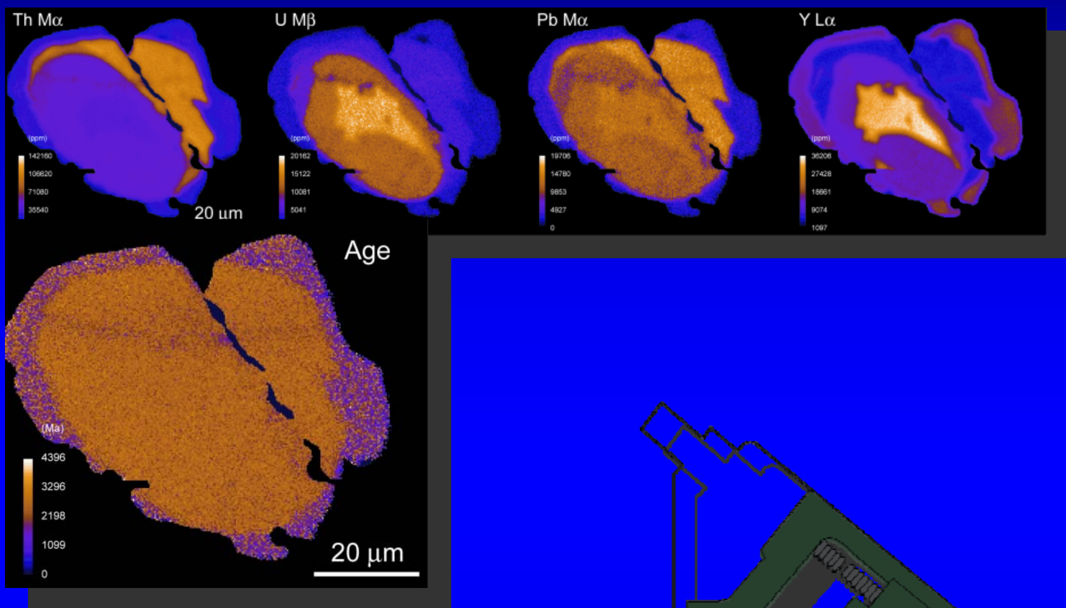
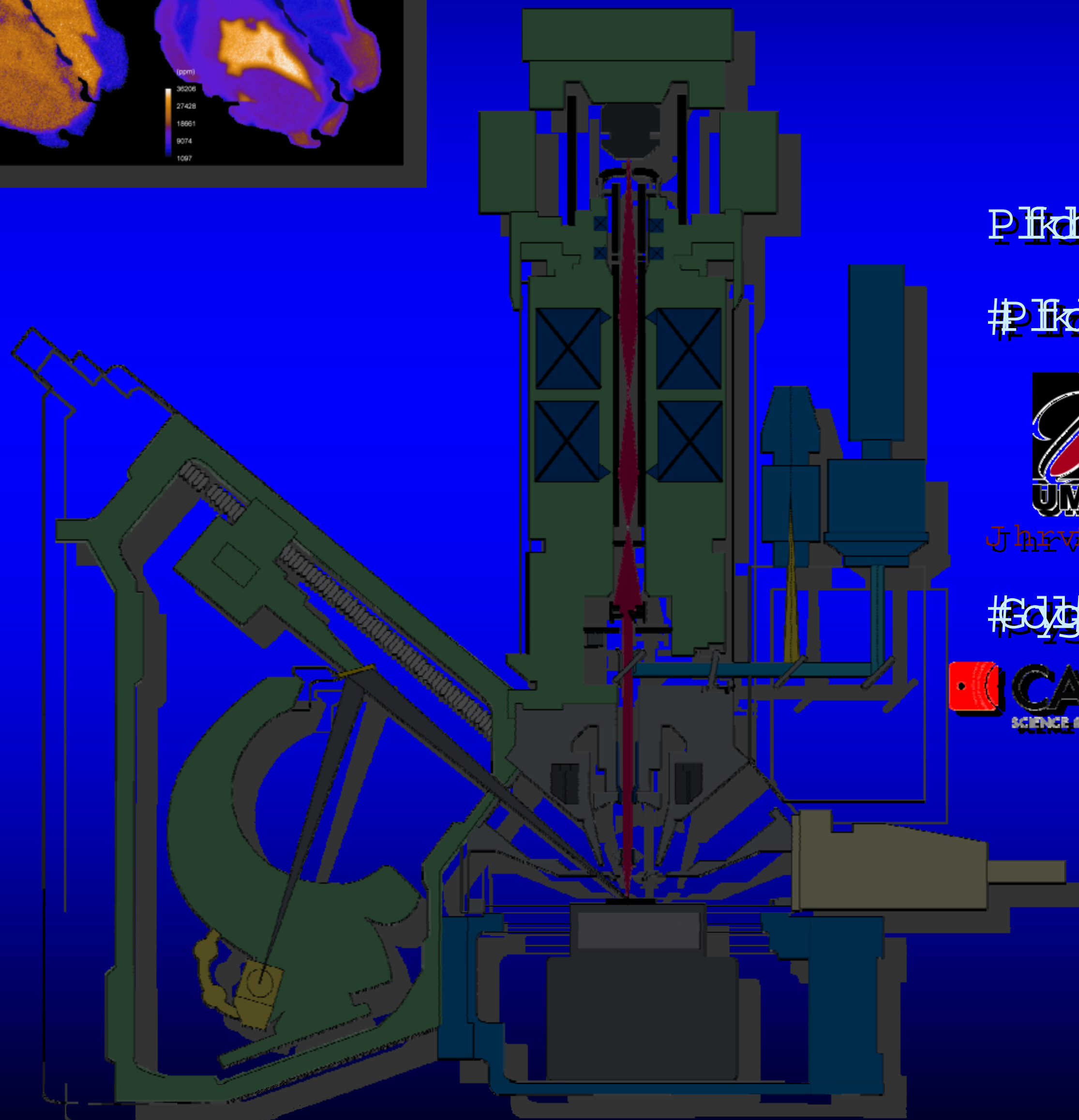
Spatial Resolution and Trace Element Sensitivity





Plfkdho#Mhuflqrylf#

#Plfkdho#Zlooldpv#

UMASS

Jhrvflhqfhv

#Gdyh#Vqrh|hqerv#

CAMECA
SCIENCE & METROLOGY SOLUTIONS

Analytical optimization…

Precision

Acquisition of as many counts as possible
Want ability to prioritize efficiency in some cases

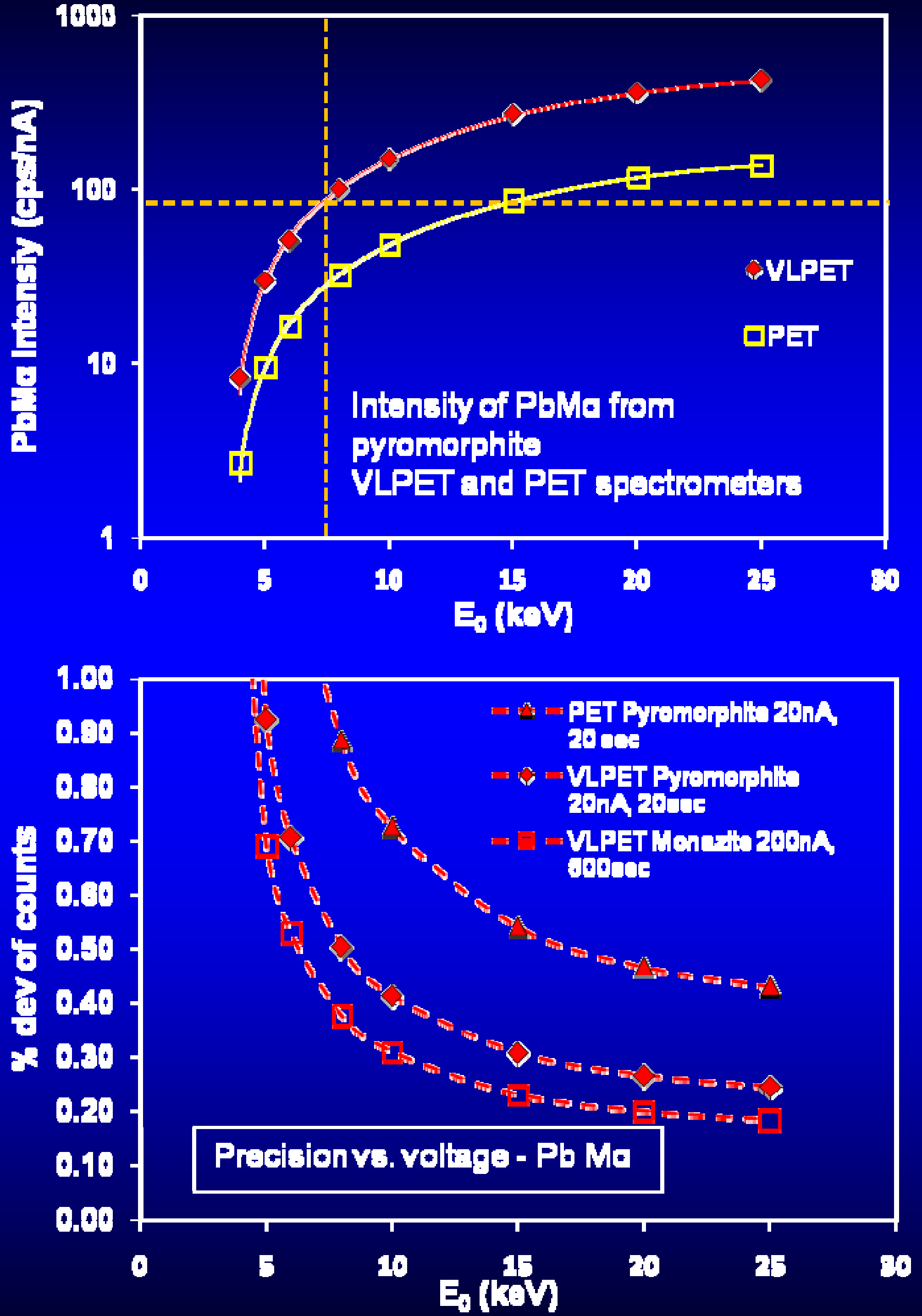
- Unlimited time?
- Unlimited current?
- Unlimited overvoltage?

Spatial Resolution

Electron scattering controls everything?
Maybe beam size makes a difference in certain circumstances

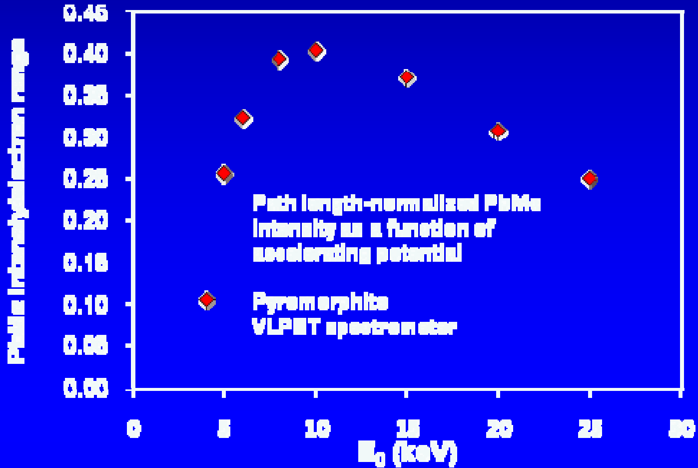
- Sufficient voltage = addressing excitation potentials
- High Z phases?

What is the realized beam diameter at high current and sufficient voltage?



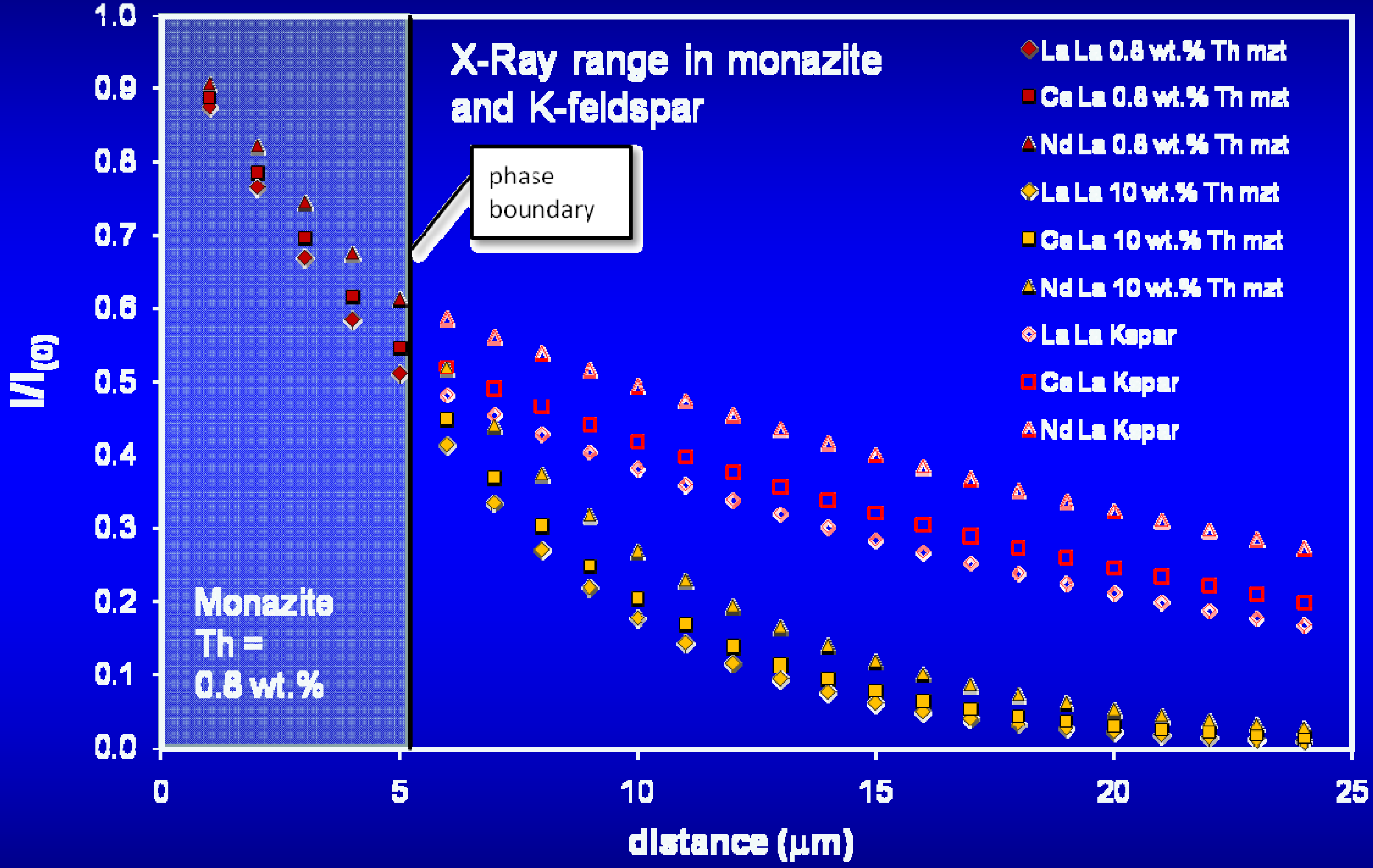
1000
100
10
1
PbMα Intensiy (cps/nA)
◆VLPET
□PET
Intensity of PbMα from
pyromorphite
VLPET and PET spectrometers
0
5
10
15
20
25
30
E0 (keV)
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
% dev of counts
PET Pyromorphite 20nA, 20 sec
VLPET Pyromorphite 20nA, 20sec
VLPET Monazite 200nA, 600sec
Precision vs. voltage - Pb Mα
E0 (keV)

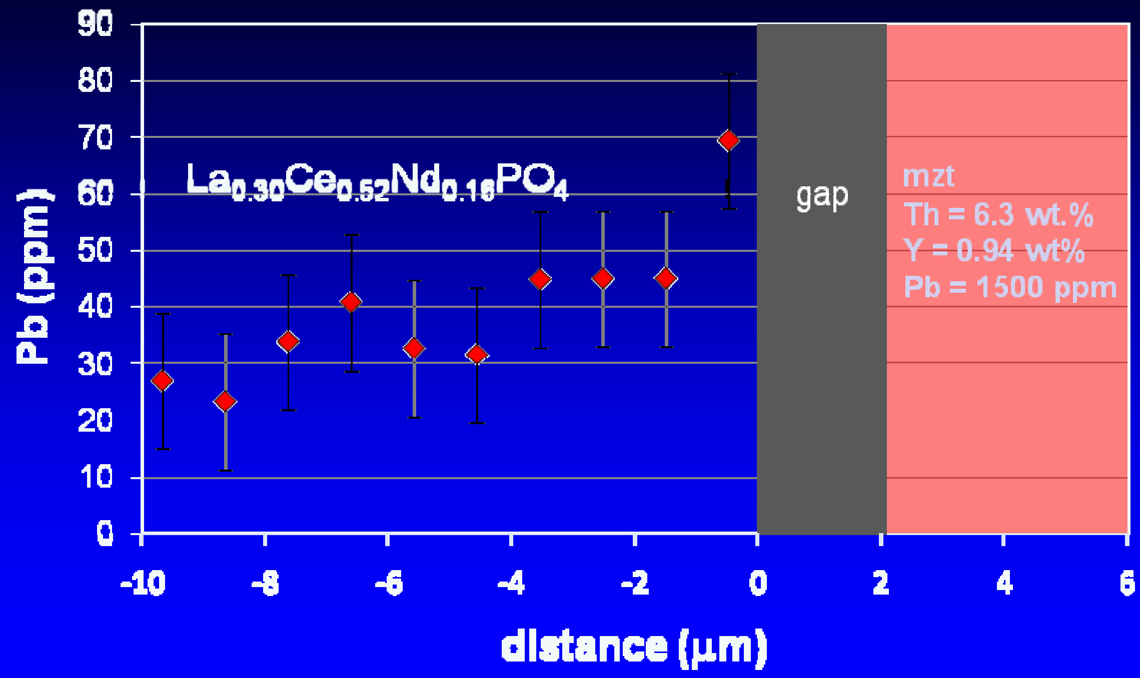
Determine the voltage you need…



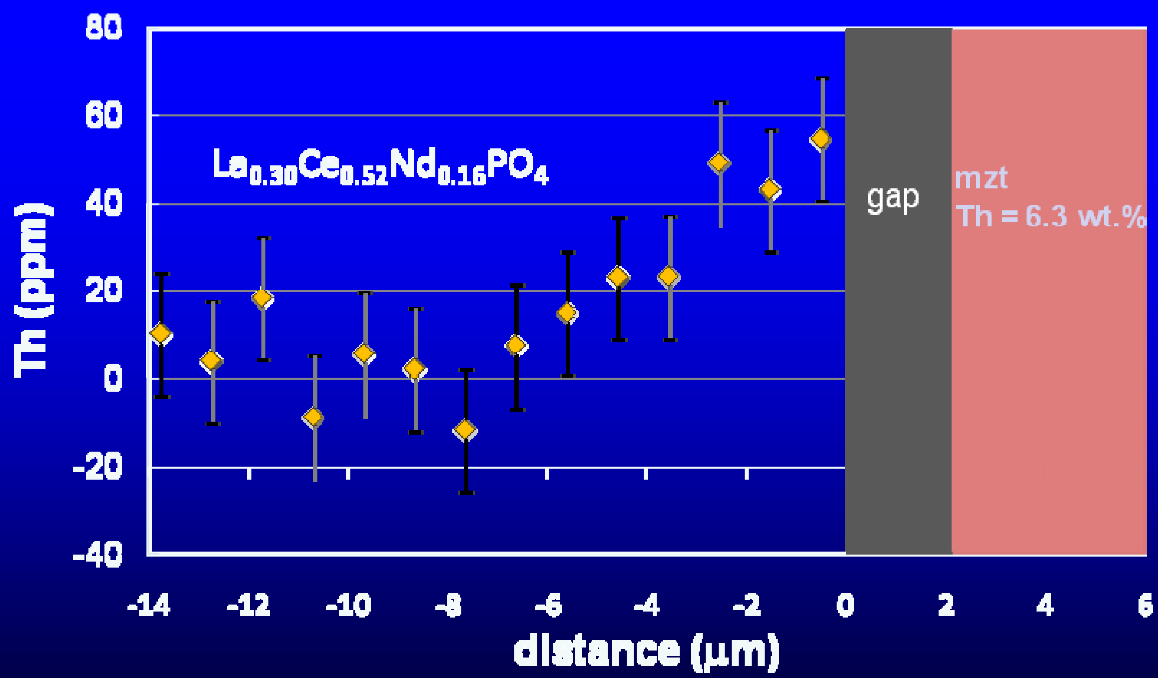
Element	Shell	Electron binding energy (keV)	E_0 at U_{opt} [1] (keV)	Characteristic line	Emission energy (keV)
Pb	MV ($3d^{5/2}$)	2.484	4.97 – 7.45	Mα1	2.3455
	MIV ($3d^{3/2}$)	2.586	5.17 – 7.76	Mβ	2.4427
	LIII ($2p^{1/2}$)	13.035	26.07 - 39.11	Lα1	10.5515
Th	MV ($3d^{5/2}$)	3.332	6.66 – 10.00	Mα	2.9961
	LIII ($2p^{1/2}$)	16.300	32.6 – 48.9	Lα1	12.6520
U	MV ($3d^{5/2}$)	3.552	7.10 – 10.66	Mα1	3.1708
	MIV ($3d^{3/2}$)	3.728	7.46 – 11.18	Mβ	3.3367
	LIII ($2p^{3/2}$)	17.166	34.33 - 51.50	Lα1	13.6147
P	K (1s)	2.146	4.29 – 6.44	Kα1	2.0137
La	LIII ($2p^{3/2}$)	5.483	10.97 – 16.45	Lα1	4.65097
				Lβ2	5.3835
	LII ($2p^{1/2}$)	5.891	11.78 – 17.67	Lβ1	5.0421
Ce	LIII ($2p^{3/2}$)	5.723	11.45 – 17.17	Lα1	4.8402
				Lβ2	5.6134
	LII ($2p^{1/2}$)	6.164	12.33 – 18.49	Lβ1	5.2622
Nd	LIII ($2p^{3/2}$)	6.208	12.42 – 18.62	Lα1	5.2304
				Lβ2	6.0894
	LII ($2P^{1/2}$)	6.722	13.44 – 20.17	Lβ1	5.7216
Yb[2]	LIII ($2p^{3/2}$)	8.944	17.89 – 26.83	Lα1	7.4156
				Lβ2	8.7588
	LII ($2p^{1/2}$)	9.978	19.96 – 29.93	Lβ1	8.4018

[1] E_0= beam energy; U_{opt} is the optimal overvoltage for the most efficient shell ionization (see text for explanation). [2] Example representing the most c

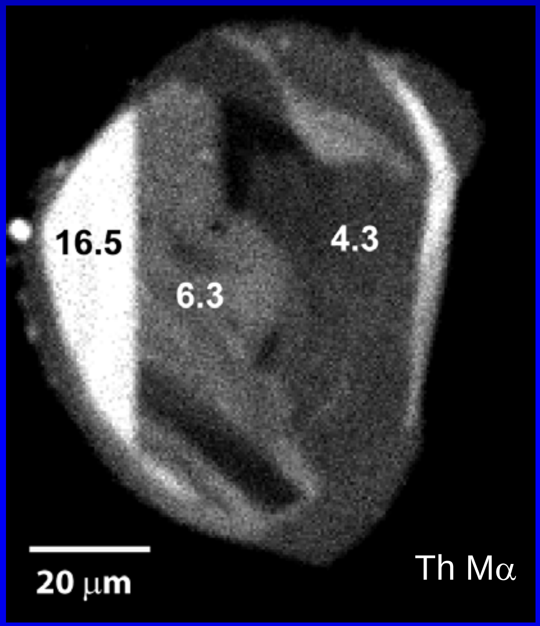

X-Ray range in monazite and K-feldspar
phase boundary
Monazite Th = 0.8 wt.%
I/I(o)
distance (µm)
La La 0.8 wt.% Th mzt
Ce La 0.8 wt.% Th mzt
Nd La 0.8 wt.% Th mzt
La La 10 wt.% Th mzt
Ce La 10 wt.% Th mzt
Nd La 10 wt.% Th mzt
La La Kspar
Ce La Kspar
Nd La Kspar
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
5
10
15
20
25



Pb (ppm)
$La_{0.30}Ce_{0.52}Nd_{0.16}PO_4$
gap
mzt
Th = 6.3 wt.%
Y = 0.94 wt%
Pb = 1500 ppm
distance (µm)



Th (ppm)
$La_{0.30}Ce_{0.52}Nd_{0.16}PO_4$
gap
mzt
Th = 6.3 wt.%
distance (µm)



16.5
6.3
4.3
20 µm
Th Mα

Quantitative analysis of complex accessory phases

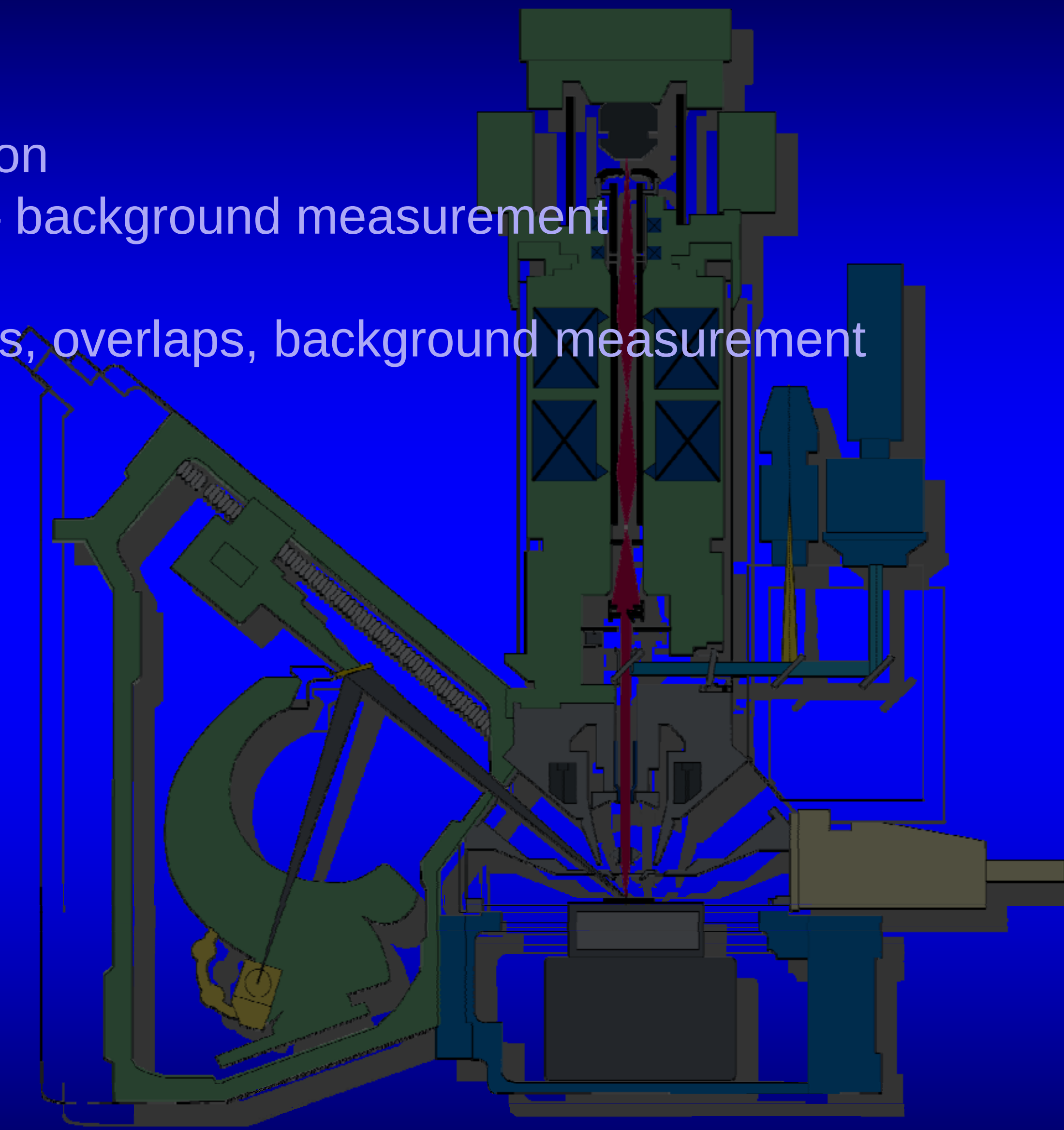
Special considerations

Analytical spatial resolution

Trace element analysis – background measurement

Heavy elements – many transitions, overlaps, background measurement

High Z



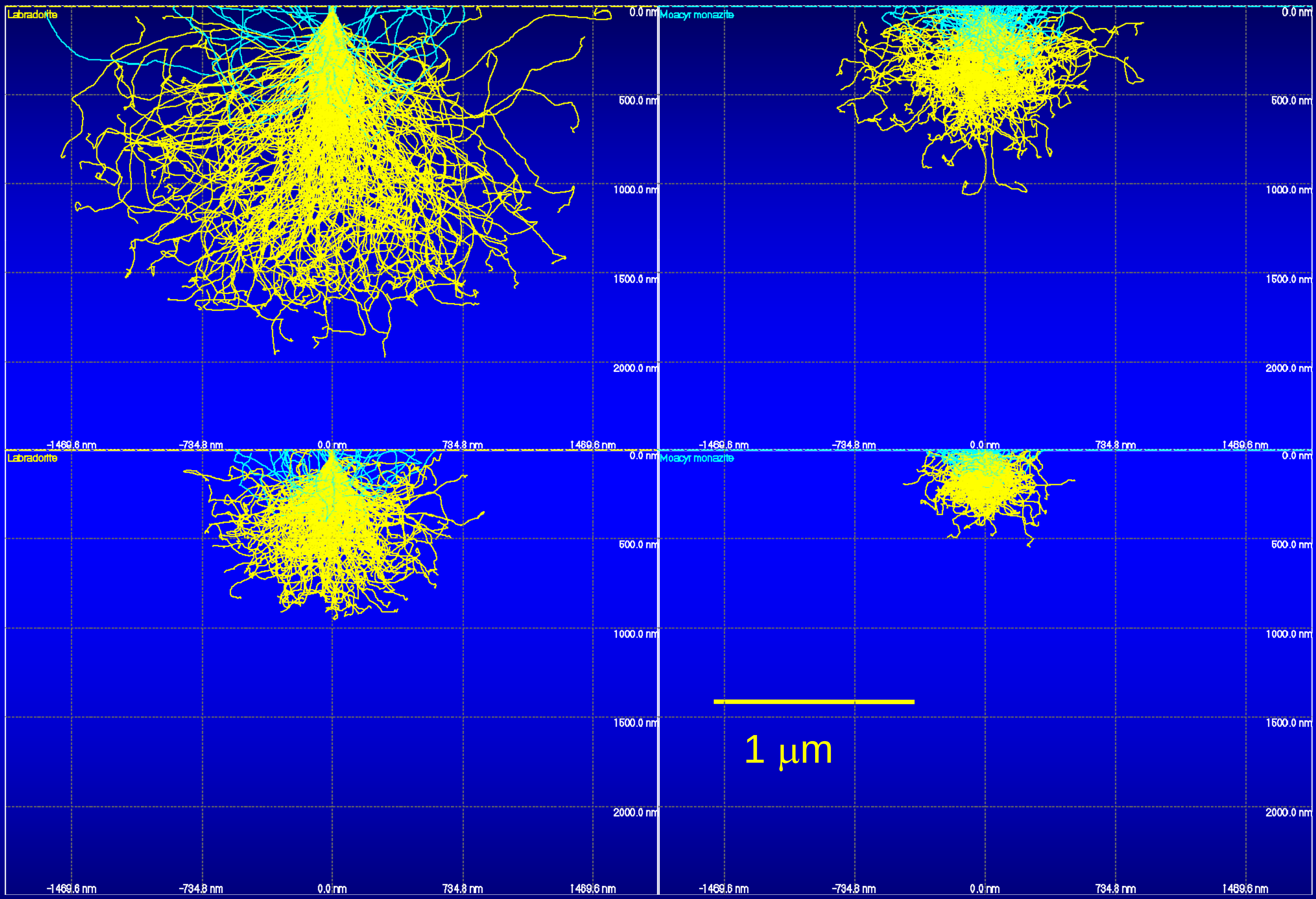
Analytical spatial resolution…

Labradorite (Z = 11)

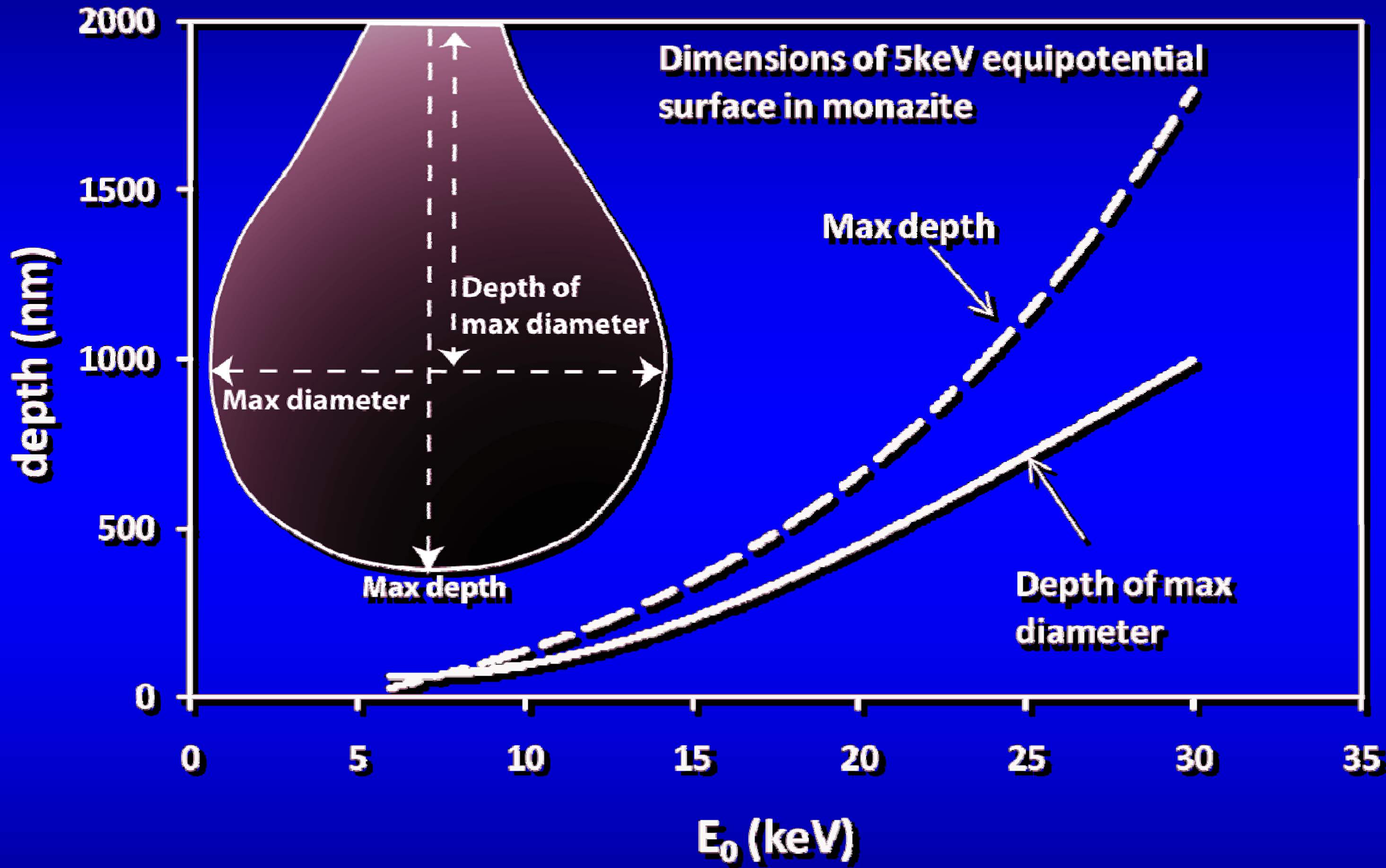
Monazite (Z = 38)

15 kV

10 kV

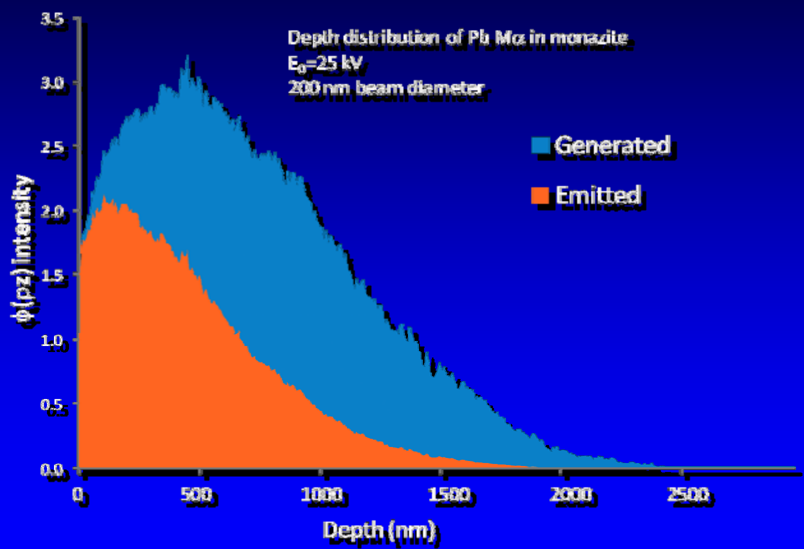


Electron trajectory modeling - Casino

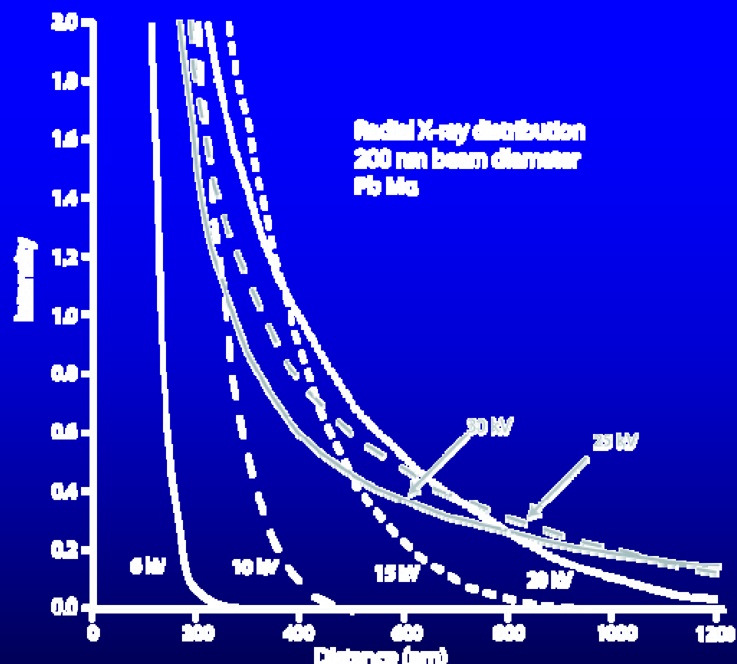


Dimensions of 5keV equipotential surface in monazite
Max depth
Depth of max diameter
Depth of
max diameter
Max diameter
Max depth
depth (nm)
2000
1500
1000
500
0
0
5
10
15
20
25
30
35
E_0 (keV)

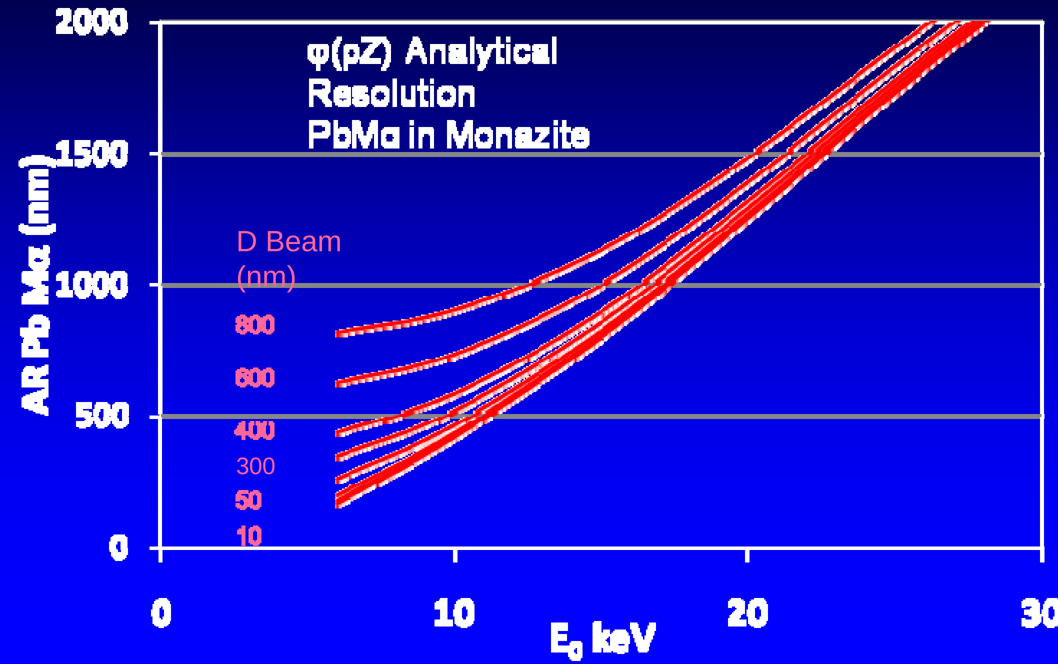
$$D_{AR} = (D_{beam}^2 + D_{scattering}^2)^{1/2}$$

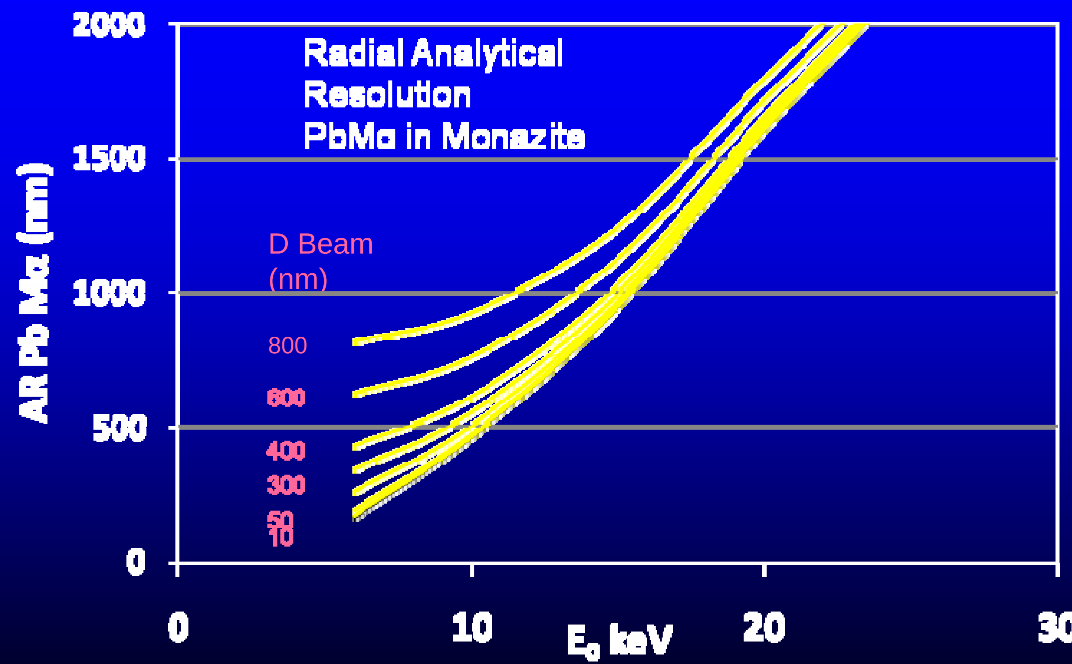


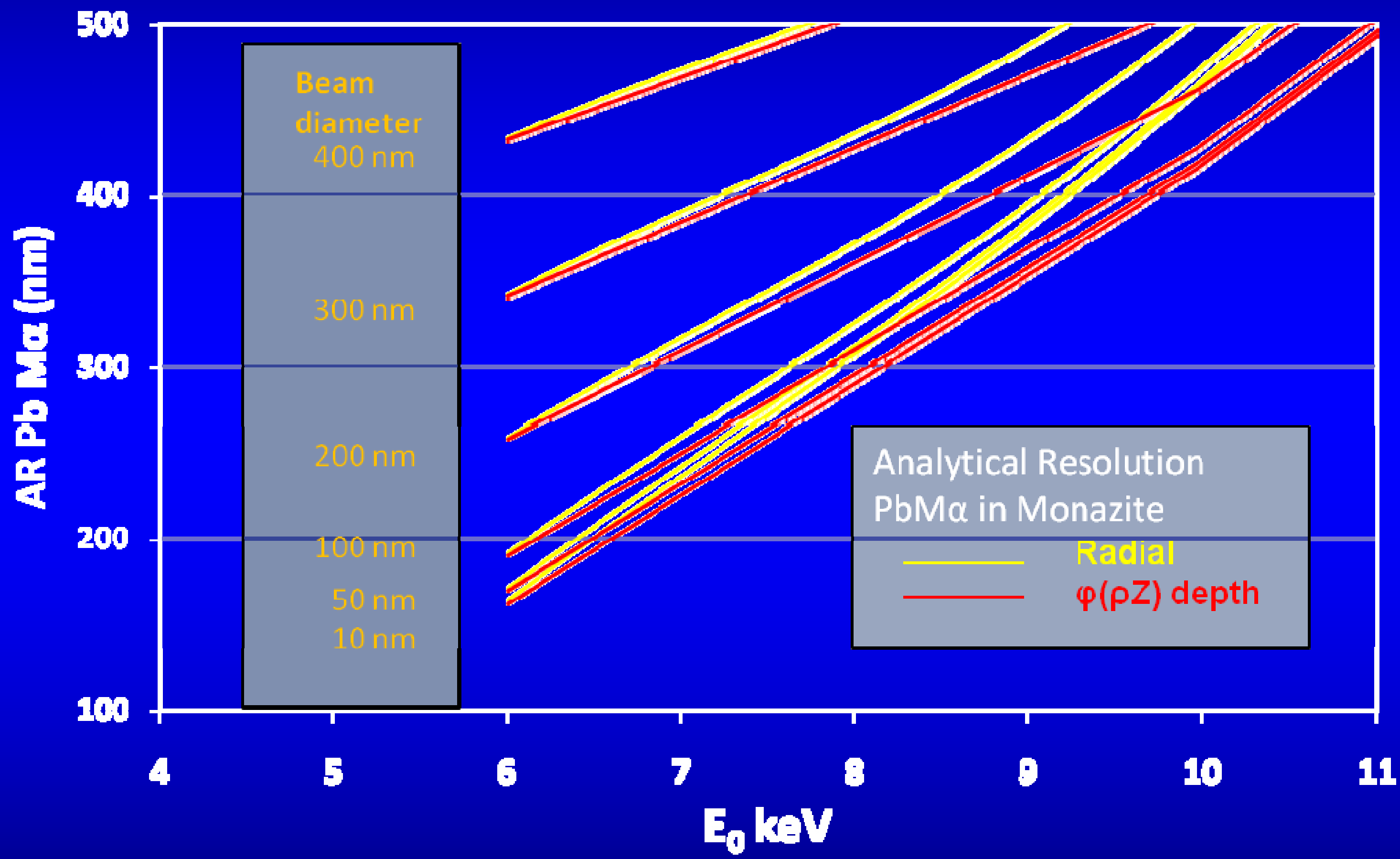
Based on depth containing 99.5% of total emitted intensity



Based on radius containing 99.5% of intensity







500
400
300
200
100
AR Pb Mα (nm)
4
5
6
7
8
9
10
11
E0 keV
Beam
diameter
400 nm
300 nm
200 nm
100 nm
50 nm
10 nm
Analytical Resolution
PbMα in Monazite
Radial
φ(ρZ) depth

Improvements in electron optics

Purpose: Large, stable current in small beam

Throughout range of voltage and current

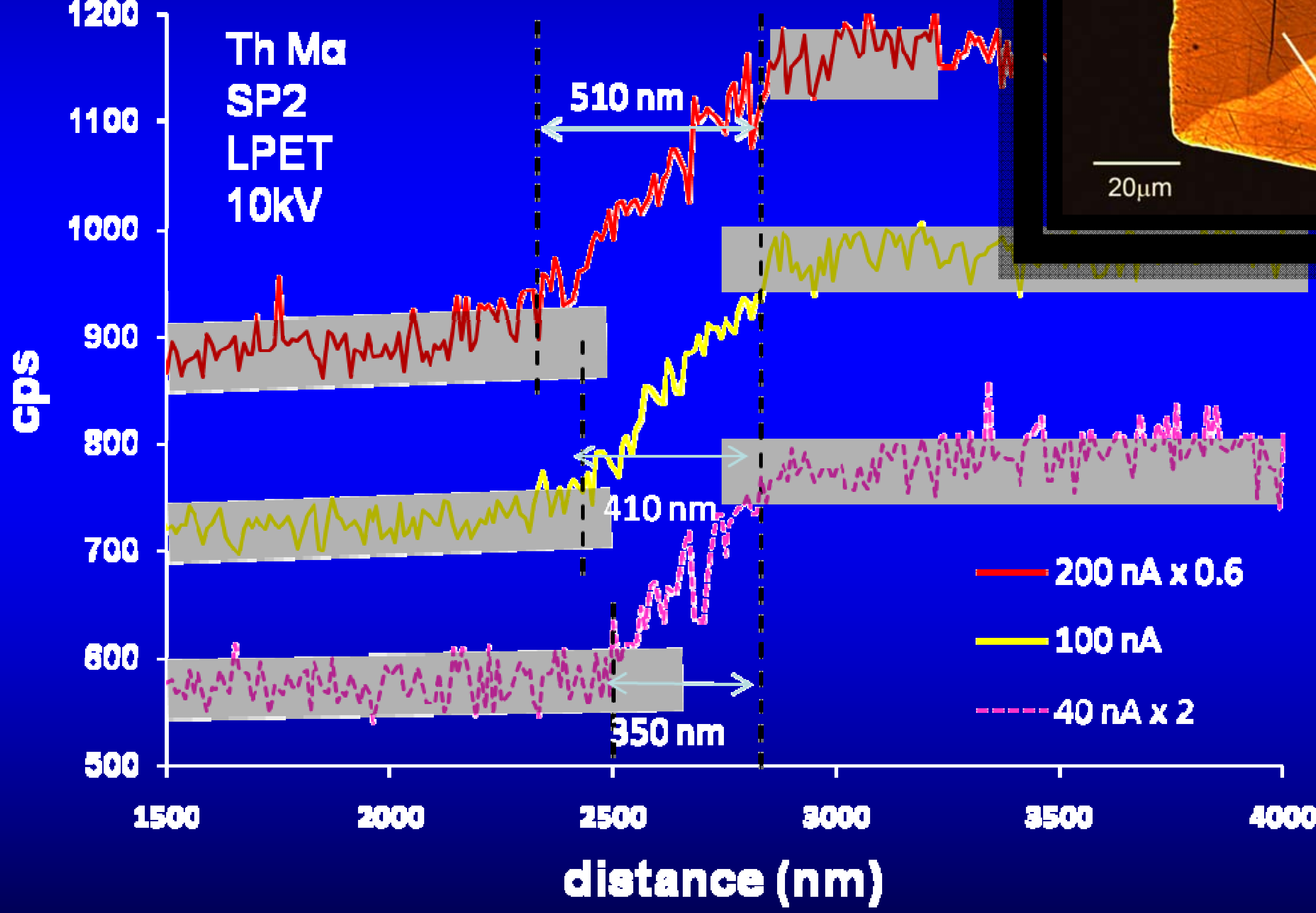
Particular attention to lower voltage, high current beam quality

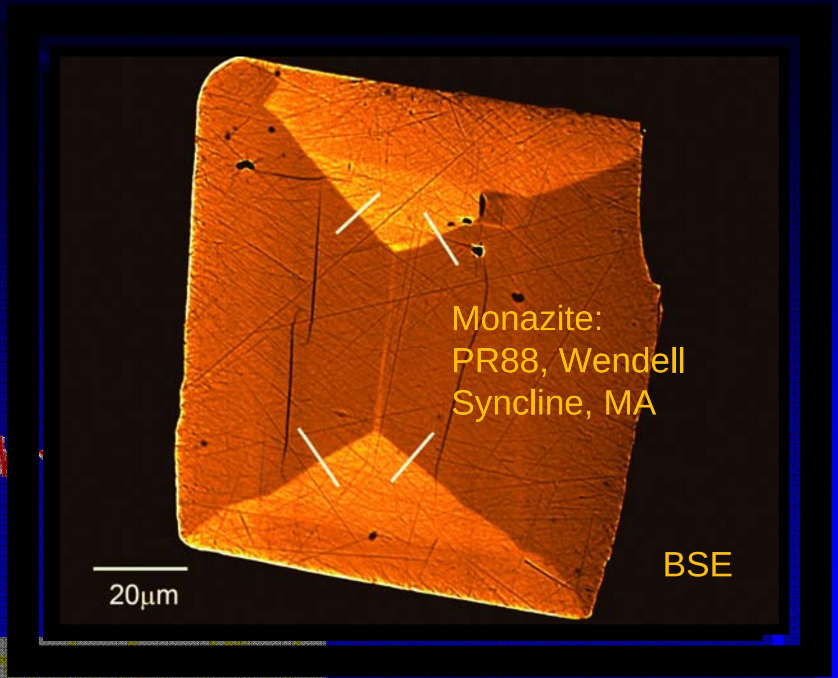
Testing theory against real monazite…

Testing analytical spatial resolution…

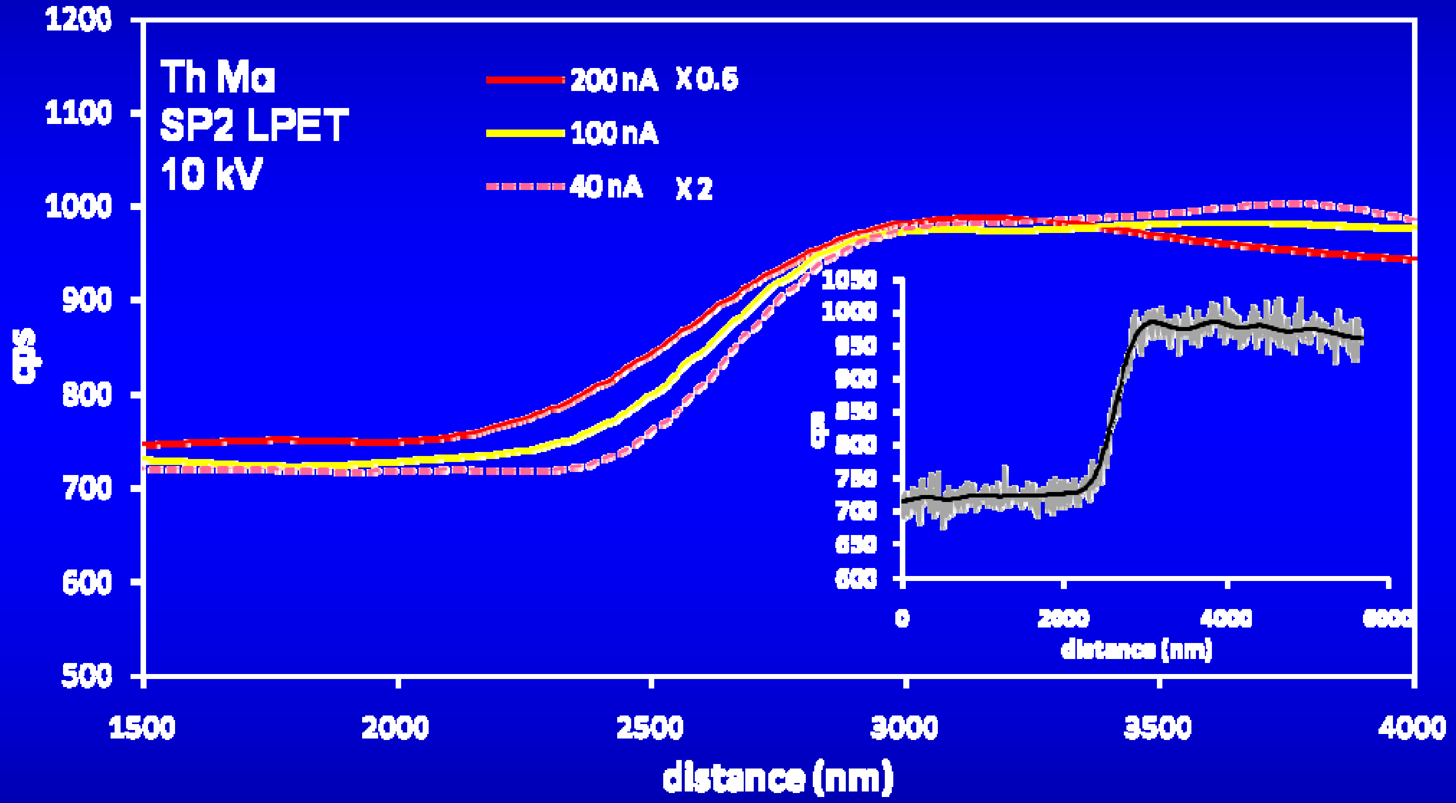
Boundary tests by beam deflection

LaB_6 ~ 3000 hrs service

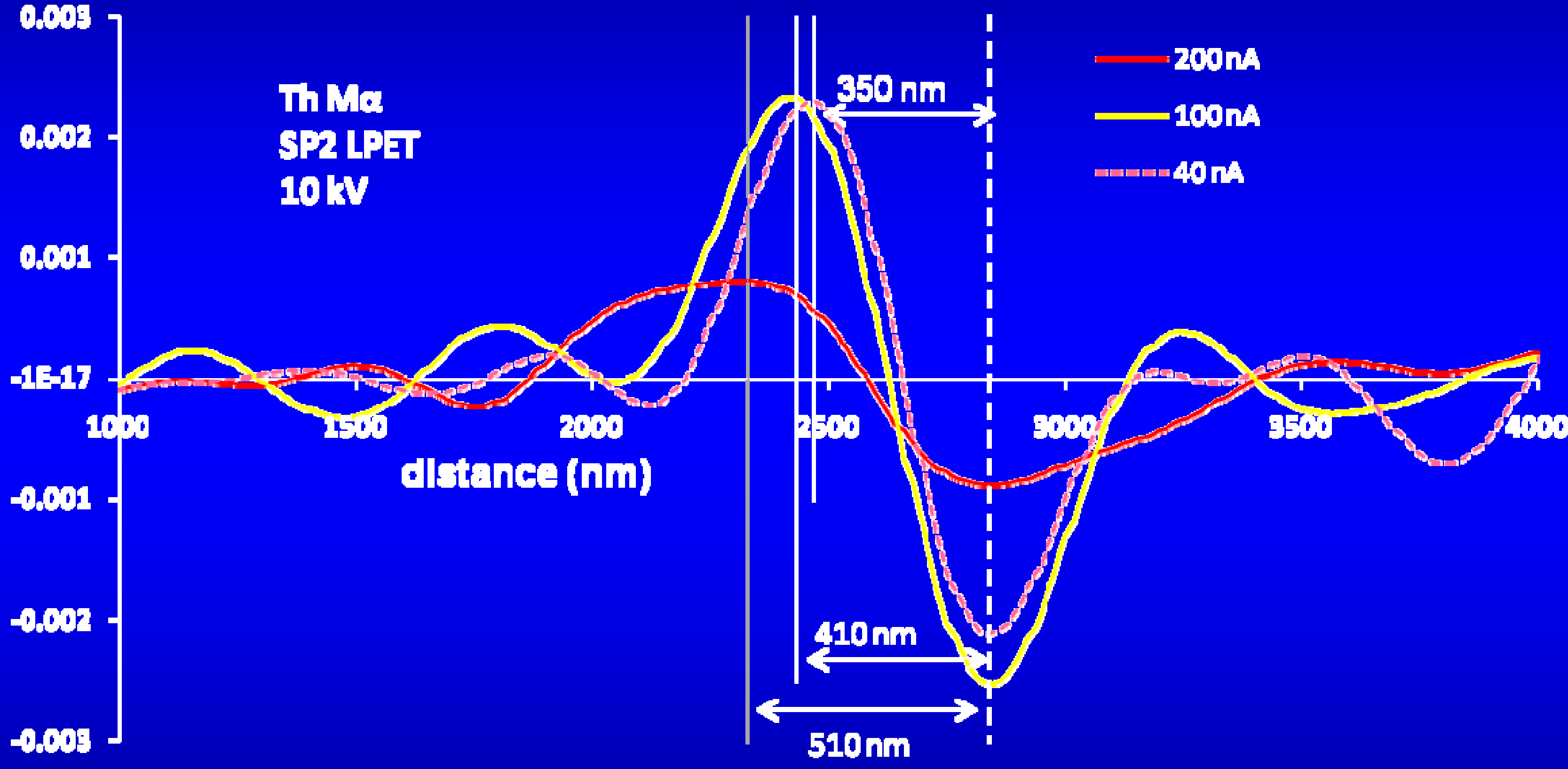




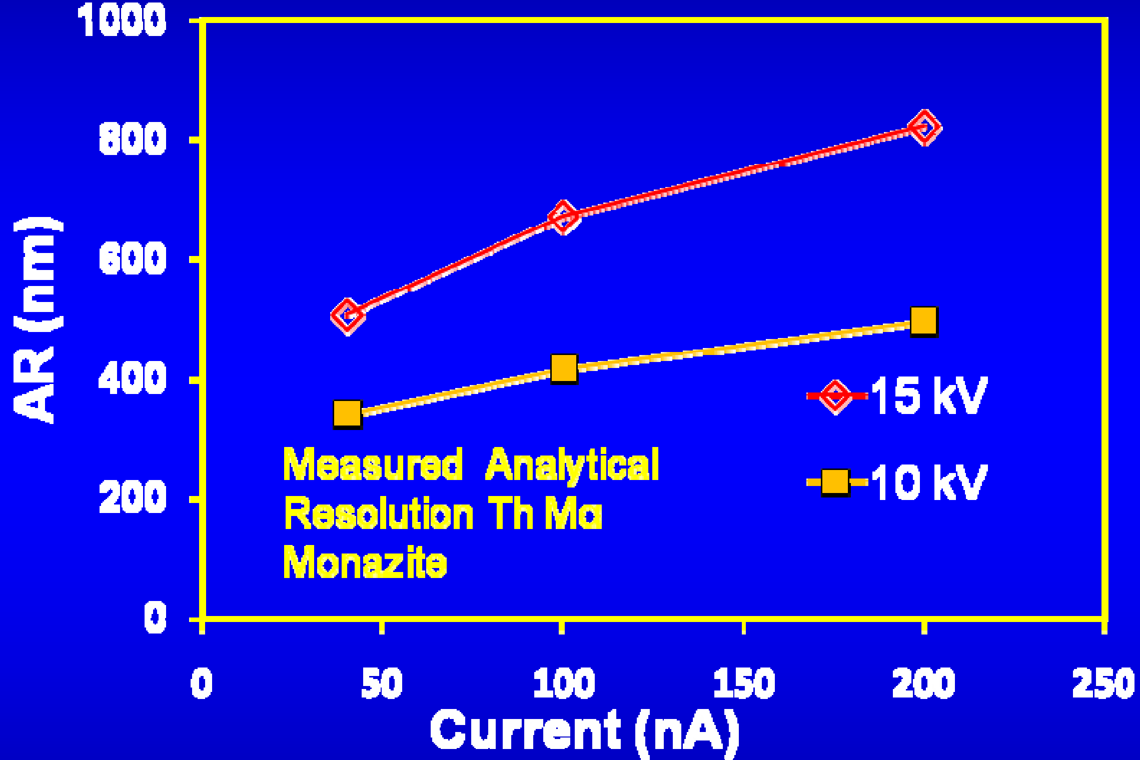
Savitsky – Golay
noise filter…

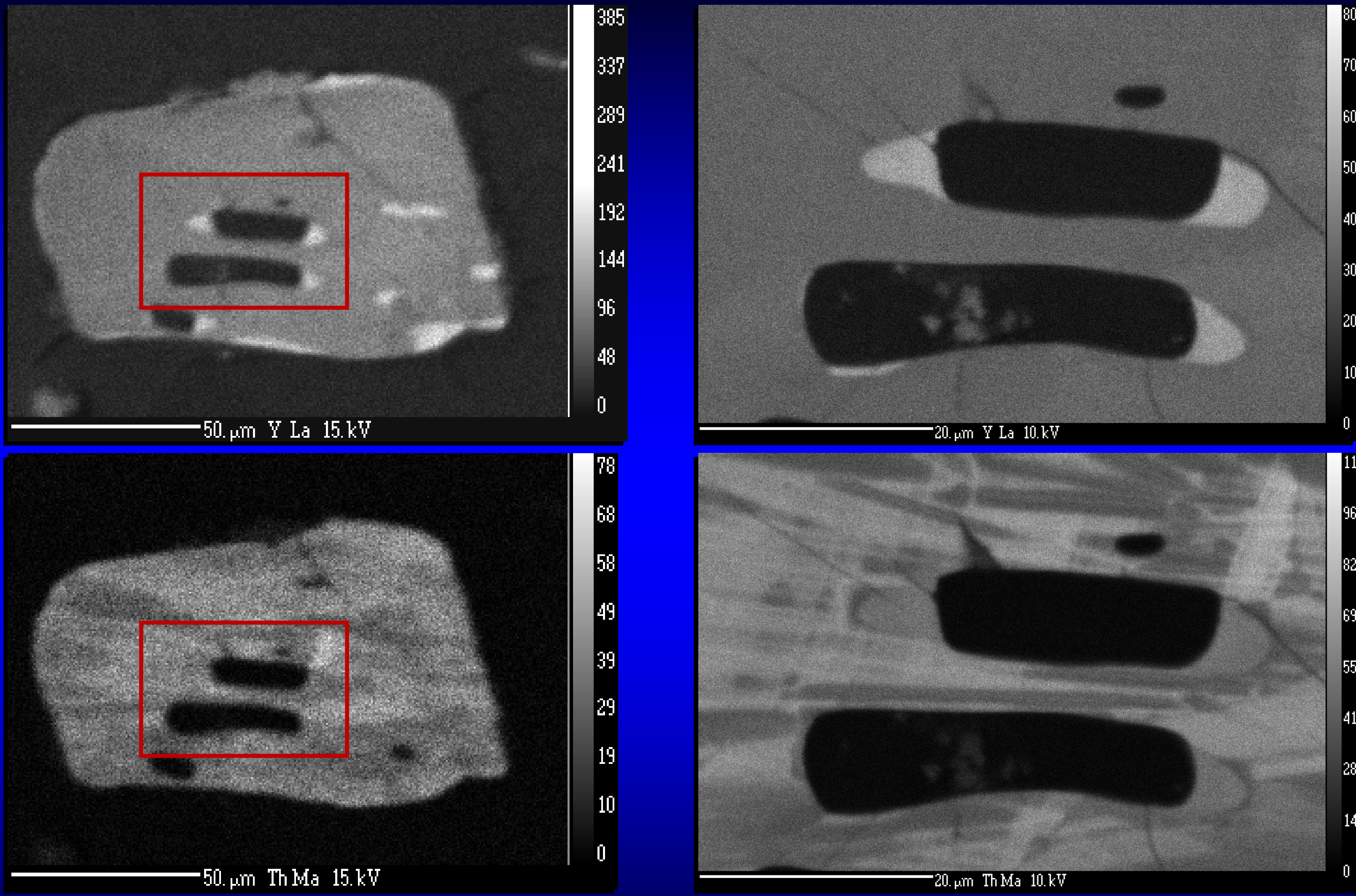


Evaluate 2nd derivative…



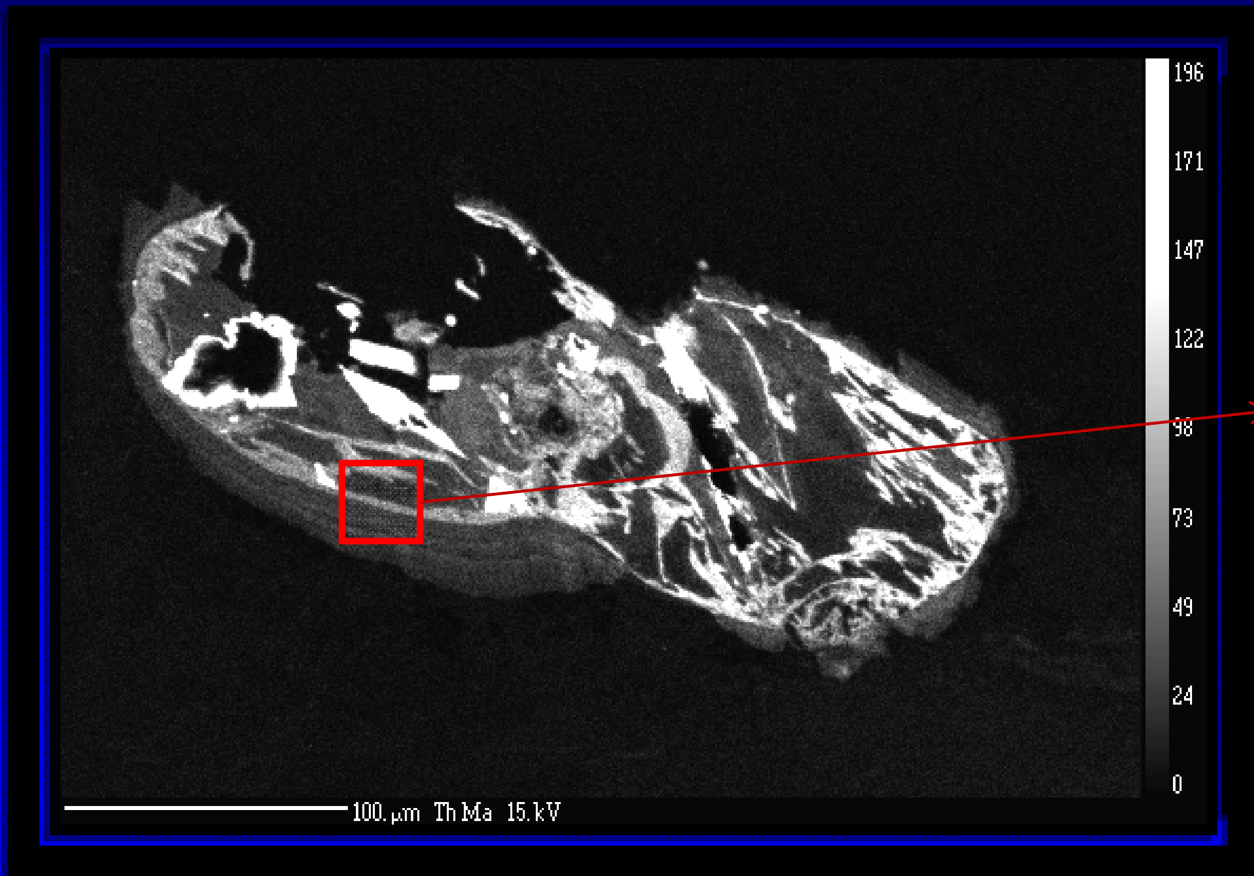
Realized analytical
spatial resolution
for Th …

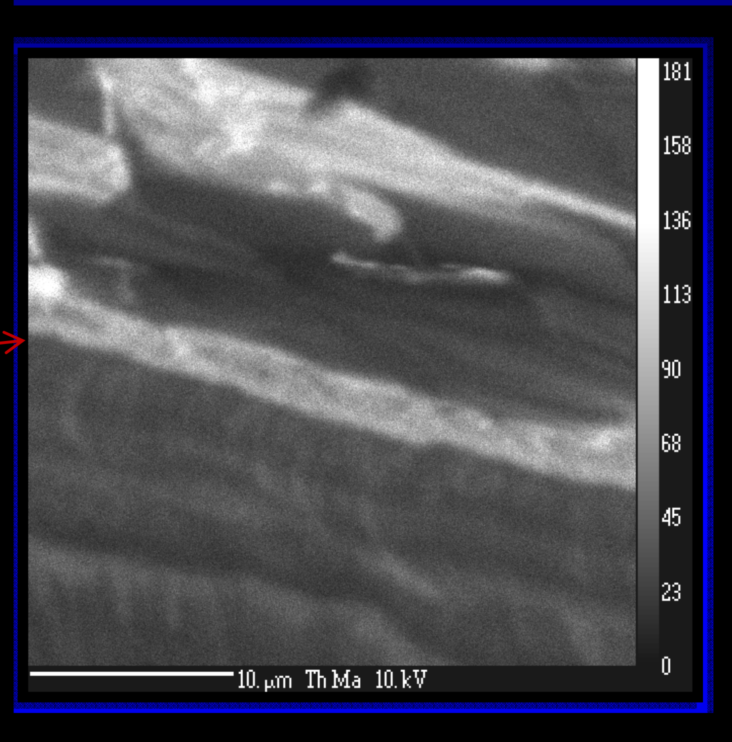




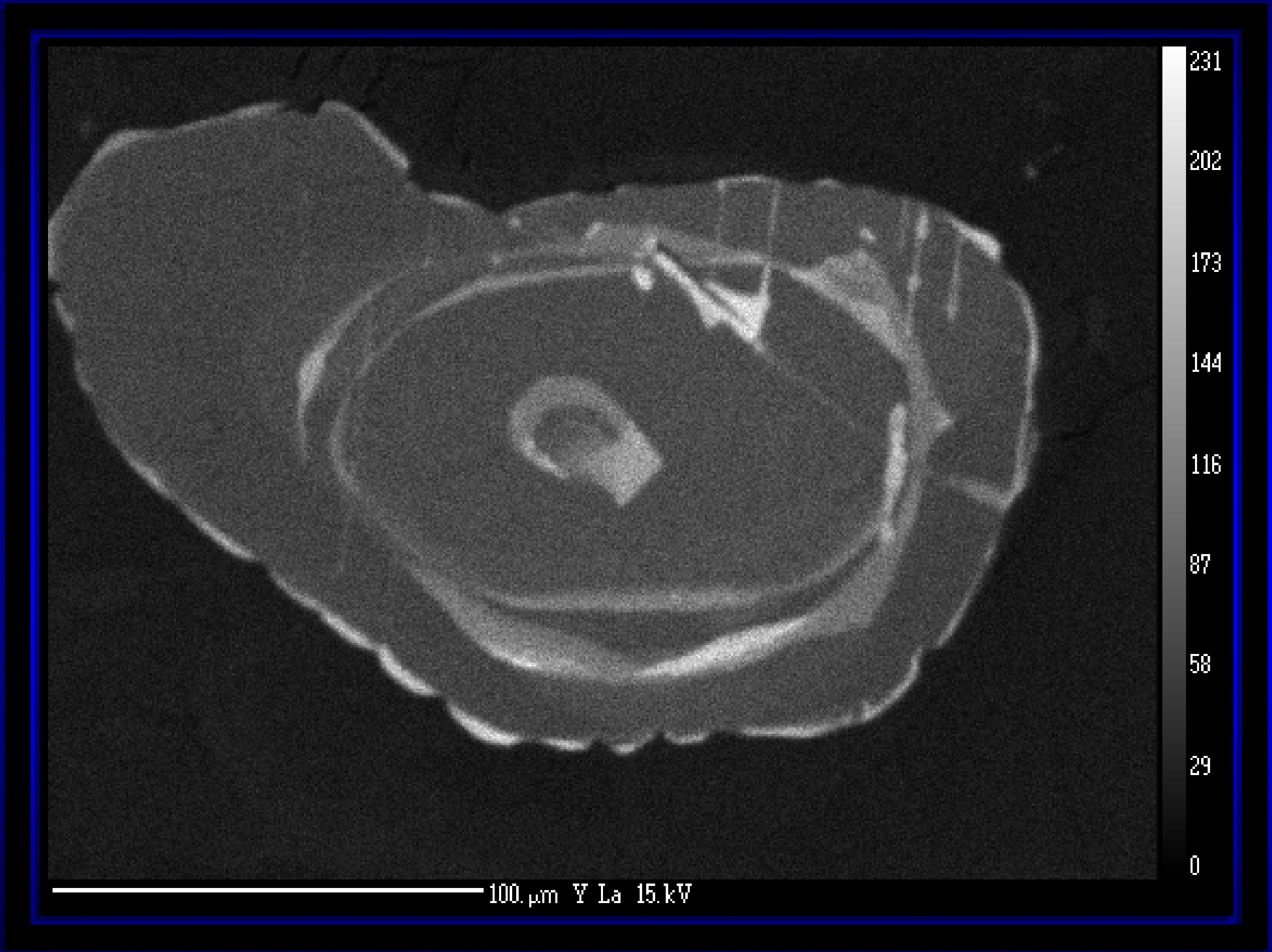
W standard column
X-Ray Mapping

LaB_6 optimized column
X-Ray Mapping


196
171
147
122
98
73
49
24
0
100. µm Th Ma 15. kV

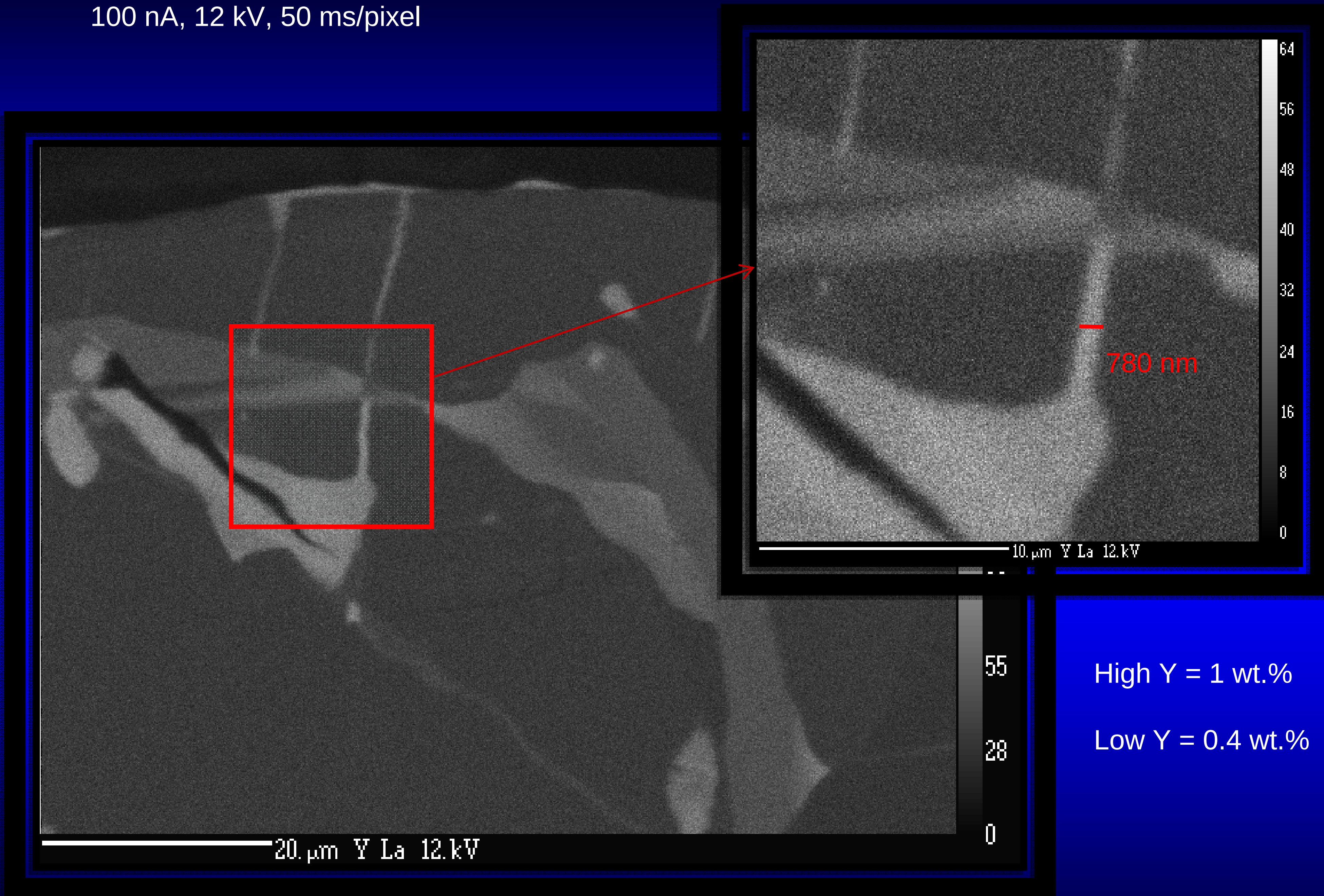

181
158
136
113
90
68
45
23
0
10. µm Th Ma 10. kV

Putting it together: High spatial resolution geochronology…*nanogeochronology*



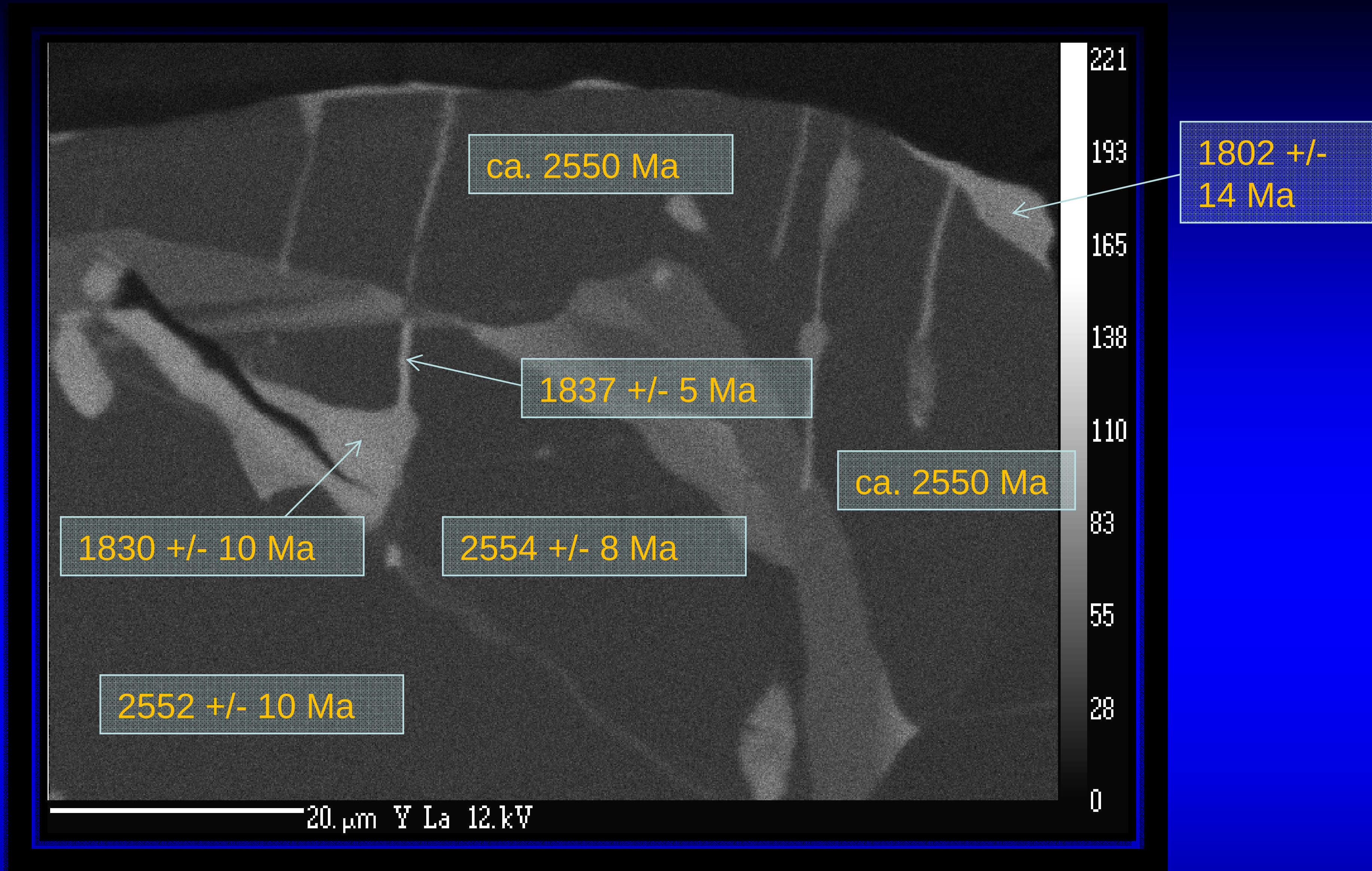
Monazite – Boothia Peninsula, northern Canada
R. Berman, GSC

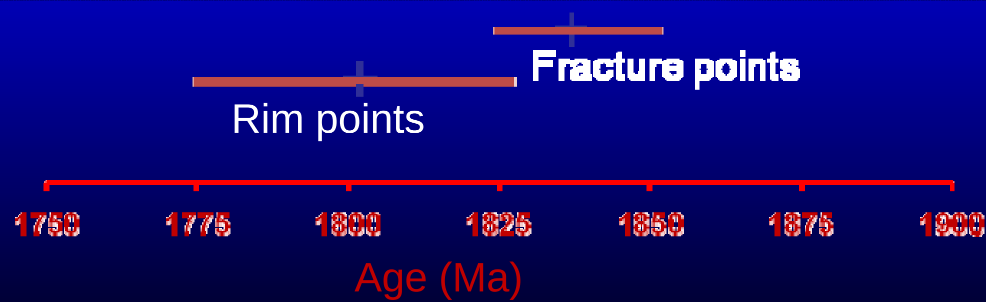
100 nA, 12 kV, 50 ms/pixel



High Y = 1 wt.%

Low Y = 0.4 wt.%


ca. 2550 Ma
1802 +/- 14 Ma
1837 +/- 5 Ma
ca. 2550 Ma
1830 +/- 10 Ma
2554 +/- 8 Ma
2552 +/- 10 Ma
221
193
165
138
110
83
55
28
0
20. μm Y La 12. kV


Fracture points
Rim points
1750
1775
1800
1825
1850
1875
1900
Age (Ma)