Low Voltage EPMA: Experiments on a New Frontier in Microanalysis

(… Opportunities and Challenges)

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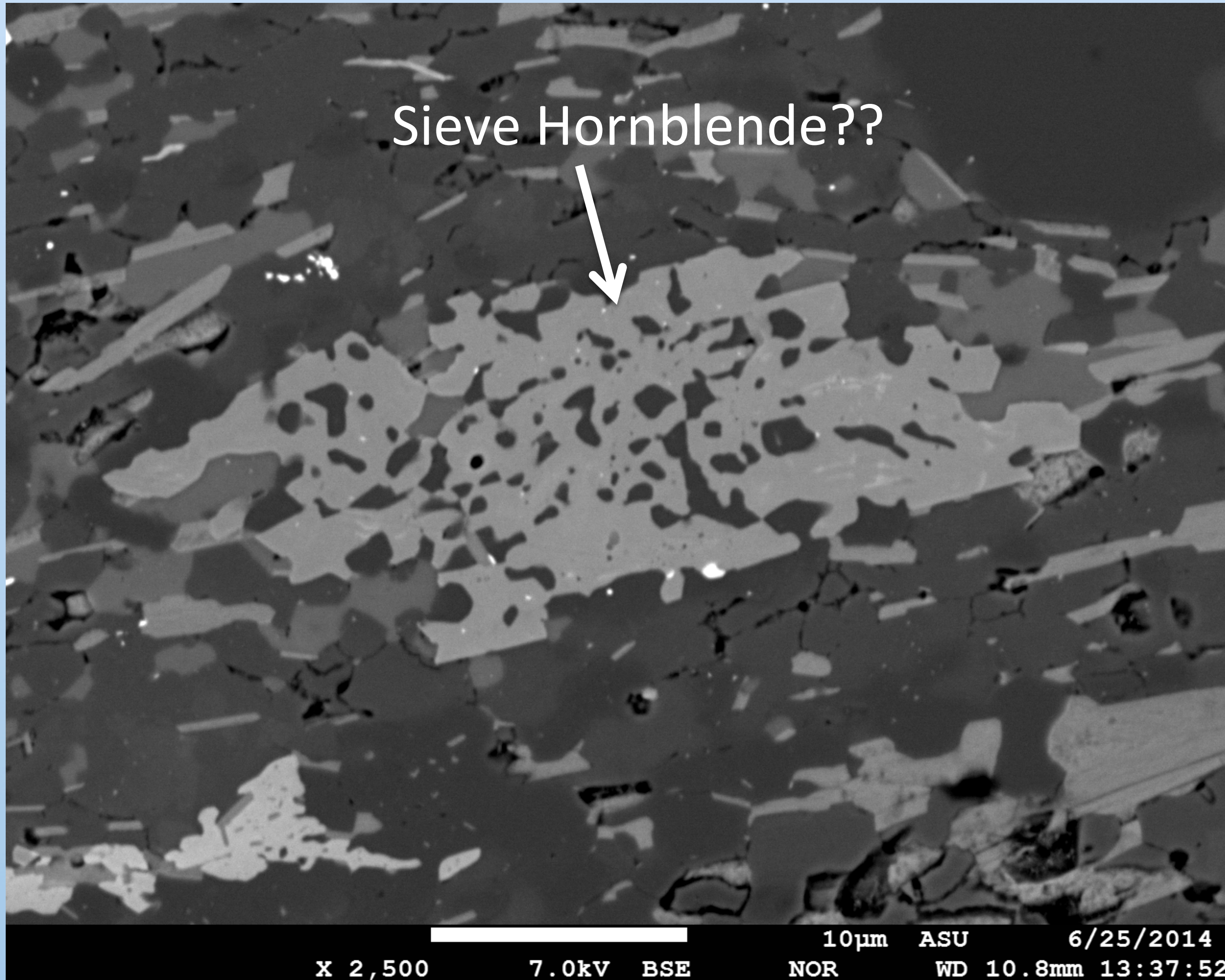
Why Field Emission EPMA?



→Accurate Probe Analysis for submicron regions

Outline

- Review:
- Experiments on spatial resolution:
- Other considerations for FE low voltage EPMA:
- What the next generation of submicron electron probes might utilize:

Part 1: Review

First a little background

- Low kV EPMA is not a new concept
- C.A. Anderson (ARL) presented in 1967
- 15 years ago Barkshire et al presented experimental data.

What is new?

- now relatively common presence of FE ‘tools’ for EPMA
- so need for further delving into capabilities and challenges…

FE vs W vs LaB6 @ 10 kV

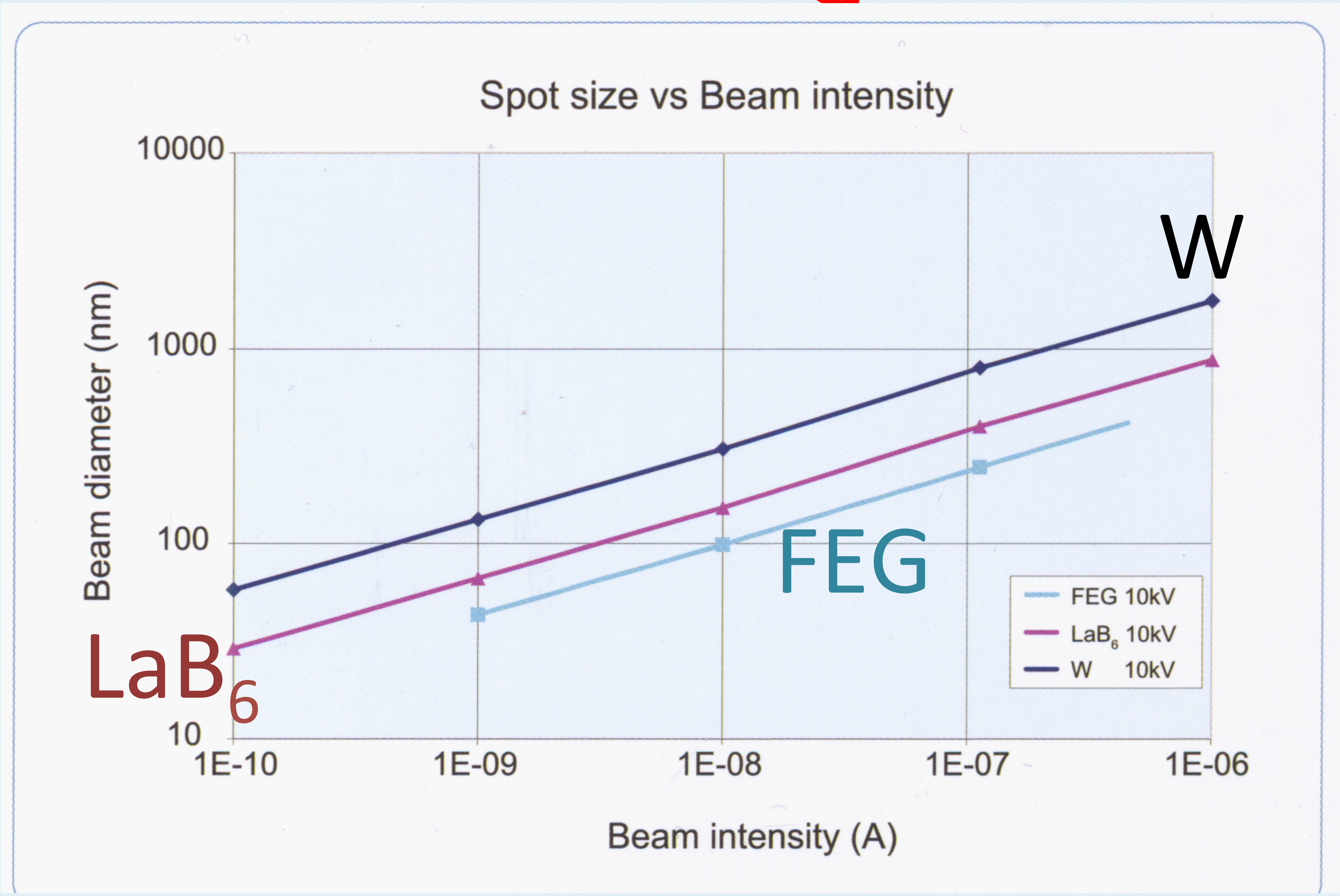


Figure 1. Effect of different electron sources and currents upon resulting beam diameter at 10 kV. (Source: CAMECA)

Effect of keV and nA

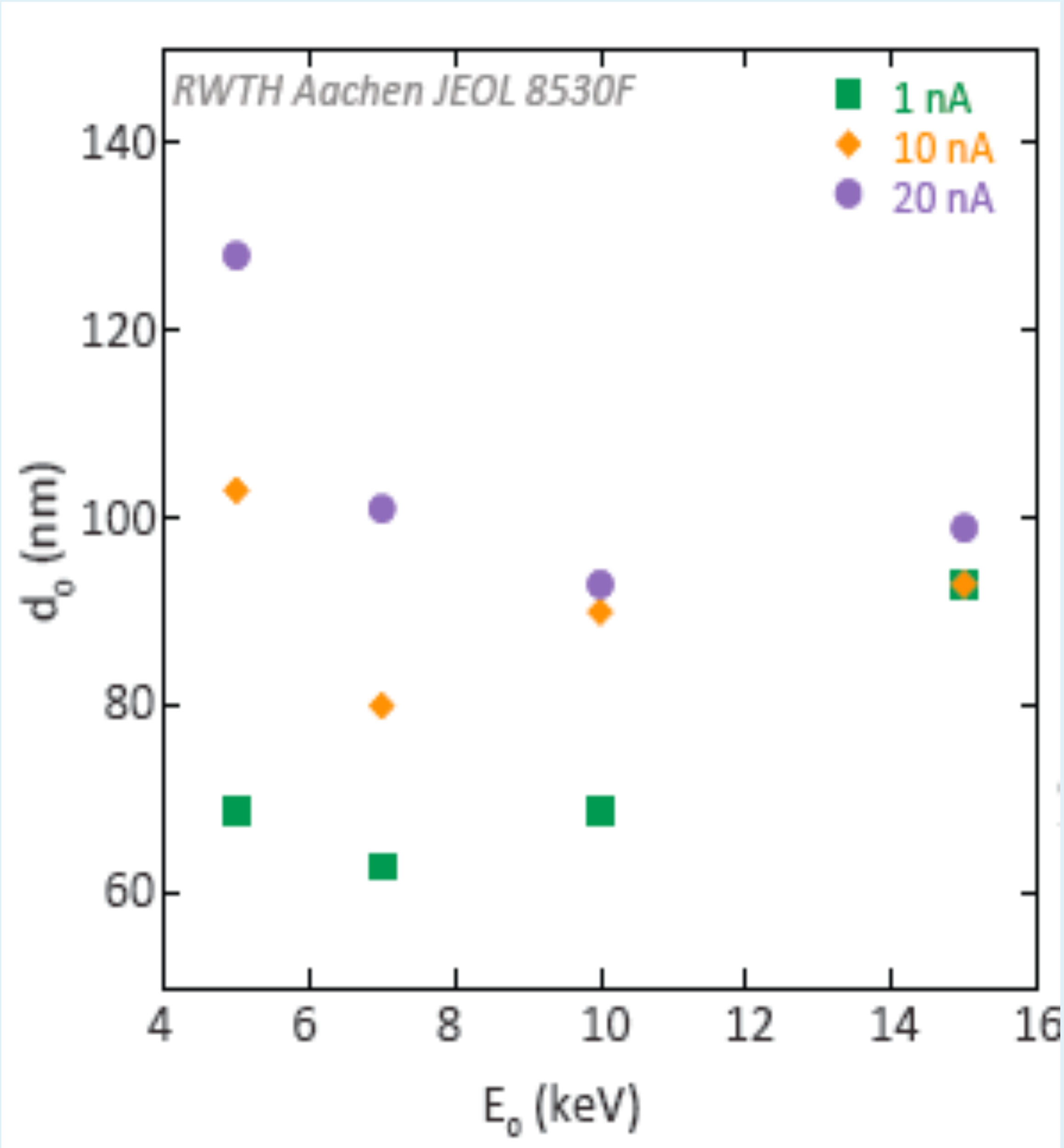


Fig 2. Effect of beam current upon beam diameter at different gun voltages. (K409 data on JEOL 8530F at RWTH Aachen)

Electron Scattering in Sample

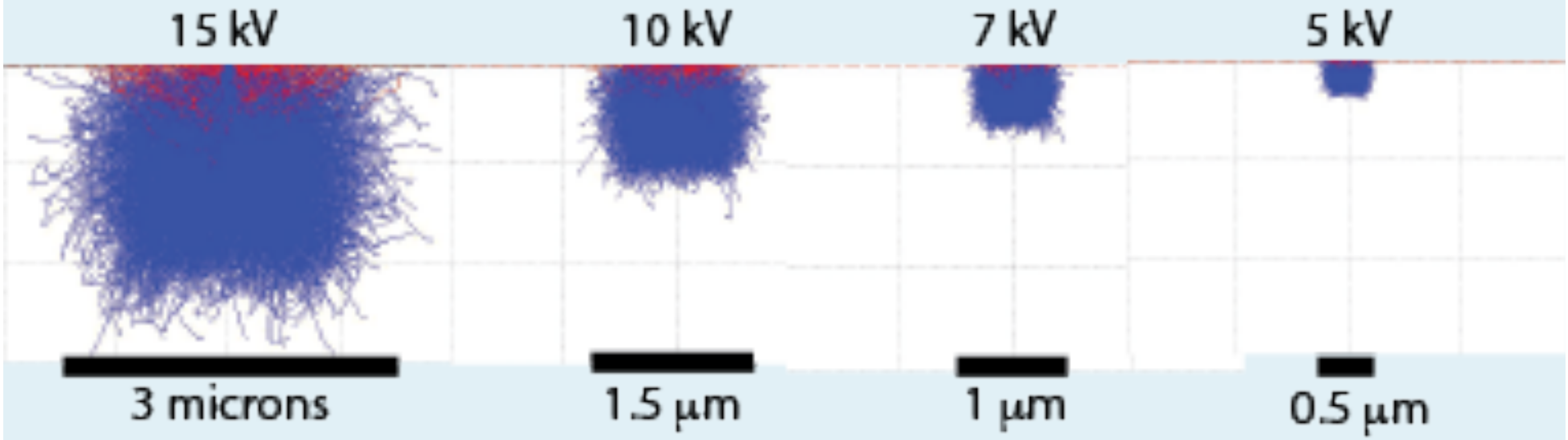
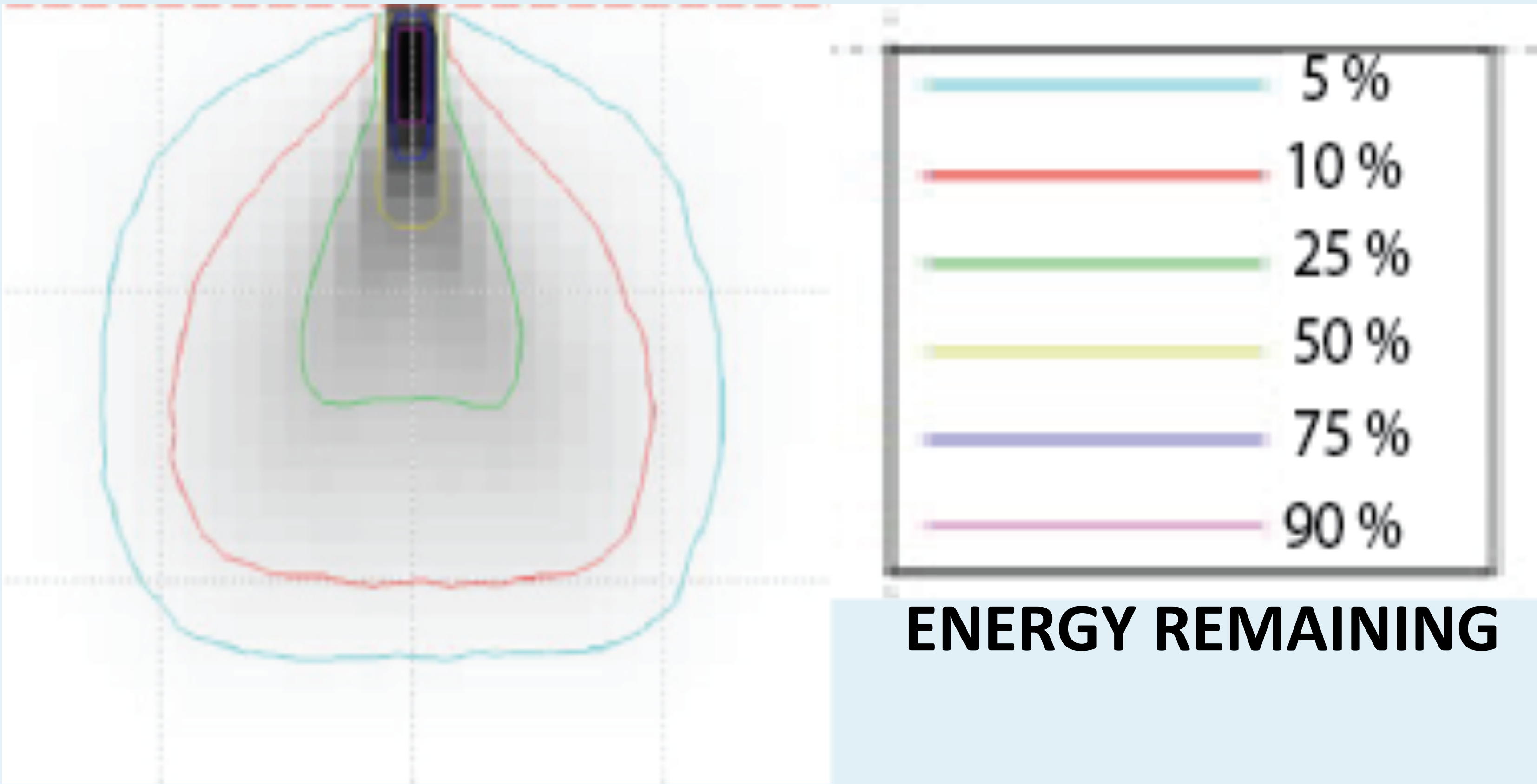


Figure 3. CASINO Monte Carlo simulations of various beam energies scattering in the same silicate glass (NIST K409). Blue shows the traces of the electrons scattered until all energy lost; red shows backscattered electrons. The electron source's beam size for all is the same.

Beam Scattering-Energy Loss



Predicted % of energy remaining of the gun E0 kV by CASINO -- here, 15 kV in olivine, (Mg,Fe)2SiO4.

Part 2:
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)

But all with similar form

Calculations of ANALYTICAL RESOLUTION

Historical Treatments:

- 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**.

Calculations of ANALYTICAL RESOLUTION

Theoretical: Equation of Merlet and Llovet (2012)

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

Simulation: CASINO, PENEPMA

Experimental:

Calculations of ANALYTICAL RESOLUTION

Theoretical: Equation of Merlet and Llovet (2012)

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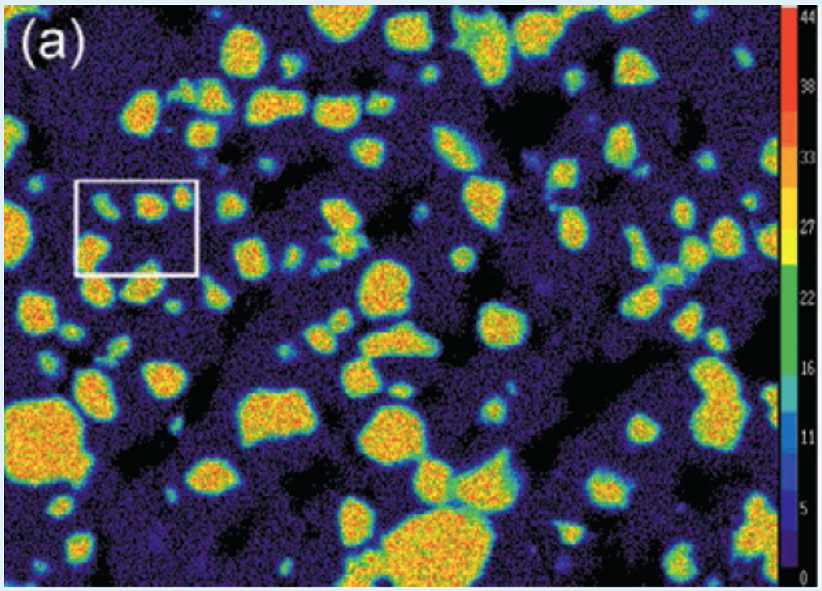
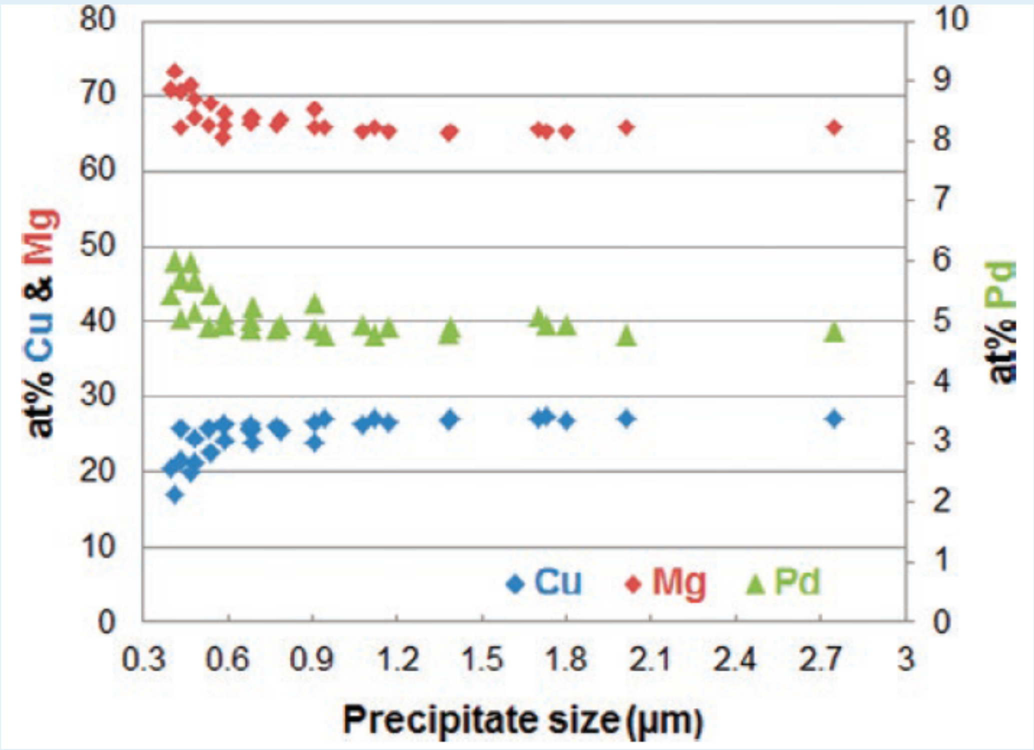
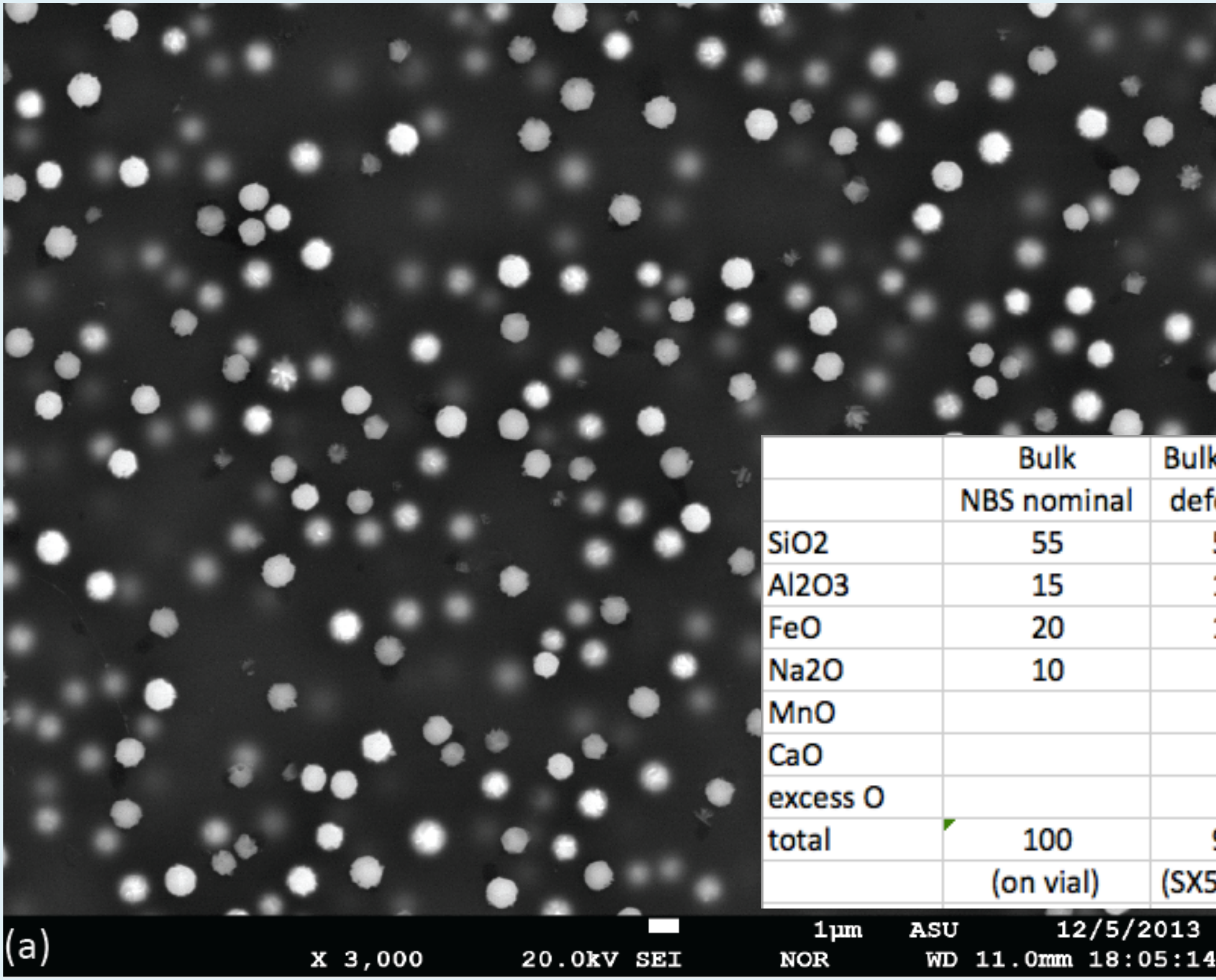


Experimental



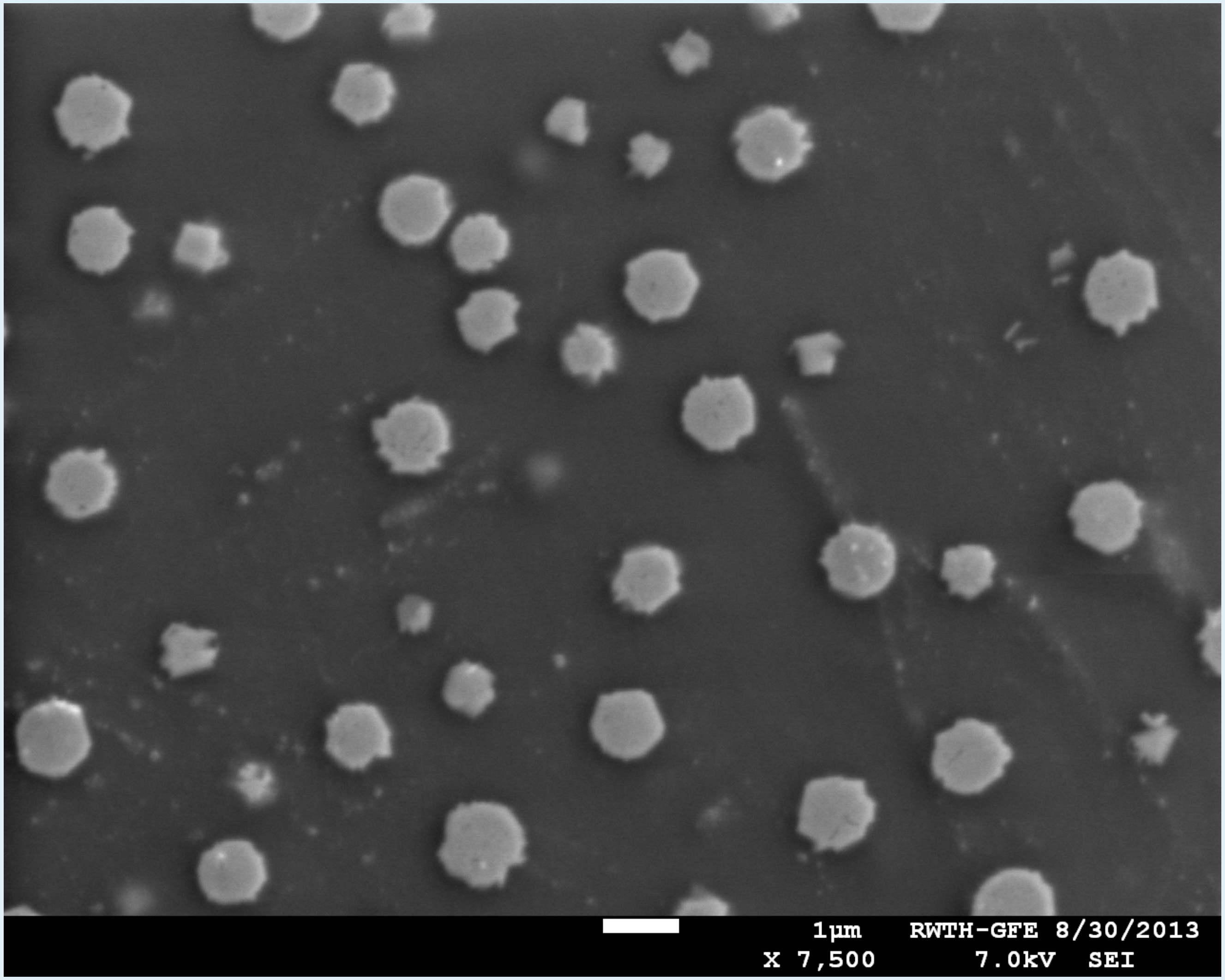
FE EPMA of various sizes of Cu-Mg-Pd phases in a Mg-Pd host (6 keV, 20 nA) from Hombourger & Outrequin, 2013

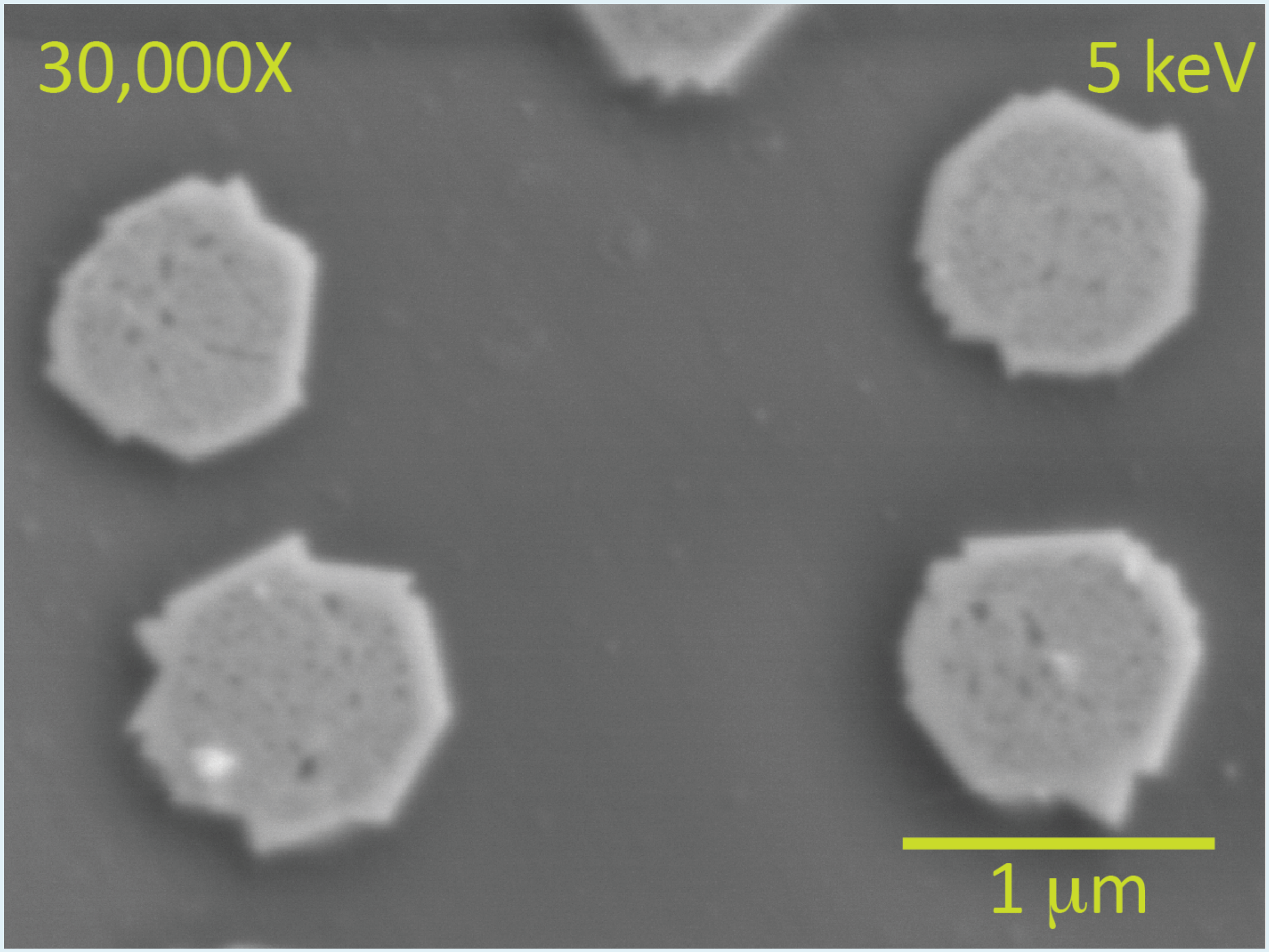
NBS/NIST K409, a 'failed experiment'



	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)

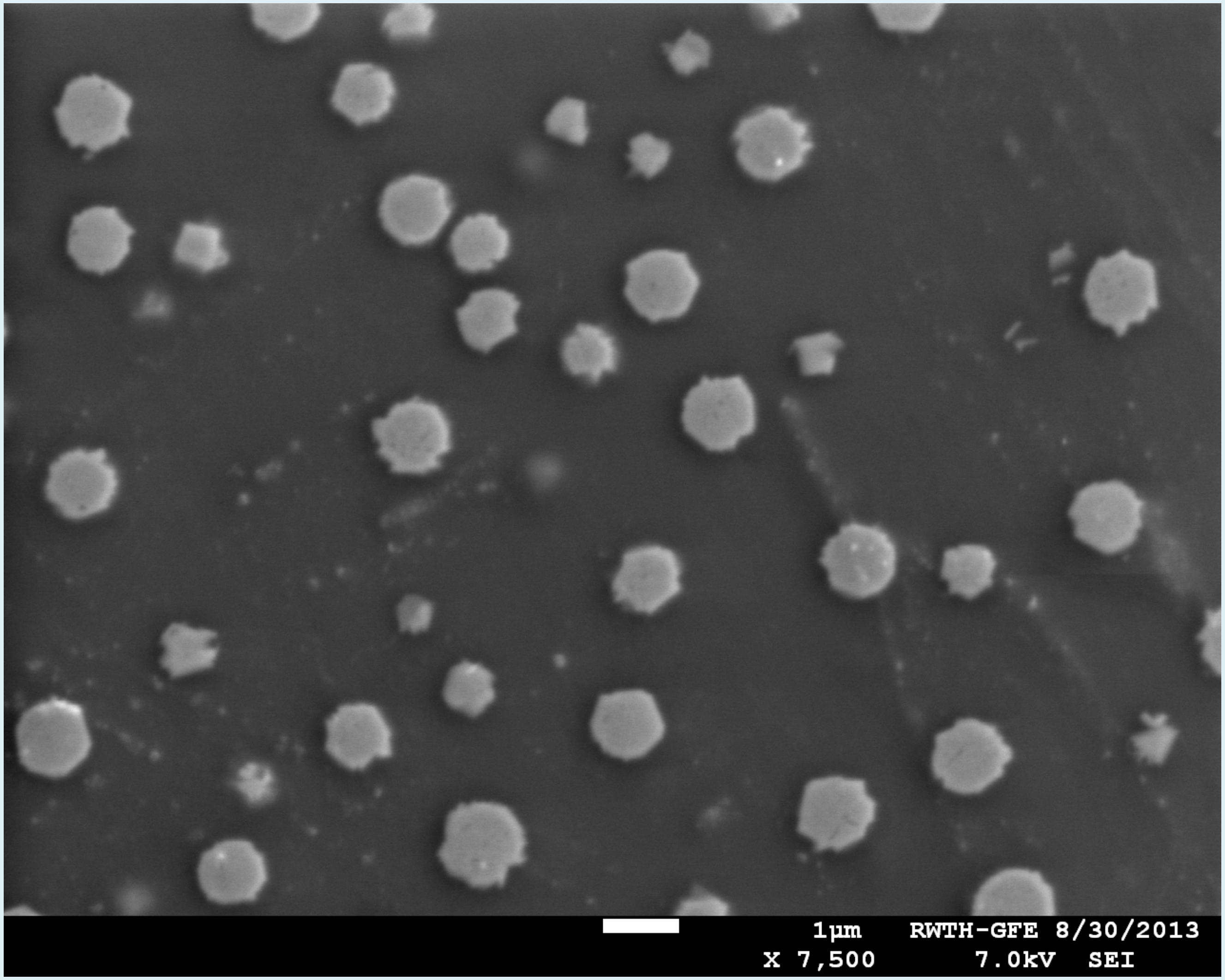
NBS/NIST K409, a ‘failed experiment’



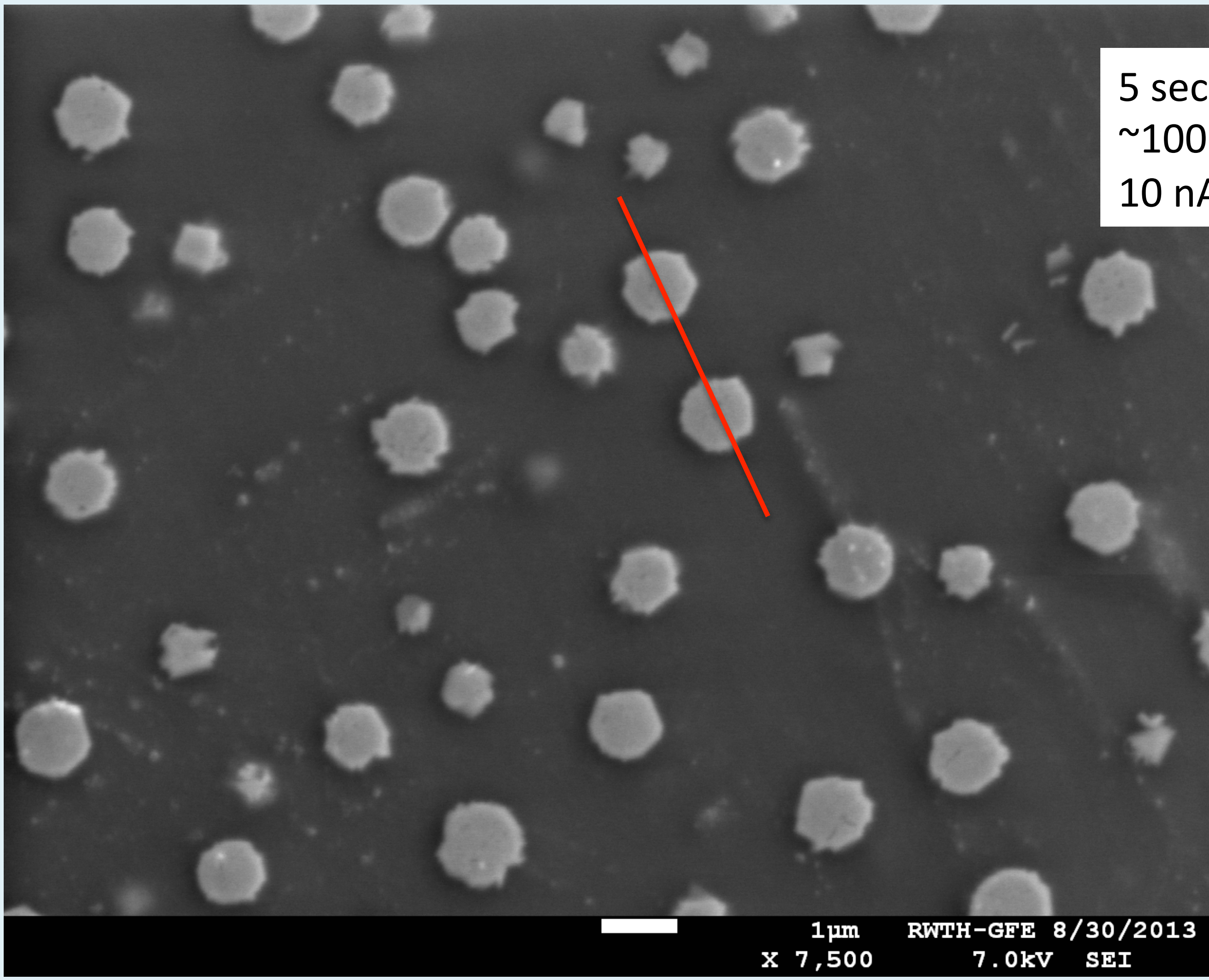


NBS/NIST K409, a 'failed experiment'

K409 …. Line Traverses

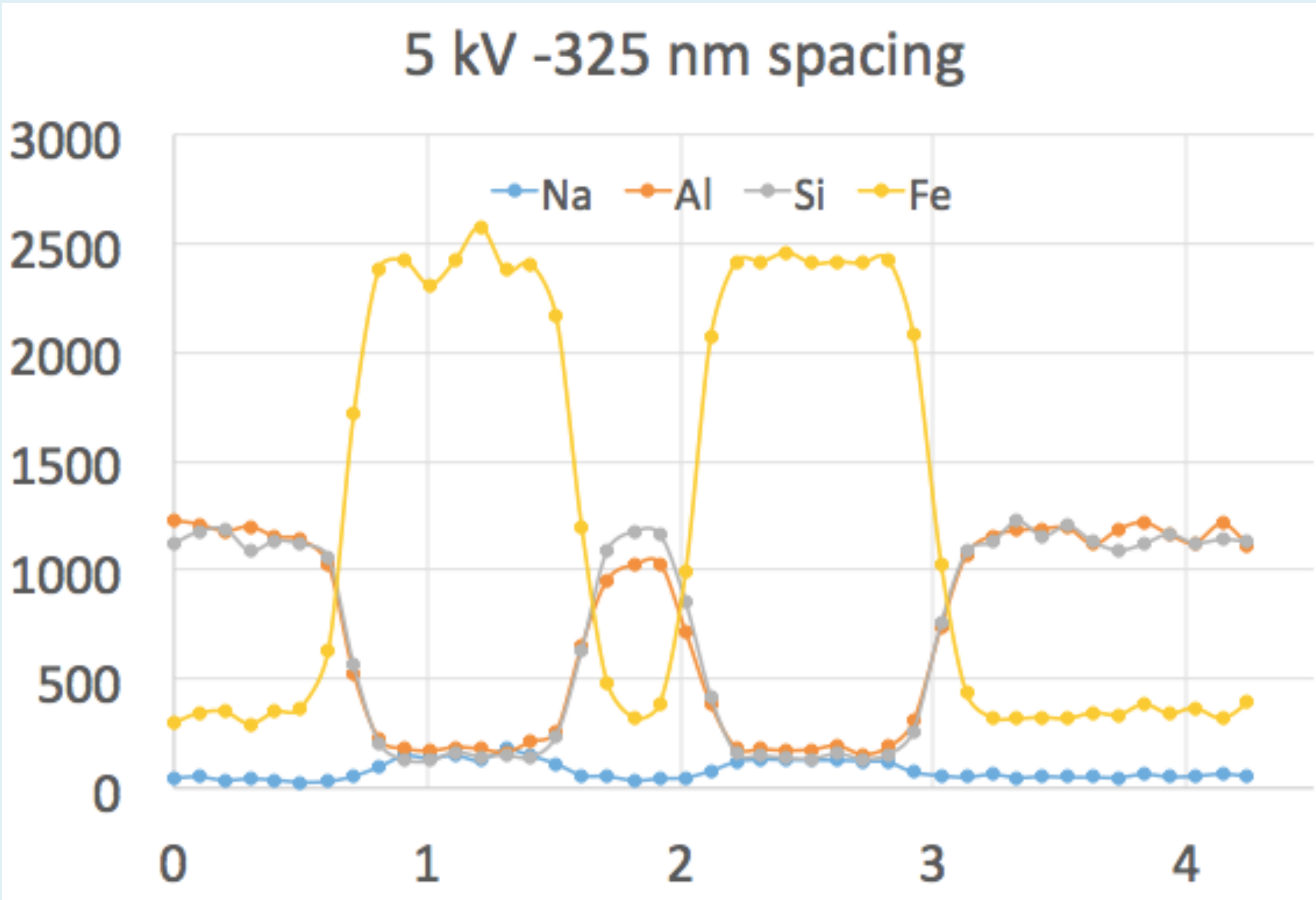


K409 …. Line Traverses – SXFive FE



5 seconds/spot
~100 nm step
10 nA

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



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’?

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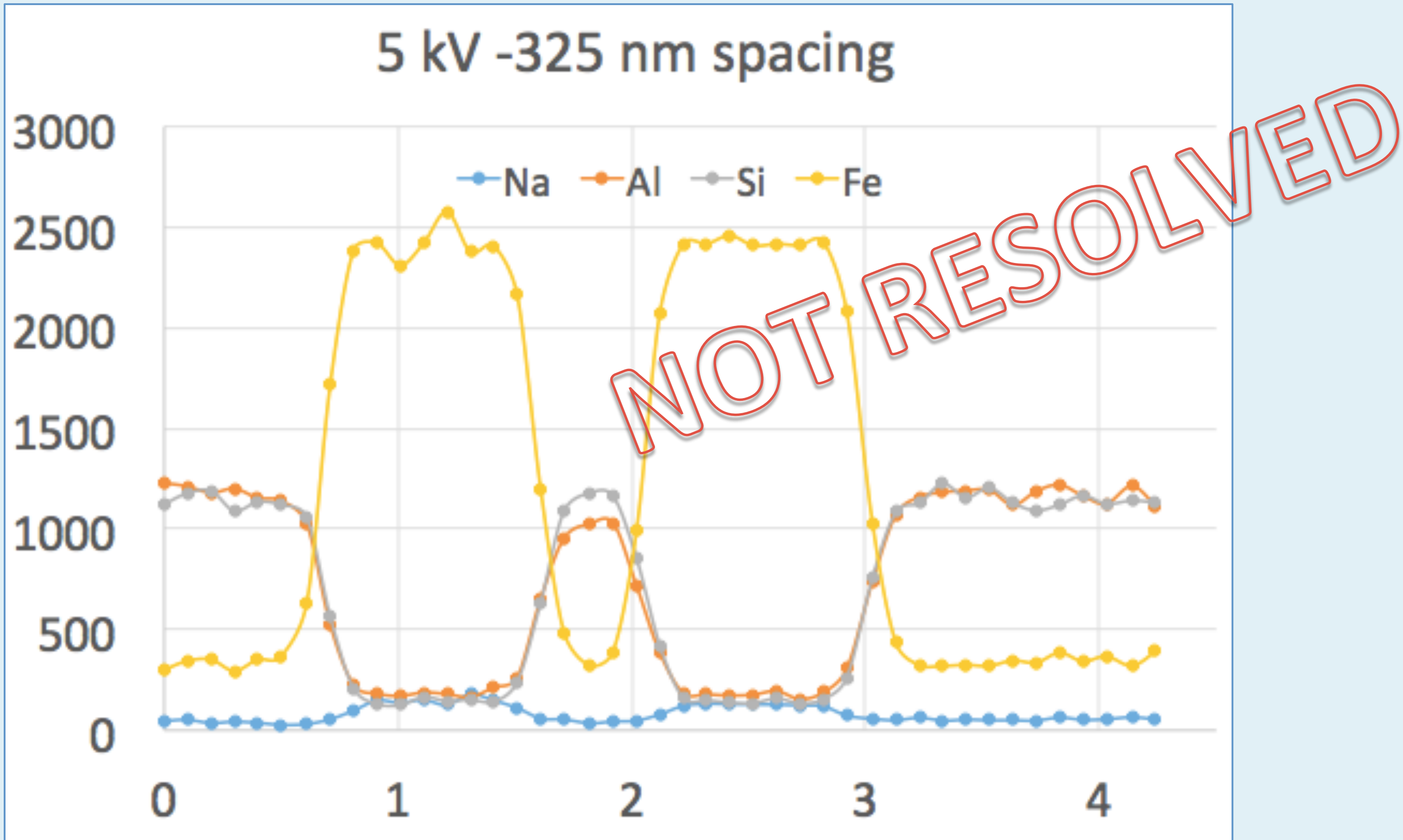
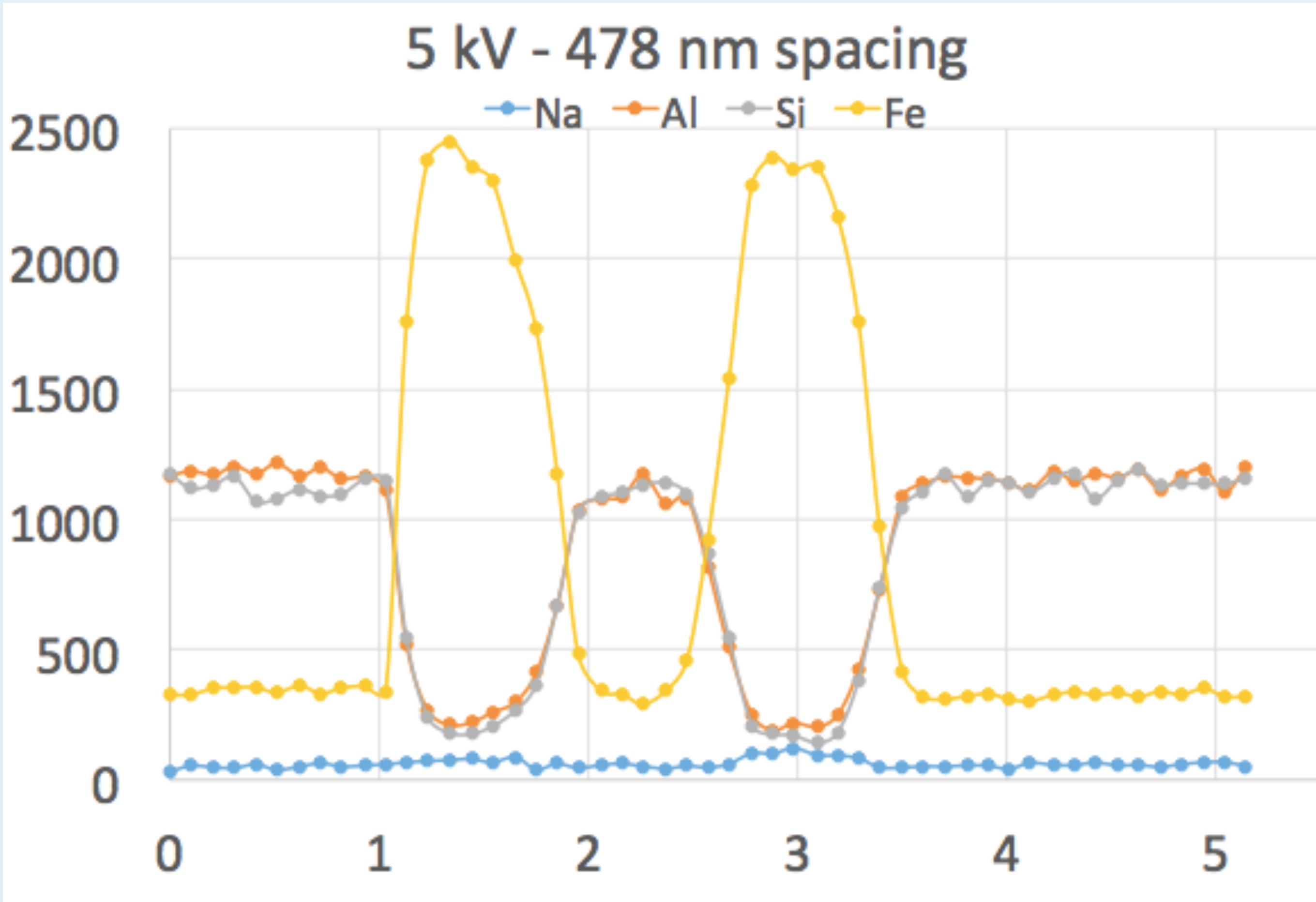
Using K409 to model low keV X-ray spatial resolution



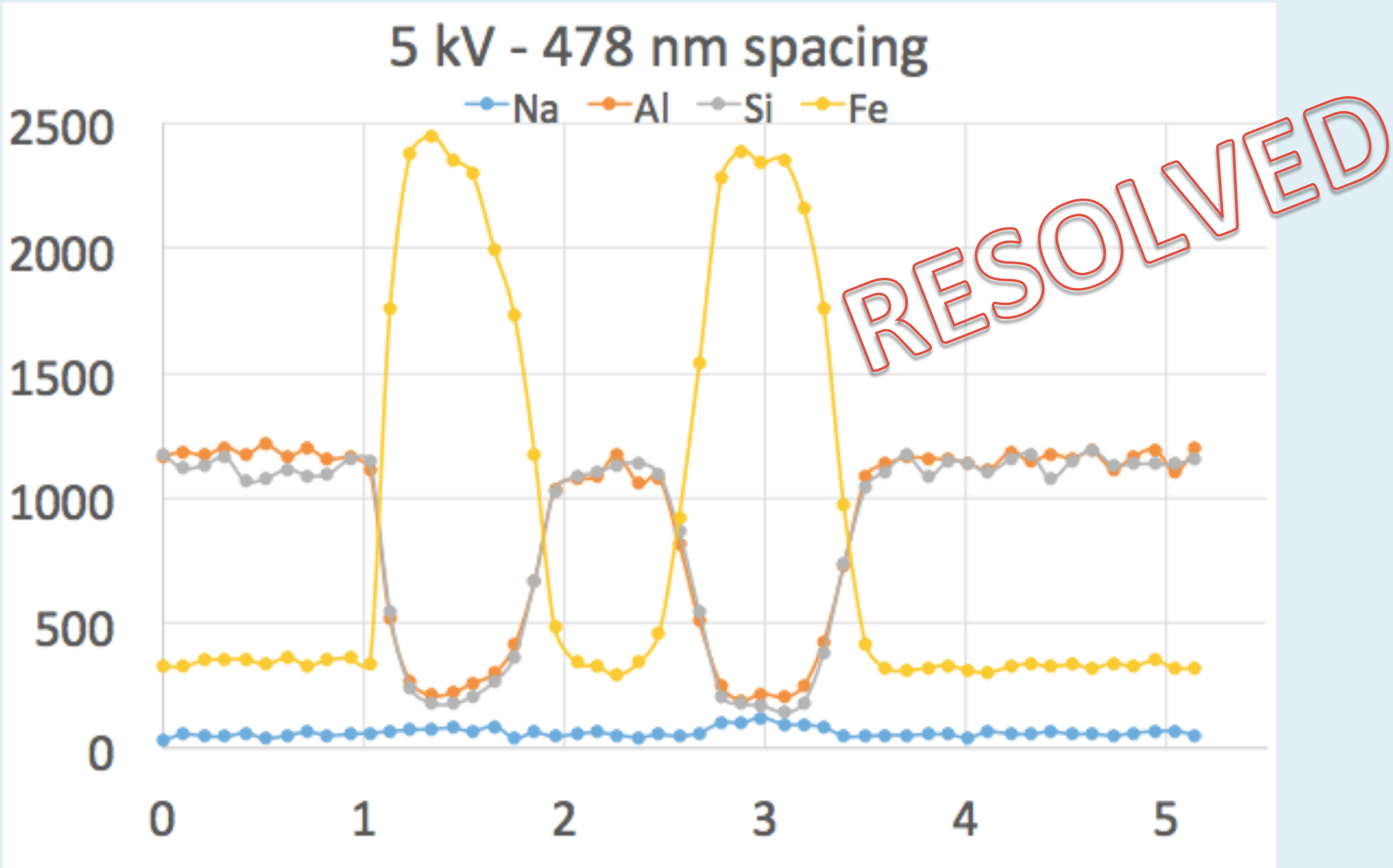
Si 1.03
Al 0.87
Fe 1.03

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’?



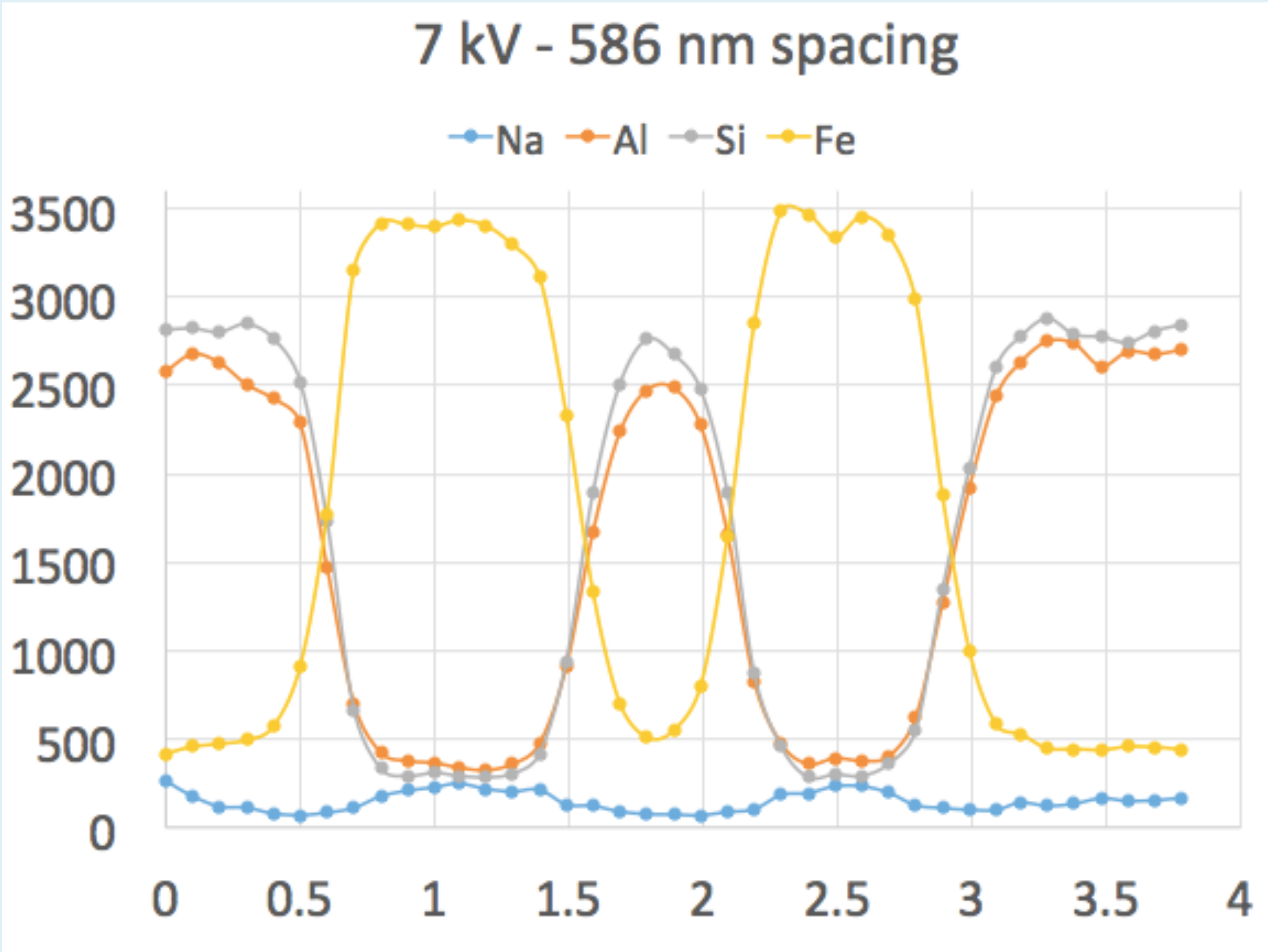
5 kV - 478 nm spacing
Na
Al
Si
Fe
2500
2000
1500
1000
500
0
0
1
2
3
4
5

Si 0.99
Al 0.94
Fe 0.98

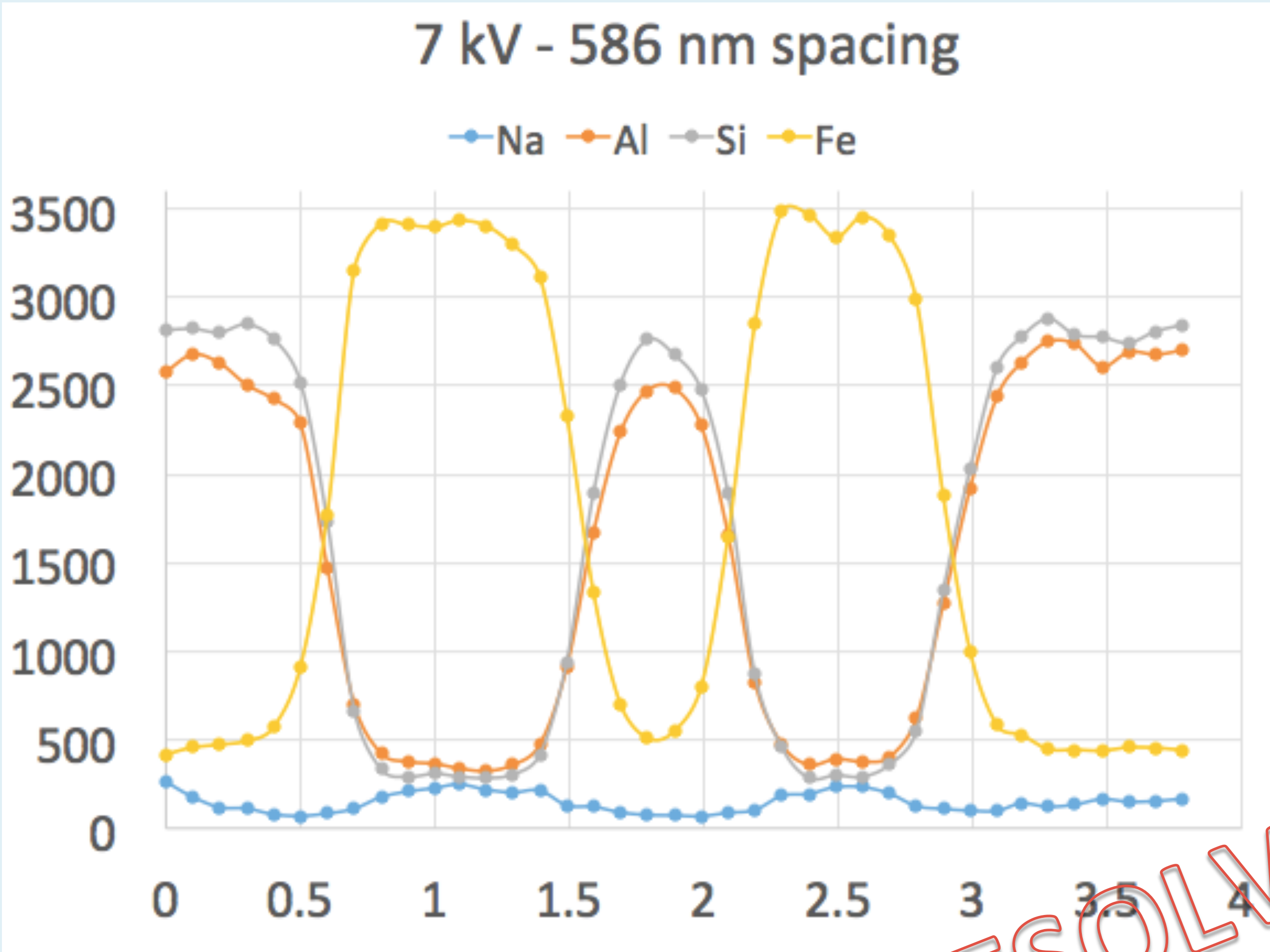


5 kV	X-ray Intensity Relative to Far Away			Plateau Points	
spacing nm	Al Ka	Si Ka	Fe La	Al, Si	Fe
300	0.81	0.91	1.20	2, 2	2
325	0.87	1.03	0.95	2, 2	0
360	0.97	0.97	1.03	2, 2	2
416	0.81	0.87	0.91	3, 3	0
478	0.94	0.99	0.98	4 , 4	4
490	1.01	0.96	0.99	3, 5	3
528	0.95	1.00	1.00	4, 4	4

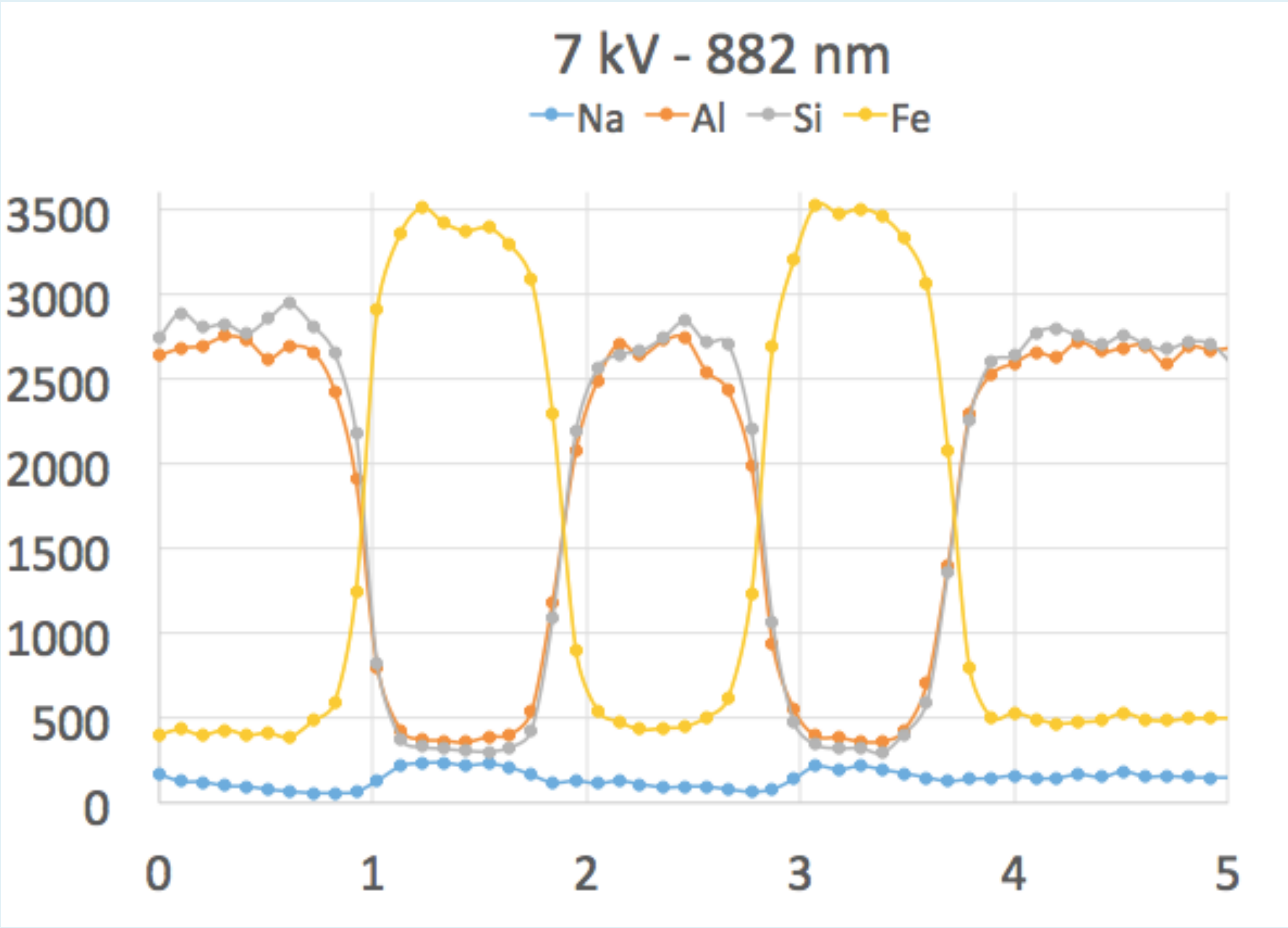
→ 450-500 nm spatial resolution @ 5 kV for Al Ka, Si Ka and Fe La in K409 glass


7 kV - 586 nm spacing
Na
Al
Si
Fe
3500
3000
2500
2000
1500
1000
500
0
0
0.5
1
1.5
2
2.5
3
3.5
4

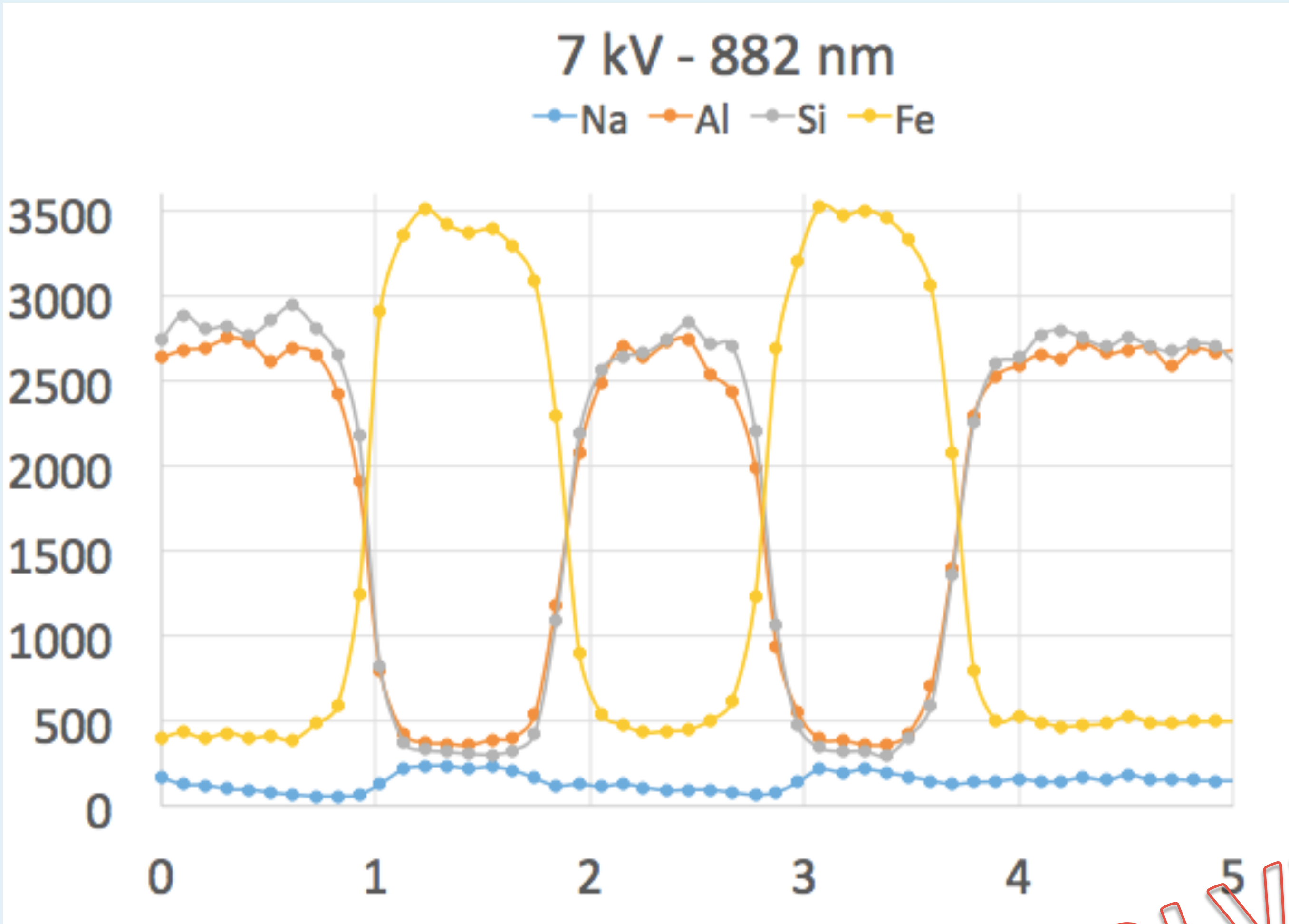
Si 0.97
Al 0.93
Fe 1.18



NOT RESOLVED


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

Si 1.01
Al 0.99
Fe 0.96



RESOLVED

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

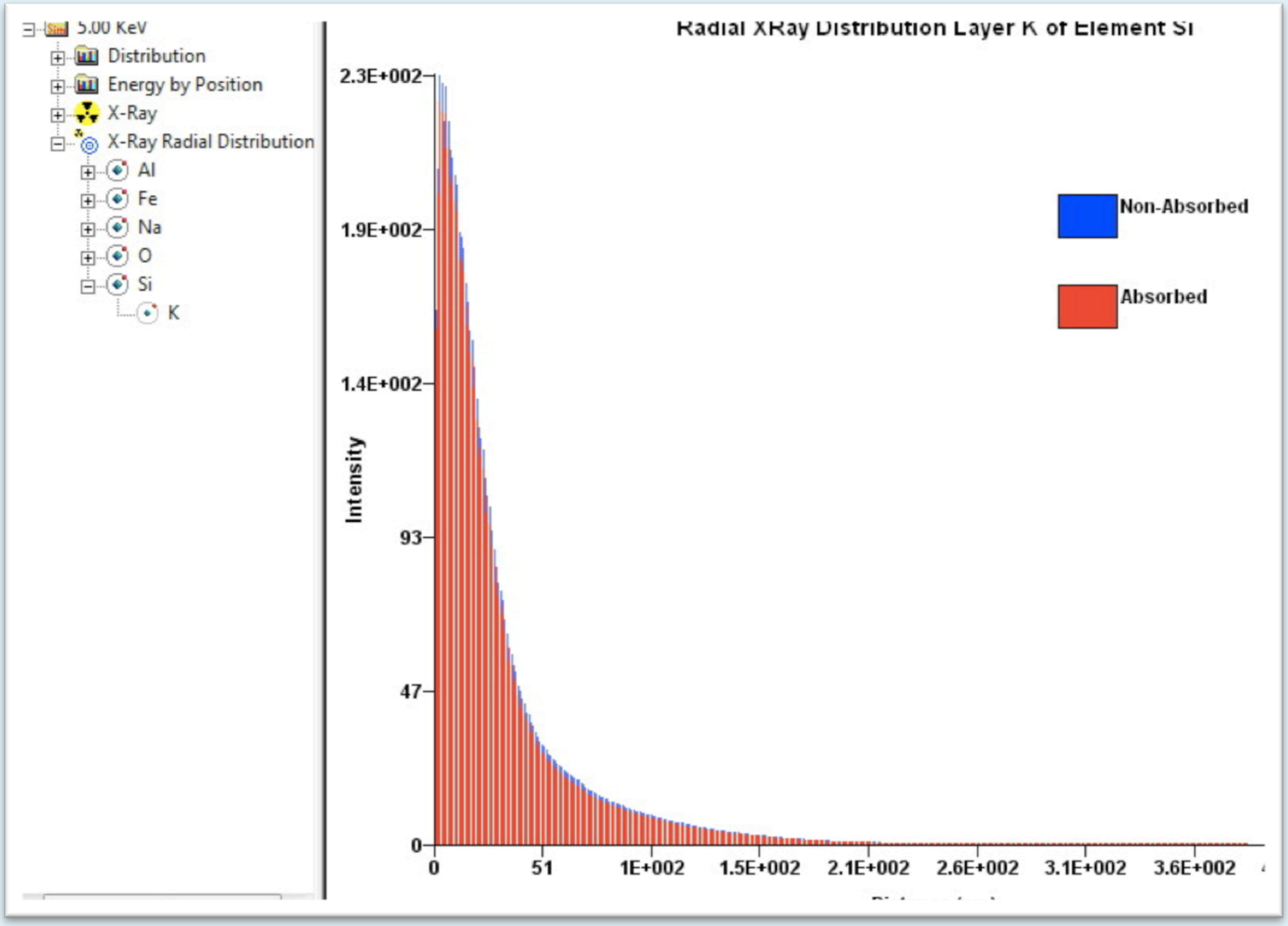
Question of statistics…

- 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	

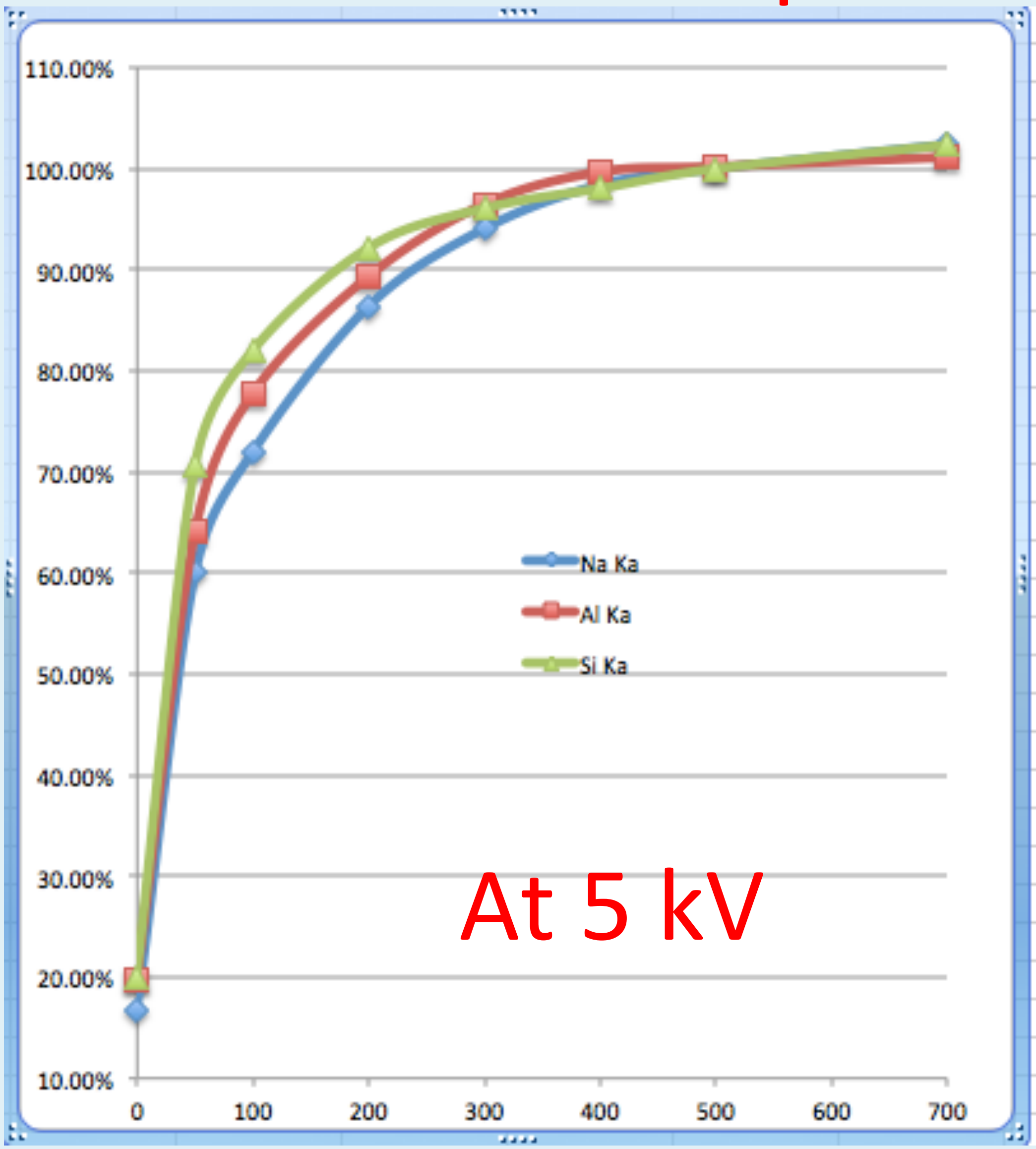
- Future: to improve statistics -- measure 3x3 grids between Fe-oxides / 3 parallel lines

CASINO Monte Carlo Simulation in K409 Experiments



At 5 kV

Penepma Monte Carlo Simulation of K409 Experiments



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
Anderson&Hasler '66	322	311	352
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

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

10 kV X-ray Ranges	Al Ka	Si Ka	Fe La	Fe Ka
Castaing 1952	1265	1205	1351	601
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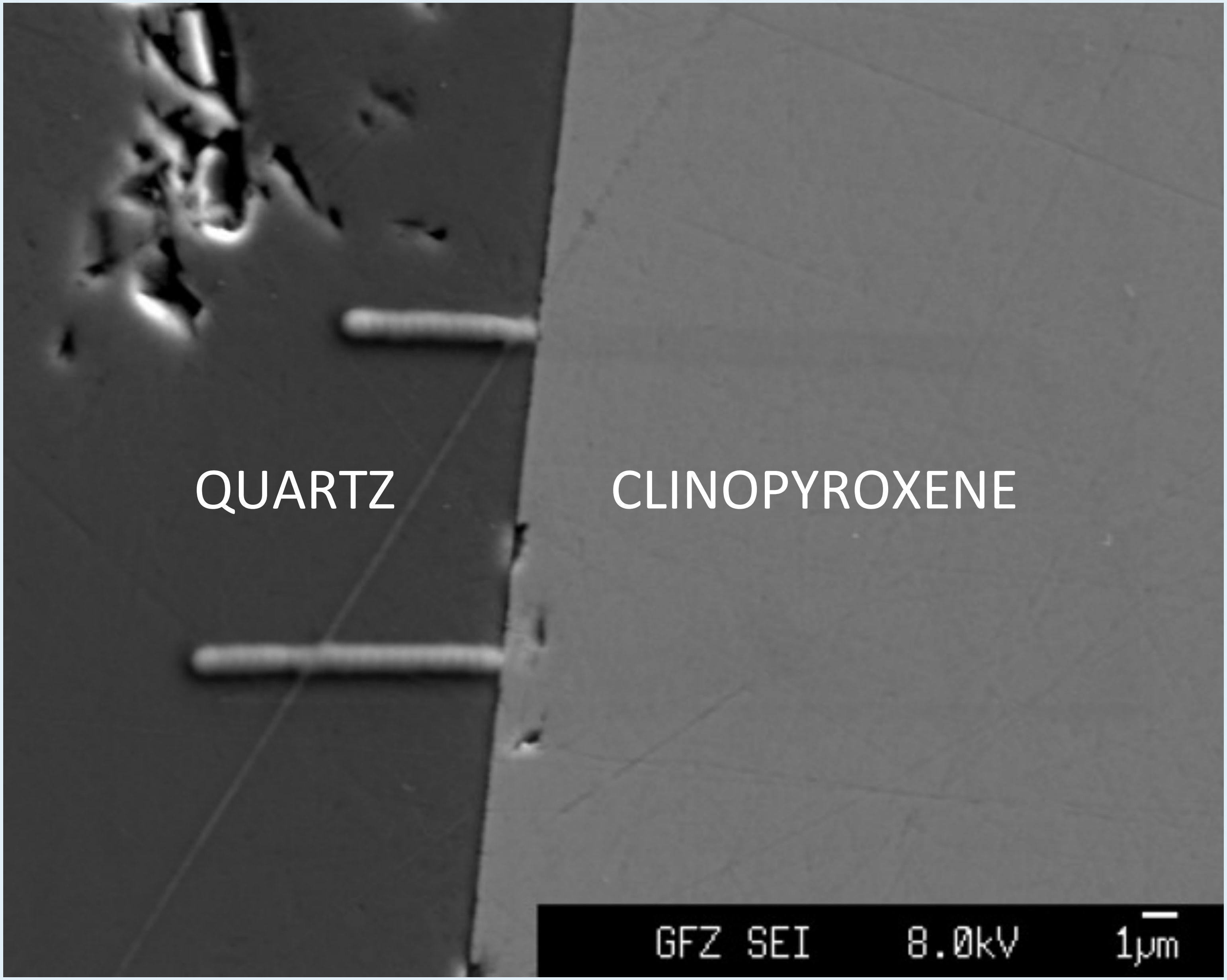
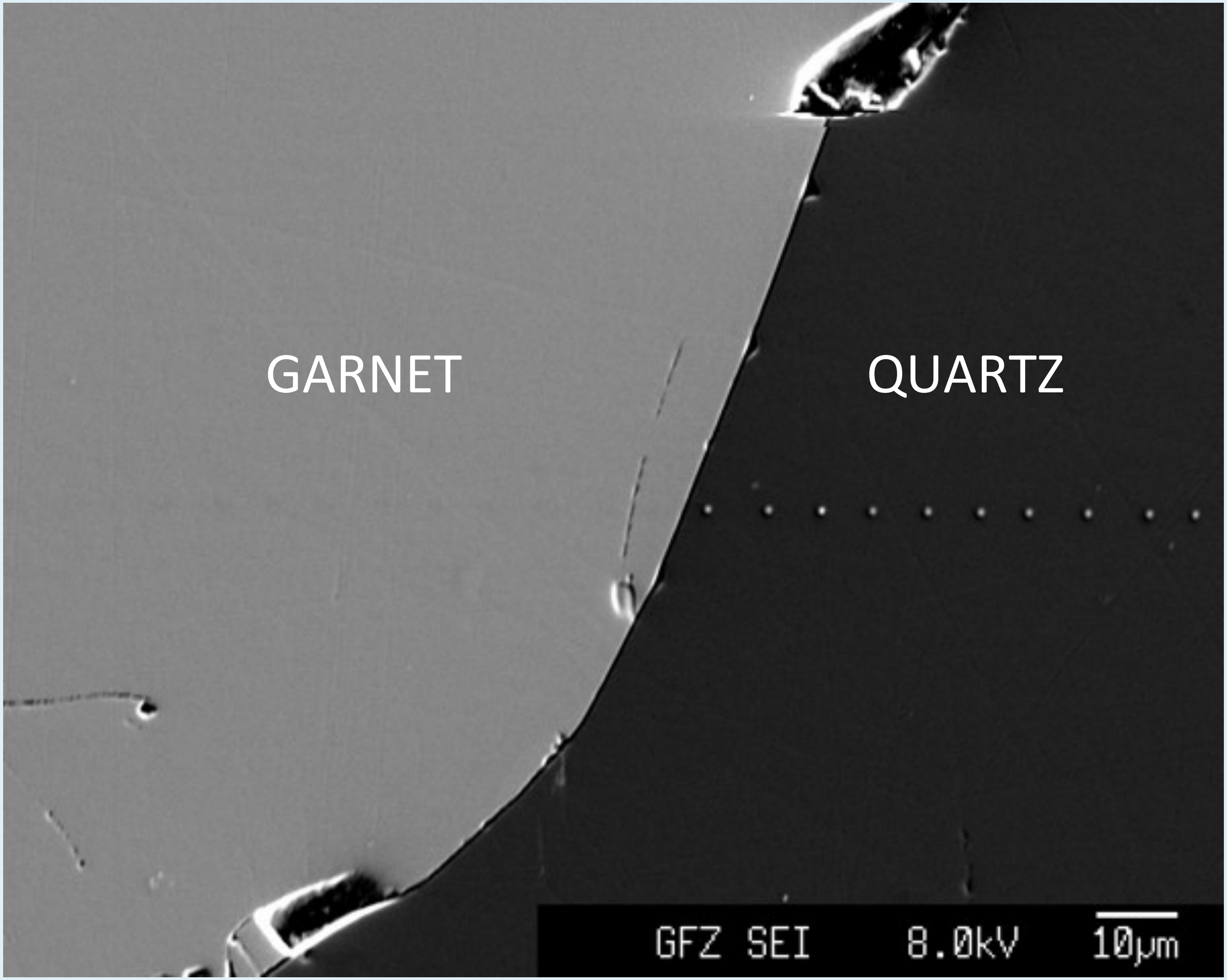
Part 3: Other considerations

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



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):

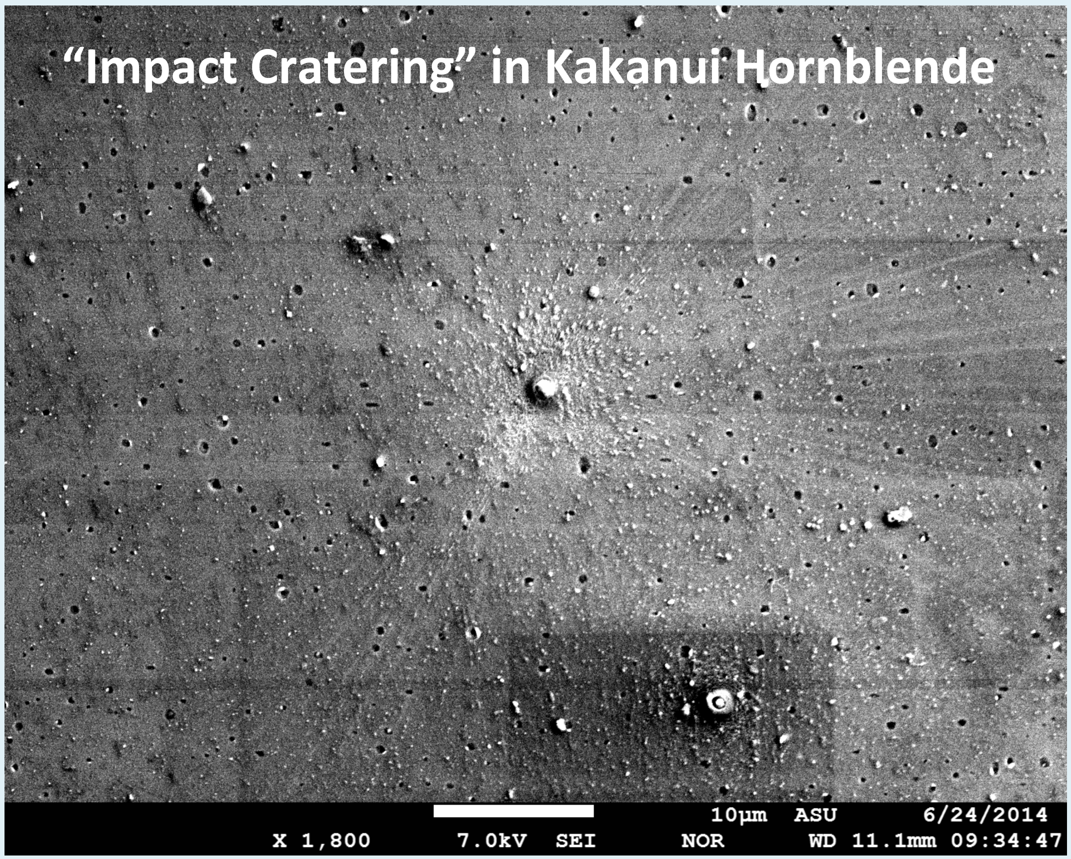
> "For routine quantitative analyses under conventional conditions, the beam diameter can be defocused to a few microns to reduce damage of the sample or the carbon coating."

→ 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

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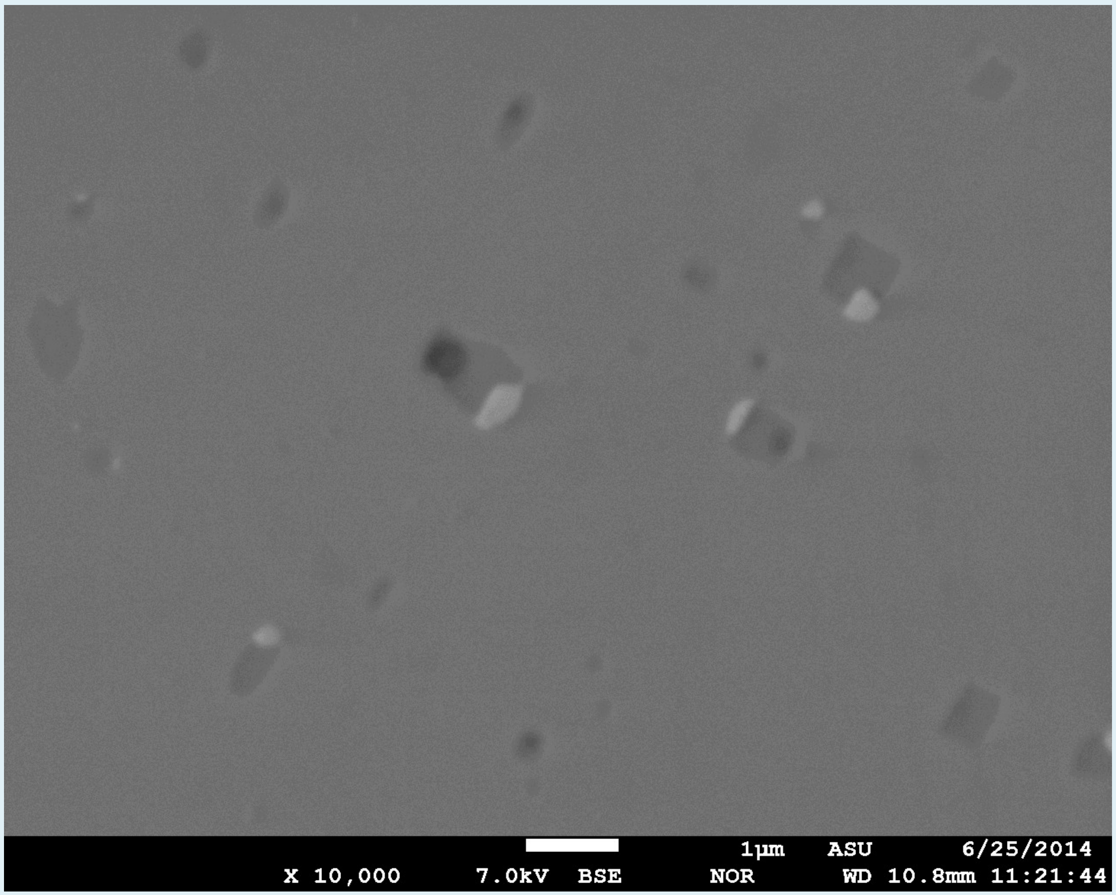
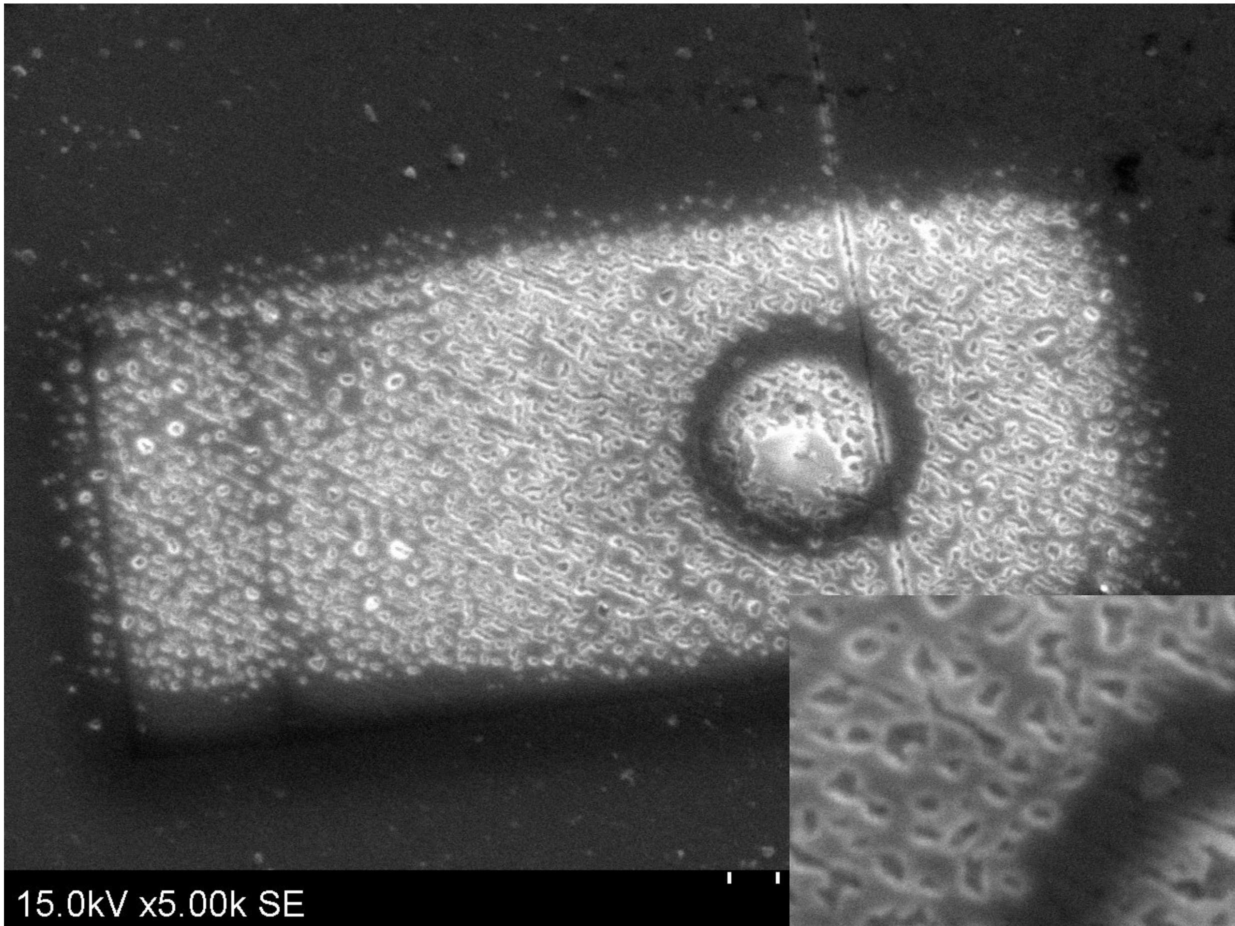
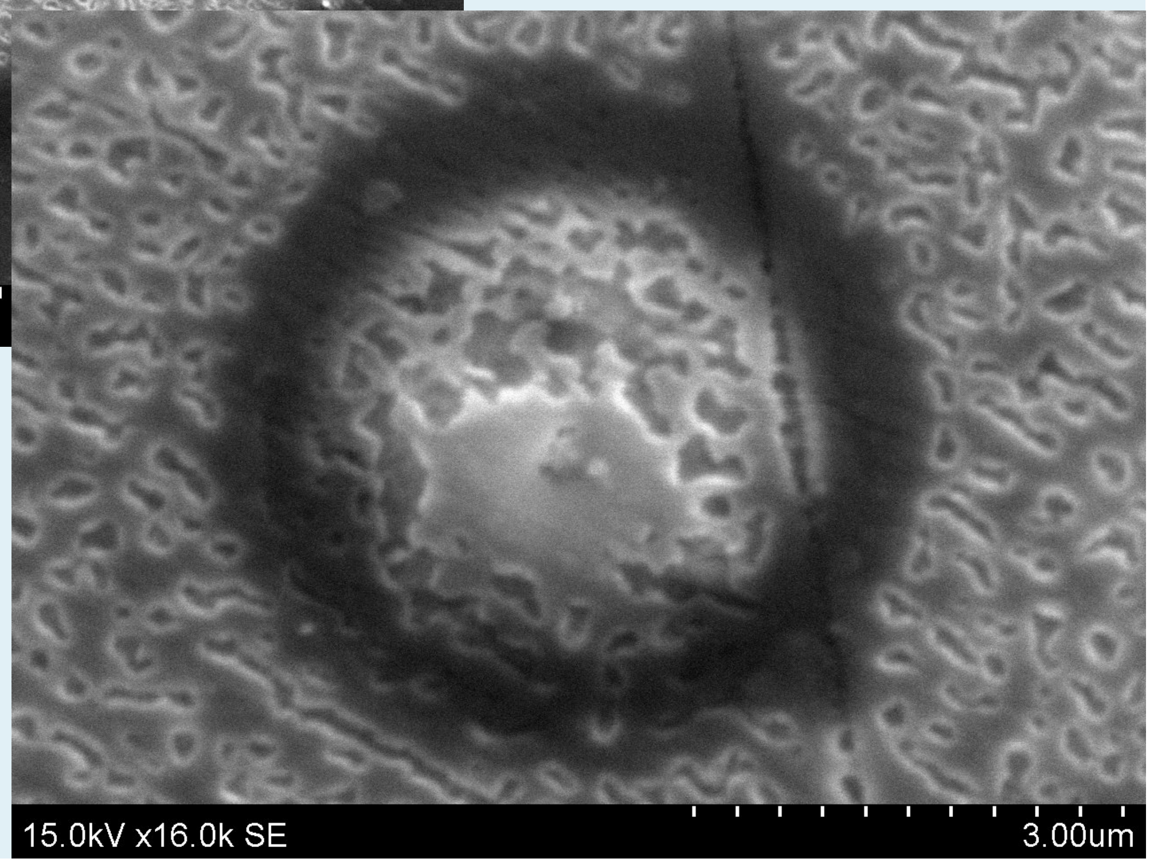


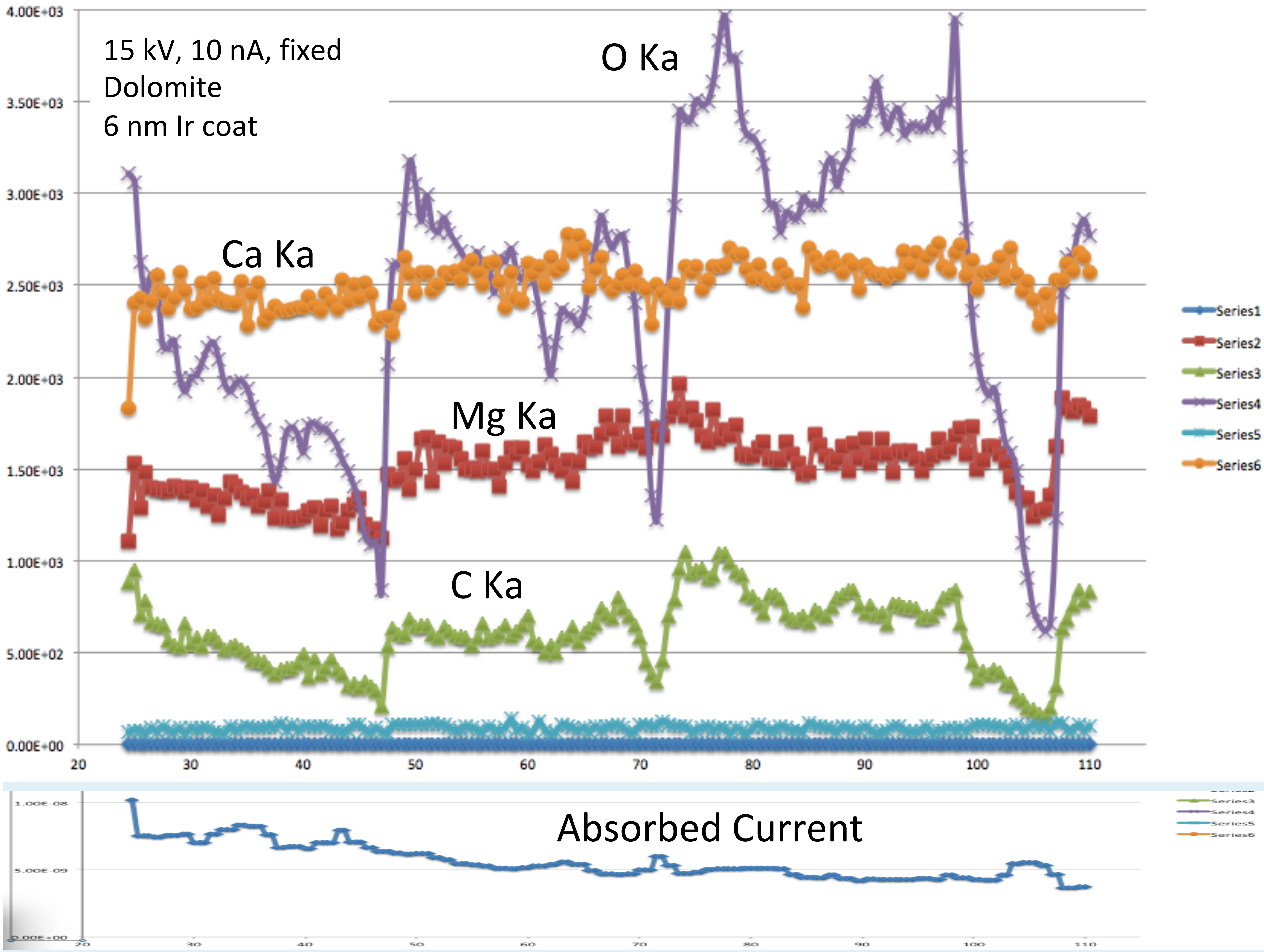
ASU 8530 Field Emission 7 keV 10 nA



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
Absorbed Current
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
1.00E-08
5.00E-09
0.00E+00

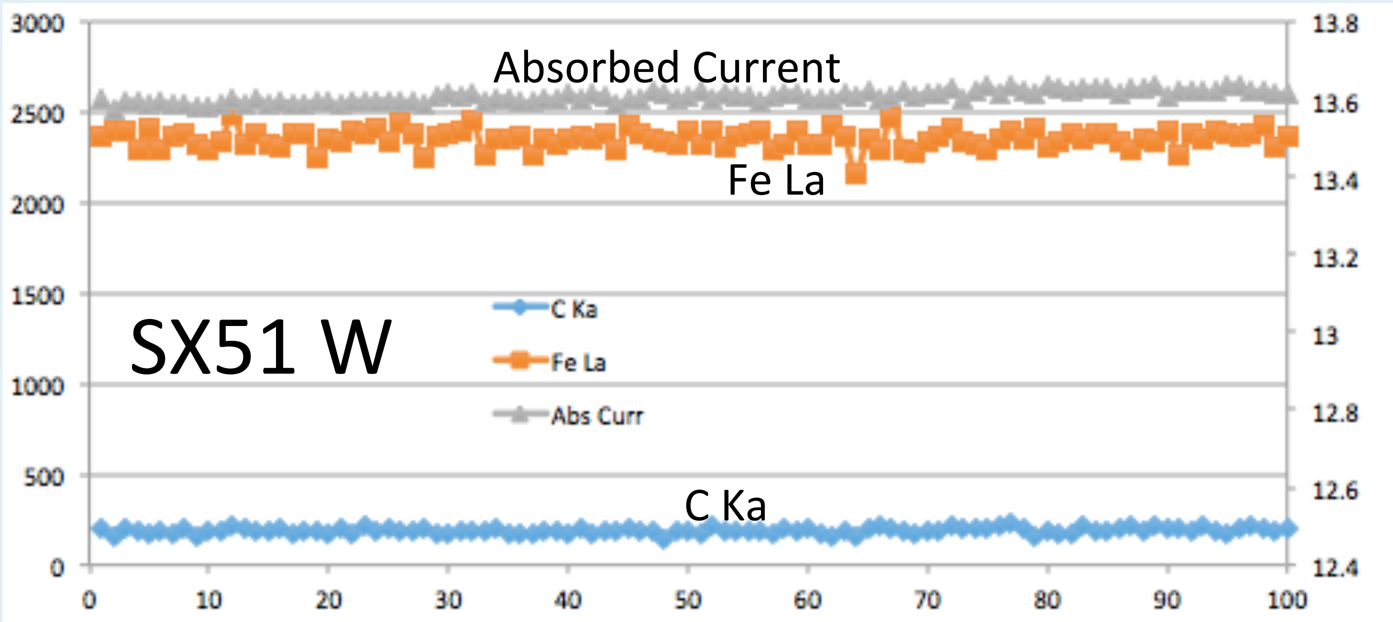
Does more intense FE beam cause different behaviors in materials?

- 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



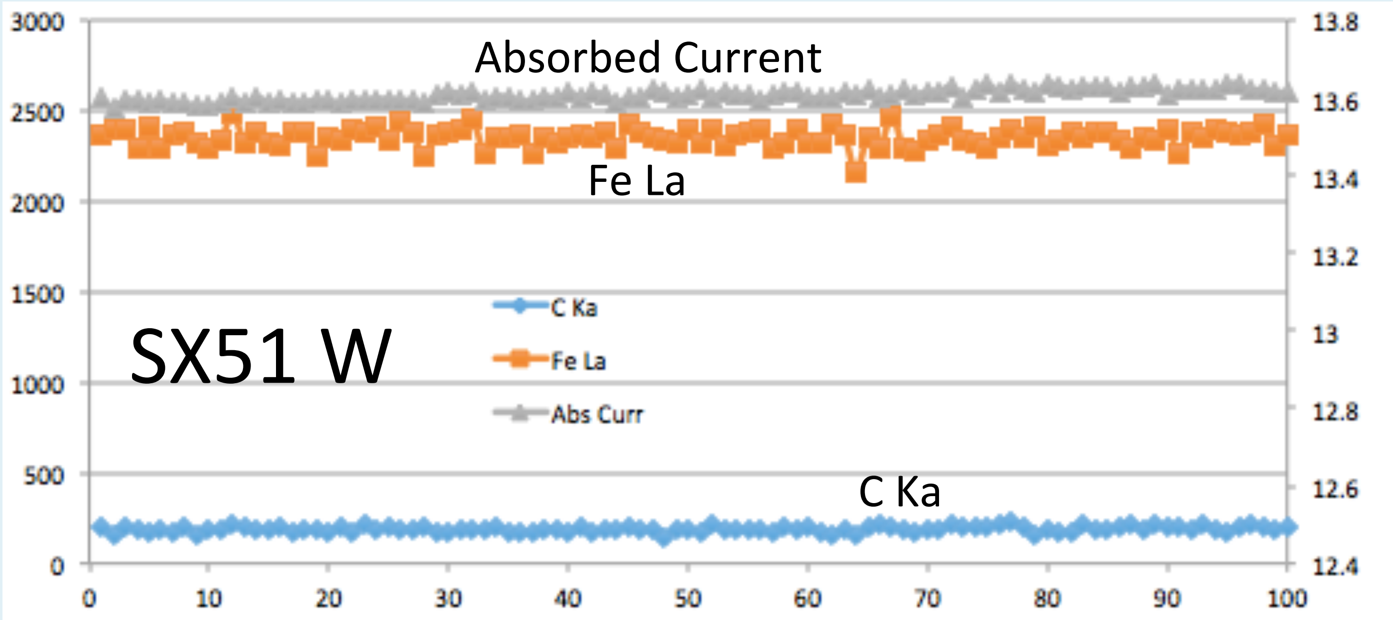
Absorbed Current

100 counting intervals ~ 250 seconds

Fe Metal: SXFive FE vs SX51 (W)

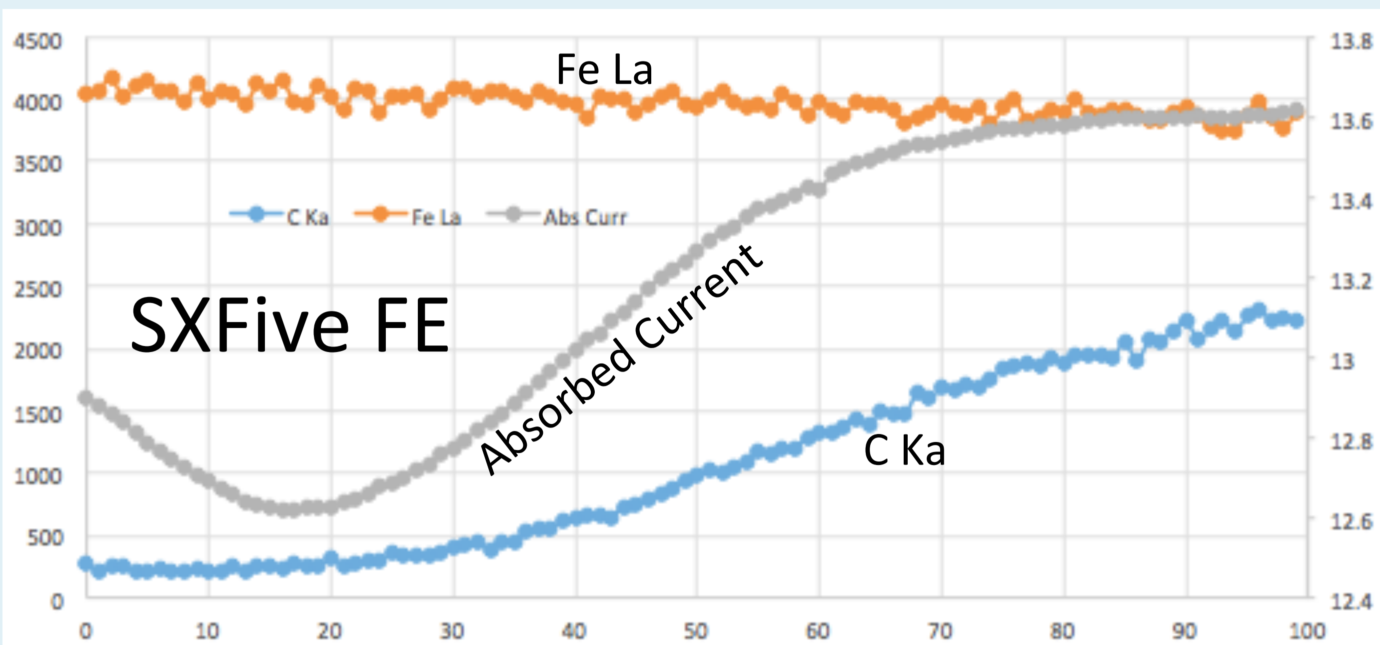
7 kV, 20 nA, LN anti-contamination

Fe La Si Ka counts



Absorbed Current

Fe La Si Ka counts

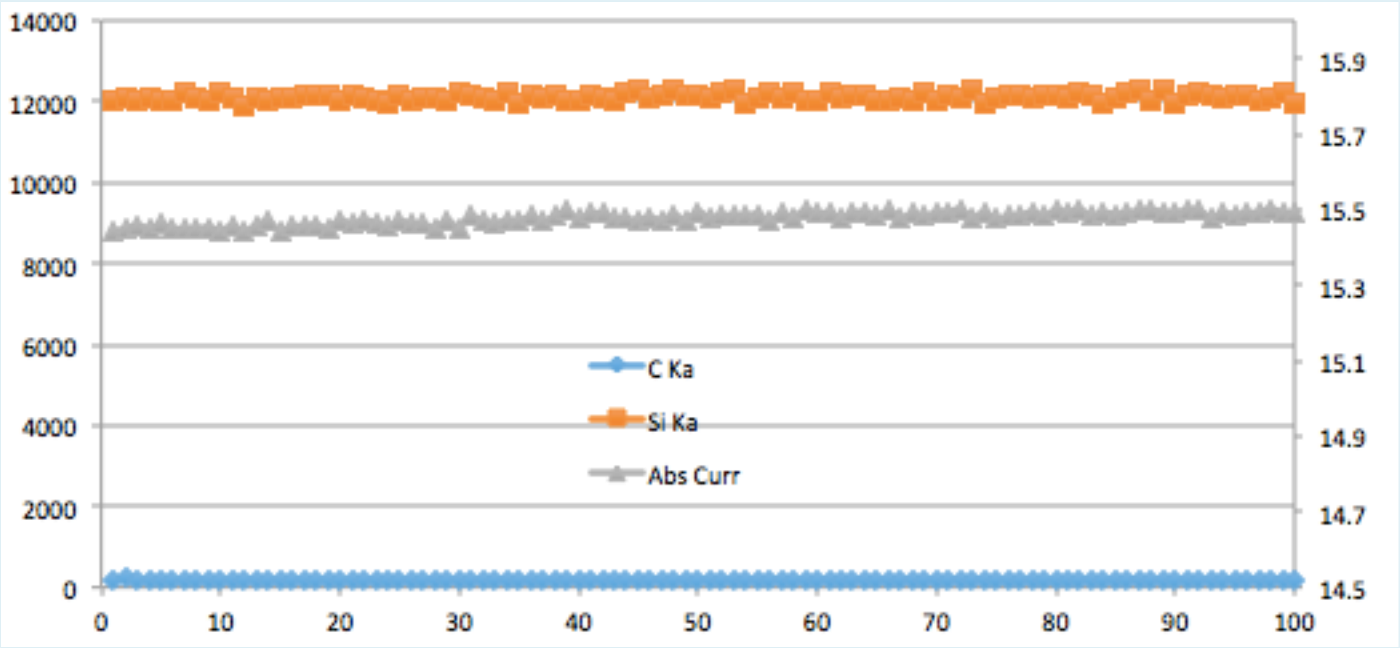


Absorbed Current

100 counting intervals ~ 250 seconds

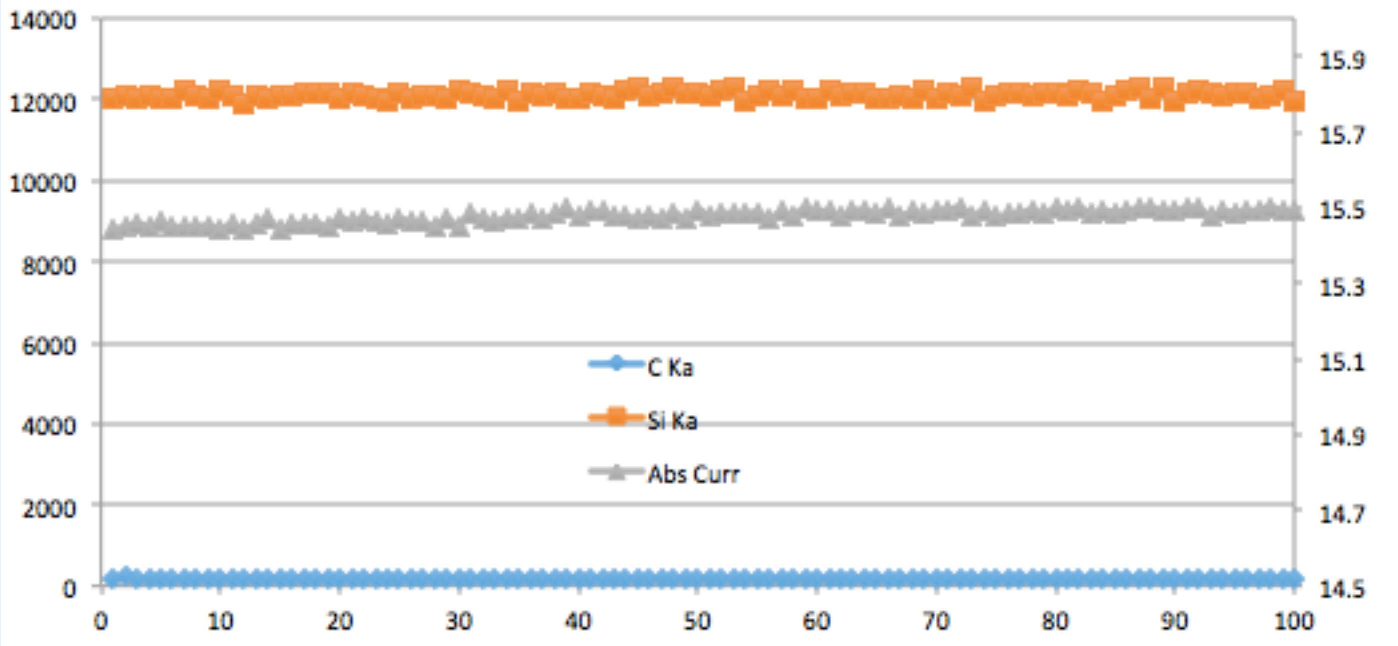
Si Metal: SX51 (W)

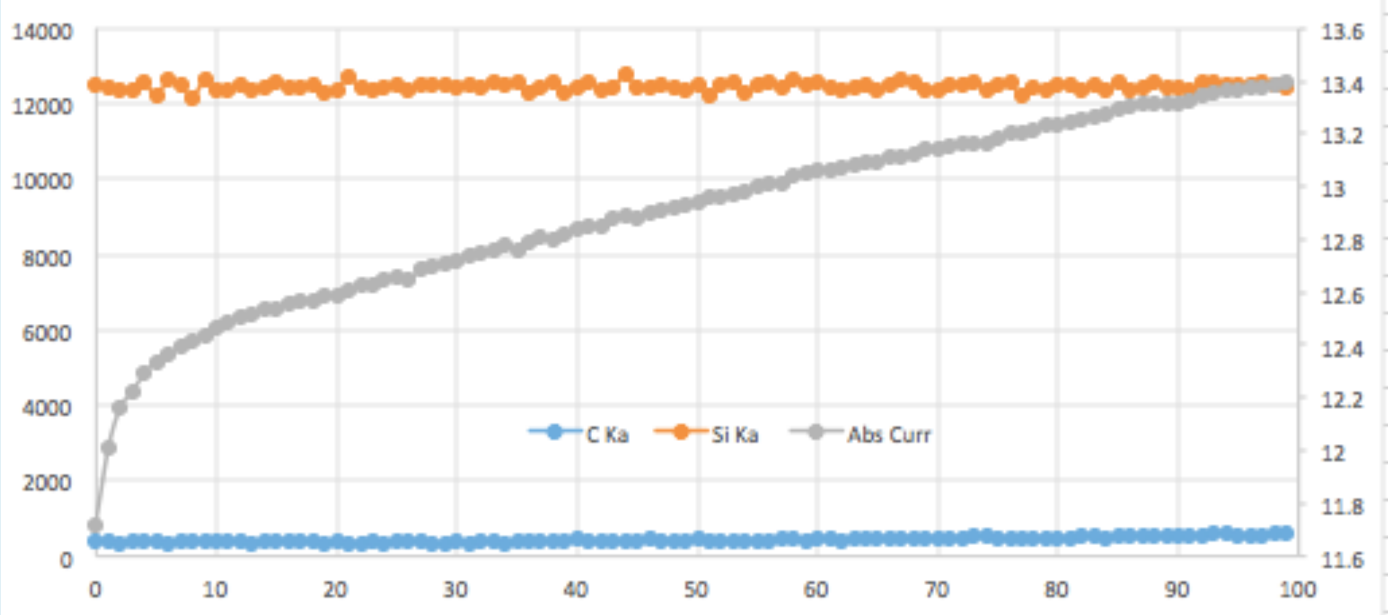
7 kV, 20 nA,
LN anti-contamination

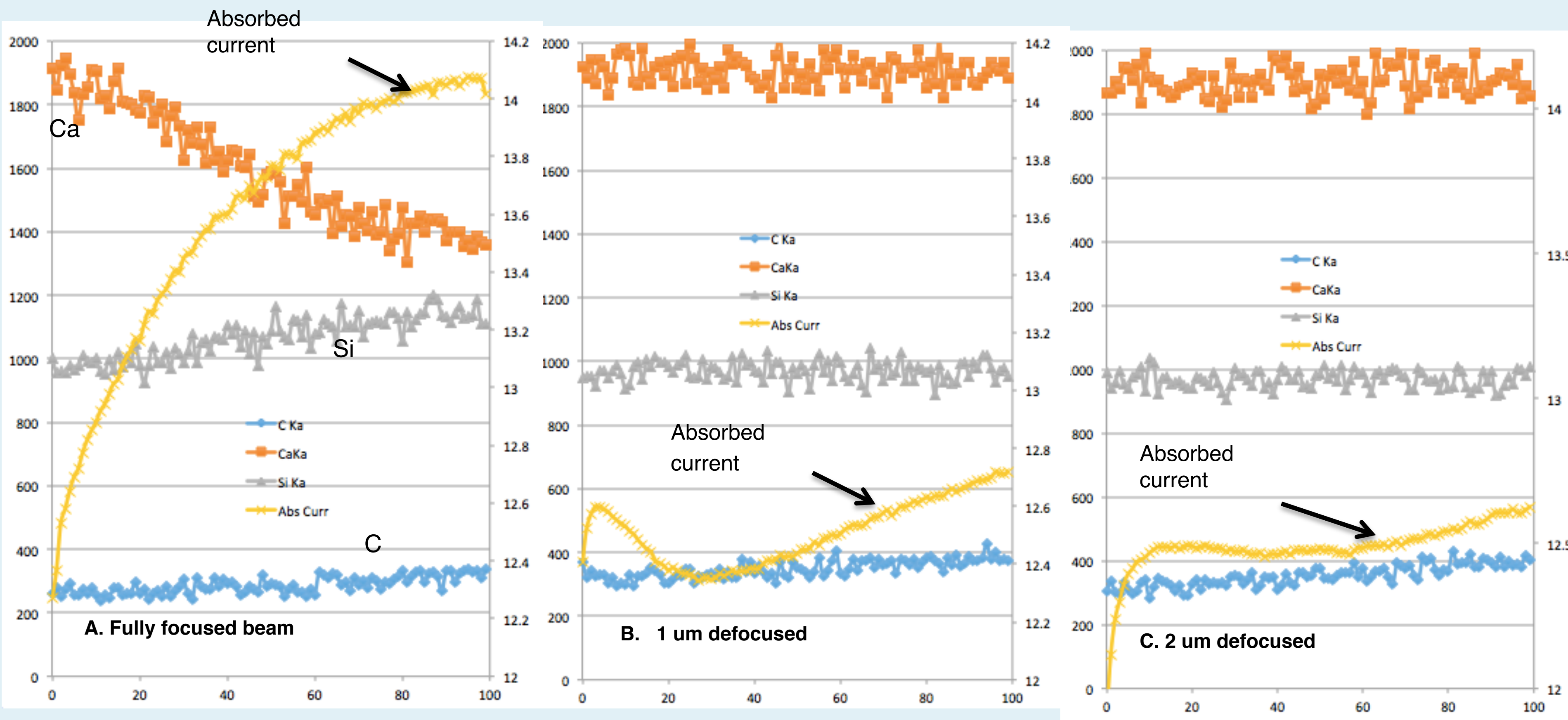


Si Metal: SXFive FE vs SX51 (W)

7 kV, 20 nA,
LN anti-contamination



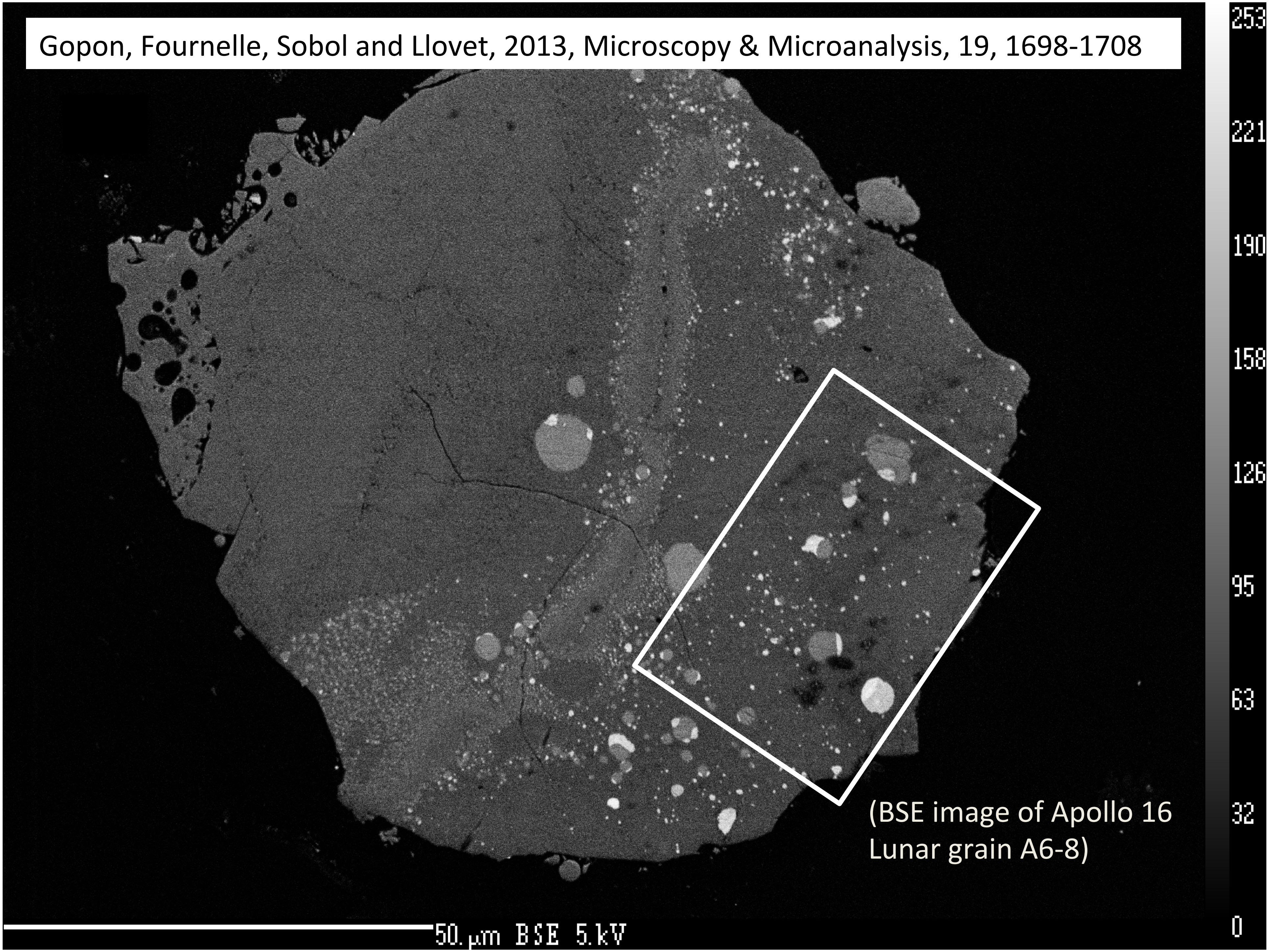




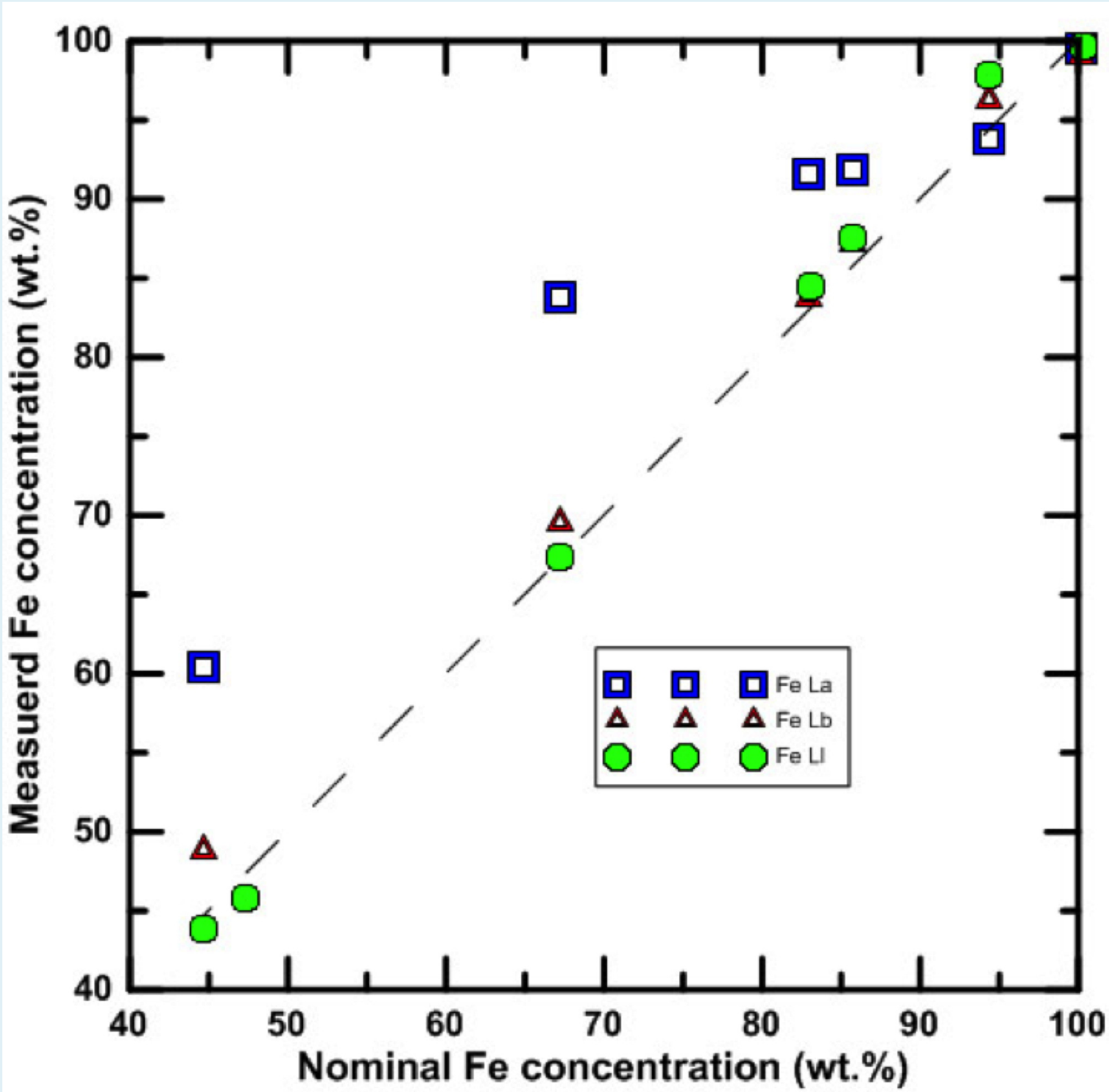
7 kV SXFive FE experiments on Wollastonite, 20 nA, from fully focused to 1 um and 2 um defocused. 100 counting intervals of 1 second each (~250 seconds total time)

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


Gopon, Fournelle, Sobol and Llovet, 2013, Microscopy & Microanalysis, 19, 1698-1708
253
221
190
158
126
95
63
32
0
(BSE image of Apollo 16 Lunar grain A6-8)
50.µm BSE 5.kV

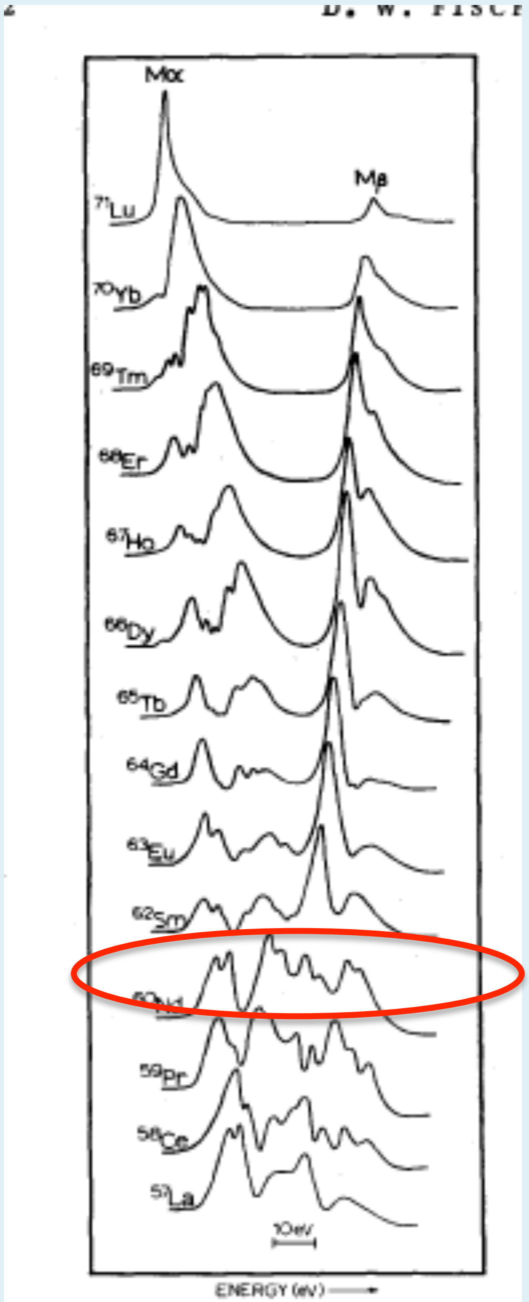
Fe-silicides: problem with Fe La



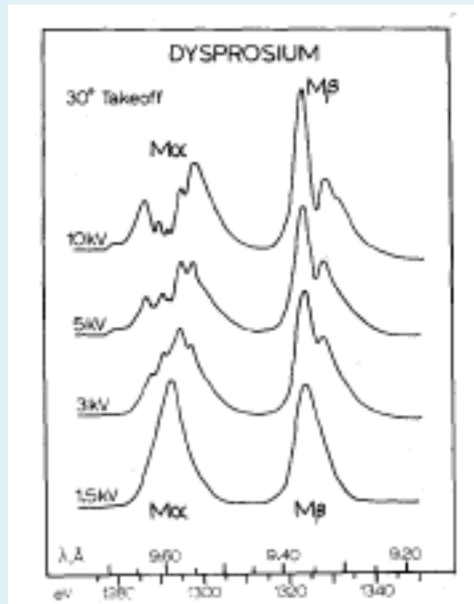
Gopon et al, 2003, Microscopy & Microanalysis

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

REEE: Ma/Mb lines can be severely affected by self-absorption—until <u>extremely low</u> kV used



Ma & Mb of REE at 10 kV

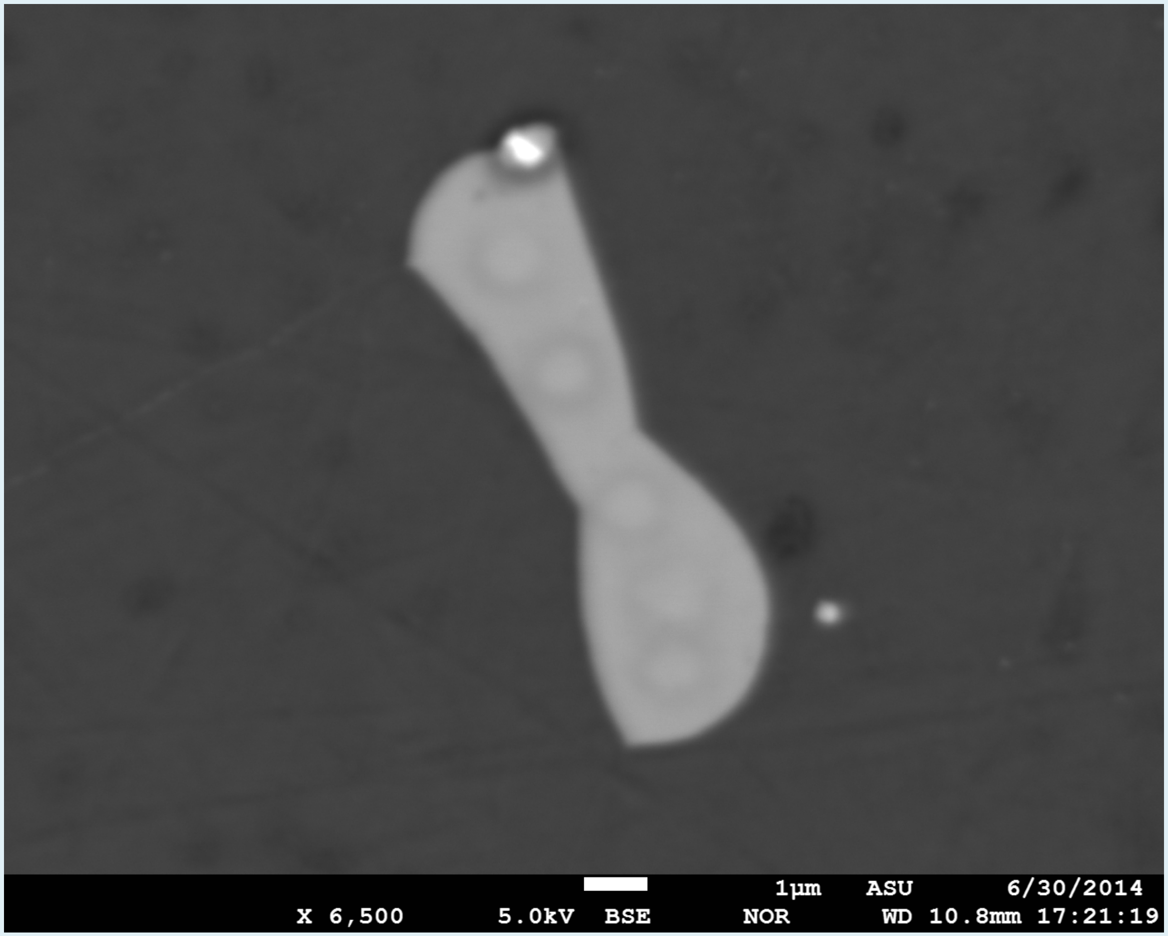


Dy Ma and Mb spectra at various kV

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

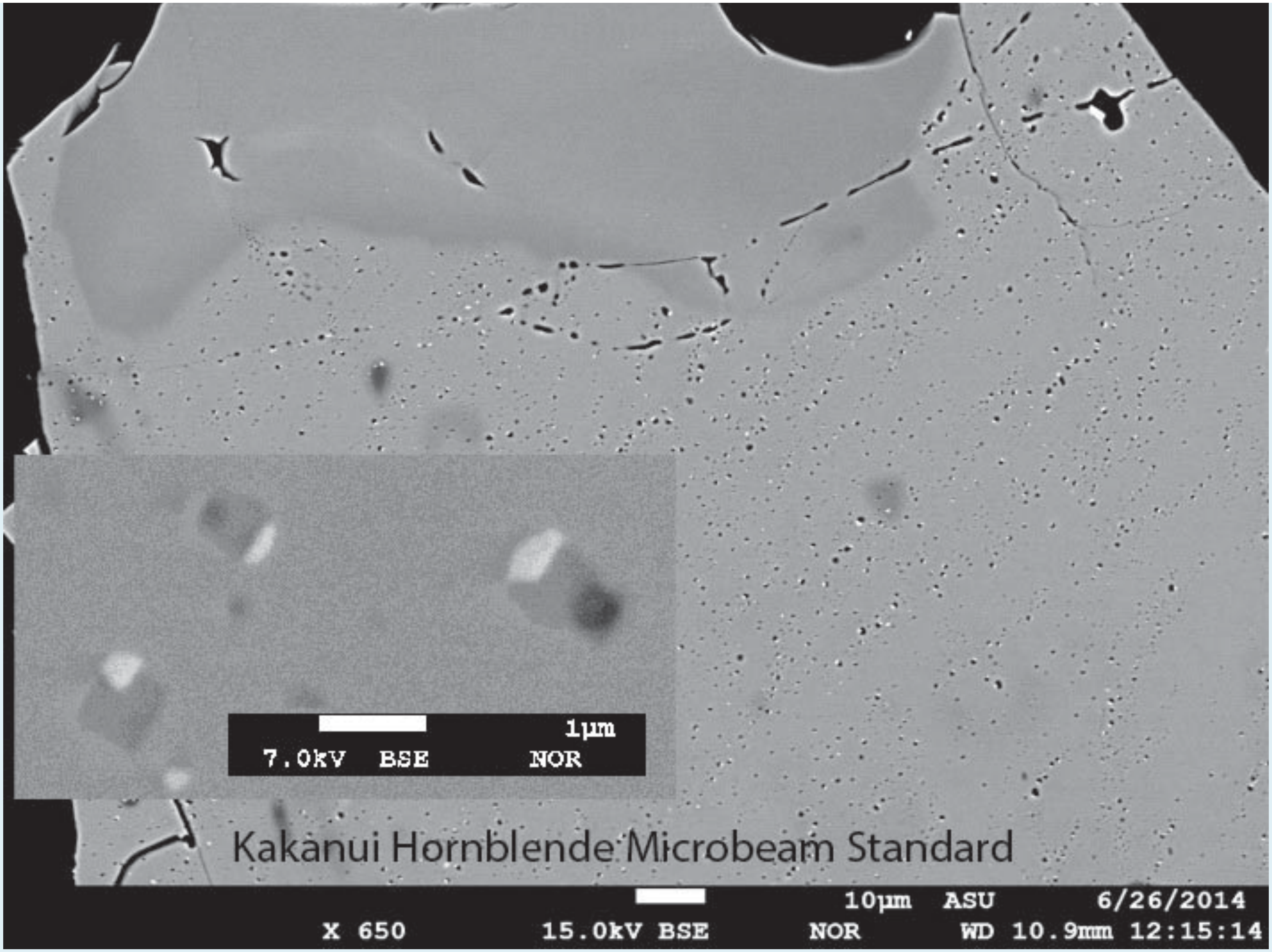
REE @ 5 kV: Nd Mz vs Nd Mb
(in Mg-Zn-Nd material)



	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

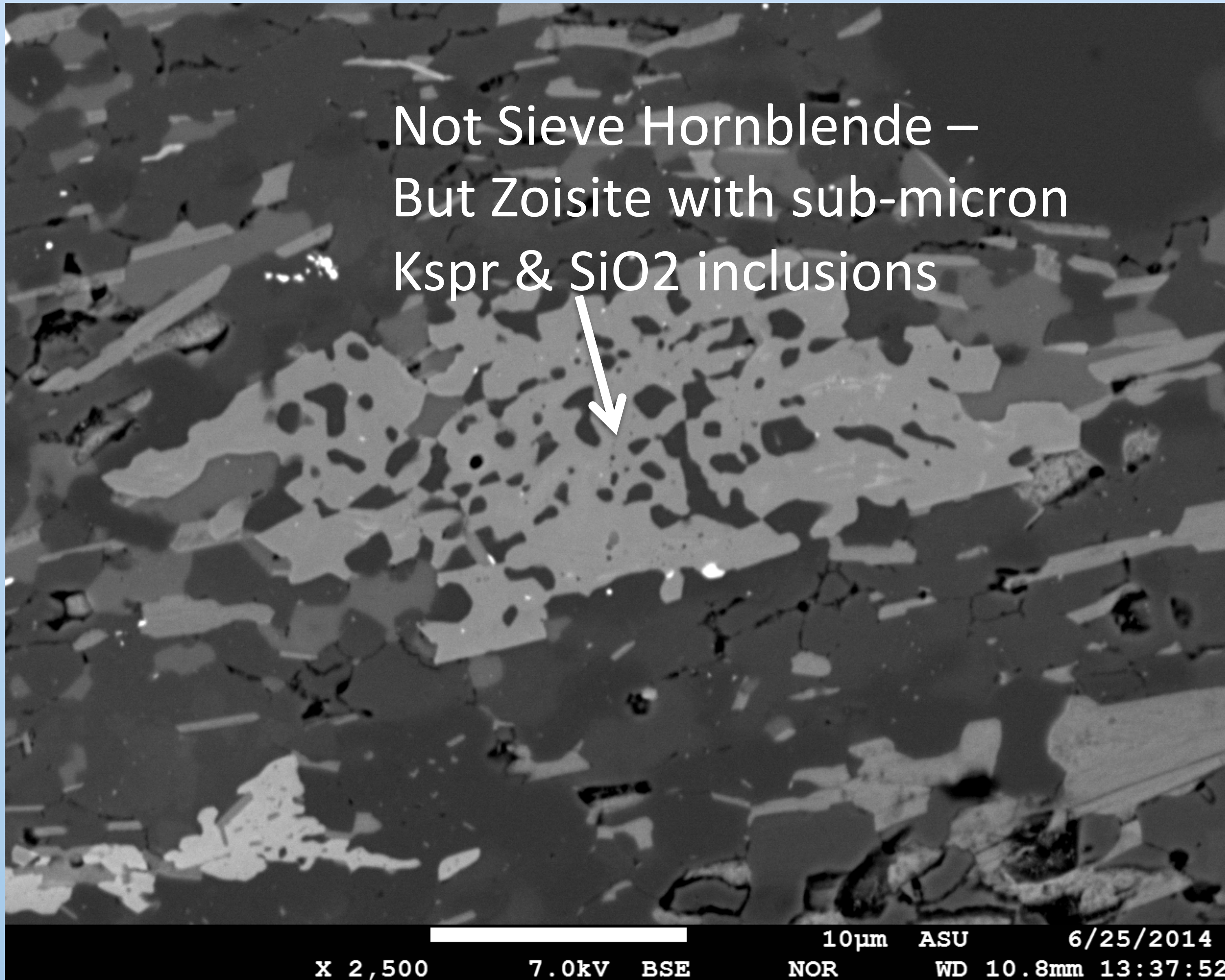


- FE EPMA can show complexity in traditional geological probe standards
- Which composition is ‘correct’? That acquired by defocused or by focused beam?

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?

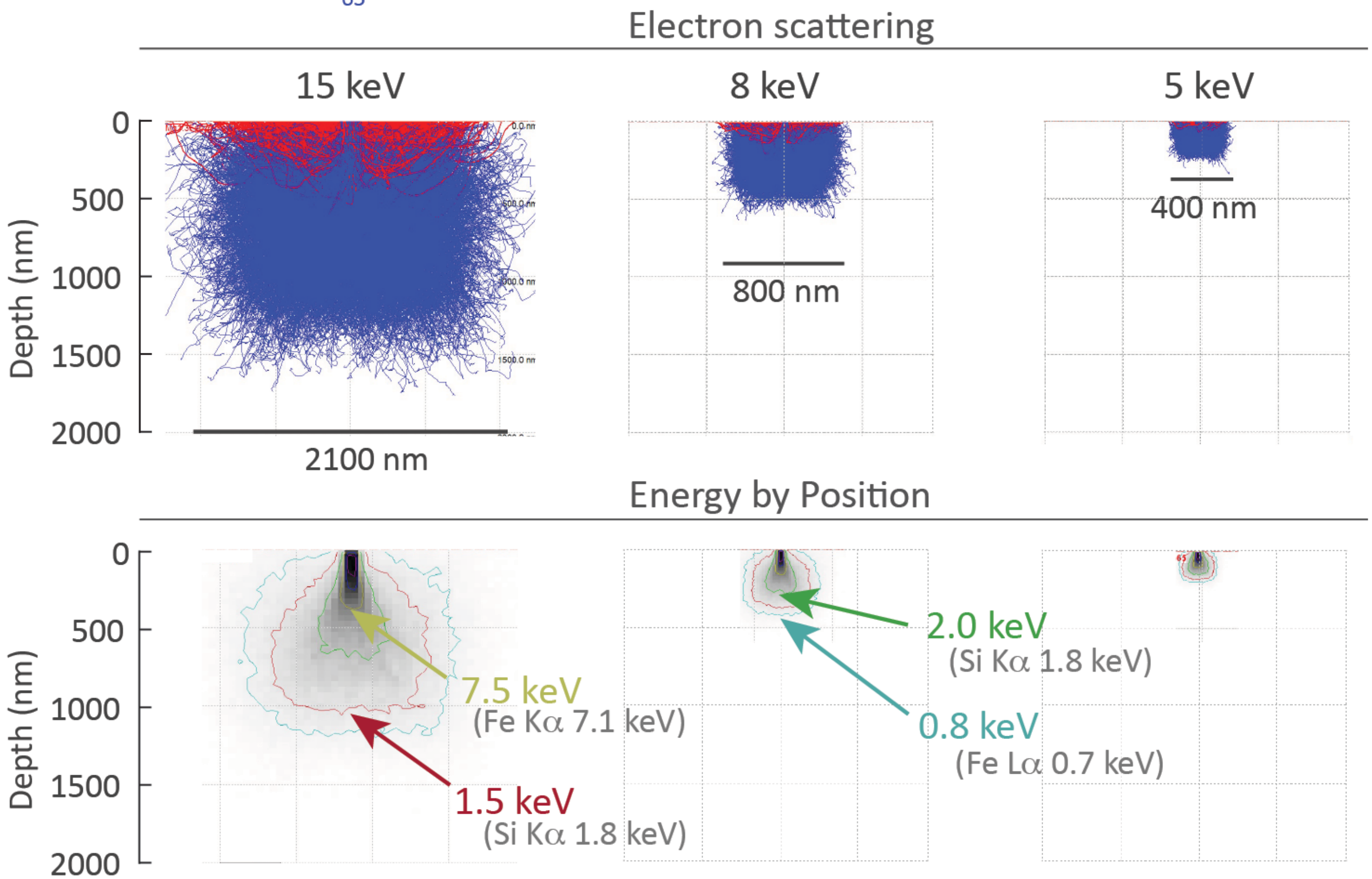


→Accurate Probe Analysis for submicron regions

Thank You

Beam Scattering-Energy Loss

Example: Olivine (Fo_{65})



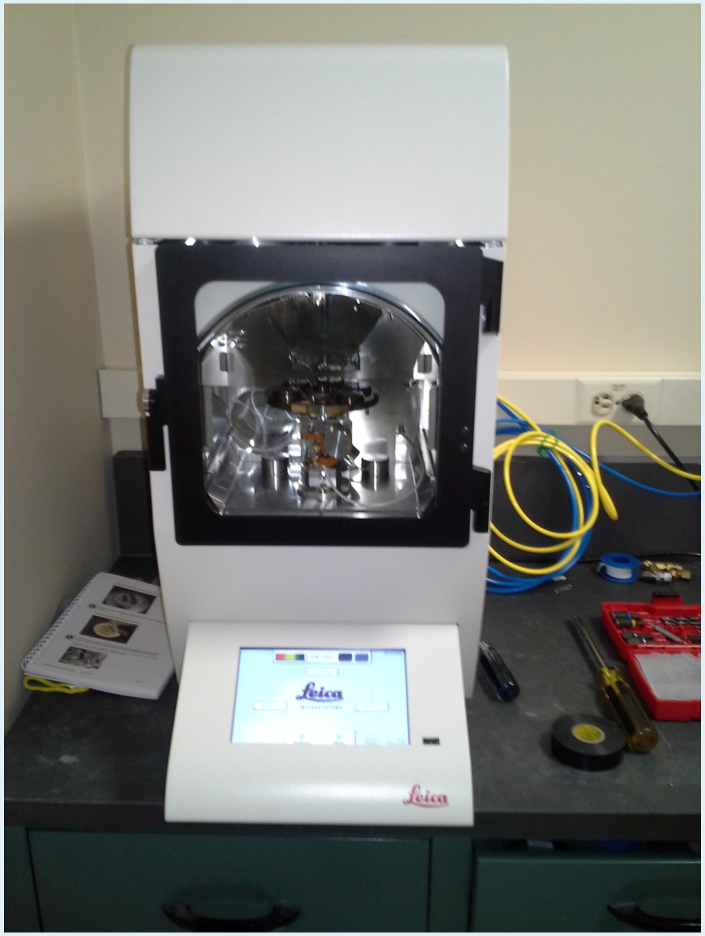
CASINO modeling

100 nm beam

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



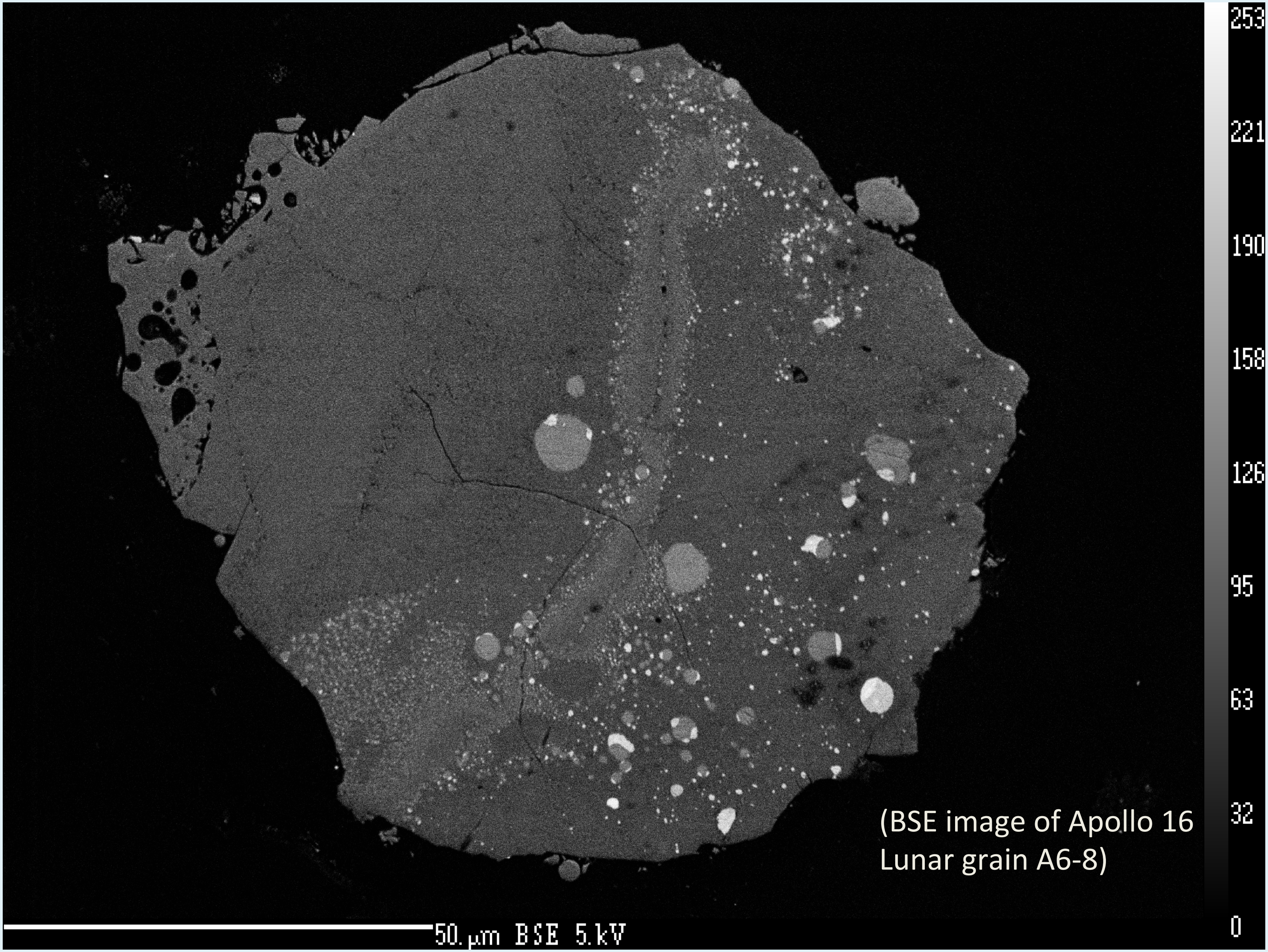
Outline

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

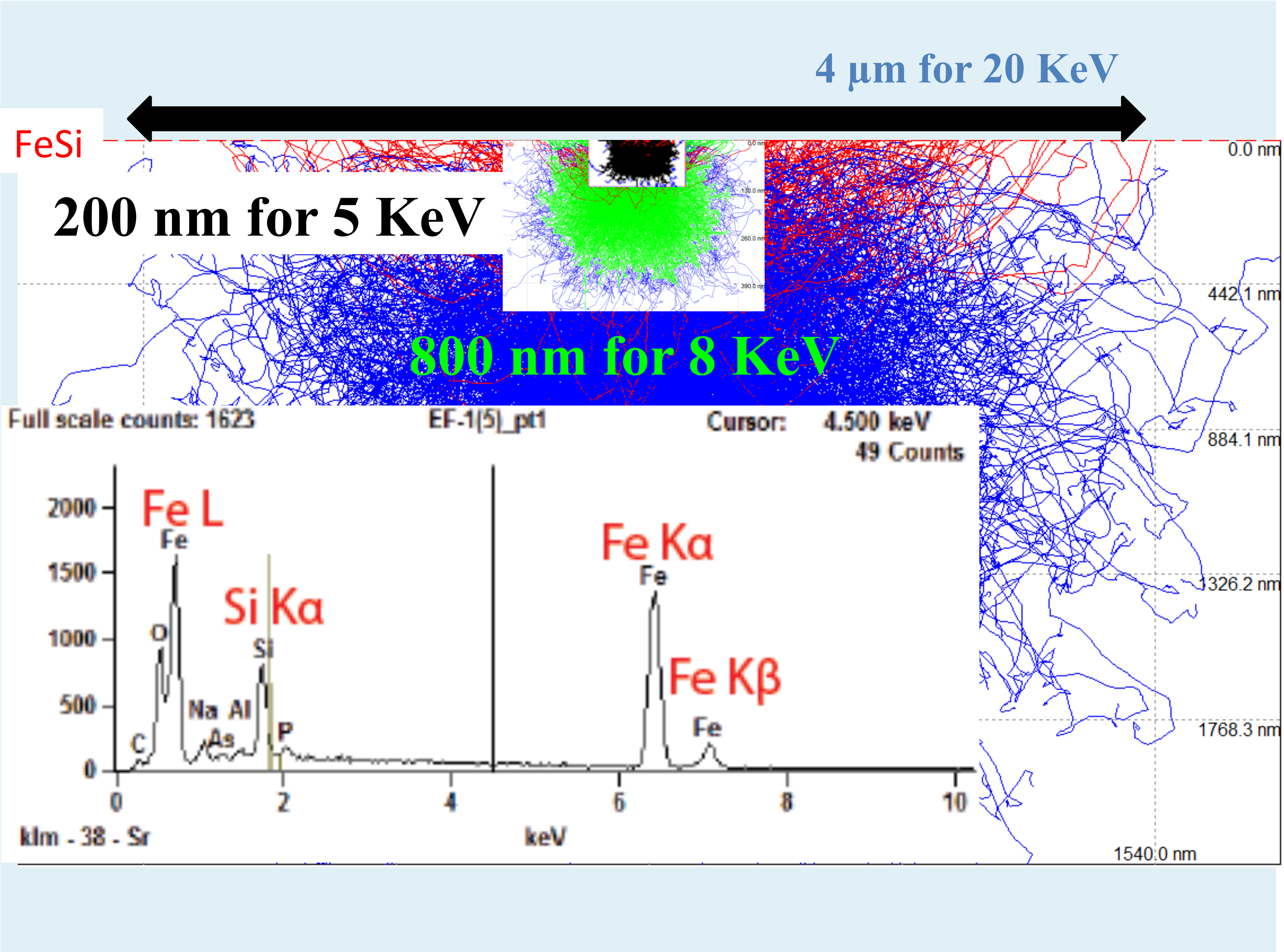
- Experiments:
  - Evaluate spatial resolution of Si and Al Ka in silicate glass K409
    - 5, 7 kV
  - Effect of high intensity FE beams on metals
  - Effect of high intensity FE beams on minerals

- 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???

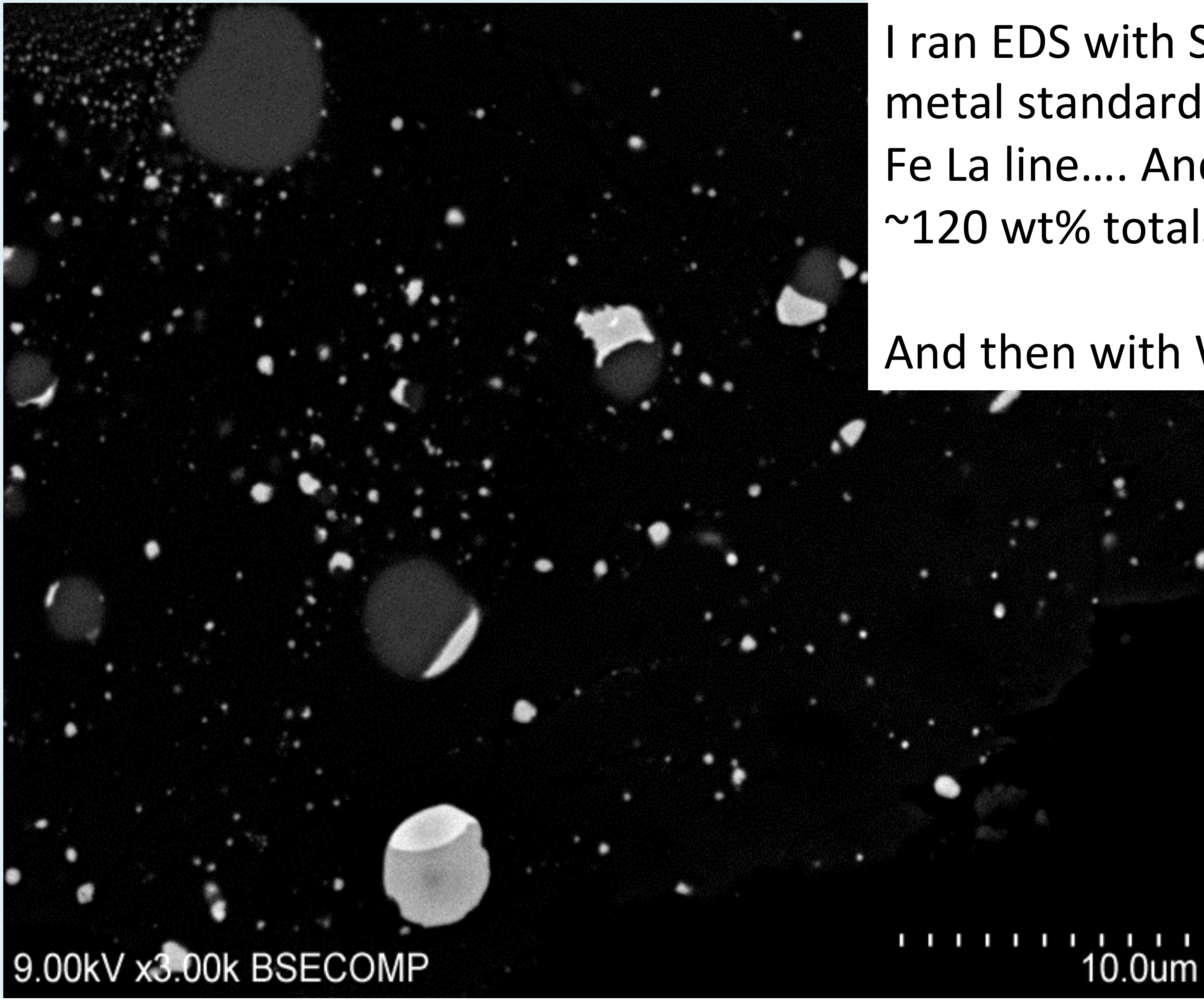


(BSE image of Apollo 16 Lunar grain A6-8)



4 µm for 20 KeV
FeSi
200 nm for 5 KeV
800 nm for 8 KeV
0.0 nm
442.1 nm
884.1 nm
1326.2 nm
1768.3 nm
1540.0 nm
Full scale counts: 1623
EF-1(5)_pt1
Cursor: 4.500 keV
49 Counts
Fe L
Fe
Si Ka
Si
O
C
Na Al
As
P
Fe Ka
Fe
Fe Kβ
Fe
2000
1500
1000
500
0
0
2
4
6
8
10
klm - 38 - Sr
keV

Sub micron analysis



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

And then with WDS….

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	---	

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 (0.02)	14.42 (0.27)	0.88 (0.25)	66.65 (0.7)	0.38 (0.04)	14.65 (0.43)	0.35 (0.03)	2.39 (0.10)	100.29
2	0.52 (0.01)	15.77 (0.14)	1.10 (0.11)	67.86 (0.5)	0.4 (0.05)	14.45 (0.27)	0.35 (0.02)	2.16 (0.04)	102.59
3	0.39 (0.02)	14.33 (0.82)	0.21 (0.28)	86.25 (1.24)	0.27 (0.05)	15.33 (0.53)	0.34 (0.01)	7.54 (0.24)	124.64
4	0.46 (0.06)	15.24 (0.35)	1.49 (0.54)	70.04 (0.3)	0.31 (0.16)	16.0 (0.6)	0.35 (0.06)	2.25 (0.15)	106.14
5	0.50 (0.004)	14.82 (0.77)	1.03 (0.06)	72.97 (0.5)	-0.04 (0.04)	15.13 (1.6)	0.39 (0.06)	2.15 (0.05)	106.99
6	0.51 (0.05)	16.91 (0.64)	0.24 (0.63)	70.36 (0.81)	"Not measured"	14.04 (0.36)	0.59 (0.18)	2.16 (0.35)	104.80

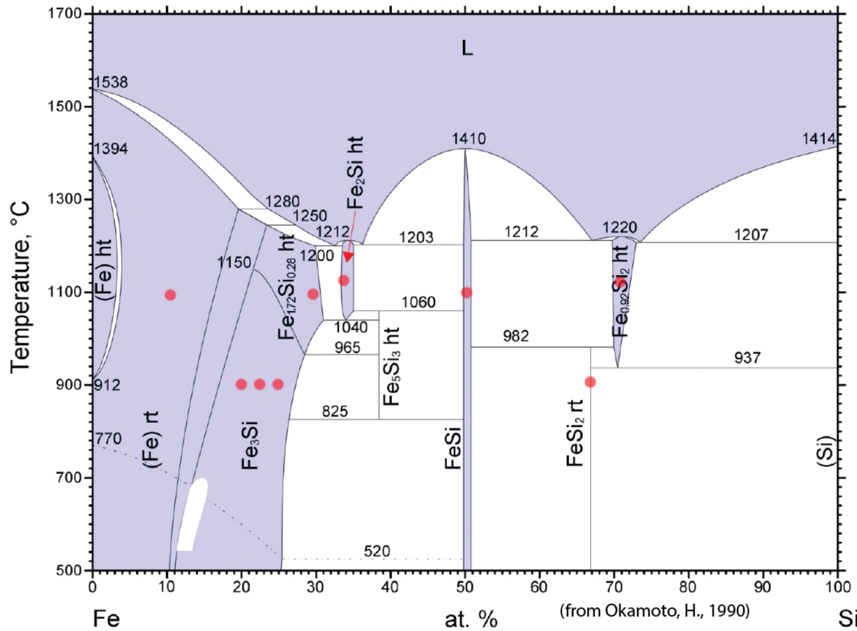
Numbers in parentheses are one standard deviation uncertainties

low (Cr)   high (Fe)   high (Ni)

Llovet, et al (2012)

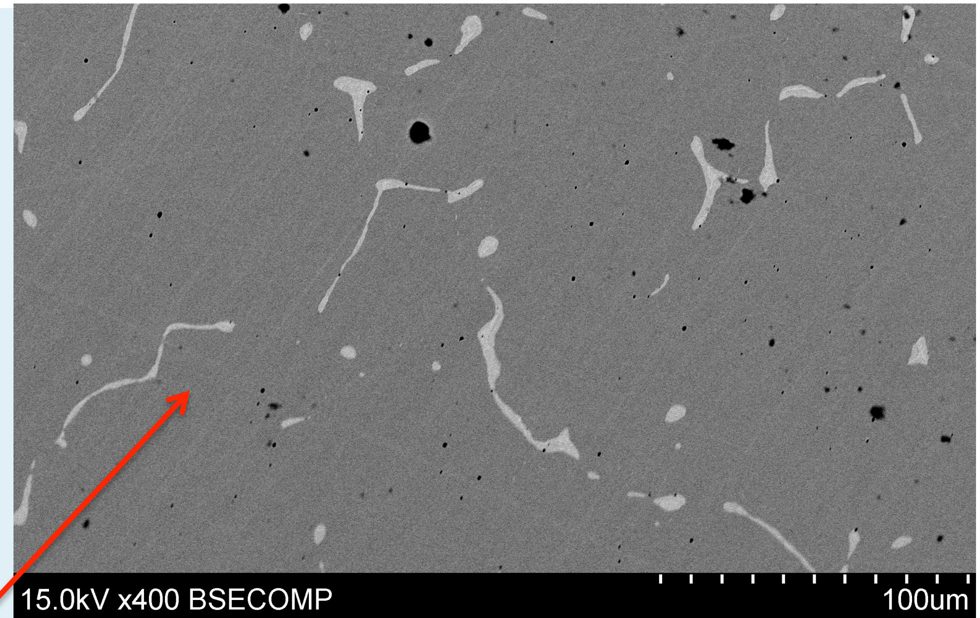
Acquire FeSi phases for understanding the apparent problem with Fe La:

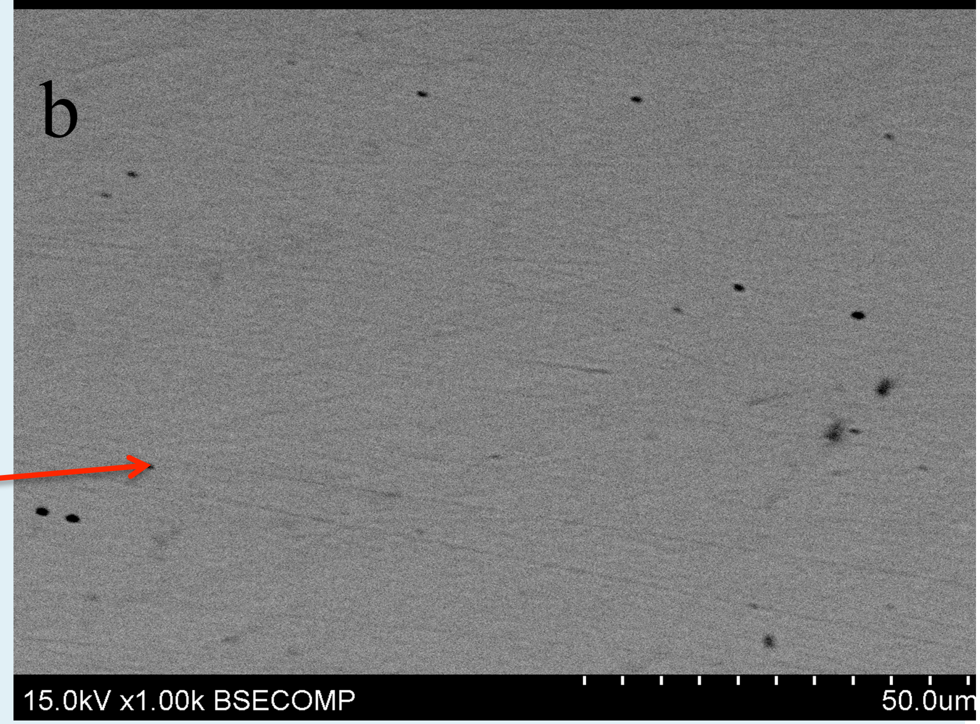
- Erkki Heikinheimo (Aalto University, Dept of Materials Science and Engineering
- University of WI material science group (John Perepezko)
- University of WI chemistry research group (Danny Fredrickson)

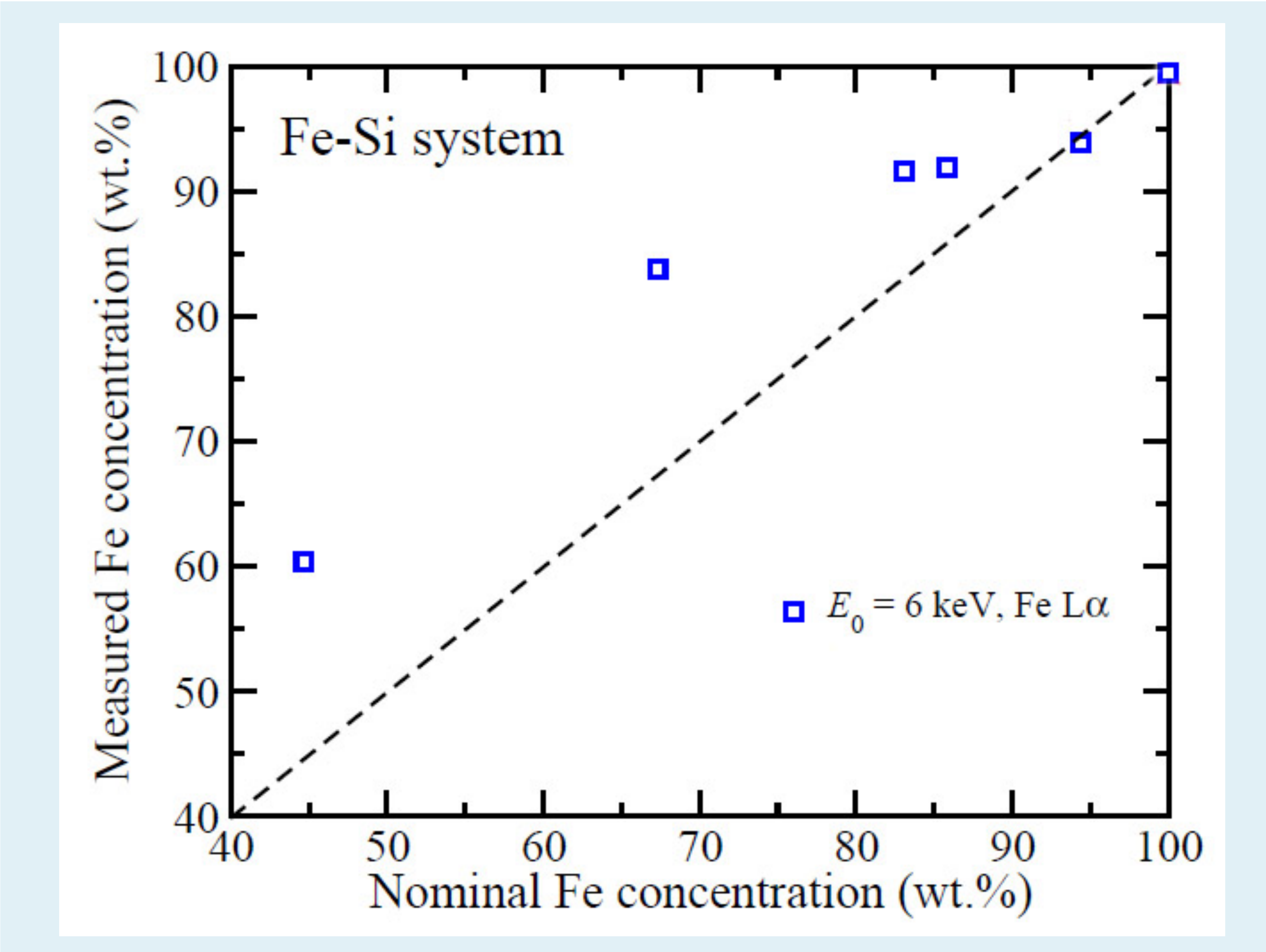


FeSi after one week at 1100°C

FeSi after 4 weeks at 1100°C







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

What could be going on here?

Initial thoughts….

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

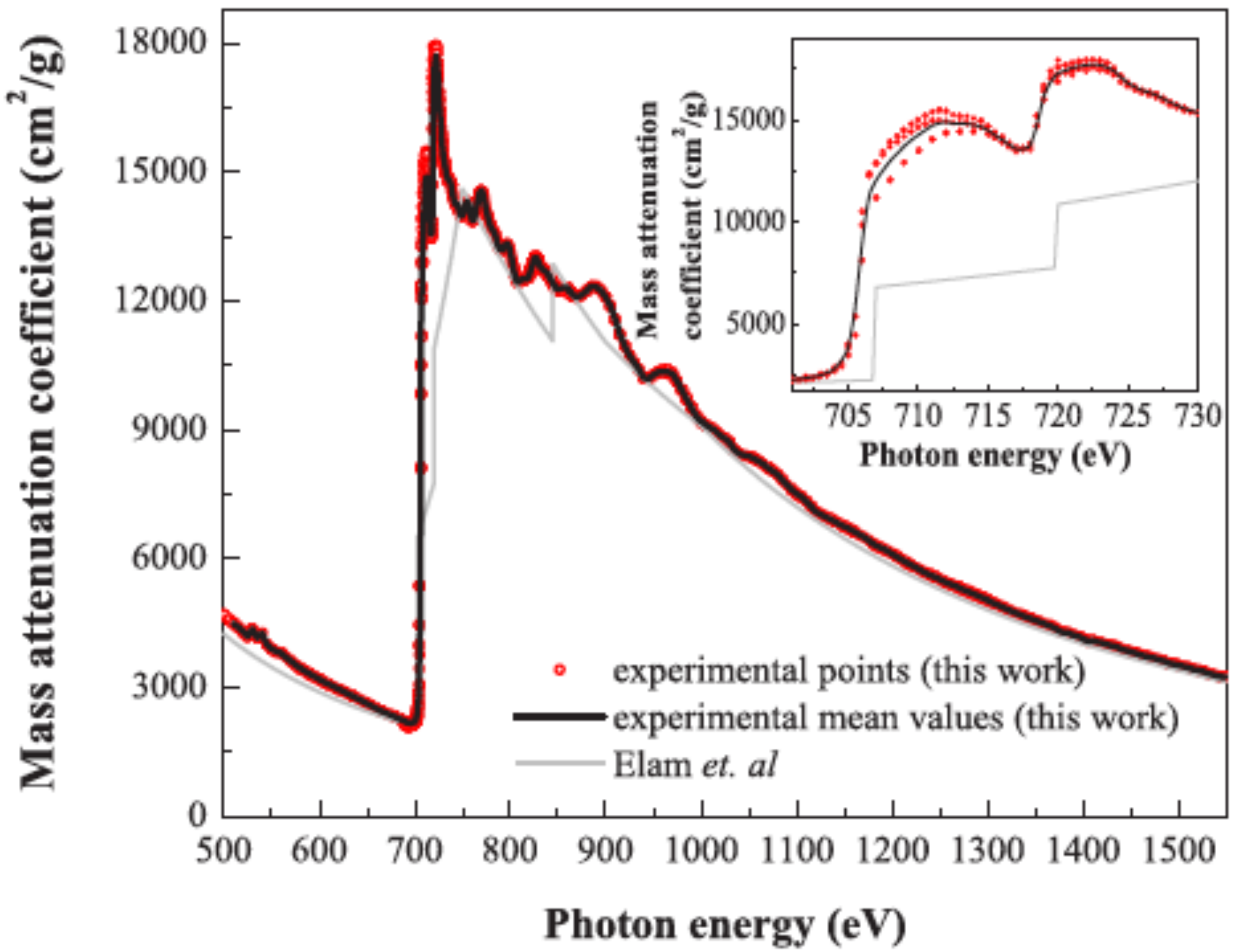
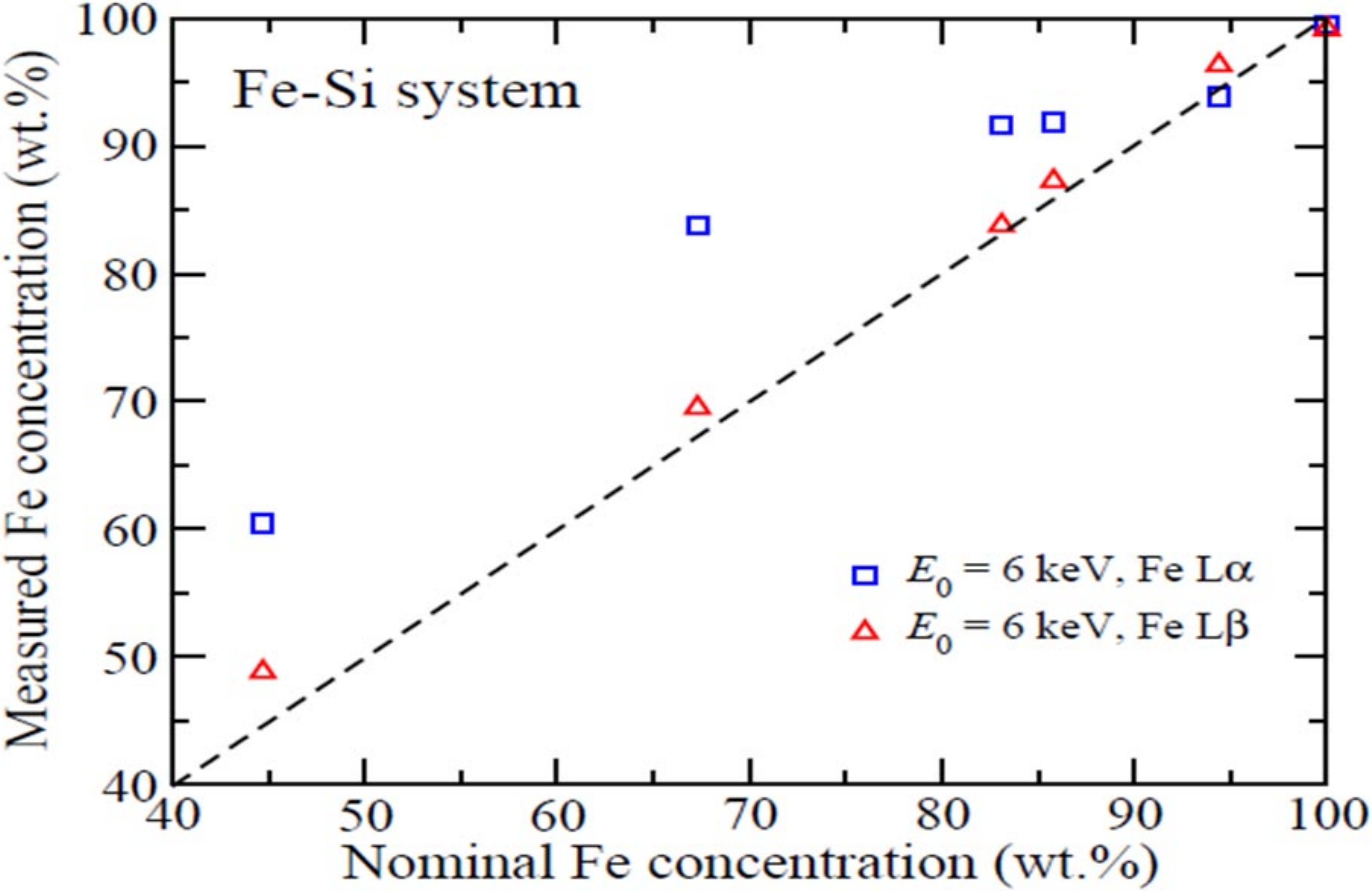


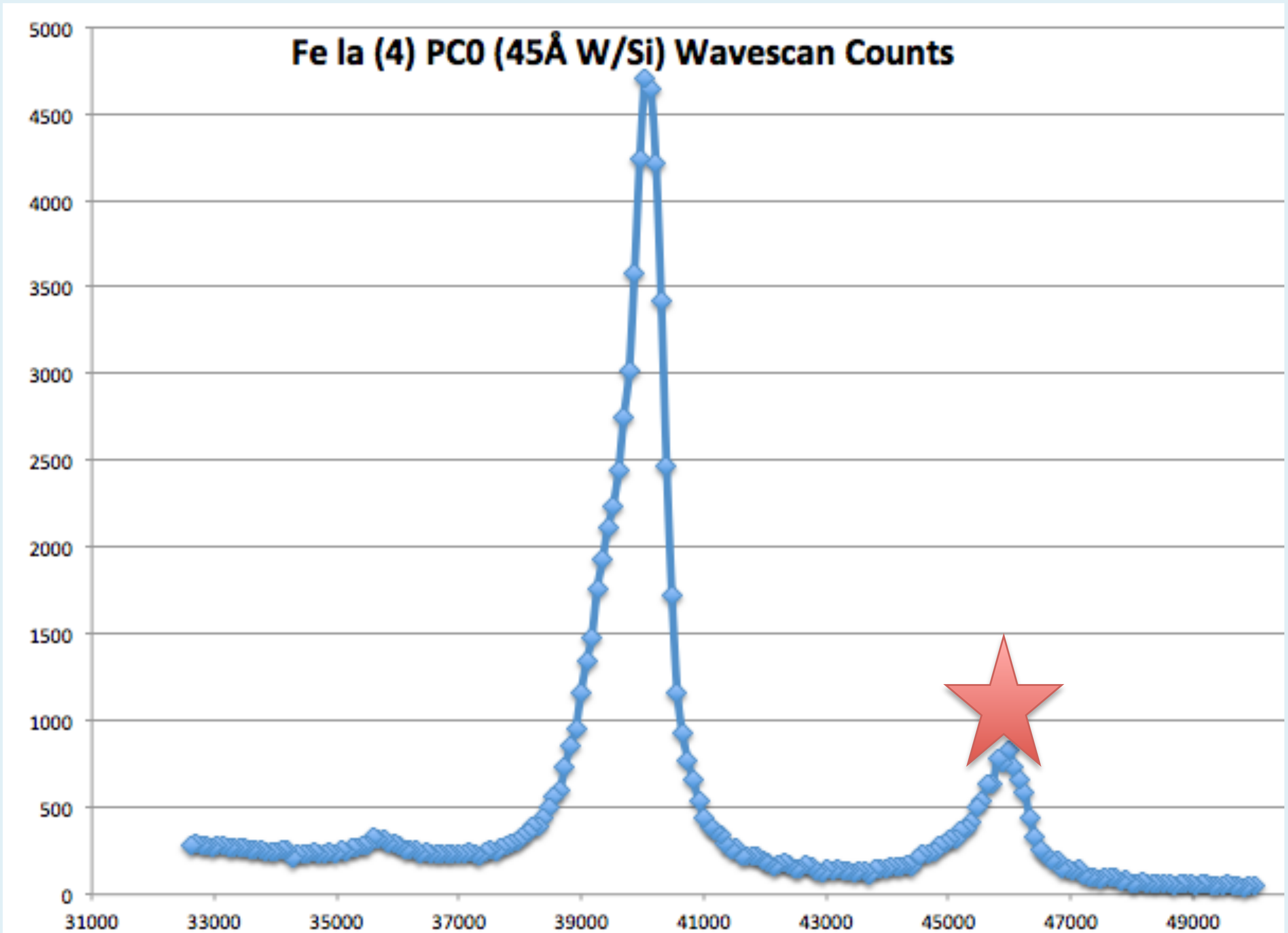
FIG. 3. (Color online) Experimental (this work) and theoretical [34] mass attenuation coefficients for metallic Fe in the energy region 500–1550 eV. The solid line represents the smoothed mean experimental values obtained by multiple transmittance energy scans.

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



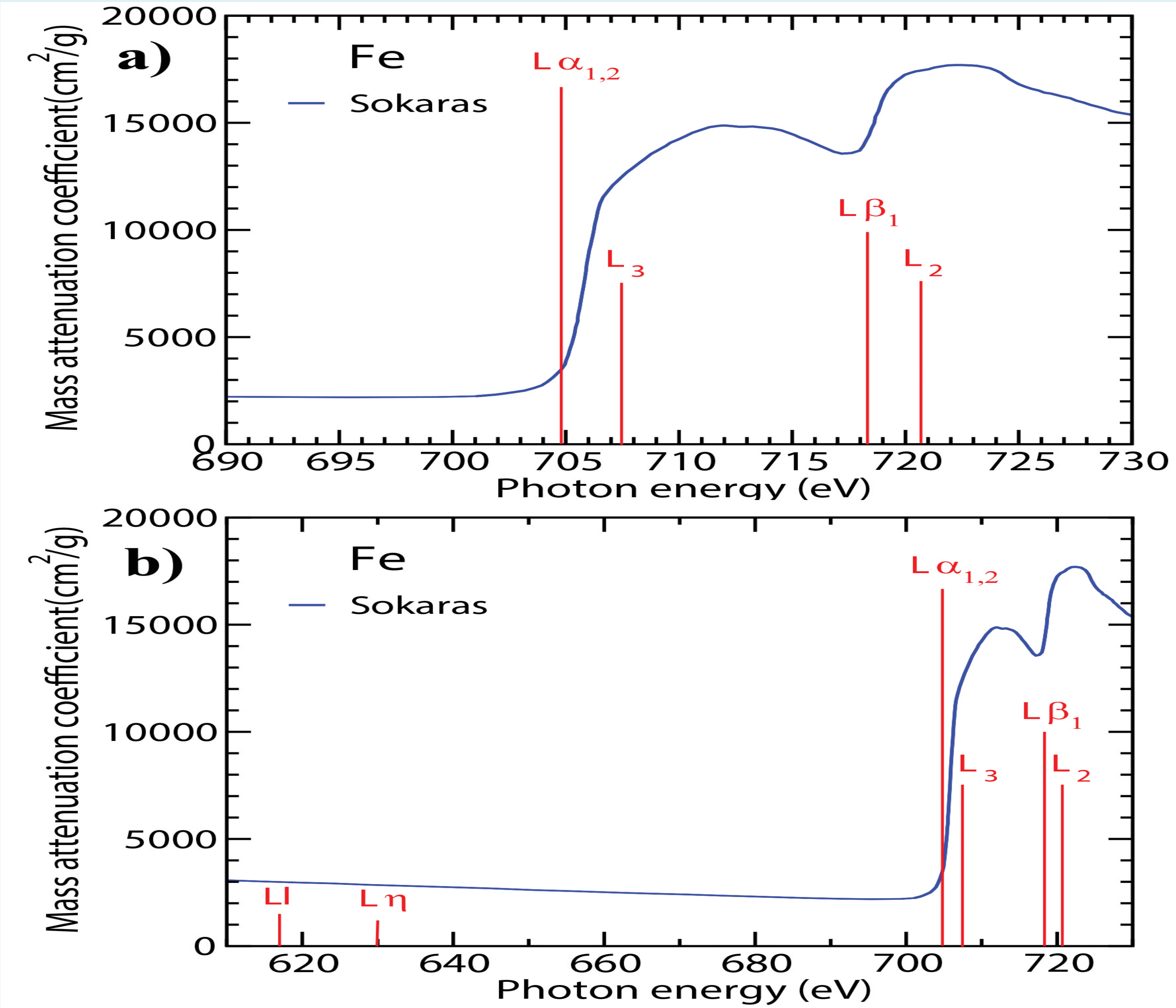
Fe-Si system
Measured Fe concentration (wt.%)
Nominal Fe concentration (wt.%)
E_0 = 6 keV, Fe Lα
E_0 = 6 keV, Fe Lβ
40
50
60
70
80
90
100

Ah ha moment…

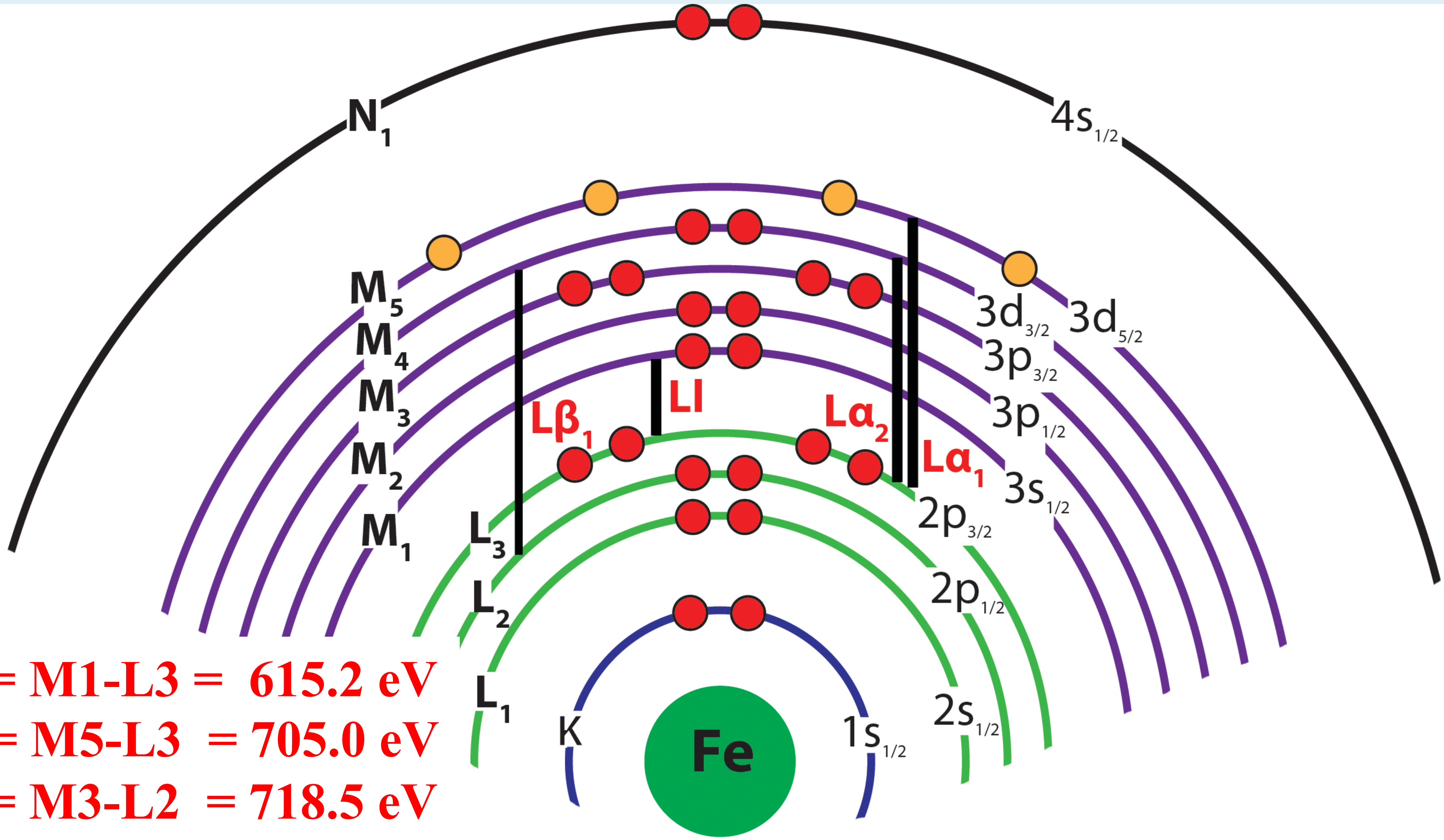


Fe la (4) PC0 (45Å W/Si) Wavescan Counts
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
31000
33000
35000
37000
39000
41000
43000
45000
47000
49000

Solution: Use the Fe Ll line for Analysis



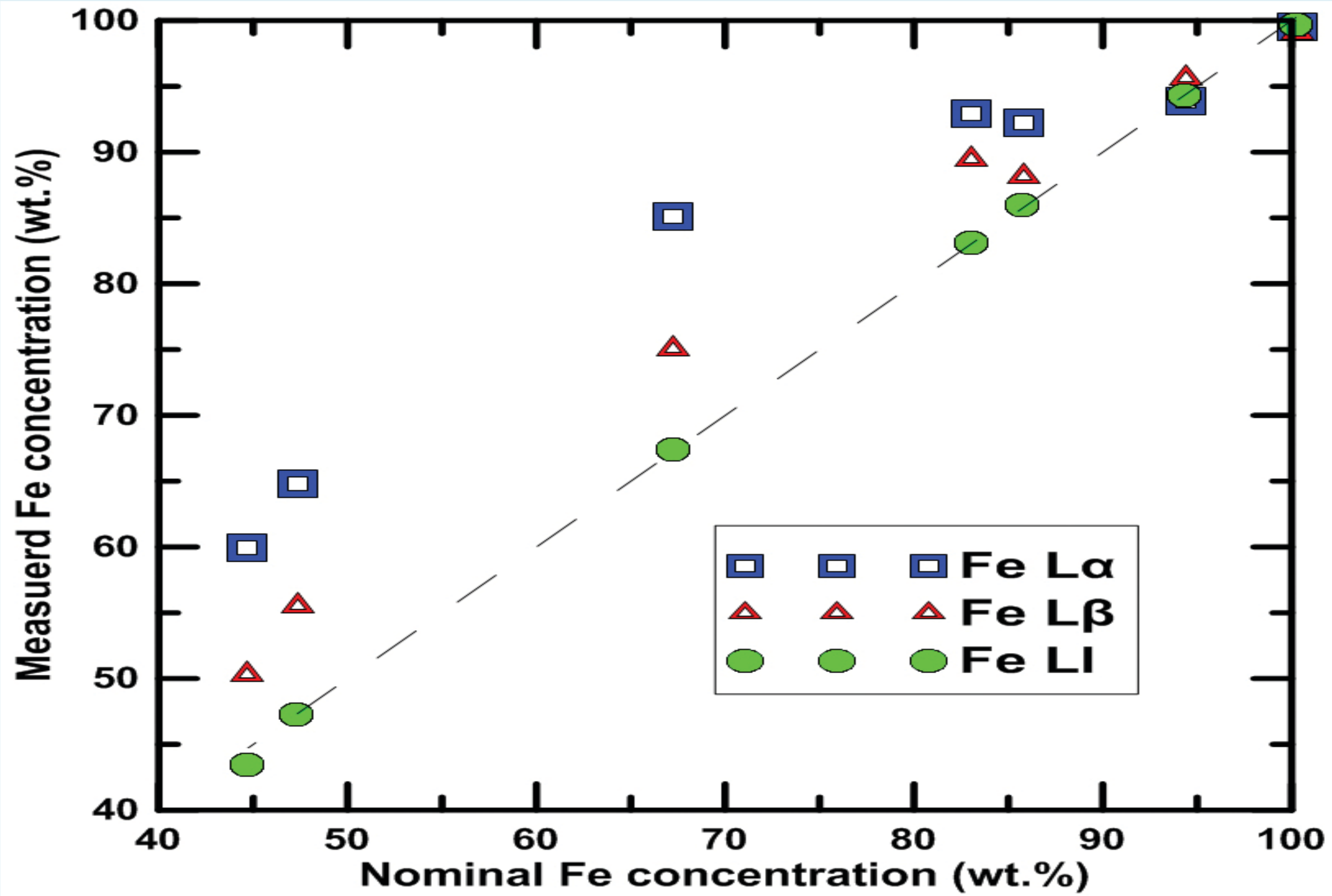
Solution: Use the Fe LL line for Analysis



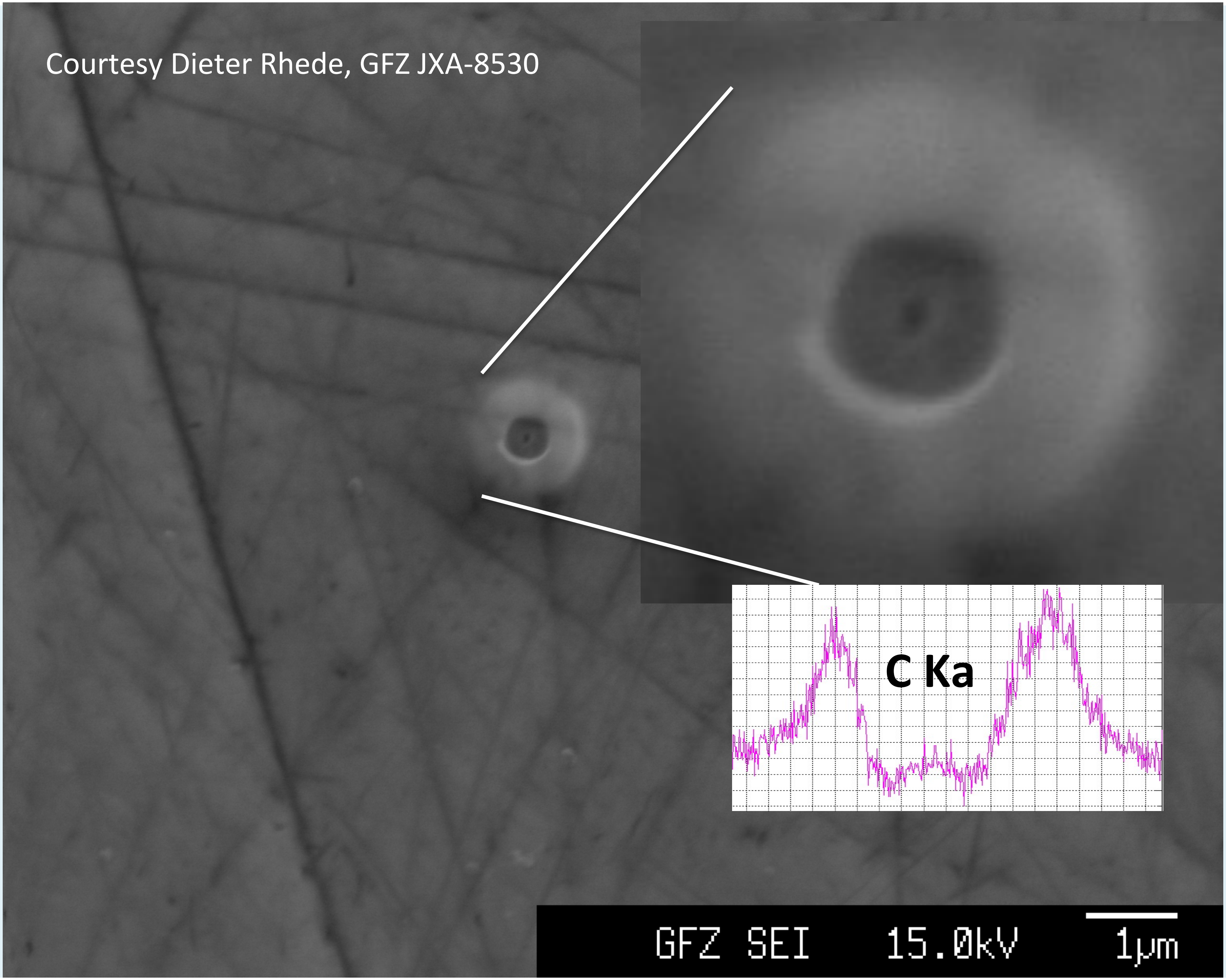
Ll = M1-L3 = 615.2 eV

Lα= M5-L3 = 705.0 eV

Lβ= M3-L2 = 718.5 eV



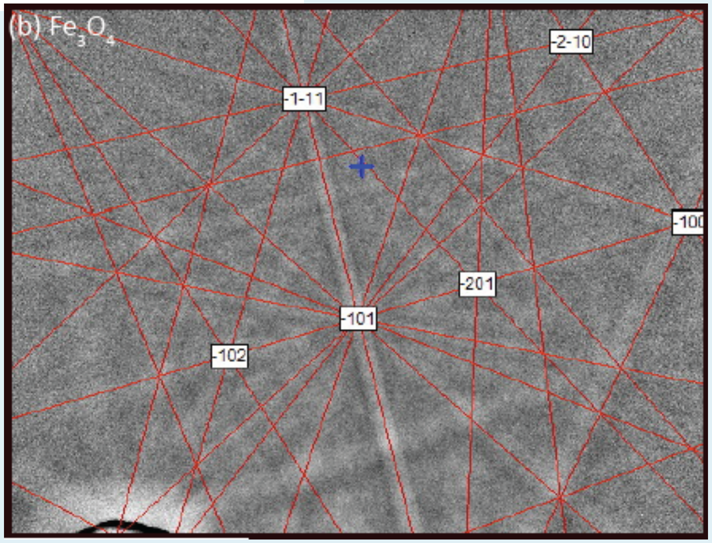
100
90
80
70
60
50
40
Measuerd Fe concentration (wt.%)
40
50
60
70
80
90
100
Nominal Fe concentration (wt.%)
Fe Lα
Fe Lβ
Fe Ll

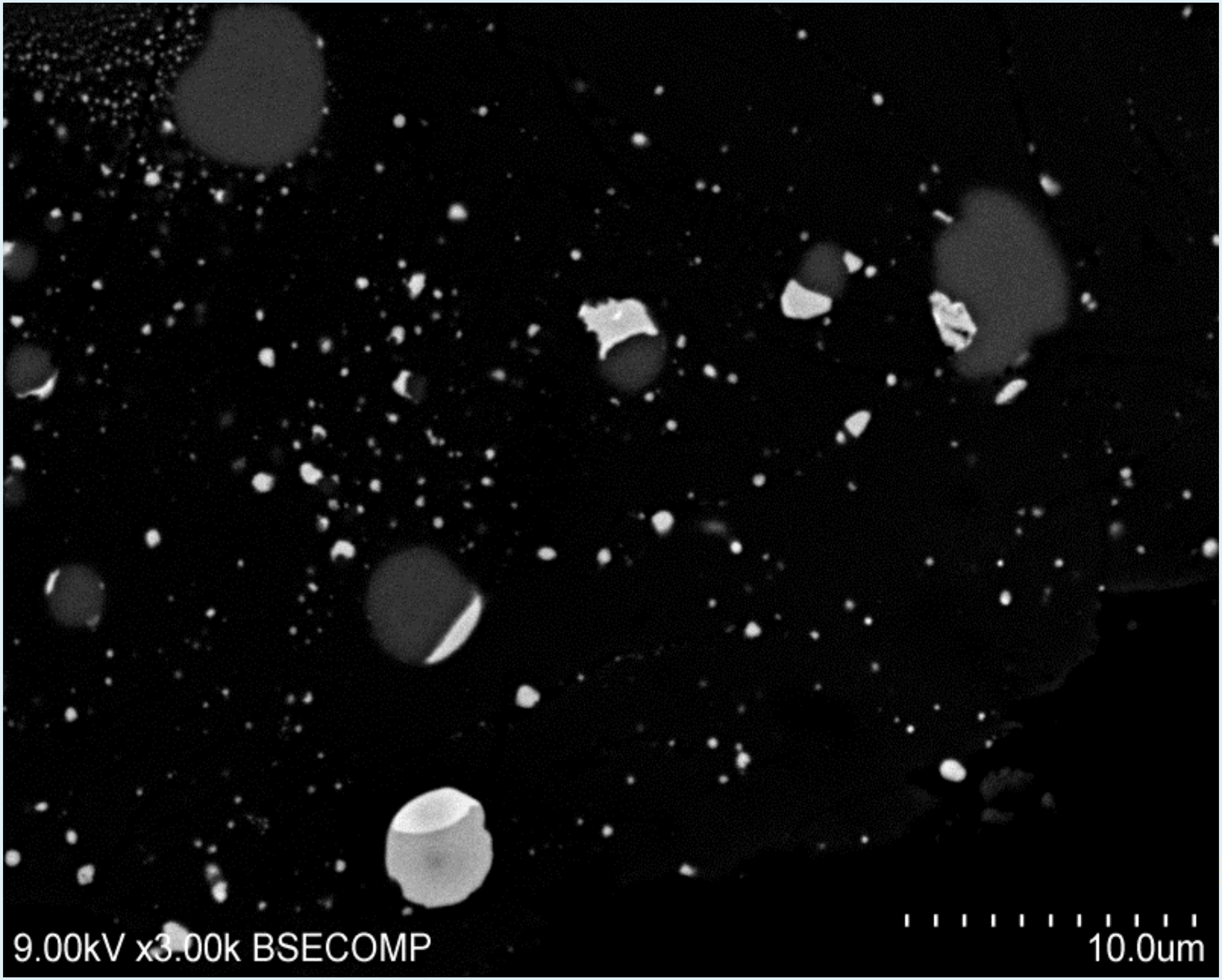

Courtesy Dieter Rhede, GFZ JXA-8530
C Ka
GFZ SEI 15.0kV 1μm

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