SAND2014-16385PE

Hyperspectral Images: Acquisition, Qualitative and Quantitative Analysis

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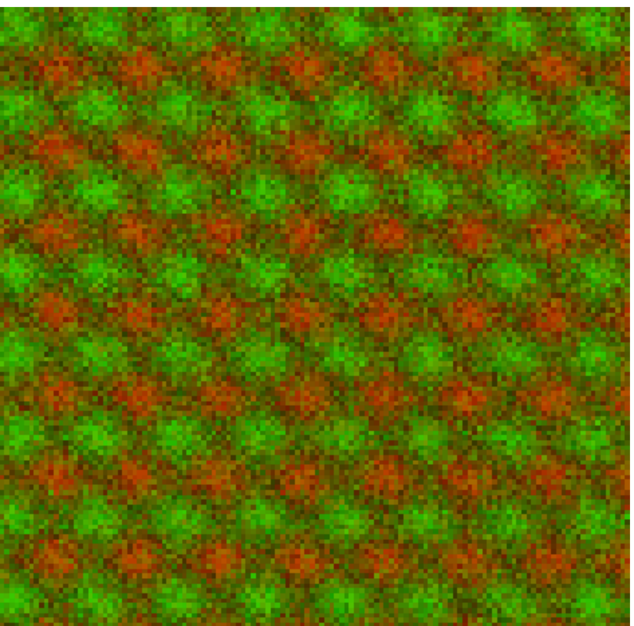

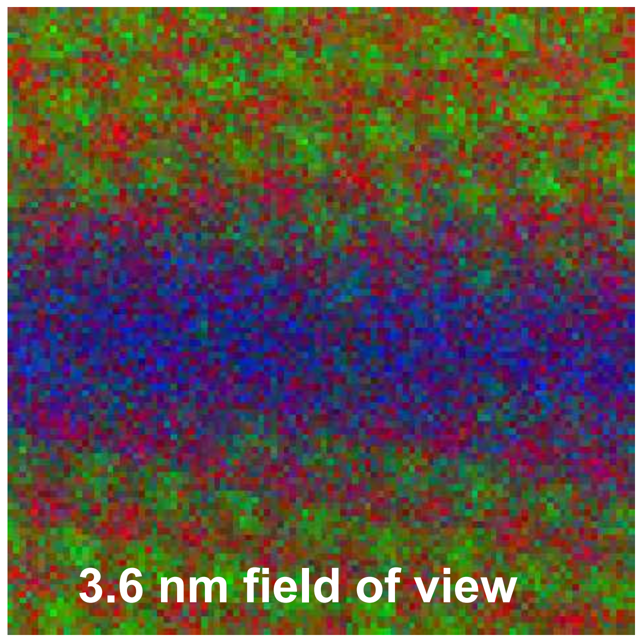

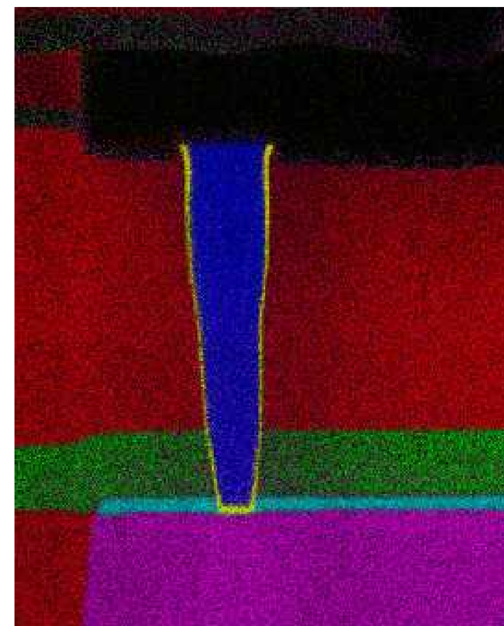

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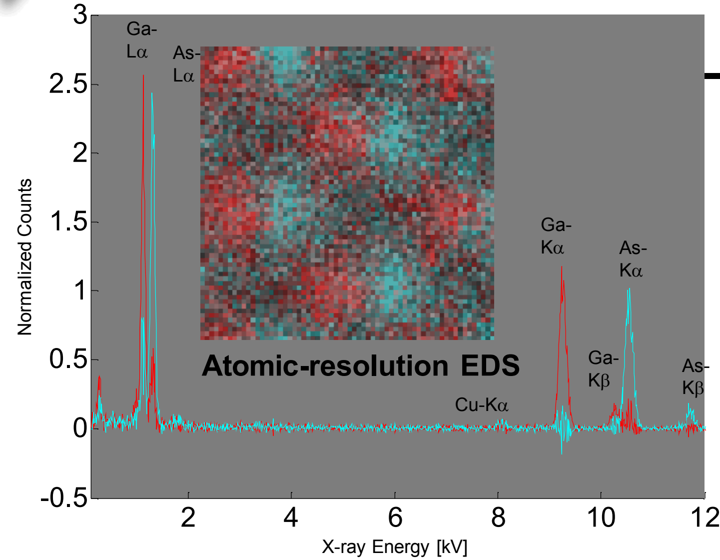
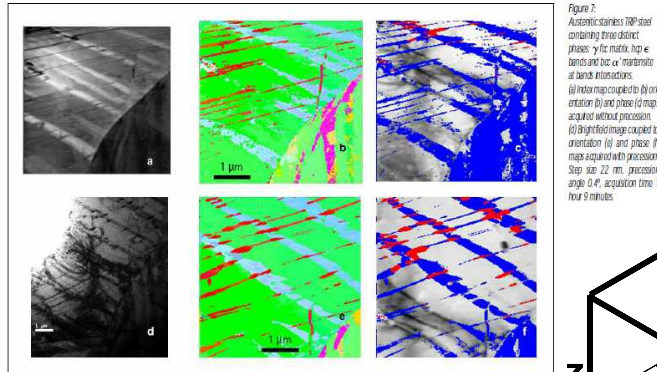
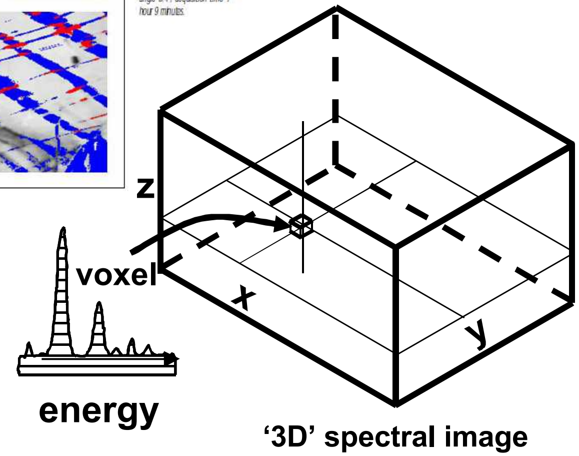
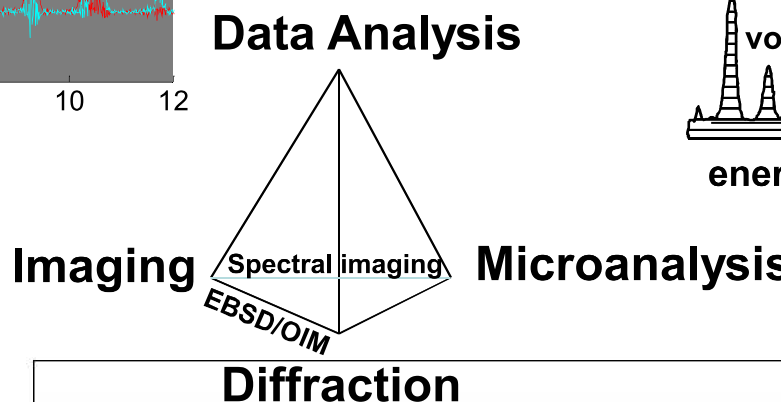
Materials Characterization Tetrahedron

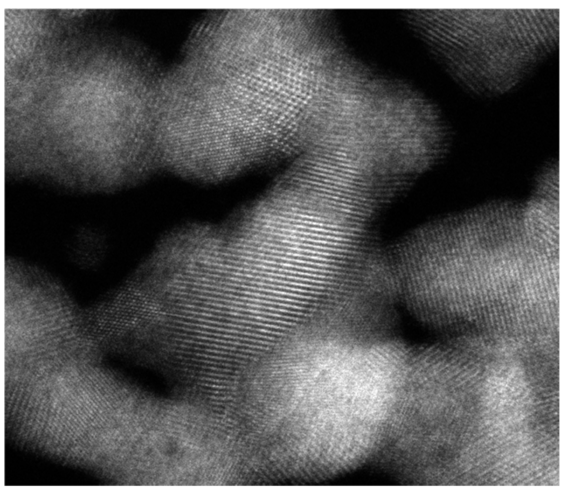




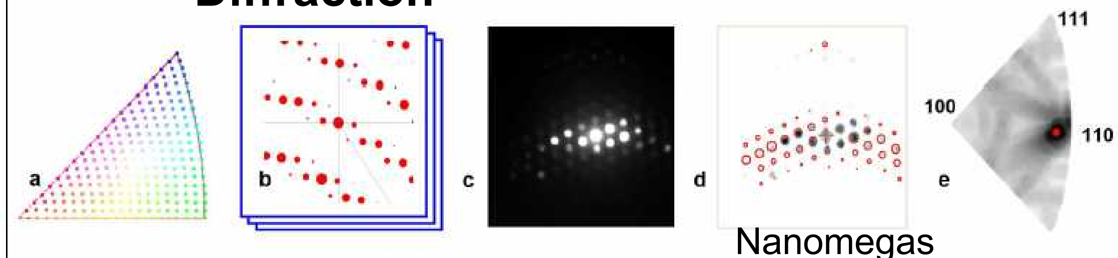
OIM in AEM







Atomic-resolution STEM image



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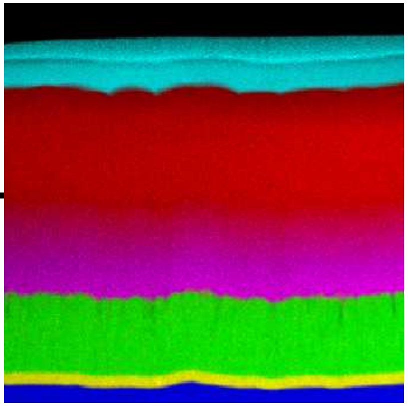
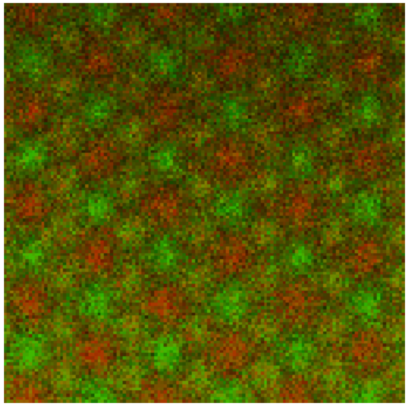
Topics



- Latest developments in instrumentation
- Spectrum imaging/data analysis
  - Spectral imaging basics
  - Multivariate statistical analysis
    - Quantitative image analysis but not quantitative compositional analysis
    - Assumptions (few) and goals (interpretability)



- Going from pretty pictures to quantitative analysis
  - Prior knowledge, assumptions, assumptions
  - Several examples

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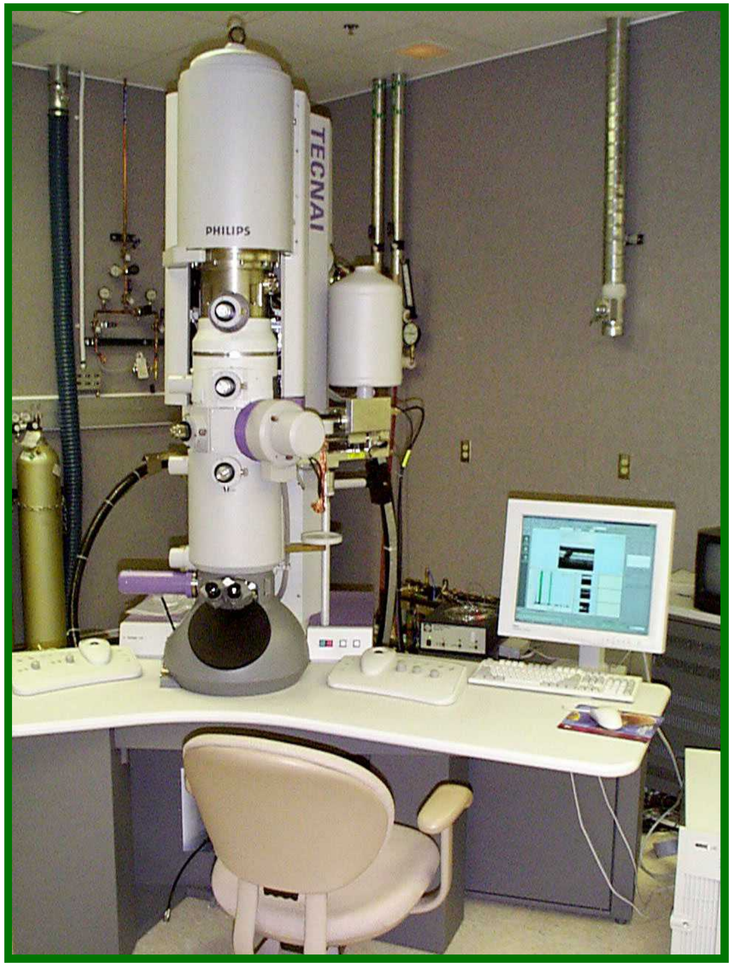
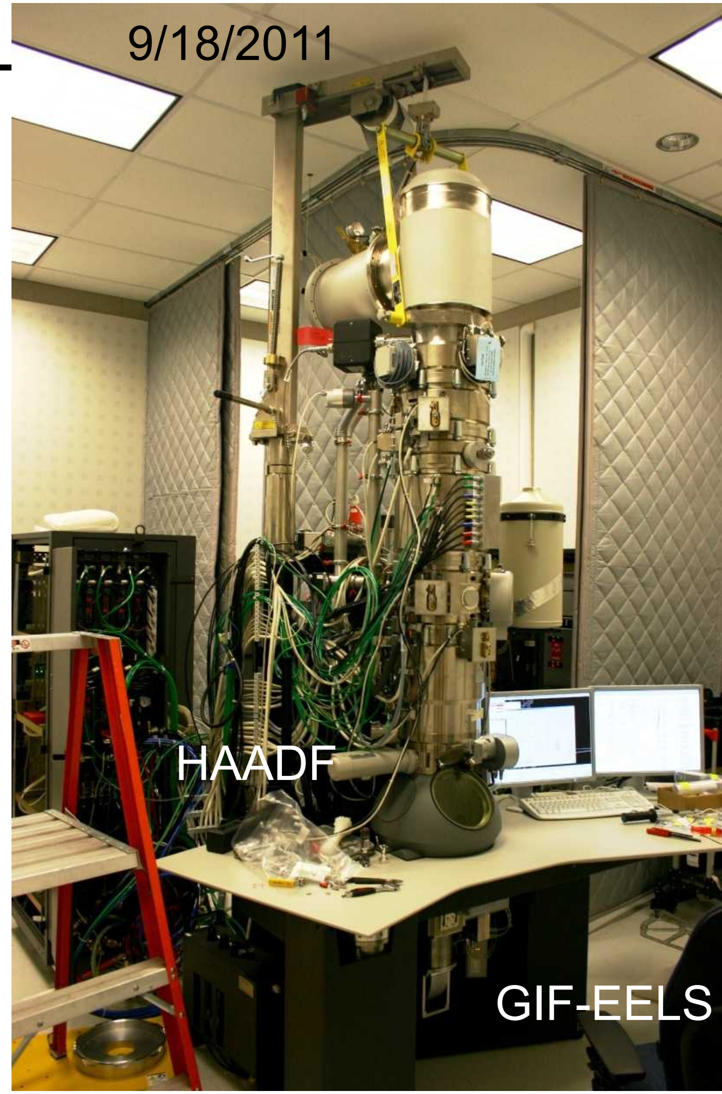
Old technology



- New in 1999
- TEM/STEM
- 300kV, field emission
- Effectively 0.06 sr EDS
- Excellent workhorse still in use today
- 1nA in 2nm FWTM probe

Titan ChemiSTEM P (G2 80-200) at Sandia



Gun

Accelerator

C1
C2
C3

-Probe corrector

-Objective lens/sample/4-SDDs

-Projector lenses

-Diffraction camera

BF, DF1, DF2
2k x 2k CCD
2k x 2k CCD

Stable room retrofitted (for lots of $$$) from CM-30 (1987) room

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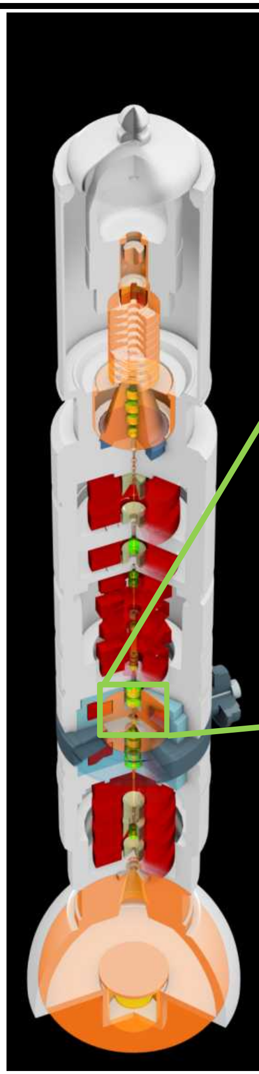
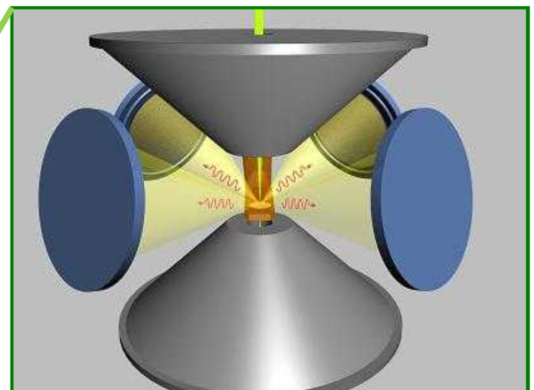
Atomic resolution x-ray microanalysis

X-FEG

DCOR
(CEOS)

Super-X





Critical elements for atomic resolution x-ray microanalysis

- High brightness gun
  - X-FEG
- Probe corrector (CEOS-DCOR)
  - 0.08nm @ 200kV
  - 0.12nm @ 80kV
- Efficient x-ray detector(s)
  - SuperX, SDD array

Analytical probe of 1.2nA in 2Å which is still a good imaging probe!

Several Titan 80-300s have gotten some of these advances

SuperX™: Large solid angle silicon drift detector array provides more flexible AEM integration

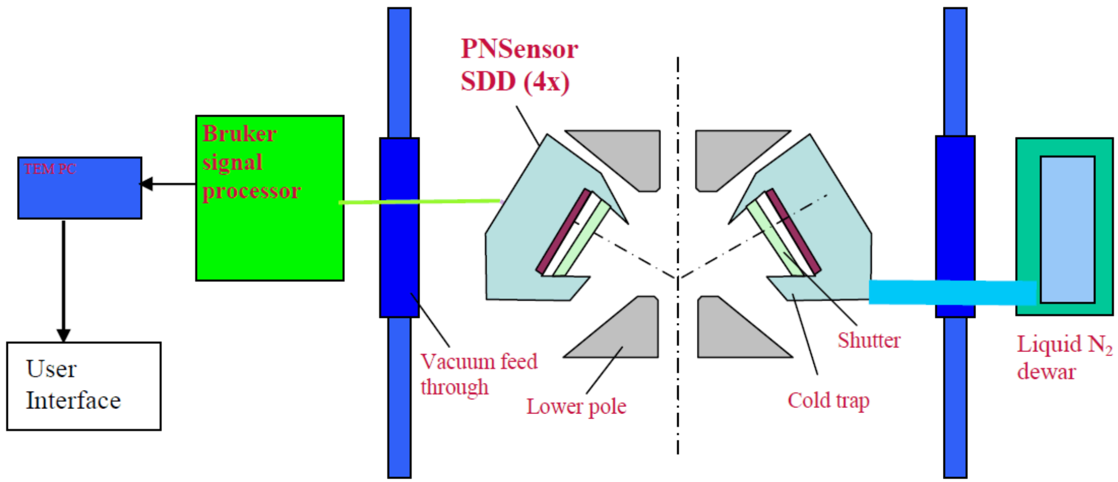
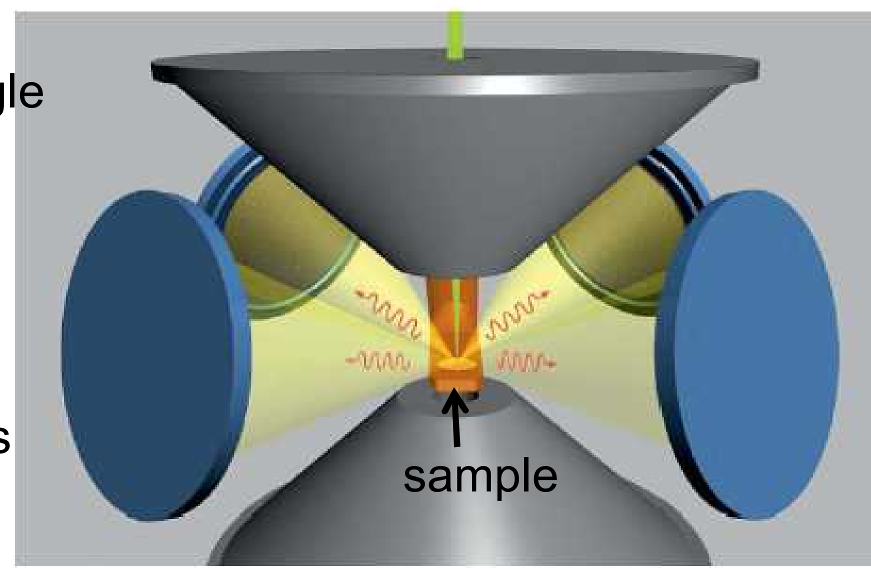


Figure 1. Schematic of Super-X detector

Conceived by FEI with collaboration from Bruker and pnSensor

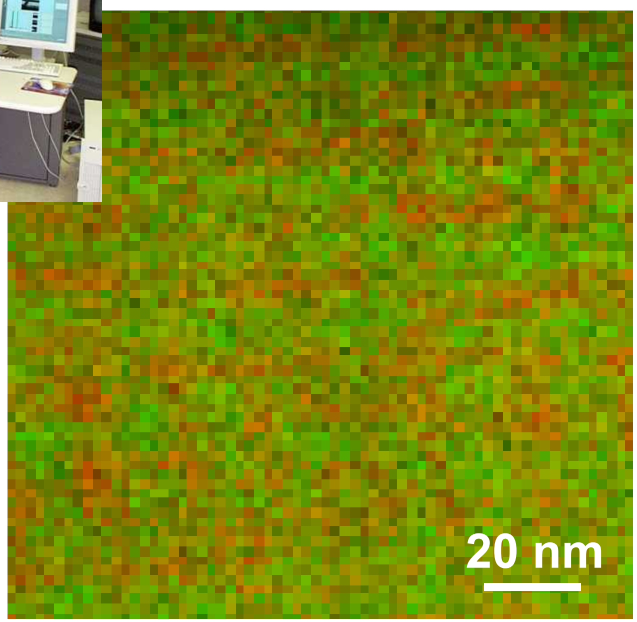
Revolutionary change in AEM-EDS

- 4-30mm^2 (120mm^2) SDDs with large solid angle
  - 0.9 sr (Osiris-uncorrected)
  - 0.7 sr (Titan-probe corrected)
  - State-of-the-art SDDs
  - Windowless & pnWindow…good light-element performance (C, N, O easily)
  - High-throughput…10 μsec instantaneous dwell times, multiple pass, drift correction



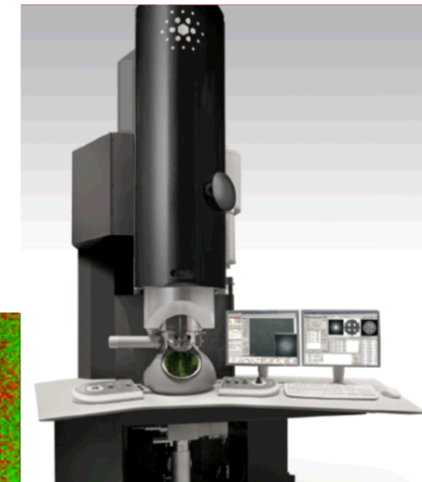
Not a fair fight really…

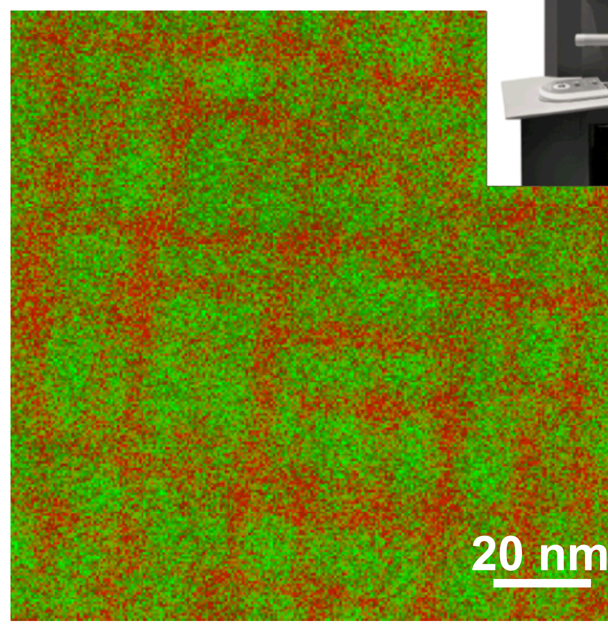
Old



120 minutes at 2nm/pixel Tecnai.

New

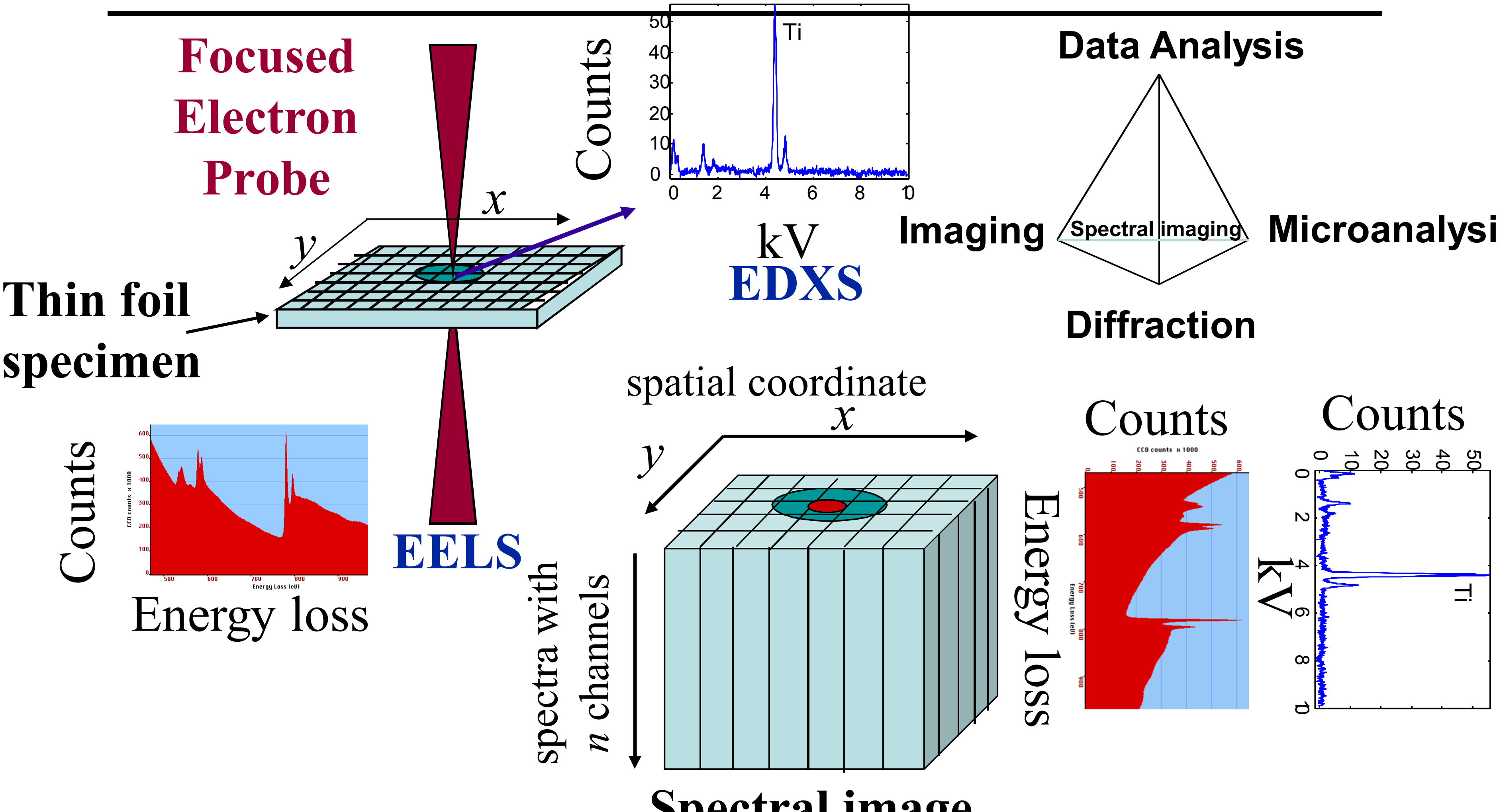




7 minutes at 0.5nm/pixel with
the Titan with ChemiSTEM

70X Improvement!

AEM Spectral Imaging



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Spectral Imaging Basics: Different ways to collect the x-ray data

- Single-pass (DigiScan-Gatan and TIA-FEI)
  – Drift correct periodically
  – All your dose to the sample one point at a time
  – Still around because of slow readout of EELS
  – Typically store everything…even zeros
- Multiple Pass (All the EDS vendors)
  – First done in 1979 in AU, for EDS by PGT in 1995
  – Event streaming/position tagged spectrometry
  – Scan the same area with 10 μsec or longer instantaneous dwell. Drift correct if needed and then scan the same area.
  – Store only the events

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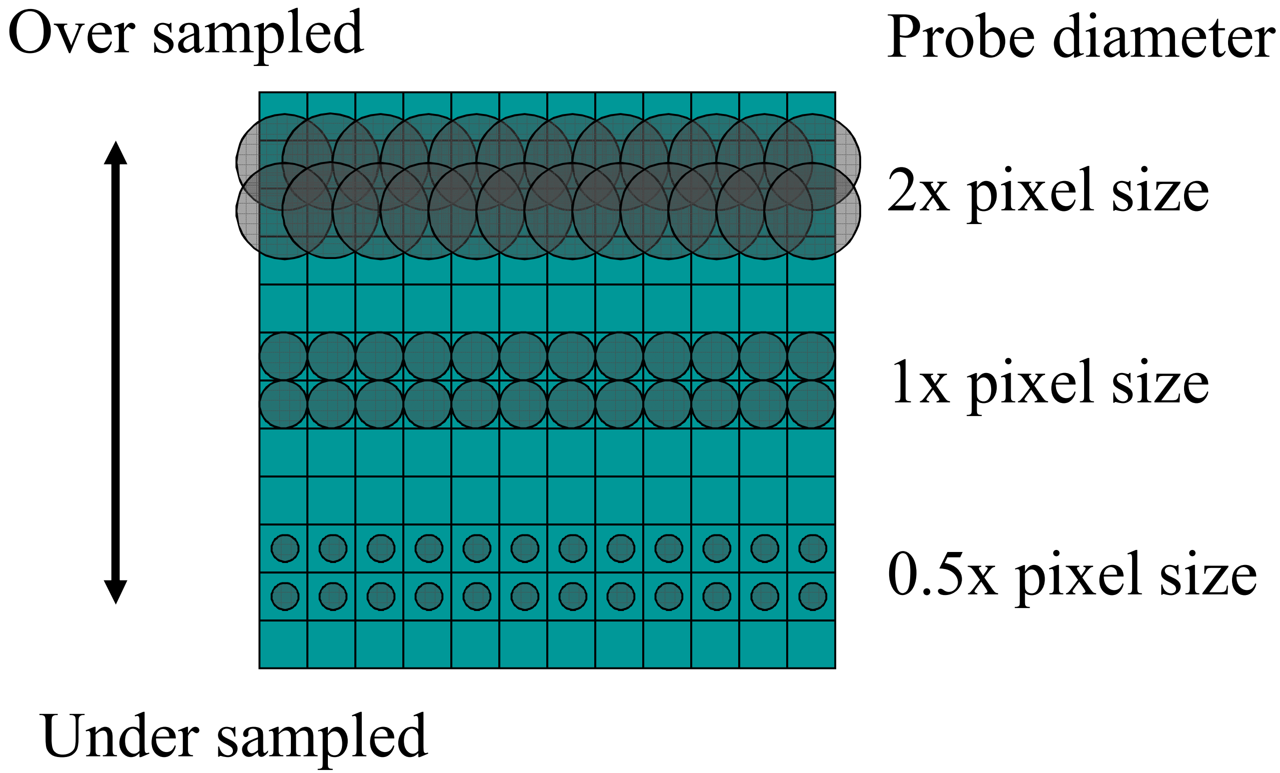
Spectral Imaging Basics: Probe vs. Pixel size



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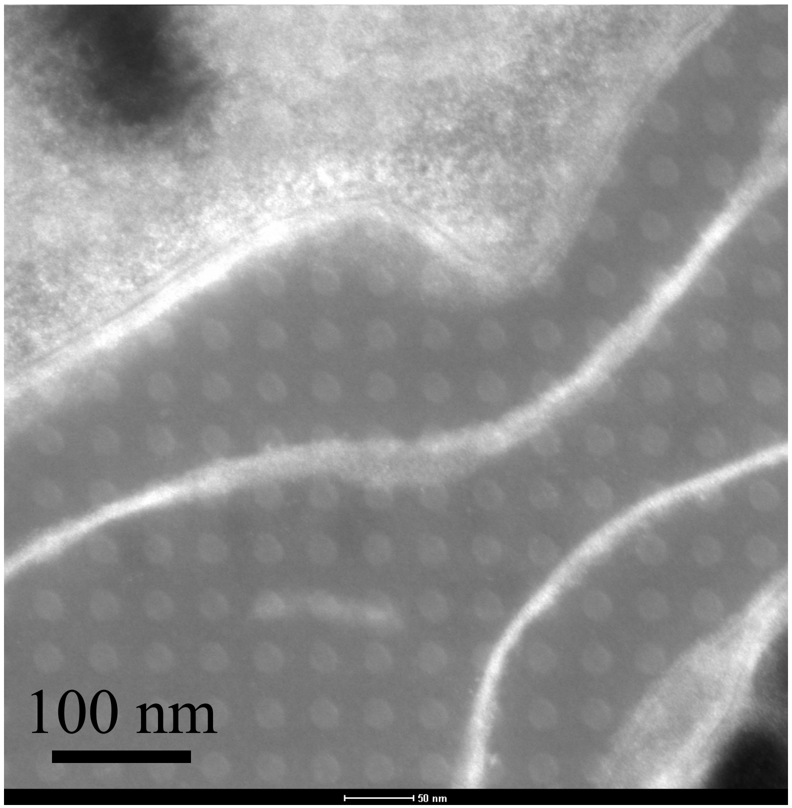
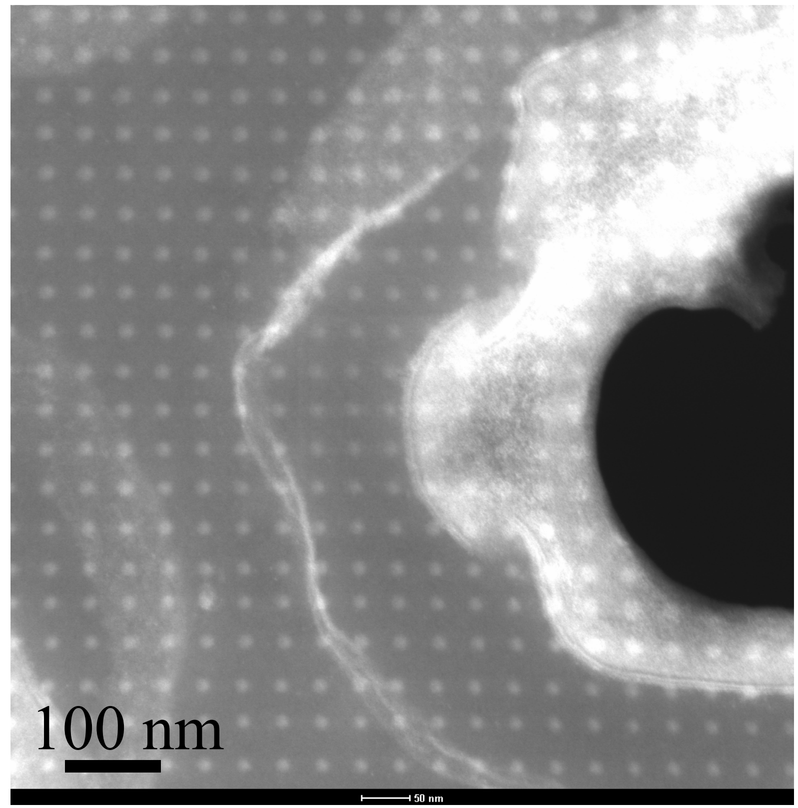
Spectral Imaging Basics: Probe vs. Pixel size



20 nm probe (defocused) with a 35 nm spacing



10 nm probe with a 40 nm spacing

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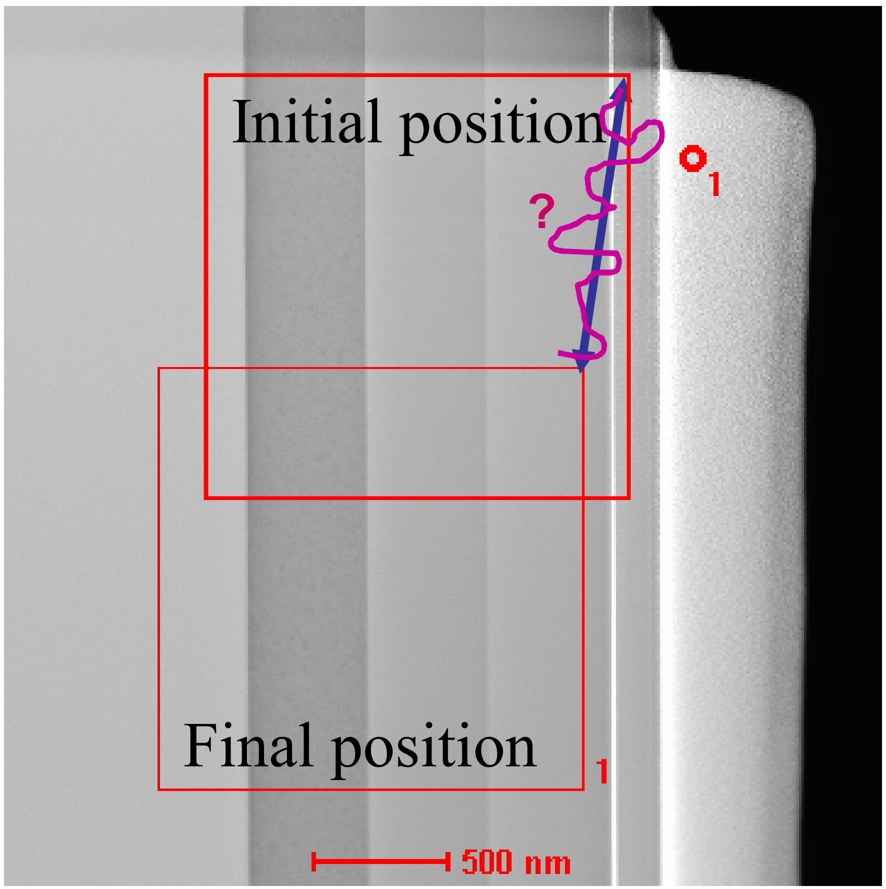
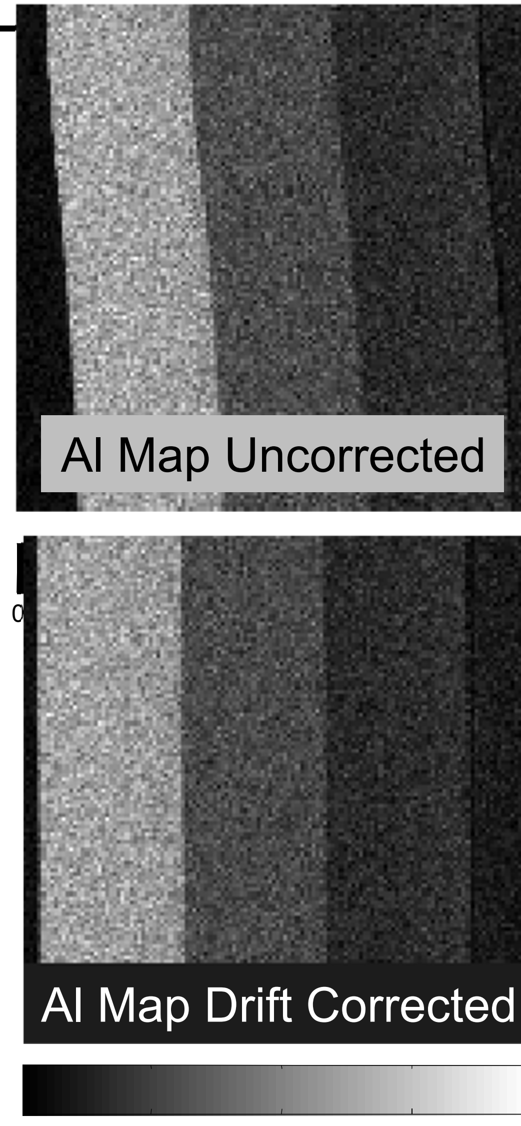
Spectral Imaging Basics: Drift Correction





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Spectral Imaging Basics: How much data to acquire?

- The probe has enough current and is the right size
- Set up STEM, look at count rate in different areas
  - Low dead time, <10%
  - Counts are more important than resolution
    - For Si(Li)…not an issue for SDDs anymore
    - Aim for 100 counts per spectrum (good rule of thumb)
    - Under-sampling is OK…saves time

Total per-pixel dwell time = ***Number of frames*** X ***Instantaneous dwell time***

Count rate X ***Total per-pixel dwell time*** = **100 counts**

Spectral Imaging Basics: Acquisition example

- Probe producing 5 kcps
- 500 x 500 pixels (250,000 pixels total)
- 40 μsec dwell per pixel per frame
- How long to get 100 counts/pixel?

  100 counts ÷ 5,000 counts/sec = 20 msec

  (500 frames @ 40 μsec/pixel/frame)
- How long* will this data set take to acquire?

  250,000 pixels X 20 msec/pixel = 5,000 sec (1.4 h)

* Doesn't include drift correction overhead

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Spectral Image Analysis

- Conventional processing
  - Maps (beware pathological overlaps/background)
  - Spectra summed from "regions of interest"
- Advanced processing…goal is interpretability
  - Multivariate statistical analysis (minimal expectations…self modeling methods)
  - Clustering, etc. (Expectation of how many clusters)
- Quantitative elemental analysis…yes but how much Ti is in that phase
  - Addition of detailed knowledge, use of standards (for k-factors), peak reference shapes

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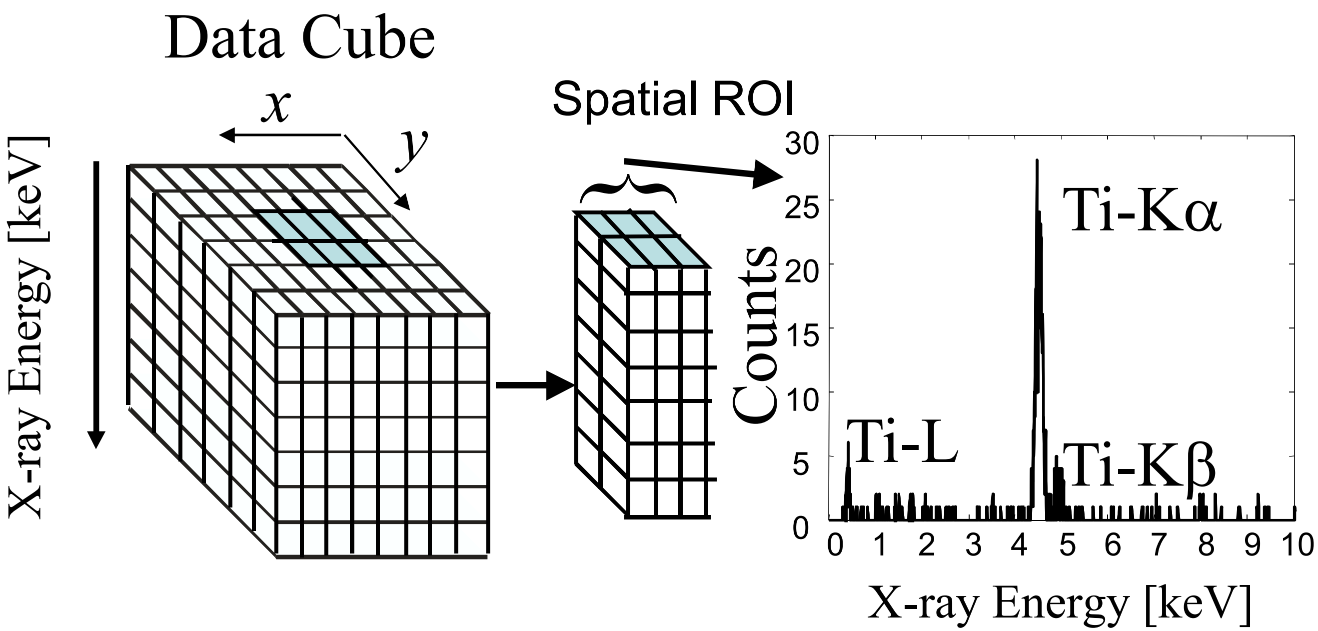
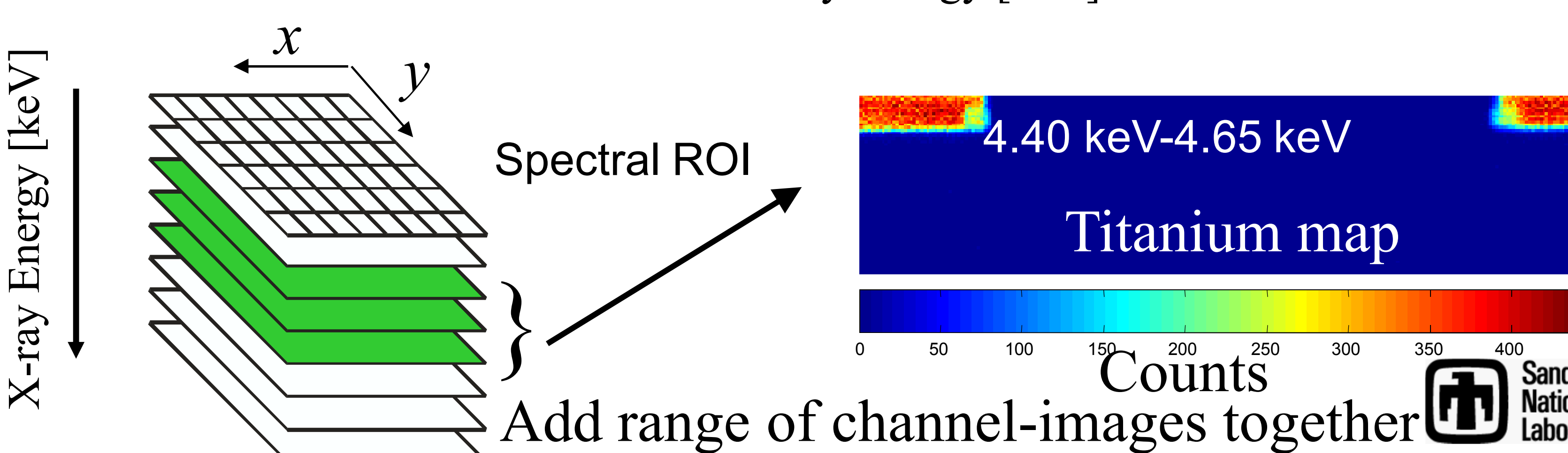
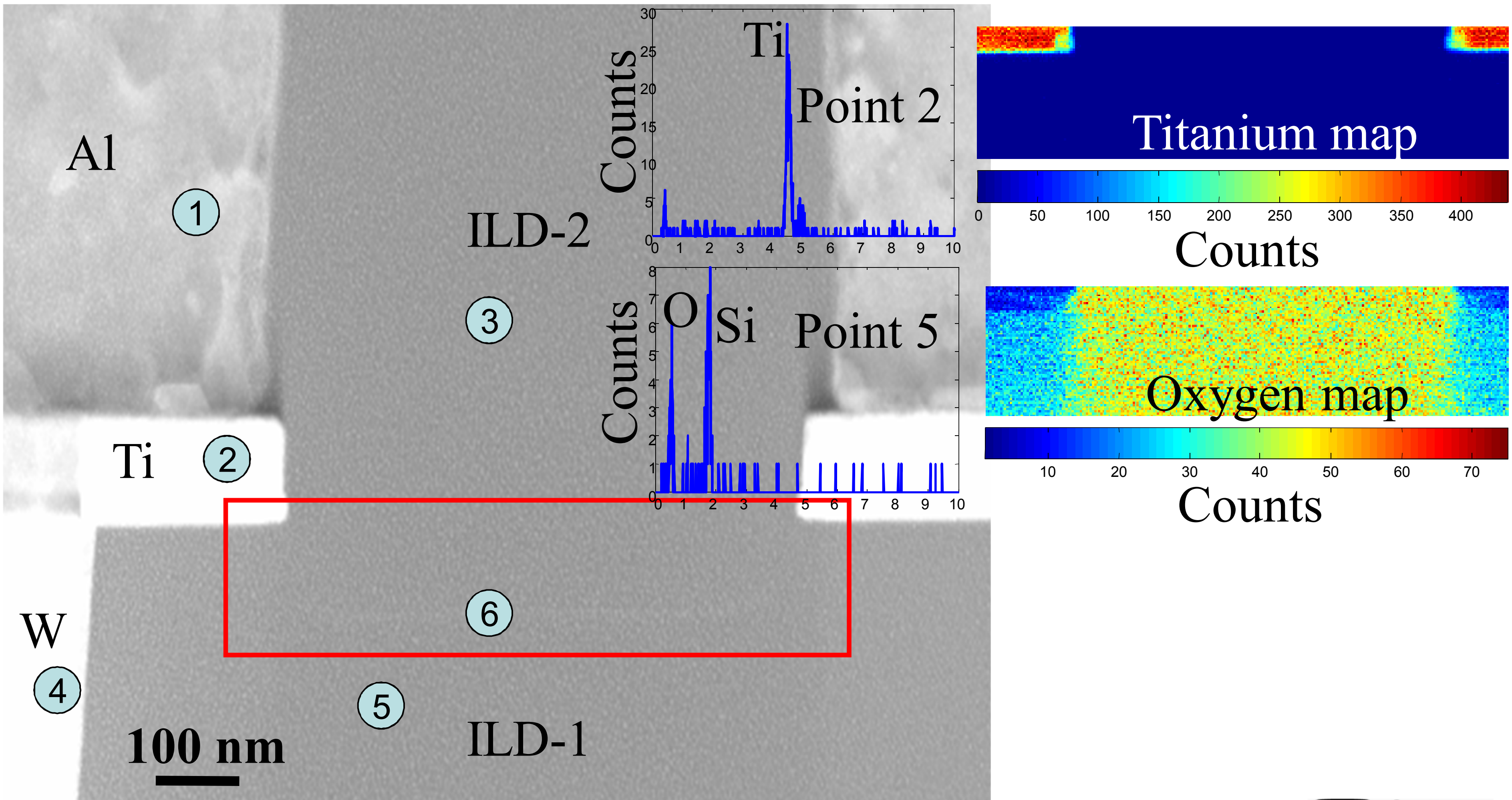
P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

Conventional Data Analysis





Example of Conventional Analysis



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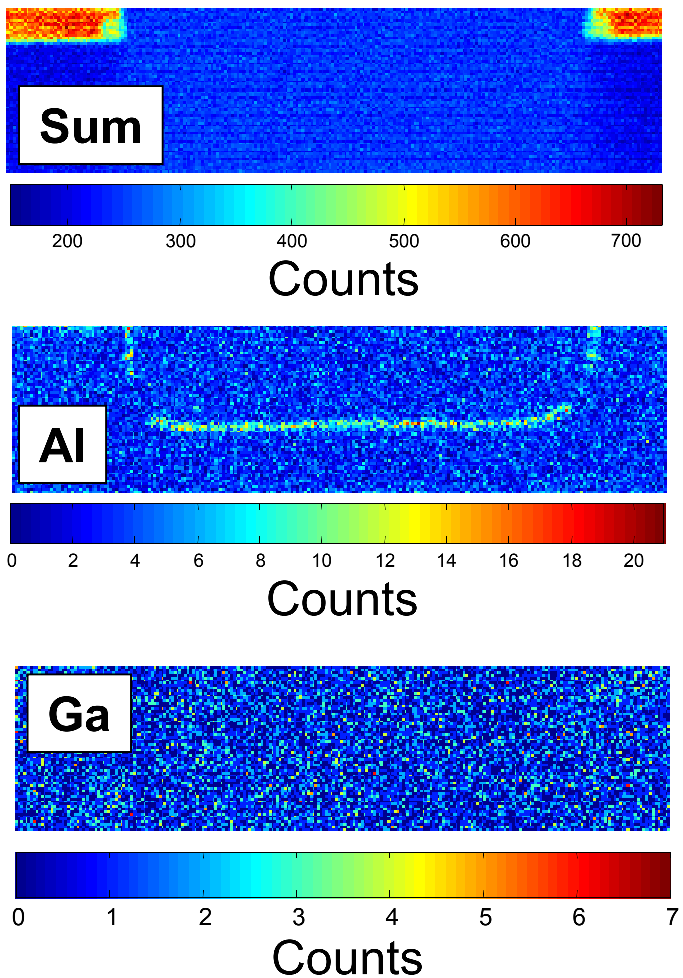
Example of Conventional Analysis



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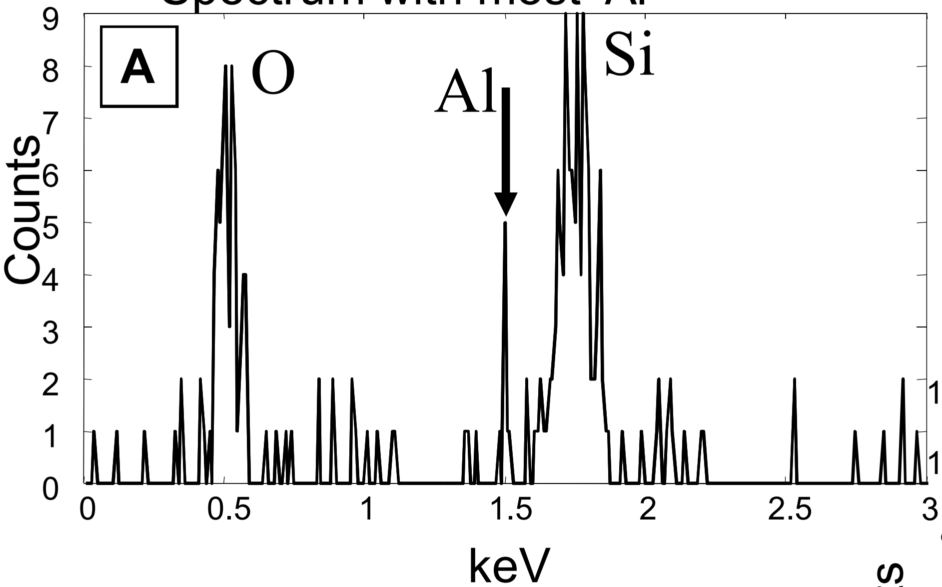
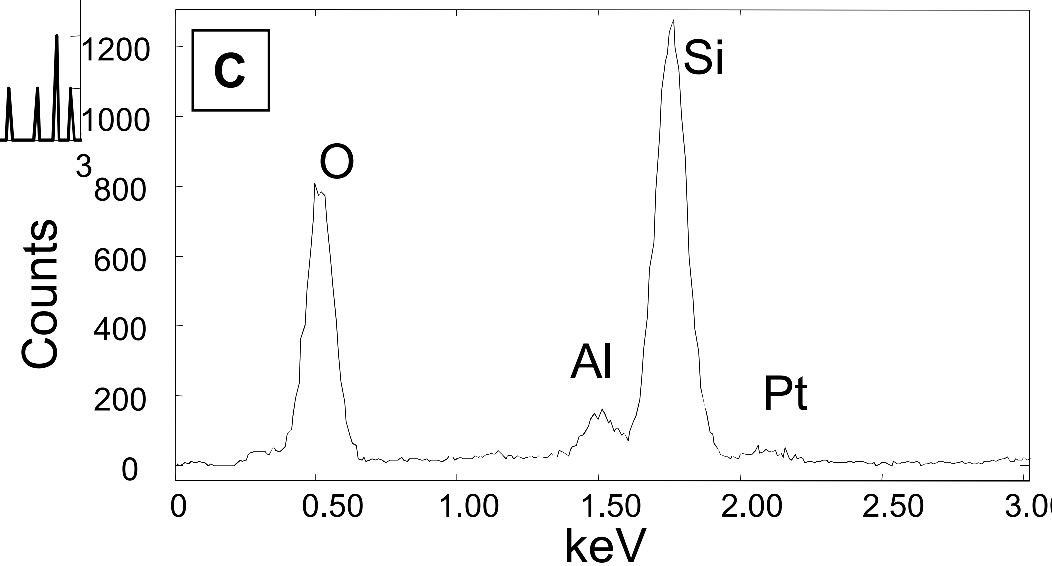
Example of Conventional Analysis

Spectrum with most ‘Al’



Binary mask of thresholded Al map



Sum spectrum from mask

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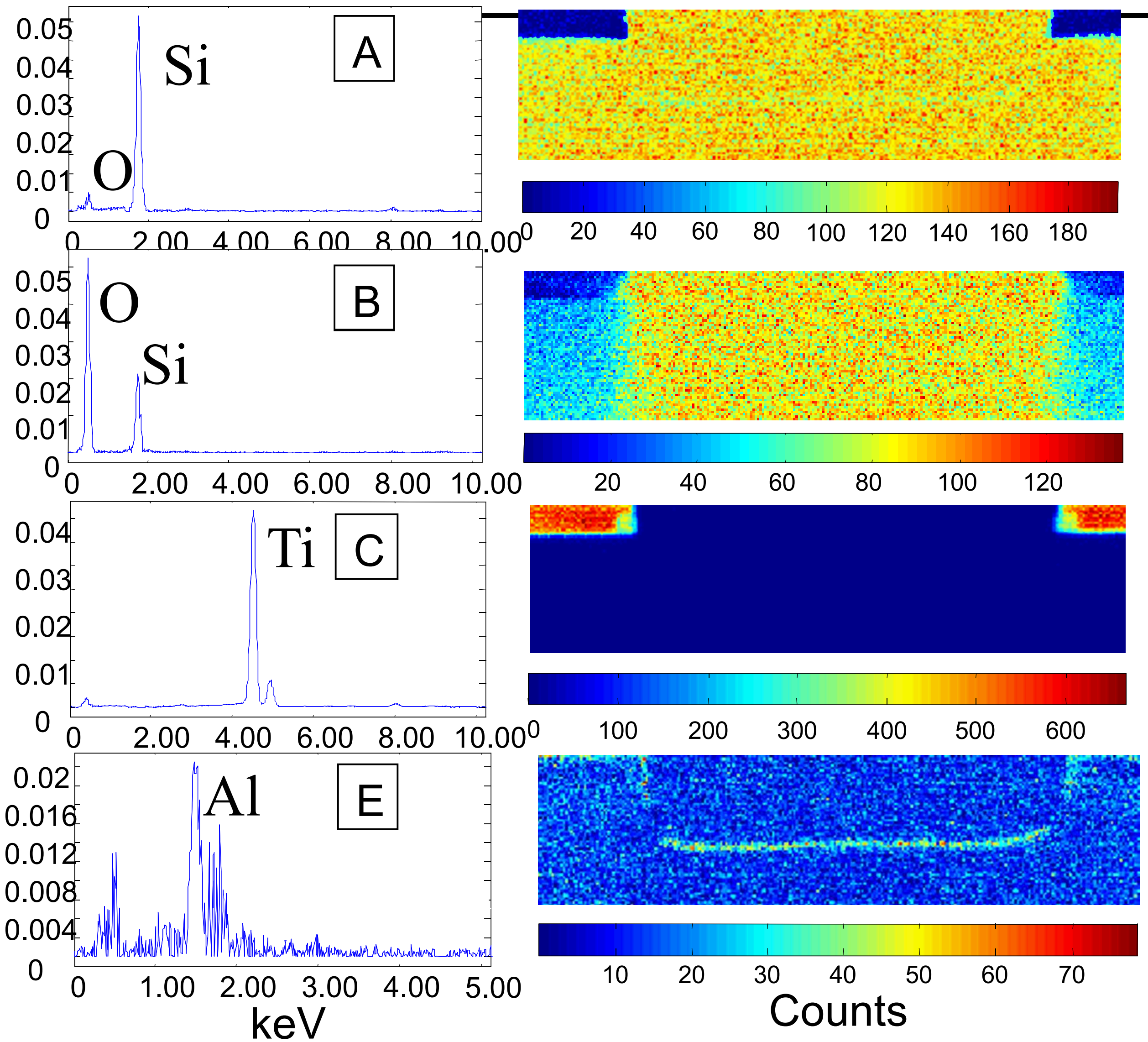
MSA of the same data



P.G. Kotula, et al. *Microsc. Microanal.* **12** [6] 538-544.

What are the basic steps of MSA?

- Keenan, M.R., *Multivariate analysis of spectral images composed of count data*, in *Techniques and applications of hyperspectral image analysis*, H. Grahn and P. Geladi, Editors. 2007, John Wiley & Sons: Chinchester.

- Scale data for non-uniform noise*
  - Down-weights large variations in intense spectral or image features which are due to noise
  - Rank 1 approximation to the noise
    - In the image domain divide by the square-root of the mean image
    - In the spectral domain divide by the square-root of the mean spectrum
    - Essentially the same answer as maximum likelihood methods with but far less computational complexity**
- Factor analysis (PCA, factor rotation, MCR)
  - **Analysis goal: compact and readily interpreted factors**
- Inverse noise scaling (very important to recover counts for quant!)

*M.R. Keenan and P.G. Kotula, *Surf. Int. Anal.* **36** (2004) 203-212

M.R. Keenan, J. Vac. Sci. Tech. A **23 [4] (2005) 746-750

Applications e.g., P.G. Kotula et al. *Microsc. Microanal.* 9 (2003) 1-17.

P.G. Kotula et al. *Microsc. Microanal.* **12** [6] 538-544.

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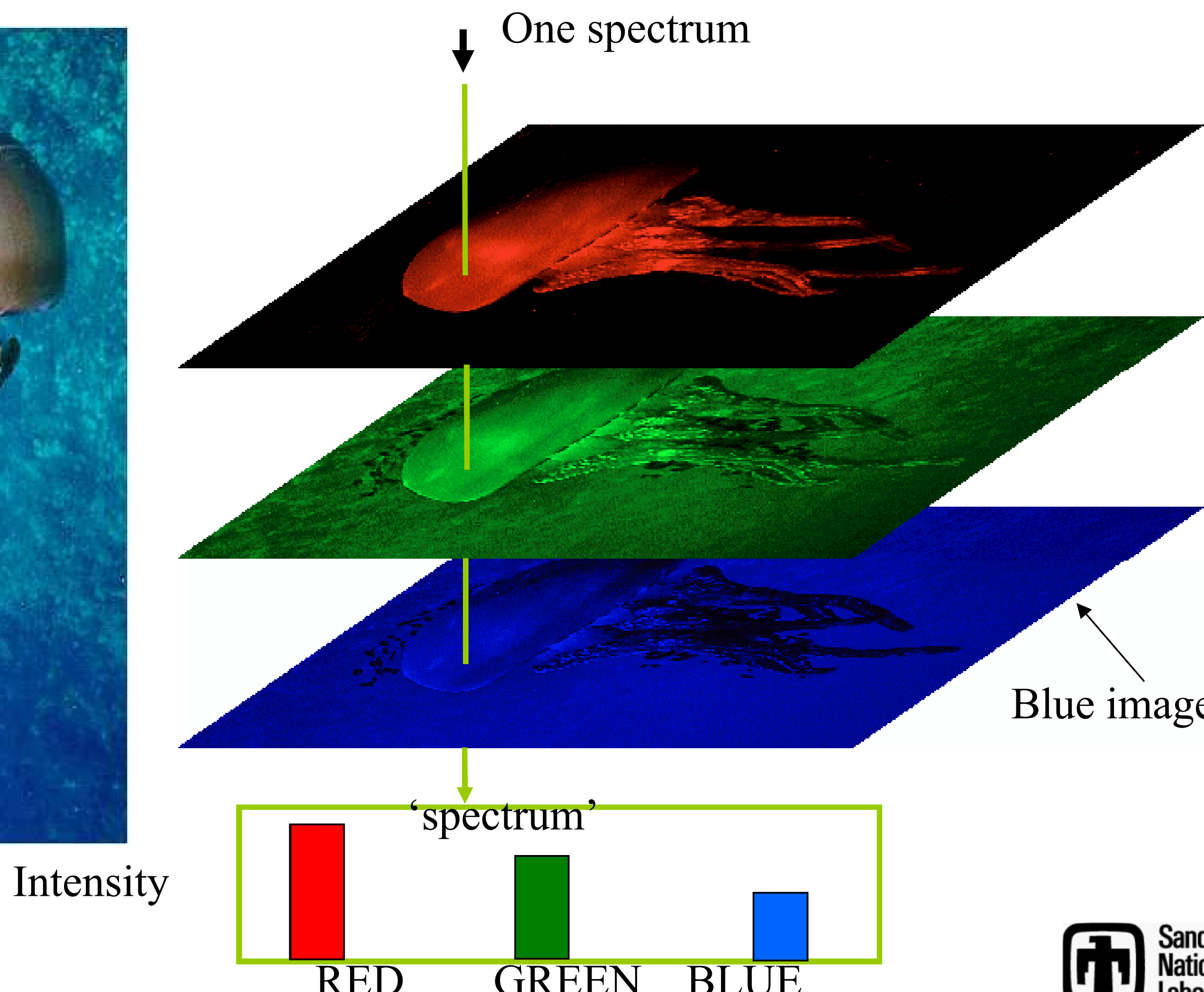
Color image: Example of a 3-channel multivariate image-variables are red, green, and blue



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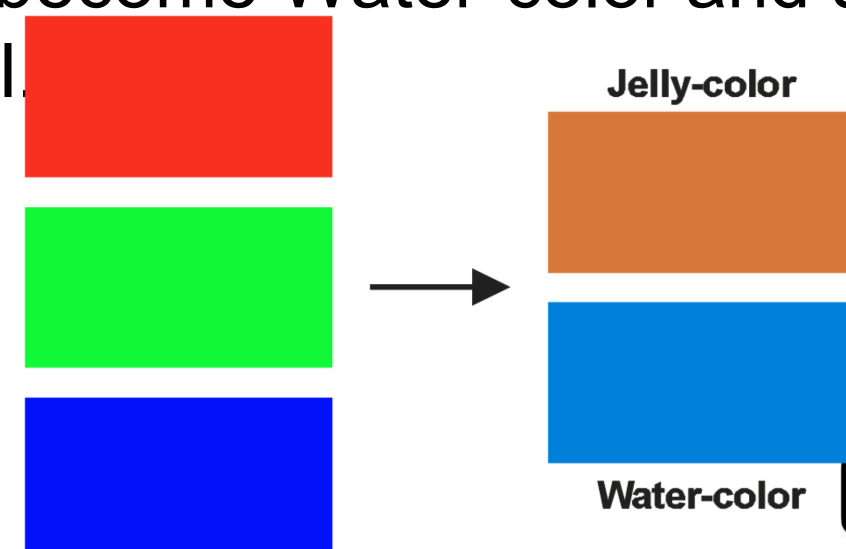
Goal of MSA, more compact and interpretable representation of the data

- There's a linear combination of the original variables that makes up new variables
- RGB is arbitrary but perhaps there's a better more interpretable representation
- Two variables describe 97% of the data set's variance
- Red, Green and Blue become Water-color and Jelly-color in the new model.



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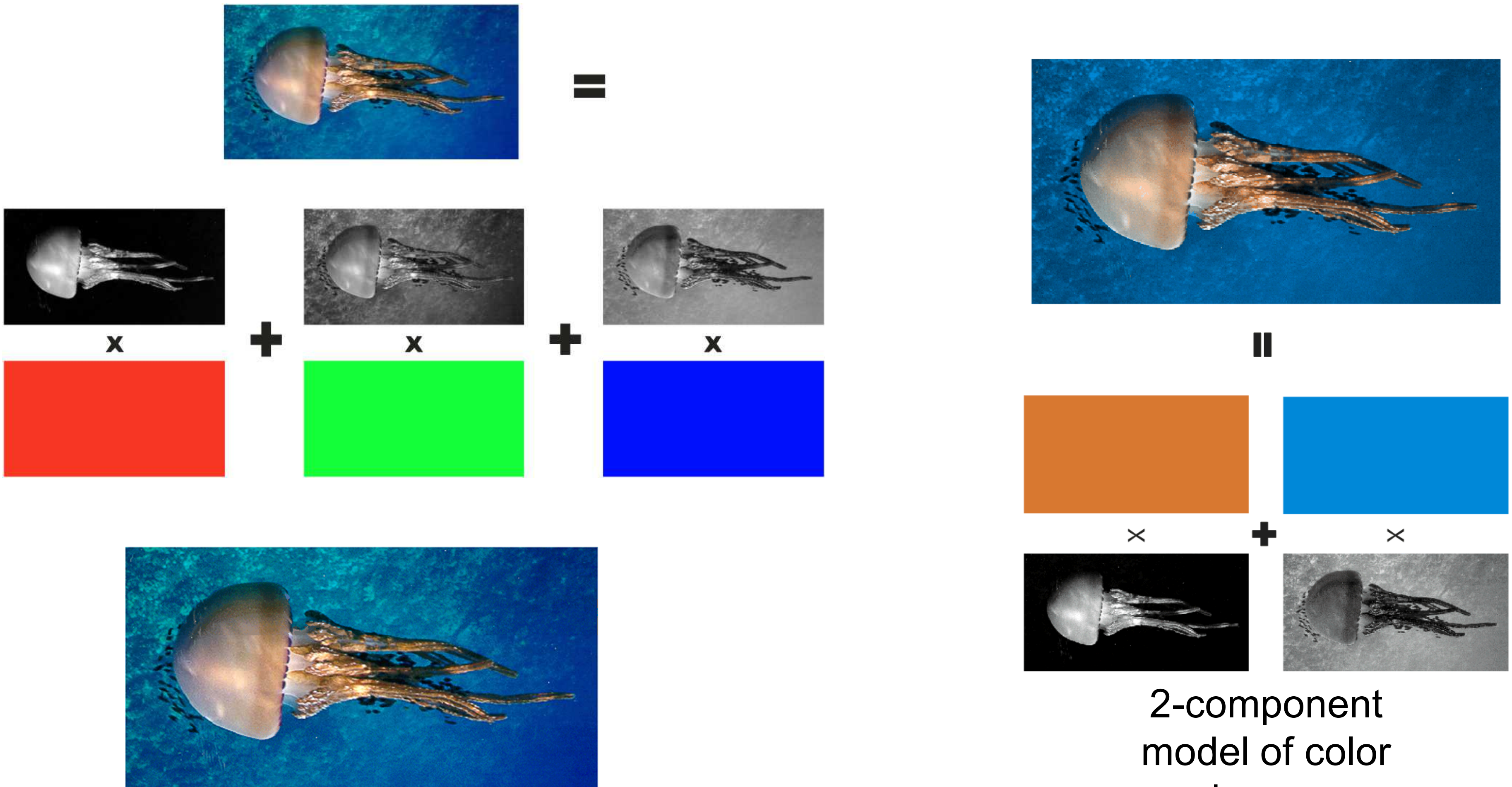
note the linearity assumption

Color Image = (Concentration) • (Spectral component)^T



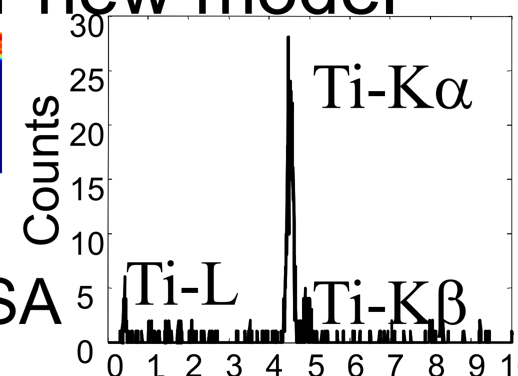
Original image

2-component model of color image

Images and analysis courtesy Michael Keenan (SNL-Ret.)

How does this translate to spectral images with 1000 or more channels/dimensions?

- In the regions with Ti, there are many channels which co-vary corresponding to the Ti-Kα, -Kβ and -L lines
- Rather than perhaps 20 of our original variables to describe this, only one is needed in our new model



- Chemically lossless compression
  - 1000 dimensions might become 5 after MSA
- New factors can be more readily interpreted
- Counts can be recovered for subsequent quantification

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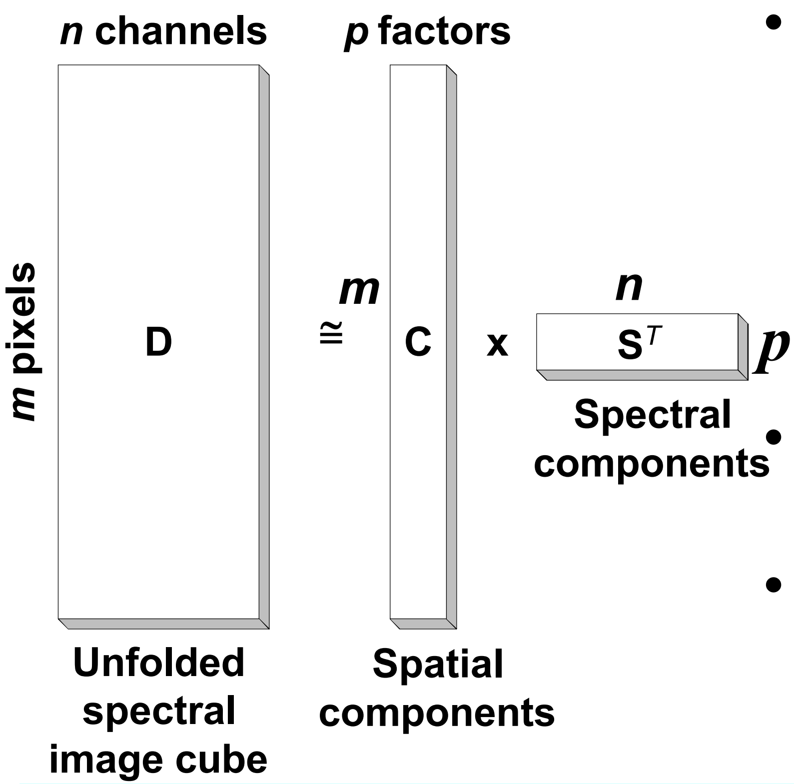
We have several options in our multivariate "Toolbox"



Analysis goal: Obtain an easily interpretable representation of the data

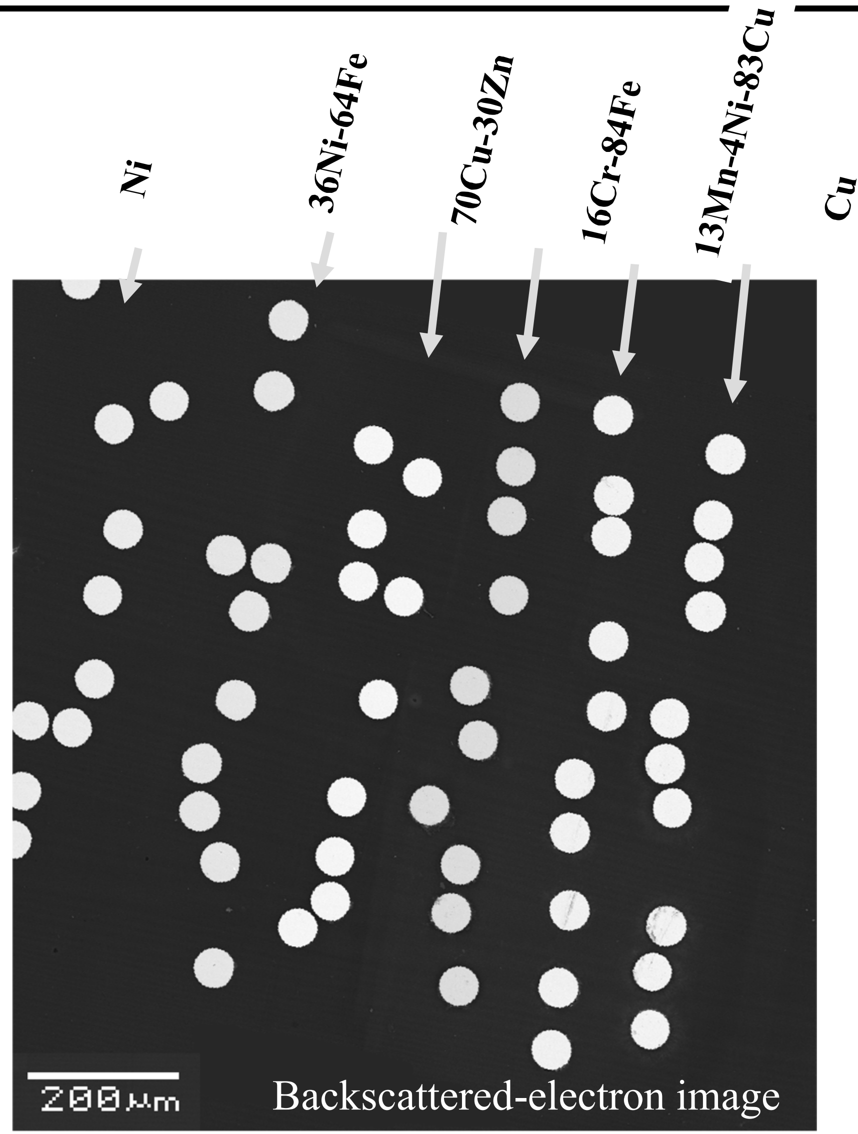
- Principal Component Analysis (PCA)
  - Factors are orthogonal
  - Factors serially maximize variance
  - Provides best LS fit to data
  - Non-physical constraints
  - Factors are abstract
- PCA + factor rotation (VARIMAX)*
  - Rotate factors to "simple structure"
- MCR-ALS**
  - A refinement of Rotated PCA
  - Non-negativity of C and/or S
  - Equality, closure and others
  - Constraints may not be effective
  - Bias due to error in variables

*M.R. Keenan, *Surf. Int. Anal.* **41** (2009) 79-87.
**P.G. Kotula, et al. *Microsc. Microanal.* 9 (2003) 1-17.

Spectral vs. Spatial Simplicity
Method: Simple wire test

Simple test structure- six different types of wires with some elements in multiple wires:

Ni
36Ni-64Fe
70Cu-30Zn
16Cr-84Fe
13Mn-4Ni-83Cu
Cu



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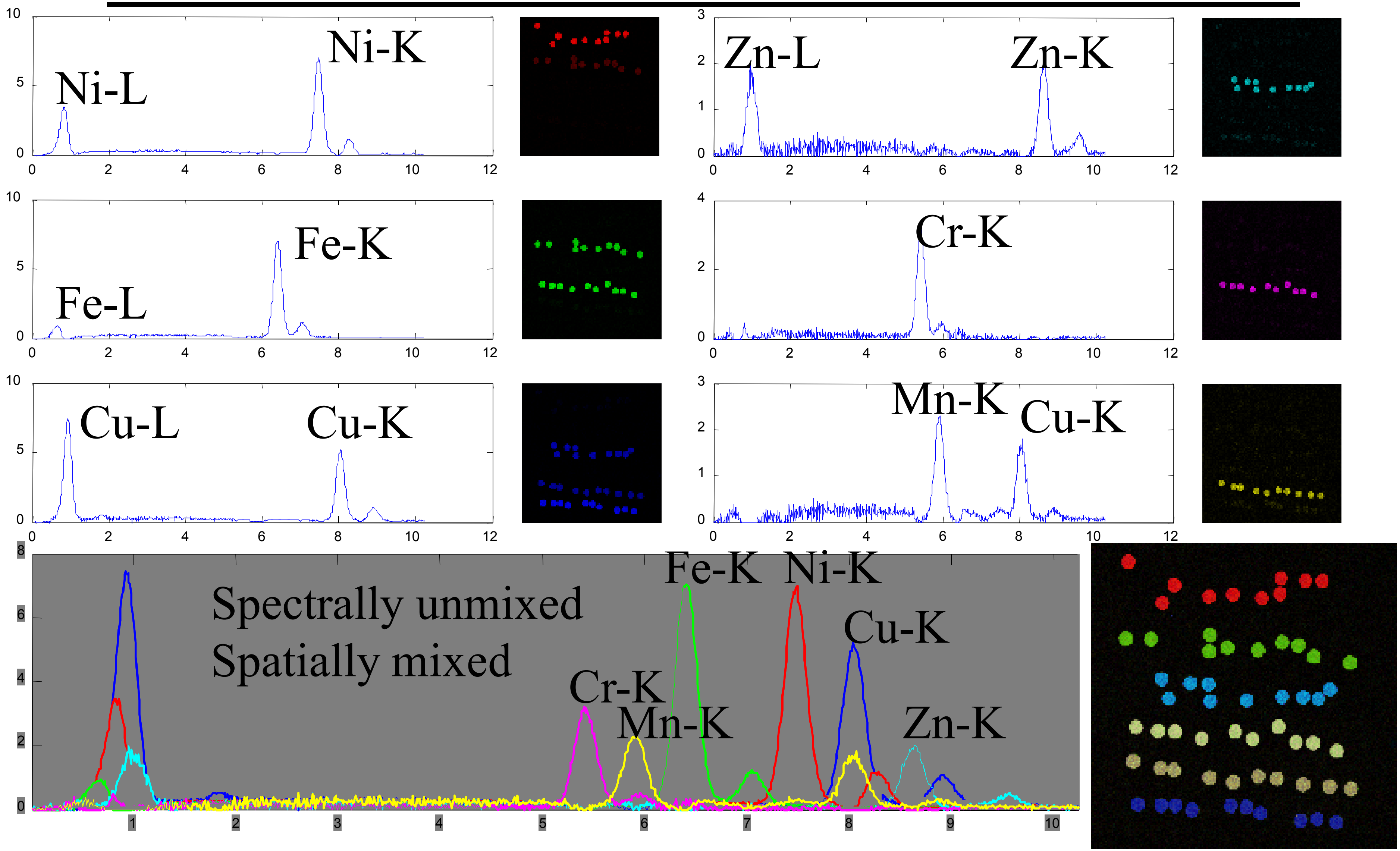
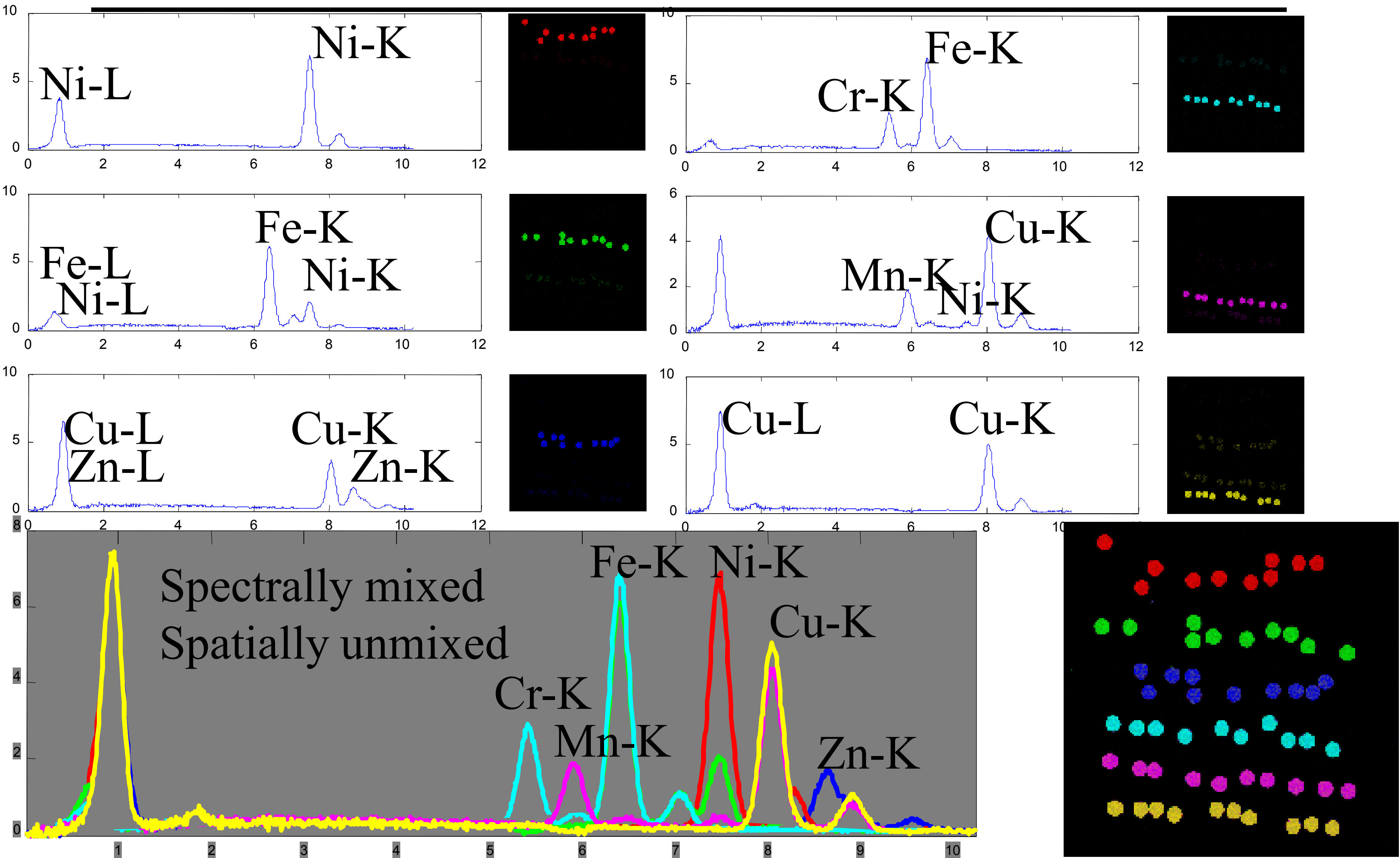
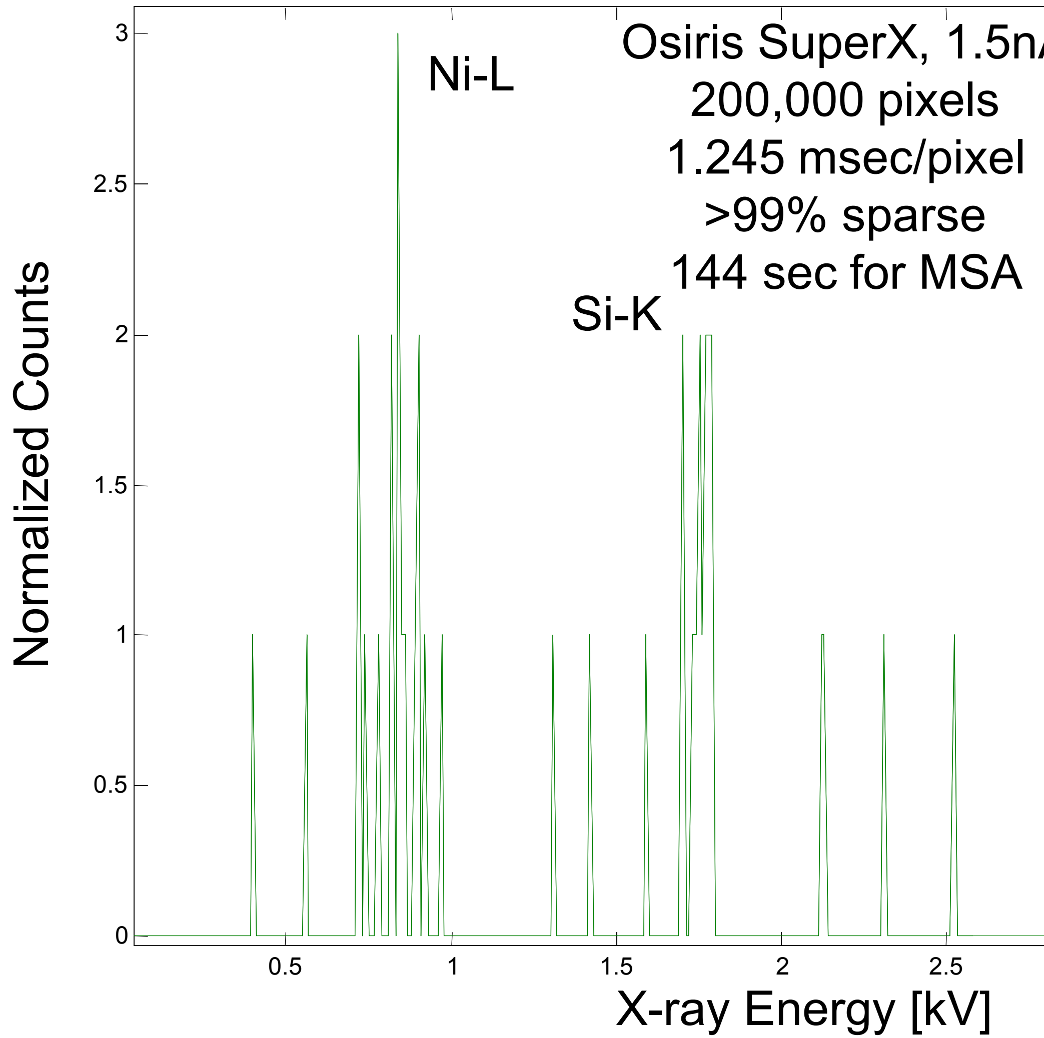
MCR-Best Spectral 'Contrast'
Often the elemental representation

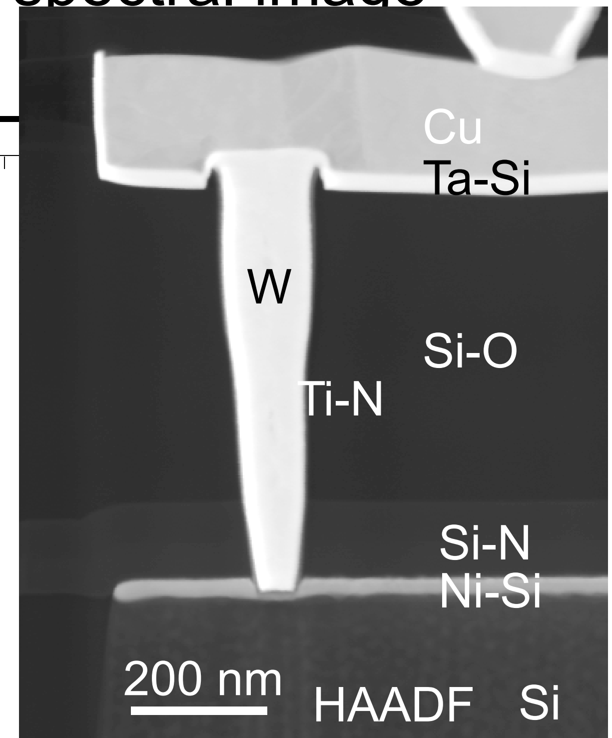


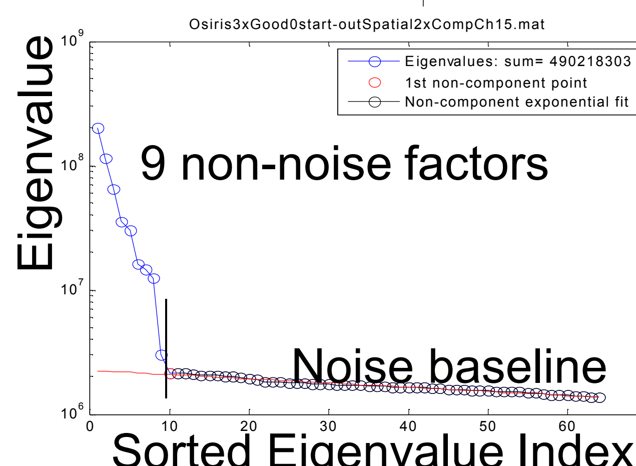
Spatial Simplicity-Best Spatial ‘Contrast’
Often the alloy or phase representation



Low end spatially, high end for sensitivity
Raw spectrum from the CMOS spectral image

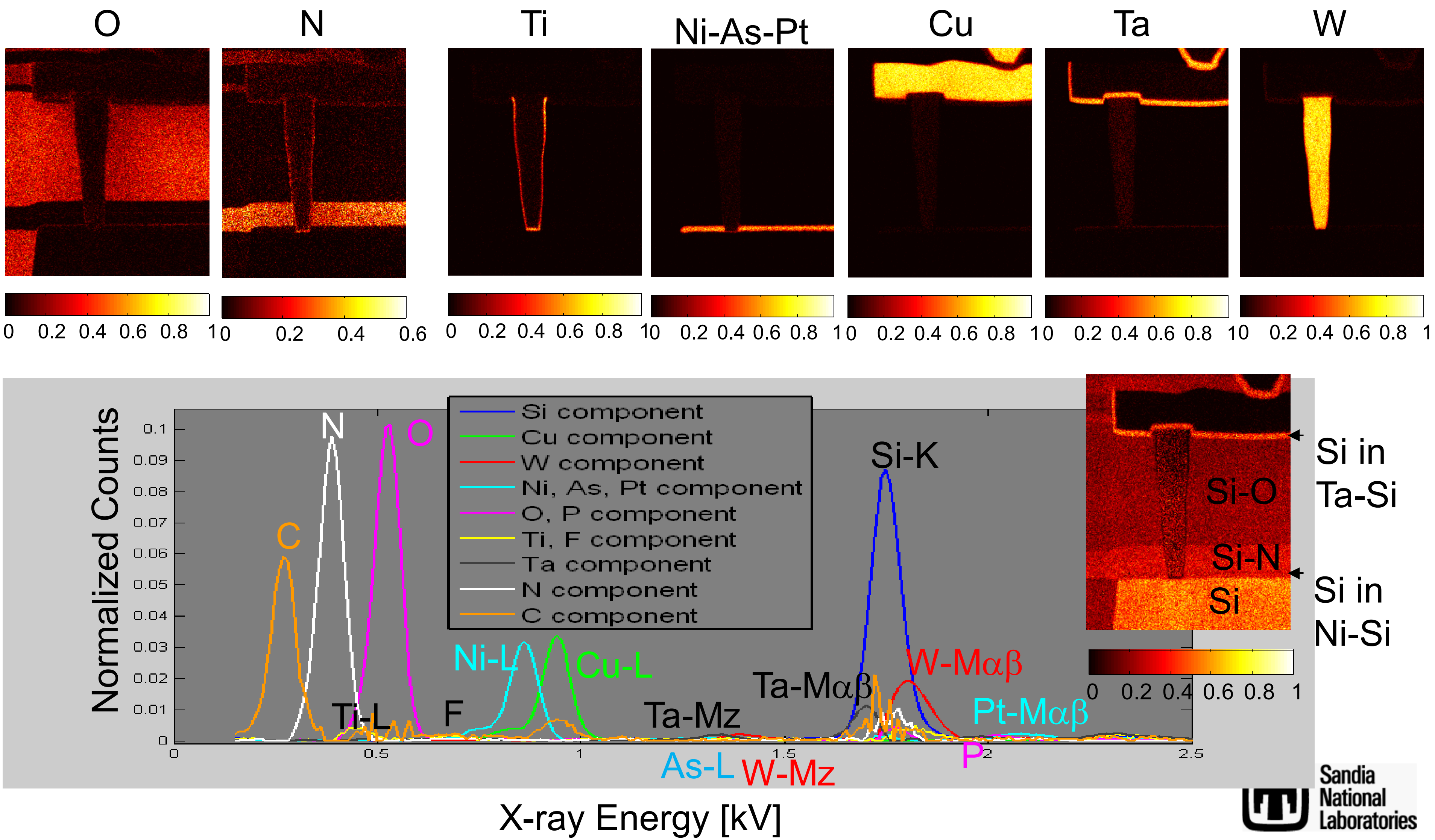




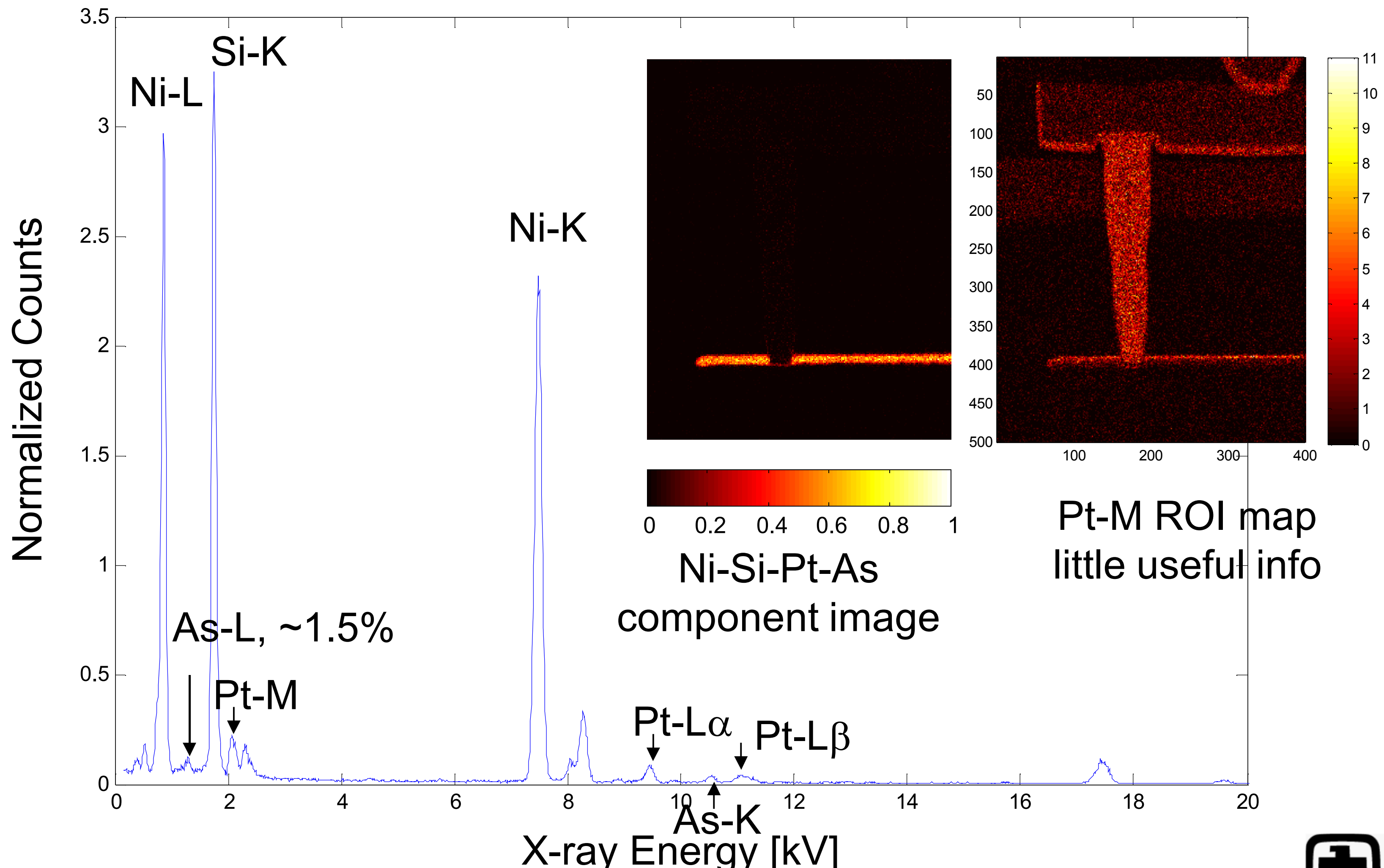


Data courtesy Dmitri Klenov, FEI on sample provide by SNL

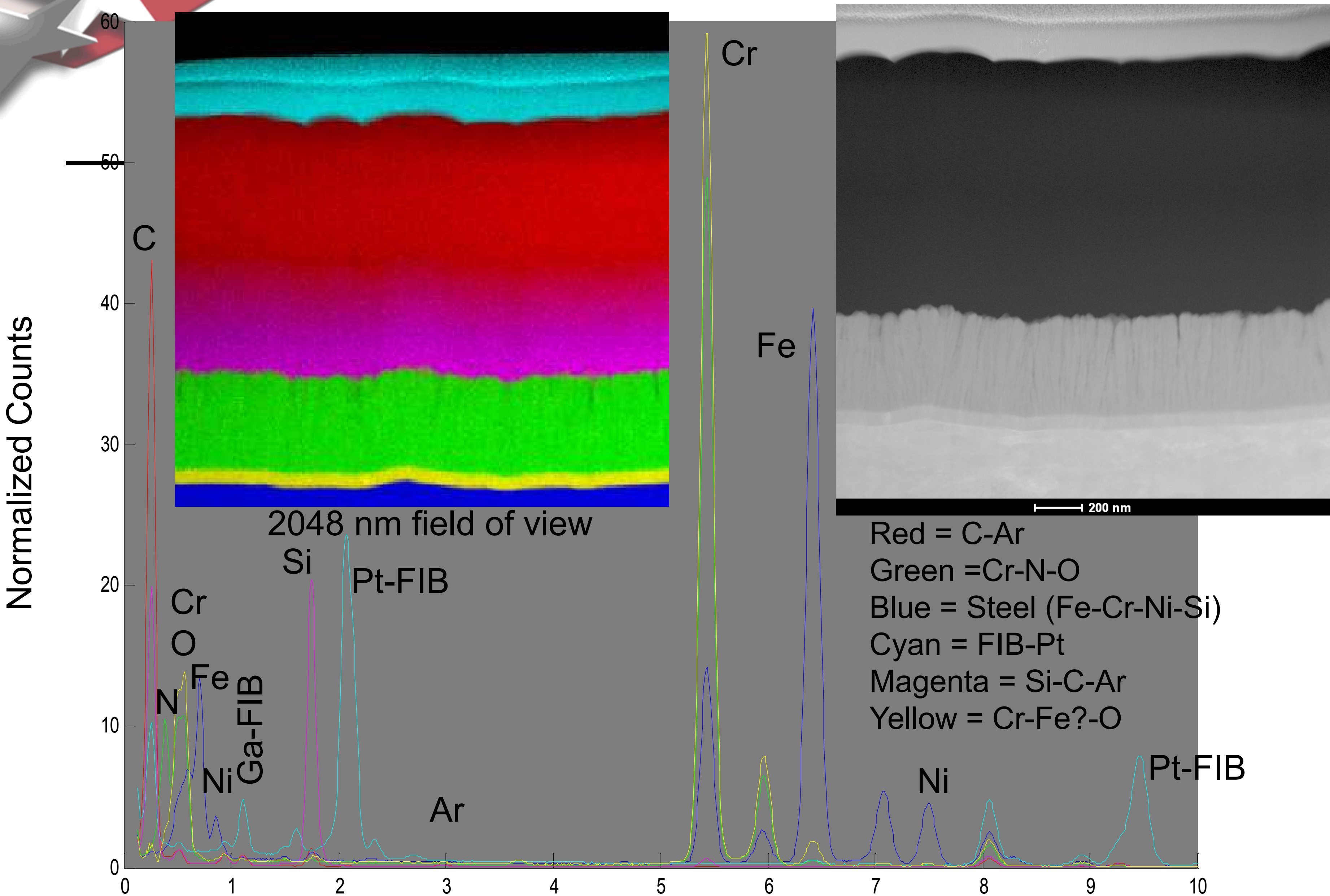
Low end, Spectral-Domain Simplicity
Best Spectral or Elemental ‘Contrast’



Low end, Spatial-Domain Simplicity
Ni-silicide contact, MSA shows minor elements



Low end…Solid-film lubricants for electromechanical devices

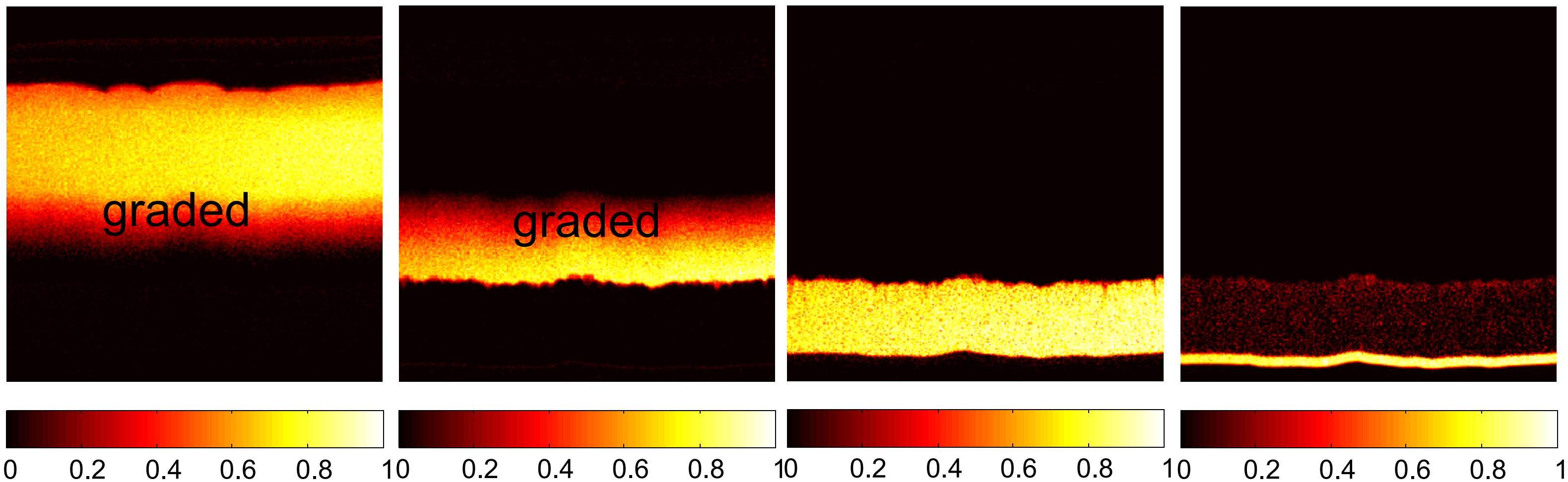


1 million pixels at 2 nm/pixel
Acquired in 20 minutes!

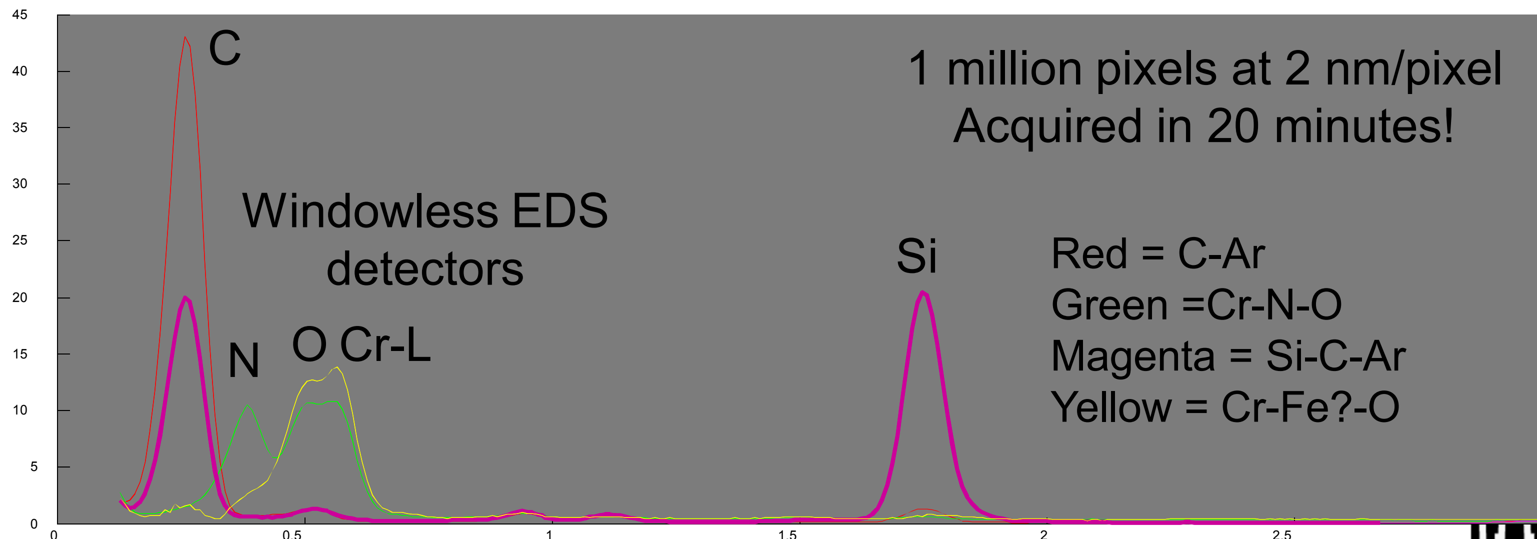
X-ray Energy [kV]

Low end…Solid-film lubricants for electromechanical devices

Red	Magenta	Green	Yellow
C-Ar	Si-C-Ar	Cr-N-O	Cr-O



2048 nm field of view



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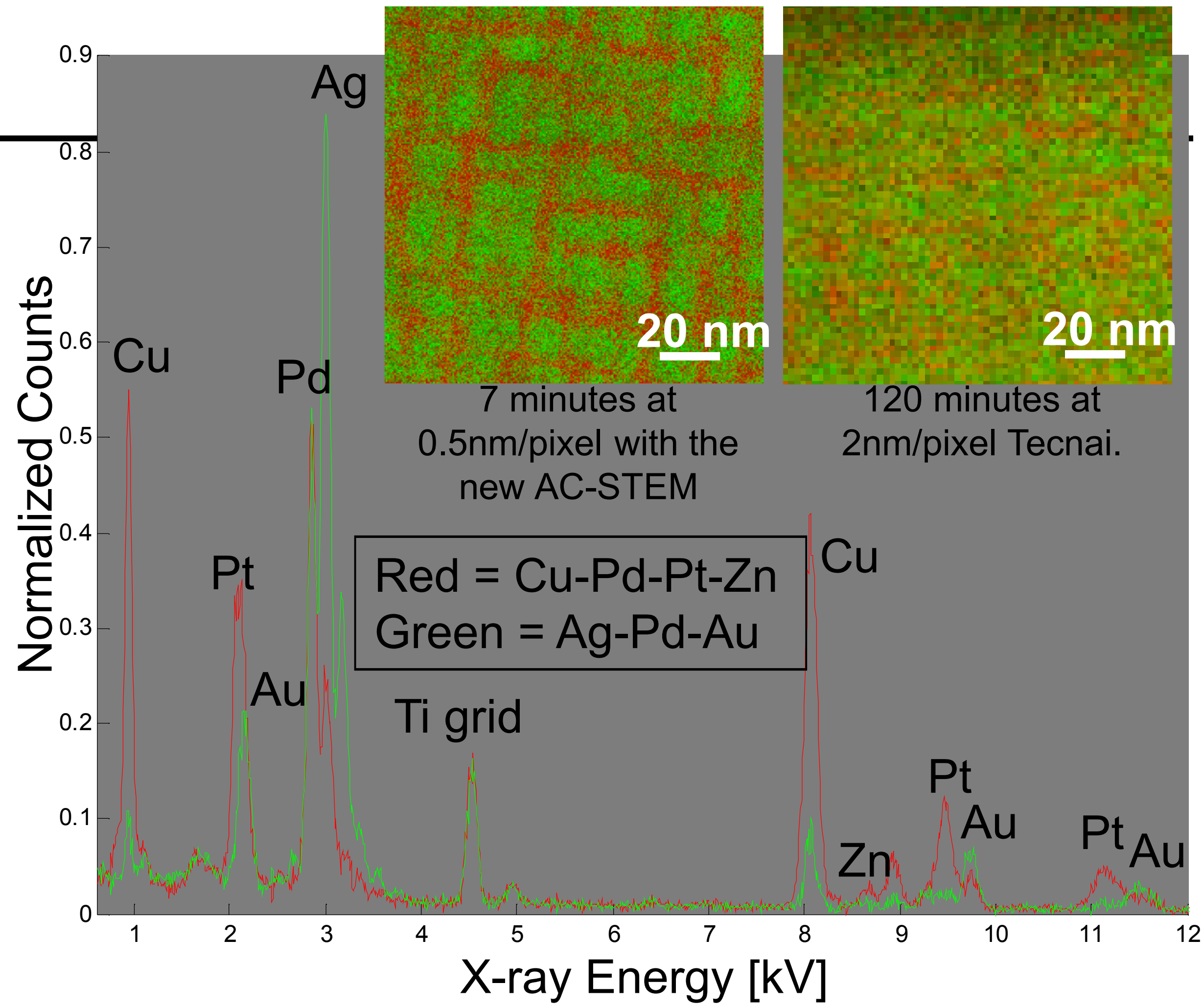
Medium end analysis
Sub-nm microanalysis of electrical contact materials

Paliney 7, electrical contact material nanometer-scale spinodal decomposition.



The analytical power of the AC-STEM is *at least* **70x** better than the older analytical microscope at Sandia.

D.F. Susan, Z. Ghanbari, P.G. Kotula, J.R. Michael & M.A. Rodriguez, *Metall. and Mat. Trans. A* **45A** (2014). DOI: 10.1007/s11661-014-2334-x

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Going from qualitative to quantitative analysis…adding more knowledge/assumptions to the problem

- Very important to first perform a comprehensive qualitative analysis
  - Conventionally, MSA or other approach
  - Make sure you understand your sample and possible interferences (like the grid fluorescence)
- Measure k-factors for elements of interest
- Measure reference-peak shapes (or use MSA-derived shapes)
- Use MSA for noise filtering
- Fit reference shapes to the noise filtered spectral image

Parish, C.M., Brennecka, G.L., Tuttle, B.A. & Brewer, L.N. (2008). *J Am Ceram Soc* **91**, 3690–3697.

Hyperspectral images to quantitative analysis

- Simple binary, MCR provides shapes/counts
  - Goldstein, J.I., Jones, R.H., Kotula, P.G. & Michael, J.R. (2007). *Meteor Planet Sci* **42**, 913–933.
- Ternary ferroelectric, ref shapes, fitting
  - Parish, C.M., Brennecka, G.L., Tuttle, B.A. & Brewer, L.N. (2008). *J Am Ceram Soc* **91**, 3690–3697.
- PCA noise filtering, fitting (not illustrated in this presentation)
  - Watanabe, M., Ackland, D.W., Burrows, A., Kiely, C.J., Williams, D.B., Krivanek, O.L., Dellby, N., Murfitt, M.F. & Szilagyi, Z. (2006). *Microsc Microanal* **12**, 515–526.
- Atomic-resolution, Rotated PCA to get pure elemental factors
  - Kotula et al., *Microsc. Microanal.* **18**, 691–698, 2012

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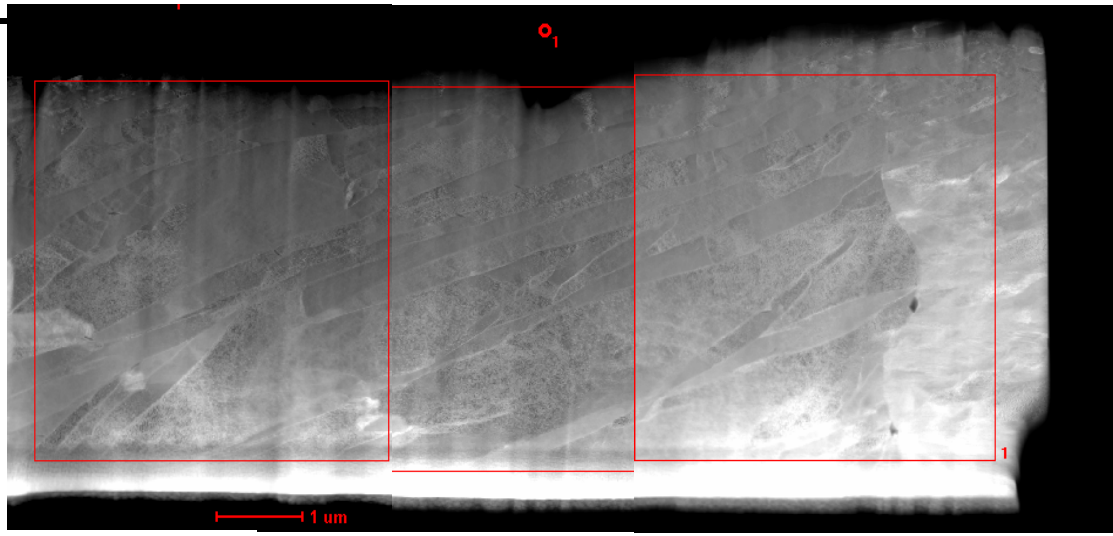
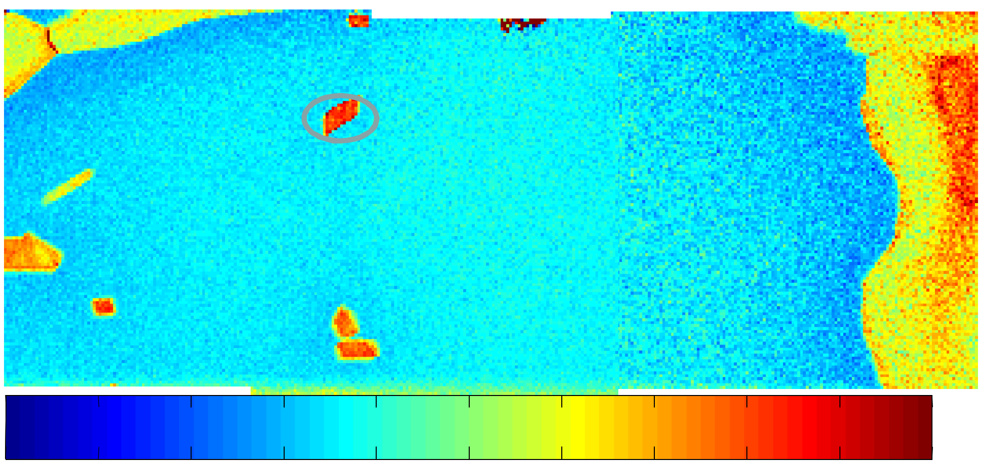
Fe-Ni Meteorite



20nm/pixel overview



Ni Concentration Wt.%

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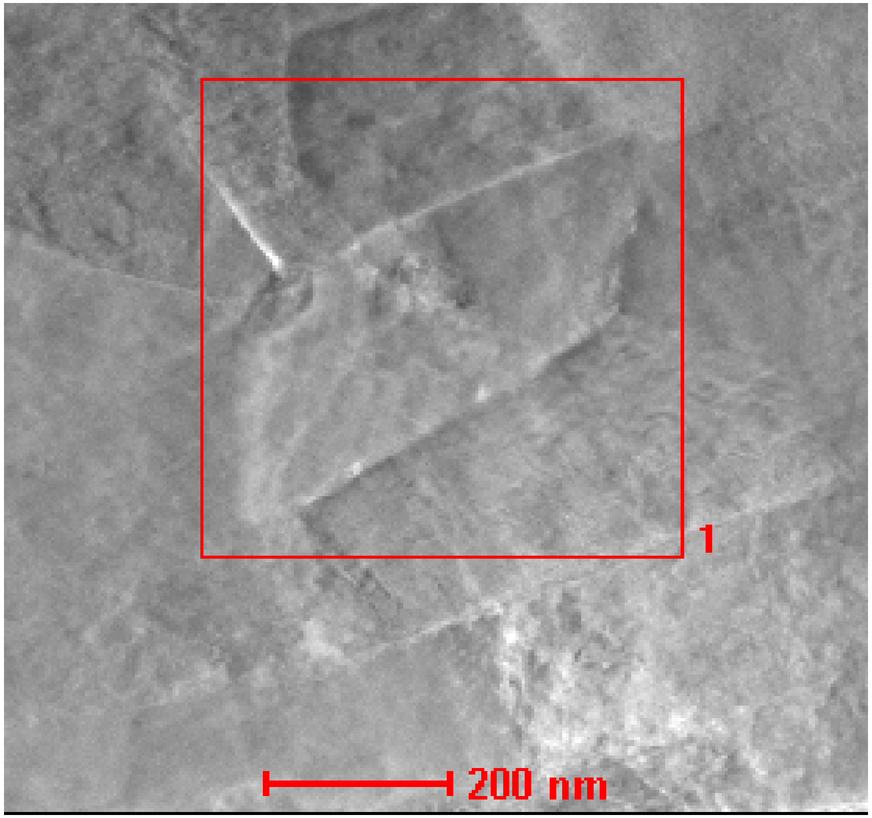
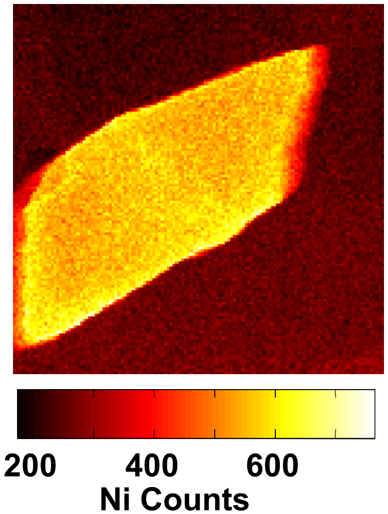
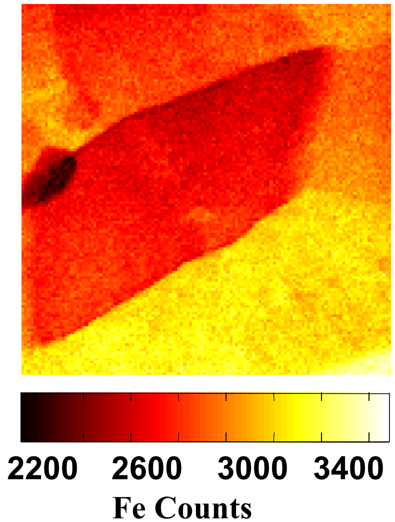
Fe-Ni Meteorite

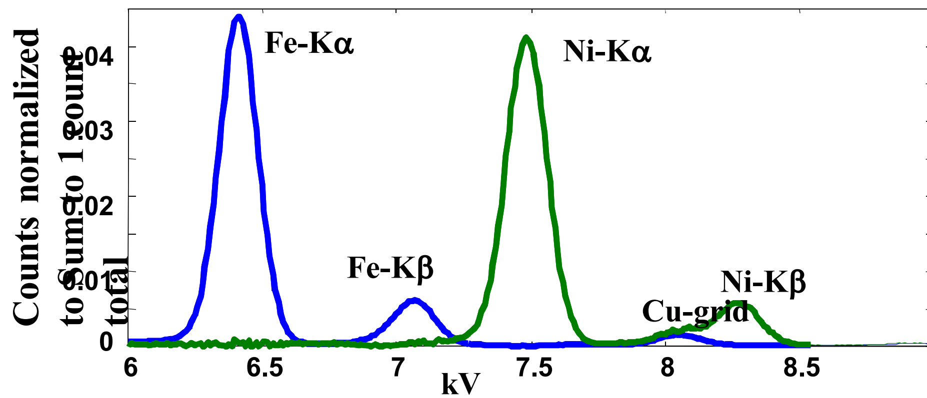
NWA739 Ni rich precipitate

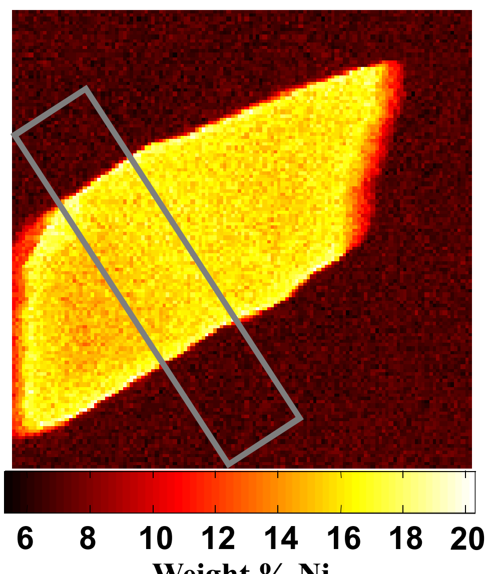


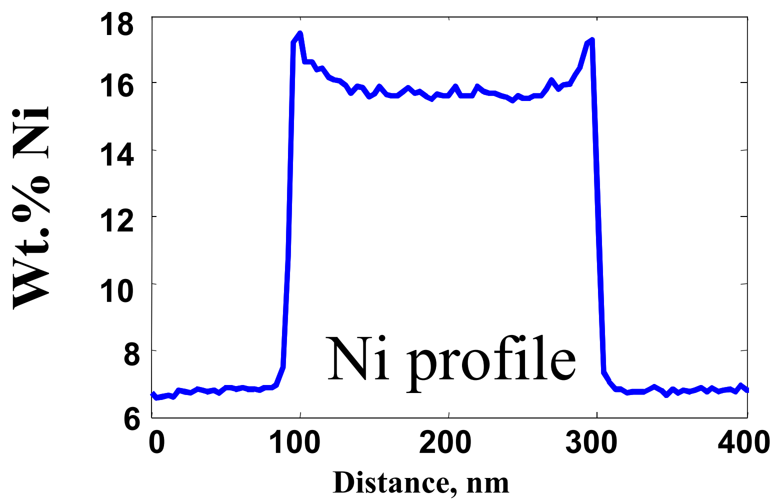
Quantitative Analysis of Fe-Ni from MCR











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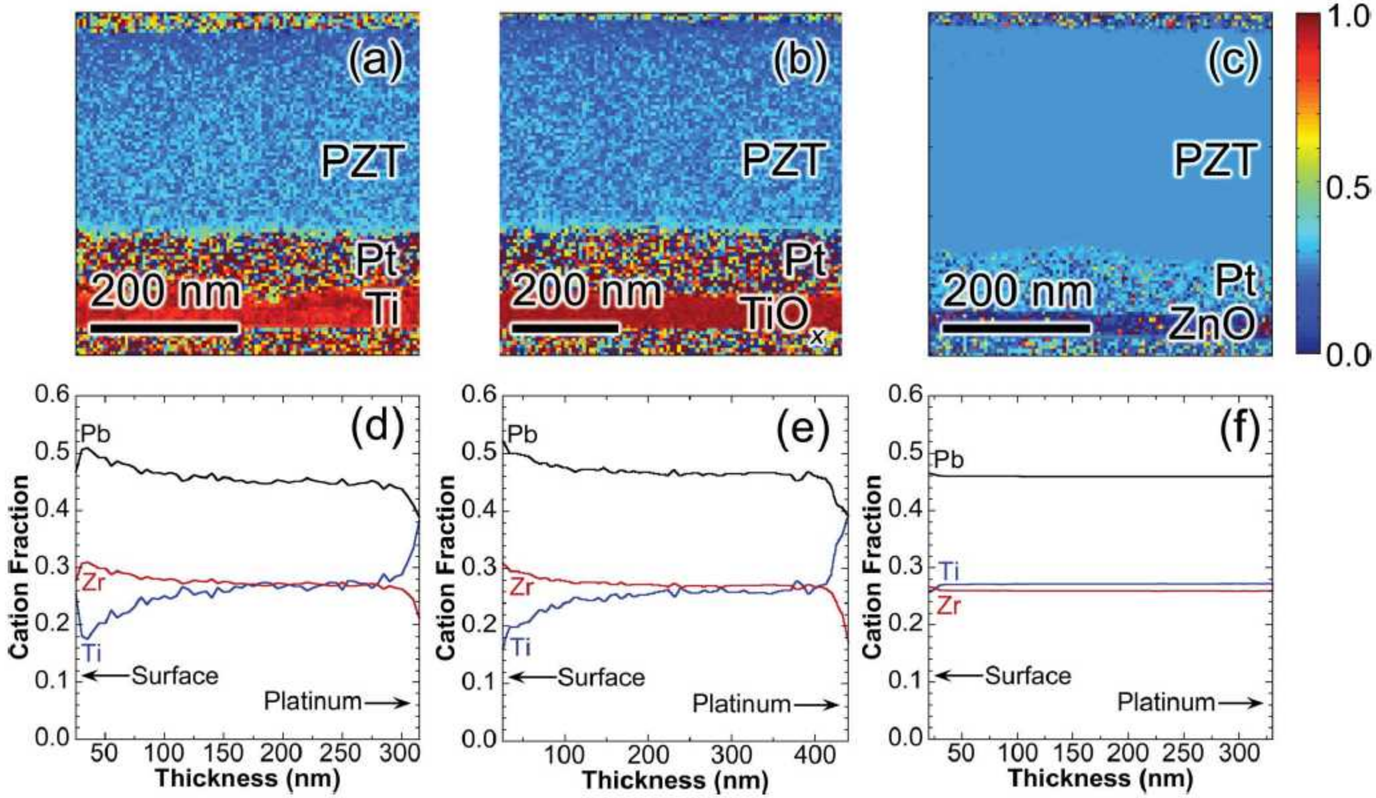
Pb-Zr-Ti Ferroelectric Quant-Tecnai

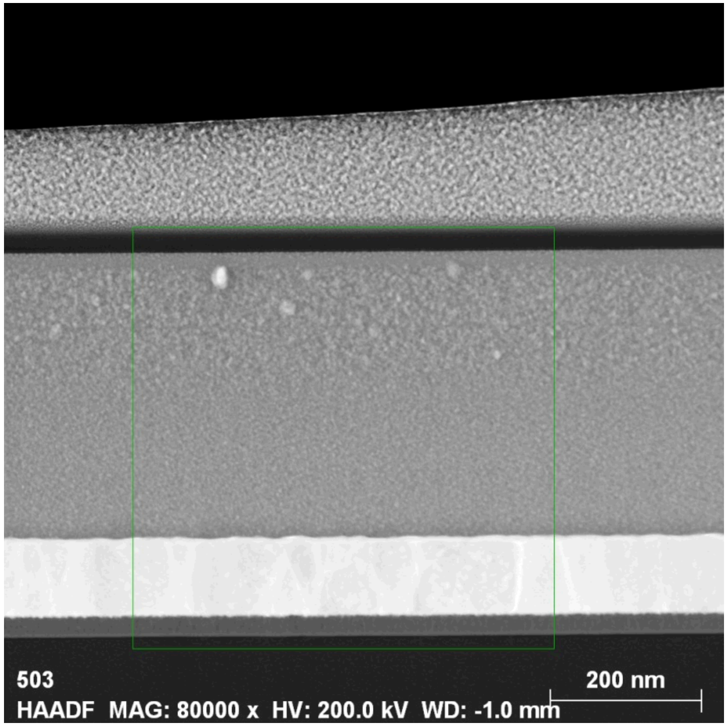


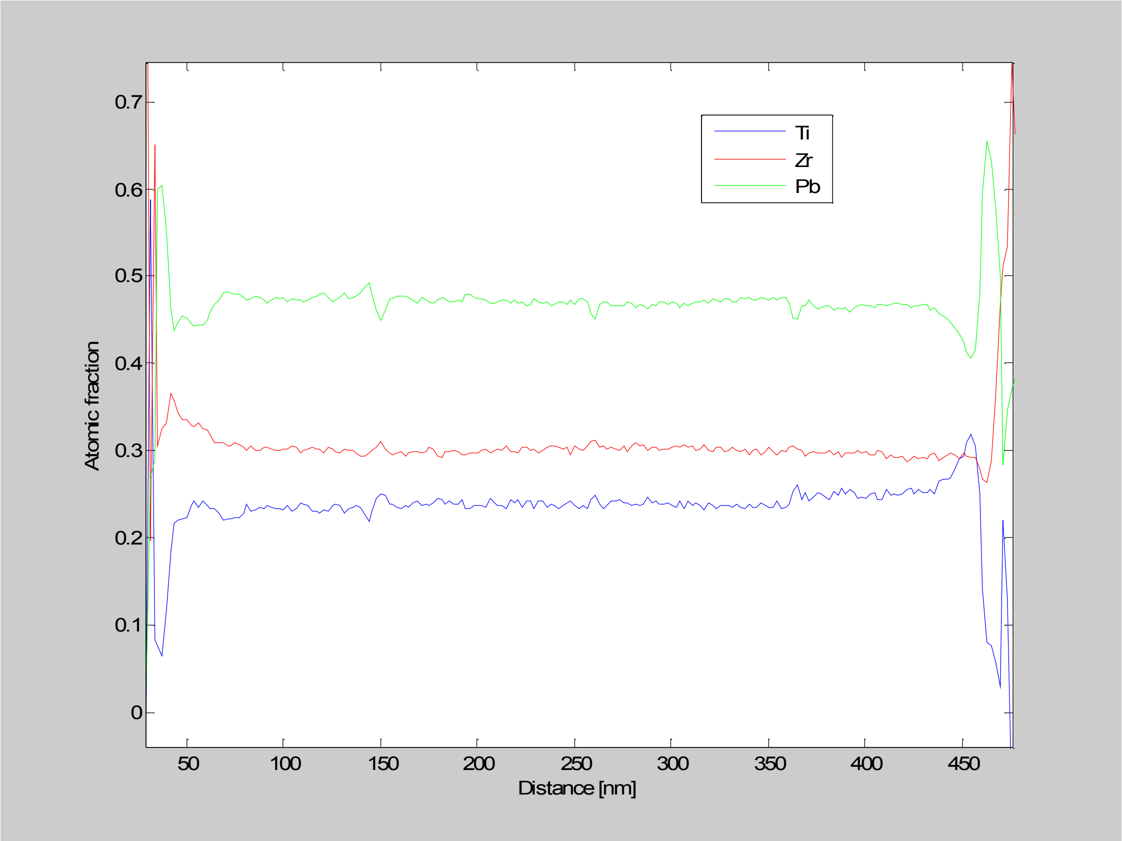
C.T. Shelton, P.G. Kotula, G.L. Brennecka, P.G. Lam, K.E. Meyer, J-P Maria, B.J. Gibbons, and J.F. Ihlefeld,"Chemically Homogeneous Complex Oxide Thin Films Via Improved Substrate Metallization," Adv. Funct. Mater. 2012, DOI: 10.1002/adfm.201103077

Titan

PZT quantitative analysis at 1 nm resolution

Solution-deposited PZT, on Pt on Ti-O on Si-O





360,000 spectra from 600 nm x 600 nm acquired in 20 minutes!
One of sixteen data set acquired that day.

Work with Jon Ihlefeld, SNL

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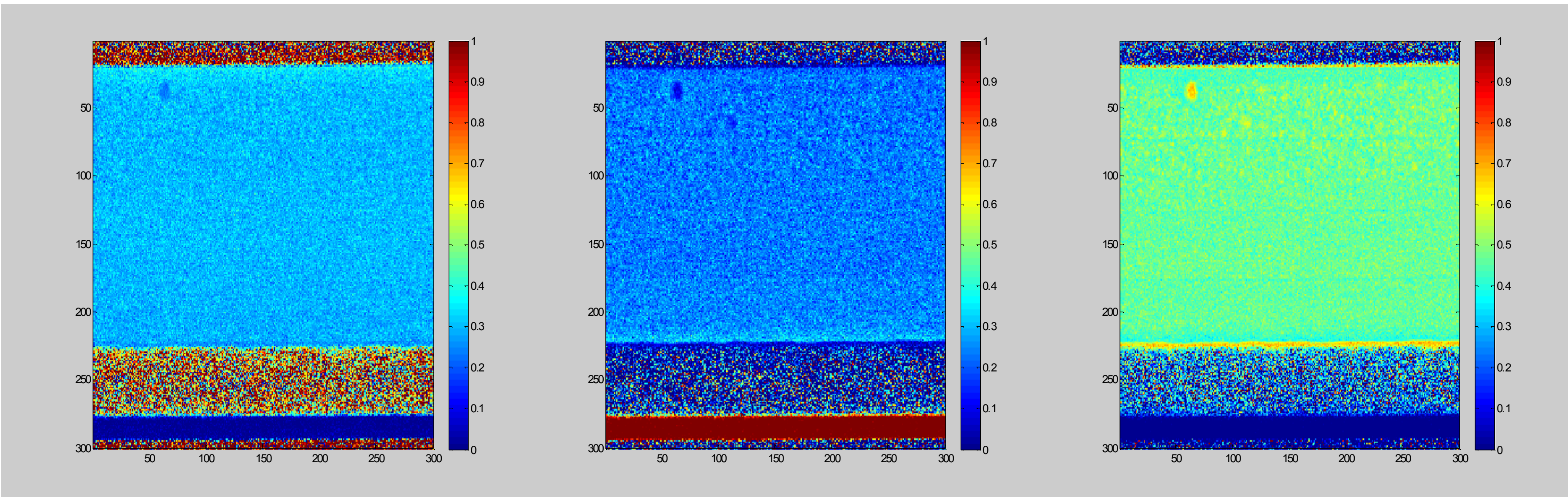
Titan

PZT quantitative analysis at 1 nm resolution



Zr atomic fraction | Ti atomic fraction | Pb atomic fraction

Work with Jon Ihlefeld (SNL)

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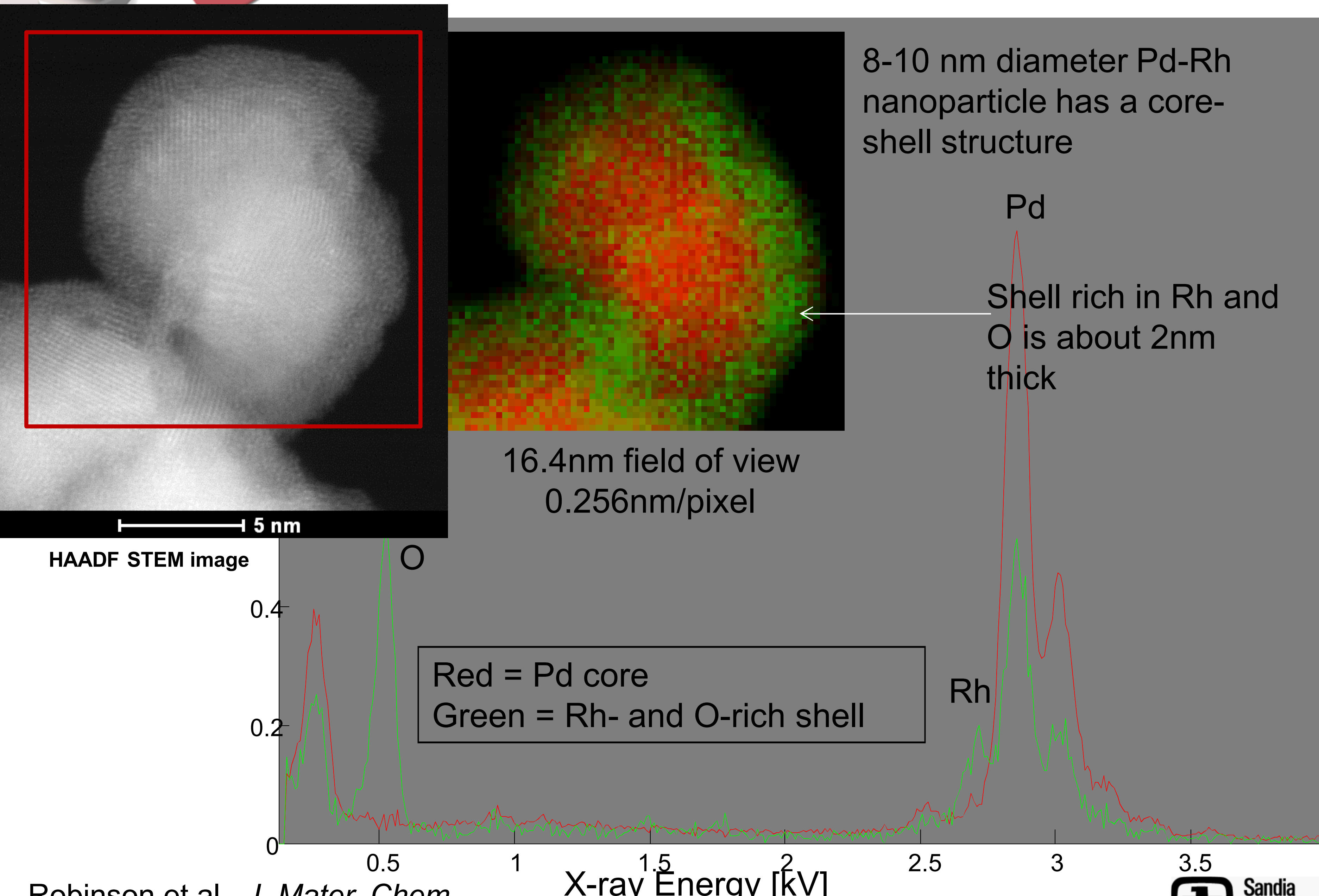
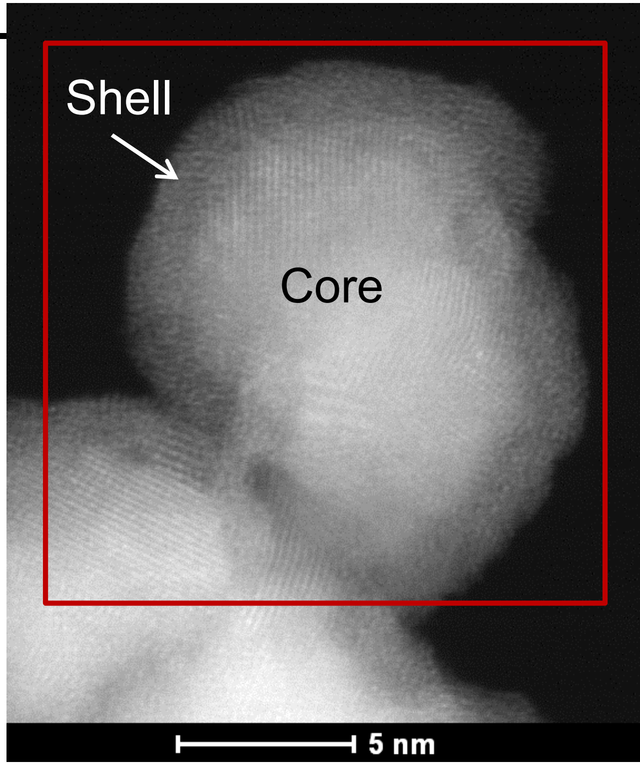
Characterization of hydrogen isotope storage materials

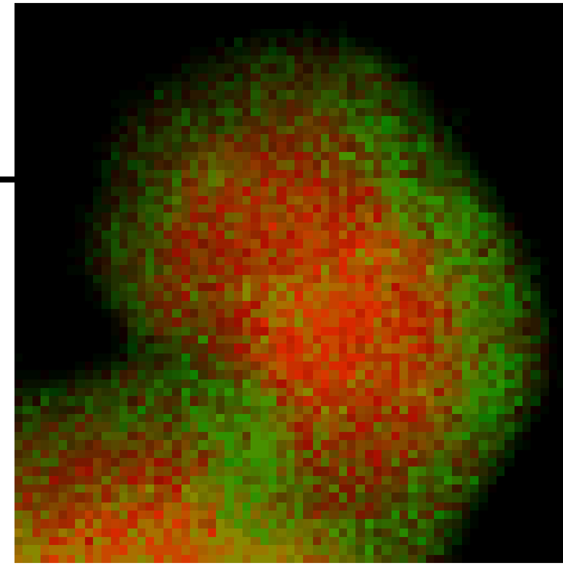


Robinson et al., *J. Mater. Chem.*, 2012, **22**, 14013

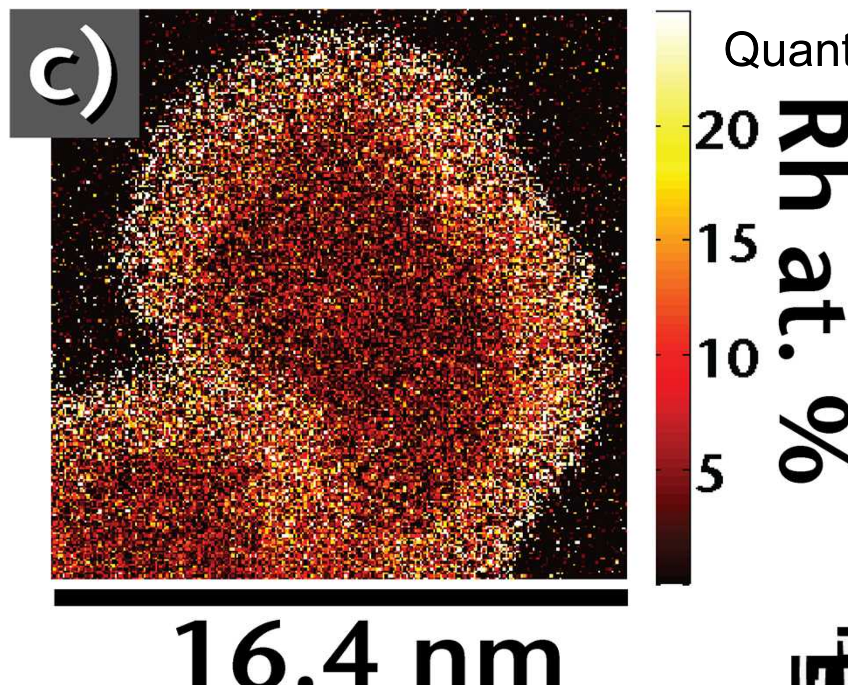
Medium end, characterization of hydrogen isotope storage materials



HAADF image



MSA results
Red = Pd-rich core
Green = Rh- and O-rich shell



Robinson et al., *J. Mater. Chem.*, 2012, **22**, 14013

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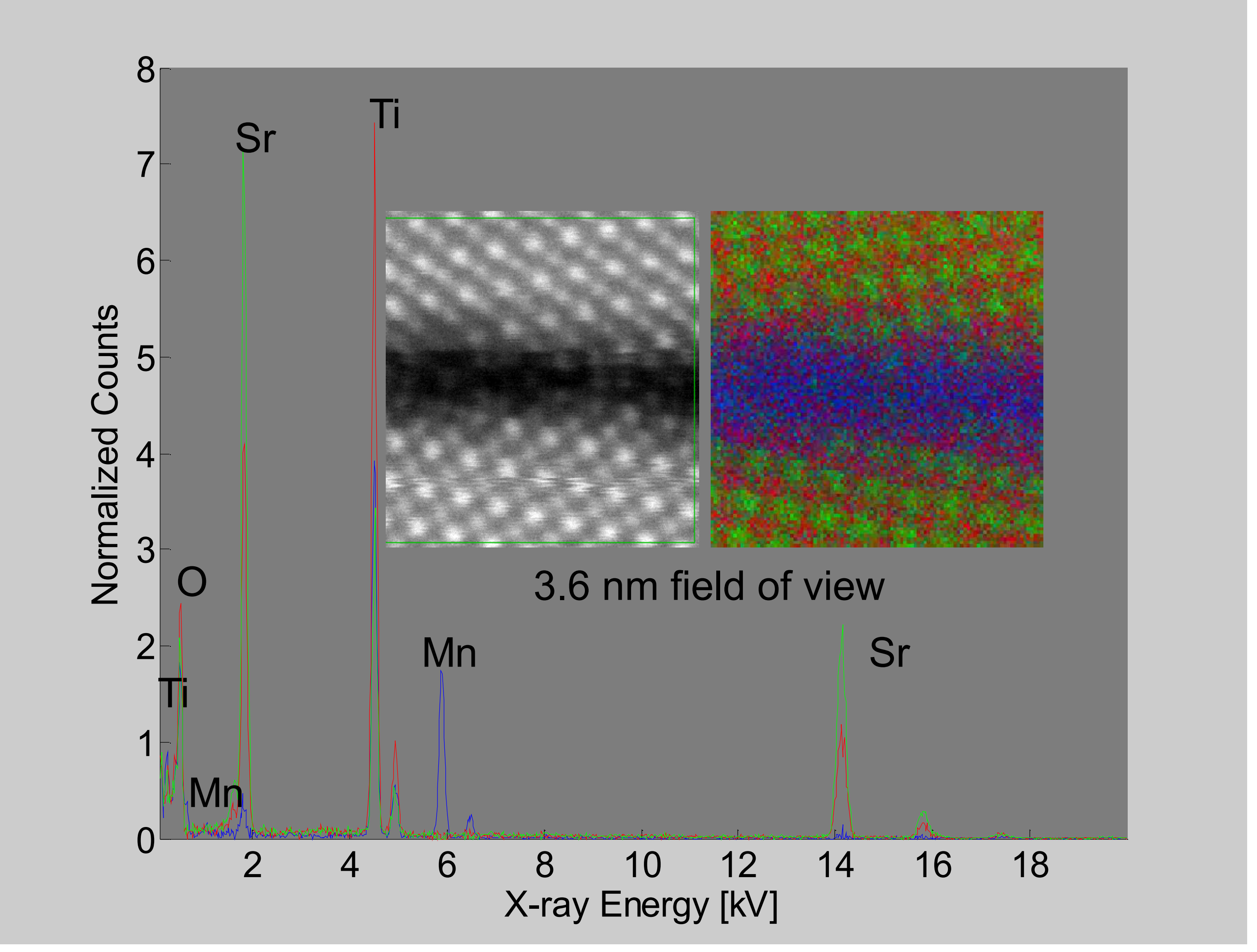
Analysis of Mn-doped STO Σ=13 Boundaries

Hao Yang, Paul G. Kotula, Yukio Sato, Yuichi Ikuhara, Nigel D. Browning. "Segregation of Mn^{2+} Dopants as Interstitials in $SrTiO_3$ Grain Boundaries," Submitted (2013).



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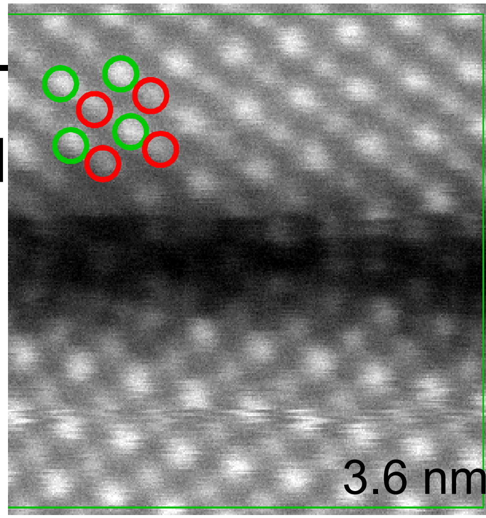
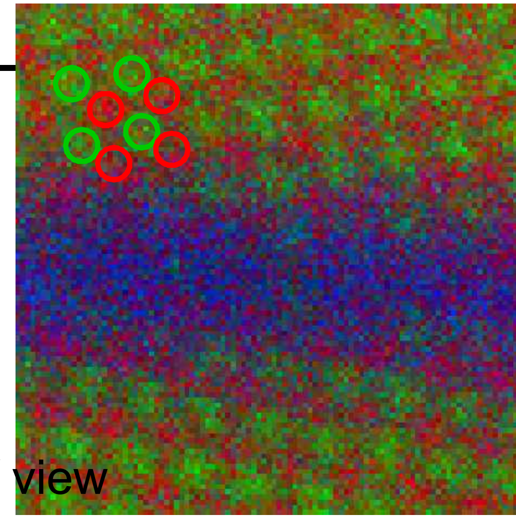
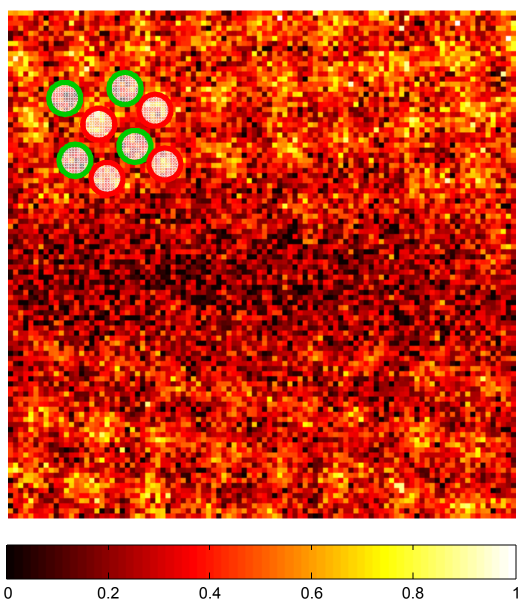
∑13 (510)/[001]
HAADF image



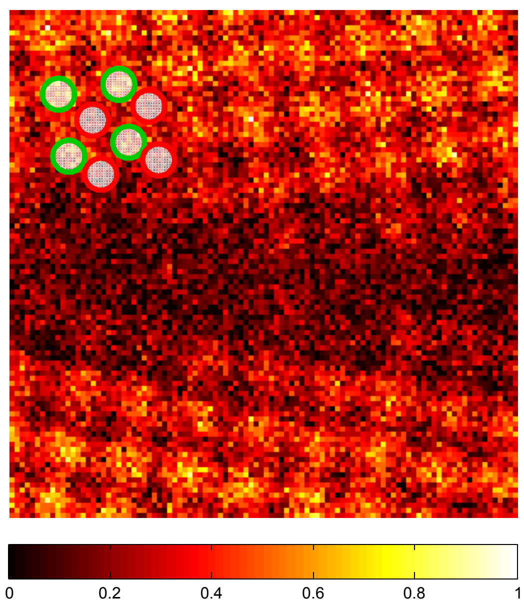


Red = Ti
Green = Sr
Blue = Mn

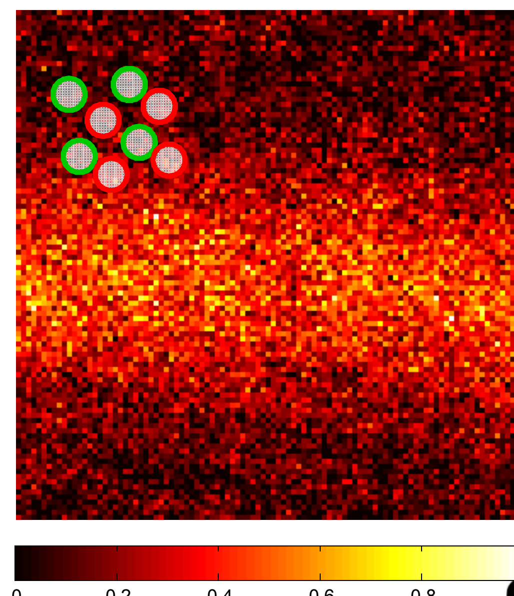
3.6 nm field of view



Ti Component



Sr Component



Mn Component

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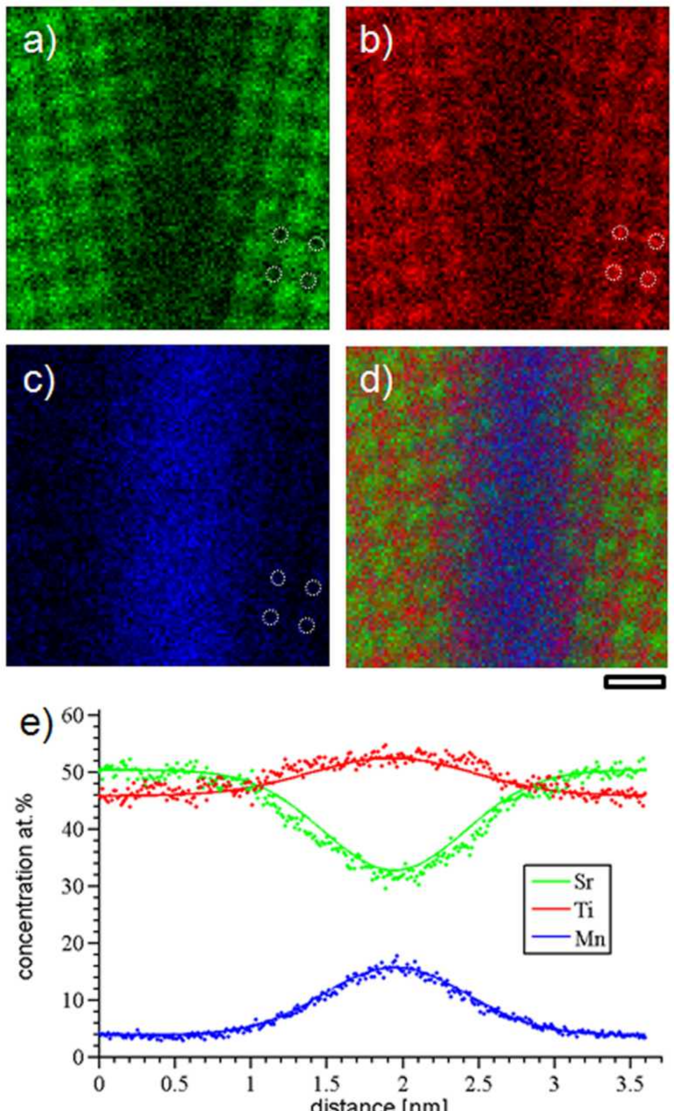
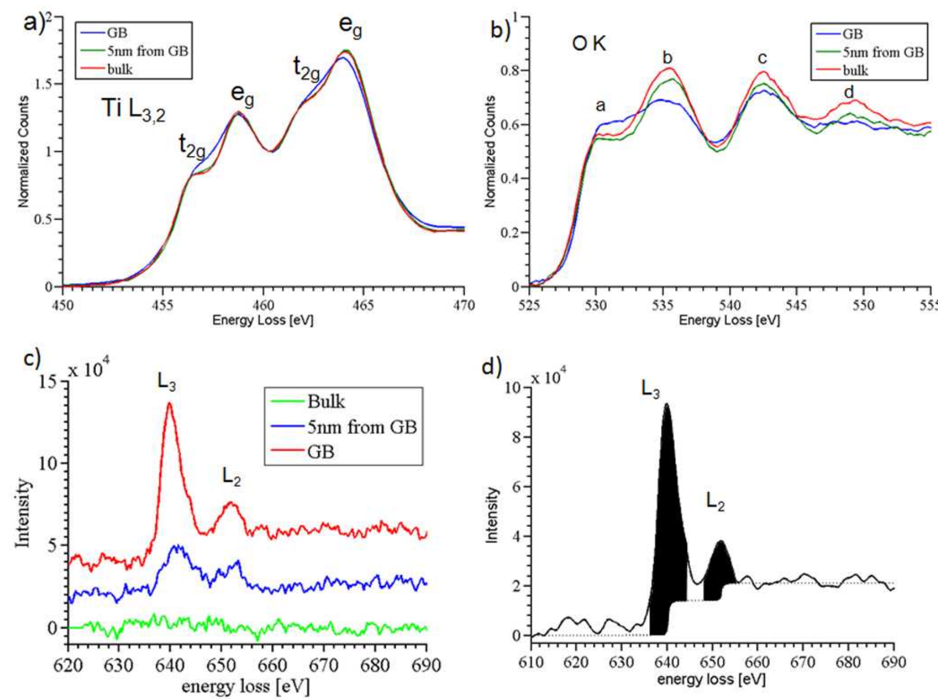
- k_{SrTi} measured from pure STO at [001]
  - k_{SrTi} = 1.34 (atomic fraction basis, Ti-K and combined Sr-L and K) was measured from a summed spectral image from the undoped material at [001]
  - k_{TiMn} = 0.9 was taken from a book value at the same kV but different microscope
  - Rotated PCA to get 'pure' elemental factors
    - Counts for each element

Analysis of Mn-doped STO Σ=13 Boundaries

∑13 (510)/[001]

Quantitative EDS and EELS





FWTM enrichment at the boundary less than 2nm

Mn^{+2} at boundary

Mn^{+4} in bulk near boundary (subsitutional with Ti)

Hao Yang, Paul G. Kotula, Yukio Sato, Yuichi Ikuhara, Nigel D. Browning. "Segregation of Mn^{2+} Dopants as Interstitials in $SrTiO_3$ Grain Boundaries," Submitted (2013).

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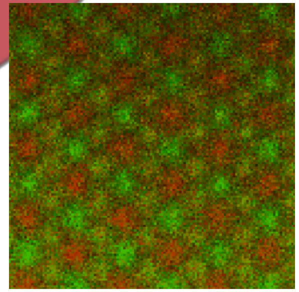
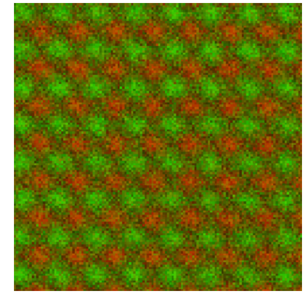
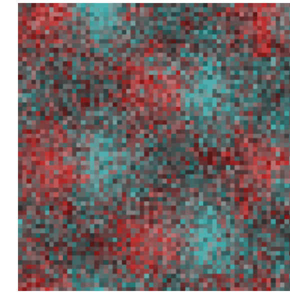


Conclusions





- Spectral image acquisition is not too difficult
- Novel detector geometries for AEM improve sensitivity and throughput.
  - Pushing to larger solid angles possible but collimation the challenge
- MSA methods are very useful for simplifying the analysis of large, complex data sets (only very simple ones shown today!)
  - Importance of Poisson normalization
  - Factor rotation, spatially or spectrally simple viewpoints
  - Unbiased analysis powerful for materials science, etc. Needle in the haystack….single atoms….
  - Quantification still additional knowledge
- New applications of SDDs and the AC-STEM come weekly

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