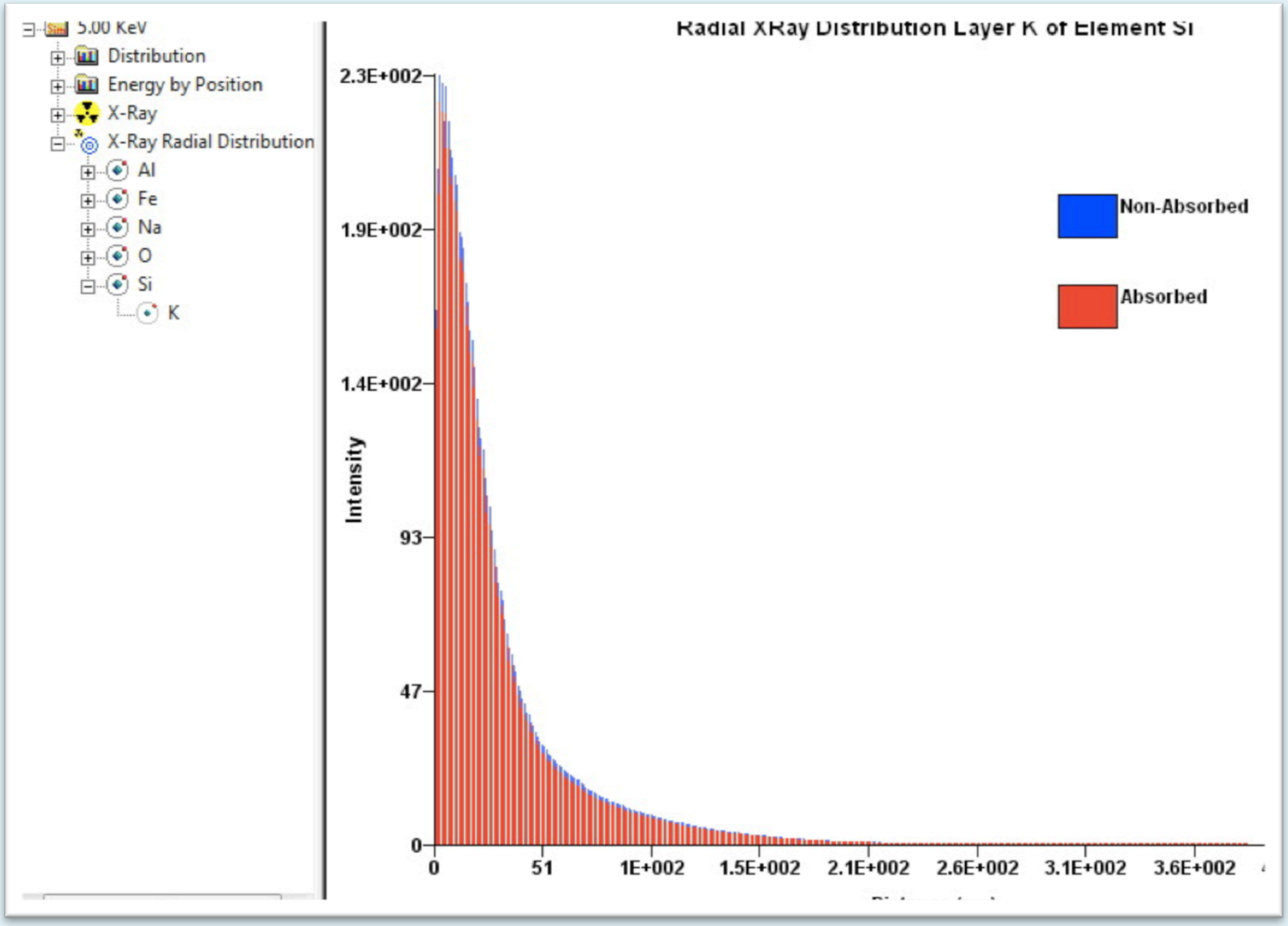
- Need to understand distinction between imaging resolution and analytical resolution
- May need to explore “non-traditional” X-ray lines if decrease beam energy
- May be a limit to “how low you can go”; here, no apparent improvement dropping from 7 to 5 keV in K409 glass example
- Fully focused beam can rapidly alter/damage some samples
- Two apps available from UW Madison EPMA lab
  - Beam size calculator
  - Lateral analytical resolution simulation (WISC-resolution)

Funding for this research: National Science Foundation grants

NSF EAR-1554269
NSF EAR-1337156

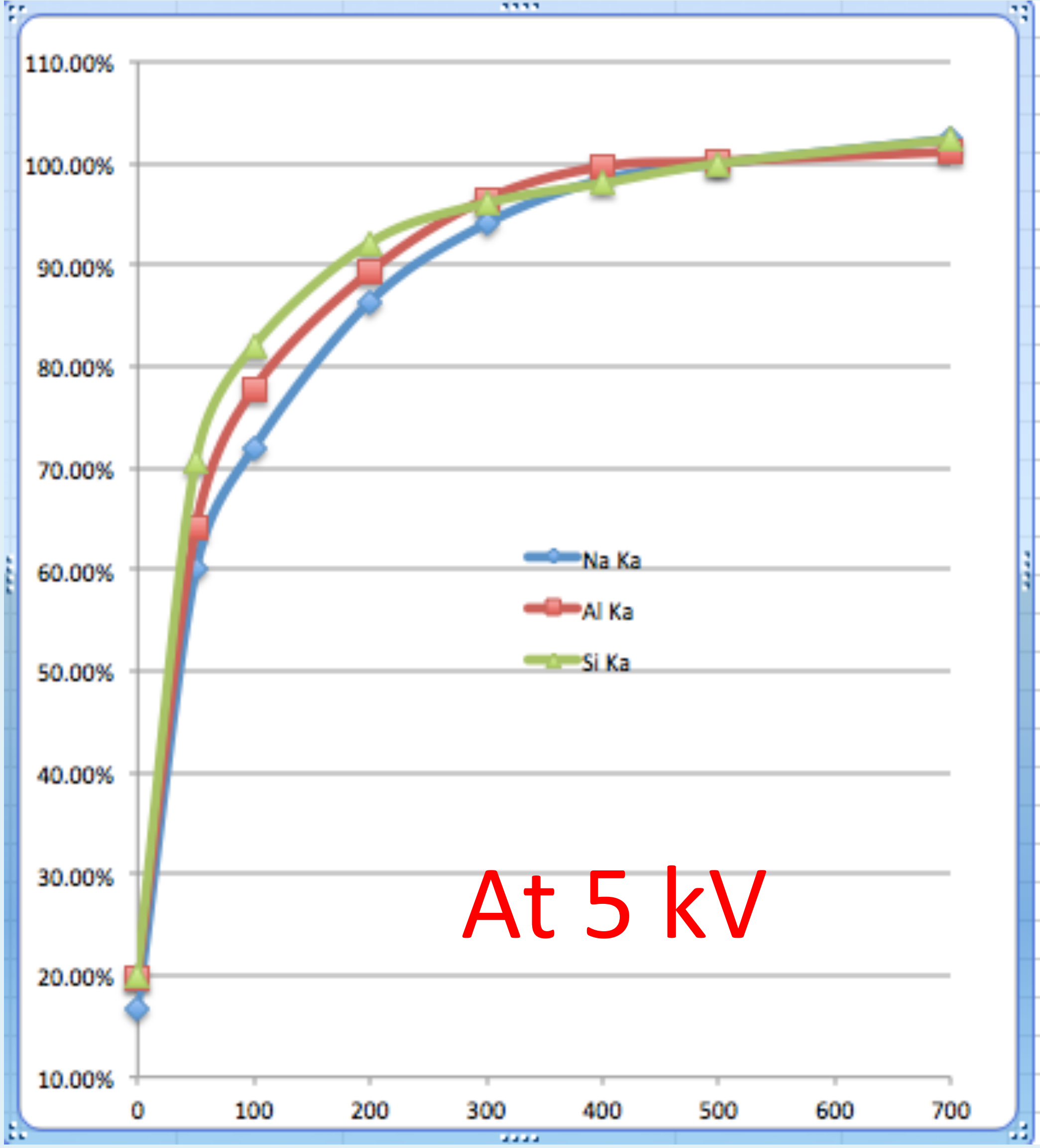

SXFiveFE
CAMECA
AMETEK
Static Beam

CASINO Monte Carlo Simulation in K409 Experiments



At 5 kV

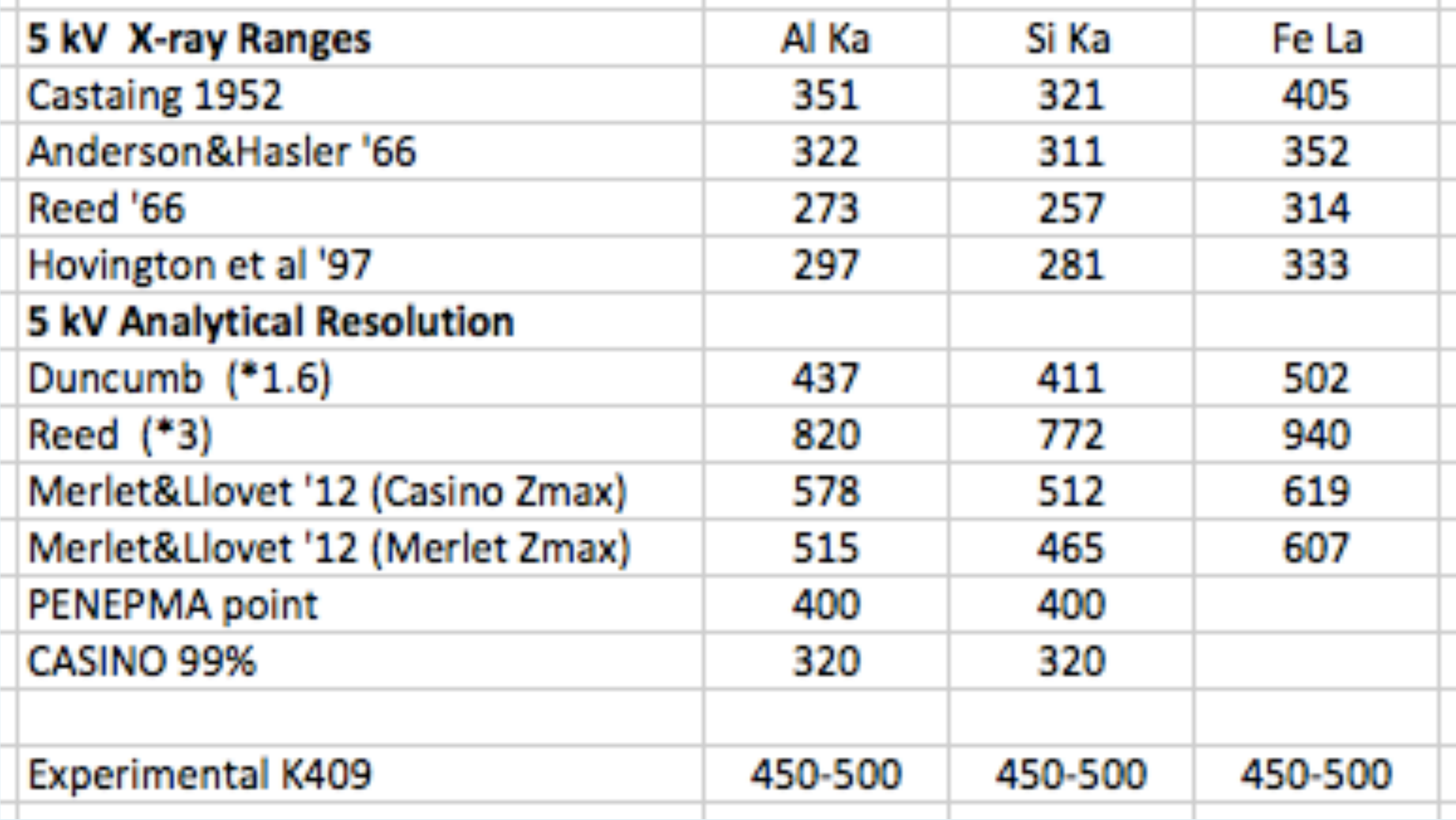
Penepma Monte Carlo Simulation of K409 Experiments



At 5 kV

5 kV

Compare Predictions of Analytical Resolution with K409 Experiments



5 kV X-ray Ranges	Al Ka	Si Ka	Fe La
Castaing 1952	351	321	405
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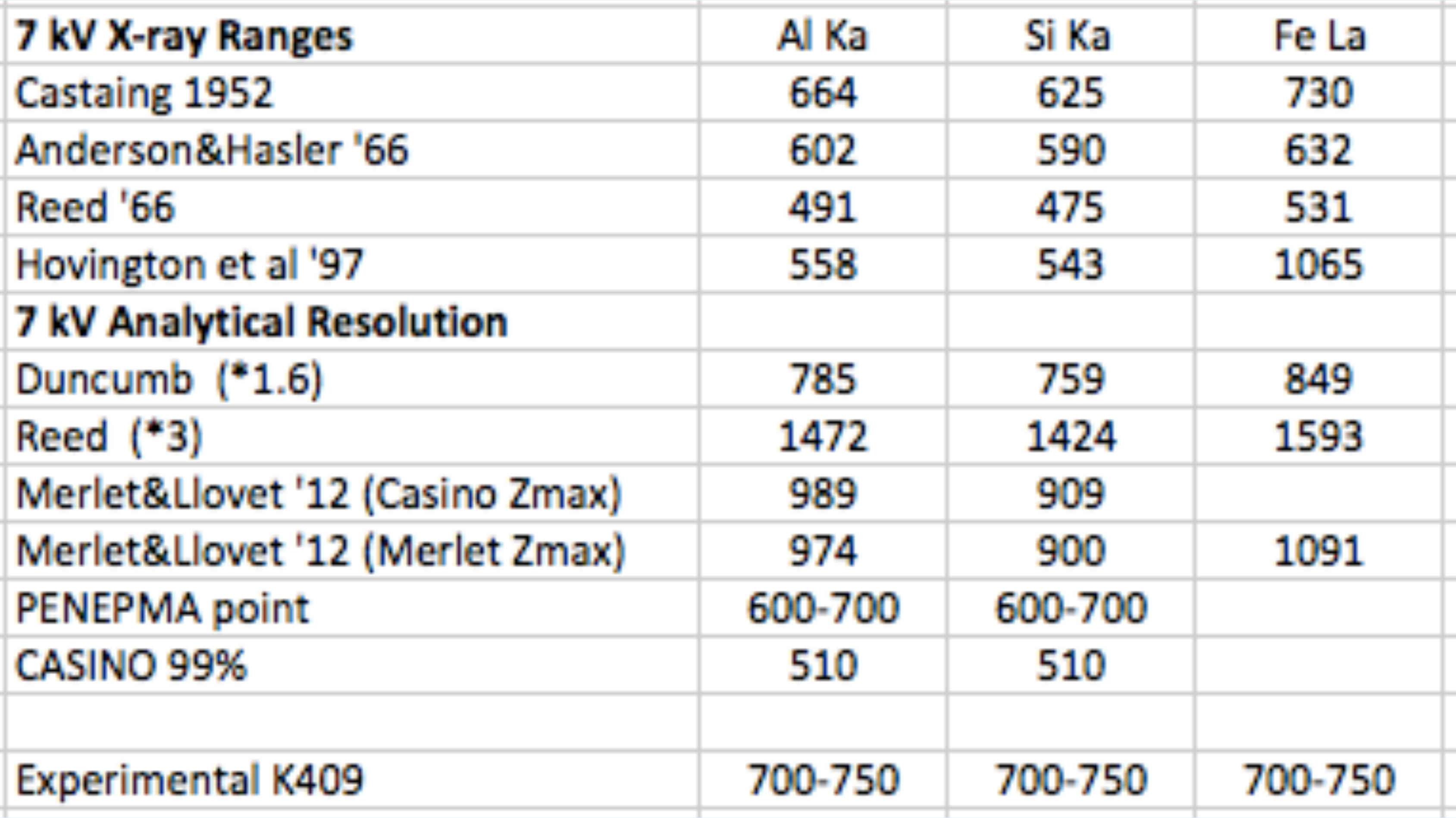
Reed '66	273	257	314
Hovington et al '97	297	281	333
5 kV Analytical Resolution			
Duncumb (*1.6)	437	411	502
Reed (*3)	820	772	940
Merlet&Llovet '12 (Casino Zmax)	578	512	619
Merlet&Llovet '12 (Merlet Zmax)	515	465	607
PENEPMA point	400	400	
CASINO 99%	320	320	
Experimental K409	450-500	450-500	450-500

7 kV

Compare Predictions of Analytical Resolution with K409 Experiments



7 kV X-ray Ranges	Al Ka	Si Ka	Fe La
Castaing 1952	664	625	730
Anderson&Hasler '66	602	590	632
Reed '66	491	475	531
Hovington et al '97	558	543	1065
7 kV Analytical Resolution			
Duncumb (*1.6)	785	759	849
Reed (*3)	1472	1424	1593
Merlet&Llovet '12 (Casino Zmax)	989	909	
Merlet&Llovet '12 (Merlet Zmax)	974	900	1091
PENEPMA point	600-700	600-700	
CASINO 99%	510	510	
Experimental K409	700-750	700-750	700-750

Problems of Soft X-ray analyses of iron

Llovet et al (2012) showed problems of Fe analyses at 5-6 keV (using Fe Lα) with interlaboratory study

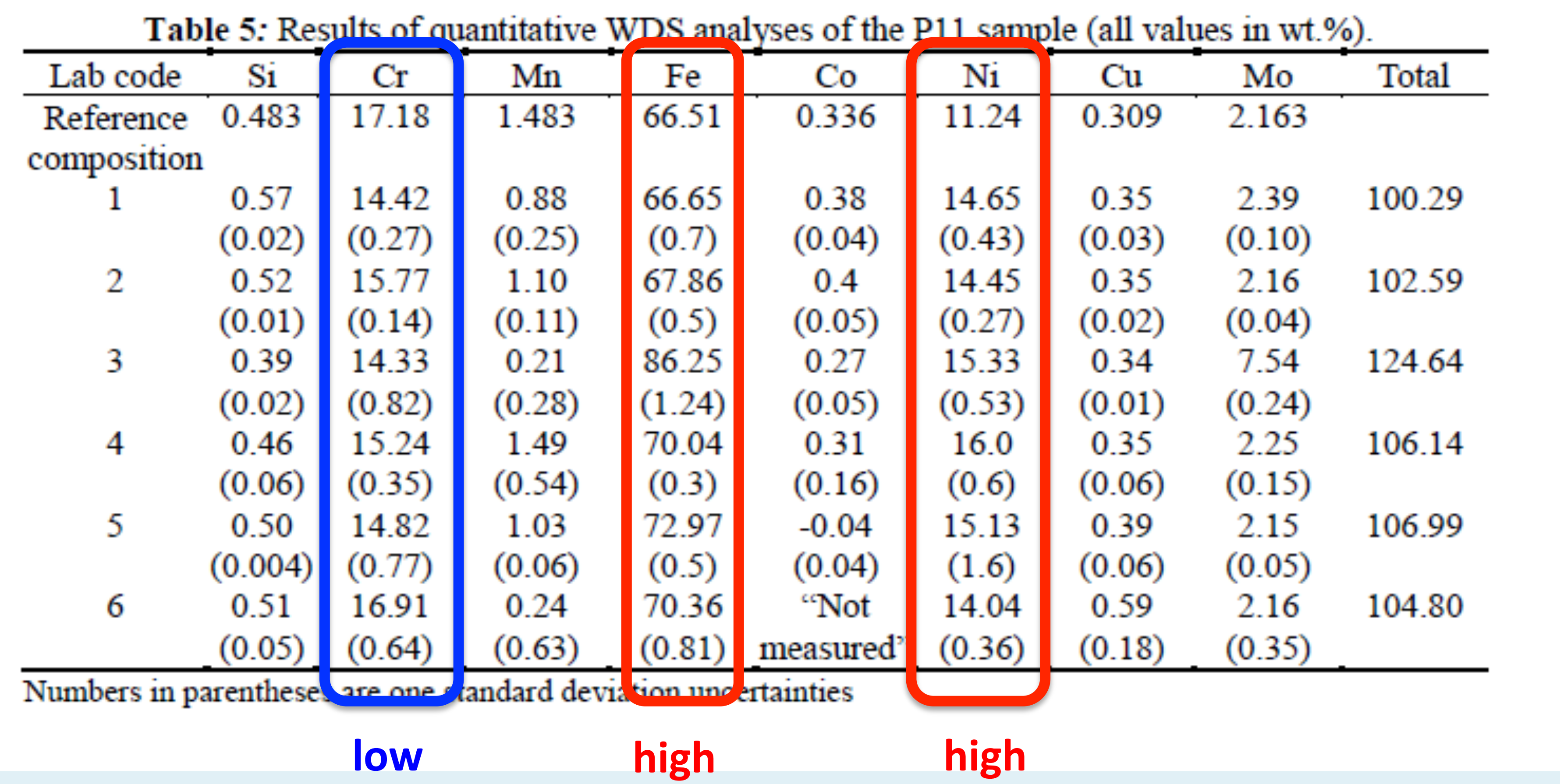


Table 5: Results of quantitative WDS analyses of the P11 sample (all values in wt.%).

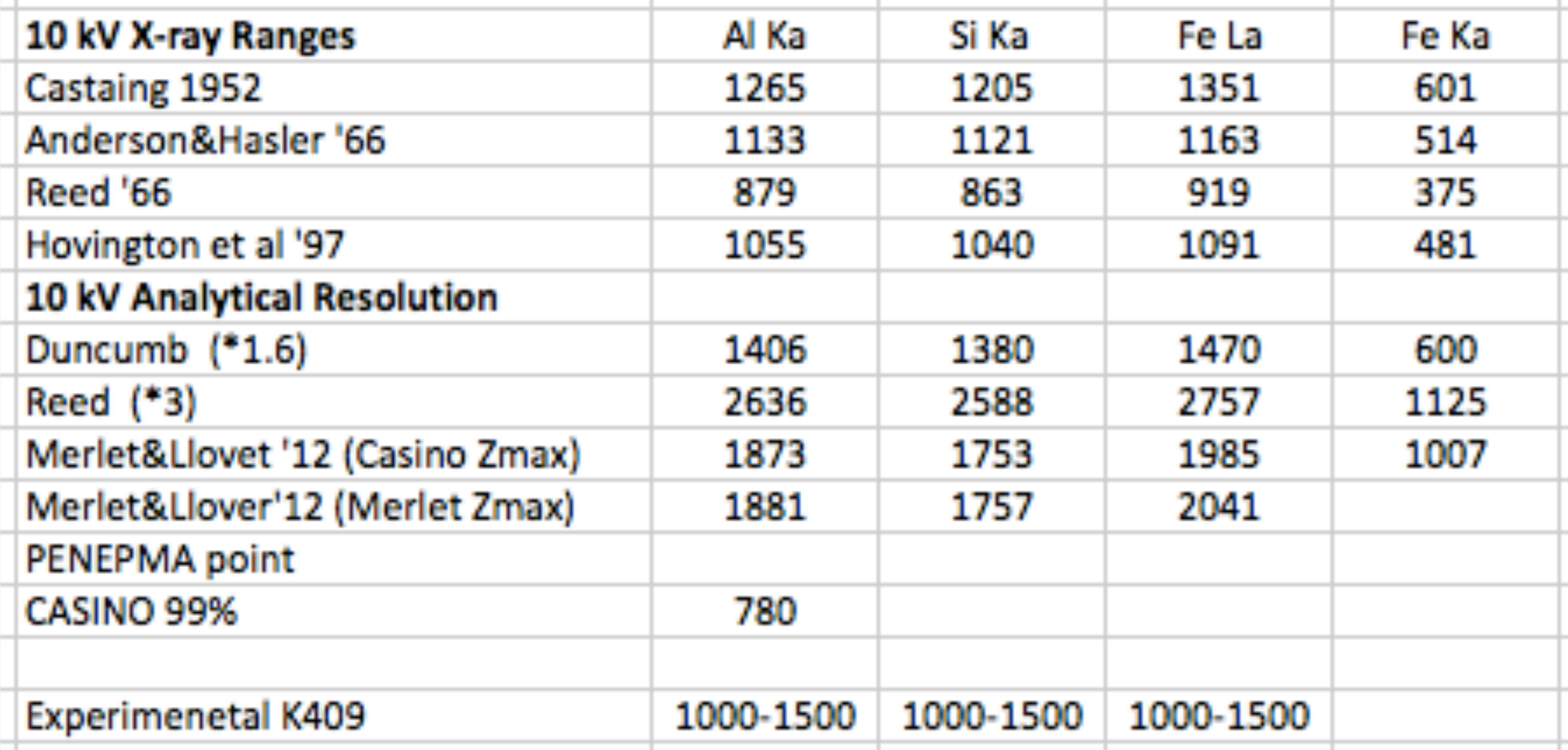
Lab code	Si	Cr	Mn	Fe	Co	Ni	Cu	Mo	Total
Reference composition	0.483	17.18	1.483	66.51	0.336	11.24	0.309	2.163	
1	0.57	14.42	0.88	66.65	0.38	14.65	0.35	2.39	100.29
	(0.02)	(0.27)	(0.25)	(0.7)	(0.04)	(0.43)	(0.03)	(0.10)	
2	0.52	15.77	1.10	67.86	0.4	14.45	0.35	2.16	102.59
	(0.01)	(0.14)	(0.11)	(0.5)	(0.05)	(0.27)	(0.02)	(0.04)	
3	0.39	14.33	0.21	86.25	0.27	15.33	0.34	7.54	124.64
	(0.02)	(0.82)	(0.28)	(1.24)	(0.05)	(0.53)	(0.01)	(0.24)	
4	0.46	15.24	1.49	70.04	0.31	16.0	0.35	2.25	106.14
	(0.06)	(0.35)	(0.54)	(0.3)	(0.16)	(0.6)	(0.06)	(0.15)	
5	0.50	14.82	1.03	72.97	-0.04	15.13	0.39	2.15	106.99
	(0.004)	(0.77)	(0.06)	(0.5)	(0.04)	(1.6)	(0.06)	(0.05)	
6	0.51	16.91	0.24	70.36	“Not	14.04	0.59	2.16	104.80
	(0.05)	(0.64)	(0.63)	(0.81)	measured”	(0.36)	(0.18)	(0.35)	

Numbers in parentheses are one standard deviation uncertainties

Llovet, et al (2012)

10 kV

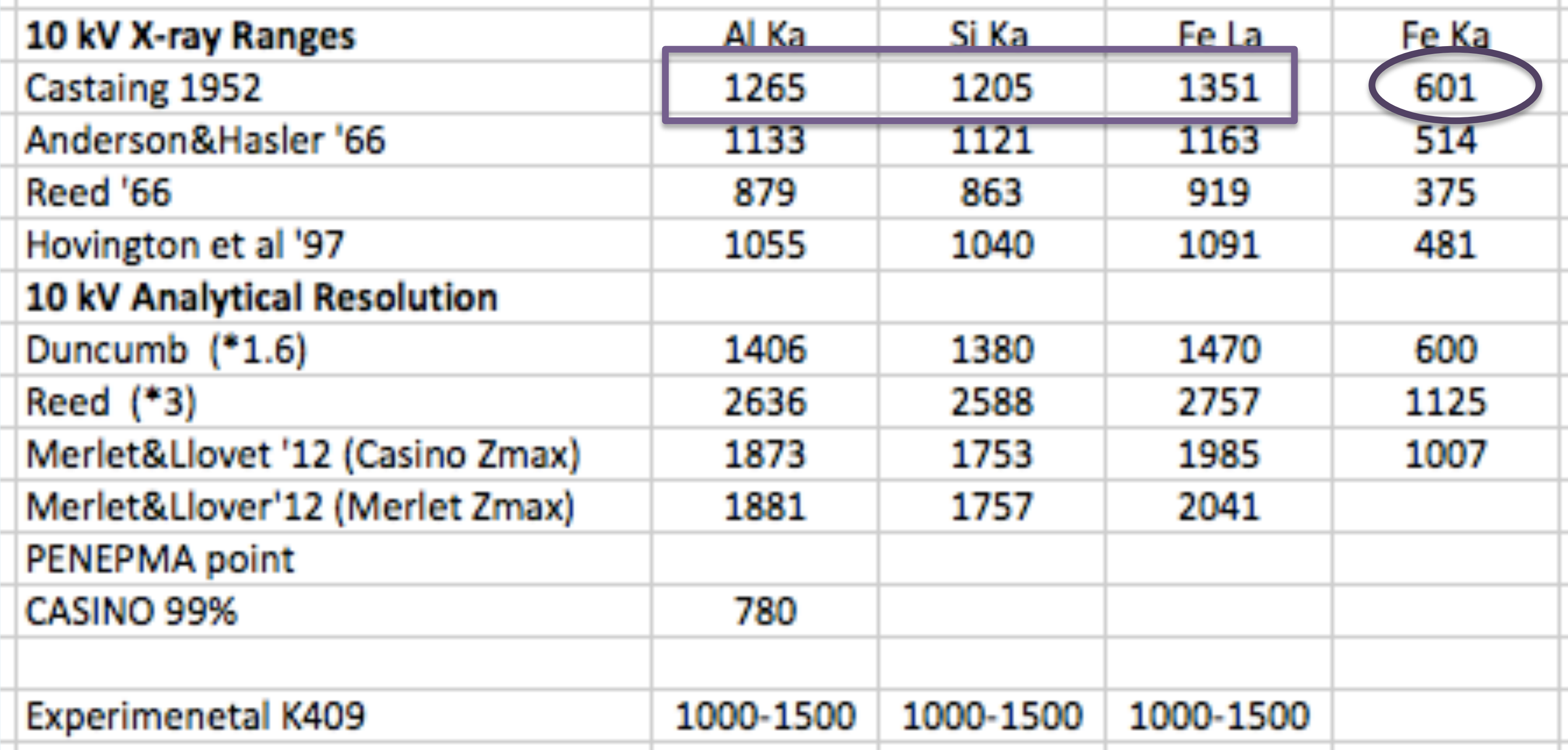
Compare Predictions of Analytical Resolution with K409 Experiments



10 kV X-ray Ranges	Al Ka	Si Ka	Fe La	Fe Ka
Castaing 1952	1265	1205	1351	601
Anderson&Hasler '66	1133	1121	1163	514
Reed '66	879	863	919	375
Hovington et al '97	1055	1040	1091	481
10 kV Analytical Resolution				
Duncumb (*1.6)	1406	1380	1470	600
Reed (*3)	2636	2588	2757	1125
Merlet&Llovet '12 (Casino Zmax)	1873	1753	1985	1007
Merlet&Llover'12 (Merlet Zmax)	1881	1757	2041	
PENEPMA point				
CASINO 99%	780			
Experimenetal K409	1000-1500	1000-1500	1000-1500	

…..Very Preliminary….

One reason low voltage may be preferable to low over-voltage



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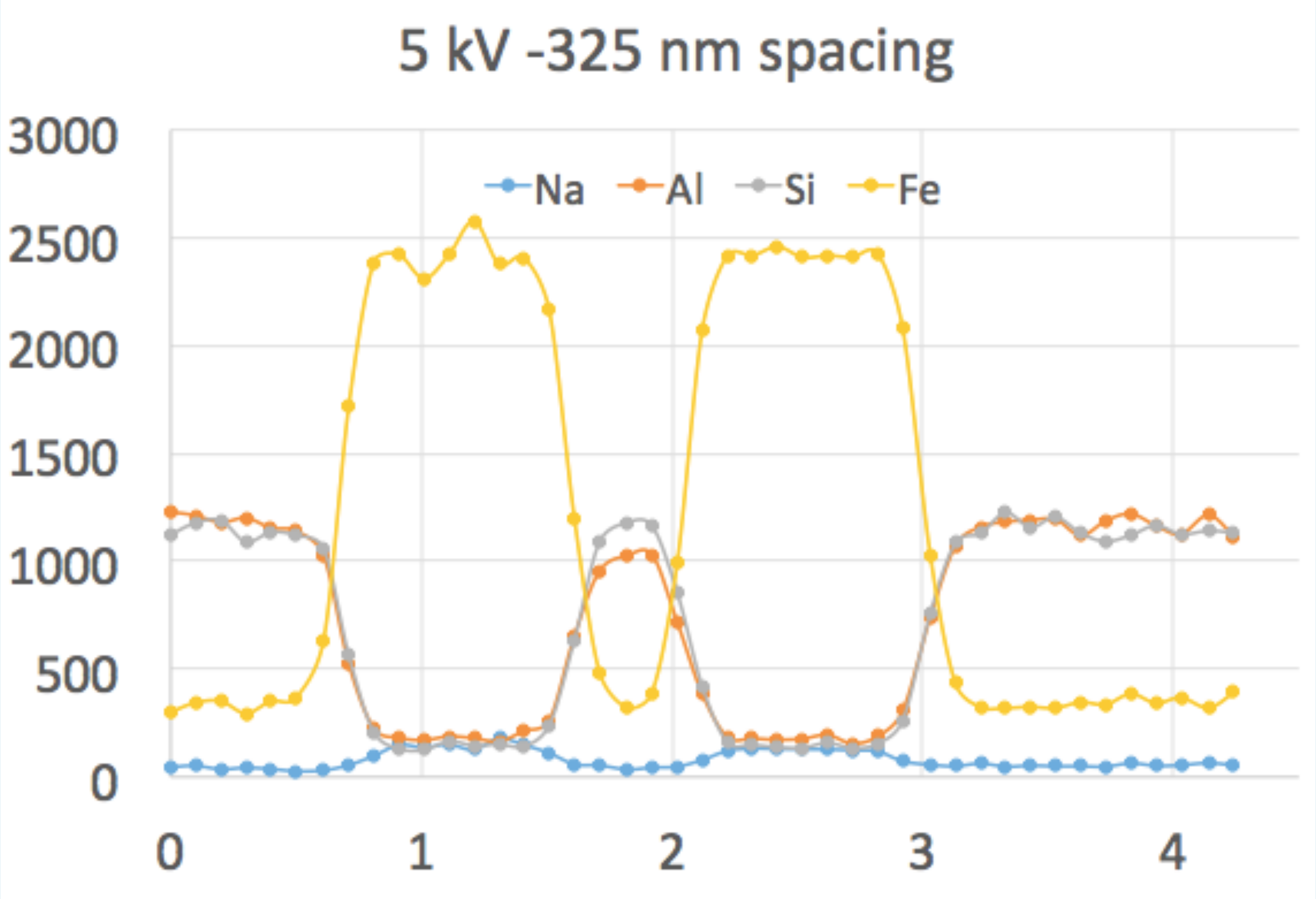
PENEPMA point				
CASINO 99%	780			
Experimenetal K409	1000-1500	1000-1500	1000-1500	

Part 3: Other considerations

Does more intense FE beam cause different behaviors in materials?

- Dieter Rhede has found that different minerals respond differently, as in having different carbon contamination spot behavior

Current research:
Using K409 to model low keV X-ray spatial resolution

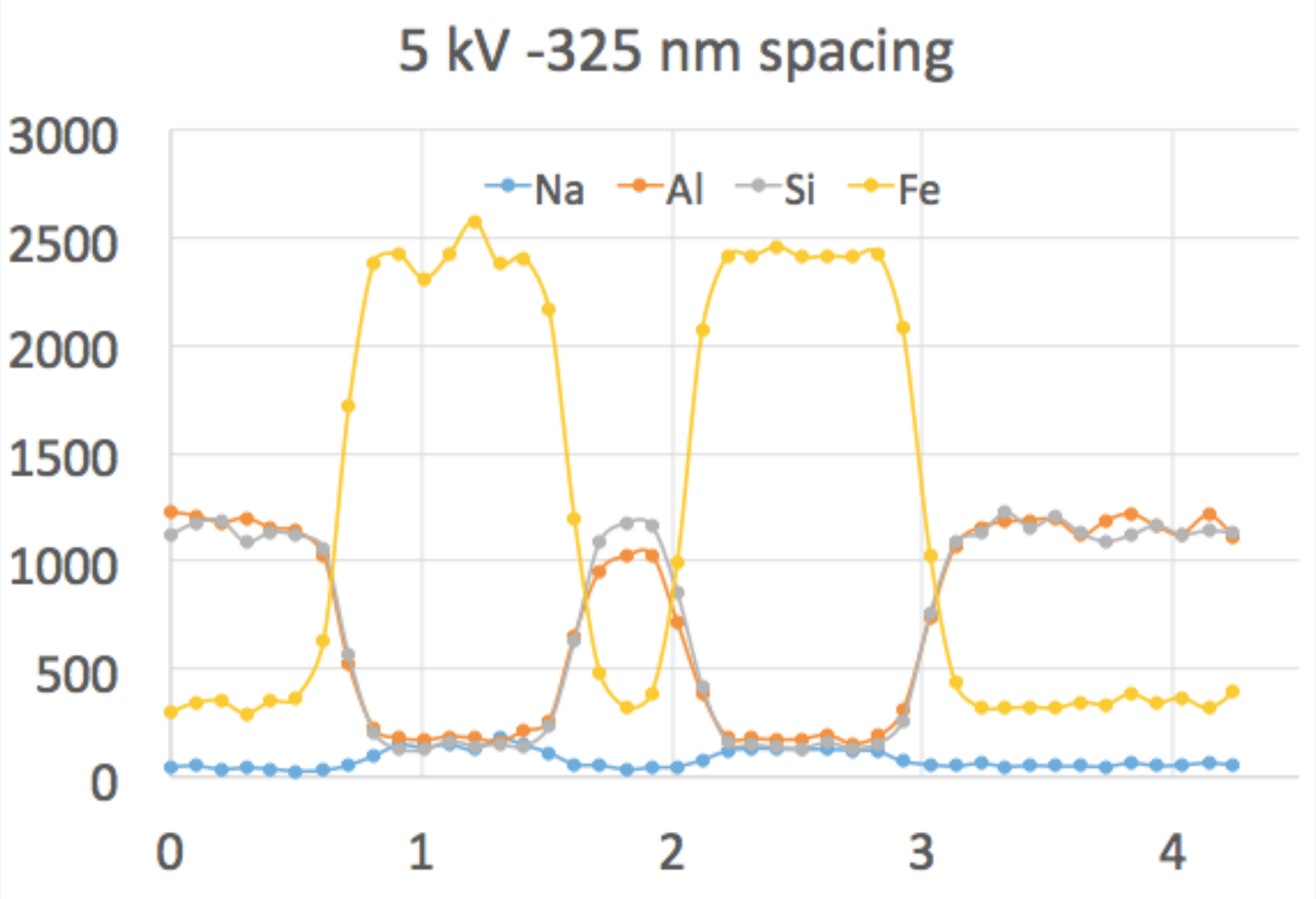


Si 0.97
Al 0.93
Fe 1.18

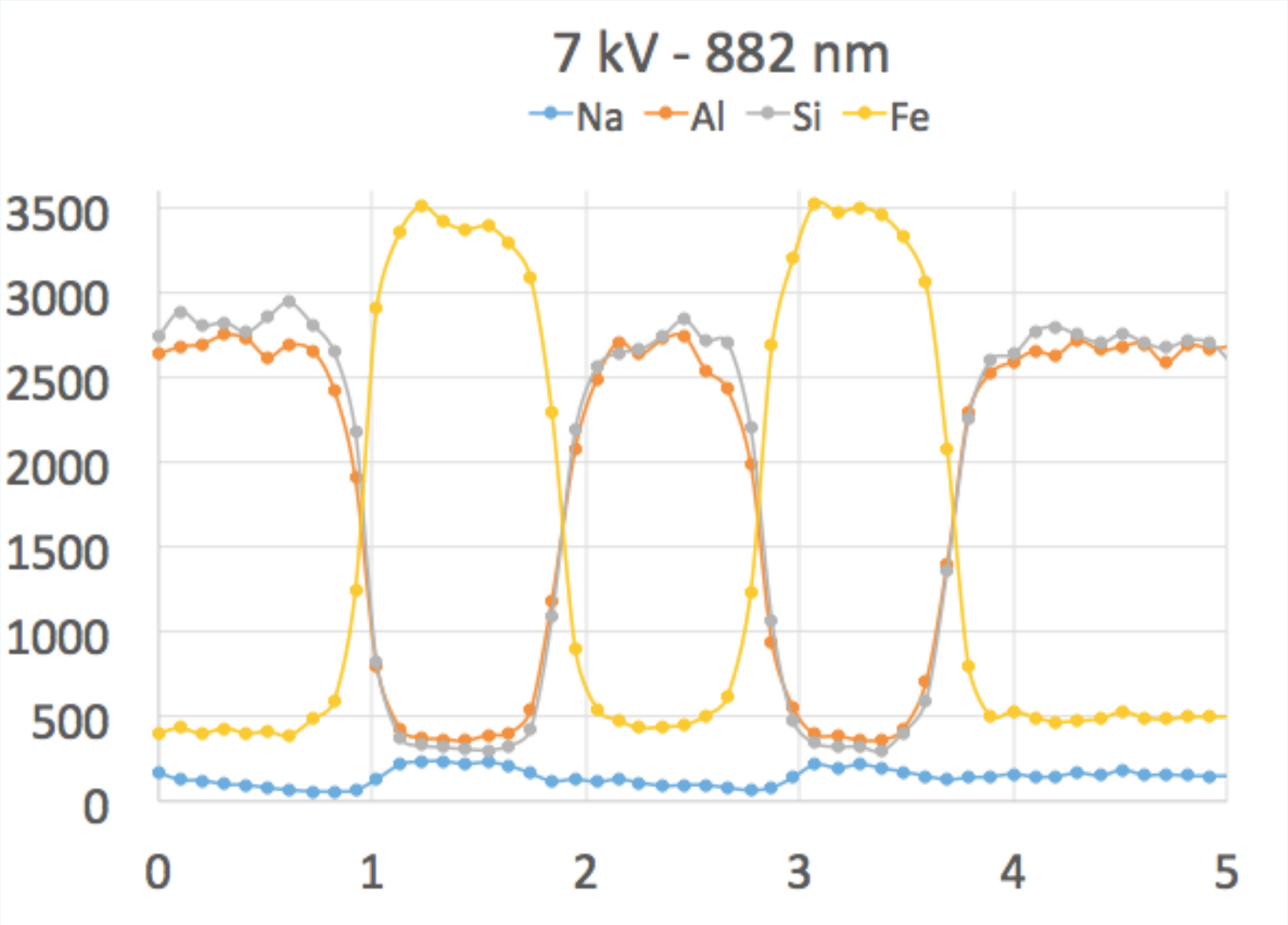
Lateral distance in microns between two K409 Fe-oxide grains = how close can they be to still achieve the same X-ray intensity as ‘far away from Fe-oxide’?

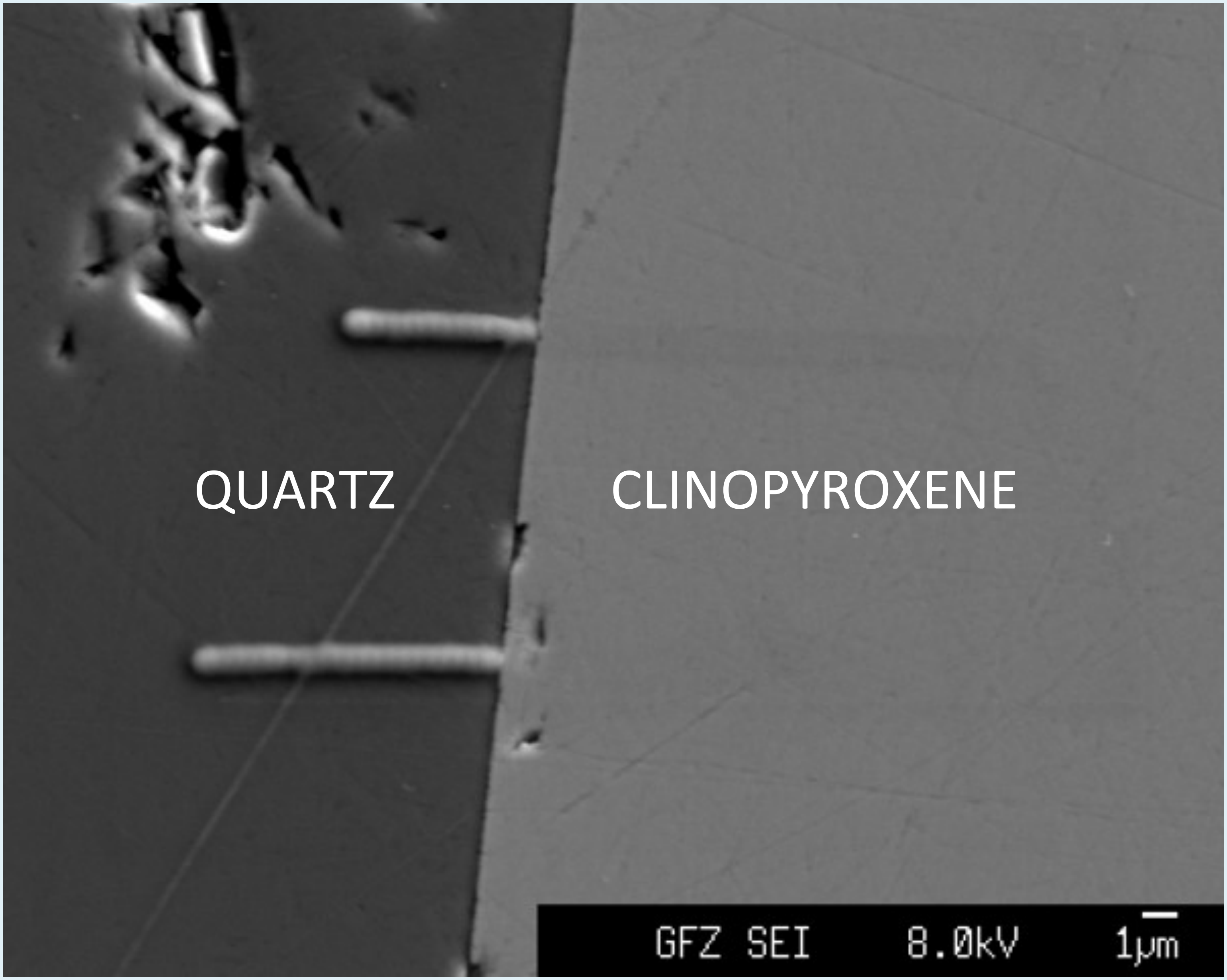
Current research:
Using K409 to model low keV X-ray spatial resolution

Si 0.97
Al 0.93
Fe 1.18

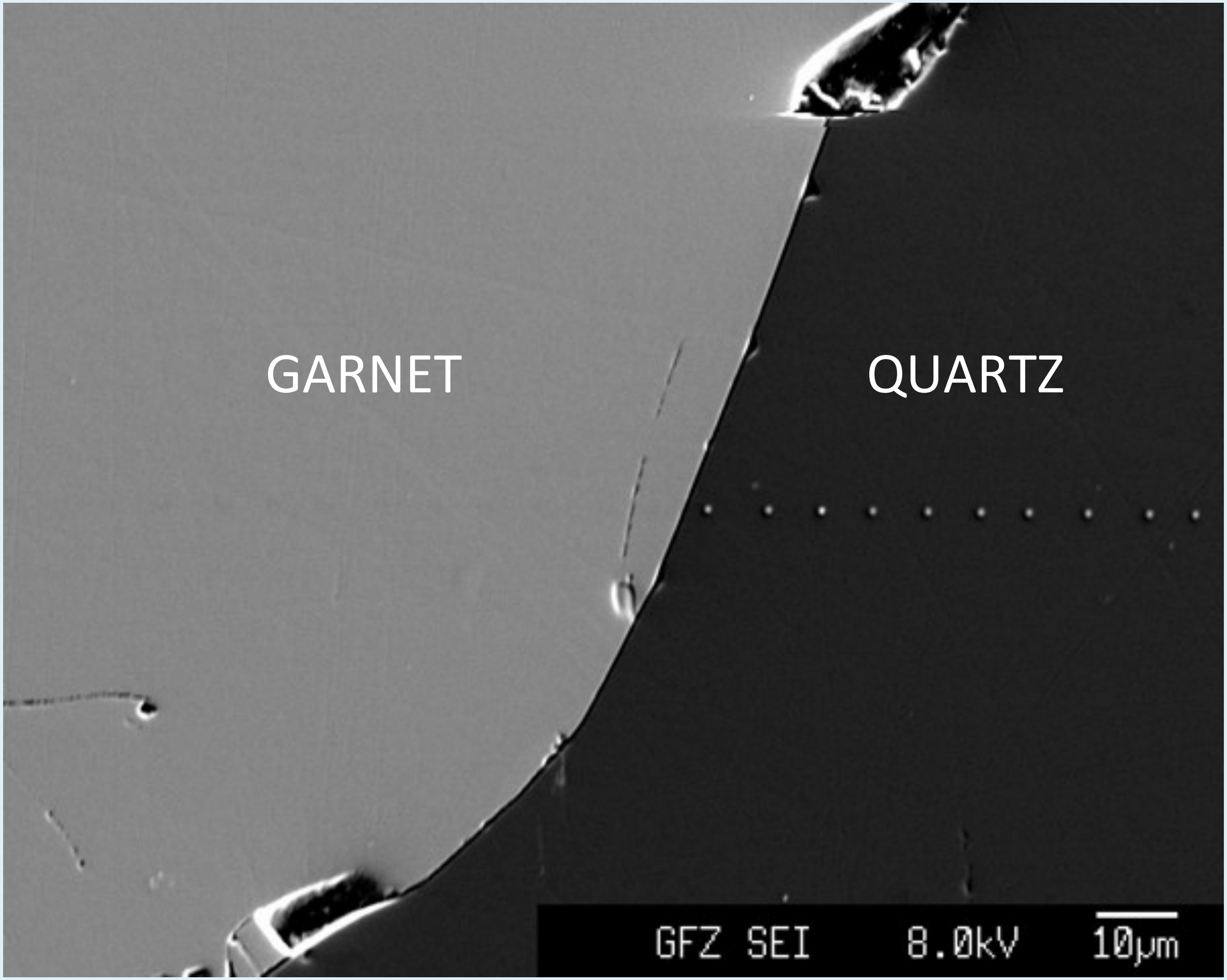


Lateral distance in microns between two K409 Fe-oxide grains = how close can they be to still achieve the same X-ray intensity as ‘far away from Fe-oxide’?


7 kV - 882 nm
Na
Al
Si
Fe
3500
3000
2500
2000
1500
1000
500
0
0
1
2
3
4
5



Courtesy Dieter Rhede, GFZ JXA-8530



Courtesy Dieter Rhede, GFZ JXA-8530

Defocus the FE beam??

- One of first things I learned from an early 8500F prober : defocus the beam (not just for glasses):

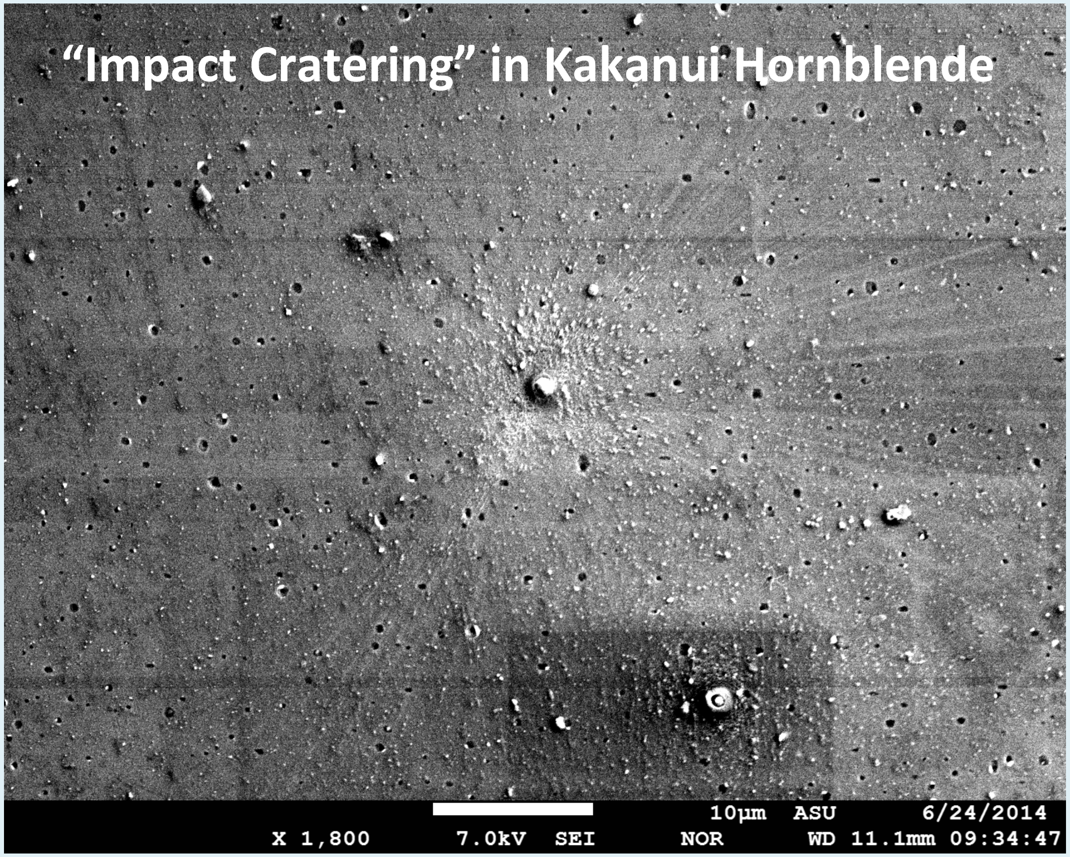
> "For routine quantitative analyses under conventional conditions, the beam diameter can be defocused to a few microns to reduce damage of the sample or the carbon coating."

→ Makes sense….but what if you want to go for very small features?

Intense FE beams → Significant Beam Damage Possible

Relative to W filament's beam

- With Temperature increase 100 X or more
- Concentrated electron charge implantation??

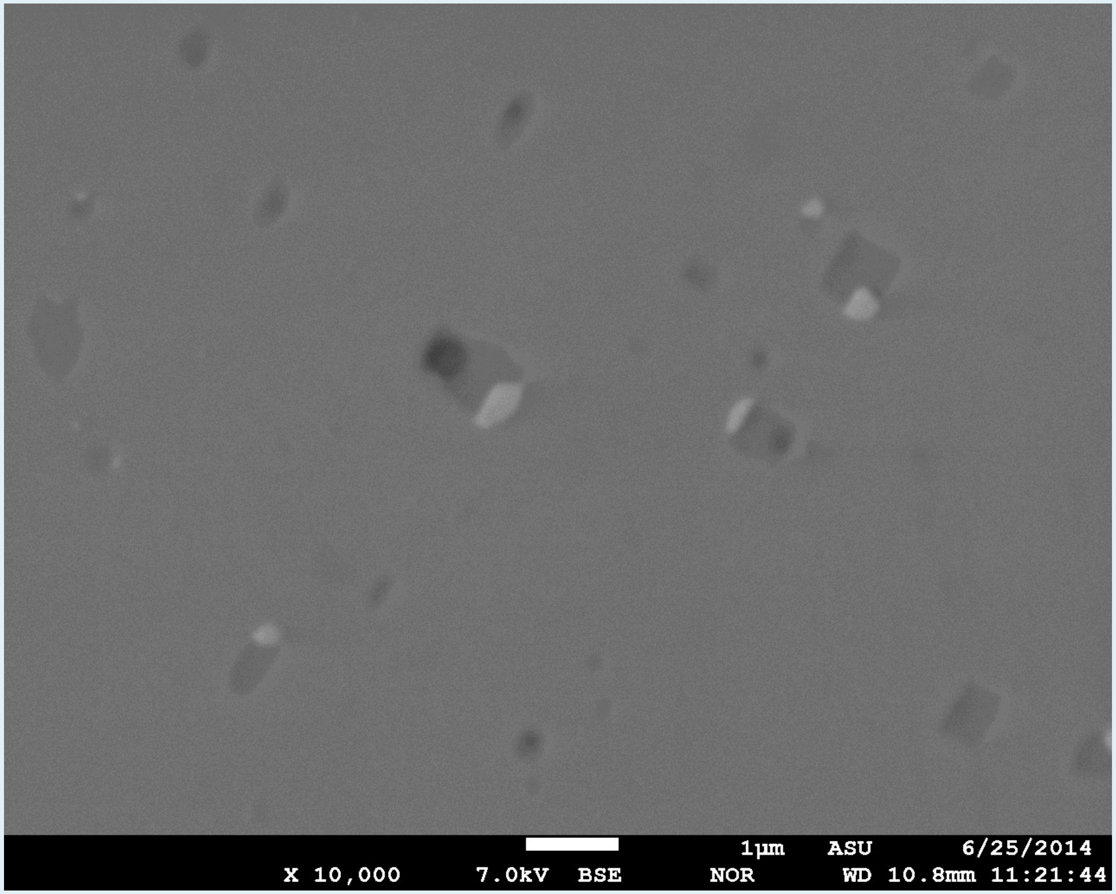


ASU 8530 Field Emission 7 keV 10 nA

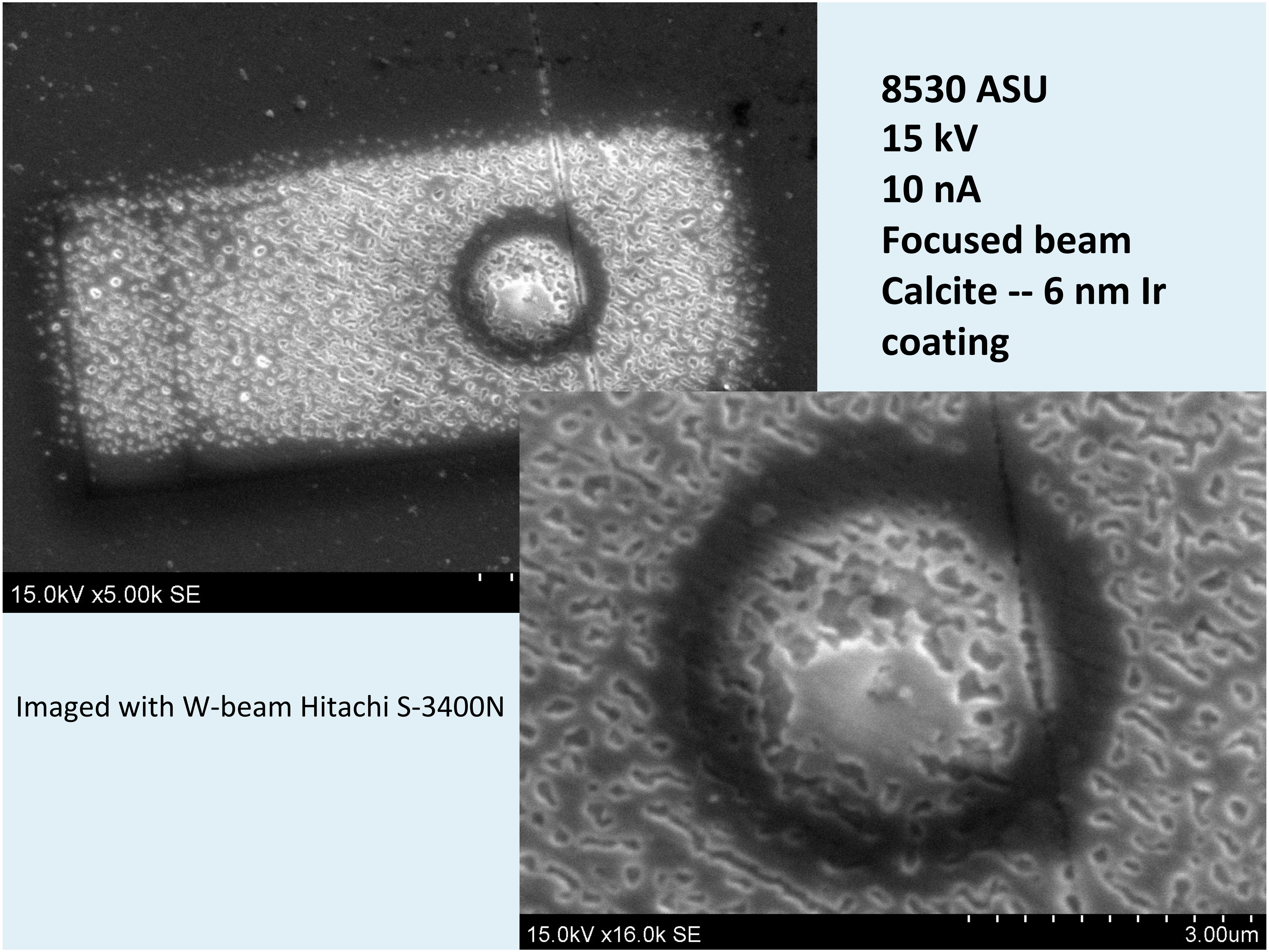
Intense FE beams → Significant Beam Damage Possible

Relative to W filament's beam

- With Temperature increase 100 X or more
- Concentrated electron charge implantation??

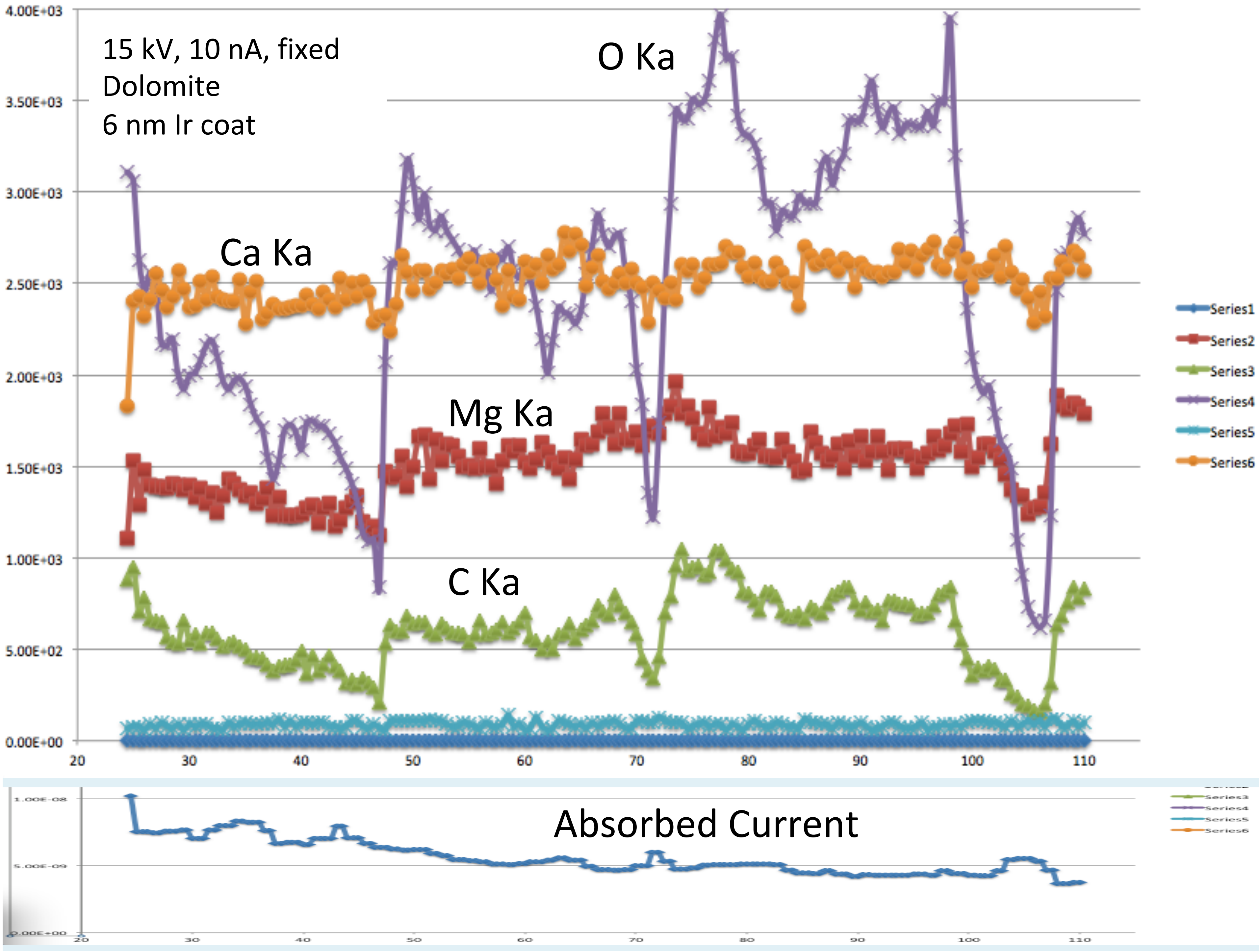


ASU 8530 Field Emission 7 keV 10 nA



8530 ASU
15 kV
10 nA
Focused beam
Calcite -- 6 nm Ir coating

Imaged with W-beam Hitachi S-3400N


15 kV, 10 nA, fixed
Dolomite
6 nm Ir coat
O Ka
Ca Ka
Mg Ka
C Ka
4.00E+03
3.50E+03
3.00E+03
2.50E+03
2.00E+03
1.50E+03
1.00E+03
5.00E+02
0.00E+00
20
30
40
50
60
70
80
90
100
110
Series1
Series2
Series3
Series4
Series5
Series6
Absorbed Current
1.00E-08
5.00E-09
0.00E+00
20
30
40
50
60
70
80
90
100
110
Series3
Series4
Series5
Series6

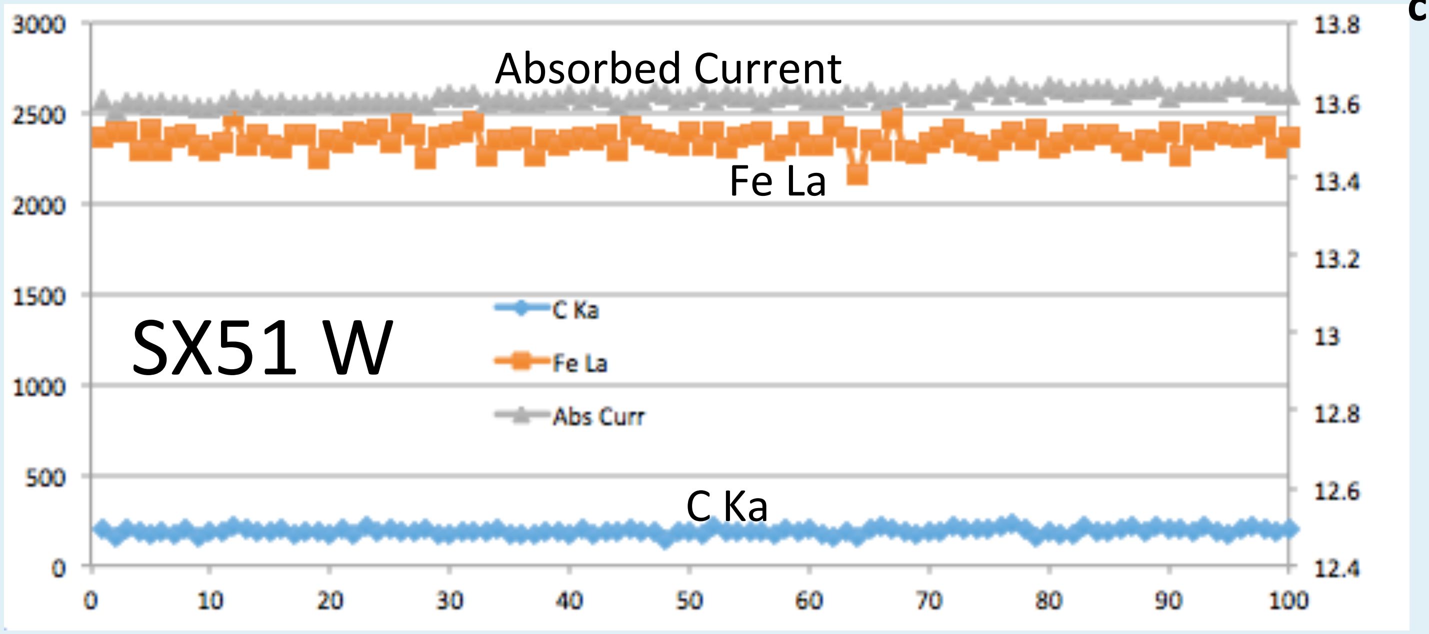
Does more intense FE beam cause different behaviors in materials?

- Consider materials which shouldn’t be impacted particularly deleteriously by the FE electron beam … Fe metal … Si metal…
- Time series experiments, 100 measurements, ~250 seconds length (“1 second measurements”)
- Comparison: FE electron probe vs traditional W filament electron probe

Fe Metal: SX51 (W)

7 kV, 20 nA,
LN anti-contamination

Fe La
Si Ka
counts



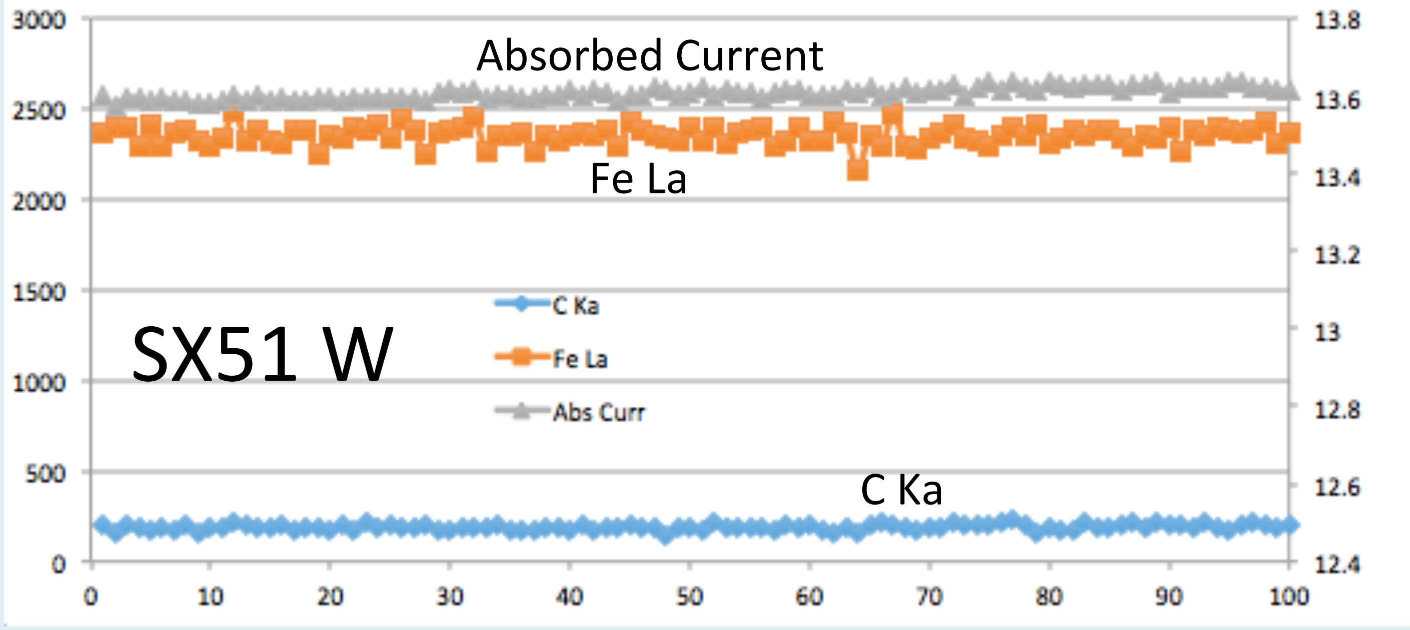
Absorbed
Current

100 counting
intervals ~
250 seconds

Fe Metal: SXFive FE vs SX51 (W)

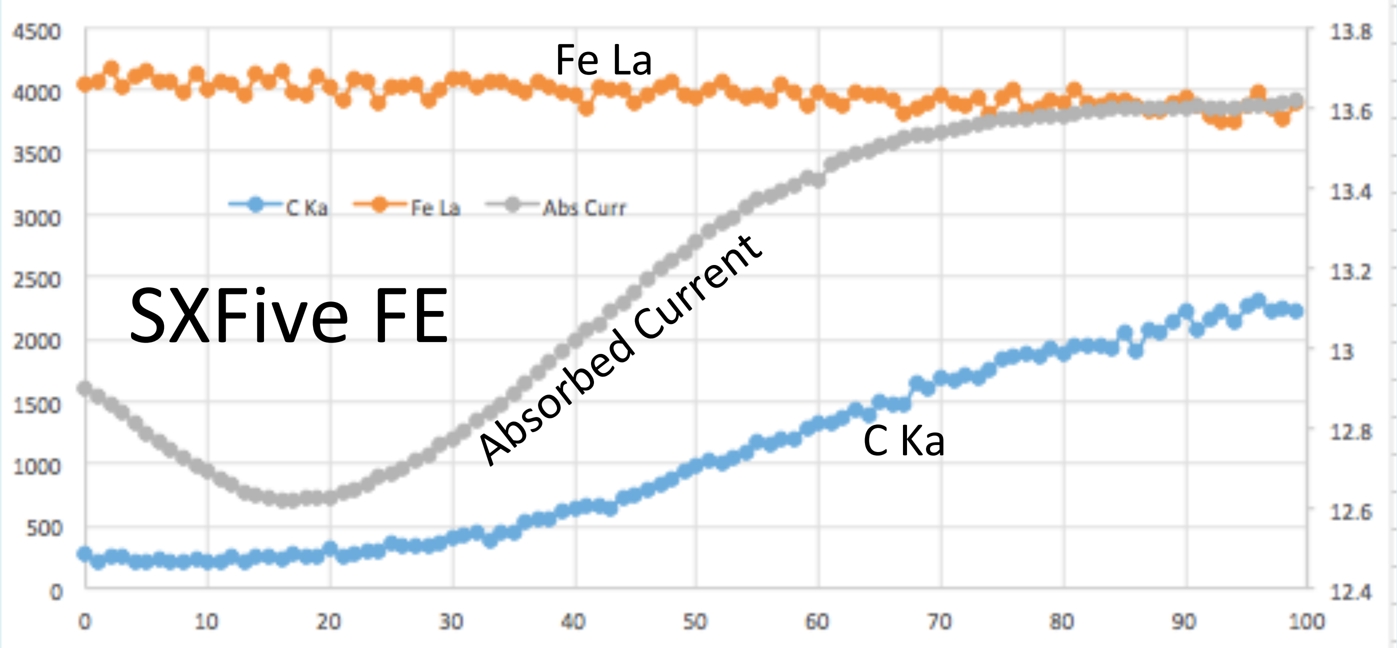
7 kV, 20 nA, LN anti-contamination

Fe La
Si Ka
counts



Absorbed
Current

Fe La
Si Ka
counts

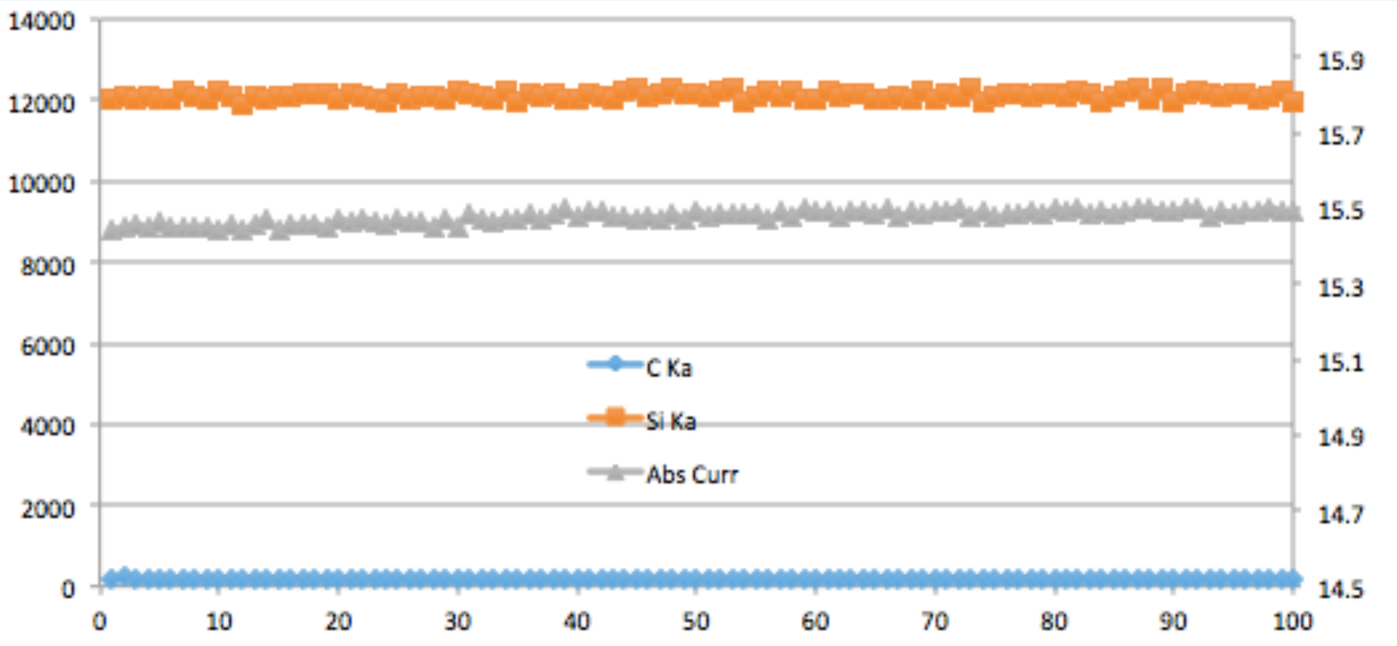


Absorbed
Current

100 counting
intervals ~
250 seconds

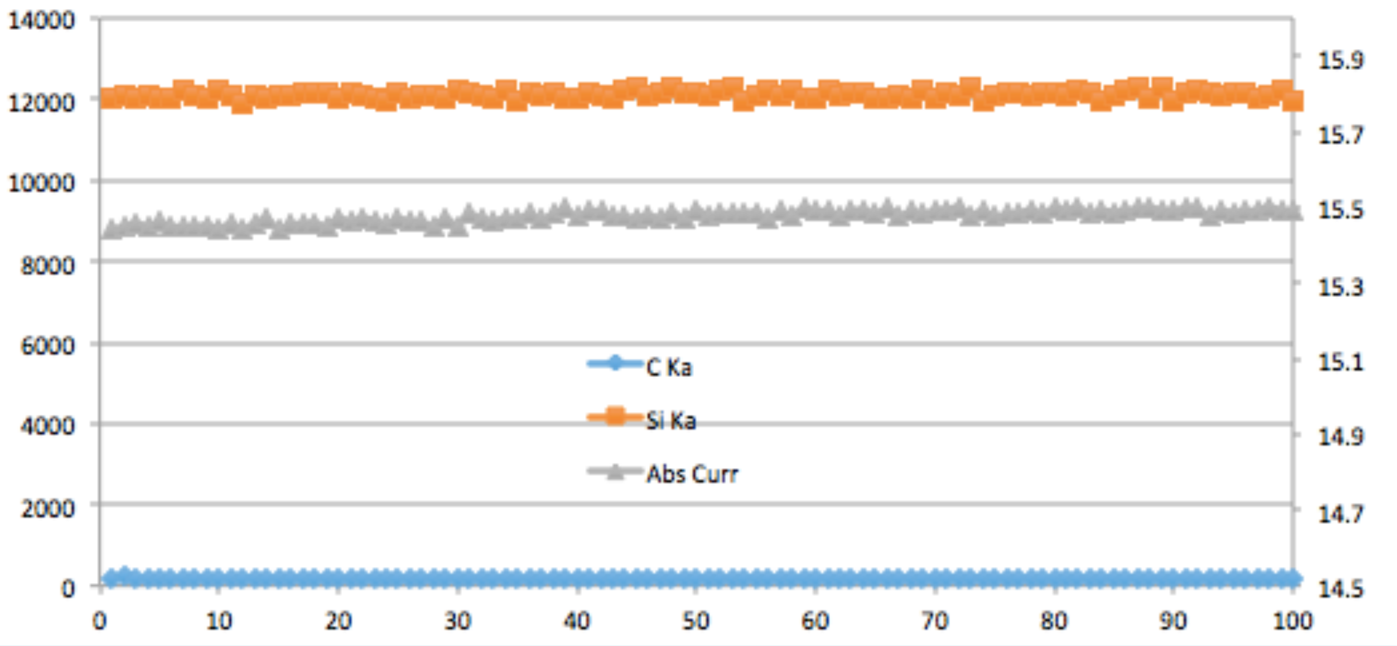
Si Metal: SX51 (W)

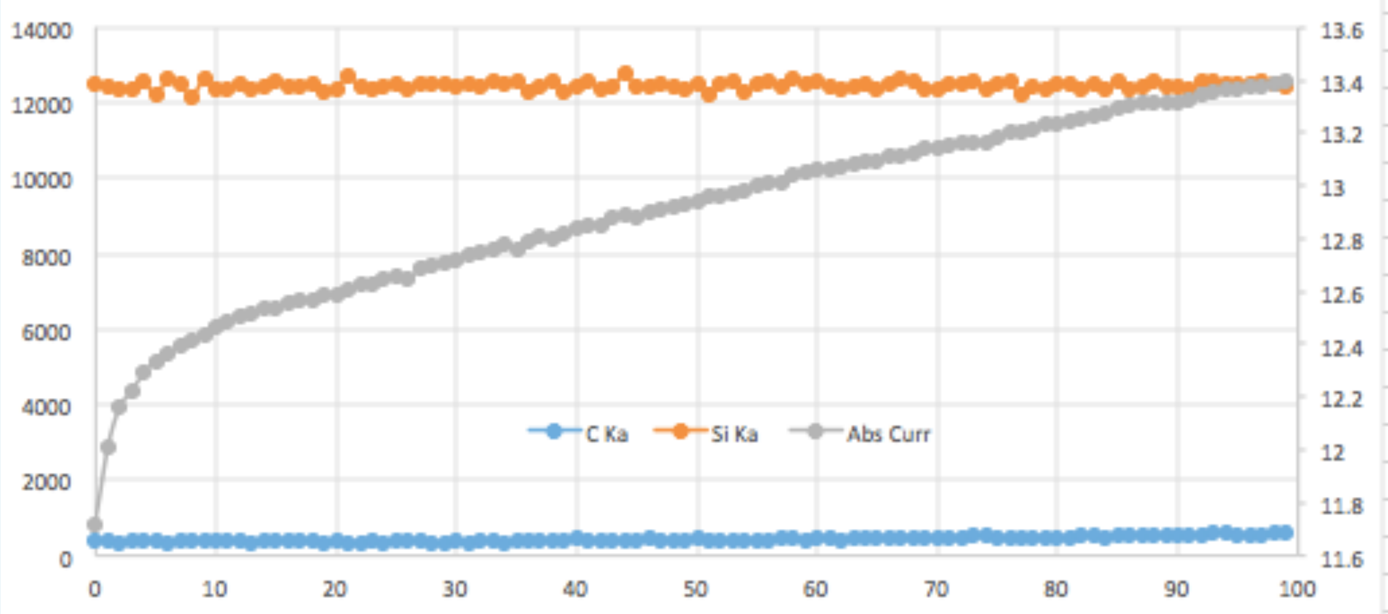
7 kV, 20 nA,
LN anti-contamination

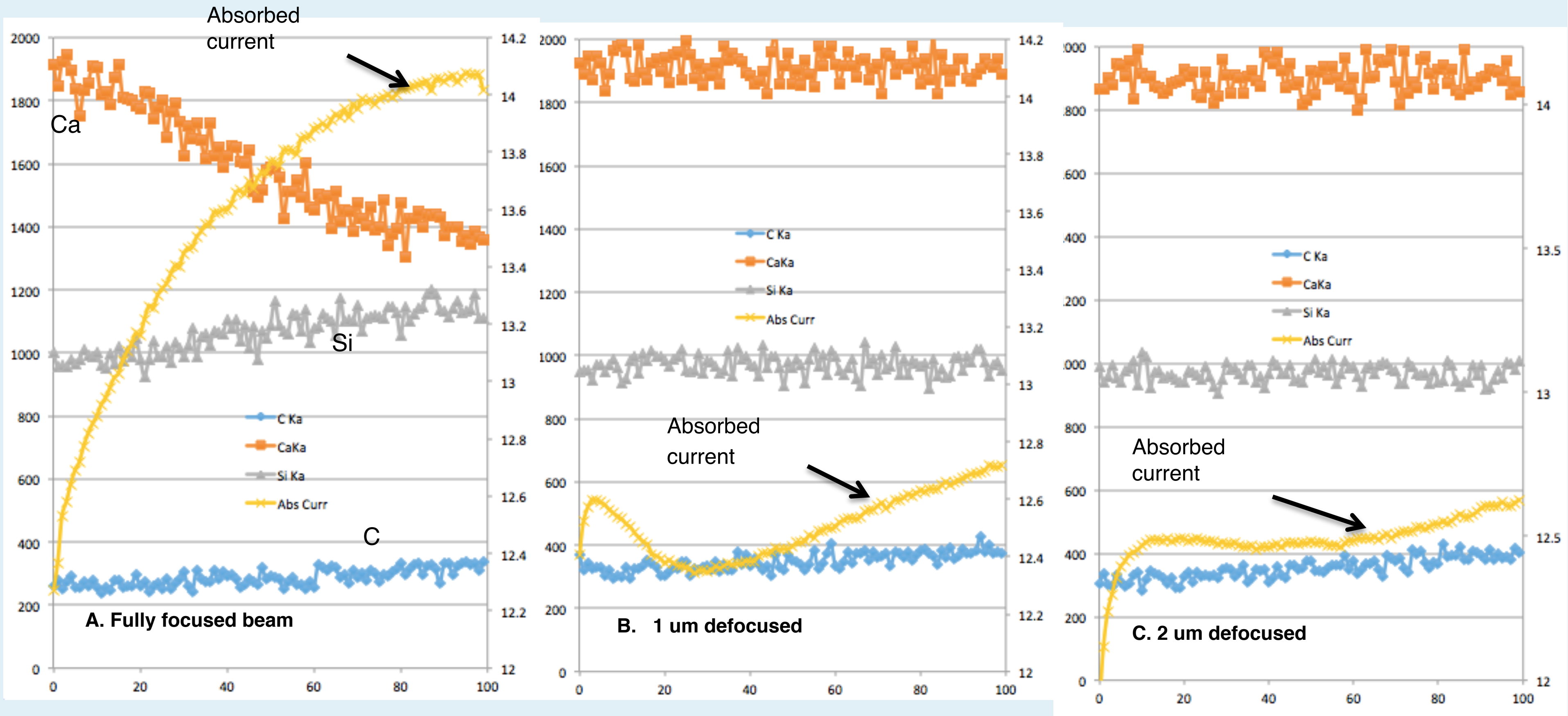


Si Metal: SXFive FE vs SX51 (W)

7 kV, 20 nA,
LN anti-contamination





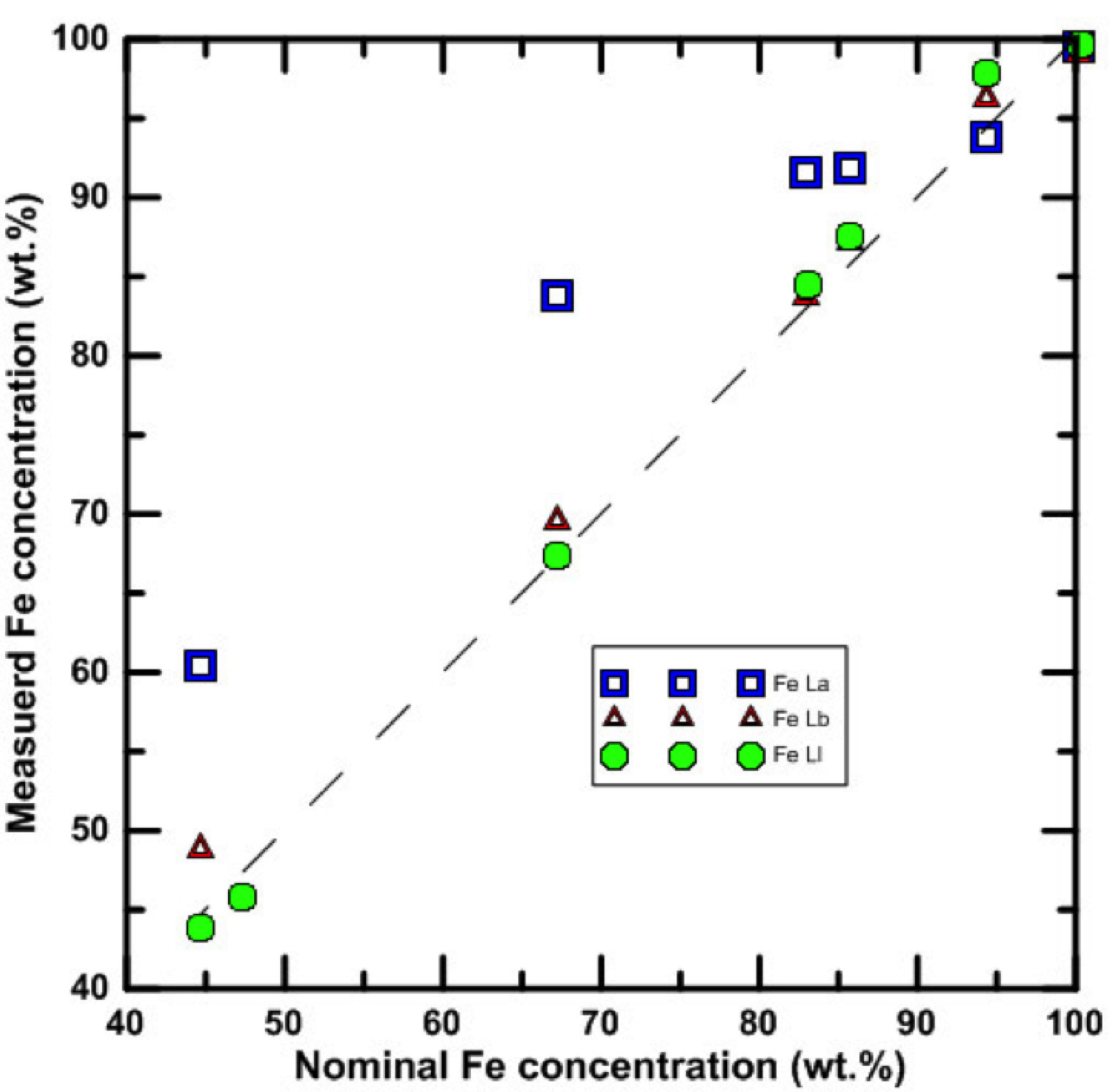


7 kV SXFive FE experiments on Wollastonite, 20 nA, from fully focused to 1 um and 2 um defocused. 100 counting intervals of 1 second each (~250 seconds total time)

Other Challenges for High Spatial Resolution EPMA with Low kV FE-EPMA

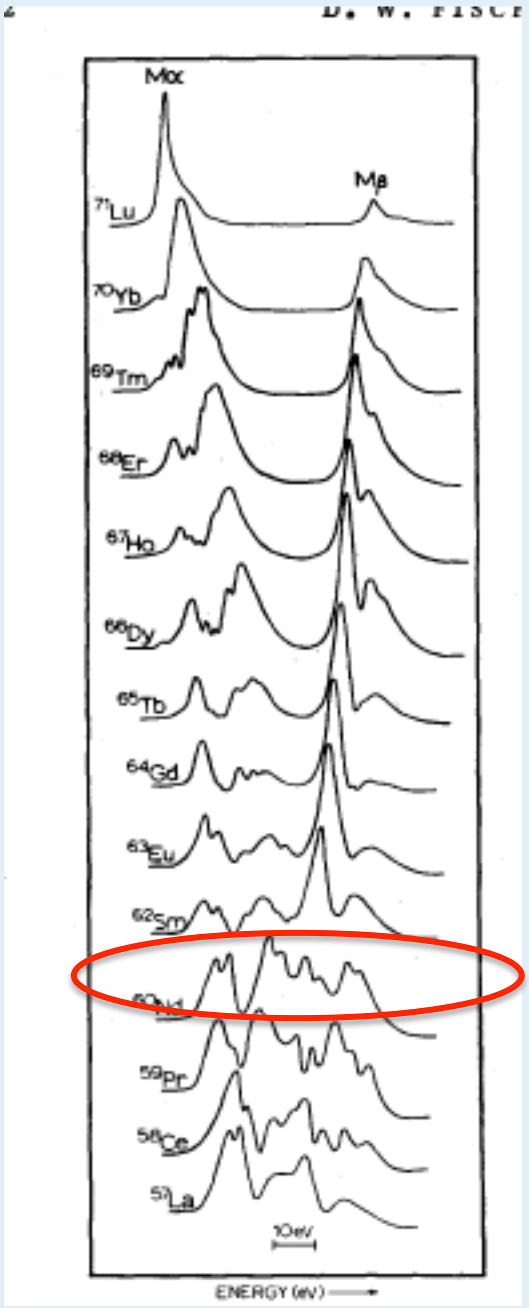
1. Traditional K and L lines no longer accessible, so use less well known L and M ones.
2. Machine stability at high mag (e.g. spectrometer movement, FA cup insertion)
3. Higher level of quality of reference materials
4. Surfaces…contamination etc

Fe-silicides: problem with Fe La



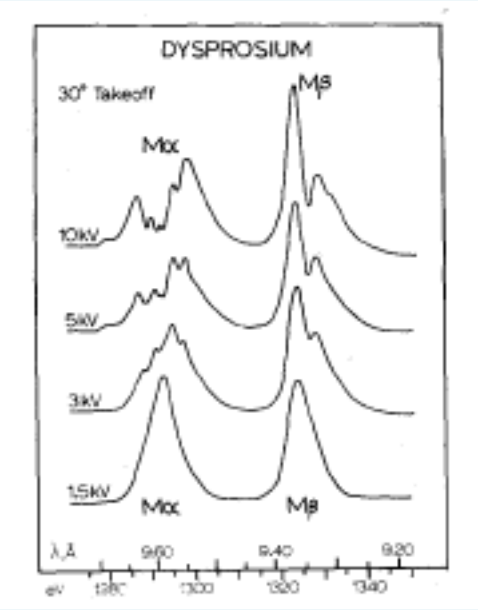
Gopon et al, 2003, Microscopy & Microanalysis

But using Ll line, avoid severe spectral issues (self-absorption etc)



Ma & Mb of REE at 10 kV

REE: Ma/Mb lines can be severely affected by self-absorption—until extremely low kV used

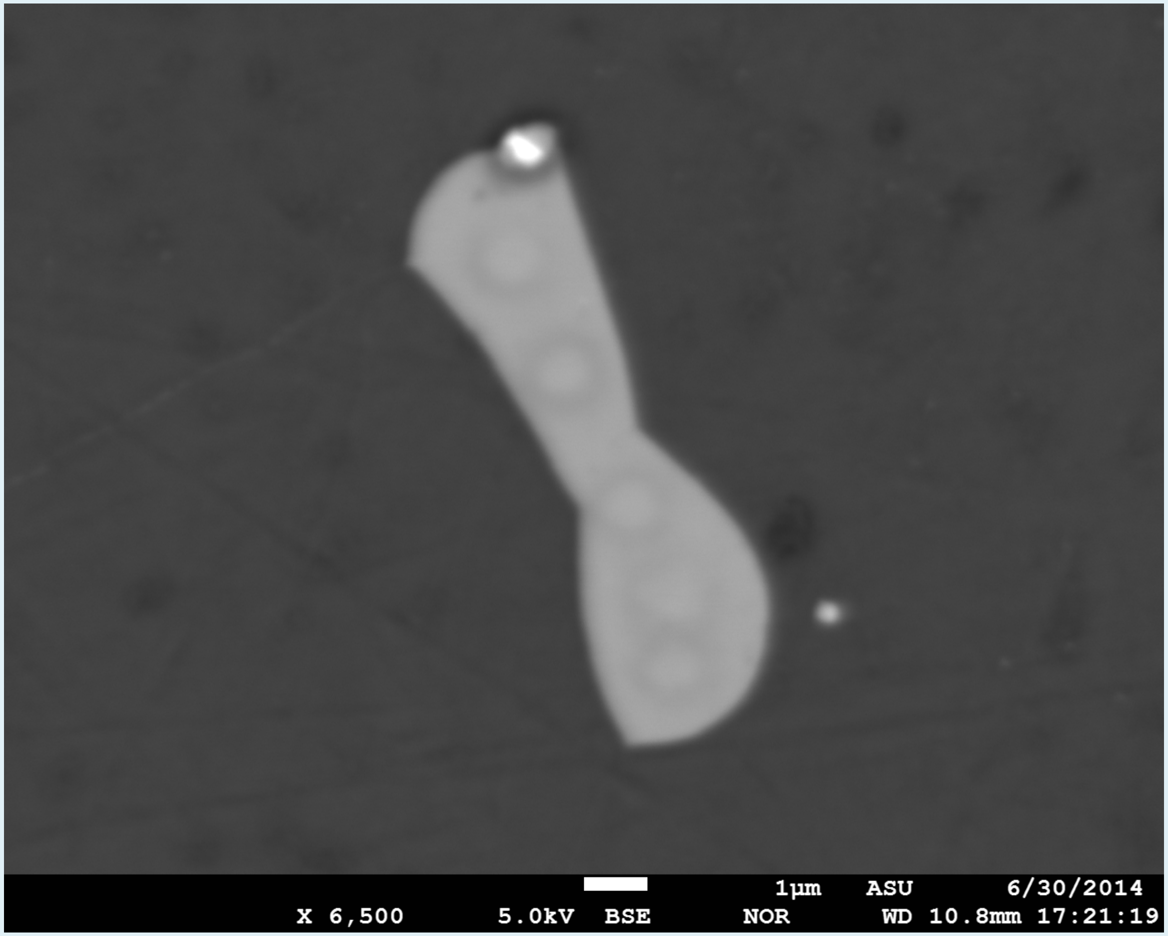


Dy Ma and Mb
spectra at various kV

Fischer and Baum, 1967, Self-Absorption effects in the soft x-ray Ma and Mb emission spectra of the REE, J. Applied Physics, 38, 4830.

Thus, need to consider "non-traditional" M lines

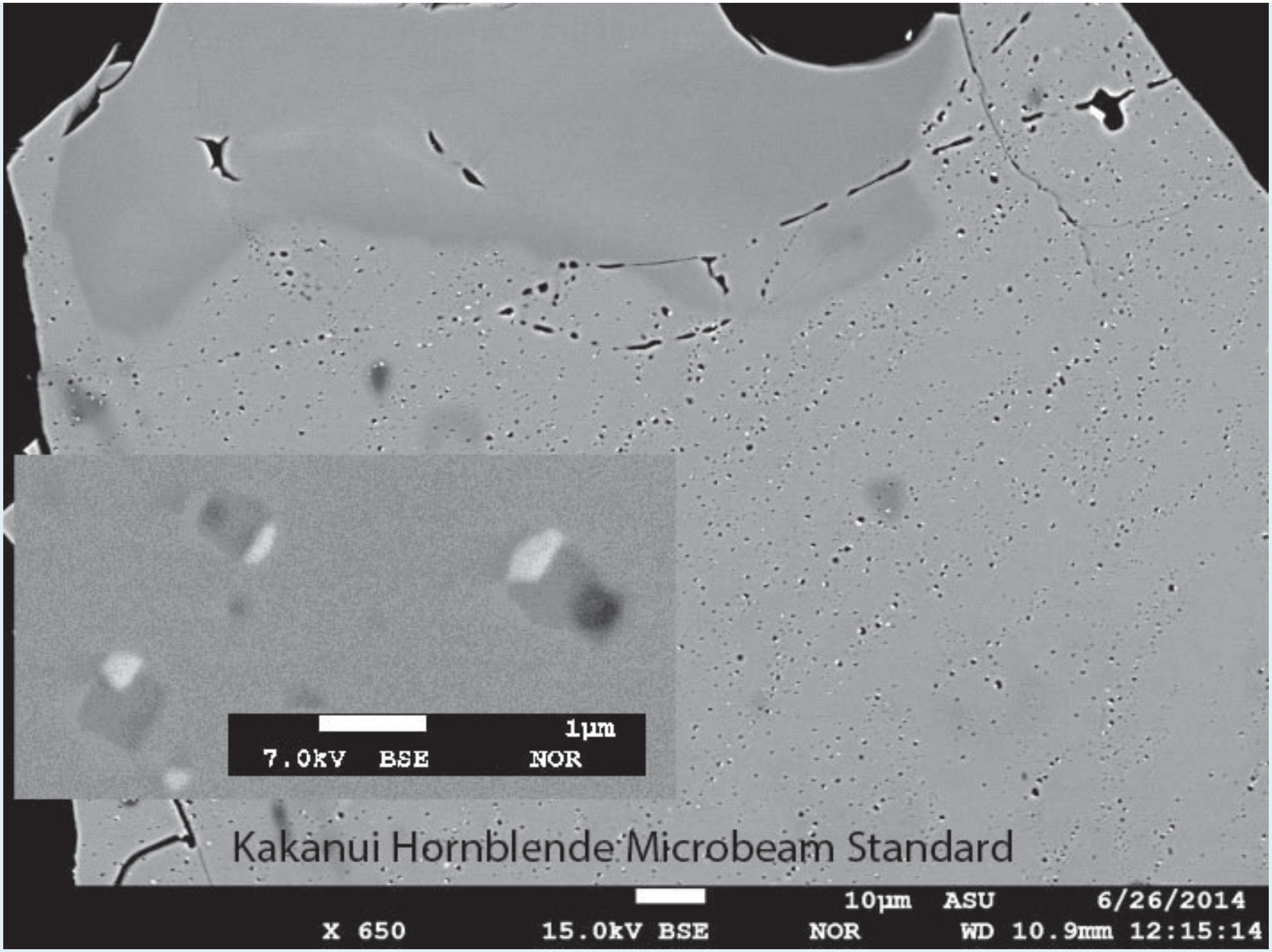
REE @ 5 kV: Nd Mz vs Nd Mb
(in Mg-Zn-Nd material)



	Nd Mb	Nd Mz	Nd Mz
Nd	72.9	35.4	39.9
Zn	1.2	1.7	1.9
Mg	55.1	56.8	57.2
O	1.9	2.1	1.8
Sum	131	96	101

Not easy to get the current software to accept Mz as analytical line…have to ‘trick it’ and this creates complications…

Kakanui hornblende – used by hundreds of EPMA labs



- FE EPMA can show complexity in traditional geological probe standards
- Which composition is ‘correct’? That acquired by defocused or by focused beam?

What could be going on here?

Initial thoughts….

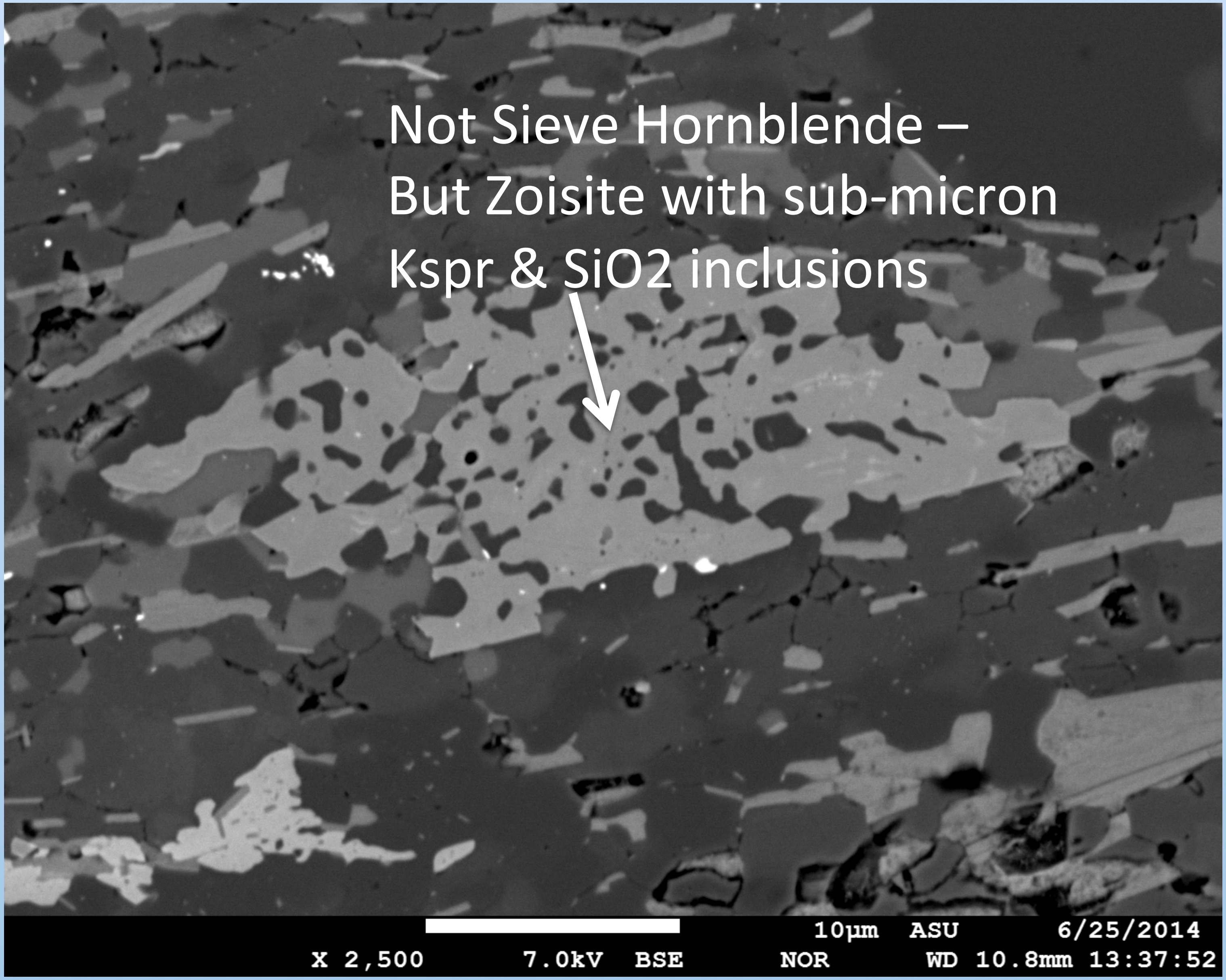
1. Chemical peak shifts?
2. Mass absorption factor errors?
   Self absorption?

Part 4:

Wish List for SubMicron EPMA

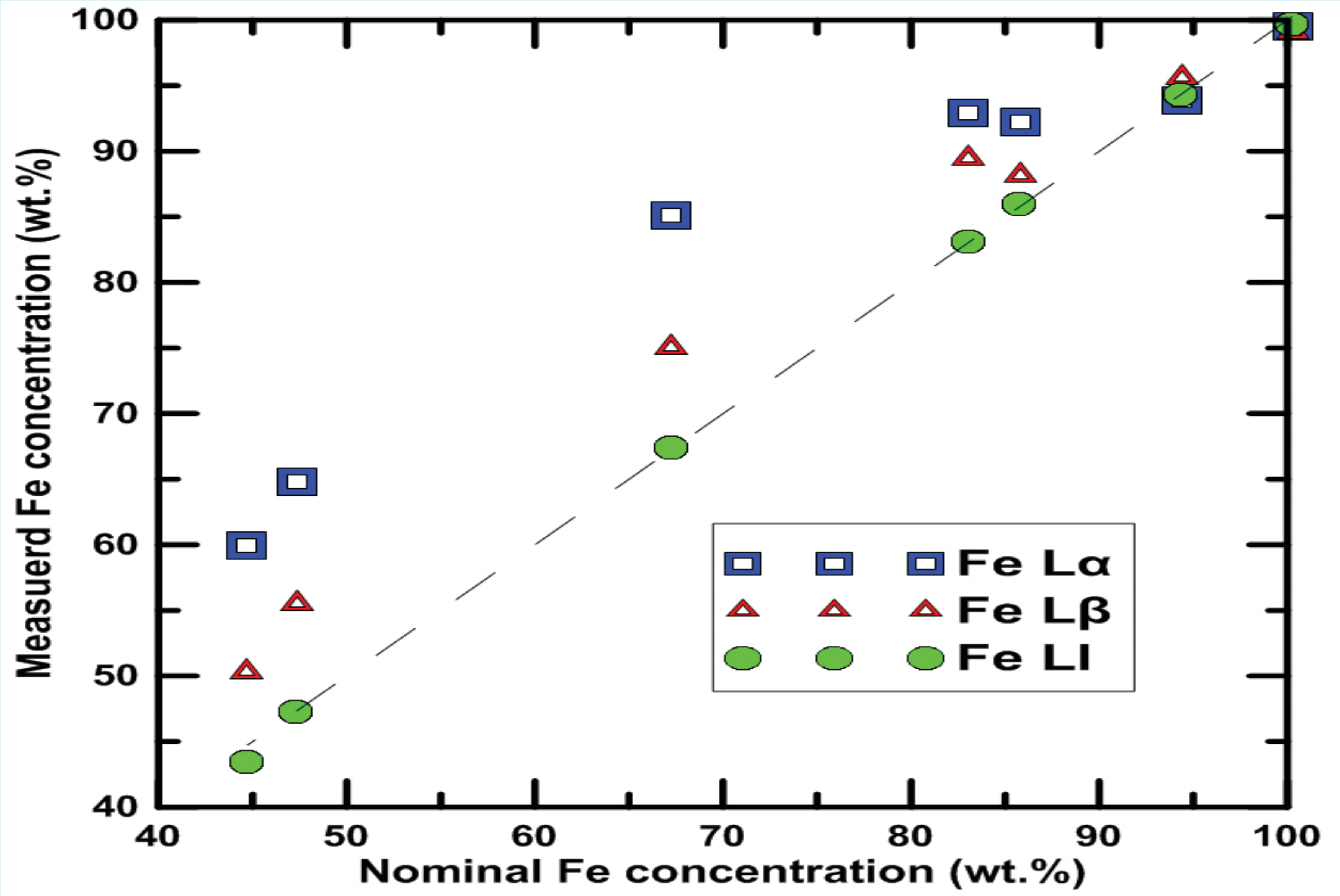
- What the next generation of submicron electron beam microanalyzers might need:
    - 24/7 “CryoTiger” closed cycle refrigerant cooled cold plate
    - Better mechanical/electronic stability at high magnification
    - In-chamber cleaner (UV?)
    - Can a sample be chilled?
    - Alternative metal coating

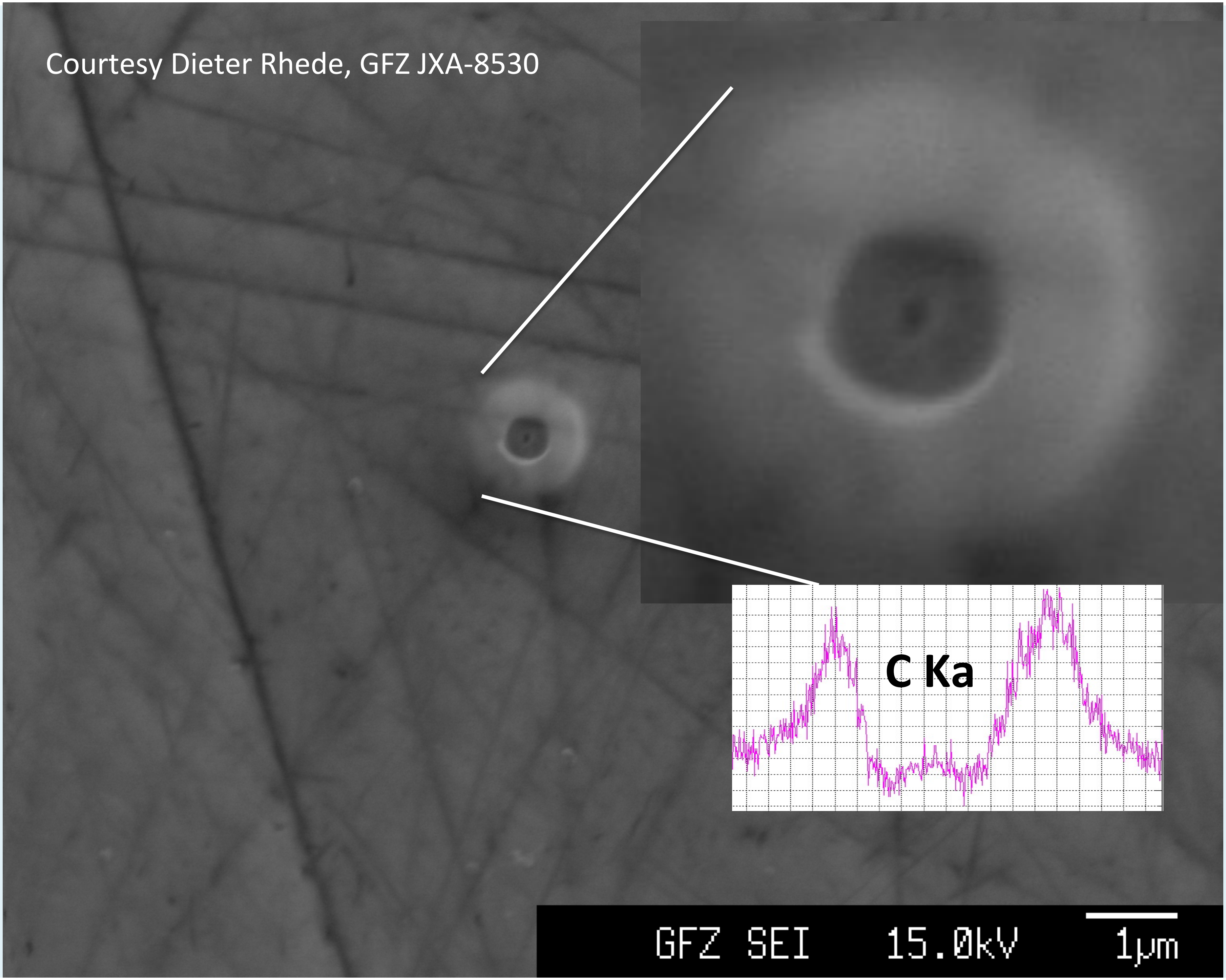
Why Field Emission EPMA?



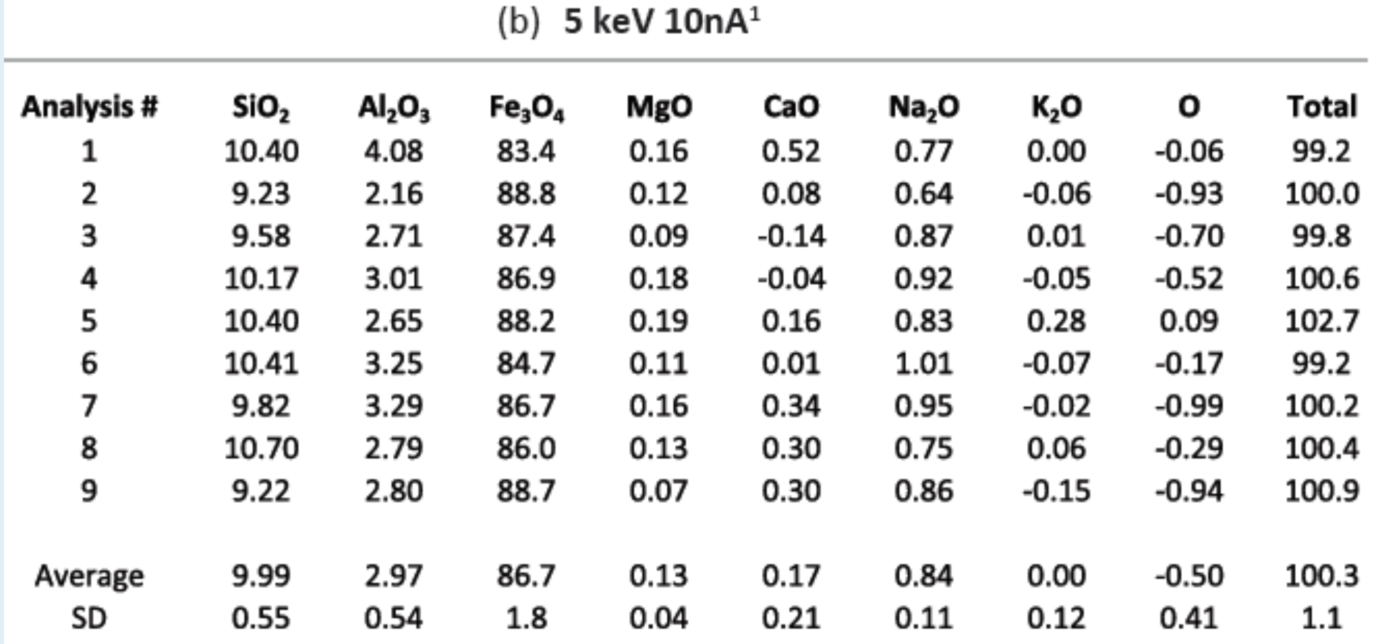
→Accurate Probe Analysis for submicron regions

Thank You


Measuerd Fe concentration (wt.%)
100
90
80
70
60
50
40
40
50
60
70
80
90
100
Nominal Fe concentration (wt.%)
Fe Lα
Fe Lβ
Fe Ll

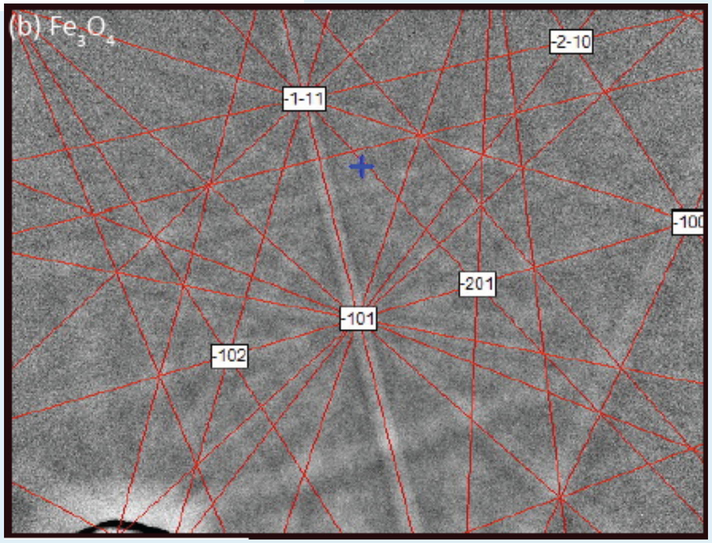

Courtesy Dieter Rhede, GFZ JXA-8530
C Ka
GFZ SEI 15.0kV 1μm

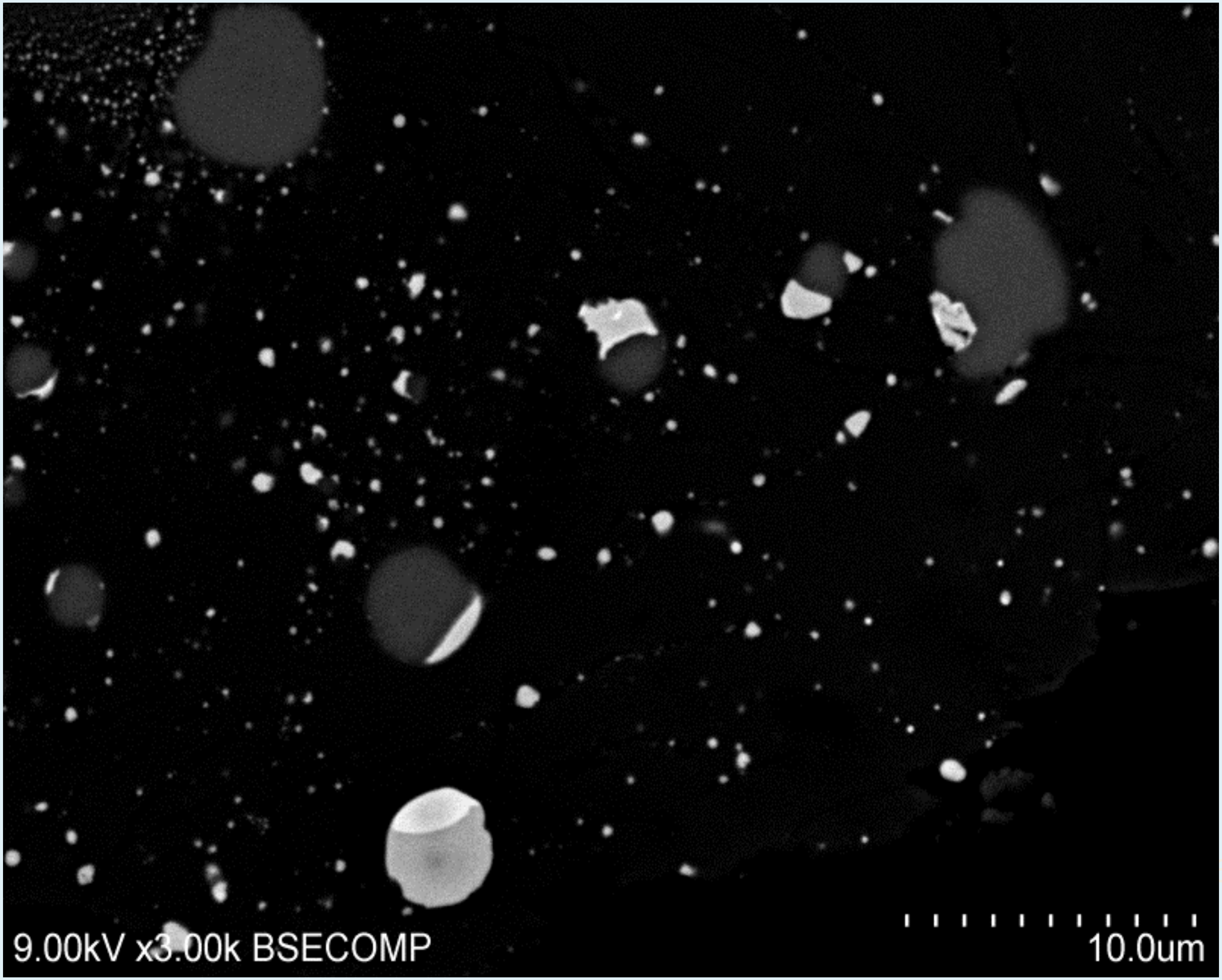
NBS/NIST K409, a ‘failed experiment’



(b) **5 keV 10nA**^{1}

Analysis #	SiO_2	Al_2O_3	Fe_3O_4	MgO	CaO	Na_2O	K_2O	O	Total
1	10.40	4.08	83.4	0.16	0.52	0.77	0.00	-0.06	99.2
2	9.23	2.16	88.8	0.12	0.08	0.64	-0.06	-0.93	100.0
3	9.58	2.71	87.4	0.09	-0.14	0.87	0.01	-0.70	99.8
4	10.17	3.01	86.9	0.18	-0.04	0.92	-0.05	-0.52	100.6
5	10.40	2.65	88.2	0.19	0.16	0.83	0.28	0.09	102.7
6	10.41	3.25	84.7	0.11	0.01	1.01	-0.07	-0.17	99.2
7	9.82	3.29	86.7	0.16	0.34	0.95	-0.02	-0.99	100.2
8	10.70	2.79	86.0	0.13	0.30	0.75	0.06	-0.29	100.4
9	9.22	2.80	88.7	0.07	0.30	0.86	-0.15	-0.94	100.9
Average	9.99	2.97	86.7	0.13	0.17	0.84	0.00	-0.50	100.3
SD	0.55	0.54	1.8	0.04	0.21	0.11	0.12	0.41	1.1




9.00kV x3.00k BSECOMP
10.0um

Issue: self-absorption artifacts related to reversible injection of electrons into partially filled 4f orbital. This is anomalous, not like normal self-absorption. Reversable transitions possible and complicate

Implanted Er into homogeneous materials

Found for Er, Mb worked well, an N6 filled (M4-N6 is Mb)

Thibault Y., 2014. Strategy for efficient high-spatial resolution X-ray microanalysis of trace REE in complex materials. Abstracts in conference program, 27th Rare earth research conference 2014, Squaw Valley, California, RERC98.

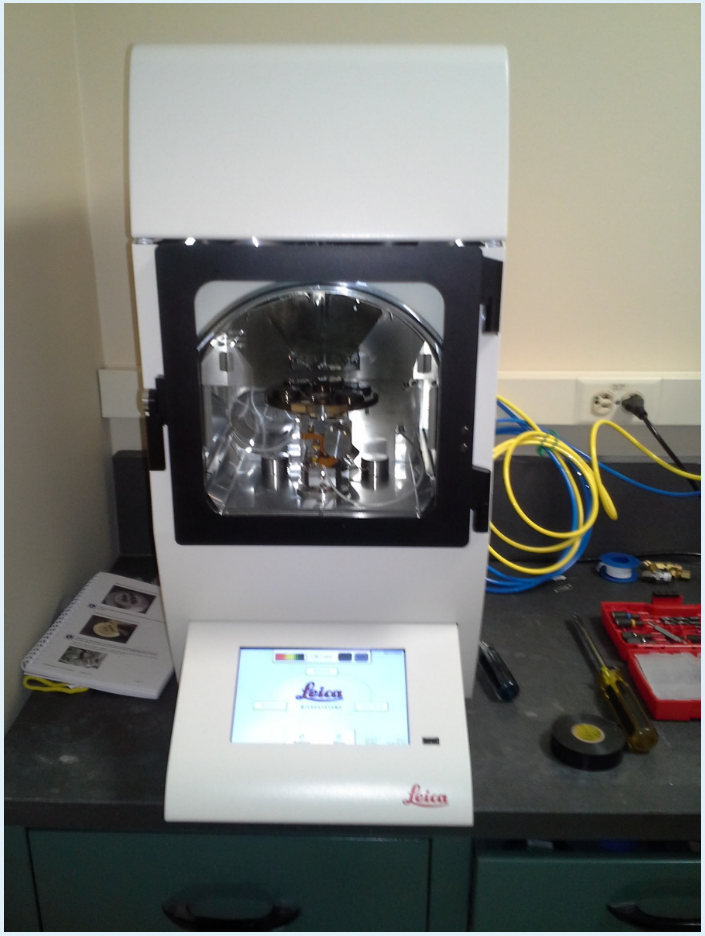
Does more intense FE beam cause different behaviors in materials?

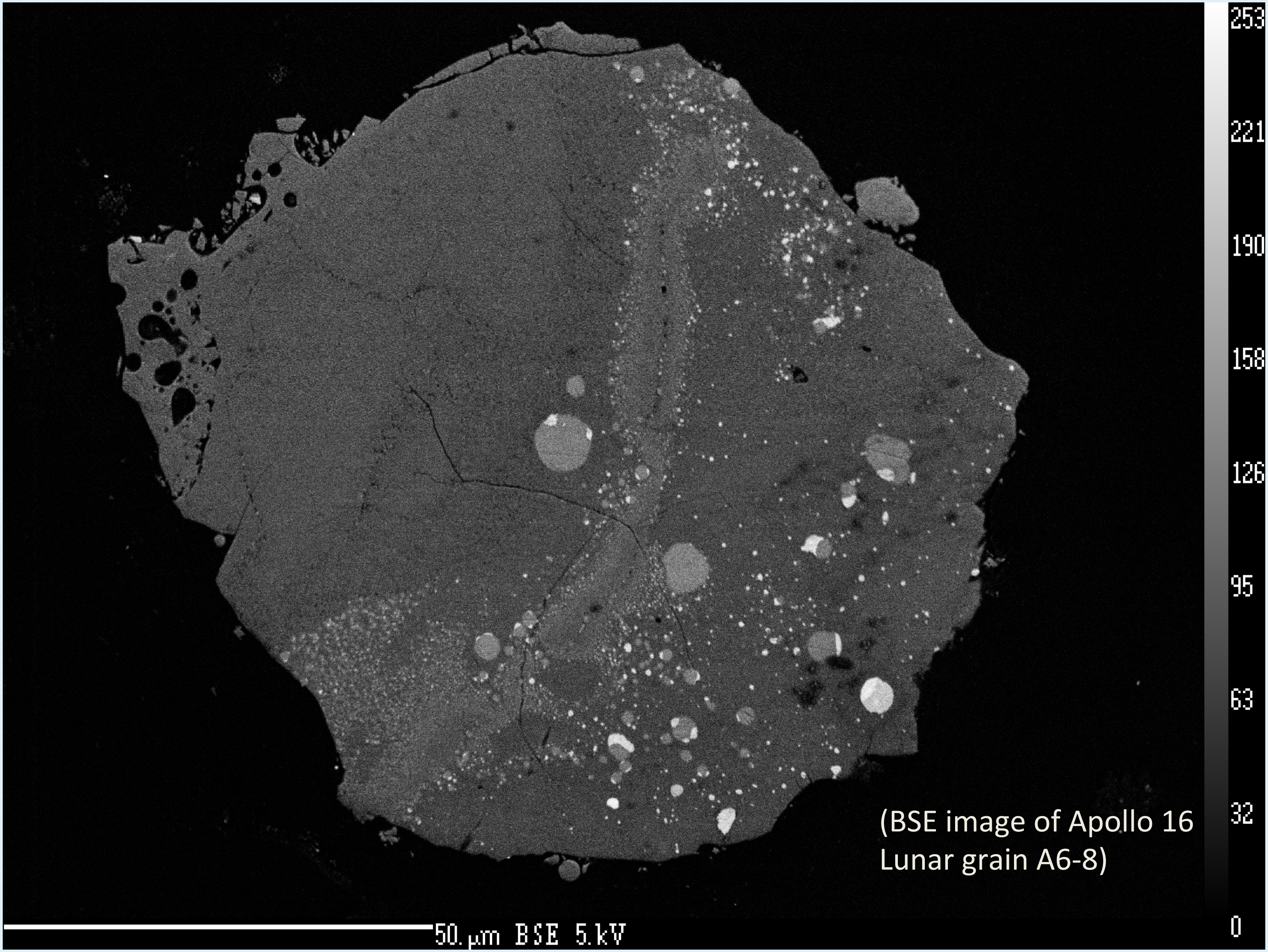
- An experiment with perhaps the most sensitive minerals, carbonates… testing out whether a thick coat of Ir might offer some ‘protection’ to beam damage

Intense FE beams → Significant Beam Damage Possible

Relative to W filament's beam
- Electron charge implantation concentrated
- With Temperature increase 25-150 X

Armstrong (2012, AGU) suggested benefits of Iridium metal coating:
- Extremely thin coats conduct well
- Possible protection by enhanced thermal conductivity vis a vis C
- Where measuring C Ka





(BSE image of Apollo 16 Lunar grain A6-8)

Outline

- Review:
  - Benefits of low kV EPMA
  - Low voltage vs low overvoltage
  - Some challenges with low kV
  - Determination of analytical spatial resolution

- Experiments:
  - Evaluate spatial resolution of Si and Al Ka in silicate glass K409
    - 5, 7 kV
  - Effect of high intensity FE beams on metals
  - Effect of high intensity FE beams on minerals

- Other considerations for FE low voltage EPMA
  - Carbon contamination differences (Dieter Rhede)
  - Re-evaluation of some standard reference materials
  - Need to experiment with non-traditional X-ray lines

- What the next generation of submicron electron beam microanalyzers need:
  - 24/7 “CryoTiger” closed cycle refrigerant cooled cold plate
  - Better mechanical/electronic stability at high magnification
  - In-chamber cleaner (UV?)
  - Can a sample be chilled???

FE vs W vs LaB6 @ 10 kV

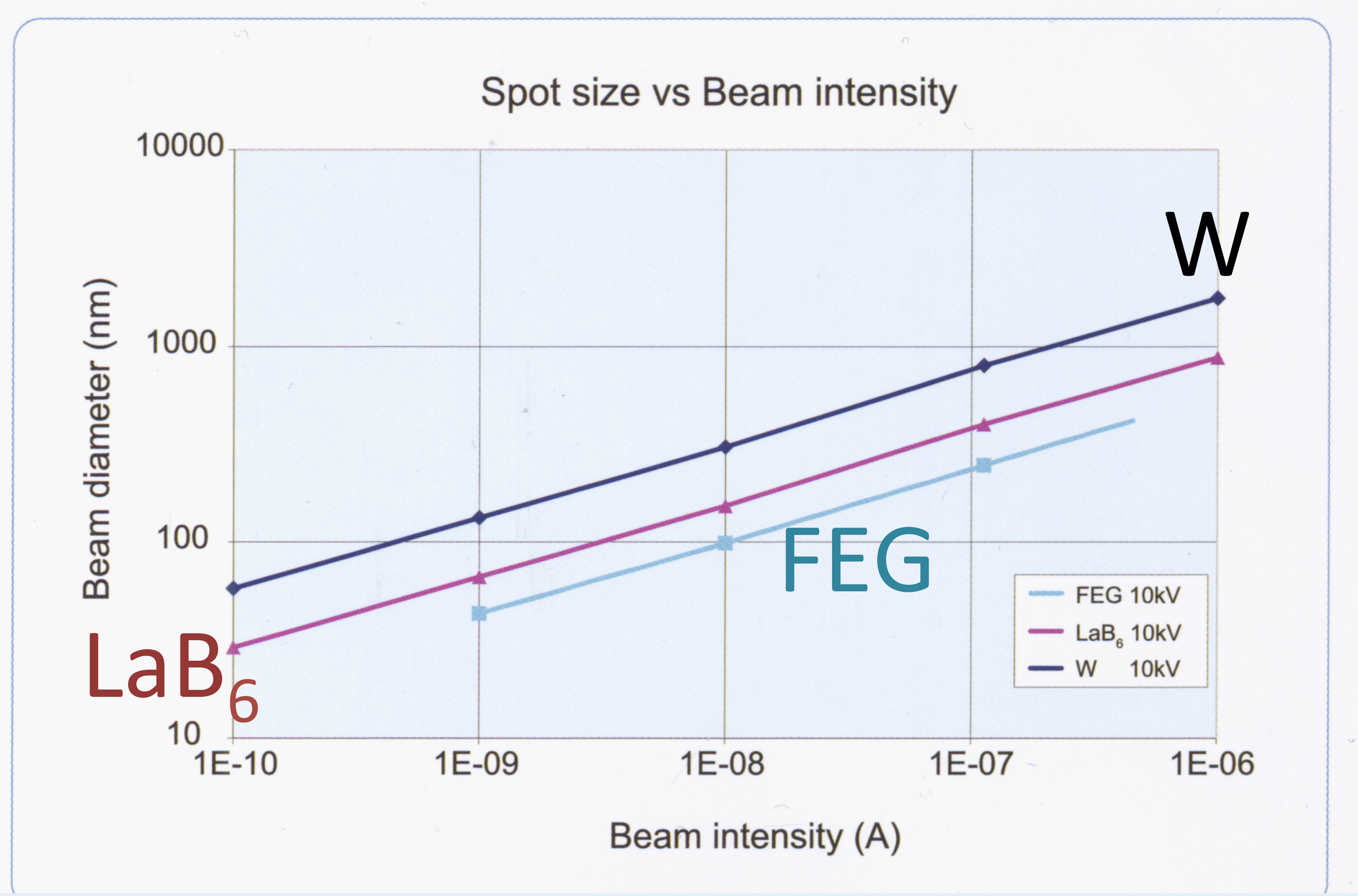
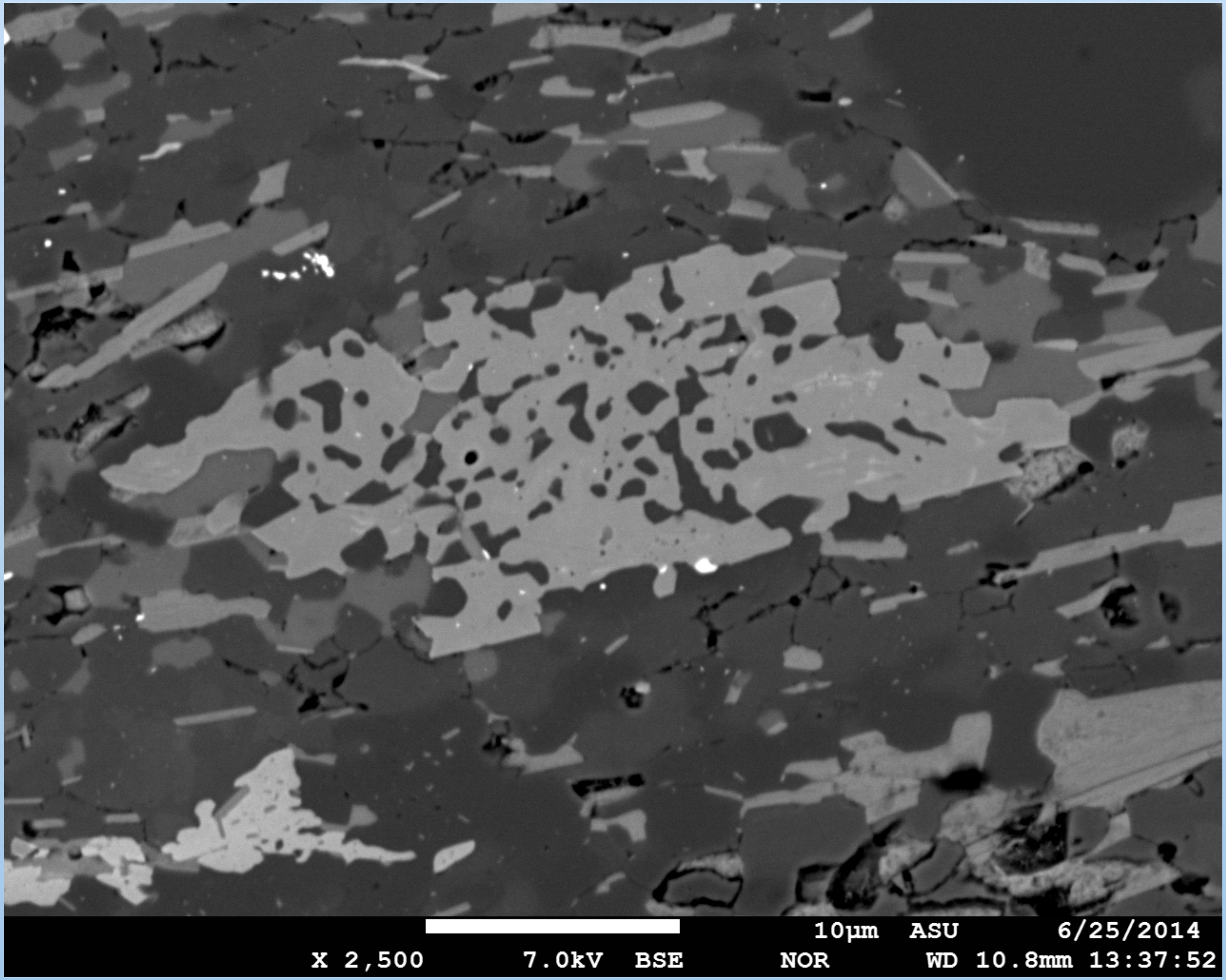


Figure 1. Effect of different electron sources and currents upon resulting beam diameter at 10 kV. (Source: CAMECA)

Field Emission image – submicron features – but EPMA?



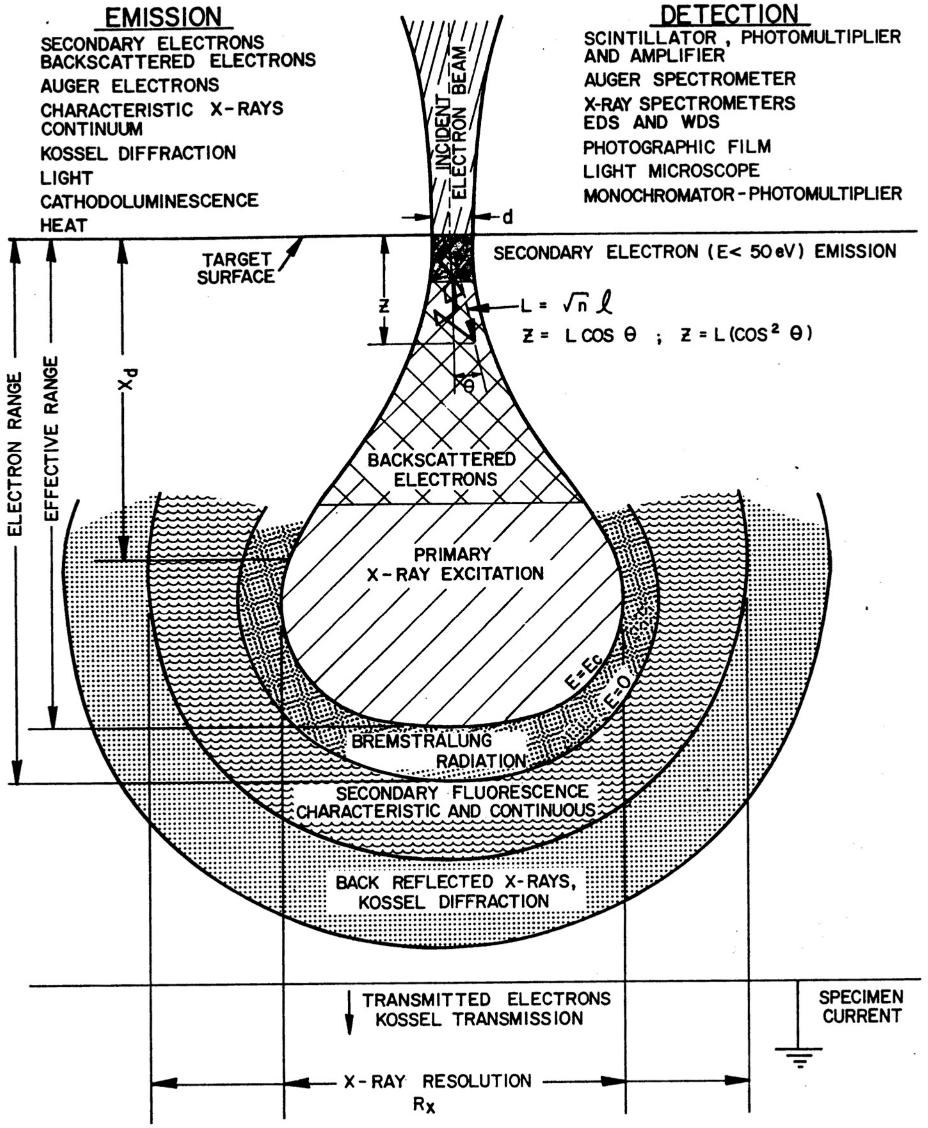


Fig. 12—*A schematic representation of the interaction of an electron beam with a solid of moderate to low atomic number. Most of the different signals emitted, their means of detection, and the diameters of the excited volumes from which they originate are shown. L is the mean free path, n the number of events, l the distance traveled between each event, E the average energy of the impinging electron, and X_d the depth where complete electron diffusion occurs.*

Electron Scattering in Sample

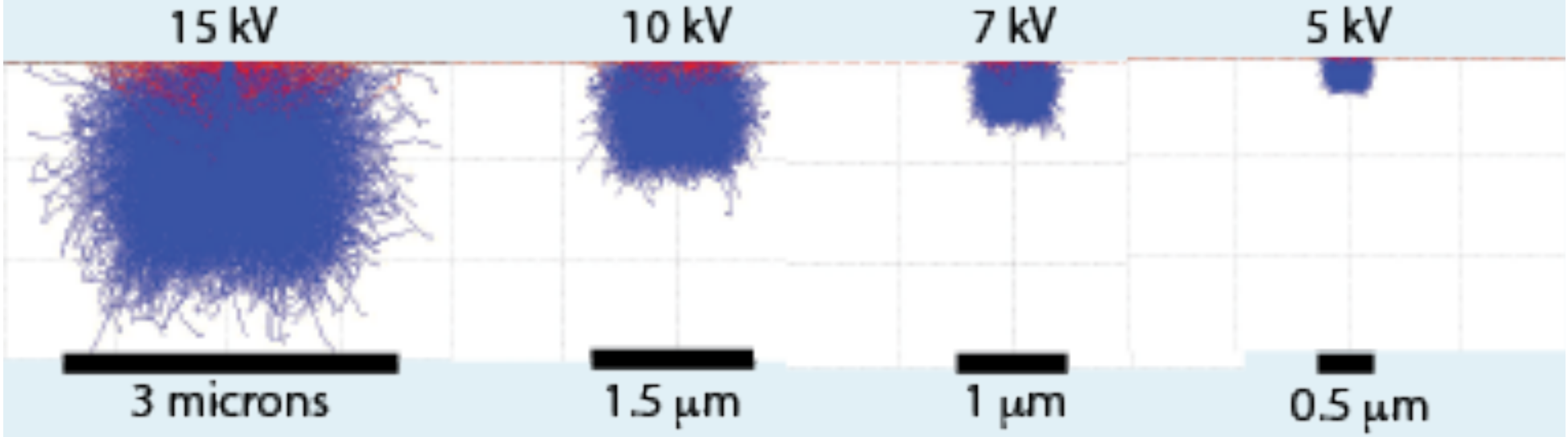
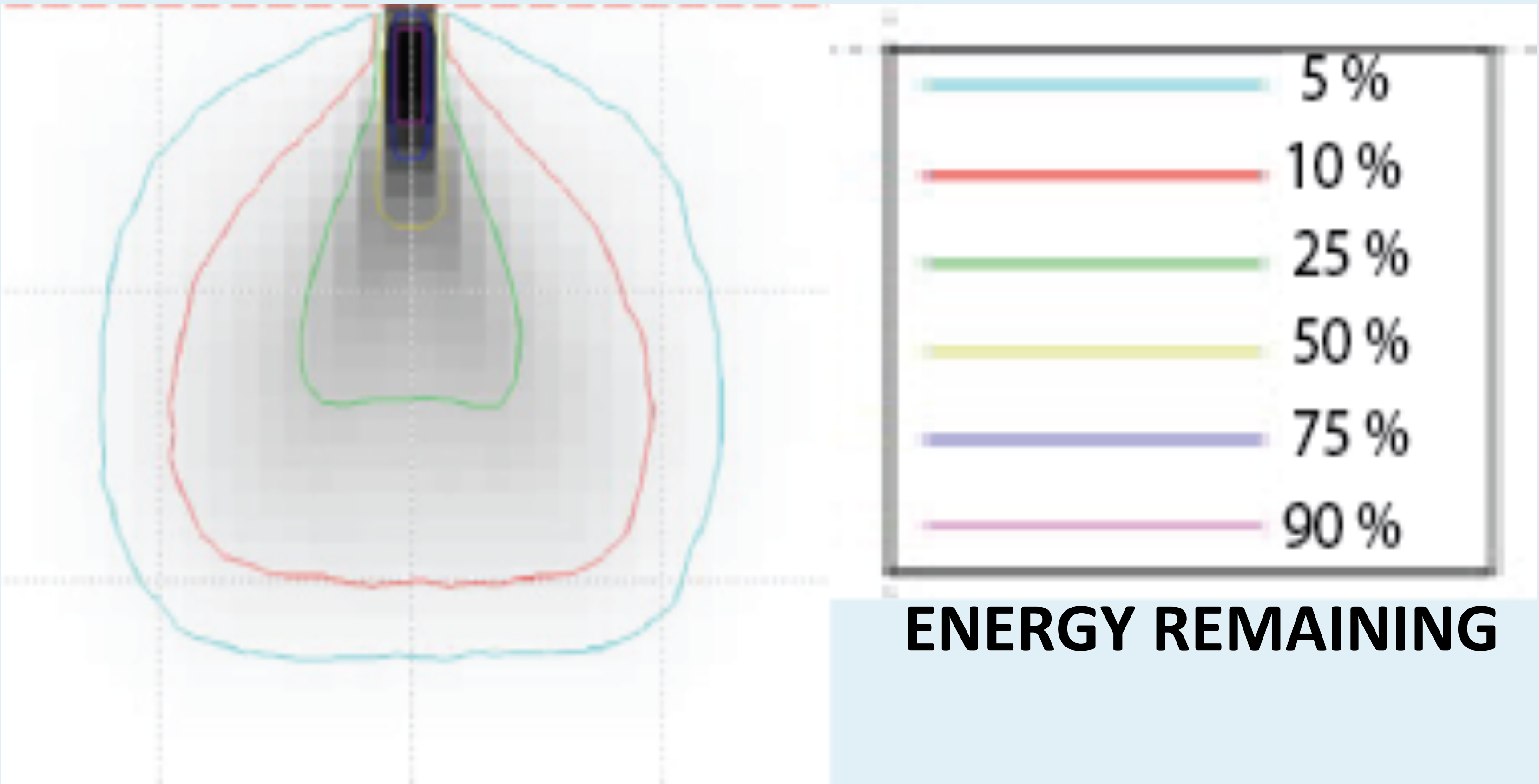


Figure 3. CASINO Monte Carlo simulations of various beam energies scattering in the same silicate glass (NIST K409). Blue shows the traces of the electrons scattered until all energy lost; red shows backscattered electrons. The electron source's beam size for all is the same.

Beam Scattering-Energy Loss

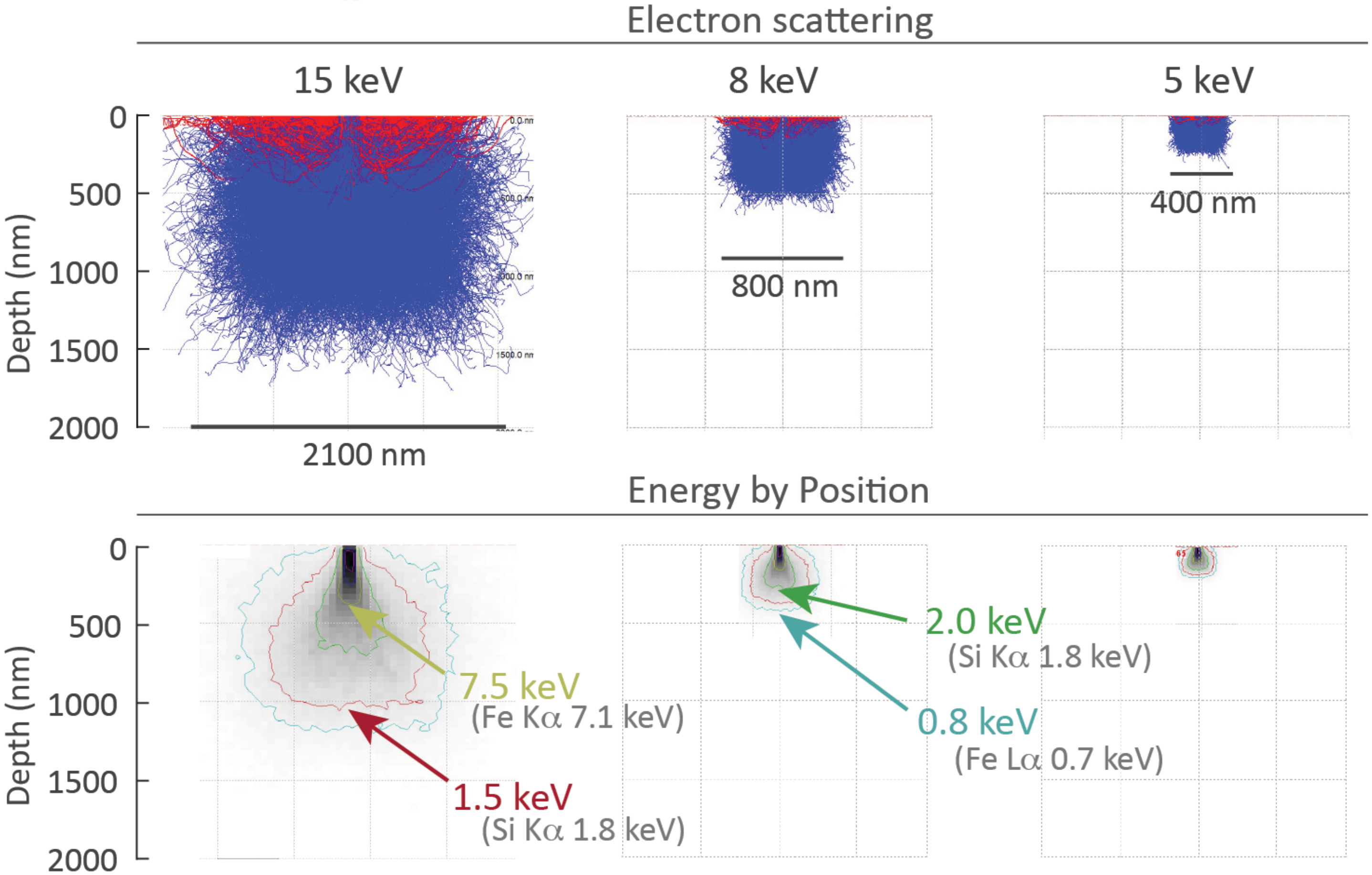


ENERGY REMAINING

Predicted % of energy remaining of the gun E0 kV by CASINO -- here, 15 kV in olivine, $(Mg,Fe)_2SiO_4$.

Beam Scattering-Energy Loss

Example: Olivine (Fo_{65})

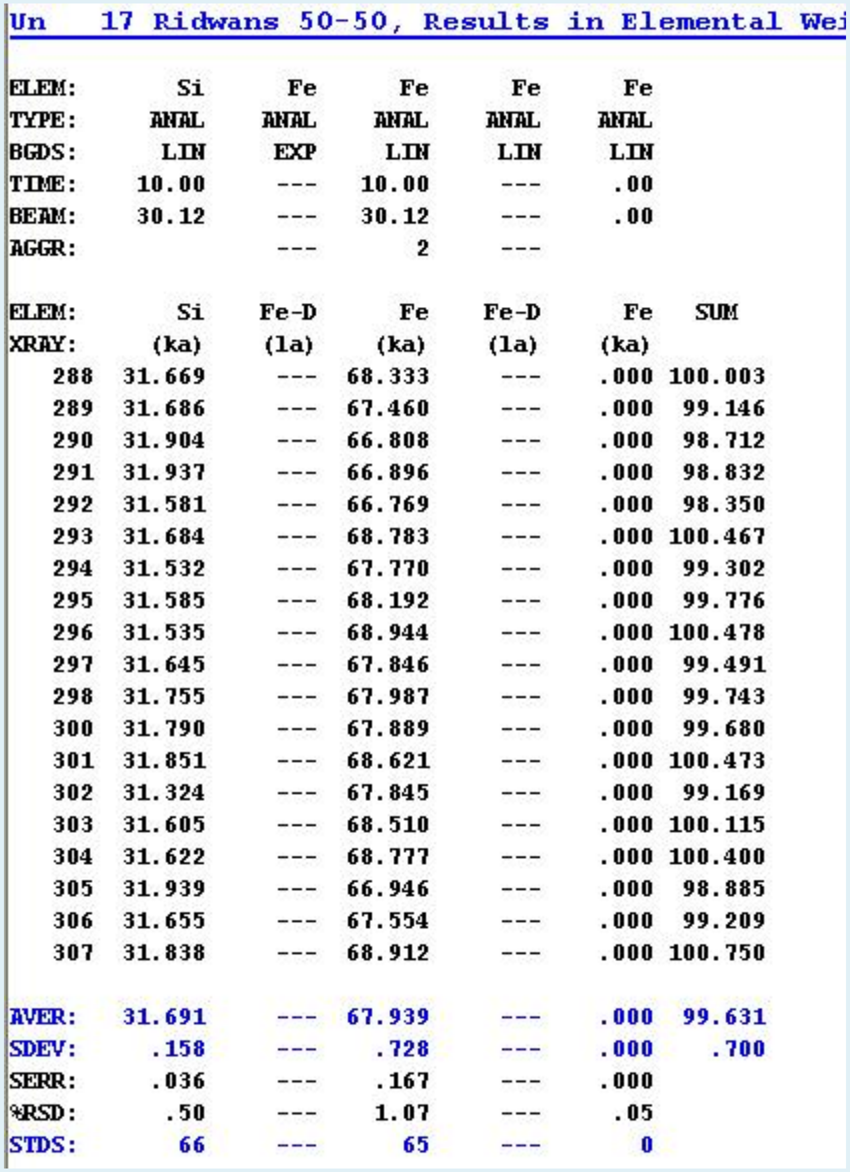


CASINO modeling

100 nm beam

Ran tests on ‘large’ commercial FeSi…

15 keV, Fe Ka



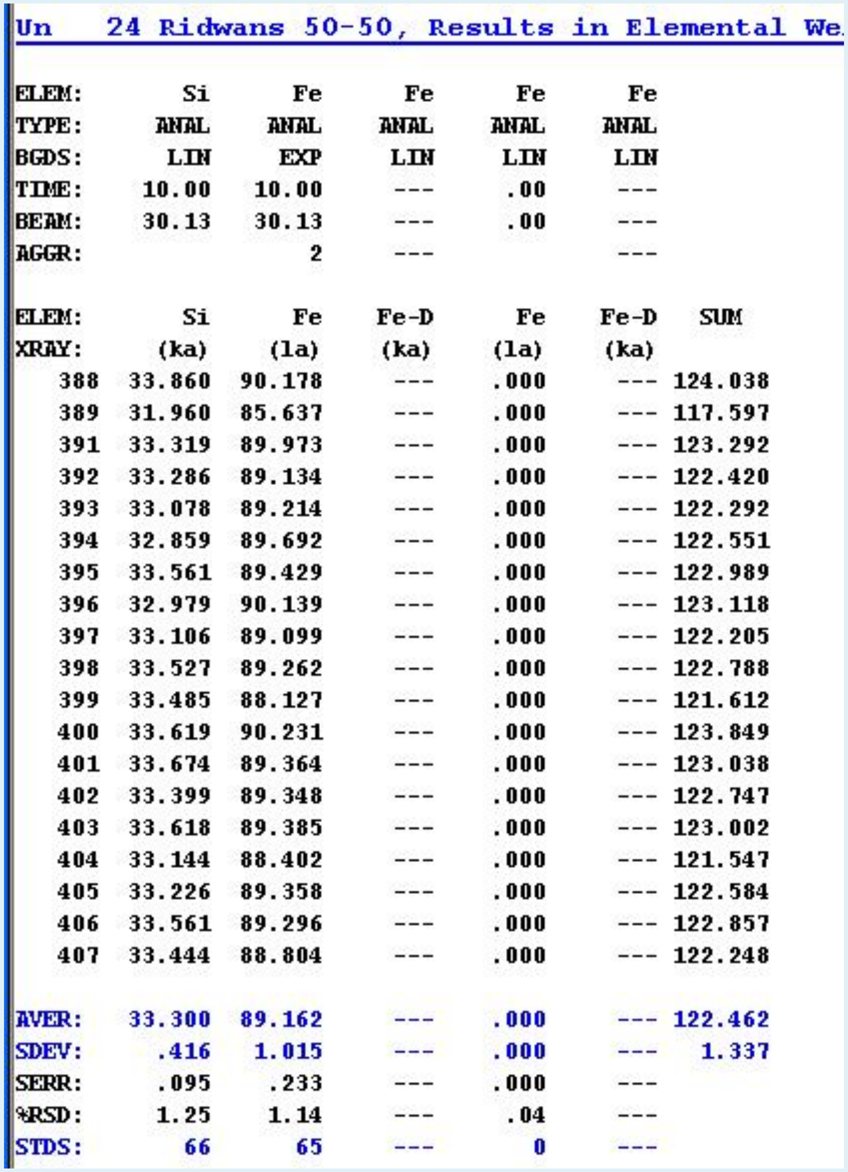
```
Un    17 Ridwans 50-50, Results in Elemental Wei

ELEM:       Si      Fe      Fe      Fe      Fe
TYPE:     ANAL    ANAL    ANAL    ANAL    ANAL
BGDS:      LIN     EXP     LIN     LIN     LIN
TIME:    10.00     ---   10.00     ---     .00
BEAM:    30.12     ---   30.12     ---     .00
AGGR:              ---       2     ---

ELEM:       Si    Fe-D      Fe    Fe-D      Fe     SUM
XRAY:     (ka)    (la)    (ka)    (la)    (ka)
   288  31.669     ---  68.333     ---    .000 100.003
   289  31.686     ---  67.460     ---    .000  99.146
   290  31.904     ---  66.808     ---    .000  98.712
   291  31.937     ---  66.896     ---    .000  98.832
   292  31.581     ---  66.769     ---    .000  98.350
   293  31.684     ---  68.783     ---    .000 100.467
   294  31.532     ---  67.770     ---    .000  99.302
   295  31.585     ---  68.192     ---    .000  99.776
   296  31.535     ---  68.944     ---    .000 100.478
   297  31.645     ---  67.846     ---    .000  99.491
   298  31.755     ---  67.987     ---    .000  99.743
   300  31.790     ---  67.889     ---    .000  99.680
   301  31.851     ---  68.621     ---    .000 100.473
   302  31.324     ---  67.845     ---    .000  99.169
   303  31.605     ---  68.510     ---    .000 100.115
   304  31.622     ---  68.777     ---    .000 100.400
   305  31.939     ---  66.946     ---    .000  98.885
   306  31.655     ---  67.554     ---    .000  99.209
   307  31.838     ---  68.912     ---    .000 100.750

AVER:   31.691     ---  67.939     ---    .000  99.631
SDEV:     .158     ---    .728     ---    .000    .700
SERR:     .036     ---    .167     ---    .000
%RSD:      .50     ---    1.07     ---     .05
STDS:       66     ---      65     ---       0
```

5 keV, Fe La



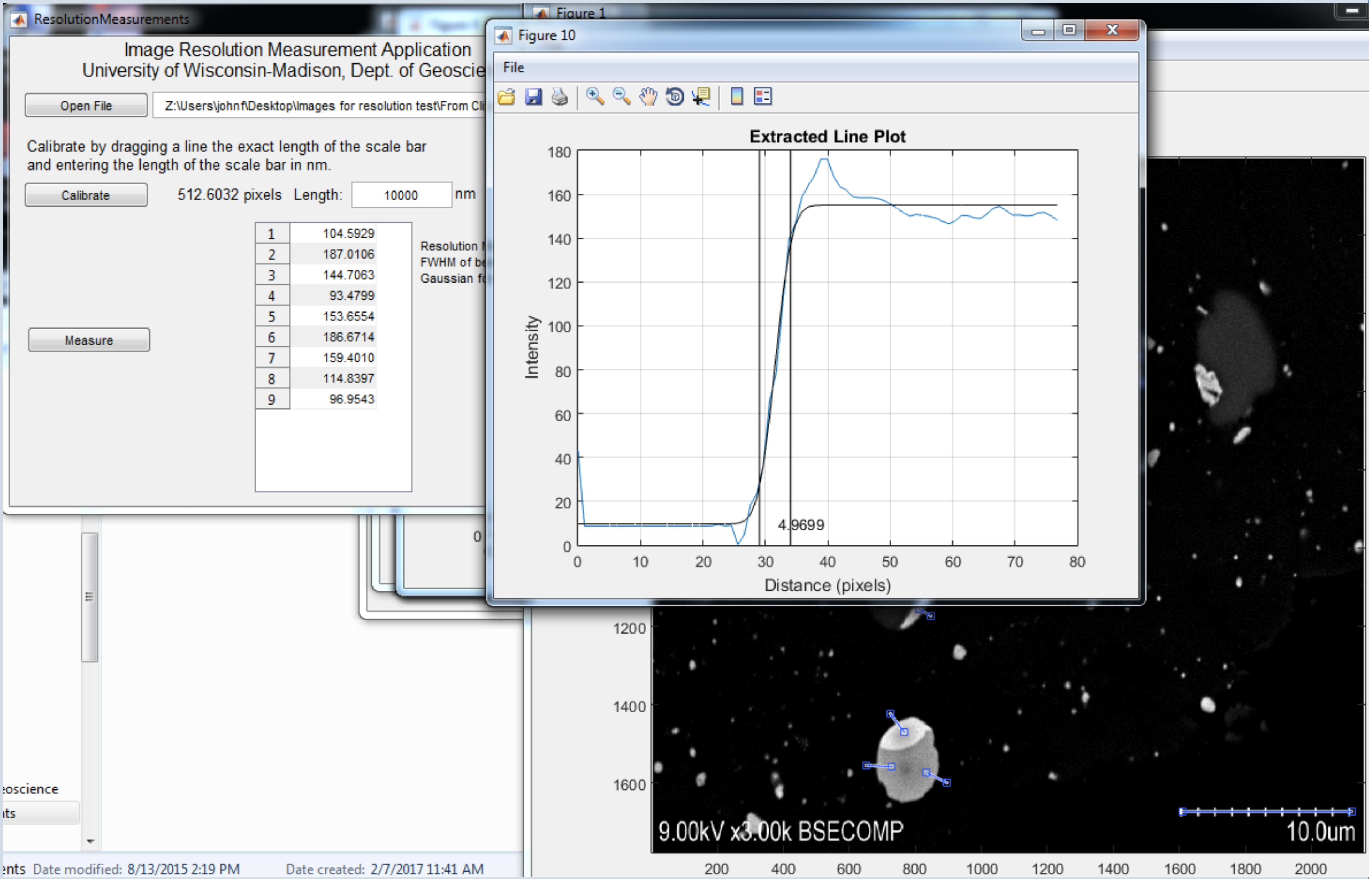
```
Un    24 Ridwans 50-50, Results in Elemental We

ELEM:       Si      Fe      Fe      Fe      Fe
TYPE:     ANAL    ANAL    ANAL    ANAL    ANAL
BGDS:      LIN     EXP     LIN     LIN     LIN
TIME:    10.00   10.00     ---     .00     ---
BEAM:    30.13   30.13     ---     .00     ---
AGGR:                2     ---             ---

ELEM:       Si      Fe    Fe-D      Fe    Fe-D     SUM
XRAY:     (ka)    (la)    (ka)    (la)    (ka)
   388  33.860  90.178     ---    .000     --- 124.038
   389  31.960  85.637     ---    .000     --- 117.597
   391  33.319  89.973     ---    .000     --- 123.292
   392  33.286  89.134     ---    .000     --- 122.420
   393  33.078  89.214     ---    .000     --- 122.292
   394  32.859  89.692     ---    .000     --- 122.551
   395  33.561  89.429     ---    .000     --- 122.989
   396  32.979  90.139     ---    .000     --- 123.118
   397  33.106  89.099     ---    .000     --- 122.205
   398  33.527  89.262     ---    .000     --- 122.788
   399  33.485  88.127     ---    .000     --- 121.612
   400  33.619  90.231     ---    .000     --- 123.849
   401  33.674  89.364     ---    .000     --- 123.038
   402  33.399  89.348     ---    .000     --- 122.747
   403  33.618  89.385     ---    .000     --- 123.002
   404  33.144  88.402     ---    .000     --- 121.547
   405  33.226  89.358     ---    .000     --- 122.584
   406  33.561  89.296     ---    .000     --- 122.857
   407  33.444  88.804     ---    .000     --- 122.248

AVER:   33.300  89.162     ---    .000     --- 122.462
SDEV:     .416   1.015     ---    .000     ---   1.337
SERR:     .095    .233     ---    .000     ---
%RSD:     1.25    1.14     ---     .04     ---
STDS:       66      65     ---       0     ---
```

Peter Sobol's "Image Resolution Measurement App" – Get @ UW Madison EPMA Lab Web Page



ResolutionMeasurements

Image Resolution Measurement Application
University of Wisconsin-Madison, Dept. of Geoscie

Open File Z:\Users\johnf\Desktop\Images for resolution test\From Cli

Calibrate by dragging a line the exact length of the scale bar and entering the length of the scale bar in nm.

Calibrate 512.6032 pixels Length: 10000 nm

1	104.5929
2	187.0106
3	144.7063
4	93.4799
5	153.6554
6	186.6714
7	159.4010
8	114.8397
9	96.9543

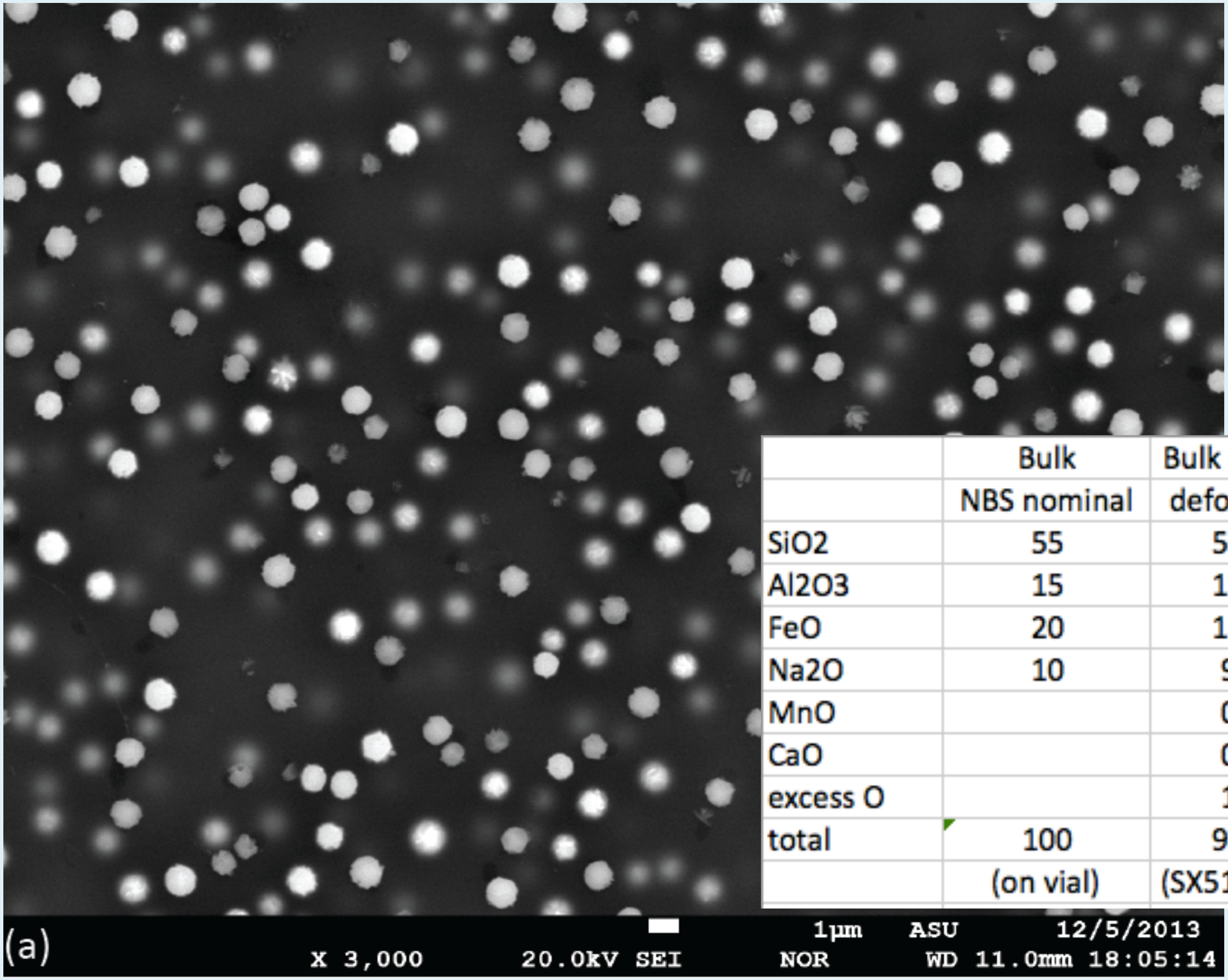
Resolution I
FWHM of be
Gaussian fc

Measure

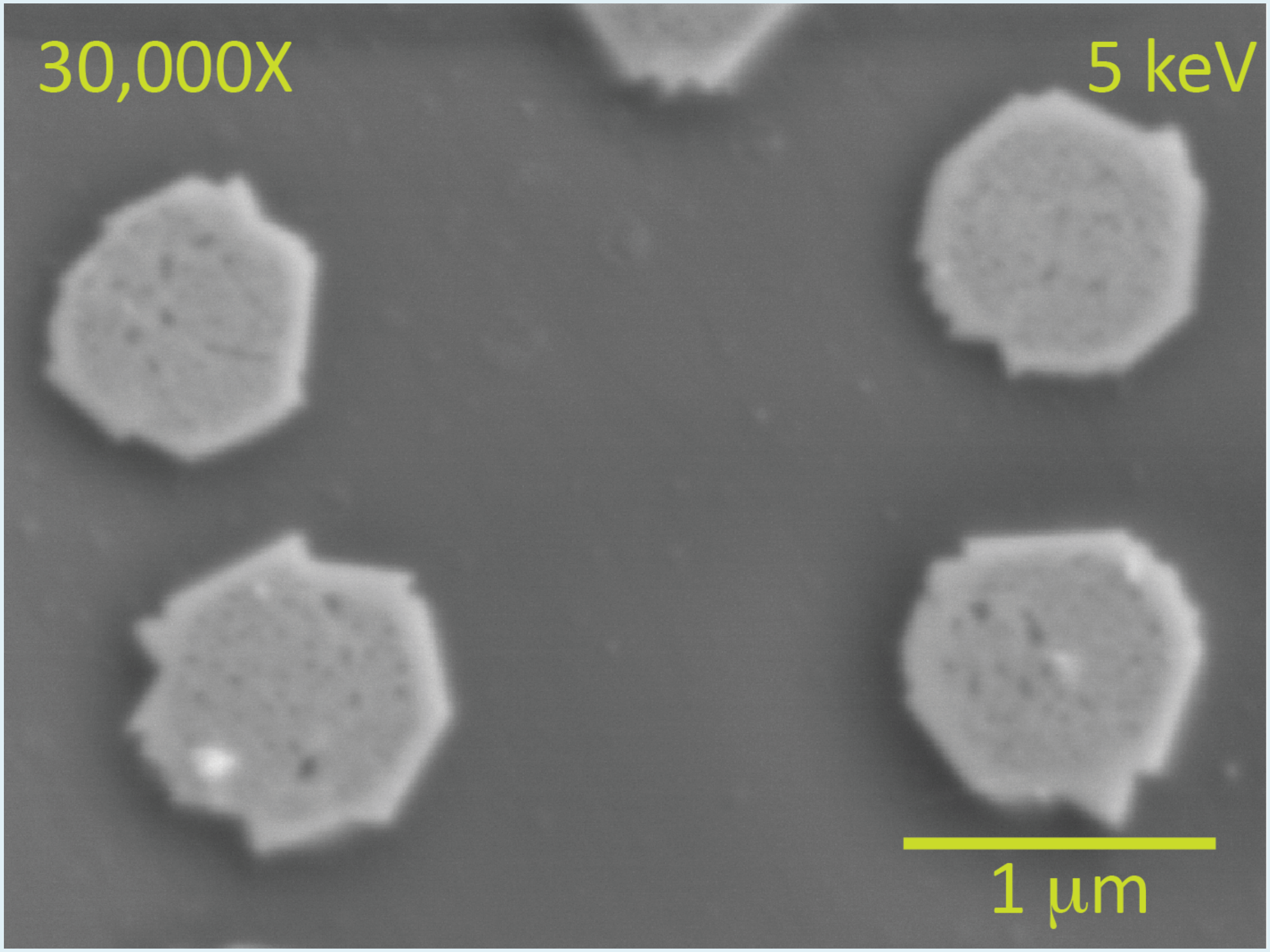
Date modified: 8/13/2015 2:19 PM Date created: 2/7/2017 11:41 AM

Uses Mathlab runtime app (also freely downloadable)

NBS/NIST K409, a 'failed experiment'

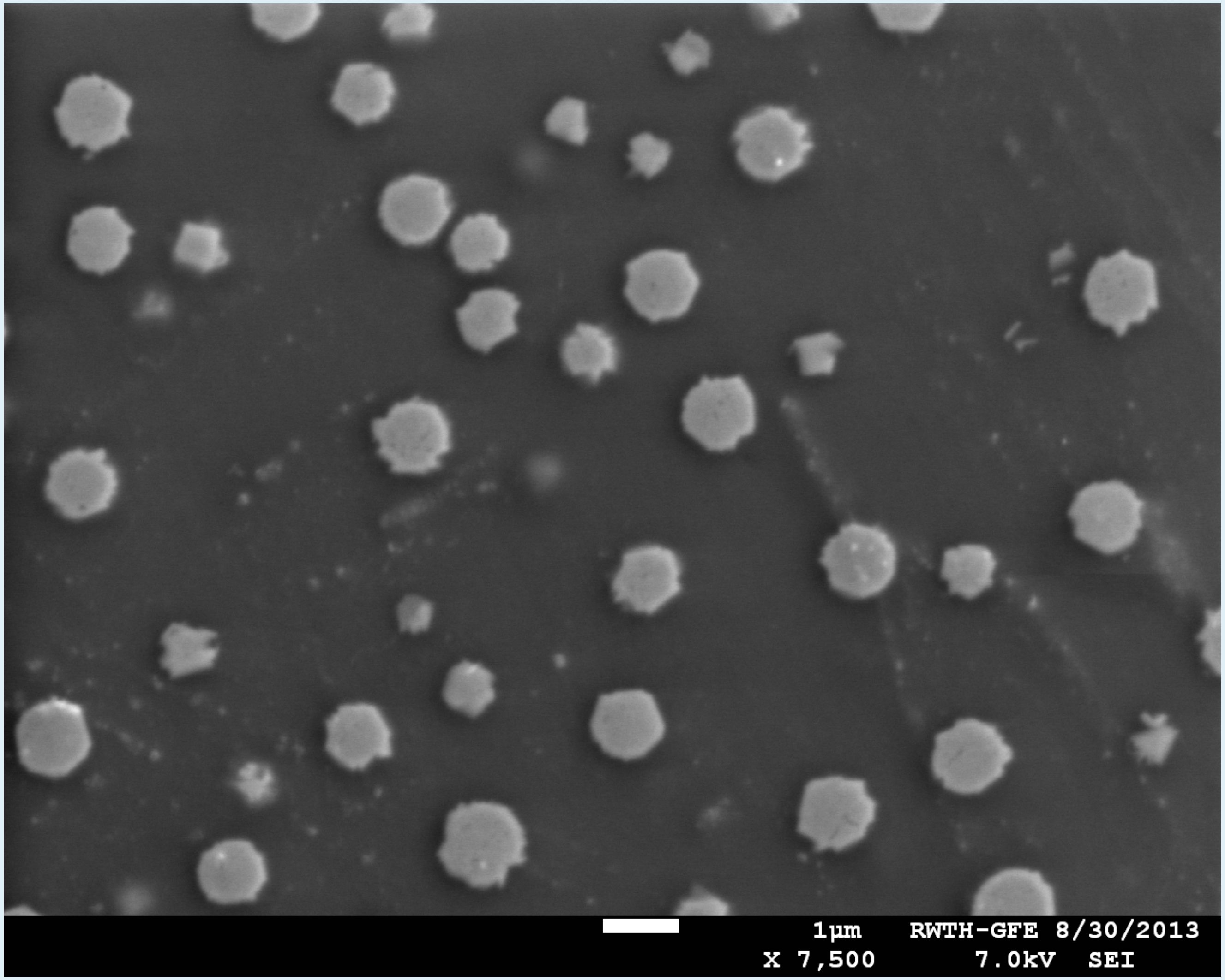


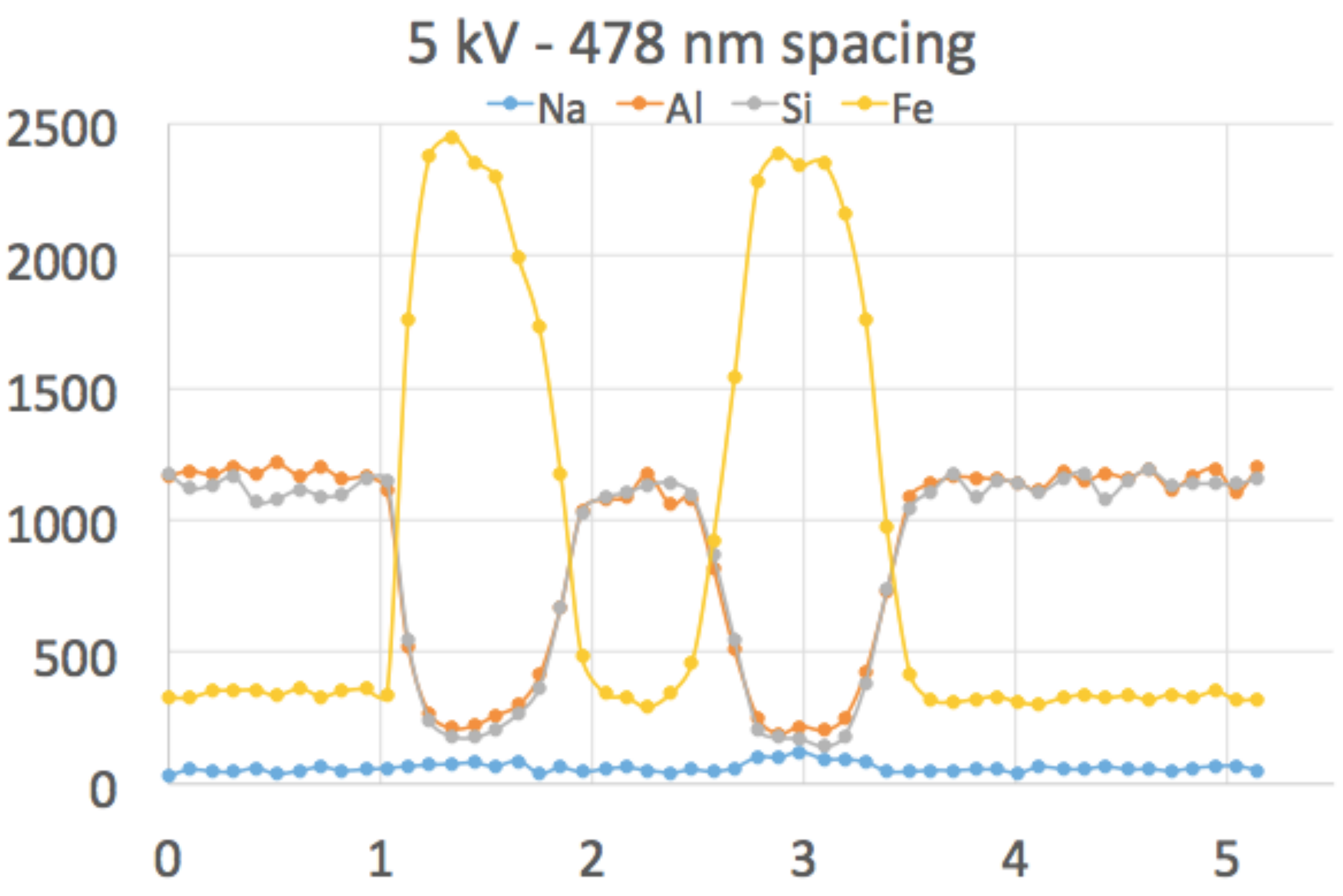
	Bulk	Bulk -EPMA	Glass
	NBS nominal	defocused	estimate of
SiO2	55	56.6	59.9
Al2O3	15	15.1	17
FeO	20	15.7	6.4
Na2O	10	9.8	10.8
MnO		0.2	
CaO		0.1	
excess O		1.8	5.9
total	100	99.3	100
	(on vial)	(SX51 2007)	(SX51 2012)



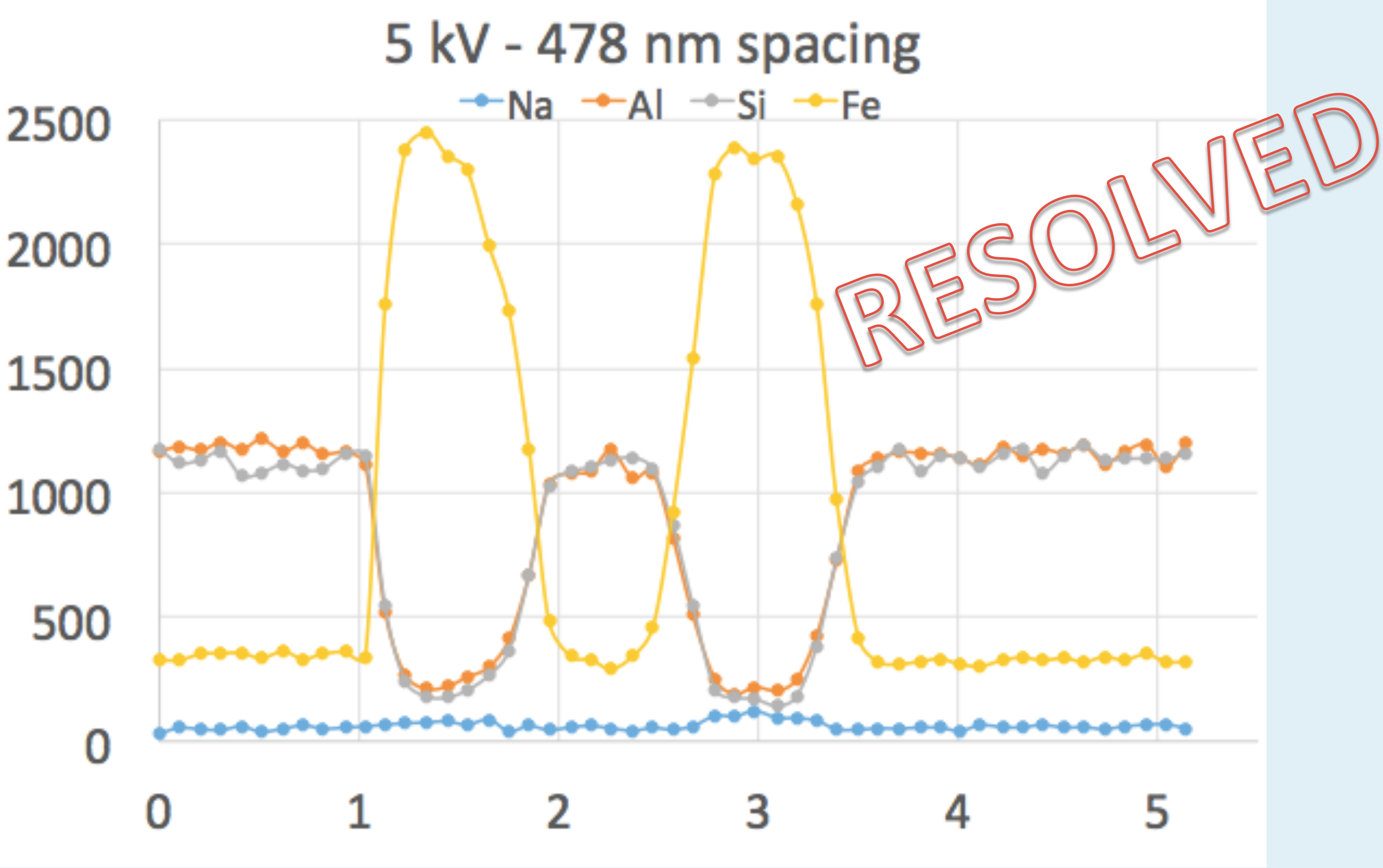
NBS/NIST K409, a ‘failed experiment’

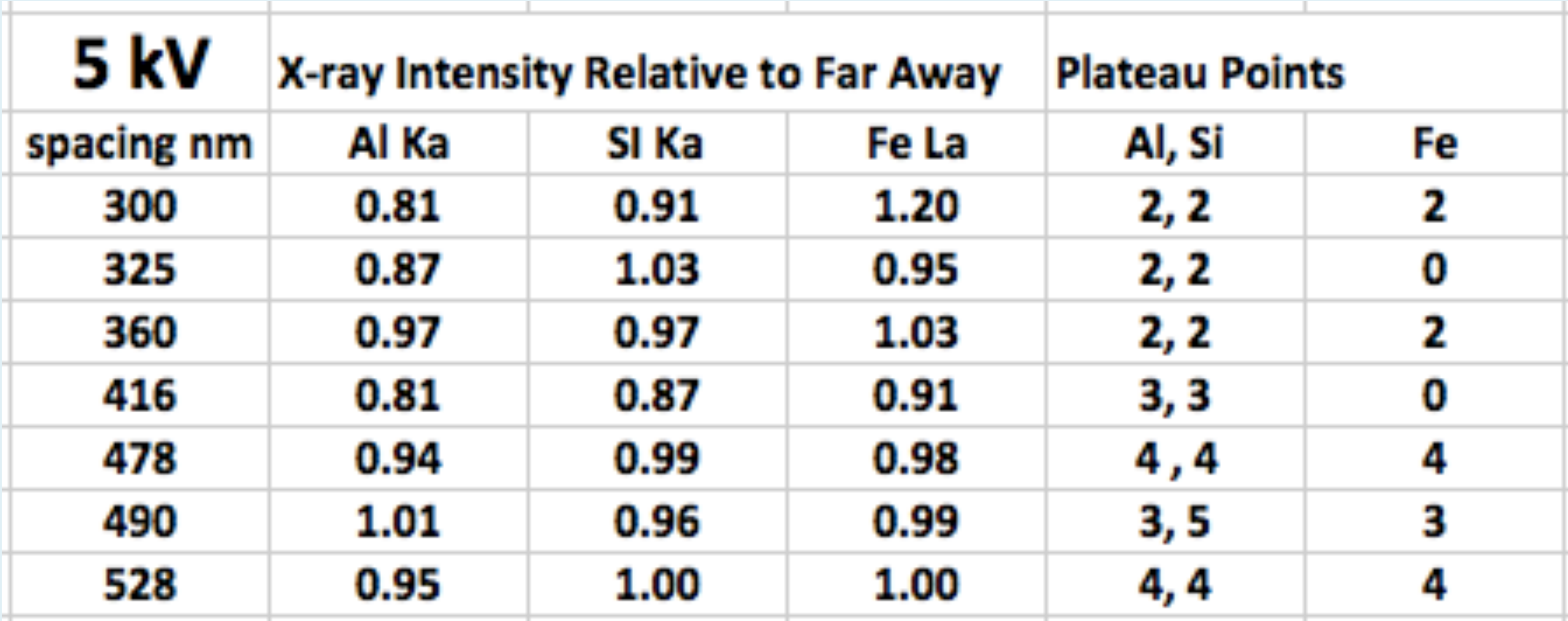
K409 …. Line Traverses




5 kV - 478 nm spacing
Na
Al
Si
Fe
2500
2000
1500
1000
500
0
0
1
2
3
4
5

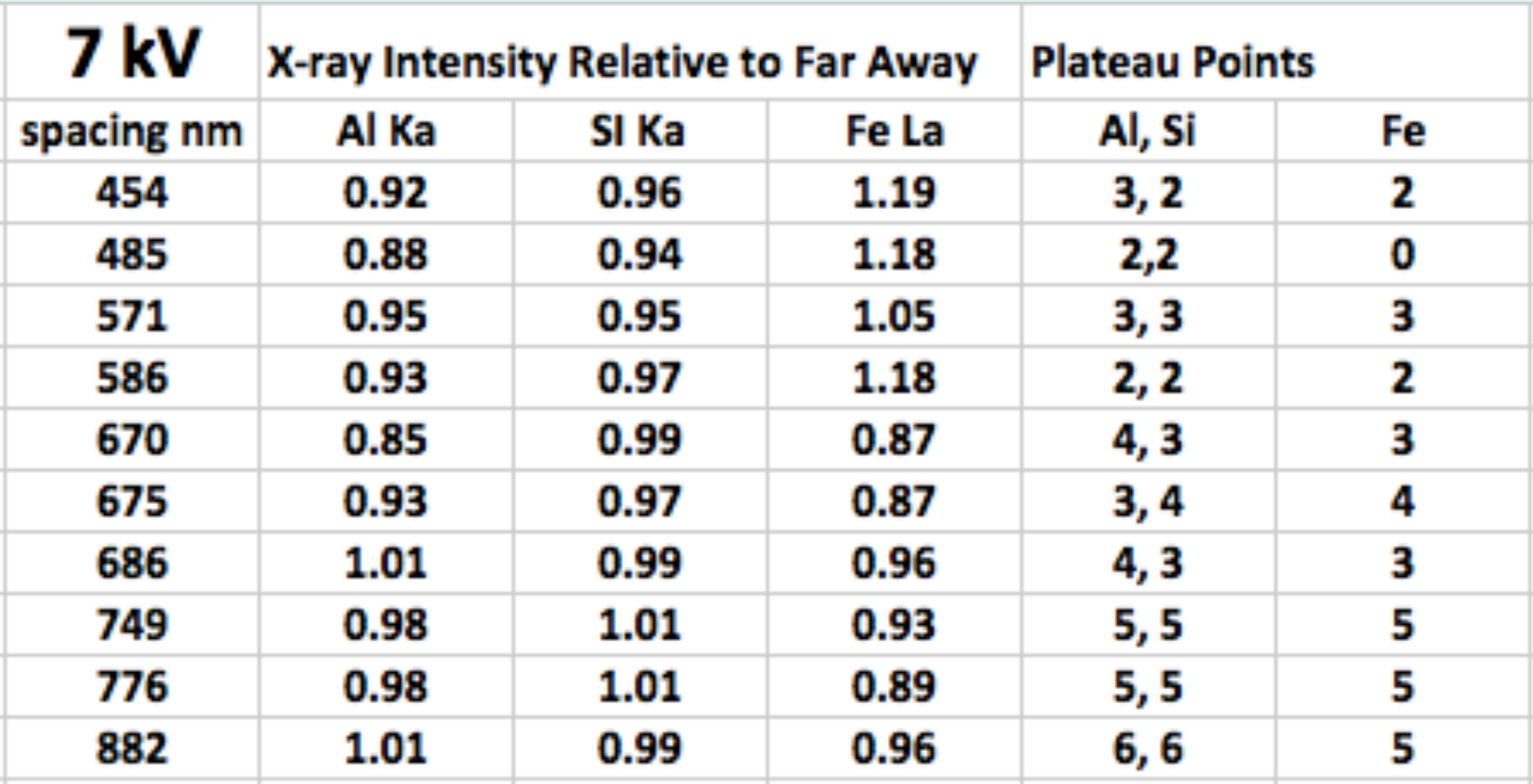
Si 0.99
Al 0.94
Fe 0.98





5 kV	X-ray Intensity Relative to Far Away			Plateau Points	
spacing nm	Al Ka	Si Ka	Fe La	Al, Si	Fe
300	0.81	0.91	1.20	2, 2	2
325	0.87	1.03	0.95	2, 2	0
360	0.97	0.97	1.03	2, 2	2
416	0.81	0.87	0.91	3, 3	0
478	0.94	0.99	0.98	4 , 4	4
490	1.01	0.96	0.99	3, 5	3
528	0.95	1.00	1.00	4, 4	4

→ 450-500 nm spatial resolution @ 5 kV for Al Ka, Si Ka and Fe La in K409 glass

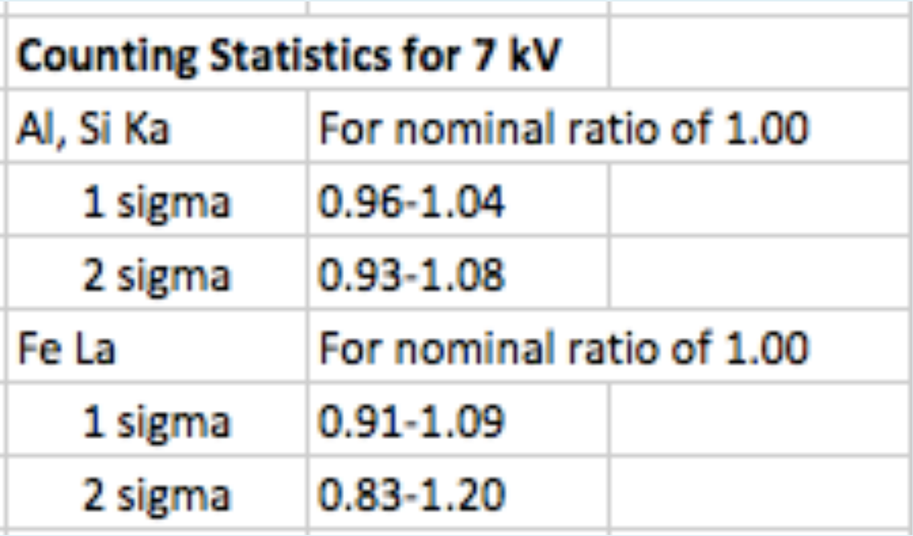


7 kV	X-ray Intensity Relative to Far Away			Plateau Points	
spacing nm	Al Ka	SI Ka	Fe La	Al, Si	Fe
454	0.92	0.96	1.19	3, 2	2
485	0.88	0.94	1.18	2,2	0
571	0.95	0.95	1.05	3, 3	3
586	0.93	0.97	1.18	2, 2	2
670	0.85	0.99	0.87	4, 3	3
675	0.93	0.97	0.87	3, 4	4
686	1.01	0.99	0.96	4, 3	3
749	0.98	1.01	0.93	5, 5	5
776	0.98	1.01	0.89	5, 5	5
882	1.01	0.99	0.96	6, 6	5

→ 700-750 nm spatial resolution @ 5 kV for Al Ka, Si Ka and Fe La in K409 glass

Question of statistics…

- Each measurement of 5 second duration: count rates limited, so wide possible variability in counting statistics



Counting Statistics for 7 kV		
Al, Si Ka	For nominal ratio of 1.00	
1 sigma	0.96-1.04	
2 sigma	0.93-1.08	
Fe La	For nominal ratio of 1.00	
1 sigma	0.91-1.09	
2 sigma	0.83-1.20	

- Future: to improve statistics -- measure 3x3 grids between Fe-oxides / 3 parallel lines